

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

Characterization of Preferential Ground-Water Seepage From a Chlorinated Hydrocarbon- Contaminated Aquifer to West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 2002–04



Scientific Investigations Report 2006–5233

Cover. West Branch Canal Creek tidal area looking south toward the Gunpowder River.

Characterization of Preferential Ground-Water Seepage From a Chlorinated Hydrocarbon-Contaminated Aquifer to West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 2002–04

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Conversion Factors and Abbreviations

Multiply	By	To obtain
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
square foot (ft ²)	0.09290	square meter (m ²)
foot per year (ft/yr)	0.3048	meter per year
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
gallon (gal)	3.785	liter
pound, avoirdupois (lb)	0.4536	kilogram (kg)
pound per cubic foot (lb/ft ³)	0.0160	gram per cubic centimeter (g/cm ³)

Other abbreviated units of measure: Water temperature, chemical concentration, and other chemical and physical properties of constituents are given in metric units. Water temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

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

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

Abbreviations

APG, Aberdeen Proving Ground

CERCLA, Comprehensive Environmental Response, Compensation, and Liability Act of 1980

CPT, Cone penetrometer tests

dhc, Dehalococcoides

DI water, Deionized water

DNA, Deoxyribonucleic acid

IRP, Installation Restoration Program

PCR, Polymerase chain reaction

PDS, Passive-diffusion sampler

qPCR, Real-time quantitative polymerase chain reaction

RPDs, Relative percent differences

TEAP, Primary terminal electron accepting process

TICs, Tentatively identified compounds

TIR, Thermal infrared

TRFLP, Terminal restriction fragment length polymorphism

USEPA, U.S. Environmental Protection Agency

USGS, U.S. Geological Survey

µg/L, micrograms per liter

µS/cm, microsiemens per centimeter

UXO, unexploded ordnance

VOC(s), volatile organic compounds

Chemical compounds

CF, chloroform

CT, carbon tetrachloride

12DCA, 1,2-dichloroethane

cDCE, *cis*-1,2-dichloroethene

tDCE, *trans*-1,2-dichloroethene

12DCE, total of *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene

MeCL, methylene chloride

PCE, tetrachloroethene

PVC, polyvinyl chloride

TeCA, 1,1,2,2-tetrachloroethane

112TCA, 1,1,2-trichloroethane

TCE, trichloroethene

TOC, total organic carbon

TSP, trisodium phosphate

VC, vinyl chloride

Characterization of Preferential Ground-Water Seepage From a Chlorinated Hydrocarbon-Contaminated Aquifer to West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 2002–04

by Emily H. Majcher, Daniel J. Phelan, Michelle M. Lorah, and Angela L. McGinty

Abstract

Wetlands act as natural transition zones between ground water and surface water, characterized by the complex interdependency of hydrology, chemical and physical properties, and biotic effects. Although field and laboratory demonstrations have shown efficient natural attenuation processes in the non-seep wetland areas and stream bottom sediments of West Branch Canal Creek, chlorinated volatile organic compounds are present in a freshwater tidal creek at Aberdeen Proving Ground, Maryland. Volatile organic compound concentrations in surface water indicate that in some areas of the wetland, preferential flow paths or seeps allow transport of organic compounds from the contaminated sand aquifer to the overlying surface water without undergoing natural attenuation. From 2002 through 2004, the U.S. Geological Survey, in cooperation with the Environmental Conservation and Restoration Division of the U.S. Army Garrison, Aberdeen Proving Ground, characterized preferential ground-water seepage as part of an ongoing investigation of contaminant distribution and natural attenuation processes in wetlands at this site. Seep areas were discrete and spatially consistent during thermal infrared surveys in 2002, 2003, and 2004 throughout West Branch Canal Creek wetlands. In these seep areas, temperature measurements in shallow pore water and sediment more closely resembled those in ground water than those in nearby surface water. Generally, pore water in seep areas contaminated with chlorinated volatile organic compounds had lower methane and greater volatile organic compound concentrations than pore water in non-seep wetland sediments. The volatile organic compounds detected in shallow pore water in seeps were spatially similar to the dominant volatile organic compounds in the underlying Canal Creek aquifer,

with both parent and anaerobic daughter compounds detected. Seep locations characterized as focused seeps contained the highest concentrations of chlorinated parent compounds, relatively low concentrations of chlorinated daughter compounds, and insignificant concentrations of methane in shallow pore water samples. These seeps were primarily along the creek edge or formed a dendritic-like pattern between the wetland and creek channel. In contrast, seep locations characterized as diffuse seeps contained relatively high concentrations of chlorinated daughter compounds (or a mixture of daughter and parent compounds) and detectable methane concentrations in shallow pore water samples. These seeps were primarily along the wetland boundary. Qualitative thermal infrared surveys coupled with quantitative verification of temperature differences, and screening for volatile organic compound and methane concentrations proved to be effective tools in determining the overall extent of preferential seepage.

Hydrologic and physical properties of wetland sediments were characterized at two focused and one diffuse seep location. In the seeps with focused discharge, measured seepage was consistent over the tidal cycle, whereas more variability with tidal fluctuation was measured in the diffuse seep location. At all locations, areas were identified within the general seep boundaries where discharge was minimal. In all cases, the geometric mean of non-zero vertical flux measurements was greater than those previously reported in the non-seep wetland sediments using flow-net analysis. Flux was greater in the focused discharge areas than in the diffuse discharge area, and all fluxes were within the range reported in the literature for wetland discharge. Vertical hydraulic conductivity estimated from seepage flux and a mean vertical gradient at seeps with focused discharge resulted in a minimum hydraulic conductivity two orders of magnitude greater than those estimated in the non-seep sediment. In contrast, vertical conductivity estimates at a diffuse seep were

similar to estimates along a nearby line of section through a non-seep area. Horizontal hydraulic conductivity appeared to be negatively correlated with increasing depth below land surface at both focused seep locations on the basis of cone penetrometer tests and particle-size analysis. When these hydrologic properties were extrapolated to focused and diffuse seep locations within West Branch Canal Creek, seep areas were estimated to account for about 1 percent of the total discharge area of the wetland. This 1 percent of wetland discharge area is estimated to contribute more than 20 percent of the total ground-water discharge to the creek, however, indicating that the seeps play an important role in the transport of ground water (and dissolved volatile organic compounds) to surface water.

Lithologic descriptions of wetland sediments in focused seep areas were consistent with descriptions elsewhere in the wetland. There was no visible evidence in the sediments of preferential pathways for ground-water discharge. Physical properties of seep sediments collected from cores showed characteristics of both organic and mineral sediments and were characteristic of organic clays with a relatively high fraction of fines. In seep sediment cores, the variation in physical properties with depth was consistent with hydrologic properties; however, the increased seepage flux in seep locations could not be explained on the basis of the physical properties analyses conducted during this study.

In the seeps with focused discharge, natural attenuation (mainly anaerobic biodegradation) is affected by the increase in vertical seepage flux and resulting decrease in residence time in the wetland sediments. This results in less reducing conditions, an accumulation of chlorinated volatile organic compounds in shallow pore water, and in some cases, a change in the microbial community. Results of surface-water-quality sampling alone were not indicative of seep location or pore water concentration at the ground-water/surface-water interface, indicating that thermal and passive pore water sampling methods such as those used in this study are more appropriate for identifying areas of preferential discharge to surface water than surface-water sampling alone.

Despite the large areal footprint of overlapping volatile organic compound plumes in the Canal Creek aquifer beneath the West Branch Canal Creek wetlands and stream bottom, natural attenuation appears to efficiently reduce concentrations in the organic-rich wetland sediments in most of the wetland area. The identification of discrete areas of preferential discharge of contaminated pore water to surface water provides an alternative approach to remediation of source zones contained within or nearby the sensitive wetland ecosystem by reducing the overall treatment area to 1 percent of the total discharge area. Targeted, passive treatment at the ground-water/surface-water interface could provide treatment immediately prior to discharge to surface water. Some limited, passive remediation in seep areas coupled with natural attenuation could preserve the wetland ecosystem and reduce the loading of volatile organic compounds to West Branch Canal Creek.

Introduction

Ground water and surface water are often investigated, described, and regulated as separate media; however, they are hydraulically connected (Winter and others, 1998). The physical and chemical interaction between the two resources is of particular importance for the fate and transport of contaminants because the U.S. Environmental Protection Agency (USEPA) reported that nearly 50 percent of regulated hazardous-waste sites have documented impacts to surface water as a result of ground-water contamination (Tomassoni, 2000). Wetlands often facilitate the interaction between ground water and surface water by acting as a natural transition zone (Winter and others, 1998; Mitsch and Gosselink, 1993). These complex ecosystems, often the receptors of ground water, have the ability to regulate the discharge of nutrients and metals (Ford, 2005), and chlorinated solvents (Lorah and others, 1997; Lorah and Olsen, 1999a). Hydrology, chemical and physical properties, and biotic ecosystem responses are interdependent in wetland environments (Mitsch and Gosselink, 1993) and are spatially and seasonally heterogeneous. The heterogeneity and complexity of these wetland systems can create conditions that provide discrete pathways for solute transport to surface water via preferential flow in the form of springs or seeps (Harvey and others, 1995; Portnoy and others, 1998; Winter and others, 1998; Conant and others, 2004). In wetlands, these discharge pathways can occur along a change in slope (fig. 1a) and at a stream bank or at low tide (fig. 1b). Although these seeps have been observed in wetlands (Harvey and others, 1995; Portnoy and

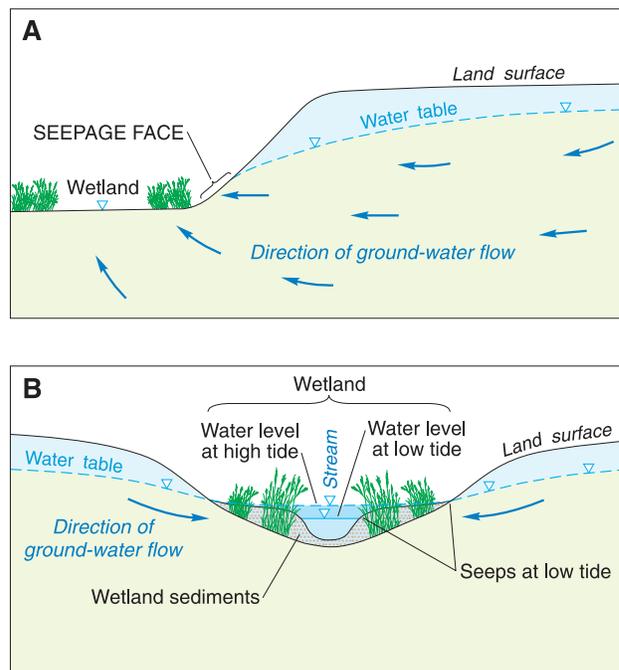


Figure 1. Conceptual model of seep and spring formation in wetlands at (A) the edge of the wetlands and (B) at low tide (modified from Winter and others, 1998).

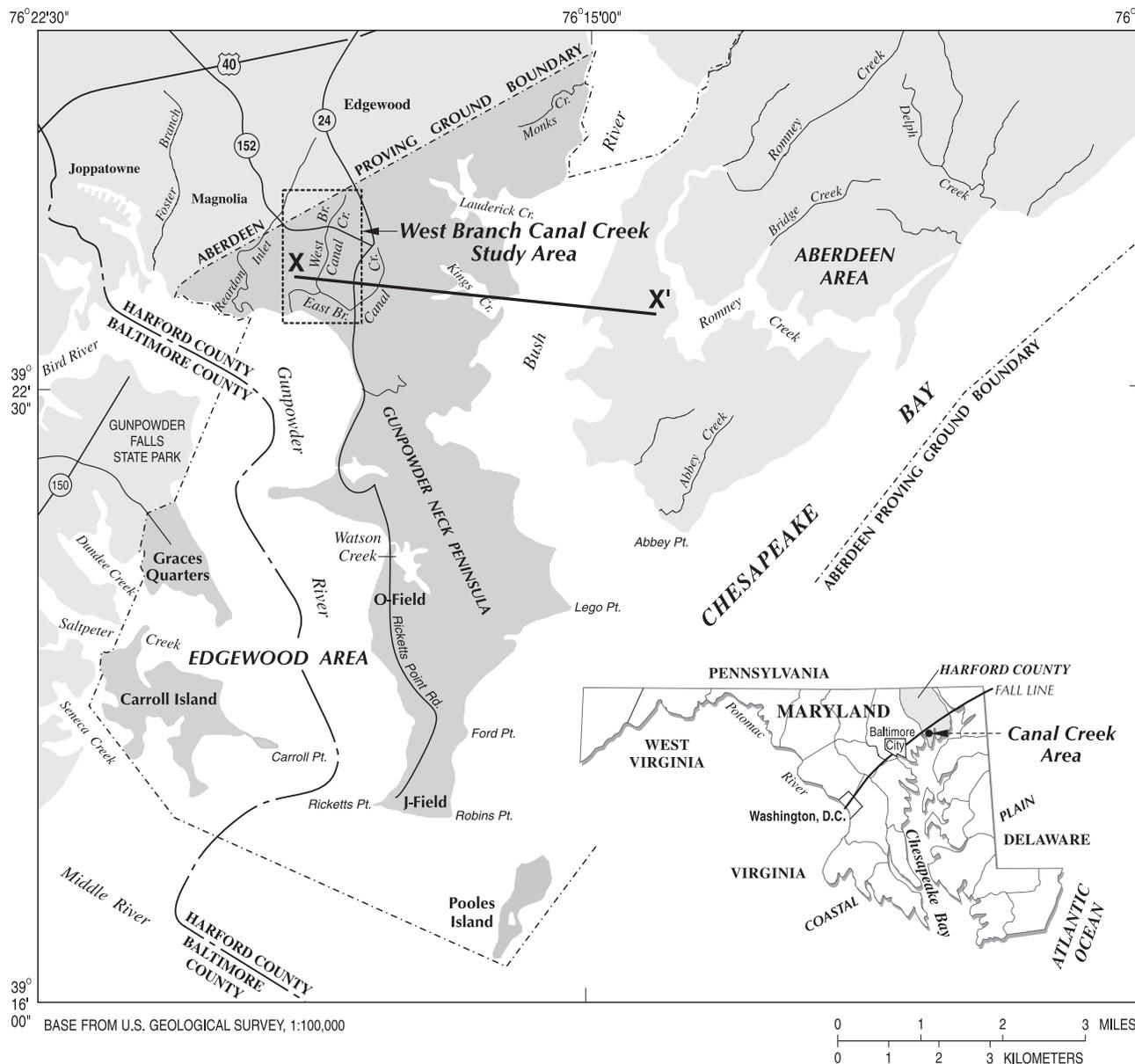


Figure 2. Location of the West Branch Canal Creek study area, Aberdeen Proving Ground, Maryland, and hydrogeologic line of section X-X' (shown in fig. 5) (modified from Phelan and others, 2002).

others, 1998; Rosenberry and others, 2000) and river beds (Conant and others, 2004), their hydrologic and physical characteristics and the role seeps play in contaminant plume discharge are poorly understood. As part of an ongoing study of contaminant distribution and natural attenuation processes, the U.S. Geological Survey (USGS) investigated relatively rapid ground-water seepage along preferential pathways from a chlorinated solvent-contaminated aquifer to West Branch Canal Creek and its surrounding wetlands at Aberdeen Proving Ground (APG), Maryland (fig. 2).

Since 1917, the Edgewood Peninsula of APG, Maryland, (fig. 2) has been a primary U.S. Army facility for research and development, manufacturing, and testing of chemical warfare agents. The main manufacturing and industrial area used

during World Wars I and II is located between two branches of a tidal creek named Canal Creek. Chlorinated organic solvents commonly were used as decontaminating agents, degreasers, and filling components during many of the activities in this area. These solvents contaminated the underlying Canal Creek aquifer, and were also discharged directly into the wetlands surrounding West Branch Canal Creek through sewer lines and disposal of construction and demolition materials (Lorah and Clark, 1996). Although no known wastes have discharged to the wetlands or creek from the manufacturing plants or sewer systems within the last three decades, comingled chlorinated solvent plumes persist in ground water that discharges to the West Branch Canal Creek bottom sediments and wetlands (Phelan and others, 2002; Weston, 2005). This area is the

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focus of an ongoing Remedial Investigation and Feasibility Study for the Installation Restoration Program (IRP) at APG, in accordance with USEPA Superfund Program.

Chlorinated solvents used during historical activities in the area included 1,1,2,2, tetrachloroethane (TeCA), trichloroethene (TCE), carbon tetrachloride (CT), chloroform (CF), and tetrachloroethene (PCE) (Nemeth, 1989; Lorah and Clark, 1996), some of which are common to other industrial and military sites. Many of these contaminants, primarily TeCA, TCE, CT, and CF, as well as PCE, hexachloroethane (HCA), and pentachloroethane (PCA), and associated chlorinated degradation by-products were detected in the Canal Creek aquifer during a series of plume delineation studies throughout the area from 1985 through 2004 (Lorah and Clark, 1996; Jacobs Engineering Group, 1995; Phelan, 2001b; Weston, 2005).

The migration of these plumes into the Canal Creek aquifer within the wetland boundaries and upward through wetland sediments along the West Branch Canal Creek

was examined along two transects (A-A' and C-C', fig. 3) downgradient from the primary manufacturing area from 1992–2001 (Lorah and others, 1997; Phelan and others, 2002) and in discrete areas south of these transects (fig. 3) in 2000 (Phelan and others, 2001b). Prior to 2002, the A-A' transect was known as A-A'', but Phelan (2002) extended the length of the transect and renamed it as A-A'. Although the chlorinated solvents tend to persist in aquifers, these and other investigations by the USGS demonstrated that the predominantly vertical discharge of ground water through organic-rich wetland sediments allows the contaminants to interact with the consistent, reducing conditions and associated microbial communities necessary for complete degradation of these contaminants (Lorah and others, 1997; Lorah and Olsen, 1999a,b; Lorah and others, 2005b). In addition to the field evidence, laboratory experiments confirmed the microbiological processes occurring in the field (Lorah and others, 2003a), indicating that monitored natural attenuation could be considered as a remedial alternative for chlorinated

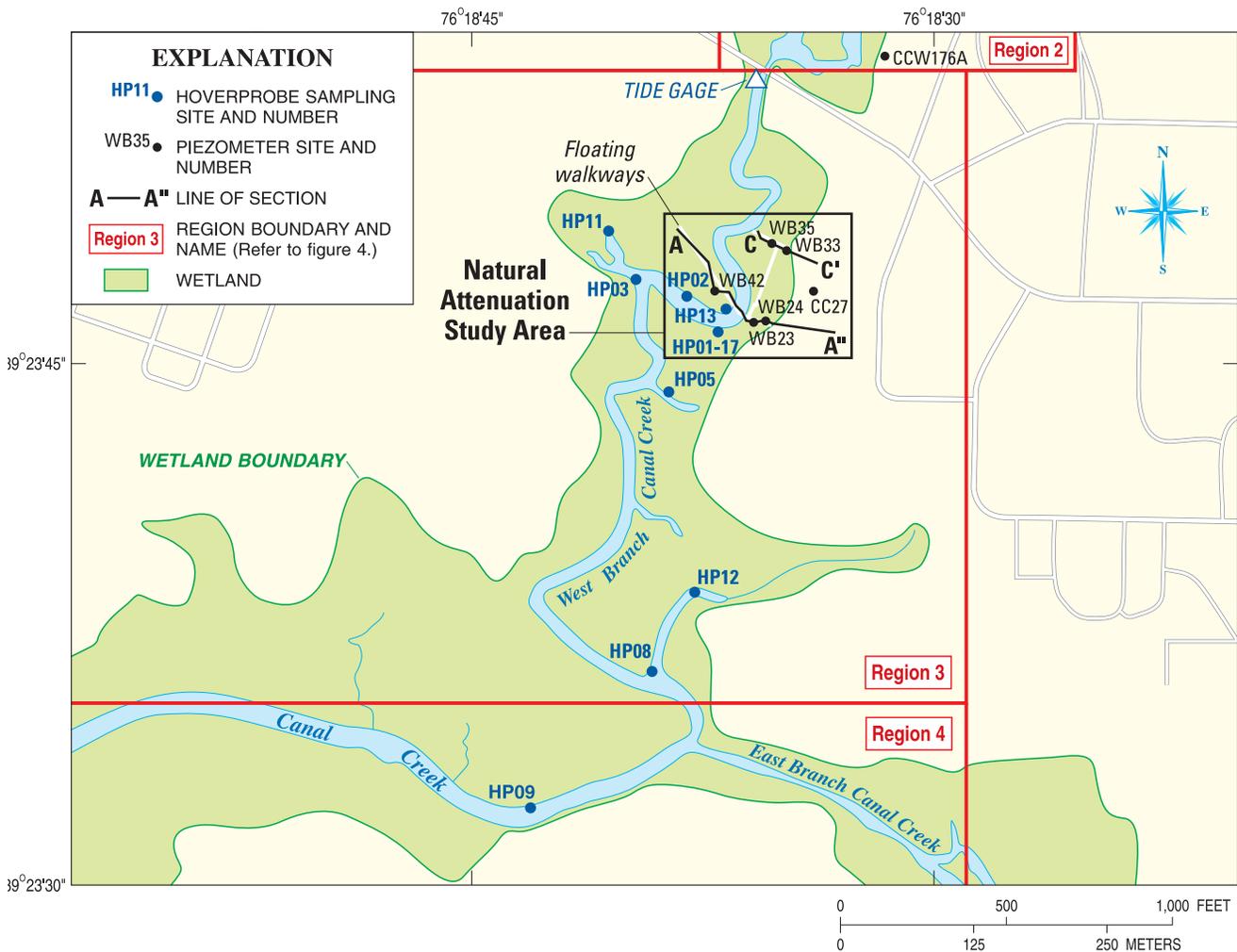


Figure 3. Location of the hoverprobe sampling sites, selected piezometers, and lines of sections A-A' and C-C', West Branch Canal Creek, Aberdeen Proving Ground, Maryland (modified from Phelan and others, 2001b).

volatile organic compound (VOC) plumes that discharge to wetlands. Although efficient natural attenuation of these chlorinated VOCs through the wetland sediments was demonstrated, VOCs (mainly CT and CF) detected in ground water (predominantly south of the natural attenuation study area) also were detected in the surface water of West Branch Canal Creek (Phelan and others, 2001a). The presence of VOCs in surface water in proportions similar to the VOCs found in ground water indicates that in some areas of the wetland, preferential flow paths of ground-water discharge or “seeps” may be present in addition to the diffuse discharge through the wetland. Ground-water discharge seeps could change the efficiency of natural attenuation processes commonly observed in the non-seep areas of the wetland and allow migration of contaminants from ground water to surface water.

The USGS investigation of preferential ground-water discharge seeps was conducted from 2002–04 in cooperation with the Environmental Conservation and Restoration Division of the Directorate for Safety, Health, and the Environment at APG. The objectives of the study were to (1) determine location, extent, and prevalence of ground-water seeps (preferential flow paths of ground-water discharge) in the wetlands along West Branch Canal Creek, predominantly in the areas impacted by upgradient chlorinated solvent plumes; (2) characterize the hydrologic and physical properties of representative seeps and evaluate the distribution of chlorinated VOCs, redox-sensitive constituents, and microbial communities and their impact on anaerobic biodegradation and surface-water quality; and (3) update the site conceptual model to include seeps and use this revised model to better define overall contaminant transport within the West Branch Canal Creek study area.

Purpose and Scope

The purpose of this report is to characterize ground-water seeps in wetland sediments that can provide a mechanism for preferential contaminant transport to the West Branch Canal Creek and surrounding wetland areas from the underlying contaminated Canal Creek aquifer. The overall occurrence and extent of the seeps within the study area is presented. The lateral distribution of chlorinated VOCs and methane (as an indicator of redox conditions appropriate for reductive dechlorination) in shallow pore water in these seep areas is described and discussed as evidence of the transport of VOCs from the contaminated aquifer to the creek. An evaluation of the hydrologic influence on the efficiency of anaerobic biodegradation is discussed as part of the focused characterization of selected seeps that are representative of different landscape locations and dominant VOCs in pore water. Hydrologic and physical properties are examined as they relate to the hydrogeology of the overall study area.

This interpretation is coupled with the evaluation of vertical distribution of both chlorinated VOCs and redox constituents in pore water. These results, in addition to sediment microbial community analysis, are used to explain the effects of seeps in the wetland system on natural attenuation processes. The impacts of these seep sites on surface-water quality are described by the comparison of overall ground-water discharge via seep flow to the diffuse flow previously reported in the non-seep wetland sediments. In addition, contaminant flux to West Branch Canal Creek is discussed, on the basis of the distribution of shallow VOCs and ground-water discharge in seep areas. The overall site conceptual model is updated to include seeps, and implications for remedial actions are presented.

In the winter of 2002, an initial aerial thermal infrared (TIR) survey was conducted and identified discrete ground-water seeps throughout the USGS West Branch Canal Creek study area wetlands and creek banks. General pore water quality relevant to natural attenuation processes (VOCs and methane) was evaluated using passive sampling methods in seep areas in spring 2002 and spring 2003. To evaluate changes in the seeps over time, additional TIR surveys were conducted in winter 2003 and winter 2004.

On the basis of observations during the TIR surveys and the results of the general pore water characterization, three seep locations were selected for additional, focused characterization from summer 2003 to fall 2004. An evaluation of the hydrology of the three seep locations was conducted through a combination of seepage meter measurements, collection of sediment cores for lithologic descriptions and physical property analysis, *in situ* dissipation tests, and temperature profiles. In addition, specially designed passive-diffusion samplers called “peepers” were used at each of three seep locations to collect fine-resolution vertical profiles of VOCs and redox-sensitive constituents including methane, ferrous iron, sulfide, and ammonia. Surface sediment samples also were collected to assess the microbial community using a deoxyribonucleic acid (DNA) fingerprinting technique used previously in the natural attenuation study (Lorah and others, 2003a). Results of this characterization were compared to previously reported results for non-seep areas to evaluate the impacts of seep flow on anaerobic biodegradation processes. The impact of VOCs in the shallow pore water on surface-water quality was estimated by the direct measurement of surface-water concentrations of VOCs in spring 2002 and spring 2003.

Estimates of seep and non-seep ground-water discharge were made to determine the hydrologic significance of the seeps. Contaminant flux to surface water from selected seep locations was calculated. Newly collected data from the seep investigations were combined with previous plume delineation results to provide a current composite of the nature and extent of the comingled VOC plume in the Canal Creek aquifer and in the wetland sediments.

Description of Study Area

The USGS West Branch Canal Creek study area is in the northwest section of the Edgewood Peninsula of APG near the northwest reaches of the Chesapeake Bay (fig. 2). This area is wholly encompassed by the APG IRP-designated Canal Creek Study Area. The land use in the USGS study area consists of grassy and wooded areas, nontidal and tidal wetlands, and impervious (paved and developed) areas that total approximately 700 acres. The West Branch Canal Creek and the nontidal and tidal wetlands surrounding it make up the western boundary of the study area. These wetlands, including those to the west of the creek, total approximately 100 acres and are the main focus of this report (fig. 4). The main industrial part of the West Branch Canal Creek study area was east of Regions 2 and 3 (fig. 4), where numerous manufacturing activities are considered likely sources of chlorinated solvent ground-water contamination detected in the underlying aquifer and the downgradient freshwater, tidal wetland (Lorah and Clark, 1996). Tidal fluctuations in these wetlands range from 0.5 to 2 ft (feet), and water frequently extends to the upland boundary.

Hydrogeologic Setting

The geology of the West Branch Canal Creek study area is characterized by thick, wedge-shaped deposits of unconsolidated Atlantic Coastal Plain sediments that dip to the southeast (fig. 5; Lorah and others, 1997). Contamination primarily occurs within the main water-bearing unit, the Canal Creek aquifer of the Patapsco Formation (hereafter referred to as the Canal Creek aquifer) that consists of medium- to coarse-grained sand and gravel, with thin clay and silt lenses. This aquifer is confined over most of the study area by an upper confining unit; however, in the vicinity the wetlands, it is typically absent allowing the Canal Creek aquifer to be largely unconfined near the West Branch Canal Creek wetland and stream (Oliveros and Vroblesky, 1989; Lorah and others, 1997; Weston, 2005). At the southern boundary of Region 2 (fig. 4) and near the West Branch Canal Creek, the continuity of the upper confining unit directly beneath the wetland and creek is unknown. It is believed to crop out in this vicinity (Oliveros and Vroblesky, 1989) but has been identified immediately to the east of the wetlands (Weston, 2005), where the Canal Creek aquifer ranges in thickness from 20 to 30 ft (Weston, 2005). Between the natural attenuation study area and the confluence of the West Branch and East Branch of Canal Creek, the Canal Creek aquifer ranges in thickness between 35 and 45 ft (Lorah and others, 1997; Phelan and others, 2001b).

The wetland and stream bottom are composed of soft, organic-rich sediments, and are typically 6 to 12 ft thick in the vicinity of the natural attenuation study area (fig. 3; Lorah and others, 1997). Sediments nearly 25 ft thick have been measured farther downstream, however (fig. 3; Phelan and

others, 2001b). The average organic content in the peat unit near the wetland study area is 18 percent (Lorah and others, 1997; Olsen and others, 1997). Flow through this peat unit is estimated to be predominantly vertical with an average specific discharge of 0.0019 to 0.0025 ft/d (feet per day) (Lorah and others, 1997).

The West Branch of Canal Creek extends from a stormwater retention pond near the northern APG boundary (fig. 4) and flows generally to the south. Approximately 1,600 ft downstream from the pond, the East Branch and West Branch merge to form the main stem Canal Creek, which discharges to the tidal Gunpowder River. The West Branch Canal Creek is tidal in all of Regions 3 and 4, and in the southern three-quarters of Region 2 (fig. 4). The base-flow conditions in the nontidal portion of the creek were estimated to range from 0.18 to 0.70 ft³/s (cubic feet per second) (Phelan and others, 2001a). Surface-water depths can range from 0 to 5 ft (Phelan and others, 2001a). On the basis of the drainage area for the tidal wetlands and creek, the exchange of water between Canal Creek and the Gunpowder River has been estimated to be approximately 9.2 million gallons per day (Phelan and others, 2001a).

Plume Delineation and Natural Attenuation Summary

A large VOC plume persists in the Canal Creek aquifer over a large part of the IRP-designated Canal Creek Study Area (fig. 6, inclusive of the USGS study areas). This area was divided for purposes of the IRP into West and East areas along a ground-water divide (fig. 6). East of the ground-water divide, contaminated ground water in the Canal Creek aquifer is pumped and treated by a ground-water treatment plant that began operating in 2001. In the western part of the study area, the plume extends from the ground-water divide west to the West Branch Canal Creek, and from north to south between the USGS stream gage and the East Branch Canal Creek (fig. 6; Weston, 2005). Multiple source areas defined within the western part of the plume include the Building 99 area, G-Street salvage yard, buildings E-5188 and E-5185, Phoshy ponds, and the former location of the pilot and chlorine plants (Lorah and Clark, 1996; Weston, 2005). Contaminants associated with these sources, coupled with the complex hydrostratigraphy of the Canal Creek aquifer have produced large, comingled plumes that consist mainly of TeCA, CT, and TCE across most of the western Canal Creek Study Area (Weston, 2005) and trend towards the wetlands along the western boundary of the study area (Lorah and Clark, 1996). The regional characteristics of ground-water flow and contaminant distribution indicate that the wetlands along the West Branch of Canal Creek serve as a receptor and that contamination does not enter the wetland from the west (General Physics Corporation, 2005) or from below the creek to the west (Lorah and Clark, 1996; Lorah and others, 1997; Weston, 2005). A preliminary natural attenuation assessment

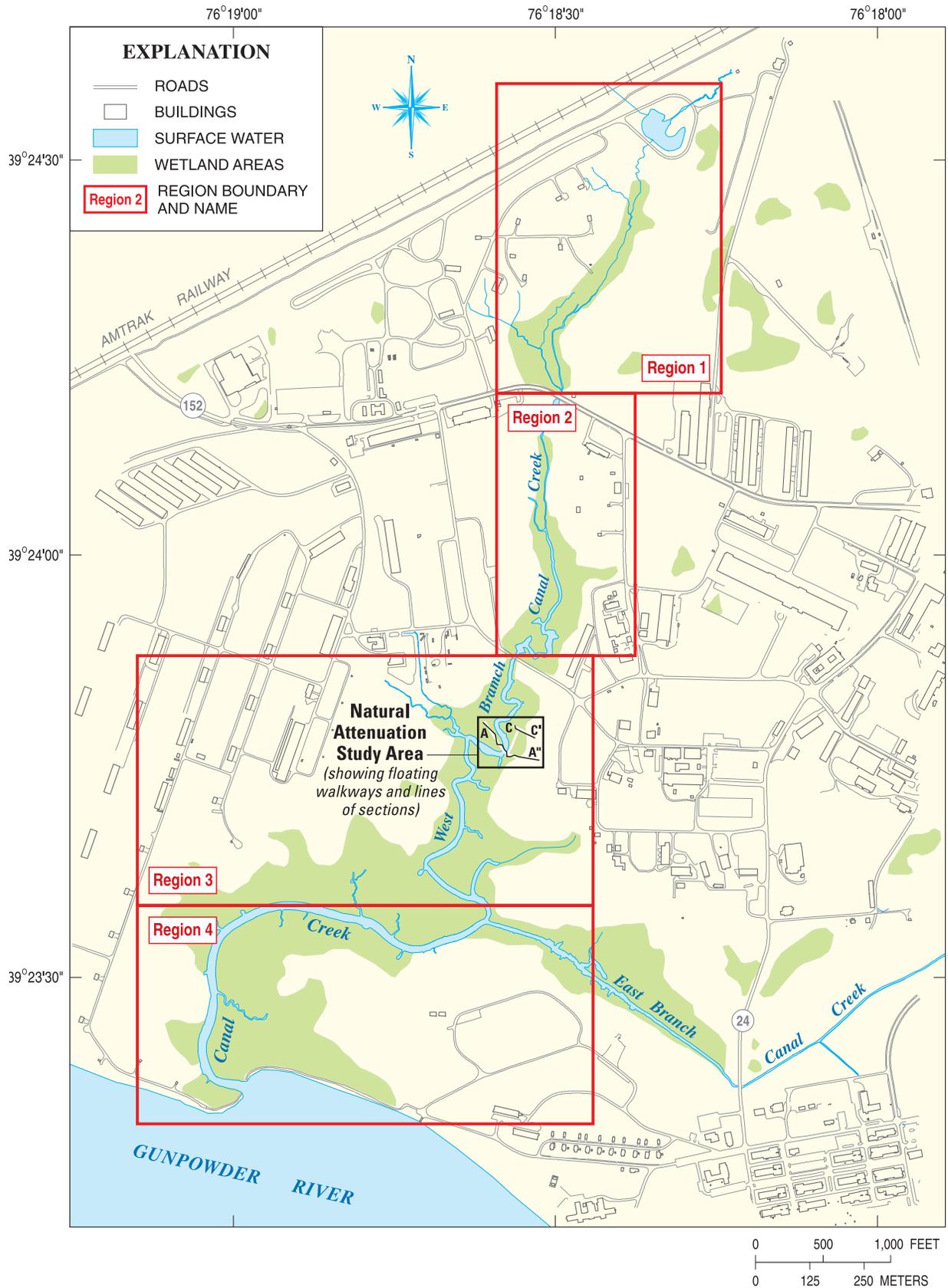
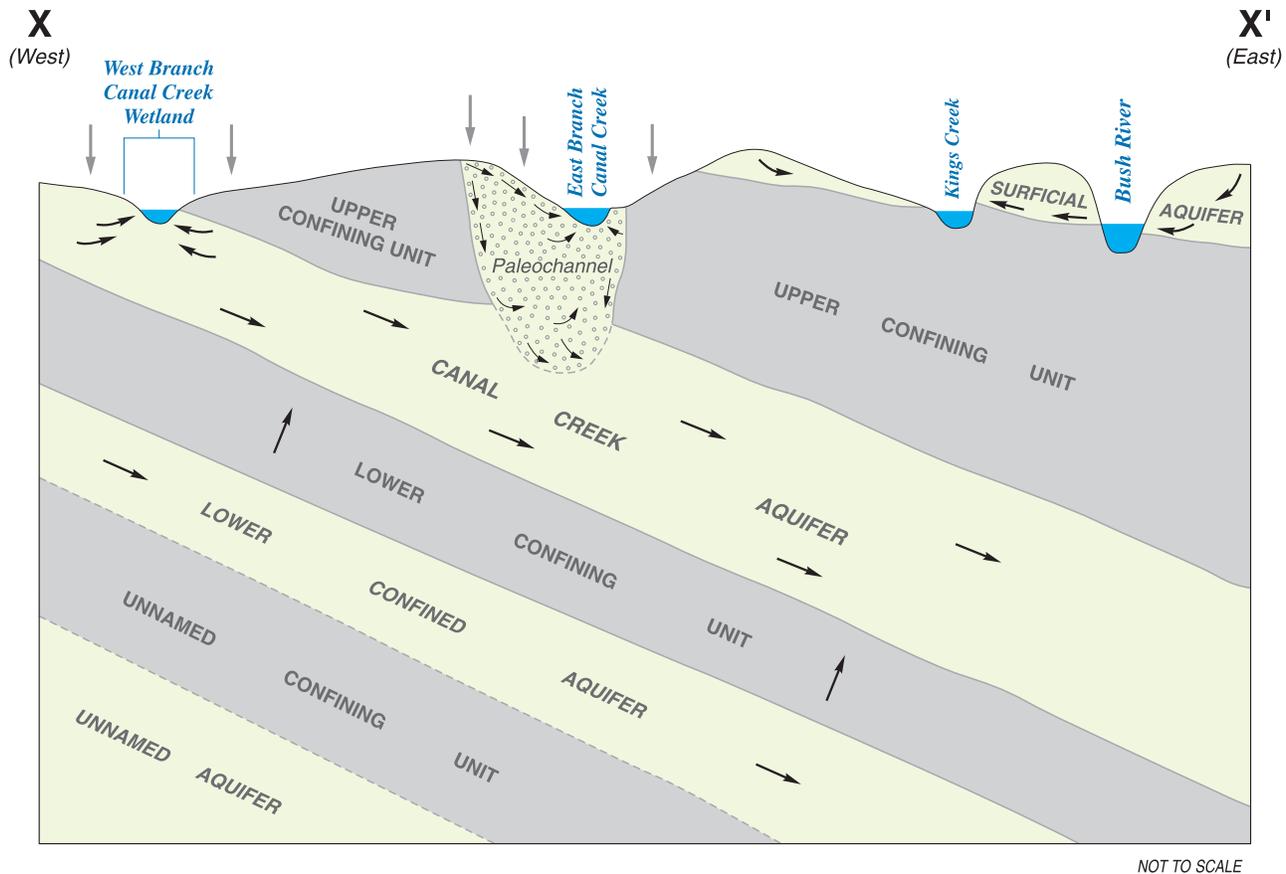


Figure 4. Location of regions, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.



EXPLANATION

 AQUIFER (Sand and gravel)	 GROUND-WATER-FLOW DIRECTION
 CONFINING UNIT (Silt and clay)	 RECHARGE

Figure 5. Generalized hydrogeologic section X-X' showing directions of ground-water flow in the Canal Creek area, Aberdeen Proving Ground, Maryland (modified from Lorah and others, 1997, p. 10). [Location of section shown in fig. 2.]

of the upland areas of the plume indicated that biodegradation is minimal prior to reaching the wetlands (Weston, 2005).

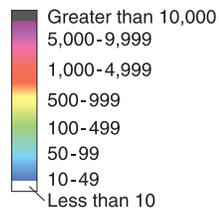
Since 1992, the USGS has conducted investigations in the discharge area downgradient of the former chlorine plant (fig. 6), predominantly within Region 3 (fig. 4) in the USGS natural attenuation study area. The purposes of these studies were to better define the fate and transport of chlorinated VOCs in the Canal Creek aquifer and West Branch wetland and stream bottom sediments (Lorah and others, 1997; 2001; Lorah and Olsen, 1999b; Lorah and others, 2005b; Phelan and others, 2002). These investigations have delineated at least two probable sources of contamination from activities in the former manufacturing area—one near the wetland/upland boundary near monitoring well CC27 (fig. 3) mainly composed of TeCA and TCE (Lorah and Clark, 1996; Lorah and others, 1997) and the second entirely within the boundaries of the wetland mainly composed of CF, CT, and PCE (Phelan and others, 2001b). Under appropriate conditions, these compounds have been shown to degrade by anaerobic reductive dechlorination to non-toxic end products (fig. 7a and b, Hollinger and others, 2003). Along the A-A'

and C-C' sections (fig. 4), TeCA and TCE were detected in the aerobic aquifer along the wetland/upland boundary in concentrations ranging from 100 to 5,000 $\mu\text{g/L}$ (micrograms per liter), whereas concentrations of degradation products were minimal or not detected (Lorah and others, 1997; Phelan and others, 2002). In the organic-rich wetland sediments where redox conditions varied from iron-reducing to methanogenic, however, daughter compounds 1,2-dichloroethene (12DCE) and vinyl chloride (VC) (and to a lesser extent 1,1,2-trichloroethane [112TCA] and 1,2-dichloroethane [12DCA]) were the dominant VOCs, whereas the parent compounds TeCA and TCE were typically not detected (Lorah and others, 1997; 2005b; Phelan and others, 2001b). The chlorinated methanes CT and CF were detected along the A-A' section at maximum concentrations of 2,000 and 2,900 $\mu\text{g/L}$, respectively, near the base of the aquifer in piezometer WB42 (fig. 3; Phelan and others, 2002). Overall, a seasonally and spatially consistent decline in total VOCs to less than 5 $\mu\text{g/L}$ was observed near the wetland surface along the lines of section (Lorah and others, 2005b; Phelan and others, 2002, fig. 3).



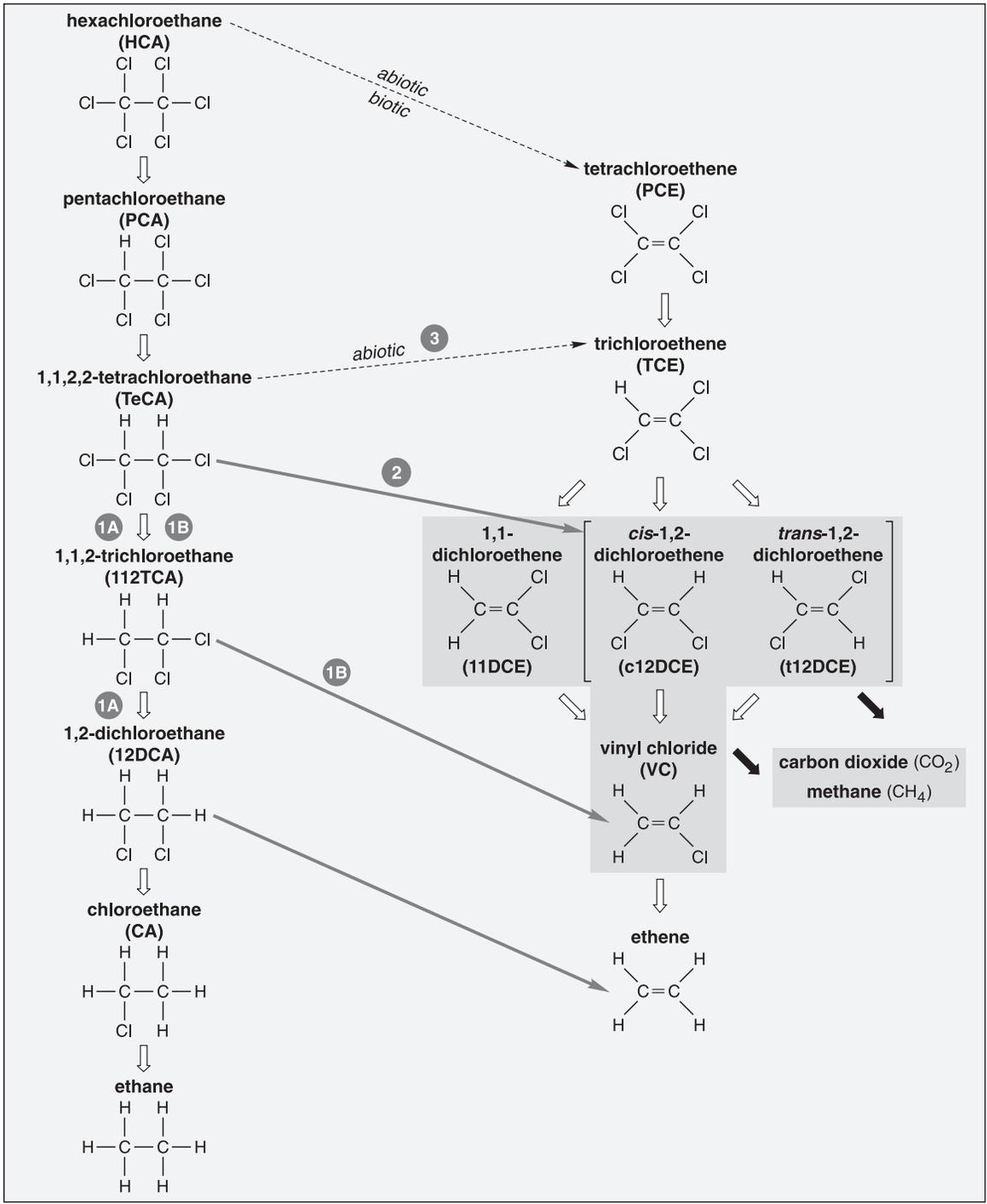
EXPLANATION

**TOTAL VOLATILE ORGANIC COMPOUND (VOC)
CONCENTRATIONS, in micrograms per liter**



- USGS STREAM GAGE
- USGS TIDE GAGE
- GROUND-WATER DIVIDE
- TREE LINE
- STREAMS
- ROADS
- BUILDINGS

Figure 6. Extent of total volatile organic compound plume in Canal Creek aquifer, Canal Creek area, Aberdeen Proving Ground, Maryland (modified from Weston Solutions, 2005, West Canal Creek study area remedial investigation).



- Pathways of TeCA degradation:**
- 1A TeCA HYDROGENOLYSIS TO 112TCA AND 12DCA
 - 1B TeCA HYDROGENOLYSIS TO 112TCA FOLLOWED BY DICHLOROELIMINATION OF 112TCA TO VC
 - 2 TeCA DICHLOROELIMINATION TO c12DCE AND t12DCE
 - 3 TeCA DEHYDROCHLORINATION TO TCE

- EXPLANATION**
- ↓ ANAEROBIC OXIDATION
 - ⇓ HYDROGENOLYSIS
 - ⇓ DICHLOROELIMINATION
 - ⇓ DEHYDROCHLORINATION

Figure 7A. Anaerobic degradation pathways for tetrachloroethene, trichloroethene, hexachloroethane, and 1,1,2,2-tetrachloroethane (modified from Lorah and others, 1997).

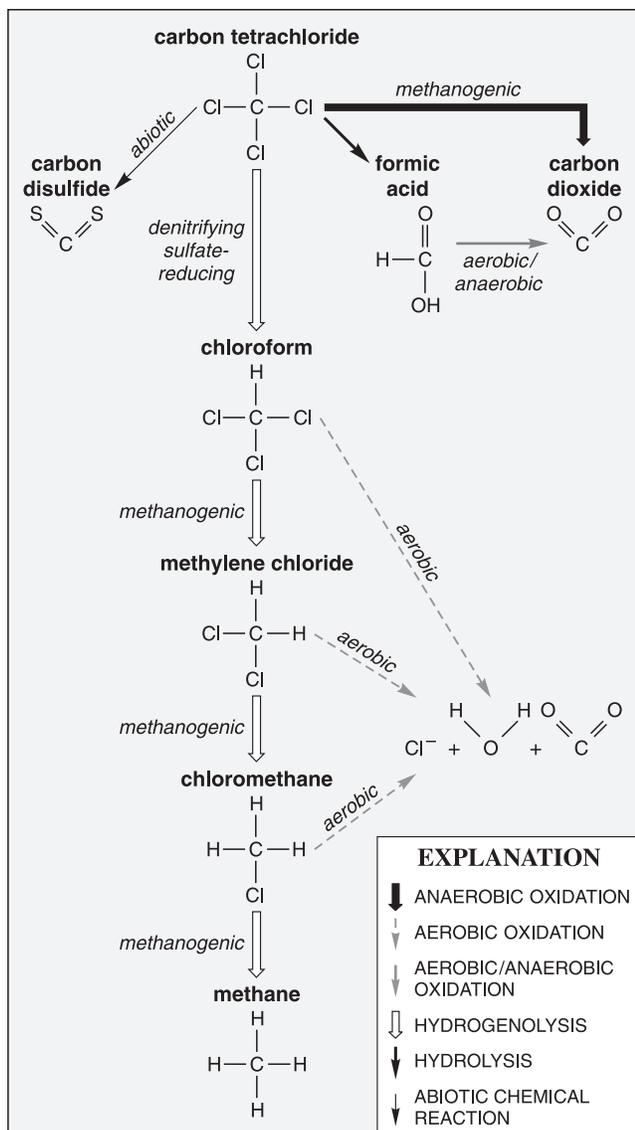


Figure 7B. Anaerobic and aerobic degradation pathways for carbon tetrachloride (modified from Criddle and others, 1991; deBest and others, 1998; Hasham and Freedman, 1995).

In spring 2000, the USGS determined VOC concentrations in nine discrete, temporary ground-water sampling locations within the wetland boundaries south of the natural attenuation study area (fig. 3). Ground-water samples from two sites in the aquifer (HP01 and HP13, fig. 3) had concentrations of total VOCs ranging from 15,000 to 50,700 $\mu\text{g/L}$, dominated by CF, CT, PCE, and the tentatively identified compounds (TICs) hexachloroethane and pentachloroethane (Phelan and others, 2001b). At five other sites, TeCA, TCE, and 12DCE were detected at concentrations less than 200 $\mu\text{g/L}$ (Phelan and others, 2001b). As in the wetland study area, the aquifer in these discrete locations was mainly aerobic (Phelan and others, 2001b). Concentrations of VOCs in shallow pore water (0.5 to 1 ft below land surface) near site HP13 were below detection limits (Spencer and others 2002) while at the same location, maximum total VOCs

(50,700 $\mu\text{g/L}$ at HP13) were detected in the aquifer 12 to 16 ft below land surface (Phelan and others, 2001).

Ground-water contamination in the Canal Creek aquifer has been delineated immediately to the east and west of the wetland boundary in the southern half of Region 2, downgradient of the former pilot plant (fig. 6; Lorah and Clark, 1996; Weston, 2005). VOCs characteristic of the upland plume (such as TeCA and CT) were detected along the eastern wetland boundary in the Canal Creek aquifer with combined concentrations ranging from 1,400 to 1,910 $\mu\text{g/L}$ (Weston, 2005). Similar monitoring on the western boundary of the wetland detected minimal to no VOCs (Weston, 2005; General Physics Corporation, 2005). Although there are no lithologic descriptions for the wetland sediments in this area, the regional chemical and hydrologic data indicate generally vertical flow and upward transport of VOCs towards the wetland and creek (Weston, 2005). The continuity of the upper confining unit immediately below the wetland sediments in this area is unknown; therefore, the hydraulic connection between the Canal Creek aquifer and the wetland sediments has not been defined.

Previous USGS investigations in the wetlands surrounding West Branch Canal Creek have identified conditions and characteristics of the wetland sediments that control the efficient natural attenuation of chlorinated VOCs (Lorah and others, 1997; Lorah and others, 2003a; Lorah and others, 2005b). Natural attenuation is defined as the physical, chemical, and biological processes that result in a reduction in dissolved-phase contaminant concentrations (National Research Council, 2000), including dispersion, dilution, sorption, volatilization, and biodegradation mechanisms (U.S. Environmental Protection Agency, 1998). Of these mechanisms, the actual destruction of contaminant mass (biodegradation, abiotic transformations) is preferable to the non-destructive mechanisms (dilution) (U.S. Environmental Protection Agency, 1998); therefore, biodegradation of TeCA (and other co-contaminants) has been the primary focus of the USGS investigations of natural attenuation in the West Branch Canal Creek wetlands.

Three factors are important for biological reductive dechlorination of the chlorinated contaminants identified in the West Branch Canal Creek study area plume(s) to proceed to non-toxic end-products (via pathways outlined in fig. 7a and b): (1) highly reducing redox conditions, (2) abundant organic substrates (dissolved organic carbon concentrations), and (3) the appropriate indigenous microbial community (U.S. Environmental Protection Agency, 1998; National Research Council, 2000; Lorah and others, 2003a). The continuously saturated conditions, high porosity, and low discharge rates of West Branch Canal Creek wetland sediments result in the formation of anaerobic (typically methanogenic or mixed iron-reducing and methanogenic) conditions, in spite of the input of aerobic water from the Canal Creek aquifer (Lorah and others, 1997). The increasing organic carbon content of wetland sediments along the vertical discharge flow path provides adequate organic substrate for

the indigenous microbial community (Lorah and others, 1997; Lorah and others, 2003). In field and laboratory studies, the mixed microbial community in the wetland study area has been shown to biodegrade TeCA and its daughter products (TCE, 12DCE, and VC) under the highly reducing conditions found in the native sediments (Lorah and others, 1997; Lorah and others, 2003a). Using molecular techniques, a recent microbial investigation of the West Branch wetland study area sediments showed that a number of diverse species or groups of bacteria and methanogens are involved in complete degradation of TeCA, one of the major ground-water and surface-water contaminants (Lorah and others, 2003a). In some steps of the TeCA degradation pathways, such as degradation of the daughter product VC, there is evidence that more than one microbial species is capable of degrading the compound and that the predominant degrading microorganism can vary at different sites in the wetland and during different seasons (Lorah and others, 2003a). Dehalorespiring bacteria reported to reductively dechlorinate 12DCE to VC and ethene, *Dehalococcoides sp.* and *Desulfuromonas sp.* (Löffler and others, 2000), have been detected in wetland sediments at West Branch Canal Creek study area (Lorah and others, 2003).

Methods and Data Analysis

From winter 2002 through summer 2004, an investigation was performed at the West Branch Canal Creek wetlands to characterize ground-water seeps. Aerial TIR and temperature data loggers were used to delineate and confirm the areas of preferential discharge. A monitoring network consisting of primarily passive diffusion-based devices was used to characterize pore water quality. Additional characterization of geochemical, hydrologic, physical, and microbiological properties was conducted at selected locations. The following sections describe the methods used to locate and characterize the seeps.

Seep Identification

The USGS conducted high-resolution, low altitude (100 to 200 ft) aerial TIR surveys of the West Branch Canal Creek, including the surrounding wetlands, to locate and confirm the presence of ground-water seeps. The West Branch Canal Creek wetlands are logistically difficult to access and investigate due to unexploded ordnance (UXO), very soft, deep sediments, and dense vegetation. Aerial TIR imaging provides an accurate, non-invasive screening tool for the identification of ground-water seeps over a large area. TIR imagery has been used as a remote sensing application to qualitatively and quantitatively assess temperature variation in natural systems including ground-water discharge (Banks and others, 1996; Portnoy and others, 1998; Torgersen and others, 2001). Previous studies have used airborne applications of thermal sensors to collect temperature data at

different resolutions (Banks and others, 1996; Torgersen and others, 2001).

Sources of error in TIR imagery in natural waters include reflective energy interference and thermal stratification (Torgersen and others, 2001). Because TIR imagery does not differentiate between reflected and emitted thermal energy during daylight hours, solar interference can negatively affect the interpretation of images. Thermal stratification occurs when the water is heated from the surface in a downward direction due to solar heating. This stratification can cause flowing waters to be biased high, particularly in times of peak sunshine. To minimize these effects, surveys are conducted pre-dawn or post-sunset, during the winter months, when the ground surface and surface water are at a maximum low temperature relative to the underlying ground water, and vegetation is least likely to obstruct the aerial view of the wetland. The aerial surveys were conducted at very low tide so that seeps that might normally discharge under surface water would be exposed for viewing.

The TIR imaging was performed in cooperation with U.S. Army Aberdeen Test Center (ATC) International Imaging Center on selected dates in January and February 2002, 2003, and 2004. A FLIR SCR1000 infrared camera was operated by ATC Imaging Center photographers from the open side door of a Bell UH-1 (Huey) helicopter operated by ATC pilots. In real time, active seeps were observed on the camera's monitor as lighter (indicating warmer) areas compared to darker (cooler) surrounding areas. Voices of the pilot, camera operators, and the USGS crew describing the locations of the seeps in relation to known landmarks in the wetland were recorded onto a digital video of the survey. Digital still images of specific seep locations also were collected. After the digital video and images were viewed and analyzed, USGS field personnel ground-truthed observations to precisely identify ground-water seep locations.

In sloped areas near the upland/wetland boundary, seepage may occur from the banks (Winter and others, 1998). In addition to the TIR surveys, visual observations were made at low tide in areas along the eastern boundary where people have altered the wetland and waste materials were known to have been disposed through discharge pipes and as part of demolition debris (Lorah and Clark, 1996). Areas that consistently maintained puddled water at the wetland surface could be attributed to ground-water discharge or reduced infiltration through lower permeability sediments. For completeness, these areas were noted as suspected seep sites and were investigated further. Once seep locations were identified, unique identifiers consisting of two letters and one number were assigned based on the geographical location. Seep locations were named with identification consisting of the region number (1–4), followed by a number (1–14) based on the north to south location within the region, and finally, a letter designating whether the seep is east or west of the creek channel (E or W).

Temperature data loggers (Onset Tidbits) were used at selected seep sites to provide quantitative evidence of the

temperature differential qualitatively observed in the TIR surveys. Tidbits were placed in both seep and non-seep locations to determine the temperature differences between the locations, determine the range of temperatures at seep sites, and corroborate the TIR data. At each location, vertical ground-water temperature gradients were measured using three temperature loggers that were attached to a 0.5-in.(inch) polyvinyl chloride (PVC) pipe and advanced to depths of approximately 0.1, 1.5, and 3.0 ft below land surface in the wetland sediment. Vertical temperature gradients were measured at a high discharge seep (3-4W) and in a background area that was not an active seep. The loggers were deployed in November 2002 and retrieved in March 2003. Both locations were along the edge of the creek channel and were equally tidally inundated. Vertical temperature gradients also were compared between three seep locations (3-4W, 3-7E, and 3-1E) from August through November 2003, and two seep locations (3-4W and 3-7E) from November 2003 through April 2004.

Monitoring Network

Given the large area encompassed by the TIR surveys and the inaccessibility of the wetland areas, temporary, passive-diffusion sampling methods were used as the primary means to characterize pore water quality in shallow ground water. Polyethylene bag passive-diffusion samplers (PDSs) and multi-level, small-chambered, passive-sampling devices called peepers were both used to characterize shallow ground water in the seep sediments throughout West Branch Canal Creek and are described in this section. These methods rely on diffusion along a concentration gradient from the surrounding ground water through a permeable membrane to a contained sample of deionized (DI) water. In order for the concentrations in these samplers to be representative of the surrounding pore water, equilibrium between the DI water contained in the sampler and surrounding porewater must be achieved. The samplers were left in place at least 3 weeks during this investigation. This equilibration time was based primarily on the ground-water velocity, ground-water temperature, and the VOC(s) present.

PDSs have increasingly gained acceptance as an effective way to sample ground water in wells (Church and Lyford, 2000; Vroblesky, 2001; Harte and others, 2000) and to delineate contamination in ground water and stream-bottom and pond-bottom sediments (Lyford and others, 2000; Savoie and others, 2000). Most VOCs, (with the exception of acetone and the gasoline additive methyl tertiary-butyl ether) have been shown to readily diffuse across a permeable polyethylene membrane. Testing of PDSs indicates that VOCs do not leach from commercially available polyethylene tubing into ground-water samples (Vroblesky, 2001). In addition, high concentrations of VOCs have not been shown to degrade the integrity of the PDS. PDSs used in this investigation were constructed of a low-density, polyethylene tubing that

was filled with organic-free, pesticide-free, DI water, then heat-sealed at each end. The PDS was placed in a protective stainless steel screen directly into the saturated sediments so that pore water came in contact with the PDS. PVC rods were attached to the samplers so that the PDSs could be located and retrieved (fig. 8).

In the middle of the stream channel where surface water was too deep to install the stainless-steel screens by hand, a deep-water PDS was used. This sampler was constructed of 2-in.-diameter PVC drilled screens that were attached onto 2-in.-diameter PVC stand pipes so the screens could be installed from a boat into the sediments to approximately 1.5 ft (fig. 9). The PDS was placed in the screens, then a coupling with an internal plug was inserted on top of the screen, and a stand pipe attached (fig. 9). The internal plug prevented the surface water that filled the pipe during installation from remaining in contact with the diffusion bag, and prevented the

(A)



(B)



Figure 8. Passive-diffusion sampler (A) polyethylene bag and (B) stainless steel mesh screen used to protect passive-diffusion sampler; shown attached to polyvinyl chloride (PVC) rod.

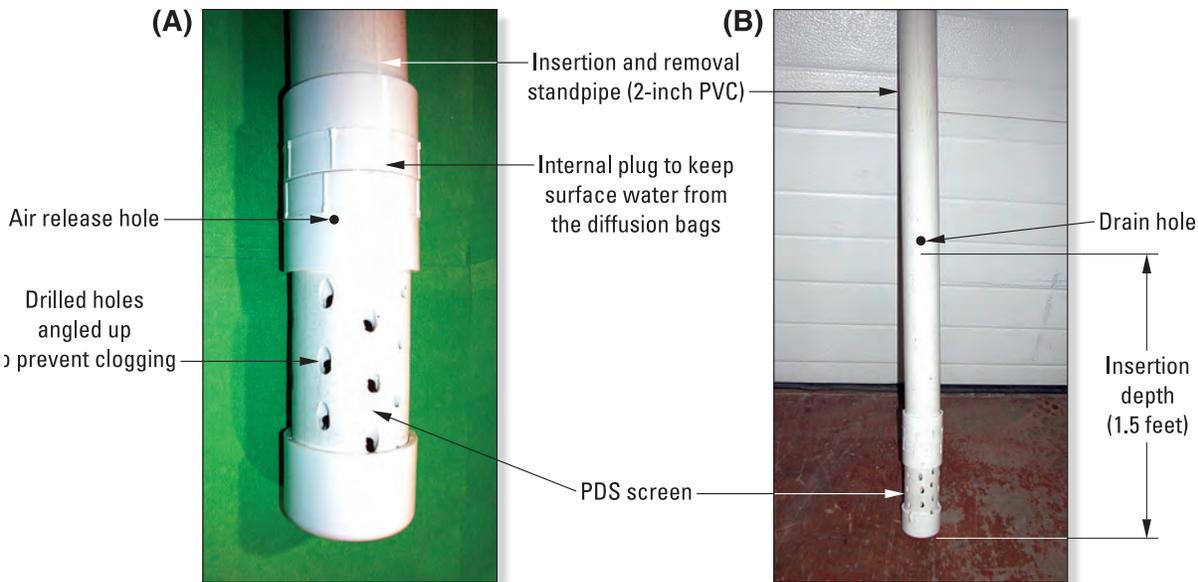


Figure 9. Deep-water passive-diffusion sampler [PDS] (A) screen and (B) standpipe (PVC, polyvinyl chloride).

methane and VOCs in the screened chamber from volatilizing to the atmosphere. The attached riser pipe filled the annulus space preventing surface water from migrating downward to the screen. The drill holes in the screen were angled so the inner portion of the hole was lower than the outer surface of the PVC casing so that mud would not be forced into the holes during installation. A hole was drilled through the side of the connector fitting so that any air in the screen area could escape while being pushed under water. A drain hole was drilled 2 feet above the plug so that surface water could reach equilibrium with the water inside the upper standpipe. No PVC glue was used in the construction of the samplers. Stainless-steel screws were used to attach the pieces together so that they remained intact during installation and removal.

Peepers, ground-water sampling tools used to gather discrete water-quality samples over a vertical section, were used at selected sites during this investigation. The original device was designed by Hesslein (1976) for the study of lake-bottom sediments. Peepers are constructed of cast acrylic, in three sections. The first section is the main body of the peeper, and the remaining two sections are overlays that secure sheets of porous membrane filter paper (0.2- μm [micron] polysulfone) over the sampling chambers (Lorah and others, 1997; Spencer and others, 2002). In most cases, the peepers used were 29 in. long and contained 21 rows of sample chambers with two chambers per row. In one case, a peeper 48 in. long, containing 22 rows of sample chambers with two chambers per row was used. Before a peeper was installed into wetland sediments, it was assembled using DI water in the cells and subsequently placed in a large tub of DI water and purged with nitrogen gas overnight to displace dissolved oxygen within the sample chambers and peeper materials (Spencer and others, 2002).

Ground-Water, Surface-Water, and Sediment Sampling and Analysis

PDSs were used during three sampling events from April through May 2002 and December 2003. An initial seep characterization was conducted in April-May 2002 using multiple pairs (1 to 11) of PDSs at 28 general locations (24 seeps plus 4 non-seep background sites) throughout the West Branch Canal Creek area (fig. 10). Multiple pairs (between 6 and 14) of PDSs were deployed at each location in March-April 2003 at six of the most contaminated seep sites—two sites in Region 2 and four sites in Region 3 (fig. 10), to confirm April-May 2002 results and establish lateral boundaries of contaminated pore water. In December 2003, PDS sampling occurred at two of the six seep locations (3-4W and 3-7E) sampled in March-April 2003 for very fine-scale lateral resolution of the seep area extent. All PDS samples were analyzed for VOCs, and were also analyzed for methane during the initial seep characterization in April-May 2002.

During PDS sampling in April-May 2002, one diffusion bag was placed in each PDS screen and two screens were deployed adjacent to each other at each sample site. During the March-April 2003 and subsequent sampling rounds, two diffusion bags were deployed in each screen, reducing the installation and removal time, and reducing variability between duplicate sample bags. During all sampling rounds, PDSs were installed at depths from 1 to 2 ft depending on the seep location. The shallow wetland sediments near the eastern upland boundary of the wetland sediments restricted placement to as little as 1 ft due to the presence of construction debris. Typical placement depths were 1.5 to 2 ft, and no samplers were placed at depths greater than 2 ft.

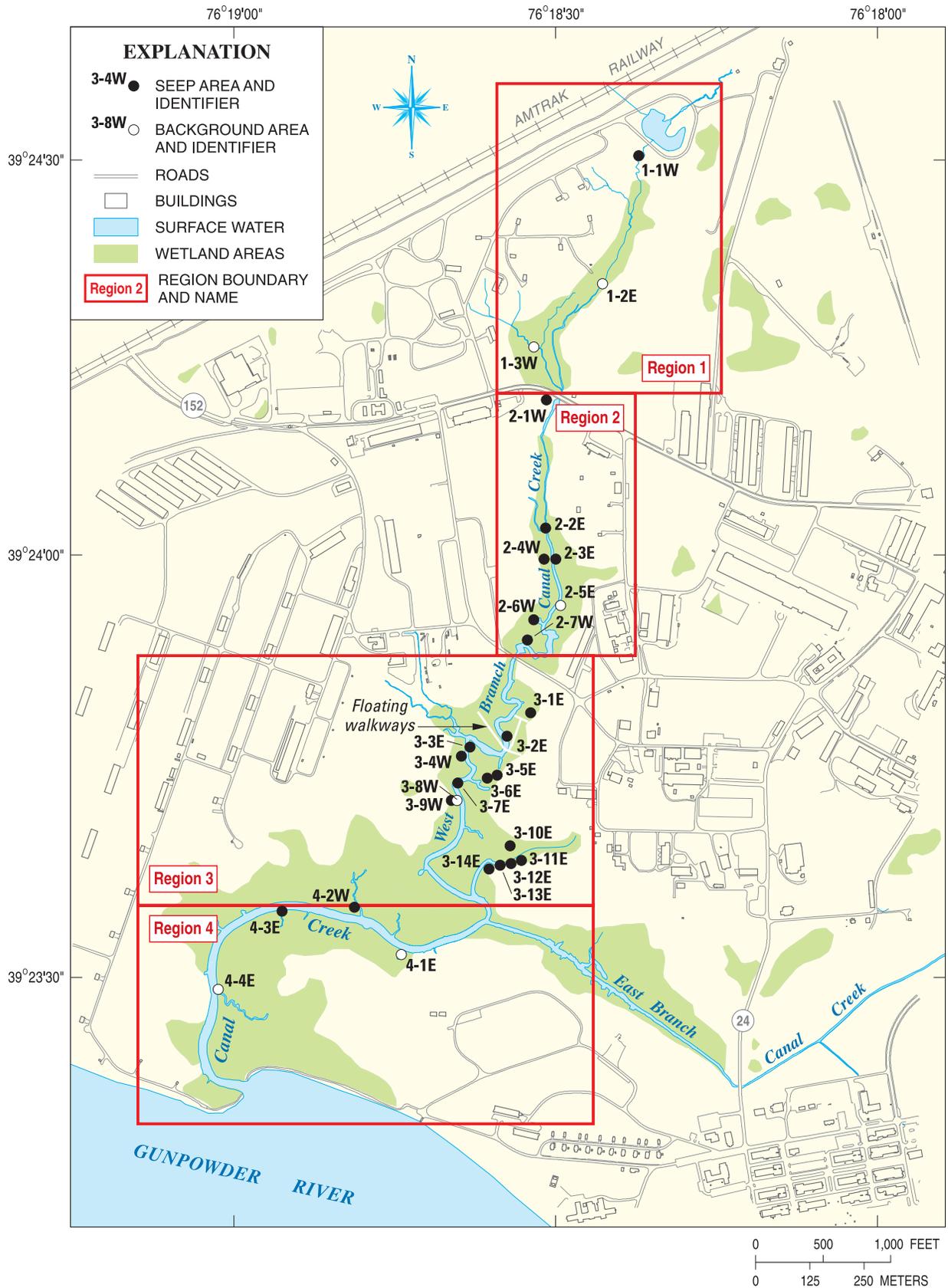


Figure 10. Location of seep areas, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

Upon retrieval, PDS bags were rinsed with DI water to remove sediment from the outside of the bag immediately before sampling. For the April-May 2002 sampling that included methane analyses, a clean 10-mL (milliliter) syringe and needle was used to penetrate the bag and withdraw duplicate methane samples. Next, a corner of the bag was cut with clean scissors, and sample water was quickly poured into duplicate VOC sample vials. The remaining water was tested for pH and specific conductance to determine if any bags had leaked prior to sampling. Sample water retained a very low specific conductance with values typically ranging between about 6 and 20 $\mu\text{S}/\text{cm}$ (microsiemens per centimeter), indicating that the bags maintained their integrity throughout the equilibration time.

A total of seven peepers were installed in sediment within the general boundaries of three seep locations (3-1E, 3-4W, and 3-7E) in July 2003. Each peeper was advanced vertically into the sediment with the uppermost cell just below the sediment surface. Following an equilibration period of approximately 3 weeks, peepers were removed from the sediment and samples were immediately collected from each of the sample chambers for measurement of redox constituents (ferrous iron, sulfide, methane, and ammonia) and analysis of VOCs. Clean syringes were used to withdraw one water sample for each analyte from each chamber and were dedicated to each chamber row. Samples for VOCs, methane, and iron were placed on ice for later analyses, and sulfide and ammonia were analyzed on site immediately after retrieval of each sample.

Surface-water samples were collected using two different methods depending on the sampling effort. During PDS retrievals, surface-water samples were collected periodically only for VOC analyses using a grab method, which involves dipping a clean stainless-steel cup in the surface water and pouring the water directly into VOC vials. Additional details for this sampling method are outlined in Aberdeen Proving Ground Standard Operating Procedure number 7 (U.S. Army Directorate of Safety, Health, and Environment, 1995).

During synoptic surface-water surveys in August 2003, small-diameter PVC pipes were used as anchors in wetland sediment at specific locations in the creek or seeps so that dedicated Teflon and tygon tubing could be attached to allow surface-water samples to be pumped from a short distance away. This technique was used to facilitate consistent locations of sampling points, and to prevent suspension of bottom sediments into samples that could be caused by movement of oars from a boat or from people walking in the wetland near the sampling site. Peristaltic pumps were attached to the other end of the dedicated tubing at each site and samples were pumped directly into bottles.

Ground-water and surface-water samples were collected and analyzed for several field parameters, redox constituents, and VOCs. Most ground-water and surface-water samples were analyzed in the field for specific electrical conductance (hereafter, specific conductance), pH, and temperature. Ground-water samples collected for redox constituents were

analyzed in the field immediately after collection and at the USGS Maryland-Delaware-D.C. (MD-DE-DC) Water Science Center Research Laboratory. Ground-water and surface-water samples were analyzed for VOCs in the USGS MD-DE-DC Water Science Center Research Laboratory.

Specific conductance, pH, and temperature were measured in the field immediately following sample collection. These parameters were measured with a commercial, multi-line meter manufactured by Wissenschaftlich-Tschnische Werstätten. The meter was calibrated daily before use with two pH and three specific conductance standard solutions.

Redox constituents analyzed included iron, methane, sulfide, and ammonia. The iron and methane samples were collected and stored in a cooler on ice until processed in the lab. Sulfide and ammonia samples were analyzed immediately in the field using colorimetric methods by the CHEMetrics (Calverton, Virginia) 1000 system (<http://www.chemetrics.com/instructions/i9503.pdf> and <http://www.chemetrics.com/instructions/i1403.pdf>). Iron samples were filtered (0.2 μm) after collection and treated in the field with the appropriate reagents to develop and fix color before storage. These iron samples were refrigerated and later analyzed using a Bausch and Lomb Spectronic 21 spectrophotometer at a wavelength of 520 nanometers according to the colorimetric method for ferrous iron described by Baedecker and Cozzarelli (1992).

Methane samples were collected and injected by syringe into sealed and preserved serum vials, which had been purged with nitrogen gas prior to sealing. Methane samples were analyzed at the USGS MD-DE-DC Water Science Center Research Laboratory using headspace gas chromatography with flame-ionization detection (GC/FID). A description of the method is detailed in Spencer and others (2002).

Prior to this investigation, methane sample vials were preserved with mercuric chloride. In this investigation, samples were preserved with trisodium phosphate (TSP) to reduce hazardous-waste disposal costs and concerns. Sufficient TSP was added to raise the pH of typical Canal Creek ground-water field samples to greater than 10 to kill microorganisms that could affect the methane production. Trials with wetland pore water from the study area showed that 800 mg/L (milligrams per liter) of TSP raised the pH above 10. Between January and June 2003, comparisons were made using both preservation methods for the same sample water over 10 time steps ranging from samples analyzed on the same day that they were collected to samples analyzed up to 5 months after the collection date. Over a 2-month holding time, both preservation methods yielded concentrations within 15 percent of the initial concentration, with no difference in analytical variability between the methods (fig. 11).

VOC analyses were conducted at the USGS MD-DE-DC Water Science Center Research Laboratory. Samples were analyzed using a purge-and-trap capillary gas chromatograph with a mass-selective detector (GC/MSD). The analytical method used for VOCs is modified from U.S. Environmental Protection Agency Method 524.2 (U.S. Environmental Protection Agency, 1988). A description of the method is

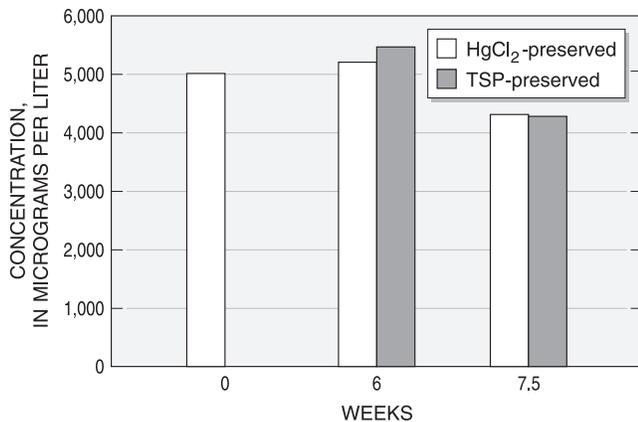


Figure 11. Comparison of mercuric chloride-preserved and trisodium phosphate-preserved methane sample concentrations. [HgCl₂, mercuric chloride; TSP, trisodium phosphate]

given in Rose and Schroeder (1995), and a description of the modifications is presented in Appendix 1. The lower reporting limit for VOC analyses generally was 0.5 µg/L (micrograms per liter) for undiluted samples but ranged as high as 24,000 µg/L for samples diluted up to 2,000 times so that the concentrations would be within the calibrated range of the instrument.

Sediment Collection and Microbial Analysis

Surficial sediment grab samples were collected for microbial community “fingerprinting” in June 2003 at six seep locations. Sediment was collected into sterile sampling tubes and immediately frozen for analysis. USGS personnel in Reston, Virginia performed analysis to characterize the bacterial community in seep sediment using a polymerase chain reaction (PCR) procedure of amplifying specific targeted DNA and performing terminal restriction fragment length polymorphism (TRFLP) analysis on the PCR products (Clement and others, 1998) as described in Lorah and others (2003a). In order to evaluate bacterial communities, 16S rDNA was targeted for analysis because it codes for a molecule present in all bacteria. TRFLP provides a molecularly derived microbial “fingerprint” that allows a relative estimate of the total bacterial abundance and diversity of the bacterial community.

Desulfuromonas can degrade TCE to *cis*-12DCE, whereas *Dehalococcoides* strains have been shown to degrade PCE, TCE, 12DCA, and VC to ethene (Hollinger and others, 2003). Therefore, in addition to the TRFLP procedures described, *Dehalococcoides spp.* and dechlorinating strains of *Desulfuromonas* were quantified in the consortium by

applying specific primers to DNA samples. DNA copy number was determined by real-time quantitative PCR (qPCR) using the Quantitect SYBR green real-time PCR kit (Qiagen, Chatsworth, CA) and the Opticon real-time PCR system (MJ Research). The 16S rDNA based primers used to target *Dehalococcoides* (*dhc*) were *dhc730f*, 5′-GCG GTT TTC TAG GTT GTC-3′ and *dhc1350r*, 5′-CAC CTT GCT GAT ATG CGG -3′ (Bunge and others, 2001). Calculations of cell numbers were based on one 16S rDNA copy per cell for *Dehalococcoides*. The detection limit of this method is estimated to be between 5 and 10 gene copies.

The *Desulfuromonas* primers (designed for specificity to *Desulfuromonas sp.* strain BB1 and *D. chloroethenica*) and conditions are previously described (Löffler and others, 2000). A standard curve was determined using Ct values of serial dilutions of plasmid containing the *dhc* amplified fragment, or the *Desulfuromonas sp.* strain BB1 amplicon of known concentration (and thus copy number), and the samples were plotted against that curve to determine abundance. The detection limit of this method is estimated to be between 5 and 10 gene copies.

Hydrologic and Physical Characterization

Seeps that showed evidence of contamination with chlorinated VOCs were investigated to determine their hydrologic and physical characteristics. Seepage meters were used to quantify discharge from the seeps, *in situ* tests were used to measure dissipation, and the lithologic and physical properties of the sediments were investigated. Descriptions of these measurements are given in the following sections.

Seepage Meters

Seepage meters have been used since the 1970s to measure rates of ground-water flow to surface-water bodies. Lee and Cherry (1978) describe the construction of the meters and the calculations required to determine flow rates. Multiple seepage meters were deployed at three seep locations over multiple days at different stages of the tidal cycle. Each seepage meter used during this investigation was made from the closed-end section of a 55-gallon steel drum that was inserted open-end down into the sediment. A fitting in the drum allows flow through a discharge tube to a sample collection bag at the sediment surface. On the basis of a method described by Lee and Cherry (1978) and successfully tested by the USGS in the fall of 2002 in the West Branch Canal Creek, a second fitting was installed into the seepage meters to allow for the escape of methane gas (fig. 12). A buildup of methane or other gas bubbles under the meter could pressurize the collection bag and reduce the amount of discharge collected. A test of a seepage meter without a vent pipe in the mid-1990s by the USGS in the wetland resulted in a buildup of gas that lifted the seepage meter almost completely out of the sediment.

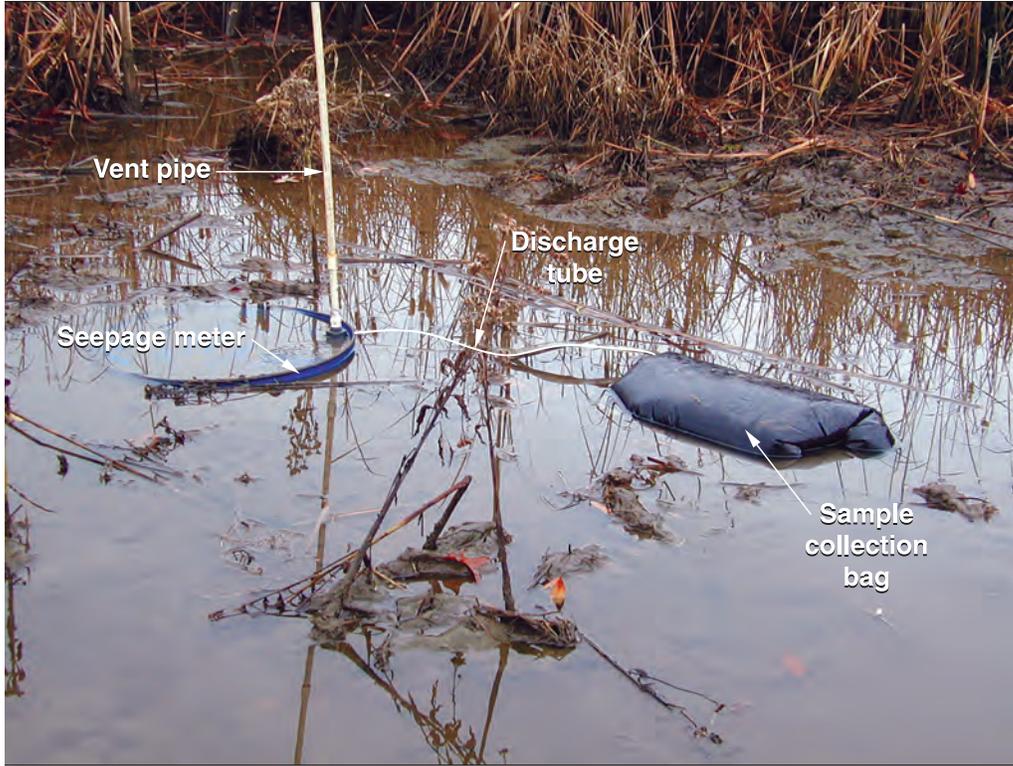


Figure 12. Deployed seepage meter at seep 3-4W at high tide in May 2002, West Branch Canal Creek, Aberdeen Proving Ground, Maryland. (Seep location shown on fig.10)

During this investigation, each collection bag was primed with 1 L (liter) of water before it was connected to the seepage meter discharge tube to prevent preferential filling of the bag due to bag memory, or the bag’s tendency to fill or empty until the bag is in its most relaxed position (Shaw and Prepas, 1989). Using this method, flow from the wetland surface to underlying sediments (hereafter referred to as recharge) would show a reduction in the amount of water in the collection bag, and flow from the underlying sediments to the wetland surface (hereafter referred to as discharge) would increase the amount of water in the bag. The collection bag was attached to the drum long enough for a measurable change in the volume of water contained in the bag, but not so long that the bag became empty or full. For seepage rates encountered at this site, times ranged from hours to 2 days, when the collection bag was removed, the contents measured, and the bag re-primed with 1 L of water.

Seepage flux was estimated from the seepage meters by use of equation 1:

$$q_v = Q/A \quad (1)$$

$$v = q_v/n \quad (2)$$

where

- q_v is seepage flux (or specific discharge),
- Q is the volume of seepage into or from the meter bag divided by the time interval,
- A is the cross-sectional area of the meter,
- v is interstitial velocity,

and

- n is effective porosity.

Seepage was considered to be positive for ground-water discharge and negative for cases where surface water flowed to ground water.

In Situ Dissipation Tests

Cone-penetrometer (CPT) tests were performed at two sites within the general boundaries of seep location 3-4W (fig. 13). A steel cone tip with sensors, attached to a friction sleeve that included a pore pressure transducer, was advanced into the wetland sediment. As the apparatus was pushed into the sediment, tip resistance, sleeve friction, and pore water pressure were continuously recorded. Additionally, dissipation tests were performed so that the advancement of the cone tip was paused and pore water pressure values were recorded with time until the built-up pore pressure dissipated and reached

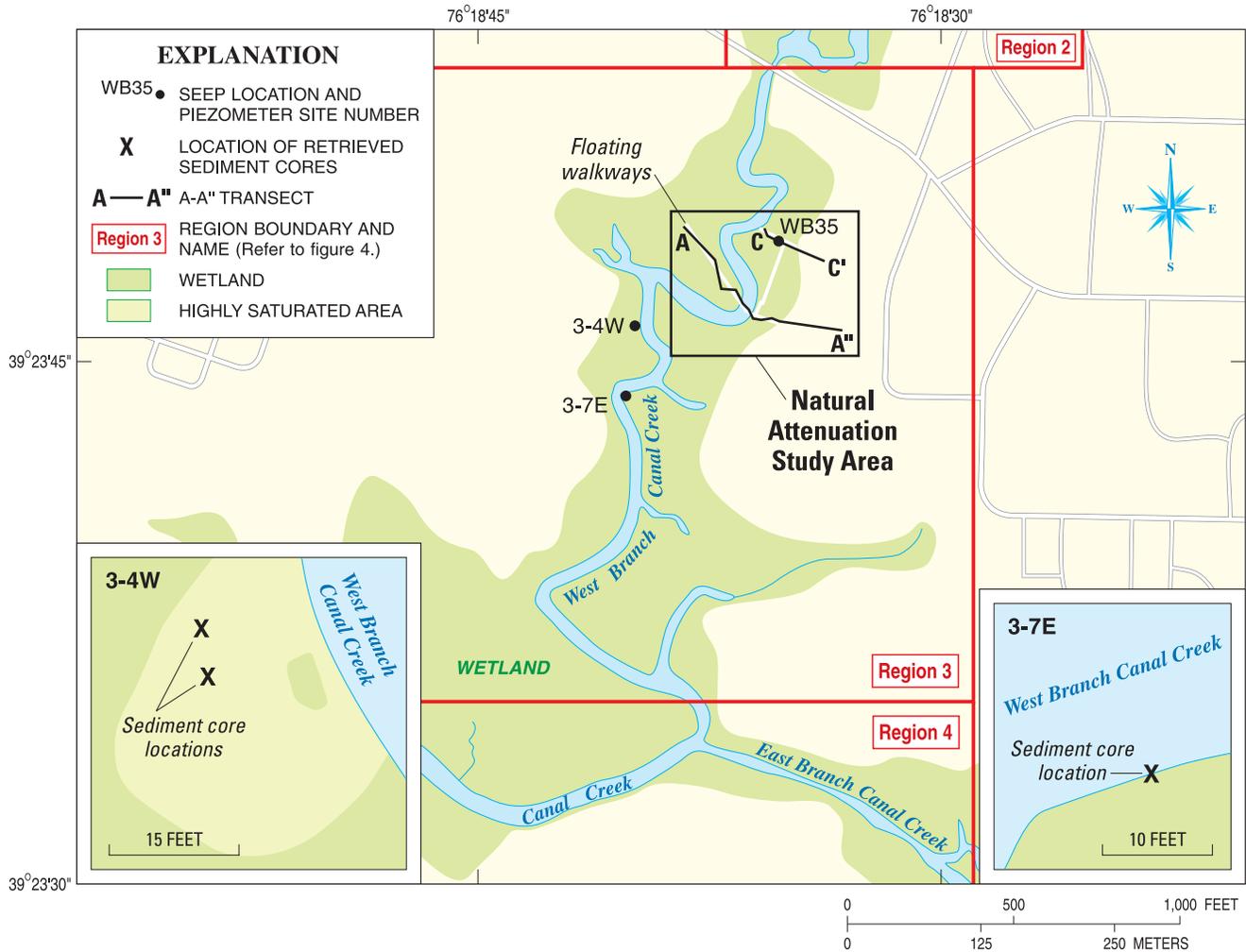


Figure 13. Approximate locations of sediment core retrieval and *in situ* cone penetrometer tests at 3-4W, 3-7E, and WB35, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

equilibrium; the dissipation data were used to calculate horizontal hydraulic conductivity of the wetland sediments. Several tests were performed at each of the two locations to determine the variability of hydraulic conductivity with depth. Three successful tests (out of eight attempts) on the north side and seven successful tests (out of ten attempts) on the south side of the seep were completed. Tests were considered unsuccessful when pore pressure did not dissipate when the tip was paused.

Dissipation tests provided information (t_{50} values) to calculate horizontal hydraulic conductivity (K_h) according to methods described by Burns and Mayne (1998), according to equation 3. A t_{50} value for a given depth interval was the time for 50 percent of the pore pressure to dissipate during the dissipation test. The velocity units used are cm/s (centimeters per second).

$$K_h(\text{cm/s}) = (251 * t_{50})^{-1.25} \quad (3)$$

Seep Sediment Lithology and Physical Properties

In March 2004, five sediment cores were retrieved from two seep locations (3-4W [3 cores] and 3-7E [1 core], fig. 13) and one reference site along the C-C' transect (near piezometer WB35 [1 core, (fig. 3)]). These sediment cores were used to describe the lithology and determine vertical variation of geotechnical parameters, physical, and chemical parameters. Two methods were used to collect cores of the wetland seep sediments. A portable vibracore drill rig on floating pontoons was used in most instances. Alternatively, if the drill rig could not be mobilized to the area, a concrete vibrator attached to a core barrel and hand-held slide hammer were used.

Cores were removed as continuous samples in schedule 80 PVC casing and sealed at both ends for laboratory analysis. Of the three wetland sediment cores retrieved at seep 3-4W, two cores were collected to the top of the aquifer using the vibracore— one on the north side of the seep (3-4WN) and the other on the south side of the seep (3-4WS). In both cases,

recovery of the wetland sediment in the cores was low. Due to the variability in compression of the wetland sediments with depth, recovery was determined by periodically measuring down within the PVC casing throughout the collection process to see how much material was in the core. The difference between the amount of casing below land surface and the depth to sediment measured inside the casing was recorded as the amount of recovered wetland sediment. These measurements were taken every foot of casing advanced. A third, shallower core was collected with the hand-held slide hammer on the north side of the seep area (3-4WN2), with the intention of improving recovery in the upper wetland sediment. Additional cores to the top of the aquifer were retrieved at seep 3-7E with the vibrocore and near piezometer WB35 (fig. 3) with the hand-held slide hammer. At the 3-4W and 3-7E cored locations, 2-in. SCH 40 PVC piezometers, screened across the bottom 1 ft, were installed to fill the annular space. The piezometers at seep location 3-4W were later renamed PTZ4C, PTZ13B, and PTZ14A. At piezometer WB35, the core hole was backfilled with bentonite.

Geotechnical analyses (Atterberg limits, wet density, and specific gravity), particle-size analysis, and total organic carbon (TOC) were determined in the laboratory from the collected cores. The Standard Test Method for Particle-Size Analysis of Soils (American Society for Testing and Materials, 2001) was performed by Waterways Experiment Station (WES). The Agricultural Analytical Services Lab at The Pennsylvania State University performed tests to determine percent TOC (Nelson and Sommers, 1996; Pella, 1990). These two tests were completed on 13 sediment samples from the cores at seep 3-4W, five samples from the core at seep 3-7E, and two samples from the core collected at piezometer WB35.

Characterization of Preferential Ground-Water Seepage

Physical and chemical methods were used to determine the extent of preferential discharge in West Branch Canal Creek. Seep areas were identified using temperature and water-quality measurements (fig. 10). Shallow pore water samples collected in a grid and analyzed for VOCs at each seep location showed the presence of VOC contamination at 10 seeps. Of these 10 locations, 3 locations that contained elevated chlorinated VOC concentrations were selected as representative locations for further hydrologic, physical, geochemical, and microbial characterization. This subset of seep locations includes both diffuse and focused locations, creek edge and wetland boundary sites, and VOCs from two main source areas. Results of this characterization were used to assess the impact of seeps on anaerobic biodegradation in shallow wetland pore water and surface-water quality throughout the West Canal Creek wetlands.

Extent of Preferential Discharge in West Branch Canal Creek

Qualitative and quantitative methods were used to estimate temperature changes in sediment and pore water as an indicator of preferential discharge. Because the Canal Creek aquifer is known to be contaminated underneath the wetland sediments, VOC concentrations were used to evaluate boundaries of seepage. Similarly, methane was used as an indicator of methanogenic conditions and was evaluated in conjunction with the presence or absence of VOCs to generally categorize locations as having either diffuse or focused discharge.

Temperature Distribution

Discrete areas of preferential discharge were identified in the wetlands and along the stream channel of West Branch Canal Creek using TIR and visual observations along the wetland boundary. Seep areas identified by both methods were observed to be spatially consistent during surveys conducted in winter 2002, 2003, and 2004 (see TIR images in Appendix 2; data on file at USGS, Baltimore, MD). The total precipitation in 2001 prior to the January 2002 flight was lower than average (fig. 14), and the total precipitation for 2003 prior to the January 2004 flight was higher, indicating that these variable climatic conditions may not impact the overall extent of preferential seepage throughout the area.

From the West Branch Canal Creek stormwater retention pond near the post boundary to the Gunpowder River, a total of 14 seep locations were consistently identified during low altitude TIR surveys, with warm water discharge appearing lighter in color than the surrounding surface temperatures (Appendix 2). An additional eight locations were suspected seep locations (table 1, fig. 10). Four suspected seep locations were inconsistently thermally warm. An additional four

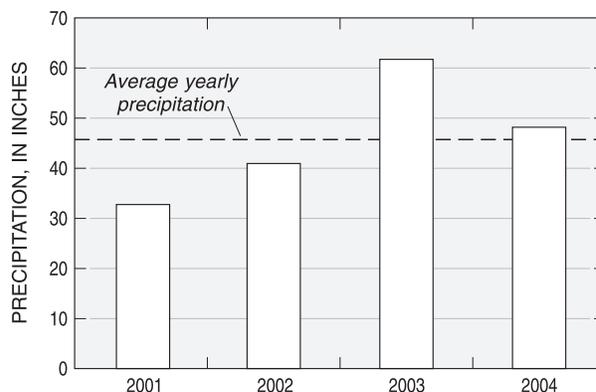


Figure 14. Precipitation from 2001-04, Phillips Army Airfield, Aberdeen Proving Ground, Maryland. (Dashed line shows average yearly precipitation from Maryland State Climatology records for Phillips Army Airfield.)

suspected seep locations were along the eastern wetland boundary where an artificial change in topography occurs. Ponded water was visually observed and thought to be diffuse discharge in these areas (fig. 10). Most of the seep locations (17 of 22) were in the tidal part of the site, upstream of the confluence with the East Branch. In addition, the majority of locations (14 of 22) were located east of the creek channel. Six background locations were selected in areas where seepage was not observed and these locations were used for sampling purposes only. They were not used to determine temperature distribution.

These areas of preferential discharge occurred in one of four landscape locations— along the creek edge, along the wetland boundary, within the central wetland, and in a dendritic-like pattern extending from the wetland to the creek edge (table 1). Two of these locations (creek edge and wetland boundary, fig. 1a, b) previously have been described in conceptual models of seep and spring formation (Winter and others, 1998). The creek edge location was most prevalent throughout all four regions and in both nontidal and tidal areas. The wetland boundary location was concentrated mainly in Region 3, where the eastern boundary of the wetland was altered by human activity and a greater change in topography exists between the uplands and wetlands. Examples of seep appearance in TIR images in the creek edge and wetland landscape locations are shown in figures 15a, 15b, and Appendix 2. Only 2 (of 22 sites) were located within the central wetland (neither near the creek edge or the wetland boundary), and both were observed within Region 3 (table 1). Three sites, all in close proximity to one another in Region 2, were observed to have a dendritic-like pattern within the wetland that extended to the creek channel (fig. 15c and Appendix 2).

Areal estimates of seep size, based on TIR images and visual observations, ranged from less than 75 ft² (feet squared) (central wetland and some creek edge locations) to greater than 300 ft² (dendritic-like pattern seep locations). The characterization of shallow pore water quality also was used to delineate the extent of the seeps and is discussed later in this section.

Whereas real-time TIR surveys were used to qualitatively identify areas of preferential discharge based on contrast between warm ground-water discharge and cold surface temperatures (Appendix 2), quantitative temperature differences were verified at some locations using temperature measurements. Various quantitative methods to measure temperature were used, including single measurement probes, analysis of TIR images, and continuous data loggers. Temperature probes were used to collect single measurements at several field locations throughout West Branch Canal Creek in March 2002 (table 2) to estimate the temperature difference between seep discharge pore water and nearby, non-seep pore water. Pore water temperature differences were measurable at all sites. Temperature difference was greatest in seep locations along the creek edge (3-4W) and in the dendritic-like pattern from the wetland to the creek channel in Region

2, ranging from 9 to 12 °C (degrees Celsius) (table 2). These measurements were consistent with temperature differences estimated by the analyses of TIR images collected during the winter 2002 TIR survey. Using the TIR camera processing software, surface temperatures were estimated in areas of the TIR images appearing as seeps and non-seeps or non-seep surface water. A relative change in surface temperatures between the surface water and seep discharge was estimated to range from 8.5 to 10 °C. This estimated temperature difference is in the range of the difference between ground-water temperature and surface-water temperature in the winter months indicating that the seep surface temperatures are similar to ground-water temperature. In the central wetland and along the eastern wetland boundary, the temperature difference between seep and non-seep areas in the images was less (3-4 °C) than observed at the other locations. Alternatively, this smaller temperature difference also may be due to spatial heterogeneities in seep temperature throughout the wetland. The relative difference between near surface temperatures in the various seep areas may indicate variable preferential discharge rates due to variable residence times of pore water within the wetland sediments.

The shorter pore water residence time in seep can be inferred by the comparison of continuous temperature measurements at variable depths below land surface at a seep along the creek edge (3-4W) to equivalent measurements in non-seep sediments upstream of the seep location. In the seep location, temperature varied by 4 °C during the period of measurement at a depth of 1.5 ft below land surface (fig. 16a). Over the period of measurement in the non-seep sediment location, temperatures varied by nearly 9 °C at this same depth (fig. 16b). This is consistent with the temperature change previously measured along the C-C' section (Lorah and others, 2005). Similarly, a greater temperature difference between depths of 0.5 and 3 ft was observed in the non-seep wetland sediments (about 7–10 °C) compared to the seep sediments (2–5 °C). Comparisons of temperature profiles between the seep and non-seep locations indicate that advection is dominating the thermal distribution in the seep areas, whereas convection is the dominant process in the non-seep areas.

Continuous vertical temperature profiles also were compared between two creek edge seeps (3-4W and 3-7E) and one eastern boundary seep (3-1E), on the basis of the range in temperature differences observed from the single measurement probes, to evaluate relative rates of discharge. Minimal variation (less than 1 °C) was observed at seep 3-4W with depth over the entire period of record (fig. 17a). At seep 3-7E, temperatures varied by a maximum of about 3 °C with depth and approximately 1.5 °C at each depth over the period of record (fig. 17b). These minimal changes were not reflected in the vertical profile of seep 3-1E temperature, where variations with depth ranged up to 7 °C and varied by 3.5 to 5 degrees over the period of record at 1.5 and 3 ft below land surface (bls), respectively (fig. 17c). These variations at 3-1E are only slightly less than changes observed along the nearby C-C' section (Lorah and others, 2005; fig. 3). Despite the smaller

22 Characterization of Preferential Ground-Water Seepage to West Branch Canal Creek, APG, Maryland

Table 1. Summary of preferential ground-water seepage locations, 2002-2004, West Branch Canal Creek wetlands and creek, Aberdeen Proving Ground, Maryland.

[TIR, thermal infrared]

Seep location identifier ¹	TIR observed location	Suspected location ²	Back-ground location	Landscape location
1-1W	x			Creek edge; nontidal
1-2E			x	Creek edge; nontidal
1-3W			x	Creek edge; nontidal
2-1W	x			Creek edge; nontidal
2-2E		x		Creek edge; nontidal
2-3E	x			Creek edge; tidal
2-4W	x			Dendritic-like pattern from wetland to creek; tidal
2-5E			x	Creek edge; tidal
2-6W	x			Dendritic-like pattern from wetland to creek; tidal
2-7W	x			Dendritic-like pattern from wetland to creek; tidal
3-1E		x ²		Eastern wetland boundary, tidal
3-2E	x			Creek edge; tidal
3-3E	x			Creek edge; tidal
3-4W	x			Creek edge; tidal
3-5E		x ²		Eastern wetland boundary; tidal
3-6E	x			East-central wetland; tidal
3-7E	x			Creek edge; tidal
3-8W			x	Western wetland boundary; tidal
3-9W	x			Creek edge; tidal
3-10E	x			East-central wetland; tidal
3-11E	x			Wetland boundary; tidal
3-12E		x		Wetland boundary; tidal
3-13E		x		Wetland boundary; tidal
3-14E		x		Wetland boundary; tidal
4-1E			x	Creek edge; tidal
4-2W		x ²		Creek edge; tidal
4-3E		x ²		Creek edge; tidal
4-4E			x	Creek edge; tidal

¹ Locations of seeps are shown in figure 10.

² Locations 3-1E, 3-5E, 4-2W, and 4-3E were either inconsistent in the TIR observations or were selected based on visual observations of seepage along the eastern wetland boundary.

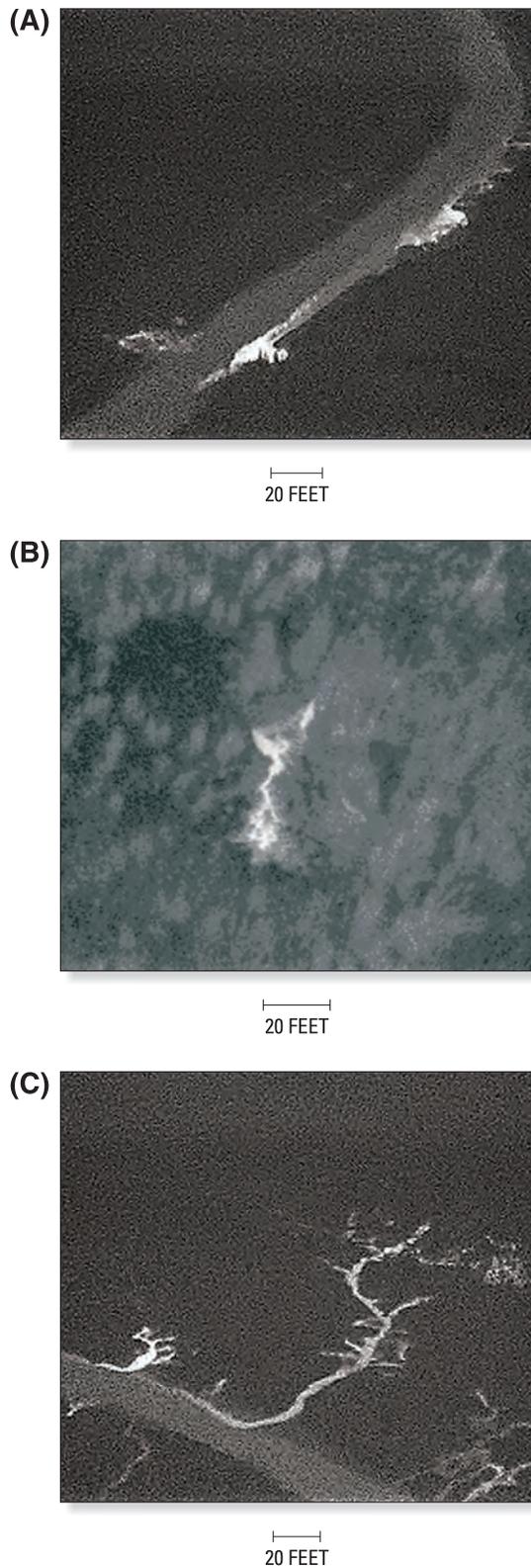


Figure 15. Thermal infrared (TIR) images of seeps in different landscape locations: (A) stream boundary, (B) wetland, and (C) dendritic-like pattern from wetland to stream. (Lighter shades represent warmer temperatures; darker shades represent cooler temperatures. All images taken during winter.)

Table 2. Measured temperature differences between seep sediment and nearby non-seep wetland sediment, March 5-6, 2002, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[Mean daily air temperature at Martin State Airport, Middle River, Maryland, for this period was -1 to 4 degrees Celsius; surface-water temperature 4.8 degrees Celsius]

Location ¹	Landscape location	Temperature differences, in degrees Celsius
2-4W	Wetland/creek, branching seep	12
2-7W	Wetland/creek, branching seep	9
3-1E	Eastern wetland boundary	4
3-5E	Eastern wetland boundary	3
3-10E	Central wetland	3
3-4W	Creek edge, tidal	10

¹ Locations of seeps are shown in figure 10.

sediment thickness along the C-C' section, previous estimates of discharge through the wetland sediments in the A-A' and C-C' sections were equivalent (Lorah and others, 1997) and are considered to represent the non-seep wetland sediments of West Branch Canal Creek. Minimal temperature changes at 3-4W and 3-7E are indicative of more focused discharge in which ground water from the aquifer is transported more rapidly through the wetland sediments to the surface, although changes at 3-1E are indicative of more diffuse discharge.

The quantitative verifications of the qualitative differences observed with TIR indicate that it is an effective tool for characterizing preferential discharge at West Branch Canal Creek. Relative differences in temperature between seeps and the non-seep sediments, as well as between seeps in different landscape locations, provide insight for the relative rate of ground-water discharge in the location. These observations are similar to those reported by Conant (2004) who correlated temperature changes to ground-water flux through the streambed of a river. Temperature mapping was used in the formation of a conceptual model that included areas of short-circuit discharge through recharge (Conant, 2004).

In addition to the winter months, temperature contrast between ground water and surface water is the greatest in the warmest part of the summer, when surface temperatures are warmer than ground-water discharge. Thermal stratification and, at West Branch Canal Creek, dense vegetation in the wetland prohibits the use of TIR during this contrasting season. Therefore, continuous temperature monitoring was used to verify the relative rate of discharge at two seep locations during various times of the year. From August through November 2003, temperature variations with depth over time were consistent with measurements from November 2003 through April 2004. As an example, figure 18 shows results from 3-4W, where changes over time are consistently less than 2.5 °C, even at shallow depths.

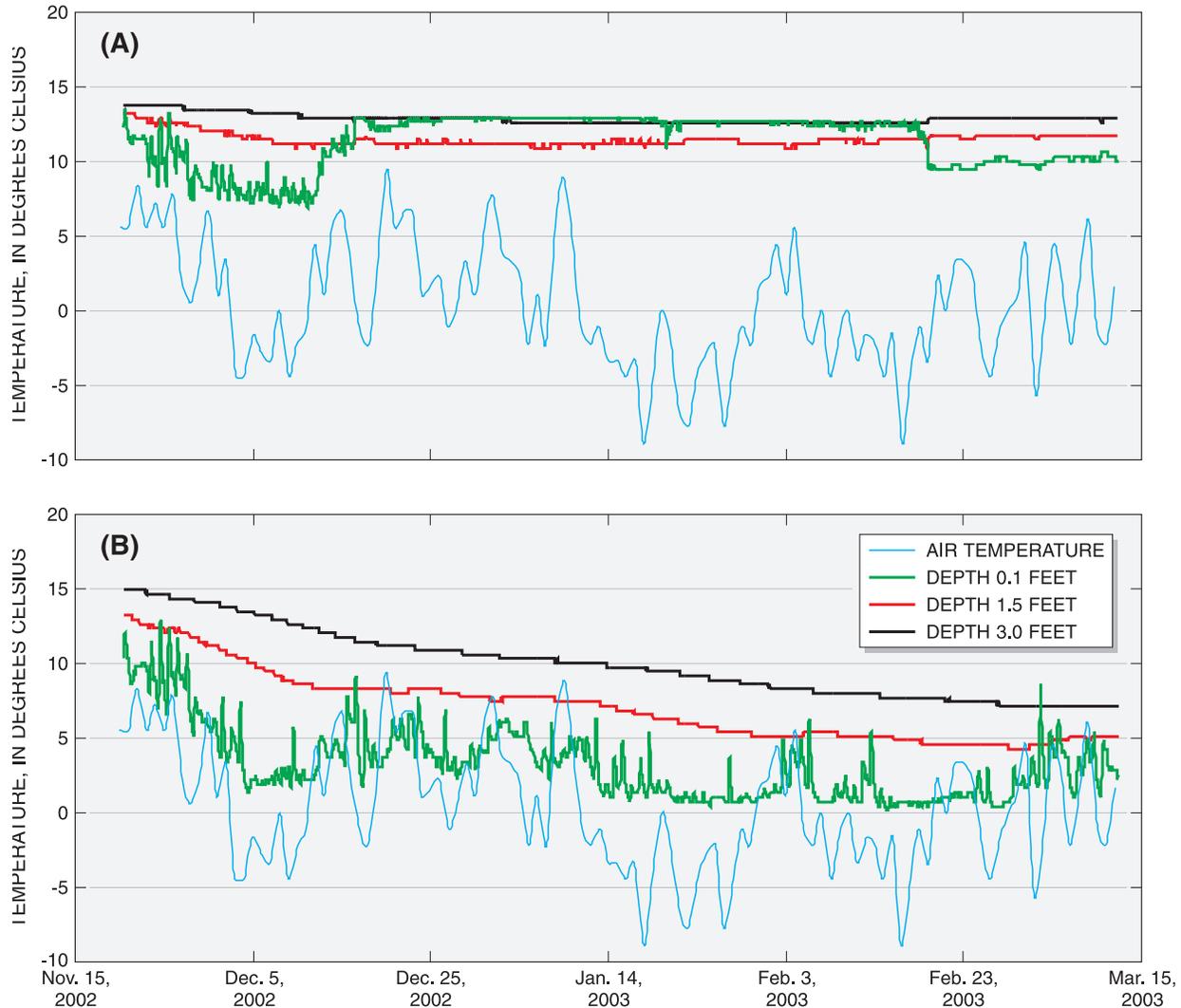


Figure 16. Comparison of temperature differences with depth below land surface, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, November 2002-March 2003, in (A) sediment beneath seep 3-4W and (B) sediment beneath a nearby area with no seeps. (Seep location shown in fig. 10.)

Volatile Organic Compound and Methane Distribution

Past site activities have resulted in the persistence of chlorinated VOCs in the Canal Creek aquifer nearby and within the boundaries of the wetlands (fig. 6). Previous investigations of shallow pore water in the wetland study area have shown that minimal concentrations of chlorinated VOC daughter compounds from underlying VOC plumes and parent compounds were not detected (Lorah and others, 1997; 2005). These parent compounds were detected in surface water, however (Phelan and others, 2001a). Therefore, the presence of chlorinated VOCs in shallow pore water in seep areas was used to infer the contaminant pathway from the aquifer to surface water. The composition, magnitude, and areal extent of the chlorinated VOCs and the presence of methane in seep pore water was used to assess the plume with which the seep

may be associated and the relative rate of discharge through the wetland sediments. Multiple pairs (1 to 11) of PDSs were used to characterize the shallow pore water quality in the 22 seep locations, plus 6 additional background locations (table 3; fig. 10; Appendix 3). These background locations are considered part of the non-seep wetland sediments and were not observed or suspected preferential discharge locations, but were located in similar landscape positions as identified seeps throughout the study area.

Pore water in all seep and background locations in Regions 1 and 4 contained minimal (less than $5 \mu\text{g/L}$) total VOCs. Similarly, samples collected from seep locations 2-1W and 2-2E, and background location 3-8W did not contain VOCs above the detection limit. Background location 2-5E contained toluene at concentrations less than $30 \mu\text{g/L}$. Toluene also was detected in shallow pore water in all landscape positions, specifically in locations 2-4W, 2-6W, 3-6E, 3-9W, 3-10E, 3-11E, 3-12E, 3-13E, and 3-14E at concentrations

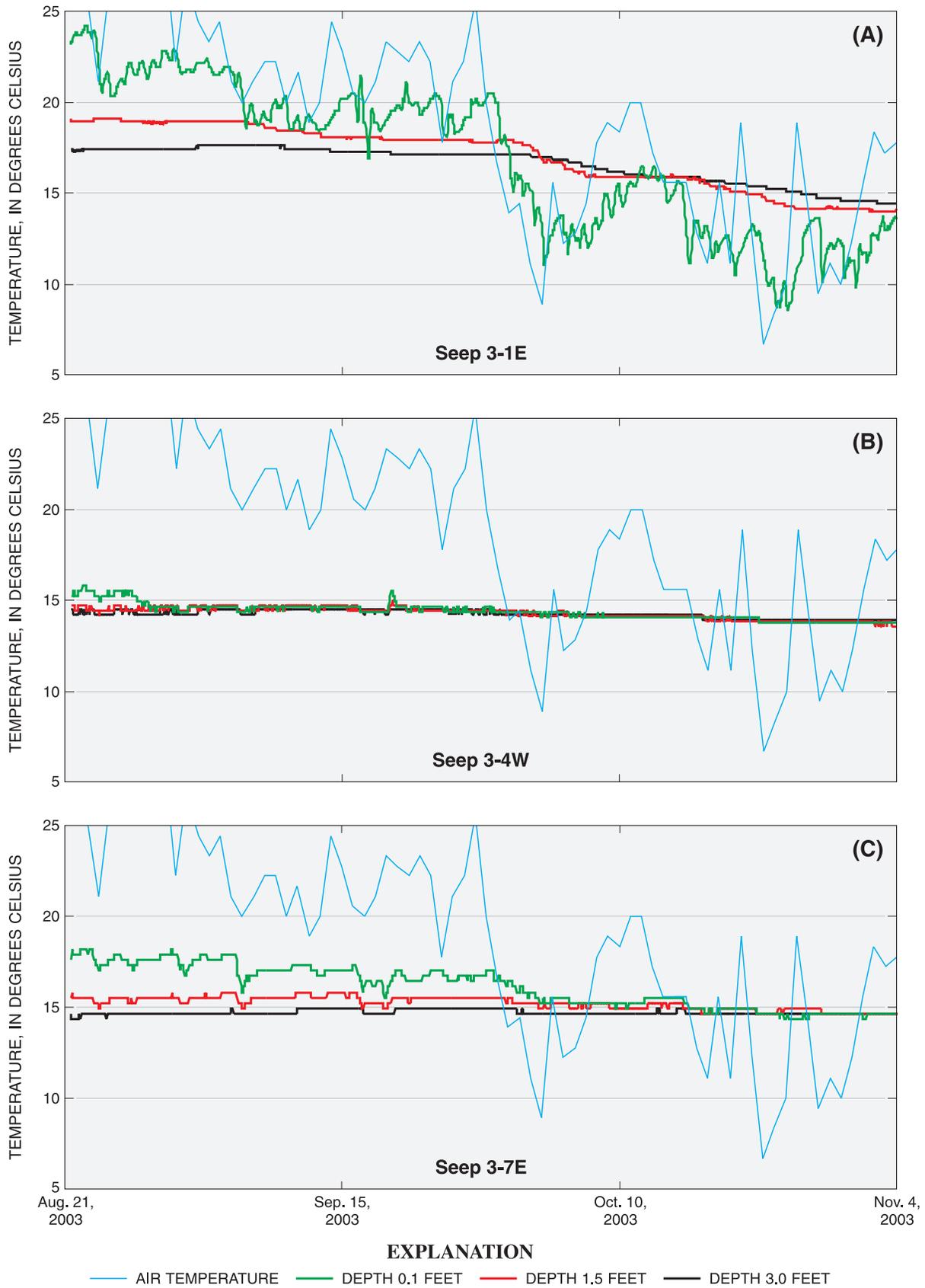


Figure 17. Comparison of temperature differences with depth below land surface at three seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, August-November 2003, (A) 3-1E, (B) 3-4W, and (C) 3-7E. (Seep locations shown in fig. 10.)

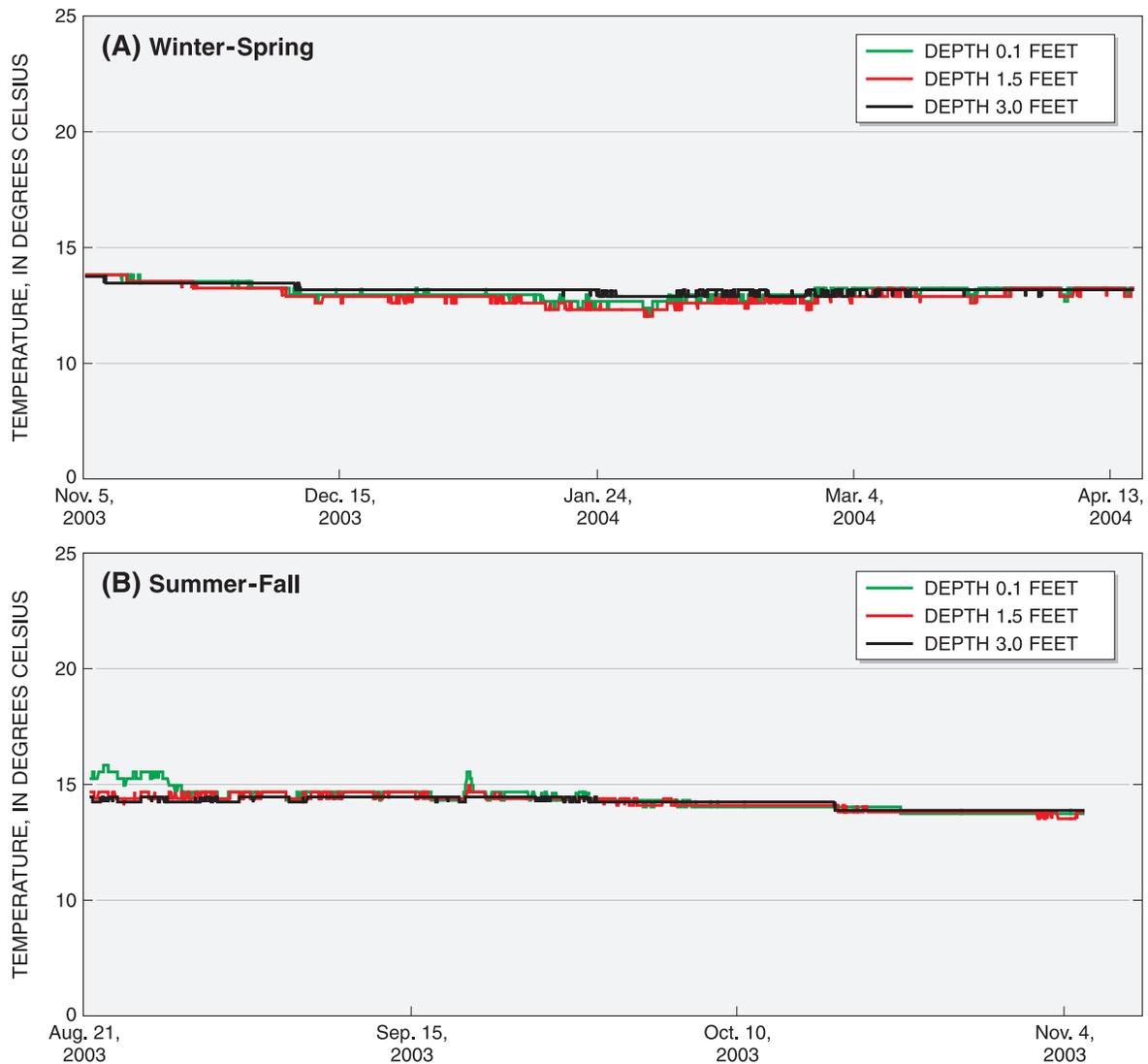


Figure 18. Temporal changes in sediment temperature with depth at seep 3-4W, August 2003-April 2004, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) winter-spring and (B) summer-fall. (Seep location shown in fig. 10.)

ranging from 3 to 516 $\mu\text{g/L}$ (table 3; Appendix 3). Toluene has been detected previously in shallow pore water, most often in the summer months (Lorah and others, 2005). In locations where both chlorinated VOCs and toluene were present, only chlorinated daughter compounds were typically identified in low concentrations. In wetland pore water, toluene may act as an electron donor for reductive dechlorination of chlorinated VOCs. Toluene was previously detected in pore water but not in the aquifer (Lorah and others, 2005), indicating that it may be from a more shallow source. Alternatively, because toluene sorbs to organic sediments more readily than other site contaminants (such as TeCA and CF) and has been shown to degrade under anaerobic conditions (Borden and others, 1997), the sporadic detections in the wetland sediments may be the remaining contamination of a plume that was more widely distributed in the past.

Chlorinated VOCs characteristic of the contaminated Canal Creek aquifer were detected in 10 of the 22 seep locations, in all landscape positions except for the central wetland areas (3-6E and 3-10E). In general, shallow pore water chlorinated VOC concentrations in these locations were higher than previously reported in the wetland sediments and were composed of both parent and anaerobic daughter compounds (table 3; fig. 19). Whereas the relative proportions of these VOCs vary between the seep areas, methane concentrations typically were lower in seep areas compared to sediments in the wetland study area (previously reported in Lorah and others, 2005). In addition, the VOC composition was spatially associated with nearby aquifer sources of contamination (seeps downgradient of the former pilot and chlorine plants contained VOCs characteristic of the ground-water plume associated with these areas, fig. 6). In

Table 3. Properties of preferential ground-water seepage locations, Spring 2002-Fall 2003, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[VOCs, volatile organic compounds; µg/L, micrograms per liter; ND, not determined; -, not detected]

Seep location identifier	Thermal infrared observed location	Suspected location ¹	Back-ground location	Landscape location	Sampling dates	Volatile organic compounds detected -compound type ²	Total VOCs ³ (µg/L)	Relative discharge
1-1W	x			Creek edge; nontidal	Mar 02	None detected	-	ND
1-2E			x	Creek edge; nontidal	Mar 02	None detected	-	ND
1-3W			x	Creek edge; nontidal	Mar 02	None detected	-	ND
2-1W	x			Creek edge; nontidal	Mar 02	None detected	-	ND
2-2E		x		Creek edge; nontidal	Mar 02	None detected	-	ND
2-4W	x			Dendritic-like pattern, wetland to creek; tidal	Mar 02	Toluene, chlorinated daughter	499	Focused
2-6W	x			Dendritic-like pattern, wetland to creek; tidal	Mar 02	Toluene	90.5	ND
2-7W	x			Dendritic-like pattern, wetland to creek; tidal	Mar 02, May 03	Chlorinated parent+daughter	324	Focused
2-3E	x			Creek edge; tidal	Mar 02, May 03	Chlorinated parent+daughter	665	Focused
2-5E			x	Creek edge; tidal	Mar 02	Toluene	26.5	ND
3-2E	x			Creek edge; tidal	Mar 02	Chlorinated parent+daughter	219	Focused
3-3E	x			Creek edge; tidal	Mar 02	Chlorinated daughter	12.5	Diffuse
3-4W	x			Creek edge; tidal	Mar 02, May 03, Dec 03	Chlorinated parent	31,800	Focused
3-7E	x			Creek edge; tidal	Mar 02, May 03, Dec 03	Parent	1,830	Focused
3-9W	x			Creek edge; tidal	Mar 02	Toluene	516	ND
4-1E			x	Creek edge; tidal	Mar 02	None detected	-	ND
4-2W		x		Creek edge; tidal	Mar 02	None detected	-	ND
4-3E		x		Creek edge; tidal	Mar 02	None detected	-	ND
4-4E			x	Creek edge; tidal	Mar 02	None detected	-	ND
3-1E		x		Eastern wetland boundary, tidal	Mar 02, May 03	Chlorinated parent+daughter	2,020	Diffuse
3-5E		x		Eastern wetland boundary, tidal	Mar 02, May 03	Chlorinated parent	437,000	Diffuse
3-8W			x	Western wetland boundary	Mar 02	None detected	-	ND
3-11E	x			Eastern wetland boundary, tidal	Mar 02	Toluene, chlorinated daughter	141	Diffuse
3-12E		x		Eastern wetland boundary, tidal	Mar 02	Benzene, toluene	30.4	ND
3-13E		x		Eastern wetland boundary, tidal	Mar 02	Toluene	3.1	ND
3-14E		x		Eastern wetland boundary, tidal	Mar 02	Benzene, toluene	85.6	ND
3-6E	x			Central wetland	Mar 02	Toluene	129	ND
3-10E	x			Central wetland	Mar 02	Toluene	97.7	ND

¹These locations were either inconsistent in the thermal infrared observations (3-1E, 3-5E, 4-2W, and 4-3E) or were identified based on visual observations of seepage along the eastern wetland boundary (2-2E, 3-12E, 3-13E, and 3-14E).

²Parent compounds at the site include 1,1,2,2-Tetrachloroethane, Tetrachloroethene, Trichloroethene, Carbon tetrachloride, or Chloroform; daughter compounds include degradation products of the parent compounds.

³Total VOCs represent the maximum combined VOC concentration from a single sampling period.

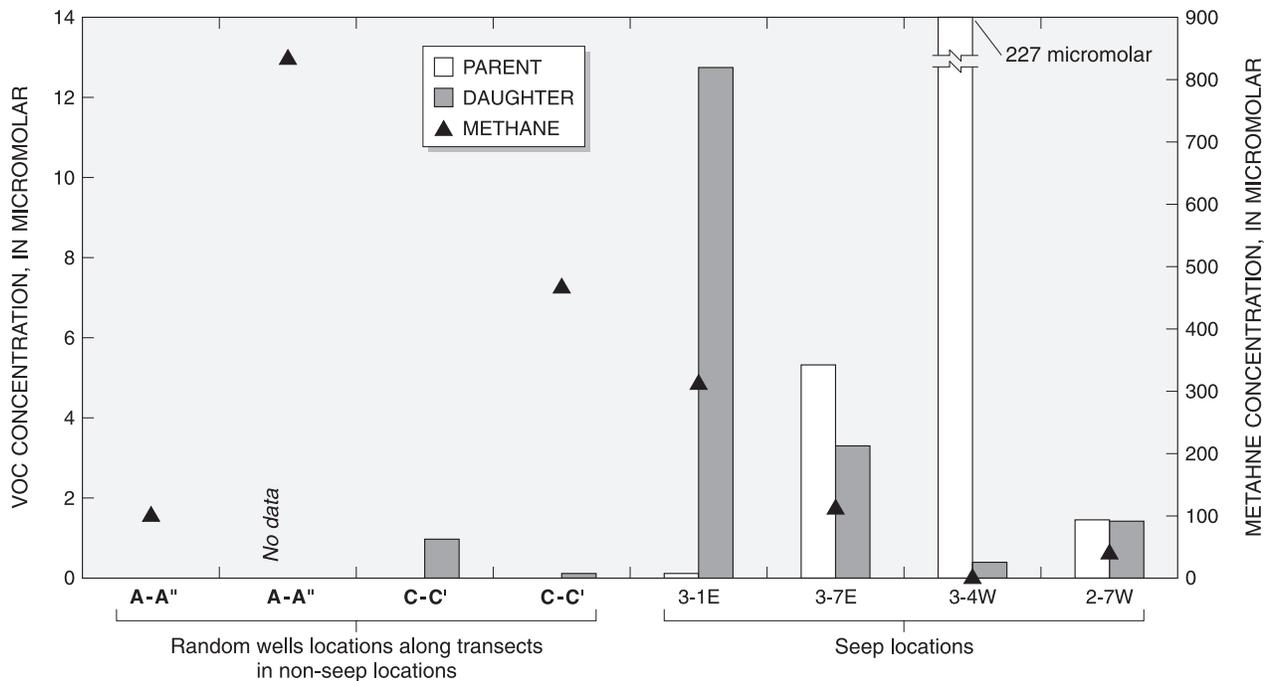


Figure 19. Comparison of chlorinated parent and daughter volatile organic compound (VOC) and methane concentrations from shallow pore water beneath non-seep wetland locations and at seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland. (Transect locations shown in fig. 3; seep locations shown in fig. 10.)

most cases, seep boundaries could be delineated by steep VOC concentration gradients over short distances (concentration changes of several orders of magnitude over a distance of 10 to 30 ft) and generally were consistent with the extent observed during TIR surveys. These characteristics indicate that seeps can be categorized as either diffuse discharge locations that may have a higher proportion of daughter compounds and moderate methane concentrations, or focused discharge locations that have a higher proportion of parent compounds and minimal methane concentrations.

Pore water samples collected from three seep locations (2-3E, 2-4W, and 2-7W) downgradient of the former pilot plant in Region 2 (figs. 4 and 6) consisted of a mixture of TeCA, TCE, and associated anaerobic daughter products, mainly DCE (both *cis*- and *trans*-isomers) and VC. Maximum total VOC concentrations in these pore water samples ranged from 324 to 665 µg/L (table 3; Appendix 3), composed mainly of the daughter compounds. Methane concentrations in the associated pore water samples were relatively low compared to previously reported concentrations in the wetland study area (Lorah and others, 1997; 2005), ranging from 42.5 to 2,800 µg/L, with most detections less than 200 µg/L.

Pore water samples collected from two seep locations near the natural attenuation study area (3-1E and 3-2E) consisted of a mixture of TeCA, TCE, and associated anaerobic daughter products, mainly DCE and VC, similar to the compounds detected along the A-A' and C-C' sections (Phelan and others, 2002; Lorah and others, 2005). The maximum concentration in samples collected from seep 3-1E near the wetland boundary was an order of magnitude greater

than the concentrations at seep 3-2E (2,020 µg/L and 219 µg/L, respectively). Samples from seep 3-1E were composed of mainly chlorinated daughter products. In both locations, methane concentrations were relatively high, ranging from 5,000 to 7,200 µg/L.

Chlorinated VOCs were detected in five seep locations south of the natural attenuation study area, both along the creek channel and the eastern wetland boundary. The greatest concentrations of chlorinated VOCs were detected in shallow pore water at nearby sites HP01 and HP13 (fig. 3), where the maximum concentrations detected in the underlying Canal Creek aquifer were previously reported (Phelan and others, 2001b). Shallow pore water at seep 3-4W contained mainly parent compounds CT, CF, PCE, HCA, and PCA for a combined total VOC concentration of 31,800 µg/L. This mixture of VOCs was similar to those detected in samples collected from the Canal Creek aquifer at sites HP01 and HP13. Seep 3-3E, located approximately 75 ft from seep 3-4W on the opposite creek bank, had total VOC concentrations of only 12.5 µg/L. Downstream of seep 3-4W and along the eastern bank of the creek channel, seep 3-7E also contained similar VOCs with a maximum total concentration of 1,830 µg/L, dominated by parent compounds. At both locations, the sampling network used PDSs that extended into the streambed sediments to define the extent of VOCs in shallow pore water because the TIR surveys could not reveal discharge under the deeper parts of the creek. In both cases, maximum concentrations were located along the creek edge. Methane concentrations were minimal in these locations.

Along the wetland boundary and more than 200 ft from the creek channel, seep 3-5E contained the highest concentration of total VOCs detected (437,000 µg/L) in the seeps (table 3, Appendix 3). The composition of VOCs in shallow pore water samples collected from this location was dominated by CF (93 percent of total molar mass), with lesser amounts of CT, PCE, TeCA, methylene chloride, and other daughter compounds (Appendix 3). The disproportionate amount of CF at this seep compared to seeps 3-4W and 3-7E, indicates that it may be the result of another intermingled source because wastes are known to have been disposed along this boundary (Lorah and Clark, 1996). Farther south along the eastern boundary, seep 3-11E had only low concentrations of chlorinated anaerobic daughter compounds (around 10 µg/L), while the rest was composed of toluene, for a total VOC concentration at this location of 141 µg/L.

Some temporal variation in shallow, non-seep sediment pore water quality has been reported previously for the natural attenuation study area (Lorah and others, 2005; 2003b). At seep 3-4W, the variation in seep pore water concentrations was not consistent with the non-seep wetland pattern of increased concentrations in the summer/fall compared to the spring (fig. 20). The relative percent difference between concentrations during spring and fall sampling events in 2003 at seep 3-4W was less than 10 percent. At seeps 2-7W, 3-1E, and 3-4W, the variation (expressed as relative percent difference) in total VOC concentration from 2002 to 2003 (years with variable precipitation preceding winter TIR surveys; fig. 14) was 15, 1, and 0 percent, respectively.

The overall magnitude and composition of VOCs detected in shallow pore water in the seep locations compared to that in the non-seep locations indicates a decreased residence time in the wetland sediments, resulting in incomplete or non-existent natural attenuation of the contaminants discharging from the aquifer, particularly in Region 3. Relatively low methane concentrations were associated with locations that had high parent compounds and low daughter compounds (fig. 19), indicating that conditions were not sufficiently reducing for complete attenuation of the VOCs. VOCs detected in shallow pore water were compared to VOCs in ground-water samples collected from nearby monitoring wells at three seep locations (fig. 21). At seep 3-4W, nearly equivalent mass of parent compounds was detected in shallow pore water compared to the aquifer, whereas at seep 3-1E, the equivalent mass of parent compounds was detected in shallow pore water as daughter compounds. These are contrasted with the VOC profile of seep 2-7W and monitoring well CCW-176A, where greater total VOC mass is detected in the underlying aquifer compared to the pore water. In the vicinity of seep 2-7W, the upper confining unit is present in at least some areas (Weston, 2005) and may restrict flow (and therefore transport of the contaminants) from the Canal Creek aquifer to the wetland surface. Alternatively, in the area south of Hanlon Road, the Canal Creek aquifer is unconfined and can directly contribute to overlying wetland sediments.

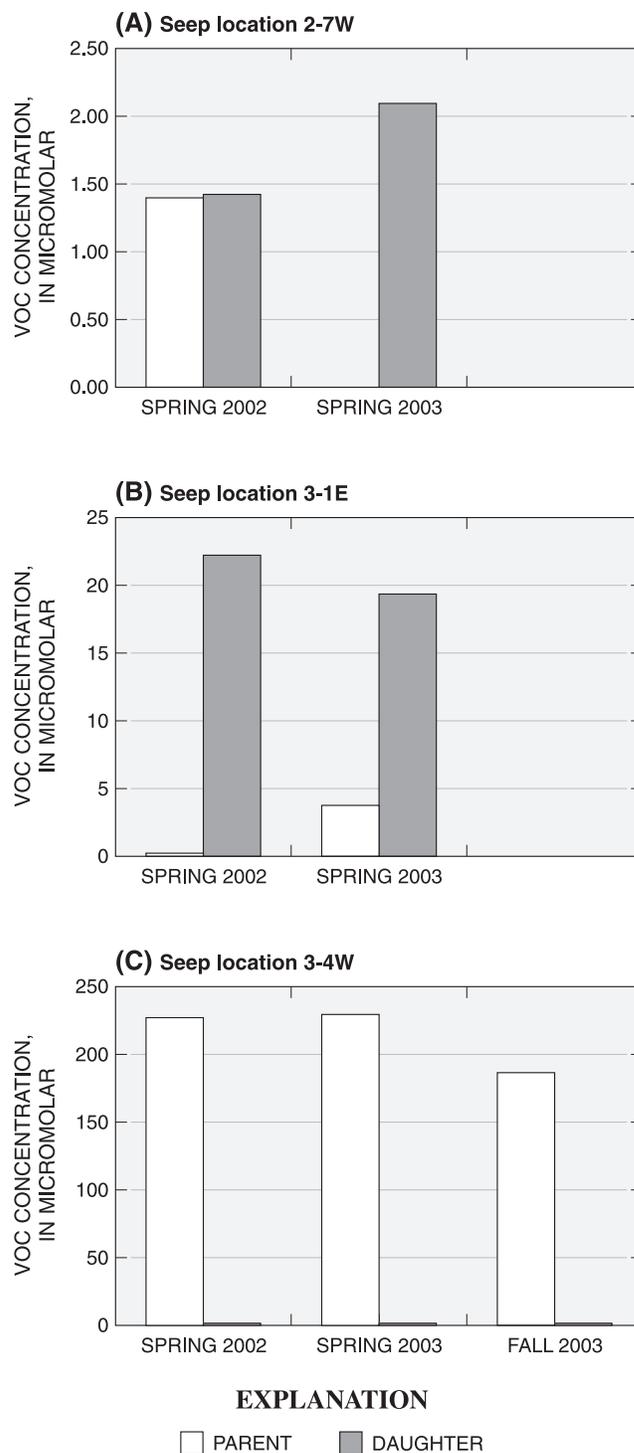


Figure 20. Temporal changes in chlorinated parent and daughter volatile organic compound (VOC) concentrations in pore water beneath three seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) 2-7W, (B) 3-1E, and (C) 3-4W. (Seep locations shown in fig. 10.)

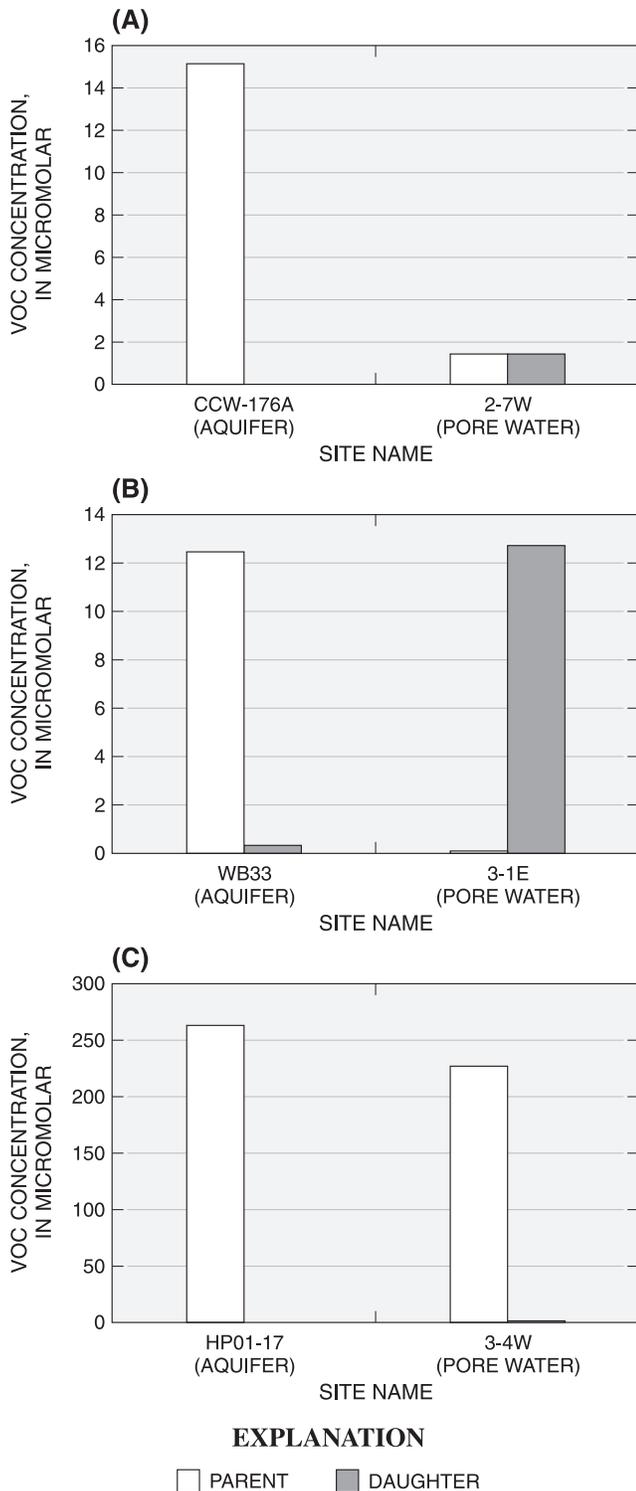


Figure 21. Comparison of chlorinated parent and daughter volatile organic compound (VOC) concentrations in pore water and in nearby aquifer at three locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) 2-7W and CCW-176A, (B) 3-1E and WB33, and (C) 3-4W and HP01-17. (Location of seeps shown in fig. 10; location of aquifer piezometers shown in fig. 3.)

In order to assess the potential for mass flux of chlorinated VOCs to surface water, seeps where chlorinated VOCs were detected were categorized as diffuse or focused preferential discharge (table 3) on the basis of the following criteria. Seeps with pore water concentrations containing mainly toluene were excluded from this generalized categorization because high methane concentrations were associated with all of these locations and may be a result of the breakdown of toluene or similar simple organics (benzene). Locations considered to be more focused discharge areas were characterized by VOCs (both compound type and magnitude) similar to those detected in the associated aquifer plume and typically were dominated by parent compounds. In addition, these locations were characterized by low methane concentrations (less than 1,000 µg/L), a high temperature contrast (greater than 5 °C) between seep and non-seep pore water, and a limited areal extent of chlorinated VOCs. Locations considered to be more diffuse preferential discharge areas (those with rates of discharge less than focused but greater than non-seep sediment locations) mostly contained daughter compounds of chlorinated VOCs typically found in the associated aquifer plume, indicating incomplete degradation. These locations were characterized by moderate methane concentrations (greater than 5,000 µg/L), a moderate temperature contrast between seep and non-seep pore water (less than 5 °C), and had a greater areal extent of chlorinated VOCs. Most locations that were characterized as focused preferential flow were either along the creek edge (seeps 2-3E, 3-4W, and 3-7E) or branched between the wetland and creek (2-4W and 2-7W), whereas most sites characterized as diffuse flow were located along the wetland boundary (seeps 3-1E, 3-11E). Some seeps (3-5E, 3-2E) had characteristics of both seep types.

Hydrologic and Physical Characterization of Focused and Diffuse Seep Locations

The presence of high concentrations of VOCs in shallow wetland pore water indicates that residence time decreased as a result of an increase in specific discharge at seep locations. Hydrologic characteristics were evaluated at three seep locations to estimate specific discharge and hydraulic conductivity in the sediment. Lithology and physical properties of these sediments are discussed in relation to the hydrologic characteristics and in comparison to non-seep wetland sediments in the wetland study area. Correlation between physical properties and the occurrence of preferential flow paths also is discussed.

Hydrologic Characterization

Hydrologic properties of organic soils and sediments are complex. Some of this complexity can be attributed to differences in the physical properties of organic soils and sediments compared to aquifer sediments. Organic soils

typically have very high porosity (near 80 percent) compared to mineral soils (40 to 50 percent) (Mitsch and Gosselink, 1993). Some studies have reported the occurrence of a dual porosity in peat and wetland sediments that affects the transport of solutes through pores, advective flow through macropores (Harvey and others, 1995; Ours and others, 1997; Blodau and Moore, 2002), and molecular diffusion into and out of dead end or isolated pores (Hoag and Price, 1995; Harvey and others, 1995). Solute transport through primarily macropore flow has been shown to largely reduce the residence time of the pore water in wetland sediments, thus increasing the solute flux to the surface (Harvey and others, 1995). Some evidence of this dual porosity has been observed during a natural gradient tracer test within the wetland study area (Olsen and Tenbus, 2004) and in measured differences in VOC concentrations using different sampling devices in the wetland sediments (Dyer and others, 2002; Lorah and others, 2005a). Diffusion-based sampling devices have been shown to preferentially sample matrix pores, while suction-based sampling devices sample macropores (Harvey and others, 1995). Lorah and others (2005a) reported a similar difference in pore water VOC concentrations analyzed in samples collected from peepers (higher VOC concentrations detected) compared to samples collected with drive-point piezometers (lower VOC concentrations detected) in the West Branch Canal Creek wetland sediments.

Various methods for the determination of hydrologic characteristics have been reported through wetland sediments. Measurement of hydraulic conductivity and water flux (Darcian approach) have been used as indicators of the transmission of water through peats and organic- and mineral-based wetland sediments, in addition to alternative methods such as a salt balance and water budgets (Portnoy and others, 1998; Nuttle and Harvey, 1995; Tobias and others, 2001; Almendiger and others, 1998). Errors and temporal changes in the method estimates of ground-water input to marshes have

been reported using both methods (Almendiger and others, 1998; Tobias and others, 2001).

Seepage flux was estimated at three locations with multiple seepage meter measurements spanning different periods of the tidal cycle. At all three sites, the geometric mean of non-zero flux measurements was greater than the mean previously reported along the wetland study area (table 4). Flux measurements in the seep areas ranged from 2.5 to 22 times greater (table 4) than those previously reported along the C-C' section, which represents the non-seep sediments (Lorah and others, 1997). Measured flux was greatest in focused discharge seeps 3-4W and 3-7E, compared to the more diffuse location 3-1E.

Variability in flux measurements during different periods of the tidal cycle differed between locations (fig. 22a). Measurements at seep 3-4W were the most consistent over the tidal cycle, with close agreement between the arithmetic and geometric means and the median values at each seepage meter (fig. 22b; table 4). Maximum discharge was typically measured at mid to low tides at all three locations (fig. 22a). Less agreement between different meters and tidal phase measurements was observed at seeps 3-1E and 3-7E, reflected in the differences between the statistics summarized in table 4; however, all seeps had areas of little-to-no ground-water discharge within the seep boundaries. Areas of greater and lesser flow were measured, similar to those observed by Rosenberry and others (2000) (fig. 22b). These observations may be due to a smaller areal extent of preferential discharge or a higher degree of heterogeneity at seeps 3-1E and 3-7E, compared to 3-4W. The diffuse discharge seep 3-1E, located near the wetland/upland boundary, appears to be more subject to reversals in flow direction than the focused discharge seeps 3-4W and 3-7E, indicated by more frequent measurements of recharge (downward seepage flux or flow of surface water into the ground). Because this seep is close to an abrupt change in slope, it may be more influenced by local hydrologic

Table 4. Summary of Darcian flux calculated from seepage measurements in June-August 2003, at seeps 3-1E, 3-4W, and 3-7E with comparisons to non-seep wetland sediments along the A-A' and C-C' sections, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[ft/d, feet per day; negative values indicate recharge, downward flux, or loss of water from the primed seepage meter bag]

Location	Number of meters used; measurements used per meter	Maximum flux range (ft/day)	Arithmetic mean flux (ft/day)	Geometric mean flux (ft/day)	Median flux; per meter ¹ (ft/day)
3-1E	4; 2-7	-0.005 to 0.18	0.019	0.006	0.001; 0.002
3-4W	4; 7	-0.024 to 0.094	0.056	0.053	0.058; 0.069; 0.072
3-7E	2; 6-8	0.018 to 0.903	0.158	0.044	0.005; 0.210

Location	Reported flux (ft/day)
A-A' section 1	0.0007 to 0.0018
C-C' section	0.003

¹Median flux only reported for meters with change in seepage meter bag volume over multiple measurements, meters without recharge or discharge not reported.

influences (runoff, precipitation) compared to the seeps farther away from this topographic change. The more focused discharge locations are a greater distance from the wetland boundaries (nearer the center of the wetland), indicating that they may be more influenced by the deeper, regional flow system. It should be noted that the magnitude of seepage measured as part of this study is on the low end of values reported in the literature for the half-barrel meter method, but is within the range of accurate measurements (Cable and others, 1997).

Individual and normalized measurements of discharge were compared to flux measurements (by seepage, water balance, and Darcy calculations) reported elsewhere. Tobias and others (2001) divided ground-water discharge into various tidal ecosystems by use of the three methods described above. Reported ranges of discharge in coastal, estuarine, and freshwater marshes are 2×10^{-5} to 0.262 ft/d, whereas subtidal discharge is reported to range from 0.007 to 0.236 ft/d (Tobias and others, 2001). Almendinger and Leete (1998) reported mean vertical discharge in a Minnesota fen to be 0.138 ft/d.

Seep discharge measured during this investigation is in the middle range of these reported values, whereas discharge from the non-seep wetland sediments is in the lower range of discharge values reported for other marsh sediments. Multiple discharge measurements at the same tidal site varied over an order of magnitude (Tobias and others, 2001), similar to the variability in this study.

Estimates of vertical and horizontal hydraulic conductivity in seep locations were made and compared to reported values for non-seep areas (Lorah and others, 1997). Mean vertical interstitial velocity and vertical hydraulic conductivity were estimated from seepage results and Darcy's law and were compared to vertical ground-water velocity and hydraulic conductivity of non-seep wetland sediments from flow net analysis (Lorah and others 1997). The vertical interstitial velocity of pore water was calculated according to equation 2 and is shown in table 5. The resulting velocity values are inversely related to effective porosity; therefore, for comparisons to the non-seep wetland sediments, an equivalent effective porosity of 0.4 was used. This porosity estimate could be overestimated if in fact a smaller proportion of pore space is driving the advective flow of seep water as described in Harvey and others (1995); therefore, the selection of this porosity value is considered to be conservative and reflects a minimum velocity.

Vertical hydraulic conductivity was calculated at three seeps (3-1E, 3-4W, and 3-7E) using Darcy's law according to equation 4, using the mean hydraulic gradient measured at the drive-point piezometers at seep 3-4W.

$$K_v = q_v / i \tag{4}$$

Table 5. Calculated seepage velocity and vertical hydraulic conductivity at seeps 3-1E, 3-4W, and 3-7E with comparisons to non-seep wetland sediments along the A-A' and C-C' sections, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[ft/d, feet per day; ft/ft, feet per foot; --, data not calculated for this report]

Location	Assumed effective porosity	Mean seepage velocity ¹ (ft/day)	Hydraulic gradient ² (ft/ft)	Vertical hydraulic conductivity ³ (ft/day)
3-1E	0.4	0.015	0.3	0.020
3-4W	0.4	0.133	0.3	0.177
3-7E	0.4	0.110	0.3	0.147
A-A' section	0.4	0.006	--	⁴ 0.003
C-C' section	0.4	0.008	--	⁴ 0.007

¹ Mean seepage velocity equals geometric mean flux (table 4) divided by the effective porosity.

² Hydraulic gradient average is from Lorah and others (2005) and measurements from 3-4W site drive-point piezometer pair.

³ Calculated as mean seepage velocity divided by the hydraulic gradient.

⁴ Reported by Lorah and others (1997).

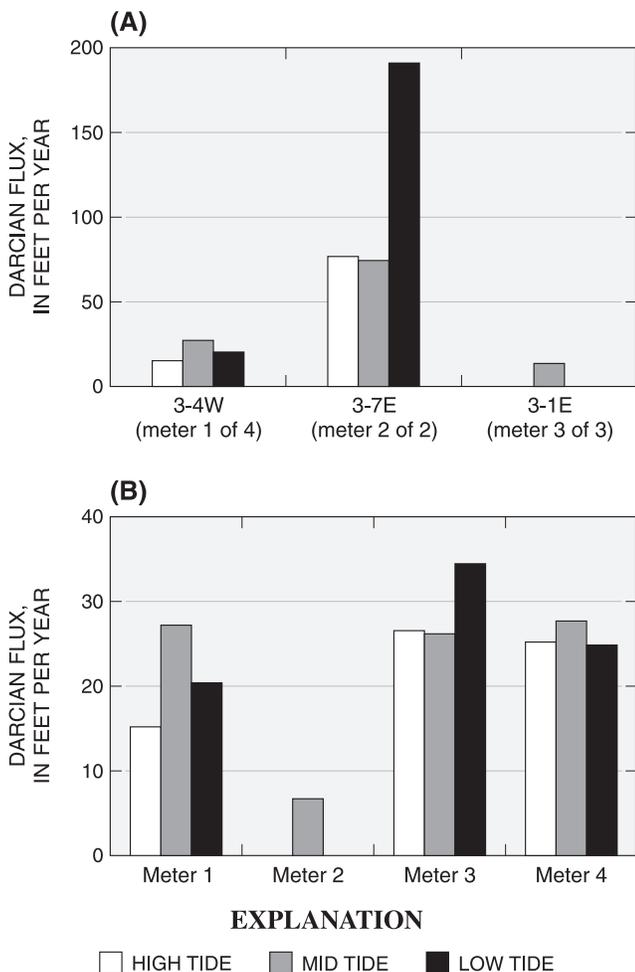


Figure 22. Variations in ground-water seepage flux (A) over the tidal cycle at different locations and (B) within the general boundaries of a seep (3-4W). (Seep locations shown in fig. 10.)

where

K_v is vertical hydraulic conductivity,
 i is the mean vertical hydraulic gradient,

and

q_v is the seepage flux (from table 4).

Vertical hydraulic gradients were measured at drive-point piezometers at seep 3-4W seven times, during both high and low tides between May and September 2004. The mean vertical gradient was 0.31 ft/ft (feet per foot), with a standard deviation of 0.04, which is equivalent to the gradient measured along the C-C' section between 1995 and 2000 (Lorah and others, 2005). This similarity indicates that the regional hydraulic gradient in the vertical direction is consistent in the non-seep sediments and seep location 3-4W. Therefore, a vertical gradient of 0.3 was assumed for all three seep locations when calculating vertical hydraulic conductivity. With this assumed average hydraulic gradient, vertical hydraulic conductivity varied between the three locations as described for flux. Vertical hydraulic conductivities at focused discharge locations 3-4W and 3-7E were estimated to be two orders of magnitude greater than the estimates for non-seep sediment (table 5; Lorah and others, 1997). Seep 3-1E was only one-half to one order of magnitude greater than previous estimates for the non-seep sediment, which is within the error reported for this calculation (Freeze and Cherry, 1979).

In addition to the vertical hydraulic conductivity calculations based on measured seepage flux, empirical estimates of horizontal hydraulic conductivity (from *in situ* dissipation tests by CPT and grain-size analysis) were conducted at specific intervals within the wetland sediment profiles to examine changes in horizontal hydraulic conductivity with depth. Results of *in situ* dissipation tests in wetland sediments at seep location 3-4W using CPT and equation 3 ranged from 9×10^{-4} to 4.1×10^{-2} ft/d (table 6). Even if the seepage discharge measurements of horizontal hydraulic conductivity are biased high, estimates from the CPT investigation are lower than estimates of vertical hydraulic conductivity. Dissipation tests have been shown to measure predominantly horizontal hydraulic conductivity. Generally, these CPT-based hydraulic conductivity measurements were in the same range as those determined in non-seep wetland sediments using slug tests, but were less than those estimated using the seepage measurements and local, vertical hydraulic gradients. Anisotropy ratios between horizontal and vertical hydraulic conductivity are typically greater than 1 and can range as high as 100 due to lateral deposition of sediments (Freeze and Cherry, 1979). In peats however, they have been reported as low as 0.2, near 1 (more isotropic), and greater than 1 (Rycroft and others, 1975).

The variability of hydraulic conductivity of West Branch Canal Creek wetland sediments in seep locations seems to be slightly correlated to depth below land surface. A decreased conductivity is observed with increased depth below land surface ($r^2 = 0.54$ for logK versus depth) for *in situ* dissipation

Table 6. Measured and calculated horizontal hydraulic conductivity in sediment at seep 3-4W with comparisons to non-seep wetland sediments along the A-A' and C-C' sections, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[ft/d, feet per day; CPT; cone penetrometer testing, Kozeny-Carmen from Kolterman and Gorelick, 1995; slug test data from Lorah and others, 1997.]

Location	Method	Hydraulic conductivity range (ft/day)	Correlation of hydraulic conductivity with depth below land surface
3-4W	<i>In-situ</i> CPT	9.0E-04 - 4.1E-02	$r^2 = 0.54$
3-4W	Kozeny-Carmen	3.3E-02 - 1.3E-01	$r^2 = 0.56$
A-A' section	Slug test	3.0E-04 - 4.0E-02	
C-C' section	Slug test	3.0E-04 - 6.0E-02	

tests at seep 3-4W. Hydraulic conductivity calculated from particle size analysis of sediments from locations 3-4W and 3-7E shows a similar pattern ($r^2=0.56$ and $r^2=0.60$, respectively, for logK versus depth), although the overall estimates were less than those calculated by other methods, likely due to the removal of organic matter prior to particle size analysis. The correlation between decreasing hydraulic conductivity with increasing depth below land surface has been previously reported in peat (Boelter and Verry, 1977) and attributed to the presence of higher fiber content (lesser degree of decomposition) in the upper parts of the sediment profile. Conflicting results have been reported in organic sediments that do not possess this varied fibric to sapric peat structure with depth (Almedinger and Leete, 1998; Chason and Siegel, 1986). Although significant woody structure is not observable in upper sediments at West Branch Canal Creek and these sediments are not truly classified as peat, a root mass is common in the upper sediments due to the presence or former presence of wetland plants, and may cause an effect similar to the effects observed in peat structure. The upper sediments of Atlantic Coastal Plain marshes have been reported to have most organic carbon associated with plant roots and not peat (Frey and Basan, 1985).

Characterization of Physical Properties

The physical properties of wetland sediments have been described previously (Rabenhorst, 2000; USACE, 1994; 2000) and the relation between particular physical properties and hydraulic properties has been discussed (Boelter and Verry, 1977; Mitsch and Gosselink, 1993; Mann and Wetzel, 2000). Commonly, organic soils, or histisols, have been described as those with at least 12 and up to 18 percent (if soil has greater than 60 percent clay) organic carbon (Rabenhorst, 2000). These organic soils are further classified on the basis of the degree of decomposition, with hydraulic conductivity decreasing and bulk density increasing with increasing extent

of decomposition (Boelter and Verry, 1977; Mitsch and Gosselink, 1993). Wetland sediments containing less than this criteria for organic carbon composition are classified as minerotrophic wetland soils and are characterized by reduced iron and manganese, causing a gleyed appearance. Ground-water discharge wetlands occurring in topographic lows can contain both minerotrophic and organic soils or sediments (Rabenhorst, 2000). Previous investigations of the West Branch Canal Creek wetland sediments indicate a high percentage of clay and an average organic content of 18 percent in the uppermost sediments (Olsen and others, 1997) and gleying has been reported in lithologic descriptions of deeper wetland sediments in the area (Phelan and others, 2001b) indicating that the wetland appears to be composed of both organic and mineral sediments, possessing characteristics of both in places.

Sediment cores of wetland sediments were collected at seeps with focused discharge and at a background location along the C-C' section (nearby piezometer WB35) for lithologic descriptions and laboratory analysis of physical properties (TOC, particle size, specific gravity, and wet density). A core was not collected from seep 3-1E, due to the presence of construction debris and difficulty in obtaining UXO clearance in this area of the wetland. Any physical differences between the previously described wetland sediments (Lorah and others, 1997; Phelan and others, 2001b) and the current background core at piezometer nest WB35, and the seep sediments were evaluated as possible influences on the occurrence of preferential flow through seep sediments.

Total depths and depths to the Canal Creek aquifer are listed in table 7 and a lithologic description of each core is provided in Appendix 4. Generally, the depth to the Canal Creek aquifer in seep locations 3-4W and 3-7E is consistent with depths reported previously at nearby sites HP05 (between the two seep areas on the east side of the channel) and HP11 (northwest of 3-4W) (Phelan and others, 2001b). The depth to the aquifer varied from the north to the south at seep location 3-4W, ranging from 11.6 to 15.1 ft bls (table 7) over a lateral

Table 7. Total core depth, depth to the Canal Creek aquifer, and method of core collection, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[ft bls, feet below land surface;-- aquifer not reached]

Site	Total core depth (ft bls)	Depth to Canal Creek aquifer (ft bls)	Core collection method
3-4WN	13.2	11.6	Vibracore
3-4WN2	5.3	--	Vibracore
3-4WS	17	15.1	Hand-held slide hammer
3-7E	14	9.5	Vibracore
WB35	6.3	6	Hand-held slide hammer

distance less than 30 ft. Compression of the organic-rich sediments overlying the Canal Creek aquifer occurred during coring operations in all cores and also was similar to that reported during previous investigations (Phelan and others, 2001b) due to high water and organic content. Lithologic descriptions of the various cores in seep areas are consistent with descriptions of wetland sediments elsewhere throughout West Branch Canal Creek (Olsen and others, 1997; Phelan and others, 2001b) and do not provide visible evidence of preferential flow paths.

Percent TOC, specific gravity, wet density, and particle size of sediment samples from all collected cores indicate that sediments possess properties of both organic and mineral sediments (table 8), which has been described for marshes of the Atlantic Coastal Plain (Rabenhorst, 2000). Percent TOC was greatest in the uppermost sediment samples from all sites and declined linearly with depth below land surface at seeps 3-4W ($r^2 = 0.96$, 0.66) and 3-7E ($r^2 = 0.86$). These surficial sediment TOC results are in the low end of the range previously reported by Olsen and others (1997) at West Branch Canal Creek. This decline in TOC in lower depths of the wetland sediment was similar to results reported in Mann and Wetzel (2000) at other wetlands, and consistent with increases in wet (or *in situ*) density and specific gravity (table 8). Values of wet density and water content (data not shown) were used to estimate bulk density by use of equation 5.

$$D_b = D_w / (1 + wc/100) \quad (5)$$

where

D_b is bulk density,

D_w is wet density,

and

wc is water content.

Calculated values of bulk density ranged from 0.25 to 0.33 g/cm³ (grams per cubic centimeter) in 3-4W and WB35 in the upper 7 ft of sediment; however, sediments at 3-7E had higher bulk density values (0.5 g/cm³) at similar depths below land surface. This location also had the lowest overall TOC (table 8). Rabenhorst (2000) reported bulk densities of organic soils and sediments in the range of 0.02 to 0.30 gm/cm³, indicating that these sediments are near or exceed the upper range for organic sediments. Wet density values are consistent with the classification of organic clays (Hayes and others, 2000).

Particle size analysis of sediment from cores collected at three seep sites (3-4WN, 3-4WS, and 3-7E) and one non-seep site (WB35) shows sediments were predominantly composed of fines (60 percent or greater) and the fine fraction is not consistently correlated with depth below land surface (r^2 ranges from 0.02 to 0.78). The sand-sized fraction was greatest in the shallowest depths at 3-4W, however, in contrast to WB35 (table 8). These particle size data are representative of the sediments without the organic fraction, which at these shallow depths is a significant part of the

Table 8. Physical properties of sediments from cores collected at seep locations 3-4W and 3-7E, and site WB35, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[pcf, pounds per cubic foot; g/cm³, grams per cubic centimeter; TOC, total organic carbon by weight; mm, millimeter; ¹sample from aquifer; N, not analyzed; -, not calculated]

Site	Approximate depth, feet below land surface	Wet density (pcf)	Wet density (g/cm ³)	Specific gravity	Percent TOC	Percent particle sizes 0.075 - 2 mm	Percent particle sizes less than 0.075 mm	Calculated bulk density (g/cm ³)
3-4WN	0 - 2.0	78.4	1.26	2.523	15.93	6.5	93.5	0.31
	2.0 - 3.0	73.8	1.18	2.550	10.31	16.3	83.7	0.32
	7.0 - 9.5	90.4	1.45	2.568	3.34	19.1	80.9	-
	9.5 - 12.0	92.5	1.48	2.550	6.87	8.8	91.2	-
	12.0 - 12.8 ¹	131.7	2.11	NA	0.07	80.1	19.9	-
3-4WS	0 - 1.8	NA	NA	NA	NA	31.3	68.7	
	1.8 - 3.3	75.7	1.21	2.591	14.85	34.2	65.8	0.25
	4.0 - 6.0	72.6	1.16	2.611	14.55	20.4	79.6	0.27
	7.0 - 9.5	83.9	1.34	2.569	6.68	2.1	97.9	0.57
	10.0 - 11.0	NA	NA	NA	5.38	5.5	94.5	-
	11.0 - 12.5	NA	NA	NA	4.02	10	90	-
	13.0 - 15.0	133.0	2.13	2.627	0.26	24	76	-
	15.0 - 16.2 ¹	129.1	2.07	NA	0.19	89.3	10.7	-
3-7E	3.0 - 4.0	80.5	1.29	2.498	4.75	20.2	79.8	0.5
	5.0-7.0	82.2	1.32	2.560	4.37	41.1	58.9	0.5
	7.0-9.5	87.2	1.40	2.552	3.47	2.8	97.2	0.64
	9.5-11.3	132.5	2.12	2.668	0.09	74.2	25.8	-
	11.3-12.0 ¹	130.8	2.10	NA	0.04	73	27	-
WB35	0-3.0	68.5	1.10	2.544	13.58	5.4	94.6	0.33
	3.0-6.3	70.7	1.13	2.617	5.71	48.9	51.1	0.37

sediment composition. Due to the shallow depth of the aquifer at siteWB35, it is difficult to ascertain if the proportion of sand-sized particles in the surficial wetland sediments at seep locations 3-4W and 3-7E is significant compared to the surficial sediments at WB35. The organic content and particle size in the surficial sediments at 3-4W and 3-7E, however, may contribute to higher hydraulic conductivity observed in these uppermost sediments at these locations.

Whereas Portnoy and others (1998) reported preferential flow in areas of observable low organic content and high permeability zones composed largely of sand, differences in physical properties of seep sediments at West Branch Canal Creek are not as apparent when compared to physical properties of non-seep sediment. Portnoy and others (1998) typically observed that ground-water discharge through marsh sediments was bypassed for more permeable zones. Although some differences in particle size were observed at West Branch Canal Creek, a specific hydrogeologic mechanism resulting in the increased specific discharge in the seep areas still remains unknown. Other possible explanations for the

increased discharge may be due to the wetland dual porosity and heterogeneity in anisotropy related to the structural distribution of the particles, or hydraulic properties of the underlying, unconfined aquifer. The very high water content of the wetland sediments at West Branch Canal Creek, combined with the high vertical hydraulic gradient, may result in shifts between macro- and matrix-pore flow with small changes in particle size distribution. Non-seep wetland sediments appear to have an anisotropic ratio (K_h/K_v) greater than 1 (Lorah and others, 1997), whereas seep areas appear to have anisotropic ratios nearer to or less than 1 (tables 5 and 6). The interconnectedness of pores and the decrease in anisotropy would require further investigation to determine whether the structural orientation of particles impacts fine-scale hydraulic properties. Alternatively, Portnoy and others (1998) and Harvey and Odum (1990) both indicated that ground-water discharge through marsh sediments can be largely affected by unconfined aquifer heterogeneities. Springs or seeps in a fringing marsh are impacted by low porosity silt and clay fingers present in the sand aquifer (Portnoy and others, 1998).

In addition, the geometry and hydraulic conductivity of the underlying aquifer have been shown to affect the pathway and magnitude of ground-water discharge to surface water (Harvey and Odum, 1990). The Canal Creek aquifer is known to be highly heterogeneous, with the presence of paleochannels and silt and clay stringers. Due to access difficulties within the wetland boundaries, the lithology of the aquifer south of the natural attenuation study area is available only at discrete points. Additional investigations would be necessary to determine whether any aquifer heterogeneities affect the local hydrogeology.

Hydrologic Influences of Preferential Discharge on Anaerobic Biodegradation

Hydrology, chemical and physical properties, and biotic ecosystem responses are interdependent in wetland environments (Mitsch and Gosselink, 1993). The hydrologic occurrence of preferential discharge limits anaerobic biodegradation because faster fluid flow through these sediments reduces the time any given parcel of water is exposed to this reducing environment. The increase in specific discharge and resulting decrease in residence time within the wetland sediment impacts several characteristics required for efficient natural attenuation, including the primary terminal electron accepting process (TEAP) and biodegradation rates. The effect of preferential flow at the seep locations is demonstrated in redox and VOC profiles, and microbial communities. These parameters are discussed for three sites to contrast how they differ in seep locations compared to the non-seep wetland sediments where natural attenuation is shown to be efficient (Lorah and others, 1997; 2005).

Redox-Sensitive Constituents

Anaerobic conditions are present throughout the non-seep wetland sediments regardless of VOC concentration (Lorah and others, 2005). The consistent artesian conditions in the wetland, coupled with the relatively low rate of discharge through the sediments, allow for the consistent methanogenic, or mixed iron-reducing and methanogenic conditions that are most conducive to reductive dechlorination (Lorah and others, 1997; 2005a). Previous investigations in the wetland sediments have indicated that measurements of the primary reduced species of ferrous iron, sulfide, and methane can determine the primary TEAP (Lorah and others, 1997).

Vertical profiles of ferrous iron, sulfide, methane, and ammonia concentrations in shallow sediments at three seep sites are shown in figure 23. Although anaerobic conditions were present in the seep sediments at all three locations, methane was detected consistently only at diffuse seep location 3-1E, following the transient appearance of sulfide. At 3-1E, the less rapid discharge rates allow for the formation of mixed iron-reducing and methanogenic conditions as indicated by the increase in methane concentrations and ferrous iron

compared to the other seep locations. This is contrasted with focused discharge locations 3-4W and 3-7E, where neither sulfide nor methane were detected in any substantial quantities in the upper 2 to 4 ft of wetland sediments. Rather, these locations with more rapid discharge and less residence time within the sediments have predominantly iron-reducing conditions in the upper sediments. Ammonia also accumulates throughout the vertical profiles at both locations (3-4W and 3-7E; fig. 23). These results are in contrast to those reported previously in non-seep areas (Lorah and others, 1997; 2005a; Lorah and Olsen, 1999b).

Chlorinated Volatile Organic Compounds

Vertical profiles of chlorinated VOCs along the C-C' section in the wetland study area during sampling events from 1995–2001 were previously reported (Lorah and others, 2005a) and used as a reference for non-seep sediments in the West Branch Canal Creek wetlands. Typically, parent chlorinated VOCs were not detected in wetland sediments along the A-A" section (Lorah and others, 1997). Along the C-C' section, low concentrations (less than 2 µg/L each) of TeCA and TCE were detected at the base of the wetland sediments, and transient accumulation of daughter products up to 250 µg/L (mainly VC and *trans*- and *cis*-isomers of 12DCE) was observed with a decrease to near detection levels at land surface (fig. 24).

In the mixed iron-reducing and methanogenic sediments at seep 3-1E, both parent and daughter compounds were detected over a larger area that could not be bounded to the east (due to the upland boundary) nor to the south (fig. 25a, b, and c). In addition, the overall areal extent of TeCA is less than the footprint of its anaerobic daughter products (tDCE and VC, shown in fig. 25a, b, and c) at seep 3-1E. Vertical concentration profiles of TeCA, tDCE, and VC showed greater concentrations of these compounds (fig. 26a and b) than those typically observed at similar depths along the nearby C-C' section; however, the vertical profile was similar to the C-C' section with most VOCs declining with decreasing depth below land surface. The depth of maximum VC concentration (fig. 23a) corresponds to the depth of maximum methane concentration (fig. 26a and b), which is consistent with the pattern observed in non-seep sediment (Lorah and others, 2005a).

Conversely, at seep 3-4W, concentrations of parent compounds CF (fig. 27a), CT (data not shown), and PCE (fig. 27b) form a similar spatial footprint (approximately 1,000 ft²) along the west bank of the West Branch Canal Creek, in which concentrations of individual contaminants range from 15,000 to less than 100 µg/L over as little as 10 ft (and not greater than 20 ft) in the predominantly iron-reducing sediments. Some daughter products were detected in discrete locations; only cDCE is present along the northern and southern fringes of the core of the seep footprint (fig. 27c), likely as a degradation product of PCE. The lack of spatially consistent daughter compounds is likely due to the mildly

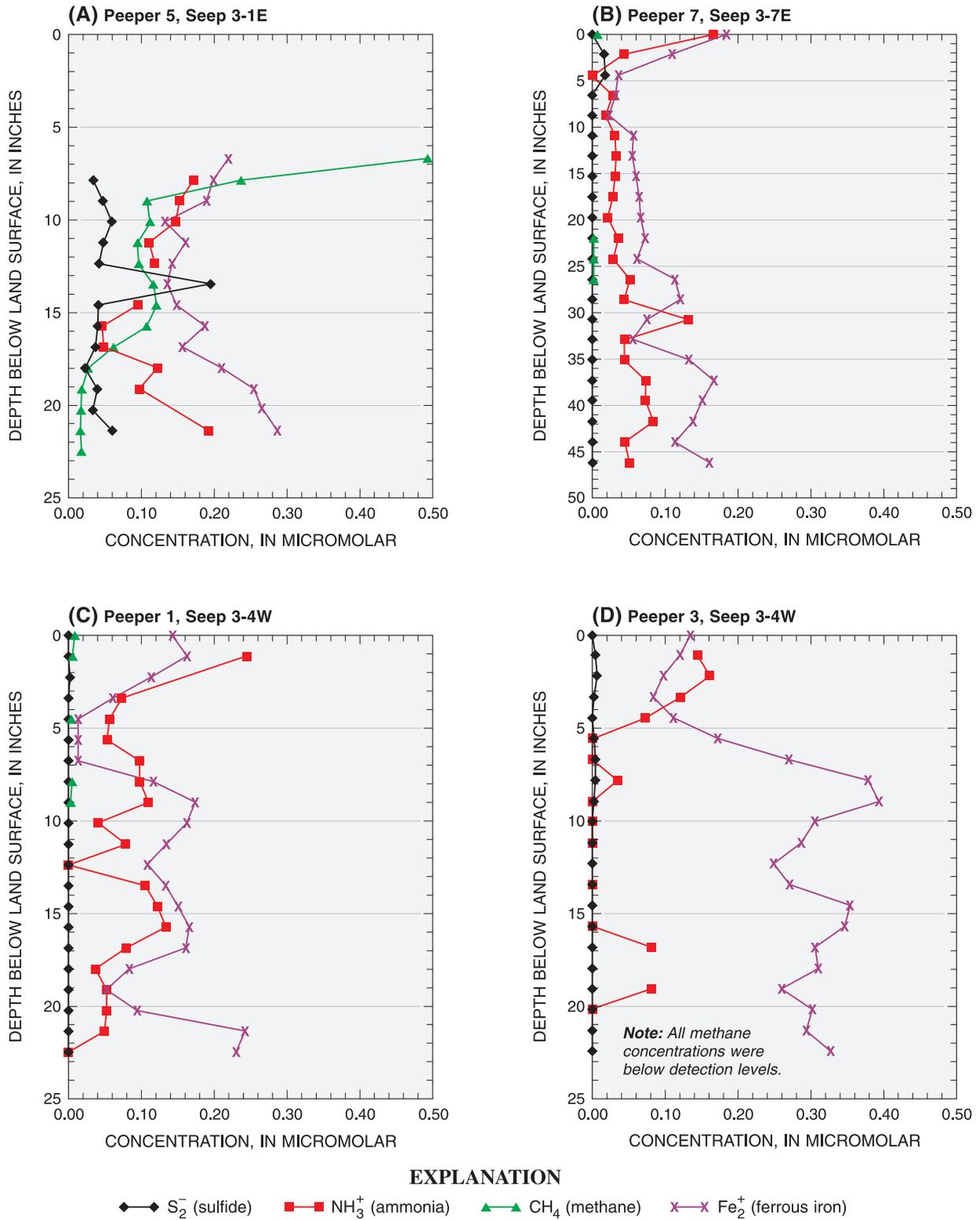


Figure 23. Vertical distribution of redox-sensitive constituents in pore water at three seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, July 2003, (A) 3-1E, (B) 3-7E, (C and D) 3-4W. (Location of seeps shown in fig. 10.)

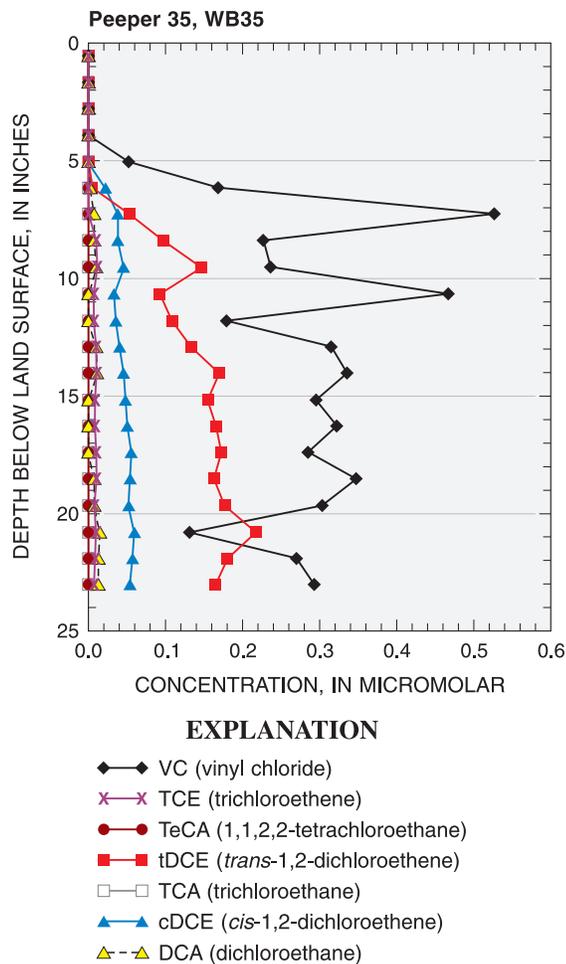


Figure 24. Vertical distribution of various chlorinated volatile organic compounds in non-seep sediment (WB35, fig. 10), May 2001, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

reducing conditions in the sediments resulting from the increased specific discharge. The presence of cDCE along the fringe may indicate that some contaminant transport is driven by diffusion into areas of lesser VOC concentrations in the non-seep sediment, near the seep boundaries. At three locations within the footprint of the seep, peepers were used to determine the vertical VOC distribution and results from two of these locations are shown in figure 28a-d (the third peeper was consistent with the others and is not shown). The increased velocity and corresponding decreased residence time in the wetland sediments results in a consistent or increasing VOC concentration profile with decreasing depth below land surface. This concentration profile indicates a conservation of CF, CT, and PCE contaminant mass along the vertical profile due to the lack of anaerobic biodegradation. In some cases, an accumulation of mass is apparent with decreasing depth below land surface, indicating that flow may not be entirely vertical in this area and that the seep may accumulate VOCs from the

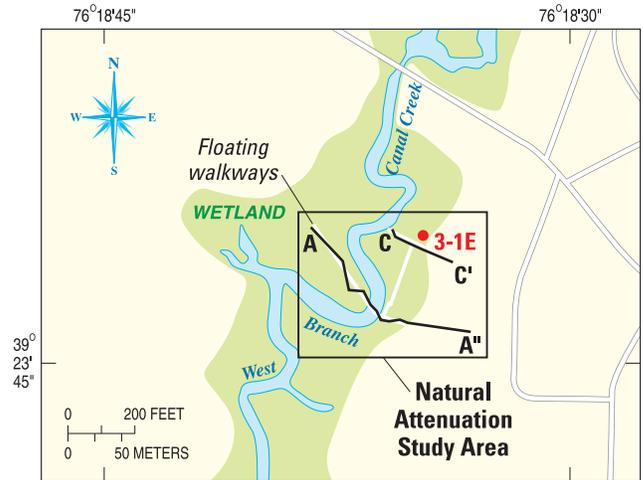
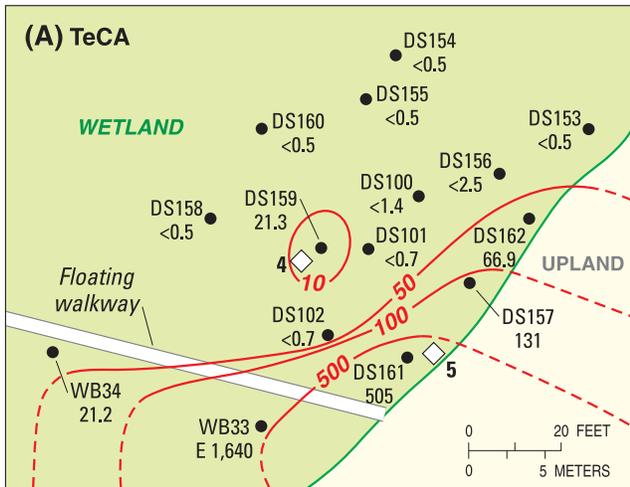
surrounding area. Discharge of the increased chlorinated VOC concentrations results in an increased contaminant mass flux to surface water compared to the non-seep wetland sediments.

Similar patterns were observed in the iron-reducing sediments found at seep location 3-7E. Maximum VOC concentrations of major parent contaminants PCE and CF were focused in a common area of about 100 ft² along the creek edge and slightly into the stream sediments (fig. 29a and b). A high degree of spatial heterogeneity was apparent in the composition, magnitude, and distribution (both lateral and vertical) of VOCs at this site, indicating that the area over which there is increased, preferential flow is very discrete or may not be entirely vertical. In the area with the greatest discharge, parent compounds were detected in shallow sediment, indicating a short residence time within the sediments. Within 5 ft laterally of these maximum concentrations of parent compounds, anaerobic daughter compounds of PCE (including 12DCE and VC) were detected in the shallow pore water. The appearance of these daughter products in this fringe area of the seep corresponded to increased methane concentrations (data not shown). In addition, vertical profile variations in chlorinated VOC composition and magnitude were apparent between the A and B cells in the same peeper, which were located at the same depth, laterally a couple of inches apart (fig. 28c and d).

Microbial Communities

Bacteria profiles of seep sediments were examined to evaluate the overall impact of the less reducing conditions and higher VOC concentrations in seep pore water on the microbial community, including the relative contribution of bacteria groups associated with dechlorination. Seep sediment profiles were compared to profiles from non-seep areas of efficient natural attenuation previously reported by Lorah and others (2003a) and Lorah and Voytek (2004). In addition, the presence of dehalorespiring organisms was estimated in order to better understand their role in anaerobic biodegradation at West Branch Canal Creek.

Comparisons of the magnitude and relative intensity of TRFLP profiles between sites can indicate the relative abundance (as determined by the overall peak area) and diversity (as determined by the overall number of peaks) of bacterial groups and species within the wetland sediments (Lorah and Voytek, 2004). Previous investigations of the microbial community in sediments within the wetland study area indicate that specific groups of bacteria associated with particular TRFLP peaks may be associated with specific steps in the reductive dechlorination of TeCA, one of the primary site VOCs (Lorah and others, 2003a). Specifically, both laboratory and field data indicate that TRFLP peaks 170, 198, 235, and 238 may be associated with the dichloroelimination of 12DCE, while the 90 and 215 base pair TRFLP peak may be associated with the hydrogenolysis of 112TCA (Lorah and others, 2003a; Lorah and Voytek, 2004). These peaks were common to surficial sediments along the A-A' and C-C'



Location of seep 3-1-E.

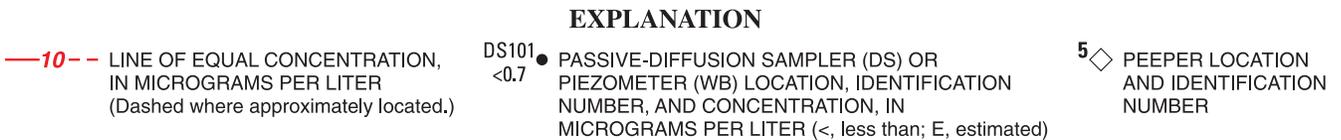
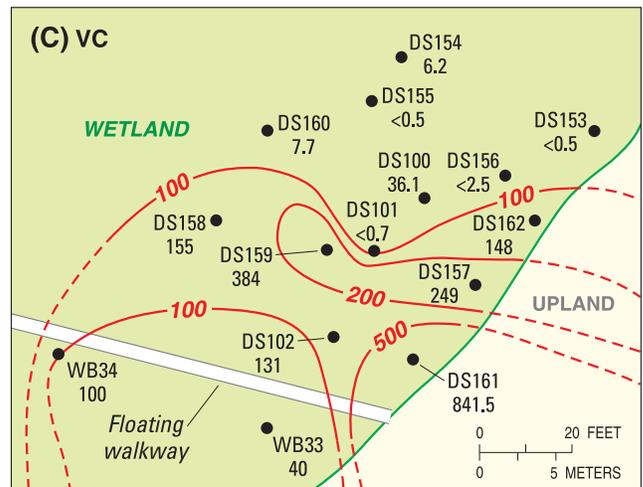
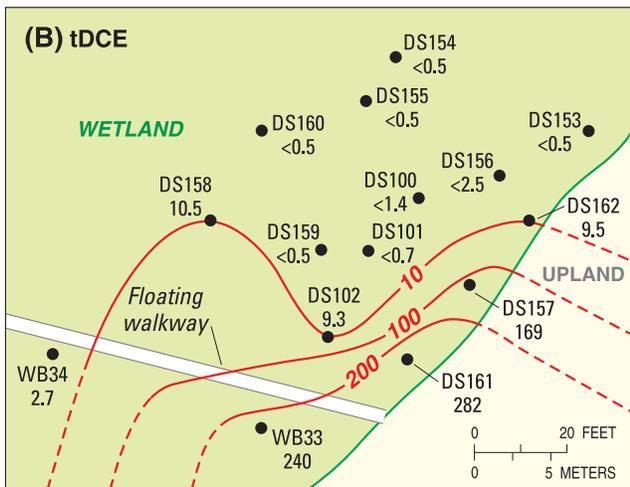


Figure 25. Distribution of selected volatile organic compounds in shallow pore water, seep location 3-1-E, May 2002 and April 2003, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) TeCA [1,1,2,2-tetrachloroethane], (B) tDCE [*trans*-1,2-dichloroethene], and (C) VC [vinyl chloride].

sections as well as the background location near piezometer WB19; however, some differences were reported between the A-A' and C-C' sections. The microbial diversity and biomass were greater along the A-A' section compared to the C-C' section, which corresponded to greater overall sediment depth to the aquifer along the A-A' section (Lorah and others, 2003a). VOC concentrations and the depth of tidal flooding was less along the A-A' section compared to the C-C' section, suggesting these factors may impact the overall community structure (Lorah and others, 2003a; fig. 30).

The dehalorespiring bacteria *Dehalococcoides* (*ethenogenes* and sp. strain FL2) and *Desulfuromonas* (strain BB1 and *chloroethenica*) have been detected in West Branch Canal Creek area wetland sediments (Lorah and others, 2003b). While *Dehalococcoides* bacteria have been shown to play a critical role in complete reductive dechlorination (Maymo-Gatell and others, 1997) and an association to field-observed degradation (Lu and others, 2004) at sites contaminated with chlorinated ethenes, the function of these bacteria in the West Branch Canal Creek sediments remains uncertain. Specifically, detections of *Dehalococcoides* in

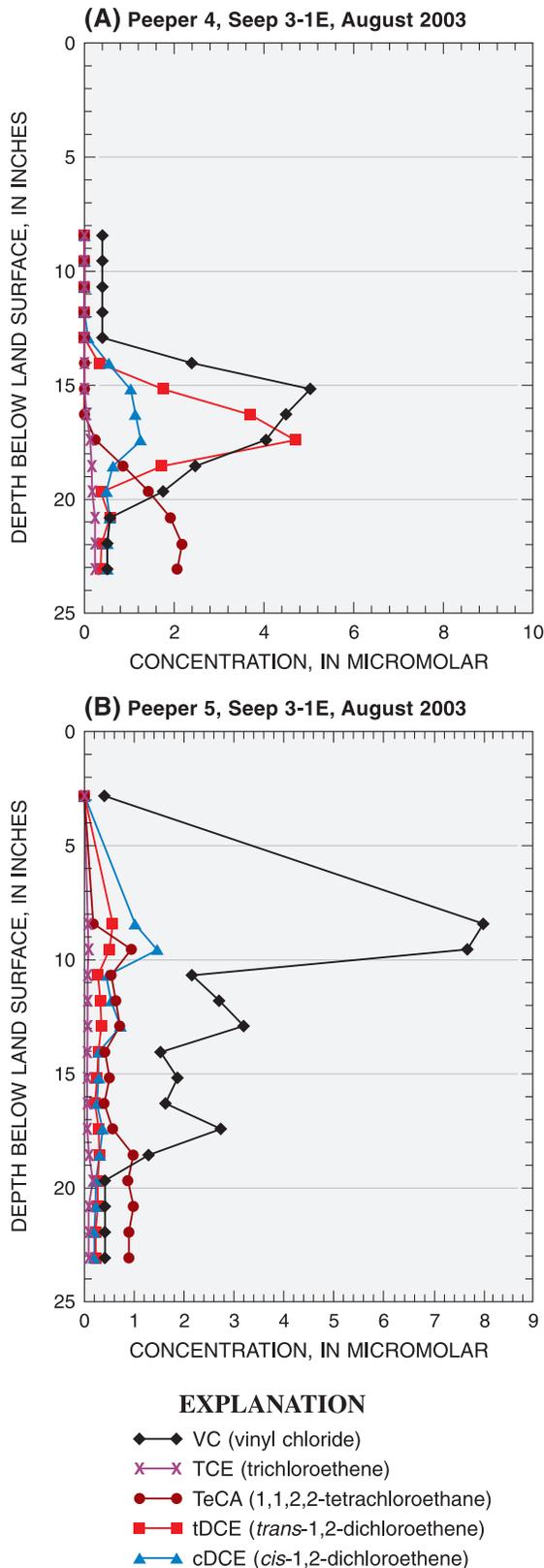
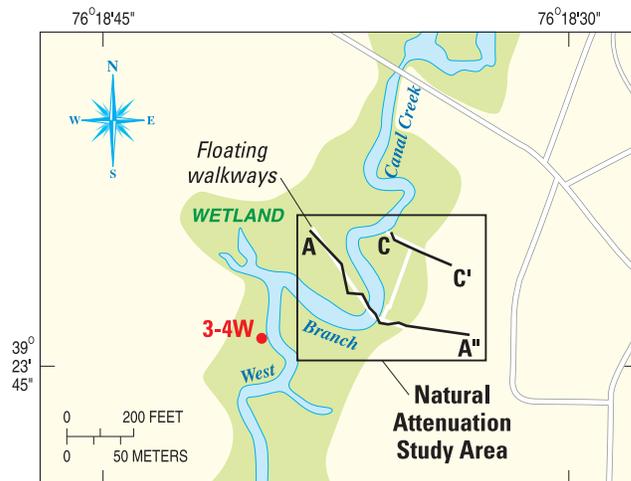
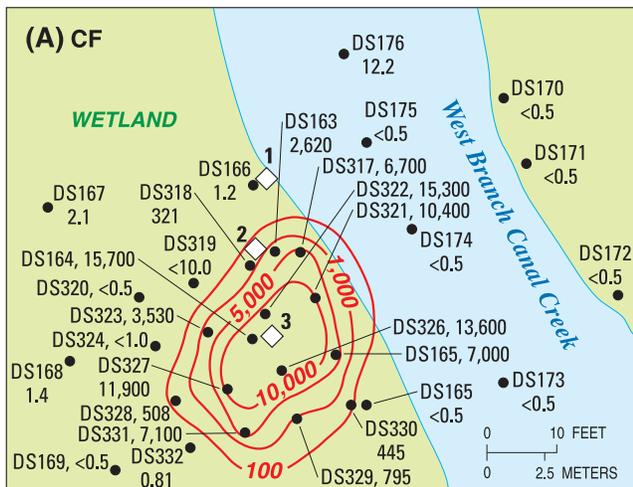


Figure 26. Vertical distribution of various chlorinated volatile organic compounds in two peepers at seep location 3-1E, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) peeper 4 and (B) peeper 5. (Location of peepers shown in fig. 25.)

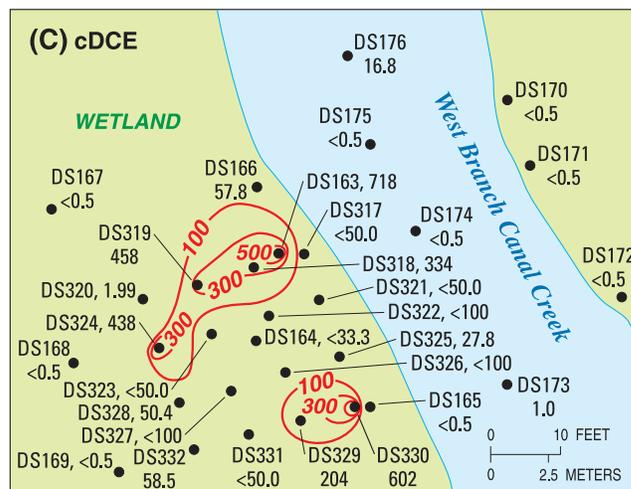
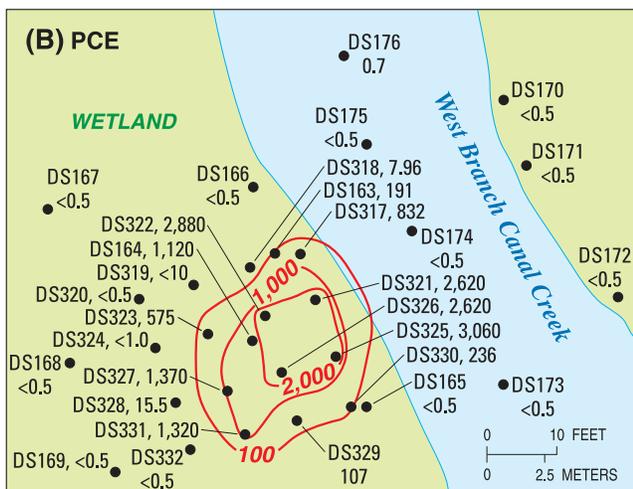
spring 1999, 2000, and summer 2000 varied from non-detect to 10^3 cells/gram (Lorah and others, 2003b). In the non-seep sediments, cell counts of *Dehalococcoides* did not correspond to VC degradation rates and cell counts were greater in the summer when degradation rates of TeCA dropped (Lorah and others, 2003b). Similarly, *Desulfuromonas* varied spatially and temporally from non-detect to 10^4 cells/gram (Lorah and others, 2003b).

The overall abundance and diversity of bacteria in sediments from seep locations generally is less than in sediments along the A-A' section or equivalent to sediments along the C-C' section, as evident in the overall dampened or equivalent relative peak intensity and total number of peaks in the TRFLP profiles (fig. 30). Like the C-C' section, many of the seep sites are located in areas where there is more tidal flooding when compared to the A-A' section. In addition, seep areas have increased VOC concentrations in shallow sediment compared to the A-A' section. Sediments in seep areas differ from the C-C' section in that the overall depth to the aquifer is typically greater; however, the rate of transport through these sediments is rapid and may result in short residence times, negating the importance of the overall sediment depth in community development. Seep sediment profiles appear to be enriched in peaks associated with dichloroelimination, with maximum peak height for the profile associated with base pairs that are suspected to be involved in the degradation of 12DCE (170/172, 198, 238). This observed "enrichment" is similar to the effect observed in the laboratory with increasing VOC concentrations (Lorah and others, 2003a). Whereas the overall abundance and diversity in some cases were less, the overall contribution of the microbial groups associated with the degradation reactions in seep sediments was similar to or greater than for non-seep sediments (fig. 31). In all cases, the total biomass attributed to peaks associated with degradation functions was greater than 30 percent of the total biomass, ranging from 30 to 290 base pair fragment lengths (fig. 31). In the case of 3-4W, where the maximum VOC concentrations were detected, these peaks accounted for 55 percent of the total biomass in this same range (fig. 31).

Quantitative PCR analysis detected *Dehalococcoides* in sediment from locations 3-1E (2×10^6 cells/gram) and 3-4W (4×10^4 cells/gram), but it was not detected in sediment from location 3-7E. Alternatively, *Desulfuromonas* was detected at locations 3-4W (3×10^4 cells/gram) and 3-7E (3×10^3 cells/gram), but was not detected in sediment from 3-1E. Detections of these two types of organisms are within the range of cell numbers detected in background and non-seep sediment locations throughout the wetland. The detection of these bacteria in the seep sediments did not appear to correspond to VOC type (PCE was detected at both 3-4W and 3-7E) and did not appear to be affected by the presence of CF at 3-4W. The accumulation of VOCs in the shallow pore water of these sediments despite the presence of one or both of these known dehalorespiring bacteria in seep sediments may be caused by several possible factors. First, the rate of pore water discharge may be too rapid for the microbial



Location of seep 3-4W.



EXPLANATION

- 100— LINE OF EQUAL CONCENTRATION, IN MICROGRAMS PER LITER
- DS169 <0.5 PASSIVE-DIFFUSION SAMPLER LOCATION, IDENTIFICATION NUMBER, AND CONCENTRATION, IN MICROGRAMS PER LITER (<, less than)
- ◇ 3 PEEPER LOCATION AND IDENTIFICATION NUMBER

Figure 27. Distribution of selected volatile organic compounds in shallow pore water, seep location 3-4W, April (DS163-DS176) and December (DS317-DS332) 2003, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) CF [chloroform], (B) PCE [tetrachloroethene], and (C) cDCE [*cis*-1,2-dichloroethene].

degradation kinetics, resulting in an existing but minimally active population. Recent studies have attempted to determine the number of bacterial cells present in association with dechlorination efficiency; however, most are based on non-native (bioaugmented) bacterial communities (Dennis and others, 2005) and therefore may not be entirely applicable to native populations. Nonetheless, in the case of bioaugmented aquifers, there appears to be a threshold population (based on the bacterial growth kinetics) that is required to observe efficient dehalorespiration of chlorinated ethenes (Dennis and others, 2005). The presence of the DNA from these bacteria

does not necessarily translate to active (living) cells; therefore, the dehalorespiring bacteria may be dead or dormant in the seep sediments. Finally, it is known that a mixed population of microorganisms is responsible for the efficient attenuation of the site contaminants (Lorah and others, 2003a; Lorah and Voytek, 2004). It is possible given the rather consistent cell counts in these wetland sediments that other microbial groups within the population may play a larger role. These results are in contrast to those reported by Lu and others (2004) of an association between *Dehalococcoides* presence and complete degradation of chlorinated ethenes to ethene. Laboratory

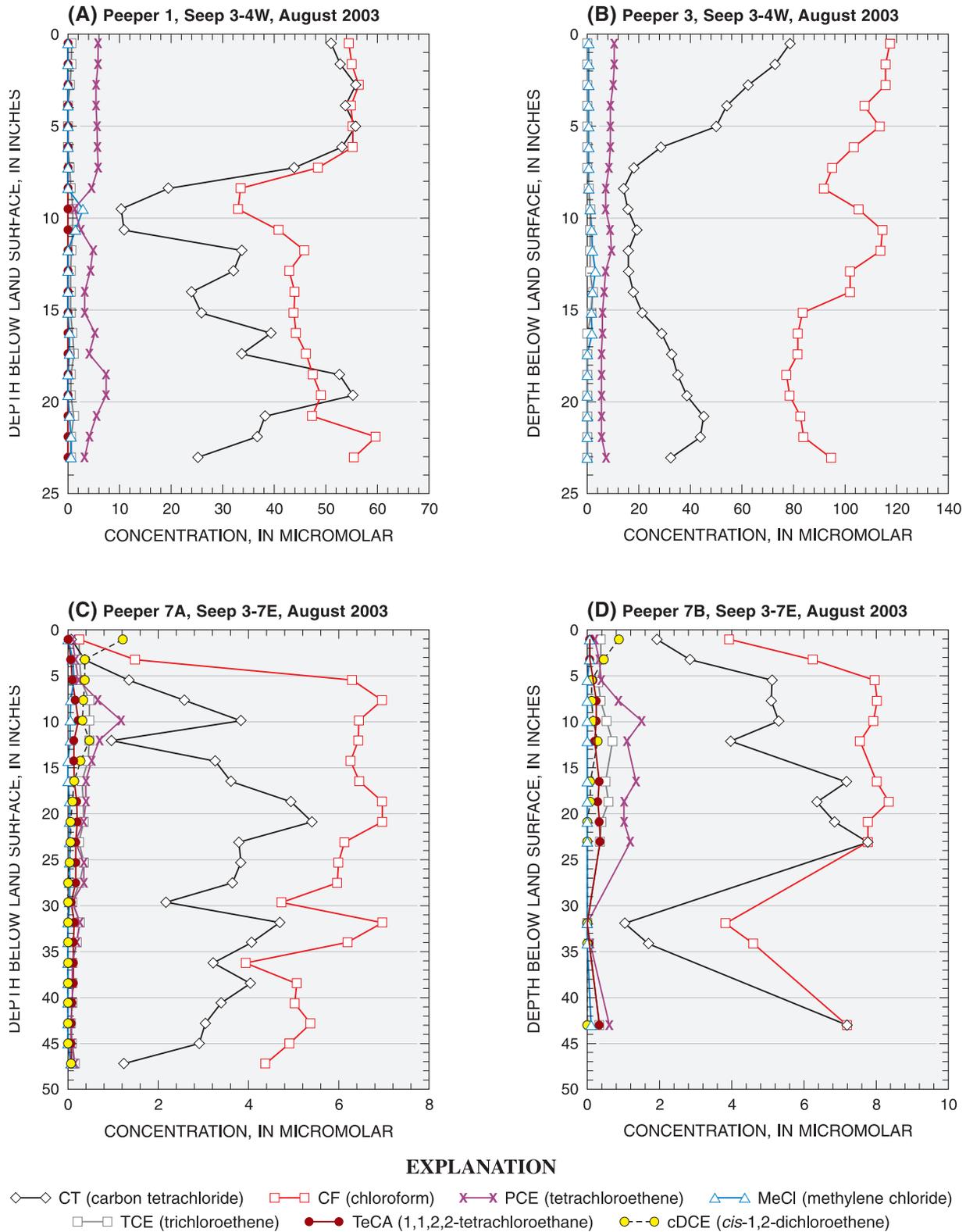
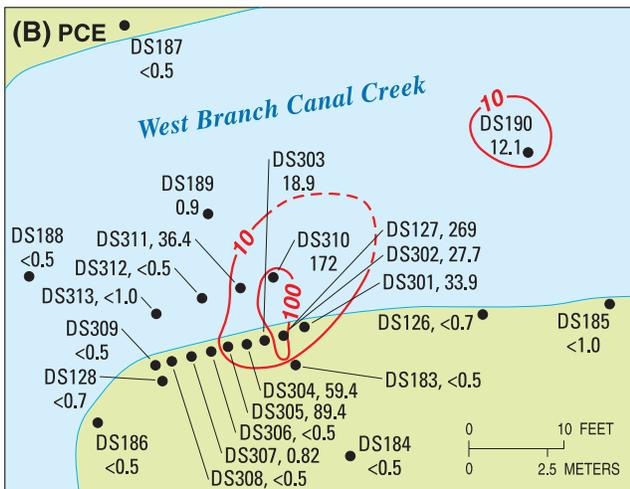
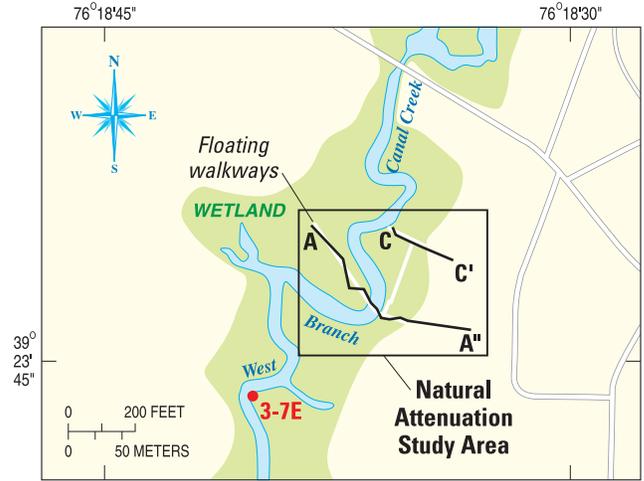
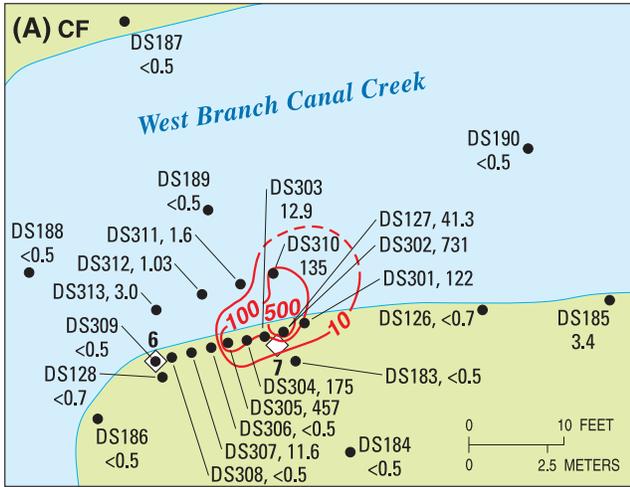


Figure 28. Vertical distribution of various chlorinated volatile organic compounds in peepers at two seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A-B) 3-4W and (C-D) 3-7E. (Location of peepers shown in figs. 27 and 29.)



EXPLANATION

- 10 — LINE OF EQUAL CONCENTRATION, IN MICROGRAMS PER LITER (Dashed where approximately located.)
- DS169 <0.5 PASSIVE-DIFFUSION SAMPLER LOCATION, IDENTIFICATION NUMBER, AND CONCENTRATION, IN MICROGRAMS PER LITER (<, less than)
- ◇ 7 PEEPER LOCATION AND IDENTIFICATION NUMBER

Figure 29. Distribution of selected volatile organic compounds in shallow pore water, seep location 3-7E, April (DS127-DS190) and December (DS301-DS313) 2003, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) CF [chloroform] and (B) PCE [tetrachloroethene].

microcosms and the further development of primers for the microbial consortium present at West Branch Canal Creek could help to answer these unknowns.

Surface-Water Quality and Mass Flux

The West Branch Canal Creek serves as a receptor for pore water discharge that contains varying concentrations of VOCs. The ground-water/surface-water interface, sometimes called the hyporheic zone in streams, is a unique transition zone that is known to be important in contaminant, nutrient, and carbon cycling and is often where the greatest populations of benthic organisms are located (Ford, 2005). While this zone is ecologically significant, the current regulatory framework does not focus on this transitional zone; instead, surface water, ground water, and sediment are regulated separately. Recently,

the USEPA has applied a new focus to the ground-water/surface-water interface with regard to flux, ecotoxicity, and threats to ground water (Ford, 2005). Previous investigations have indicated that non-seep surface-water sampling is not an adequate indicator of concentrations in upwelling zones, such as seeps (Conant and others, 2004; Greenberg and others, 2002). Surface-water samples were collected in conjunction with pore water samples during this investigation.

For this study, a total of 49 surface-water samples were collected and analyzed from within the seep location boundaries, near specific pore water sample locations. Surface-water samples were collected during periods of low tide when the surface of the wetland sediments was exposed and water was flowing or ponding along the sediment surface; therefore, these samples are largely undiluted by creek water. VOCs were detected only near seep locations in the tidal part

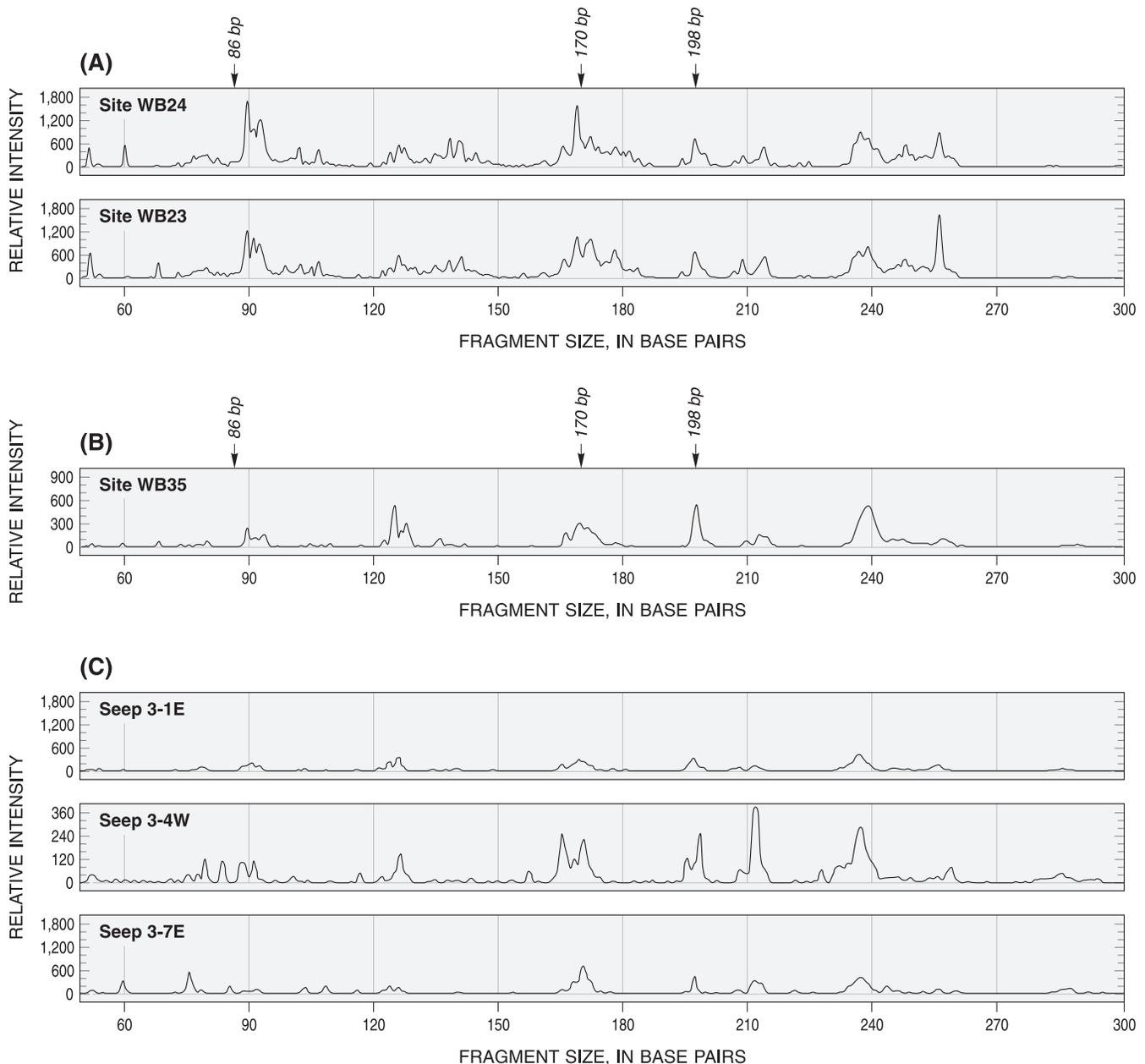


Figure 30. Terminal-restriction fragment length polymorphism scans of wetland sediment, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) A-A' transect, 1999, (B) C-C' transect, 1999, and (C) seep locations 3-1E, 3-4W, and 3-7E, 2003. (Locations of transects shown in fig. 3; locations of seeps shown in fig. 10.)

of the creek. Generally, the parent VOCs most commonly detected in pore water—CT, CF, TeCA, and TCE—also were detected most frequently and in the greatest magnitude in surface-water samples; however, some daughter compounds also were detected. Of the seep locations within the tidal part, seven locations (2-4W, 2-6W, 3-6E, 3-13E, 4-1E, 4-2W, and 4-3E) had no detections of VOCs above their reporting limits (fig. 32a; Appendix 3). The maximum concentrations of 12 of 14 chlorinated VOCs were found at two seep locations: 3-4W and 3-5E (table 9, fig. 32a and b). Maximum concentrations of CT, PCE, TCE, TeCA, 112TCA, PCA, and

HCA were detected in surface-water samples collected near 3-4W (fig. 32b). Maximum concentrations of cDCE, 12DCA, methylene chloride (MeCL), and CF were detected in surface-water samples collected near 3-5E. Although toluene was detected in pore water at concentrations greater than 500 $\mu\text{g/L}$, it was not detected frequently in surface water (one detection of less than 1 $\mu\text{g/L}$).

As in the current investigation, Phelan and others (2001a) reported primarily CF, CT, TeCA (and to a lesser extent PCE and TCE) in surface water. Results of surface-water sampling at Canal Creek from November 1999 to September 2000

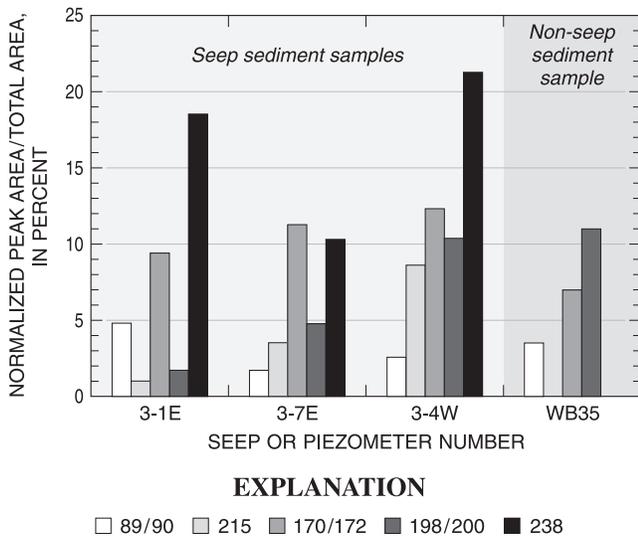


Figure 31. Proportion of bacterial peaks attributed to dechlorination in seep sediment samples compared to a non-seep sediment sample. (Location of seeps shown in fig. 10; location of WB35 shown in fig. 3.)

indicated that concentrations of VOCs in the creek channel were not statistically different between years, but tended to show a pattern of increased concentrations during low and mid tides compared to high tide (Phelan and others, 2001a). Maximum concentrations were centralized around the area between the natural attenuation study area and the confluence with the East Branch Canal Creek (Phelan and others, 2001a), where several contaminated seeps were identified during this investigation.

Additional sampling of surface water was conducted during a tidal cycle in the creek to observe the effects of pore water discharge on nearby non-seep surface water. Sampling of surface-water from fixed locations at 9 different times during a tidal cycle conducted near focused (3-4W) and diffuse (3-1E) seep locations indicated that the highest VOC concentrations (fig. 33a and b) corresponded to periods of the tidal cycle when the highest ground-water discharge was measured (see discussion in “Hydrologic and Physical Characterization” section). Sampling difficulties were experienced during two collection times (High mid-tide [HM] and mid-tide [M1]) during this event and are not shown in figure 33a. At focused discharge location 3-4W, where ground-water discharge was found to be consistent during the tidal cycle, surface-water VOC concentrations also were consistent (fig. 33a). At diffuse discharge location 3-1E, surface-water VOC concentrations and ground-water discharge were greatest at the mid-low tide. During this sampling event, surface-water samples were collected from both upstream and downstream locations near 3-4W, and from two locations spaced between 3-1E seep and the creek channel. Concentrations of VOCs in

surface water decreased by two to three orders of magnitude within 30 ft of both observable seep locations (Appendix 3). Surface-water samples collected upstream of 3-4W along the western bank consisted of VOCs common to the seep location and were greatest during the incoming mid-tide, whereas VOC concentrations in surface water collected downstream along the western bank were greatest during outgoing mid-tide, indicating that the VOCs in seep pore water were affecting surface water in these locations during this event. The median surface-water VOC concentration of samples collected in cross-section during the outgoing mid-tide from the western to eastern creek bank near 3-4W was 8 µg/L, however. Conversely, surface-water samples collected between 3-1E and West Branch Canal Creek were not characteristic of nearby seep discharge, as most surface-water VOCs detected were not present in pore water at 3-1E; VOCs found in 3-4W were detected in the creek channel near 3-1E.

Overall, these surface-water data indicate that surface-water sampling alone is not a good indicator of the location or magnitude of pore water concentrations, particularly in tidal environments. Conant and others (2004) and Majcher (2001) observed similar results in nontidal environments. Conant and others (2004) reported that PCE pore water concentrations discharging to a river varied by up to 5,000 times over very short lateral distances, but PCE was rarely detected in surface water due to dilution. Similarly, *in situ* eco-toxicity testing in a riverine upwelling zone indicated greater bioaccumulation and exposure of benthics to chlorobenzenes when compared to downwelling zones (Greenberg and others, 2002), an observation not likely to be made in *ex situ* toxicity tests with non-seep surface water. The results from this study support the conclusions of these previous studies that pore water characterization is required to clearly define the contaminant input at the ground-water/surface-water interface and may have bearing on ecological toxicity to sediment-dwelling organisms. Due to the variability and diluted concentrations of VOCs detected in surface water, concentrations typically did not exceed chronic toxicity values, particularly in the tidal environment at West Branch Canal Creek. Porewater concentrations in seep areas may exceed chronic toxicity values, however, reinforcing the importance of pore water characterization.

Updated Site Conceptual Model and Implications for Remediation

Ground-water data collected as part of several previous studies (Phelan and others, 2001b; 2002; Weston, 2005; General Physics Corporation, 2005) and the current study were combined to provide an updated composite of the VOC plume in plan view from 1999–2003. Overlapping plumes in the Canal Creek aquifer likely originating from multiple sources are shown in figure 34a and b. The consistent pattern of CF (as well as CT and PCE, data not shown) in

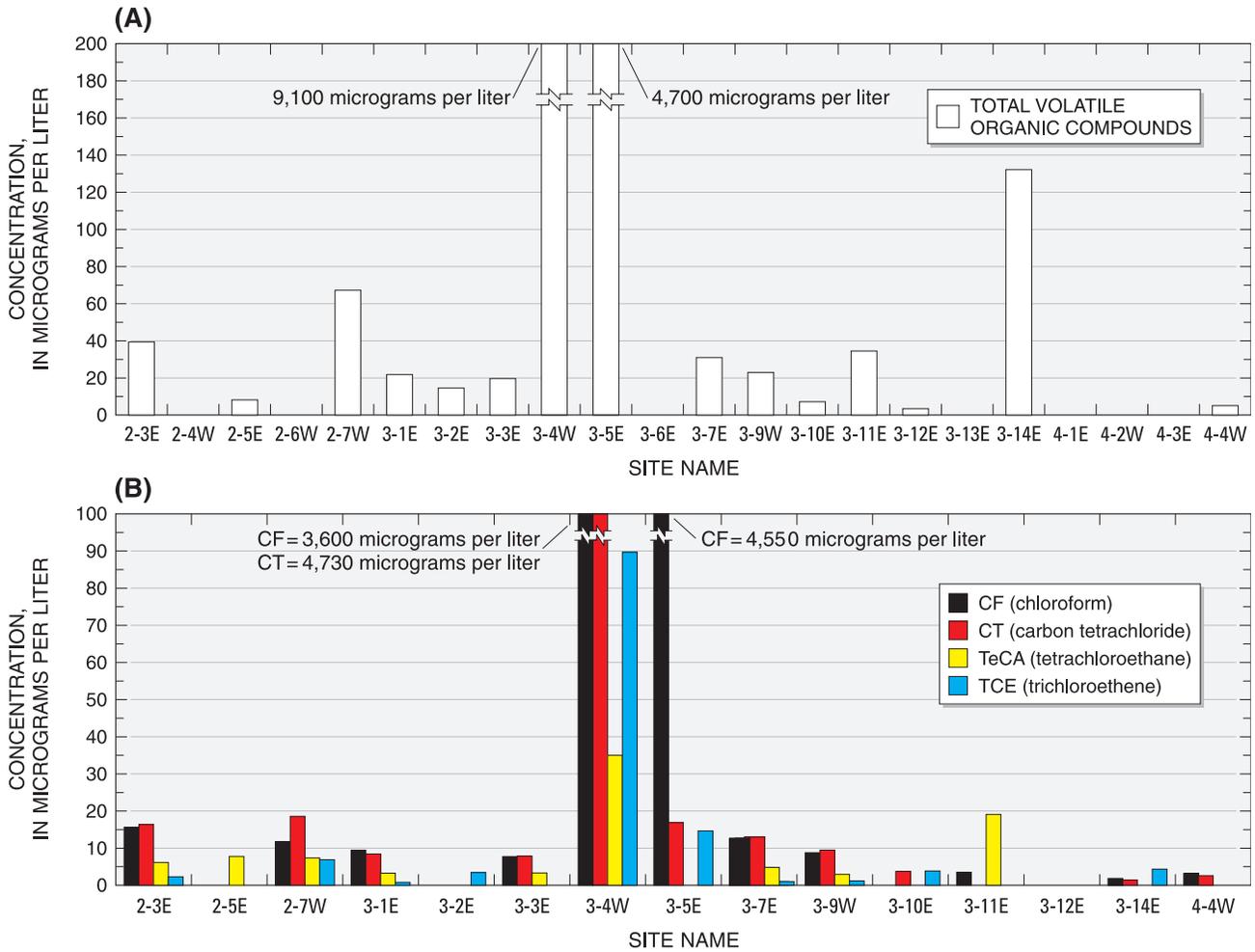


Figure 32. Maximum concentrations of volatile organic compounds measured in surface water during May 2002 and April 2003 next to seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) total volatile organic compounds and (B) select volatile organic compounds. (Locations shown in fig. 10.)

the aquifer south of the A-A" section and TeCA (and TCE, data not shown) near and north of the A-A" section shows that these were likely separate sources in the past, but have overlapped due to dispersion over time. The large area of the VOC plume in the Canal Creek aquifer is not reflected in the overlying pore water, as shown in figure 35a and b. Discrete, consistent areas of preferential discharge exist in the wetlands surrounding West Branch Canal Creek and allow for the transport of rather undiluted ground water to surface water. These areas do not appear to be interconnected, but rather are spatially correlated to nearby sources. In these discrete areas of preferential discharge, natural attenuation, specifically anaerobic biodegradation, is affected to varying degrees based on the rate of discharge. Generally, more diffuse locations appear to be mixed iron-reducing and methanogenic, allowing for some degradation of parent compounds in the aquifer and resulting in the presence of both parent and daughter compounds. More focused discharge locations appear to be in iron-reducing conditions, with mainly parent VOCs detected. Both areas have a decreased abundance and diversity of

bacteria compared to the A-A" section of the wetland study area. Although natural attenuation does not appear to be efficient in these areas, these seep areas account for only about 1 percent of the total discharge area. Therefore, it appears that in most of the wetland system, the first conceptual model presented for the wetland system by Lorah and others (1997) is valid—natural attenuation mechanisms efficiently attenuate upgradient dissolved plumes and plumes within the wetland boundaries as ground water travels along mostly upward discharge pathways characteristic of the regional flow system. The seep areas, however, are an exception to this past model.

An estimate of the contribution of seep discharge to overall discharge from the wetland was made by extrapolating the linear velocity at the focused and diffuse discharge locations to other seep locations throughout the study area. Additional assumptions made for this calculation are listed here.

1. Seeps with focused discharge have an average discharge rate similar to that measured at 3-4W (42 ft/yr) (feet per

Table 9. Summary concentrations of volatile organic compounds in surface-water samples collected near seeps in spring 2002 and spring 2003, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

[VC, vinyl chloride; *t*12DCE, *trans*-1,2-dichloroethene; *c*12DCE, *cis*-1,2-dichloroethene; 12DCA, 1,2-dichloroethane; 112TCA, 1,1,2-trichloroethane; 1112TeCA, 1,1,1,2-tetrachloroethane; 1122TeCA, 1,1,2,2-tetrachloroethane; TCE, trichloroethene; PCE, tetrachloroethene; MeCl, methylene chloride; CF, chloroform; CT, carbon tetrachloride; PCA, pentachloroethane; HCA, hexachloroethane; µg/L, micrograms per liter; > greater than; n, number]

	VC	<i>t</i> 12DCE	<i>c</i> 12DCE	12DCA	112TCA	1112TeCA	1122TeCA		
Maximum (µg/L)	82.6	24.4	47	17.2	4.9	13.9	35		
Number of detections	2	3	5	4	2	2	17		
Median (µg/L, n>2)		4.15	6.6	4			4.6		
	TCE	PCE	MeCl	CF	CT	PCA	HCA	Toluene	
Maximum (µg/L)	89.6	586.6	788.4	4550	4730	24.5	118	0.7	
Number of detections	14	8	2	17	20	1	1	1	
Median (µg/L, n>2)	2.9	3.1		10.35	7.9				

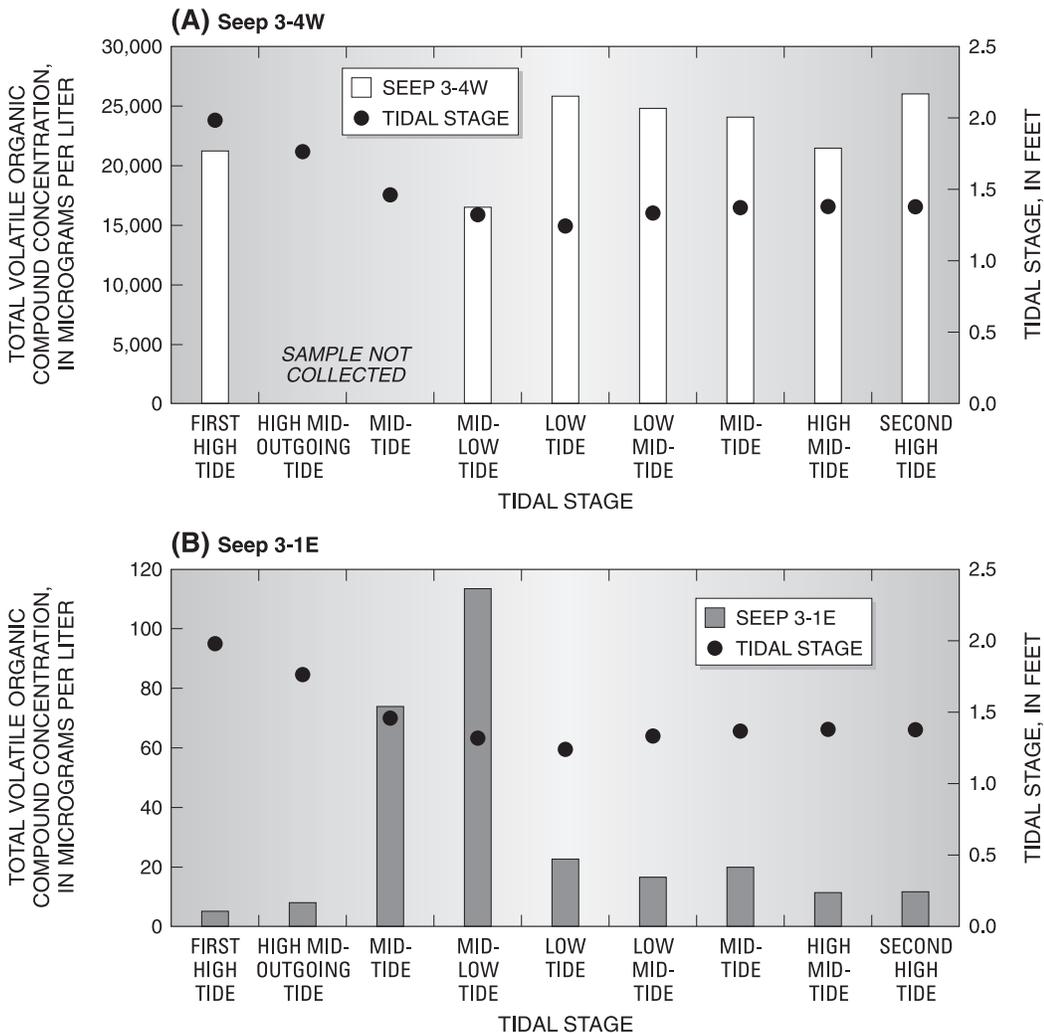
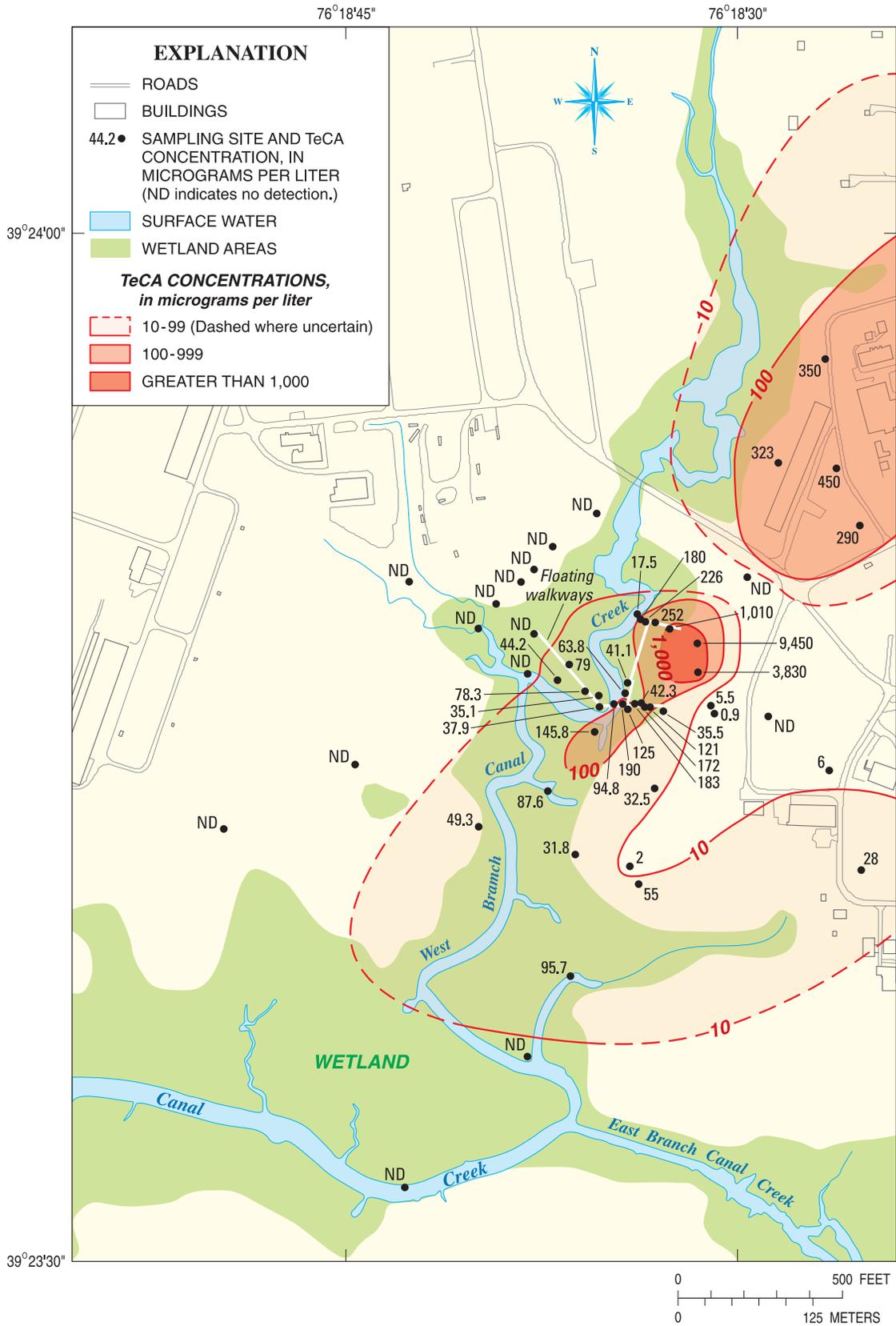


Figure 33. Total volatile organic compound concentrations in surface water collected during a tidal cycle in August 2003 at two seep locations, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, (A) 3-4W and (B) 3-1E. (Seep locations shown in fig. 10.)



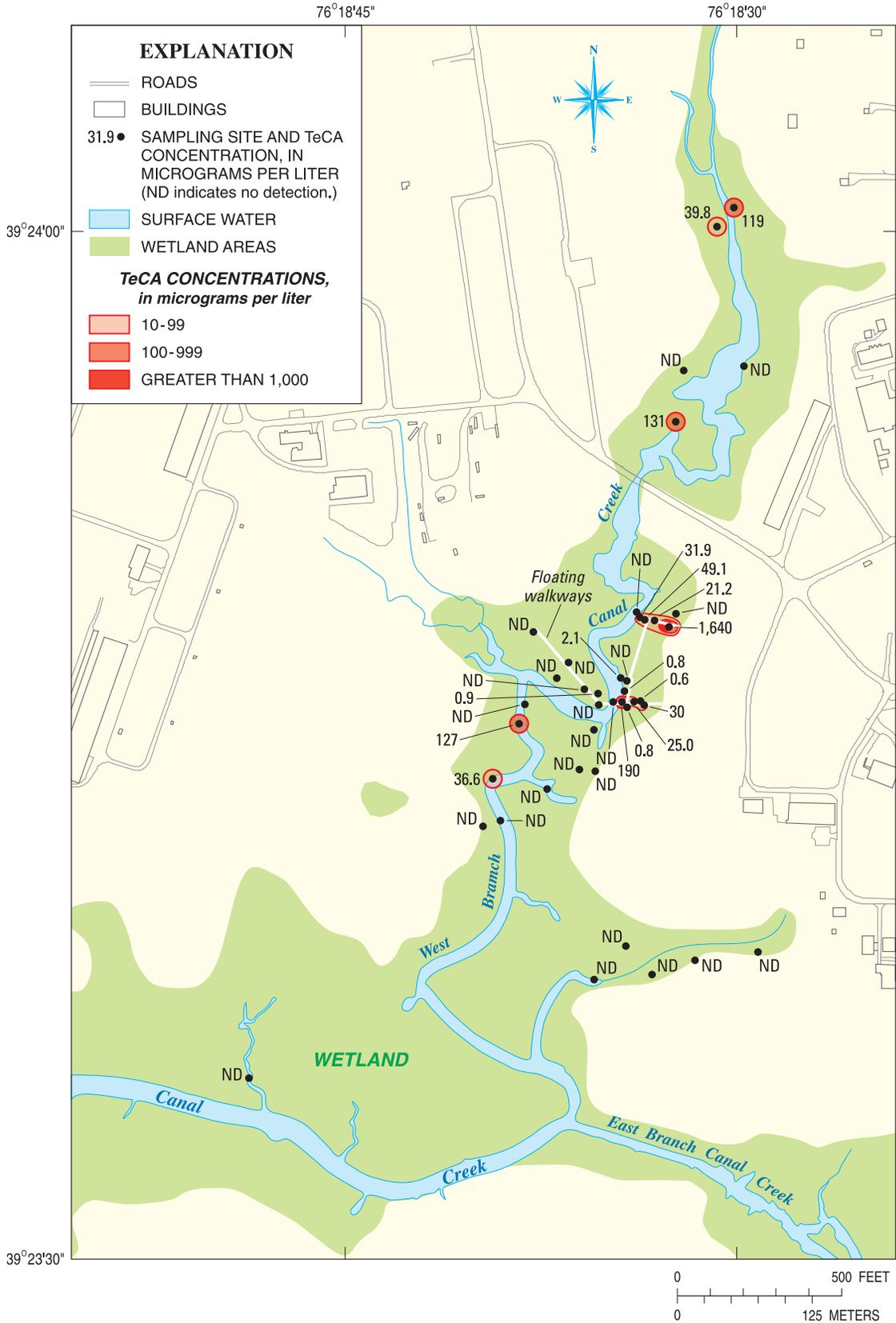


Figure 35A. Distribution of 1,1,2,2-tetrachloroethane [TeCA] in ground-water samples from the upper peat unit, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 1999–2002.

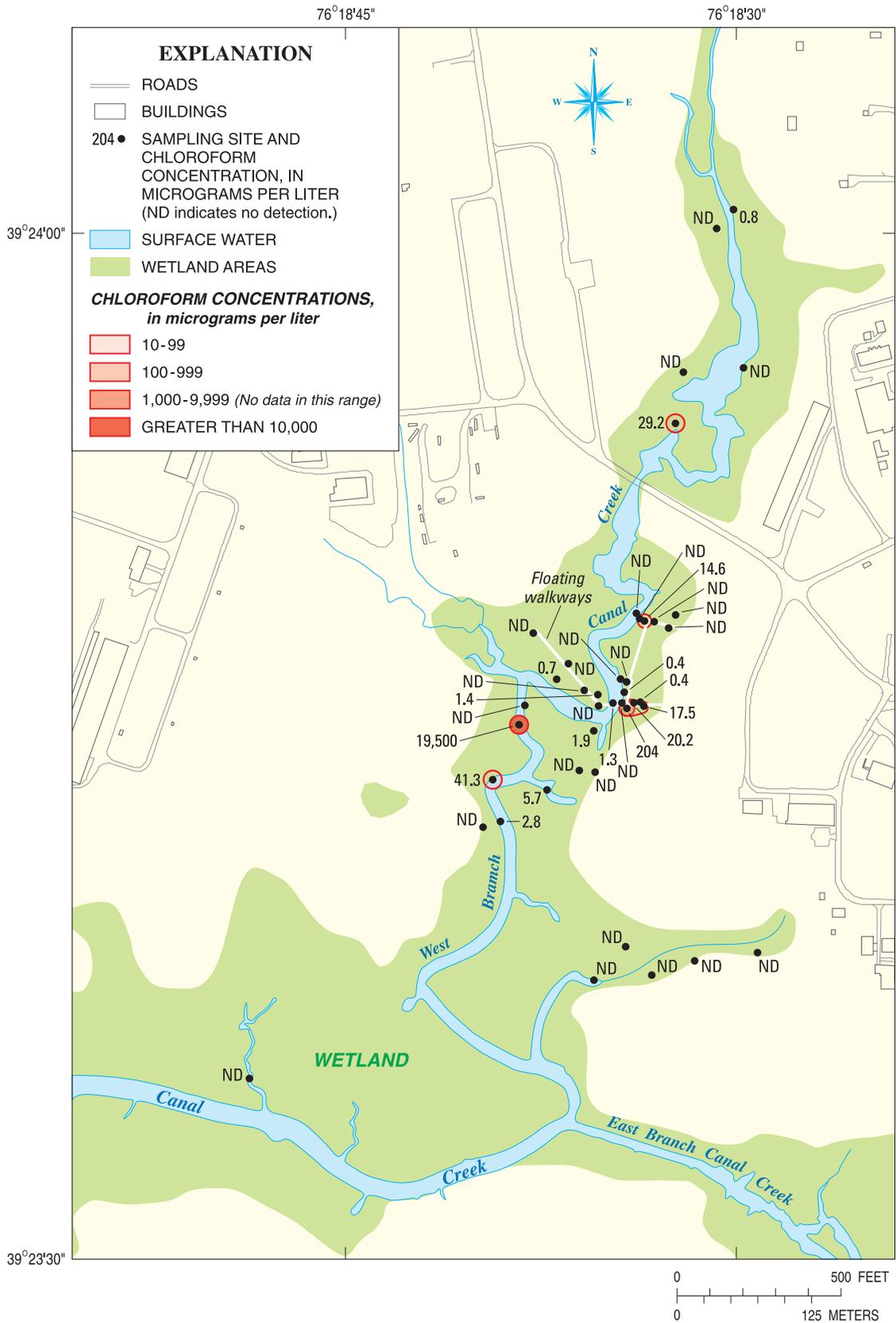


Figure 35B. Distribution of chloroform in ground-water samples from the upper peat unit, West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 1999-2002.

year); diffuse seep locations have an average discharge rate similar to that measured at 3-1E (29 ft/yr).

2. Given the presence of several diffuse seep locations along the eastern wetland boundary, the area along this boundary from the wetland study area to the pushout area near the East Branch was assumed to be a diffuse seep area with a rate of 29 ft/yr.
3. Non-seep (bulk) wetland discharge was calculated from the total areal extent of the wetlands and creek bottom sediments minus the extent of the seep areas and the linear velocity estimated within the wetland study area.

Using these assumptions, the seep discharge area is only 1 percent of the potential non-seep discharge area of the wetland. The discharge through this 1 percent of the area contributes approximately 21 percent of the estimated ground-water discharge through the system. However, other factors in the water balance such as evapotranspiration and recharge were not evaluated; therefore, this estimate is considered conservative as these other factors may play a larger role, thus reducing discharge in the non-seep sediments. The lack of unsaturated conditions at low tide throughout the wetland indicates that, at a minimum, ground-water discharge exceeds the balance between evapotranspiration and precipitation. Although this can only be considered a crude estimate compared to a rigorous water balance, it demonstrates that the discrete seep locations play a large role in the hydrologic system of the wetland at West Branch Canal Creek.

Despite the relatively small areal extent of the seep discharge, volumetric estimates of input to surface water may be important, particularly for contaminated ground-water discharge. An estimate of mass flux (defined as the contaminant mass per unit time) was calculated for major VOCs detected in pore water at seep locations 3-1E, 3-4W, and 3-7E, by use of equation 6,

$$F = \Sigma[V \times A \times X_c] \quad (6)$$

where

- F is mass flux (kg/yr),
 V is mean seepage velocity (ft/day),
 A is area within the contour shown in figures 25, 27, and 29 (ft²),

and

- X_c is the VOC contour concentration for a given compound (kg/ft³).

Using only the primary contributing VOCs at these three locations, flux was calculated to range from 0.032 kg/yr (kilograms per year) to 6.90 kg/yr at seeps 3-7E and 3-4W, respectively. The estimated flux at location 3-1E was estimated to be 0.250 kg/yr. These three locations combined contribute a minimum of nearly 7.26 kg/yr of chlorinated VOCs to the Gunpowder River. These results indicate a positive correlation between parent contaminant concentration

and magnitude of discharge, resulting in the greatest overall flux at seep location 3-4W. This correlation is consistent with some previous studies at another site of transport across the ground-water/surface-water interface (Ford, 2005). It is not consistent, however, with observations by Conant and others (2004) at other sites, who reported that the highest VOC concentrations were detected in low-discharge zones attributed to desorption.

Whereas surface-water monitoring does not indicate any exceedances of USEPA freshwater criteria for VOCs, pore water concentrations exceeded surface water concentrations by 5 orders of magnitude and may exceed these criteria in some cases. Although VOCs are generally not considered in the evaluation of ecological risks, the effects of upwelling zones on benthic organisms are being considered by the regulatory community (Ford, 2005). Existing, engineered remediation technologies are incompatible with the Canal Creek wetland environment, particularly for at least one source area within the boundaries of the wetland. Focused, passive remediation at the ground-water/surface-water interface could provide an alternative to more invasive approaches by enhancement of the biological processes identified elsewhere in the wetland.

Summary and Conclusions

From 2002 through 2004, the U. S. Geological Survey, in cooperation with the Environmental Conservation and Restoration Division of the U.S. Army Garrison, Aberdeen Proving Ground, characterized preferential ground-water seepage as part of an ongoing investigation of contaminant distribution and natural attenuation processes in wetlands at West Branch Canal Creek, Aberdeen Proving Ground, Maryland. Increased understanding of preferential seepage in the creek wetland sediments was needed to determine the overall efficiency of biodegradation at the site and the source of surface-water contamination.

Wetlands act as natural transition zones between ground water and surface water, characterized by the complex interdependency of hydrology, chemical and physical properties, and biotic effects. Chlorinated volatile organic compounds (mainly carbon tetrachloride and chloroform) are present in the creek, despite field and laboratory demonstration of efficient natural attenuation processes in the non-seep wetland and stream-bottom sediments. Surface-water volatile organic compound concentrations indicate that in some areas of the wetland, preferential flow paths or seeps allow transport of the compounds from the contaminated sand aquifer to the overlying surface water. The presence of these compounds in surface water in proportions similar to those found in ground water indicates that in some areas of the wetland, preferential flow paths allowed transport of non-attenuated compounds from the Canal Creek aquifer to West Branch Canal Creek. The location, extent, and prevalence of preferential seepage were determined through thermal infrared

imaging and follow-up temperature verification by use of instantaneous temperature probes and continuous temperature loggers. The distribution of volatile organic compounds and methane was determined by use of passive diffusion samplers and these results were used to determine boundaries of seep areas and generally categorize the rate of preferential discharge. Hydrologic properties were evaluated at selected seep locations using seepage meters, cone penetrometer *in situ* dissipation tests, and laboratory physical property analysis including particle size, total organic carbon, specific gravity, and wet density. The hydrologic effects on anaerobic biodegradation were examined by comparing vertical distributions of redox-sensitive constituents and volatile organic compounds and analyzing the microbial community in surficial sediments for specific dechlorinating bacteria.

Seep areas were discrete and spatially consistent during thermal infrared surveys and visual observations made in 2002, 2003, and 2004. This time span included years with both high and low precipitation. Seeps occurred in one of four landscape locations—along the creek edge, along the wetland boundary, within the central wetland, or in a dendritic-like pattern between the central wetland to the creek edge. Seeps were most prevalent along the creek edge. Seeps characterized by the dendritic-like pattern were identified only north of the tide gage in an area where the upper confining unit crops out. Seep locations south of the tide gage were spatially compact, possibly as a result of the absence of the upper confining unit in this area. Instantaneous and continuous temperature measurements were made during the winter months in seep sediments identified during thermal infrared surveys. These measurements confirmed that higher near-surface temperatures in the seeps are more indicative of deeper ground-water temperatures than temperatures from shallow ground water in non-seep sediments, verifying the results of the thermal infrared measurements. The opposite relation between seep and non-seep sediments was observed during the summer months, indicating that preferential discharge appears to be consistent throughout the year at these locations. The relative difference in temperature with depth and over the period of record was used to infer relative rates of ground-water discharge as either focused or diffuse. In addition to temperature, concentrations of volatile organic compounds and methane in shallow pore water were used to delineate seep boundaries and categorize areas as having either focused or diffuse discharge in seep locations. Generally, seep locations dominated by chlorinated volatile organic compounds had lower methane and higher volatile organic compound concentrations compared to non-seep wetland sediment. Volatile organic compounds detected in shallow pore water seeps were spatially similar to the dominant compounds in the underlying Canal Creek aquifer, with parent and anaerobic daughter compounds detected. Seeps with focused discharge contained the highest parent volatile organic compound concentrations, had non-detectable methane concentrations, and were located along the creek edge (2-3E, 3-4W, and 3-7E) or formed a dendritic-like pattern

between the wetland and creek channel (2-4W and 2-7W). In contrast, seeps with diffuse discharge contained relatively high concentrations of chlorinated daughter compounds (or a mixture of daughter and parent compounds), had detectable concentrations of methane, and were located along the wetland boundary (3-1E and 3-11E). The qualitative thermal infrared surveys, coupled with quantitative verification of temperature differences and screening for volatile organic compounds and methane concentrations, proved to be effective tools for delineating contaminated seeps.

Hydrologic and physical properties of wetland sediments were characterized at two seeps with focused discharge (3-4W and 3-7E) and one seep with diffuse discharge (3-1E). In the focused seeps, measured seepage was consistent over the tidal cycle, whereas more variability with tidal fluctuation was measured in the diffuse seep. At all locations, areas within the general seep boundaries where discharge was minimal were identified. In all cases, the geometric mean of non-zero vertical flux measurements was greater than the means previously reported in the non-seep wetland sediments using flow-net analysis. Vertical flux was greater in the focused discharge areas compared to the diffuse discharge area, and all fluxes were within the range reported in the literature for wetland discharge. Vertical hydraulic conductivity estimated from seepage flux and a mean vertical gradient at seep locations 3-4W and 3-7E resulted in a minimum hydraulic conductivity two orders of magnitude greater than that estimated in the non-seep sediments, whereas hydraulic conductivity estimates at 3-1E were similar to nearby estimates along the C-C' section. Estimates of horizontal hydraulic conductivity at seep 3-4W made by use of *in situ* dissipation and cone penetrometer tests were within the range previously reported for non-seep wetland sediments at West Branch Canal Creek, and are lower than the estimates of vertical hydraulic conductivity. This anisotropic relationship (K_h/K_v less than 1) has been previously reported in peats and differs from the non-seep wetland sediments along the two sections. Horizontal hydraulic conductivity appeared to be negatively correlated to increasing depth below land surface at both 3-4W and 3-7E on the basis of cone penetrometer tests and particle-size analysis. Extrapolating these hydrologic properties to focused and diffuse seep locations within West Branch Canal Creek, seep areas were estimated to be only about 1 percent of the total discharge area of the wetland. This 1 percent of wetland area is estimated to contribute more than 20 percent of the total ground water to the creek, however, indicating that the seeps play a significant role in the transport of ground water to surface water.

Lithologic descriptions of wetland sediments in seep areas 3-4W and 3-7E are consistent with descriptions elsewhere in the wetland. There was no visible evidence in the sediments of preferential pathways for ground-water discharge, unlike those reported in areas other than Canal Creek. Physical properties of seep sediments collected from cores at locations 3-4W and 3-7E and non-seep wetland sediment location WB35 were characteristic of both organic

and mineral sediments, and characteristic of organic clays with a relatively high fraction of fines. The shallow depth of the core (and thus the low number of samples) from WB35 made comparisons of physical properties between seep and non-seep sediments difficult; however, most physical properties were similar between the various sites at various depths. In seep sediment cores, the variation in physical properties with depth was consistent with hydrologic properties; however, the increased seepage flux in seep locations could not be explained on the basis of the physical properties analyses conducted for this study.

In the preferential seepage areas, natural attenuation dominated mainly by anaerobic biodegradation is affected by the increase in vertical seepage flux and resulting decrease in residence time within the wetland sediments. This results in less-reducing conditions, an accumulation of chlorinated volatile organic compounds in shallow pore water, and in some cases, a change in the microbial community. Vertical distribution of redox-sensitive constituents in diffuse seep 3-1E indicated mixed methanogenic and iron-reducing conditions; in contrast, the focused seeps 3-4W and 3-7E were dominated by iron-reducing conditions, indicating a correlation with discharge rates. The less-reducing conditions in these sediments appear to be a result of decreased residence time of the aerobic ground water in the Canal Creek aquifer through the wetland sediments. This less-reduced primary terminal electron-accepting process corresponded to greater accumulation of chlorinated daughter compounds (vinyl chloride) at seep 3-1E and parent compounds at seeps 3-4W and 3-7E (chloroform, carbon tetrachloride, and tetrachloroethene). These compounds did not decline with decreased depth below land surface and, in some cases, parent concentrations actually increased in the upper sediments. The concentrations of chlorinated parent and daughter compounds were several orders of magnitude higher than concentrations previously reported at these depths. Total shallow pore water volatile organic compound concentrations ranged from 4 micromolar at seep 3-1E to greater than 200 micromolar at seep 3-4W. This vertical distribution indicates that little to no biodegradation was occurring in the upper 2 to 4 feet of wetland sediment in these locations and corresponds to the less-reducing primary terminal electron-accepting process. The lateral extent of chlorinated volatile organic compounds at these sites was greatest at the more diffuse discharge location (3-1E) compared to the more focused discharge locations (3-4W and 3-7E) where lateral concentration gradients were very steep. In the focused discharge seeps, concentrations varied by several orders of magnitude over less than 20 feet. In these areas, diffusion into the non-seep sediments was apparent by the detection of chlorinated anaerobic daughter compounds along the "fringe" of the seep footprint. This pattern was not apparent in the seeps with diffuse discharge where parent and daughter compounds were both present in the seep area.

Microbial fingerprinting indicated that the overall abundance and diversity of bacteria in sediments from seeps

varied from less than (when compared to the A-A' section) or equivalent to (when compared to the C-C' section) the abundance and diversity in the non-seep sediments. This was evidenced by the relative peak intensity and total number of peaks in terminal restriction fragment length polymorphism profiles of polymerase chain reaction products. Seep sediment profiles appear to be enriched in peaks associated with dichloroelimination, however, and the contribution of these peaks to the overall bacterial profile is similar to that measured in non-seep sediments where natural attenuation has been shown to be efficient. Using real-time polymerase chain reaction, two known dehalorespiring bacteria, *Dehalococcoides* (*ethenogenes* and strain FL2) and *Desulfuromonas* (strain BB1 and *chloroethenica*), were detected in surficial sediments collected from seep areas in some samples reaching levels observed in non-seep sediments in the natural attenuation study area. DNA from these organisms was not correlated with contaminant type or discharge rates; therefore, their role or activity in the seep sediments is largely unknown.

Parent volatile organic compounds most commonly detected in pore water (carbon tetrachloride, chloroform, 1,1,2,2-tetrachloroethane, and trichloroethene) also were detected most frequently and in the greatest magnitude in surface-water samples collected during April-May 2002 and 2003. Daughter compounds also were detected in surface water, but less frequently. The maximum concentrations of 12 of 14 chlorinated compounds were detected in samples collected from two seeps (3-4W and 3-5E), with total volatile organic compound concentrations of 9,100 and 4,700 micrograms per liter, respectively. Surface-water concentrations of volatile organic compounds at 3-4W were approximately 25 percent of pore water concentrations at this location. In addition, mid-tide sampling of the cross section of West Branch Canal Creek surface water resulted in a median total volatile organic compound concentration of 8 micrograms per liter. Surface-water volatile organic compound concentrations do not appear to be accurate predictors of seep location or pore water concentrations and underscore the need for pore water sampling. A more accurate reflection of the impact on surface water may be determined by the calculation of flux to surface water, based on pore water concentrations and areal contours. By use of this method, the predicted load of primary volatile organic compounds to West Branch Canal Creek from three contaminated seep locations would be nearly 16 pounds per year.

In spite of the large, areal footprint of overlapping volatile organic compound plumes in the Canal Creek aquifer beneath the West Branch Canal Creek wetlands and stream bottom, natural attenuation appears to efficiently reduce volatile organic compound concentrations in the organic-rich wetland sediments through the majority of the site. Only about 1 percent of the total discharge area was identified as a seep zone; these areas were discrete and bounded by decreased concentrations of volatile organic compounds in the pore water. Surface-water sampling alone was not indicative of seep

locations or of the magnitude of the pore water concentration at the ground-water/surface-water interface, indicating that thermal and passive pore water sampling methods, such as those used in this study, are more appropriate for identifying areas of preferential discharge to surface water.

The identification of discrete areas of preferential discharge of ground water to surface water can provide an alternative approach to remediation of source zones contained within or near a sensitive wetland ecosystem. Targeted, passive treatment at the ground-water/surface-water interface could also provide treatment immediately prior to discharge to surface water. Some limited, active remediation in seep areas coupled with natural attenuation could help preserve the wetland ecosystem and reduce volatile organic compound loading to West Branch Canal Creek or other wetland, riverine, and estuarine environments.

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