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

Temporal Changes in Indicators of Natural Attenuation and Physical Controlling Factors for a Freshwater Tidal Wetland Contaminated With Chlorinated Volatile Organic Compounds, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 1995–2001

Scientific Investigations Report 2005-5057

U.S. Department of the Interior
U.S. Geological Survey

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By Michelle M. Lorah, Tracey A. Spencer, and Angela L. McGinty

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Conversion Factors and Datums

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
	Flow rate	
meter per year (m/yr)	3.281	foot per year (ft/yr)

Temperature in degrees Celsius (^{o}C) may be converted to degrees Fahrenheit (^{o}F) as follows:

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

Vertical coordinate information is referenced to the North American Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given either in micrograms per liter (µg/L), or micromoles per liter (µmol/L), or micromolar (µM).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25^{o}C).

Water year is the 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 2000, is called the "2000 water year."

Abbreviations

APG	Aberdeen Proving Ground
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
12DCA	1,2-dichloroethane
c12DCE	*cis*-1,2-dichloroethene
t12DCE	*trans*-1,2-dichloroethene
12DCE	total of *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene
ESTCP	Environmental Security Technology Certification Program
DNAPL(s)	dense non-aqueous-phase liquid(s)
MLSs	multilevel samplers
NWQL	National Water Quality Laboratory
RPDs	relative percent differences
TeCA	1,1,2,2-tetrachloroethane
112TCA	1,1,2-trichloroethane
TCE	trichloroethene
USGS	U.S. Geological Survey
VC	vinyl chloride
VOCs	volatile organic compound(s)

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Abstract

Since 1992, the U.S. Geological Survey has studied natural attenuation processes occurring as chlorinated volatile organic compounds (VOCs) discharge to a freshwater tidal wetland along West Branch Canal Creek, Aberdeen Proving Ground, Maryland. Field and laboratory studies have shown that anaerobic biodegradation is a major natural attenuation process in the wetland sediments and that monitored natural attenuation could be an effective ground-water remediation method for the VOCs at this site. In this study, temporal changes in the contaminated aquifer and wetland porewater were characterized using water-quality and physical data collected during 1995–2001 to assist in defining natural attenuation efficiency throughout the year and in developing long-term monitoring plans.

The major contaminants in the aquifer within the natural attenuation study area are 1,1,2,2-tetrachloroethane and trichloroethene. The major contaminants in the wetland porewater are the anaerobic daughter compounds of 1,1,2,2-tetrachloroethane and trichloroethene, including 1,2-dichloroethene and vinyl chloride. A consistent seasonal pattern of higher VOC concentrations in the summer/fall (June–November) than in the winter/spring (December–May) was observed in the aquifer in the upland area. Little seasonal change was observed in VOC concentrations in the aquifer and deeper wetland sediments within the wetland boundary, however. Major ions and constituents indicative of oxidation-reduction (redox) reactions did not show a consistent seasonal variation in the aquifer in either the upland or within the wetland, except for elevated chloride and other inorganic constituents in the uplands during 1996.

Porewater collected at 3-centimeter intervals along upward flowpaths through the wetland sediments showed that complete natural attenuation of the VOCs typically occurred before land surface was reached, although low VOC concentrations sometimes were detectable within the upper 10 centimeters during the summer (June–August). A distinct temporal variation in VOC concentrations in the shallow porewater was observed, with VOC concentrations low in the winter/spring and increasing by a factor of 2 to 4 in the summer/fall. VOC concentrations were highest in June 2000. Concentrations of redox-sensitive constituents, including methane, ferrous iron, and sulfide, in porous-membrane diffusion samplers (peepers) indicated that the shallow wetland porewater was anaerobic at all times of the year. Methane concentrations were higher in the summer/fall than in the winter/spring, whereas ferrous iron and sulfide concentrations showed an opposite temporal pattern of lower concentrations in the summer/fall compared to the winter/spring.

Major physical factors that could potentially control temporal variations in the wetland and aquifer geochemistry include ground-water head gradients and flow patterns, surface-water levels and tidal fluctuations, and sediment temperature. Water levels measured in the aquifer in the upland indicated a consistent seasonal pattern of rising water levels with increased recharge to the aquifer in the late winter and spring, and decreasing water levels in the summer. The lower winter/spring VOC concentrations detected in the aquifer in the uplands could be associated with dilution caused by increased recharge. In contrast, water levels and horizontal and vertical head gradients were remarkably constant throughout the study within the wetland area. Upward discharge from the aquifer was sufficient to maintain water-saturated or nearly saturated (within 10 centimeters of land surface) conditions in the wetland sediments throughout the sampling period, despite summer evapotranspiration demands and below normal precipitation during 1997–1999. Thus, the water-saturated, anaerobic conditions needed for reductive dechlorination and efficient natural attenuation of the VOCs were prevalent throughout the study.

Vertical head gradients from the aquifer to the wetland sediments were relatively constant—around 0.2 meter/meter from 1995 through 2000. Horizontal head gradients in the wetland porewater were lower, typically ranged from about 0 to 0.04 (meter/meter), and also were relatively constant throughout much of the study period. During March and June 2000, however, a strong negative horizontal gradient (-0.18 meter/meter) indicated a prolonged period of wetland

porewater flow in an inland direction from the creek channel. Mean creek stage was 20 to 25 percent higher in the spring and summer of 2000 compared to the previous 2 years, which probably caused the prolonged flow reversal and the unusual increase in shallow porewater VOC concentrations in 2000.

Although temperatures varied seasonally in the wetland sediments, changes were greatest in the upper 0.15 meters of sediment and were dampened greatly with depth. The temperature fluctuations apparently did not significantly decrease biodegradation because VOC concentrations in the shallow wetland porewater were substantially lower in the winter/spring compared to the summer without breakthrough of parent VOCs to the wetland surface.

Overall, the results of this 6-year temporal study indicate that anaerobic conditions and efficient biodegradation of the VOCs is maintained throughout the year in the wetland sediments, supporting earlier conclusions that monitored natural attenuation could be an effective ground-water remediation method at this site. The relatively constant hydrologic and temperature conditions in the wetland sediment appear to assist in maintaining efficient natural attenuation of the VOCs throughout the year. Although a clear cause of the annual, transient increases in VOC concentrations in the shallow porewater was not determined, the most extreme increases in concentrations of inorganic constituents in 1996 and of VOCs in the summer of 2000 were associated with unusual hydrologic events—above normal precipitation in 1996 and prolonged high creek stage in 2000. Monitoring these physical factors could provide an indication of when unusual concentrations might occur in the wetland porewater; a sampling event could then be initiated.

Introduction

Evaluation of monitored natural attenuation as a remediation method or as a component of a remedy for contaminated ground water requires a comprehensive understanding of the processes affecting contaminant distribution and transformation, and of the variability of these processes with time (Wiedemeier and others, 1998). In cooperation with the U.S. Army Garrison, Aberdeen Proving Ground (APG), Maryland since 1992, the U.S. Geological Survey (USGS) has studied natural attenuation processes occurring as plumes of chlorinated volatile organic compounds (VOCs) discharge to a freshwater tidal wetland along West Branch Canal Creek at APG (Lorah and others, 1997; Lorah and Olsen 1999a, 1999b; Lorah and others, 2003) (fig. 1). The major contaminants in the shallow aquifer (less than about 15 m, or meters deep) at this site are 1,1,2,2-tetrachloroethane (TeCA) and trichloroethene (TCE), which can be a daughter product of TeCA degradation in addition to being a widely used solvent itself. The major contaminants in the wetland porewater are relatively low concentrations of anaerobic daughter compounds of TeCA and TCE, including *cis*-1,2-dichloroethene (c12DCE), *trans*-1,2-dichloroethene (t12DCE), vinyl chloride (VC), 1,1,2-trichloroethane (112TCA), and 1,2-dichloroethane (12DCA) (fig. 2). Previous field and laboratory studies showed that anaerobic biodegradation is a dominant natural attenuation process in the wetland sediments and that monitored natural attenuation could be an effective ground-water remedy at this site (Lorah and others, 1997; Lorah and others, 2003).

Wetlands are dynamic surficial systems that could show greater seasonal variability in contaminant distribution and biodegradation rates than observed in deeper ground-water systems. Previous evaluations of contaminant distributions and indicators of natural attenuation by biodegradation at this site have primarily used results from two comprehensive sampling events—one in the summer of 1995 and one in the summer of 2000 (Lorah and others, 1997; Phelan and others, 2002). Previous analysis of seasonal changes observed in the aquifer and wetland porewater was limited to field data collected during 1995–1996 (Lorah and others, 1997). Laboratory experiments to measure potential changes in anaerobic TeCA biodegradation rates also were conducted using wetland sediment collected during three different seasons in 1999–2000 and incubated at 19 ° (degrees) Celsius (the average wetland porewater temperature in the summer) (Lorah and others, 2003). High potential seasonal variability in biodegradation rates was observed in these laboratory experiments, with biodegradation rates unexpectedly low in microcosms constructed with wetland sediment collected in the summer compared to those constructed with sediment collected in the late winter/early spring and in the fall (Lorah and others, 2003). In addition, microbial community analyses of the wetland sediment showed relatively low microbial biomass and microbial diversity in the summer, potentially indicating a lower abundance of critical microorganisms needed to biodegrade TeCA and its anaerobic daughter products in the summer. It is unclear, however, if the lower potential biodegradation rates measured in the laboratory microcosms would be reflected in the field data. The sediment for these microcosms and microbial community analyses was collected from a depth of 0 to 0.25 m below land surface, whereas the contaminated wetland sediments range up to 3.6 m in thickness in the study area. In addition, the colder wetland sediment temperatures in the winter/early spring cause lower biodegradation rates, which would counteract the high potential biodegradation rate measured in the seasonal microcosms incubated at 19 °Celsius (Lorah and others, 2003).

The temporal variability needs to be understood to determine natural attenuation efficiency throughout the year and to develop long-term monitoring plans. The purpose of this study was to characterize temporal changes in the contaminated aquifer and wetland porewater, using water-quality and physical data collected at selected sites during multiple sampling events between 1995–2001. Seasonal sampling over a multiyear period was needed to discern consistent patterns in ground-water chemistry. This temporal study was conducted as part of the ongoing USGS study of natural attenuation processes in the West Branch Canal Creek wetland area at APG.

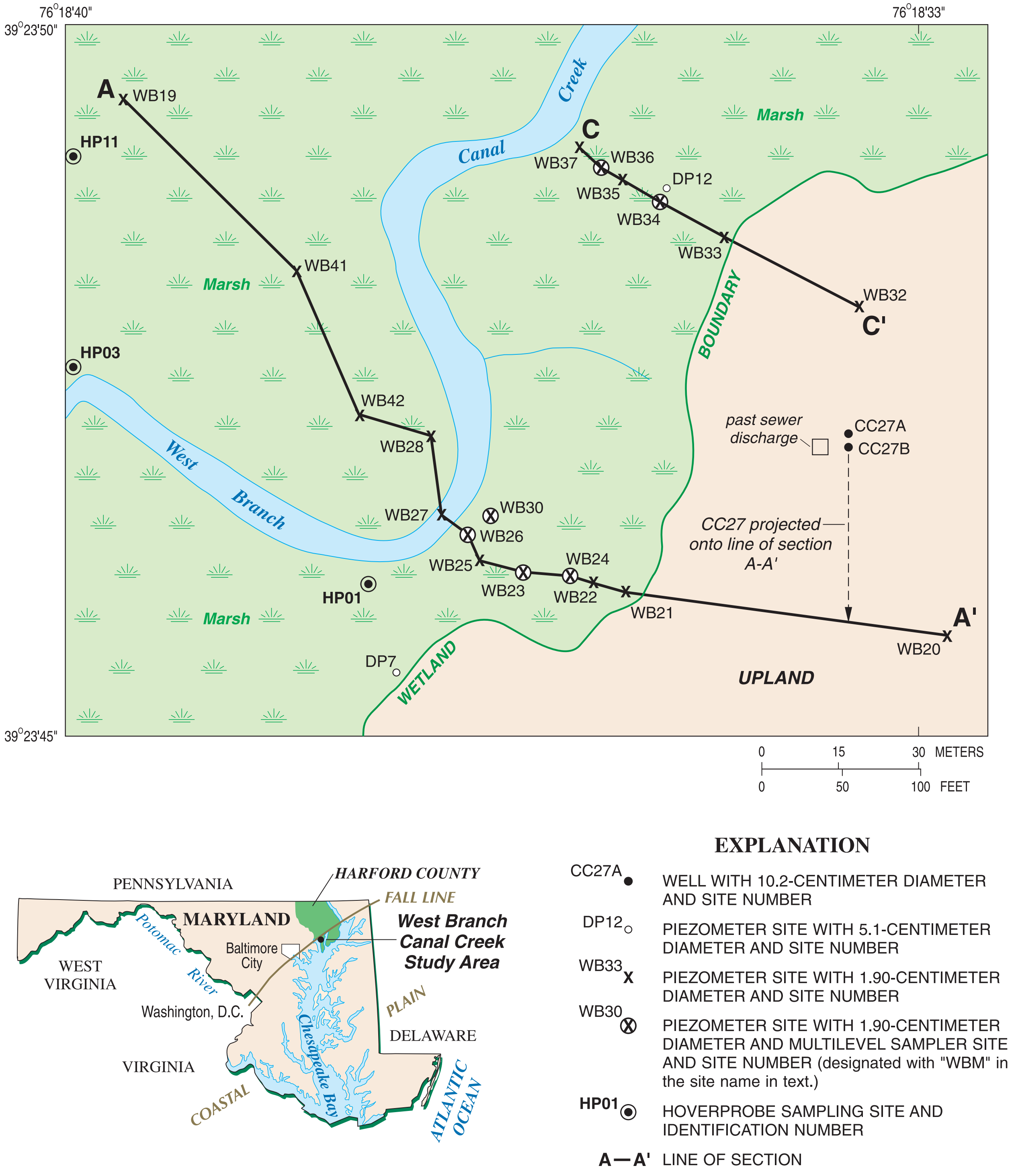


Figure 1. Location of sampling sites and sections A-A' and C-C' in the wetland study area along West Branch Canal Creek, Aberdeen Proving Ground, Maryland (modified from Lorah and others, 2003).

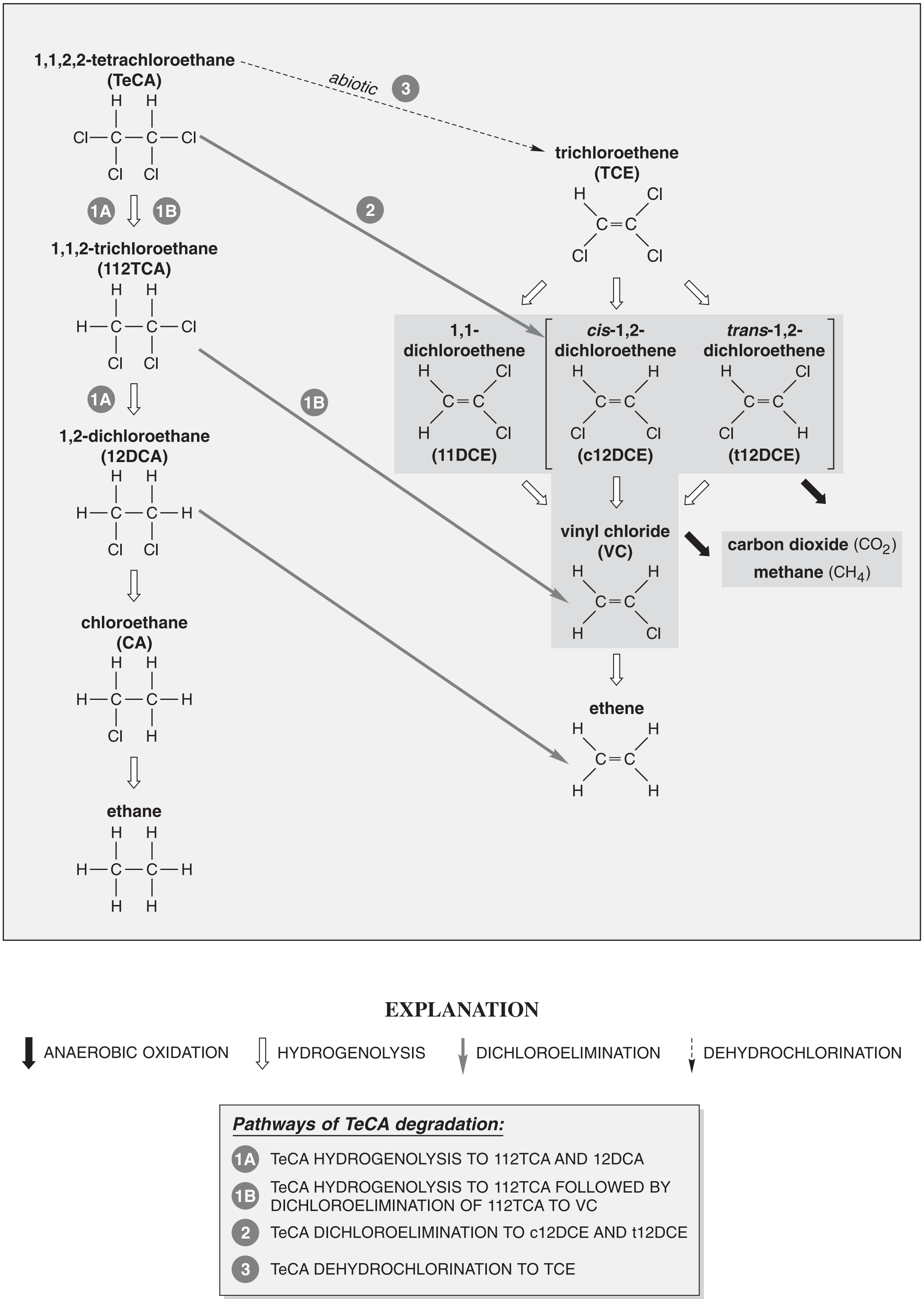


Figure 2. Anaerobic degradation pathways for 1,1,2,2-tetrachloroethane and trichloroethene (modified from Lorah and others, 1997).

Purpose and Scope

The purpose of this report is to characterize the temporal changes in (1) chemical constituents that are indicators of natural attenuation of chlorinated VOCs in ground water in the West Branch Canal Creek wetland study area, and (2) possible physical factors that could be controlling these changes. Evaluation of the ground-water chemistry focuses on indicators of anaerobic biodegradation reactions that are known from previous studies to be a major natural attenuation process of the VOCs. These indicators include concentrations of TeCA, TCE, chlorinated daughter products, and redox-sensitive constituents (ferrous iron, sulfide, and methane). Ground-water chemistry in the wetland sediments and aquifer is evaluated using samples collected from 26 drive-point piezometers and 2 wells that were sampled during nine sampling events between 1995–2000. In addition, detailed vertical profiles of shallow (less than 120 cm, or centimeters deep) wetland porewater chemistry is evaluated using data from porous-membrane samplers, or peepers, that were installed at two to six sites and sampled as many as 10 times between 1995–2001. Temporal analysis of the water-quality data includes evaluating differences on a yearly and seasonal basis, where seasons are broadly divided into before and during the growing season. Possible physical factors that could control temporal changes in natural attenuation include water levels in the aquifer, stage in the creek, tidal fluctuations, and sediment temperature. Implications of the observed temporal changes on a monitored natural attenuation remedy for the VOCs discharging to the wetland sediments are discussed.

Description of Study Area and Site History

The study area is in a small section of the freshwater tidal wetlands along the West Branch Canal Creek at APG, a U.S. Army base in Maryland near the head of the Chesapeake Bay (fig. 1). The wetland vegetation along the eastern bank of the creek in the study area is dominated by *Phragmites*, or common reed, whereas the vegetation along the western bank contains a mix of common reed, southern wild rice, and narrow-leaf cattail (Lorah and others, 1997). Tidal amplitude in the creek ranges from about 0.15 to 0.60 m, and the wetland is regularly flooded to the wetland boundary. Floating walkways were installed in 1994 to allow access to the study area and to minimize disturbance to the wetland sediments and vegetation during sampling and other field activities. Land-surface elevations range from sea level to about 5 m in the uplands to the east of the wetland boundary. Landfilling in the past narrowed the wetland area along the eastern bank. The upland immediately east of the wetland boundary currently consists of wooded and some open field areas, with office buildings and abandoned manufacturing facilities further east.

APG has been the primary chemical-warfare research and development center for the United States since 1917, and the area to the east of the West Branch Canal Creek was APG's major industrial area. Chemical manufacturing and other military related activities were greatest during World Wars I and II; many of the plants have since been demolished or abandoned. Historical activities in the Canal Creek area are detailed in Nemeth (1989) and are summarized in Lorah and Clark (1996). Until the 1970s, chemical wastes were discharged with little or no treatment to sewerlines that were constructed of vitrified clay during World War I. Several sewerlines discharged near the current boundary or within the wetland area along the West Branch Canal Creek (Lorah and Clark, 1996), although the ends of the sewerlines are now buried and have not been located. Release of waste products by spills, landfilling, and discharge to sewers during chemical manufacturing operations near the creek resulted in ground-water contamination (Lorah and Clark, 1996; Lorah and others, 1997). Chlorinated solvents, including TeCA, TCE, carbon tetrachloride, and chloroform, were widely used in manufacturing and other military-related activities and are the major ground-water contaminants. Dense non-aqueous-phase liquid (DNAPL) contaminant source areas have not been found in the upland near the wetland study area, but continued dissolution of residual DNAPLs in the aquifer could be a continuous source for the plumes discharging to the wetland (Lorah and Clark, 1996; Lorah and others, 1997). Ground-water contamination in the uplands surrounding the West Branch Canal Creek was first described in USGS studies in the Canal Creek area during 1985–1993 (Lorah and Vroblesky, 1989; Lorah and Clark, 1996). In 1990, APG was placed on the National Priorities List established under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), and the U.S. Army and U.S. Environmental Protection Agency Region III signed an Interagency Agreement for investigation and remediation of the area.

Previous Investigations and Background on Natural Attenuation

Until 1992, when the USGS began the natural attenuation study in the wetland area, investigations of ground-water contamination near the West Branch Canal Creek were conducted only in the upland areas. Oliveros and Vroblesky (1989) and Lorah and Vroblesky (1989) reported that the Canal Creek aquifer (in the Patapsco Formation), which is the major contaminated aquifer in the Canal Creek area, is unconfined or semiconfined near the West Branch Canal Creek and that local recharge and discharge occurs. Recharge from rainfall infiltration occurs upgradient from the wetlands on both sides of the creek. Large bends in the potentiometric surface of the Canal Creek aquifer near the West Branch Canal Creek indicated that heads were strongly controlled by surface water in hydraulic connection with the aquifer (Oliveros and Vroblesky, 1989). Lorah and Vroblesky (1989) and Lorah and Clark (1996) found extensive areas of VOC contamination in the Canal Creek aquifer along the eastern side of West Branch Canal Creek. The Canal Creek aquifer in the upland areas surrounding West Branch Canal Creek was predominantly aerobic, and little evidence of biodegradation of the chlorinated VOCs was observed (Lorah and Clark, 1996).

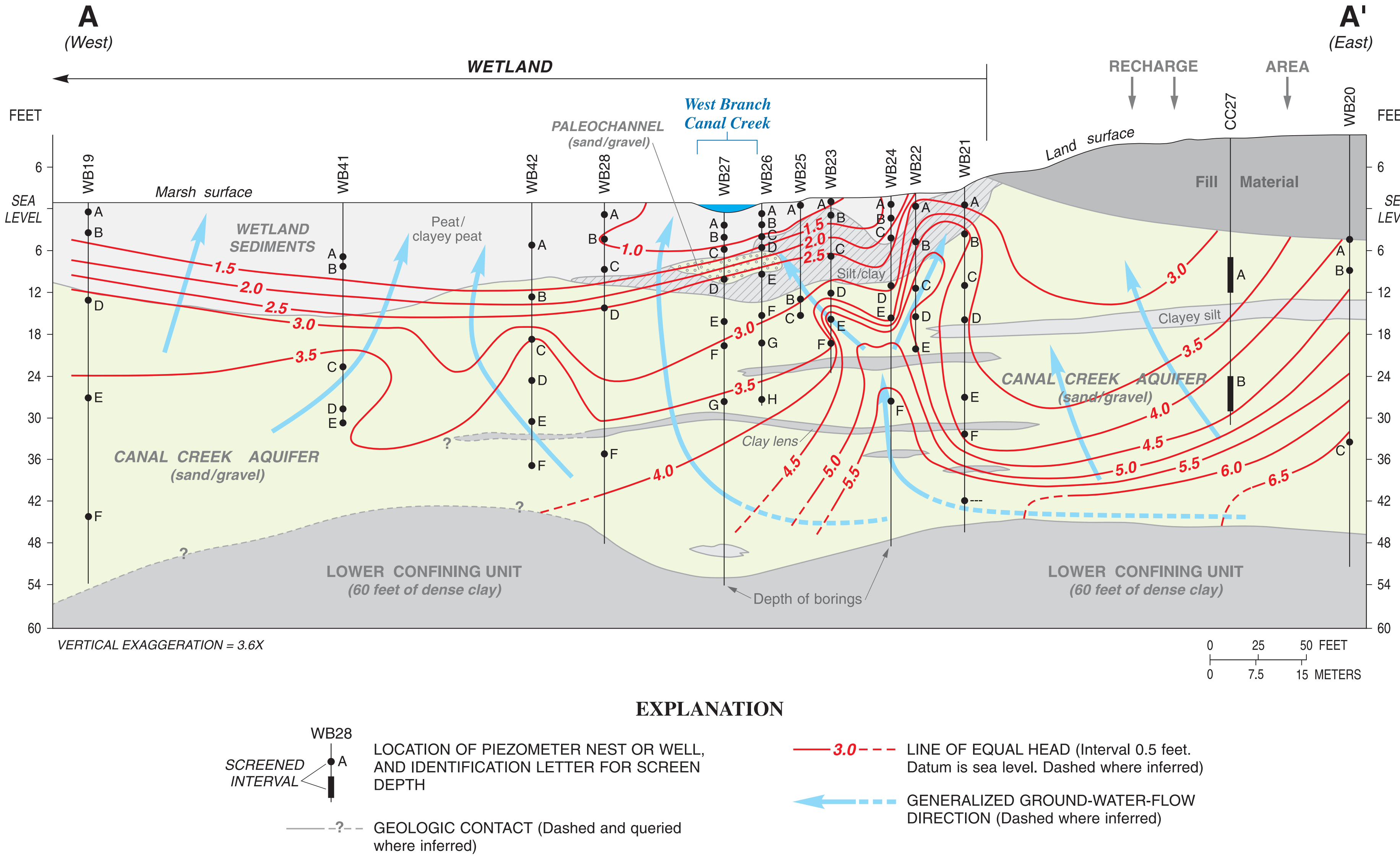
In 1992, the USGS began a study of the wetland area along the West Branch Canal Creek to investigate the hypothesis that natural attenuation by anerobic biodegradation would occur as the chlorinated VOCs in the Canal Creek aquifer discharged upward through anaerobic wetland and creek-bottom sediments (Lorah and others, 1997). A relatively small wetland area was selected downgradient of monitoring well site CC27 (fig. 1), which was known to contain VOCs in the range of several thousand µg/L (micrograms per liter). The study focused on extensive characterization of the contaminant distribution and natural attenuation processes along two transects through the wetlands area (figs. 1, 3, and 4), rather than on defining the areal extent of contamination within the wetland area. The two transects are aligned along the general direction of ground-water flow in the aquifer. During 1994–1995, about 100 drive-point piezometers were installed in nests with screens placed at different intervals in the wetland sediments and the Canal Creek aquifer (Lorah and others, 1997; Lorah and Olsen, 1999a). Piezometer nests WB41 and WB42 were added in November 2000 to better define the contaminant distribution and hydrogeology along section A–A′ (Phelan and others, 2002) (fig. 3). Peepers also were used to define porewater chemistry in the upper 60 cm of the wetland sediment (Lorah and others, 1997; Lorah and Olsen, 1999a, b).

The Canal Creek aquifer is about 12 to 14 m thick near West Branch Canal Creek and consists mainly of medium- to coarse-grained sand and gravel that is typical of the unconsolidated Coastal Plain sediments in the area (figs. 3, 4). Wetland sediments that overlie the Canal Creek aquifer consist of two distinct layers that have a combined thickness of about 1.8 to 3.6 m—a lower unit of silty to sandy clay or clayey sand and an upper unit of peat mixed with variable amounts of clay and silt (Lorah and others, 1997) (figs. 3, 4). The total organic carbon content of the peat unit ranges from 6.9 to 32.6 percent, averaging about 18 percent (Lorah and others, 1997; Olsen and others, 1997). Ground-water-flow directions in the aquifer within the wetland area are laterally toward the creek from both sides and upward through the wetland and creek-bottom sediments (figs. 3, 4). The ground-water divide representing the convergence of flow from the east and west sides is near the center of the wetland, in the general vicinity of sites WB41 and WB42 (Phelan and others, 2002) (fig. 3). Reversals in ground-water-flow directions are evident at high tide in some places and affect contaminant distributions (Lorah and others, 1997; Lorah and Olsen, 1999a). Seasonal variations in head distributions and ground-water flow were not evident in the 1995–1996 data evaluated in the earlier natural attenuation study (Lorah and others, 1997, p. 36).

TeCA (fig. 5) and TCE (data not shown) had similar distributions along section A–A′, with the highest total concentrations (about 3,000 µg/L) at CC-27 near the eastern edge of the wetland (Lorah and others, 1997; Phelan and others, 2002). Concentrations of TeCA (fig. 5) and TCE were each in the range of 100 µg/L directly beneath the wetland sediments. The TeCA and TCE plumes along section A–A′ extended to the western side of the creek channel, which confirmed measurements of head gradients that indicated a lateral component of ground-water flow in the aquifer beneath the creek and discharge to wetland sediments on the western side of the channel along this section (Lorah and others, 1997; Phelan and others, 2002). TeCA was the major contaminant in the ground water along section C–C′, occurring at a maximum concentration of about 2,000 µg/L in the aquifer at sites WB32 and WB33 at the eastern edge of the wetland (fig. 6). Unlike section A–A′, where both TeCA and TCE were major ground-water contaminants, TCE concentrations were a factor of 10 lower than TeCA concentrations in the aquifer and wetland sediment along section C–C′ (Lorah and others, 1997; Phelan and others, 2002).

Distributions of redox-sensitive constituents showed that the ground water became increasingly anaerobic along upward flowpaths through the wetland sediments. Concurrent with a change to predominantly iron-reducing conditions and then to predominantly methanogenic conditions, concentrations of the parent VOCs (primarily TeCA and TCE) decreased, while concentrations of VOCs that are anaerobic daughter compounds showed a transient increase in the wetland sediments. The concentrations of the daughter compounds decreased so that VOCs were low or nondetectable before land surface or the surface water was reached along these sections (Lorah and others, 1997; Lorah and Olsen, 1999a).

Laboratory microcosm experiments conducted during 1996–1997 with TeCA and TCE confirmed the rapid and complete degradation of these compounds in the wetland sediments under anaerobic conditions through reductive dechlorination reactions (Lorah and others, 1997, 2001; Lorah and Olsen, 1999b). Continued microcosm and enrichment experiments during 1999–2001 defined some of the factors controlling degradation reactions and evaluated microbial communities associated with these reactions (Lorah and others, 2003; Lorah and Voytek, 2004). Both TeCA and TCE degradation produced 12DCE (c12DCE and t12DCE) and VC as the daughter compounds that showed the greatest transient accumulation in the anaerobic microcosms. 12DCE is produced from dichloroelimination of TeCA; VC is produced from dichloroelimination of 112TCA, which is a hydrogenolysis product of TeCA, and from hydrogenolysis of the 12DCE produced by dichloroelimination (fig. 2). Hydrogenolysis of the TCE produced by abiotic degradation of TeCA (fig. 2) accounted for a minor percentage of the 12DCE and VC in TeCA-amended microcosms (Lorah and others, 1997, 2003). In TCE-amended microcosms, 12DCE and VC were the only chlorinated daughter products observed (Lorah and others, 1997, 2001). The daughter products 112TCA and 12DCA, which can be produced by hydrogenolysis of TECA, also were commonly observed in the field and in anaerobic microcosms but generally not in concentrations as high as those observed for 12DCE and VC. Ethene, a non-chlorinated and non-toxic end product of TeCA and TCE degradation (fig. 2) was observed infrequently and only in trace quantities in the field and anaerobic laboratory microcosms (Lorah and others, 1997, 2003). Later enrichment experiments, how-



EXPLANATION

WB28 — SCREENED INTERVAL — LOCATION OF PIEZOMETER NEST OR WELL, AND IDENTIFICATION LETTER FOR SCREEN DEPTH

3.0 — LINE OF EQUAL HEAD (Interval 0.5 feet. Datum is sea level. Dashed where inferred)

GEOLOGIC CONTACT (Dashed and queried where inferred)

GENERALIZED GROUND-WATER-FLOW DIRECTION (Dashed where inferred)

Figure 3. Section A-A' showing the hydrogeology and locations of piezometer nests and screen depths (modified from Phelan and others, 2002).

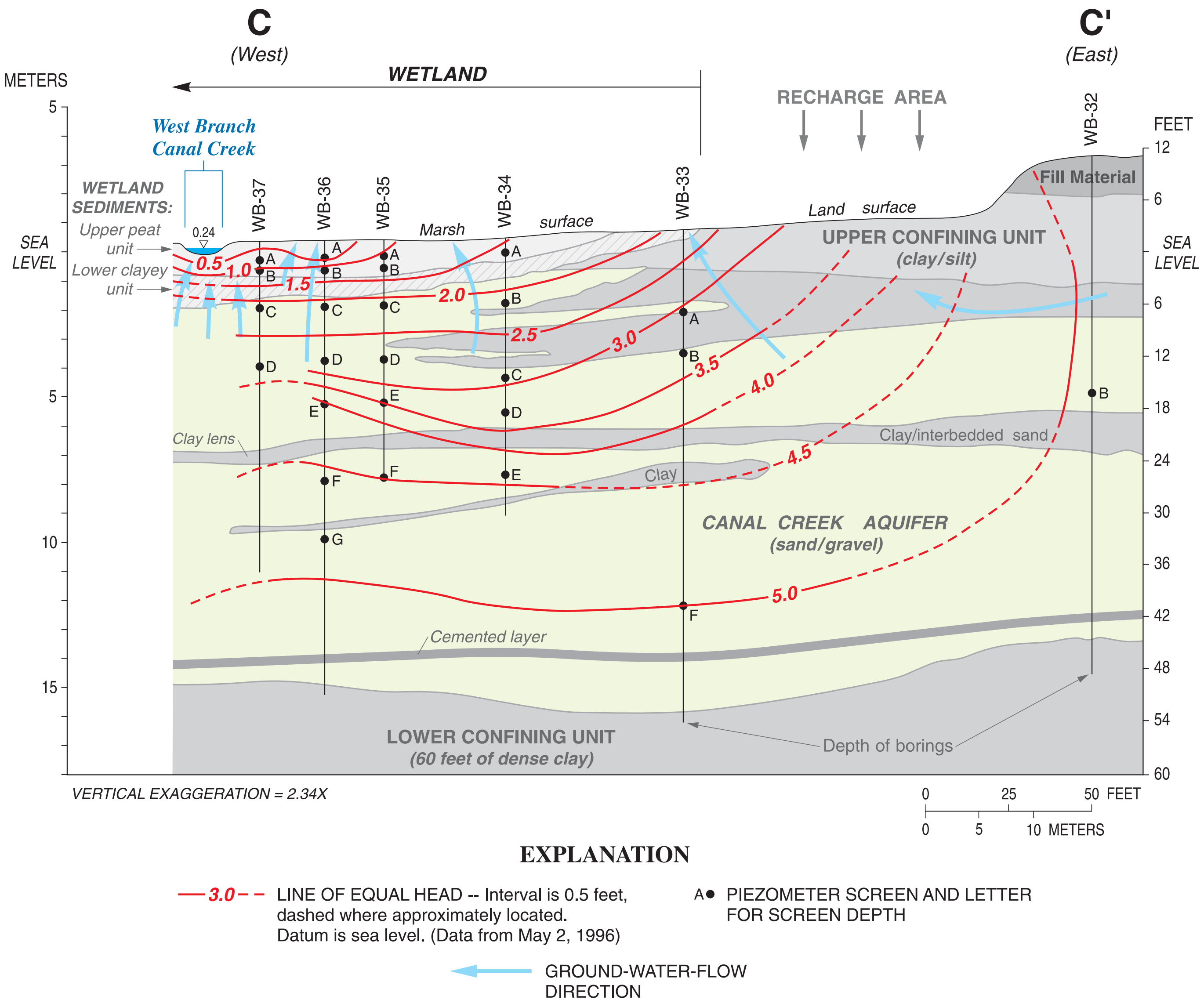


Figure 4. Section C-C' showing the hydrogeology and locations of piezometer nests and screen depths (modified from Lorah and others, 1997).

ever, showed that ethene is produced but is rapidly mineralized to carbon dioxide under anaerobic conditions in the wetland sediment (Lorah and others, 2003; Elizabeth Jones, USGS, written commun., 2004). A microbial consortium, rather than one individual microbial species or group, is involved in the anaerobic degradation of TeCA and TCE in the wetland sediments at West Branch Canal Creek (Lorah and others, 2003).

In addition to anaerobic degradation of the lower chlorinated daughter products such as 12DCE and VC, aerobic degradation is possible around plant roots and near land surface in the wetland. Lorah and others (1997, 2001) showed in aerobic laboratory experiments that methanotrophs, bacteria that require oxygen and utilize methane as a substrate, could rapidly degrade 12DCE and VC to non-chlorinated end products.

As part of the natural attenuation investigation in the West Branch wetland area, additional drilling and ground-water sampling was done outside of the area of the transects (Phelan and others, 2001). Drilling and ground-water-quality profiling was done at 12 sites along the creek channel south of section A–A′ using the USGS hoverprobe, which is a hovercraft with a vibrocore drill rig mounted on it (hoverprobe sites near A–A′ are shown in fig. 1). This water-quality profiling found two sites immediately south of section A–A′ that had high concentrations (greater than 10,000 µg/L) of carbon tetrachloride and chloroform (Phelan and others, 2001) and lower concentrations of chlorinated

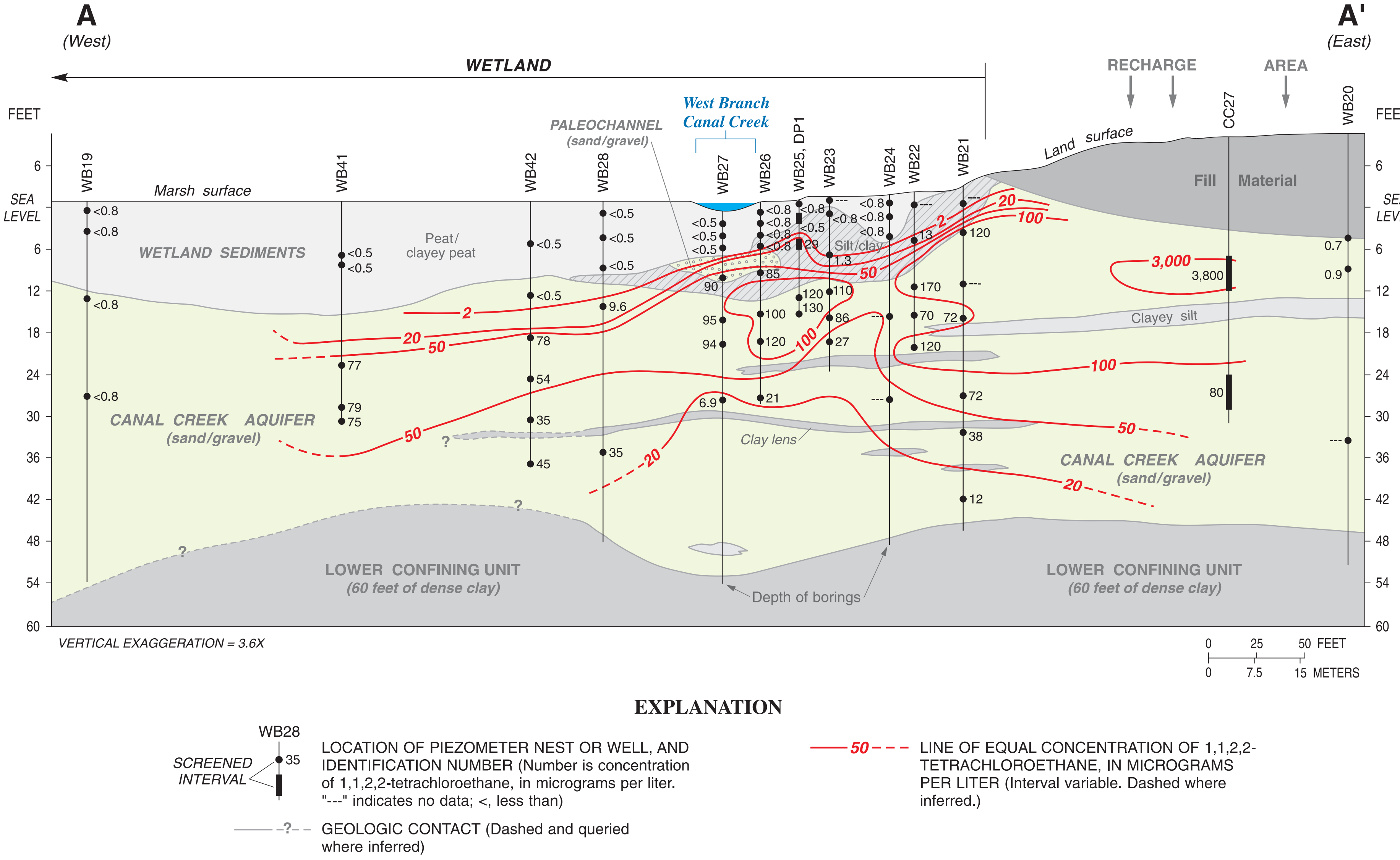


Figure 5. Distribution of 1,1,2,2-tetrachloroethane (TeCA) in ground water in section A-A', 2000-01 (modified from Phelan and others, 2002).

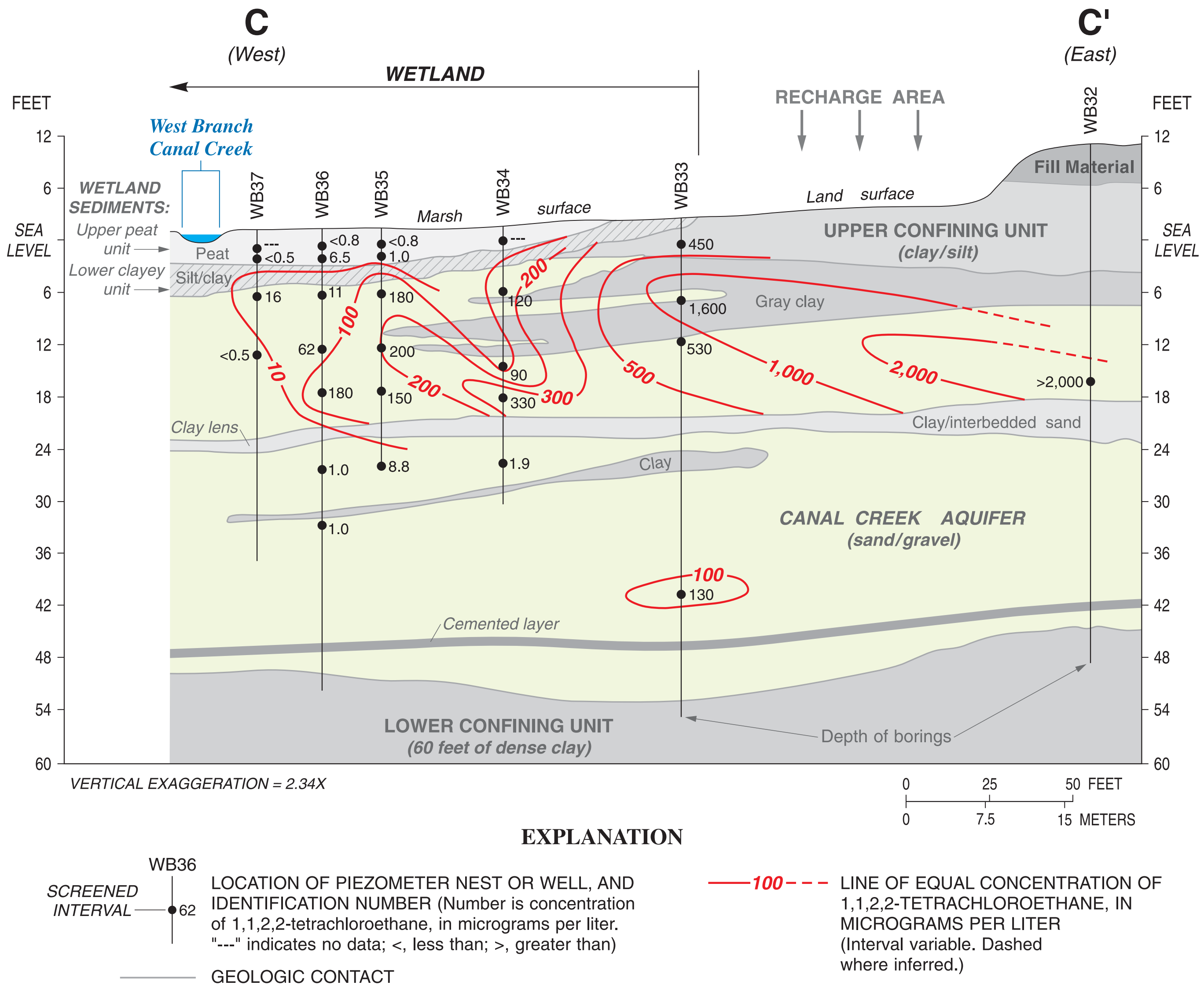


Figure 6. Distribution of 1,1,2,2-tetrachloroethane (TeCA) in ground water in section C-C', June-August 2000, West Branch Canal Creek, Aberdeen Proving Ground, Maryland (from Phelan and others, 2002).

ethanes and ethenes. These results indicated another plume in addition to the TeCA- and TCE-dominated plumes along sections A–A′ and C–C′ (Phelan and others, 2002). Piezometer nests were added at sites WB41 and WB42 along section A–A′ (fig. 3), and sampling confirmed the presence of carbon tetrachloride and chloroform in concentrations ranging from 1,000 to 2,000 µg/L near the bottom of the aquifer (about 11 m below sea level) at these sites (Phelan and others, 2002). Elsewhere along sections A–A′ and C–C′, concentrations of carbon tetrachloride and chloroform ranged from 10 to 100 µg/L (Phelan and others, 2002).

Methods and Data Analysis

Water-Quality Monitoring Network

Temporal changes in ground-water chemistry were evaluated using data collected from a network of piezometers, wells, and multilevel samplers (MLSs) that are permanently installed at the site and from the periodic installation and removal of peepers (tables 1–3). The piezometer network in the wetland study area consists predominantly of about 100 drive-point piezometers that are 1.9-cm-diameter stainless steel. These were installed in nests of 5 to 10 piezometers along sections A–A′ and C–C′ between July 1994 and February 1995 (fig. 1). Each piezometer has a

1.3-cm-diameter inner Teflon-lined polyethylene tube that extends from above land surface to the top of the screened interval, which consists of 15.2-cm-long stainless-steel mesh screen (Lorah and others, 1997). Two 10.2-cm wells (CC27A and CC27B) in the upland that were installed during the previous Canal Creek ground-water investigation also were sampled as part of this wetland study (fig. 1). These piezometers and wells were sampled as part of comprehensive sampling events during the summers of 1995 and 2000 (Lorah and others, 1997; Phelan and others, 2002). As part of the study of seasonal ground-water dynamics, 26 of the 1.9-cm piezometers were sampled in March–April 1996, June 1996, August 1996, March 1999, May 1999 (ended June 1), July–August 1999, and March–April 2000, in addition to the summer 1995 and summer 2000 events (tables 1 and 2). Only data from the 26 piezometers and two 10.2-cm wells that were included in the seasonal sampling events are discussed in this report (table 1); other piezometers sampled only during the comprehensive sampling events in the summers of 1995 and 2000 are not discussed here because of insufficient temporal data.

In addition, samples from peepers and multilevel samplers were used to obtain more detailed delineation of changes in ground-water quality along vertical flowpaths in the wetland sediments during different seasons (tables 1–3). Peepers are passive ground-water sampling devices that contain discrete sampling chambers that are filled with deionized water before installation in the wetland sediment. Peepers have been used previously to sample porewater for a wide range of inorganic constituents (major ions, nutrients, trace metals), dissolved gases, and dissolved organic carbon (Carignan and others, 1985). The length of time commonly allowed for peeper equilibration, during which the surrounding porewater diffuses through the membrane into the peeper chamber, is about 2 weeks (Carignan, 1984; Carignan and others, 1994; Webster and others, 1998). Webster and others (1998) determined a theoretical equilibration period of 15 days for molecular diffusion of inorganic constituents in freshwater sediments, using a peeper cell length and polysulfone membrane similar to those used in the present study. Considering only molecular diffusion as a solute transport method provides the most conservative estimate of required equilibration time. In this study, a 2.5- to 3-week equilibration period was used before the peeper was removed for sampling. The peepers were installed in shallow wetland sediments adjacent to existing piezometers, and are therefore associated with the locations listed in table 1. The sampling sites and periods for the peepers are summarized in table 3. The peepers are constructed of Lexan or acrylic in three sections—the main body of the peeper that contains sampling chambers and two overlays that secure sheets of filter paper (0.2-µm, or micrometer polysulfone membrane) over the sampling chambers (Lorah and others, 1997; Spencer and others, 2000). For most sampling events, 61-cm-long peepers containing 21 rows of sampling chambers, with two sampling chambers in a row, were used. A 122-cm-long peeper was also placed at one site in March and June 2000 (PL36 in table 3). The 122-cm-long peeper contains 22 rows of sampling chambers that hold about twice the sample volume (about 23 mL, or milliliters in each chamber) than the 61-cm-long peepers.

The MLSs were installed at existing piezometer sites in July–August 1999 as part of a Department of Defense ESTCP study (Dyer and others, 2002) (table 1). Some of the screened intervals of the MLSs coincide with the screened interval of the 1.9-cm piezometers at the sites, but the MLSs generally had more screened intervals in the wetland sediment. Because the MLS installed at site WB26 showed evidence of cross-contamination between screened intervals, the nested 1.9-cm drive-point piezometers are used in this report in the analysis of vertical flowpaths for site WB26. The MLSs were sampled in March 2000 and June 2000. For the peepers placed at site DP12, wetland porewater data from deeper than 60 cm was obtained from selected 0.64-cm-diameter stainless-steel piezometers that were sampled as part of a tracer test during 1999 (Spencer and others, 2000; Olsen and Tenbus, 2005) (table 1). These 0.64-cm piezometers have inverted screens inside the bottom of the pipe, providing a discrete sampling point. Ground-water-quality data from the piezometers, wells, peepers, and multilevel samplers are reported in Olsen and others (1997), and Spencer and others (2000, 2002).

Ground-Water Sampling and Analysis

Ground-water samples were collected from the piezometers and MLSs for analysis of field parameters, redox constituents, inorganic constituents, and VOCs. Seasonal sampling events of the 1.9-cm piezometers (table 2) generally took 2 weeks to complete. Methods of sampling varied, depending on sampler type, piezometer depth, water recovery rate, and sampling event. Sampling and analysis methods, the associated data, and quality control and assurance results have been reported previously in Lorah and others (1997), Olsen and others (1997), and Spencer and others (2000, 2002), and are briefly summarized here. In general, piezometers installed in the wetland sediments were purged and sampled using a stainless-steel bailer during 1995–1996 sampling events, and a syringe with Teflon tubing in post-1996 sampling events. Some piezometers screened in the aquifer also were sampled using these methods if the water recovery rate was poor. A peristaltic pump was used in all sampling events for piezometers that had faster recovery rates. Between sample collections, the equipment was decontaminated using a soapy water wash, rinsed three times with deionized water, and then pre-rinsed with sample water. Quality control and assurance samples that were collected included field blanks, trip blanks, and duplicate samples (generally a minimum of 15 percent of the total number of piezometers sampled).

Before installation, peepers were placed in a large tub of deionized water and purged with nitrogen gas overnight to remove oxygen from the water within the sample chambers and from the plastic. The peepers were manually pushed downward into the wetland sediment until the top of the first

Table 1. Well-construction data for piezometers and multilevel samplers included in the temporal analysis, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 1995–2000

[Site identification number represents the latitude, longitude, and piezometer number within the cluster and is used for tracking water-quality samples; --, no data; DP, 1.90-centimeter (cm) drive-point piezometer with 15.24-cm-long screened interval; W4, 10.2-cm well with 152-cm-long screened interval; MLS, multilevel sampler with 7.62-cm-long screened intervals; TP, tracer test 0.64-cm piezometer with 1.25-cm-long inverted screen. Screened depth given as meters below land surface to midpoint.]

Site name	Device used at the site	Site identification number	Hydrogeologic unit	Screened depth (meters below land surface)	Land-surface elevation (meters)
		1.90-centimeter piezometer/10.2-centimeter well network			
CC-27A	W4	392343076183301	Canal Creek aquifer	6.25	3.41
CC-27B	W4	392343076183302	Canal Creek aquifer	11.43	3.47
WB19B	DP	392354076183702	Wetland sediments, upper peat unit	1.36	0.46
WB19E	DP	392354076183705	Canal Creek aquifer	8.76	0.45
WB22B	DP	392342076183402	Wetland sediments, upper peat unit	2.21	0.8
WB22D	DP	392342076183404	Canal Creek aquifer	5.26	0.75
WB23B	DP	392341076183402	Wetland sediments, lower clayey unit	0.75	0.23
WB23C	DP	392341076183403	Wetland sediments, lower clayey unit	2.67	0.32
WB23D	DP	392341076183404	Canal Creek aquifer	3.89	0.31
WB24A	DP	392343076183401	Wetland sediments, upper peat unit	0.35	0.56
WB24B	DP	392343076183402	Wetland sediments, upper peat unit	0.99	0.54
WB24E	DP	392343076183405	Canal Creek aquifer	5.11	0.56
WB26A	DP	392343076183502	Wetland sediments, upper peat unit	0.38	0.12
WB26B	DP	392343076183503	Wetland sediments, upper peat unit	0.84	0.14
WB26C	DP	392343076183504	Wetland sediments, upper peat unit	1.30	0.06
WB26D	DP	392343076183505	Wetland sediments, lower clayey unit	1.75	0.10
WB26F	DP	392343076183507	Canal Creek aquifer	4.65	0.10
WB33A	DP	392353076183301	Canal Creek aquifer	2.73	0.90
WB33B	DP	392353076183302	Canal Creek aquifer	4.34	0.90
WB34A	DP	392348076183410	Wetland sediments, upper peat unit	0.53	0.44
WB34B	DP	392348076183411	Canal Creek aquifer	2.30	0.42
WB35A	DP	392354076183402	Wetland sediments, upper peat unit	0.53	0.36
WB35B	DP	392354076183403	Wetland sediments, upper peat unit	0.93	0.39
WB35C	DP	392354076183404	Canal Creek aquifer	2.27	0.39
WB35E	DP	392354076183406	Canal Creek aquifer	5.56	0.39
WB36A	DP	392355076183402	Wetland sediments, upper peat unit	0.59	0.39
WB36B	DP	392355076183403	Wetland sediments, upper peat unit	0.90	0.30
WB36C	DP	392355076183404	Canal Creek aquifer	2.24	0.32
		Multilevel samplers (MLSs)			
WBM23A	MLS	392341076183407	Wetland sediments, upper peat unit	0.23	0.43
WBM23B	MLS	392341076183408	Wetland sediments, upper peat unit	0.46	0.43
WBM23C	MLS	392341076183409	Wetland sediments, lower clayey unit	0.76	0.43
WBM23D	MLS	392341076183410	Wetland sediments, lower clayey unit	1.52	0.43
WBM23E	MLS	392341076183411	Wetland sediments, lower clayey unit	2.67	0.43
WBM23F	MLS	392341076183412	Wetland sediments, lower clayey unit	3.28	0.43
WBM23G	MLS	392341076183413	Canal Creek aquifer	3.89	0.43

Table 1. Well-construction data for piezometers and multilevel samplers included in the temporal analysis, West Branch Canal Creek, Aberdeen Proving Ground Maryland, 1995–2000—Continued

Site name	Device used at the site	Site identification number	Hydrogeologic unit	Screened depth (meters below land surface)	Land-surface elevation (meters)
Multilevel samplers (MLSs)—Continued					
WBM24A	MLS	392343076183411	Wetland sediments, upper peat unit	0.37	0.56
WBM24B	MLS	392343076183412	Wetland sediments, upper peat unit	0.67	0.56
WBM24C	MLS	392343076183413	Wetland sediments, upper peat unit	1.01	0.56
WBM24D	MLS	392343076183414	Wetland sediments, upper peat unit	1.83	0.56
WBM24E	MLS	392343076183415	Wetland sediments, lower clayey unit	2.44	0.56
WBM24F	MLS	392343076183416	Canal Creek aquifer	3.66	0.56
WBM24G	MLS	392343076183417	Canal Creek aquifer	5.12	0.56
WBM30A	MLS	392344076183406	Wetland sediments, upper peat unit	0.35	0.50
WBM30B	MLS	392344076183407	Wetland sediments, lower clayey unit	0.69	0.50
WBM30C	MLS	392344076183408	Wetland sediments, lower clayey unit	0.99	0.50
WBM30D	MLS	392344076183409	Wetland sediments, lower clayey unit	1.45	0.50
WBM30E	MLS	392344076183410	Wetland sediments, lower clayey unit	2.06	0.50
WBM30F	MLS	392344076183411	Wetland sediments, lower clayey unit	2.97	0.50
WBM30G	MLS	392344076183412	Canal Creek aquifer	3.89	0.50
WBM34A	MLS	392348076183416	Wetland sediments, upper peat unit	0.53	0.55
WBM34B	MLS	392348076183417	Wetland sediments, upper peat unit	0.84	0.55
WBM34C	MLS	392348076183418	Wetland sediments, upper peat unit	1.14	0.55
WBM34D	MLS	392348076183419	Wetland sediments, lower clayey unit	1.45	0.55
WBM34E	MLS	392348076183420	Canal Creek aquifer	1.75	0.55
WBM34F	MLS	392348076183421	Canal Creek aquifer	2.01	0.55
WBM34G	MLS	392348076183422	Canal Creek aquifer	2.29	0.55
WBM36A	MLS	392348076183416	Wetland sediments, upper peat unit	0.30	--
WBM36B	MLS	392348076183417	Wetland sediments, upper peat unit	0.61	--
WBM36C	MLS	392348076183418	Wetland sediments, upper peat unit	0.91	--
WBM36D	MLS	392348076183419	Wetland sediments, upper peat unit	1.22	--
WBM36E	MLS	392348076183420	Wetland sediments, upper peat unit	1.52	--
WBM36F	MLS	392348076183421	Canal Creek aquifer	1.83	--
WBM36G	MLS	392348076183422	Canal Creek aquifer	2.26	--
Tracer test 0.64-centimeter piezometers					
E07-307	TP		Wetland sediments, upper peat unit	0.76	--
E14-082	TP		Wetland sediments, upper peat unit	0.76	--
E14-217	TP		Wetland sediments, upper peat unit	0.76	--
F07-015	TP		Wetland sediments, upper peat unit	0.91	--
F14-292	TP		Wetland sediments, upper peat unit	0.91	--
G14-225	TP		Wetland sediments, upper peat unit	1.07	--
G18-180	TP		Wetland sediments, upper peat unit	1.07	--
H07-210	TP		Wetland sediments, upper peat unit	1.22	--
H14-060	TP		Wetland sediments, upper peat unit	1.22	--
IO7-112	TP		Wetland sediments, upper peat unit	1.37	--

Table 2. Temporal sampling periods for piezometers and multilevel samplers, 1995–2000

Collection year	Collection season	Collection months	Number of samples collected
		Piezometers	
1996	Winter/Spring	March–April	23
1999	Winter/Spring	March; May	50
2000	Winter/Spring	March	25
1995	Summer/Fall	Comprehensive (June–October)	27
1996	Summer/Fall	June; August	45
1999	Summer/Fall	August	23
2000	Summer/Fall	June; Comprehensive (July)	28
		Multilevel samplers (MLSs)	
2000	Winter/Spring	March	41
2000	Summer/Fall	June	41
		Tracer Test 0.64-centimeter piezometers	
1999	Winter/Spring	February–March; May	4; 5
1999	Summer/Fall	August	5

row of sampling chambers was level with land surface. After the 3-week equilibration period, samples were collected from the individual chambers of the peeper by puncturing the porous membrane and immediately withdrawing the sample water using a glass syringe and rigid Teflon tubing. Generally, three peepers could be sampled in a day. Constituents analyzed in the peepers included redox-sensitive constituents (ferrous or total dissolved iron, sulfide, and methane) and VOCs (table 3). Chloride also was analyzed in the 122-cm long peepers (PL36), which held a larger sample volume than the 61-cm long peepers (table 3).

Analyses for specific conductance, pH, temperature, and alkalinity were done in the field for samples collected from the piezometers and MLSs. A commercial pH meter coupled with a temperature-compensated gel-filled probe was used to measure pH and temperature. Alkalinity as bicarbonate was determined by filtering the sample through a 0.45-µm filter, then analyzed using the inflection-point titration method. Major and selected trace cation and anion constituents were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Samples for NWQL cation analysis were filtered (0.45 µm) and acidified to pH less than 2.0 with ultrapure nitric acid; samples for NWQL anion analysis were filtered (0.45 µm) and chilled. Methods used by NWQL for analysis of inorganic constituents in water samples are given in Fishman and Friedman (1989) and in Fishman (1993). The median relative percent differences (RPDs) in replicate samples generally were 17 percent for the cations and anions analyzed by NWQL in 1995 and 1996, 1.6 percent in sample year 1999, and 0.33 percent in sample year 2000.

Redox constituents analyzed in the field or in the USGS on-site laboratory included iron, sulfide, and methane. Ferrous and total dissolved iron samples were filtered through a 0.2-µm filter, preserved with reagents in the field according to the colorimetric bipyridine technique (Brown and others, 1970; Baedecker and Cozzarelli, 1992), and then analyzed with a Bausch and Lomb Spectronic 21 spectrophotometer at 520 nm (nanometers). Sulfide was measured in the field on an unfiltered sample using a CHEMetrics A-1051 photometer kit. Methane samples were collected in duplicate for each piezometer by injection into sealed serum vials that contained mercuric chloride and nitrogen gas (Baedecker and Cozzarelli, 1992). Methane samples were analyzed using a gas chromatograph with a flame-ionization detector at the USGS on-site laboratory. Methane detection limits generally ranged from 55 µg/L to 133 µg/L; median RPDs in replicate samples generally were less than 20 percent during 1995–1996, 3.2 percent during 1999, and 1.7 percent during 2000.

VOC samples were collected in 8-mL glass vials and analyzed at the on-site USGS laboratory at West Branch Canal Creek. One exception is that samples collected from the MLSs in June 2000 were analyzed at the USGS District office in Trenton, New Jersey, using a gas chromatograph with an electrolytic conductivity detector. VOCs were analyzed at the on-site USGS laboratory using a gas chromatograph with a mass-selective detector following a modified U.S. Environmental Protection Agency (USEPA) method 524.2 (Rose and Schroeder, 1995). This method was modified to include an additional standard injected into each

Table 3. Peeper sampling dates and constituents analyzed, 1995–2001

[Peepers were installed 2 to 3 weeks prior to sampling date; V, volatile organic compounds; CH_4, methane; Fe, total dissolved iron; Fe^{2+}, ferrous iron; S, sulfide; Cl^-, chloride. Blanks indicate that peeper was not sampled.]

Sampling month	Peeper name (Piezometer site where peeper was installed)									
	P24 (WB24)	**P25 (WB25)**	**P26 (WB26)**	**P12 (DP12)**	**P19 (WB19)**	**P34 (WB34)**	**P35 (WB35)**	**P36 (WB36)**	**PL36 (WB36)**	**P37 (WB37)**
October/November 1995 [1]	10/25/1995 V, CH_4	10/25/1995 CH_4	10/25/1995 V, CH_4				11/03/1995 V, CH_4			11/03/1995 V
December 1995 [1]	12/15/1995 V	12/15/1995 V	12/15/1995 V							
March/April 1996 [2]							03/26/1996 V, CH_4	03/26/1996 V		04/03/1996 V
June 1996 [1]							06/01/1996 V, CH_4, Fe, Fe^{2+}, S	06/01/1996 V, CH_4		
November 1998 [3]				11/30/1998 V, CH_4, Fe, S	11/30/1998 V, CH_4, Fe, S		11/30/1998 V, CH_4, Fe, S			
February 1999 [3]				02/17/1999 V, CH_4, Fe, S	02/17/1999 V, CH_4, Fe, S		02/17/1999 V, CH_4, Fe, S	02/17/1999 V, CH_4, Fe, S		
May 1999 [3]				05/13/1999 V, CH_4, Fe, S	05/13/1999 V, CH_4, Fe, S		05/13/1999 V, CH_4, Fe, S	05/13/99 V, CH_4, Fe, S		
August 1999 [3]				08/04/1999 V, CH_4, Fe, S	08/04/1999 V, CH_4, Fe, S		08/04/1999 V, CH_4, Fe, S	08/04/1999 V, CH_4, Fe, S		
March 2000 [4]				03/27/2000 V, CH_4, Fe, S	03/27/2000 CH_4, Fe, S	03/23/2000 V, CH_4, Fe, S	03/27/2000 V, CH_4, Fe, S	03/23/2000 V, CH_4, Fe, S	03/23/2000 V, CH_4, Fe, Fe^{2+}, S, Cl^-	
June 2000 [4]				06/26/2000 V, CH_4, Fe^{2+}, S	06/26/2000 V, CH_4, Fe^{2+}, S	06/21/2000 V, CH_4, Fe^{2+}, S	06/26/2000 V, CH_4, Fe^{2+}, S	06/21/2000 V, CH_4, Fe^{2+}, S	06/21/2000 V, CH_4, Fe, Fe^{2+}, S, Cl^-	
May 2001 [4]							05/23/2001 V, CH_4, Fe^{2+}, S	05/18/2001 V, CH_4, Fe^{2+}, S		

[1] Data not reported previously.

[2] Data in Olsen and others (1997).

[3] Data in Spencer and others (2000).

[4] Data in Spencer and others (2002). Duplicate peepers (P35 and P35S) were installed and sampled at site WB35 in May 2001.

sample for validation purposes; three standards are injected instead of the two stipulated in the USEPA 524.2 method. The method also was modified to utilize a 5-mL sample volume, rather than the 25 mL required by USEPA method 524.2, to accommodate the limited sample volumes that could be collected from the piezometers and peepers. The lower detection limit for the VOCs typically ranged from 0.2 µg/L to 10 µg/L, depending on the specific analyte, instrument performance, and dilutions. The upper calibration limit ranged from 100 µg/L to 250 µg/L. Based on long-term observations, the instrument response is fairly linear to concentrations twice the calibration limit; therefore, concentrations detected between 250 and 500 µg/L were reported although they exceed the upper reporting limit of 250 µg/L. The median RPDs for replicate VOC analyses were 14.6 percent during 1995–1996, 21.2 percent during 1999, and 6.6 percent during 2000.

Hydrologic and Temperature Measurements

Synoptic water-level measurements were made in the piezometer network along both sections through the wetland approximately monthly between March 1995 and January 1996, and at least prior to each piezometer sampling event after 1996 (Olsen and others, 1997; Spencer and others, 2000). In addition, water levels were measured in water-table wells installed at several piezometer sites in the wetland and screened from 0 to 0.61 m below land surface (Olsen and others, 1997; Spencer and others, 2000). Water levels were measured using a steel tape and reported as elevations above or below mean sea level using surveyed elevations of the measuring point for each piezometer. Synoptic water-level measurements were made at high and low tides on most dates. A water-level data recorder in well CC27A has been used to obtain semi-continuous measurements of water levels in the aquifer in the uplands throughout this study. Thermistors were installed in the wetland sediment near site DP12 (fig. 1) and monitored with automatic-recording devices to obtain temporal measurements of temperatures during 1997–2001. Thermistors were set at depths of 0.15, 0.61, 1.07, and 2.13 m, giving measurements through the wetland sediment and to the top of the aquifer. Air temperature was monitored at the same location.

Temporal Changes in Indicators of Natural Attenuation

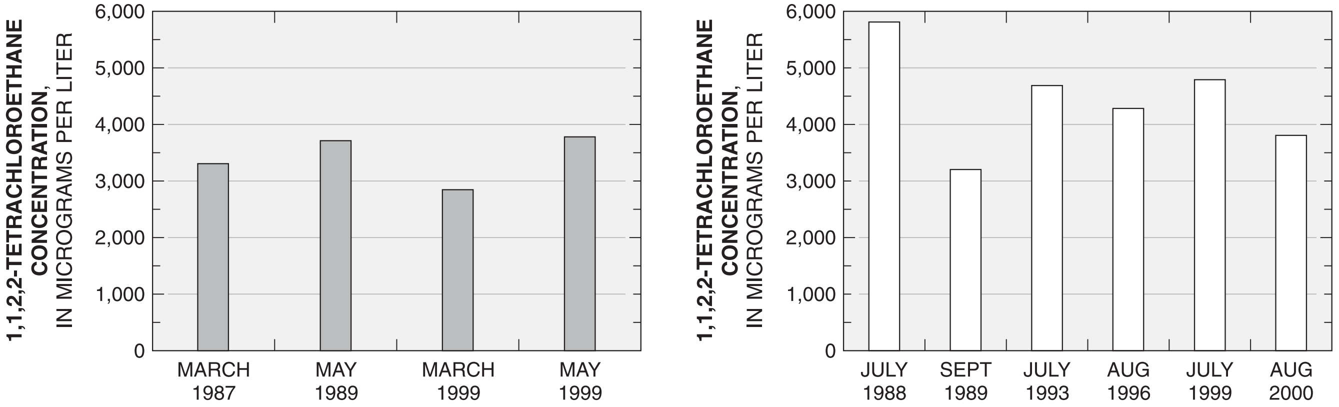
Areal Analysis

To conduct an areal analysis of temporal changes in the plumes along the two sections in the study area (fig. 1), changes in geochemistry were evaluated using the upland wells at site CC27, the upland piezometers at site WB33, and the piezometers within the wetland boundary that were selected for seasonal sampling during 1995–2000. Site WB33 is directly at the upland/wetland boundary along section C–C′ and about 30 m away from site CC27, located between the two sections (fig. 1). Concentrations in the aquifer at these two sites should be representative of concentrations entering the wetland area at the two sections. Additional sampling events prior to 1995 were included for the upland wells at site CC27 to evaluate the stability of the contaminant concentrations entering the wetland. For the piezometers in the wetland area, changes in contaminant concentrations in samples collected from piezometers screened in the aquifer and the wetland sediments were compared. The screens in all but four of these piezometers were placed deeper than 60 cm, screened in deeper wetland sediments and the aquifer. The piezometer sampling events were divided into two categories for temporal analysis on a seasonal basis—summer (June–September), which corresponds with the time of active plant growth, and spring (March–May), which corresponds with the time of plant quiescence through the initiation of growth (table 2). Variations in water-quality concentrations on a yearly basis also were evaluated.

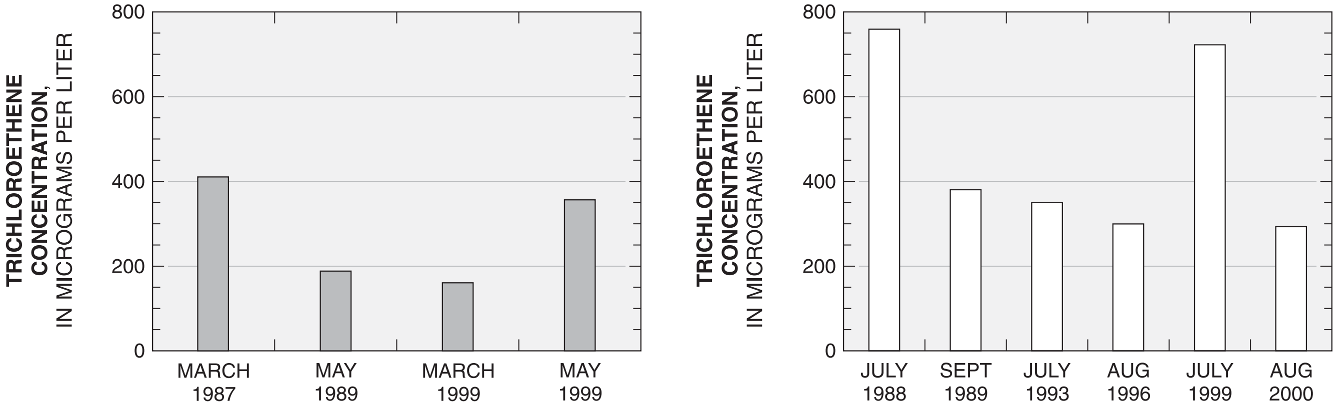
Chlorinated Volatile Organic Compounds

Although some seasonal change in VOC concentrations was observed in samples collected from the upland wells and piezometers screened in the aquifer at sites CC27 and WB33 (fig. 7), little seasonal change was observed in samples collected from the piezometers screened in the aquifer and deeper wetland sediments within the wetland boundary (fig. 8). The parent compounds TeCA and TCE were the major contaminants in the upland wells at CC27, while TeCA was the only major VOC in the upland piezometers at WB33. Concentrations of TeCA and TCE in CC27A and WB33A, which are screened at a shallow depth in the aquifer (figs. 3 and 4), generally were higher in samples collected in the summer than those collected in the spring (figs. 7a–f). TeCA concentrations commonly were 4,000 µg/L or higher in CC27A in the summer and less than 4,000 µg/L in the spring (figs. 7a–b); a similar trend of higher summer concentrations was observed for TCE (figs. 7c–d). In samples from WB33A, TeCA concentrations were between 1,500 and 2,400 µg/L in the summer, whereas concentrations were 1,000 µg/L or less in most samples collected in the spring (figs. 7e–f). The difference in spring and summer VOC concentrations at CC27A and WB33A generally was greater than the highest median RPD for replicate VOC analyses of 21 percent that was obtained in 1999; the median RPDs for replicate VOC analyses were less than 15 percent for other sampling years. Samples from deeper in the aquifer (wells CC27B and WB33B) at these upland sites had TeCA and TCE concentrations that were a factor of 5 to 10 lower than those observed at shallow depths in the aquifer at CC27A and WB33A (figs. 3 and 4). VOC concentrations in CC27B and WB33B were consistently higher in the summer compared to the spring (data not shown), as observed at shallow depth in the aquifer (figs. 7a–f).

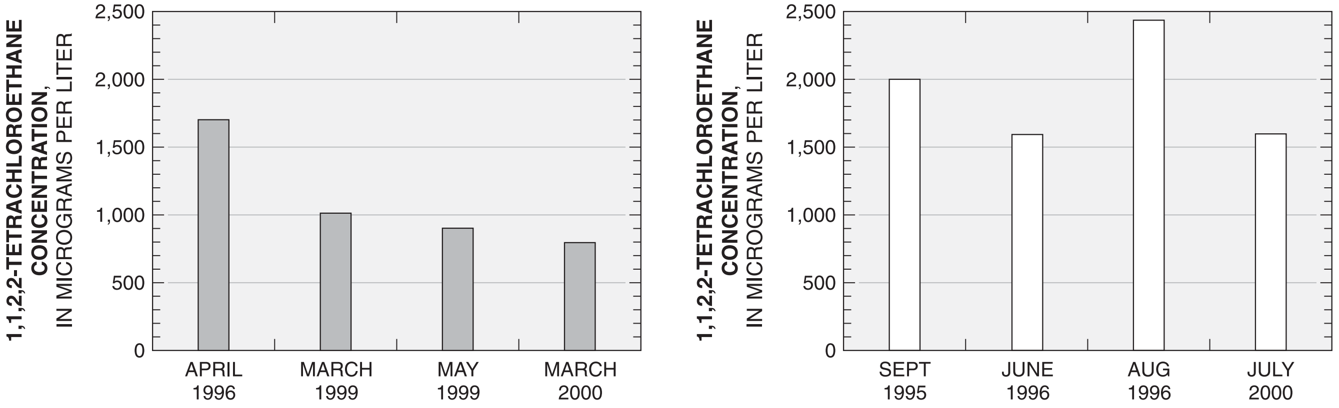
Although seasonal fluctuations apparently occurred, VOC concentrations over the more than 10 years that samples have been collected at site CC27 did not show a substantial decline that would indicate a change in the source mass (fig. 7). Instead, the contaminant plume entering the


(a) Well CC27A, Spring

(b) Well CC27A, Summer


(c) Well CC27A, Spring

(d) Well CC27A, Summer


(e) Well WB33A, Spring

(f) Well WB33A, Summer

Figure 7. Temporal changes in concentrations of chlorinated volatile organic compounds in the aquifer at the upland sites CC27 and WB33: **(a)** concentrations of 1,1,2,2-tetrachloroethane (TeCA) in samples collected from well CC27A in the spring; **(b)** concentrations of TeCA in samples collected from well CC27A in the summer; **(c)** concentrations of trichloroethene (TCE) in samples collected from well CC27A in the spring; **(d)** concentrations of TCE in samples collected from well CC27A in the summer; **(e)** concentrations of TeCA in samples collected from well WB33A in the spring; and **(f)** concentrations of TeCA in samples collected from well WB33A in the summer.

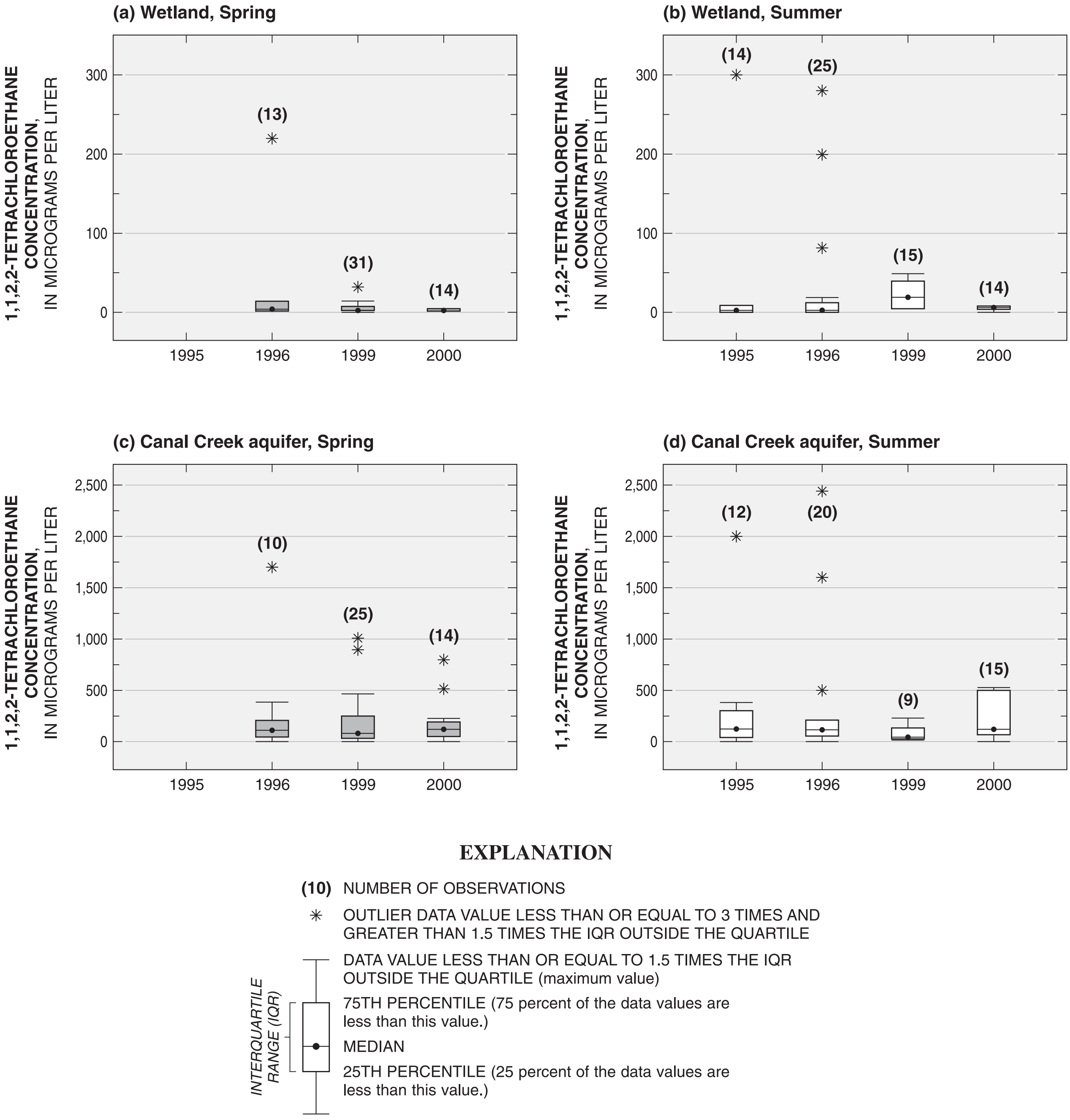


Figure 8. Concentrations of 1,1,2,2-tetrachloroethane (TeCA) in piezometer samples from the wetland sediment in the **(a)** spring and **(b)** summer, and from the Canal Creek aquifer in the **(c)** spring and **(d)** summer.

wetland appears to be at steady state, which is consistent with the hypothesis that continued dissolution of residual DNAPL provides a long-term source of contamination (Lorah and others, 1997).

The pattern of higher VOC concentrations in the summer compared to the spring was not evident in samples collected from piezometers within the wetland boundary and screened in the aquifer or wetland sediments (table 4; fig. 8). Median TeCA concentrations in the aquifer were between 80 and 125 µg/L in both the summer and spring, except for a lower median concentration of 38 µg/L in the summer of 1999 (table 4, figs. 8c–d). TCE, carbon tetrachloride, and chloroform are parent VOCs that also were detected frequently and in relatively high concentrations in the piezometer aquifer samples without showing an apparent seasonal trend (tables 4 and 5). Median TeCA concentrations in the piezometer samples from the wetland sediments were substantially lower than in the aquifer, ranging from 1.5 to 5.7 µg/L in all except one sampling event without showing an apparent seasonal trend (table 4). In addition, no seasonal trend was apparent in concentrations or detection frequency of the daughter compounds 12DCE, VC, 112TCA, and 12DCA in the piezometer samples from the wetland sediments or aquifer (tables 4 and 5). In the piezometer samples collected from the wetland sediments, the daughter compounds 12DCE and VC were commonly detected (40 to 79 percent), and had median concentrations (2.6 to 15.2 µg/L) as high or higher than those of the parent compounds TeCA and TCE. The chlorinated daughter compounds 12DCE, 112TCA, and 12DCA commonly were detected in more than 50 percent of the piezometer samples collected from the aquifer, but their median concentrations were about a factor of 10 lower than those of the parent compounds TeCA, TCE, carbon tetrachloride, and chloroform in the aquifer (tables 4 and 5).

Major Ions and Other Geochemical Parameters In contrast to the VOCs, a consistent seasonal change in concentrations of major inorganic constituents and specific conductance was not observed in the upland/boundary wells at sites CC27 and WB33. Chloride, which typically acts as a conservative constituent in ground water, is shown in figure 9 as an example of temporal variation in major ions. Because chloride analyses were not available for all sampling periods, especially for WB33A samples, specific conductance also is shown. Comparison of chloride concentrations and specific conductance values for well CC27A shows that specific conductance variations are indicative of chloride variations (figs. 9a–d). Chloride concentrations and specific conductance values were the same or slightly lower in CC27A in the summer compared to the spring. Although major ions and specific conductance varied from year to year, spring and summer concentrations were not substantially different. Specific conductance in CC27A was about 400 µS/cm (microsiemens per centimeter) in the spring of 1987 and 1989 and also about 400 µS/cm in the summer of 1988 and 1989; specific conductance increased to about 800 µS/cm in spring of 1999 and a similar value of about 700 µS/cm was then seen in the summer of 1999 (figs. 9c,d). A large increase in chloride and specific conductance in CC27A was seen in August 1996, but corresponding spring data were not collected. Specific conductance values in WB33A were approximately the same in the summer and spring samples (figs. 9e,f). The large increase observed in well CC27A in August 1996 was not observed at WB33A. The deeper aquifer wells CC27B and WB33B also showed similar ranges of specific conductance values in the spring compared to the summer, although too few chloride analyses were available to discern a temporal pattern (data not shown). The chloride and specific conductance data contrast with the consistently higher VOC concentrations in the summer compared to the spring at both sites.

For the piezometers in the wetland area, no substantial seasonal variation was observed in concentrations of inorganic constituents and field parameters, which is consistent with the lack of seasonal variation in VOCs observed in these piezometers (tables 4 and 6). Tables 6 and 7 summarize the median and maximum concentrations and the detection frequency of representative major ions (chloride and sulfate), field parameters (pH and specific conductance), and redox-sensitive constituents (ferrous iron, methane, and sulfide). Chloride concentrations in the spring and summer piezometer samples also are shown in figure 10. Chloride had approximately the same median and range of concentrations in the spring as those in the summer for the piezometers screened in the wetland sediment (figs. 10a–b). A similar lack of seasonal difference in chloride concentrations was observed for the piezometers screened in the aquifer (figs. 10c–d). During the 1995–2000 sampling period, chloride concentrations in the aquifer were highest in 1996 with medians of 82 mg/L (milligrams per liter) in the spring and 73 mg/L in the summer. In comparison, median chloride concentrations in the aquifer were between 40 and 56 mg/L during the other sampling years (table 6). Specific conductance values showed a similar temporal trend as chloride concentrations. Sulfate concentrations were more variable than the chloride or specific conductance, but also did not show a consistent seasonal difference for the upland or wetland piezometers (table 6).

Vertical Flowpath Analysis

Temporal changes in distributions of chlorinated VOCs, redox-sensitive constituents, and chloride were evaluated along vertically upward flowpaths through the wetland sediments using the peeper data collected between 1995–2001 (table 3) and the MLS data collected in 2000. The 61-cm-long peepers provide high spatial resolution of chemical changes in the upper 61 cm of the upper peat unit of the wetland sediments, whereas only 4 of the 28 piezometers that were sampled seasonally have screens less than 61 cm deep (table 1). Comparison of the peeper results to the results from the peepers and MLSs during the ESTCP study indicated that the peepers give the most reliable data in this upper 61 cm of sediment (Dyer and others, 2002).

The MLSs, which are located at two sites along section A–A′, two sites along section C–C′, and one site in between the two sections (fig. 1), were used to evaluate temporal

Table 4. Median and maximum concentrations of volatile organic compounds in water samples from piezometers screened in wetland and aquifer sediments, comparing spring and summer sampling events

[All concentrations in micrograms per liter. Duplicate samples not included. Max, maximum concentration; --, not detected or only one detection]

				Parent Compounds										Daughter Compounds									
				1,1,2,2-Tetrachloroethane		Tetrachloroethene		Trichloroethene		Carbon tetrachloride		Chloroform		*cis*-1,2-Dichloroethene		*trans*-1,2-Dichloroethene		Vinyl chloride		1,1,2-Trichloroethane		1,2-Dichloroethane	
Collection year	**Collection season**	**Collection months**	**Screen location**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**	**Median**	**Max**
1996	Spring	March–April	Wetland	2.6	220	4.3	6.8	11	160	--	--	6.0	8.1	9.1	35.5	3.5	74	8.4	97	8.0	28	2.7	15
1999	Spring	March–May	Wetland	3.0	32	1.8	2.3	9.0	60	--	--	4.8	10	5.2	40.7	4.0	66	10	41	4.9	38	1.3	2.1
2000	Spring	March	Wetland	3.2	4.8	--	--	6.2	15	--	--	--	--	2.6	48	15	37	5.3	18	2.3	3.2	1.2	2.3
1995	Summer	June–October	Wetland	1.5	300	1.8	2.2	9.8	69	--	--	4.2	6.3	10	26	1.9	25	5.5	59	0.90	32	1.2	6.4
1996	Summer	June–August	Wetland	2.4	280	2.6	5.8	11	160	22	43	5.1	110	9.4	47	6.6	72	4.0	27	3.9	36	3.1	17
1999	Summer	August	Wetland	18	49	2.9	4.2	13	74	7.1	11	16	17	5.3	45.8	12	55	8.4	22	6.2	400	3.3	4.6
2000	Summer	June–July	Wetland	5.7	11	1.4	1.7	7.5	62	--	--	1.4	2.2	4.25	45.8	6.0	52	11	32	2.3	2.8	1.6	3.1
1996	Spring	March–April	Aquifer	110	1,700	5.1	8.5	42	160	36	110	20	310	3.35	17	0.6	18	--	--	1.4	22	2.5	6.2
1999	Spring	March–May	Aquifer	81	1,000	2.2	6.3	29	110	10	140	25	240	3.0	29.4	0.8	21	4.8	9.4	1.7	40	2.6	6.3
2000	Spring	March	Aquifer	125	800	1.8	5.1	57	110	11	100	15	160	2.25	9.2	1.9	12	--	--	3.6	12	4.1	4.4
1995	Summer	June–October	Aquifer	120	2,000	1.1	6.5	30	130	8.5	77	15	230	1.6	23	0.6	13	1.6	2.3	1.2	24	1.0	4.8
1996	Summer	June–August	Aquifer	110	2,440	3.8	14	66	320	26	160	26	330	4.25	24	1.6	21	4.6	5.5	1.4	21	2.3	6.7
1999	Summer	August	Aquifer	38	230	2.0	5.8	35	100	14	110	40	140	3.35	40.1	1.6	69	--	--	4.0	4.5	2.1	3.5
2000	Summer	June–July	Aquifer	120	530	2.9	4.8	60	130	7.8	88	10	150	6.4	17.3	1.6	30.9	9.4	17	1.5	24	2.3	4.4

Table 5. Number of samples collected and the detection frequency for volatile organic compounds in water samples from piezometers screened in wetland and aquifer sediments, comparing spring and summer sampling events

					Detection frequency as percentage of total number of samples (number of detections)									
					Parent Compounds					Daughter Compounds				
Collection year	Collection season	Collection months	Screen location	Total number of samples collected	1,1,2,2-Tetra-chloro-ethane	Tetra-chloro-ethene	Tri-chloro-ethene	Carbon tetra-chloride	Chloro-form	*cis*-1,2-Dichloro-ethene	*trans*-1,2-Dichloro-ethene	Vinyl chloride	1,1,2-Trichloro-ethane	1,2-Di-chloro-ethane
1996	Spring	March–April	Wetland	13	54 (7)	15 (2)	54 (7)	7 (1)	15 (2)	69 (9)	69 (9)	54 (7)	23 (3)	15 (2)
1999	Spring	March, May	Wetland	27	59 (16)	11 (3)	78 (21)	0 (0)	11 (3)	63 (17)	44 (12)	67 (18)	44 (12)	19 (5)
2000	Spring	March	Wetland	13	23 (3)	0 (0)	38 (5)	0 (0)	0 (0)	54 (7)	38 (5)	61 (8)	23 (3)	31 (4)
1995	Summer	June–October	Wetland	14	36 (5)	14 (2)	43 (6)	0 (0)	14 (2)	79 (11)	64 (9)	50 (7)	36 (5)	43 (6)
1996	Summer	June–August	Wetland	25	80 (20)	20 (5)	56 (14)	8 (2)	24 (6)	68 (17)	48 (12)	44 (11)	28 (7)	44 (11)
1999	Summer	August	Wetland	15	27 (4)	13 (2)	53 (8)	13 (2)	13 (2)	60 (9)	40 (6)	47 (7)	27 (4)	20 (3)
2000	Summer	June–July	Wetland	14	29 (4)	14 (2)	50 (7)	0 (0)	14 (2)	57 (8)	50 (7)	57 (8)	29 (4)	43 (6)
1996	Spring	March–April	Aquifer	10	90 (9)	50 (5)	100 (10)	70 (7)	90 (9)	80 (8)	70 (7)	10 (1)	60 (6)	50 (5)
1999	Spring	March, May	Aquifer	23	91 (21)	65 (15)	100 (23)	69 (16)	83 (19)	74 (17)	61 (14)	13 (3)	57 (13)	35 (8)
2000	Spring	March	Aquifer	12	100 (12)	75 (9)	100 (12)	83 (10)	100 (12)	83 (10)	25 (3)	8 (1)	33 (4)	50 (6)
1995	Summer	June–October	Aquifer	13	85 (11)	93 (12)	85 (11)	77 (10)	93 (12)	85 (11)	100 (13)	15 (2)	85 (11)	85 (11)
1996	Summer	June–August	Aquifer	20	90 (18)	70 (14)	85 (17)	70 (14)	90 (18)	80 (16)	40 (8)	10 (2)	55 (11)	65 (13)
1999	Summer	August	Aquifer	8	88 (7)	88 (7)	100 (8)	88 (7)	88 (7)	75 (6)	50 (4)	13 (1)	38 (3)	38 (3)
2000	Summer	June–July	Aquifer	14	93 (13)	64 (9)	100 (14)	71 (10)	100 (14)	93 (13)	50 (7)	29 (4)	86 (12)	71 (10)

Table 6. Median and maximum concentrations of selected inorganic constituents and field parameters in water samples from piezometers screened in wetland and aquifer sediments, comparing spring and summer sampling events

[Duplicate samples not included. mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter; --, not detected or only one detection; NA, not analyzed]

Collection year	Collection season	Collection months	Screen location	Chloride, mg/L as Cl		Sulfate, mg/L as SO_4		pH, standard units		Specific conductance, µS/cm		Iron, Ferrous mg/L as Fe		Methane µg/L		Sulfide µg/L as S	
				Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum	Median	Maximum
1996	Spring	March–April	Wetland	100	250	48	140	6.14	6.62	510	1,260	4.27	34.2	2,900	12,000	15	660
1999	Spring	March, May	Wetland	96	450	3.7	120	6.19	7.30	470	3,210	4.86	72.2	1,860	14,200	10	62
2000	Spring	March	Wetland	98	440	22	120	5.90	6.80	470	1,800	3.60	92.2	1,360	13,600	1	25
1995	Summer	June–October	Wetland	110	340	16	78	6.20	6.91	560	3,690	4.73	16.2	1,060	7,900	22	920
1996	Summer	June–August	Wetland	93	240	46	120	5.90	6.39	490	1,090	4.49	15.2	1,650	12,000	100	1,300
1999	Summer	August	Wetland	NA	NA	NA	NA	6.17	7.06	590	3,730	4.79	95.6	1,090	13,600	7	72
2000	Summer	June–July	Wetland	77	370	47	140	5.90	6.60	490	2,040	7.10	56.9	1,300	14,200	5	75
1996	Spring	March–April	Aquifer	82	350	110	200	4.82	7.26	510	1,100	0.05	0.94	--	--	0	0
1999	Spring	March, May	Aquifer	40	88	81	120	4.68	6.87	450	1,150	0.25	2.86	304	697	4	140
2000	Spring	March	Aquifer	43	270	84	130	4.70	6.90	380	620	0.10	0.2	0	451	0	10
1995	Summer	June–October	Aquifer	56	120	110	210	4.81	5.87	450	860	0.10	1.96	0	550	0	590
1996	Summer	June–August	Aquifer	73	110	99	190	4.80	7.03	460	860	0.15	0.53	103	170	0	50
1999	Summer	August	Aquifer	NA	NA	NA	NA	4.70	7.31	430	700	0.07	0.49	--	--	8	74
2000	Summer	June–July	Aquifer	46	97	75	140	4.65	6.10	430	660	0.06	2.9	0	353	0	120

Table 7. Number of samples collected and the detection frequency for selected inorganic constituents and field parameters in water samples from piezometers screened in wetland and aquifer sediments, comparing spring and summer sampling events

					Detection frequency as percentage of total number of samples (number of detections)						
Collection year	Collection season	Collection months	Screen location	Total number of samples collected	Chloride	Sulfate	pH	Specific conductance	Iron, Ferrous	Methane	Sulfide
1996	Spring	March–April	Wetland	13	92 (12)	92 (12)	92 (12)	100 (13)	92 (12)	85 (11)	92 (12)
1999	Spring	March, May	Wetland	26	50 (13)	46 (12)	100 (26)	96 (25)	85 (22)	77 (20)	62 (16)
2000	Spring	March	Wetland	13	69 (9)	69 (9)	92 (12)	92 (12)	85 (11)	100 (13)	85 (11)
1995	Summer	June–October	Wetland	14	86 (12)	86 (12)	100 (14)	93 (13)	93 (13)	100 (14)	100 (14)
1996	Summer	June–August	Wetland	26	85 (22)	85 (22)	92 (24)	96 (25)	100 (26)	85 (22)	100 (26)
1999	Summer	August	Wetland	14	7 (1)	7 (1)	100 (14)	93 (13)	86 (12)	79 (11)	50 (7)
2000	Summer	June–July	Wetland	14	57 (8)	57 (8)	93 (13)	93 (13)	100 (14)	100 (14)	100 (14)
1996	Spring	March–April	Aquifer	9	100 (9)	100 (9)	100 (9)	100 (9)	9 (5)	11 (1)	78 (7)
1999	Spring	March, May	Aquifer	24	63 (15)	63 (15)	100 (24)	100 (24)	38 (9)	17 (4)	50 (12)
2000	Spring	March	Aquifer	11	82 (9)	82 (9)	100 (11)	100 (11)	82 (9)	100 (11)	82 (9)
1995	Summer	June–October	Aquifer	12	100 (12)	100 (12)	92 (11)	92 (11)	100 (12)	100 (12)	83 (10)
1996	Summer	June–August	Aquifer	20	100 (20)	100 (20)	100 (20)	100 (20)	45 (9)	10 (2)	95 (19)
1999	Summer	August	Aquifer	11	0 (0)	0 (0)	100 (11)	91 (10)	36 (4)	9 (1)	82 (9)
2000	Summer	June–July	Aquifer	12	75 (9)	75 (9)	100 (12)	100 (12)	100 (12)	100 (12)	100 (12)

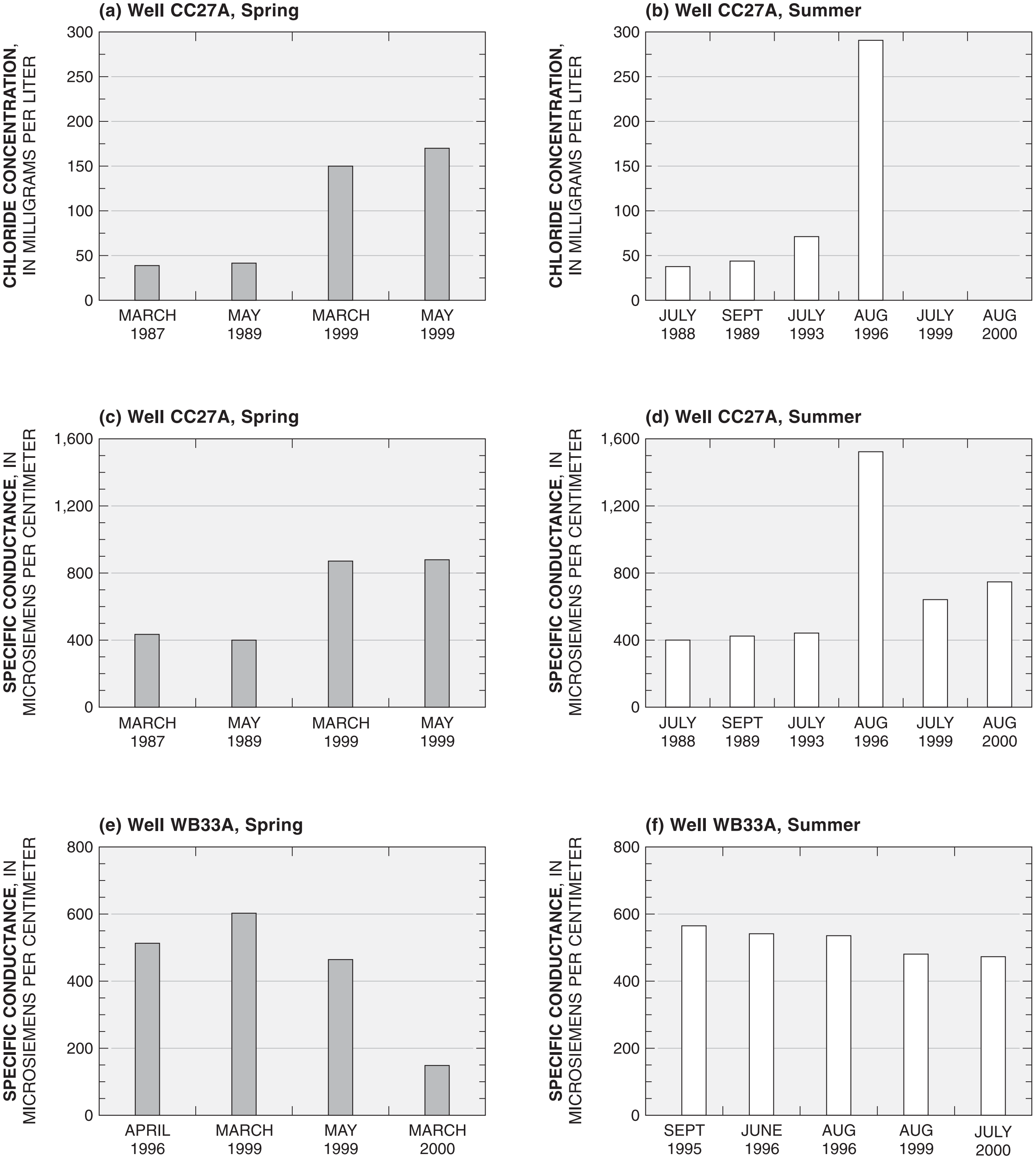


Figure 9. Temporal changes in concentrations of chloride and specific conductance in the aquifer at the upland sites CC27 and WB33: **(a)** concentrations of chloride in samples collected from well CC27A in the spring; **(b)** concentrations of chloride in samples collected from well CC27A in the summer; **(c)** specific conductance in samples collected from well CC27A in the spring; **(d)** specific conductance in samples collected from well CC27A in the summer; **(e)** specific conductance in samples collected from well WB33A in the spring; and **(f)** specific conductance in samples collected from well WB33A in the summer.

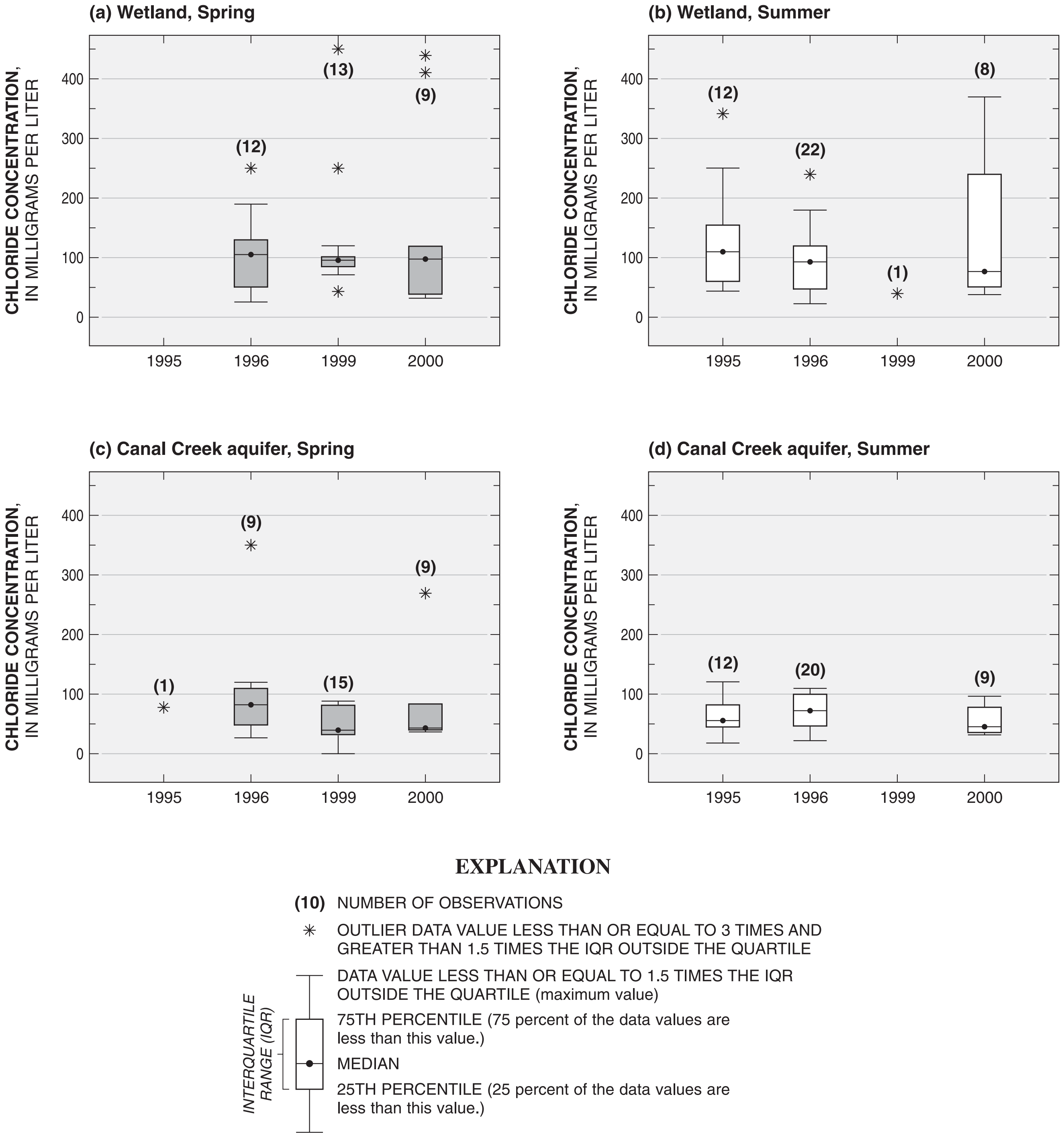


Figure 10. Concentrations of chloride in piezometer samples from the wetland sediment in the **(a)** spring and **(b)** summer, and from the Canal Creek aquifer in the **(c)** spring and **(d)** summer.

changes along vertically upward flowpaths in the deeper wetland sediments, including the lower clayey unit. The 1.9-cm-diameter piezometer nest at site WB26 along section A–A′ also was used to evaluate temporal change along flowpaths in the deeper wetland sediments because screened depth intervals are comparable to the MLSs at this site. Although the MLSs do not provide as high a degree of vertical resolution as the peepers, they do provide an indication of changes throughout the entire thickness of wetland sediment and across the study area. Temporal analysis of the MLS data, however, was limited because data from only two sampling events were available.

Chlorinated Volatile Organic Compounds Temporal changes in chlorinated VOC concentrations in the shallow porewater of the upper peat unit could only be evaluated for the section C–C′, where VOC concentrations were consistently detectable. Little or no VOC contamination was found in the upper 61 cm of wetland sediment along section A–A′. During two seasons in 1995, peepers were sampled at three sites along section A–A′, where contaminated ground water is known to discharge vertically upward through the wetland sediments—sites WB24, WB25, and WB26 (fig. 1; table 1). These peeper samples did not have detectable concentrations of chlorinated VOCs (data on file, USGS, Baltimore, Maryland), indicating that natural attenuation processes in the deeper wetland sediments had removed the VOCs before the upper 61 cm of sediment was reached. The non-detectable concentrations in the peepers placed along section A–A′ were consistent with those in the piezometers (fig. 5). In addition, VOCs were not detectable in peepers installed at background site WB19 along section A–A′. The VOC concentrations most likely are higher in the shallow sediment along section C–C′ compared to A–A′ because the thinner wetland sediments along C–C′ result in a shorter residence time for anaerobic biodegradation and other natural attenuation processes to occur. Along section C–C′, the greatest number of peeper sampling events occurred at sites WB35, WB36, and DP12 (table 3). VOCs were not detectable in the peepers placed at the edge of the plume at site WB37.

The VOCs detected in all peeper samples consisted primarily of daughter compounds of TeCA or TCE; parent compounds TeCA or TCE were detected infrequently and in lower concentrations than the daughter compounds. Of 495 samples collected from peepers along section C–C′ between 1995–2001, the most frequently detected VOCs were the daughter compounds VC, c12DCE, and t12DCE, which were detected in more than half the samples (table 8). In contrast, the parent compound TeCA was detected in only 35 peeper samples. Although TCE was detected in more peeper samples than TeCA, TCE could be both a parent and a daughter compound (fig. 2). Mean concentrations of the daughter compounds VC, c12DCE, and t12DCE were 26.3, 7.71, and 11.6 µg/L, respectively, whereas TeCA and TCE had mean concentrations of 1.63 and 1.69 µg/L, respectively (table 8).

A consistent temporal pattern in VOC concentrations was observed in samples from peepers installed at sites WB35 and WB36 between 1995–2001 (figs. 11a–b). Concentrations of total chlorinated VOCs at these two sites were substantially higher in the summer/fall than those in the winter/spring. Between about 30 and 60 cm below land surface at site WB35, total chlorinated VOC concentrations ranged from 1.0 to 4.0 µM (micromolar) in the 5 sampling events that occurred in the fall/summer, whereas concentrations were consistently below 0.6 µM in the 5 sampling events in the winter/spring (fig. 11a). At the same depths (30 and 60 cm below land surface) at site WB36, total chlorinated VOC concentrations ranged from 0.6 to 2.0 µM in the fall/summer sampling events, whereas concentrations generally were below 0.5 µM in the winter/spring sampling events (fig. 11b). The highest VOC concentrations at both sites were measured in the two June sampling events (figs. 11a–b). Total VOC concentrations were below detection in the upper 10 cm at site WB35 at all sampling events (fig. 11a), but low VOC concentrations remained near land surface in several of the spring sampling events at site WB36 (fig. 11b). The non-detectable or low VOC concentrations in the shallow porewater throughout the year indicate that natural attenuation is effective during all seasons.

No consistent temporal pattern could be discerned in the peepers sampled at site DP12, which is closer to the wetland/upland boundary than sites WB35 and WB36 (figs. 6 and 11c). For three of the six peeper sampling events at site DP12, VOCs were non-detectable over most or all the 60-cm depth interval. For the remaining three sampling events at DP12, similar VOC concentrations were detected between 30 and 60 cm below land surface in the summer/fall and winter/spring (fig. 11c). The two peeper sampling events at site WB34, which is located near site DP12 (fig. 1), showed that VOC concentrations were about twice as high in the summer than in the spring at depths between about 40 and 60 cm below land surface (fig. 11d). VOCs were not detected in the upper 40 cm of wetland sediment at WB34, as was the case at site DP12.

At sites WB35 and WB36, where temporal changes in total chlorinated VOCs were evident, only the concentrations of daughter compounds changed, while concentrations of the parent compound TeCA remained undetectable in the peeper samples during each sampling event. Concentration profiles for TeCA and for each of the possible chlorinated daughter compounds under anaerobic conditions are shown for the peepers at site WB35 during 1995–2000 (fig. 12). As in previous studies at this site, 12DCE and VC were the predominant daughter compounds observed. Concentration profiles for the individual compounds at site WB36 (data not shown) were similar to those at site WB35, except for a greater predominance of VC than 12DCE (fig. 13). During the sampling events of 1995–1996 and 1998–1999, concentrations of 12DCE and VC showed the same temporal increase from winter to summer with little change in the depths at which the peak concentration of each compound occurred (fig. 12). In 1999, for example, 12DCE was the dominant daughter compound at depths of 30 to 60 cm

Table 8. Summary of concentrations and frequency of detections of volatile organic compounds in peepers sampled at sites WB34, WB35, WB36, WB37, and DP12 along the C–C′ transect, 1995–2001

[Concentrations are in micrograms per liter. A total of 495 samples were collected from peepers at these sites, but all values less than 0.2 micrograms per liter were excluded from the statistical summary.]

	1,1,2,2-Tetrachloroethane	1,1,2-Trichloroethane	1,2-Dichloroethane	Chloroethane	Trichloroethene	1,2-*trans*-dichloroethene	1,2-*cis*-dichloroethene	Vinyl chloride	Toluene
Mean	1.63	1.61	2.90	7.45	1.69	11.6	7.71	26.3	21.3
Median	1.43	1.25	1.47	4.77	1.18	5.85	5.54	15.8	3.41
Minimum	.53	.33	.27	.65	.50	.25	.23	.50	.28
Maximum	5.93	10.1	18.5	24.5	5.68	61.9	49.5	233	295
Count	35	66	149	16	115	278	313	340	113

below land surface, and VC was the dominant daughter compound in a relatively narrow zone of 15 to 25 cm below land surface during each sampling event. Peak concentrations of 12DCE and VC within these zones increased by a factor 3 to 4 from February 1999 (winter) to August 1999 (summer) (fig. 12). Although the concentrations varied between the different sampling periods of 1995–1996, 1998–1999, and 2000, this general seasonal pattern within each period was the same. On most sampling dates, 12DCE concentrations decreased along the upward flowpath as VC concentrations increased, which is consistent with 12DCE degradation to VC by reductive dechlorination. In fact, the peak molar concentrations of 12DCE and VC at site WB35 often were nearly equal (fig. 12), indicating a relatively good mass balance. One exception to this pattern and the general 12DCE:VC mass balance at site WB35 was seen in June 2000, when VC concentrations were dominant at all depths and reached concentrations nearly four times as high as the 12DCE concentrations.

The anomalously higher VC concentrations in June 2000 at site WB35 compared to concentrations during other sampling events are evident when VC concentrations are plotted against 12DCE concentrations for all peeper samples collected (figs. 13a–b). If reductive dechlorination of the measured 12DCE accounted for all VC detected, then sample concentrations would fall on the 12DCE:VC 1:1 line (fig. 14). Sample concentrations were well above the 1:1 line in June 2000 for site WB35, whereas concentrations were in a fairly uniform band around the 1:1 line during all other sampling events. At site WB36, however, sample concentrations were above the 1:1 line during all sampling events, indicating that VC concentrations were consistently higher than could be accounted for by reductive dechlorination of the12DCE detected in peeper samples at the site (figs. 13c–d). Although dichloroelimination of 112TCA also produces VC, 112TCA was detected infrequently and in concentrations lower than 12DCE (total of *cis*- and *trans*- isomers) by a factor of 10 in the peeper samples (table 8). Thus, the unusually high proportion of VC at site WB36, and at site WB35 in June 2000, indicates the presence of a different contaminant plume than the one originating from the upland and flowing toward the creek along section C–C′. The possible existence of another contaminant plume is discussed further in the section on Ground-Water Flow.

No temporal change in the 12DCE to VC ratio was observed at either site. Excluding the June 2000 peeper samples at site WB35, the 12DCE:VC concentrations showed the same general trend lines for each site in the winter/spring compared to the summer/fall, with concentrations of both constituents higher in the summer/fall (figs. 13b,d). Concentrations of the *cis*- and *trans*- isomers of 12DCE also showed the same ratio in the winter/spring compared to the summer/fall, with concentrations of both constituents higher in the summer/fall (figs. 14a–b). Thus, the phenomenon causing the temporal variation in VOC concentrations equally affects the production or transport of c12DCE, t12DCE, and VC, rather than a change in rate in one part of the degradation pathway or in the transport of one constituent. Possible physical factors that could control these temporal changes are discussed in the section on Temporal Changes in Physical Controlling Factors.

Toluene was the only contaminant other than the chlorinated VOCs observed in substantial concentrations in the peeper samples. Toluene, however, was not detected during all sampling events at a site (figs. 15a–d). Toluene was detected in peepers at sites WB35 and WB36 in June 1996, at site WB34 in June 2000, and at site DP12 in August 1999 and June 2000 (figs. 15a–d). Peepers were not sampled at sites WB34 and DP12 in June 1996; peepers were sampled at sites WB35 and WB36 in June 2000, but toluene concentrations were near or below detection levels. As was observed with the chlorinated VOCs, the highest toluene concentra-

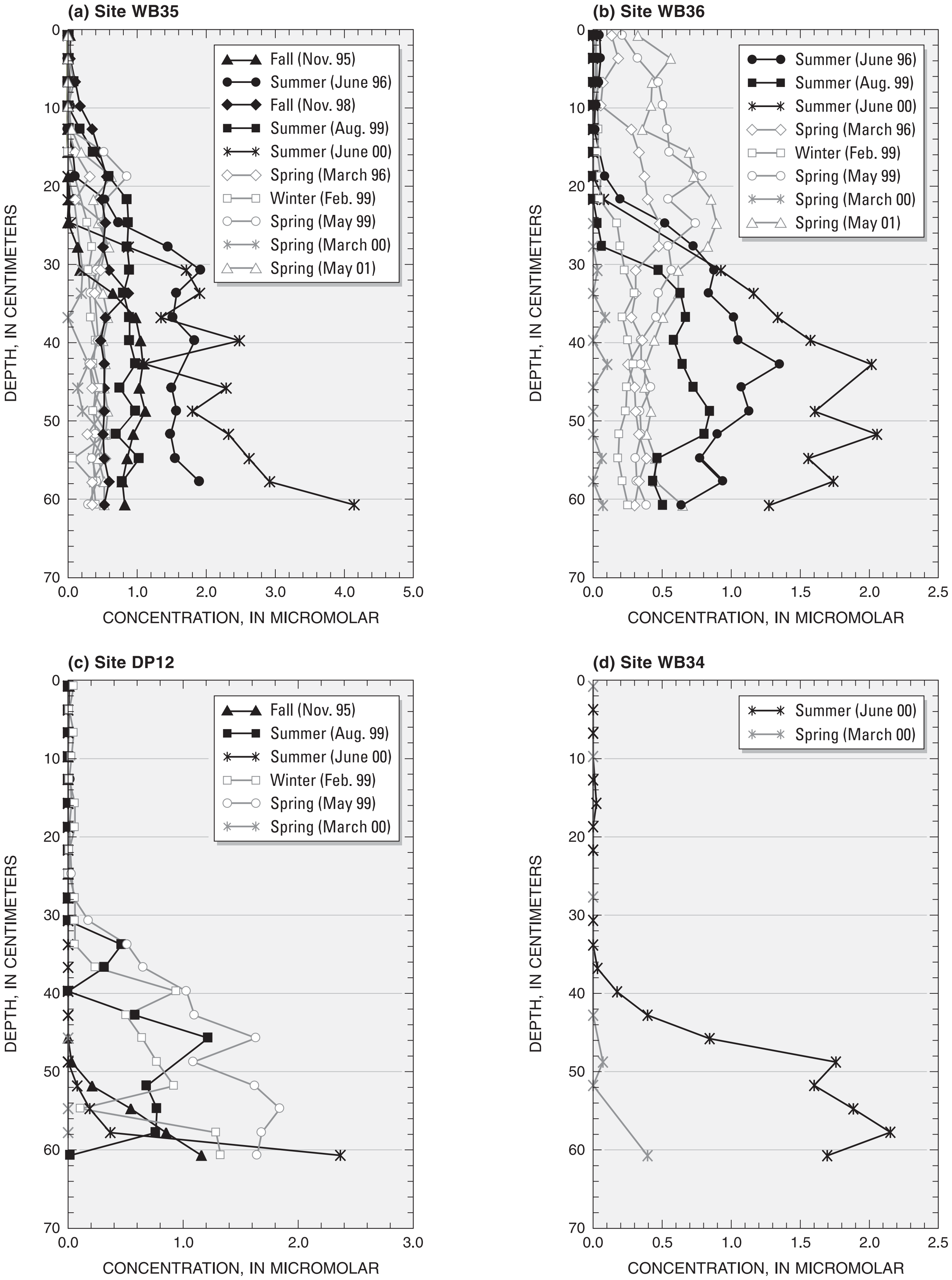
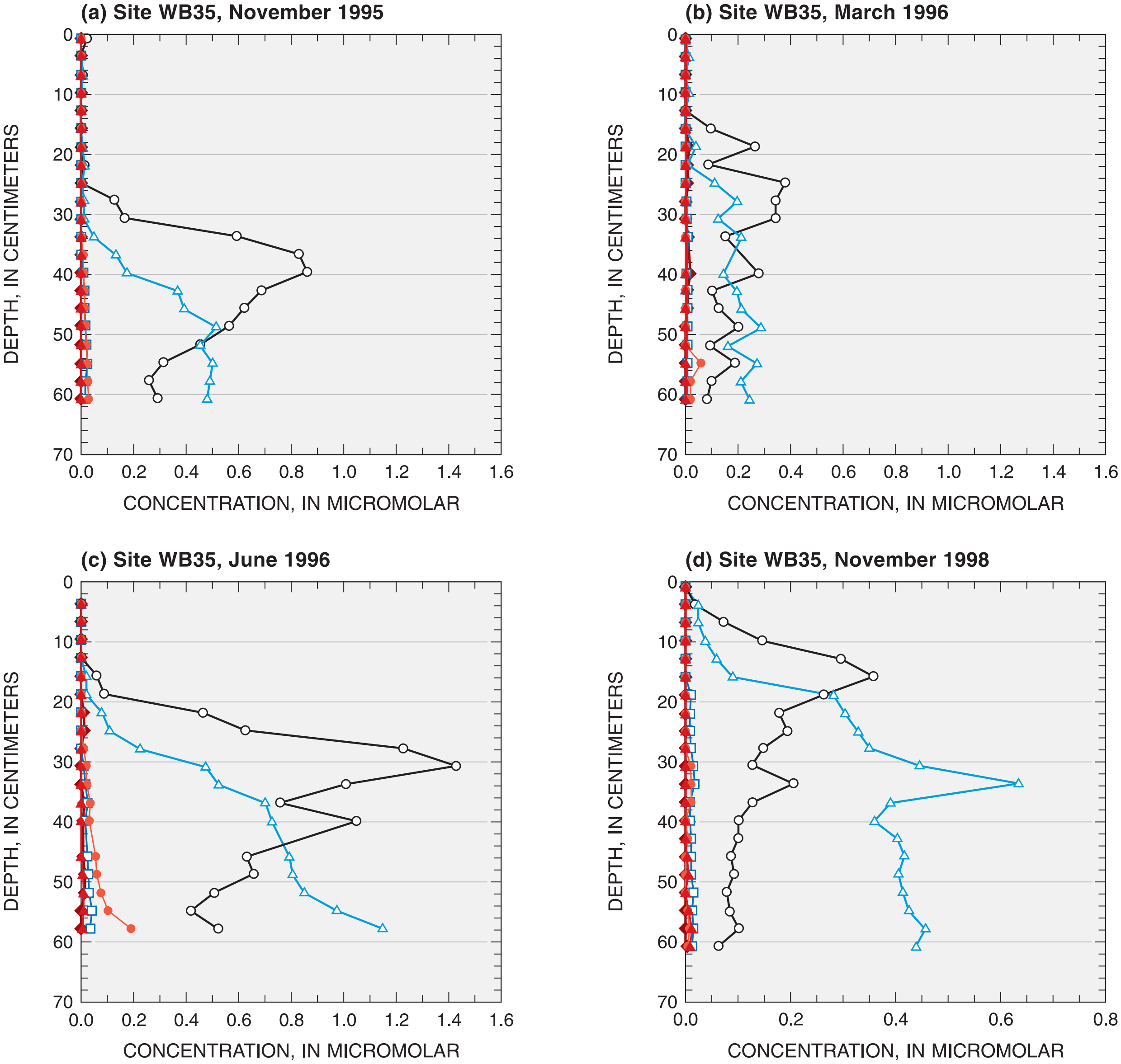
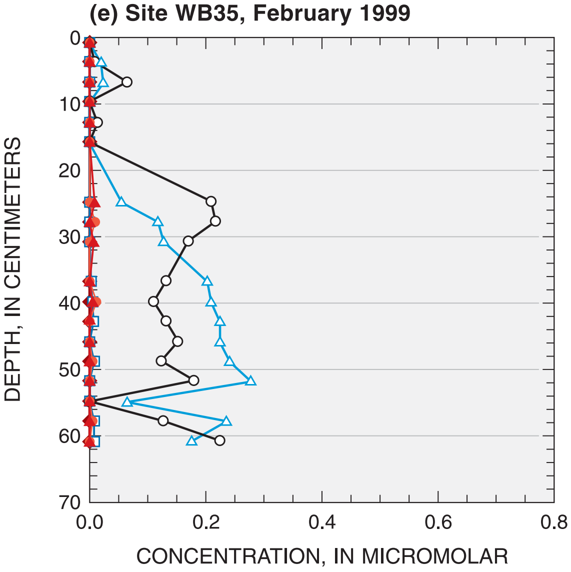


Figure 11. Concentrations of total chlorinated volatile organic compounds observed in wetland porewater in peepers sampled during the winter/spring compared to the summer/fall at sites **(a)** WB35, **(b)** WB36, **(c)** DP12, and **(d)** WB34.





EXPLANATION

◆ TeCA
▲ 112TCA
● 12DCA
□ TCE
△ 12DCE
○ VC

Figure 12. Concentrations of 1,1,2,2-tetrachloroethane (TeCA) and its daughter compounds [1,1,2-trichloroethane (112TCA); 1,2-dichloroethane (12DCA); trichloroethene (TCE); 1,2-dichlororethene (12DCE, total of *cis*- and *trans*- isomers); and vinyl chloride (VC) chlorinated volatile organic compounds (total VOCs)] observed in wetland porewater at site WB35 in peepers sampled during 1995-2000. **(a)** November 1995, **(b)** March 1996, **(c)** June 1996, **(d)** November 1998, and **(e)** February 1999.

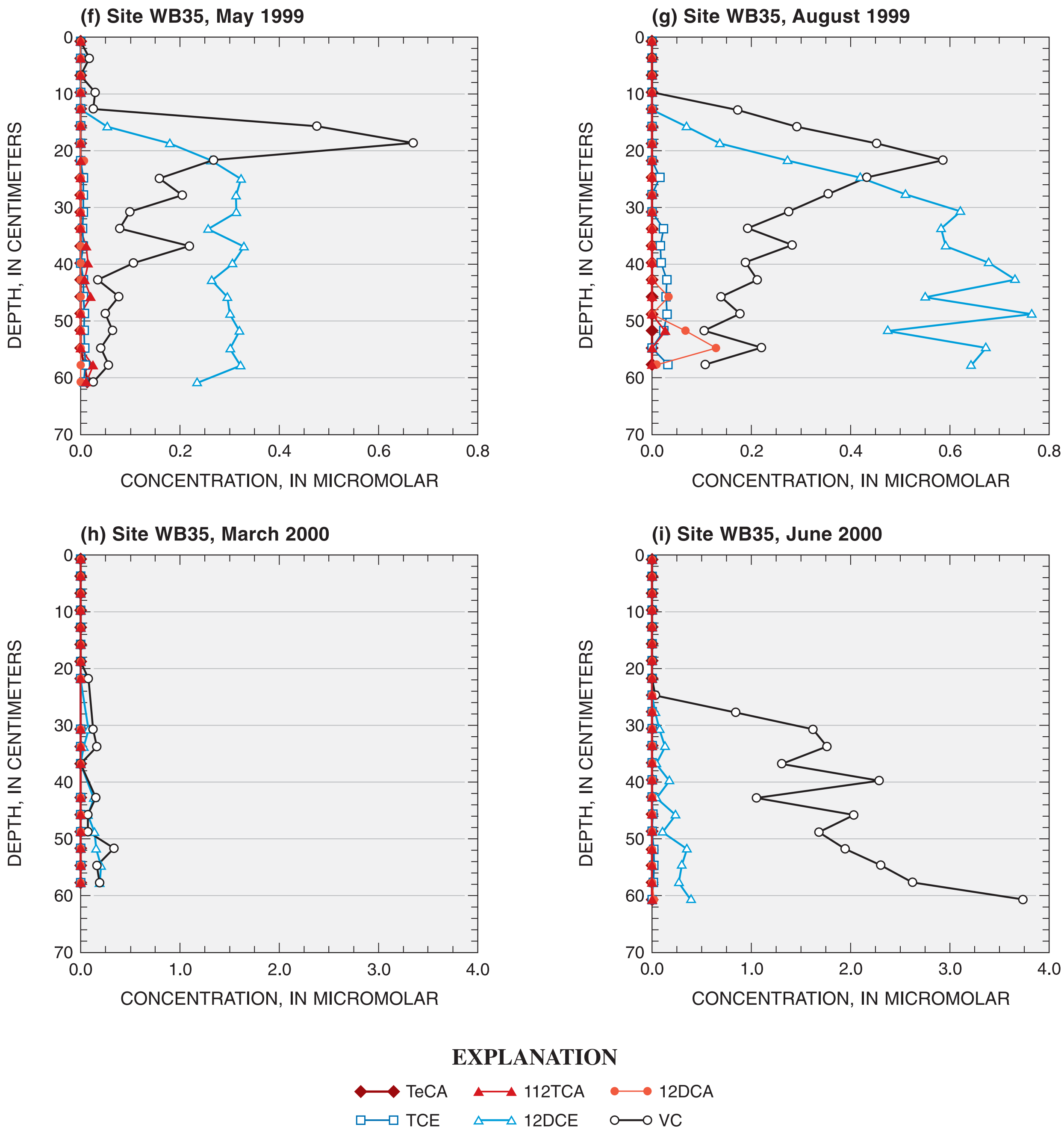
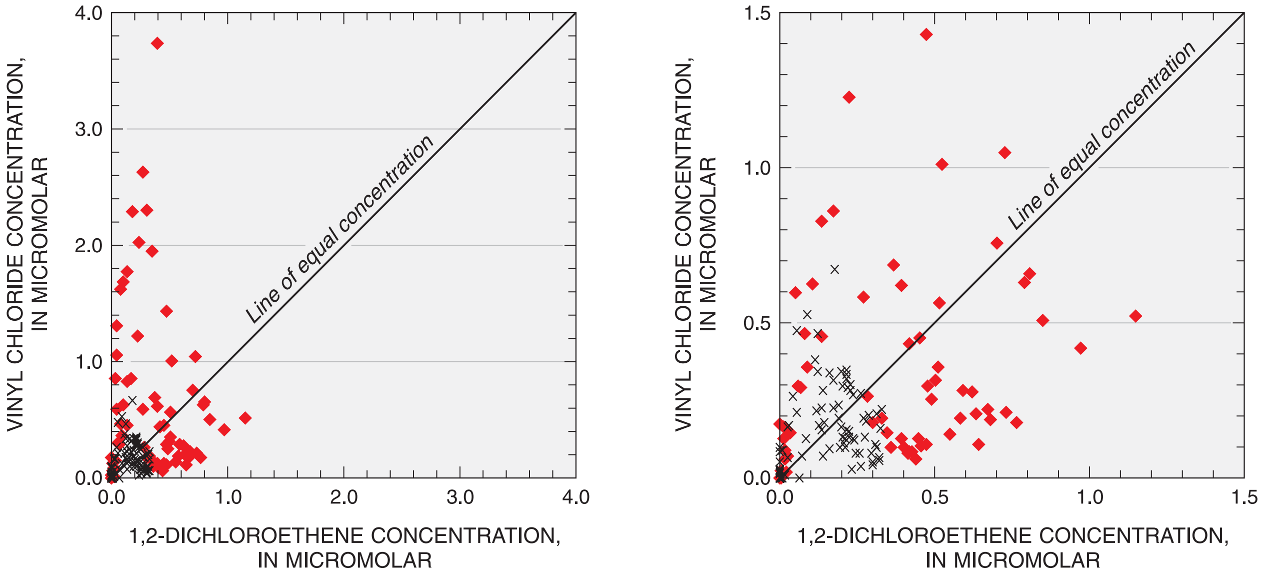
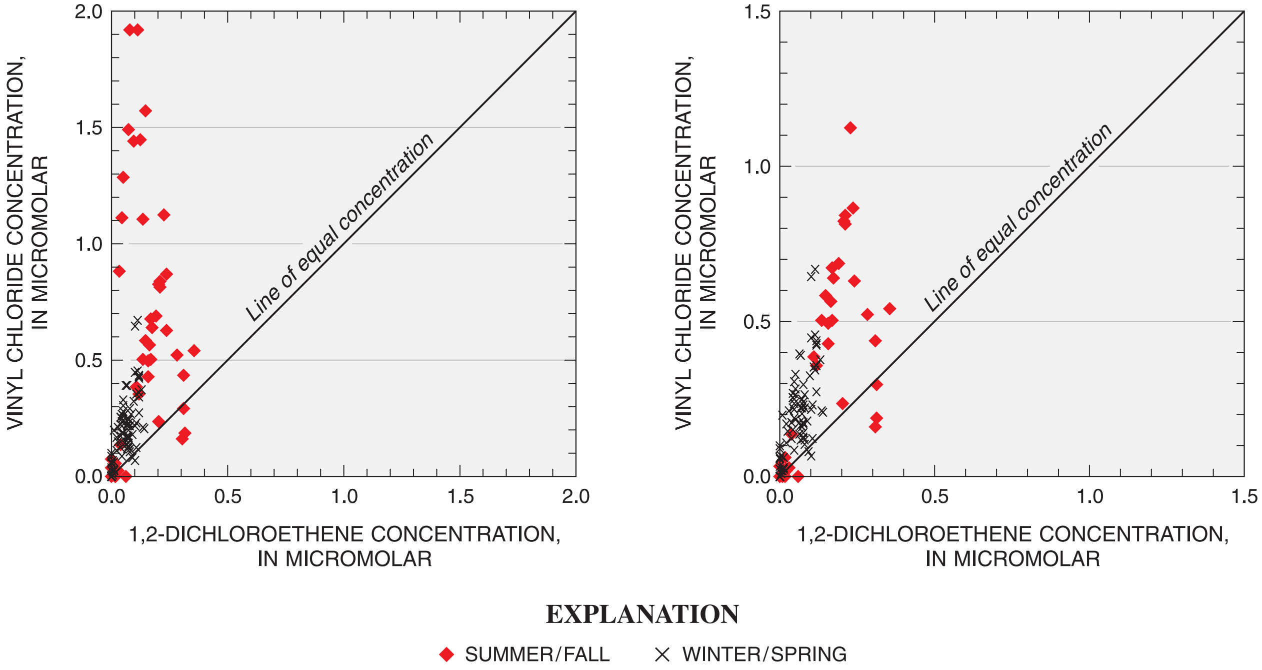


Figure 12. Concentrations of 1,1,2,2-tetrachloroethane (TeCA) and its daughter compounds [1,1,2-trichloroethane (112TCA); 1,2-dichloroethane (12DCA); trichloroethene (TCE); 1,2-dichlororethene (12DCE, total of *cis*- and *trans*- isomers); and vinyl chloride (VC) chlorinated volatile organic compounds (total VOCs)] observed in wetland porewater at site WB35 in peepers sampled during 1995-2000. **(f)** May 1999, **(g)** August 1999, **(h)** March 2000, and **(i)** June 2000. -- Continued



(a) Site WB35, with June 2000 sampling

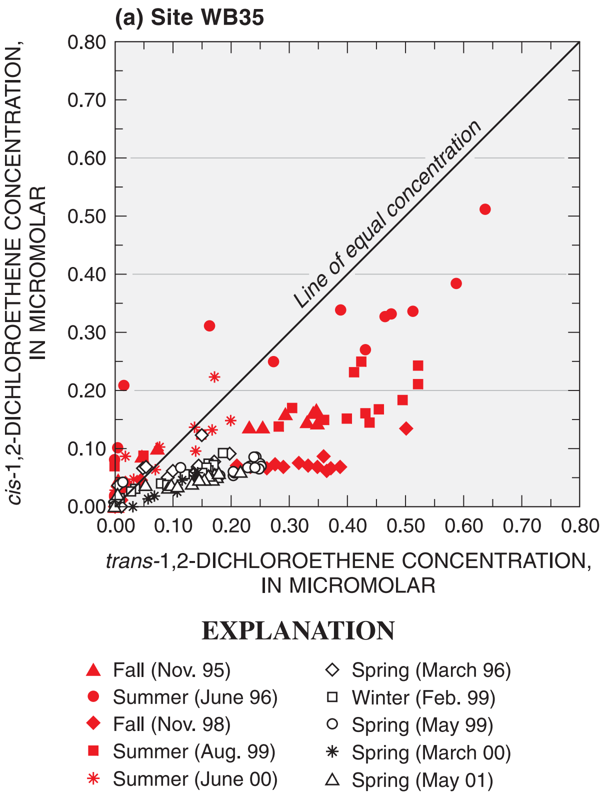
(b) Site WB35, without June 2000 sampling



(c) Site WB36, with June 2000 sampling

(d) Site WB36, without June 2000 sampling

Figure 13. Concentrations of 1,2-dichloroethene (total of *cis*- and *trans*- isomers) compared to vinyl chloride in wetland porewater in peepers sampled at site WB35 **(a)** with and **(b)** without the June 2000 sampling event, and at site WB36 **(c)** with and **(d)** without the June sampling event.


(a) Site WB35

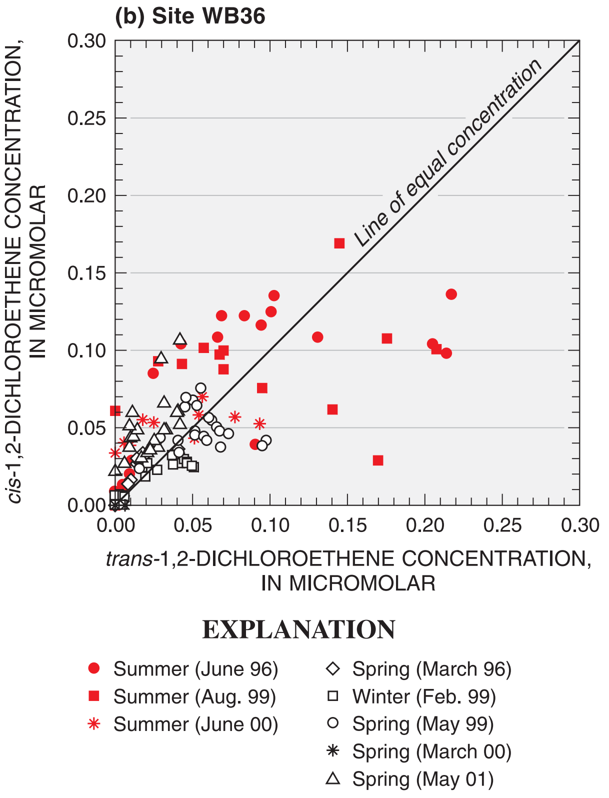

(b) Site WB36

Figure 14. Concentrations of *cis*-1,2-dichloroethene compared to *trans*-1,2-dichloroethene observed in wetland porewater in peepers sampled during the winter/early spring and the summer/fall at sites **(a)** WB35 and **(b)** WB36.

ions were observed in samples collected during the summer. Toluene concentrations were as high as 300 µg/L (3.3 µM) in the peeper samples at sites WB35 and WB36 in June 1996, which was higher than the concentrations of total chlorinated VOCs during this sampling event (figs. 11a,b; figs. 15a,b). The highest toluene concentrations occurred between about 10 and 30 cm below land surface at each site; concentrations decreased to below detection levels before land surface was reached, as was observed with the chlorinated VOCs (figs. 11 and 15). The periodic presence of toluene in the wetland porewater could affect natural attenuation of the chlorinated VOCs by serving as a readily available electron donor to support reductive dechlorination. Additional electron donor would be expected to enhance reductive dechlorination rates; however, this potential enhancement was not observed because the toluene was detected in the wetland porewater only during the summer when concentrations of chlorinated VOCs were relatively high.

In contrast to the shallow (less than or equal to 60 cm) wetland porewater chemistry observed with the peeper data, the deeper porewater in the wetland and top of the aquifer that was sampled from the MLSs generally did not show a temporal shift in VOC concentrations in the summer event (June 2000) compared to the spring event (March 2000) (figs. 16a–d). Unlike the peepers, substantial concentrations of both parent and daughter chlorinated VOCs were observed in the deeper porewater sampled with the MLSs, and neither type of VOC showed substantial difference in March 2000 compared to June 2000. Parent VOC concentrations were highest near the contact between the lower confining unit of the wetland sediments and the aquifer at each site. Parent VOC concentrations decreased upward in the MLSs, while daughter VOC concentrations increased and then decreased in a pattern similar to that observed in the peepers. The lack of temporal variation in the deeper wetland porewater was observed at MLSs along sections A–A′ and C–C′ (figs. 16a–d). At the two sites along section C–C′ where MLS data show little temporal change (WBM34 and WBM36, figs. 16b and 16d), shallow peeper samples showed a two- to ten-time increase in concentrations detected during June 2000 compared to those detected during March 2000 (figs. 11b and 11d). The lack of temporal variation in VOC concentrations in the deeper porewater sampled with the MLSs is consistent with the lack of temporal variation observed in concentrations from the wetland and aquifer from piezometer samples (fig. 8). Toluene was not detected in any samples collected from MLSs or piezometers screened at depths greater than 60 cm (deeper than the peepers), indicating that the toluene source is shallow.

Redox-Sensitive Constituents and Chloride Concentrations of ferrous iron, sulfide, and methane in peeper samples indicated that the shallow wetland porewater was anaerobic during all sampling events at both contaminated sites (figs. 17–18) and the uncontaminated site (fig.19). Thus, conditions are suitable for reductive dechlorination of VOCs throughout the year. As noted in earlier studies at this site (Lorah and others, 1997, p. 65; Lorah and Olsen 1999a),

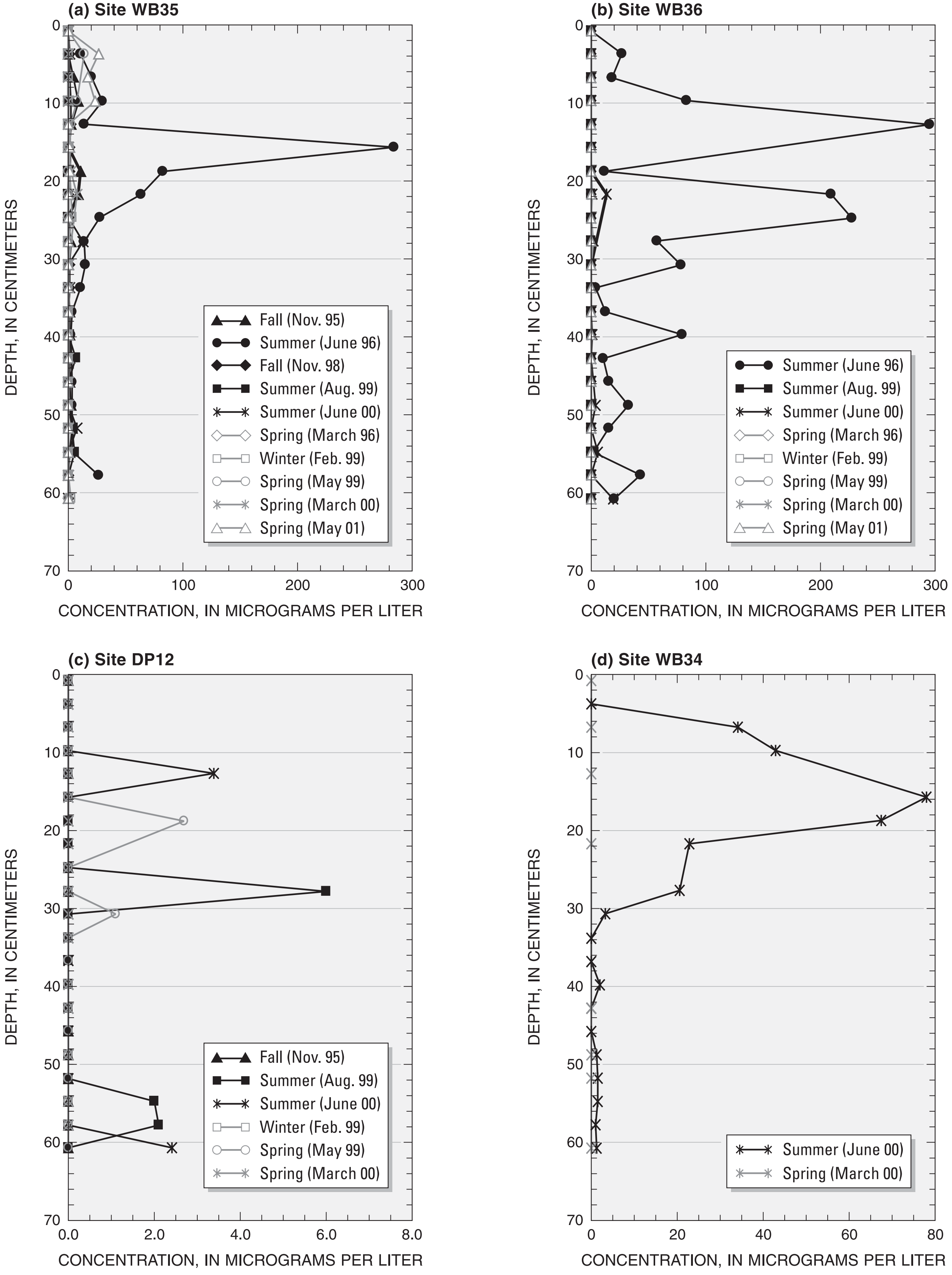


Figure 15. Concentrations of toluene observed in wetland porewater in peepers sampled during the winter/spring compared to the summer/fall at sites **(a)** WB35, **(b)** WB36, **(c)** DP12, and **(d)** WB34.

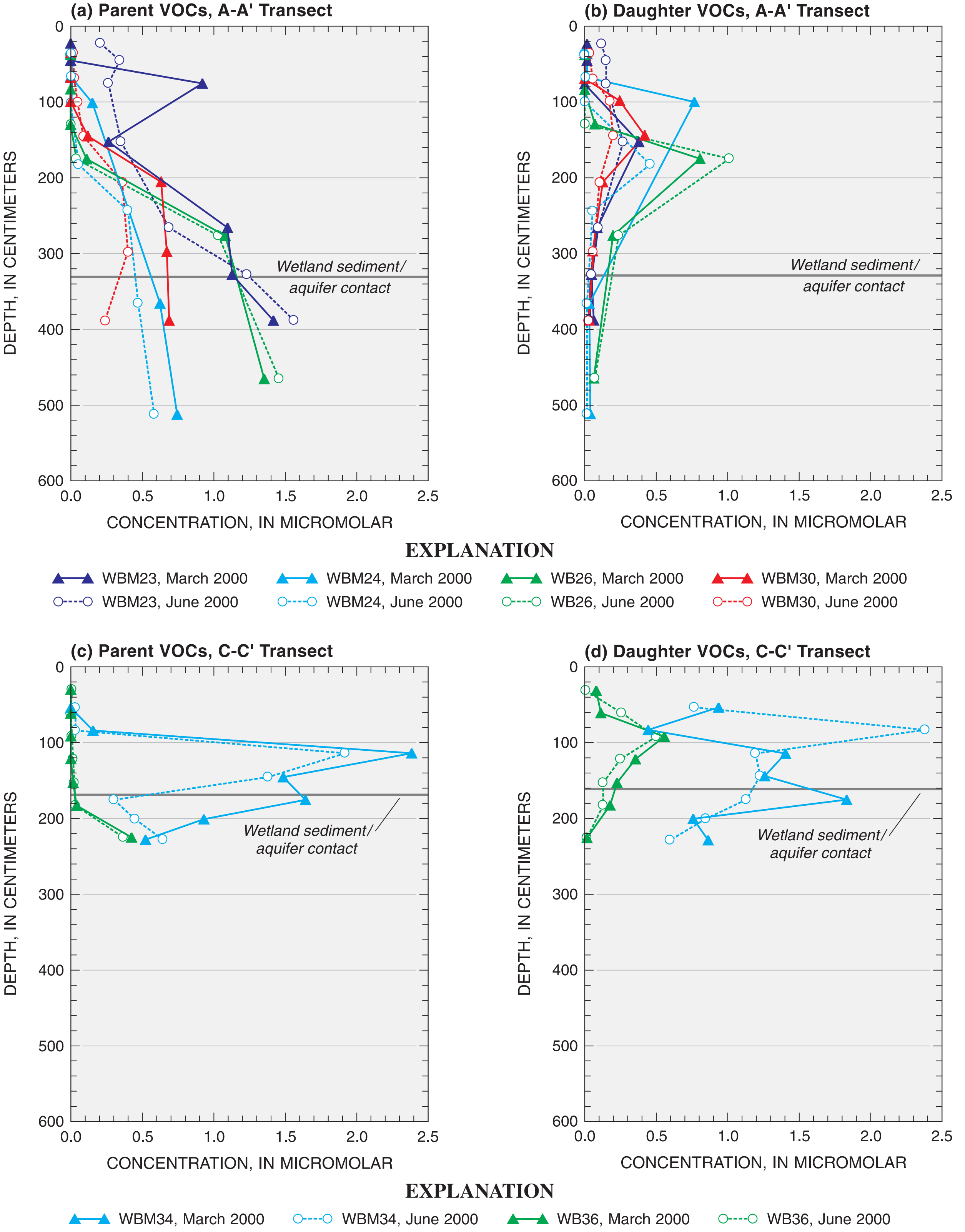


Figure 16. Concentrations of chlorinated volatile organic compounds (VOCs) in multi-level samplers and selected piezometers in March 2000 compared to June 2000: **(a)** the sum of parent VOCs (1,1,2,2-tetrachloroethane and trichloroethene) at sites along the A-A' transect; **(b)** the sum of daughter VOCs (1,1,2-trichloroethane; 1,2-dichloroethane; chloroethane; *cis*-1,2-dichloroethene; *trans*-1,2-dichloroethene; and vinyl chloride) at sites along the A-A' transect; **(c)** the sum of parent VOCs (1,1,2,2-tetrachloroethane and trichloroethene) at sites along the C-C' transect; and **(d)** the sum of daughter VOCs (1,1,2-trichloroethane; 1,2-dichloroethane; chloroethane; *cis*-1,2-dichloroethene; *trans*-1,2-dichloroethene; and vinyl chloride) at sites along the C-C' transect.

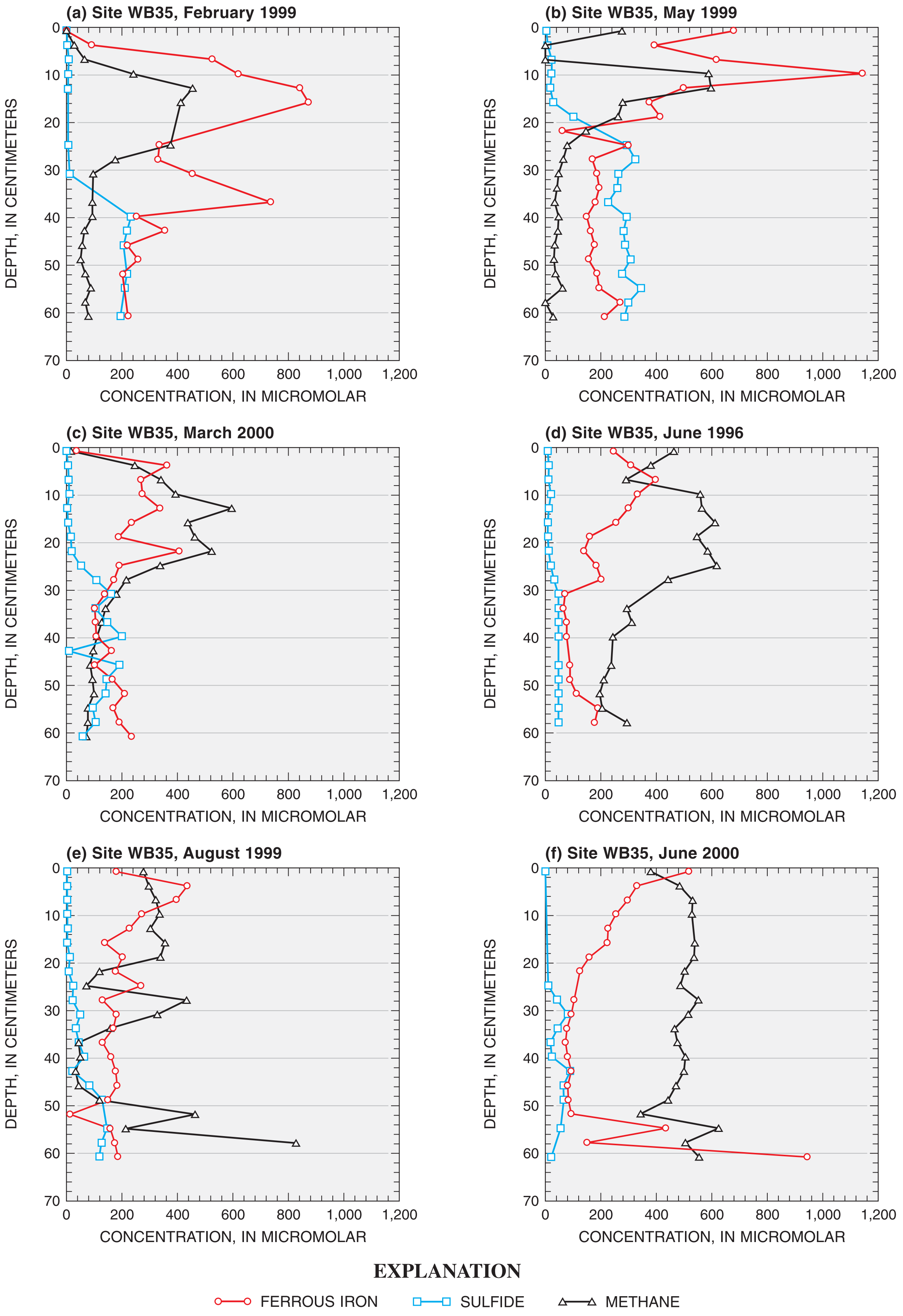
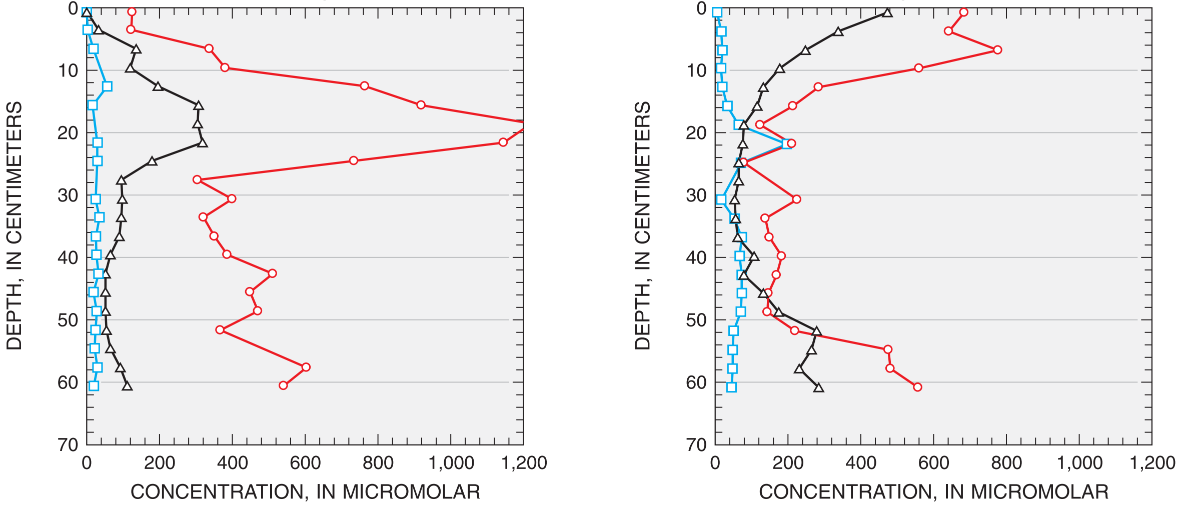
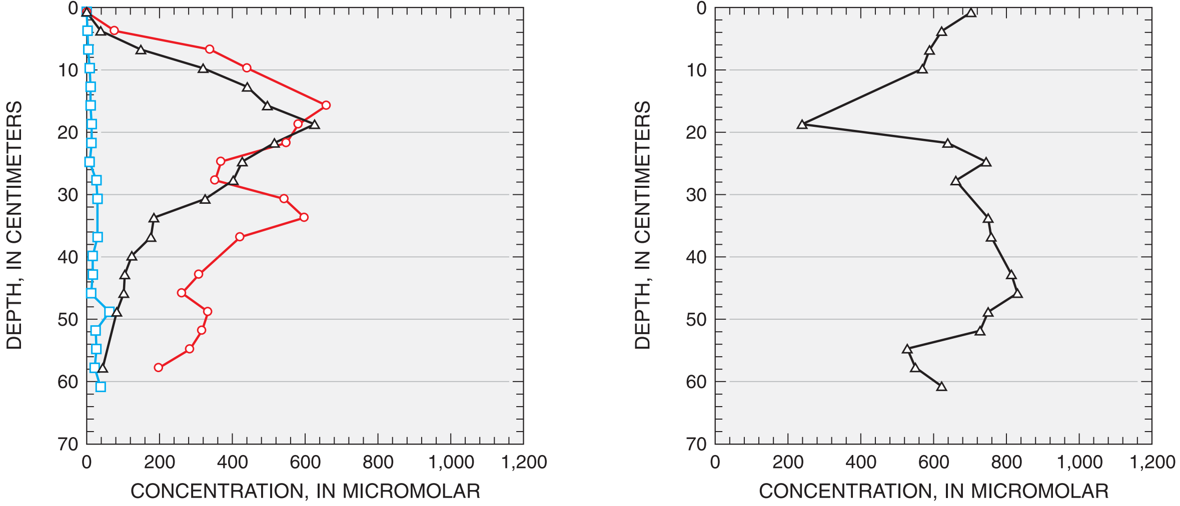


Figure 17. Concentrations of redox-sensitive constituents observed in wetland porewater at site WB35 in peepers during winter/spring sampling events in **(a)** February 1999, **(b)** May 1999, and **(c)** March 2000 compared to summer/fall sampling events in **(d)** June 1996, **(e)** August 1999, and **(f)** June 2000.

(a) Site WB36, February 1999 (b) Site WB36, May 1999



(c) Site WB36, March 2000 (d) Site WB36, June 1996



(e) Site WB36, August 1999 (f) Site WB36, June 2000

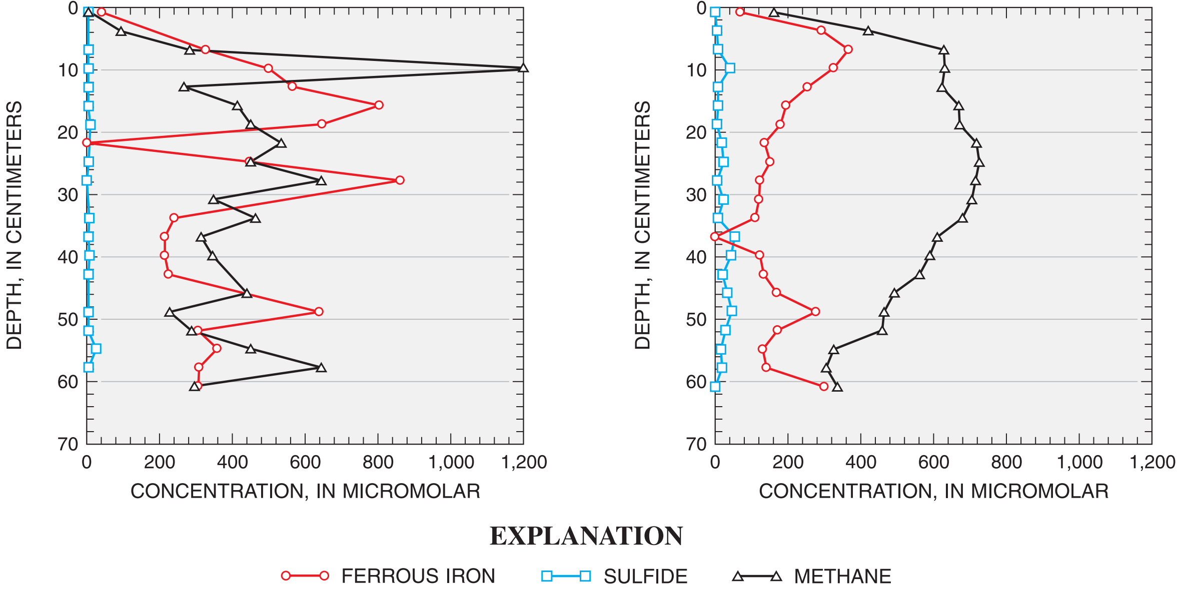
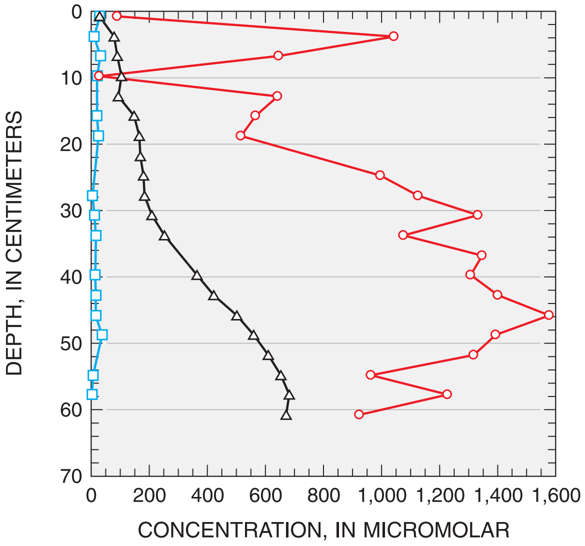
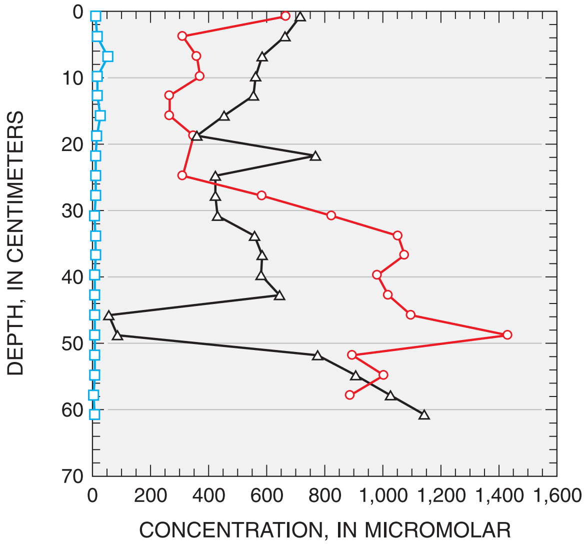
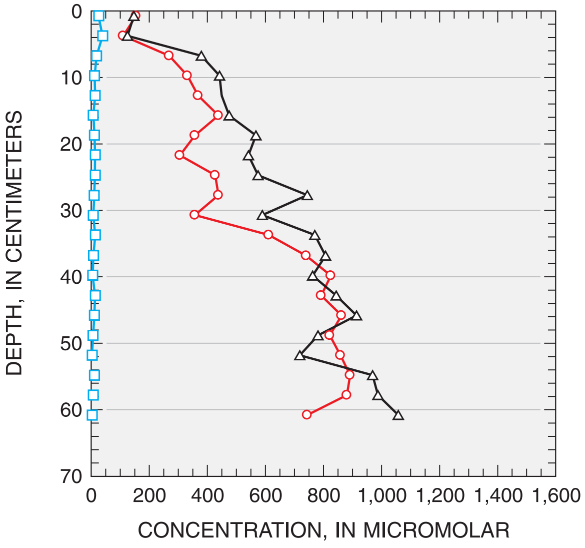
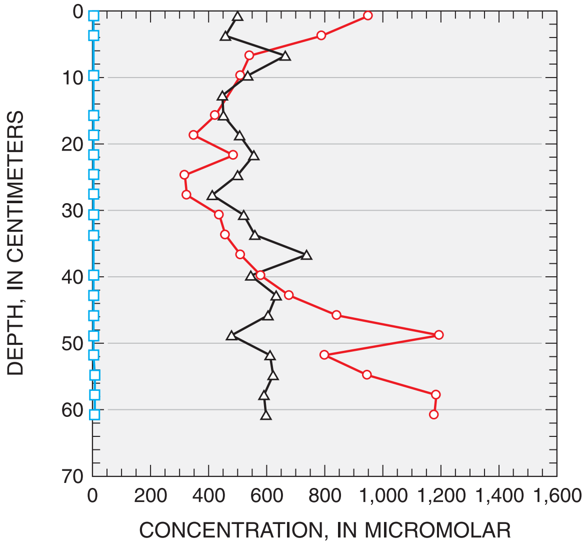


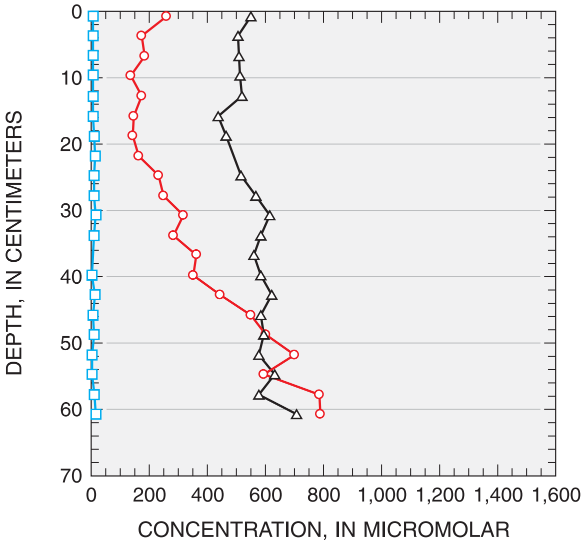
Figure 18. Concentrations of redox-sensitive constituents observed in wetland porewater at site WB36 in peepers during winter/spring sampling events in **(a)** February 1999, **(b)** May 1999, and **(c)** March 2000 compared to summer/fall sampling events in **(d)** June 1996, **(e)** August 1999, and **(f)** June 2000.


(a) Site WB19, February 1999


(b) Site WB19, May 1999


(c) Site WB19, March 2000


(d) Site WB19, August 1999


(e) Site WB19, June 2000

EXPLANATION

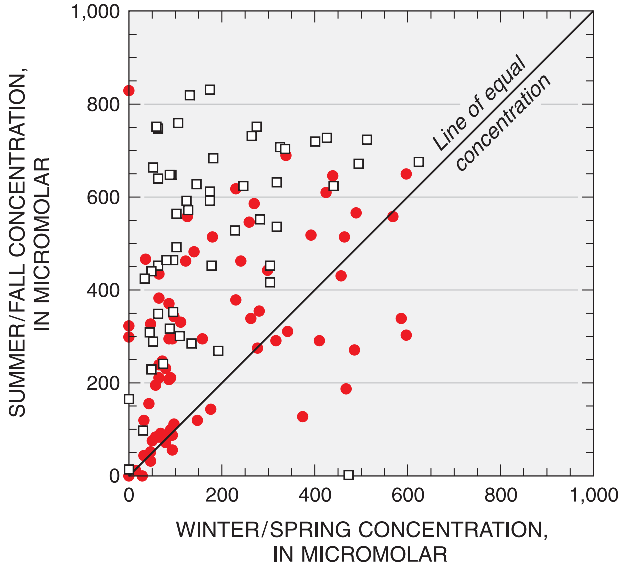
○ FERROUS IRON   □ SULFIDE   △ METHANE

Figure 19. Concentrations of redox-sensitive constituents observed in wetland porewater at site WB19 in peepers during the winter/spring sampling events in **(a)** February 1999, **(b)** May 1999, and **(c)** March 2000 compared to summer/fall sampling events in **(d)** August 1999, and **(e)** June 2000.

the final reductive dechlorination reactions of production and degradation of VC generally coincide with the zone of highest methane concentrations in the wetland porewater (figs. 12 and 17). The similar concentrations and temporal changes of redox-sensitive constituents at the contaminated sites compared to the background site WB19 (figs. 17–19) indicate that the discharge of VOCs has little effect on the natural redox conditions in the wetland sediment. It should be noted that the reduced iron species, ferrous iron, was directly measured during some sampling events, whereas total dissolved iron (sum of ferrous and ferric iron) was measured during other sampling events (table 3). During three sampling events, both total dissolved iron and ferrous iron were measured, giving a total of 61 values to compare within a concentration range of 0.10 to 70 mg/L. Linear regression of these 61 measurements of total dissolved iron versus ferrous iron concentrations gave an equation with a slope of 0.986 and a correlation coefficient of 0.987. Total dissolved iron and ferrous iron concentrations, therefore, can be considered equivalent in the wetland porewater.

The relative distributions of ferrous iron, sulfide, and methane showed some consistent temporal variations at the two contaminated sites, WB35 and WB36 (figs. 17 and 18) and at the background site WB19 (fig. 19). In the shallow wetland porewater at the contaminated and background sites, iron-reducing conditions seemed to be predominant over the 60-cm depth profiles in the winter sampling event of February 1999, as indicated by the substantially higher micromolar concentrations of ferrous iron compared to methane (figs. 17a, 18a, and 19a). The nearly equimolar concentrations of ferrous iron and methane over the 60-cm depth profiles during the spring events (May 1999 and March 2000) indicate nearly equal predominance of iron reduction and methanogenesis. In contrast, methanogenesis became predominant relative to ferrous iron concentrations in the wetland porewater at each site during the summer sampling events, especially in June 1996 and 2000 (figs. 17d–f, 18d–f, and 19d–e). During the June 2000 event, methane concentrations were uniformly high with depth at the contaminated and uncontaminated sites (figs.17f, 18f, and 19e)—methane concentrations were about 600 µM from about 5 to 60 cm below land surface at sites WB35 and WB36 in June 2000.

(a) Methane, Sites WB35 and WB36



(b) Ferrous Iron, Sites WB35 and WB36

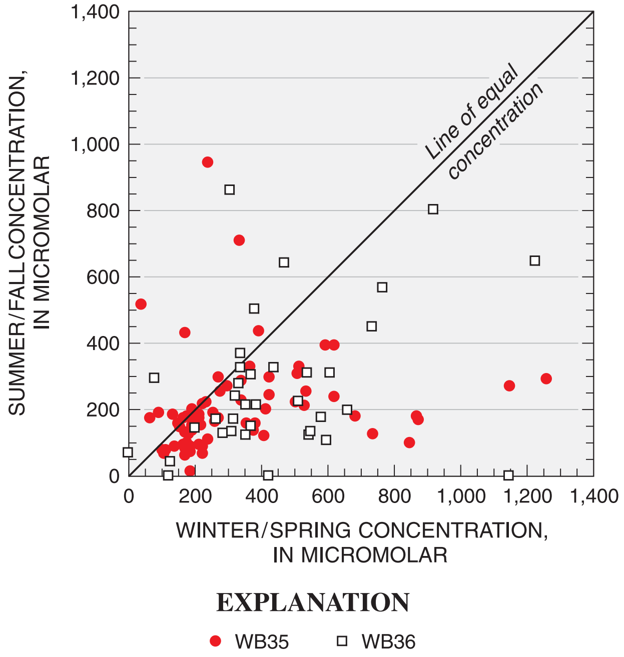


Figure 20. Concentrations of **(a)** methane and **(b)** ferrous iron during winter/spring sampling events compared to summer/fall sampling events of peepers placed at sites WB35 and WB36.

The higher overall methane concentrations in the summer/fall compared to the winter/spring are evident when plotted against one another (fig. 20a). Other studies in anaerobic freshwater environments have shown an increase in the methane production rate with increasing temperatures (Sinke and others, 1992; Schulz and Conrad, 1997; Fey and Conrad, 2000). It should be noted that methane concentrations are not directly indicative of methane production rates. Methane can be removed from the shallow wetland porewater by ebullition, transport through plants, volatilization near land surface, and oxidation by methanotrophs (Fiedler and Sommer, 2000; Rosenberry and others, 2003). All of these processes would be expected to be more prevalent during the summer than during the winter/spring; thus, actual methane production in the summer most likely is higher than indicated by the increase in measured methane concentrations in the wetland porewater.

Ferrous iron concentrations showed an opposite temporal pattern from methane concentrations, with lower concentrations in the summer/fall compared to the winter/spring (fig. 20b). Studies with wetland plants have shown that iron plaque formation occurs around plant roots when oxygen is drawn from the air to their roots (Hansel and others, 2002). Formation of the iron plaque, which can be comprised of amorphous iron hydroxides, lepidocrocite, goethite, and siderite, occurs with seasonal development of emergent biomass and peaks with peak photosynthetic activity. Thus, oxidation of dissolved ferrous iron during iron plaque formation could decrease dissolved iron concentrations in the summer. Iron oxyhydroxide coloration was observed around plant roots during sediment coring (Lorah and others, 1997). The bulk sediment porewater remained anaerobic throughout the summer, despite oxygen transport to plant roots (figs. 17–19). As was observed with methane concentrations, ferrous iron concentrations might not be indicative of actual iron reduction rates because ferrous iron and sulfide commonly can precipitate to form minerals. Thus, increased sulfide production and precipitation of iron sulfides also could lower iron concentrations. Although sulfide production was evident at site WB35 throughout the year, it was not evident at site WB19 (fig. 19). Both sites, however, showed low ferrous iron concentrations during the summer sampling events compared to the winter/spring sampling events, indicating that precipitation of iron sulfides was not a factor (fig. 19). The highest sulfide concentrations were measured at site WB35 during the winter/spring sampling events, when ferrous iron concentrations also were highest (fig. 17).

Although limited data are available, temporal variation in concentrations of the conservative constituent chloride in the shallow wetland porewater contrasted with the temporal variations in VOC concentrations (figs. 11 and 21). Whereas VOC concentrations in the shallow wetland porewater measured with the peepers were higher in the summer/fall than the winter/spring (fig. 11), chloride concentrations were lower in the summer (June 2000) than in the spring (March 2000) (fig. 21). This temporal pattern was observed at two sites—contaminated site WB36 and the background site WB19. As was observed with the VOCs, the temporal change in chloride concentrations was observed only in the upper 40 cm at WB36. Approximately equivalent chloride concentrations were observed below 40 cm at site WB36 in the winter/spring and summer/fall in the peepers (fig. 21). The deeper wetland and shallow aquifer porewater data from the MLSs also showed little temporal variation in chloride concentrations (data not shown). The decreased chloride in the shallow wetland porewater in the summer could result from dilution of the wetland porewater by greater upward flux of aquifer ground water to the wetland porewater in the summer, or by less downward flux of surface water in the summer. The aquifer consistently had concentrations of chloride about an order of a magnitude lower than the wetland porewater at all times of the year (fig. 10); thus, the ground-water flux would need to change to account for a lower chloride concentration in the summer. The surface water typically had higher chloride concentrations than the wetland porewater in 1995–1996 (Olsen and others, 1997), but surface-water data are unavailable for 2000, when peepers were sampled for chloride. Alternatively, the lower chloride concentrations in the wetland porewater in June 2000 could have resulted from lateral mingling of different contaminant plumes with changing flow conditions. Ground-water-flow conditions and other possible physical factors controlling the wetland chemistry are discussed in the next section.

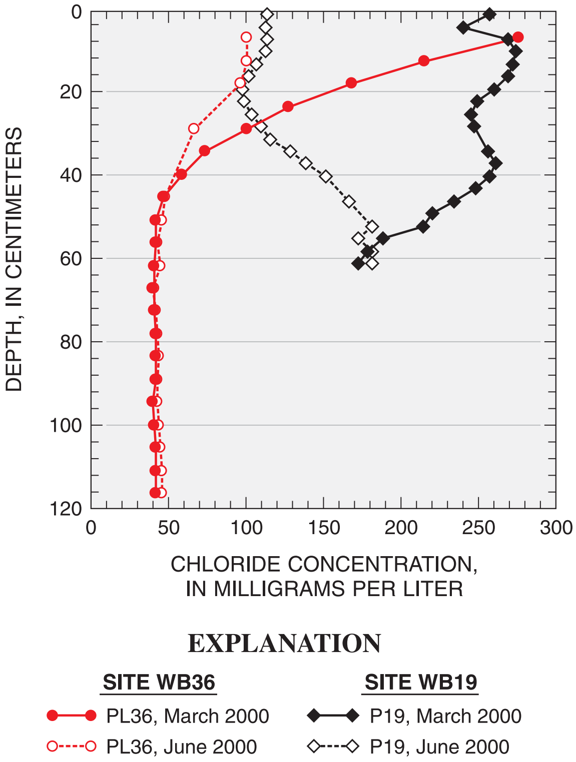


Figure 21. Concentrations of chloride in peepers sampled at sites WB36 (peeper PL36) and WB19 (peeper P19) in spring (March 2000) compared to summer (June 2000) sampling events.

Temporal Changes in Physical Controlling Factors

Major potential physical factors that could control temporal variations in the wetland and aquifer geochemistry include ground-water head gradients and flow, surface-water levels and tidal fluctuations, and sediment temperature. Possible interactions between geochemical and physical factors are complex in ground-water/surface-water environments. For example, recharge events have been shown to affect the availability of dissolved organic carbon, nutrients, and electron donors and acceptors that sustain microbial activity (McGuire and others, 2000). Variation in the flux of one electron acceptor, such as oxygen or sulfate, can shift the predominant redox reaction in the wetland sediments, which could affect the efficiency of natural attenuation through biodegradation reactions. Recharge events or other hydrologic factors that increase ground-water flow to the wetland sediments also could affect the VOC concentrations more directly—decreasing concentrations by dilution or increasing concentrations by increased contaminant flux from source areas. Possible tidal effects from long-term (over a period of weeks or months) shifts in surface-water elevations are evaluated by comparing ground-water head gradients at low and high tides, and by evaluating surface-water elevations measured at the tide gage along the West Branch Canal Creek, located about 250 m north of the transects in the study area. Short-term diurnal fluctuations in water levels also occur from tidal effects, but sampling was not conducted over the short time scales that would be necessary to observe this potential effect.

Another possible physical factor that could affect the redox and contaminant geochemistry in the shallow wetland porewater that is not directly evaluated here is the growth of wetland plants in the spring and their activity through September or October. Possible effects of plant growth on the redox geochemistry were discussed earlier, and the possible effect of evapotranspiration associated with plant activity is discussed in the section on Ground-Water Flow. Wetland plants are known to decrease concentrations of dissolved gases such as methane in wetland porewater through transportation from the plant roots to the atmosphere (Salhani and Stengel, 2001). Chlorinated VOCs could be transported with methane through plant roots. Pardue (2002) observed uptake of chlorobenzene by wetland plants in laboratory reactors. However, plant-driven efflux of VOCs would be expected to lower VOC concentrations in the wetland porewater during their most active summer/fall period (Salhani and Stengel, 2001), whereas higher porewater VOC concentrations occurred during the summer than during the winter (fig. 11). Stimulation of methanotrophic bacteria and their oxidation of chlorinated VOCs also could peak in the summer while plants are actively transporting oxygen to roots. Ratios of 12DCE:VC in the wetland porewater do not indicate a substantial effect from methanotrophic activity, however. Methanotrophs degraded VC faster than 12DCE in laboratory experiments with wetland sediment from the West Branch site (Lorah and others, 2001), but 12DCE:VC ratios in the wetland porewater remained about the same in the summer compared to the winter/spring (figs. 13 b and 13d). Wetland plants also could indirectly affect porewater VOC concentrations by exuding organic acids from the roots that stimulate microbial degradation (Pardue, 2002). Evaluation of these complex plant-microbical interactions was beyond the scope of this study.

Ground-Water Flow

Because of the shallow ground-water flow system in the wetland area, water-level elevations were expected to show strong temporal fluctuations from seasonal variations in recharge from precipitation in the upland areas and from evapotranspiration in the wetland area during the growing season. Although water levels were seasonally variable in the aquifer in the uplands (fig. 22), water levels and gradients within the wetland area were relatively constant (figs. 23 and 24). A hydrograph of semi-continuous water levels measured in 1998 in the aquifer at site CC27 in the uplands shows that water levels were high in the late winter and spring when recharge is greatest (fig. 22). Water levels then started to decline in June and were low through the summer and fall. Although hydrographs from 1999–2001 (data not shown) were less complete, they showed a similar seasonal pattern. The higher detected VOC concentrations in the uplands in the summer compared to the winter/spring (fig. 7) could be associated with the generally lower water levels in the summer. With declining recharge in the summer, less dilution of the contaminant plume might occur. However, a corresponding increase was not observed in chloride concentrations or specific conductance values in the upland aquifer (fig. 9) to support a hypothesis of decreased dilution of the contaminant plume in the summer.

In the wetland area, a consistent pattern of seasonal variation in water levels was not observed in the aquifer or the wetland sediments. Boxplots showing selected water levels in the wetland sediment and aquifer are shown in figure 23. Water levels measured in the same wells along each section during winter/spring and summer/fall were compared. For each section, the median and range in water levels in the wetland sediment and aquifer were approximately the same in the winter/spring compared to the summer/fall (fig. 23). Water levels in the wetland sediment along section A–A′ showed a greater range than those measured in the wetland sediment along section C–C′, which probably reflects the greater thickness and lithologic variability in the wetland sediments along section A–A′ (figs. 3–4). For both sections, however, a generally upward head gradient was indicated by the higher water levels in the aquifer than the wetland sediments during winter/spring and summer/fall (fig. 23). Water levels measured at low tide in water-table wells (screened 0 to 0.61 m below land surface) along section A–A′ through the wetland indicate that upward discharge from the aquifer was sufficient to maintain water-saturated or nearly saturated conditions in the wetland sediments throughout the year (fig. 25). The persistence of anaerobic conditions throughout the study in the shallow wetland porewater (figs. 17–19) reflects the consistently water-saturated conditions. Water levels were at or above land-surface elevations at sites WB26 and WB28 (fig. 25), which are closest to the creek banks and at the lowest land-surface elevations (fig. 1). The high water levels above land surface probably indicate hydrostatic loading with the tides at these bank sites. During the spring of 1996, the water table was 0.10 m above land surface at site WB24, which is about 23 m east of the creek bank (fig. 1). The water table then remained within 0.05 m of land surface in the summer of 1996 and throughout 1999 at site WB24, and within 0.10 m of land surface at site WB22, which is closer to the wetland-upland boundary (fig. 25). Unusually high precipitation

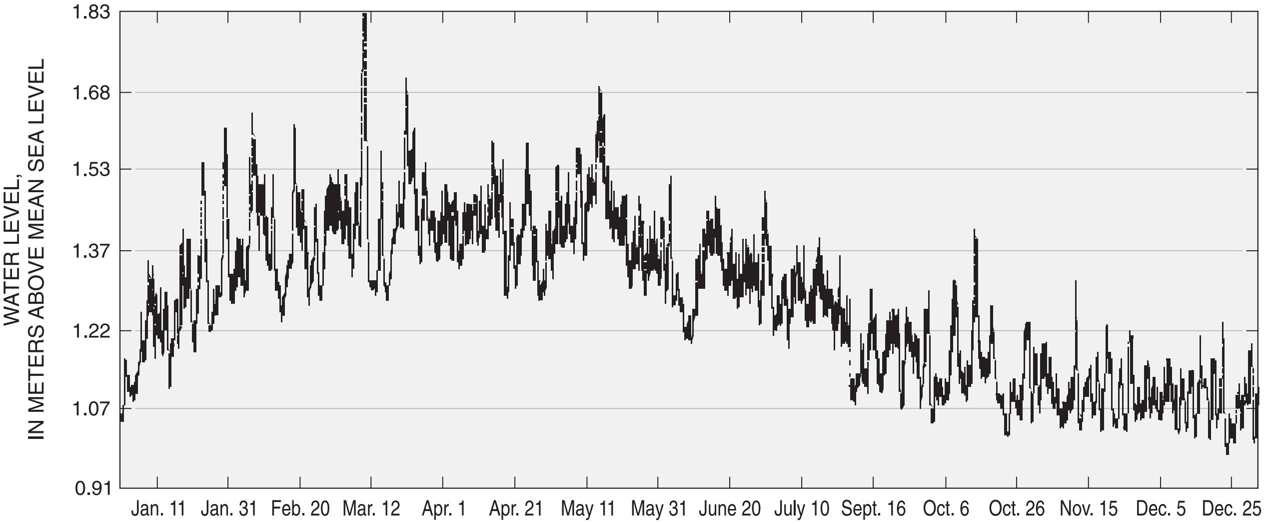


Figure 22. Hydrograph showing water levels in the upland well CC27A, 1998.

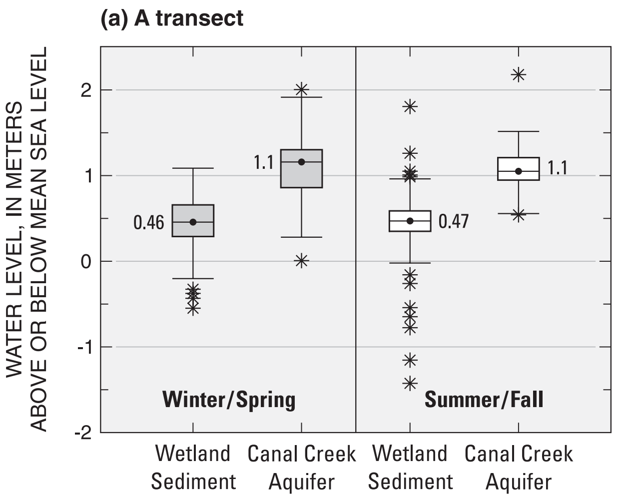
resulted in high recharge in the winter and spring of 1996 (Lorah and others, 1997), and accounts for the higher water table in spring 1996. Precipitation was below or near the normal annual level for 1997, 1998, and 1999 (fig. 26). In 1999, precipitation was below normal most of the year, except for September when high rainfall due to Hurricane Floyd added 30 cm of rain.

The fact that the water table remained near land surface through seasonal evapotranspiration demand and throughout an extended drought period indicates that there is a strong upward discharge from the aquifer to the wetland sediments. In laboratory mesocosm experiments, Mann and Wetzel (2000) found that evapotranspiration from emergent macrophytes in wetlands increased head gradients and groundwater-flow rates within sand sediments but had no effect in predominantly clay sediments. The clayey wetland sediments at West Branch Canal Creek, therefore, could also contribute to the lack of seasonal variation observed. In addition, plant roots in the wetland were observed to extend to the top of the Canal Creek aquifer at some locations (Lorah and others, 1997). Tapping of the aquifer by plant roots would diminish the effect of evapotranspiration on the wetland sediments.

A possible cause of the consistently higher VOC concentrations in the shallow wetland porewater in the summer/fall compared to the winter/spring could be a higher mass flux of VOCs to the wetland sediments from the aquifer in the summer/fall. Because VOC concentrations in the aquifer were consistent between the seasons, a higher head gradient between the aquifer and wetland sediments would have to occur to increase the mass flux of VOCs to the wetland sediment. A comparison of the median head differences (delta h) between the aquifer and wetland sediments in the winter/spring to the summer/fall for 1995–2000 does not indicate a seasonal change in mass flux, however (fig. 24). Because the same piezometers were measured during each event, the median head difference (delta h) is representative of the median head gradient. Vertical head gradients remained about the same in the winter/spring compared to the summer/fall for the two sections, plotting within 25 percent of the 1:1 equivalent line (fig. 24). One exception was the relatively high head gradients in the winter/spring of 1996. The above normal precipitation (fig. 26) that resulted in high recharge in 1996 (Lorah and others 1997) likely accounts for the higher median head gradients along section A–A′ during winter/spring 1996.

The high chloride and specific conductance observed in the summer of 1996 (spring 1996 measurements were not available) in the uplands near section A–A′ (site CC27 in fig. 9) may reflect the high recharge and water levels at section A–A′ in winter/spring of 1996. VOC concentrations in the upland, however, were not higher in 1996 than in other years (fig. 7), indicating different sources for the chloride and VOCs. Salt was stored in the upland region near site CC27 during historical operation of a chlorine manufacturing plant (Lorah and Clark, 1996), and the high recharge in 1996 may have resulted in transport of residual chloride in the soil to the aquifer. The high chloride observed at site CC27A in summer 1996 was not observed at site WB33A (fig. 9), which is at the beginning of section C–C′ and distant from the historical chloride source.

Synoptic water-level measurements generally were made both at high tide and low tide on the same day, and these measurements gave similar median head differences


(a) A transect

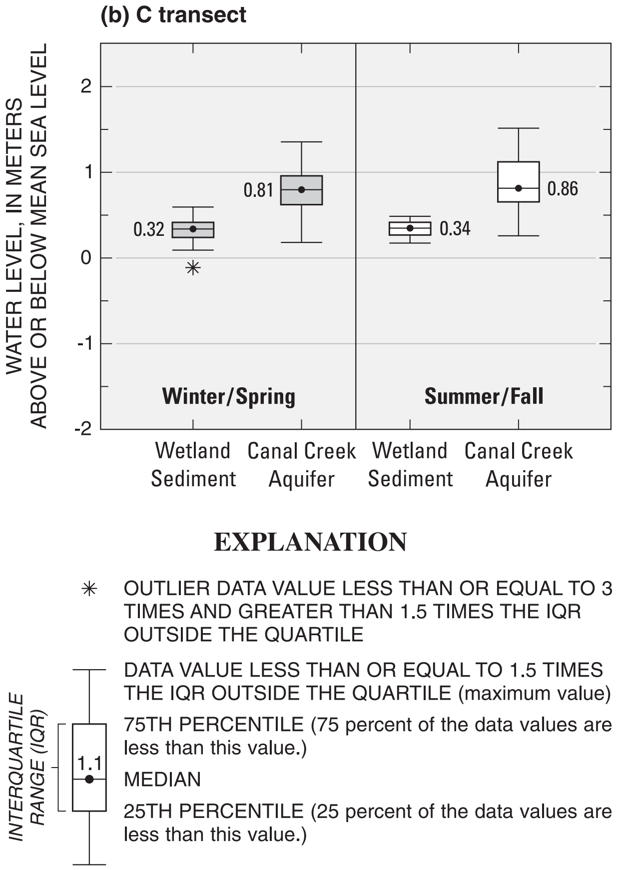

(b) C transect

Figure 23. Water-level elevations measured in the winter/spring and summer/fall for the wetland sediment and aquifer within the wetland boundary along the **(a)** A transect and **(b)** C transect in 1995.

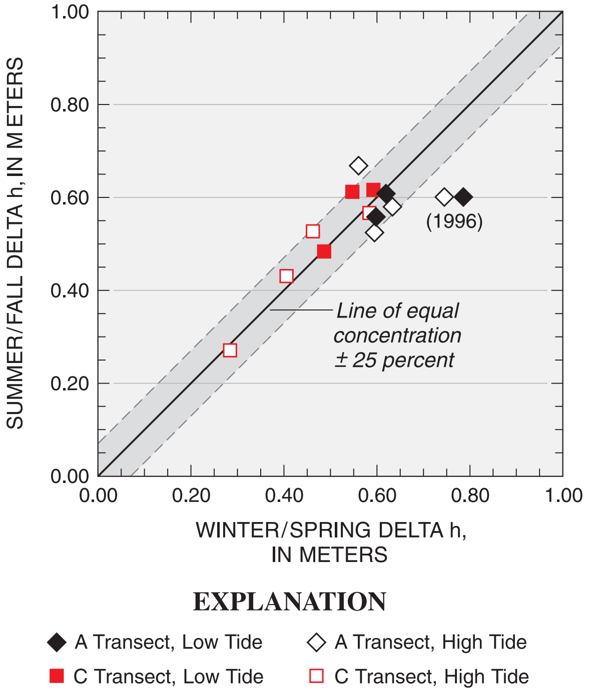


Figure 24. Comparison of median vertical head differences (median head in the wetland porewater subtracted from median head in the aquifer) in the winter/spring and summer/fall, 1995-2000.

between the aquifer and wetland sediment for both sections A–A′ and C–C′ (fig. 24). Water-level measurements were made only at high tide in June (summer) 2000 along section C–C′, and unusually low median head differences were observed (about 0.3 m compared to greater than 0.4 m for other years) (fig. 24). However, the vertical head difference measured in 2000 in the summer/fall was equivalent to that measured in the winter/spring, as observed for other years (fig. 24). The possible relation between vertical head gradient from the aquifer to wetland and the shallow porewater VOC concentrations is shown in more detail in figure 27 for one site along section C–C′, where peeper measurements consistently showed higher concentrations in the summer/fall compared to the spring/winter. Water-level measurements made at high and low tides at site WB35 on each day usually gave equivalent vertical head gradients (fig. 27). Vertical head gradients, and thus vertical mass flux to the wetland sediments, varied little during 1995 to 2000, in contrast to the annual variation in VOC concentrations in the shallow porewater (fig. 27). These results contrast with another study that has shown a seasonal change in groundwater discharge in a wetland fringing an estuary in southeastern Virginia; discharge maxima occurred in the spring and minima in the early fall (Tobias and others, 2001).

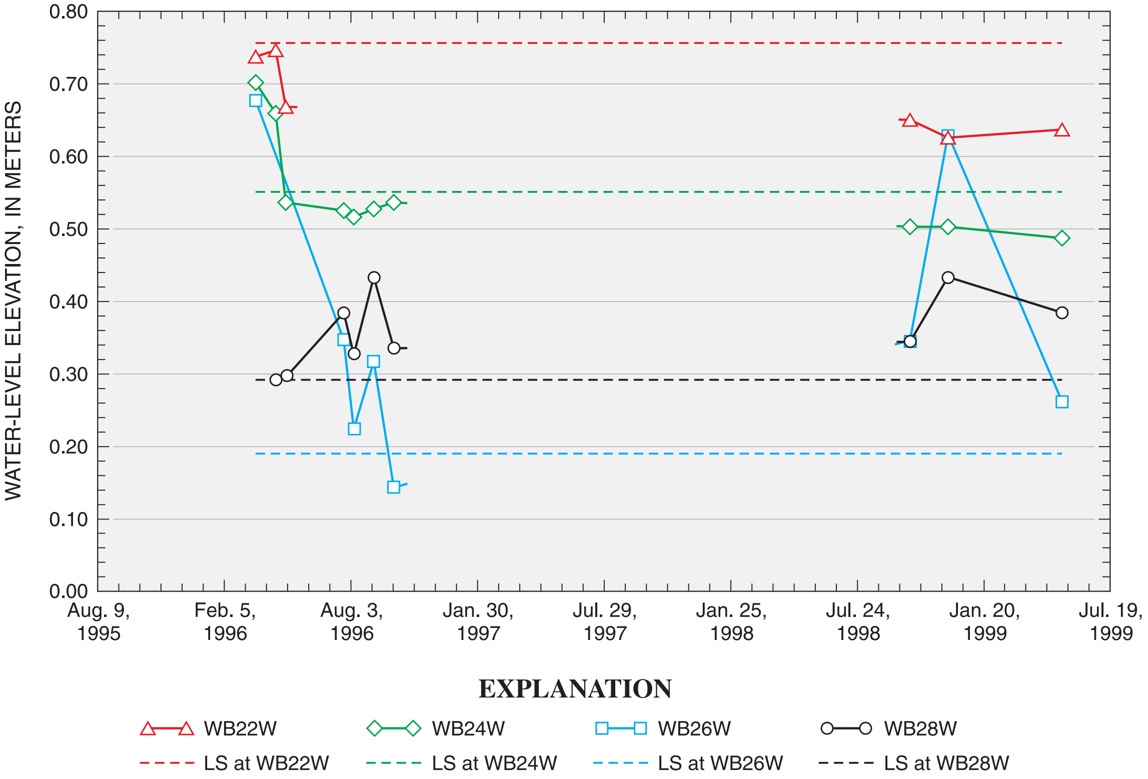


Figure 25. Water-level elevations measured at low tide in water-table wells in the wetland sediments during 1996-99 and land-surface (LS) elevations.

Overall, it is apparent that water-level changes in the shallow ground water in the West Branch wetland area show less seasonal variation than in the aquifer in the upland region, although VOC concentrations show a greater seasonal variation in the shallow wetland porewater. Seeps, or areas of focused ground-water discharge, have been delineated recently in the creek channel and the surrounding wetlands in the West Branch Canal Creek area (Majcher and others, 2003). It is possible that flow to the seep areas may increase following annual periods of recharge in the uplands, while flow in the non-seep areas remains more uniform. Because many of the seeps are contaminated with VOCs, these possible temporal variations in seep flow could have a substantial effect on flux of VOCs to the creek.

Another possible factor causing the seasonal increase in VOC concentrations in the shallow wetland porewater is changes in horizontal head gradients in the shallow ground water, which are possibly causing transport of VOCs from areas of variable VOC concentrations that were not measured along the transects through the wetland. The periodic detections of toluene in the peepers along section C–C′, particularly in the summer/fall (fig. 15), indicate such a possible intermingling of shallow contaminant plumes, because toluene was not detected in the aquifer along the section. Hori-

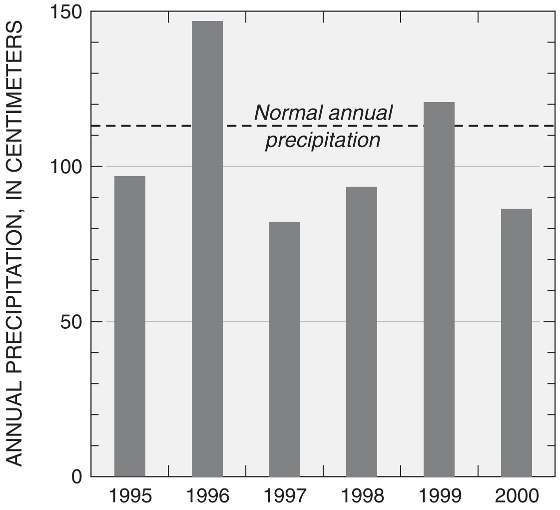


Figure 26. Total annual precipitation, 1995-2000, measured at Aberdeen Proving Ground, Maryland. (Rainfall data from U.S. Army Aberdeen Test Center Meteorology Team. Normal annual precipitation reported at *http://www.atmos.umd.edu/~climate/apg/norm.html* for data collected from 1971-2000.)

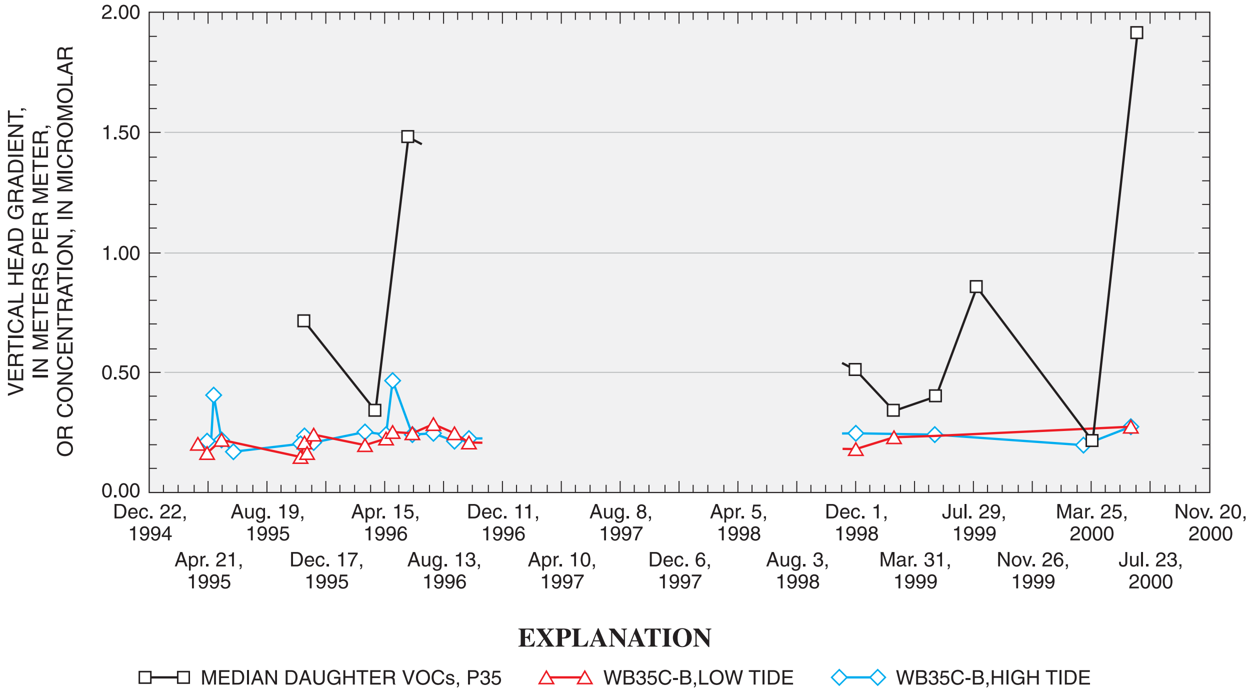


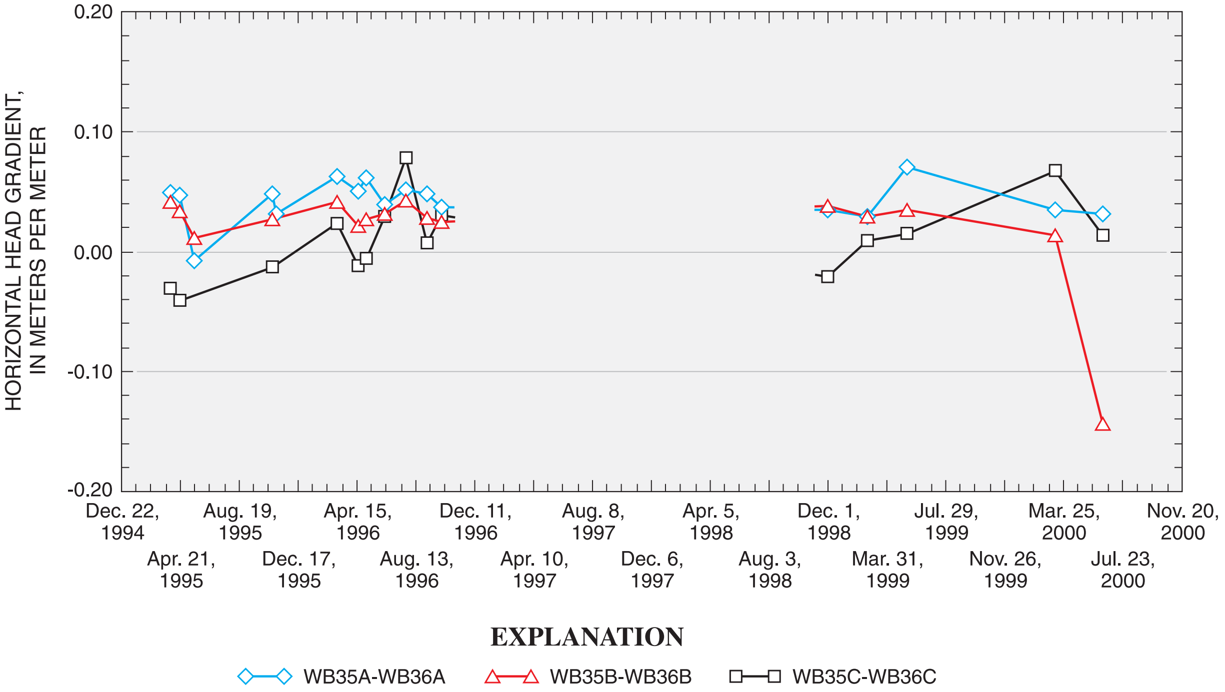
Figure 27. Fluctuations in the vertical head gradient from the aquifer to the wetland sediments and the median total concentration of daughter volatile organic compounds (VOCs) at site WB35 along section C-C', 1995-2000. (A positive head gradient indicates upward flow. Head gradient calculated by using the water-level elevations in WB35B and WB35C, and the distance between the midpoints of their screened intervals. Median VOCs were calculated using the detected concentrations of daughter VOCs in peepers sampled at site WB35 on each date; parent VOCs were not detected in these peepers.)

zontal gradients are shown in figure 28 for three sites along section C–C′, comparing the head gradients in the wetland sediments (A and B screened intervals) and the aquifer (C screened interval). Horizontal head gradients in the wetland porewater typically ranged from 0 to 0.04 m/m and were as much as an order of magnitude lower than the vertical head gradient (about 0.2 m/m) from the aquifer to the wetland sediments (figs. 27–28). The constant low horizontal head gradients in the West Branch Canal Creek wetland area contrast with other coastal wetlands, where horizontal head gradients dominated flow at all times (Harvey and others, 1987) or at times of high recharge in the spring (Tobias and others, 2001).

As was observed for the vertical head gradients, a seasonal pattern of changing horizontal ground-water-flow directions every summer/fall that could correlate with the summer/fall increases in VOC concentrations in the shallow porewater was not evident (fig. 11). Horizontal head gradients were near zero most of the time in the wetland porewater, except in March and June 2000, when there was a strong negative horizontal gradient (-0.18 m/m) between piezometers WB35B and WB36B (flow toward WB35B) and between piezometers WB36A and WB37A (flow toward WB36A) (figs. 28a, b). The negative horizontal head gradient in 2000 indicates that flow was inland toward site WB35 from site WB37, which is near the creek channel. Although short-term reversals in flow direction have been observed previously at high tide at these sites (Lorah and others, 1997; Lorah and Olsen, 1999a), the unusually high negative gradient in both March and June 2000 indicates a more prolonged period of flow reversal.

This prolonged flow reversal in the wetland porewater could explain the higher VOC concentrations in June 2000 at sites WB35 and WB36 compared to any other summer sampling period (fig. 11). At site WB35, maximum VC concentrations in the shallow porewater were about four times higher in June 2000 compared to previous years (fig. 12). In addition, both the ratios of VC and 12DCE (fig. 13) and the redox chemistry (fig. 17) in the peepers at site WB35 were similar to those at site WB36 in June 2000, whereas distinct profiles were observed previously at the two sites. Thus, the porewater chemistry at site WB35 apparently reflects the prolonged period of horizontal flow from site WB36 and impact from a different ground-water contaminant plume flowing from near the creek channel and inland to the east. Further confirmation or delineation of another plume is not possible with the current monitoring network. The surface water did not contain significant concentrations of VC (Phelan and others, 2001) that could be a source of this contamination. In contrast to the shallow wetland porewater,

(a) WB35 to WB36, C Transect



(b) WB36 to WB37, C Transect

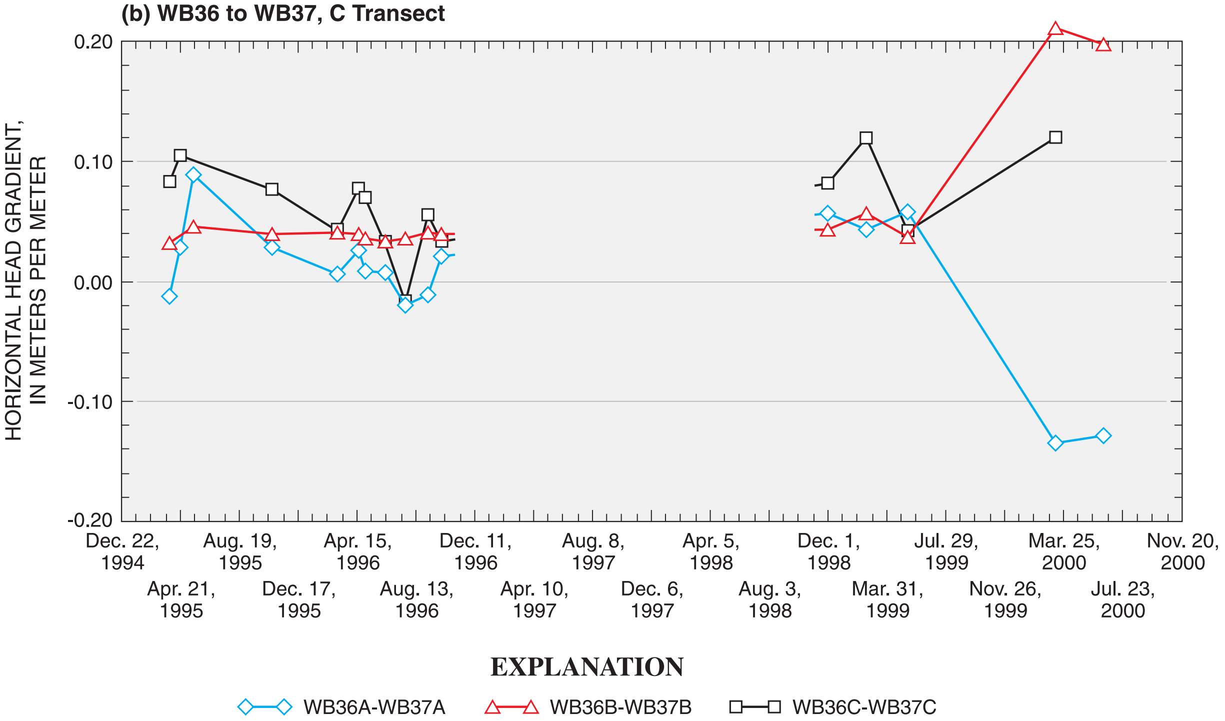


Figure 28. Fluctuations in the horizontal head gradients in the wetland porewater and aquifer between sites **(a)** WB35 and WB36, and **(b)** sites WB36 and WB37 along section C-C', 1995-2000. (Horizontal head gradients calculated using the water-level elevations measured at low tide in the piezometers and the horizontal distance between them. In June 2000, only high-tide water-level measurements were made.)

Table 9. Mean surface-water elevations measured at a tide gage in the West Branch Canal Creek at Hanlon Road for water years 1998–2000

[Tide gage located about 100 meters north of C transect (fig. 1); mean water-level elevations in meters are given for 3-month seasonal periods]

Season	1998 Water Year (October 1997–September 1998)	1999 Water Year (October 1998–September 1999)	2000 Water Year (October 1999–September 2000)
Fall (October–December)	0.28	0.28	0.26
Winter (January–March)	0.35	0.23	0.17
Spring (April–June)	0.39	0.37	0.47
Summer (July–September)	0.38	0.38	0.44

ground water in the aquifer (C screened interval) showed consistent horizontal head gradients (figs. 28a, b), and VOC concentrations were consistent in June 2000 with previous measurements (fig. 15; table 4).

Surface-Water Levels and Tidal Fluctuations

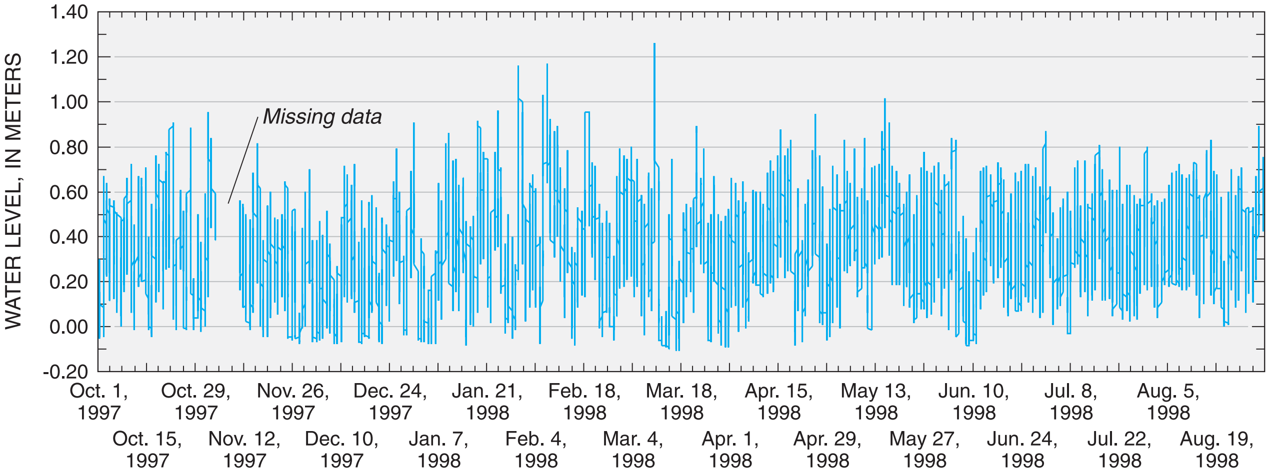
Surface-water elevations from a tide gage in the West Branch Canal Creek are available for 3 water years during the period of ground-water sampling (fig. 29). Water levels fluctuated daily in the creek, ranging from elevations of 0 to 1 m. Winter surface-water elevations were most variable between the different years, probably because of variable durations and extent of freezing (table 9). Surface-water levels for fall, spring, and summer were about the same during water years 1998 and 1999, with mean water levels for the 2 years agreeing within 5 percent (table 9). During water year 2000, the mean surface-water elevations of 0.47 and 0.44 m in the spring and summer, respectively, were 20 to 25 percent higher than the 1998–1999 water levels during the same seasons (table 9). This increase in surface-water elevations in the spring could account for the unusually low vertical head gradient that was observed between the aquifer and wetland sediments in 2000 (fig. 27), and for the strong negative horizontal gradient (inland flow direction from the creek channel) in the shallow wetland porewater along section C–C′ in March and June 2000 (fig. 28). Thus, the prolonged high creek stage corroborates the prolonged reversal in ground-water flow indicated by the head gradients and the unusual increase in shallow porewater VOC concentrations along section C–C′ during this period. These results indicate that monitoring of creek stage could be used as one method of determining when a sampling event may be needed during implementation of monitored natural attenuation as a remediation method for the plumes of chlorinated VOCs entering the wetland area.

Sediment Temperature

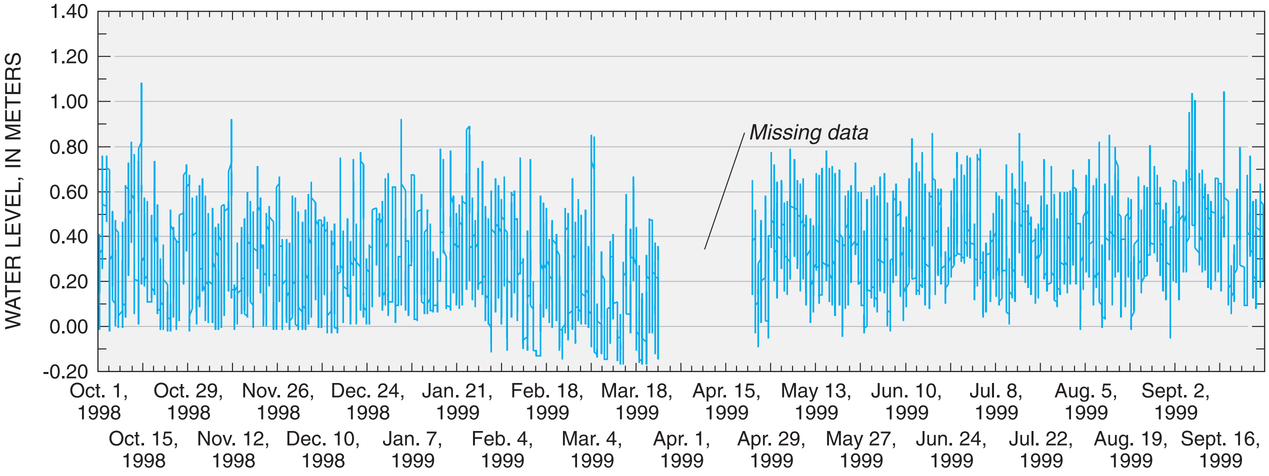
Temperatures did vary seasonally in the wetland sediments, but temperature changes were greatest in the upper 0.15 m of sediment and were dampened greatly with depth (figs. 30a, b). At the shallow depth of 0.15 m, the wetland sediment temperature responded closely to air temperature, with the sediment temperature ranging between 0 and 5 °C in the winter/early spring and increasing to maximum temperatures between 20 and 25 °C in summer. At a depth of 0.61 m, the sediment temperature remained around 10 °C in the winter/early spring and then increased only by 6 to 8 °C in the summer (figs. 30a, b). At a depth of 2.1 m, sediment temperatures remained between 10 and 15 °C throughout the year.

It was previously hypothesized that lower degradation rates of the VOCs may occur in the winter because the colder temperatures would decrease microbial activities. The sediment temperature data, however, indicate that temperatures are between 10 to 20 °C throughout the year in all except the upper 0.15 m of sediment (fig. 30), which should allow biodegradation to proceed at all times. Concentrations of daughter VOCs in the shallow wetland porewater were substantially lower in the winter/spring compared to the summer in the limited field data previously reported (Lorah and others, 1997), and in the more extensive field data presented here. If the lower concentrations of daughter products were indicative of lower biodegradation rates in the winter/spring, breakthrough of parent VOCs to the shallow wetland porewater probably would have been observed in the winter/spring. Parent VOCs remained near or below detection levels in the shallow porewater in the winter/spring, however, showing no evidence of a decrease in biodegradation rates. Laboratory-measured biodegradation rates of TeCA actually indicated a higher potential biodegradation rate in the winter/spring sediment than in summer sediment (Lorah and others, 2003). When all microcosms were incubated at 19 °C, TeCA degradation rates were higher in microcosms constructed with wetland sediment collected in the late winter/early spring compared to those constructed with wetland sediment collected in the summer (Lorah and others, 2003). Microcosms constructed with late winter sediment that were incubated at 5 °C showed substantial TeCA degradation, although the rate of TeCA loss was about 50 percent lower than the rate observed at 19 °C (Lorah and others, 2003). Microbial diversity and biomass were greater in the shallow

(a) 1998 Water Year



(b) 1999 Water Year



(c) 2000 Water Year

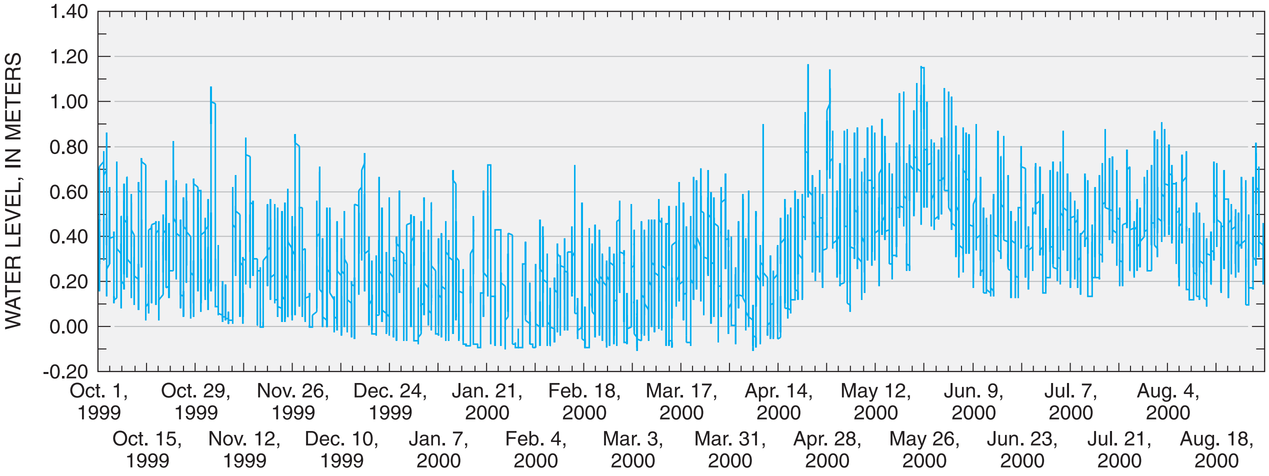
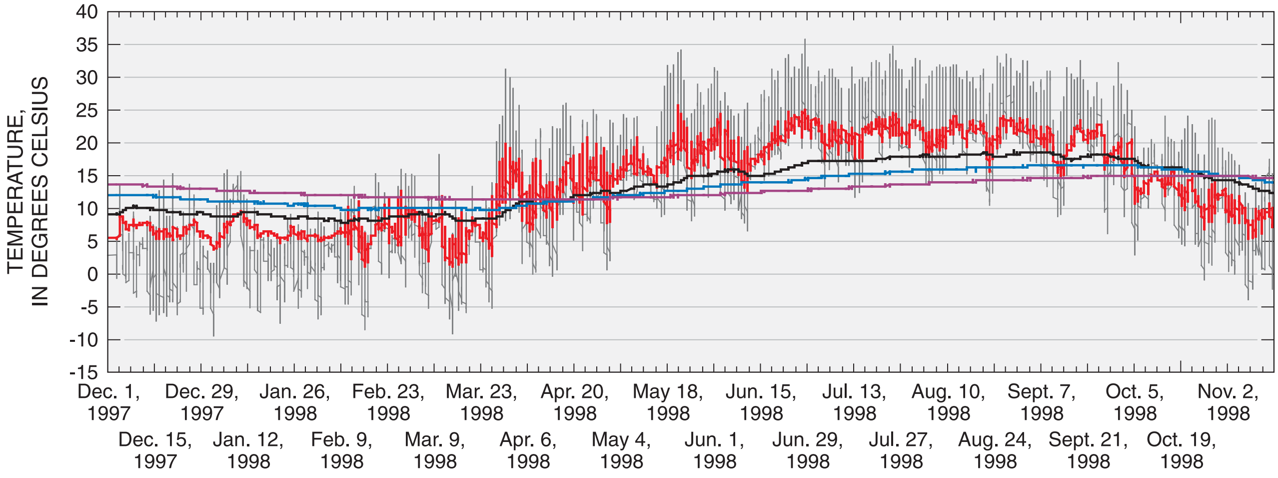


Figure 29. Tidal fluctuations at the Hanlon Road tide gage, West Branch Canal Creek, for **(a)** 1998, **(b)** 1999, and **(c)** 2000 water years. [Tide gage located about 100 meters north of C transect (fig. 1).]

(a) December 1997-1998



(b) December 2000-2001

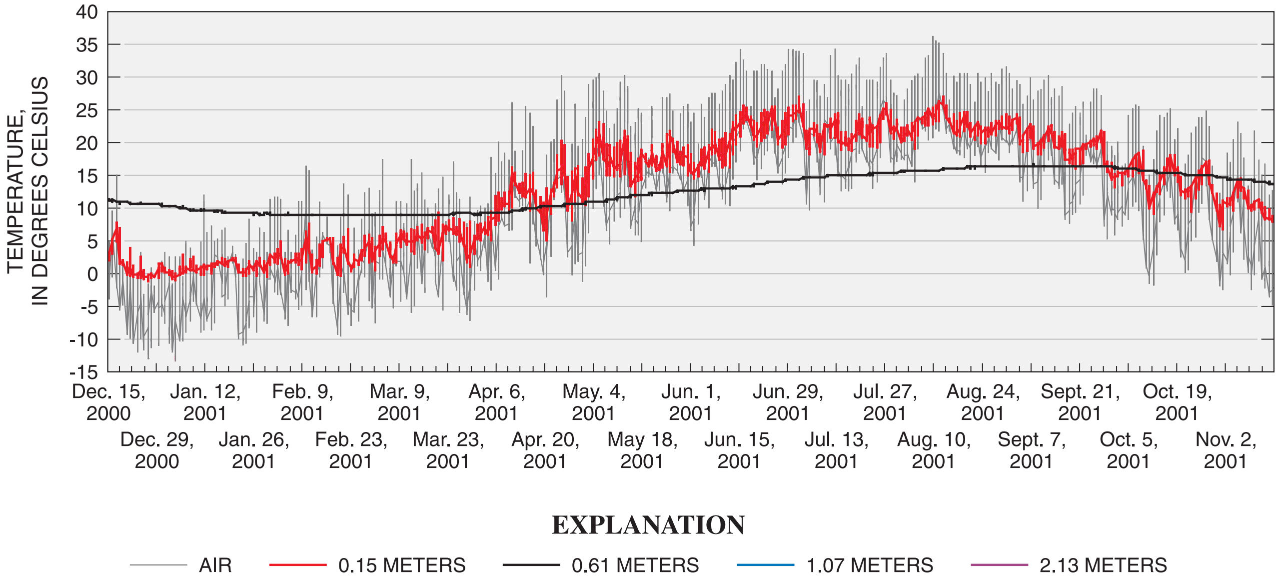


Figure 30. Temperature of air and wetland sediment (in meters below land surface) measured near site DP12 along the C transect in **(a)** December 1997-1998 and **(b)** December 2000-2001.

(less than 0.25 m) wetland sediment collected in the winter/early spring than in shallow sediment collected in the summer (Lorah and others, 2003). It is possible that the effect of lower sediment temperatures on microbial activity could be balanced by the greater microbial biomass in the winter/early spring, resulting in fairly uniform biodegradation rates throughout the year. Overall, the patterns observed in the sediment temperature data and in the field and laboratory biogeochemical data are not consistent with a direct effect of colder winter temperatures decreasing the microbial degradation of the VOCs.

Freezing and thawing of the sediment is an indirect temperature-related effect that could alter the distribution of VOCs and inorganic constituents in the shallow wetland porewater. A rapid period of warming typically was observed at the 0.15 m depth at the end of March to early April (figs. 30a, b). Freeze-thaw events can increase the amounts and forms of nutrient and organic carbon released into soil solution, causing an increase in microbial activity with thawing (Grogan and others, 2004). Although VOC concentrations were low in spring in the wetland porewater, as might occur with increased microbial degradation on thawing, concentrations were equally low in February (fig. 12). Temperature changes also influence microbial community structure in anaerobic sediments. Several studies have found that lower sediment temperatures and freezing conditions shift the community to dominance of acetogens and acetate-consuming methanogens compared to sulfate-reducing bacteria and hydrogen-consuming methanogens (Fey and Conrad, 2000; Mountfort and others, 2003). Methanosarcinaceae is a methanogen group that includes all those that can utilize acetate to generate methane. In our previous laboratory study of VOC biodegradation in the West Branch wetland sediments, high biodegradation rates in sediment collected in early spring 1999 (immediately after thawing) were correlated with an increase in the relative proportion of Methanosarcinaceae in the methanogen population (Lorah and others, 2003; Lorah and Voytek, 2004). This effect was observed in microcosms constructed with sediment from site WB30 but not site WB23 (fig. 1). A similar increase in the proportion of Methanosarcinaceae and increase in biodegradation in sediment from site WB30 compared to sediment collected from site WB23 was observed in microcosms constructed in October 2000 (Lorah and others, 2003; Lorah and Voytek, 2004). Thus, it is unclear if temperature-related shifts in the methanogen community were a factor in these experiments, and if such a microbial community shift could account for the lower VOC concentrations observed in the winter/spring in the wetland porewater (figs. 11–12).

Summary and Conclusions

In cooperation with the U.S. Army Garrison, Aberdeen Proving Ground, Maryland since 1992, the U.S. Geological Survey has studied natural attenuation processes occurring as plumes of chlorinated volatile organic compounds (VOCs) discharge to a freshwater tidal wetland along West Branch Canal Creek, Aberdeen Proving Ground. Field and laboratory studies have shown that anaerobic biodegradation is a dominant natural attenuation process in the wetland sediments, and that monitored natural attenuation could be an effective ground-water remediation method for the VOCs at this site. Only limited temporal analysis of VOC concentrations and other indicators of natural attenuation were reported previously, however. An evaluation of temporal variability assists in defining natural attenuation efficiency throughout the year and in developing long-term monitoring plans. In this study, temporal changes in the contaminated aquifer and wetland porewater were characterized using data on water-quality and physical controlling factors collected at selected sites during multiple sampling events between 1995–2001.

The major contaminants in the aquifer within the natural attenuation study area are 1,1,2,2-tetrachloroethane and trichloroethene, which can be a daughter product of 1,1,2,2-tetrachloroethane degradation in addition to being a widely used solvent itself. The major contaminants in the wetland porewater are relatively low concentrations of anaerobic daughter compounds of 1,1,2,2-tetrachloroethane and trichloroethene, including *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene, vinyl chloride, 1,1,2-trichloroethane, and 1,2-dichloroethane. A consistent seasonal pattern of higher VOC concentrations in the summer/fall than in the winter/spring was observed in the aquifer in the upland area. However, little seasonal change was observed in VOC concentrations in the aquifer and deeper wetland sediments within the wetland boundary. Major ions and redox constituents did not show a consistent seasonal variation in the aquifer in either the upland or the wetland.

Changes in porewater chemistry also were evaluated over small vertical intervals (3 centimeters) along upward flowpaths through the wetland sediments using peepers, a type of passive diffusion sampler. Peepers installed at sites along section A–A′ through the wetland did not have detectable concentrations of VOCs, indicating that natural attenuation was largely completed before the shallow porewater (upper 61 centimeters) measured with the peepers was reached along this section. VOCs were detected in this shallow porewater along section C–C′, where the wetland sediments are thinner and thus the contaminants have a shorter residence time to be affected by natural attenuation processes. Concentrations of parent VOCs were low (less than 2 micrograms per liter) or undetectable in the shallow porewater measured with the peepers along section C–C′, but chlorinated VOCs that are anaerobic daughter products of 1,1,2,2-tetrachloroethane and trichloroethene were observed. Distribution of VOCs in the peepers along upward flowpaths reflected the sequential reductive dechlorination of 1,1,2,2-tetrachloroethane and trichloroethene—production of 1,2-dichloroethene occurred at depth, followed by production of vinyl chloride, and then decreasing concentrations of all VOCs toward land surface. A distinct temporal variation was observed in VOC concentrations in this shallow porewater. VOC concentrations in the peepers were low in the winter/spring and increased by a factor of 2 to 4 in the summer/fall. Of all the peeper sampling events between 1995–2001, VOC concentrations were highest in June 2000. Detection of toluene in the peeper samples, but not in the deeper wetland porewater or in the aquifer, indicate some lateral intermingling with unknown plume sources. Toluene concentrations typically were highest in the summer, as observed for the chlorinated VOCs in the shallow porewater. These temporal variations indicate that monitoring of VOC concentrations in the shallow wetland porewater in the summer is crucial. Although complete natural attenuation of the VOCs typically was observed before land surface was reached, low concentrations of VOCs sometimes were detectable within the upper 10 centimeters during the summer.

Concentrations of redox-sensitive constituents, including methane, ferrous iron, and sulfide, in the peepers indicated that the shallow wetland porewater was anaerobic at all times of the year. Methane concentrations were higher in the summer/fall than in the winter/spring, whereas ferrous iron concentrations showed an opposite temporal pattern of lower concentrations in the summer/fall compared to the winter/spring. Because of low sample volumes from the peepers, only VOCs and redox constituents typically were analyzed. Chloride concentrations also were determined in the shallow porewater in March 2000 and June 2000, however, and were lower during the summer sampling event than during the spring sampling event.

Major physical factors that could potentially control temporal variations in the wetland and aquifer geochemistry include head gradients and ground-water-flow directions, surface-water levels and tidal fluctuations, and sediment temperature. Water levels measured in the aquifer in the upland indicated a consistent seasonal pattern of rising water levels in the late winter and spring, and decreasing water levels in the summer. The higher summer VOC concentrations detected in the aquifer in the uplands could reflect a decrease in dilution of contaminant concentrations with the decrease in recharge to the aquifer. In contrast, water levels and horizontal and vertical head gradients were surprisingly constant throughout the study within the wetland area. The median and range in water levels in the wetland sediment and aquifer within the wetland area were approximately the same in the winter/spring compared to the summer/fall. Water levels measured in water-table wells in the wetland indicate that upward discharge from the aquifer was sufficient to maintain water-saturated or nearly saturated (within 10 centimeters of land surface) conditions in the wetland sediments throughout the sampling period, despite summer evapotranspiration demands and below-normal precipitation during 1997–1999. The consistent anaerobic conditions in the wetland sediments also indicate that the wetland sediments remained water-saturated. Thus, conditions needed for reductive dechlorination and efficient natural attenuation of the VOCs were prevalent at all times. Vertical head gradients between the aquifer and wetland sediments were about the same in the winter/spring compared to the summer/fall for the two sections, with the exception of relatively high head gradients along section A–A′ in the winter/spring of 1996. Above-normal precipitation resulted in high recharge in 1996, and likely accounts for the higher head gradients and chloride concentrations observed along section A–A′ during winter/spring 1996.

Vertical head gradients from the aquifer to the wetland sediments along section C–C′ were relatively constant—around 0.2 meter/meter through 1995–2000. Horizontal head gradients in the wetland porewater were lower, typically ranged from about 0 to 0.04 (meter/meter), and were relatively constant throughout much of the study period. During March and June 2000, however, a strong negative horizontal gradient (-0.18 meter/meter) indicated a prolonged period of wetland porewater flow in an inland direction from the creek channel. Mean creek stage was 20 to 25 percent higher in the spring and summer of 2000 compared to the previous 2 years, causing the prolonged flow reversal indicated by the head gradients. The unusual increase in VOC concentrations in shallow porewater along section C–C′ during this period probably resulted from this prolonged period of flow reversal.

Although temperatures varied seasonally in the wetland sediments, changes were greatest in the upper 0.15 meters of sediment and were dampened greatly with depth. At the shallow depth of 0.15 meters, the wetland sediment temperature responded closely to air temperature, with the sediment temperature ranging between 0 and 5 degrees Celsius in winter-early spring and increasing to maximum temperatures between 20 and 25 degrees Celsius in summer. In contrast, at a depth of 2.1 meters at the top of the aquifer, sediment temperatures remained between 10 and 15 degrees Celsius throughout the year. The fact that concentrations of VOCs in the shallow wetland porewater were substantially lower in the winter/spring compared to the summer indicates that the temperature fluctuations did not substantially decrease biodegradation rates.

In summary, the relatively constant hydrologic and temperature conditions in the wetland sediment appear to assist in maintaining efficient natural attenuation of the VOCs throughout the year. Although a clear cause of the annual increases in VOC concentrations in the shallow porewater was not determined, the most extreme increases in concentrations of inorganic constituents in 1996 and of VOCs in the summer of 2000 were associated with unusual hydrologic events—above-normal precipitation in 1996 and prolonged high creek stage in 2000. Monitoring these physical factors could provide an indication of when unusual concentrations might occur in the wetland porewater. A sampling event could then be initiated if monitored natural attenuation is implemented as the remediation strategy.

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