

Prepared in cooperation with the Naval Facilities Engineering Command Southeast

**Investigation of Ground-Water Contamination at a
Drainage Ditch, Installation Restoration Site 4, Naval Air
Station Corpus Christi, Corpus Christi, Texas, 2005–06**

Scientific Investigations Report 2007–5155

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By Don A. Vroblesky and Clifton C. Casey

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Contents

Abstract.....	1
Introduction.....	1
Purpose and Scope	2
Site Description.....	2
Methodology.....	3
Chlorobenzene Contamination at the Drainage Ditch	5
Summary.....	6
References Cited.....	7

Figures

1–3. Maps showing—	
1. Location of Naval Air Station Corpus Christi, Corpus Christi, Texas.....	1
2. Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas.....	2
3. Sampling locations in and adjacent to the drainage ditch, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas	3

Tables

1. Descriptions of sampling points in the drainage ditch, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.....	3
2. Concentrations of selected volatile organic compounds in water samples, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.....	4
3. Concentrations of inorganic constituents in water samples, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.....	4

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Volume		
gallon (gal)	3.785	liter (L)

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

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

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Elevation, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Abbreviations

CB	Chlorobenzene
1,2-DCB	1,2-Dichlorobenzene
1,4-DCB	1,4-Dichlorobenzene
Fe ²⁺	Iron, dissolved
IR	Installation Restoration
K_{oc}	Soil sorption coefficient
mL/min	Milliliter per minute
NAS	Naval Air Station
NTU	Nephelometric turbidity units
PDB	Polyethylene diffusion bag
PVC	Polyvinyl chloride
USGS	U.S. Geological Survey
VOC	Volatile organic compound

Investigation of Ground-Water Contamination at a Drainage Ditch, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06

By Don A. Vroblesky and Clifton C. Casey

Abstract

The U.S. Geological Survey, in cooperation with the Naval Facilities Engineering Command Southeast, used newly developed sampling methods to investigate ground-water contamination by chlorobenzenes beneath a drainage ditch on the southwestern side of Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, during 2005–06. The drainage ditch, which is a potential receptor for ground-water contaminants from Installation Restoration Site 4, intermittently discharges water to Corpus Christi Bay. This report uses data from a new type of pore-water sampler developed for this investigation and other methods to examine the subsurface contamination beneath the drainage ditch. Analysis of ground water from the samplers indicated that chlorobenzenes (maximum detected concentration of 160 micrograms per liter) are present in the ground water beneath the ditch. The concentrations of dissolved oxygen in the samples (less than 0.05–0.4 milligram per liter) showed that the ground water beneath and near the ditch is anaerobic, indicating that substantial chlorobenzene biodegradation in the aquifer beneath the ditch is unlikely. Probable alternative mechanisms of chlorobenzene removal in the ground water beneath the drainage ditch include sorption onto the organic-rich sediment and contaminant depletion by cattails through uptake, sorption, and localized soil aeration.

Introduction

Ground-water contamination by volatile organic compounds (VOCs) is present at Installation Restoration (IR) Site 4, Naval Air Station (NAS) Corpus Christi, on the Gulf of Mexico near the city of Corpus Christi, Texas (figs. 1 and 2) (Terraine, Inc., 2006). IR Site 4 was an aircraft firefighter training area that operated from the 1960s to 1991. A drainage ditch on the southwestern side of IR Site 4 intermittently discharges ground water to Corpus Christi Bay.

The primary VOC of concern at the drainage ditch is chlorobenzene. A study was conducted by the U.S. Geological Survey (USGS), in cooperation with the Naval Facilities Engineering Command Southeast, to determine whether chlorobenzene in the ground water discharges to the drainage ditch southwest of IR Site 4.

Chlorobenzene, which has no known natural sources, can be released to the environment as a pesticide carrier (Meek and others, 1994a), in the manufacture of rubber polymers, as a carrier for textile dyes, in the production of phenol and nitrochlorobenzene, in the formulation of herbicides, and as a solvent in the manufacture of adhesives, paints, resins, dyes, and drugs (Grosjean, 1991; Mackay and others, 1996; World Health Organization, 2004).

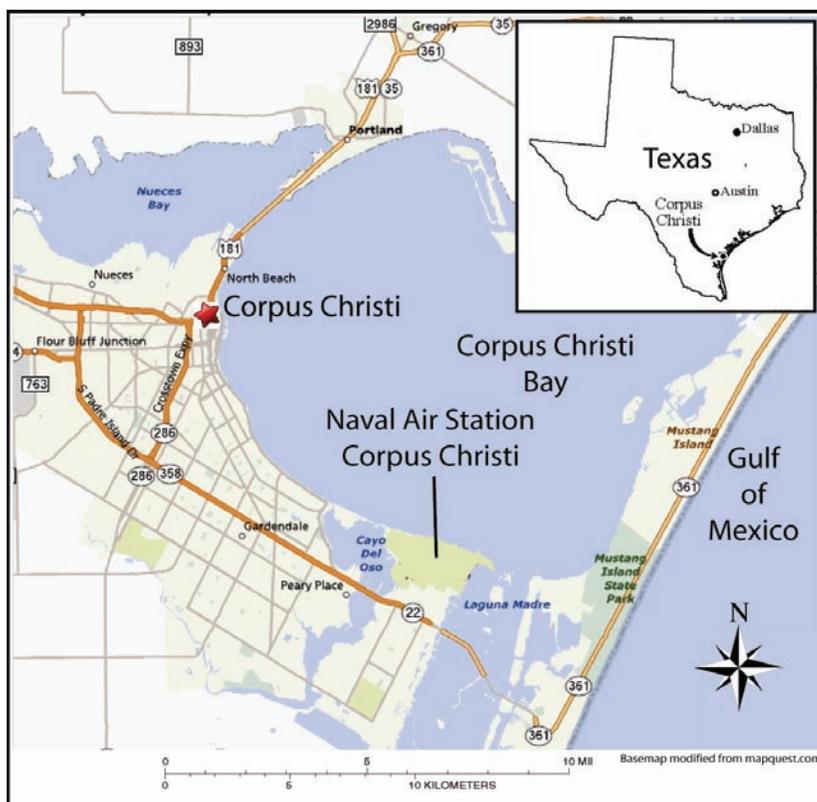


Figure 1. Location of Naval Air Station Corpus Christi, Corpus Christi, Texas.

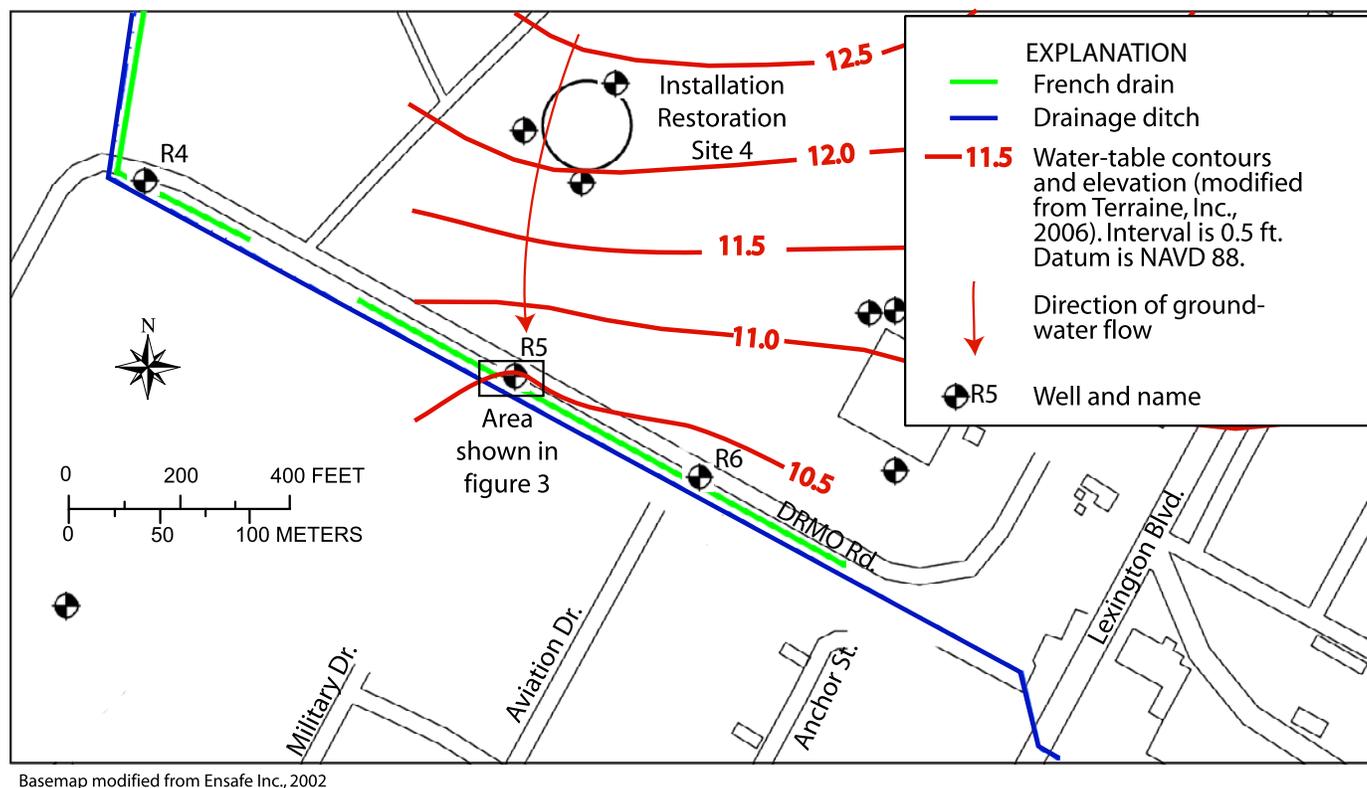


Figure 2. Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas.

In addition to chlorobenzene, 1,2-dichlorobenzene (1,2-DCB) and 1,4-dichlorobenzene (1,4-DCB) also are present in the ground water near the drainage ditch (Terraine, Inc., 2006). The compound 1,2-DCB is used as a solvent for carbon and grease from metals and in the synthesis of organic chemicals such as toluene diisocyanate (Grosjean, 1991; Meek and others, 1994b). The compound 1,4-DCB is used as an intermediate in the production of other chemicals, such as polyphenylene sulfide resins, and in controlling tree-boring insects, ants, and blue mold in tobacco seedbeds (Grosjean, 1991). It also is used in air fresheners, urinal deodorants, and moth and bird repellents, but these uses release 1,4-DCB primarily to the atmosphere (Meek and others, 1994c; World Health Organization, 2004).

Purpose and Scope

This report presents an evaluation of the presence of chlorobenzene in ground water discharging to the drainage ditch southwest of IR Site 4 and the potential for chlorobenzene depletion by biodegradation, sorption, or plant uptake in the drainage ditch. Six newly developed pore-water samplers were used for this investigation (Vroblesky and Casey, 2007). Four newly developed samplers were installed 1.25 to 1.6 feet (ft) beneath the drainage ditch. In addition, one of the newly developed samplers was installed in surface water near the ditch, and one new sampler and three standard polyethylene

diffusion bag (PDB) samplers were installed 0.2 to 0.25 ft beneath the ditch. Ground-water samples were collected from a nearby well. A total of 17 water samples were collected and analyzed for VOCs during 2005–2006. The concentrations of VOCs and other constituents in those samples are presented.

Site Description

NAS Corpus Christi, Texas, is surrounded on three sides by water: Cayo Del Oso (west), Corpus Christi Bay (north), and Laguna Madre (east) (fig. 1). IR Site 4 is underlain by an unconfined aquifer composed of fine-grained sand to silty or clayey sand. Contour maps of the water table indicate that ground-water flow at IR Site 4 is toward a gaining reach of a drainage ditch, on the southwestern side of the site (EnSafe Inc., 2002; Terraine, Inc., 2006) (fig. 2). Bottom sediment in the drainage ditch consists of organic-rich detritus and mud.

The depth to ground water at IR Site 4 is less than 10 ft. A French-drain structure approximately 20 to 30 ft northeast of the ditch intercepts ground water discharging to the ditch from the contaminated aquifer (fig. 2). When the French drain is in operation, a pump collects ground water in the drain and transfers it to a granular activated carbon tank. The water is then discharged to the sanitary sewer. The French drain was not in operation, however, during this investigation. The drainage ditch is intermittently flooded and is heavily vegetated with cattails.

Methodology

For this investigation, newly developed pore-water samplers (Vroblesky and Casey, 2007) and standard water-filled PDB samplers were installed in a drainage ditch on the southwest side of IR Site 4. The samplers were installed at five sites, within approximately 20 ft of each other near well R5, in surface water and at depths of less than 1 ft and about 1.5 ft below the ditch bed (table 1; fig. 3).

The samplers remained in place approximately 5 months prior to the collection of water samples. The water samples were collected by connecting a peristaltic pump to the nylon tubing attached to the inner pipe of the sampler. After three sampler volumes were purged, a pore-water sample was collected for laboratory analysis for VOCs. Selected samples were analyzed for turbidity, pH, specific conductance, sulfide, carbon dioxide, alkalinity, and dissolved iron (Fe^{2+}) (tables 2 and 3).

Low-flow sampling methodology (Barcelona and others, 1994; Shanklin and others, 1995; Sevee and others, 2000) was used to collect ground-water samples from well R5. During low-flow sampling, the well was purged using a peristaltic pump at a rate of approximately 250 milliliters per minute (mL/min), until the temperature, pH, dissolved oxygen, and specific conductance stabilized and no additional water-level drawdowns were observed. Stabilization of water properties was monitored using a flow-through cell containing temperature, pH, dissolved oxygen, and specific conductance sensors. The water properties were considered to be stabilized when the observed changes over three 3-minute intervals were within ± 3 percent for temperature and specific conductance, within ± 0.1 units for pH, and within ± 10 percent for dissolved oxygen.

Table 1. Descriptions of sampling points in the drainage ditch, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.

Site shown in figure 3	Sampler identifier	Sampler type	Sampler depth, in feet below drainage-ditch bed
1	WDS1	1.4-inch-diameter pore-water sampler	1.5
1	PDBWD1	Polyethylene diffusion bag sampler	.25
1	SW1	1.4-inch-diameter pore-water sampler	.2
1	SW4	1.4-inch-diameter pore-water sampler	In surface water above ditch bed
2	WDS2	2.5-inch-diameter pore-water sampler	1.25
3	WDS3	2.5-inch-diameter pore-water sampler	1.6
3	PDBWD3	Polyethylene diffusion bag sampler	.25
4	WDS4	1.4-inch-diameter pore-water sampler	1.4
5	PDBWD4	Polyethylene diffusion bag sampler	.25

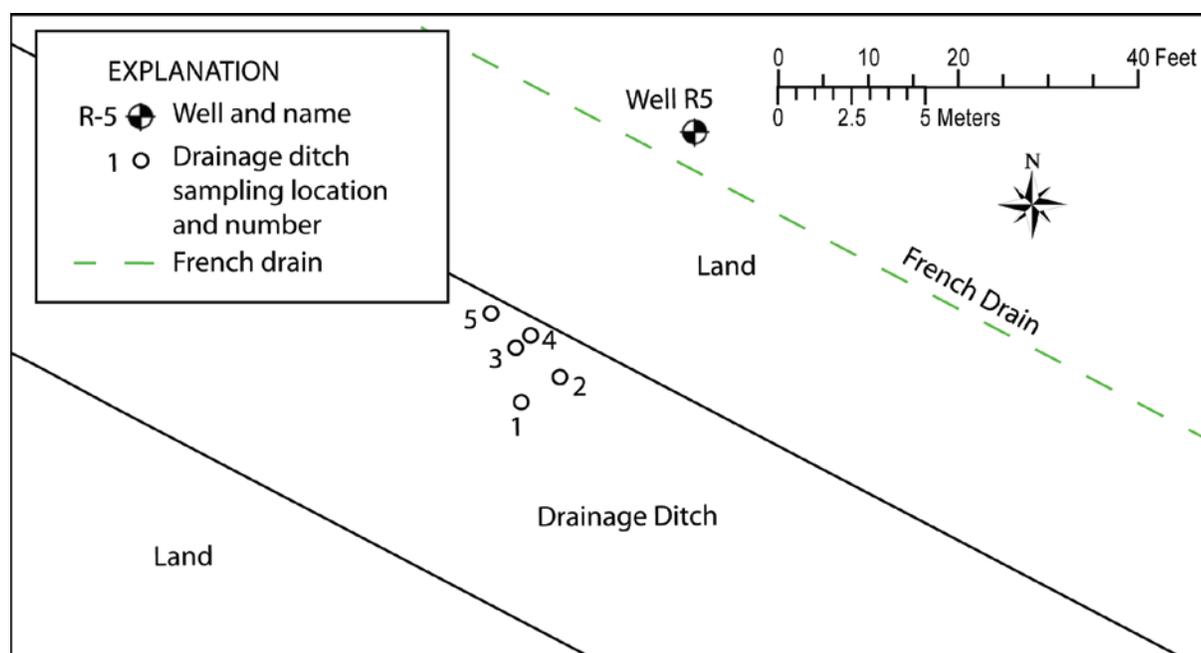


Figure 3. Sampling locations in and adjacent to the drainage ditch, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas. (Site location shown in figure 2.)

4 Investigation of Ground-Water Contamination at a Drainage Ditch, Naval Air Station Corpus Christi

Table 2. Concentrations of selected volatile organic compounds in water samples, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.

[CB, chlorobenzene; 1,2-DCB, 1,2-dichlorobenzene; 1,4-DCB, 1,4-dichlorobenzene; <, less than; J, estimated value; —, no sample; all concentrations are in micrograms per liter; suffix R represents a duplicate sample]

Location	Sampler number	Date	CB	1,2-DCB	1,4-DCB	Ethane	Methane
R5	R5	9/19/2005	57	<1.4	6.5	—	—
R5	R5	8/15/2006	72	1.45	7.18	<2	2,670
1	WDS1	9/19/2005	160	<5.6	16J	11	4,300
1	WDS1	8/15/2006	50.3	1.67	11.8	<2	1,730
1	PDBWD1	9/19/2005	74	<2.2	7.1J	—	—
1	SW1	9/19/2005	36	<5.6	<6.7	.66J	1,500
1	SW1	8/15/2006	3.05	.281	4.08	—	—
1	SW4	9/19/2005	2.3J	<1.4	<1.7	—	—
1	SW4	8/15/2006	15.6	<.25	1.08	—	—
2	WDS2	9/19/2005	85	<2.2	3.1J	—	—
2	WDS2R	9/19/2005	110	<3.5	5.1J	—	—
2	WDS2	8/15/2006	54.5	.452	2.86	—	—
3	WDS3	9/19/2005	140	<3.5	8.9J	—	—
3	PDBWD3	9/19/2005	76	<.56	5.8	—	—
4	WDS4	9/19/2005	68	1.8	7.5	—	—
4	WDS4	8/15/2006	79.4	1.58	8.67	<2	2,850
5	PDBWD4	9/19/2005	16	.64J	2.8	—	—

Table 3. Concentrations of inorganic constituents in water samples, Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, 2005–06.

[mg/L, milligrams per liter; S.U., standard units; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NTU, Nephelometric turbidity units; —, data not collected; <, less than; >, greater than]

Location	Sampler number	Date	Dissolved oxygen (mg/L)	Temperature (Celsius)	Turbidity (NTU)	pH (S.U.)	Specific conductance (µS/cm)	Sulfide (mg/L)	Carbon dioxide (mg/L)	Alkalinity (mg/L)	Iron(II) (mg/L)
R5	R5	9/19/2005	<0.05	—	—	—	—	<0.1	—	—	—
R5	R5	8/15/2006	.1	30.42	3.7	6.46	898	<.1	70	325	16
1	WDS1	9/19/2005	.05	—	—	—	—	—	—	—	—
1	WDS1	8/15/2006	.1	28.13	15.5	6.6	1,873	<.1	100	375	>10
1	SW1	8/15/2006	<.05	29.04	11.2	6.77	3,394	—	—	—	—
1	SW4	8/15/2006	.1	28.48	66	6.94	895	—	—	—	—
2	WDS2	8/15/2006	.2	28.13	33.7	6.58	—	—	—	—	—
4	WDS4	9/19/2005	.15	—	—	—	—	—	—	—	—
4	WDS4	8/15/2006	.3	30.65	571	6.45	537	<.1	100	350	>10

Chlorobenzene Contamination at the Drainage Ditch

Analytical results for water collected from the pore-water samplers in and beneath the drainage ditch at IR Site 4 showed the presence of chlorobenzene and other organic constituents (table 2). The chlorobenzene concentrations in ground-water samples collected at well R5, upgradient from the ditch, were 57 micrograms per liter ($\mu\text{g/L}$) in September 2005 and 72 $\mu\text{g/L}$ in August 2006. Other recent concentrations of chlorobenzene found in water samples collected from well R5 were 12 $\mu\text{g/L}$ in January 2005, 109 $\mu\text{g/L}$ in June 2005, and 88.4 $\mu\text{g/L}$ in January 2006 (Terraine, Inc., 2006), indicating a degree of temporal variation in chlorobenzene concentrations at this location.

During the 2005 sampling, the chlorobenzene concentrations in water collected from all of the pore-water samplers installed deeper than 1 ft below the top of the ditch bed sediments were higher than concentrations in water collected from well R5. There are several possible explanations for the difference in concentrations between samples collected from the pore-water samplers and those collected from well R5. One explanation is that the chlorobenzene concentrations may be higher in the ground water beneath the ditch than at well R5. Alternatively, there could be a heterogeneous distribution of chlorobenzene concentrations across the approximately 6.3 ft of saturated screened interval in well R5. Pumped water from well R5 is a flow-weighted mixture of concentrations from across the screened interval; therefore, the highest chlorobenzene concentrations that discharge to the stream may be under-represented by well R5. This error is reduced by using pore-water samplers because the samplers have a much shorter screen length (0.7 ft) than the wells, allowing the pore-water sampler concentrations to more closely represent local pore-water concentrations.

Another possible explanation for the difference between chlorobenzene concentrations in samples collected from well R5 and those from pore-water samplers is that the use of very coarse-grained sand (1,410 to 2,000 microns) as a filter pack in these prototype pore-water samplers allowed the pumped water from the samplers to be turbid (table 3). Because chlorobenzene sorbs to sediment, the chlorobenzene concentrations in the turbid water from the pore-water samplers may have caused the dissolved chlorobenzene concentration to be over-represented.

Finally, some of the differences in chlorobenzene concentrations among the samplers could be due to sampling or analytical variation. Chlorobenzene concentrations in duplicate samples collected in September 2005 differed by approximately 19 percent (85 $\mu\text{g/L}$ and 110 $\mu\text{g/L}$ for sampler WDS2, table 2). For this set of samples, that difference indicates the range of uncertainty.

Water collected by the PDB samplers at sites 1, 3, and 5 (PDBWD1, PDBWD3, and PDBWD4) also contained chlorobenzene (table 2). These samplers were buried just beneath the surface of the ditch bottom. Because the polyethylene

membrane of the PDB samplers excludes turbidity, these concentrations probably accurately represent chlorobenzene concentrations in pore water from the sediment just below the surface of the ditch bed.

Pore-water sampler SW1 was located near PDB sampler PDBWD1. Samples collected with SW1 contained slightly lower concentrations of chlorobenzene than samples collected with the PDB sampler. Because pore-water sampler SW1 obtained water from directly below the sediment surface, the concentrations could represent a mixture of pore water and surface water, potentially resulting in lower concentrations of chlorobenzene than the concentration in pore water alone (table 2).

The above information indicates that chlorobenzene concentrations in pumped water samples from well R5 should be considered the minimum for chlorobenzene concentrations in pore water at that well. With the exception of concentrations in pore water collected with sampler SW1, the chlorobenzene concentrations in water collected with the pore-water samplers should be considered the maximum chlorobenzene concentrations at those locations. Thus, it is unlikely that more than 160 $\mu\text{g/L}$ of chlorobenzene was present in the pore water beneath the ditch at the locations sampled (table 2).

Water collected with the pore-water samplers contained less than 0.4 mg/L of dissolved oxygen, indicating that anaerobic conditions are present in the aquifer beneath the ditch (table 3). Although chlorobenzene readily biodegrades under aerobic conditions by oxidative dechlorination, biodegradation under anaerobic conditions occurs at a slower rate and monochlorobenzene has been reported to be stable under anaerobic conditions (Masunaga and others 1996; Susarla and others, 1996; World Health Organization, 2004). Under methanogenic and sulfate-reducing conditions, degradation of chlorobenzenes is limited to dechlorination with no breakdown of the aromatic structure (World Health Organization, 2004), leaving benzene as a daughter product. Because benzene concentrations in water collected with the pore-water samplers were less than 0.5 $\mu\text{g/L}$ (data not shown), it is unlikely that substantial chlorobenzene biodegradation is taking place in the anaerobic ground water beneath the ditch.

Concentrations of chlorobenzene in water samples from sites 1 and 3 show that the concentrations decrease from about 1.5 ft below the ditch to immediately below the ditch (0.2 ft; tables 1 and 2). Although there is some uncertainty in these findings related to sample turbidity, the data are consistent with expectations that sorption will deplete chlorobenzene concentrations in water discharging upward through the organic-rich bottom sediment of the drainage ditch. The soil sorption coefficients (K_{oc}) are 466 for chlorobenzene, 987 for 1,2-DCB, and 1,470 for 1,4-DCB (World Health Organization, 2004), indicating a strong tendency for the chlorobenzenes to sorb onto aquifer organic matter. Thus, the decrease in chlorobenzene concentrations with decreasing depth is consistent with chlorobenzene removal by sorption along the transport pathway through the organic-rich ditch bed sediment.

The presence of cattails (*Typha* spp.) also offers a potential depletion mechanism for chlorobenzene in the sediments beneath the drainage ditch near IR Site 4. Cattails have been found to be efficient in uptake of metals (Carvalho and Martin, 2001; Goulet and others, 2005), explosives (Miller and others, 1997), perchlorate (Nzengung and McCutcheon, 2003), and other dissolved constituents. Dietz and Schnoor (2001) found that chlorobenzene is strongly bound to roots. Furthermore, sorption isotherm experiments have shown these binding reactions to be irreversible, meaning that it is a biochemical bonding behavior and not hydrophobic partitioning behavior.

In addition, some wetland plants, such as cattails and salt-marsh rush (*Juncus gerardii*) can aerate marsh soils (Bertness and Hacker, 1994; Hacker and Bertness, 1995, 1999; Callaway and King, 1996). Thus, there is a potential for cattail-induced soil aeration in the drainage ditch bed sediments to provide localized conditions favorable to chlorobenzene oxidation. In an effort to increase the potential for cattail-related contaminant removal near IR Site 4, a tree in the drainage ditch near well R5 that was preventing cattail growth was removed in 2005. By 2006, the cattail population had increased and filled the formerly shaded area. Further investigation is warranted to evaluate potential uptake by the increased cattail population.

Summary

The USGS, in cooperation with the Naval Facilities Engineering Command Southeast, used newly developed sampling methods to investigate ground-water contamination by chlorobenzenes beneath a drainage ditch on the southwestern side of Installation Restoration Site 4, Naval Air Station Corpus Christi, Corpus Christi, Texas, during 2005–06. The drainage ditch, which is a potential receptor for ground-water contaminants from Installation Restoration Site 4, intermittently discharges water to Corpus Christi Bay.

Water samples obtained from the pore-water samplers in and beneath the drainage ditch at IR Site 4 contained the presence of chlorobenzene and other organic constituents.

In 2005, all water samples collected from pore-water samplers positioned deeper than 1 ft below the top of the ditch bed sediments contained higher chlorobenzene concentrations than water samples collected from well R5. There are several possible explanations for this difference in measured chlorobenzene concentrations. One explanation is that the chlorobenzene concentrations may be higher in the ground water beneath the ditch than at well R5. Alternatively, the difference could be the result of a mixture of water; a constituent concentration in a sample is a flow-weighted average of concentrations in water across the saturated screened interval, which is about 6.3 ft long for well R5 but only 0.7 ft long for the pore-water samplers. If there is vertical heterogeneity in contaminant concentrations across the screened interval of well R5, then the sample from well R5 under-represents the highest chlorobenzene concentrations intersecting the screened interval. The pumped pore-water samplers reduce this error by having a much smaller screen length (0.7 ft), allowing the pumped concentrations to more closely represent aqueous concentrations in local pore water. It is also possible that the pumped pore-water samplers overestimated the chlorobenzene concentrations because the very coarse-grained sand used as a filter in these samplers allowed the pumped water from the samplers to be turbid, and the turbid water may have included sorbed chlorobenzene. Turbidity in the water sample can be reduced or eliminated by using a finer-grained filter sand pack in the pore-water samplers. Analytical results from PDB samplers that eliminate turbidity, however, show that even without the uncertainty associated with collecting turbid water, approximately 16 to 76 $\mu\text{g/L}$ of dissolved chlorobenzene was present in the pore water collected a few inches beneath the drainage ditch in 2005.

The anaerobic conditions in the aquifer beneath the ditch make substantial chlorobenzene biodegradation unlikely. The soil sorption coefficients for the chlorobenzenes, however, indicate a strong tendency for these compounds to sorb onto the organic-rich ditch bed sediments. In addition, the presence of cattails in the drainage ditch provides a potential removal mechanism for chlorobenzene by uptake and sorption onto roots and by aeration of the sediment near the roots.

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