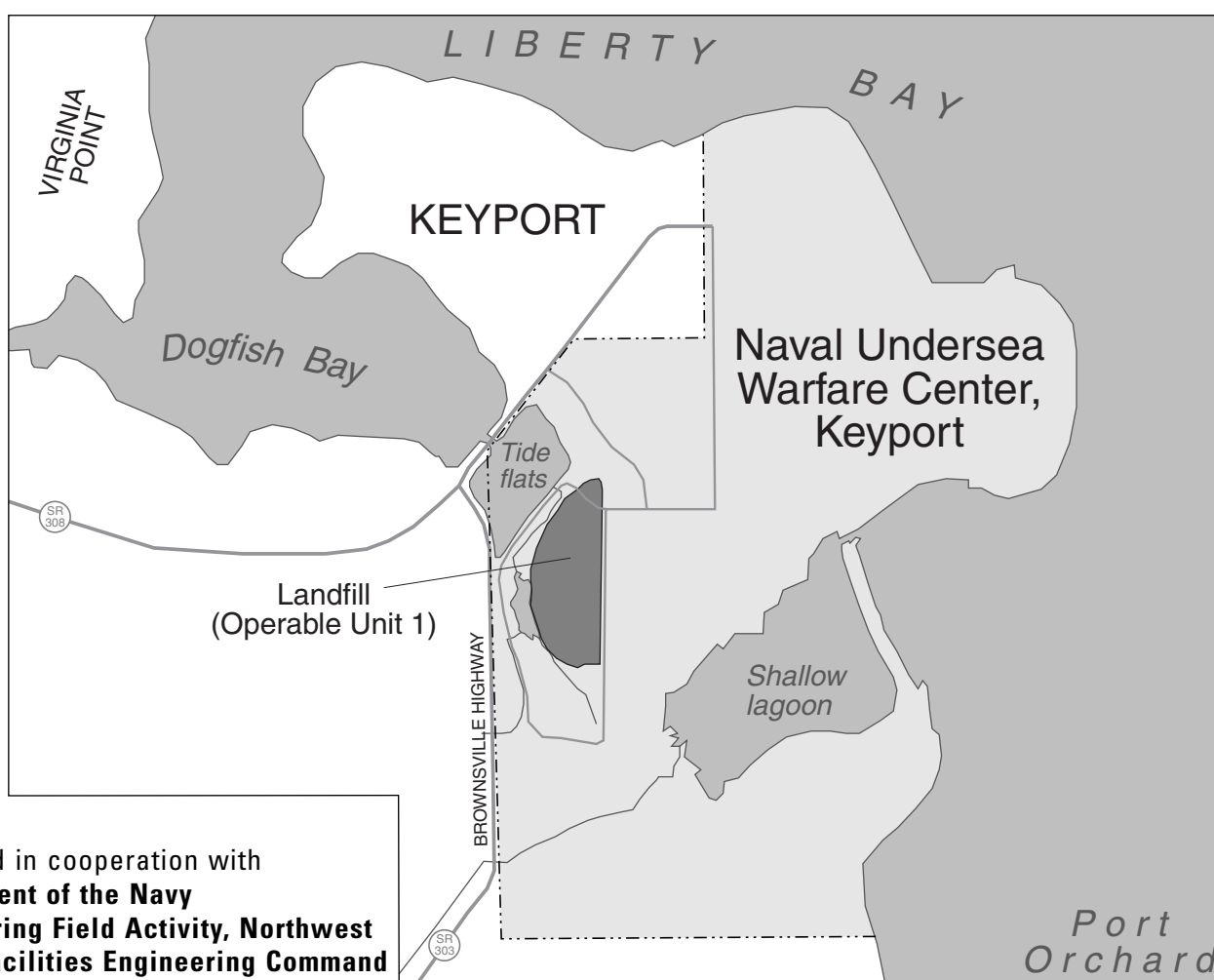**U.S. Department of the Interior**
U.S. Geological Survey

Natural Attenuation of Chlorinated Volatile Organic Compounds in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

Water-Resources Investigations Report 02-4119

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By R.S. Dinicola, S.E. Cox, J.E. Landmeyer, and P.M. Bradley

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U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
Length		
inch (in)	2.54	centimeter
inch (in)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
Area		
acre	4,047	square meter
acre	0.004047	square kilometer
Flow rate		
foot per day (ft/d)	0.3048	meter per day
foot per year (ft/yr)	0.3048	meter per year
Mass		
gram (g)	0.03527	ounce, avoirdupois

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=1.8 °C+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

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

Altitude, as used in this report, refers to distance above or below sea level.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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EXECUTIVE SUMMARY

The U.S. Geological Survey (USGS) evaluated the natural attenuation of chlorinated volatile organic compounds (CVOCs) in ground water beneath the former landfill at Operable Unit 1 (OU 1), Naval Undersea Warfare Center, Division Keyport, Washington. The predominant contaminants in ground water are trichloroethene (TCE) and its degradation byproducts *cis*-1,2-dichloroethene (*cis*DCE) and vinyl chloride (VC). The Navy planted two hybrid poplar plantations on the landfill in spring of 1999 to remove and control the migration of CVOCs in shallow ground water. Previous studies provided evidence that microbial degradation processes also reduce CVOC concentrations in ground water at OU 1, so monitored natural attenuation is a potential alternative remedy if phytoremediation is ineffective. This report describes the current (2000) understanding of natural attenuation of CVOCs in ground water at OU 1 and the impacts that phytoremediation activities to date have had on attenuation processes. The evaluation is based on ground-water and surface-water chemistry data and hydrogeologic data collected at the site by the USGS and Navy contractors between 1991 and 2000. Previously unpublished data collected by the USGS during 1996–2000 are presented.

Natural attenuation of CVOCs in shallow ground water at OU 1 is substantial. For 1999–2000 conditions, approximately 70 percent of the mass of dissolved chlorinated ethenes that was available to migrate from the landfill was completely degraded in shallow ground water before it could migrate to the intermediate aquifer or discharge to surface water. Attenuation of CVOC concentrations appears also to be substantial in the intermediate aquifer, but biodegradation appears to be less significant; those conclusions are less certain because of the paucity of data downgradient of the landfill beneath the tide flats. Attenuation of CVOC concentrations is also substantial in surface water as it flows through the adjacent marsh and out to the tide flats. Attenuation processes other than dilution reduce the CVOC flux in marsh surface water by about 40 percent by the time the water discharges to the tide flats. Despite the importance of natural attenuation processes at reducing both the contaminant concentrations and the contaminant mass at OU 1, natural attenuation alone was not effective enough in the year 2000 to meet current numerical remediation goals for the site. That was in part due to the relatively short distance between the landfill and the adjacent marsh, and in part due to the extremely high CVOC concentrations directly beneath the landfill.

Additional hydrogeologic and geochemical characterization was completed as part of this investigation to improve our understanding of the fate and transport of CVOCs at OU 1. Oxygen- and hydrogen-isotope and common-ion data were interpreted to identify two distinct flowpaths for contaminant migration into the intermediate aquifer, one through the middle aquitard and downgradient to the slightly contaminated intermediate-aquifer well beneath the Highway 308 causeway, and the other through a permeable window in the middle aquitard to currently uncontaminated deeper intermediate-aquifer wells beneath Highway 308.

A more detailed distribution of total CVOCs in shallow ground water was determined by integrating data from existing monitoring wells with new data from piezometers in the landfill and diffusion samplers in the adjacent marsh. The refined distribution shows that the highest CVOC concentrations beneath the landfill are about four times greater than previously thought, and that the pattern of CVOC concentrations in shallow marsh ground water correlates well with the pattern observed beneath the landfill. The latter observation was evidence that the diffusion samplers used to collect marsh CVOC samples worked as intended and reasonably represent shallow ground-water conditions.

Ground-water redox conditions beneath the former landfill were found to be generally favorable for complete degradation of CVOCs through either reductive dechlorination alone or through the combined processes of reductive dechlorination and mineralization. Redox conditions were determined by quantifying oxidized and reduced inorganic compounds as well as steady-state dissolved hydrogen (H_2) concentrations throughout the contaminant plume. Two areas of strongly reducing (sulfate reduction or methanogenesis) ground water favorable for reductive dechlorination were identified beneath the landfill—one beneath the northern part of the landfill and one beneath the southern part. Those areas were surrounded by mildly reducing (iron or manganese reducing) ground waters that are possibly more favorable for mineralization of less chlorinated CVOCs. The landfill is a substantial source of organic carbon in shallow ground water, and the correlation between high organic carbon concentration and strongly reducing conditions is clear evidence that redox conditions are being controlled by microbially mediated processes. Ground-water redox conditions within the intermediate aquifer were generally less favorable for reductive dechlorination, but were possibly favorable for mineralization of less chlorinated CVOCs. Organic carbon concentrations were elevated in contaminated intermediate aquifer

wells, but were substantially lower than those found in shallow ground water beneath the landfill.

The evaluation of natural attenuation found consistent evidence for both partial and complete degradation of CVOCs in upper-aquifer ground water at OU 1. Temporal changes in CVOC concentrations between 1991 and 2000 at shallow wells beneath the landfill, and changes in recent (1999-2000) CVOC and redox-sensitive geochemical concentrations along shallow ground-water flowpaths indicated substantial attenuation and degradation beneath the landfill. Total CVOC concentrations continued to attenuate along ground-water flowpaths between the landfill and the marsh, and the proportions of CVOCs changed from predominantly highly chlorinated compounds to less chlorinated compounds along selected flowpaths. Concentrations of redox-sensitive compounds also changed, following a pattern consistent with active reductive dechlorination along those same flowpaths. Overall, the evidence indicated the most substantial attenuation and degradation occurred beneath the southern part of the northern plantation and beneath the northern part of the southern plantation.

The evaluation found evidence for limited attenuation and degradation in the intermediate aquifer. Temporal changes in CVOC concentrations at individual wells in the most contaminated part of the intermediate aquifer indicated limited attenuation and degradation, whereas changes in CVOC and geochemical concentrations along ground-water flowpaths between the upper aquifer and the main body of the intermediate aquifer indicated substantial attenuation but uncertain biodegradation. Further downgradient of the landfill, it could only be concluded that contaminants have not migrated to beneath the Highway 308 causeway in the main body of the intermediate aquifer.

That could be a result of biodegradation, dilution, or discharge of ground water to the tide flats upgradient of Highway 308; or it could simply be that not enough time has passed for the contaminants to reach the deeper wells at the Highway 308 causeway. Along the newly identified ground-water flowpath between the upper aquifer and the sole contaminated Highway 308 well, the evidence suggested substantial attenuation, but the causes of the attenuation were uncertain because of the lack of observation points beneath the tide flats.

There have been no clear long-term changes in CVOC concentrations at individual surface-water sites in the marsh, but there has been substantial attenuation of concentrations in surface water as it flows through the marsh and out to the tide flats. Biodegradation is likely insignificant in surface water, but volatilization (as well as dilution) substantially attenuate contaminant concentrations in the downstream direction.

Flux-based contaminant-mass-degradation rate calculations indicate that the majority of dissolved chlorinated ethenes in landfill ground water are degraded in ground water before they have an opportunity to migrate to the intermediate aquifer or discharge to surface water. Of the mass of dissolved chlorinated ethenes available to migrate from the landfill, nearly all TCE is degraded, about 60 percent of the cisDCE is degraded, and about 40 percent of the VC is degraded before discharging to surface water. Additional calculations using surface-water concentration data suggest that the actual fluxes of TCE and cisDCE to the marsh may be about 100 and 30 percent greater, respectively, than the flux-based estimates, because the diffusion samplers did not fully represent contaminant discharge to the southeastern portion of the marsh. The surface-water-based calculations also suggest there was a net loss of about 30 percent of the TCE flux, 40 percent of the cisDCE flux, and 50 percent of the VC flux as surface water flows through the marsh and out to the tide flats. The losses were likely due to nondestructive attenuation processes such as volatilization.

Comparison of calculated attenuation rates of chlorinated ethene concentrations for different ground-water flowpaths confirmed the previous findings regarding where biodegradation is most effective at OU 1. Attenuation rates varied throughout the upper aquifer beneath the landfill in close accordance with the location of favorable redox conditions, and attenuation rates in the intermediate aquifer were substantially slower than those calculate for the upper aquifer.

Based on data collected through June 2000, natural attenuation alone was not effective enough to meet the numerical remediation goals for ground water or surface water at OU 1. CVOC concentration goals were not met in upper-aquifer ground water beneath the landfill in five wells sampled as part of the long-term monitoring program and in all nine piezometers sampled during this investigation. CVOC concentrations in intermediate aquifer ground water were greatly attenuated when compared to landfill concentrations; nevertheless, ground-water remediation goals for *cis*DCE and/or VC were not met in three intermediate-aquifer wells. CVOC concentrations in marsh ground water also were greatly attenuated when compared to landfill concentrations, but the VC ground-water remediation goal for the protection of surface water was not met in nine of the 16 diffusion samplers. And finally, CVOC concentrations in surface water were also greatly attenuated when compared to landfill concentrations, but surface-water remediation goals for VC were not met at three of the five surface-water sites that are part of the long-term monitoring program, and the TCE remediation goal was not met at one site.

Phytoremediation activities had some apparent effect on contaminant concentrations in ground water and surface water, but ground-water redox conditions to date (2000) were not affected by the February 1999 asphalt removal for tree planting. Water-level monitoring by the Navy during 1999 and 2000 showed that ground-water flow directions and gradients were consistent with those found previous to asphalt removal.

The poplar trees in the phytoremediation plantations were not yet mature in 2000, so the lack of discernible changes to date is understandable. Redox conditions in the upper aquifer did not change substantially after the initiation of phytoremediation activities. However, concentrations of some redox-sensitive compounds did decrease, suggesting that increased recharge following asphalt removal diluted ambient landfill ground water or led to precipitation of oxidized iron and manganese compounds. There was no evidence of geochemical changes in the intermediate aquifer as a result of asphalt removal. CVOC concentrations increased in some downgradient wells in both the northern and southern plantations after asphalt removal, whereas CVOC concentrations decreased in some upgradient wells in the southern plantation. There was no evidence for CVOC changes in the intermediate aquifer that could be attributed to asphalt removal. A clear increase in CVOC concentrations in marsh surface water followed asphalt removal, apparently from increased contaminant discharge in ground water beneath the southern plantation.

The results of the natural attenuation evaluation suggest than minor modifications to the current sampling plan may be beneficial to understanding the future impacts of phytoremediation and natural attenuation on the fate and distribution of CVOCs at OU 1. Current plans call for sampling analytes related to natural attenuation at eight wells once every year through 2004 and once every 5 years after 2004. With regard to sampling frequency, it would be informative to sample in March and September during at least a single year after the plantation canopy closes and tree roots have reached the water table. Those data would give more convincing evidence about effects of phytoremediation activities on ground-water redox conditions. Also, the decision to switch to a 5-year sampling cycle could best be made nearer the year 2004, when additional data will be available to evaluate whether ground-water conditions are relatively stable. With regard to the number of wells sampled, the eight wells identified for sampling may be inadequate. Adding at least one upgradient well in the upper aquifer and one in the intermediate aquifer would provide comparison data to determine how geochemical conditions change as water flows to beneath the landfill. In addition, the landfill piezometers are located in the most contaminated parts of the landfill, so it would be worthwhile to sample CVOCs and geochemistry at those sites at least every other year through 2004. It would be worthwhile to sample the CVOCs and geochemistry in a deeper intermediate-aquifer well at the Highway 308 causeway to monitor possible contaminant migration in the main body of that aquifer. The passive diffusion samplers provided very valuable information on overall contaminant attenuation in ground water, and it would be worthwhile to sample those same sites (with a few modifications) a few years after the plantation canopy closes. It would be informative to deploy diffusion samplers in March and September to coincide with the proposed one-time seasonal sampling, but sampling CVOCs in surface water could be used as a reasonable proxy for those seasonal data. With regard to analytes sampled, the list of geochemicals identified is adequate. DOC is thought to be a somewhat better measure of bioavailable organic carbon, so future sampling could include DOC rather than TOC. It would be useful to measure redox-sensitive compounds in diffusion samplers if that capability is available in the near future, and it would be useful to measure surface-water discharge directly in the marsh during the proposed seasonal sampling events or during the year when diffusion samplers are deployed. Those data could be used to confirm the hypothesis of seasonal or no ground-water discharge to the marsh from the northern part of the landfill.

ABSTRACT

The U.S. Geological Survey (USGS) evaluated the natural attenuation of chlorinated volatile organic compounds (CVOCs) in ground water beneath the former landfill at Operable Unit 1 (OU 1), Naval Undersea Warfare Center, Division Keyport, Washington. The predominant contaminants in ground water are trichloroethene (TCE) and its degradation byproducts *cis*-1,2-dichloroethene (*cis*DCE) and vinyl chloride (VC). The Navy planted two hybrid poplar plantations on the landfill in spring of 1999 to remove and control the migration of CVOCs in shallow ground water. Previous studies provided evidence that microbial degradation processes also reduce CVOC concentrations in ground water at OU 1, so monitored natural attenuation is a potential alternative remedy if phytoremediation is ineffective. This report describes the current (2000) understanding of natural attenuation of CVOCs in ground water at OU 1 and the impacts that phytoremediation activities to date have had on attenuation processes. The evaluation is based on ground-water and surface-water chemistry data and hydrogeologic data collected at the site by the USGS and Navy contractors between 1991 and 2000. Previously unpublished data collected by the USGS during 1996-2000 are presented.

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Phytoremediation activities had some apparent effect on contaminant concentrations in ground water and surface water, but ground-water redox conditions to date (2000) were not affected by the February 1999 asphalt removal for tree planting. The poplar trees in the phytoremediation plantations were not yet mature in 2000, so the lack of discernible changes to date is understandable. Concentration changes of some redox-sensitive compounds suggest that increased recharge following asphalt removal diluted ambient landfill ground water. CVOC concentrations increased in some downgradient wells in both the northern and southern plantations after asphalt removal, whereas CVOC concentrations decreased in some upgradient wells in the southern plantation. A clear increase in CVOC concentrations in marsh surface water followed asphalt removal, apparently from increased contaminant discharge in ground water beneath the southern plantation.

The results of the natural attenuation evaluation suggest than minor modifications to the current sampling plan may be beneficial to understanding the future impacts of phytoremediation and natural attenuation on the fate and distribution of CVOCs at OU 1.

INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) have migrated to ground water beneath the 9-acre former landfill at Operable Unit 1 (OU 1), Naval Undersea Warfare Center (NUWC), Division Keyport (referred to in this report as NUWC Keyport), Wash. ([fig. 1](#)). The predominant contaminants in ground water are trichloroethene (TCE) and its degradation byproducts *cis*-1,2-dichloroethene (*cis*DCE) and vinyl chloride (VC); the compound 1,1,1-trichloroethane (TCA) and its degradation byproducts 1,1-dichloroethane (1,1-DCA), 1,1-dichloroethene (1,1-DCE) and chloroethane (CA) are of concern at a few locations at the site. A need for remedial action was identified because those hazardous compounds present a potential risk to humans, primarily through drinking contaminated ground water or through ingesting seafood harvested from contaminated surface water (URS Consultants, Inc., 1998).
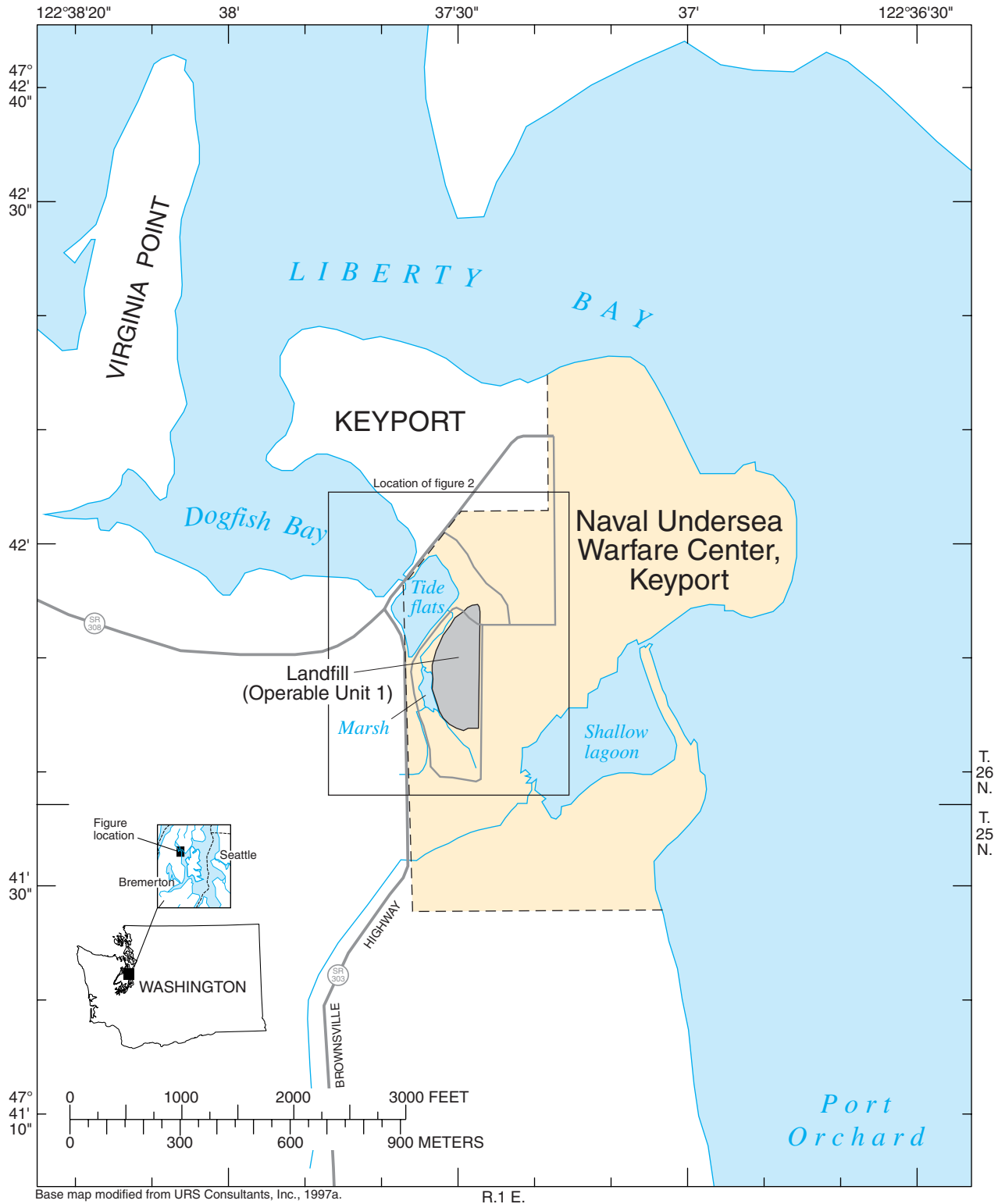
Figure 1.   Location of the Operable Unit 1 study area, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.

In spring of 1999 two hybrid poplar plantations were planted on the northern and southern parts of the OU 1 landfill ([fig. 2](#)) to remove and destroy CVOCs from shallow ground water and to reduce the potential for CVOC migration from the site (URS Greiner, Inc., 1999). If that phytoremediation strategy is later determined to be ineffective at the site, the Record of Decision (ROD) specifies that monitored natural attenuation should be evaluated as an alternative remedy (URS Consultants, Inc., 1998). The ROD also specifies that potentially adverse impacts of phytoremediation activities (which included removing asphalt cover from parts of the landfill) on in-situ microbial degradation of contaminants be evaluated.

The Navy began a cooperative effort with the U.S. Geological Survey (USGS) in 1995 to investigate various natural attenuation mechanisms at OU 1. Results from previous field and laboratory studies have provided evidence that microbial degradation processes can reduce CVOC concentrations in ground water at OU 1 (Bradley and others, 1998; URS Consultants, Inc., 1997a). Ground-water reduction-oxidation (redox) conditions are favorable for microbially mediated CVOC degradation beneath OU 1, the concentrations and distributions of parent compounds and degradation products are in general accord with expected degradation processes, and laboratory experiments demonstrated that microorganisms indigenous to the site can successfully biodegrade selected contaminants of concern under ambient ground-water conditions. Since those preliminary investigations in 1998, the USGS has collected additional natural-attenuation data both before and after the initial phytoremediation activities, and methods for collecting and interpreting those data have improved. The U.S. Navy is interested in documenting the current understanding of natural attenuation of CVOCs in ground water at OU 1 and identifying if phytoremediation activities to date (2000) have had any adverse impacts on attenuation processes.

Purpose and Scope

The purpose of this report is to present the results of evaluating natural attenuation in the study area including: (1) a description of the current (2000) understanding of natural attenuation of CVOCs in ground water at OU 1, NUWC Keyport, and (2) an evaluation of whether phytoremediation activities have had any adverse impacts on attenuation processes. The data used for the evaluation of natural attenuation included hydrogeologic, contaminant chemistry, geochemistry, and environmental tracer data collected by the USGS from 1996 to 2000 and by the Navy from 1991 to 2000.

Description of the Study Area

NUWC Keyport is located mostly on a small peninsula in Kitsap County, Wash., in an extension of Puget Sound called Liberty Bay ([fig. 1](#)). The NUWC occupies the eastern half of the peninsula and the town of Keyport occupies the western half. The highest point on the Keyport peninsula (about 43 feet above sea level) is located near the center, and the peninsula is connected to the mainland by a narrow strip of land just above sea level that was mostly tidal wetland before much of it was filled in by the Navy by the 1940s. The mainland to the southwest of Keyport peninsula rises steeply to rolling uplands 200–400 feet above sea level.

The 9-acre former landfill at OU 1, located on the narrow strip of connecting land, is between 9 and 14 feet above sea level and is essentially flat. It is adjacent to some tide flats that are an extension of Dogfish Bay and Liberty Bay. Most of the landfill was formerly a marshland extending inland from the tide flats, and a portion of the original marsh remains to the west and south of the landfill. The landfill is unlined at the bottom, and the southern two-thirds of its surface was covered with asphalt when this investigation began (1996). Some of the asphalt cover was removed during February 1999 in order to plant hybrid poplar trees for phytoremediation.

Keyport has a temperate marine climate characterized by warm, dry summers and cool, wet winters (Washington State University, 1968). Mean annual temperature is about 51 degrees Fahrenheit; January is the coolest month and July is the warmest. Mean annual precipitation is about 31 inches, 77 percent of which falls from October through March. Snowfall is infrequent and rainfall is generally not intense.

More-detailed discussions of the study area and its setting can be found in the Remedial Investigation (RI) report (URS Consultants, 1993) and the Summary Data Assessment Report (URS Consultants, 1997a).
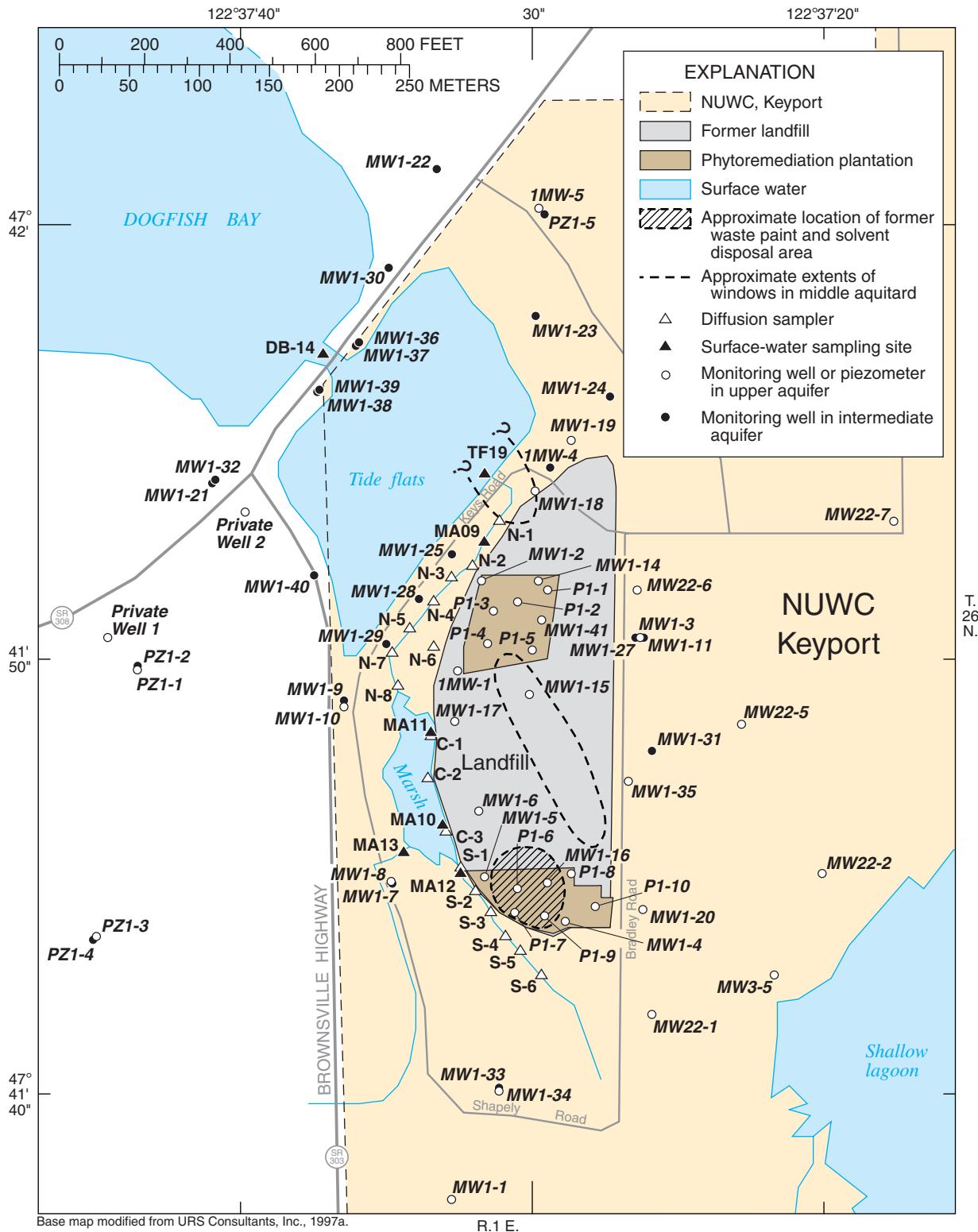
Figure 2. Location of the former landfill and other features and of the data-collection sites at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.

Hydrogeologic Setting

NUWC Keyport lies within the Puget Sound Lowland, a topographic and structural depression between the Cascade Range on the east and the Olympic Mountains on the west. The Keyport peninsula and surrounding areas are composed primarily of unconsolidated Pleistocene glacial and interglacial deposits overlying Tertiary and older bedrock (Blunt and others, 1987). A veneer of more recent alluvium, including stream, beach, landslide, and marsh deposits, covers the youngest glacial deposits in some areas. The unconsolidated deposits are more than 1,500 feet thick beneath the Keyport peninsula (Jones, 1999).

Ground water beneath OU 1 occurs within a series of aquifers that are composed of permeable sand, gravel, or fill materials separated by finer-grained silt or clay layers. Contamination at OU 1 is known to occur only in about the top 60 feet of the unconsolidated deposits, so those units are described in this report; recent information on deeper sediments can be found in Kahle (1998) and Jones (1999). Twenty-one stratigraphic units and six primary hydrogeologic units were identified beneath the study area (URS Consultants, Inc., 1997a). The hydrogeologic units, from top to bottom, are referred to as the unsaturated zone, upper aquifer, middle aquitard, intermediate aquifer, Clover Park aquitard, and Clover Park coarse-grained zone (figs. 3 and 4). Those six units are described below. Additional cross sections, original borehole logs, and a discussion of the relation between stratigraphic and hydrogeologic units can be found in a report by URS Consultants, Inc. (1997a).

The unsaturated zone at OU 1 consists primarily of fill materials including a mix of silt, sand, gravel, clay, and trash debris. The unit also includes organic-rich silt or silty-sand marsh deposits and silt or silty-sand estuary and tide flats deposits. The unit ranges from 0 to about 20 feet thick. The permeability of this zone is highly variable due its heterogeneity.

The upper aquifer at OU 1 consists primarily of sand or silty-sand and gravel with localized zones of marsh, estuary, and tide flats deposits. The saturated portion of the OU 1 landfill materials is also included in this unit. The unit is nearly continuous across OU 1 and ranges from about 4 to 22 feet thick. The permeability of the upper aquifer is relatively high where coarse-grained, although scattered deposits of finer-grained materials suggest that preferential flow

pathways are likely over short distances. The unit is less permeable near the northern tip of the landfill, and the unit is essentially absent west of the landfill in the vicinity of well MW1-8, where it is truncated by fine-grained glaciolacustrine clay and silt deposits. Estimated hydraulic conductivity for the upper aquifer ranges from 0.2 to 4.1 feet per day (ft/d) (URS Consultants, Inc., 1997a).

The middle aquitard at OU 1 separates the upper and intermediate aquifers and consists primarily of silt, clay, and fine sand with localized peat. The unit is nearly continuous across OU 1 and ranges from about 1 to 40 feet thick. The middle aquitard is notably absent beneath the central part of the landfill; an eroded window of about 1 acre extends northwest for about 500 feet from the southeastern edge of the landfill (fig. 2). The unit is also essentially absent where it grades into more permeable silt and sand interbeds in the vicinity of well MW1-18 at the northwestern margin of the landfill. The permeability of the middle aquitard is mostly very low, with an estimated vertical hydraulic conductivity of 0.0001 ft/d (URS Consultants, Inc., 1993).

The intermediate aquifer at OU 1 consists primarily of sand and gravel with localized silt and glacial till lenses. The unit is continuous across OU 1 except in the vicinity of well MW1-7, where it is truncated by fine-grained glaciolacustrine clay and silt deposits. The intermediate aquifer thins to less than 1 foot and is indistinct near well MW1-18 at the northwestern margin of the landfill where fine-grained sediments predominate. It increases to about 30–40 feet in thickness upgradient (south) and downgradient (northwest) of the landfill. Somewhere beneath the tide flats and in the vicinity of the Highway 308 causeway, the aquifer is divided into an upper and lower permeable zone by as much as 16 feet of a compacted glacial till deposit. The permeability of the intermediate aquifer is relatively high, with an estimated hydraulic conductivity of 3.3 ft/d (URS Consultants, Inc., 1997a).

The Clover Park aquitard is a regionally extensive unit consisting of hard silt, peat, and clay. It is continuous beneath OU 1 and ranges from 100 to 200 feet thick. Localized permeable zones occur in the aquitard and were distinguished as a separate hydrogeologic unit. The permeability of the Clover Park aquitard is mostly very low, with an estimated vertical hydraulic conductivity of 0.01 to 0.0001 ft/d (URS Consultants, Inc., 1993).
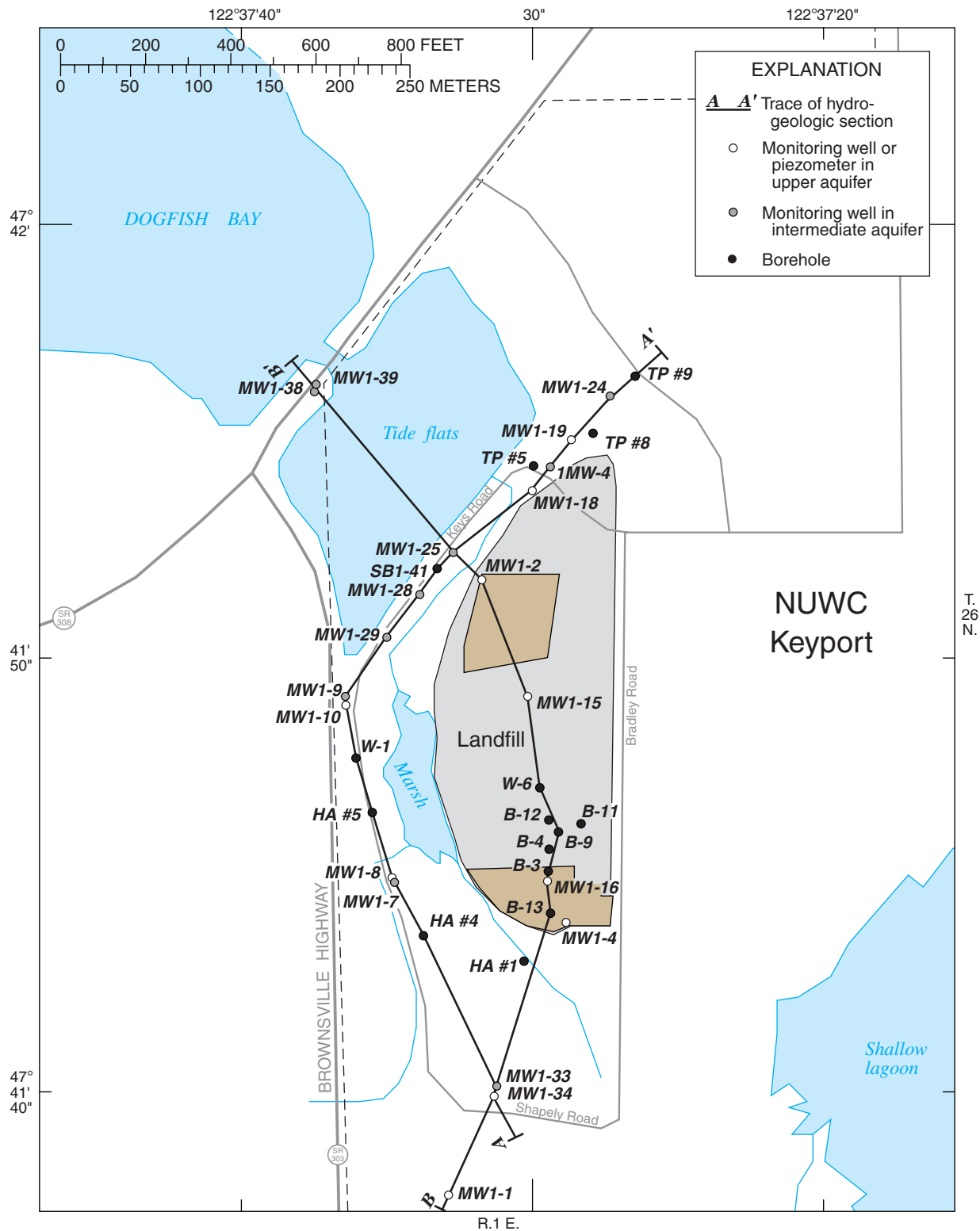
Figure 3. Location of the hydrogeologic sections shown in figure 4, Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
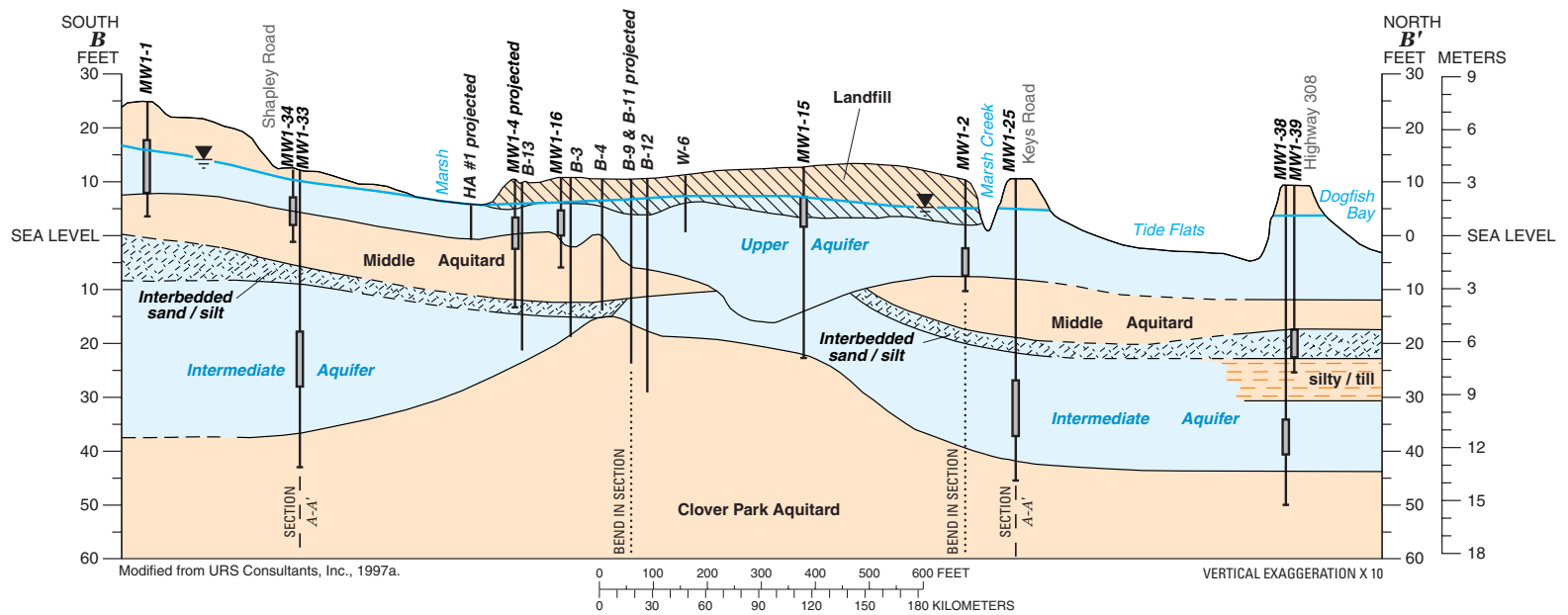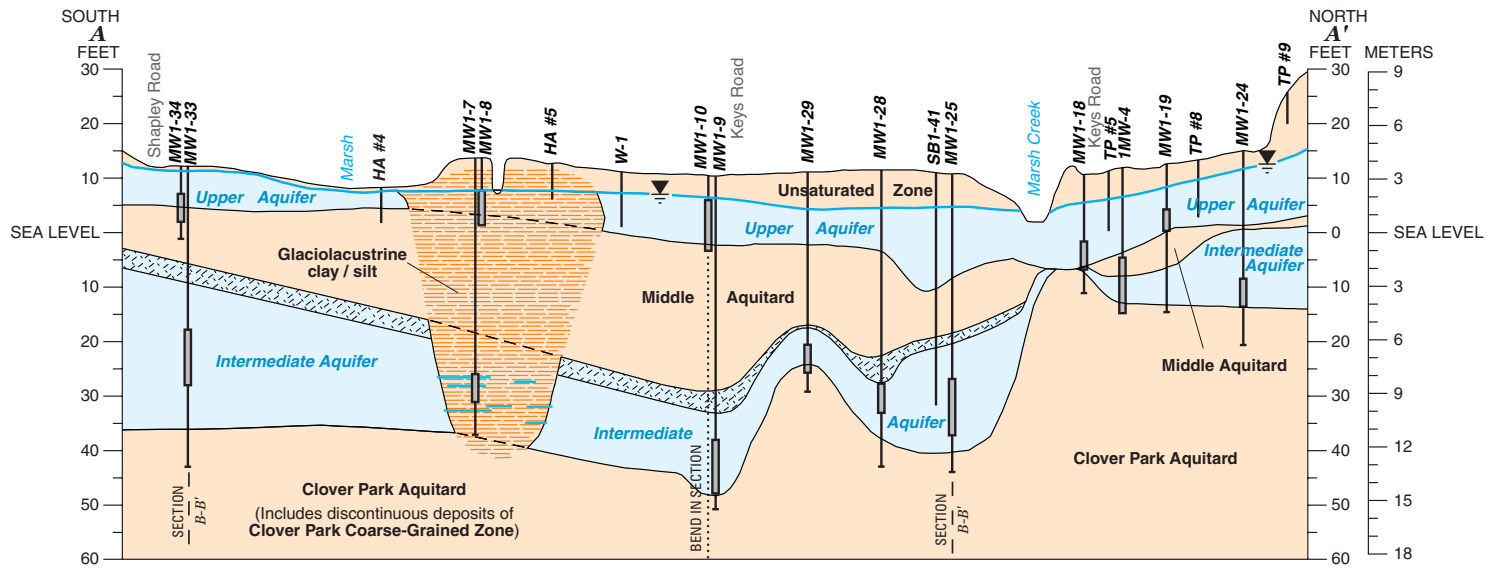
Figure 4. The six primary hydrogeologic units at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. Modified from URS Consultants, Inc., 1997a.)

The Clover Park coarse-grained zone consists of large discontinuous deposits of sand and gravel with silt embedded throughout the Clover Park aquitard. The unit was identified in a few borings at OU 1, but the coarse-grained lenses are not thought to be interconnected. Selected lenses may be hydraulically connected to the intermediate aquifer.

The NUWC Keyport water-supply well and a nearby Kitsap Public Utility District water-supply well are completed in a deeper aquifer 700 to 800 feet below sea level. A thorough inventory of private wells, completed in 1996-97, showed no water-supply wells completed in shallower units at locations downgradient from OU 1 (URS Consultants, Inc., 1997a).

Surface-Water and Ground-Water Flow

The descriptions of surface-water and ground-water flow and their interaction are summarized from two reports by URS Consultants, Inc. (1993 and 1997a). The reports relied on data from multiple water-level measurements from wells and piezometers and surface-water stations collected during 1995-96, hourly observations of water level and salinity collected during a 48-hour tidal/salinity investigation in July 1996, and rising-head slug-test data collected from monitoring wells between 1991–96.

Two perennial freshwater creeks drain into the marsh adjacent to the OU 1 landfill (fig. 2). The eastern creek begins in a partly emergent wetland area located immediately south of the landfill, and the western creek drains the upland area to the southwest of OU 1. Both creeks flow into a perennial marsh pond that feeds a single outlet creek. The outlet creek flows past the northern part of the landfill, through a culvert and tide gate, and into the tide flats. Most storm-water runoff from the OU 1 landfill drains directly into the marsh, and limited amounts of storm-water runoff from other parts of NUWC Keyport flow into the marsh at points just south of the landfill and near the mouth of the outlet creek. Storm-water runoff also enters the marsh from the creek draining the western uplands. During periods of no runoff, surface water in the marsh is entirely ground-water discharge.

Surface water in the tide flats and upstream to the marsh pond is affected by the 10- to 12-ft diurnal tidal fluctuations in Dogfish Bay. During high tides, water levels in the tide flats are at the same water-level elevation as Dogfish Bay. However, the tide gate at the marsh outlet automatically closes during a rising tide

and limits the flow of seawater into the marsh. As a result, the high-tide surface-water level at the marsh outlet is generally 1.5 to 2.5 ft less than the water level in the tide flats. The incoming seawater rarely extends upstream beyond the marsh pond, where the tidal fluctuation is less than 0.5 ft. On a falling tide, surface water from the marsh again drains into the tide flats and the tide flats drain to Dogfish Bay. When the water-level elevation in Dogfish Bay drops below about -2 ft, a sill beneath the Highway 308 bridge limits the discharge to Dogfish Bay and maintains the water level in the tide flats at about -2 ft. The water-level elevation in Dogfish Bay falls below -2 ft about one-third of the time. On a rising tide the situation is reversed; seawater from Dogfish Bay flows into the tide flats once the water-level elevation in the Bay exceeds -2 ft, and seawater from tide-flats flows into the marsh once the tide flats water level elevation exceeds about 0.5 ft.

Ground water in the unconfined upper aquifer beneath the OU 1 landfill generally flows from east to west (figs. 5 and 6). All of the upper-aquifer ground water beneath the landfill was previously thought to discharge primarily to the marsh, because of an inferred ground-water flow divide beneath Keys Road, the elevated roadway that separates the marsh from the tide flats. New data presented in the section "Evaluation of Natural Attenuation" suggest, however, that at least during part of the year, ground water from the northern half of the landfill flows beneath the marsh and discharges directly to the tide flats. A ground-water flow divide east of the landfill separates westward ground-water flow from eastward groundwater flow beneath the neck of the Keyport peninsula. The primary source of upper-aquifer ground water is recharge of precipitation through the landfill itself and through pervious areas to the immediate east and northeast of the landfill. The removal of asphalt from the phytoremediation plantations in February 1999 has likely resulted in increased recharge through the landfill itself, but no discernable changes in flow directions or gradients had been observed by the year 2000 (CH2MHill Constructors, Inc., 2001). Although upper-aquifer water levels and flow directions beneath the northwestern part of the landfill are influenced by tidal changes, there does not appear to be a substantial flux of seawater into the upper aquifer during high tides. Ground water in wells MW1-2 and 1MW-1 is not saline, and the salinity did not fluctuate as a function of tide during the 24-hour tidal study.
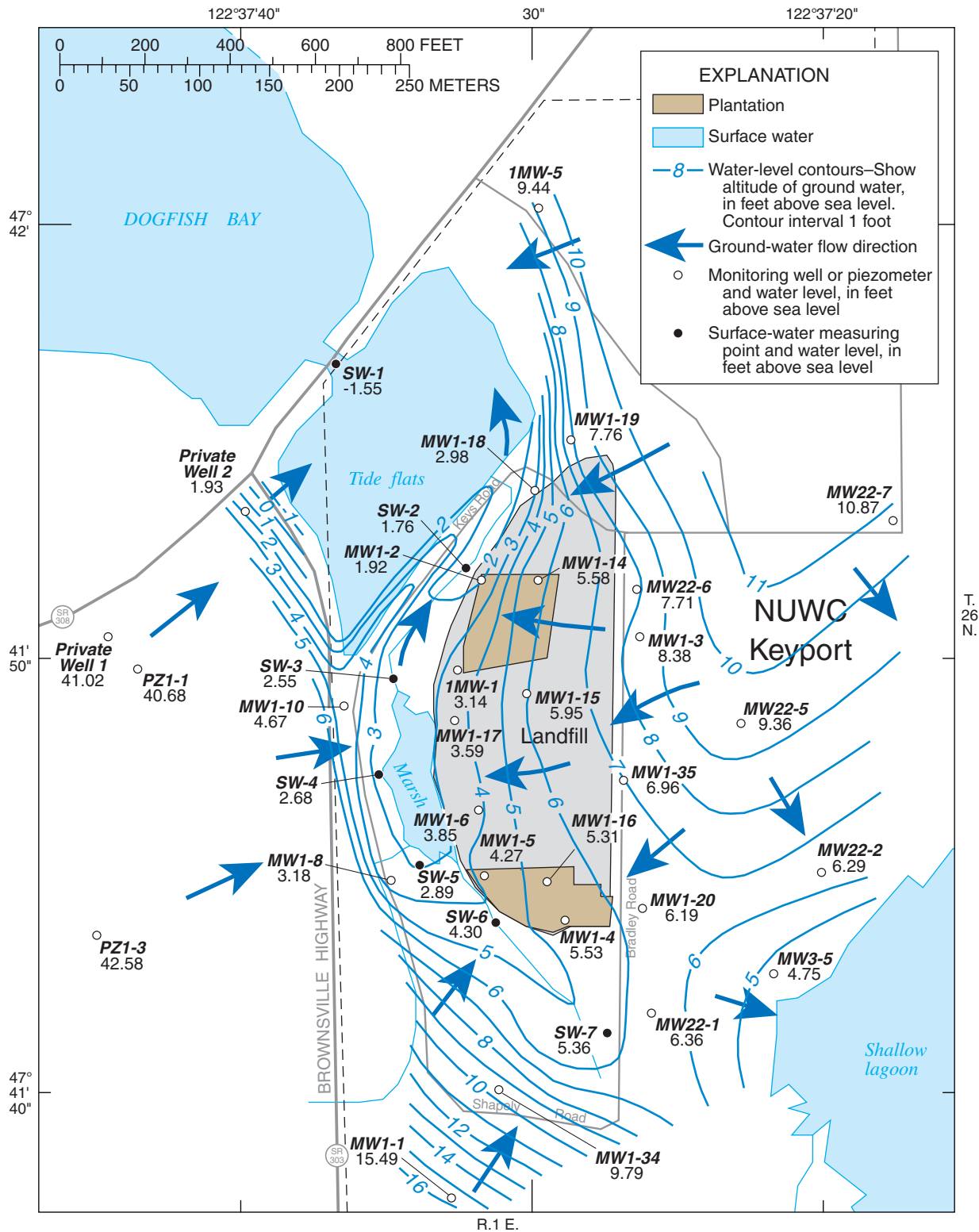
Figure 5.   Ground-water levels and flow in the shallow aquifer during a low tide, September 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. (Modified from URS Consultants, Inc., 1997a.)
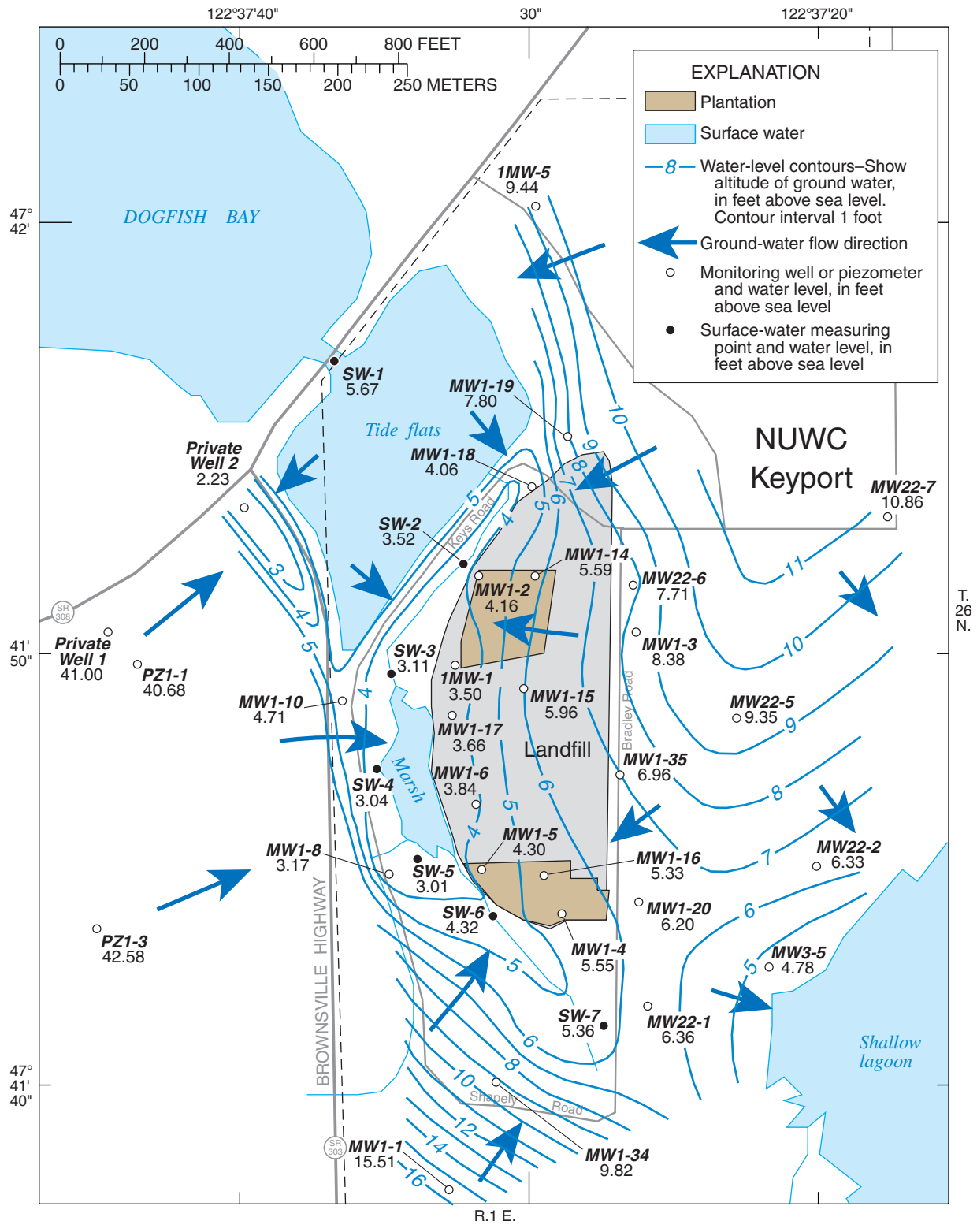
Figure 6.   Ground-water levels and flow in the shallow aquifer during a high tide, September 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. (Modified from URS Consultants, Inc., 1997a.)

Ground water in the predominantly confined intermediate aquifer beneath the OU 1 landfill generally flows from the south and west to the northwest (figs. 7 and 8). Ground-water flow in this aquifer converges beneath the tide flats and Dogfish Bay from three directions and ultimately discharges directly to seawater. The primary sources of ground water in the intermediate aquifer are recharge of precipitation in areas more than 1,000 ft south of the landfill where the middle aquitard is absent, and downward flow from the upper aquifer in areas within and northeast of OU 1 where permeable windows penetrate the middle aquitard. Ground-water levels and flow directions in the intermediate aquifer beneath and adjacent to the tide flats are influenced by tidal changes, however the flux of seawater into and out of the aquifer beneath OU 1 during a single tidal cycle is negligible. Observed changes in intermediate-aquifer water levels result from a pressure wave that propagates inland because of the increased load of seawater on aquifer sediments during a high tide. Over a timescale of perhaps centuries, there has been a flux of saline water (or possibly a flux of dissolved solids only through dispersion) into the intermediate aquifer. Ground water in the intermediate aquifer upgradient of the landfill is fresh; at the down-gradient margin of the landfill it is somewhat brackish; and further downgradient at Highway 308 it is brackish north of the bridge, somewhat brackish in the lower part of the aquifer south of the bridge, and not brackish in the upper part of the aquifer south of the bridge (well MW1-39). Together, these observations and interpretation of new data presented in this report suggest that the downgradient well MW1-39 is hydraulically connected to the upper aquifer and is not screened within the main body of the intermediate aquifer, as previously inferred.

Some ground water in the contaminated portion of the upper aquifer flows downward into the intermediate aquifer. Observed water levels indicate that there is a downward gradient for ground-water flow between the upper and intermediate aquifers beneath the northeastern third of the landfill, and that there is an upward gradient beneath the remainder of the landfill and perhaps the entire marsh. The delineated zone of downward gradient partially overlaps both of the identified windows in the middle aquitard (fig. 2).

Ground-water flow rates along multiple flow paths in the upper and intermediate aquifers (figs. 9 and 10) were estimated using observed water levels and calculated hydraulic conductivities from slug-tests in monitoring wells. In the upper aquifer, ground-water flow rates were estimated to be 29 to 83 ft/yr for the five east-west flowpaths shown on figure 9. In the intermediate aquifer, ground-water flow rates were estimated to be 28 to 89 ft/yr beneath the landfill and 10 ft/yr beneath the tide flats (fig. 10). These estimates are used later in this report for calculating contaminant mass degradation rates and field attenuation rates at OU 1. The USGS collected additional data related to ground-water flow rates in the intermediate aquifer, and they too are presented in this report.

Contamination and Remediation

The OU 1 landfill was the primary disposal area for both domestic and industrial wastes generated by NUWC Keyport from the 1930s through 1973. Mixed trash and demolition debris were burned at the northern end of the landfill from the 1930's to the 1960's, and unburned or partially burned materials were buried in the landfill or pushed into the marsh. Paints, thinners, solvents, acids, dried sludge from a wastewater treatment plant, and other industrial wastes were disposed of at various locations in the landfill from the 1930s through 1973. The most concentrated disposal area for waste paints and solvents was located at the southern end of the landfill (fig. 2). That location coincides with the highest observed concentrations of CVOCs in ground water at OU 1. Few, if any, intact and full drums of waste were thought to be buried in the landfill. Instead, most drum contents were emptied into the landfill and the drums were then reused or crushed and buried.

The CVOCs identified as chemicals of concern at OU 1 are tetrachloroethene (PCE), TCE, *cis*DCE, trans-1,2-dichloroethene (*trans*DCE), VC, TCA, 1,2-dichloroethane (1,2-DCA), 1,1-DCA, and 1,1-DCE. The primary CVOCs originally disposed of were likely PCE, TCE, TCA, and 1,2-DCA. The other contaminants are known degradation products of those original contaminants and likely developed within the landfill itself.
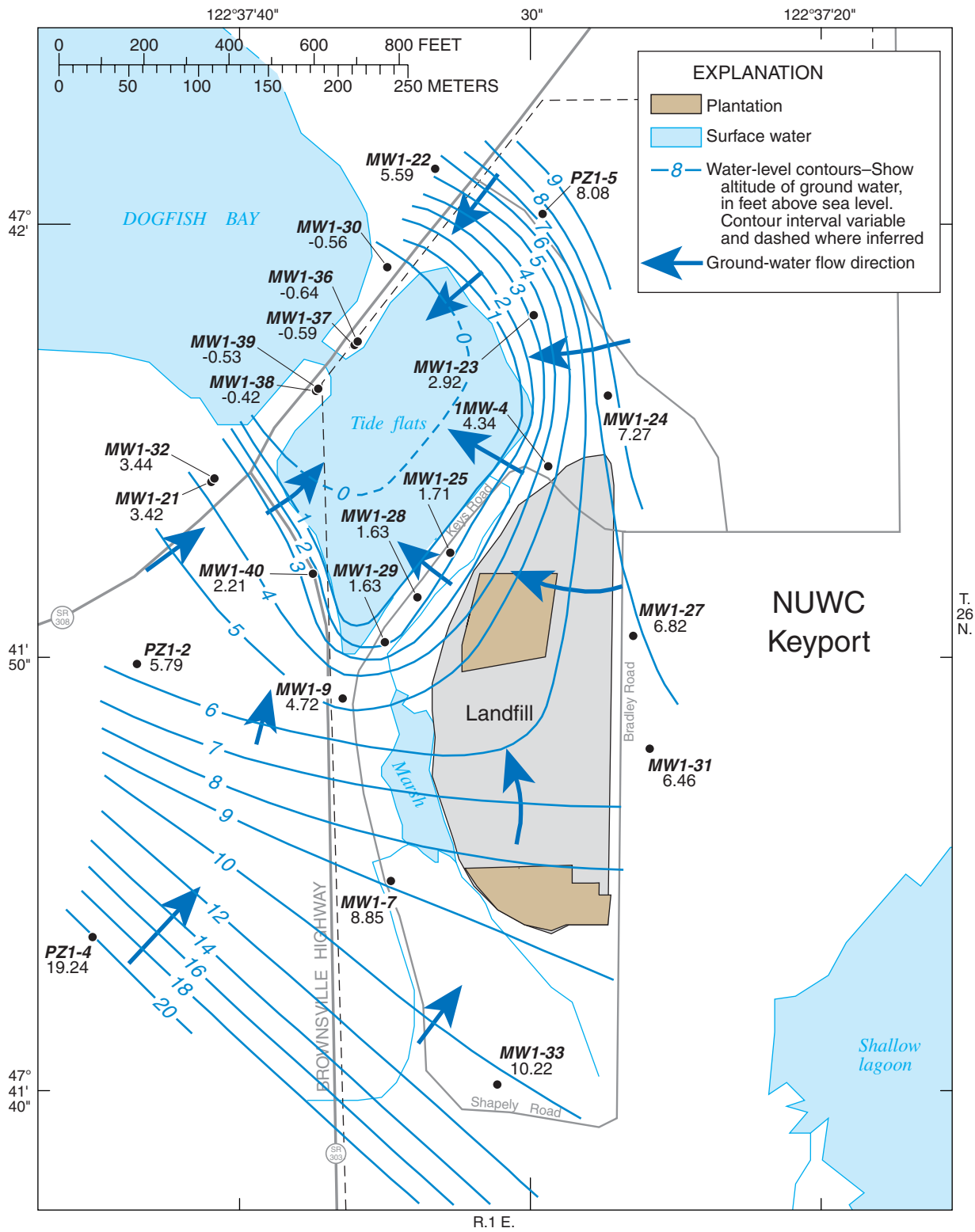
Figure 7. Ground-water levels and flow in the intermediate aquifer during a low tide, September 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. (Modified from URS Consultants, Inc., 1997a.)
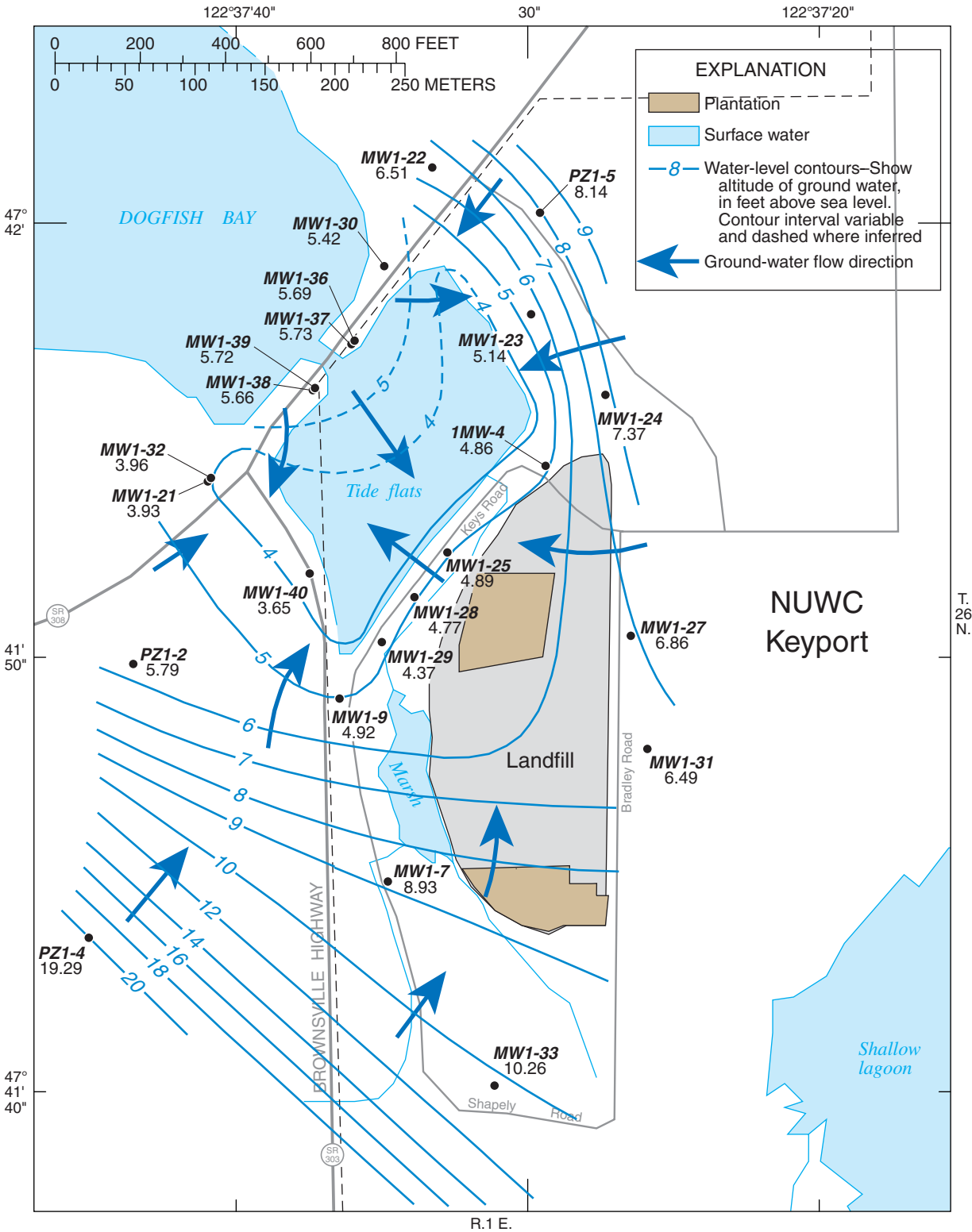
Figure 8. Ground-water levels and flow in the intermediate aquifer during a high tide, September 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. (Modified from URS Consultants, Inc., 1997a.)

Figure 9. Ground-water flow directions and flow rates in the upper aquifer at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. (Modified from URS Consultants, Inc., 1997a.)

Figure 10. Ground-water flow directions and flow rates in the intermediate aquifer at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
(Modified from URS Consultants, Inc., 1997a.)
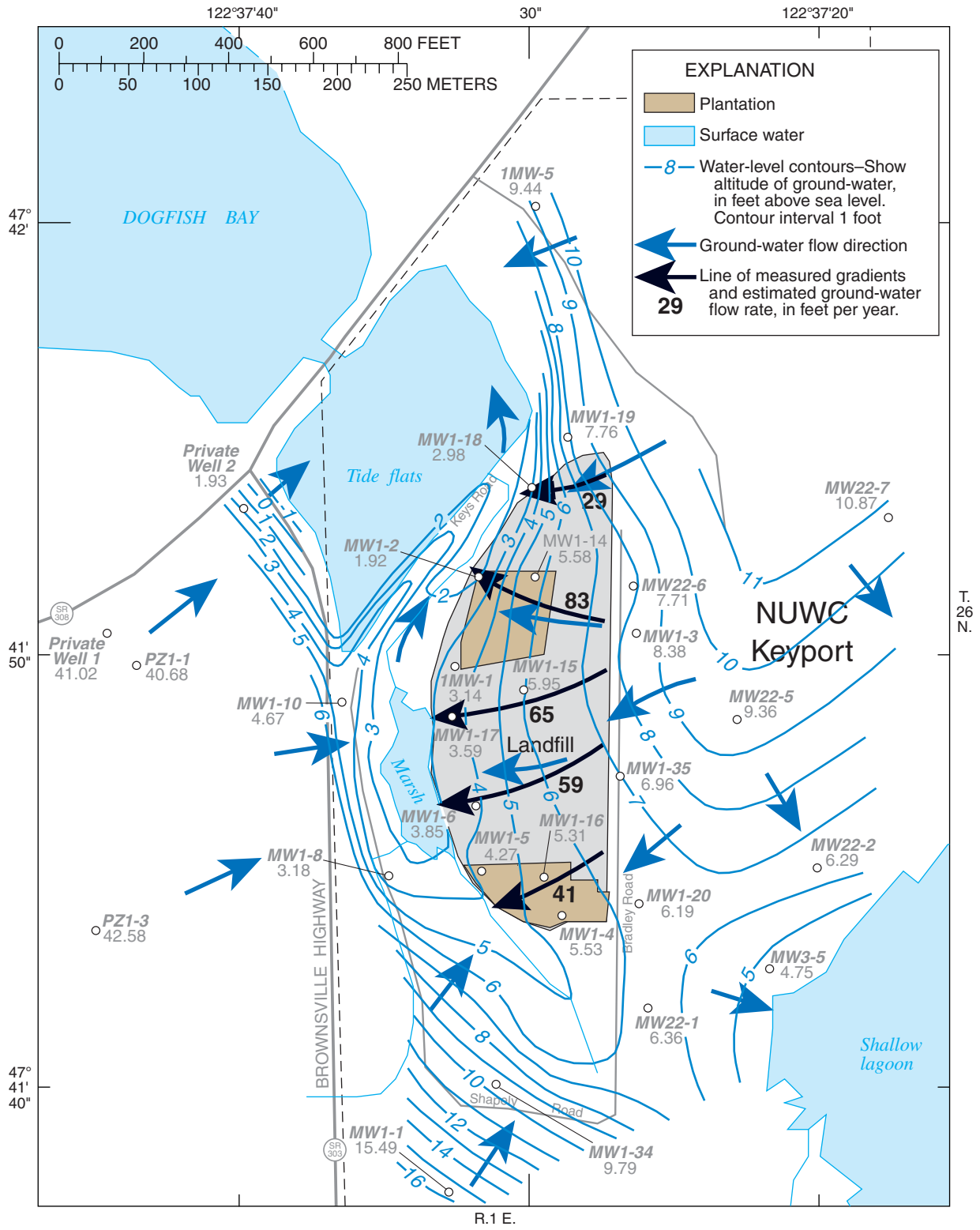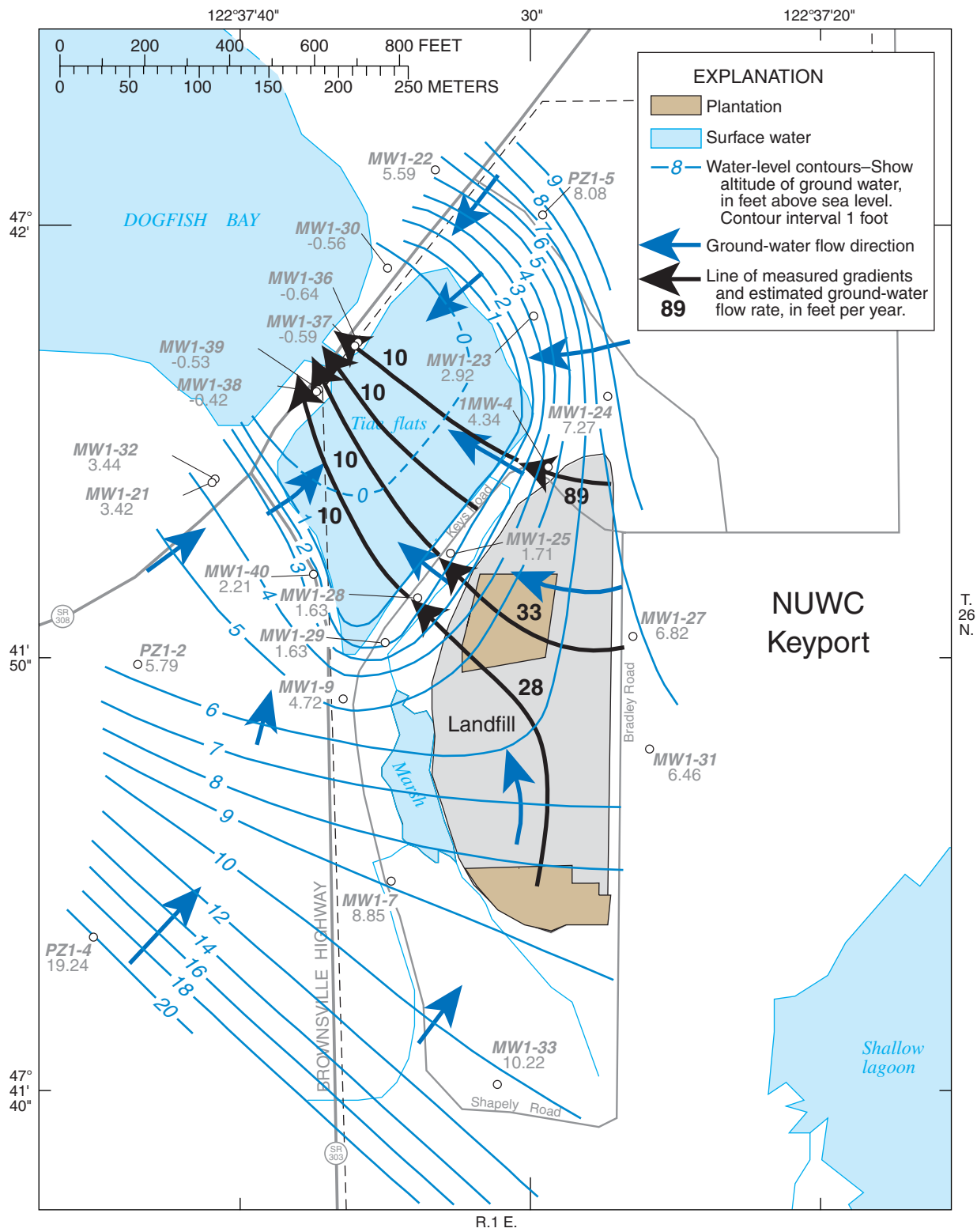
Chlorinated VOCs are present in the upper and intermediate aquifers and in surface water at OU 1. The highest contaminant concentrations are found in the upper aquifer beneath the southern part of the landfill (fig. 11). Less is known about contaminant concentrations in the intermediate aquifer beneath the landfill, although the contaminant plume downgradient of the landfill is well characterized (fig. 12). Based on the disposal history and observed contaminant concentrations, some contaminants probably are present in the upper aquifer in their non-dissolved phase as non-aqueous phase liquids (NAPLs).

The remediation strategy selected by the Navy for CVOCs at OU 1 includes removal and treatment of the contaminants from the upper aquifer by phytoremediation with hybrid poplar trees, retaining the asphalt cover over the remaining paved portions of the landfill to minimize ground-water recharge, short-term process monitoring, long-term performance monitoring, and institutional controls to prevent undue exposures to landfill contaminants (URS Consultants, Inc., 1998). Two plantations of hybrid poplar trees were planted in spring of 1999. Asphalt was removed, about 1 to 2 feet of topsoil was added, and the sites were prepared for planting during February 1999. Performance monitoring during 1999 and 2000 showed the trees were overall in good health, and ground-water flow directions and gradients are consistent with historical findings (URS Greiner, Inc., 2000). The trees were not yet mature in 2000 and the roots had not reached the water table, so the lack of discernible water-level changes was expected. Changes in contaminant concentrations in upper-aquifer ground water and in surface water have been observed after the introduction of phytoremediation (CH2MHill Constructors, Inc., 2001). Those changes are described and interpreted later in this report in section "Evaluation of Natural Attenuation".

Acknowledgments

Figure 11. Concentrations of chlorinated volatile organic compounds (CVOCs) in surface water and upper-aquifer ground water, 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
(Modified from URS Consultants, Inc., 1997a).
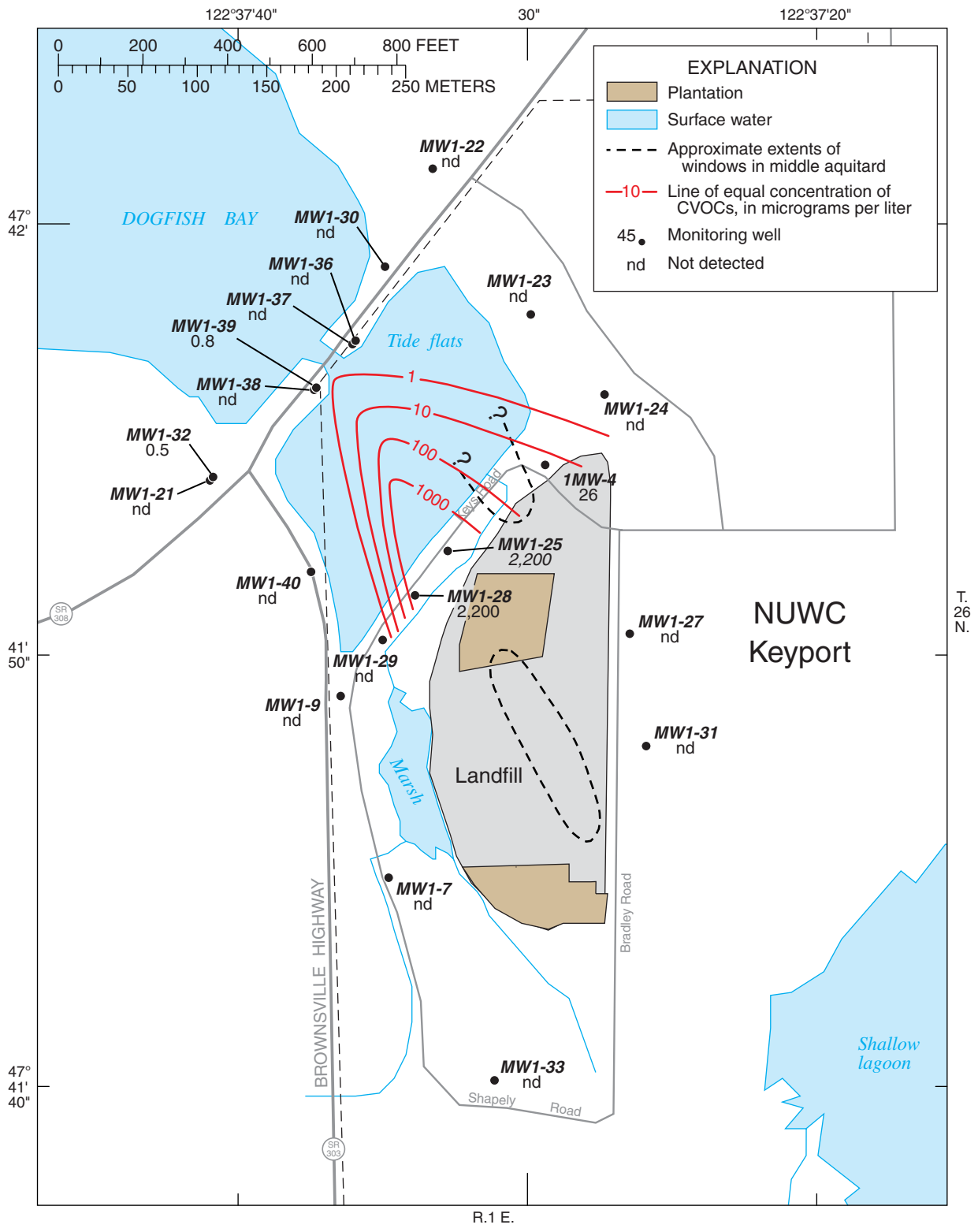
Figure 12. Concentrations of chlorinated volatile organic compounds (CVOCs) in intermediate-aquifer ground water, 1996, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
(Modified from URS Consultants, Inc., 1997a).

REDOX CONDITIONS IN CONTAMINATED GROUND WATER

Evaluation of redox conditions in ground-water contaminant plumes is a prerequisite for understanding the behavior of contaminants and for evaluating the effectiveness of natural attenuation processes. That is because ground-water redox conditions greatly control the occurrence and rate of nearly all biodegradation processes.

Most biodegradation processes involve redox reactions in which electrons are transferred from one compound (the electron donor) to another (the electron acceptor). Depending on the particular compound and redox condition, CVOCs can serve as either electron donors or electron acceptors. Possible electron donors in contaminated ground water include various organic-carbon compounds in landfill leachate, and hydrocarbon fuels. The less chlorinated VOCs, such as VC and dichlorinated ethenes and ethanes, can also act as electron donors under aerobic or mildly reducing redox conditions. Possible electron acceptors include the inorganic constituents oxygen, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide, as well as highly chlorinated VOCs such as PCE, TCE, and TCA. VC and dichlorinated ethenes and ethanes may also act as electron acceptors under strongly reducing redox conditions.

Indigenous microorganisms that require carbon and energy to sustain their growth facilitate most ground-water redox reactions. A variety of microorganisms often compete for the supply of available electron-donating organic carbon in ground water, but they are more specialized in their use of the different electron acceptors. Oxygen-reducing microorganisms (those that use oxygen as an electron acceptor) can out-compete all others when dissolved oxygen (DO) is present. However, if the supply of DO in ground water is depleted and electron-donating compounds are still available, oxygen reducers will become dormant and nitrate reducers will predominate until the supply of nitrate is depleted. This sequence continues through manganese reduction, iron reduction, sulfate reduction, and carbon-dioxide reduction (methanogenesis). The result of this competitive exclusion is the formation of somewhat discrete redox zones in an aquifer.

Redox conditions are named according to the inorganic compound that is acting as the predominant electron acceptor in a given portion of an aquifer. Thus, the common redox conditions in ground water are oxygen reducing (or aerobic), nitrate reducing, manganese reducing, iron reducing, sulfate reducing, and carbon-dioxide reducing (methanogenic). Nitrate reduction, manganese reduction, and iron reduction are often together referred to as mildly reducing conditions, whereas sulfate reduction and methanogenesis are often referred to as strongly reducing conditions. That distinction is made because different types of biodegradation processes are favored under mildly and strongly reducing conditions.

Determination of redox conditions in contaminated ground water is not a simple task and no universally accepted procedures exist. The rationale behind characterizing redox conditions in ground water at Keyport is summarized here. Additional information about characterizing redox conditions can be found in Cozzarelli and others (2000), Christensen and others (2000), Wiedemeier and Chappelle (1998), and Weidemeier and others (1998).

Redox conditions in contaminated ground water can sometimes be deduced by quantifying various oxidized and reduced inorganic compounds in ground water samples (Cozzarelli and others, 2000; Christensen and others, 2000; Wiedemeier and Chappelle, 1998). The identification of aerobic conditions is relatively simple; they are predominant if DO concentrations in ground water are greater than about 1 milligram per liter (mg/L). Identification of the various anaerobic redox conditions (in which DO concentrations are less than 1 mg/L) is more difficult. If nitrate concentrations exceed about 0.5 mg/L in anaerobic ground water, then nitrate reduction is likely. If anaerobic ground water lacks nitrate, and if reduced manganese ($Mn(II)$) or iron ($Fe(II)$) concentrations increase along a ground-water flow path, then manganese or iron reduction is indicated. If anaerobic ground water lacks nitrate, if sulfate (oxidized sulfur) concentrations decrease along a ground-water flow path, and if concentrations of hydrogen sulfide (reduced sulfur) exceed about 0.05 mg/L, then sulfate reduction is indicated. Finally, if anaerobic ground water lacks nitrate, sulfate, and hydrogen sulfide, and if methane concentrations exceed about 0.2 mg/L, then carbon dioxide reduction (methanogenesis) is indicated.

Many conditions at the OU 1 landfill complicate the determination of redox conditions. Contaminated ground water beneath landfills often is not at a thermodynamic steady-state or chemical equilibrium, so several electron-accepting processes may be occurring simultaneously (Cozzarelli and others, 2000; Christensen and others, 2000). As fresh ground water mixes with saline ground water in a near shore environment such as the OU 1 landfill, the natural supply of sulfate may increase substantially along a flowpath and effectively mask any sulfate consumption by redox reactions. Redox-sensitive compounds such as sulfate, methane, or iron (II) may leach to ground water from many locations in a landfill, and could also mask any concentration changes resulting from redox reactions in the local ground water. Redox-sensitive species such as methane, iron (II), or manganese (II) often migrate away from where they were produced, blurring the interpretation of where one redox zone ends and another begins. Precipitation of iron, manganese, and sulfur species can also affect the identification of a redox condition at a given point. And finally, redox conditions and concentrations of redox-sensitive compounds can change dramatically over very short distances in contaminant plumes, making it difficult to obtain a ground-water sample that represents a single discrete redox zone even in monitoring wells with relatively short (5-foot) open intervals. These confounding conditions cannot be avoided, but an awareness of them can put the interpretation and use of the identified redox zones into proper perspective.

An alternative method for identifying the predominant redox processes in anaerobic ground water is through direct measurement and interpretation of dissolved-hydrogen (H_2) concentrations in ground water. Hydrogen is continuously produced and consumed by different microorganisms during anaerobic decomposition of organic matter, and for natural ground waters the different microorganisms that facilitate nitrate-, manganese-, iron-, sulfate-, and carbon dioxide-reduction reactions exhibit different efficiencies in utilizing H_2 (Lovely and Goodwin, 1988). Nitrate-reducers are very efficient at utilizing H_2, so they keep H_2 concentrations in ground water at very low levels of less than 0.1 nanomolar (nM). Manganese- and iron-reducers use H_2 less efficiently, so they keep H_2 concentrations between 0.1–0.2 and 0.2–0.8 nM, respectively. Sulfate-reducers are less

efficient still, so they keep H_2 concentrations at between 1 and 4 nM, and carbon-dioxide reducers are relatively inefficient, resulting in H_2 concentrations greater than 5 nM. The result of that competition for H_2 is that each anaerobic redox condition is characterized by a distinct H_2 concentration in ground water (table 1) (Chapelle and others, 1995; Lovely and others, 1994).

Table 1. Characteristic dissolved-hydrogen concentrations for different anaerobic redox conditions in ground water

Redox condition	Characteristic dissolved-hydrogen concentration (nanomolar)
Nitrate reduction	Less than 0.1
Manganese reduction	0.1 — 0.2
Iron reduction	0.2 — 0.8
Sulfate reduction	1 — 4
Methanogenesis	Greater than 5

It has more recently been argued that identifying redox conditions from specific steady-state H_2 concentrations is not applicable to all contaminant plumes (Hoehler and others, 1998; Jakobsen and others, 1998; Christensen and others, 2000). Uncertainties arise from observations that H_2 concentrations alone do not account for complicating effects from different absolute concentrations of dissolved redox species, that there is much variability in the iron-oxide minerals that can serve as electron acceptors, that ground-water temperature affects equilibrium H_2 concentrations, and that redox conditions may be overlapping and not exclusive. Despite those limitations, H_2 concentrations do indicate redox conditions in a relative sense, in that higher H_2 concentrations are consistently found in more strongly reduced ground waters. And in terms of contaminant biodegradation, identifying the presence of strongly reducing conditions or knowing where H_2 concentrations exceed 1 nM may be more important than knowing the specific inorganic compound that is the predominant electron acceptor. Thus, quantifying oxidized and reduced inorganic compounds as well as steady-state H_2 concentrations throughout a contaminant plume can be used with reasonable confidence to identify favorable and less favorable conditions for contaminant biodegradation.

NATURAL ATTENUATION IN GROUND WATER

Natural attenuation refers to a variety of physical, chemical, and biological processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water (U.S. Environmental Protection Agency, 1997). Processes relevant to natural attenuation of CVOCs in ground water include destructive processes such as abiotic and biotic degradation and non-destructive processes such as dispersion, sorption, and volatilization. Destructive processes are preferred when relying on natural attenuation for site remediation (U.S. Environmental Protection Agency, 1997), so contaminant degradation was a primary focus of this investigation. Processes that could naturally attenuate chlorinated ethenes and ethanes in ground water at the OU 1 landfill are summarized here.

Destructive Attenuation Processes

Contaminant degradation is the transformation of a chemical compound (the parent compound) into one or more other compounds (the daughter products). Biodegradation reactions are mediated by subsurface microorganisms, whereas abiotic degradation reactions are not. Daughter products resulting from degradation of CVOCs may be more or less toxic than the parent compound, but most intermediate daughter products can be further degraded into nontoxic compounds. From a remediation standpoint, degradation is most desirable when a contaminant is ultimately transformed into innocuous inorganic by-products such as carbon dioxide, water, and chloride.

Over the past two decades, numerous field and laboratory studies have shown that microbes indigenous to ground-water systems can degrade chlorinated ethenes and ethanes. It has also been shown that local subsurface redox conditions are a primary factor controlling the occurrence and rate of biodegradation reactions, although the occurrence and rate of abiotic degradation reactions are usually independent of redox conditions. The most important degradation reactions for the chlorinated ethenes TCE, DCE, *cis*DCE, and VC and the chlorinated ethanes TCA, 1,1-DCA, and chloroethane (CA) are presented here.

Trichloroethene and Other Chlorinated Ethenes

Abiotic degradation of chlorinated ethenes occurs very slowly under conditions commonly found in aquifers (Vogel, 1994). Although considerable discrepancies exist, half-lives for abiotic degradation of TCE and DCE have been reported to be as long as 10^6–10^8 years (Jeffers and others, 1989). Abiotic degradation half-lives of TCE can be as short as minutes to a few days in systems amended with an abundance of zero-valent iron (Gillham and O'Hannesin, 1994), but abundant zero-valent iron is uncommon in natural settings.

Biodegradation of chlorinated ethenes can be very rapid under conditions often found in aquifers, and at least two pathways for complete biodegradation of chlorinated ethenes have been demonstrated in field and laboratory studies (fig. 13). The first pathway consists solely of sequential dechlorination reactions in which the chlorinated ethenes serve as electron acceptors. TCE can be rapidly degraded to ethene by this pathway, but the dechlorination often slows or stops at *cis*DCE or VC in many ground-water systems. The second pathway consists of a partial sequence of dechlorination reactions, followed by mineralization of the resulting *cis*DCE or VC. Mineralization (or direct oxidation) is the process in which organic compounds are transformed into inorganic by-products. In mineralization reactions, *cis*DCE and VC serve as electron donors. This combination of dechlorination of TCE followed by mineralization of *cis*DCE and VC has been shown to result in complete biodegradation of chlorinated ethene contaminants in many ground-water systems (Weidemeier and Chappelle, 1998).

Reductive dechlorination of TCE by microorganisms requires anaerobic ground-water redox conditions. TCE serves as an electron acceptor during this process, and a chlorine atom is removed and replaced with a hydrogen atom to form (primarily) *cis*DCE. All three isomers of dichloroethene can theoretically be produced, but *cis*DCE is by far the most common daughter product (Bouwer, 1994). Because TCE is reduced during this process, the reaction must be coupled with the oxidation of another compound. Organic compounds such as natural organic matter, fuel hydrocarbons, or various compounds found in landfill leachate are common electron donors that are oxidized during the reduction of TCE.

EXPLANATION

▢ Parent compound

⬭ Organic daughter compounds

⬡ Inorganic daughter compounds

——▶ Reductive dechlorination

- - -▶ Abiotic reaction

------▶ Mineralization reaction

Trichlorethene (TCE)

1,1,1-Trichlorethane (TCA)

cis-1,2-Dichloroethene (cisDCE)

1,1-Dichloroethene (DCE)

1,1-Dichloroethane (DCA)

Vinyl Chloride (VC)

Acetate

Chloroethane (CA)

Ethene

Carbon Dioxide, Water, Chloride

Figure 13. Possible degradation pathways for trichloroethene and for 1,1,1-trichloroethane.

Reductive dechlorination of TCE has been demonstrated under all anaerobic conditions, but it is reported to be most efficient under the strongly reducing conditions of sulfate reduction (Gossett and Zinder, 1996) or methanogenesis (McCarty and Semprini, 1994). Reductive dechlorination can also degrade cisDCE to VC to ethene, but the sequence often is interrupted because of a change to mildly reducing redox conditions as contaminants are transported downgradient by ground-water flow. TCE is the chlorinated ethene most susceptible to reductive dechlorination, followed by cisDCE and then VC.

Microbially mediated mineralization of all DCE isomers or VC can occur in either aerobic or mildly reducing anaerobic ground water. The CVOCs serve as

electron donors during this process and are degraded to carbon dioxide, water, and chloride. Because DCE or VC is oxidized in this process, the reactions must be coupled with the reduction of another compound. Oxygen, manganese (IV), and iron (III) are common electron acceptors that can be reduced during mineralization of DCE and VC (Bradley and others, 1998; Bradley and Chapelle, 1996, 1997, and 1998; Davis and Carpenter, 1990). Mineralization of DCE and VC is most efficient under aerobic conditions, is moderately efficient under iron or manganese reducing conditions, and is negligible under sulfate reducing and methanogenic conditions. The rates of DCE mineralization are usually somewhat less than those for VC mineralization, and TCE is not readily mineralized.

Given the above processes, the complete degradation of TCE into carbon dioxide, water, and chloride is most effective in aquifers that are either (1) sulfate reducing or methanogenic throughout the extent of contamination, or (2) sulfate reducing or methanogenic near the TCE source area, and become aerobic or manganese or iron reducing downgradient of the source area (Chapelle, 1996). The first situation is favorable for complete reductive dechlorination of TCE, *cis*DCE, and VC, whereas the second situation is favorable for reductive dechlorination of TCE and possibly *cis*DCE, followed by mineralization of the resulting *cis*DCE and VC. Both situations require a substantial source of organic carbon to create strongly reducing conditions near the TCE source area.

1,1,1-Trichloroethane and Other Chlorinated Ethanes

In contrast to TCE, the chlorinated ethane 1,1,1-TCA can be degraded at significant rates by both abiotic and biotic reactions. Abiotic degradation of TCA can occur through two different pathways (fig. 13). Reported half-lives for the abiotic degradation of TCA into acetate range from 0.5–1.7 years and half-lives for abiotic degradation of TCA into DCE range from 0.8–2.5 years (Vogel and McCarty, 1987). Those half-lives reflect conditions at a temperature of 20 degrees Celsius (°C). Expected field half-lives for TCA at 15°C, a representative ground-water temperature for Area 6, would be about twice as long (1.6 to 5 years) based on data from Jeffers and others (1989). Abiotic degradation of TCA is essentially independent of redox conditions or pH, so it occurs throughout most aquifers. Abiotic degradation of 1,1-DCA and 1,2-DCA is not an important natural attenuation process (Jeffers and others, 1989)—their reported half-lives are about 60 to 70 times greater than those for TCA. However, abiotic degradation of CA is very rapid, with a reported half-life of only 0.12 year at 20°C (Bouwer and McCarty, 1983).

Reductive dechlorination of chlorinated ethanes is similar to the process for chlorinated ethenes. TCA can be reductively dechlorinated to 1,1-DCA and then to CA. The process occurs under anaerobic conditions only, and is most effective under the more strongly reducing conditions of sulfate reduction and methanogenesis. TCA is more susceptible to reductive dechlorination than are 1,1-DCA and CA. Less is known about mineralization of chlorinated ethanes.

Mineralization of 1,2-DCA under aerobic conditions (Klecka and others, 1998) and under anaerobic conditions (Dinicola and others, 2000) has been demonstrated previously. Mineralization of 1,1-DCA has been inferred but not well studied, and mineralization of CA is suspected to be much slower than abiotic degradation of that compound.

Similar to the degradation of TCE, the complete degradation of TCA into carbon dioxide, water, and chloride is also most efficient in aquifers that are either (1) sulfate reducing or methanogenic throughout the extent of contamination, or (2) sulfate reducing or methanogenic near the TCA source area, and become aerobic or manganese or iron reducing downgradient of the source area. However, the potential for substantial abiotic degradation of TCA suggests that even in an aerobic aquifer, TCA can degrade into acetate and 1,1-DCE, which could subsequently be degraded into innocuous daughter products. Given that degradation of 1,1-DCE (a known carcinogen) could possibly be a rate-limiting step in the process, a fully aerobic aquifer system would probably not be as conducive to TCA degradation as would an aquifer system that is anaerobic at the source area.

Nondestructive Attenuation Processes

Nondestructive natural attenuation processes include those that reduce contaminant concentration but do not reduce the total contaminant mass in a system. The most important nondestructive attenuation processes for CVOCs in ground water are volatilization, dispersion, and sorption.

With regard to natural attenuation of contaminants in ground water, volatilization is a transfer of contaminants from ground water to soil gas. Volatilization can reduce the total contaminant mass in ground water, but only by transferring the mass to soil gas and the atmosphere. Volatilized chemicals in soil gas can also be transferred back to ground water by infiltrating water, resulting in little loss of mass but an attenuation of chemical concentrations. Volatilization can be a very important mechanism for the loss of chemicals from the soil to the air or from surface water to the air, but volatilization of chemicals from ground water is constrained much more by the rate of vapor transport upward through the unsaturated zone.

The rate at which a chemical volatilizes from ground water is affected by many factors, such as soil properties, chemical properties, and environmental conditions, and commonly used methods used to estimate volatilization are not particularly accurate (Rathbun, 1998).

Dispersion is the mixing of different waters due to effects of heterogeneity in the permeability of aquifer materials. It causes a contaminant plume to spread out in directions that are longitudinal and transverse to the direction of ground-water flow. Dispersion is relevant to natural attenuation because it dilutes contaminant concentrations by spreading the contaminant into a larger volume of aquifer. Dispersion is attributed to both mechanical and molecular diffusion processes, but mechanical dispersion is the dominant process at normal ground-water flow velocities (Davis and others, 1993). Dispersion is greater in more heterogeneous aquifer materials.

Sorption is the partitioning of dissolved solutes from the ground water onto sediment particles. Sorption is relevant to natural attenuation because it retards the movement of a contaminant plume. Sorption is largely a reversible process, so contaminants may not be permanently removed from solution. Sorption is a complex process than includes several mechanisms, but sorption of CVOCs is primarily dependent on the amount of organic carbon present in the aquifer materials and the hydrophobicity of the contaminant. The amount of sorption is often quantified by a distribution coefficient (K_d). A K_d for a given contaminant in a given material is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration, and K_d increases directly with the total organic carbon content of aquifer materials (Schwarzenbach and Westall, 1981). The equilibrium distribution of contaminants between the sorbed and dissolved phases generally can be described by a linear sorption isotherm, where K_d is always equal to the amount of contaminant sorbed to the solid phase divided by the amount in solution. Although such an equilibrium between contaminant concentrations in the sorbed and solution phases is often assumed, numerous experiments have shown that desorption can be rate-limiting, and previously sorbed contaminants can be slowly released into solution over a period of weeks or months (Harmon and others, 1989).

METHODS AND DATA ANALYSIS

This evaluation of natural attenuation at OU 1 was patterned after existing guidelines and protocols from Wiedemeier and Chapelle (1998), Weidemeier and others (1998), and U.S. Environmental Protection Agency (1997). The data used for the evaluation included hydrogeologic, contaminant chemistry, geochemistry, and environmental tracer data collected by the Navy during 1991-2000 and by the USGS during 1996-2000. The focus was on documenting and quantifying contaminant degradation in ground water, although data on contaminant attenuation in surface water are also presented.

The evaluation considered the following evidence. First, ground-water CVOC concentration data from 1991-2000 were examined to ascertain any long-term trends in contaminant concentrations. Temporal changes in concentration attributed to natural attenuation were identified separately from changes that could be attributed to recent phytoremediation activities. Temporal changes in the relative amounts of parent compounds and daughter compounds were also examined to help ascertain the importance of biodegradation over other attenuation mechanisms. Changes in CVOC concentrations and redox-sensitive geochemicals along selected ground-water flow paths for recent (1999–2000) conditions were then examined to determine the magnitude of natural attenuation and the importance of degradation in creating the observed changes. The rate at which the dissolved contaminant mass at OU 1 is degraded in ground water, and the rate at which contaminants are discharged to surface water, were then estimated for recent (1999–2000) conditions. Contaminant attenuation rates, which are a measure of the attenuation of contaminant concentrations rather than mass, were also calculated from observed data along selected ground-water flowpaths. And finally, the overall effectiveness of natural attenuation at meeting site remediation goals was evaluated.

Hydrogeologic Data Collection

The Navy has routinely measured water-level altitudes in wells, piezometers, and nearby streams since 1991 (URS Consultants, 1993 and 1997a; URS Greiner, Inc., 2000; CH2M Hill Constructors, Inc., 2001).

Measurement points were all surveyed and referenced to existing NUWC Keyport benchmarks, and all altitudes were referenced to sea level as defined by the National Geodetic Vertical Datum of 1929. The Navy conducted rising-head slug tests in most wells to estimate the hydraulic conductivity of subsurface materials, and those hydraulic conductivity values were calculated using the Hvorslev (1951) method.

Chemical Sampling and Analyses

The Navy collected and analyzed ground-water and surface-water chemical samples at NUWC Keyport during 1991-2000. The USGS collected and analyzed ground-water chemical samples at NUWC Keyport during 1996-2000.

The Navy's ground-water chemistry data were collected from a varying network of monitoring wells (fig. 2). The specific wells sampled at different times and the methods and analyses used by the Navy for collecting and analyzing ground-water samples are described by URS Consultants, Inc. (1993 and 1997a), URS Greiner, Inc. (2000), and CH2M Hill Constructors, Inc. (2001). In general, samples were collected with bottom-filling bailers during 1991, and with submersible or peristaltic pumps after 1991. Bailer samples were collected after purging at least three well volumes of water from the wells. Pumped samples were collected using a modification of the Puls and Barcelona (1996) low-flow sampling method in which dedicated pumps were not used. Samples were collected after allowing ground-water temperature, pH, specific conductance, and turbidity measurements to stabilize to within 10 percent. The Navy's ground-water analytical results that were used in this investigation included concentrations of VOCs, total metals, and dissolved metals determined using the U.S. Environmental Protection Agency's Contract Laboratory Program (CLP) methods that were applicable at the time of sampling.

The Navy's surface-water chemistry data were collected from a network of sampling sites located along the creek that flows through the marsh, the marsh pond, the tide flats, and into Dogfish Bay (fig. 2). The specific sites that were sampled at different times and the methods and analyses used for collecting and analyzing surface-water samples are described by URS Consultants, Inc. (1993 and 1997a) and CH2M Hill Constructors, Inc. (2001). In general, all surface-water samples were single-grab samples collected by hand in small containers. The Navy's surface-water analytical results used in this investigation also included determinations for VOCs, total metals, and dissolved metals using the U.S. Environmental Protection Agency's CLP methods that were applicable at the time of sampling.

The USGS collected ground-water samples from various wells and piezometers between 1996 and 2000. All samples were collected with a peristaltic pump after purging at least three well volumes of water from the wells. Most samples were collected after allowing ground-water temperature, pH, specific conductance, and DO measured in a flow-through chamber to stabilize to within 10 percent; purge water from wells sampled from September 1996 through March 1998 was not monitored.

Usually, ground-water temperature, specific conductance, and pH were measured in the field immediately before collection of unfiltered samples; DO was always measured in the field. Specific conductance and temperature were measured using a temperature-compensated probe and meter that were checked daily with standard reference solutions. The pH was measured using a temperature-compensated meter calibrated daily with two pH standards. Dissolved oxygen was measured using one or more methods, including a modified Winkler titration (Radtke and others, 1998), a temperature-compensated meter that was calibrated daily with water-saturated air, or 0–1 mg/L CHEMettes Rhodazine-D™ colorimeteric ampules. Multiple DO analyses were often done to confirm concentrations of less than 1 mg/L. Alkalinity was measured by field titration of an unfiltered sample and concentration of the bicarbonate ion (HCO_3^-) was calculated.

Concentration of manganese, iron (II), total iron, and hydrogen sulfide were measured in the field immediately after collection and filtration of samples through a 0.45-micrometer membrane filter. Analyses were made using a Hach Model 2010 spectrophotometer, according to Hach analytical method numbers 8039, 8034, 8146, 8008, and 8131 (Hach Company, 1998). Selected samples also were filtered into polyethylene bottles, acidified with nitric acid to a pH of less than 2, chilled, and sent to the USGS National Water Quality Laboratory (NWQL) for measurement of manganese and iron using inductively coupled plasma (ICP) spectroscopy.

Those lab analyses were done to check the accuracy of the field analyses, and the data were found to be comparable to the field analyses (data not shown). Samples for sulfate and chloride analyses were filtered into polyethylene bottles with no preservatives added, and analyte concentrations were measured using ion chromatography at the NWQL or at the USGS Microbial Studies Group Laboratory (MSGL) in Columbia, S.C.

VOC samples were collected in 40-mL glass vials, acidified to a pH of less than 2 with hydrochloric acid, sealed, placed on ice, and shipped to one of three laboratories for analysis using EPA Method 8260A: the MSGL, the NWQL, and a NWQL contract laboratory (Quanterra) in Denver, Colo. Total organic carbon (TOC) was measured in the USGS laboratory in Ocala, Fla., using EPA Method 415.1. The unfiltered TOC samples were collected in amber glass bottles and chilled to less than 4°C before shipment to the laboratory. Dissolved methane, ethene, and ethane samples were collected in serum bottles and sealed with Teflon® septa. The samples were preserved with mercuric chloride, chilled, and analyzed using gas chromatography (Kampbell and others, 1989) at the MSGL or at Transglobal Environmental Geosciences Northwest, Inc., in Lacey, Wash.

Dissolved H_2 in ground water was sampled using the bubble-strip method of Chapelle and others (1997) and concentrations were measured in the field using a gas chromatograph equipped with a reduction gas detector. Initial gas samples were collected and analyzed after 20 minutes of stripping; subsequent samples were collected and analyzed at about 5-minute intervals until measured H_2 concentrations stabilized to within 10 percent.

Oxygen-18 and hydrogen-2 (deuterium) samples were unfiltered and were collected in 250-mL polyethylene bottles. Oxygen-18 concentrations were measured using the CO_2 equilibration technique (25°C) of Epstein and Mayeda (1953). Deuterium concentrations were measured using a hydrogen equilibration technique (Coplen and others, 1991).

Samples for tritium/helium age dating were collected in 12-inch-long, 3/8-inch-diameter copper tubes. The tubes were crimped closed while the contents were under pressure from the sampling pump to eliminate atmospheric contamination. The analyses for tritium and helium isotopes and the estimated age dates for each sample were determined at Lamont-Doherty Earth Observatory of Columbia University, Palisades, N.Y. (Ludin and others, 2001).

VOCs in shallow ground water directly beneath the marsh stream and pond were sampled at 17 locations (fig. 2) using passive diffusion samplers. Such sampling devices have proven to be effective in sampling ground water in wells (Vroblesky, 2001), and there is no theoretical reason that they would not be equally effective at sampling ground water directly in saturated sediments. The samplers consisted of 8-in-long by 2-in-diameter polyethylene lay-flat tubing that was filled with deionized water and heat sealed at both ends; they were constructed by the USGS in Tacoma, Wash. The filled bags were inserted into plastic mesh sleeves to protect them from damage. Sixteen samplers were buried by hand in about 12-in of mud beneath the marsh creek and pond, and one sampler was buried beneath an isolated puddle. The holes were backfilled with native materials and tamped down and left to equilibrate with pore water for more than 2 weeks. The locations of the samplers were marked with wooden stakes and approximately located on a site map. Samplers were retrieved by hand and immediately processed. A corner of each bag was cut and three 40-mL glass VOC vials were filled, acidified to a pH of less than 2 with HCl, sealed, and kept on ice for shipment to the NWQL.

Calculation of Contaminant Mass-Degradation Rates in Ground Water and Discharge to Surface Water

The rate at which the contaminant mass at OU 1 was degraded in ground water and the rate at which contaminants were discharged to surface water were calculated for recent (1999–2000) conditions using mass-balance equations. Comparison of the two rates provides a measure of the effectiveness of destructive attenuation mechanisms. The mass degradation and discharge rates represent recent conditions only and are not appropriate for extrapolating contaminant degradation long into the future; if ground-water flow rates change or if the mass of dissolved contaminants in ground water decreases due to phytoremediation, the mass degradation and discharge rates may also change. However, the rates presented in this report can in the future be compared to rates calculated from additional data collected after phtytoremediation is fully implemented to provide insight into the effects of phytoremediation.

The mass degradation and discharge rates were calculated using a flux-based approach that accounts for the entire dissolved mass of chlorinated ethenes in ground water. The approach compared the flux of chlorinated ethenes that is available to migrate from the landfill to the flux that actually migrates from the landfill to beneath the marsh, to the intermediate aquifer, and ultimately to surface water. The difference between the flux available to migrate from the landfill and the flux that actually migrates is an estimate of the mass of contaminants degraded in ground water over a given duration. Data used for the calculations included contaminant concentration data primarily from 1999 and 2000, and ground-water flux estimates from a previous site-characterization investigation (URS Consultants Inc., 1997b). The mass of non-dissolved contaminants in the landfill (such as that sorbed to sediment or present as non-aqueous phase liquids) is unknown, so the calculations considered only contaminants dissolved in ground water.

Chlorinated ethene fluxes across three separate transects positioned approximately perpendicular to ground-water flow were calculated by multiplying ground-water fluxes determined by URS Consultants Inc. (1997b) by observed contaminant concentrations, with the appropriate unit conversions. The flux across the most upgradient transect represented the mass of contaminants available to migrate from the landfill; the upgradient transect was oriented north to south beneath the landfill and connected the most highly contaminated wells in the upper aquifer (specific wells used are identified in the tables presenting the flux calculations and results). The flux across a downgradient transect in the upper aquifer represented the mass of contaminants that actually migrates from the landfill in the upper aquifer; that transect was oriented north to south beneath the marsh and connected the line of diffusion sampler sites. Finally, the flux across a downgradient transect in the intermediate aquifer transect represented the mass of contaminants that actually migrates from the landfill in that deeper unit; that transect was oriented northeast to southwest in the intermediate aquifer downgradient from the landfill and connected the row of intermediate aquifer wells at that location.

Once the chlorinated ethene fluxes were calculated for the three transects, the mass degraded in ground water per day was calculated as the difference between the flux across the upgradient (landfill) transect and the sum of the fluxes across the

downgradient (marsh and intermediate aquifer) transects. There were too few data to estimate mass degradation beyond the marsh and intermediate aquifer transects, so it was conservatively assumed that all chlorinated ethenes that flowed past those downgradient transects discharged to surface water. The validity of the mass balance calculations was partly assessed by independently calculating the flux of chlorinated ethenes into the marsh using available surface-water flow and contaminant concentration data. No similar data were available to calculate the actual flux of contaminants to the tide flats and Dogfish Bay.

The flux-based mass balance was based on the following assumptions. First, the ground-water sampling locations were assumed to adequately represent conditions throughout the site. That assumption is reasonable for the relatively dense network of wells and piezometers in the landfill and intermediate aquifer, although it is less certain that the diffusion samplers adequately represent shallow ground water beneath the marsh. It was also assumed that steady-state conditions applied to ground-water flow, the supply of dissolved contaminants, and contaminant degradation rates. Historical and recent water-level data suggest that ground-water flow was at or near steady-state conditions (URS Greiner, Inc., 2000). Generally stable or slowly decreasing CVOC concentrations in the most contaminated landfill wells suggest that the supply of dissolved contaminants has been relatively steady. Less is known about the history of contaminant degradation rates, although the landfill has been closed for many years and enough time has passed for redox conditions to stabilize and the microbial community to acclimate. The final assumption was that there was no substantial contaminant loss in ground water through sorption or volatilization. Volatilization losses were probably minimal because volatilization of chemicals from ground water is greatly constrained by the rate of vapor transport upward through the unsaturated zone. Sorption losses may have been important in the organic-rich marsh sediments, but contaminants have been flowing through those sediments for many decades, so the bulk of the sorption capacity was probably filled long ago. Contaminant losses through both of these mechanisms are inherently included in the reported calculated mass degradation rates.

Calculation of Contaminant Attenuation Rates

The contaminant attenuation rate is the first-order approximation of the rate at which ground-water contaminant concentrations decrease in the downgradient direction. The calculated attenuation rates could change as a result of changing redox conditions, but the rates are more appropriate than mass degradation rates for extrapolating contaminant degradation into the future because they are not dependent on the absolute concentrations of CVOCs. The attenuation rates presented in this report can also be compared in the future with similarly calculated results based on new data that could be collected after phtytoremediation is fully implemented to provide insight into the effects of phytoremediation on CVOC degradation.

The attenuation rates are presented as half-lives ($T_{1/2}$), in years, which are measures of the time required to reduce the concentration of a contaminant to one-half of its initial value. Attenuation rates were estimated using the simple one-dimensional first-order rate equation

$$C_x = C_o e^{-kt} , \qquad (1)$$

where
- C_x is the contaminant concentration at a distance x feet downgradient of C_o,
- C_o is the contaminant concentration at an upgradient location,
- t is time required for contaminants to travel distance x, and
- k is the first-order rate constant.

If C_o and C_x are known, the equation can be rearranged as follows to solve for k;

$$k = [(\ln C_o / C_x)]/t \qquad (2)$$

k can be converted to a half-life ($T_{1/2}$) by

$$T_{1/2} = \ln(2)/k \qquad (3)$$

and

$$T_{1/2} = 0.693/k \qquad (4)$$

The concentration values used in the equation were from individual sampling locations along presumed flow paths, or were from average concentrations for transects aligned perpendicular to the ground-water flow direction (specific wells used are identified in the tables presenting the attenuation rate calculations and results). Transect averages were used to overcome uncertainties about whether individual wells lie exactly along the centerline of a flowpath. Estimates of ground-water travel-times used in the calculations were from URS Consultants, Inc. (1997a) and from data presented in this report.

HYDROGEOLOGIC AND GEOCHEMICAL CHARACTERIZATION FOR NATURAL ATTENUATION

Site characteristics used to evaluate natural attenuation included the direction and rate of ground-water flow, the redox conditions of ground water, and the distribution of the various CVOCs. The Navy did much of the hydrogeologic and contaminant characterization at the site (URS Consultants, Inc., 1997a). The focus of this section of the report is on new data and interpretations concerning ground-water flow directions, the rates and distribution of contaminants, and ground-water redox conditions.

Ground-Water Flow Directions and Rates

Previous estimates of ground-water flow directions and rates at Area 1 are shown in figures 9 and 10. Some important uncertainties regarding ground-water flowpaths and flow rates in the intermediate aquifer remained after publication of those estimates (URS Consultants, Inc., 1997a). Although the human health risk from contaminants in the intermediate aquifer was demonstrated to be minimal, the contaminants are still a concern because they are migrating beyond the landfill and may eventually pose an environmental risk in the marine environment.

Ground-Water Flowpaths Between the Upper and Intermediate Aquifers

The flowpath followed by contaminants from the landfill out to the intermediate aquifer well MW1-39 beneath the Highway 308 causeway is uncertain, in large because the chemistry of ground water in well MW1-39 is substantially different from that in the other three wells on the causeway. In particular, detectable concentrations of CVOCs have been found only in MW1-39, and ground water at MW1-39 has a specific conductance that is 65 to 95 percent lower than that observed at the three nearby wells. The specific conductance in well MW1-39 is also 60 to 80 percent lower than that observed at the contaminated intermediate-aquifer wells closer to the landfill (MW1-25 and MW1-28) that are presumably upgradient from MW1-39. URS Consultants, Inc. (1997a) suggested two possible flowpaths from the landfill that could explain the data. One flowpath presumed the contaminants migrated in the top layer of the intermediate aquifer above more saline ground water represented by MW1-25 and MW1-28, and the other presumed contaminated ground water from MW1-25 and MW1-28 mixed with fresh uncontaminated ground water flowing beneath the tide flats from the southwest. The flowpath that contaminants follow from the landfill to MW1-39 was further examined in this study using new common-ion, oxygen-18 (^{18}O), and hydrogen-2 (deuterium or ^{2}H) data.

Details about the hydrogeologic setting and well characteristics of the area between the landfill and Highway 308 are as follows. Four intermediate-aquifer wells are located near the center of the Highway 308 causeway: MW1-36, MW1-37, MW1-38, and MW1-39 (fig. 2). Wells MW1-37 and MW1-39 are screened immediately below the approximately 5-ft-thick middle aquitard at a depth of about 27 feet, whereas wells MW1-36 and MW1-38 are screened about 12 feet below that altitude at the bottom of the intermediate aquifer. All wells have 5-ft-long screen intervals. Of the shallower wells, MW1-39 is screened in a non-glacial silty sand and MW1-37 is screened in a glacial sand and gravel; both are underlain by a relatively silty subunit within the intermediate aquifer (fig. 4). Both of the deeper wells, MW1-36 and MW1-38, are screened in a glacial sand and gravel that is similar to the unit screened by the intermediate-aquifer wells MW1-25

and MW1-28 nearer the landfill. Between the two pairs of wells on the causeway, the specific conductance of ground water is substantially higher northeast of the highway bridge, and within each well pair, the specific conductance is higher in the deeper wells.

^{2}H and ^{18}O isotope samples were collected during June 2000 in eight wells at OU 1, including an uncontaminated upgradient intermediate-aquifer well (MW1-33), two upper-aquifer wells in the landfill (MW1-16 and MW1-41), three intermediate-aquifer wells near the downgradient margin of the landfill (MW1-29, MW1-28, and MW1-25), and two downgradient wells on the causeway at Highway 308 (MW1-38 and MW1-39). ^{2}H and ^{18}O isotopes are ideal conservative tracers for ground water because they are chemically stable and are physically a part of the water molecule. The isotope "signature" of a specific type of ground water is simply its concentration of ^{2}H and ^{18}O. Isotope concentrations are reported as so-called "delta" values in units of parts per thousand relative to Vienna Standard Mean Ocean Water, and a negative delta value indicates that water is depleted in the heavy isotope relative to the standard.

Analysis of the isotope data suggests that the deeper well MW1-38 is on the primary intermediate-aquifer flowpath that originates at MW1-33 and passes through MW1-25 and MW1-28, but the shallower well MW1-39 is part of a different flowpath (fig. 14). Ground water at MW1-39, the only contaminated well on the causeway, is isotopically distinct from ground water at all the other wells sampled, whereas ground water in the deeper uncontaminated deeper well MW1-38 is isotopically similar to contaminated intermediate-aquifer ground water nearer the landfill (MW1-25 and 28) as well as uncontaminated upgradient water (MW1-33). The ground water at MW1-39 is isotopically distinct in that it is relatively depleted in the heavier isotopes. It is beyond the scope of this report to fully investigate the cause of that depletion, but one documented mechanism that can deplete heavier isotopes in ground-water systems is ultra-filtration through fine-grained geologic materials such as a confining bed (Coplen and Hanshaw, 1973).
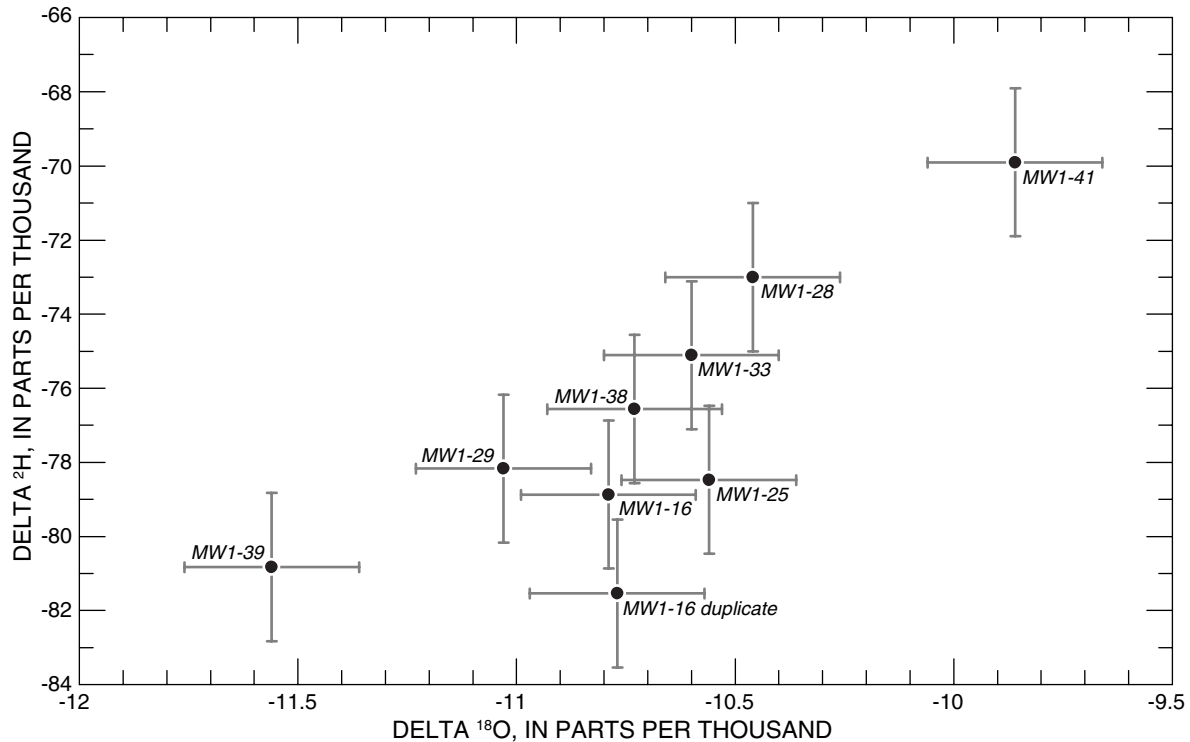
Figure 14. Concentrations of oxygen-18 and hydrogen-2 isotopes in ground water in selected wells, June 2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

That possible mechanism suggests an alternate flowpath for contamination to reach Highway 308 from the landfill: percolation of contaminated upper-aquifer ground water from the northern part of the landfill directly through the fine-grained middle aquitard to the layer screened by MW1-39.

Ground water at well MW1-41, the only upper-aquifer well sampled for isotopes in the northern part of the landfill, is also isotopically distinct from that at all other wells sampled because it is enriched in the heavier isotopes. Isotope enrichment from evaporation during recharge is the likely cause of that difference; the well is located in the northern plantation in an area where ponded water and saturated surface soils have inhibited tree growth. Ground water in upper-aquifer well MW1-16 in the southern plantation is more similar in composition to ground water in the intermediate-aquifer wells, and no ponded water has been noted at its location. Given that contaminants are able to migrate directly from the upper aquifer to the main body of the intermediate aquifer through the

window in the middle aquitard beneath the central landfill, it is likely that contaminants in MW1-25 and MW1-28 have followed that flowpath. The results of the isotope analysis suggest the hypothesis of two distinct flowpaths for contaminants in the intermediate aquifer, one through the aquitard itself to MW1-39 and the other through the aquitard window to MW1-25 and 28. This hypothesis was further explored by an evaluation of common-ion data collected in June 2000.

The common-ion data highlight a number of known and hypothesized characteristics of ground-water flowpaths at OU 1. Common-ion data from selected wells were plotted on a variation of a trilinear diagram (fig. 15a) , a graphical tool that illustrates differences in the ionic composition of various samples as well as the effects of mixing waters with different ionic compositions (Hill 1940; Piper 1944). The diameters of the circles around individual points in the diagram are directly proportional to the concentration of total dissolved solids (TDS) in the sample.

The trilinear diagram shows clear differences between ground water at different locations. Uncontaminated intermediate-aquifer water that is not affected by seawater (light blue symbols on fig. 15) is calcium/magnesium-bicarbonate type with relatively low TDS concentration, which is typical for uncontaminated ground water in Kitsap County, Wash. (Greene, 1997). The exception in this group is well MW1-7 which is screened in a fine-grained unit that is not truly part of the intermediate aquifer; the contaminated intermediate-aquifer well 1MW-4 is also screened in finer-grained materials and plots closely to MW1-7. Uncontaminated (or minimally contaminated) upper-aquifer water (purple symbols on fig. 15) is also calcium/magnesium-bicarbonate type except where wells are screened in finer-grained materials (such as MW1-35 and MW1-20). Contaminated upper-aquifer water beneath most of the landfill (red symbols on fig. 15) is usually somewhat enriched in sodium and potassium and consistently has elevated TDS concentrations due to mixing with landfill leachate. Contaminated upper-aquifer wells near the downgradient margin of the northern part of the landfill (1MW-1, MW1-2 and MW1-19; grey symbols on fig. 15) are substantially enriched in sodium and potassium and have elevated TDS concentrations due to mixing with landfill leachate of a different composition. And finally, intermediate-aquifer water downgradient of the landfill (green symbols for wells near landfill and pink symbols for wells near the Highway 308 causeway on fig. 15) is enriched with chloride and sodium as a result of mixing with seawater—the ionic composition of seawater (without the TDS circle) is shown on fig. 15 for comparison. Specific differences between seawater—affected wells in the intermediate aquifer are discussed below.

The observed ionic differences support the hypothesis that there are two distinct flowpaths for contaminants to reach intermediate-aquifer wells. Mixing of two different waters is illustrated by a straight line joining two points on a trilinear diagram (assuming ions are not added or removed by processes such as ion exchange, precipitation, or dissolution of salts). Line "AA" in figure 15b illustrates the salinization of intermediate-aquifer ground water when uncontaminated intermediate-aquifer water flows from the upgradient area to the south of OU 1 (MW1-33), to beneath the southern tip of the tide flats shoreline (MW1-29), and eventually towards seawater in Dogfish Bay. Lines labeled BB illustrate the contamination and salinization of intermediate-aquifer water by mixing with two different waters; uncontaminated intermediate-aquifer water from south of the landfill (MW1-33) mixes with contaminated upper-aquifer water from the central part of the landfill (1MW-1 and MW1-16), and the resulting mix flows towards seawater past MW1-25 out to MW1-36 or MW1-37. Similar lines that included MW1-28 rather than MW1-25 could be drawn. Sodium and potassium concentrations in MW1-25 and MW1-28 are elevated above the level expected for straight mixing of intermediate-aquifer water with seawater (line AA), suggesting that sodium/potassium-enriched upper-aquifer water from the northern plantation is part of the mix. Lines labeled CC illustrate the contamination and salinization of intermediate-aquifer ground water by mixing with one (or possibly two) different waters along the newly hypothesized flowpath; contaminated sodium/potassium-enriched upper-aquifer water from the northern part of the landfill (1MW-1 or MW1-2) diffuses through the middle aquitard and mixes with seawater as it flows out towards Highway 308 (MW1-39). Water at MW1-39 has a lower TDS concentration than contaminated landfill water, so the landfill water may also be mixed along the flowpath with a third, unidentified type of water with lower TDS concentration. The lower TDS concentration in MW1-39 may also be a result of dissolved solids removal from the landfill water by ultra-filtration or precipitation within the fine-grained unit, or it may reflect a preferential flowpath between the landfill and MW1-39 that is not reflected in the chemistry found in existing landfill wells. Although the isotope and common-ion data are not definitive, they do support the hypotheses that contaminated ground water in MW1-39 comes directly from the northern part of the landfill and not from the main body of the intermediate aquifer represented by MW1-25 and MW1-28.
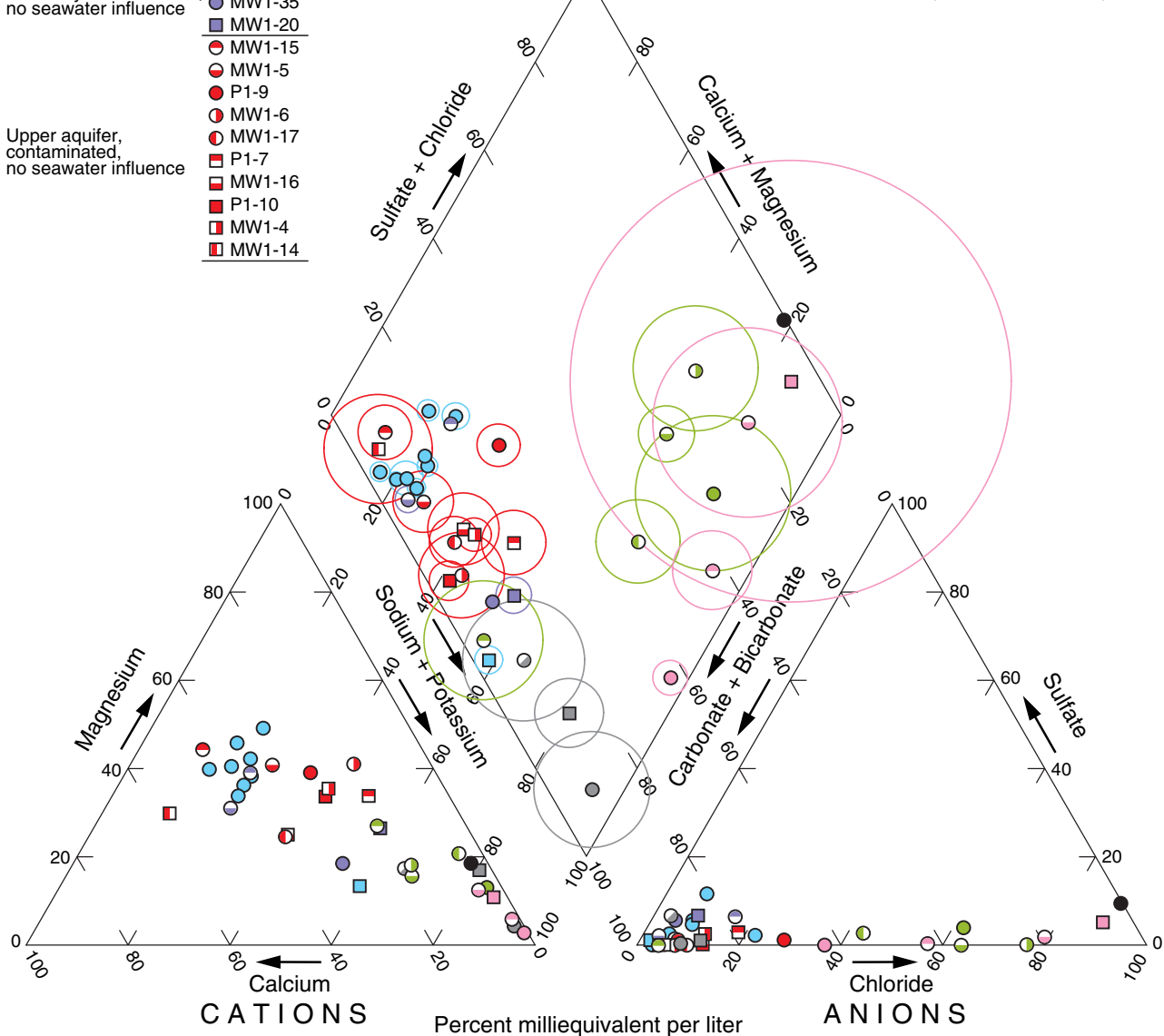
Figure 15. Trilinear diagrams showing (A) differences in ionic composition of water at selected wells and (B) mixing of ground waters along two flowpaths at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

B.
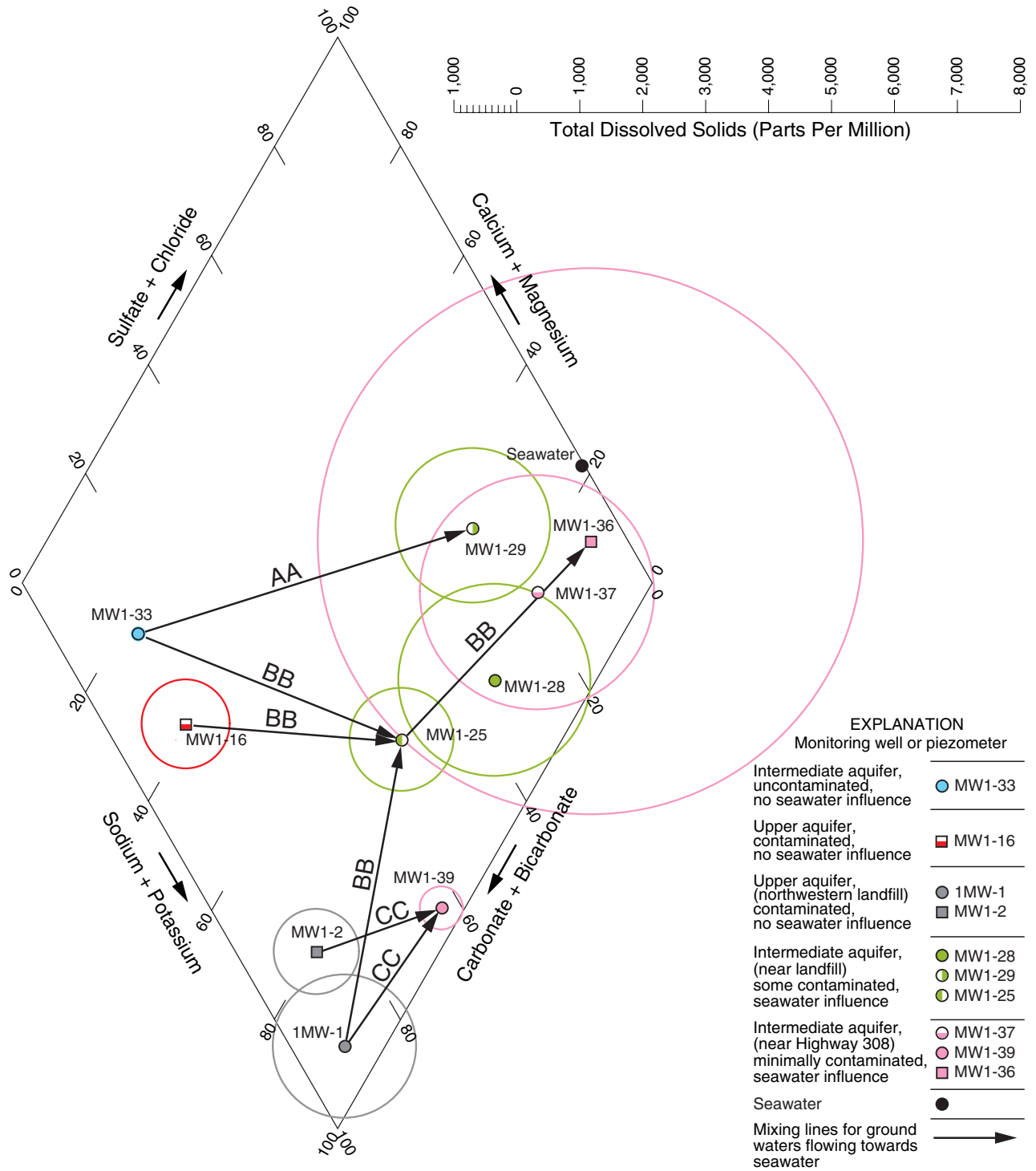
Figure 15. *Continued*

Ground-Water Flow Rates in the Intermediate Aquifer

Previous flow-rate estimates for ground water in the intermediate aquifer downgradient of the landfill were inconsistent. The USGS previously collected and interpreted tritium data from selected wells at OU 1 and estimated that the flow rate in the intermediate aquifer between the landfill margin and Highway 308 was about 25 ft/yr (Appendix A in URS Consultants, Inc., 1997a). That estimate was more than twice the 10 ft/yr rate estimated using hydraulic-gradient and conductivity data (fig. 10). For this study, the USGS collected and analyzed data for use in a more accurate tritium/helium age-dating method (Solomon and Cook, 2000) to derive independent estimates of ground-water flow rates in the intermediate aquifer. The tritium/helium method allows age-date estimation not only by quantifying the amount of tritium in a sample, but also by quantifying the amount of the ^{3}helium isotope in a sample that resulted from radioactive decay of tritium. An expanded discussion with references on the theory and application of tritium/helium age dating can be found in Solomon and Cook (2000) and is not repeated in this report.

The previous flow-rate estimates and the new tritium/helium flow-rate estimate are consistent if the newly hypothesized flowpath out to well MW1-39 is presumed true. Tritium/helium age dates were calculated for ground-water samples collected by USGS in September 1996 from intermediate-aquifer wells MW1-31, MW1-25, and MW1-39 (table 2). A sample was also collected from shallow well MW1-15, but it was contaminated in the laboratory and unusable. The calculated tritium/helium age dates of ground water (a measure of the time between when the ground water was recharged and when it was sampled) were 11 years for MW1-31, 24 years for MW1-25, and 38 years for MW1-39. Ground-water flow rates were estimated by dividing the distance traveled between wells by the difference in age dates for water from two wells. The distance between upgradient well MW1-31 and MW1-25 is 660 ft. Assuming that upper-aquifer water does not mix with intermediate-aquifer water along the flow path from MW1-31 to MW1-25, the estimated ground-water flow rate would be about 50 ft/yr, which is faster than rate of 33 ft/yr estimated in 1997. However, some "younger" upper-aquifer water is know to reach the intermediate aquifer between the two wells (MW1-25 is contaminated), so the 50 ft/yr flow rate estimate must be too high and the actual flow rate is more likely similar to the hydraulics-based estimate of 33 ft/yr. The tritium/helium flow rate beneath the tide flats between wells MW1-25 and MW1-39 was similarly calculated to be 36 ft/yr [500 ft / (38 yrs – 24 yrs)], but those two wells are now hypothesized to be on different flowpaths. The calculated flow rate from tritium age dates reported in 1997 was similar (25 ft/yr), but that estimate was also based on the erroneous assumption that the wells are on the same flowpath. Both of those age-date-based estimates are much higher than the hydraulics-based estimate of 10 ft/yr. However, presuming that MW1-39 is on a more shallow flowpath coming from the upper aquifer (as indicated by isotope and common-ion data), and assuming that the upper-aquifer water at the margin of the landfill is about 5 years old, then the tritium/helium based flow rate beneath the tide flats between wells MW1-2 and MW1-39 would be about 15 ft/yr [500 ft / (38 yr - 5 yr)].

Table 2. Age dates calculated using tritium/helium data from ground water sampled September 19, 1996, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[TU, tritium unit; ccSTPg^{-1}, cubic centimeters at standard temperature and pressure per gram]

Well identification No.	Tritium (TU)	^{3}Helium/ ^{4}Helium 10^{-6}	^{4}Helium 10^{-8}	Neon (ccSTPg^{-1})	Uncorrected age (years)	Corrected age (years)
MW1-31	5.92	1.63	5.13	21.9	12	11
MW1-25	5.91	2.03	5.24	20.9	22	24
MW1-39	1.64	1.56	7.17	24.6	27	38

That estimate is similar to the 1997 hydraulics-estimated rates of 10 ft/yr. No tritium/helium data were collected at other wells located on the Highway 308 causeway that are likely on the same flowpath as MW1-25, so the hydraulics-based estimate of about 10 ft/yr is the only estimate available for the main body of the intermediate aquifer.

Changes in Ground-Water Flow from Phytoremediation Activities

Performance monitoring of the phytoremediation activities by the Navy during 1999 and 2000 showed that ground-water flow directions and gradients are consistent with historical findings (URS Greiner, Inc., 2000). The poplar trees in the phytoremediation plantations were not yet mature in 2000, so the lack of discrenable water-level changes to date is not unexpected. Thus, for this report, it is presumed that the overall ground-water flow directions and rates have not yet been affected by phytoremediation activities.

Redox Conditions in Ground Water

Characterizing ground-water redox conditions was required because redox conditions greatly control the occurrence and rate of nearly all contaminant biodegradation processes. The redox conditions of ground water in the upper and intermediate aquifers at OU 1 were characterized using ground-water geochemistry data collected by the USGS between during 1996-2000 (table 7, back of report). The geochemical data were not always consistent with theory or easy to interpret for reasons previously described in this report. The two approaches for identifying redox conditions described in the methods section of this report were generally followed, except in the following three cases.

1. A reliable DO concentration of greater than 1 mg/L indicated aerobic conditions, and the reliability of a DO measurement was determined by comparing the measurement with dissolved iron and manganese concentrations. It is relatively easy to contaminate an anaerobic ground-water sample with oxygen and is quite difficult to contaminate an aerobic sample with dissolved iron and manganese. Thus, a sample with a measured DO concentration greater than 1 mg/L that also had dissolved iron (II) or manganese concentrations exceeding about 0.2 mg/L was

considered to be anaerobic. Conflicting DO and dissolved metals data were most frequent in the September 1996 data, and most wells with DO concentrations greater than 1 mg/L in 1996 were found to be anaerobic in all subsequent sampling rounds. The suspect 1996 DO data most likely result from inadequate well purging before sampling (purging was done up to 24 hours prior to sampling in 1996 only), or from inadvertent sample aeration during collection.

2. The unique relationship between dissolved H_2 concentrations and redox conditions shown in table 1 was assumed to be reasonable for ground water at OU 1. However, it was recognized that a pumped sample from a well screened 5 ft or longer likely included ground water from different redox zones in the highly heterogeneous environment of the landfill. Thus, additional geochemistry data were often used to assign a redox condition different than the condition indicated by dissolved H_2 concentration alone. In particular, if sulfide and iron (II) were detected in the same sample at elevated concentrations, sulfate-reducing conditions were assigned even if dissolved H_2 concentrations were less than 1 nM. This was justified in part because the temperature of ground water at Keyport (12–15°C) is colder than that on which the equilibrium H_2 concentrations are based. It was also justified because iron (II) and sulfide are expected to react quite rapidly and precipitate from solution, so a detection of both analytes in a sample suggested on-going production of sulfide through sulfate reduction.

3. The detection of methane in a well was not necessarily interpreted as signifying methanogenic conditions at that well. Elevated methane concentrations were found throughout the landfill, indicating that methanogenic conditions in OU 1 ground water are common but perhaps limited to small areas distributed throughout the landfill. Methane is relatively mobile in ground water, so elevated methane concentrations in wells located near the margin or downgradient of the landfill were not considered conclusive evidence for methanogenic conditions in those downgradient locations.

Upper Aquifer

Redox conditions in many of the wells in the upper aquifer varied widely over time (table 7, back of report). Some of that variability may be actual changes in redox conditions over time, but some of it can be attributed to technical shortcomings in sampling highly heterogeneous ground water or to non-equilibrium redox conditions.

Despite the variability in geochemistry sample data, a consistent spatial pattern of redox conditions in the upper aquifer was ascertained from the data. There were two areas of strongly reducing ground water beneath the OU 1 landfill—one in the vicinity of the northern plantation and one in the southern plantation-and those areas were surrounded by mildly reducing ground waters. The site-wide redox conditions can be shown by mapping the average dissolved H_2 concentrations from all sampling rounds for each well, and then delineating zones of aerobic ground water, mildly reducing ground water (dissolved H_2 concentrations less than 1 nM), and strongly reducing ground water (dissolved H_2 concentrations greater than 1 nM) (fig. 16). Those three redox classifications are particularly relevant to natural attenuation because biodegradation through reductive dechlorination is generally limited to strongly reducing ground water, and biodegradation through direct mineralization is most effective in aerobic or mildly reducing ground water.

The distribution of redox conditions in the upper aquifer corresponds well to the distribution of total organic carbon in ground water (fig. 17). It is clear that the landfill is a substantial source of organic carbon in shallow ground water, and the former waste-paint disposal area at the southern end of the landfill is a particularly abundant source of organic carbon. Because organic carbon is a basic necessity for microbial respiration, the correlation between organic carbon and redox conditions is clear evidence that microbially mediated processes are controlling redox conditions. Specific organic acids were analyzed in September 1996 ground-water samples, and organic-acid concentrations (particularly acetic acid) in southern plantation well MW1-16 were more than three orders of magnitude greater than those found in any other well (data not shown). Organic acids are compounds that can be readily metabolized by microorganisms, whereas TOC includes many carbon compounds that are not so easily metabolized.

Changes in Upper-Aquifer Redox Conditions from Phytoremediation Activities

The overall spatial pattern of redox conditions in the upper aquifer has not changed substantially over the six sampling rounds, but concentration changes in some redox-sensitive compounds suggest that ground-water chemistry was somewhat affected after asphalt was removed in February 1999. Beneath the southern plantation, a greater than 50-percent reduction in the concentrations of the relatively mobile compounds manganese, iron (II), and TOC between October 1998 and June 2000 may indicate a flushing or dilution of those analytes near the northern margin of the plantation near MW1-16 (fig. 18). A post-asphalt removal decrease in specific conductance at MW1-16 from 3,370 microseimens per centimeter (μS/cm) to 902 μS/cm (table 7, back of report) supports that hypothesis, as do decreased contaminant concentrations described later in this report. Specific conductance also decreased substantially in MW1-5 after asphalt removal, although concentration changes in redox analytes were not consistent, which suggests that all geochemical changes were not related to dilution alone. Beneath the northern plantation, a similar response to asphalt removal was not evident (fig. 19), probably because much of that area was not paved prior to phytoremediation. There was little evidence indicating a change in the historically strong reducing conditions beneath the centers of the plantations as a result of asphalt removal (see dissolved H_2 trends in figs. 18 and 19), although the piezometers with the high H_2 concentrations were not installed until after the asphalt removal. A substantial change in redox conditions is unlikely because even with the observed decrease in TOC after asphalt removal, there remained abundant organic carbon to quickly consume any additional dissolved oxygen that might be carried downward with increased recharge. Additional data would be needed to track the changes into the future, but ground-water consumption by the maturing poplar trees may induce more substantial changes in ground-water chemistry.
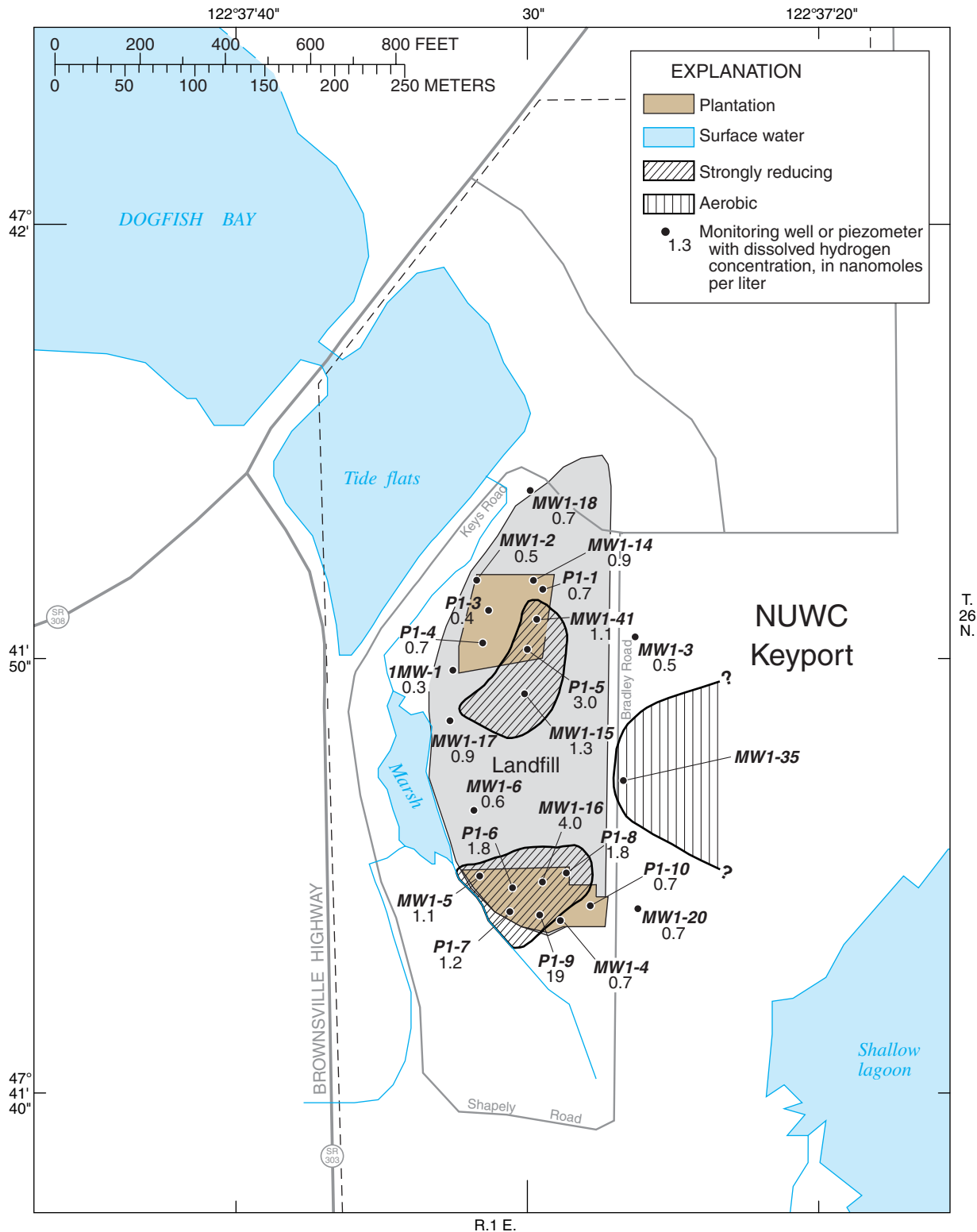
Figure 16. Average dissolved hydrogen (H$_2$) concentrations at sampled wells and delineated redox conditions in the upper aquifer at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.

Ground water not delineated as strongly reducing or aerobic is mildly reducing.
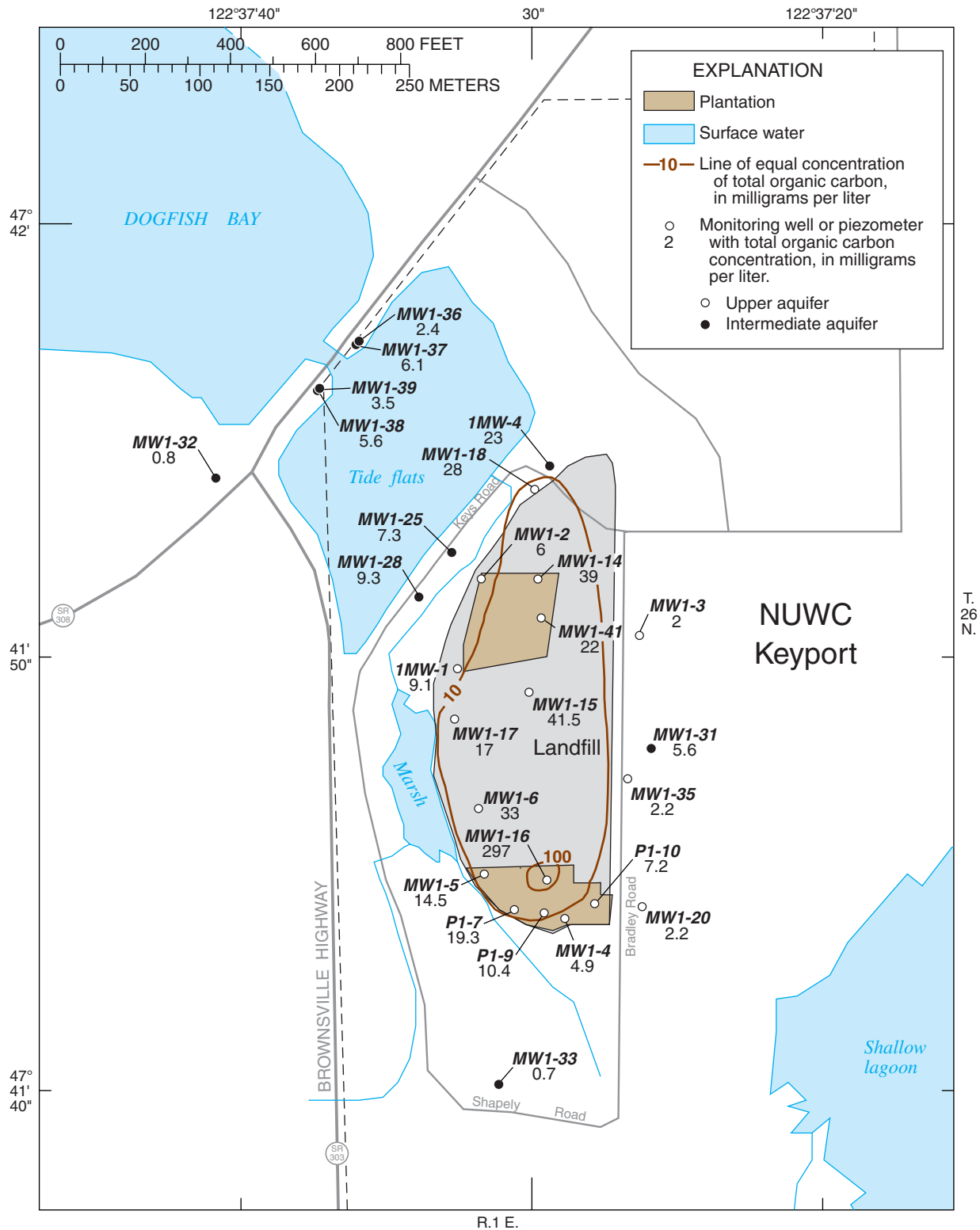
Figure 17. Concentrations of total organic carbon in ground water, 1999, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
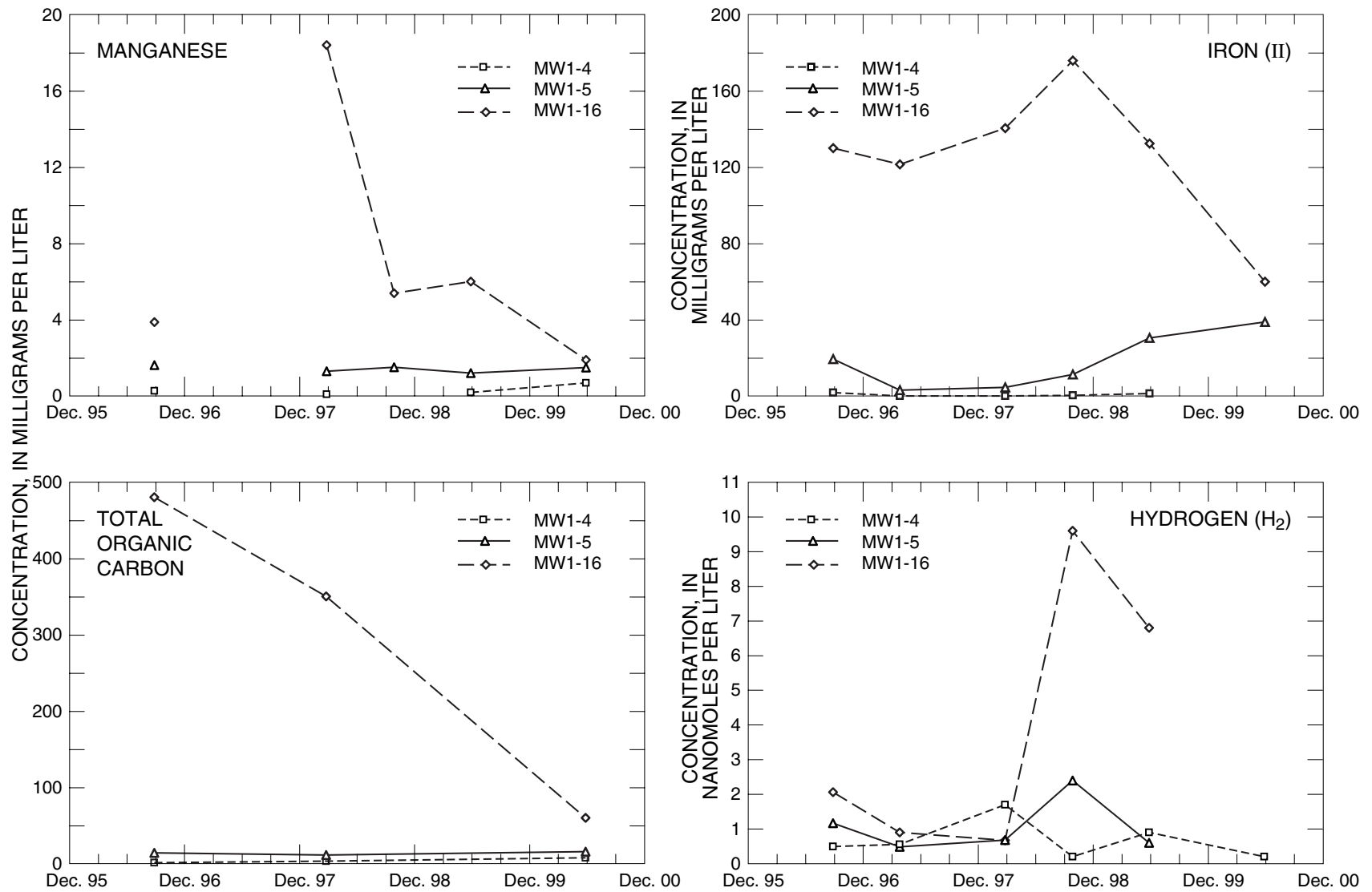
Figure 18. Concentrations of manganese, iron (II), total organic carbon, and hydrogen (H$_2$), 1996–2000, in wells MW1-4, MW1-5, and MW1-16 in the southern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.
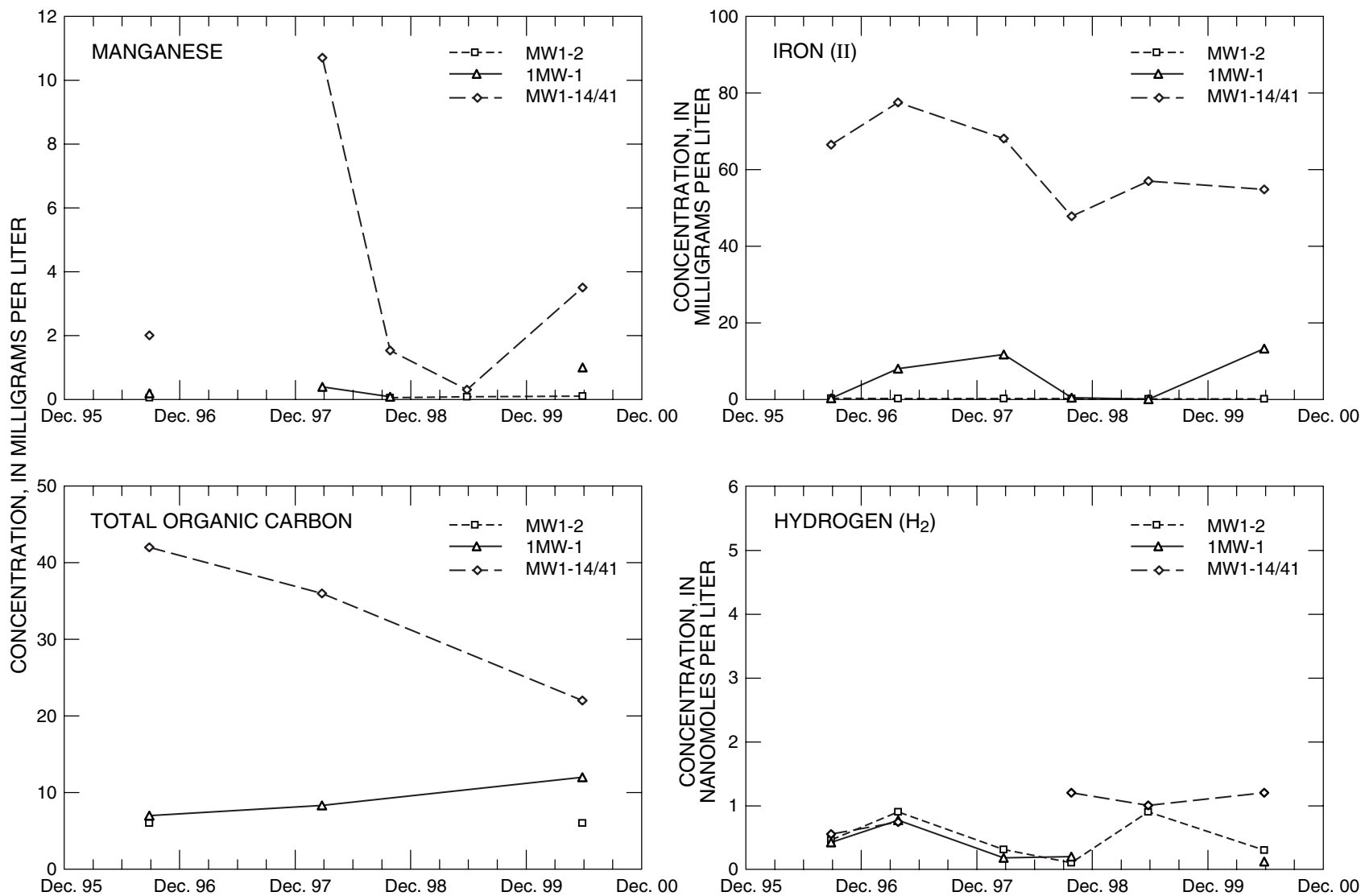
Figure 19. Concentrations of manganese, iron (II), total organic carbon, and hydrogen (H_2), 1996–2000, in wells MW1-2, 1MW-1, and MW1-14/41 in the northern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

Intermediate Aquifer

Background redox conditions in the intermediate aquifer are aerobic to the south of the landfill (MW1-33) and are iron or manganese reducing to the east of the landfill (MW1-31) and to the southwest of the tide flats (MW1-32) (table 7, back of report). At the downgradient margin of the landfill, conditions range from strongly reducing near the northern tip of the landfill (1MW-4) to iron or manganese reducing near the central landfill (MW1-25, MW1-28, and MW1-29) (fig. 20), and TOC concentrations are elevated in the wells contaminated with leachate (wells MW1-25, MW1-28, and 1MW-4 in fig. 17). Redox conditions have been more variable further downgradient in the intermediate aquifer beneath Highway 308 (fig. 21). The upper part of the intermediate aquifer at that location (MW1-37 and MW1-39) appears to switch between iron- and sulfate-reducing conditions, whereas the lower part of the aquifer (MW1-36 and MW1-38) appears to be consistently iron or manganese reducing. The alternating redox conditions may be related to tidal-induced changes in the intermediate aquifer (water levels in the wells along Highway 308 fluctuate in close accordance to tide level), but the specific mechanism causing the variability is unknown. It was observed that stronger reducing conditions were present in MW1-39 when samples were taken on a falling tide within 2 hours of the high tide. As would be expected in this deeper aquifer, there was no evidence that the redox conditions were affected by asphalt removal or other phytoremediation activities.

Distribution of Chlorinated VOCs in Upper-Aquifer Ground Water and Surface Water

The Navy has monitored the distribution of CVOCs in ground water at OU 1 since 1991. In this section of the report, some of those historical data are integrated with new CVOC data collected by the USGS from piezometers at the northern and southern plantations, and from passive diffusion samplers within the marsh. The distribution of CVOCs in ground water is required to evaluate natural attenuation because decreasing concentrations along flowpaths are evidence for natural attenuation, and because

increasing predominance of degradation products relative to parent compounds along flowpaths is evidence that biodegradation is a contributor to the attenuation. Interpretation of historical and new CVOC data is presented later in the "Evaluation of Natural Attenuation."

A more detailed distribution of total CVOCs in the upper aquifer was determined by integrating data from monitoring wells, piezometers, and diffusion samplers (fig. 22). The data shown were collected primarily in June 1999 for wells and piezometers, and in June 2000 for diffusion samplers; some data from April 1997 are included for wells that were not sampled more recently (table 8, back of report). Although the data are from different times, they reasonably represent the distribution of CVOCs in the landfill at about the time that phytoremediation activities began. As will be described in the following section of this report, changes in CVOC concentrations attributed to the first 2 years of phytoremediation activities have been noticeable in only a few selected wells. The distribution of CVOCs in the intermediate aquifer has changed little from that shown previously in figure 12.

The more detailed distribution of CVOCs in the upper aquifer is similar to the distribution determined previously (fig. 11), with a few notable exceptions. First, data from piezometers in the north and south plantations show that the highest CVOC concentrations in the shallow aquifer are about four times greater than previously thought. Because CVOC concentrations in most monitoring wells have changed little over time, the refined distribution reflects the increased number of measurement points rather than any substantial change in site CVOC concentrations. The overall pattern of CVOC concentrations in shallow ground water beneath the marsh correlates well with the pattern observed beneath the landfill. That is evidence that the passive diffusion samplers used to collect marsh CVOC samples worked as intended and are representative of shallow ground-water conditions.
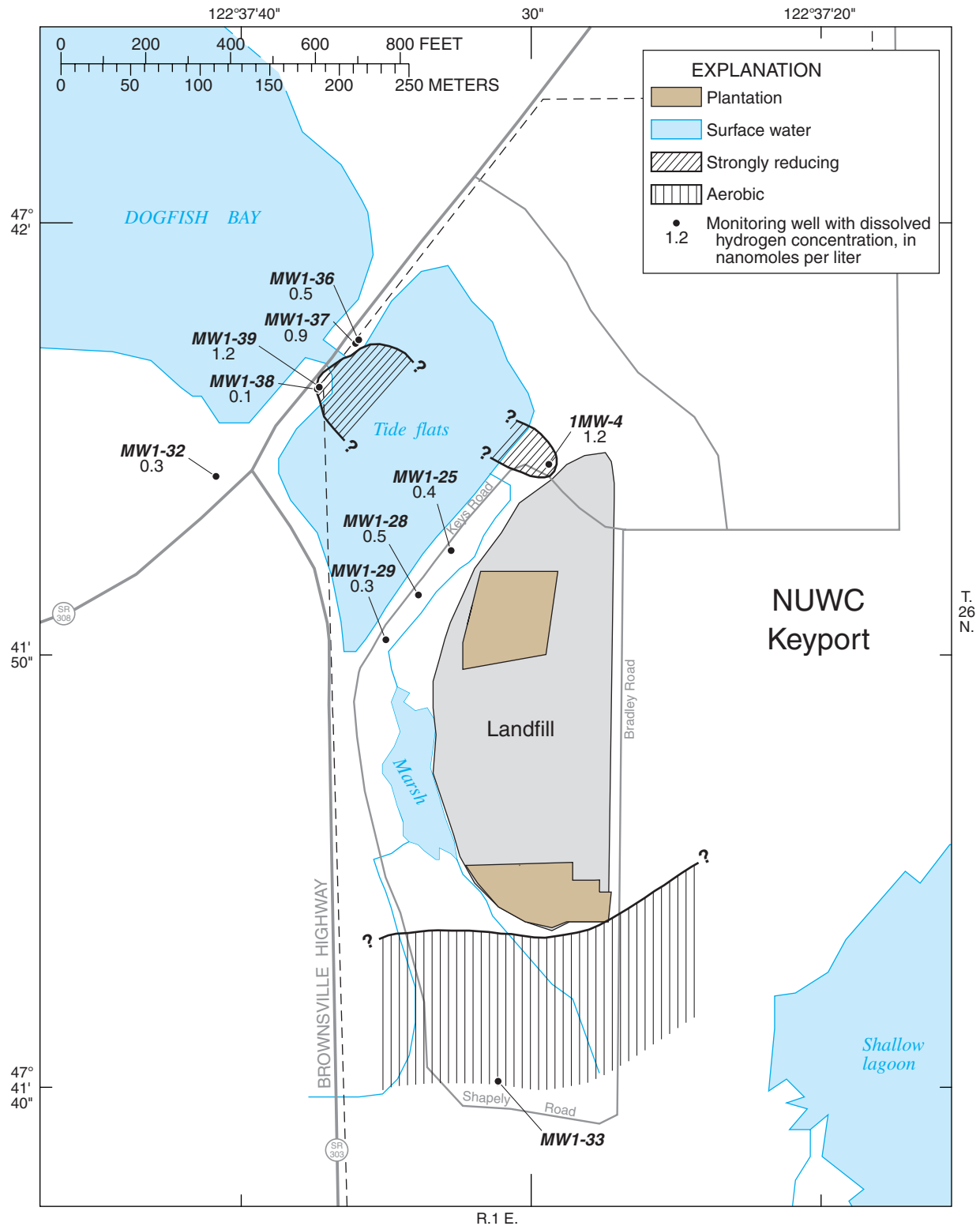
Figure 20. Average dissolved hydrogen (H$_2$) concentrations at sampled wells and delineated redox conditions in the intermediate aquifer at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
Ground water not delineated as strongly reducing or aerobic is mildly reducing.
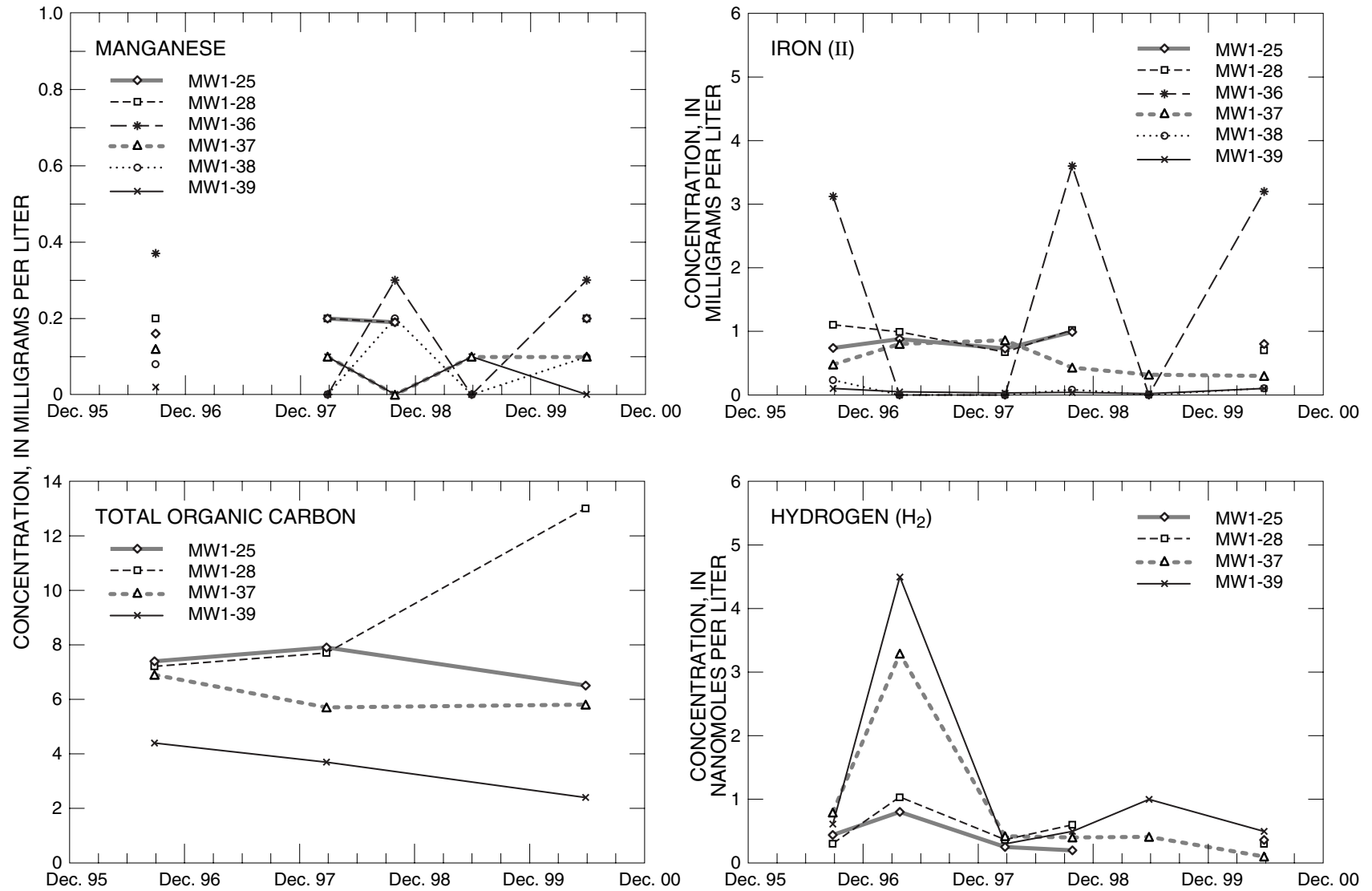
Figure 21. Concentrations of manganese, iron (II), total organic carbon, and hydrogen, 1996–2000, in selected intermediate-aquifer wells at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.
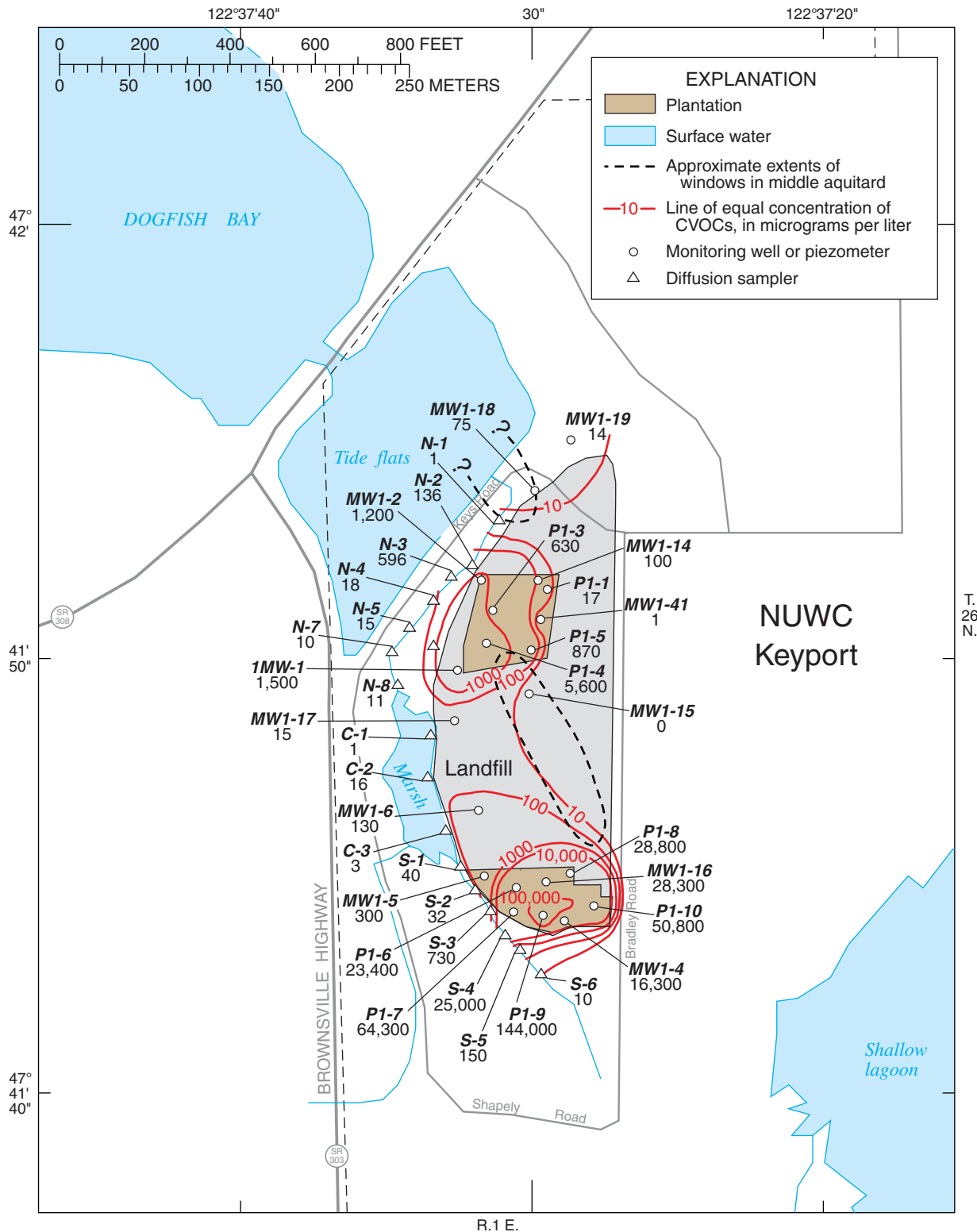
Figure 22. Concentrations of chlorinated volatile organic compounds (CVOCs) in upper-aquifer ground water, 1999, at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.

EVALUATION OF NATURAL ATTENUATION

The first step in evaluating natural attenuation at OU 1 was to look for trends over time in the contaminant concentration data from 1991–2000. Decreasing contaminant concentrations over time were evidence for natural attenuation, and an increasing predominance over time of degradation products relative to parent compounds were evidence for biodegradation. The changes in concentration over time were divided into those attributable to post-1998 phytoremediation activities and those attributable to natural attenuation. The second step was to examine changes in CVOC concentrations and redox-sensitive compounds along selected ground-water flowpaths at a specific time. Again, decreasing contaminant concentrations along a flowpath were evidence for natural attenuation, and an increasing predominance of degradation products relative to parent compounds along a flowpath were evidence for biodegradation. The evidence is presented separately for the upper aquifer beneath the northern plantation, the upper aquifer beneath the southern plantation, the intermediate aquifer, and surface water.

There is clear evidence for substantial natural attenuation and degradation of CVOCs in ground water at OU 1. The rate of degradation was quantified by calculating how much dissolved contaminant mass was degraded in ground water each day assuming recent (1999-2000) site conditions. For comparison, the mass of dissolved contaminants that were discharged to surface water each day was also calculated. The rate of natural attenuation was also quantified by calculating the first-order attenuation rates for contaminant concentrations along selected ground-water flowpaths. The rate calculations are presented for OU 1 as a whole and for specific locations.

Natural Attenuation in the Upper Aquifer Beneath the Northern Plantation

Changes in contaminant and geochemical concentrations over time and along ground-water flowpaths indicate that natural attenuation and degradation are substantial beneath the northern plantation, particularly at its southern end. Flowpath data also indicate that there is continued contaminant attenuation between the landfill and the marsh, and

possibly between the landfill and intermediate-aquifer well MW1-39 at the Highway 308 causeway. Some of the post-1998 decrease in contaminant concentrations can be attributed to the effects of asphalt removal for phytoremediation.

Changes in CVOC Concentrations Over Time

Evaluation of 1991-2000 CVOC data (tables 9 and 10, back of report) for northern plantation wells showed decreasing CVOC concentrations over the long term at the southern end of the plantation that are attributed to biodegradation. Increased concentrations after 1998 beneath the southwestern corner of the plantation are attributed to the effects of asphalt removal. CVOC concentrations have been relatively stable beneath the northern part of the plantation, which indicates biodegradation has been less active and attenuation has been less pronounced. The northern part of the plantation was never paved and post-1998 changes were not evident.

Total chlorinated ethene concentrations at 1MW-1, just outside the southwestern corner of the northern plantation, steadily decreased from 1991 through March 1998, but that trend reversed after asphalt removal during February 1999 (fig. 23). The proportion of VC relative to TCE and *cis*DCE has steadily increased since 1991, which is evidence for VC production from the reductive dechlorination of TCE and *cis*DCE. The absolute concentration of VC has not increased over the long term, which is evidence for reductive dechlorination and(or) mineralization of VC. The post-1998 increase in concentration at 1MW-1 was coincidental with asphalt removal over the southern part of the plantation, which suggests that the resulting increase in recharge may have flushed some additional contamination from the unsaturated zone into ground water. Chlorinated ethanes (and the TCA abiotic degradation compound 1,1-DCE) have also been above concentrations of concern at 1MW-1, and the temporal changes in ethane concentrations have been similar to those observed for chlorinated ethenes. There has been a long-term decrease in total chlorinated ethane concentrations since 1991, followed by an increase after 1998. There has also been a noticeable increase in the proportion of the daughter product DCA and a noticeable decrease in the proportion of the abiotic degradation product 1,1-DCE.
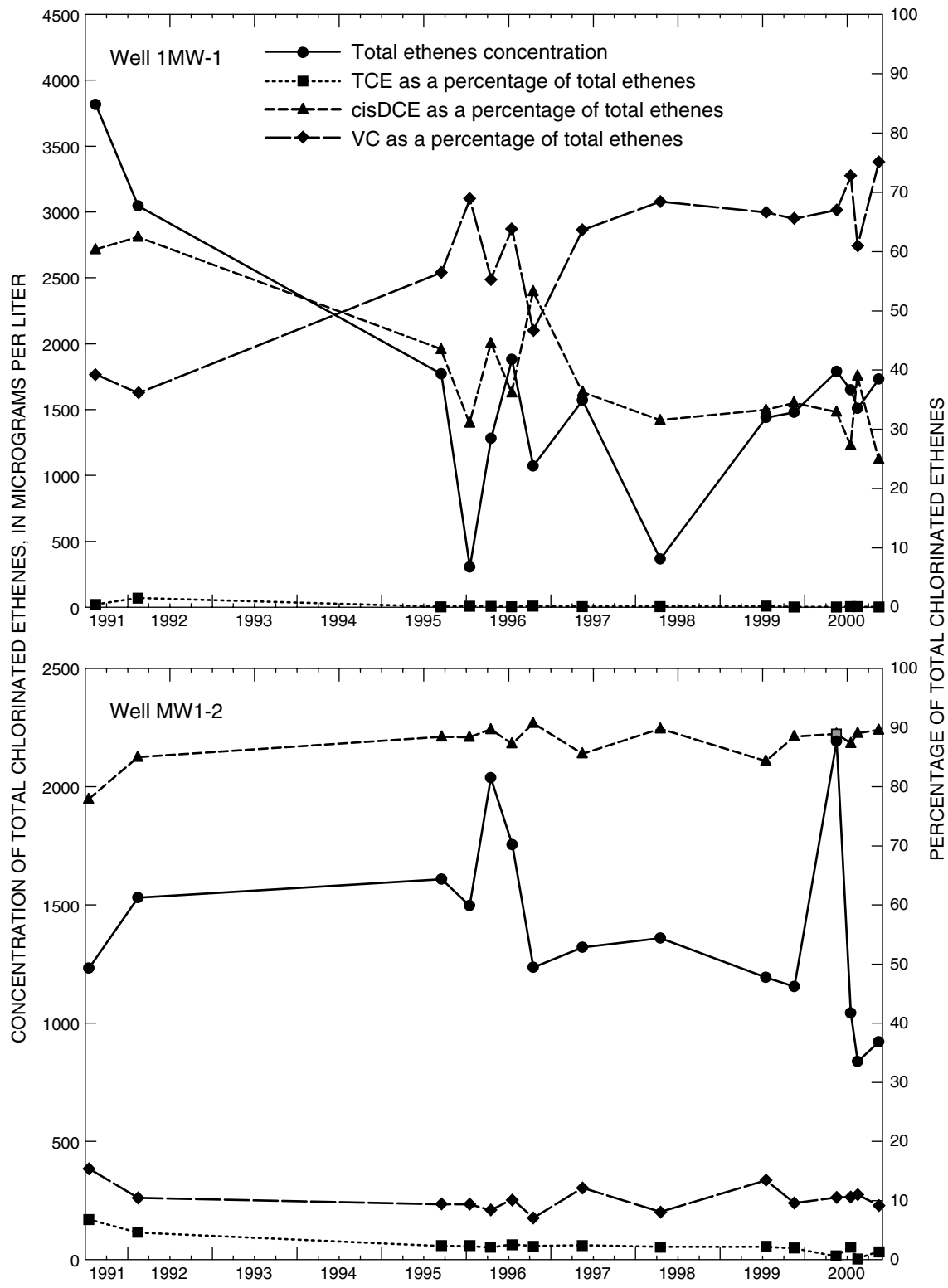
Figure 23. Concentrations of chlorinated ethenes in wells 1MW-1 and MW1-2 in the northern plantation, 1991–2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

Beneath the northern part of the plantation at well MW1-2, there has been a more subtle decrease in total chlorinated ethene concentrations between 1991 and 2000 and little change in the predominance of *cis*DCE (fig. 23). Those observations suggest that biodegradation has been less active at MW1-2, and that much of the degradation of TCE to *cis*DCE and some VC occurs upgradient of the well. The only chlorinated ethane-related compound of concern at MW1-2 has been the abiotic degradation product 1,1-DCE. The lack of the TCA biodegradation products DCA and CA at MW1-2 further indicates that reductive dechlorination has been less active. No consistent changes due to post-1998 asphalt removal were evident at MW1-2, likely because the northern part of the northern plantation had never been paved. There are no long-term observations of CVOC concentrations upgradient from the western margin of the northern plantation available to evaluate trends.

Changes in CVOC and Geochemical Concentrations Along Flowpaths

Changes in CVOC and geochemical concentrations along ground-water flowpaths beneath the northern plantation show additional evidence for natural attenuation and biodegradation, and the data confirm that biodegradation has been most active beneath the southern part of the plantation. Flowpath data also indicate continued attenuation of CVOCs between the landfill and the marsh, and possibly between the landfill and intermediate-aquifer well MW1-39 at the Highway 308 causeway.

Two specific point-to-point flowpaths were evaluated for the northern plantation (fig. 24), as well as a transect-to-transect averaged flowpath. Flowpath A is located along the northern margin of the northern plantation and is assumed to terminate in the marsh or extend beneath the tide flats to MW1-39. Flowpath B is located along the southern margin of the plantation and likely terminates in the marsh near N-7, although some ground water along this path may also continue on to MW1-39. The transect-to-transect flowpath consists of four 300-ft-wide north-south transects oriented perpendicular to the direction of ground-water flow. The upgradient and easternmost transect is represented by the upgradient well MW1-3. The next downgradient transect includes sites MW1-14, P1-1, MW1-41, P1-5, and MW1-15, followed by the third transect that includes MW1-2, P1-3, P1-4, and 1MW-1. The final

and westernmost transect includes all diffusion samplers between N-2 and N-8. Well MW1-39 represents an alternative possible end point for the transect-to-transect flowpath. Data used for the flowpath evaluations were collected primarily during June 1999 from the wells and piezometers, and during June 2000 from the diffusion samplers (tables 7 and 8, back of report); data collected at other times were used only for wells where 1999 or 2000 data were not available. The transect-to-transect flowpath was evaluated to overcome uncertainties in the assumption that specific wells on the point-to-point flowpaths are indeed on the same flowpath. The average concentrations for each transect were estimated by weighting the observed concentrations at individual points by the proportion of a transect's length represented by each sampling point. The transect-to-transect approach does mask the observed differences between the northern and southern parts of the plantation, but it was found to reasonably represent conditions beneath the plantation as a whole.

CVOC concentrations increase substantially as ground water flows beneath the plantation, but then decrease as ground water flows beneath the marsh and the tide flats (fig. 25). The predominant ethene compound changes from TCE to *cis*DCE or VC in the downgradient direction, indicating reductive dechlorination of TCE and *cis*DCE along the flowpaths. The short-lived degradation product ethene was detected at 1MW-1 (at 8.6 μg/L) during June 2000 (table 9, back of report), indicating active reductive dechlorination of VC beneath the southern part of the plantation. Only 0.2 μg/L of ethene was detected at MW1-2, indicating limited reductive dechlorination of VC beneath the northern part of the plantation. The average total CVOC concentrations decreased by more than a factor of 20 between the downgradient margin of the landfill and the marsh, indicating continued contaminant attenuation beyond the landfill. Downgradient of the marsh and tide flats at MW1-39, the detection of only trace amounts of *cis*DCE and VC and the switch to VC as the predominant ethene compound may indicate continued reductive dechlorination of TCE and *cis*DCE beneath the tide flats, although there are alternative explanations for the observations. It is possible that TCE and *cis*DCE have been sorbed more effectively than VC has; for the same aquifer materials, TCE sorption may be as much as 10 times greater and *cis*DCE sorption up to 3 times greater than VC sorption (Howard, 1993).
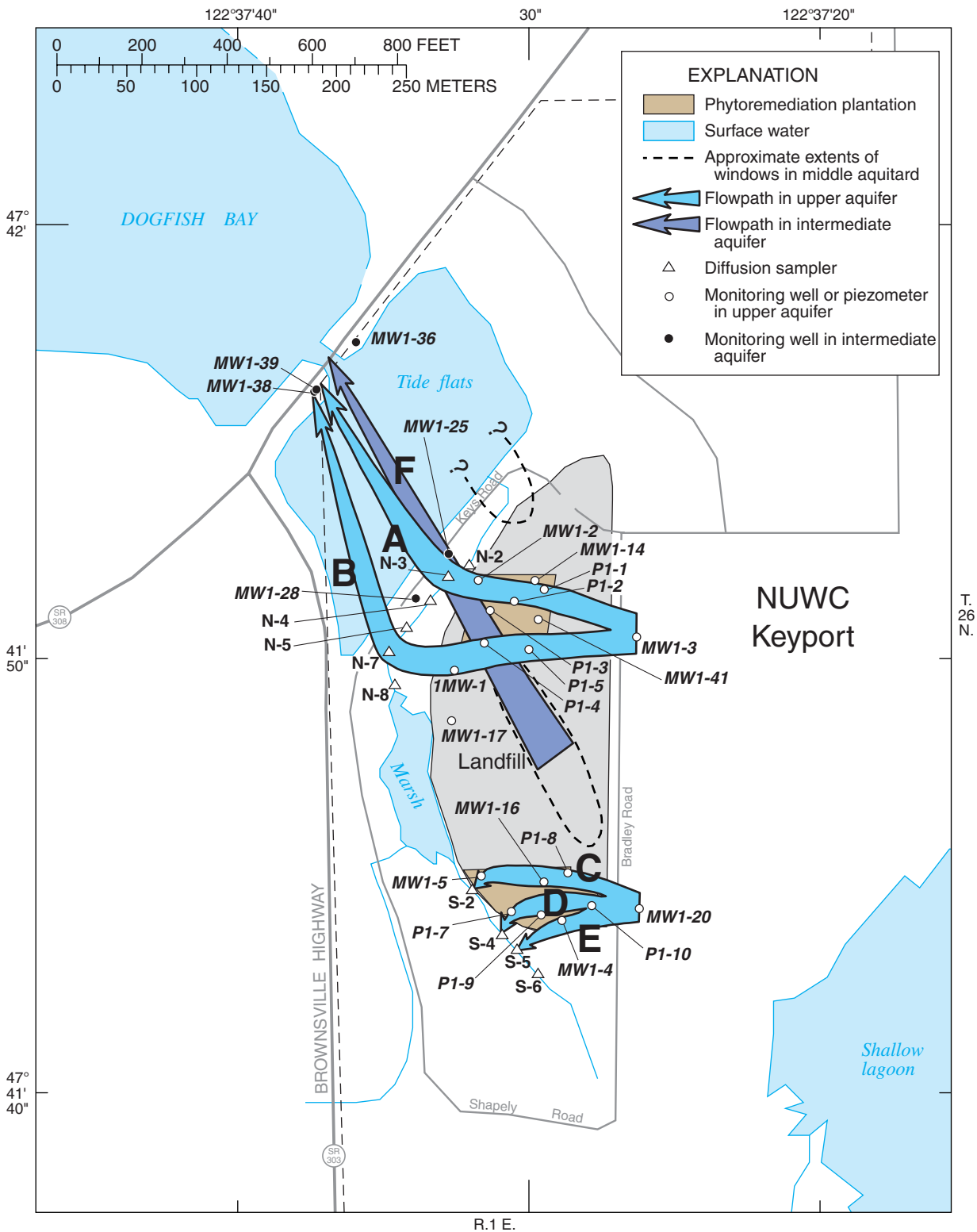
Figure 24. Locations of ground-water flow paths used to evaluate natural attenuation at Operable Unit 1, Naval Undersea Warfare Center (NUWC), Division Keyport, Washington.
Flowpaths A through E are in the upper aquifer and flowpath F is in the intermediate aquifer.
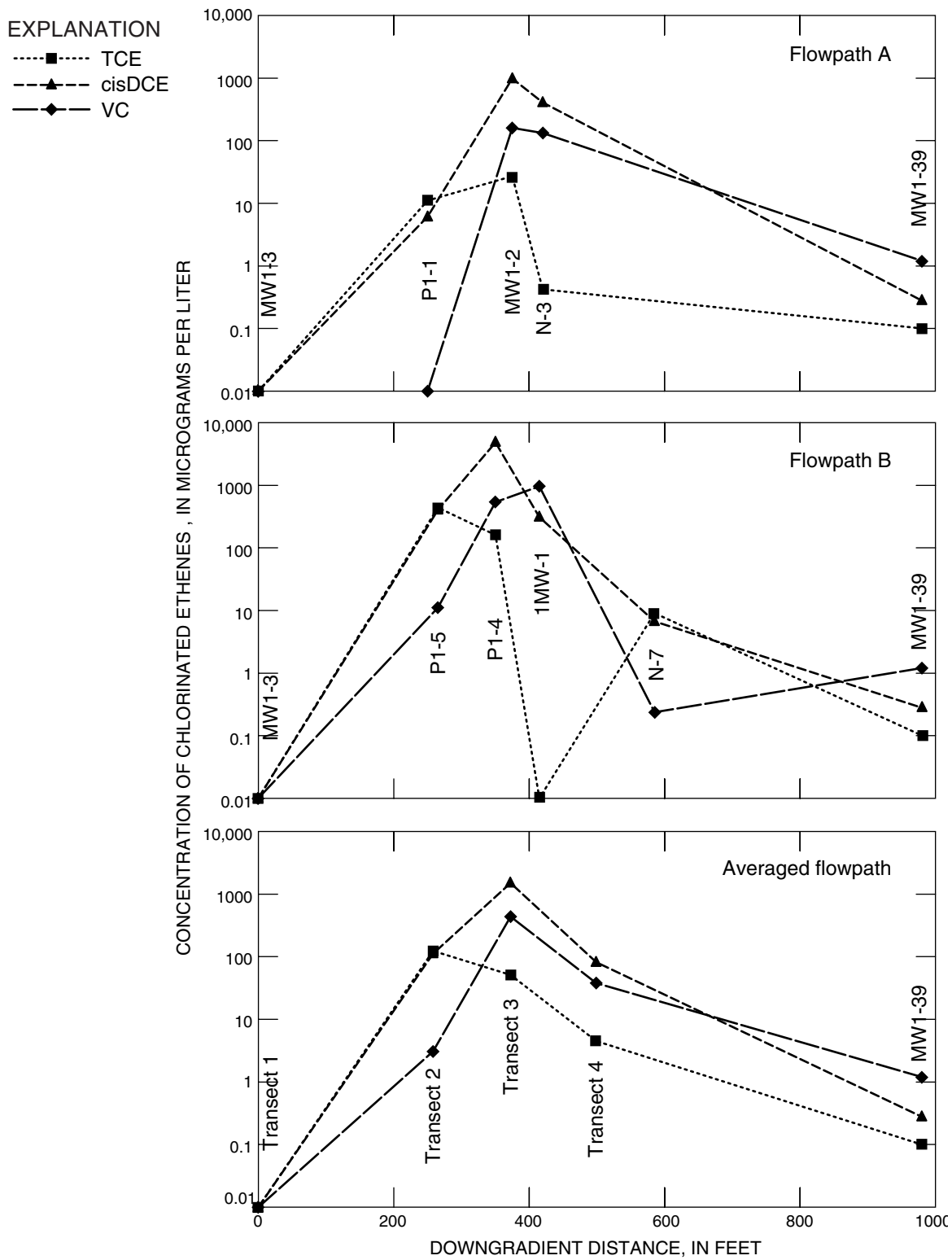
Figure 25. Concentrations of chlorinated ethenes, 1999, along ground-water flowpaths A and B and along an averaged flowpath in the northern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

It is also possible that not enough time has passed for the core of the CVOC plume to reach MW1-39. The estimated travel time of ground water between the landfill and the well is 20-25 years, but the contaminant travel time may be longer due to retardation from sorption. Given the paucity of hydrogeologic information from beneath the tide flats, continued long-term monitoring would be the most certain way to determine the actual attenuation downgradient from the marsh.

Changes in concentrations of redox-sensitive compounds along the northern flow paths provide additional evidence for active biodegradation, and they again indicate that biodegradation is most active beneath the southern part of the plantation (fig. 26). (Redox-sensitive compounds could not be measured in the diffusion samplers because of the sampler design used.) The increase in total organic carbon (TOC) beneath the plantation correlates well with the enhanced microbial activity, and the subsequent downgradient decrease in TOC illustrates consumption of the organic carbon by microorganisms. The increase in H_2 concentrations beneath the southern part of the plantation indicates favorable conditions for reductive dechlorination. The increase in HCO_3^- beneath the plantation indicates production of carbon dioxide by microbial mineralization of organic compounds, possibly including *cis*DCE and VC. The increase in reduced iron (II) and sulfide and the decrease in sulfate indicate that the electron acceptors iron (III) and sulfate are being consumed. The increase in specific conductance (SC) beneath the plantation indicates landfill leachate reaching ground water, and the downgradient decrease in specific conductance of about 50 percent between the marsh and MW1-39 suggests that perhaps half of the observed downgradient attenuation can be attributed to dilution of contaminants through mixing with less-contaminated water. There were not enough methane data to show on the flowpath illustrations, but the data in table 7 (back of report) indicate substantial methane production beneath the northern plantation, particularly at or near 1MW-1.

Natural Attenuation in the Upper Aquifer Beneath the Southern Plantation

Changes in contaminant and geochemical concentrations over time and along ground-water flowpaths suggest that natural attenuation, including both abiotic and biotic degradation, is also substantial beneath the southern plantation, although the data are quite variable. Attenuation and degradation have been substantial beneath the northern part of the southern plantation. Biodegradation processes are less effective beneath the southern part of the plantation, due in part to lower H_2 concentrations that are less favorable for sustained reductive dechlorination. Attenuation processes in general also appear to be less effective along ground-water flowpaths because remaining NAPL is likely an on-going source of dissolved contaminants. Contaminant concentrations continued to decrease at a possibly accelerated rate beneath the northern part of the plantation after the1999 asphalt removal, but concentrations were highly variable beneath the southern part of the plantation after 1998.

Changes in CVOC Concentrations Over Time

Evaluation of the 1991-2000 CVOC data (tables 9 and 10, back of report) showed that long-term concentrations have overall, but inconsistently, decreased beneath the northern part of the southern plantation, whereas concentrations tended to increase beneath the southern part. Much of the long-term decrease beneath the northern part of the plantation can be attributed to biodegradation, although changes after 1998 are likely due in part to asphalt removal for phytoremediation. Changes in CVOC concentrations were inconsistent after asphalt removal beneath the southern part of the plantation.

Near the northwest corner of the southern plantation at MW1-5, total chlorinated ethene concentrations decreased over the long term, and the predominant compound by far has been VC (fig. 27). Total ethene concentrations continued to decrease after the asphalt removal. Total chlorinated ethane concentrations also decreased over the long and short term. At MW1-5, DCA was increasingly the predominant ethane compound through 1998, after which it has alternated with chloroethane in predominance. Those observations are clear evidence for reductive dechlorination of both chlorinated ethenes and ethanes.

Near the northern margin of the plantation at MW1-16, total chlorinated ethene and ethane concentrations have varied but have generally decreased over the long term (fig. 27). The 1999 asphalt removal appears to have enhanced the concentration decrease.
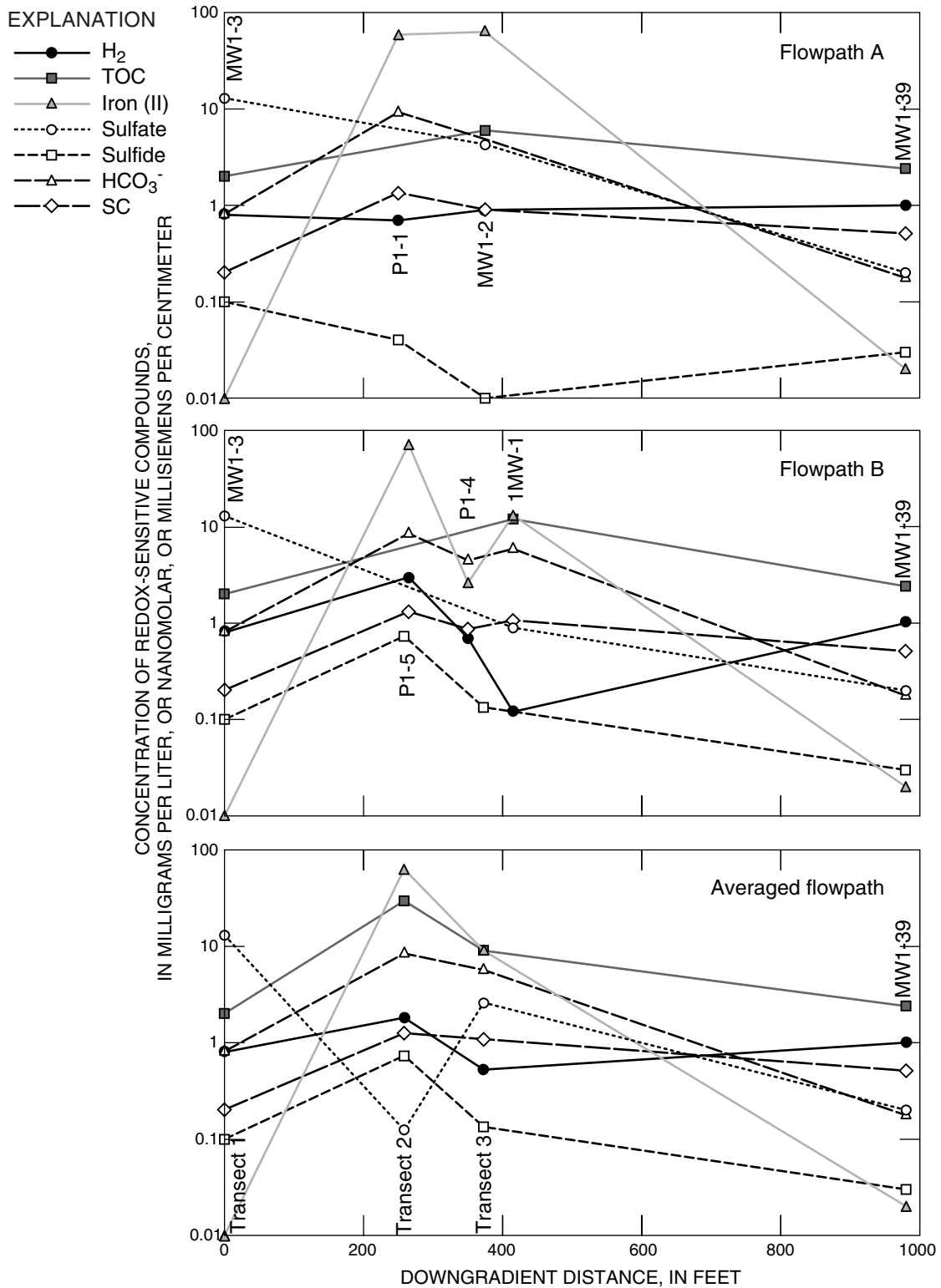
Figure 26. Concentrations of redox-sensitive compounds, 1999, along ground-water flowpaths A and B and along an averaged flowpath in the northern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.
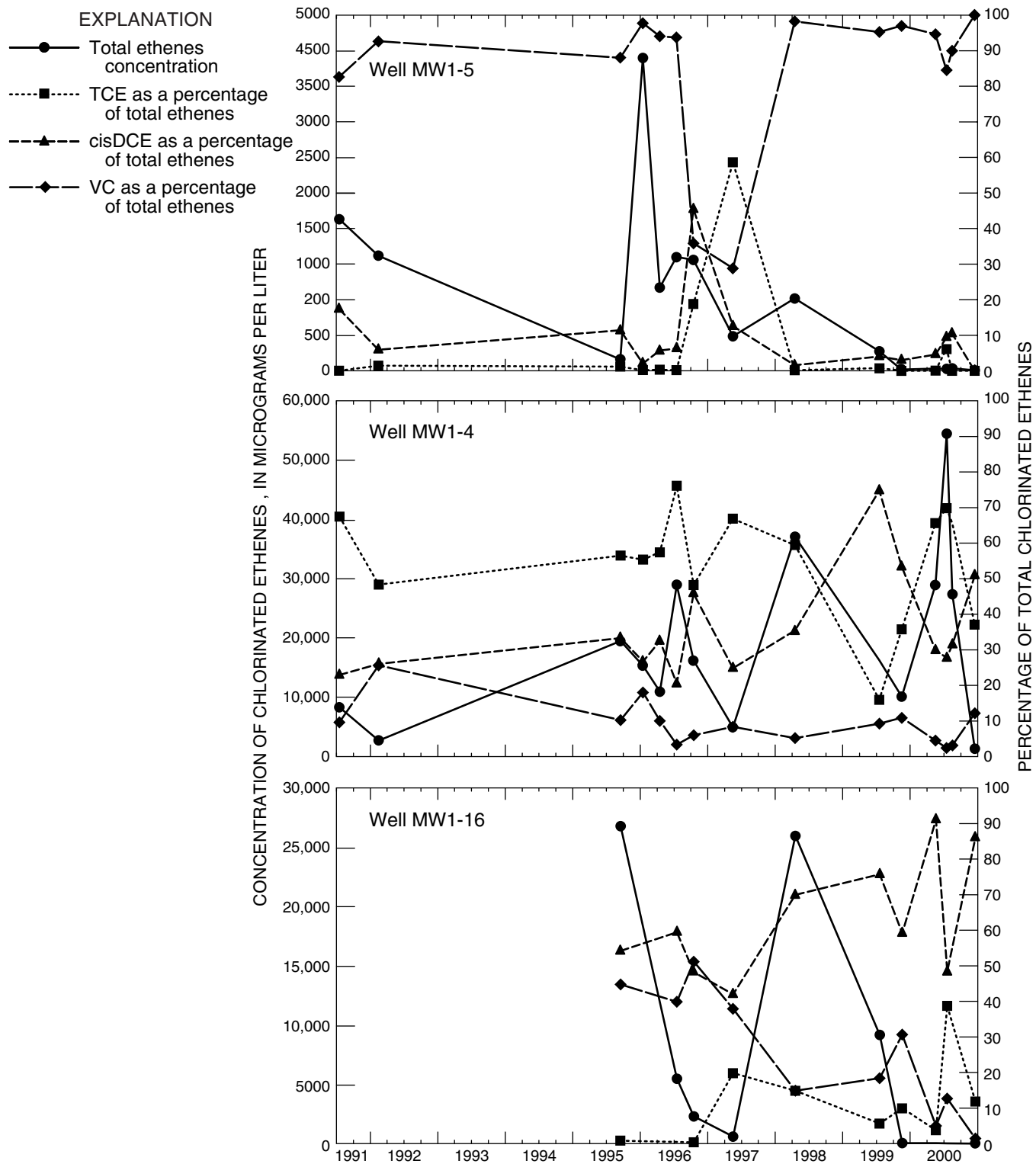
Figure 27. Chlorinated ethenes, 1991–2000, in wells MW1-4, MW1-5, and MW1-16 in the southern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

At MW1-16, *cis*DCE was the predominant ethene compound, and DCA was the predominant ethane compound. The observations clearly show that the historically high chlorinated ethene and ethane concentrations have been greatly attenuated in the vicinity of MW1-16, and that biodegradation has been the reason for at least part of that attenuation.

In contrast, in the southern part of the plantation chlorinated ethene concentrations have increased over the long term at MW1-4 (fig. 27). TCE was consistently the predominant compound before 1999 and has since alternated with *cis*DCE for predominance. Chlorinated ethane concentrations have been sporadic and relatively low over the long term at MW1-4, and the abiotic degradation product 1,1-DCE has been predominant. Those observations indicate that biodegradation at MW1-4 has not been rapid enough to fully attenuate the incoming contaminant flux. The 1999 asphalt removal was followed by a sharp rise and then a fall in concentrations, which is difficult to interpret with the available data.

There are no long-term observations of CVOC concentrations from the newer piezometers throughout the plantation, but the limited available data from 1999-2000 indicate that CVOC concentrations beneath the southern part of the plantation (P1-7 and P1-9) increased slightly during the year. CVOC concentrations beneath the eastern part of the plantation (P1-10) decreased by about a factor of two during the same year.

The effects of asphalt removal on CVOC concentrations beneath the southern plantation have varied, depending on the specific location. However, recent increased CVOC concentration changes in the marsh surface water (described later in this section) indicate that, overall, the asphalt removal has resulted in increased chlorinated ethene flux to the marsh from the southern plantation.

Changes in CVOC and Geochemical Concentrations Along Flowpaths

Changes in CVOC and geochemical concentrations along ground-water flowpaths beneath the southern plantation show evidence for substantial attenuation and biodegradation, particularly toward the northern margin of the plantation. Biodegradation processes are less effective beneath the southern part of the plantation, due in part to lower H_2 concentrations that are less favorable for sustained reductive

dechlorination, but attenuation processes in general also appear to be less effective along ground-water flowpaths because remaining NAPL is likely an on-going source of dissolved contaminants.

Point-to-point ground-water flowpaths were difficult to define beneath the southern plantation, in part because of the large spatial variation in concentrations of CVOC and redox-sensitive geochemicals observed in wells and piezometers. Ground-water flow is east to west beneath the plantation, except near the southern landfill margin where the lower-altitude marshlands induce a more southerly flow direction. Flow direction and geochemistry data were used to delineate three presumed point-to-point flowpaths beneath the southern plantation (fig. 24). Flowpath C is an east-west track beneath the northern part of the plantation, flowpath D is an east-west track beginning nearer the center of the plantation, and flowpath E is a northeast-southwest track beneath the southeastern corner of the plantation. All flow paths were assumed to terminate in the marsh. An averaged transect-to-transect flowpath was not constructed for the southern plantation.

There is a substantial increase in CVOC concentrations as ground water flows into the southern plantation, and the magnitude of subsequent downgradient attenuation varies greatly between the three flowpaths evaluated (fig. 28). There is substantial attenuation and biodegradation of CVOCs beneath the northern part of the plantation and marsh along flowpath C. TCE was consistently the least abundant ethene, and the switch in predominance from *cis*DCE to VC at MW1-5 indicates active reductive dechlorination along the flow path. The short-lived degradation product ethene was detected in MW-16 (at 70 µg/L) and MW1-5 (at 8.6 µg/L) during June 2000 (table 9, back of report), also indicating active reductive dechlorination of VC. The total chlorinated ethene concentrations decreased by about a factor of 100 between the center of flowpath C and the margin of the landfill in June 1999; before the February 1999 asphalt removal the decrease was still substantial at about a factor of 20-30. The total chlorinated ethene concentrations decreased by about an additional factor of 10 to less than 16 µg/L between the margin of the landfill and the marsh. Those decreases all indicate sustained attenuation along flowpath C.
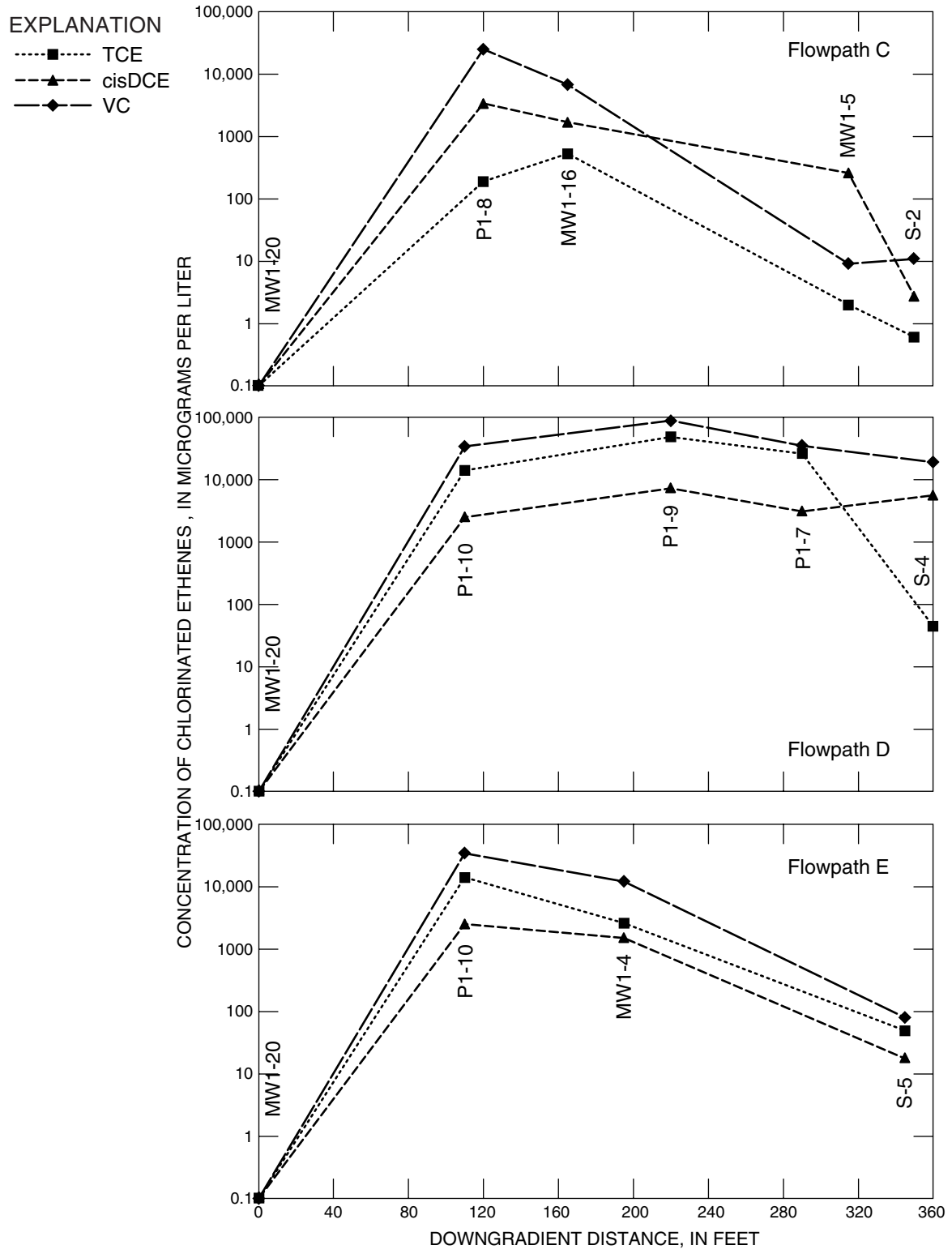
Figure 28. Concentrations of chlorinated ethenes, 1999, along ground-water flowpaths C, D, and E in the southern plantation at Operable Unit 1, Naval Undersea Warfare Center, Divison Keyport, Washington.

Chlorinated ethane concentrations were high enough to be of concern along this flowpath (table 10, back of report), and attenuation (including biodegradation) of those compounds is similar to the ethenes. Chlorinated ethane concentrations decreased substantially along flowpath C, the relative abundance of the intermediate products DCA and CA increased along the flowpath, and the short-lived ethane was detected at 3.6 - 6.6 µg/L.

There is less attenuation of CVOCs beneath the southern part of the plantation and marsh along flowpaths D and E, perhaps because remaining NAPL is an on-going source of dissolved contaminants. TCE is less abundant than *cis*DCE, but more abundant than VC, which suggests less-complete reductive dechlorination along the flow paths. However, the short-lived degradation product ethene was detected along flowpath D in P1-10, P1-9, and P1-7 at 2, 37, and 69 µg/L, respectively, during June 2000 (table 9, back of report), and was also detected along flowpath E in P1-10 and MW1-4 at 2 and 12 µg/L. Those detections of ethene indicate active reductive dechlorination of VC along both flowpaths. The total chlorinated ethene concentrations decreased somewhat along flowpaths D and E beneath the landfill, and they decreased more substantially between the margin of the landfill and the marsh. The attenuation along flowpath D between the landfill and the marsh is likely due both to accelerated biodegradation of TCE and cisDCE in the organic-rich marsh sediments and to preferential sorption of TCE in the sediments. The more substantial attenuation shown for flowpath E is likely an artifact of the marsh sampling locations. Site S-5 may not adequately represent ground-water discharge coming from MW1-4 because there are saturated marshlands between the landfill margin and S-5 where more highly contaminated ground water may discharge. The TCE concentration at surface-water station MA12 during June 2000 was about twice as high as that observed at S-5 or any other diffusion sampler site, which indicates an unmeasured discharge of TCE to the marsh. Chlorinated ethanes are far less abundant than ethenes (and of less concern) along flowpaths D and E.

Changes in concentrations of redox-sensitive compounds along flow paths in the southern plantation (fig. 29) provide additional evidence for active biodegradation, particularly in the northern part of the southern plantation. The increase in total organic carbon (TOC) beneath the plantation indicates a reason for the enhanced microbial activity. Subsequent downgradient decrease in TOC along the northern flowpath illustrates consumption of the electron-donor material by microorganisms, whereas the continuing increase in TOC along the southern flowpaths indicates continuing sources of organic carbon. Increasing H_2 concentrations along flowpaths C and D reflect increasingly anaerobic conditions, and the concentrations are high enough to sustain reductive dechlorination. H_2 concentrations along the southernmost flowpath E are lower and less favorable for sustained reductive dechlorination. The increase in HCO_3^- along the northern flowpath indicates production of carbon dioxide by microbial mineralization of organic compounds, possibly including *cis*DCE and VC. The increase in reduced iron (II) and sulfides along flowpath C and the decrease in sulfate indicate that the electron acceptors iron (III) and sulfate are being consumed. Although sulfate decreases along the southern flowpaths D and E, no coincident increase in sulfide was observed; the sulfide and iron (II) may be precipitating along those paths. The downgradient decrease in specific conductance (SC) of about 50 percent along flowpath C suggests that perhaps half of the observed attenuation could be attributed to dilution of contaminants through recharge of relatively clean water.

Natural Attenuation in the Intermediate Aquifer

Changes in contaminant and geochemical concentrations over time and along ground-water flowpaths indicate that attenuation is substantial but degradation is uncertain in the most contaminated part of the intermediate aquifer. CVOC concentrations have decreased slightly over the long term beneath the downgradient margin of the landfill, but the lack of observation points beneath the tide flats indicates only that contaminants have not migrated to beneath Highway 308. That may reflect either biodegradation, dilution, discharge of ground water to the tide flats upgradient of Highway 308, or simply that not enough time has passed for the contaminants to reach most Highway 308 wells. There is no evidence for changes in the intermediate aquifer that could be attributed to asphalt removal.
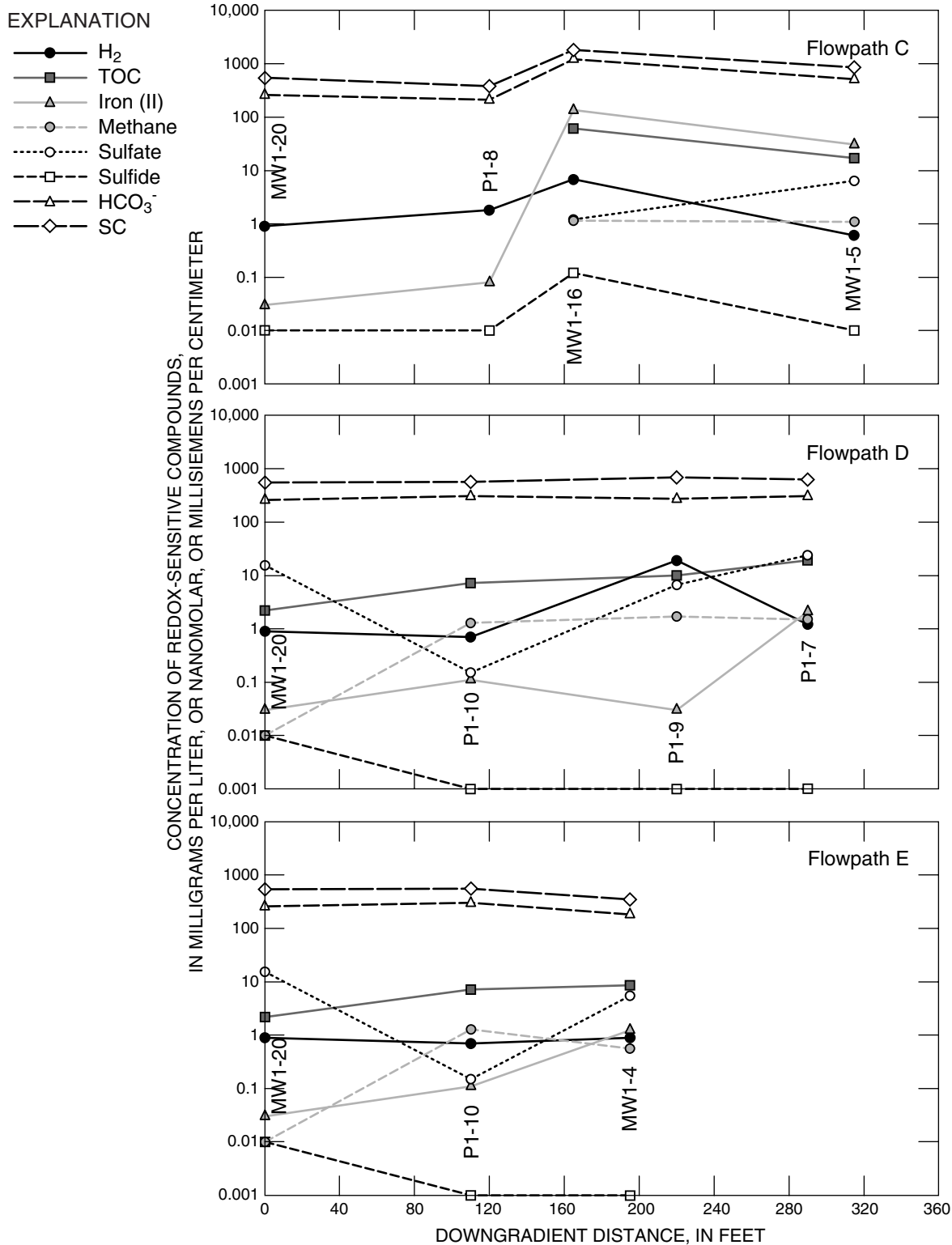
Figure 29. Concentrations of redox-sensitive compounds, 1999, along ground-water flowpaths C, D, and E in the southern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

Changes in CVOC Concentrations Over Time

Evaluation of CVOC data from 1991-2000 for intermediate aquifer wells indicates a substantial long-term decrease in concentrations at the moderately contaminated well 1MW-4, but only a small long-term decrease in concentrations at the highly contaminated wells MW1-25 and MW1-28 (fig. 30). The predominant compound has generally been VC at 1MW-4, and had been consistently been *cis*DCE at MW1-25 and MW1-28. The data indicate that VC has been effectively biodegraded at 1MW-4. The reason for the apparent increase in *cis*DCE at 1MW-4 in 1996–97 is unknown. Redox conditions at 1MW-4 were identified as strongly reducing during 1996 and 1997, and methane concentrations were some of the highest observed at OU 1, so it does not appear that the elevated 1996-97 *cis*DCE concentrations resulted from less favorable conditions for biodegradation.

The predominance of *cis*DCE in the intermediate aquifer indicates that most of the transformation of TCE to *cis*DCE and VC occurs upgradient, likely in the upper aquifer. The continued biodegradation (and attenuation in general) of CVOCs in the most contaminated part of the intermediate aquifer is not evident in the long-term data at MW1-25 and MW1-28. The stable concentrations and predominance of *cis*DCE do not provide much insight into attenuation and biodegradation in the intermediate aquifer. Changes in CVOC concentrations along ground-water flow paths, as described below, do suggest continued attenuation in the intermediate aquifer, but continued biodegradation is uncertain. There is no evidence for CVOC changes in the intermediate aquifer that could be attributed to asphalt removal.

Changes in CVOC and Geochemical Concentrations Along Flowpaths

Because there were no intermediate-aquifer observation points beneath the tide flats, point-to-point ground-water flowpaths indicate only that the contaminants have not migrated to beneath Highway 308. That may be because of biodegradation, dilution through mixing with seawater, or discharge of ground water to the tide flats upgradient of Highway 308.

A single flowpath was evaluated for the intermediate aquifer (F on fig. 24). The precise location of the contaminant source for the flowpath is unknown, so the contaminants and geochemical concentrations from two wells (1MW-1 and MW1-16) at opposite ends of the window through the middle aquitard were averaged and assumed to be representative of the source water. The flowpath is assumed to begin in the upper aquifer, although it is recognized that some uncontaminated and aerobic water from upgradient parts of the intermediate aquifer contributes to the flowpath. The contaminant and geochemical concentrations at wells MW1-25 and MW1-28 were averaged to represent the second point along the flowpath; the chemical composition of ground water is quite similar in the two wells. The flowpath is shown to continue beneath the tide flats to well MW1-36 or MW1-38, the deeper wells of each of the nested pairs on either side of the Highway 308 bridge. It is recognized that some intermediate-aquifer ground water may actually discharge into the tide flats and never flow as far as the Highway 308 wells.

There is substantial attenuation of CVOCs along the presumed intermediate aquifer flowpath (fig. 31), although much of the attenuation is likely due to mixing with uncontaminated water. TCE concentrations decrease by about a factor of 10 between the upper and intermediate aquifers, *cis*DCE concentrations decrease by a factor of 2, and VC concentrations decrease by a factor of 3. Those data suggest some additional reductive dechlorination of TCE between the two aquifers, although H_2 concentrations within the intermediate aquifer are likely too low to sustain additional reductive dechlorination. A 25-percent increase in HCO_3^- concentrations between the upper and intermediate aquifer wells (fig. 31) is most likely due mixing with seawater, although some of the increase could also be due to mineralization of *cis*DCE and VC along the flowpath. Other changes in geochemistry indicate a gradual decrease in the strength of reducing conditions and mixing with seawater. Changes in common-ion concentrations between wells MW1-25 and MW1-28 and wells MW1-36 and MW1-38 also indicate mixing with seawater beneath the tide flats (see fig. 15).
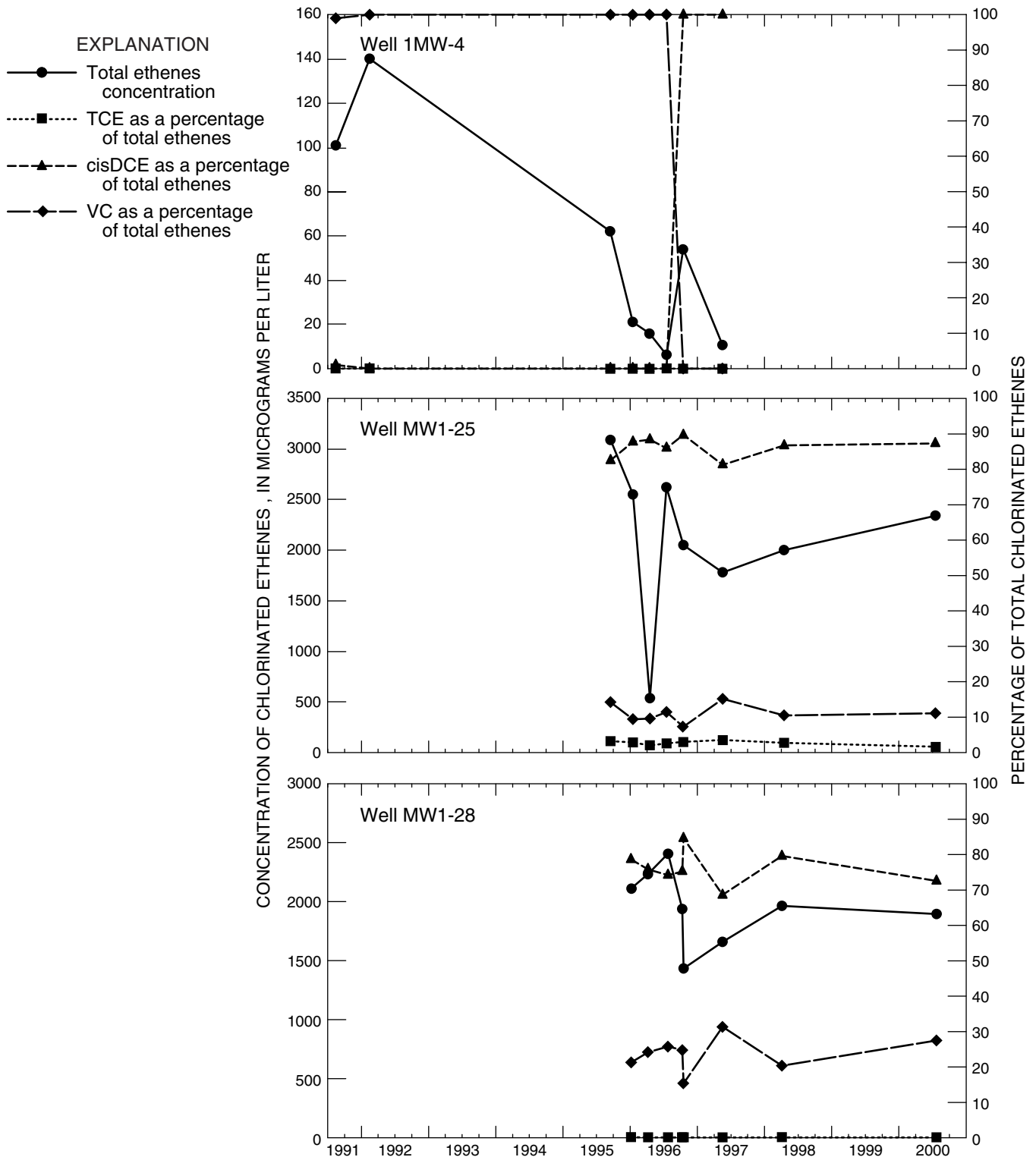
Figure 30. Concentrations of chlorinated ethenes, 1991–2000, in intermediate-aquifer wells 1MW-4, MW1-25, and MW1-28 in the southern plantation at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.
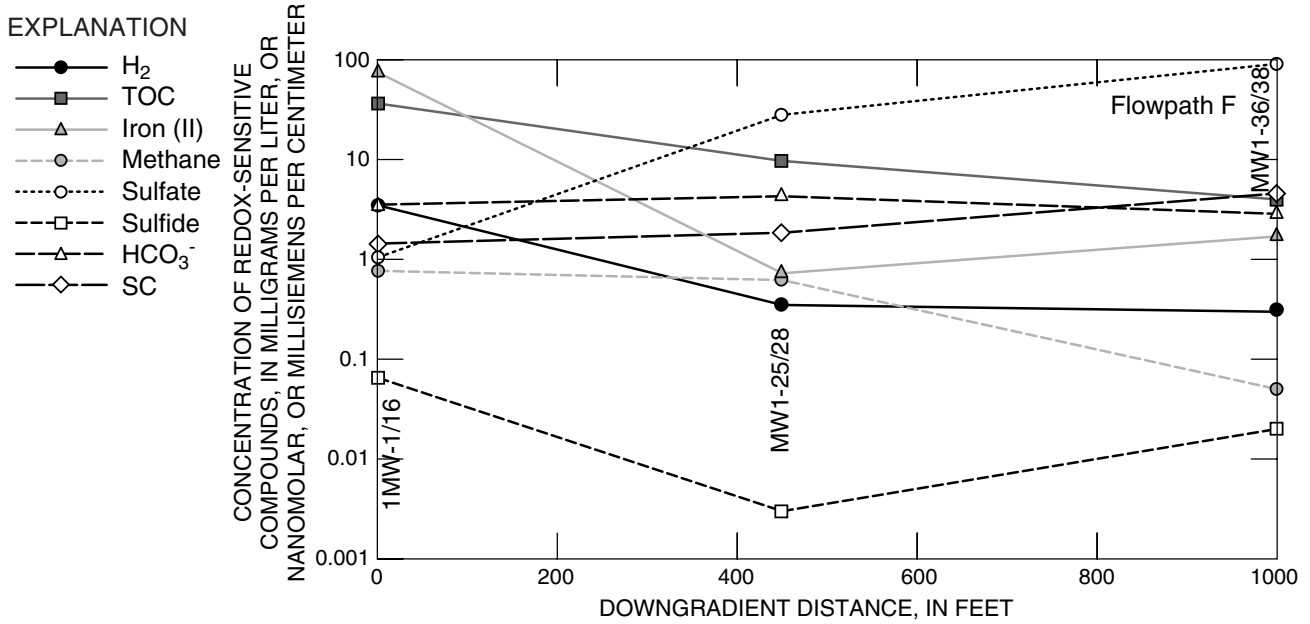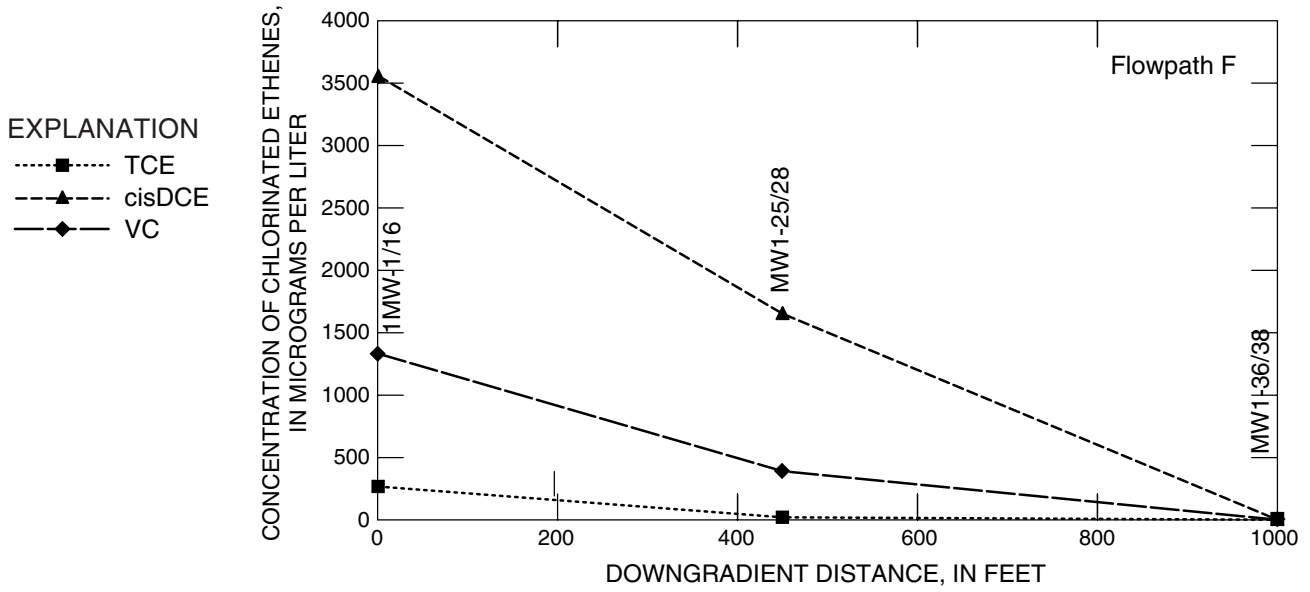
Figure 31. Concentrations of chlorinated ethenes and redox-sensitive compounds along flowpath F in the intermediate aquifer at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

Natural Attenuation in Surface Water

There have been no clear long-term changes in contaminant concentrations at surface-water sites in the marsh, but there is substantial attenuation of concentrations in surface water as it flows through the marsh and across the tide flats. An increase in surface-water contaminant concentrations after 1998 can be attributed to increased discharge of ground-water contaminants to surface water after asphalt removal from the southern plantation.

Changes in CVOC Concentrations Over Time

The presence of a pattern of long-term trends in CVOC data for 1991-2000 for surface-water sites in the marsh is inconclusive, but a clear increase in concentrations after 1998 (tables 9 and 10, back of report) can be attributed to increased discharge of ground-water contaminants to surface water after asphalt removal in the southern plantation (fig. 32). *cis*DCE has been the predominant ethene compound at the most highly contaminated upstream site, MA-12, although the relative abundance of VC has been increasing. Likewise, DCA has been the predominant ethane compound at MA-12, although the relative abundance of CA has also been increasing. As expected, those observations correspond with the observed temporal pattern of daughter product predominance in most southern plantation wells. Biodegradation is likely insignificant in surface water, but dilution of contaminant concentrations from other surface-water inflows to the marsh, and contaminant loss presumably through volatilization, result in a substantial change in concentrations in the downstream direction, as described below.

Changes in CVOC Concentrations Along Flowpaths

There is substantial attenuation of CVOC concentrations in surface water as it flows through the marsh and across the tide flats (fig. 33). The data shown are from June 2000, and the total chlorinated ethene concentration in shallow ground water beneath the marsh creek and pond is included for comparison. The data confirm that most surface-water contamination results from ground-water discharge to the marsh from beneath the southern plantation. Standing water and saturated soils persist year around in the marshland adjacent to the southern plantation, which indicates perennial ground-water discharge to the southern marsh.

In contrast, the marshland adjacent to the northern plantation is not consistently saturated at the surface. For example, diffusion sampler N-6 was buried in saturated soils beneath a small pond near the north-central landfill margin in late June 2000, but the pond was dry and the soil surrounding the sampler was unsaturated when the sampler was retrieved 2 weeks later. Those observations suggest that ground water from the northern plantation may not be discharging to the marsh, and that conclusion is supported by the lack of an observable increase in surface-water contaminant concentrations where the marsh ground-water contaminant concentrations increase between downgradient distances of 800 to 1,200 feet. Flowpath A (fig. 24) crosses the marsh in the vicinity where ground-water discharge to the surface may be absent, which further explains why contaminated ground water continues flowing westward out to well MW1-39.

Concentrations of surface-water contaminants increased slightly between the most downgradient marsh station (MA-09) and the discharge point to the tide flats (TF19). This increase has been observed consistently since 1996, and upper-aquifer contamination at the far northern tip of the landfill is the most likely cause for it.

The predominance of *cis*DCE in surface water confirms that biodegradation of chlorinated ethenes is not complete in upper-aquifer ground water, and the consistent ratios of TCE, *cis*DCE, and VC indicate that biodegradation ceases in surface water. The observed attenuation of CVOCs is thus a result of volatilization, dispersion, and mixing.
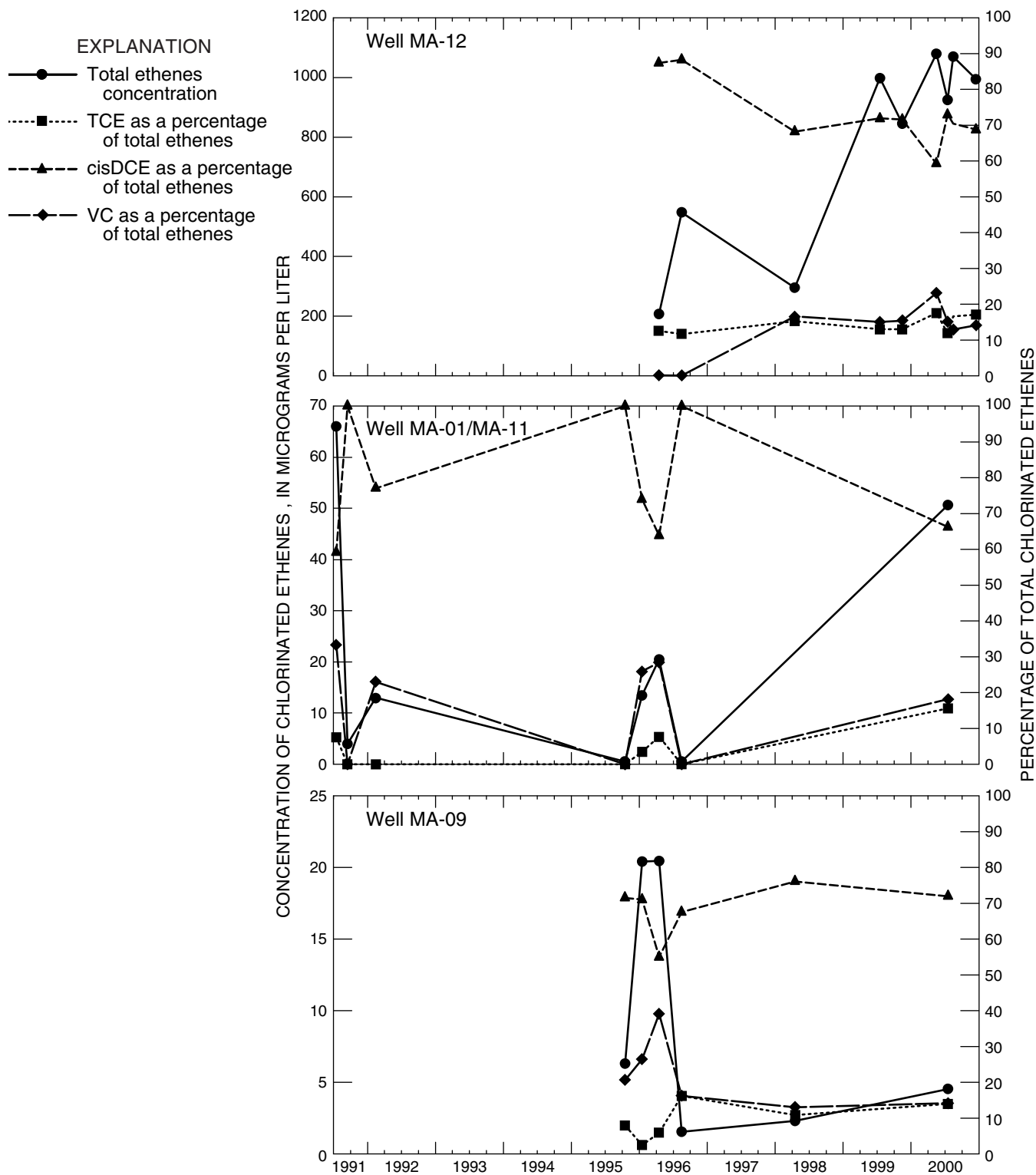
Figure 32. Concentrations of chlorinated ethenes, 1991–2000, for surface-water stations MA-12, MA01/MA-11, and MA-09 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.
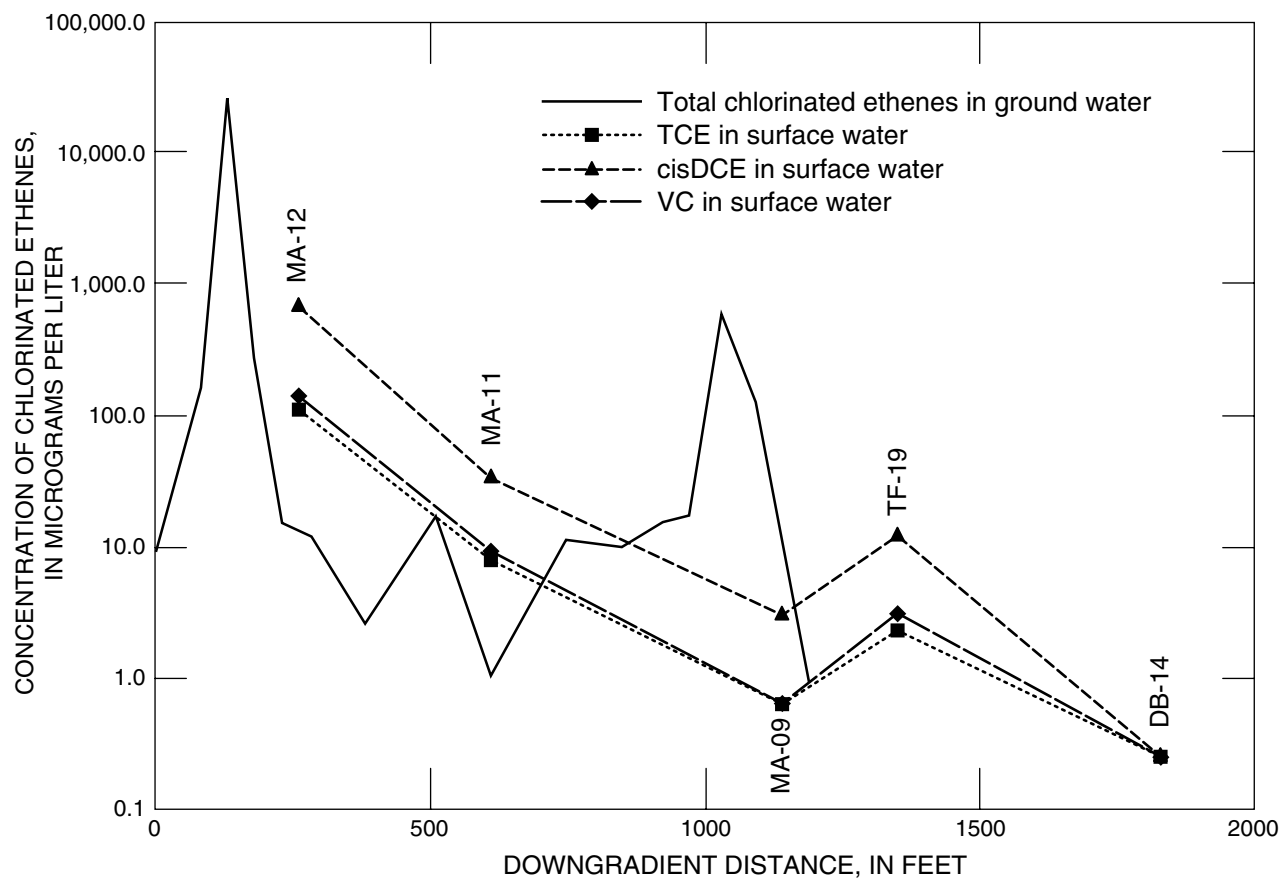
Figure 33. Concentrations of chlorinated ethenes in surface water as it flows through the marsh and across the tideflats at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington. Total chlorinated ethene concentration in ground water beneath the marsh creek and pond is included for comparison.

Degradation Rates of Chlorinated Ethene Mass in Ground Water and Mass Discharge to Surface Water

The rate at which the dissolved contaminant mass is degraded in ground water, and the rate at which the remaining contaminant mass is discharged to surface water, were estimated for recent (2000) conditions at OU 1 using the approach described in the "Methods and Data Analysis" section of this report. The data used to estimate those rates were primarily from June 1999 and 2000, and the results are thought to represent conditions at OU 1 before phytoremediation activities have substantially affected ground water. Ranges in mass-degradation rates were reported for

*cis*DCE and VC. The minimum rates were based only on the observed differences in fluxes between transects for a specific compound. The maximum rates for *cis*DCE were calculated by assuming that the estimated mass of TCE that was degraded produced an equivalent number of moles of *cis*DCE that were also degraded. Likewise, the maximum rates for VC were calculated by assuming the estimated mass of *cis*DCE that was degraded produced an equivalent number of moles of VC that were also degraded. Only one mass removal rate is reported for TCE because the amount of PCE available to degrade into TCE was negligible. The calculations were done only for the chlorinated ethenes; the mass of chlorinated ethanes in the landfill is substantially less.

Overall, the results indicate that the majority of dissolved chlorinated ethenes are degraded in ground water before they have an opportunity to discharge to surface water (table 3; additional data in table 11 at back of report). Of the 71 grams per day (g/d) of chlorinated ethenes available to migrate from the landfill (table 11), only about 27 percent (19 g/d) actually migrates past downgradient transects and discharges to surface water (table 3). Thus, 73 percent of the dissolved contaminant mass is degraded in ground water.

Of the 24 g/d of TCE available to migrate from the landfill, less than 1 percent (0.2 g/d) actually migrates past downgradient transects and discharges to surface water. The degradation of dissolved TCE in landfill ground water appeared to be very effective, but the amount degraded is likely overestimated. Probably, not all of the TCE that migrates from the southern plantation to the marsh was measured in the diffusion samplers because no samplers were located directly adjacent to the southernmost margin of the landfill.

The degradation of dissolved *cis*DCE appeared to be somewhat less effective than that of TCE; of the 41 g/d of *cis*DCE that is originally available to migrate from the landfill, almost 40 percent (16 g/d) migrates past downgradient transects and discharges to surface water. However, the total mass of *cis*DCE degraded each day (25 to 43 g/d) is greater than the mass of TCE degraded. That is because initially there was more *cis*DCE available to degrade, and because the degradation of TCE is an ongoing source for additional *cis*DCE. About three-quarters of the *cis*DCE that is not degraded migrates to the intermediate aquifer and likely discharges to the tide flats and Dogfish Bay.

The degradation of dissolved VC appeared to be least efficient of the compounds examined; of the 5.5 g/d of VC that is originally available to migrate from the landfill, 60 percent (3.4 g/d) migrates past downgradient transects and discharges to surface water. The mass of VC degraded each day (2.2 to 18 g/d) is the least of all of the compounds examined, but the total mass of VC discharging to surface water is still much less than the mass of *cis*DCE that discharges.

An alternate estimate of chlorinated ethene discharge to the marsh was made by summing the appropriate ground-water and surface-water fluxes to the marsh upstream of two surface-water monitoring sites (MA-12 and TF-19) and multiplying those total streamflow estimates by the average chlorinated ethene concentrations measured at the surface-water sites. Streamflow has not been measured directly at OU 1, so the ground-water and surface-water discharge estimates were instead used to represent non-storm period streamflow through the marsh.

The results of the alternative estimate (table 4) suggest that discharge of TCE and *cis*DCE to surface water from the southern plantation may be about 98 and 27 percent greater, respectively, than that calculated using the flux-based approach. Those results are consistent with the hypothesis that the diffusion samplers did not fully represent contaminant discharge to the southeastern portion of the marsh; TCE and *cis*DCE are the predominant contaminants in well MW1-4 along the margin of the landfill in that vicinity. The two estimates of VC discharge from the southern plantation are in close agreement.

The results of the alternative estimate also suggest there is a net loss of contaminants in marsh surface water as it flows from MA-12 to the outlet at TF-19. About 30 percent of the TCE flux, 40 percent of the *cis*DCE flux, and 50 percent of the VC flux flowing past the upstream site are lost to other destructive attenuation processes such as volatilization before discharging to the tide flats.

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Natural Attenuation of CVOCs in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

Table 3. Degradation rates of chlorinated ethene mass and discharge to surface water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Chlorinated ethene mass removal rate between landfill transect and downgradient transects**: **cisDCE**, Upper range estimate for *cis*DCE mas removal rate assumes all TCE mass removal was converted to *cis*DCE; **VC**, Upper range estimate for VC mass removal rate assumes all *cis*DCE mass removed was converted to VC. TCE, trichloroethene; *cis*DCE, cis-1,2-dichloroethene; VC, vinyl chloride; ft, feet; g/d, grams per day; –, not applicable]

Sub-transect name	Ground-water sample sites in transects	Chlorinated ethene mass removal rate between landfill transect and downgradient transects			Chlorinated ethene discharge to marsh			Chlorinated ethene discharge to tide flats/Dogfish Bay		
		TCE (g/d)	*cis*DCE (g/d)	VC (g/d)	TCE (g/d)	*cis*DCE (g/d)	VC (g/d)	TCE (g/d)	*cis*DCE (g/d)	VC (g/d)
1 – Landfill										
North	MW1-18	-0.002	0.006	0.010	–	–	–	–	–	–
North-central	MW1-2, P1-3, P1-4	0.4	6.7 – 7	0.4 – 4.7	–	–	–	–	–	–
Central	MW1-17	0.001	-0.008	0.01 -0.02	–	–	–	–	–	–
South-central	MW1-6	0.2	0.02 – 0.2	0.01 – 0.03	–	–	–	–	–	–
South	P1-6, P1-7, MW1-4	23	18 – 35	1.8 – 13	–	–	–	–	–	–
Subtotals		24	25 – 43	2.2 - 18	–	–	–	–	–	–
2 – Marsh										
North	N1	–	–	–	–	–	–	0.0001	0.0004	0.0001
North-central	N2, N3, N4, N5, N7, N8	–	–	–	–	–	–	0.02	0.5	0.2
Central	C1, C2	–	–	–	0.0001	0.009	0.01	–	–	–
South-central	C3	–	–	–	0.0001	0.004	0.001	–	–	–
South	S1, S2, S3, S4, S5, S6	–	–	–	0.02	3.5	1.1	–	–	–
Subtotals		–	–	–	0.02	3.5	1.1	0.02	0.5	0.2
3 – Intermediate aquifer										
North[1]	1MW-1	–	–	–	–	–	–	0.002	0.02	0.001
North-central[2]	1MW-4, MW1-25	–	–	–	–	–	–	0.01	0.5	0.07
South-central[3]	MW1-25	–	–	–	–	–	–	0.2	9.2	1.2
South[4]	MW1-28	–	–	–	–	–	–	0.0	2.0	0.8
Subtotals		–	–	–	–	–	–	0.2	11.7	2.1
TOTALS		24	25 – 43	2.2 – 18	0.02	3.5	1.1	0.2	12.2	2.3

[1]North intermediate-aquifer CVOC flux comes from northern part of the landfill

[2]North-central intermediate-aquifer CVOC flux comes from northern part of the landfill (0.6 percent) and the north-central part (99.4 percent).

[3]South-central intermediate-aquifer CVOC flux comes from north-central part of the landfill (50 percent) and southern part (50 percent).

[4]South intermediate-aquifer CVOC flux comes from north-central part of the landfill (50 percent) and southern part (50 percent).

Table 4. Results of alternate method of estimating chlorinated ethene discharge to the marsh at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Water flux:** Ground-water and surface-water flux estimates not shown in table 11 were from Appendix F, URS Inc., 1997b. **Observed chlorinated ethene concentrations**: Chlorinated ethene data from table 9 (sites MA-12 and TF-19) and table 8 (diffusion sampler transects). TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; VC, vinyl chloride; gal/min, gallons per minute; µg/L, micrograms per liter; g/d, grams per day]

Location	Water flux (gal/min)	Observed chlorinated ethene concentration			Calculated and observed chlorinated ethene flux		
		TCE (µg/L)	*cis*DCE (µg/L)	VC (µg/L)	TCE (g/d)	*cis*DCE (g/d)	VC (g/d)
Upstream of station MA-12							
Ground water from south side of marsh	1.1	0	0	0	0	0	0
Ground water from landfill	0.2	16	3,200	980	0.02	3.5	1.1
Calculated flux to surface water upstream of MA-12	1.3				0.02	3.5	1.1
Observed flux in surface-water at MA-12	1.3	110	670	140	0.8	4.7	1.0
Percent difference between calculated and observed					98	27	-7
Upstream of station TF-19							
Surface water from creek draining lands west of marsh	40	0	0	0	0	0	0
Ground water from west of marsh pond	0.6	0	0	0	0	0	0
Ground water from south-central landfill	0.3	0.05	2.2	0.44	0.0001	0.004	0.001
Ground water from central landfill	0.4	0.06	4.1	6.1	0.0001	0.009	0.01
Calculated flux to surface water upstream of TF-19	43				0.02	3.5	1.1
Observed flux in surface-water at TF-19	43	2.3	12	2	0.5	2.8	0.5
Percent difference between calculated and observed					97	-25	-121
Percent difference observed between MA-12 and TF-19					31	41	51

Chlorinated Ethene Attenuation Rates

The approximate first-order rates at which CVOC concentrations are attenuated in ground water were also estimated for recent conditions at OU 1. The data used to calculate attenuation rates using equations (2) and (3) were primarily from June 1999 for ground water beneath the landfill and in the intermediate aquifer, and from June 2000 for ground water beneath the marsh. Like the mass degradation rate estimates, the results presented are thought to represent natural attenuation rates at OU 1 before phytoremediation activities have substantially affected ground water, although some of the initial effects of asphalt removal, site preparation, and tree planting are inherent in the estimates.

Attenuation rates were calculated for TCE, *cis*DCE, and VC (table 5; additional data in table 12 at back of report) between pairs of sampling locations (segments) along ground-water flowpaths shown on figure 24. Attenuation rates were not calculated for the first segment of most flowpaths between upgradient wells and landfill wells where contaminant concentrations consistently increased. The negative half-lives calculated for a few segments indicate there was a net gain in downgradient concentration due to additional source material. Ranges in attenuation degradation rates are reported for *cis*DCE and VC when the two estimates were significantly different. The minimum rates were calculated using only the point-to-point concentration changes observed for a flowpath segment.

The maximum rates for *cis*DCE were calculated by assuming that all TCE lost along a flowpath segment produced an equivalent number of moles of *cis*DCE, and the maximum rates for VC were calculated by assuming that all *cis*DCE lost along a flowpath segment produced an equivalent number of moles of VC. That approach assumes that TCE and *cis*DCE are attenuated by reductive dechlorination only. Only one attenuation rate is reported for TCE because the amount of PCE remaining in the landfill was negligible. The calculations were done only for the chlorinated ethenes.

Comparison of calculated attenuation rates for different flowpaths ([table 5](#) and [table 12](#)) confirms the previous findings regarding where biodegradation is most effective at OU 1. Beneath the southern part of the northern plantation, relatively short TCE and *cis*DCE half-lives were estimated (flowpath B, segment 2) where redox conditions were favorable for reductive dechlorination. In contrast, longer TCE and *cis*DCE half-lives and shorter VC half-lives were calculated at the downgradient margin of the northern part of landfill (flowpath A, segment 2; flowpath B, segment 3) where redox conditions were less favorable for reductive dechlorination, but were more favorable for mineralization of VC. Attenuation half-lives for the flowpath segments from the marsh to Highway 308 were substantially longer than those determined for upgradient segments, which suggest that contaminant degradation slows substantially once ground water leaves the organic-carbon-rich aquifer beneath the landfill.

In the southern plantation, the longest attenuation half-lives were most often found along the more southern flowpaths D and E. For flowpath D, segment 2, the likely cause of the long half-life for TCE is that there is an additional source for TCE along the segment; redox conditions are very favorable for reductive dechlorination along the segment. For flowpath E, segment 2, the relatively long TCE half-life is likely due to limited reductive dechlorination; redox conditions along the segment are less favorable for that degradation mechanism. For the more northern flowpath C, redox conditions are very favorable for reductive dechlorination of TCE and *cis*DCE along the upgradient segment of the flowpath, and redox conditions may be favorable for mineralization of VC along downgradient segments. Those conditions are reflected in TCE half-lives that increase and VC half-lives that decrease in the downgradient direction. The

negative half-life for TCE at the beginning of flowpath C indicates that an additional source of TCE is available along the segment.

In the intermediate aquifer, the calculated attenuation half-lives are substantially longer than those determined for the upper aquifer, which again suggests a decrease in contaminant degradation once ground water leaves the organic-carbon-rich aquifer beneath the landfill. Rates could not be calculated for the flowpath segment between MW1-25/28 and Highway 308 because contaminants have not been detected in the downgradient wells as of 2000.

Effectiveness of Natural Attenuation at Meeting Remediation Goals

There is clear evidence for substantial degradation and overall attenuation of CVOCs at OU 1. However, for natural attenuation to be an effective sole remedy under the 1998 Record of Decision, it would need to meet the specific remediation goals for a site. The numerical remediation goals related to chlorinated VOCs in ground water and surface water at OU 1 are shown in [table 6](#).

In June 2000, natural attenuation alone was not effective enough to meet the numerical remediation goals for ground water or surface water at OU 1. Chlorinated VOC concentrations in upper-aquifer ground water beneath the landfill substantially exceeded remediation goals; multiple ground-water remediation goals were exceeded in five wells that were sampled as part of the long-term monitoring program (1MW-1, MW1-2, MW1-4, MW1-5, and MW1-16)(CH2MHill Constructors, Inc., 2001), and one or more ground-water remediation goals were exceeded at all nine upper-aquifer piezometers sampled during this investigation.

Chlorinated VOC concentrations in intermediate-aquifer ground water were greatly attenuated when compared to landfill concentrations, but ground-water remediation goals for *cis*DCE and VC were still notably exceeded in two intermediate-aquifer wells (MW1-25 and MW1-28), and the goal for VC was slightly exceeded in a downgradient well (MW1-39).

Table 5. First-order attenuation half-lives of chlorinated ethene for segments of selected flowpaths at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; VC, vinyl chloride]

Flowpath and segment	First-order attenuation half-life $T_{1/2}$		
	TCE (years)	cisDCE (years)	VC (years)
Upper Aquifer			
North landfill to marsh			
Flowpath A, segment 2	0.5	0.3	1.3 – 0.1
Flowpath B, segment 2	0.1	0.1	-0.5 – 0.3
Flowpath B, segment 3	-0.1	0.2	0.2
Average flowpath, segment 2	0.3	0.2	0.3 – 0.2
Marsh to Highway 308			
Flowpath A, segment 3	2.7	3.6 – 3.5	5.5 – 4.2
Average flowpath, segment 3	2.6	3.9	6.5 – 4.8
South landfill to marsh			
Flowpath C, segment 2	-0.9	0.7	1.3 – 0.4
Flowpath C, segment 3	0.3	0.3	1 – 0.5
Flowpath C, segment 4	0.4	-2.5 – -13	0.1
Flowpath D, segment 2	1.4	1 – 0.8	1.1 – 0.3
Flowpath D, segment 3	0.1	1.5 – 0.8	-1.5 – 0.7
Flowpath E, segment 2	1.0	1.6 – 1.3	3.3 – 0.6
Flowpath E, segment 3	0.5	0.4	0.4 – 0.3
Intermediate aquifer			
Upper aquifer to intermediate aquifer			
Flowpath F, segment 1	1.7	5.6 – 5.1	3.5 – 2
Intermediate aquifer to Highway 308	3.9	2.7	3.0 – 2.7

Chlorinated VOC concentrations in marsh ground water were also greatly attenuated when compared to landfill concentrations, but the VC ground-water remediation goal for the protection of surface water was exceeded in eight of the 16 diffusion samplers (N-2, N-3, N-4, N-8, C-2, S-3, S-4, and S-5); the remediation goal for 1,1-DCE was also exceeded in the S-4 diffusion sampler.

And finally, CVOC concentrations in surface water were also greatly attenuated when compared to landfill concentrations, but surface-water remediation goals for VC were exceeded at three of the five surface-water sites that are part of the long-term monitoring program (MA-12, MA-11, and TF-19). The TCE goal was also exceeded at site MA-12 near the southern plantation where the VC exceedance was most substantial.

Table 6. Numerical remediation goals for concentrations of chlorinated volatile organic compounds in ground water and surface water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[μg/L, micrograms per liter; –, no criterion]

Chemical of concern	Ground-water remediation goal for drinking-water protection (μg/L)	Ground-water remediation goal for surface-water protection (μg/L)	Surface-water remediation goal (μg/L)
Tetrachloroethene	5	4.2	4.2
Trichloroethene	5	56	56
cis-1,2-dichloroethene	70	–	–
trans-1,2-dichloroethene	100	33,000	33,000
Vinyl chloride	0.5	2.9	2.9
1,1,1-trichloroethane	200	41,700	41,700
1,1-dichloroethane	800	–	–
1,2-dichloroethane	5	59	59
1,1-dichloroethene	0.5	1.9	1.9

CONCLUSIONS

Current Understanding of Natural Attenuation at OU 1

Natural attenuation of CVOCs in shallow ground water at OU 1 is substantial. Approximately 70 percent of the mass of dissolved chlorinated ethenes that is available to migrate from the landfill is completely degraded in shallow ground water and does not migrate to the intermediate aquifer or discharge to surface water. Attenuation of CVOC concentrations appears also to be substantial in the intermediate aquifer, but biodegradation appears to be less active. The conclusions regarding the intermediate aquifer are less certain and more difficult to quantify because of the paucity of data downgradient of the landfill beneath the tide flats. Attenuation of CVOC concentrations also is substantial in surface water as it flows through the adjacent marsh and out to the tide flats. Attenuation processes other than dilution reduce the flux of CVOCs in marsh surface water by about 40 percent by the time the water discharges to the tide flats. Despite the importance of natural attenuation processes at reducing both the contaminant concentrations and the contaminant mass at OU 1, natural attenuation alone was not effective enough in the year 2000 to meet current numerical remediation goals for the site. That was due in part to the relatively short distance between the landfill and the adjacent marsh, and in part to the high CVOC concentrations beneath the landfill.

Most of the data needed to characterize the hydrogeology were collected and reasonably interpreted before this investigation. Additional interpretation of existing data and new data collected for this study, including stable-isotope and common-ion concentrations, suggest that there are likely two distinct flowpaths for contaminant migration into the intermediate aquifer. The first flowpath begins with contaminated shallow ground water beneath the northern plantation and flows through the middle aquitard and downgradient to the slightly contaminated intermediate well MW1-39. The second flowpath begins with contaminated shallow ground water from beneath perhaps both plantations and flows through a permeable window in the middle aquitard to the moderately contaminated intermediate aquifer wells MW1-25 and 28.

The second flowpath likely continues downgradient to currently uncontaminated wells screened deeper in the intermediate aquifer (MW1-36 or MW1-38), but it may flow upward to discharge into the tide flats. Interpretation of new ground-water age-date estimates based on tritium/helium analysis reconciled some past discrepancies between ground-water flow rates in the intermediate aquifer that were estimated using different techniques.

With regard to geochemical characterization, the distribution of total CVOCs in shallow ground water was determined in greater detail by integrating data from existing monitoring wells with newly collected data from piezometers in the landfill and diffusion samplers beneath the adjacent marsh. The refined distribution shows that the highest CVOC concentrations beneath the landfill are about four times greater than previously thought, and that the pattern of CVOC concentrations in shallow marsh ground water correlates well with the pattern observed beneath the landfill. The latter observation was evidence that the diffusion samplers used to collect CVOC samples from the marsh worked as intended and are representative of shallow ground-water conditions.

Also with regard to geochemical characterization, ground-water redox conditions beneath the former landfill were found to be generally favorable for complete degradation of CVOCs through either reductive dechlorination alone or through the combined processes of reductive dechlorination and mineralization. Two areas of strongly reducing ground water (sulfate reduction or methanogenesis) that are favorable for reductive dechlorination were delineated beneath the landfill—one in the vicinity of the northern plantation and one in the southern plantation. Those areas were surrounded by mildly reducing ground waters (iron or manganese reducing) that may be favorable for mineralization of CVOCs. The landfill is a substantial source of organic carbon in shallow ground water, and the correlation between organic carbon and redox conditions is clear evidence that microbially mediated processes are controlling redox conditions.

Ground-water redox conditions within the intermediate aquifer were generally less favorable for reductive dechlorination, but were somewhat favorable for mineralization of CVOCs. Redox conditions in contaminated intermediate aquifer wells ranged from strongly reducing to mildly reducing. Organic carbon concentrations were somewhat elevated in contaminated intermediate-aquifer wells, but were substantially less than those found in shallow ground water beneath the landfill.

The evaluation of natural attenuation found consistent evidence for both partial and complete degradation of CVOCs in ground water at OU 1, particularly within the upper aquifer beneath the landfill. The evidence included temporal changes in CVOC concentrations at individual wells between 1991 and 2000 and changes in 1999 CVOC concentrations and redox-sensitive geochemicals along ground-water flowpaths.

Temporal changes in CVOC concentrations at individual wells in shallow ground water beneath the landfill indicated substantial attenuation and degradation of CVOCs. Beneath the northern plantation, CVOC concentrations decreased beneath the southern part of the plantation due to biodegradation, but were unchanged beneath the northern part. Beneath the southern plantation, CVOC concentrations generally decreased beneath the northern part of the plantation, but increased beneath the southern part. Much of the long-term concentration decrease could be attributed to biodegradation.

Changes in CVOC and geochemical concentrations along ground-water flowpaths beneath the landfill also indicated substantial attenuation and degradation. Total CVOC concentrations decreased along ground-water flowpaths between the landfill and the marsh, and along many flowpaths the predominant CVOC switched from a more highly chlorinated compound to a less chlorinated compound. That switch indicates active reductive dechlorination. Also along many flowpaths, concentrations of redox-sensitive compounds such as H_2, HCO_3^-, iron (II), and sulfide increased while TOC and sulfate concentrations decreased. That pattern is consistent with conditions suitable for active reductive dechlorination. Similar to the historical CVOC evidence, the flowpath evidence indicated more substantial attenuation and degradation beneath the southern part of the northern plantation, and beneath the beneath the northern part of the southern plantation.

Temporal changes in CVOC concentrations at individual wells in the most contaminated part of the intermediate aquifer indicated little attenuation or degradation. There was substantial attenuation and degradation beneath the far northern margin of the landfill in the intermediate aquifer where CVOC concentrations were much lower to begin with.

Changes in CVOC and geochemical concentrations along ground-water flowpaths between the upper aquifer and the main body of the intermediate aquifer indicated substantial attenuation but uncertain degradation; H_2 concentrations in the main body of the intermediate aquifer were not indicative of the strongly reducing conditions needed to sustain reductive dechlorination. Along flowpath segments farther downgradient of the landfill in the main body of the intermediate aquifer, it could only be concluded that contaminants have not migrated to beneath Highway 308. The lack of observation points beneath the tide flats did not allow rigorous evaluation of attenuation processes, and the available data could reflect either biodegradation, dilution, discharge of ground water to the tide flats upgradient of Highway 308, or simply that not enough time has passed for the contaminants to reach most Highway 308 wells. Along the newly identified ground-water flowpath between the upper aquifer and the Highway 308 intermediate aquifer well MW1-39 at the Highway 309 bridge, the evidence suggested substantial attenuation but was again uncertain because of the lack of observation points beneath the tide flats.

There have been no clear long-term changes in CVOC concentrations at surface-water sites in the marsh, but there is substantial attenuation of concentrations in surface water as it flows through the marsh and across the tide flats. The predominant ethenes and ethanes in surface water have been *cis*DCE and DCA, respectively, but the relative abundance of VC and CA has been increasing. Those observations reflect the observed temporal pattern of ethene and ethane predominance in most southern plantation wells where most surface-water contaminants originate. Biodegradation is likely insignificant in surface water, but dilution and volatilization substantially attenuate contaminant concentrations in the downstream direction.

Flux-based calculations of the degradation rates of contaminant mass indicate that the majority of dissolved chlorinated ethenes in landfill ground water are degraded in ground water before they have an opportunity to discharge to surface water. Of the mass of dissolved chlorinated ethenes available to migrate from the landfill, an estimated 73 percent is degraded in ground water and only 27 percent actually discharges to surface water. Nearly all TCE is degraded, about 60 percent of the *cis*DCE is degraded, and about 40 percent of the VC is degraded. An alternate estimate of chlorinated ethene discharge to the marsh indicated that the actual TCE and *cis*DCE discharge rates might be about 100 and 30 percent greater, respectively, than the flux-based estimates. The flux-based estimates were low because the diffusion samplers did not fully represent contaminant discharge to the southeastern portion of the marsh. Additional calculations suggest there was a net loss of about 30 percent of the TCE flux, 40 percent of the *cis*DCE flux, and 50 percent of the VC flux contaminants in surface water as it flows through the marsh and out to the tide flats. The loss was likely due to nondestructive attenuation processes such as volatilization before discharging to the tide flats.

Comparison of calculated attenuation rates of chlorinated ethene concentration for different ground-water flowpaths confirmed the previous findings regarding where biodegradation is most effective at OU 1. Attenuation rates varied throughout the upper aquifer beneath the landfill in close accordance with the location of favorable redox conditions, and attenuation rates in the intermediate aquifer were substantially slower.

Based on data collected through June 2000, natural attenuation alone was not effective enough to meet the numerical remediation goals for ground water or surface water at OU 1. CVOC concentrations in upper-aquifer ground water beneath the landfill substantially exceeded remediation goals; multiple remediation goals were exceeded in five wells that were sampled as part of the long-term monitoring program, and one or more remediation goals were exceeded at all nine upper aquifer piezometers sampled during this investigation. CVOC concentrations in intermediate-aquifer ground water were greatly attenuated when compared to landfill concentrations, but ground-water remediation goals for *cis*DCE and VC were still notably exceeded in two intermediate-aquifer wells, and the goal for VC was slightly exceeded in a third well. CVOC concentrations in marsh ground water were also greatly attenuated when compared to landfill concentrations, but the ground-water remediation goal for VC for the protection of surface water was exceeded in eight of the 16 diffusion samplers.

And finally, CVOC concentrations in surface water were also greatly attenuated when compared to landfill concentrations, but surface-water remediation goals for VC were exceeded at three of the five surface-water sites that are part of the long-term monitoring program, and the TCE remediation goal was exceeded at one site.

Current Impacts of Phytoremediation Activities on Natural Attenuation

Phytoremediation activities apparently had some impact on contaminant concentrations in ground water and surface water, but ground-water redox conditions to date (2000) were not affected by the removal of asphalt in February 1999 for tree planting. Performance monitoring by the Navy during 1999 and 2000 showed that ground-water flow directions and gradients were consistent with historical findings. The poplar trees in the phytoremediation plantations were not yet mature in 2000, so the lack of discernable changes to date is not unexpected.

Redox conditions in the upper aquifer did not change substantially after the initiation of phytoremediation activities, but decreased concentrations of some redox-sensitive compounds suggest that increased recharge following the February 1999 asphalt removal somewhat diluted ambient landfill ground water. In selected southern plantation wells, concentrations of the relatively mobile compounds manganese, iron (II), and TOC decreased by more than 50 percent between October 1998 and June 2000. A similar response to asphalt removal was not evident in the northern plantation, likely because much of that area was not paved prior to phytoremediation. There was no evidence of geochemical changes in the intermediate aquifer as a result of asphalt removal.

Increases in CVOC concentrations after 1998 in downgradient wells in the northern and southern plantations were coincidental with asphalt removal for phytoremediation. The northern part of the northern plantation was never paved, so post-1998 changes were not evident. Decreases in CVOC concentrations after 1998 in upgradient wells in the southern plantation were also coincidental with asphalt removal for phytoremediation.

There was no evidence for CVOC changes in the intermediate aquifer that could be attributed to asphalt removal. A distinct post-1998 increase in CVOC concentrations in marsh surface water was coincidental with the asphalt removal, and the increase appeared to have resulted from increased contaminant discharge from the southern plantation.

Continued Monitoring of Natural Attenuation

Current plans call for sampling of analytes related to natural attenuation at eight wells once every year through 2004 and once every 5 years after 2004. The wells identified for sampling are 1MW-1 and MW1-2 in the northern plantation; MW1-4, MW1-5, and MW1-6 in the southern plantation; and MW1-25, MW1-28, and MW1-39 in the intermediate aquifer. The analytes identified for sampling are those shown in tables 7 and 8 of this report. The Navy and regulatory agencies may mutually agree to adjust the sampling locations, frequencies, and analytes.

With regard to sampling frequency, it would be informative to sample in March and September during at least a single year after the plantation canopy is closed completely and tree roots have reached the water table. The first possible year for that will likely be 2002. Data from seasonal sampling would give more definitive evidence on effects of phytoremediation activities on ground-water redox conditions. The growing season begins and the recharge season ends in March, and both the growing season and dry season are nearly over in September. Also, the decision to switch to a 5-year sampling cycle would best be made nearer the year 2004 when additional data will be available to evaluate whether ground-water conditions are relatively stable.

With regard to sampling locations, the eight wells identified for sampling may be too few. Past natural-attenuation sampling rounds have included 12 to 20 wells or piezometers to fully characterize site redox conditions. Including at least one upgradient well in the upper aquifer (MW1-3 or MW1-20) and one in the intermediate aquifer (MW1-33) will provide comparison data to assess how geochemical conditions change beneath the landfill.

The landfill piezometers are also located in the most contaminated parts of the landfill, so it would be beneficial to sample VOCs and geochemistry at those sites at least every other year through 2004. And given the newly hypothesized flowpaths for the intermediate aquifer, it would be worthwhile to sample the VOCs and geochemistry in another intermediate aquifer well at Highway 308 (MW1-38) to monitor possible contaminant migration from MW1-25 and MW1-28. The passive diffusion samplers provided valuable information on overall contaminant attenuation in ground water, and it would be useful to sample those same sites (with a few modifications to better monitor ground-water discharge in the vicinity of MW1-4) a few years after the plantation canopy is closed and tree roots have reached the water table. Multilevel diffusion samplers (referred to as "peepers") rather than single samplers would allow better documentation of attenuation processes in marsh sediments. It would be informative to deploy diffusion samplers or peepers in March and September to coincide with the proposed one-time seasonal sampling, but sampling VOCs in surface water could be used as a reasonable proxy for those seasonal data.

With regard to analytes sampled, the list of geochemicals identified is adequate. In June 2001, the USGS collected and analyzed both total and dissolved organic carbon (TOC and DOC) at 19 wells. DOC is thought to be a somewhat better measure of bioavailable organic carbon, so future sampling could include DOC rather than TOC with little loss of continuity. It would be useful to measure redox-sensitive compounds in diffusion samplers if that capability is available in the near future; the capability is available now to measure dissolved oxygen and possibly methane in diffusion samplers. And it would be useful to measure surface-water discharge directly in the marsh during the proposed seasonal sampling events, or at least during the year when diffusion samplers are deployed. Those data could be used to confirm the hypothesis of seasonal or no ground-water discharge to the marsh from the northern part of the landfill.

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TABLES 7, 8, 9, 10, 11, AND 12

Table 7. Predominant redox conditions at selected wells and ground-water chemistry data collected from 1996 to 2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[U, upper aquifer; I, intermediate aquifer; Fe, iron reducing; S, sulfate reducing; Mn, manganese reducing; M, methanogenic; A, aerobic; H_2, hydrogen; nM, nanomolar; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter; <, less than; >, greater than; –, not analyzed]

Well identification No.	Date sampled	Hydro-geologic unit	Pre-dominant redox condition	Ground-water chemistry data											
				Dissolved H_2 (nM)	Dissolved oxygen (mg/L)	Total organic carbon (mg/L)	Nitrate (mg/L)	Dissolved manganese (mg/L)	Dissolved iron (II) (mg/L)	Dissolved sulfate (mg/L)	Dissolved sulfide (mg/L)	Dissolved methane (mg/L)	Total bicarbonate (mg/L)	pH (units)	Specific conductance (μS/cm)
1MW-1	09-17-96	U	Fe	0.4	2.8	7.0	<0.02	0.18	0.24	7.5	0.00	10	640	7.9	–
	04-16-97		Fe	0.8	0.4	–	0.11	–	8.0	1.4	0.01	29	1,140	7.2	–
	03-05-98		Fe/S	0.2	0.1	8.3	–	0.39	12	–	0.06	–	–	–	–
	10-09-98		Fe	0.2	0.5	–	–	0.08	0.39	–	0.01	–	660	7.7	1,080
	06-21-00		Mn/Fe	0.1	0.5	12	<0.05	0.96	13	0.9	0.00	0.39	590	7.0	1,070
1MW-4	09-17-96	I	S/M	0.6	1.6	23	<0.02	0.77	1.4	0.04	0.00	16	780	7.3	–
	04-16-97		S/M	1.8	0.0	–	0.03	–	1.7	0.36	0.02	47	1,280	7.3	–
MW1-2	09-17-96	U	Fe	0.5	2.4	6.0	<0.02	0.05	0.23	4.6	0.00	1.2	510	6.9	–
	04-16-97		S	1.1	0.2	–	<0.02	–	0.13	4.6	0.00	2.5	1,140	6.7	–
	03-02-98		Fe	0.3	0.1	–	–	–	0.16	–	–	–	–	–	–
	10-07-98		Fe	0.1	0.1	–	–	0.05	0.14	–	0.00	–	300	6.7	868
	06-09-99		Fe	0.9	0.2	–	–	0.08	0.09	–	0.00	–	490	6.8	901
	06-21-00		Fe	0.3	0.1	6.0	<0.05	0.06	0.10	4.3	0.00	0.04	460	6.8	870
MW1-3	06-09-99	U[1]	Fe	0.8	0.4	–	–	0.07	<0.01	–	0.01	–	81	6.0	202
	06-20-00		Fe	0.2	0.3	2.0	0.99	0.08	<0.01	13	0.00	0.02	82	5.9	205
MW1-4	09-17-96	U	Fe	0.5	2.8	2.0	<0.02	0.28	1.8	7.1	0.00	1.2	130	6.9	–
	04-16-97		Fe	0.6	0.4	–	0.24	–	0.00	8.6	0.00	0.70	270	7.4	–
	03-03-98		S	1.7	0.2	4.0	–	0.10	0.01	–	0.00	–	–	–	–
	10-08-98		Fe	0.2	0.5	–	–	–	0.28	–	0.00	–	170	6.7	368
	06-07-99		Fe	0.9	0.1	–	–	0.20	1.2	–	0.00	–	180	6.6	350
	06-22-00		Fe	0.2	0.1	8.6	–	0.70	–	5.5	0.00	0.56	230	6.8	412
MW1-5	09-17-96	U	S	1.2	0.0	15	<0.02	1.6	19	6.4	0.01	2.4	330	6.7	–
	04-16-97		Fe	0.5	0.0	–	0.08	–	3.1	2.8	0.03	18	1,380	6.6	–
	03-04-98		Fe	0.7	0.0	12	–	1.3	4.5	–	0.00	–	–	–	–
	10-08-98		S	2.4	0.0	–	–	1.5	11	–	0.00	–	410	6.4	1,740
	06-08-99		Fe	0.6	0.3	–	–	1.2	30	–	0.01	–	510	6.5	855
	06-22-00		Fe	–	0.0	17	–	1.5	39	6.4	0.01	1.1	460	6.6	790

Table 7. Predominant redox conditions at selected wells and ground-water chemistry data collected from 1996 to 2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well identi-fication No.	Date sampled	Hydro-geologic unit	Pre-dominant redox condition	Ground-water chemistry data											
				Dissolved H_2 (nM)	Dis-solved oxygen (mg/L)	Total organic carbon (mg/L)	Nitrate (mg/L)	Dis-solved man-ganese (mg/L)	Dis-solved iron (II) (mg/L)	Dis-solved sulfate (mg/L)	Dis-solved sulfide (mg/L)	Dis-solved methane (mg/L)	Total bicar-bonate (mg/L)	pH (units)	Specific conduc-tance (µS/cm)
MW1-6	09-17-96	U	S	1.1	0.0	33	1.2	1.2	30	0.10	0.00	7.0	840	6.7	–
	04-16-97		S	0.5	0.0	–	0.07	–	36	4.2	0.15	14	1,140	6.5	–
	10-08-98		Fe	0.2	0.0	–	–	1.1	32	–	0.01	–	720	6.4	1,170
MW1-14	09-17-96	U	S/M	0.6	0.0	42	<0.02	2.0	67	0.27	0.00	9.2	1,260	6.4	–
	04-16-97		S/M	0.7	0.0	–	0.05	–	78	0.13	0.00	46	1,750	6.4	–
	03-04-98		Fe/S	–	0.1	36	–	11	68	–	0.05	–	–	–	–
	10-07-98		S	1.2	0.0	–	–	1.5	48	–	0.01	–	600	6.3	1,450
	06-09-99		S	1.0	0.3	–	–	0.30	57	–	0.36	–	810	6.4	1,220
MW1-15	09-16-96	U	S/M	0.2	0.0	50	<0.02	5.7	68	0.11	0.00	8.8	1,160	–	–
	04-16-97		S/M	0.8	0.0	–	<0.02	–	77	0.08	0.03	44	1,630	6.3	–
	03-05-98		S	1.2	0.0	33	–	18	51	–	0.00	–	–	–	–
	10-09-98		S	2.9	0.0	–	–	5.8	64	–	0.01	–	750	6.3	1,110
MW1-16	09-17-96	U	S	2.1	0.0	480	<0.02	3.9	130	0.17	0.00	4.3	1,350	6.5	–
	04-16-97		S/M	1.0	0.0	–	<0.02	–	120	2.0	0.06	29	1,840	6.5	–
	03-04-98		Fe	0.7	0.3	350	–	18	100	–	0.01	–	–	–	–
	10-08-98		M	9.6	0.0	–	–	5.4	180	–	0.01	–	1,560	6.3	3,370
	06-07-99		M	6.8	0.6	–	–	>5	140	–	0.12	–	1,210	6.7	1,820
	06-22-00		S	–	0.1	61	–	1.9	60	1.2	0.02	1.2	510	6.7	902
MW1-17	09-17-96	U	Fe/S	0.9	0.0	23	<0.02	1.3	62	4.3	0.00	8.9	760	6.5	--
	04-16-97		Fe	0.6	0.0	–	<0.02	–	37	68	0.02	23	1,200	6.6	--
	10-09-98		Fe	–	0.0	–	–	0.80	56	–	0.02	–	510	6.4	1,740
	06-22-00		S	1.2	0.0	11	–	–	68	–	0.02	2.8	450	6.5	1,260
MW1-18	09-17-96	U	Fe/S	1.0	0.3	28	<0.02	4.0	12	4.6	0.00	11	880	7.0	–
	04-16-97		Fe	0.5	0.0	–	0.05	–	23	8.2	0.00	52	1,510	6.8	–
	10-07-98		Fe	–	0.2	–	–	0.77	3.3	–	0.01	–	920	7.3	1,780
MW1-20	06-08-99	U[1]	Fe	0.9	0.3	–	–	0.35	0.03	–	0.01	–	260	6.7	546
	06-21-00		Fe	0.4	0.0	2.2	<0.05	0.24	0.11	16	0.00	0.01	240	6.8	530
MW1-25	09-17-96	I	Fe	0.4	2.7	7.4	0.14	0.16	0.74	16	0.01	3.6	360	7.1	–
	04-17-97		Fe	0.8	0.1	–	<0.02	–	0.88	15	0.01	7.9	1,010	7.0	–
	03-05-98		Fe	0.3	0.3	7.9	–	0.20	0.73	–	0.00	–	–	–	–
	10-05-98		Fe	0.2	0.1	–	–	0.19	0.99	–	0.01	–	450	6.9	1,240

Table 7. Predominant redox conditions at selected wells and ground-water chemistry data collected from 1996 to 2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well identi-fication No.	Date sampled	Hydro-geologic unit	Pre-dominant redox condition	Ground-water chemistry data											
				Dissolved H$_2$ (nM)	Dis-solved oxygen (mg/L)	Total organic carbon (mg/L)	Nitrate (mg/L)	Dis-solved man-ganese (mg/L)	Dis-solved iron (II) (mg/L)	Dis-solved sulfate (mg/L)	Dis-solved sulfide (mg/L)	Dis-solved methane (mg/L)	Total bicar-bonate (mg/L)	pH (units)	Specific conduc-tance (µS/cm)
MW1-25	06-22-00		Fe	0.4	0.2	6.5	–	0.16	0.80	12	0.00	0.79	380	6.9	1,230
MW1-28	09-16-96	I	Fe	0.5	2.1	7.2	<0.02	0.20	1.0	48	0.00	1.7	350	–	–
	04-17-97		Fe	1.0	0.0	–	0.04	–	0.99	51	0.01	5.3	1,100	7.4	–
	03-05-98		Fe	0.4	0.5	7.7	–	0.20	0.67	–	0.00	–	–	–	–
	10-07-98		Fe	0.6	0.0	–	–	0.19	1.0	–	0.02	–	320	6.6	2,630
	06-22-00		Fe	0.3	0.0	13	–	0.16	0.66	44	0.01	0.45	480	7.3	2,460
MW1-29	09-16-96	I	Mn/Fe	0.0	1.9	–	<0.02	0.86	2.0	1.8	0.02	8.1	300	–	–
	04-17-97		Fe	0.7	0.0	–	0.29	–	2.1	1.1	0.01	18	710	7.3	–
MW1-31	09-16-96	I[1]	Mn/Fe	–	–	5.6	–	3.6	0.32	–	–	–	–	–	–
MW1-32	09-16-96	I[2]	Fe	0.5	2.7	0.8	0.07	0.23	1.3	16	0.01	<0.01	110	–	–
	04-17-97		Fe	–	1.2	–	0.17	–	0.87	17	0.01	<0.01	300	7.1	–
	03-02-98		Fe	–	<1.0	–	–	0.10	1.1	–	0.01	–	–	–	–
	10-05-98		Fe	0.1	0.0	–	–	0.36	1.0	–	0.01	–	130	7.2	270
MW1-33	10-07-98	I[1]	A	–	3.3	0.1	–	0.003	0.0	–	0.01	–	78	6.6	177
	06-21-00		A	–	3.8	0.7	1.3	<0.002	0.0	7.5	0.00	0.05	74	6.7	164
MW1-35	10-07-98	U[1]	A	–	2.4	1.9	–	0.15	0.0	–	0.00	–	110	6.4	301
	06-08-99		A	–	2.1	–	–	–	--	–	–	–	76	6.4	187
	06-20-00		A	–	3.0	2.2	0.16	<0.002	0.0	3.9	0.00	0.01	77	6.6	151
MW1-36	10-09-98	I[3]	Fe	–	0.0	–	–	0.30	3.6	–	0.01	–	280	7.3	8,610
	06-20-00		Fe	0.5	0.1	2.4	<0.05	0.28	3.2	180	0.02	0.01	270	7.3	7,940
MW1-37	09-16-96	I[4]	Fe	0.8	1.2	6.9	<0.02	0.12	0.48	23	0.03	0.30	280	–	–
	04-17-97		S	3.3	0.0	–	<0.02	–	0.80	27	0.02	0.90	730	7.7	–
	03-03-98		Fe	0.4	0.4	5.7	–	0.10	0.86	–	0.00	–	–	–	–
	10-09-98		Fe	0.4	0.0	–	–	<0.01	0.43	–	0.01	–	340	7.9	2,440
	06-07-99		Fe	0.4	0.4	–	–	0.10	0.32	–	0.03	–	340	7.7	2,920
	06-20-00		Fe	0.1	0.1	5.8	<0.05	0.13	0.30	28	0.02	0.07	350	7.6	3,240
MW1-38	10-09-98	I[3]	Fe	–	0.1	–	–	0.20	0.08	–	0.02	–	310	7.8	1,460
	06-20-00		Fe	0.1	0.2	5.6	<0.05	0.08	0.10	2.3	0.03	0.10	300	7.8	1,240

Table 7. Predominant redox conditions at selected wells and ground-water chemistry data collected from 1996 to 2000, at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well identi-fication No.	Date sampled	Hydro-geologic unit	Pre-dominant redox condition	Ground-water chemistry data											
				Dissolved H_2 (nM)	Dis-solved oxygen (mg/L)	Total organic carbon (mg/L)	Nitrate (mg/L)	Dis-solved man-ganese (mg/L)	Dis-solved iron (II) (mg/L)	Dis-solved sulfate (mg/L)	Dis-solved sulfide (mg/L)	Dis-solved methane (mg/L)	Total bicar-bonate (mg/L)	pH (units)	Specific conduc-tance (μS/cm)
MW1-39	09-16-96	I[4]	Fe	0.6	2.0	4.4	<0.02	0.02	0.0	0.71	0.04	1.6	140	–	–
	04-17-97		S	4.5	0.0	–	<0.02	–	0.05	13	0.06	6.1	360	7.9	–
	03-03-98		Fe	0.3	0.3	3.7	–	0.10	0.03	–	0.05	–	–	–	–
	10-09-98		Fe/S	0.5	0.0	–	–	<0.01	0.04	–	0.07	–	170	8.1	502
	06-07-99		Fe/S	1.0	0.3	–	–	0.10	0.02	–	0.00	–	180	8.0	512
	06-20-00		S	0.5	0.1	2.4	<0.05	0.01	0.10	0.2	0.08	0.41	180	8.0	481
MW1-41	06-09-99	U	S	1.0	0.3	–	–	2.2	60	–	0.01	–	860	6.6	1,260
	06-21-00		S/M	1.2	0.1	22	<0.05	3.5	55	<0.3	0.00	1.9	1,030	6.5	1,500
P1-1	06-09-99	U	Fe	0.7	0.4	–	–	4.0	59	–	0.00	–	930	6.4	1,350
P1-3	06-09-99	U	Fe	0.4	0.2	–	–	1.0	19	–	0.04	–	730	6.8	1,470
P1-4	06-09-99	U	Fe	0.7	0.3	–	–	0.34	2.6	–	0.02	–	450	7.0	867
P1-5	06-08-99	U	S	3.0	0.3	–	–	3.1	72	–	0.01	–	850	6.2	1,320
P1-6	06-08-99	U	S	1.8	0.1	–	–	0.12	0.02	–	0.04	–	300	6.8	574
P1-7	06-08-99	U	S	1.2	0.1	–	–	0.61	2.09	–	0.00	–	310	6.7	627
	06-22-00		Fe	–	0.1	19	–	2.6	3.8	24	0.00	1.5	400	6.8	851
P1-8	06-07-99	U	S	1.8	0.0	–	–	0.20	0.08	–	0.01	–	210	7.6	381
P1-9	06-08-99	U	M	19	0.3	–	–	0.90	0.03	–	0.00	–	270	6.6	680
	06-22-00		S/M	–	0.1	10	–	0.69	0.20	6.6	0.00	1.7	250	6.8	548
P1-10	06-07-99	U	Fe	0.7	0.3	–	–	0.10	0.11	–	0.00	–	300	6.7	560
	06-22-00		S/M	–	0.0	7.2	–	0.03	0.30	<0.31	0.01	1.3	290	7.1	500

[1]Background well

[2]Cross-gradient well, uncontaminated

[3]Lower part of intermediate aquifer

[4]Upper part of intermediate aquifer.

Table 8. Concentrations of chlorinated volatile organic compounds in ground water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[Laboratory data qualifier codes, such as "J" for estimated value and "D" for dilution, are not shown. PCE, tetrachloroethene; TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; *trans*DCE, *trans*-1,2-dichloroethene; VC, vinyl chloride; 1,1,1-TCA, 1,1,1-trichloroethane; 1,1,-DCA, 1,1-dichloroethane; CA, chloroethane; 1,1-DCE, 1,1-dichloroethene; BTEX, benzene, tolune, ethylbenzene, and xylenes; CVOCs, chlorinated volatile organic compounds; μg/L, micrograms per liter; <, less than; –, not analyzed or calculated; nd, none detected at unspecified level]

Well identi- fication No.	Date sampled	PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	1,1,1-TCA (μg/L)	1,1-DCA (μg/L)	CA (μg/L)	1,1-DCE (μg/L)	Total BTEX (μg/L)	Total CVOCs (μg/L)
1MW-1	06-11-99	<3	<3	310	170	960	<3	19	9.0	4.0	nd	1,500
1MW-4	04-16-97	<3.3	<2.6	11	<1.9	<1.3	–	–	–	<1.9	–	11
MW1-2	06-11-99	<3	27	980	26	160	<3	<3	<3	5.0	nd	1200
MW1-3	10-20-99	<0.5	0.70	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	0.70
MW1-4	06-14-99	4.0	2,600	12,000	140	1,500	<3	2.0	2.0	24	7.0	16,000
MW1-5	06-14-99	<3	2	9.0	2.0	260	<3	9.0	18	<3	29	300
MW1-6	04-16-97	<3.3	108	16	<1.9	9.4	–	–	–	<1.9	–	130
MW1-14	04-16-97	<3.3	<2.6	<1.9	<1.9	<1.3	–	–	–	<1.9	–	nd
MW1-15	04-16-97	<3.3	<2.6	<1.9	<1.9	<1.3	–	–	–	<1.9	–	nd
MW1-16	06-14-99	1.0	530	6,800	160	1,700	140	15,000	3,900	48	2,300	2,8000
MW1-17	04-16-97	<3.3	<2.6	16	<1.9	<1.3	–	–	–	<1.9	–	16
MW1-18	04-16-97	<3.3	<2.6	47	<1.9	28	–	–	–	<1.9	–	75
MW1-20	10-20-99	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-25	03-04-98	<0.5	56	1,700	35	210	<0.5	2.4	<0.5	5.3	nd	2,000
MW1-28	03-04-98	<0.5	0.98	1,500	64	400	<0.5	1.3	<0.5	4.3	nd	2,000
MW1-29	04-17-97	<3.3	<2.6	<1.9	<1.9	<1.3	–	–	–	<1.9	–	nd
MW1-31	09-12-96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-32	03-02-98	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-33	06-24-96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-35	09-09-96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-36	09-11-96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-37	06-07-99	<1	<1	<1	<0.5	<2	<1	<1	<2	<1	nd	nd
MW1-38	09-10-96	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	nd	nd
MW1-39	06-07-99	<1	<1	0.28	<0.5	1.2	<1	<1	<2	<1	nd	1
MW1-41	10-20-99	<0.5	<0.5	0.60	<0.5	<0.5	<0.5	<0.5	–	–	–	1

Table 8. Concentrations of chlorinated volatile organic compounds in ground water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well identi-fication No.	Date sampled	PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	1,1,1-TCA (μg/L)	1,1-DCA (μg/L)	CA (μg/L)	1,1-DCE (μg/L)	Total BTEX (μg/L)	Total CVOCs (μg/L)
P1-1	06-09-99	<2	11	6.1	<1	<4	<2	0.24	<4	<2	19	17
P1-3	06-09-99	<16	35	450	20	120	<16	<16	3.6	<16	nd	630
P1-4	06-09-99	<130	160	4,800	56	540	<130	<130	<270	<130	nd	5,600
P1-5	06-08-99	<13	440	400	3.5	11.0	<13	<13	15	<13	47	870
P1-6	06-08-99	<400	74	16,000	170	5,400	<400	1,500	300	<400	nd	23,000
P1-7	06-08-99	<670	26,000	35,000	210	3,100	<670	<670	<1,300	<670	nd	64,000
P1-8	06-07-99	<710	190	25,000	210	3,400	<710	<710	<1,400	<710	nd	29,000
P1-9	06-08-99	<2,000	48,000	88,000	470	7,200	<2,000	<2,000	<4,000	<2,000	nd	144,000
P1-10	06-07-99	<1,000	14,000	34,000	270	2,500	<1,000	<1,000	<2,000	<1,000	nd	51,000
S1	07-07-00	<0.1	1.4	8.2	0.69	1.5	<0.1	4.7	24	<0.1	2.6	40
S2	07-07-00	<0.1	0.60	11	1.3	2.8	<0.1	6.1	10	<0.1	2.6	32
S3	07-07-00	<0.1	0.63	9.9	9.5	220	<0.1	460	36	<0.1	5.9	730
S4	07-07-00	<0.1	45	19,000	140	5,600	<0.1	0.91	20	76	5.1	25,000
S5	07-07-00	<0.1	49	80	1.3	17	<0.1	<0.1	–	0.17	0.15	150
S6	07-07-00	<0.1	0.24	8.0	0.22	1.1	<0.1	<0.1	–	<0.1	0.62	10
C1	07-07-00	<0.1	<0.1	0.51	0.28	0.25	<0.1	<0.1	–	<0.1	1.4	1
C2	07-07-00	<0.1	0.11	3.8	0.25	12	<0.1	0.11	–	<0.1	2.7	16
C3	07-07-00	<0.1	<0.1	2.2	<0.1	0.44	<0.1	<0.1	–	<0.1	nd	3
N1	07-07-00	<0.1	0.13	0.68	<0.1	<0.2	<0.1	<0.1	–	<0.1	nd	1
N2	07-07-00	<0.1	0.42	46	2.5	86	<0.1	1.61	–	<0.1	0.57	140
N3	07-07-00	<0.1	16	410	13	130	<0.1	<0.1	–	1.2	nd	570
N4	07-07-00	<0.1	0.77	13	0.72	3.4	<0.1	<0.1	–	<0.1	0.14	18
N5	07-07-00	<0.1	0.83	13	0.35	0.24	<0.1	0.22	–	<0.1	0.28	15
N7	07-07-00	<0.1	0.91	6.7	0.23	1.9	<0.1	0.15	–	<0.1	0.27	10
N8	07-07-00	<0.1	0.12	7.6	0.23	3.2	<0.1	0.12	–	<0.1	0.13	11

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Data source code**: **1**, URS Consultants, Inc., 1993. **2**, URS Consultants, Inc., 1997a; Round 1. **3**, URS Consultants, Inc., 1997a; Round 2. **4**, URS Consultants, Inc., 1997a; Round 3. **5**, URS Consultants, Inc., 1997a; Round 4. **6** , URS Consultants, Inc., 1997a; Round 5. **7**, USGS, this report; 1996-97 data from Microbial Studies Group Laboratory, Columbia, SC by gas chromatography with flame-ionization detector. 1999-2000 data from Quanterra laboratory, EPA methods SW846 8260B, except ethene and ethane from Transglobal Env. Geo. NW, Inc., by modified EPA method 8015. **8** , Navy pre-ROD sampling Round 6; personal communication, Renee Wallis; U.S. Navy, EFA NW, Poulsbo, WA; EPA Method 8260. **9**, URS Greiner, Inc., 2000. **10**. CH2MHill Constructors, Inc., 2001. **Ethene**: Ethene data for September 1996 and April 1997 are reported as micromoles (µM) in the headspace of the sample vial. They are suitable for comparison between wells sampled during the same times only. Laboratory data qualifier codes, such as "J" for estimated value and "D" for dilution, are not shown. **Acroymns:** PCE, tetrachloroethene; TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; *trans*DCE, *trans*-1,2-dichloroethene; VC, vinyl chloride; 1,1,1-TCA, 1,1,1-trichloroethane; CA, chloroethane; 1,1-DCE, 1,1-dichloroethene; BTEX, benzene, toluene, ethylbenzene, and xylenes; CVOCs, chlorinated volatile organic compounds. **Abbreviations**: µg/L, micrograms per liter. **Symbols:** <, less than; --, not analyzed or calculated; nd, none detected at unspecified level]

Well or site No.	Date sampled	Data source code	PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	Total BTEX (µg/L)
										Ethene compounds →	**Specific chlorinated ethene as a percentage of total ethenes** →		
										Monitoring wells			
1MW-1	07-09-91	1	<0.01	15	2,300	–	1,500	–	3,800	0	60	39	5.0
	01-20-92	1	<10	45	1,900	–	1,100	–	3,000	1	62	36	nd
	08-25-95	2	<1	<1	590	180	1,000	–	1,800	0	43	56	nd
	12-06-95	3	<1	<1	87	7.7	210	–	300	0	31	69	1.6
	03-12-96	4	<0.5	0.62	450	120	710	–	1,300	0	45	55	1.2
	06-26-96	5	<0.5	0.51	460	220	1,200	–	1,900	0	36	64	nd
	09-17-96	7	<3.3	<2.6	410	160	500	<1	1,100	0	53	47	nd
	04-16-97	7	<3.3	<2.6	450	120	1,000	<1	1,600	0	36	64	–
	03-03-98	8	<0.5	<0.5	81	34	250	–	360	0	31	68	0.33
	06-11-99	9	<3	<3	310	170	960	–	1,400	0	33	67	nd
	10-20-99	9	<0.5	<0.5	320	190	970	–	1,500	0	34	66	–
	04-26-00	9	<0.5	<0.5	380	210	1,200	–	1,800	0	33	67	nd
	06-21-00	10	<0.5	0.58	240	210	1,200	8.6	1,700	0	27	73	0.20
	07-24-00	9	<25	<25	380	210	920	–	1,500	0	39	61	–
	10-31-00	9	<1	<1	270	160	1,300	–	1,700	0	25	75	–
1MW-4	07-09-91	1	<0.01	<0.01	1.0	–	100	–	100	0	1	99	3.0
	01-21-92	1	<10	<10	<10	–	140	–	140	0	0	100	nd
	08-21-95	2	<1	<1	<1	<1	62	–	62	0	0	100	0.62
	12-05-95	3	<1	<1	<1	<1	21	–	21	0	0	100	nd
	03-12-96	4	<0.5	<0.5	<0.5	<0.5	16	–	16	0	0	100	nd

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (µg/L)
			PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
							Monitoring wells—*Continued*						
1MW-4	06-26-96	5	<0.5	<0.5	<0.5	<0.5	6.2	–	6.2	0	0	100	nd
	09-17-96	7	<3.3	<2.6	54	<2	<1.4	<1	54	0	100	0	nd
	04-16-97	7	<3.3	<2.6	11	<2	<1.4	<1	11	0	100	0	–
MW1-2	06-19-91	1	<0.01	83	960	–	190	–	1,200	7	78	15	nd
	01-20-92	1	<10	70	1,300	–	160	–	1,500	5	85	10	nd
	08-28-95	2	<1	36	1,400	23	150	–	1,600	2	88	9	nd
	12-06-95	3	<1	35	1,300	22	140	–	1,500	2	88	9	nd
	03-11-96	4	<0.5	41	1,800	26	170	–	2,000	2	90	8	nd
	06-25-96	5	<0.5	43	1,500	31	180	–	1,800	2	87	10	nd
	09-17-96	7	<3.3	28	1,100	21	87	<1	1,200	2	91	7	nd
	04-16-97	7	<3.3	30	1,100	30	160	<1	1,300	2	86	12	–
	03-02-98	8	<0.5	29	1,200	21	110	–	1,400	2	90	8	nd
	06-11-99	9	<3	27	980	26	160	–	1,200	2	84	13	nd
	10-20-99	9	<0.5	23	1,000	21	110	–	1,200	2	88	10	–
	04-26-00	9	<0.5	13	1,900	49	230	–	2,200	1	89	10	0.60
	06-21-00	10	<0.5	22	890	21	110	0.26	1,000	2	87	11	0.30
	07-24-00	9	<25	<25	750	<25	87	–	840	0	89	11	–
	10-31-00	9	<1	12	810	15	84	–	920	1	90	9	–
MW1-3	06-20-91	1	<0.01	<0.01	<5	–	<0.01	–	nd	–	–	--	nd
	01-20-92	1	<10	<10	<10	–	<10	–	nd	–	–	--	nd
	03-08-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	4.4
	06-21-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	nd
	09-11-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	nd
	10-20-99	9	<0.5	0.70	<0.5	<0.5	<0.5	–	0.7	100	0	0	–
	04-26-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	nd
	06-20-00	7	–	–	–	–	–	0.12	–	–	–	--	–
	07-24-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	–
	10-31-00	9	<1	<1	<1	<1	<1	–	nd	–	–	--	–

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

| Well or site No. | Date sampled | Data source code | Ethene compounds | | | | | | | Specific chlorinated ethene as a percentage of total ethenes | | | Total BTEX (μg/L) |
			PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μm, or μg/L)	Total (μg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
						Monitoring wells—*Continued*							
MW1-4	06-19-91	1	<0.01	5,600	1,900	–	800	–	8,300	67	23	10	nd
	01-23-92	1	<10	1,300	700	–	690	–	2,700	48	26	26	nd
	08-23-95	2	2.2	11,000	6,400	80	2,000	–	19,000	56	33	10	2.2
	12-05-95	3	1.7	8,600	3,900	<500	2,800	–	15,000	55	27	18	nd
	03-05-96	4	0.96	6,300	3,500	56	1,100	–	11,000	58	32	10	1.2
	06-20-96	5	4.0	22,000	5,900	41	970	–	29,000	76	21	3	3.3
	09-17-96	7	20	7,800	7,300	109	970	2.0	16,000	48	46	6	6.0
	04-16-97	7	<3.3	3,300	1,200	24	410	<1	4,900	67	25	8	–
	03-03-98	8	3.8	22,000	13,000	140	1,900	–	37,000	59	35	5	9.9
	06-14-99	9	4.0	2,600	12,000	140	1,500	–	16,000	16	75	9	7.0
	10-20-99	9	0.70	3,600	5,300	70	1,100	–	10,000	36	53	11	–
	04-26-00	9	2.9	19,000	8,500	160	1,300	–	29,000	66	30	4	5.8
	06-22-00	10	<250	38,000	15,000	100	1,300	12	54,000	70	28	2	nd
	07-24-00	9	<250	18,000	8,500	<250	860	–	27,000	65	31	3	–
	11-09-00	9	<1	490	660	12	160	–	1,300	37	51	12	–
MW1-5	06-25-91	1	<0.01	<0.01	370	–	1,762	–	2,100	0	17	83	16
	01-23-92	1	<10	23	95	–	1,500	–	1,600	1	6	93	nd
	08-23-95	2	<1	1.9	17	1.3	140	–	160	1	11	88	2.3
	12-05-95	3	<1	7.3	74	16	4,300	–	4,400	0	2	98	1.8
	03-06-96	4	<0.5	3.0	60	7.0	1,100	–	1,200	0	6	94	6.2
	06-20-96	5	<0.5	1.7	93	6.5	1,500	–	1,600	0	6	94	8.4
	09-17-96	7	<3.3	292	709	<2	560	2.0	1,600	19	45	36	14
	04-16-97	7	<3.3	285	60	<2	140	<1	490	59	13	29	–
	03-04-98	8	<0.5	1.6	8.9	7.2	1,000	–	1,000	0	2	98	12
	06-14-99	9	<3	2.0	9.0	2.0	260	–	270	1	4	95	29
	10-20-99	9	<0.5	<0.5	0.50	<0.5	18	–	19	0	3	97	–
	04-26-00	9	<0.5	<0.5	1.2	<0.5	30	–	31	0	5	95	3.4

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (µg/L)
			PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
Monitoring wells—Continued													
MW1-5	06-22-00	10	<0.5	1.6	1.8	0.64	22	8.6	26	6	9	84	–
	07-25-00	9	<0.5	<0.5	3.4	<0.5	31	–	34	0	10	90	–
	11-06-00	9	<1	<1	<1	<1	7.0	–	7.0	0	0	100	–
MW1-6	06-25-91	1	<0.01	<0.01	2.0	–	<0.01	–	2.0	0	100	0	1.0
	01-23-92	1	<10	<10	<10	–	<10	–	nd	–	–	--	6.0
	08-24-95	2	<1	<1	<1	<1	<1	–	nd	–	–	--	9.6
	12-12-95	3	<1	<1	<1	<1	<1	–	nd	–	–	--	4.6
	03-07-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	4.6
	06-20-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	--	4.8
	09-17-96	7	<3.3	150	290	<2	89	<1	530	28	55	17	6.0
	04-16-97	7	<3.3	110	16	<2	9.4	<1	140	81	12	7	–
MW1-14	08-28-95	2	<1	<1	<1	<1	0.53	–	0.53	0	0	100	10
	09-17-96	7	<3.3	<2.6	99	<1.9	<1.2	<1	99	0	100	0	nd
	04-16-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	--	–
MW1-15	08-30-95	2	<1	<1	<1	<1	0.53	–	0.53	0	0	100	185
	09-16-96	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	--	7.0
	04-16-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	--	–
MW1-16	08-31-95	2	0.51	250	14,000	520	12,000	–	27,000	1	54	45	94
	06-20-96	5	1.3	34	3,100	180	2,200	–	5,500	1	59	40	2,500
	09-17-96	7	<3.3	11	1,100	29	1,200	12	2,300	0	48	51	390
	04-16-97	7	45	126	220	46	240	25	630	20	42	38	–
	03-04-98	8	1.5	3,900	18,000	180	3,900	–	26,000	15	70	15	1,600
	06-14-99	9	1.0	530	6,800	160	1,700	–	9,200	6	76	18	2,300
	10-20-99	9	1.2	9.2	28	26	28	–	91	10	59	31	–
	04-26-00	9	0.69	3.3	70	7.4	4.3	–	85	4	91	5	560
	06-22-00	10	1.0	20	13	12	6.6	70	52	39	48	13	1,100

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (µg/L)
			PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	

Monitoring wells—Continued

Well or site No.	Date sampled	Data source code	PCE	TCE	*cis*DCE	*trans*DCE	VC	Ethene	Total	% TCE	% trans/cis DCE	% VC	Total BTEX
MW1-16	07-25-00	9	<50	<50	<50	<50	<50	–	nd	–	–	–	–
	11-06-00	9	<1	4.1	12	16	0.5	–	33	12	86	2	–
MW1-17	08-29-95	2	<1	<1	6.4	0.94	6.9	–	14	0	50	47	12
	12-04-95	3	<1	<1	5.1	<1	4.3	–	9.4	0	54	41	11
	03-06-96	4	<0.5	<0.5	0.32	0.29	0.47	–	1.1	0	46	35	9.6
	06-24-96	5	<0.5	<0.5	1.4	0.51	1.2	–	3.1	0	57	36	14
	09-17-96	7	<3.3	<2.6	34	<2	52	<1	86	0	40	59	nd
	04-16-97	7	<3.3	<2.6	16	<2	0.62	<1	16	0	90	3	–
	06-22-00	10	<0.5	0.30	0.25	0.64	0.25	<0.1	1.4	21	62	17	4.0
MW1-18	08-28-95	2	<1	<1	<1	<1	34	–	34	0	0	100	nd
	12-05-95	3	<1	<1	<1	<1	35	–	35	0	0	100	nd
	03-12-96	4	<0.5	<0.5	<0.5	<0.5	66	–	66	0	0	100	nd
	06-26-96	5	<0.5	<0.5	<0.5	<0.5	45	–	45	0	0	100	nd
	09-17-96	7	<3.3	<2.6	137	<1.9	0.62	<1	140	0	99	1	nd
	04-16-97	7	<3.3	<2.6	47	<1.9	28	<1	75	0	63	37	–
MW1-20	08-30-95	2	<1	<1	<1	<1	<1	–	nd	–	–	–	nd
	12-08-95	3	<1	<1	<1	<1	<1	–	nd	–	–	–	nd
	03-11-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-27-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	10-20-99	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	–
	04-26-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-21-00	7	–	–	–	–	--	<0.1	nd	–	–	–	–
	07-25-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	–
	10-31-00	9	<1	<1	<1	<1	<1	–	nd	–	–	–	–
MW1-25	08-17-95	2	<1	100	2,500	49	440	–	3,100	3	83	14	0.60
	12-06-95	3	<1	74	2,200	38	240	–	2,600	3	88	9	nd
	03-11-96	4	<0.5	11	470	6.3	52	–	540	2	88	10	2.5

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

| Well or site No. | Date sampled | Data source code | Ethene compounds | | | | | | | Specific chlorinated ethene as a percentage of total ethenes | | | Total BTEX (μg/L) |
			PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μm, or μg/L)	Total (μg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
						Monitoring wells—Continued							
MW1-25	06-25-96	5	<0.5	70	2,200	51	300	–	2,600	3	86	11	nd
	09-17-96	7	<3.3	62	1,800	39	150	<1	2,100	3	90	7	nd
	04-17-97	7	<3.3	64	1,400	46	270	<1	1,800	4	81	15	–
	03-04-98	8	<0.5	56	1,700	35	210	–	2,000	3	87	10	nd
	06-22-00	10	<0.5	39	2,000	41	260	5.8	2,300	2	87	11	0.63
MW1-28	12-07-95	3	<1	2.3	1,600	61	450	–	2,100	0	79	21	nd
	03-08-96	4	<0.5	1.6	1,600	94	540	–	2,200	0	76	24	nd
	06-25-96	5	<0.5	2.2	1,700	85	620	–	2,400	0	74	26	nd
	09-09-96	6	<0.5	1.2	1,400	58	480	–	1,900	0	75	25	nd
	09-16-96	7	<3.3	<2.6	1,165	49	220	<1	1,400	0	85	15	nd
	04-17-97	7	<3.3	<2.6	1,065	75	520	<1	1,700	0	69	31	–
	03-04-98	8	<0.5	0.98	1,500	64	400	–	2,000	0	80	20	nd
	06-22-00	10	<0.5	0.81	1,300	74	520	2.6	1,900	0	73	27	nd
MW1-29	12-07-95	3	<1	<1	<1	<1	<1	–	nd	–	–	–	nd
	03-08-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-18-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-09-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-16-96	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	nd
	04-17-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	–
MW1-31	12-11-95	3	<1	<1	<1	<1	<1	–	nd	–	–	–	nd
	03-13-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-21-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-12-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
MW1-32	03-18-96	4	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-18-96	5	<0.5	0.46	<0.5	<0.5	<0.5	–	0.46	100	0	0	nd
	09-12-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-16-96	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	nd
	04-17-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	–
	03-02-98	8	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (μg/L)
			PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μm, or μg/L)	Total (μg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
						Monitoring wells—*Continued*							
MW1-33	06-24-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-21-00	7	–	–	–	–	–	0.18	nd	–	–	–	–
MW1-35	06-25-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-09-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-20-00	7	–	–	–	–	–	0.37	nd	–	–	–	–
MW1-36	06-17-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-11-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-20-00	7	–	–	–	–	–	<0.1	nd	–	–	–	nd
MW1-37	06-17-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-10-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-16-96	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	nd
	04-17-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	–
	06-07-99	7	<1	<1	<1	<0.5	<2	–	nd	–	–	–	nd
	06-20-00	7	–	–	–	–	–	–	nd	–	–	–	–
MW1-38	06-19-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-10-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	06-20-00	7	–	–	–	–	–	0.57	nd	–	–	–	–
MW1-39	06-17-96	5	<0.5	<0.5	<0.5	<0.5	0.80	–	0.80	0	0	100	4.6
	09-10-96	6	<0.5	<0.5	<0.5	<0.5	0.76	–	0.76	0	0	100	nd
	09-16-96	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	nd
	04-17-97	7	<3.3	<2.6	<1.9	<1.9	<1.2	<1	nd	–	–	–	–
	03-03-98	8	<0.5	<0.5	0.34	<0.5	1.40	–	1.7	0	20	80	nd
	06-07-99	7	<1	<1	0.28	<0.5	1.20	–	1.5	0	19	81	nd
	06-20-00	10	<0.5	<0.5	0.40	<0.5	2.00	0.26	2.7	0	17	83	nd
MW1-41	10-20-99	9	<0.5	<0.5	0.60	<0.5	<0.5	–	0.60	0	100	0	–
	04-26-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	1.7

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (μg/L)
			PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μm, or μg/L)	Total (μg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
							Monitoring wells—*Continued*						
MW1-41	06-21-00	10	<0.5	<0.5	0.82	<0.5	0.53	<0.1	1.3	0	0	100	3.0
	07-24-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	–
	11-02-00	9	<1	<1	<1	<1	<1	–	nd	–	–	–	–
							Piezometers						
P1-1	06-09-99	7	<2	11	6.10	<1	<4	–	17	65	35	0	19
P1-3	06-09-99	7	<16	35	450	20	120	–	620	6	75	19	nd
P1-4	06-09-99	7	<130	160	4,800	56	540	–	5,600	3	87	10	nd
P1-5	06-08-99	7	<13	440	400	3.5	11	–	860	51	47	1	47
P1-6	06-08-99	7	<400	74	16,000	170	5,400	–	22,000	0	75	25	nd
P1-7	06-08-99	7	<670	26,000	35,000	210	3,100	–	64,000	40	55	5	nd
	06-22-00	7	3.61	26,600	44,000	220	3,800	69	75,000	36	59	5	16
P1-8	06-07-99	7	<710	190	25,000	210	3,400	–	29,000	1	88	12	nd
P1-9	06-08-99	7	<2,000	48,000	88,000	470	7,200	–	140,000	33	62	5	nd
	06-22-00	7	4.99	88,000	64,000	320	5,800	37	160,000	56	41	4	22
P1-10	06-07-99	7	<1,000	14,000	34,000	270	2,500	–	51,000	28	68	5	nd
	06-22-00	7	1.04	8,730	13,000	100	2,260	2.3	24,000	36	54	9	12
							Seep						
SP1-1	05-16-90	1	<5	<5	<5	–	<5	–	nd	–	–	–	nd
	07-01-91	1	<0.01	<0.01	14	–	59	–	73	0	19	81	25
	01-22-92	1	<10	<10	55	–	160	–	210	0	26	74	4.0
	09-05-95	2	<1	<1	<1	<1	0.66	–	0.66	0	0	100	5.6
	12-05-95	3	<1	<1	<1	<1	<1	–	nd	–	–	–	1.0
	03-13-96	4	<0.5	<0.5	170	1.8	420	–	590	0	29	71	5.4
	07-02-96	5	<0.5	<0.5	7.4	0.76	31	–	39	0	21	79	4.7
	09-10-96	6	<0.5	<0.5	0.33	<0.5	1.1	–	1.1	0	23	77	8.8

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	Total BTEX (µg/L)
											Specific chlorinated ethene as a percentage of total ethenes		
					Ethene compounds								

Well or site No.	Date sampled	Data source code	PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µm, or µg/L)	Total (µg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	Total BTEX (µg/L)
						Seep—*Continued*							
SP1-1	06-11-99	9	<3	<3	4.0	<3	32	–	36	0	11	89	14
	10-20-99	9	<0.5	<0.5	0.60	<0.5	0.25	–	0.85	0	100	0	–
	04-26-00	9	<0.5	1.7	32	2.5	210	–	250	1	14	85	15
	07-25-00	9	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	–
	11-09-00	9	<1	<1	<1	<1	<1	–	nd	–	–	–	–
					Surface-water sites in downstream order								
MA01	06-10-91	1	<5	5.0	39	–	22	–	66	8	59	33	nd
	08-21-91	1	<5	<5	4.0	–	<10	–	4.0	0	100	0	nd
	01-14-92	1	<10	<10	10	–	3.0	–	13	0	77	23	nd
MA09	09-05-95	2	<1	<1	4.0	<1	1.3	–	5.3	0	75	25	nd
	12-05-95	3	<1	<1	14	<1	5.4	–	19	0	72	28	nd
	03-14-96	4	<0.5	1.2	11	<0.5	8.0	–	20	6	55	39	nd
	07-02-96	5	<0.5	<0.5	0.79	<0.5	<0.5	–	0.79	0	100	0	nd
	03-03-98	8	<0.5	<0.5	1.5	<0.5	0.30	–	1.8	0	83	17	nd
	06-01-00	10	<0.5	0.63	3.0	<0.5	0.64	–	4.3	15	70	15	nd
MA10	09-06-95	2	<1	<1	1.9	<1	0.64	–	2.5	0	76	24	nd
	12-06-95	3	<1	2.5	36	<1	17	–	56	4	65	30	nd
	03-13-96	4	<0.5	3.2	30	0.36	15	–	49	7	63	31	nd
	07-02-96	5	<0.5	0.49	6.3	<0.5	1.2	–	7.5	6	79	15	nd
MA11	09-06-95	2	<1	<1	0.51	<1	<1	–	0.51	0	100	0	nd
	12-06-95	3	<1	<1	10	<1	3.5	–	14	3	74	26	nd
	03-13-96	4	<0.5	1.6	13	<0.5	5.9	–	21	8	64	28	nd
	07-02-96	5	<0.5	<0.5	0.52	<0.5	<0.5	–	0.52	0	100	0	nd
	06-01-00	10	<0.5	7.9	33	0.56	9.2	–	51	16	66	18	nd
MA12	03-14-96	4	<0.5	26	180	1.6	<0.5	–	210	13	87	0	nd
	07-01-96	5	<0.5	64	480	3.5	<0.5	–	550	12	88	0	nd
	03-04-98	8	<0.5	45	200	1.6	49	–	300	15	68	17	0.28
	06-11-99	7	<3	130	710	8.0	150	–	1,000	13	72	15	nd
	10-20-99	9	<0.5	110	600	5.5	130	–	850	13	72	15	–

Table 9. Cumulative summary of concentrations of chlorinated ethenes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethene compounds							Specific chlorinated ethene as a percentage of total ethenes			Total BTEX (μg/L)
			PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μm, or μg/L)	Total (μg/L)	Percentage of TCE	Percentage of *trans* and *cis*DCE	Percentage of VC	
								*Surface-water sites in downstream order—Continued*					
MA12	04-26-00	9	<0.5	190	630	10	250	–	1,100	18	59	23	nd
	06-01-00	10	<0.5	110	670	5.5	140	–	930	12	73	15	nd
	07-25-00	9	<25	180	750	<25	140	–	1,100	17	70	13	–
	11-09-00	9	<1	170	680	4.6	140	–	1,000	17	69	14	–
TF16	06-11-91	1	<5	<5	<5	–	<10	–	nd	–	–	–	nd
	08-21-91	1	<5	<5	<5	–	<10	–	nd	–	–	–	nd
	01-14-92	1	<5	<5	3.0	–	<10	–	3.0	–	–	–	nd
TF19	09-05-95	2	<1	<1	4.0	<1	0.92	–	4.9	0	80	20	nd
	12-04-95	3	<1	<1	8.7	<1	3.1	–	12	0	74	26	nd
	03-12-96	4	<0.5	1.3	19	0.26	19	–	40	3	49	48	nd
	07-01-96	5	<0.5	0.70	5.9	<0.5	2.4	–	9.0	8	65	27	nd
	09-10-96	6	<0.5	<0.5	1.4	<0.5	<0.5	–	1.4	0	100	0	nd
	03-03-98	8	<0.5	2.6	16	0.31	6.1	–	25	10	65	24	nd
	06-01-00	10	<0.5	2.3	12	0.20	3.1	–	18	13	69	18	nd
DB14	09-05-95	2	<1	<1	<1	<1	<1	–	nd	–	–	–	nd
	12-04-95	3	<1	<1	1.9	<1	<1	–	1.9	–	–	–	nd
	03-13-96	4	<0.5	<0.5	0.35	<0.5	<0.5	–	nd	–	–	–	nd
	07-01-96	5	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	09-10-96	6	<0.5	<0.5	<0.5	<0.5	<0.5	–	nd	–	–	–	nd
	03-03-98	8	<0.5	<0.5	1.50	<0.5	0.58	–	2.1	–	–	–	0.28
	06-01-00	10	<0.5	<0.5	0.59	<0.5	<0.5	–	0.59	–	–	–	nd

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Data source code**: **1**, URS Consultants, Inc., 1993. **2**, URS Consultants, Inc., 1997a; Round 1. **3**, URS Consultants, Inc., 1997a; Round 2. **4**, URS Consultants, Inc., 1997a; Round 3. **5**, URS Consultants, Inc., 1997a; Round 4. **6** , URS Consultants, Inc., 1997a; Round 5. **7**, USGS, this report; 1996-97 data from Microbial Studies Group Laboratory, Columbia, SC by gas chromatography with flame-ionization detector. 1999-2000 data from Quanterra laboratory, EPA methods SW846 8260B, except ethene and ethane from Transglobal Env. Geo. NW, Inc., by modified EPA method 8015. **8** , Navy pre-ROD sampling Round 6; personal communication, Renee Wallis; U.S. Navy, EFA NW, Poulsbo, WA; EPA Method 8260. **9**, URS Greiner, Inc., 2000. **10**, CH2MHill Constructors, Inc., 2001. **Ethene**: Ethene data for September 1996 and April 1997 are reported as micromoles (μM) in the headspace of the sample vial. They are suitable for comparison between wells sampled during the same times only. Laboratory data qualifier codes, such as "J" for estimated value and "D" for dilution, are not shown. **Acroymns:** 1,1-DCE, 1,1-dichloroethene; 1,1,1-TCA, 1,1,1-trichloroethane; 1,1,-DCA, 1,1-dichloroethane; CA, chloroethane; **Abbreviations**: μg/L, micrograms per liter. **Symbols**: <, less than; –, not analyzed or calculated; nd, none detected at unspecified level]

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (μg/L)	1,1-DCA (μg/L)	CA (μg/L)	Ethane (μg/L)	1,1-DCE (μg/L)	Total (μg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
Monitoring wells												
1MW-1	07-09-91	1	<5	20	11	–	13	44	5	43	24	28
	01-20-92	1	<10	18	9.0	–	14	41	11	39	20	30
	08-25-95	2	<1	14	<1	–	5.1	19	2	70	2	25
	12-06-95	3	<1	1.0	2.2	–	<1	3.2	12	24	52	12
	03-12-96	4	<0.5	8.5	<0.5	–	2.6	11	2	73	2	22
	06-26-96	5	<0.5	15	0.50	–	3.2	19	1	79	3	17
	09-17-96	7	–	–	–	–	<2	–	–	–	–	–
	04-16-97	7	–	–	–	–	7.8	7.8	0	0	–	100
	03-03-98	8	<0.5	4.5	1.3	–	0.40	6.2	4	70	20	6
	06-11-99	9	1.5	19	9.0	–	4.0	34	4	57	27	12
	10-20-99	9	<3	17	–	–	2.9	20	0	85	–	15
	04-26-00	9	<0.5	18	6.9	–	3.1	28	1	64	24	11
	06-21-00	10	<0.5	13	5.8	19	1.7	39	1	63	28	8
	07-24-00	9	<0.5	<25	–	–	<25	nd	–	–	–	–
	10-31-00	9	<1	<1	–	–	2.0	2.0	0	0	–	100
1MW-4	07-09-91	1	<5	<5	<10	–	<5	nd	–	–	–	–
	01-21-92	1	<10	<10	<10	–	<10	nd	–	–	–	–
	08-21-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-05-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-12-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–

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Natural Attenuation of CVOCs in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
						Monitoring wells—Continued						
1MW-4	06-26-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-16-97	7	–	–	–	–	<1.9	–	–	–	–	–
MW1-2	06-19-91	1	<5	<5	1.0	–	2.0	3.0	0	0	33	67
	01-20-92	1	<10	<10	<10	–	4.0	4.0	0	0	0	100
	08-28-95	2	<1	<1	<1	–	4.2	4.2	0	0	0	100
	12-06-95	3	<1	<1	<1	–	3.5	3.5	0	0	0	100
	03-11-96	4	<0.5	<0.5	<0.5	–	4.8	4.8	0	0	0	100
	06-25-96	5	<0.5	0.23	<0.5	–	5.1	5.3	0	4	0	100
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-16-97	7	–	–	–	–	7.8	–	–	–	–	–
	03-02-98	8	<0.5	<0.5	<0.5	–	3.4	3.4	0	0	0	100
	06-11-99	9	<3	<3	<3	–	5.0	5.0	0	0	0	100
	10-20-99	9	<0.5	<0.5	–	–	3.4	3.4	0	0	–	100
	04-26-00	9	<0.5	<0.5	<0.5	–	6.0	6.0	0	0	0	100
	06-21-00	10	<0.5	0.30	0.30	0.24	3.2	4.0	0	8	8	80
	07-24-00	9	<25	<25	–	–	<25	nd	–	–	–	–
	10-31-00	9	<1	<1	–	–	2.2	2.2	0	0	0	100
MW1-3	06-20-91	1	<0.01	<5	<10	–	<5	nd	–	–	–	–
	01-20-92	1	<10	<10	<10	–	<10	nd	–	–	–	–
	03-08-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-21-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-11-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	10-20-99	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	04-26-00	9	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-20-00	7	–	–	–	0.19	–	0.19	–	–	–	–
	07-24-00	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	10-31-00	9	<1	<1	–	–	<1	nd	–	–	–	–

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
						Monitoring wells—Continued						
MW1-4	06-19-91	1	<5	1.0	2.0	–	5.0	8.0	24	10	19	48
	01-23-92	1	<10	<10	<10	–	<10	nd	–	–	–	–
	08-23-95	2	<1	<1	<1	–	7.7	7.7	0	0	0	100
	12-05-95	3	<1	<1	<1	–	5.2	5.2	0	0	0	100
	03-05-96	4	<0.5	0.67	<0.5	–	5.6	5.6	0	7	0	93
	06-20-96	5	<0.5	0.64	<0.5	–	13	14	0	5	2	92
	09-17-96	7	–	–	–	–	27	–	–	–	–	–
	04-16-97	7	–	–	–	–	<2	–	–	–	–	–
	03-03-98	8	<0.5	<0.5	<0.5	–	16	16	0	1	1	96
	06-14-99	9	<3	2.0	2.0	–	24	28	0	7	7	81
	10-20-99	9	<0.5	0.80	–	–	10	11	0	7	0	93
	04-26-00	9	<0.5	16	0.84	–	16	33	0	48	4	48
	06-22-00	10	<250	<250	<250	4.1	<250	4.1	–	–	–	–
	07-24-00	9	<250	<250	–	–	<250	nd	–	–	–	–
	11-09-00	9	<1	<1	–	–	0.9	0.9	0	0	–	100
MW1-5	06-25-91	1	<5	13	9.0	–	<5	22	0	59	41	0
	01-23-92	1	<10	30	8.0	–	<10	38	0	79	21	0
	08-23-95	2	<1	5.8	2.8	–	<1	8.6	0	67	33	0
	12-05-95	3	<1	110	<1	–	<1	110	0	100	0	0
	03-06-96	4	<0.5	34	<0.5	–	<0.5	34	0	100	0	0
	06-20-96	5	<0.5	29	<0.5	–	<0.5	29	0	100	0	0
	09-17-96	7	–	–	–	–	<2	–	–	–	–	–
	04-16-97	7	–	–	–	–	<2	–	–	–	–	–
	03-04-98	8	<0.5	67	2.8	–	<0.5	70	0	96	4	0
	06-14-99	9	<3	9.0	18	–	<3	27	0	33	67	0
	10-20-99	9	<0.5	9.6	–	–	<0.5	10	0	100	–	0
	04-26-00	9	>0.5	1.1	11	–	>0.5	12	0	10	90	0

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
Monitoring wells—Continued												
MW1-5	06-22-00	10	<0.5	6.9	9.3	3.6	<0.5	20	0	34	47	0
	07-25-00	9	<0.5	1.8	–	–	<0.5	1.8	0	100	--	0
	11-06-00	9	<1	1.7	–	–	<1	1.7	0	100	--	0
MW1-6	06-25-91	1	<0.01	<5	12	–	<5	12	0	0	100	0
	01-23-92	1	<10	<10	12	–	<10	12	0	0	100	0
	08-24-95	2	<1	<1	6.7	–	<1	6.7	0	0	100	0
	12-12-95	3	<1	<1	4.4	–	<1	4.4	0	0	100	0
	03-07-96	4	<0.5	<0.5	4.1	–	<0.5	4.1	0	0	100	0
	06-20-96	5	<0.5	<0.5	6.9	–	<0.5	6.9	0	0	100	0
	09-17-96	7	–	–	–	–	<2	–	–	–	–	–
	04-16-97	7	–	–	–	–	<2	–	–	–	–	–
MW1-14	08-28-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-16-97	7	–	–	–	–	<1.9	–	–	–	–	–
MW1-15	08-30-95	2	<1	<1	<1	–	<1	nd	–	–	--	--
	09-16-96	7	–	–	–	–	<1.9	–	–	–	--	--
	04-16-97	7	–	–	–	–	<1.9	–	–	–	--	--
MW1-16	08-31-95	2	5,600	12,000	44	–	680	18,000	31	65	0	4
	06-20-96	5	430	30,000	1,900	–	180	33,000	1	92	6	1
	09-17-96	7	–	–	–	–	99	–	–	–	–	–
	04-16-97	7	–	–	–	–	72	–	–	–	–	–
	03-04-98	8	840	24,000	3,800	–	110	29,000	3	83	13	0
	06-14-99	9	140	15,000	3,900	–	48	19,000	1	79	20	0
	10-20-99	9	23	6,500	–	–	5.0	6,500	0	100	–	0
	04-26-00	9	16	1,700	430	–	<0.5	2,100	1	79	20	0
	06-22-00	10	29	2,500	590	6.6	2.0	3,100	1	80	19	0

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
						Monitoring wells—Continued						
MW1-16	07-25-00	9	25	2,300	–	–	<50	2,300	1	98	–	0
	11-06-00	9	21	3,900	–	–	<1	3,900	1	99	–	0
MW1-17	08-29-95	2	<1	<1	0.86	–	<1	0.86	0	0	100	0
	12-04-95	3	<1	<1	2.2	–	<1	2.2	0	0	100	0
	03-06-96	4	<0.5	<0.5	2.5	–	<0.5	2.5	0	0	100	0
	06-24-96	5	<0.5	<0.5	3.3	–	<0.5	3.3	0	0	100	0
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-16-97	7	–	--	–	–	<1.9	–	–	–	–	–
	06-22-00	10	<0.5	0.10	1.3	17	<0.5	18	0	0	7	0
MW1-18	08-28-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-05-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-12-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-26-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-16-97	7	–	–	–	–	<1.9	–	–	–	–	–
MW1-20	08-30-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-08-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-11-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-27-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	10-20-99	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	04-26-00	9	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-21-00	7	–	–	–	<0.1	–	nd	–	–	–	–
	07-25-00	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	10-31-00	9	<1	<1	–	–	<1	nd	–	–	–	–
MW1-25	08-17-95	2	<1	4.8	<1	–	7.3	12	0	40	0	60
	12-06-95	3	<1	3.9	<1	–	6.1	10	0	39	0	61
	03-11-96	4	<0.5	1.1	<0.5	--	0.98	2.1	0	53	0	47

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

| Well or site No. | Date sampled | Data source code | Ethane compounds and 1,1-DCE | | | | | | Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE | | | |
			1,1,1-TCA (μg/L)	1,1-DCA (μg/L)	CA (μg/L)	Ethane (μg/L)	1,1-DCE (μg/L)	Total (μg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
						Monitoring wells—Continued						
MW1-25	06-25-96	5	<0.5	4.7	<0.5	–	7.5	12	0	37	0	63
	09-17-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
	03-04-98	8	<0.5	2.4	<0.5	–	5.3	7.7	0	34	0	66
	06-22-00	10	<0.5	6.9	2.3	1.6	7.2	18	0	38	13	40
MW1-28	12-07-95	3	<1	1.1	<1	–	5.1	6.2	0	16	0	84
	03-08-96	4	<0.5	2.1	<0.5	–	5.0	7.1	0	29	0	71
	06-25-96	5	<0.5	2.4	<0.5	–	6.3	8.7	0	28	0	72
	09-09-96	6	<0.5	2.3	<0.5	–	5.4	7.7	0	29	0	71
	09-16-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
	03-04-98	8	<0.5	1.3	<0.5	–	4.3	5.6	0	23	0	77
	06-22-00	10	<0.5	3.2	0.97	0.67	5.1	10	0	32	10	51
MW1-29	12-07-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-08-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-18-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-09-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-16-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
MW1-31	12-11-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-13-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-21-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-12-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
MW1-32	03-18-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-18-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-12-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-16-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
	03-02-98	8	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
							Monitoring wells—Continued					
MW1-33	06-24-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-21-00	7	–	–	–	11	–	11	–	–	–	–
MW1-35	06-25-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-09-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-20-00	7	–	–	–	<0.1	–	nd	–	–	–	–
MW1-36	06-17-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-11-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-20-00	7	–	–	–	<0.1	–	nd	–	–	–	–
MW1-37	06-17-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-16-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
	06-07-99	7	<1	<1	<2	–	<1	nd	–	–	–	–
	06-20-00	7	–	–	–	–	–	–	–	–	–	–
MW1-38	06-19-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-20-00	7	–	–	–	1.7	–	–	–	–	–	–
MW1-39	06-17-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-16-96	7	–	–	–	–	<1.9	–	–	–	–	–
	04-17-97	7	–	–	–	–	<1.9	–	–	–	–	–
	03-03-98	8	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-07-99	7	<1	<1	<2	–	<1	nd	–	–	–	–
	06-20-00	10	<0.5	<0.5	<0.5	<0.1	<0.5	nd	–	–	–	–
MW1-41	10-20-99	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	04-26-00	9	<0.5	<0.5	1.8	–	<0.5	1.8	0	0	100	0

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
Monitoring wells—Continued												
MW1-41	06-21-00	10	<0.5	0.20	1.9	1.4	<0.5	3.5	0	6	54	0
	07-24-00	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	11-02-00	9	<1	<1	–	–	<1	nd	–	–	–	–
Piezometers												
P1-1	06-09-99	7	<2	0.24	<4	–	<2	0.2	0	100	0	0
P1-3	06-09-99	7	<16	<16	3.6	–	<16	3.6	0	100	0	0
P1-4	06-09-99	7	<130	<130	<270	–	<130	nd	–	–	–	–
P1-5	06-08-99	7	<13	<13	15	–	<13	15	0	0	100	0
P1-6	06-08-99	7	<400	1,500	300	–	<400	1,800	0	83	17	0
P1-7	06-08-99	7	<670	<670	<1,300	–	<670	nd	–	–	–	–
	06-22-00	7	0.24	17	8.4	11	72	110	0	16	66	–
P1-8	06-07-99	7	<710	<710	<1,400	–	<710	nd	–	–	–	–
P1-9	06-08-99	7	<2,000	<2,000	<4,000	–	<2,000	nd	–	–	–	–
	06-22-00	7	<10	2.6	<20	<1.0	47	49	0	4	0	96
P1-10	06-07-99	7	<1,000	<1,000	<2,000	–	<1,000	nd	–	–	–	–
	06-22-00	7	<0.1	1.2	0.13	0.42	16	17	0	7	0	93
Seep												
SP1-1	05-16-90	1	<5	<5	<10	–	<5	nd	–	–	–	–
	07-01-91	1	<5	<5	3.0	–	<5	3.0	–	–	–	–
	01-22-92	1	<10	<10	<10	–	<10	nd	–	–	–	–
	09-05-95	2	<1	<1	1.3	–	<1	1.3	–	–	–	–
	12-05-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-13-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	07-02-96	5	<0.5	<0.5	0.20	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	1.8	–	<0.5	1.8	–	–	–	–

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE

Seep—*Continued*

Well or site No.	Date sampled	Data source code	1,1,1-TCA	1,1-DCA	CA	Ethane	1,1-DCE	Total	%TCA	%DCA	%CA	%DCE
SP1-1	06-11-99	9	<3	<3	2.0	–	<3	2.0	–	–	–	–
	10-20-99	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	04-26-00	9	<0.5	<0.5	2.1	–	<0.5	2.1	–	–	–	–
	07-25-00	9	<0.5	<0.5	–	–	<0.5	nd	–	–	–	–
	11-09-00	9	<1	<1	–	–	<1	nd	–	–	–	–

Surface-water sites in downstream order

MA01	06-10-91	1	<5	1.0	<10	–	<5	nd	–	–	–	–
	08-21-91	1	<5	<5	<10	–	<5	nd	–	–	–	–
	01-14-92	1	<10	<10	<10	–	<10	nd	–	–	–	–
MA09	09-05-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-05-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-14-96	4	<0.5	0.29	<0.5	–	<0.5	0.29	–	–	–	–
	07-02-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	03-03-98	8	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-01-00	10	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
MA10	09-06-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-06-95	3	<1	1.2	<1	–	<1	1.2	–	–	–	–
	03-13-96	4	<0.5	0.93	<0.5	–	<0.5	0.93	–	–	–	–
	07-02-96	5	<0.5	0.23	<0.5	–	<0.5	0.23	–	–	–	–
MA11	09-06-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-06-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-13-96	4	<0.5	0.43	<0.5	–	<0.5	0.44	–	–	–	–
	07-02-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-01-00	10	<0.5	1.2	<0.5	–	<0.5	1.2	–	–	–	–
MA12	03-14-96	4	<0.5	<5	0.52	–	0.56	1.1	–	–	–	–
	07-01-96	5	<0.5	11	0.54	–	1.0	13	–	–	–	–
	03-04-98	8	<0.5	3.9	<0.5	–	<0.5	3.9	–	–	–	–
	06-11-99	7	<3	15	3.0	–	2.0	20	–	–	–	–
	10-20-99	9	<0.5	12	–	–	1.9	14	–	–	–	–

Table 10. Cumulative summary of concentrations of chlorinated ethanes and other volatile organic compounds in ground and surface water, 1991–2000, from selected sites at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well or site No.	Date sampled	Data source code	Ethane compounds and 1,1-DCE						Specific chlorinated ethane and 1,1-DCE as a percentage of total ethanes and 1,1-DCE			
			1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	Ethane (µg/L)	1,1-DCE (µg/L)	Total (µg/L)	Percentage TCA	Percentage DCA	Percentage CA	Percentage DCE
					Surface-water sites in downstream order—Continued							
MA12	04-26-00	9	<0.5	21	5.0	–	1.3	27	–	–	–	–
	06-01-00	10	<0.5	16	7.3	–	<0.5	23	–	–	–	–
	07-25-00	9	<25	<25	–	–	<25	nd	–	–	–	–
	11-09-00	9	<1	14	–	–	1.2	15	–	–	–	–
TF16	06-11-91	1	<5	<5	<10	–	<5	nd	–	–	–	–
	08-21-91	1	<5	<5	<10	–	<5	nd	–	–	–	–
	01-14-92	1	<5	<5	<10	–	<5	nd	–	–	–	–
TF19	09-05-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-04-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-12-96	4	<0.5	0.43	<0.5	–	<0.5	0.43	–	–	–	–
	07-01-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	03-03-98	8	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-01-00	10	<0.5	0.40	<0.5	–	<0.5	0.40	–	–	–	–
DB14	09-05-95	2	<1	<1	<1	–	<1	nd	–	–	–	–
	12-04-95	3	<1	<1	<1	–	<1	nd	–	–	–	–
	03-13-96	4	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	07-01-96	5	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	09-10-96	6	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	03-03-98	8	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–
	06-01-00	10	<0.5	<0.5	<0.5	–	<0.5	nd	–	–	–	–

Table 11. Data used to calculate degradation rates of chlorinated ethene mass and discharge to surface water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Transect length and ground-water flux**: Cross-section length and ground-water flux estimates from Table 3-11, URS Inc., 1997a. **Average chlorinated ethene concentration**: CVOC concentration data from table 8, this report; VC, vinyl chloride; ft, feet; gal/min, gallons per minute; μg/L, micrograms per liter; g/d, grams per day;–, not applicable]

Sub-transect name	Ground-water sample sites in transects	Transect length (ft)	Ground-water flux (gal/min)	Average chlorinated ethene concentration			Chlorinated ethene flux across transect		
				TCE (μg/L)	*cis*DCE (μg/L)	VC (μg/L)	TCE (g/d)	*cis*DCE (g/d)	VC (g/d)
1 – Landfill									
North	MW1-18	275	0.1	0.50	46	28	0.0003	0.03	0.02
North-central	MW1-2, P1-3, P1-4	315	1.2	72.	2,000	260	0.5	13	1.7
Central	MW1-17	300	0.4	0.30	0.25	0.25	0.001	0.001	0.0005
South-central	MW1-6	250	0.3	110	16	9.4	0.2	0.03	0.02
South	P1-6, P1-7, MW1-4	225	0.2	22,000	25,000	3,500	23	27	3.8
Subtotals		1,365	2.2	–	–	–	24	41	5.5
2 – Marsh									
North	N1	275	0.1	0.13	0.68	0.1	0.00007	0.0004	0.0001
North-central	N2, N3, N4, N5, N7, N8	315	1.2	3.2	82	38	0.02	0.5	0.2
Central	C1, C2	300	0.4	0.06	4.1	6.1	0.0001	0.009	0.01
South-central	C3	250	0.3	0.05	2.2	0.44	0.0001	0.004	0.001
South	S1, S2, S3, S4, S5, S6	225	0.2	16	3,200	980	0.02	3.5	1.1
Subtotals		1,365	2.2	–	–	–	0.04	4.0	1.3
3 – Intermediate aquifer									
North[1]	1MW-1	160	0.3	1.3	11	0.72	0.002	0.02	0.001
North-central[2]	1MW-4, MW1-25	110	0.1	20.	1,000	130	0.01	0.55	0.07
South-central[3]	MW1-25	185	0.8	39	2,000	260	0.2	9.2	1.2
South[4]	MW1-28	130	0.3	0.81	1,300	520	0.001	2.0	0.8
Subtotals		585	1.5	–	–	–	0.2	12	2
TOTALS		–	–	–	–	–	–	–	–

[1]North intermediate aquifer CVOC flux comes from northern part of the landfill.
[2]North-central intermediate aquifer CVOC flux comes from northern part of the landfill (0.6 percent) and the northcentral part (99.4 percent).
[3]South-central intermediate aquifer CVOC flux comes from north-central part of the landfill (50 percent) and southern part (50 percent).
[4]South intermediate aquifer CVOC flux comes from north-central part of the landfill (50 percent) and southern part (50 percent).

Table 12. Data used to calculate first-order attenuation half-lives of chlorinated ethene for segments of selected flowpaths at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; VC, vinyl chloride; CVOC, chlorinated volatile organic compound; ft, feet; μg/L, micrograms per liter; ft/d, feet per day]

Flowpath and segment	Upgradient sample sites	Upgradient CVOC concentration C_O		
		TCE (μg/L)	*cis*DCE (μg/L)	VC (μg/L)
Upper aquifer				
North landfill to marsh				
Flowpath A, segment 2	MW1-2	27	980	160
Flowpath B, segment 2	P1-4	160	4,800	540
Flowpath B, segment 3	1MW-1	0.001	310	960
Average flowpath, segment 2	MW1-2, P1-3, P1-4, 1MW-1	51	1,500	440
Marsh to Highway 308				
Flowpath A, segment 3	N3	16	410	130
Average flowpath, segment 3	N2, N3, N4, N5, N7, N8	4.5	82	38
South landfill to marsh				
Flowpath C, segment 2	P1-8	190	25,000	3,400
Flowpath C, segment 3	MW1-16	530	6,800	1,700
Flowpath C, segment 4	MW1-5	2	9	260
Flowpath D, segment 2	P1-9	48,000	88,000	7,200
Flowpath D, segment 3	P1-7	26,000	35,000	3,100
Flowpath E, segment 2	P1-10	14,000	34,000	3,100
Flowpath E, segment 3	MW1-4	2,600	12,000	1,500
Intermediate aquifer				
Upper aquifer to intermediate aquifer				
Flowpath F, segment 1	MW1-16, 1MW-1	265	3,600	1,300
Intermediate aquifer to Highway 308				
Flowpath F, segment 2	MW1-25, MW1-28	20	1,600	390

Table 12. Data used to calculate first-order attenuation half-lives of chlorinated ethene for segments of selected flowpaths at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Flowpath and segment	Upgradient sample sites	Downgradient CVOC concentration C_X		
		TCE (μg/L)	*cis*DCE (μg/L)	VC (μg/L)
Upper aquifer				
North landfill to marsh				
Flowpath A, segment 2	N3	16	410	130
Flowpath B, segment 2	1MW-1	0.58	240	1,200
Flowpath B, segment 3	N7	9	6.7	1.9
Average flowpath, segment 2	N2, N3, N4, N5, N7, N8	4.5	82	38
Marsh to Highway 308				
Flowpath A, segment 3	MW1-39	0.001	0.28	1.2
Average flowpath, segment 3	MW1-39	0.001	0.28	1.2
South landfill to marsh				
Flowpath C, segment 2	MW1-16	530	6,800	1,700
Flowpath C, segment 3	MW1-5	2	9	260
Flowpath C, segment 4	S2	0.60	11	2.8
Flowpath D, segment 2	P1-7	26,000	35,000	3,100
Flowpath D, segment 3	S4	45	19,000	5,600
Flowpath E, segment 2	MW1-4	2,600	12,000	1,500
Flowpath E, segment 3	S5	49	80	17
Intermediate aquifer				
Upper to intermediate				
Flowpath F, segment 1	MW1-25, MW1-28	20	1,600	390
Intermediate to Highway 308				
Flowpath F, segment 2	MW1-37	0.001	0.001	0.001

Table 12. Data used to calculate first-order attenuation half-lives of chlorinated ethene for segments of selected flowpaths at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Flowpath and segment	Down-gradient distance x (ft)	Ground-water flow rate (ft/d)	Travel time t (days)	First-order attenuation half-life T$_{1/2}$		
				TCE (years)	*cis*DCE (years)	VC (years)
Upper aquifer						
North landfill to marsh						
Flowpath A, segment 2	45	0.34	132	0.5	0.3	1.3 – 0.1
Flowpath B, segment 2	65	0.34	191	0.1	0.1	-0.5 – 0.3
Flowpath B, segment 3	170	0.34	500	-0.1	0.2	0.2
Average flowpath, segment 2	127	0.34	374	0.3	0.2	0.3 – 0.2
Marsh to Highway 308						
Flowpath A, segment 3	560	0.04	13,659	2.7	3.6 – 3.5	5.5 – 4.2
Average flowpath, segment 3	481	0.04	11,732	2.6	3.9	6.5 – 4.8
South landfill to marsh						
Flowpath C, segment 2	45	0.10	474	-0.9	0.7	1.3 – 0.4
Flowpath C, segment 3	150	0.15	1,000	0.3	0.3	1 – 0.5
Flowpath C, segment 4	35	0.15	233	0.4	-2.5 – -13	0.1
Flowpath D, segment 2	70	0.15	467	1.4	1 – 0.8	1.1 – 0.3
Flowpath D, segment 2	70	0.15	467	0.1	1.5 – 0.8	-1.5 – 0.7
Flowpath E, segment 2	85	0.10	895	1.0	1.6 – 1.3	3.3 – 0.6
Flowpath E, segment 3	150	0.15	1,000	0.5	0.4	0.4 – 0.3
Intermediate aquifer						
Upper to intermediate						
Flowpath F, segment 1	450	0.2	2,250	1.7	5.6 – 5.1	3.5 – 2
Intermediate to Highway 308						
Flowpath F, segment 2	550	0.03	20,370	3.9	2.7	3.0 – 2.7

APPENDIX A. QUALITY ASSURANCE AND CONTROL OF U.S. GEOLOGICAL SURVEY GEOCHEMICAL SAMPLING

APPENDIX A. QUALITY ASSURANCE AND CONTROL OF U.S. GEOLOGICAL SURVEY GEOCHEMICAL SAMPLING

Quality assurance and control of geochemical sampling included collecting duplicate samples for redox-sensitive analytes and VOCs and analyzing field blank samples for VOCs. Duplicates were collected for various redox-sensitive analytes during all sampling events, and were collected for VOCs only during the four events when numerous VOC samples were collected. A field blank collected during June 1999 was collected by pumping VOC-free water through previously used and cleaned tubing. Those results represent possible sampling contamination in samples collected at known contaminated wells only; new tubing was used to sample from wells that were known to be uncontaminated or slightly contaminated and from piezometers sampled for the first time. A diffusion sampler field blank was collected from an extra passive diffusion sampler that was carried along in the backpack with other samplers during the entire day of sampler installation. All diffusion samplers including the field blank were filled with deionized, rather than VOC-free water. Those blank results represent possible sampling contamination in diffusion samples that could result from many sources during the course of sampler installation, such as the ambient environment, or from VOCs present in the deionized water. Selected laboratory quality assurance and control data, including the method blank results for methane, ethene, and ethane analyses done by Transglobal Environmental Geosciences Northwest, Inc., in Lacey, Wash., are provided in table A1. The complete data set is on file in the USGS office in Tacoma, Wash.

Duplicate sample results compared favorably for all constituents (table A1). The relatively high variation in duplicate sulfide analyses from October 1998 and June 1999 was attributed to a delay in adding reagents to the samples after filling the sample vials; sulfide concentrations can change substantially in just a few minutes once anaerobic ground water is exposed to the atmosphere. Dissolved H_2 concentrations in samples from some wells during some sampling events changed upward and downward and failed to stabilize around a single value, even after repeated sampling and analysis for more than 3 hours. Repeated H_2 analyses for a given sample were consistent, so analytical errors were not the cause of the variation. The variation may reflect the likely heterogeneity of redox conditions beneath the landfill. As more water was pumped during extended sampling, ground water with different H_2 concentrations and redox conditions from slightly different zones in the aquifer may have been sampled. Variability in H2 and sulfide analyses adds some uncertainty to the determination of redox conditions for a given well at a specific time. However, that uncertainty was reduced by considering multiple redox-sensitive constituents in determining redox conditions, and by sampling redox constituents multiple times at most wells.

Trace amounts of chlorinated ethenes and BTEX compounds were detected in the field blank sample of pumped VOC-free water (MW1-14FB). As previously mentioned, this blank was collected by pumping VOC-free water through previously used and cleaned tubing, so those results represent possible sampling contamination only in samples collected at known contaminated wells. A trace amount of *cis*DCE detected in the diffusion sampler field blank (S-1FB) could have come from the deionized water used in the sampler, or it could have diffused into the sampler from the ambient air above the marsh. Finally, a trace amount of methane was detected in the June 2000 method blank, indicating low-level contamination at the laboratory.

Table A1. Quality assurance and control data collected by the U.S. Geological Survey at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[Laboratory data qualifier codes, such as "J" for estimated value and "D" for dilution, are not shown. **Well identification No**.: D denotes duplicate sample; FB denotes field blank sample. **Dissolved H$_2$**: Multiple dissolved H$_2$ samples were analyzed at all wells. The duplicate data shown are the lowest and highest concentrations measured at wells where consecutive concentrations never stablized at a consistent value. **Ethene**: Ethene data for September 1996 and April 1997 are reported as micromoles (μM) in the headspace of the sample vial. They are suitable for comparison between wells sampled during the same times only. nM, nanomolar; mg/L, milligrams per liter; μg/L, micrograms per liter; μM, micromolar; PCE, tetrachloroethene; TCE, trichloroethene; *cis*DCE, *cis*-1,2-dichloroethene; *trans*DCE, *trans*-1,2-dichloroethene; VC, vinyl chloride; TCA, 1,1,1-trichloroethane; 1,1-DCA, 1,1-dichloroethane; CA, chloroethane; 1,1-DCE, 1,1-dichloroethene; BTEX, benzene, toluene, ethylbenzene, and xylenes; <, less than; nd, none detected; –, not analyzed]

Well identification No.	Date sampled	Dis-solved H$_2$ (nM)	Dis-solved oxygen (mg/L)	Dis-solved nitrate (mg/L)	Dis-solved man-ganes (mg/L)	Dis-solved iron (mg/L	Dis-solved iron (II) (mg/L)	Dis-solved sulfate (mg/L)	Dis-solved sulfide (mg/L)	Dis-solved methane (mg/L)	pH (unit)	Total bicarbon ate (mg/L)	Total organic carbon (mg/L)
MW1-2	September 1996	–	2.4	<0.02	–	–	0.23	4.6	<0.01	1.2	6.9	510	–
MW1-2D	September 1996	–	1.9	<0.02	–	–	0.18	5.1	<0.01	0.9	6.8	480	–
MW1-6	September 1996	0.9	0.0	1.2	–	–	30	0.10	<0.01	7.0	6.7	690	–
MW1-6D	September 1996	1.1	0.0	0.81	–	–	35	<0.01	<0.01	7.1	6.6	670	–
MW1-16	April 1997	0.8	0.0	–	–	–	120	–	0.06	29	6.5	1,110	–
MW1-16D	April 1997	1.0	0.0	–	–	–	110	–	0.06	29	6.5	1,510	–
MW1-2	March 1998	–	–	–	–	0.19	0.16	–	–	–	–	–	–
MW1-2D	March 1998	–	–	–	–	0.18	0.12	–	–	–	–	–	–
MW1-14	October 1998	–	0.0	–	1.5	–	48	–	0.01	–	6.3	600	–
MW1-14D	October 1998	–	0.0	–	1.4	–	43	–	0.03	–	6.3	600	–
MW1-28	October 1998	0.1	–	–	–	–	–	–	–	–	–	–	–
MW1-28D	October 1998	0.6	–	–	–	–	–	–	–	–	–	–	–
MW1-14	June 1999	–	–	–	0.30	–	57	–	0.4	–	–	–	–
MW1-14D	June 1999	–	–	–	0.20	–	64	–	0.03	–	–	–	–
MW1-16	June 1999	2.5	–	–	–	–	–	–	–	–	–	–	–
MW1-16D	June 1999	6.8	–	–	–	–	–	–	–	–	–	–	–
P1-1	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
P1-1D	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
P1-7	June 1999	0.6	–	–	–	–	–	–	–	–	–	–	–
P1-7D	June 1999	1.2	–	–	–	–	–	–	–	–	–	–	–
MW1-14FB	June 1999	–	–	–	–	–	–	–	–	–	–	–	–

Table A1. Quality assurance and control data collected by the U.S. Geological Survey at Operable Unit 1, Naval Undersea Warfare Center, Divison Keyport, Washington—*Continued*

Well identification No.	Date sampled	PCE (µg/L)	TCE (µg/L)	*cis*DCE (µg/L)	*trans*DCE (µg/L)	VC (µg/L)	Ethene (µM or µg/L)	TCA (µg/L)	1,1-DCA (µg/L)	CA (µg/L)	1,1-DCE (µg/L)	Ethane (µg/L)	BTEX (µg/L)
MW1-2	September 1996	<3.3	28	1,100	21	87	<10	–	–	–	<1.9	–	nd
MW1-2D	September 1996	<3.3	26	1,100	19	88	<10	–	–	–	<1.9	–	nd
MW1-6	September 1996	<3.3	150	290	<1.9	89	<10	–	–	–	<1.9	–	6.0
MW1-6D	September 1996	<3.3	140	240	<1.9	66	6.0	–	–	–	<1.9	–	6.0
MW1-16	April 1997	45	130	220	46	240	25	–	–	–	72	–	–
MW1-16D	April 1997	38	87	160	42	210	25	–	–	–	68	–	–
MW1-2	March 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-2D	March 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-14	October 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-14D	October 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-28	October 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-28D	October 1998	–	–	–	–	–	–	–	–	–	–	–	–
MW1-14	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
MW1-14D	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
MW1-16	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
MW1-16D	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
P1-1	June 1999	<2	11	6.1	<1	<4		<2	0.24	<4	<2	--	19
P1-1D	June 1999	<2	11	5.7	<1	<4		<2	0.23	<4	<2	--	18
P1-7	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
P1-7D	June 1999	–	–	–	–	–	–	–	–	–	–	–	–
MW1-14FB	June 1999	<1	0.34	1.4	0.17	<2	–	<1	<1	<2	<1	–	0.54

Table A1. Quality assurance and control data collected by the U.S. Geological Survey at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

Well identification No.	Date sampled	Dis-solved H$_2$ (nM)	Dis-solved oxygen (mg/L)	Dis-solved nitrate (mg/L)	Dis-solved man-ganes (mg/L)	Dis-solved iron (mg/L	Dis-solved iron (II) (mg/L)	Dis-solved sulfate (mg/L)	Dis-solved sulfide (mg/L)	Dis-solved methane (mg/L)	pH (unit)	Total bicarbon ate (mg/L)	Total organic carbon (mg/L)
MW1-17	June 2000	–	–	–	–	–	–	–	–	2.8	–	–	11.0
MW1-17D	June 2000	–	–	–	–	–	–	–	–	1.8	–	–	9.9
MW1-20	June 2000	0.1	–	–	–	–	–	–	–	0.008	–	–	–
MW1-20D	June 2000	0.5	–	–	–	–	–	–	–	0.007	–	–	–
MW1-36	June 2000	–	–	–	–	–	–	–	0.02	0.009	–	–	–
MW1-36D	June 2000	–	–	–	–	–	–	–	0.02	0.009	–	–	–
MW1-37	June 2000	–	–	–	–	–	–	–	0.02	–	–	–	–
MW1-37D	June 2000	–	–	–	–	–	–	–	0.02	–	–	–	–
S-1FB	June 2000	–	–	–	–	–	–	–	–	–	–	–	–
Method Blank	June 2000	–	–	–	–	–	–	–	–	0.002	–	–	–

Well identification No.	Date sampled	PCE (μg/L)	TCE (μg/L)	*cis*DCE (μg/L)	*trans*DCE (μg/L)	VC (μg/L)	Ethene (μM or μg/L)	TCA (μg/L)	1,1-DCA (μg/L)	CA (μg/L)	1,1-DCE (μg/L)	Ethane (μg/L)	BTEX (μg/L)
MW1-17	June 2000	–	–	–	–	–	<0.1	–	–	–	–	17	–
MW1-17D	June 2000	–	–	–	–	–	<0.1	–	–	–	–	9.0	–
MW1-20	June 2000	–	–	–	–	–	<0.1	–	–	–	–	<0.1	–
MW1-20D	June 2000	–	–	–	–	–	<0.1	–	–	–	–	<0.1	–
MW1-36	June 2000	–	–	–	–	–	<0.1	–	–	–	–	<0.1	–
MW1-36D	June 2000	–	–	–	–	–	<0.1	–	–	–	–	<0.1	–
MW1-37	June 2000	–	–	–	–	–	–	–	–	–	–	–	–
MW1-37D	June 2000	–	–	–	–	–	–	–	–	–	–	–	–
S-1FB	June 2000	<0.1	<0.1	0.13	<0.1	<0.2	--	<0.1	<0.1	--	<0.1	--	<0.1
Method Blank	June 2000	–	–	–	–	–	<0.1	–	–	–	–	<0.1	–

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