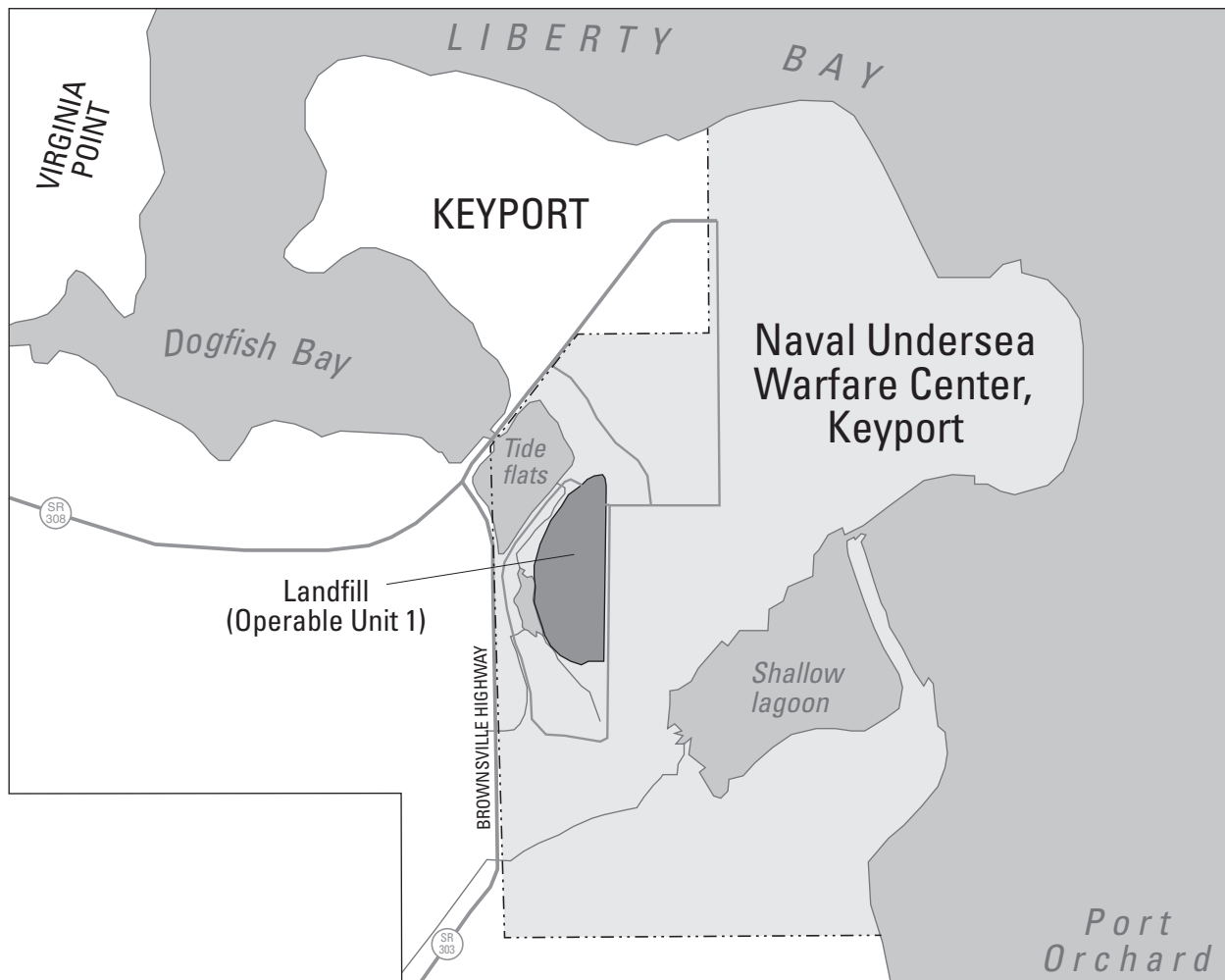


Prepared in cooperation with Department of the Navy Engineering Field Activity,  
Northwest Naval Facilities Engineering Command

## Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2002



Open File Report 2004-1203

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

# Report Documentation Page

Form Approved  
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>2004</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2002</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>U.S. Department of the Interior U.S. Geological Survey 1849 C. Street, NW Washington, DC 20240</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

# **Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2002**

By R.S. Dinicola

Prepared in cooperation with the  
Department of the Navy  
Engineering Field Activity, Northwest  
Naval Facilities Engineering Command

Open-File Report 2004-1203

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

**U.S. Department of the Interior**  
Gale A. Norton, Secretary

**U.S. Geological Survey**  
Charles G. Groat, Director

**U.S. Geological Survey, Reston, Virginia: 2004**

For sale by U.S. Geological Survey, Information Services  
Box 25286, Denver Federal Center  
Denver, CO 80225-0286

For more information about the USGS and its products:  
Telephone: 1-888-ASK-USGS  
World Wide Web: <http://www.usgs.gov/>

Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

*Suggested citation:*

*Dinicola, R.S., 2004, Selected natural attenuation monitoring data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2002: U.S. Geological Survey Open-File Report 2004-1203, 19 p.*

# Contents

Abstract.....	1
Introduction .....	2
Purpose and Scope .....	2
Acknowledgments.....	2
Methods and Data Analysis.....	6
Natural Attenuation Monitoring Data .....	7
Geochemical Data and Predominant Redox Conditions .....	7
Volatile Organic Compounds .....	16
June 2003 Sampling.....	16
Summary.....	16
References Cited.....	18

## Figures

Figure 1.	Map showing location of Operable Unit 1 study area, Naval Undersea Warfare Center, Division Keyport, Washington .....	3
Figure 2.	Map showing location of June 2002 data-collection sites and other features at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington .....	4

## Tables

Table 1.	Construction data and water-level measurements for monitoring wells and piezometers sampled during June 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington .....	5
Table 2.	Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington .....	8
Table 3.	Concentrations of selected chlorinated volatile organic compounds in ground water from piezometers and monitoring wells sampled from 1999 to 2002 by the U.S. Geological Survey at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington .....	17

## Conversion Factors and Datum

### CONVERSION FACTORS

	<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
	acre	4,047	square meter
	acre	0.4047	hectare
	feet (ft)	0.3048	meters

Temperature in degrees Celsius ( $^{\circ}\text{C}$ ) may be converted to degrees Fahrenheit ( $^{\circ}\text{F}$ ) as follows:

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

Temperature in degrees Fahrenheit ( $^{\circ}\text{F}$ ) may be converted to degrees Celsius ( $^{\circ}\text{C}$ ) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8.$$

Concentrations of chemical constituents in water are given in milligrams per liter, micrograms per liter, or nanomoles per liter (nanomolar). One milligram per liter is equivalent to one thousand micrograms per liter. One microgram per liter is equivalent to "parts per billion."

### DATUMS

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1988 (NGVD of 1988). Horizontal coordinate information is referenced to the NAD27.

### ABBREVIATIONS

#### Organizations

USGS	U.S. Geological Survey
EFANW	Naval Facilities Engineering Command, Engineering Field Activity, Northwest
NUWC	Naval Undersea Warfare Center
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
Other	
CA	Chloroethane
<i>cis</i> DCE	<i>cis</i> -1,2-dichloroethene
CVOCs	Chlorinated volatile organic compounds
DO	Dissolved oxygen
H <sub>2</sub>	Dissolved hydrogen
HCO <sub>3</sub> <sup>-</sup>	Bicarbonate
nM	Nanomolar
mg/L	Milligrams per liter
ORP	Oxidation-reduction potential
OU 1	Operable Unit 1
TCA	1,1,1-trichloroethane
TCE	Trichloroethene
VC	Vinyl chloride
VOC	Volatile organic compound
μm	Micrometer
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene

# Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2002

By R.S. Dinicola

## Abstract

Previous investigations indicated that natural attenuation and biodegradation of chlorinated volatile organic compounds (CVOCs) are substantial in shallow ground water beneath the 9-acre former landfill at Operable Unit 1 (OU 1), Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. The U.S. Geological Survey (USGS) has continued to monitor ground-water geochemistry to assure that conditions remain favorable for contaminant biodegradation. This report presents the geochemical and selected CVOC data for ground water at OU 1, collected by the USGS during June 10-14, 2002, in support of long-term monitoring for natural attenuation.

Overall, the geochemical data for June 2002 indicate that redox conditions in the upper-aquifer water remain favorable for reductive dechlorination of chlorinated VOCs because strongly reducing conditions persisted beneath much of the former landfill. Redox conditions in the intermediate aquifer downgradient of the landfill also remained favorable for reductive dechlorination, although the 2002 dissolved hydrogen ( $H_2$ ) concentration from well MW1-28 is questionable. Changes in redox conditions were observed at certain wells during 2002, but a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting redox conditions and if biodegradation processes are changing over time. The Navy

intends to complete a more thorough interpretation in preparation for the 5-year review of OU 1 scheduled for 2004.

There were a few substantial differences between the 2002 concentrations and previously observed concentrations of volatile organic compounds. Total CVOC concentrations in 2002 samples decreased substantially in all piezometers sampled in the northern plantation, and the largest percentages of decrease were for the compounds trichloroethene (TCE) and *cis*-1,2-dichloroethene (*cis*-DCE). Changes in total CVOC concentrations in the southern plantation were less consistent. Historically high concentrations were observed in samples from three piezometers, with particularly substantial increases in TCE and *cis*-DCE concentrations, and historically low concentrations were observed in two piezometers, with particularly substantial decreases in TCE and *cis*-DCE concentrations. Similarly to the redox chemistry, a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting CVOC concentrations and if biodegradation processes are changing over time.

No changes in monitoring plans are proposed for June 2003, although the practice of deploying a data sonde downhole while purging the wells will be discontinued. Downhole monitoring added uncertainty to selected measured dissolved  $H_2$  concentrations because of the possibility that the sonde and cable created a bridge that resulted in non-equilibrium dissolved  $H_2$  concentrations at the wells.

# Introduction

Chlorinated volatile organic compounds (CVOCs) have migrated to ground water beneath the 9-acre former landfill at Operable Unit 1 (OU 1) of the Naval Undersea Warfare Center (NUWC), Division Keyport. The NUWC is located mostly on a small peninsula in Kitsap County, Wash., in an extension of Puget Sound called Liberty Bay ([fig. 1](#)). The 9-acre former landfill at OU 1 is on the narrow strip of connecting land and is adjacent to some tidal flats that are an extension of Dogfish and Liberty Bays. The OU 1 landfill is unlined at the bottom and was constructed in a former marshland. The landfill was the primary disposal area for domestic and industrial wastes generated by NUWC Keyport from the 1930s through 1973. Paints, thinners, solvents, acids, dried sludge from a wastewater-treatment plant, and other industrial wastes were disposed of at various locations in the landfill. The most concentrated disposal area for waste paints and solvents was at the southern end of the landfill.

CVOCs are present in the upper and intermediate aquifers and in surface water at OU 1. 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 in the hydrogeologic units referred to as the unsaturated zone, the upper aquifer, the middle aquitard, and the intermediate aquifer. Ground water in the unconfined upper aquifer generally flows from the east to the west toward Dogfish Bay. Ground water in the predominately confined intermediate aquifer flows from the south and west toward the landfill, and then northwest from the landfill toward Dogfish bay. Two perennial freshwater creeks drain the marsh adjacent to the landfill.

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 OU 1. A need for remedial action was identified because those hazardous compounds present a potential risk to humans (URS Consultants, Inc., 1998). Phytoremediation combined with on-going natural attenuation processes was chosen by the Navy as the preferred remedy (URS Consultants, Inc., 1998). The Navy planted two hybrid poplar plantations on the landfill ([fig. 2](#)) in spring of 1999 to remove and control the migration of CVOCs in shallow ground water (URS Greiner, Inc., 1999).

# Purpose and Scope

The Navy began a cooperative effort with the USGS in 1995 to investigate various natural attenuation mechanisms at OU 1. Field and laboratory studies conducted from 1996 through 2000 have shown that natural attenuation and biodegradation of CVOCs in shallow ground water at OU 1 are substantial (URS Consultants, Inc., 1997; Bradley and others, 1998; Dinicola and others, 2002). The USGS has continued to monitor the geochemistry of ground water to assure that conditions remain favorable for contaminant biodegradation.

This report presents the ground-water chemical and selected CVOC data collected by the USGS at OU 1 during June 10-14, 2002, in support of the long-term monitoring for natural attenuation. USGS data collected from 1996 through 2001 were presented in Dinicola and others (2002) and Dinicola (2003). The June 2002 data collection focused on constituents used to evaluate ground-water redox conditions. The USGS collected ground-water samples from 13 wells and 9 piezometers ([table 1](#) and [fig. 2](#)). Concentrations of various geochemicals were determined in all samples, however concentrations of VOCs were determined by the USGS in samples from all 9 piezometers and from only 4 of the 13 monitoring wells. The Navy collected samples to determine VOC concentrations at other OU 1 monitoring wells, and those data are presented in a different report (The TEC LTM Team, 2003). The June 2002 data were not interpreted in detail for this report because natural attenuation will be thoroughly evaluated again at OU 1 in support of the 5-year review scheduled for 2004.

# Acknowledgments

The author thanks Matthew Butler of the Naval Facilities Engineering Command, Engineering Field Activity, Northwest (EFANW) for his guidance and funding for the continued monitoring. Mick Butterfield of EFANW and Gene Ellis of NUWC Keyport provided logistic support for field activities. Stephen Cox, Raegan Huffman, and Greg Justin of the U.S. Geological Survey, Tacoma, Wash., assisted with data collection and analysis.

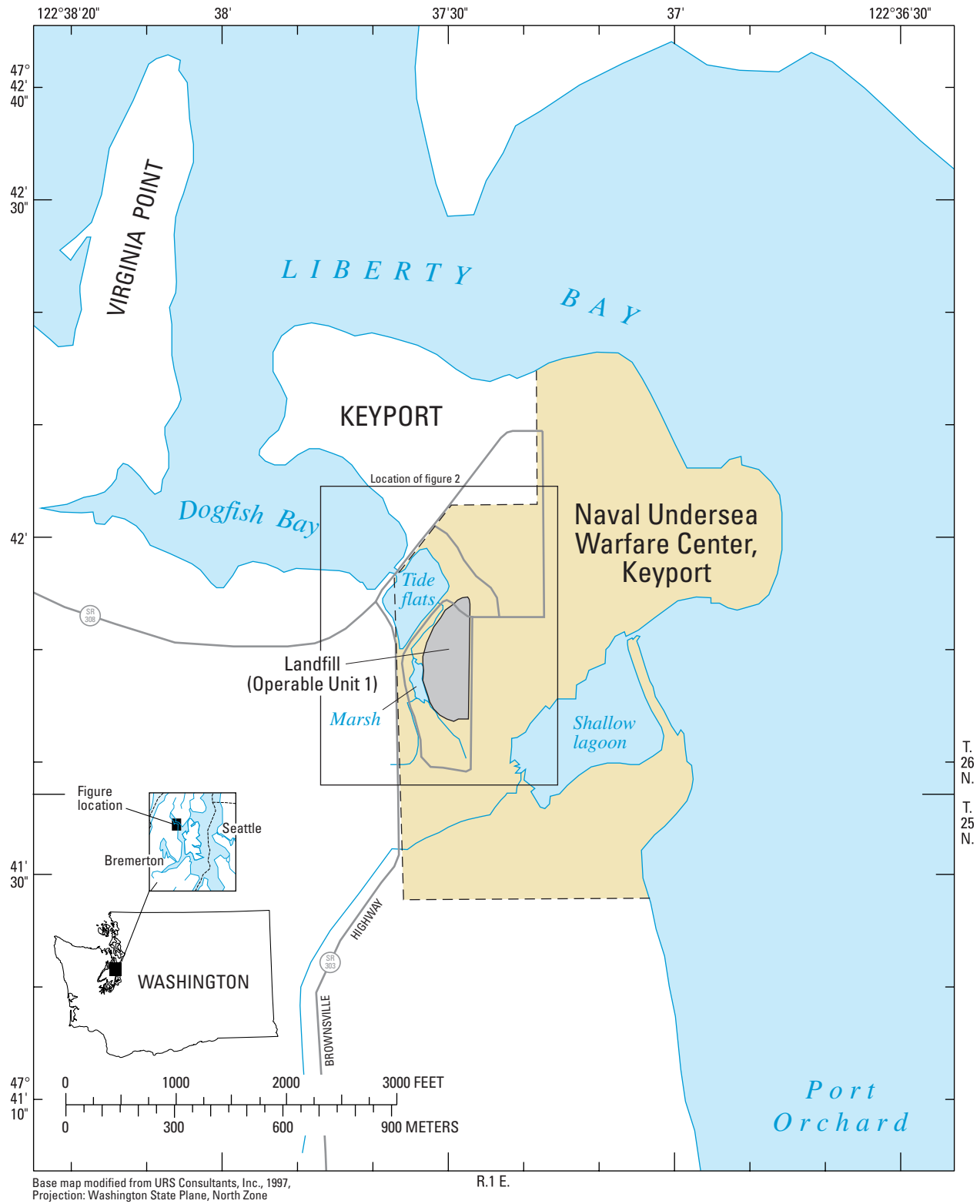
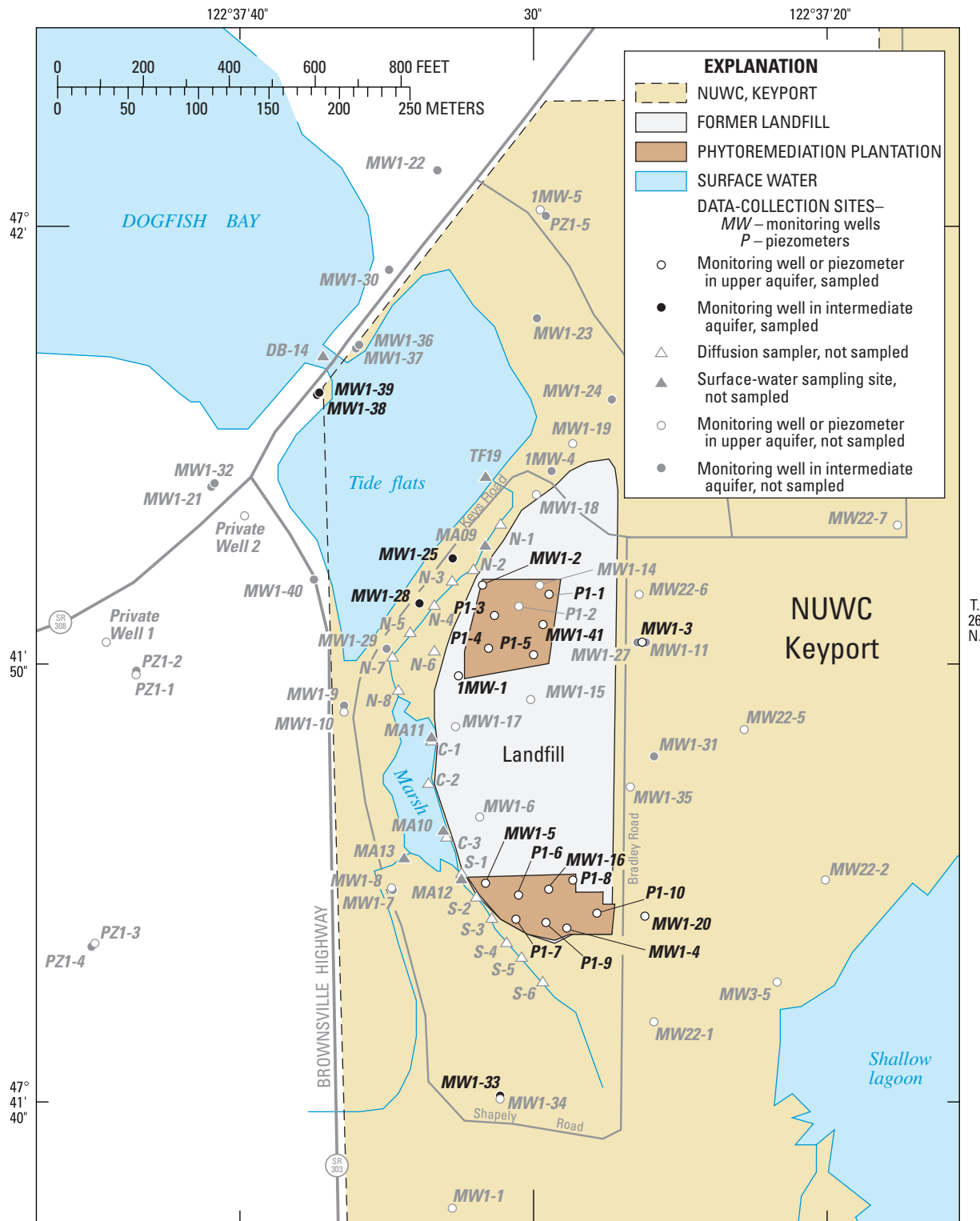


Figure 1. Location of Operable Unit 1 study area, Naval Undersea Warfare Center, Division Keyport, Washington.

4 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002



Base map modified from URS Consultants, Inc., 1997,  
 Projection: Washington State Plane, North Zone

R.1 E.

**Figure 2.** Location of June 2002 data-collection sites and other features at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

**Table 1.** Construction data and water-level measurements for monitoring wells and piezometers sampled during June 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[**Well No.:** MW, monitoring well; P, piezometer. **USGS site No.:** Unique number for each site based on latitude and longitude of the site. First six digits are latitude, next seven digits are longitude, and final two digits are a sequence number to uniquely identify each site. **Altitudes of water levels and measuring points** are given in feet above or below (-) NAVD88. **Water level** is in feet below measuring point (bmp). **Depth of well and screened interval** are in feet below land surface. **Measuring point:** Water levels in wells are usually reported as depths below land surface, although the measuring point can be any convenient fixed place near the top of the well. For these wells and piezometers, the measuring points are marked points on the tops of well casings—they vary from being near the ground surface to a few feet above ground surface. The altitude of the measuring point is commonly recorded so that static water levels can also be reported as altitudes. **Abbreviations:** ft, foot; in, inch; USGS, U.S. Geological Survey; ROD, Record of Decision; dup, field duplicate sample. **Symbols:** –, not measured; na, not applicable]

Well No.	USGS site No.	Date	Time sampled	Water-level altitude (ft)	Water-level (ft bmp)	Altitude of measuring point (ft)	Depth of well (ft)	Casing diameter (in.)	Screened interval (ft)	VOCs sampled by		Geochemical sampling specified in ROD
										USGS	Navy	
1MW-1	474151122373201	06-10-02	15:00	3.08	6.98	10.06	16.5	2	5.5-15.5		X	X
MW1-2	474153122373101	06-11-02	10:35	3.04	8.85	11.89	18.5	4	12.5-17.5		X	X
MW1-3	474152122372501	06-10-02	13:00	9.50	4.05	13.55	11.5	4	5.5-10.5			
MW1-4	474145122372801	06-13-02	12:45	5.60	6.60	12.2	13.0	4	7-12		X	X
MW1-5	474146122373201	06-13-02	15:30	4.24	8.84	13.08	12.0	4	6-11		X	X
MW1-16	474146122372801	06-13-02	11:30	5.44	7.39	12.83	12.0	2	6-11		X	X
MW1-20	474145122372501	06-12-02	15:00	6.53	3.91	10.44	16.0	2	10-15	X		
MW1-25	474154122373201	06-14-02	13:00	2.22	9.69	11.91	49.0	2	38-48	X	X	X
MW1-28	474153122373301	06-14-02	13:30	-.81	11.04	10.23	45.0	2	39-44	X	X	X
MW1-33	474140122373201	06-10-02	16:35	11.02	.48	11.50	41.0	2	30-40			
MW1-38	474156122373701	06-12-02	12:00	-.57	10.40	9.83	51.0	2	–	X		
MW1-39	474157122373701	06-11-02	12:45	-.72	10.57	9.85	33.7	2	27.7-32.7		X	X
MW1-41	474152122372901	06-10-02	16:35	6.81	8.40	15.21	15.0	2	5-15		X	
P1-1	474153122372801	06-11-02	14:15	–	8.31	na	15.0	1	10-15	X		
P1-3	474153122373101	06-11-02	10:30	–	9.77	na	15.0	1	10-15	X		
P1-4	474152122373101	06-11-02	12:45	4.30	8.25	12.55	15.0	1	10-15	X		
P1-5	474152122372801	06-10-02	16:30	–	9.15	na	15.0	1	10-15	X		
P1-6	474146122373001	06-14-02	14:15	5.17	7.59	12.76	15.0	1	10-15	X		
(dup)			14:16							X		
P1-7	474145122373101	06-14-02	11:00	6.88	5.24	12.12	15.0	1	10-15	X		
P1-8	474147122372801	06-13-02	11:00	6.06	6.00	12.06	15.0	1	10-15	X		
(dup)			11:01									
P1-9	474145122372901	06-13-02	16:00	5.39	6.52	11.91	15.0	1	10-15	X		
P1-10	474145122372601	06-12-02	13:45	6.42	5.44	11.86	15.0	1	10-15	X		

## Methods and Data Analysis

Sample collection, processing, and field analyses were in accordance with applicable USGS procedures (U.S. Geological Survey, 1997 to 2002). The analytical methods used for the June 2002 data-collection activities were generally consistent with previous USGS data-collection activities at OU 1.

The geochemical measures and concentrations determined for samples from all wells and piezometers included dissolved H<sub>2</sub>, dissolved oxygen (DO), filtered organic carbon, filtered nitrate plus nitrite, filtered manganese, filtered iron (II), filtered sulfate, unfiltered sulfide, dissolved methane, dissolved carbon dioxide, filtered bicarbonate, pH, specific conductance, oxidation-reduction potential (ORP), and filtered chloride. The concentrations of 64 VOCs, including all CVOCs of interest at OU 1, also were determined for samples from the piezometers and selected monitoring wells. Monitoring wells and piezometers sampled at OU 1 are of different depths and diameters (table 1), but all were constructed with PVC casings and screens with sand filter packs.

All samples were collected with a peristaltic pump and single-use polyethylene tubing. A stainless-steel weight was attached to the bottom of the pre-measured length of tubing to accurately collect the sample from the mid-screen elevation in each well or piezometer. Samples were collected after approximately three casing volumes of water were purged from the wells or piezometers and after allowing pH, specific conductance, and DO to stabilize within  $\pm 0.1$  units, 5 percent, and 0.3 mg/L (milligrams per liter), respectively. Those three analytes, as well as oxidation-reduction potential, were measured in a flow-through chamber using temperature compensated probes from a YSI™ data sonde. The specific-conductance probes were checked daily with standard reference solutions; the pH probes were calibrated daily with two pH standards; and the DO probes were calibrated daily with water-saturated air and occasionally verified with zero-dissolved-oxygen solution. DO analyses were confirmed for most samples using 0 to 1 mg/L CHEMetes Rhodazine- D™ colorimetric ampoules (manufactured by CHEMetrics, Inc., Calverton, Va.). The ampoules were filled directly from the sampling tube after well purging was complete.

The purge-related analytes were measured using two different techniques. At seven monitoring wells (1MW-1, MW1-2, MW1-5, MW1-16, MW1-20, MW1-28, and MW1-41), the analytes were measured by deploying the sonde into the wells at a depth immediately above the mid-screen level of the sample tubing, and the sonde readings were monitored

remotely while purging. At the remaining monitoring wells and the piezometers, sample water was pumped through a flow-through chamber attached to the sonde or stand-alone probes at the wellhead. The difference in techniques is relevant because the downhole sonde deployment may have affected the quality of the dissolved H<sub>2</sub> data (as discussed later in this report.)

Bicarbonate concentration (HCO<sub>3</sub><sup>-</sup>) was measured in the field by titration of a sample filtered through a 0.45-micrometer (μm) membrane filter, and the concentration was calculated from the titration results. The inflection points of the titration curve were used to determine equivalence end-points. Iron (II) concentrations were measured in the field in a sample filtered through a 0.45-μm membrane filter using a colorimetric 1,10 phenanthroline indicator method and a Hach Model 2010 spectrophotometer according to Hach analytical method number 255 (Hach Company, 1998). Concentrations of sulfide were measured in the field using a colorimetric methylene-blue indicator method using the same spectrophotometer according to analytical method number 690 (Hach Company, 1998). Information about the methodologies used to determine field iron and sulfide concentrations is described at <http://www.hach.com>.

Dissolved H<sub>2</sub> 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 from each well or piezometer were collected and analyzed after at least 20 minutes of stripping; subsequent samples were collected and analyzed at about 5-minute intervals until consecutive H<sub>2</sub> concentrations stabilized to within 10 percent. If dissolved H<sub>2</sub> did not stabilize and did not consistently increase or decrease over time, the range over which the concentrations fluctuated was reported.

Samples for analysis of nitrate, manganese, sulfate, and chloride were filtered through a 0.45-μm membrane filter into polyethylene bottles, chilled, and sent to the USGS National Water Quality Laboratory (NWQL) in Lakewood Colo. The manganese sample was acidified in the field with nitric acid to a pH of less than 2, and then analyzed at NWQL by inductively coupled plasma as described by Fishman (1993). Chloride and sulfate were analyzed using ion chromatography as described by Fishman and Friedman (1989). Nitrate plus nitrite (reported as nitrite plus nitrate as N) were analyzed calorimetrically by cadmium reduction and diazotization as described by Fishman (1993). The results for the nitrate plus nitrite analyses are referred to simply as nitrate in this report because of the expected small contribution of nitrite to the total concentration determined.

Samples for filtered (dissolved) organic carbon were filtered through a 0.45- $\mu\text{m}$  filter and collected in amber glass bottles, acidified in the field with sulfuric acid to a pH of less than 2, chilled to less than 4°C (degrees Celsius), and shipped to the USGS laboratory in Ocala, Fla., for analysis. Organic carbon concentrations were determined using high-temperature combustion according to Standard Method 5310B as described by Franson (1992).

Dissolved methane and carbon dioxide samples were collected in 150-ml glass bottles, sealed with rubber stoppers, chilled to less than 4°C, and analyzed at the USGS Dissolved Gas Laboratory in Reston, Va. Samples were analyzed using a gas chromatograph with a flame-ionization detector as described at [http://water.usgs.gov/lab/dissolved-gas/lab/DG\\_method.html](http://water.usgs.gov/lab/dissolved-gas/lab/DG_method.html).

VOC samples were collected in 40-mL glass vials, acidified to a pH of less than 2 with hydrochloric acid, sealed, and placed on ice. The samples were shipped to the NWQL for analysis using purge-and-trap capillary-column gas chromatography/mass spectrometry (Conner and others, 1998).

## Natural Attenuation Monitoring Data

The data collected in support of long-term monitoring for natural attenuation included geochemical and selected CVOC data. The predominant redox conditions at each sample location were determined from the geochemical data.

### Geochemical Data and Predominant Redox Conditions

The June 2002 data and the previous geochemical data collected by USGS at OU 1 (Dinicola and others, 2002; Dinicola, 2003) are shown in [table 2](#). Duplicate samples were collected at piezometers P1-6 and P1-8 and analyzed for concentrations of organic carbon, manganese, sulfate, and chloride. The duplicate results for those constituents agreed within 7 percent. Duplicate methane and carbon dioxide samples were collected and analyzed at all wells according to the Reston laboratory protocols. The duplicate methane concentrations were within 0 to 21 percent for all samples except those with very low concentrations (less than 0.1 mg/L). Duplicate carbon dioxide concentrations were within 40 percent. Carbon dioxide concentrations were not analyzed for

OU 1 samples prior to 2002, but were analyzed during 2002 because they are included in the methane analysis schedule from the Reston laboratory. The analyte is of interest for natural attenuation because it is a direct measure of the primary byproduct of microbial respiration, whereas bicarbonate concentration is an indirect measure of the carbon dioxide concentration.

The predominant redox conditions for June 2002 samples were determined primarily by DO and dissolved H<sub>2</sub> concentrations. The process and uncertainties in determining the predominant redox conditions from geochemical data are described in greater detail in Dinicola and others (2002). Generally, DO concentrations greater than 1 mg/L indicate aerobic conditions, and DO concentrations less than 1 mg/L indicate anaerobic conditions. More specific anaerobic conditions are indicated by dissolved H<sub>2</sub> concentrations: 0.2-0.8 nM (nanomolar) indicates iron reduction, 1-5 nM indicates sulfate reduction, and greater than 5 nM indicates methanogenesis. Anaerobic ground water with a dissolved H<sub>2</sub> concentration less than 1 nM is referred to as mildly reducing, and water with a dissolved H<sub>2</sub> concentration greater than 1 nM is referred to as strongly reducing. These general terms for describing anaerobic redox conditions are useful because reductive dechlorination of CVOC contaminants is more likely to occur under strongly reducing conditions (McCarty and Semprini, 1994; Gossett and Zinder, 1996).

The selected predominant redox conditions for 1996-2001 shown in [table 2](#) were updated during 2002 after consideration of the variation and contradictions in the data. The updated redox determinations are based primarily on a more strict interpretation of DO and dissolved H<sub>2</sub> concentration data, as described in the previous paragraph. Samples with a DO concentration less than 1 mg/L and no associated H<sub>2</sub> concentration data were assigned a general anaerobic (An) redox condition. For the few samples (mostly from 1996) where DO concentrations exceeded 1 mg/L and where iron (II) concentrations were greater than 0.5 mg/L, the iron (II) data were assumed to be better indicators of actual aquifer conditions. Therefore, less weight was given to the DO data and the samples were considered anaerobic. The updated redox assignments better reflect our understanding of the assignment of specific redox conditions, although they do not change the overall conclusion that redox conditions in the upper aquifer are favorable for reductive dechlorination of chlorinated VOCs because strongly reducing conditions persisted beneath much of the former landfill.

## 8 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Date sampled	Predominant redox condition	Dissolved hydrogen (nM)	Dissolved oxygen (mg/L)	Unfiltered (total) organic carbon (mg/L)	Filtered (dissolved) organic carbon (mg/L)	Filtered nitrate + nitrite (mg/L as N)	Filtered manganese (mg/L)	Filtered iron (II) (mg/L)
1MW-1	09-17-96	Fe	0.4	2.8	7.0	–	<0.02	0.18	0.24
	04-16-97	Fe	.8	.4	–	–	.11	–	8.0
	03-05-98	Fe/S	.2	.1	8.3	–	–	.39	12
	10-09-98	Fe	.2	.5	–	–	–	.08	.39
	06-21-00	Mn/Fe	.1	.5	12	–	<.05	.96	13
	06-11-01	Fe	.6	.7	13	12	<.05	.24	2.9
	06-10-02	Fe	.4	.2	14	–	<.05	.37	7.3
1MW-4	09-17-96	Fe	.6	1.6	23	–	<.02	.77	1.5
	04-16-97	S	1.8	.0	–	–	.03	–	1.7
MW1-2	09-17-96	A	.5	2.4	6.0	–	<.02	.05	.23
	04-16-97	Fe	.7	.2	–	–	<.02	–	.13
	03-02-98	Fe	.3	–	–	–	–	–	.16
	10-07-98	Fe	.1	.1	–	–	–	.05	.14
	06-09-99	Fe	.9	.2	–	–	–	.08	.09
	06-21-00	Fe	.3	.1	6.0	–	<.05	.06	.10
	06-12-01	S	3.5	.3	5.3	5.0	<.05	.08	.29
	06-11-02	An	>20	.1	45	–	<.05	.09	.27
MW1-3	06-09-99	Fe	.8	.4	–	–	–	.07	<.01
	06-20-00	Fe	.2	.3	2.0	–	.99	.08	<.01
	06-12-01	A	–	4.0	2.3	1.1	1.1	.04	.02
	06-10-02	S	2.7	.4	1.4	–	1.6	.10	.01
MW1-4	09-17-96	Fe	.5	2.8	2.0	–	<.02	.28	1.8
	04-16-97	Fe	.6	.4	–	–	.24	–	<.01
	03-03-98	S	1.7	.2	4.0	–	–	.10	.01
	10-08-98	Fe	.2	.5	–	–	–	–	.28
	06-07-99	Fe	.9	.1	–	–	–	.20	1.2
	06-22-00	Fe	.2	.1	8.6	–	–	.70	–
	06-14-01	S	.9 - 3.2	.5	2.9	2.5	.08	.54	1.6
	06-13-02	S	2.4	.1	3.8	–	.08	.47	1.2
MW1-5	09-17-96	S	1.2	.0	15	–	<.02	1.6	19
	04-16-97	Fe	.5	.0	–	–	.08	–	3.1
	03-04-98	Fe	.7	.0	12	–	–	1.3	4.5
	10-08-98	S	2.4	.0	–	–	–	1.5	11
	06-08-99	Fe	.6	.3	–	–	–	1.2	31
	06-22-00	Fe	–	.0	17	–	–	1.5	39
	06-13-01	Fe	.8	.3	10	9.6	.12	1.5	25
	06-13-02	S	3.4	.5	11	–	.14	1.5	20
MW1-6	09-17-96	S	1.1	.0	33	–	1.2	1.2	30
	04-16-97	Fe/S	.5	.0	–	–	.07	–	36
	10-08-98	Fe	.2	.0	–	–	–	1.1	32
MW1-14	09-17-96	Fe	.6	.0	42	–	<.02	2.0	67
	04-16-97	Fe	.7	.0	–	–	.05	–	78
	03-04-98	Fe/S	–	.1	36	–	–	11	68
	10-07-98	S	1.2	.0	–	–	–	1.5	48
	06-09-99	S	1.0	.3	–	–	–	.30	57

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; ORP, oxidation reduction potential; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Dissolved carbon dioxide (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance ( $\mu$ S/cm)	ORP (mV)	Filtered chloride (mg/L)
1MW-1	7.5	<0.01	10		640	7.9	–	–	43
	1.4	.01	29		1,100	7.2	–	–	–
	–	.06	–		–	–	–	–	–
	–	.01	–		660	7.7	1,080	--	--
	.9	<.01	.39		590	7.0	1,070	-92	44
	2.2	<.01	5.6		550	7.1	974	-110	50
	1.7	<.01	14 (15)	77 (81)	520	7.7	835	-160	54
1MW-4	.04	<.01	16		780	7.3	–	–	25
	.36	.02	47		1,300	7.3	–	–	–
MW1-2	4.6	<.01	1.2		510	6.9	–	–	50
	4.6	<.01	2.5		1,100	6.7	–	–	–
	–	–	–		–	–	–	–	–
	–	<.01	–		300	6.7	868	–	–
	–	<.01	–		490	6.8	901	–	–
	4.3	<.01	.04		460	6.8	870	37	36
	5.4	<.01	.78		470	6.5	853	27	48
MW1-3	4.2	<.01	.92 (.92)	200 (200)	500	6.6	829	200	37
	–	<.01	–		81	6.0	202	–	–
	13	<.01	.02		82	5.9	205	180	8.4
	14	<.01	.12		90	6.1	203	220	10
11	<.01	.06 (0.02)	140 (140)	80	5.8	182	400	9.7	
MW1-4	7.1	<.01	1.2		130	6.9	–	–	15
	8.6	<.01	.70		270	7.3	–	–	–
	–	<.01	–		–	–	–	–	–
	–	<.01	–		170	6.7	368	–	–
	–	<.01	–		180	6.6	350	–	–
	5.5	<.01	.56		230	6.8	412	-26	19
	5.4	<.01	3.7		180	6.5	360	-8	22
MW1-5	5.5	<.01	5.2 (5.5)	60 (65)	190	6.6	442	-14	20
	6.4	<.01	2.4		410	6.7	–	–	21
	2.8	.03	18		1,400	6.6	–	–	–
	–	<.01	–		–	–	–	–	–
	–	<.01	–		410	6.4	1,740	–	–
	–	.01	–		510	6.5	855	–	–
	6.4	<.01	1.1		460	6.6	790	-80	19
6.0	.01	2.4		470	6.4	766	-70	12	
MW1-6	6.3	.02	7.4 (7.2)	180 (180)	740	6.5	608	-77	9.6
	.10	<.01	7.0		840	6.7	–	–	27
	4.1	.15	15		1,100	6.5	–	–	--
MW1-14	–	.01	–		720	6.4	1,170	–	–
	.27	<.01	9.2		1,200	6.4	–	–	25
	.13	<.01	46		1,800	6.4	–	–	–
	–	.05	–		–	–	–	–	–
	–	.01	–		600	6.3	1,450	–	–
–	.04	–		810	6.4	1,220	–	–	

## 10 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Date sampled	Predominant redox condition	Dissolved hydrogen (nM)	Dissolved oxygen (mg/L)	Unfiltered (total) organic carbon (mg/L)	Filtered (dissolved) organic carbon (mg/L)	Filtered nitrate + nitrite (mg/L as N)	Filtered manganese (mg/L)	Filtered iron (II) (mg/L)
MW1-15	09-16-96	Fe	0.2	0.0	50	–	<0.02	5.7	68
	04-16-97	Fe/S	.8	.0	–	–	<.02	–	77
	03-05-98	S	1.2	.0	33	–	–	18	51
	10-09-98	S	2.9	.0	–	–	–	5.8	64
MW1-16	09-17-96	S	2.1	.0	480	–	<.02	3.9	130
	04-16-97	Fe/S	.8	.0	–	–	<.02	–	120
	03-04-98	Fe	.7	.3	350	–	–	18	100
	10-08-98	M	9.6	.0	–	–	–	5.4	180
	06-07-99	M	6.8	.6	–	–	–	>5	140
	06-22-00	S	–	.1	61	–	–	1.9	60
	06-14-01	S	1.7	.2	64	66	.33	2.4	56
06-13-02	M	4.6 - 7.6	.9	71	–	<.05	3.2	38	
MW1-17	09-17-96	Fe	.7	.0	23	–	<.02	1.3	62
	04-16-97	Fe	.6	.0	–	–	<.02	–	37
	10-09-98	Fe	–	.0	–	–	–	.80	56
	06-22-00	S	1.2	.0	11	–	–	1.2	68
	06-12-01	S	2.0 - 2.7	.4	9.2	8.0	<.05	1.2	48
MW1-18	09-17-96	Fe/S	1.0	.0	28	–	<.02	4.0	12
	04-16-97	Fe	.5	.0	–	–	.05	–	23
	10-07-98	Fe	–	.2	–	–	–	.77	3.3
MW1-20	06-08-99	Fe	.9	.3	–	–	–	.35	.03
	06-21-00	Fe	.4	.0	2.2	–	<.05	.24	.11
	06-13-01	S	2.1	.2	3.0	1.4	<.05	.28	.01
	06-12-02	An	>100	.1	1.4	–	<.05	.16	.01
MW1-25	09-17-96	Fe	.4	2.7	7.4	–	.14	.16	.74
	04-17-97	Fe	.8	.1	–	–	<.02	–	.88
	03-05-98	Fe	.3	.3	7.9	–	–	.20	.73
	10-05-98	Fe	.2	.1	–	–	–	.19	.99
	06-22-00	Fe	.4	.2	6.5	–	–	.16	.80
	06-12-01	S	2.8 - 4.3	.2	7.1	6.8	<.05	.16	.99
	06-14-02	S	0.7 - 2.4	.1	6.2	–	<.05	.18	1.1
MW1-28	09-16-96	Fe	.3	2.1	7.2	–	<.02	.20	1.0
	04-17-97	Fe	1.0	.0	–	–	.04	–	.99
	03-05-98	Fe	.4	.5	7.7	–	–	.20	.67
	10-07-98	Fe	.6	.0	–	–	–	.19	1.0
	06-22-00	Fe	.3	.0	13	–	–	.16	.66
	06-12-01	S/M	4.1 - 5.7	.5	10	6.9	<.05	.16	.90
	06-14-02	An	>100	.1	7.0	–	<.05	.16	.92
MW1-29	09-16-96	Mn/Fe	.0	1.9	–	–	<.02	.86	2.0
	04-17-97	Fe	.7	.0	–	–	.29	–	2.1

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; ORP, oxidation reduction potential; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Dissolved carbon dioxide (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance ( $\mu$ S/cm)	ORP (mV)	Filtered chloride (mg/L)
MW1-15	0.11	<0.01	8.8		1,200	–	–	–	18
	.08	.03	44		1,600	6.3	–	–	–
	–	<.01	–		–	–	–	–	–
	–	<.01	–		750	6.3	1,110	–	–
MW1-16	.17	<.01	4.3		1,400	6.5	–	–	150
	2.2	.06	29		1,800	6.5	–	–	–
	–	.01	–		–	–	–	–	–
	–	<.01	–		1,600	6.3	3,370	–	–
	–	.01	–		1,200	6.7	1,820	–	–
	1.2	.02	1.2		510	6.7	902	-130	43
	1.1	.08	10		610	6.4	953	–	40
.4	.04	24 (21)	270 (270)	700	6.5	1,400	-140	17	
MW1-17	4.3	<.01	8.9		760	6.5	–	–	61
	68	.02	23		1,200	6.6	–	–	–
	–	.02	–		510	6.4	1,740	–	–
	–	.02	2.8		450	6.5	1,260	-41	160
MW1-18	12	.01	9.4		500	6.5	1,200	-280	120
	4.6	<.01	11		880	7.0	–	–	86
	8.2	<.01	52		1,500	6.8	–	–	–
MW1-20	–	<.01	–		920	6.6	1,780	–	–
	–	<.01	–		260	6.7	546	–	–
	16	<.01	.01		240	6.8	530	79	14
	20	<.01	.27		260	6.4	544	250	33
MW1-25	17	<.01	.06 (.05)	97 (99)	250	7.0	701	180	29
	16	<.01	3.6		360	7.1	–	–	140
	15	<.01	7.9		1,000	7.0	–	–	–
	–	<.01	–		–	–	–	–	–
	–	<.01	–		450	6.9	1,240	--	--
	13	<.01	.79		380	6.9	1,230	-49	170
	13	<.01	4.7		440	6.7	1,180	-36	160
9.7	<.01	7.0 (7.1)	83 (83)	370	6.7	1,030	-60	170	
MW1-28	48	<.01	1.7		350	--	–	–	380
	51	<.01	5.3		1,100	7.4	–	–	–
	–	<.01	–		–	–	–	–	–
	–	.02	–		320	6.6	2,630	–	–
	44	<.01	.45		480	7.3	2,460	-87	510
	45	<.01	4.1		480	7.4	2,200	-220	490
	39	<.01	3.9 (4.0)	40 (40)	470	7.2	2,580	-110	460
MW1-29	1.8	.02	8.1		300	–	–	–	500
	1.1	<.01	18		710	7.3	–	–	–

## 12 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Date sampled	Predominant redox condition	Dissolved hydrogen (nM)	Dissolved oxygen (mg/L)	Unfiltered (total) organic carbon (mg/L)	Filtered (dissolved) organic carbon (mg/L)	Filtered nitrate + nitrite (mg/L as N)	Filtered manganese (mg/L)	Filtered iron (II) (mg/L)
MW1-31	09-16-96	Mn/Fe	–	–	5.6	–	–	3.6	0.32
MW1-32	09-16-96	Fe	0.4	2.7	.8	–	0.07	0.23	1.3
	04-17-97	Fe	–	1.2	–	–	.17	–	.87
	03-02-98	Fe	–	<1.0	–	–	–	.10	1.1
	10-05-98	Fe	.1	.0	–	–	–	.36	1.0
MW1-33	10-07-98	A	–	3.3	.1	–	–	.003	<.01
	06-21-00	A	–	3.8	.7	–	1.3	<.002	<.01
	06-11-01	A	–	3.8	1.5	1.4	1.1	<.003	<.01
	06-10-02	A	–	3.4	1.2	–	1.1	<.002	<.01
MW1-35	10-07-98	A	–	2.4	1.9	–	–	.15	<.01
	06-08-99	A	–	2.1	–	–	–	–	–
	06-20-00	A	–	3.0	2.2	–	.16	<.002	<.01
MW1-36	10-09-98	Fe	–	.0	–	–	–	.30	3.6
	06-20-00	Fe	.5	.1	2.4	–	<.05	.28	3.2
MW1-37	09-16-96	Fe	.8	1.5	6.9	–	<.02	.12	.48
	04-17-97	S	3.3	.0	–	–	<.02	–	.80
	03-03-98	Fe	.4	.4	5.7	–	–	.10	.86
	10-09-98	Fe	.4	.0	–	–	–	<.01	.43
	06-07-99	Fe	.4	.4	–	–	–	.10	.32
	06-20-00	Fe	.1	.1	5.8	–	<.05	.13	.25
MW1-38	10-09-98	Fe	–	.1	–	–	–	.20	.08
	06-20-00	Fe	.1	.2	5.6	–	<.05	.08	.10
	06-12-02	S	1.4	.0	5.0	–	<.05	.08	0.42
MW1-39	09-16-96	Fe/S	.6	2.0	4.4	–	<.02	.02	<.01
	04-17-97	S	4.5	.0	–	–	<.02	–	.05
	03-03-98	Fe/S	.3	.3	3.7	–	–	.10	.03
	10-09-98	Fe/S	.5	.0	–	–	–	<.01	.04
	06-07-99	Fe/S	1.0	.3	–	–	–	.10	.02
	06-20-00	Fe/S	.5	.1	2.4	–	<.05	.01	.07
	06-12-01	S	1.4	.3	3.4	3.3	<.05	.01	<.01
	06-12-02	M	>30	.0	2.8	–	<.05	.01	0.1
MW1-41	06-09-99	S	1.0	.3	–	–	–	2.2	60
	06-21-00	S	1.2	.1	22	–	<.05	3.5	55
	06-11-01	S	2.0	.3	14	14	<.05	3.7	66
	06-10-02	S	2.2	.8	20	–	<.05	3.6	52
P1-1	06-09-99	Fe	.7	.4	–	–	–	4.0	59
	06-11-02	S	1.4	.0	17	–	<.05	2.7	40
P1-3	06-09-99	Fe	.4	.2	–	–	–	1.0	19
	06-11-02	Fe	.3	.0	45	–	<.05	2.6	39

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; ORP, oxidation reduction potential; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Dissolved carbon dioxide (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance ( $\mu$ S/cm)	ORP (mV)	Filtered chloride (mg/L)
MW1-31	–	–	–	–	–	–	–	–	–
MW1-32	16	0.01	<0.01	–	110	–	–	–	7.4
	17	.01	<.01	–	300	7.1	–	–	–
	–	<.01	–	–	–	–	–	–	–
	–	<.01	–	–	130	7.2	270	–	–
MW1-33	--	<.01	–	–	78	6.6	177	–	–
	7.5	<.01	.05	–	74	6.7	164	160	4.0
	8.2	<.01	.07	–	71	6.2	154	300	3.6
	7.3	<.01	.004 (0.000)	31 (32)	81	6.5	138	360	3.4
MW1-35	–	<.01	–	–	110	6.4	301	–	–
	–	–	–	–	76	6.4	187	–	–
	3.9	<.01	.01	–	77	6.6	151	360	2.3
MW1-36	–	<.01	–	–	280	7.3	8,610	–	–
	180	.02	.01	–	270	7.3	7,940	-130	2,300
MW1-37	23	.03	.30	–	280	–	–	–	660
	27	.02	.90	–	730	7.7	–	–	–
	–	<.01	–	–	–	–	–	–	–
	–	<.01	–	–	340	7.9	2,440	–	–
	–	.03	–	–	340	7.7	2,920	–	–
	29	.02	.07	–	350	7.6	3,240	-160	840
MW1-38	–	.02	–	–	310	7.8	1,460	–	–
	2.3	.03	.10	–	300	7.8	1,240	-130	230
	2.9	.04	1.1 (1.1)	7.7 (7.9)	310	7.6	1,350	-160	230
MW1-39	.71	.04	1.6	–	140	–	–	–	85
	13	.06	6.1	–	360	7.9	–	–	–
	–	.05	–	–	–	–	–	–	–
	–	.07	–	–	170	8.1	502	--	--
	–	<.01	–	–	180	8.0	512	--	--
	.2	.08	.41	–	180	8.0	481	-130	61
	.1	.05	2.7	–	170	7.8	472	-130	61
	.1	.06	4.8 (4.8)	2.4 (2.4)	180	7.9	464	-120	60
MW1-41	–	.01	–	–	860	6.6	1,260	–	–
	<.3	<.01	1.9	–	1,000	6.5	1,500	-75	8.3
	30	.02	25	–	980	6.3	1,330	-89	9.9
	.4	.04	21 (26)	540 (530)	830	6.3	1,190	-68	7.9
P1-1	–	<.01	–	–	930	6.4	1,350	–	–
	<.1	<.01	29 (29)	400 (400)	650	6.3	987	-80	9.3
P1-3	–	.04	–	–	730	6.8	1,470	–	–
	1.0	.03	24 (19)	400 (400)	820	6.4	1,340	-73	61

## 14 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu$ S/cm, microsiemens per centimeter at 25° Celsius; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Date sampled	Predominant redox condition	Dissolved hydrogen (nM)	Dissolved oxygen (mg/L)	Unfiltered (total) organic carbon (mg/L)	Filtered (dissolved) organic carbon (mg/L)	Filtered nitrate + nitrite (mg/L as N)	Filtered manganese (mg/L)	Filtered iron (II) (mg/L)
P1-4 (duplicate)	06-09-99	Fe	0.7	0.3	–	–	–	0.34	2.6
	06-13-01	Fe	.1	.5	9.8	8.7	<0.05	.38	3.4
	06-13-01	Fe	–	–	8.4	6.2	<.05	.38	3.6
	06-11-02	Fe	.2	.1	8.0	–	<.05	2.6	3.7
P1-5	06-08-99	S	3.0	.3	–	–	–	3.1	72
	06-10-02	S	1.7	.1	25	–	<.05	2.6	62
P1-6 (duplicate)	06-08-99	S	1.8	.1	–	–	–	.12	.02
	06-14-01	S	1.8	.2	34	34	.23	.45	.95
	06-13-02	S	1.6	.0	–	26	<.05	.88	1.0
	06-13-02	–	–	–	–	–	<.05	.84	–
P1-7	06-08-99	S	1.2	.1	–	–	–	.61	2.1
	06-22-00	Mn/Fe	–	.1	19	–	–	2.6	3.2
	06-14-01	Mn/Fe	.2	.2	11	11	<.05	2.3	2.0
	06-14-02	Mn/Fe	.2	1.3	8.9	–	<.05	2.2	1.9
P1-8 (duplicate)	06-07-99	S	1.8	.0	–	–	–	.20	.08
	06-14-01	Fe	.7	.1	4.8	4.7	.06	.16	.22
	06-13-02	Fe	.6	.3	8.8	–	<.05	.21	.38
	06-13-02	–	–	–	9.0	–	<.05	.21	–
P1-9	06-08-99	M	19	.3	–	–	–	.90	.03
	06-22-00	S/M	–	.1	10	–	–	.69	.20
	06-14-01	M	6.7	.1	2.3	1.7	<.05	.19	.05
	06-13-02	An	–	.6	9.8	–	<.05	1.2	.42
P1-10	06-07-99	Fe	.7	.3	–	–	–	.10	.11
	06-22-00	Fe	–	.0	7.2	–	–	.07	.25
	06-13-01	S	2.0	.2	3.0	4.2	<.05	.07	.20
	06-12-02	Fe	.3	.1	3.5	–	<.05	.05	.41

**Table 2.** Predominant redox conditions and ground-water geochemical data collected from 1996 to 2002 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington—*Continued*

[All data except those shaded were published previously in Dinicola and others (2002), Dinicola (2003); 2002 dissolved methane and carbon dioxide concentrations were collected and analyzed in duplicate. **Predominant redox conditions:** A, aerobic; Fe, iron reducing; M, methanogenic; Mn, manganese reducing; S, sulfate reducing. **Abbreviations:** nM, nanomolar; mg/L, milligrams per liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25° Celsius; ORP, oxidation reduction potential; mV, millivolt. **Symbols:** <, actual value is less than value shown; >, actual value is greater than value shown; –, not analyzed]

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Dissolved carbon dioxide (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	ORP (mV)	Filtered chloride (mg/L)
P1-4 (duplicate)	–	0.02	–	–	450	6.9	867	–	–
	3.8	<.01	0.9	–	390	6.6	761	-78	53
	3.8	<.01	3.2	–	390	–	–	–	53
	3.5	<.01	5.9 (6.7)	90 (86)	380	6.7	734	-86	56
P1-5	–	.01	–	–	850	6.2	1,320	–	–
	<.6	.02	23 (25)	400 (570)	730	6.2	1,200	-59	17
P1-6 (duplicate)	–	.04	–	–	300	6.8	574	–	–
	4.9	.12	6.3	–	350	6.4	657	-38	47
	4.3	.11	11 (11)	170 (170)	380	6.4	604	-11	37
	4.6	–	–	–	–	–	–	–	38
P1-7	–	<.01	–	–	310	6.7	627	–	–
	24	<.01	1.5	–	400	6.8	851	-35	55
	18	<.01	4.0	–	320	6.5	666	-32	41
	12	<.01	6.0 (6.5)	87 (95)	300	6.6	601	-41	60
P1-8 (duplicate)	–	.01	–	–	210	7.6	381	–	–
	.13	.02	6.9	–	200	7.0	363	-73	18
	.3	.02	11 (–)	40 (–)	104	6.9	482	-46	35
	.3	–	–	–	–	–	–	–	35
P1-9	–	<.01	–	–	270	6.6	680	–	–
	6.6	<.01	1.7	–	250	6.8	548	-17	59
	7.6	<.01	1.4	–	200	7.8	289	-120	14
	5.6	<.01	7.5 (7.5)	91 (94)	280	6.5	601	17	71
P1-10	–	<.01	–	–	300	6.7	560	–	–
	<.31	<.01	1.3	–	290	7.1	500	-19	15
	.06	<.01	4.9	–	290	7.2	476	-24	15
	<.1	<.01	18 (18)	51 (54)	270	6.8	438	8	14

## 16 Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA, June 2002

Dissolved H<sub>2</sub> concentrations from wells MW1-2, MW1-20, MW1-28, and MW1-39 were extremely high (greater than 20 nM) during June 2002, and it is questionable whether those data represent actual aquifer conditions. Erroneous gas-chromatography analyses were rejected as a cause of the high readings after a review of calibration notes and quality assurance/quality control data for the dissolved H<sub>2</sub> measurements. Three other possible causes for extreme increases in dissolved H<sub>2</sub> concentrations were considered: (1) chemical reactions involving pulverized aquifer materials that may have occurred during and immediately after well drilling, (2) a sudden increase in the bioavailability of organic carbon (such as following injection of acetate to an aquifer to stimulate reductive dechlorination), or (3) sampling with electric submersible pumps, sampling wells with steel casing, or other sampling procedures that create a "bridge" between different redox zones from the ground surface to the bottom of the well (Chapelle and others 1997). The first possible cause was ruled out for OU 1 data because all of the wells were installed years ago. The second possible cause is unlikely at most OU 1 wells, although it may have played a role at well MW1-2, where organic carbon concentration increased from 5 to 45 mg/L between 2001 and 2002. The third possible cause is the most likely explanation for the 2002 data. The first three of the four wells with extremely high dissolved H<sub>2</sub> concentrations were purged and sampled while the YSI™ sonde was deployed down the well, and it is possible that the sonde and cable created a bridge that resulted in non-equilibrium production of dissolved H<sub>2</sub>. There is some uncertainty in this explanation because the sonde was also deployed downhole in four additional wells (1MW-1, MW1-5, MW1-16, and MW1-41), where 2002 dissolved H<sub>2</sub> concentrations were similar to historical data. The practice of deploying a data sonde downhole while purging the wells will be discontinued for future monitoring.

Overall, geochemical data from June 2002 indicate that redox conditions in the upper-aquifer water remain favorable for reductive dechlorination of chlorinated VOCs because strongly reducing conditions persisted beneath much of the landfill. Those strong reducing conditions are maintained by generally abundant organic carbon beneath the landfill that ranges in concentration from 4-71 mg/L, as compared to 1.4 mg/L in the upgradient wells MW1-3 and MW1-20. Redox conditions in ground water from the intermediate aquifer just downgradient of the landfill (wells MW1-25 and MW1-28) also remained favorable for reductive dechlorination, although

the 2002 dissolved H<sub>2</sub> concentration from MW1-28 is questionable. Although changes in redox conditions were observed at certain wells during 2002, a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting redox condition and if biodegradation processes are changing over time. The Navy intends to complete a more thorough interpretation in preparation for the 5-year review of OU 1 scheduled for 2004.

### Volatile Organic Compounds

June 2002 and previous CVOC data (Dinicola and others, 2002; Dinicola 2003) collected by the USGS at OU 1 are shown in [table 3](#). Duplicate samples were collected and analyzed for piezometers P1-6 and P1-8 and the CVOC concentrations agreed within 6 percent ([table 3](#)). A field blank that was subject to all aspects of sample collection and field processing was also collected. Concentrations of the compounds of interest were not detected in the field blank. Complete analytical results, including chlorinated and non-chlorinated VOCs, for June 2002 and previous years are available from the USGS National Water Information System (NWIS) web site <http://waterdata.usgs.gov/wa/nwis/qwdata>.

There were a few obvious differences between the 2002 and previously observed VOC concentrations. Total CVOC concentrations decreased substantially in all piezometers sampled in the northern plantation (P1-1, -3, -4, and -5), and the largest percentage decreases were observed for the compounds TCE and *cis*-DCE. Changes in total CVOC concentrations in the southern plantation were less consistent. Historically high concentrations of TCE and *cis*-DCE were observed in P1-7, -8, and -9, and historically low concentrations were observed in P1-6 and -10. Similarly to the redox chemistry, a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting CVOC concentrations and if biodegradation processes are changing over time.

### June 2003 Sampling

No changes in monitoring plans are proposed for June 2003, although the practice of deploying a data sonde downhole while purging the wells will be discontinued.



## Summary

Previous investigations have shown that natural attenuation and biodegradation of chlorinated volatile organic compounds (CVOCs) are substantial in shallow ground water beneath the 9-acre former landfill at Operable Unit 1 (OU 1), Naval Undersea Warfare Center (NUWC), Division Keyport, Washington. The U.S. Geological Survey (USGS) has continued to monitor ground-water geochemistry to assure that conditions remain favorable for contaminant biodegradation. This report presents the ground-water geochemical and selected CVOC data collected at OU 1 by the USGS during June 10-14, 2002, in support of long-term monitoring for natural attenuation.

Overall, the June 2002 geochemical data indicate that redox conditions in the upper-aquifer water remain favorable for reductive dechlorination of chlorinated VOCs because strongly reducing conditions persisted beneath much of the former landfill. Redox conditions in the intermediate aquifer downgradient of the landfill also remained favorable for reductive dechlorination, although the 2002 dissolved hydrogen (H<sub>2</sub>) concentration from well MW1-28 is questionable. Although changes in redox conditions were observed at certain wells during 2002, a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting redox condition and if biodegradation processes are changing over time. The Navy intends to complete a more thorough interpretation in preparation for the 5-year review of OU 1 scheduled for 2004.

There were a few significant differences between the 2002 concentrations and previously observed VOC concentrations. Total CVOC concentrations decreased substantially in all northern plantation piezometers sampled, and the largest percentages of decrease between 2002 and previous data were for the compounds TCE and *cis*-DCE. Changes in total CVOC concentrations in the southern plantation were less consistent. Historically high concentrations were observed in three piezometers, with particularly substantial increases in TCE and *cis*-DCE concentrations, and historically low concentrations were observed in two piezometers, with particularly substantial decreases in TCE and *cis*-DCE concentrations. Similarly to the redox chemistry, a longer monitoring period and more thorough interpretation are needed to ascertain if phytoremediation activities are affecting CVOC concentrations and if biodegradation processes are changing over time.

No changes in monitoring plans are proposed for June 2003, although the practice of deploying a data sonde downhole while purging the wells will be discontinued. Downhole monitoring added uncertainty to selected measured dissolved H<sub>2</sub> concentrations due to the possibility that the sonde and cable created a bridge that resulted in non-equilibrium dissolved H<sub>2</sub> concentrations at the wells.

## References Cited

- Bradley, P.M., Landmeyer, J.E., and Dinicola, R.S., 1998, Anaerobic oxidation of [1,2-<sup>14</sup>C] dichloroethene under Mn(IV)-reducing conditions: Applied and Environmental Microbiology, v. 64, no. 4, p. 1,560-1,562.
- Chapelle, F.H., Vroblesky, D.A., Woodward, J.C., and Lovely, D.R., 1997, Practical considerations for measuring hydrogen concentrations in groundwater: Environmental Science and Technology, v. 31, no. 10, p. 2,873-2,877.
- Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829, 78 p.
- Dinicola, R.S., 2003, Natural attenuation monitoring data during June 2001, Naval Undersea Warfare Center, Division Keyport, Washington: U.S. Geological Survey Open-File Report 03-344, 17 p.
- Dinicola, R.S., Cox, S.E., Landmeyer, J.E., and Bradley, P.M., 2002, Natural attenuation of chlorinated volatile organic compounds in ground water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington: U.S. Geological Survey Water-Resources Investigations Report 02-4119.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Franson, M.H., ed. 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federation, variously paged.
- Gossett, J.M., and Zinder, S.H., 1996, Microbiological aspects relevant to natural attenuation of chlorinated ethenes, *in* Proceedings of the symposium on natural attenuation of chlorinated organics in ground water: EPA/540/R-96/509, Dallas, TX, September 1996, variously paged.
- Hach Company, 1998, DR/2010 spectrophotometer procedures manual: Loveland, Colo., Hach Company, variously paged.
- McCarty, P.L., and Semprini, L., 1994, Ground-water treatment for chlorinated solvents, *in* Handbook of Bioremediation: Boca Raton, Lewis Publishers, p. 87-116.

- The TEC LTM Team, 2003, 2002 annual report Operable Unit 1, Area 1, former base landfill, Naval Undersea Warfare Center Division, Keyport, Washington: Prepared by CH2MHill Constructors, Inc., Seattle, Wash., for Engineering Field Activity, Northwest, Naval Facilities Engineering Command, Poughkeepsie, Wash., 28 p.
- URS Consultants, Inc., 1997, Final summary data assessment report for Operable Unit 1 Naval Undersea Warfare Center Division Keyport, Washington: Prepared by URS Consultants, Seattle, Wash., for Engineering Field Activity, Northwest, Naval Facilities Engineering Command, Poughkeepsie, Wash., 3 v.
- URS Consultants, Inc., 1998, Final record of decision for Operable Unit 1 Naval Undersea Warfare Center Division Keyport, Washington: Prepared by URS Consultants, Seattle, Wash., for Engineering Field Activity, Northwest, Naval Facilities Engineering Command, Poughkeepsie, Wash., 111 p.
- URS Greiner, Inc., 1999, Phytoremediation closure report for Operable Unit 1 Naval Undersea Warfare Center Division Keyport, Washington: Prepared by URS Greiner, Inc., Seattle, Wash., for Engineering Field Activity, Northwest, Naval Facilities Engineering Command, Poughkeepsie, Wash., variously paged.
- U.S. Geological Survey, 1997 to 2002, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, 2 v., variously paged. [Also available online at <http://pubs.water.usgs.gov/twri9A>. Chapters originally were published from 1997-1999; updates and revisions are ongoing and are summarized at: <http://water.usgs.gov/owq/FieldManual/mastererrata.html>.

Manuscript approved for publication, April 21, 2004

Prepared by the Publishing Group, U.S. Geological Survey,  
Washington Water Science Center, Tacoma, Washington

USGS Publishing staff  
Judith A. Wayenberg  
Bill Gibbs  
Linda S. Rogers

For more information concerning the research in this report, contact the  
Washington Water Science Center Director,  
U.S. Geological Survey, 1201 Pacific Avenue – Suite 600  
Tacoma, Washington 98402  
<http://wa.water.usgs.gov>



1879–2004