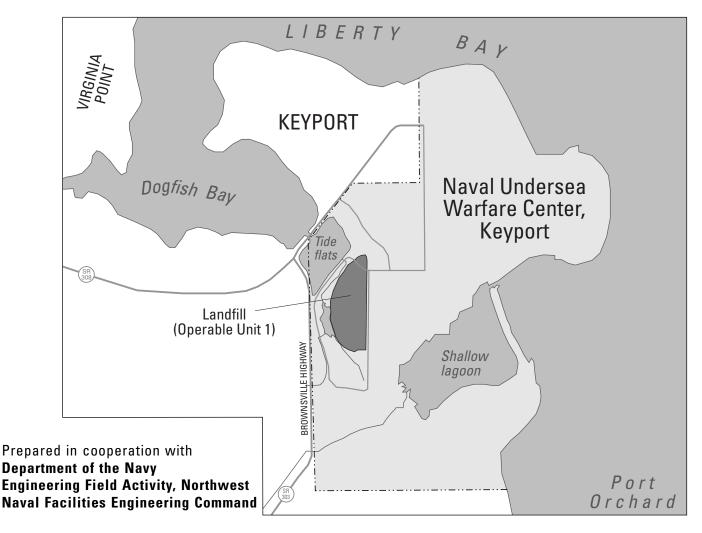
Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington, June 2001

Open-File Report 03-344





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By R.S. Dinicola

U.S. GEOLOGICAL SURVEY

Open-File Report 03-344

Prepared in cooperation with DEPARTMENT OF THE NAVY ENGINEERING FIELD ACTIVITY, NORTHWEST NAVAL FACILITIES ENGINEERING COMMAND

Tacoma, Washington 2003

U.S. DEPARTMENT OF THE INTERIOR

GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND DATUMS

CONVERSION FACTORS

Multiply	Ву	To obtain
acre	4,047	square meter
acre	0.4047	hectare
foot (ft)	0.3048	meter

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.

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.

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ABSTRACT

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 groundwater geochemical and selected CVOC data collected at OU 1 by the USGS during June 11-14, 2001 in support of the long-term monitoring for natural attenuation.

Overall, the June 2001 data indicate that redox conditions in the upper aquifer remain favorable for reductive dechlorination of CVOCs because strongly reducing conditions persisted beneath much of the former landfill. Redox conditions in the intermediate aquifer down gradient of the landfill appear to have become more favorable for reductive dechlorination because June 2001 dissolved hydrogen concentrations indicated strongly reducing conditions there for the first time. Although changes in redox conditions were observed at certain wells during 2001, a longer monitoring period is needed to ascertain if phytoremediation activities are affecting the ground-water chemistry.

A minor change to future monitoring is proposed. Filtered organic carbon (previously referred to as dissolved, and defined as that which passes through a 0.45-micrometer membrane filter) should be analyzed in the future rather than unfiltered (previously referred to as total) organic carbon because the filtered analysis may be a better measure of bioavailable organic carbon. Unfiltered and filtered organic carbon data were collected during June 2001 for comparison. Filtered organic carbon data collected in the future could be reasonably compared with historical unfiltered organic carbon data by multiplying the historical data by a factor of about 0.9.

INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) have migrated to ground water beneath the 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, Washington, 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.

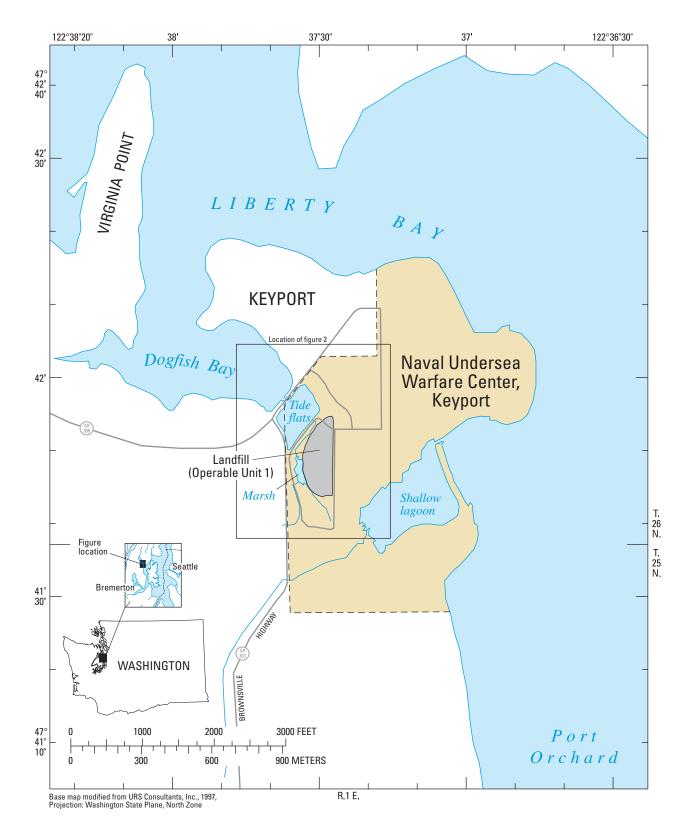


Figure 1. Location of Operable Unit 1 study area, Naval Undersea Warfare Center, Division Keyport, Washington.

Chlorinated VOCs 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 east to west towards Dogfish Bay. Ground water in the predominantly confined intermediate aquifer generally flows from south and west to beneath the landfill, and then to the northwest towards 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 by-products 1,1dichloroethane (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 were 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 the spring of 1999 to remove and control the migration of CVOCs in shallow ground water (URS Greiner, Inc., 1999).

Purpose and Scope

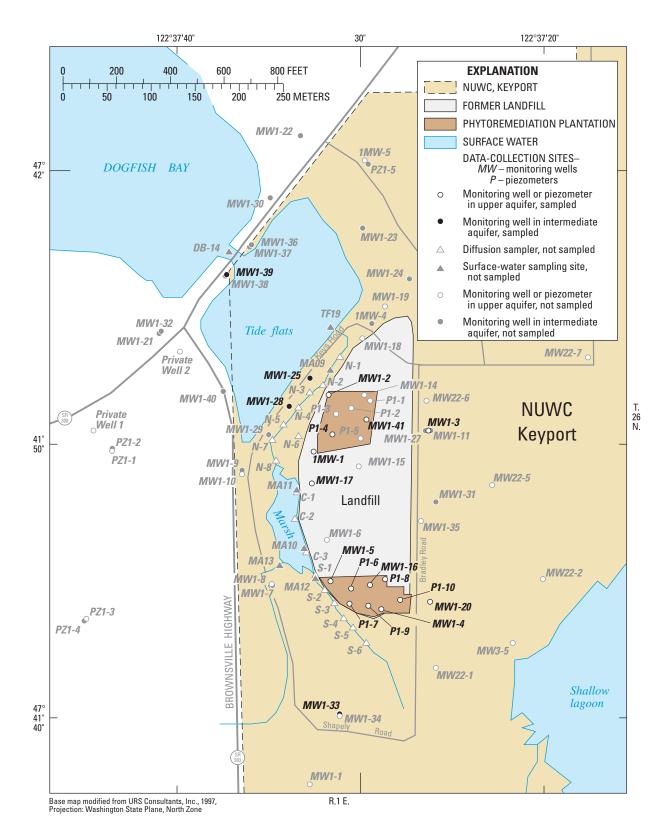
The Navy began a cooperative effort with the USGS in 1995 to investigate various natural attenuation mechanisms at OU 1. Field and laboratory studies conducted from 1996 through 2000 have shown that

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, a critical mechanism of natural attenuation.

This report presents the ground-water geochemical and selected CVOC data collected by the USGS at OU 1 during June 11-14, 2001 in support of the long-term monitoring for natural attenuation. USGS data collected from 1996 through 2000 were presented in Dinicola and others (2002). The June 2001 data collection focused on constituents used to evaluate ground-water redox conditions. The USGS collected ground-water samples from 13 wells and 6 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 the six piezometers only. The Navy collected additional samples to determine VOC concentrations at OU 1 monitoring wells, and those data were presented in The TEC LTM Team (2002). The June 2001 data were not interpreted in detail for this report because natural attenuation will again be thoroughly evaluated at OU 1 in support of the 5-year review scheduled for 2004.

Acknowledgments

The author thanks Sandra Keinholz and Matthew Butler of the Naval Facilities Engineering Command, Engineering Field Activity, Northwest (EFANW) for their guidance and funding for the continued monitoring. James Reeves of EFANW and Gene Ellis of Naval Undersea Warfare Center, Keyport provided logistic support for field activities. Stephen Cox, CG Laird, and Rose Eppers of the U.S. Geological Survey, Tacoma, Washington assisted with data collection and analysis.



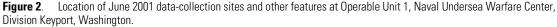


 Table 1.
 Construction data and water-level measurements for monitoring wells and piezometers sampled during June 2001 at Operable Unit 1, Naval

 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. Volatile organic compounds (VOCs) sampled: USGS, U.S. Geological Survey. Abbreviations: ROD, Record of Decision; dup, field duplicate sample. Symbols: –, not sampled]

Well No.	USGS site No.	Date/time sampled	Water- level altitude (ft)	Water- level (ft bmp)	Altitude of mea- suring point (ft)	Depth of well (ft)	Casing diameter (in)	Screened interval (ft)	<u>VOCs san</u> USGS	<u>ipled by</u> Navy	Geochem- ical sampling specified in ROD
1MW-1	474151122373201	06-11-01 15:00	3.06	7.00	10.06	16.5	2	5.5–15.5	_	Х	Х
MW1-2	474153122373101	06-12-01 17:15	1.84	10.05	11.89	18.5	4	12.5–17.5	_	Х	Х
MW1-3	474152122372501	06-12-01 10:30	9.34	4.21	13.55	11.5	4	5.5–10.5	_	_	-
MW1-4	474145122372801	06-14-01 10:30	5.67	6.53	12.20	13.0	4	7–12	_	Х	Х
MW1-5	474146122373201	06-13-01 15:45	4.33	8.75	13.08	12.0	4	6–11	_	Х	Х
MW1-16	474146122372801	06-14-01 10:40	5.53	7.30	12.83	12.0	2	6–11	-	Х	Х
MW1-17	474150122373201	06-12-01 11:15	3.92	8.02	11.94	13.5	2	7.5–12.5	_	Х	_
MW1-20	474145122372501		6.68	3.76	10.44	16.0	2	10–15	_	_	_
MW1-25	474154122373201		2.29	9.62	11.91	49.0	2	38–48	_	-	Х
MW1-28	474153122373301		-0.75	10.98	10.23	45.0	2	39–44	_	-	Х
MW1-33	474140122373201		11.12	0.38	11.50	41.0	2	30–40	_	_	_
MW1-39	474157122373701		-0.42	10.27	9.85	33.7	2	27.7–32.7	_	Х	Х
MW1-41	474152122372901		6.41	8.80	15.21	15.0	2	5–15	_	Х	_
P1-4	474152122373101		4.74	7.81	12.55	15.0	1	10–15	Х	-	-
Dup		14:01							Х		
P1-6	474146122373001	06-14-01 15:00	5.39	7.37	12.76	15.0	1	10–15	Х	-	-
P1-7	474145122373101	06-14-01 13:15	5.23	6.89	12.12	15.0	1	10–15	Х	-	_
P1-8	474147122372801	06-14-01 16:15	6.19	5.87	12.06	15.0	1	10–15	Х	-	-
P1-9	474145122372901		5.48	6.43	11.91	15.0	1	10–15	х	-	_
P1-10	474145122372601		6.59	5.27	11.86	15.0	1	10–15	Х	-	_

METHODS AND DATA ANALYSIS

Sample collection, processing, and field analyses were in accordance with applicable USGS procedures (U.S. Geological Survey, 1997 to 2001). The analytical methods used for the June 2001 data-collection activities generally were consistent with previous USGS data-collection activities at OU 1, with the exception that the laboratories used to determine methane concentrations changed from year to year.

The geochemical concentrations determined for samples from all wells and piezometers included dissolved hydrogen (H₂), dissolved oxygen, unfiltered and filtered organic carbon, filtered nitrate plus nitrite, filtered manganese, filtered iron (II), filtered sulfate, unfiltered sulfide, dissolved methane, filtered bicarbonate, pH, specific conductance, oxidationreduction 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. Monitoring wells and piezometers sampled at OU 1 are of different depths and diameters (<u>table 1</u>), but all were constructed with PVC casings and screens with sand filter packs.

All samples were collected with a peristaltic pump and single-use polyurethane tubing. A stainlesssteel weight was attached to the bottom of the premeasured length of tubing to accurately collect a sample from the mid-screen altitude 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 dissolved oxygen to stabilize within 0.1 units, 5 percent, and 0.3 mg/L, respectively. Those three analytes, as well as oxidation reduction potential, were measured in a flowthrough chamber using temperature compensated probes and meters. The specific conductance probe was checked daily with standard reference solutions; the pH probe was calibrated daily with two pH standards; and the dissolved oxygen probe was calibrated daily with water-saturated air and occasionally verified with zero dissolved oxygen solution. Dissolved oxygen analyses were confirmed with samples from selected wells or piezometers using 0 to-1 milligram per liter (mg/L) CHEMets Rhodazine-DTM colorimetric ampoules (manufactured by CHEMetrics, Inc., Calverton, Virginia). The ampoules were filled directly from the sampling tube after well purging was complete.

Bicarbonate (HCO⁻₃) concentration was measured in the field by titration of a sample passed through 0.45-micrometer (μ m) 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. Concentrations of iron (II) were measured in the field in a sample passed through 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 on an unfiltered sample using a colorimetric methylene blue indicator method using the same spectrophotometer according to analytical method number 690 (Hach Company, 1998).

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 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 hydrogen concentrations stabilized to within 10 percent. If dissolved H_2 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 passed through 0.45-µm membrane filter into polyethylene bottles, chilled, and sent to the USGS National Water Quality Laboratory (NWQL). 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 colorimetrically by cadmium reduction and diazotization, as described by Fishman (1993). The results for the nitrite plus nitrate analyses are referred to as simply nitrate in this report because of the expected small contribution of nitrite to the total concentration determined.

Unfiltered (total) organic carbon and filtered (dissolved) organic carbon samples were collected in amber glass bottles, chilled to less than 4 °C, and shipped to the USGS laboratory in Ocala, Florida., for analysis. The filtered sample was passed through a 0.45- μ m membrane filter between the pump and the bottle. Organic carbon concentrations were determined using high temperature combustion according to Standard Method 5310B, as described by Franson (1992).

Dissolved methane samples were collected in serum bottles, preserved with mercuric chloride, sealed with Teflon® septa, chilled, and analyzed at the USGS Washington Water Science Center laboratory in Lakewood, Washington, using a gas chromatograph with a flame-ionization detector as described by Kampbell and others (1989). The same method was used for methane analyses of OU 1 samples prior to 2001, although the 1996-97 samples were analyzed at the USGS Microbial Studies Group Laboratory in Columbia, South Carolina and the 2000 samples were analyzed at Transglobal Environmental Geosciences Northwest, Inc. in Lacey, Washington. It is uncertain if the same sample processing and holding-time protocols were followed at the three different laboratories.

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 (Connor 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. Both unfiltered and filtered organic carbon data were collected in June 2001 in order to compare the two types of analyses.

Geochemical Data and Predominant Redox Conditions

The June 2001 data and the previous geochemical data collected by USGS at OU 1 (Dinicola and others, 2002) are shown in <u>table 2</u>. Duplicate samples were collected and analyzed for piezometer P1-4. With the exception of methane concentrations, the duplicate sample analyses were consistent within 0 to 30 percent. Methane concentrations determined for duplicate samples collected from P1-4 during 2001 were substantially different (0.9 and 3.2 mg/L). A possible cause of that difference was different laboratory holding times for the duplicate samples, although the laboratory documentation on holding-time protocols used is incomplete.

The predominant redox conditions for June 2001 samples were determined primarily by dissolved oxygen and dissolved H₂ 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, dissolved-oxygen concentrations greater than 1 mg/L indicated aerobic conditions, and dissolved-oxygen concentrations less than 1 mg/L indicated anaerobic conditions. More specific anaerobic conditions were indicated by dissolved H₂ concentrations: 0.2 to 0.8 nanomolar (nM) indicated iron reduction, 1 to 5 nM indicated sulfate reduction, and greater than 5 nM indicated methanogenesis. Anaerobic ground water with a dissolved H₂ concentration less than 1 nM is referred to as mildly reducing, and water with a dissolved H₂ concentration greater than 1 nM is referred to as strongly reducing. Those more general terms for describing anaerobic redox conditions are useful because reductive dechlorination of CVOC contaminants is much more likely to occur under strongly reducing conditions (McCarty and Semprini, 1994; Gossett and Zinder, 1996).

Table 2. Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

Well No.	Date sampled	Predominant redox condition	Dissolved H ² (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	0.8	0.4	-	-	0.11	-	8.0
	03-05-98	Fe/S	0.2	0.1	8.3	-	_	0.39	12
	10-09-98	Fe	0.2	0.5	-	-	-	0.08	0.39
	06-21-00	Mn/Fe	0.1	0.5	12	-	< 0.05	0.96	13
	06-11-01	Fe	0.6	0.7	13	12	< 0.05	0.24	2.9
1MW-4	09-17-96	Fe	0.6	1.6	23	_	< 0.02	0.77	1.5
	04-16-97	S	1.8	0.0	_	-	0.03	_	1.7
MW1-2	09-17-96	Fe	0.5	2.4	6.0	_	< 0.02	0.05	0.23
	04-16-97	Fe	0.7	0.2	_	_	< 0.02	_	0.13
	03-02-98	Fe	0.3	_	_	_	_	_	0.16
	10-07-98	Fe	0.1	0.1	_	_	_	0.05	0.14
	06-09-99	Fe	0.9	0.2	_	_	_	0.08	0.09
	06-21-00	Fe	0.3	0.1	6.0	_	< 0.05	0.06	0.10
	06-12-01	S	3.5	0.3	5.3	5.0	< 0.05	0.08	0.29
MW1-3	06-09-99	Fe	0.8	0.4	_	_	_	0.07	< 0.01
	06-20-00	Fe	0.2	0.3	2.0	_	0.99	0.08	< 0.01
	06-12-01	А	-	4.0	2.3	1.1	1.1	0.04	0.02
MW1-4	09-17-96	Fe	0.5	2.8	2.0	_	< 0.02	0.28	1.8
	04-16-97	Fe	0.6	0.4	_	_	0.24	_	< 0.01
	03-03-98	S	1.7	0.2	4.0	_	_	0.10	0.01
	10-08-98	Fe	0.2	0.5	_	_	_	_	0.28
	06-07-99	Fe	0.9	0.1	_	_	_	0.20	1.2
	06-22-00	Fe	0.2	0.1	8.6	_	_	0.70	_
	06-14-01	S	0.9 - 3.2	0.5	2.9	2.5	0.08	0.54	1.6
MW1-5	09-17-96	S	1.2	0.0	15	_	< 0.02	1.6	19
	04-16-97	Fe	0.5	0.0	_	_	0.08	_	3.1
	03-04-98	Fe	0.7	0.0	12	_	_	1.3	4.5
	10-08-98	S	2.4	0.0	_	_	_	1.5	11
	06-08-99	Fe	0.6	0.3	_	_	_	1.2	31
	06-22-00	Fe	_	0.0	17	_	_	1.5	39
	06-13-01	Fe	0.8	0.3	10	9.6	0.12	1.5	25
MW1-6	09-17-96	S	1.1	0.0	33	_	1.2	1.2	30
	04-16-97	Fe/S	0.5	0.0	_	_	0.07	_	36
	10-08-98	Fe	0.2	0.0	-	-	-	1.1	32
MW1-14	09-17-96	Fe	0.6	0.0	42	_	< 0.02	2.0	67
	04-16-97	Fe	0.7	0.0	_	_	0.05	_	78
	03-04-98	Fe/S	-	0.1	36	_	_	11	68
	10-07-98	S	1.2	0.0	_	-	_	1.5	48
	06-09-99	S	1.0	0.3	-	-	_	0.30	57
MW1-15	09-16-96	Fe	0.2	0.0	50	_	< 0.02	5.7	68
	04-16-97	Fe/S	0.8	0.0	_	-	< 0.02	_	77
	03-05-98	S	1.2	0.0	33	_	-	18	51
	10-09-98	S	2.9	0.0	_	_	_	5.8	64

 Table 2.
 Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea

 Warfare Center, Division Keyport, Washington—Continued

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance (µS/cm)	ORP (mV)	Filtered chloride (mg/L)
1MW-1	7.5	< 0.01	10	640	7.9	_	_	43
	1.4	0.01	29	1,100	7.2	-	-	-
	_	0.06	_	-	-	-	-	-
	-	0.01	_	660	7.7	1,080	-	-
	0.9	< 0.01	0.39	590	7.0	1,070	-92	44
	2.2	< 0.01	5.6	550	7.1	974	-110	50
1MW-4	0.04	< 0.01	16	780	7.3	_	_	25
	0.36	0.02	47	1,300	7.3	_	_	
		0.04						-
MW1-2	4.6	< 0.01	1.2	510	6.9	-	-	50
	4.6	< 0.01	2.5	1,100	6.7	-	-	-
	-	-	-	-	-	-	-	-
	-	<0.01 <0.01	-	300	6.7 6.8	868 901	-	-
	4.3	<0.01 <0.01	0.04	490 460	6.8	901 870	37	- 36
	5.4	<0.01	0.78	400	6.5	853	27	48
	5.4	<0.01	0.78	470	0.5	055	27	40
MW1-3	-	< 0.01	_	81	6.0	202	_	-
	13	< 0.01	0.02	82	5.9	205	180	8.4
	14	< 0.01	0.12	90	6.1	203	220	10
MW1-4	7.1	< 0.01	1.2	130	6.9	_	_	15
	8.6	< 0.01	0.70	270	7.3	_	_	-
	_	< 0.01	_	_	_	_	_	_
	_	< 0.01	_	170	6.7	368	_	_
	_	< 0.01	_	180	6.6	350	_	_
	5.5	< 0.01	0.56	230	6.8	412	-26	19
	5.4	< 0.01	3.7	180	6.5	360	-8	22
MW1-5	6.4	< 0.01	2.4	330	6.7	_	_	21
IVI VV 1-J	2.8	0.03	18	1,400	6.6	_	_	- 21
	2.0	< 0.01	-	-	-	_	_	_
	_	<0.01	_	410	6.4	1,740	_	_
	_	0.01	_	510	6.5	855	_	_
	6.4	< 0.01	1.1	460	6.6	790	-80	19
	6.0	0.01	2.4	470	6.4	766	-70	12
	0.10	0.01	5.0	2.40	6.7			27
MW1-6	0.10	< 0.01	7.0	840	6.7	-	-	27
	4.1	0.15 0.01	15	1,100 720	6.5 6.4	1,170	-	-
	-	0.01	_	720	0.4	1,170	-	-
MW1-14	0.27	< 0.01	9.2	1,300	6.4	-	-	25
	0.13	< 0.01	46	1,800	6.4	-	-	-
	_	0.05	_	-	-	-	-	-
	_	0.01	_	600	6.3	1,450	-	-
	_	0.04	_	810	6.4	1,220	-	-
MW1-15	0.11	< 0.01	8.8	1,200	_	_	_	18
	0.08	0.03	44	1,600	6.3	_	_	- 10
	-	< 0.01		-	-	_	_	_

 Table 2.
 Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea

 Warfare Center, Division Keyport, Washington—Continued

Well No.	Date sampled	Predominant redox condition	Dissolved H ² (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)
MW1-16	09-17-96	S	2.1	0.0	480	_	< 0.02	3.9	130
	04-16-97	Fe/S	0.8	0.0	-	_	< 0.02	_	120
	03-04-98	Fe	0.7	0.3	350	_	_	18	100
	10-08-98	М	9.6	0.0	-	_	_	5.4	180
	06-07-99	М	6.8	0.6	-	_	_	>5	140
	06-22-00	S	-	0.1	61	-	-	1.9	60
	06-14-01	S	1.7	0.2	64	66	0.33	2.4	56
MW1-17	09-17-96	Fe	0.7	0.0	23	_	< 0.02	1.3	62
	04-16-97	Fe	0.6	0.0	-	-	< 0.02	-	37
	10-09-98	Fe	_	0.0	_	_	_	0.80	56
	06-22-00	S	1.2	0.0	11	_	_	_	68
	06-12-01	S	2.0 - 2.7	0.4	9.2	8	< 0.05	1.2	48
MW1-18	09-17-96	Fe/S	1.0	0.0	28	_	< 0.02	4.0	12
	04-16-97	Fe	0.5	0.0	_	_	0.05	_	23
	10-07-98	Fe	-	0.2	_	-	-	0.77	3.3
MW1-20	06-08-99	Fe	0.9	0.3	_	_	_	0.35	0.03
	06-21-00	Fe	0.4	0.0	2.2	_	< 0.05	0.24	0.11
1	06-13-01	S	2.1	0.2	3.0	1.4	< 0.05	0.28	0.01
MW1-25	09-17-96	Fe	0.4	2.7	7.4	_	0.14	0.16	0.74
	04-17-97	Fe	0.8	0.1	_	_	< 0.02	_	0.88
	03-05-98	Fe	0.3	0.3	7.9	_	_	0.20	0.73
	10-05-98	Fe	0.2	0.1	_	_	_	0.19	0.99
	06-22-00	Fe	0.4	0.2	6.5	_	_	0.16	0.80
1	06-12-01	S	2.8 - 4.3	0.2	7.1	6.8	< 0.05	0.16	0.99
MW1-28	09-16-96	Fe	0.3	2.1	7.2	_	< 0.02	0.20	1.0
	04-17-97	Fe	1.0	0.0	_	_	0.04	_	0.99
	03-05-98	Fe	0.4	0.5	7.7	_	_	0.20	0.67
	10-07-98	Fe	0.6	0.0	_	_	_	0.19	1.0
	06-22-00	Fe	0.3	0.0	13	_	_	0.16	0.66
	06-12-01	S/M	4.1 - 5.7	0.5	10	6.9	< 0.05	0.16	0.90
MW1-29	09-16-96	Mn/Fe	0.0	1.9	_	_	< 0.02	0.86	2.0
	04-17-97	Fe	0.7	0.0	_	_	0.29	-	2.1
MW1-31	09-16-96	Mn/Fe	_	_	5.6	_	-	3.6	0.32
MW1-32	09-16-96	Fe	0.4	2.7	0.8	_	0.07	0.23	1.3
	04-17-97	Fe	_	1.2	_	_	0.17	_	0.87
	03-02-98	Fe	_	<1.0	_	_	_	0.10	1.1
	10-05-98	Fe	0.1	0.0	-	-	_	0.36	1.0
MW1-33	10-07-98	А	_	3.3	0.1	_	_	0.003	< 0.01
	06-21-00	A	_	3.8	0.7	_	1.3	< 0.002	< 0.01
	06-11-01	A	-	3.8	1.5	1.4	1.1	< 0.003	< 0.01
MW1-35	10-07-98	А	_	2.4	1.9	_	_	0.15	< 0.01
	06-08-99	A	_	2.4	-	_	_	-	
	00 00 //			2.1					

 Table 2.
 Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea

 Warfare Center, Division Keyport, Washington—Continued

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance (µS/cm)	ORP (mV)	Filtered chloride (mg/L)
MW1-16	0.17	< 0.01	4.3	1,400	6.5	_	_	150
	2.2	0.06	29	1,800	6.5	-	_	-
	-	0.01	_	-	-	-	-	-
	-	< 0.01	_	1,600	6.3	3,370	-	-
	_	0.01	_	1,200	6.7	1,820	_	-
	1.2	0.02	1.2	510	6.7	902	-130	43
	1.1	0.08	10	610	6.4	953	-	40
MW1-17	4.3	< 0.01	8.9	760	6.5	_	_	61
	68	0.02	23	1,200	6.6	_	_	-
	_	0.02	_	510	6.4	1,740	_	_
	_	0.02	2.8	450	6.5	1,260	-41	160
	12	0.01	9.4	500	6.5	1,200	-280	120
MW1-18	4.6	< 0.01	11	880	7.0	_	_	86
	8.2	< 0.01	52	1,500	6.8	_	_	_
	_	< 0.01	_	920	6.6	1,780	_	_
MW1 20		-0.01		260	67	546		
MW1-20	-	<0.01 <0.01	0.01	260 240	6.7 6.8	546 530		 14
	16 20	<0.01	0.01	240	6.4	544	250	33
	20	<0.01	0.27	200	0.4	544	230	55
MW1-25	16	< 0.01	3.6	360	7.1	-	-	140
	15	< 0.01	7.9	1,000	7.0	-	-	-
	-	< 0.01	-	-	-	-	-	-
	-	< 0.01	_	450	6.9	1,240	_	-
	13	< 0.01	0.79	380	6.9	1,230	-49	170
	13	< 0.01	4.7	440	6.7	1180	-36	160
MW1-28	48	< 0.01	1.7	350	_	_	_	380
	51	< 0.01	5.3	1,100	7.4	_	_	-
	_	< 0.01	-	_	_	-	_	-
	-	0.02	_	320	6.6	2,630	-	-
	44	< 0.01	0.45	480	7.3	2,460	-87	510
	45	< 0.01	4.1	480	7.4	2,200	-220	490
MW1-29	1.8	0.02	8.1	300	_	_	_	500
	1.1	< 0.01	18	710	7.3	_	_	_
MW1-31	_	_	_	_	_	_	_	_
	16	0.01	0.01	110				-
MW1-32	16	0.01	<0.01	110	7 1	-	-	7.4
	17	0.01 <0.01	< 0.01	300	7.1	-	_	-
	_	<0.01	_	130	7.2	270	_	_
MW1 22								
MW1-33	- 7 5	<0.01	-	78 74	6.6	177	150	-
	7.5 8.2	<0.01 <0.01	0.05	74	6.7 6.2	164 154	150 300	4.0
	0.2		0.07				500	- 3.0
MW1-35	_	< 0.01	_	110	6.4	301	-	-
	-	-	-	76	6.4	187	-	-
	3.9	< 0.01	0.01	77	6.6	151	360	2.3

Table 2. Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea

 Warfare Center, Division Keyport, Washington—Continued

Well No.	Date sampled	Predominant redox condition	Dissolved H ² (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)
MW1-36	10-09-98	Fe	_	0.0	_	_	_	0.30	3.6
	06-20-00	Fe	0.5	0.1	2.4	-	< 0.05	0.28	3.2
MW1-37	09-16-96	Fe	0.8	1.5	6.9	_	< 0.02	0.12	0.48
	04-17-97	S	3.3	0.0	-	-	< 0.02	-	0.80
	03-03-98	Fe	0.4	0.4	5.7	-	-	0.10	0.86
	10-09-98	Fe	0.4	0.0	-	-	-	< 0.01	0.43
	06-07-99	Fe	0.4	0.4	_	_	_	0.10	0.32
	06-20-00	Fe	0.1	0.1	5.8	-	< 0.05	0.13	0.25
MW1-38	10-09-98	Fe	_	0.1	_	_	_	0.20	0.08
	06-20-00	Fe	0.1	0.2	5.6	-	< 0.05	0.08	0.10
MW1-39	09-16-96	Fe/S	0.6	2.0	4.4	_	< 0.02	0.02	< 0.01
	04-17-97	S	4.5	0.0	_	_	< 0.02	_	0.05
	03-03-98	Fe/S	0.3	0.3	3.7	_	-	0.10	0.03
	10-09-98	Fe/S	0.5	0.0	_	_	_	<0.01	0.03
	06-07-99	Fe/S	1.0	0.3	_	_	_	0.10	0.04
	06-20-00	Fe/S	0.5	0.5	2.4	_	_ <0.05	0.10	0.02
	06-12-01	S S	1.4	0.1	3.4	3.3	< 0.05	0.01	< 0.01
MW1-41	06-09-99	S	1.0	0.3	_	_	-	2.2	60
101 00 1-41	06-21-00	S	1.0	0.5	22	_	< 0.05	3.5	55
	06-11-01	S	2.0	0.1	14	14	<0.05	3.7	66
P1-1	06-09-99	Fe	0.7	0.4	_	_	_	4.0	59
P1-3	06-09-99	Fe	0.4	0.2	_	_	_	1.0	19
P1-4	06-09-99	Fe	0.7	0.3	-	-	-	0.34	2.6
(1 1	06-13-01	Fe	0.1	0.5	9.8	8.7	< 0.05	0.38	3.4
(duplicate)	06-13-01	Fe	-	-	8.4	6.2	< 0.05	0.38	3.6
P1-5	06-08-99	S	3.0	0.3	-	-	-	3.1	72
P1-6	06-08-99	S	1.8	0.1	_	_	-	0.12	0.02
	06-14-01	S	1.8	0.2	34	34	0.23	0.45	0.95
P1-7	06-08-99	S	1.2	0.1	_	_	_	0.61	2.1
	06-22-00	Mn/Fe	_	0.1	19	_	_	2.6	3.2
	06-14-01	Mn/Fe	0.2	0.2	11	11	< 0.05	2.3	2.0
P1-8	06-07-99	S	1.8	0.0	_	_	_	0.20	0.08
	06-14-01	Fe	0.7	0.1	4.8	4.7	0.06	0.16	0.22
P1-9	06-08-99	М	19	0.3	_	_	_	0.90	0.03
/	06-22-00	S/M	_	0.1	10	_	_	0.69	0.20
	06-14-01	M	6.7	0.1	2.3	1.7	< 0.05	0.19	0.05
P1-10	06-07-99	Fe	0.7	0.3	_	_	_	0.10	0.11
	06-22-00	Fe	_	0.0	7.2	_	_	0.10	0.11
	06-13-01	S	2.0	0.0	3.0	4.2	< 0.05	0.07	0.20

 Table 2.
 Predominant redox conditions and ground-water geochemical data collected from 1996 to 2001 at Operable Unit 1, Naval Undersea

 Warfare Center, Division Keyport, Washington—Continued

Well No.	Filtered sulfate (mg/L)	Unfiltered sulfide (mg/L)	Dissolved methane (mg/L)	Filtered bicarbonate (mg/L)	pH (units)	Specific conductance (µS/cm)	ORP (mV)	Filtered chloride (mg/L)
MW1-36	_	< 0.01	_	280	7.3	8,610	_	_
	180	0.02	0.01	270	7.3	7,940	-130	2,300
MW1-37	23	0.03	0.30	280	_	_	_	660
	27	0.02	0.90	730	7.7	_	-	_
	-	< 0.01	-	-	-	-	-	-
	-	< 0.01	-	340	7.9	2,440	-	-
	-	0.03	_	340	7.7	2,920	_	_
	29	0.02	0.07	350	7.6	3,240	-160	840
MW1-38	_	0.02	_	310	7.8	1,460	-	-
	2.3	0.03	0.10	300	7.8	1,240	-130	230
MW1-39	0.71	0.04	1.6	140	_	_	_	85
	13	0.06	6.1	360	7.9	_	_	_
	_	0.05	_	_	_	_	_	_
	_	0.07	_	170	8.1	502	_	_
	-	< 0.01	_	180	8.0	512	_	—
	0.2	0.08	0.41	180	8.0	481	-130	61
	0.1	0.05	2.7	170	7.8	472	-130	61
MW1-41	_	0.01	_	860	6.6	1,260	_	_
	< 0.3	< 0.01	1.9	1,000	6.5	1,500	-75	8.3
	30	0.02	25	980	6.3	1,330	-89	9.9
P1-1	-	< 0.01	-	930	6.4	1,350	-	_
P1-3	-	0.04	_	730	6.8	1,470	_	_
P1-4	_	0.02	_	450	6.9	867	-	-
	3.8	< 0.01	0.9	390	6.6	761	-78	53
duplicate)	3.8	< 0.01	3.2	390	-	-	-	53
P1-5	_	0.01	_	850	6.2	1,320	_	_
P1-6	-	0.04	-	300	6.8	574	-	-
	4.9	0.12	6.3	350	6.4	657	-38	47
P1-7	_	< 0.01	_	310	6.7	627	_	_
	24	< 0.01	1.5	400	6.8	851	-35	55
	18	< 0.01	4.0	320	6.5	666	-32	41
P1-8	_	0.01	_	210	7.6	381	_	_
110	0.13	0.02	6.9	200	7.0	363	-73	18
D1 0								
P1-9	-	< 0.01	- 17	270	6.6	680 548	- 17	-
	6.6 7.6	<0.01 <0.01	1.7 1.4	250 200	6.8 7.8	548 289	-17 -120	59 14
	7.0	\0.01	1.4			207	-120	14
P1-10	_	< 0.01	_	300	6.7	560	-	-
	< 0.31	< 0.01	1.3	290	7.1	500	-19	15
	0.06	< 0.01	4.9	290	7.2	476	-24	15

Overall, geochemical data from water samples collected in June 2001 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 ground water from the intermediate aquifer just down gradient of the landfill (wells MW1-25 and MW1-28) appear to have become more favorable for reductive dechlorination; dissolved H₂ concentrations indicated strongly reducing conditions there for the first time. The range over which dissolved H₂ concentrations fluctuated was reported if dissolved H₂ did not stabilize and did not consistently increase or decrease over time. Although changes in redox conditions were observed at certain wells during 2001, a longer monitoring period is needed to ascertain if phytoremediation activities are affecting the ground-water chemistry.

Comparison of Unfiltered (Total) and Filtered (Dissolved) Organic Carbon Concentrations

Prior to 2001, only unfiltered organic carbon data were collected by the USGS at OU 1. However, filtered organic carbon may be a better measure of bioavailable organic carbon. Unfiltered and filtered organic carbon analyses were done for all samples collected in June 2001 in order to compare the two types of data.

As expected, the unfiltered organic carbon concentrations were slightly greater than filtered organic carbon concentrations for 18 of 20 samples (table 2 and fig. 3). On average, unfiltered organic carbon concentrations were 0.5 mg/L (11 percent)

greater than filtered organic carbon concentrations, and the median difference between the two measures was 0.4 mg/L (6 percent). Thus, filtered organic carbon data collected in the future could be reasonably compared with historical unfiltered organic carbon data by multiplying the historical data by a factor of about 0.9.

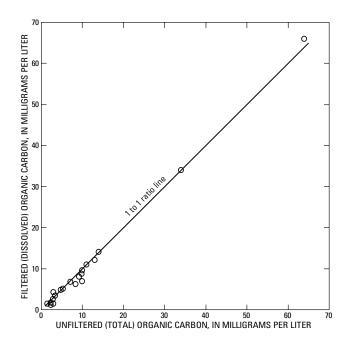


Figure 3. Unfiltered and filtered organic carbon concentrations for June 2001 at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington.

Chlorinated Volatile Organic Compound Data

June 2001 and previous CVOC data (Dinicola and others, 2002) collected from piezometers by the USGS at OU 1 are shown in <u>table 3</u>. Duplicate CVOC samples were collected and analyzed for piezometer P1-4 and the CVOC concentrations agreed within 7 percent (<u>table 3</u>). Complete analytical results, including chlorinated and non-chlorinated VOCs, for June 2001

and previous years are available from the USGS NWISweb site <u>http://waterdata.usgs.gov/wa/nwis/</u> <u>qwdata</u>. There were a few substantial differences between the June 2001 and previously measured CVOC concentrations, but neither the cause of those differences nor the relation between redox conditions and CVOC concentrations throughout OU 1 are evaluated in this report.

Table 3. Concentrations of selected chlorinated volatile organic compounds in ground water from piezometers sampled from 1999 to 2001 by the U.S.

 Geological Survey at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington

[All data except those shaded were published previously in Dinicola and others (2002). **Chlorinated volatile organic compounds (CVOCs)**: 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 xylene; CVOCs, chlorinated volatile organic compounds. **Abbreviations**: $\mu g/L$, micrograms per liter. **Symbols**: <, actual value is less than value shown; –, not analyzed; nd, not detected]

Piezo- meter No.	Date sampled	ΡCE (μg/L)	ТСЕ (µ g/L)	<i>cis-</i> DCE (μg/L)	<i>trans-</i> 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
	06-13-01	<20	<20	4,900	46	650	<20	<20	<20	<20	nd	5,600
(duplicate)	06-13-01	<20	<20	5,000	44	670	<20	<20	<20	<20	nd	5,700
P1-5	06-08-99	<13	440	400	3.5	11	<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
	06-14-01	<20	370	16,000	220	9,900	<20	4,800	610	11	88	32,000
P1-7	06-08-99	<670	26,000	35,000	210	3,100	<670	<670	<1,300	<670	nd	64,000
	06-22-00	3.6	27,000	44,000	220	3,800	0.24	17	8.4	72	16	75,000
	06-14-01	<20	26,000	37,000	190	4,000	<20	<20	<20	44	nd	68,000
P1-8	06-07-99	<710	190	25,000	210	3,400	<710	<710	<1,400	<710	nd	29,000
	06-14-01	<20	810	8,600	62	4,200	<20	<20	<20	<20	nd	14,000
P1-9	06-08-99	<2,000	48,000	88,000	470	7,200	<2,000	<2,000	<4,000	<2,000	nd	140,000
	06-22-00	5.0	88,000	64,000	320	5,800	<10	2.6	<20	47	22	160,000
	06-14-01	<40	29,000	7,300	32	450	<40	<40	<40	<40	nd	37,000
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
	06-22-00	1.0	8,700	13,000	100	2,300	< 0.1	1.2	0.13	16	12	24,000
	06-13-01	<20	6,600	12,000	68	1,900	<20	<20	<20	11	nd	21,000

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 11-14, 2001 in support of the long-term monitoring for natural attenuation.

Overall, the June 2001 data indicate that redox conditions in the upper aquifer remain favorable for reductive dechlorination of CVOCs because strongly reducing conditions persisted beneath much of the former landfill. Redox conditions in the intermediate aquifer down gradient of the landfill appear to have become more favorable for reductive dechlorination because June 2001 dissolved hydrogen concentrations indicated strongly reducing conditions there for the first time. Although changes in redox conditions were observed at certain wells during 2001, a longer monitoring period is needed to ascertain if phytoremediation activities are affecting the groundwater chemistry.

A minor change to future monitoring is proposed. Filtered organic carbon (previously referred to as dissolved, and defined as that which passes through a 0.45-micrometer membrane filter) should be analyzed in the future rather than unfiltered (previously referred to as total) organic carbon because the filtered analysis may be a better measure of bioavailable organic carbon. Unfiltered and filtered organic carbon data were collected during June 2001 for comparison. Filtered organic carbon data collected in the future could be reasonably compared with historical unfiltered organic carbon data by multiplying the historical data by a factor of about 0.9.

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