

Prepared under interagency agreement with the U.S. Environmental Protection Agency

Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions and Potentiometric Surfaces in Two Trichloroethene-Contaminated Zones at the Double Eagle and Fourth Street Superfund Sites in Oklahoma City, Oklahoma

Scientific Investigations Report 2004–5050, version 2

Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions and Potentiometric Surfaces in Two Trichloroethene-Contaminated Zones at the Double Eagle and Fourth Street Superfund Sites in Oklahoma City, Oklahoma

By Christopher L. Braun

Prepared under interagency agreement with the U.S. Environmental Protection Agency

Scientific Investigations Report 2004–5050, version 2

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, Austin, Texas: 2004 Revised: 2007

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.

Braun, C.L., 2004 [revised 2007], Reductive dechlorination of chlorinated ethenes under oxidation-reduction conditions and potentiometric surfaces in two trichloroethene-contaminated zones at the Double Eagle and Fourth Street Superfund Sites in Oklahoma City, Oklahoma (version 2): U.S. Geological Survey Scientific Investigations Report 2004–5050, 20 p. [Online only].

Contents

Abstract 1
Introduction
Purpose and Scope
Subsurface Description of the Study Area2
Data Collection and Analytical Methods
Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions
Volatile Organic Compounds
Dissolved Oxygen
Nitrate and Nitrite
Ferrous Iron and Total Iron
Sulfate and Sulfide
Methane
Potentiometric Surfaces
Summary
References Cited

Figures

1.	Map showing location of study area, Oklahoma City, Oklahoma	. 2
2.	Map showing locations of Double Eagle Refining Superfund site and Fourth Street	
	Abandoned Refinery Superfund site within the study area	. 3
3ab.	Sequence diagrams showing concentrations of trichloroethene (TCE), cis-dichloroethene	
	(<i>cis</i> -DCE), vinyl chloride, ethene, and chloride in the:	
	a. Shallow zone of the Garber-Wellington aquifer, February 2002 (except ethene,	
	December 2001)	12
	b. Deep zone of the Garber-Wellington aquifer, February 2002	13
4a–b.	Sequence diagrams showing concentrations of dissolved oxygen, nitrate, ferrous iron,	
	sulfate, and methane in the:	
	a. Shallow zone of the Garber-Wellington aquifer, December 2001	14
	b. Deep zone of the Garber-Wellington aquifer, February–March 2002	15
5.	Map showing potentiometric surface and flow directions in the shallow zone of the Garber-	
	Wellington aquifer, Double Eagle Refining Superfund site and Fourth Street Abandoned	
	Refinery Superfund site, December 2001	18
6.	Map showing potentiometric surface and flow directions in the deep zone of the Garber-	
	Wellington aquifer, Double Eagle Refining Superfund site and Fourth Street Abandoned	
	Refinery Superfund site, February 2002	19

Tables

1.	General information for wells sampled in the Garber-Wellington aquifer at the Double	
	Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site,	
	Oklahoma City, Oklahoma, by the U.S. Geological Survey and the Oklahoma Department	
	of Environmental Quality, December 2001 and February–March 2002	4

2.	Selected constituents, methods, and procedures used to evaluate natural attenuation processes in ground water at the Double Eagle Refining Superfund site and the Fourth	
	Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma	5
3.	Analytical results for volatile organic compounds and chloride from well-water samples at	
	the Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department of	
	Environmental Quality, February 2002.	. 7
4.	Historical analytical results for selected volatile organic compounds from well-water	
	samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned	
	Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department	
	of Environmental Quality	. 9
5.	Analytical results for selected properties and inorganic constituents from well-water	
	samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned	
	Refinery Superfund site, Oklahoma City, Oklahoma, collected by the U.S. Geological Survey,	
	December 2001 and February–March 2002	16
6.	Analytical results for carbon dioxide, methane, ethane, and ethene from well-water samples	
	at the Double Eagle Refinery Superfund site and the Fourth Street Abandoned Refinery	
	Superfund site, Oklahoma City, Oklahoma, collected by the U.S. Geological Survey,	
	December 2001 and February–March 2002	17
7.	Measured and computed data from wells used to construct potentiometric surfaces at the	
	Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery	
	Superfund site, Oklahoma City, Oklahoma, December 2001 and February 2002	18

Vertical Datum

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions and Potentiometric Surfaces in Two Trichloroethene-Contaminated Zones at the Double Eagle and Fourth Street Superfund Sites in Oklahoma City, Oklahoma

By Christopher L. Braun

Abstract

The Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site are in northeast Oklahoma City, Oklahoma, adjacent to one another. The Double Eagle facility became a Superfund site on the basis of contamination from lead and volatile organic compounds; the Fourth Street facility on the basis of volatile organic compounds, pesticides, and acid-base neutral compounds. The study documented in this report was done to investigate whether reductive dechlorination of chlorinated ethenes under oxidation-reduction conditions is occurring in two zones of the Garber-Wellington aquifer (shallow zone 30-60 to 75 feet below land surface, deep zone 75 to 160 feet below land surface) at the sites; and to construct potentiometric surfaces of the two water-yielding zones to determine the directions of groundwater flow at the sites. The presence in some wells of intermediate products of reductive dechlorination, dichloroethene and vinyl chloride, is an indication that reductive dechlorination of trichloroethene is occurring. Dissolved oxygen concentrations (less than 0.5 milligram per liter) indicate that consumption of dissolved oxygen likely had occurred in the oxygen-reducing microbial process associated with reductive dechlorination. Concentrations of nitrate and nitrite nitrogen (generally less than 2.0 and 0.06 milligrams per liter, respectively) indicate that nitrate reduction probably is not a key process in either aquifer zone. Concentrations of ferrous iron greater than 1.00 milligram per liter in the majority of wells sampled indicate that iron reduction is probable. Concentrations of sulfide less than 0.05 milligram per liter in all wells indicate that sulfate reduction probably is not a key process in either zone. The presence of methane in ground water is an indication of strongly reducing conditions that facilitate reductive dechlorination. Methane was detected in all but one well. In the shallow zone in the eastern part of the study area, ground water flowing from the northwest and south coalesces in a potentiometric trough, then moves westward and ultimately northwestward. In the western part of the study area, ground water in the shallow zone flows northwest. In the deep zone in the eastern part of the study area, ground water generally flows northwestward; and in the western part of the study area, ground water in the deep zone generally flows northward.

Introduction

The Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site are in northeast Oklahoma City, Okla., about 0.5 mile north of the North Canadian River (figs. 1, 2). The Double Eagle facility re-refined used motor oil from 1929 until the early 1980s using a process of acidulation and filtration (U.S. Environmental Protection Agency, 2001a). In March 1989, the site was placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List (NPL) on the basis of soil, sludge, and water samples collected in October 1987. The principal contaminants at the site were lead and the volatile organic compounds (VOCs) xylene, ethylbenzene, and trichloroethene. Prior to being placed on the NPL, the facility processed about 500,000 to 600,000 gallons of used oil into finished lubricating oil each month (Fluor Daniel, Inc., 1993). About 80,000 gallons of oily sludge (waste) was generated by this process each month; the sludge was disposed of on-site in the sludge lagoon or one of the seven numbered impoundments shown in figure 2 (Ecology and Environment, Inc., 1988).

The Fourth Street site, located about 500 feet northeast of the Double Eagle site, operated as a waste-oil reclamation facility from about 1940 until the early 1960s (U.S. Environmental Protection Agency, 2001b). The USEPA collected samples at the site from June 1985 until December 1987. The results of the sampling indicated elevated concentrations of VOCs, pesticides, and acid-base neutral compounds in the soil and sludge. The site was placed on the NPL in March 1989.

In spring 2001, a 5-year review of the Double Eagle/Fourth Street sites was completed, which resulted in a short-term study supported by an interagency agreement between the U.S. Geological Survey (USGS) and the USEPA. The primary objective of the study was to investigate whether reductive dechlorination of chlorinated ethenes under oxidation-reduction (redox) conditions is occurring in two water-yielding zones of the Garber-Wellington aquifer at the sites; the secondary objective was to construct potentiometric surfaces of the two water-yielding zones to determine the directions of ground-water flow in the zones at the sites.

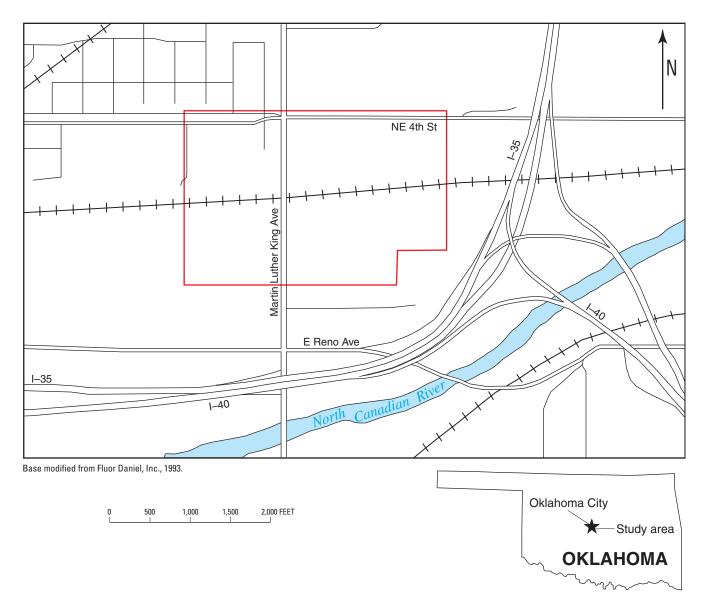


Figure 1. Location of study area, Oklahoma City, Oklahoma.

Purpose and Scope

The purpose of this report is to document the sampling and analytical methods used to obtain ground-water-quality data for assessing the extent of reductive dechlorination; to assess the extent of reductive dechlorination on the basis of controlling redox processes; and to present potentiometric surfaces, with flow directions indicated, for two water-yielding zones. The assessment of reductive dechlorination was made using data from 14 water samples from 13 wells (seven in the shallow zone, six in the deep zone). The potentiometric surfaces were constructed from measured pressures (converted to hydraulic heads) at the bottoms of the screened intervals of the 13 wells; thus the two potentiometric surfaces are based on seven and six head measurements, respectively.

Subsurface Description of the Study Area

The study area overlies alluvial deposits of Recent geologic age. The deposits are from 30 to 60 feet thick and consist primarily of unconsolidated and interfingering lenses of silt, sand, gravel, and clay (Fluor Daniel, Inc., 1993). Beneath the alluvial deposits in the study area is the Garber-Wellington aquifer, which comprises interbedded sandstone, shale, and siltstone of Permian age (Carr and Marcher, 1977). Rocks of the Hennessey Group (predominantly shale) commonly separate the alluvial deposits from the Garber-Wellington aquifer in the Oklahoma City area, but previous test drilling indicated that those rocks are not present in the study area (Kathleen Buckley, Oklahoma Department of Environmental Quality, written commun., 2002). Test drilling in the study area also indicated that the Garber-Wellington aquifer contains a shale layer at a

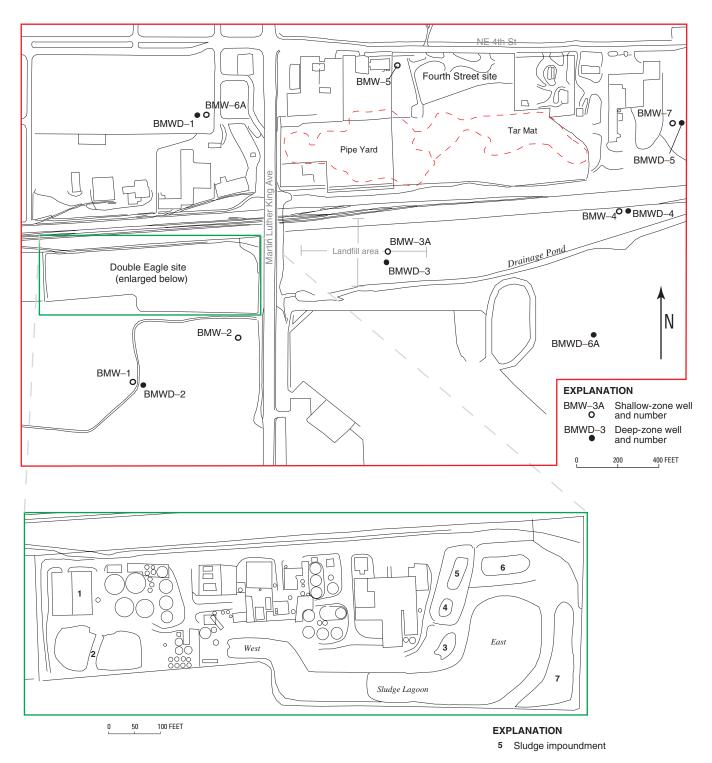


Figure 2. Locations of Double Eagle Refining Superfund site and Fourth Street Abandoned Refinery Superfund site within the study area.

depth below land surface of about 160 feet. For this report, the aquifer from its top at the base of the alluvial deposits to a depth below land surface of about 75 feet is defined as the shallow zone; and the aquifer from the base of the shallow zone to the shale layer at about 160 feet is defined as the deep zone.

The Oklahoma City Oil Field underlies the study area at depths that exceed 1,000 feet (Amy Johnson, Oklahoma Department of Environmental Quality, written commun., 2003). Salinity in both zones of the Garber-Wellington aquifer exceeds 10,000 parts per million in the area as a result of brine contamination associated with oil-field activities (Kathleen Buckley, Oklahoma Department of Environmental Quality, written commun., 2002).

Data Collection and Analytical Methods

Data for this study were collected and analyzed by the USGS and the Oklahoma Department of Environmental Quality (ODEQ) or their contractors in accordance with a Quality Assurance Project Plan (Kathleen Buckley, Oklahoma Department of Environmental Quality, written commun., 2002). The USGS collected water samples from seven wells open to the shallow zone of the Garber-Wellington aquifer and from six wells open to the deep zone (fig. 2, table 1). The shallow-zone wells and one deep-zone well (BMWD-5) were sampled in December 2001, and the deep-zone wells were sampled in February–March 2002. The USGS analyzed samples in the field for specific conductance, pH, alkalinity, temperature, dissolved oxygen (DO), nitrate and nitrite nitrogen, ferrous iron, total

Table 1. General information for wells sampled in the Garber-Wellington aquifer at the Double Eagle Refining Superfund siteand the Fourth Street Abandoned Refinery Superfund site, Okla-homa City, Oklahoma, by the U.S. Geological Survey and the Okla-homa Department of Environmental Quality, December 2001 andFebruary–March 2002

Aquifer zone and well number (fig. 2)	Altitude of TOC (feet above NGVD 29)	Total depth (feet below TOC)	Screened interval (feet below TOC)
Shallow			
BMW-1	1,173.55	74	59–69
BMW-2	1,168.58	44	31-41
BMW-3A	1,171.97	62	47–57
BMW-4	1,171.88	¹ 48	35–45
BMW-5	1,170.41	48	35–45
BMW-6A	1,174.06	72	61–71
BMW-7	1,169.30	46	33-43
Deep			
BMWD-1	1,174.02	154	140-150
BMWD-2	1,178.11	149	140-150
BMWD-3	1,171.16	159	140-150
BMWD-4	1,172.29	156	140-150
BMWD-5	1,168.69	156	140-150
BMWD–6A	1,175.33	¹ 146	135–145

¹ Estimated on the basis of depth setting of pressure transducer (see table 7).

iron, sulfate, sulfide; and the dissolved gases carbon dioxide, methane, and hydrogen, which were analyzed using field gas chromatographs. The methods used to collect gas samples likely resulted in elevated hydrogen concentrations. The pump used by ODEQ to purge the wells before USGS sampling had metal parts that came into contact with the water, which likely generated some hydrogen. Thus, analyses of hydrogen gas data are not included in this report. The USGS collected and sent samples for analyses of ethane, ethene, and methane to a contract laboratory (Microseeps, Inc., Pittsburg, Pa.).

Unfiltered ground-water samples were collected from the shallow-zone wells using a peristaltic pump and from the deepzone wells using a bladder pump. Wells were pumped for at least 30 minutes before sample collection. The field or laboratory methods and procedures used to analyze selected constituents are listed in table 2.

Decontamination procedures between wells consisted of equipment cleaning and rinsing with deionized water¹ and a dilute detergent solution (as needed). Equipment cleaned included glassware used for chemical analyses, monitoring probes, glass bubblers (for headspace analysis), Teflon® tubing for the bladder pump, and the bladder pump itself. New Tygon® tubing was used in sampling each of the shallow-zone wells.

The USGS measured DO concentration in the field using the indigo carmine method (Gilbert and others, 1982). Ground water was pumped through Teflon® tubing (with a low oxygendiffusion coefficient) into a sampling cell. A vacuum-sealed ampoule was placed into the overflowing sample cell, and the tip was broken to draw a fixed size of sample into the ampoule. The tip was covered to ensure against atmospheric contamination of the sample. The ampoule was inverted carefully several times to mix the color-developing reagents with the sample and allowed to react for 2 minutes. Then the ampoule was placed in a CHEMetrics VVR multivariate photometer and the DO concentration recorded. The lower and upper method detection limits for DO using this method and instrumentation are 0 and 15.0 milligrams per liter (mg/L), respectively.

Nitrate concentrations were measured in the field using the cadmium reduction method (HACH Co., 1989). At least 40 milliliters (mL) of ground water were collected in a glass beaker. The tip of a vacuum-sealed ampoule was then snapped against the side of the beaker to draw a fixed volume of sample into the ampoule. The ampoule was inverted repeatedly during a 1-minute period to mix the reagent and sample. The cadmium reduction reaction was allowed to proceed for 5 minutes. After 5 minutes, a blank sample was placed into the HACH DR/890 colorimeter. The blank sample was removed, the sample cell containing the ground-water sample was placed in the colorimeter, and the concentration of total nitrate as nitrogen was read and recorded in the field notebook. The lower and upper detection limits for total nitrate as nitrogen using this method and instrumentation are 0 and 5.0 mg/L, respectively.

Nitrite concentrations were measured in the field using the azo dye formation method (American Public Health Association, 1992). A sample cell was filled with 25 mL of ground

Constituent	Method	Procedure
Dissolved oxygen	Indigo carmine ^{1,2}	Colorimetric analysis (field)
Nitrate	Cadmium reduction ³	Colorimetric analysis (field)
Nitrite	Azo dye formation ²	Colorimetric analysis (field)
Ferrous iron	1,10 Phenanthroline ⁴	Colorimetric analysis (field)
Total iron	FerroVer ³	Colorimetric analysis (field)
Sulfate	SulfaVer 4 ²	Colorimetric analysis (field)
Sulfide	Methylene blue, colorimetric ^{2,4}	Colorimetric analysis (field)
Dissolved carbon dioxide and methane	Bubble strip ⁵	Gas chromatographic analysis
Dissolved methane, ethane, and ethene	Bubble strip ⁵	Gas chromatographic analysis

 Table 2.
 Selected constituents, methods, and procedures used to evaluate natural attenuation processes in ground water at the Double

 Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma

¹ Gilbert and others, 1982.

² American Public Health Association, 1992.

³ HACH Co., 1989.

⁴ U.S. Environmental Protection Agency, 1979.

⁵ Chapelle, 1996.

water; the tip of a vacuum-sealed ampoule was then snapped against the side of the beaker to draw a fixed volume of sample into the ampoule. The ampoule was inverted several times to mix the reagent and sample. The azo dye was allowed to develop for 10 minutes. After 10 minutes, a blank sample was placed into the CHEMetrics VVR multivariate photometer. The blank sample was removed, the sample cell containing the ground-water sample was placed in the photometer, and the concentration of total nitrite as nitrogen was read and recorded in the field notebook. The lower and upper method detection limits for total nitrite as nitrogen using this method and instrumentation are 0 and 0.8 mg/L, respectively.

The concentration of ferrous iron was measured in the field using the 1,10-phenanthroline method (American Public Health Association, 1992). A minimum of 40 mL of ground water was collected in a glass beaker. The tip of a vacuum-sealed ampoule was then snapped against the side of the beaker to draw a fixed volume of sample into the ampoule. The ampoule was inverted several times, and the reaction was allowed to proceed for 3 minutes. After 3 minutes, a blank sample was placed into the HACH DR/890 colorimeter. The blank sample was removed, the sample cell containing the ground-water sample was placed in the colorimeter, and the concentration of ferrous iron was read and recorded in the field notebook. The lower and upper method detection limits for ferrous iron using this method and instrumentation are 0.01 and 3.00 mg/L, respectively. If a sample concentration was greater than 3 mg/L, a 50-percent dilution of the sample with deionized water¹ was used, and the sample was re-analyzed. Two to five dilutions were required at nine wells; all analyses that required dilution are considered approximations. The ferrous iron samples collected at three wells were cloudy, causing incorrect readings on the colorimeter.

The concentration of total iron was measured in the field using the FerroVer colorimetric method (HACH Co., 1989). A minimum of 40 mL of ground water was collected in a glass beaker. The tip of a vacuum-sealed ampoule was then snapped against the side of the beaker to draw a fixed volume of sample into the ampoule, and the ampoule was inverted several times. The reaction was allowed to proceed for 3 minutes. After 3 minutes, a blank sample was placed into the HACH DR/890 colorimeter. The blank sample was removed, the sample cell containing the ground-water sample was placed in the colorimeter, and the concentration of total iron was read and recorded in the field notebook. The lower and upper method detection limits for total iron using this method and instrumentation are 0.01 and 3.00 mg/L, respectively. If a sample concentration was greater than 3 mg/L, a 50-percent dilution of the sample with deionized water¹ was used, and the sample was re-analyzed. Two to five dilutions were required at nine wells; all analyses that required dilution are considered approximations.

Sulfate concentrations were measured in the field using the SulfaVer 4 method (American Public Health Association, 1992). A minimum of 40 mL of ground water was collected in a glass beaker. The tip of a vacuum-sealed ampoule was snapped against the side of the beaker to draw a fixed volume of sample into the ampoule. The ampoule was inverted repeatedly during a 1-minute period to mix the reagent and sample. The reaction was allowed to proceed for 5 minutes. After 5 minutes, a blank sample was placed into the HACH DR/890 colorimeter. The blank sample was removed, the sample cell

¹The analyte of interest was not detected in an analysis of the deionized water.

containing the ground-water sample was placed in the colorimeter, and the concentration of sulfate was read and recorded in the field notebook. The lower and upper detection limits for sulfate using this method and instrumentation are 0 and 70 mg/L, respectively. If a sample concentration was greater than 70 mg/L, a 50-percent dilution of the sample with deionized water¹ was used, and the sample was re-analyzed. Two to five dilutions were required at 12 wells; all analyses that required dilution are considered approximations.

Sulfide concentrations were measured in the field using the methylene blue colorimetric method (American Public Health Association, 1992; U.S. Environmental Protection Agency, 1979). Three drops of the sulfide reagent were added to a sample cell containing 25 mL of ground water and mixed by stirring with the tip of the ampoule containing the sulfide reagent. After mixing, the tip of the ampoule was snapped against the side of the sample cell, and the ampoule was filled. The ampoule was inverted several times to mix the reagent and sample. The methylene blue color was allowed to develop for 5 minutes. After 5 minutes, a blank sample was placed into the VVR multivariate photometer. The blank sample was removed, the sample cell containing the ground-water sample was placed in the photometer, and the concentration of total sulfide was read and recorded in the field notebook. The lower and upper detection limits for total sulfide using this method and instrumentation are 0.001 and 1.5 mg/L, respectively.

The concentrations of dissolved carbon dioxide and methane were measured in the field using the "bubble strip" method (Chapelle, 1996). Ground water was pumped through a glass bubbler fitted with a septum. Once flow was established at about 300 mL per minute and the bubbler was filled and free of gas bubbles, 20 mL of helium was injected. The induced headspace was allowed to equilibrate with the flowing ground water for about 30 minutes. After 30 minutes, 10 mL of the headspace gas was withdrawn using a 10-mL gas-tight syringe with a valve; after 5 minutes, a second 10-mL sample of the headspace gas was withdrawn into a second syringe. Both samples were analyzed using an MTI dual-column gas chromatograph equipped with a thermal conductivity detector calibrated with standard gases.

A second gas sample also was collected using the "bubble strip" method and was sent (at ambient air temperature) to the Microseeps, Inc., laboratory for analysis of dissolved methane, ethane, and ethene. After the samples were collected for the analysis of dissolved carbon dioxide and methane, another 20 mL of helium was injected into the bubbler and allowed to equilibrate for about 15 minutes. The sample then was extracted with a 50-mL disposable syringe and injected into a 22-mL sample bottle that had been evacuated previously by Microseeps, Inc.

The ODEQ collected water samples from the 13 wells in February 2002 for analysis of selected VOCs. The samples were analyzed by a contract laboratory using U.S. Environmental Protection Agency (1999) method 8260.

Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions

The most common redox processes in ground water are the reduction of oxygen, nitrate (denitrification), ferric iron, sulfate, and carbon dioxide (methanogenesis). The reduced chemical species produced during redox reactions are used in biological processes that facilitate reductive dechlorination of chlorinated ethenes. The efficiency of the reductive dechlorination process varies depending on redox conditions. Dechlorination of the more highly chlorinated ethenes (trichloroethene [TCE] and tetrachloroethene [PCE]) can occur in mildly reducing environments, such as those associated with ferric iron reduction, but dechlorination is more efficient in sulfate-reducing or methanogenic conditions (Chapelle, 1996; Suarez and Rifai, 1999). The reduced intermediate products dichloroethene (DCE) and vinyl chloride (VC) typically require a more strongly reducing environment, methanogenic conditions, to be degraded to the end product, ethene (Bradley and Chapelle, 1998).

Hydrogen is produced during anaerobic microbial metabolism. Hydrogen is then used by respirative microorganisms that most commonly use ferric iron, sulfate, or carbon dioxide as electron acceptors. Dissolved hydrogen concentrations can be used to identify which redox process is dominant at a particular location (Chapelle, 1996). In addition to dissolved hydrogen concentrations, concentrations of the reduced species nitrite, ferrous iron, sulfide, and methane are useful for identifying redox processes.

Determination of dissolved hydrogen concentrations might not be necessary; when concentrations of the reduced species produce conflicting information, hydrogen concentrations are critical. For example, ferrous iron, sulfide, and methane can be transported by ground-water flow in the subsurface. The constituents could be produced upgradient and transported to the well where the measurement is made.

The methods used to collect gas samples in this study likely resulted in elevated hydrogen concentrations. As a result these data are not included in this report, and determination of the dominant redox process is deduced from other redox indicators, such as reduced species.

Volatile Organic Compounds

Table 3 summarizes laboratory analyses of all VOCs in samples collected from the wells in February 2002. Table 4 lists historical analytical results for five VOCs in samples collected from December 1996 through February 2002.

The concentrations of chlorinated ethenes at the site are controlled partially by reductive dechlorination, which in turn is controlled by redox processes in ground water. Under anaerobic

Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions 7

Table 3. Analytical results for volatile organic compounds and chloride from well-water samples at the Double Eagle Refining Super-fund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department ofEnvironmental Quality, February 2002

[TOC, top of casing; NGVD 29, National Geodetic Vertical Datum of 1929; DTW, depth to water; $\mu g/L$, micrograms per liter; mg/L, milligrams per liter; <, less than; E, estimated]

Aquifer zone and well number (fig. 2)	Date sampled	Altitude of TOC (feet above NGVD 29)	DTW (feet below TOC)	Screened interval (feet below TOC)	Ace- tone (µg/L)	Ben- zene (µg/L)	Bromo- form (μg/L)	Carbon disulfide (µg/L)	Carbon tetra- chloride (µg/L)	Chloro- benzene (µg/L)	Chloro- dibromo- methane (µg/L)	Chloro- ethane (µg/L)	2-Chloro- ethyl- vinyl ether (μg/L)	Chloro- form (µg/L)	Dichloro- bromo- methane (µg/L)
Shallow															
BMW-1	02/28/02	1,173.55	18.80	59–69	<50	39	<25	<25	<25	<25	<25	<50	<25	<25	<5
BMW-2	02/28/02	1,168.58	10.33	31-41	<100	E45	<50	<50	<50	350	<50	<100	<50	<50	<50
BMW-3A	02/27/02	1,171.97	15.93	47–57	<50	E20	<25	<25	<25	<25	<25	<50	<25	<25	<25
BMW-4	02/27/02	1,171.88	13.92	35–45	<10	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5
BMW-5	02/28/02	1,170.41	12.58	35–45	<100	E16	<50	<50	<50	<50	<50	<100	<50	<50	<50
BMW-6A	02/27/02	1,174.06	23.53	61–71	<500	<250	<250	<250	<250	<250	<250	<500	<250	<250	<250
BMW-7	02/27/02	1,169.30	11.18	33–43	<50	<25	<25	<25	<25	<25	<25	<50	<25	E6	<25
Deep															
BMWD-1	02/27/02	1,174.27	66.45	140-150	<100	130	<50	<50	<50	<50	<50	<100	<50	<50	<50
BMWD-2	02/28/02	1,178.29	65.15	140-150	<10	12	<5	<5	<5	<5	<5	<10	<5	<5	<5
BMWD-3	02/27/02	1,170.90	62.00	140-150	<100	60	<50	<50	<50	<50	<50	<100	<50	<50	<50
BMWD-4	02/27/02	1,172.29	64.35	140-150	<100	120	<50	<50	<50	<50	<50	<100	<50	E10	<50
BMWD-5	02/27/02	1,168.65	58.30	140-150	<10	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5
BMWD-6A	02/27/02	1,175.33		135–145	<10	<5	<5	<5	<5	<5	<5	<10	<5	<5	<5

Aquifer zone and well number (fig. 2)	1,1- Dichloro- ethane (μg/L)	1,2- Dichloro- ethane (μg/L)	1,1- Dichloro- ethene (µg/L)	<i>cis</i> -1,2- Dichloro- ethene (μg/L)	<i>trans</i> -1,2- Dichloro- ethene (μg/L)	1,2- Dichloro- propane (µg/L)	<i>cis</i> -1,3- Dichloro- propene (μg/L)	<i>trans</i> -1,3- Dichloro- propene (μg/L)	Ethyl- benzene (µg/L)	2-Hex- anone (µg/L)	Methyl bromide (µg/L)	Methyl chloride (µg/L)
Shallow												
BMW-1	E13	52	<25	73	<25	<25	<25	<25	<25	<50	<50	<50
BMW-2	<50	<50	<50	E34	<50	<50	<50	<50	<50	<100	<100	<100
BMW-3A	E8	35	<25	41	<25	<25	<25	<25	E7	<50	<50	<50
BMW-4	<5	<5	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10
BMW-5	E11	E29	<50	E19	<50	<50	<50	<50	<50	<100	<100	<100
BMW-6A	E82	<250	E110	1,700	E66	<250	<250	<250	<250	<500	<500	<500
BMW-7	<25	<25	<25	<25	<25	<25	<25	<25	<25	<50	<50	<50
Deep												
BMWD-1	E15	E27	<50	320	<50	<50	<50	<50	E10	<100	<100	<100
BMWD-2	E2	8	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10
BMWD-3	<50	<50	<50	E12	<50	<50	<50	<50	<50	<100	<100	<100
BMWD-4	<50	<50	<50	E18	<50	<50	<50	<50	E16	<100	<100	<100
BMWD-5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10
BMWD-6A	<5	<5	<5	<5	<5	<5	<5	<5	<5	<10	<10	<10

8 Reductive Dechlorination and Potentiometric Surfaces at Two Superfund Sites, Oklahoma City, Oklahoma

 Table 3.
 Analytical results for volatile organic compounds and chloride from well-water samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department of Environmental Quality, February 2002—Continued

Aquifer zone and well number (fig. 2)	Methyl- ene chloride (μg/L)	Methyl- ethyl ketone (µg/L)	Methyl- iso- butyl ketone (µg/L)	Styrene (µg/L)	1,1,2,2- Tetra- chloro- ethane (μg/L)	Tetra- chloro- ethene (μg/L)	1,1,1- Trichloro- ethane (μg/L)	1,1,2- Tri- chloro- ethane (μg/L)	Tri- chloro- ethene (μg/L)	Toluene (µg/L)	Vinyl acetate (µg/L)	Vinyl chloride (µg/L)	Xylene (μg/L)	Chloride (mg/L)
Shallow														
BMW-1	<25	<50	<50	<25	<25	<25	<25	<25	E5	<25	<50	E23	<25	14,900
BMW-2	<50	<100	<100	<50	<50	<50	<50	<50	<50	<50	<100	67	<50	4,650
BMW-3A	<25	<50	<50	<25	<25	<25	<25	<25	<25	<25	<50	<50	E14	18,700
BMW-4	<5	<10	<10	<5	<5	<5	<5	<5	<5	<5	<10	<10	<5	93.5
BMW-5	<50	<100	<100	<50	<50	<50	<50	<50	<50	<50	<100	E10	<50	17,700
BMW-6A	<250	<500	<500	<250	<250	<250	<250	<250	850	<250	<500	E61	<250	11,600
BMW-7	<25	<50	<50	<25	<25	<25	<25	<25	<25	<25	<50	<50		547
Deep														
BMWD-1	<50	<100	<100	<50	<50	<50	<50	<50	160	<50	<100	E31	E10	21,300
BMWD-2	<5	<10	<10	<5	<5	<5	<5	<5	<5	<5	<10	<10	<5	13,500
BMWD-3	<50	<100	<100	<50	<50	<50	<50	<50	<50	<50	<100	<100	<50	20,100
BMWD-4	<50	<100	<100	<50	<50	<50	<50	<50	<50	<50	<100	<100	E20	29,500
BMWD-5	<5	<10	<10	<5	<5	<5	<5	<5	<5	<5	<10	<10	<5	19,900
BMWD-6A	<5	<10	<10	<5	<5	<5	<5	<5	<5	<5	<10	<10	<5	2,580

conditions, reductive dechlorination of TCE proceeds as follows:

$$TCE \Rightarrow DCE + Cl \Rightarrow VC + 2Cl \Rightarrow ethene + 3Cl.$$
(1)

Normally DCE is not used as a primary solvent; it is an intermediate product of reductive dechlorination of a more highly chlorinated compound. The presence of DCE in samples from eight of the 13 wells and also VC in five of the 13 samples (fig. 3; table 3) is thus an indication that reductive dechlorination of TCE is occurring. Concentrations of these intermediate products of reductive dechlorination were larger than concentrations of TCE in samples from several wells.

Dissolved Oxygen

DO concentrations (table 5) greater than about 0.50 mg/L indicate that oxygen reduction is the dominant microbial process (U.S. Environmental Protection Agency, 1999). Oxygen reduction under aerobic conditions proceeds according to the equation

$$CH_2O + O_2 => CO_2 + H_2O.$$
 (2)

Both anaerobic (DO less than 0.50 mg/L) and aerobic (DO greater than 0.50 mg/L) ground-water conditions were observed in samples from wells at various locations. DO concentrations were in the anaerobic range in the majority of wells sampled, indicating that consumption of DO likely had occurred in the oxygen-reducing microbial process. The DO concentration in the sample from well BMWD-6A was large (4.3 mg/L) compared to those from the other wells. Some fraction of the water tapped by this well might be from the nearby Canadian River (fig. 1).

Nitrate and Nitrite

Nitrate (NO_3^-) is reduced to nitrite (NO_2^-) (table 5) as follows:

$$CH_2O + 2NO_3^- => 2NO_2^- + CO_2 + H_2O.$$
 (3)

After dissolved oxygen has been depleted, nitrate might function as an electron acceptor for anaerobic biodegradation of organic carbon by denitrification. The generally low concentrations of nitrate (less than 2.0 mg/L in nine of 11 samples) and nitrite (0.06 mg/L or less in all samples) (fig. 4; table 5) indicate that nitrate reduction probably is not a key process in either the shallow or deep zones of the Garber-Wellington aquifer.

 Table 4.
 Historical analytical results for selected volatile organic compounds from well-water samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department of Environmental Quality

[In micrograms per liter; --, not sampled; E, estimated; <, less than]

Date								Well	number						
sampled	BMW-1	BMW-2	BMW–3	BMW–3A	BMW-4	BMW–5	BMW-6A	BMW-7	BMWD-1	BMWD-2	BMWD–3	BMWD-4	BMWD–5	BMWD–6	BMWD–6A
								Benzene							
12/03/96	70	68	100		E3	190	110	<5	<5	52	89	<5	<5	<5	
)3/06/97	66	68	61		8	150	120	<5	<5	68	160	24	<5	<5	
6/01/97	83	73	64		<5	140	120	<5	13	21	120	89	<5	<5	
9/01/97	78	63	78		<5	220	110	<5	66	83	150	140	<5	<5	
2/01/97	58	61	61		<5	150	54	<5	64	37	35	68	<5	<5	
3/01/98	30	13	34		E2	72	74	<5		7	10	108	E2	<5	
6/01/98	60	66	62		6	130	75	<5	160	13	65	110	<5	<5	
9/01/98	74	86	85		<5	152	41	<5	158	17	161	63	26	<5	
6/10/99	69	51			<5	41	99	<5	150	5	93	168	50	<5	
0/04/99	24	64		110	<5	110	31	<5	130	13	18	100	23	<5	
2/07/99	23	44		120	<5	130	65	<5	140	<5	91	130	<5	<5	
4/14/00	91.4	50.5		121.2	<5	120	88	<5	132.8	17.9	144	43.8	8.33	<1	
9/27/00	46	44		36	<5	62	66	<5	120	23	97	80	33	<5	
03/05/01	18	9		41	<5	52	22	<5	130	11	61	120	<5	<5	
2/28/02	39	E45		E20	<5	E16	<250	<25	130	12	60	120	<5		<5
							<i>cis</i> -1	,2-Dichloroe	ethene						
12/03/96	10	21	14		<5	130	230	<5	<5	<5	15	<5	<5	<5	
)3/06/97	12	19	9		<5	100	250	<5	<5	7	19	<5	<5	<5	
6/01/97	17	26	13		<5	100	270	<5	26	5	18	6	<5	<5	
9/01/97	17	22	13		<5	120	230	<5	110	11	23	6	<5	<5	
2/01/97	36	24	11		<5	100	170	<5	120	7	11	<5	<5	<5	
3/01/98	29	10	11		<5	52	165	<5		4	8	5	<5	<5	
6/01/98	26	31	12		<5	100	230	<5	300	7	12	6	<5	<5	
9/01/98	30	38	21		<5	124	310	<5	274	8	24	4	<5	<5	
6/10/99	42	24			<5	35	420	<5	250	6	15	8	<5	<5	
0/04/99	65	30		39		96	730		230	10	5	5		<5	
2/07/99	59			51		100	590		240		16	6			
4/14/00				51		93		<1	215	13.01	23.13				
9/27/00	55	25		35		43	500		230	15	17	11			
3/05/01	60	15		36	<5	33	1,200	<5	230	11	13	13	<5	<5	
2/28/02	73	E34		41	<5	E19	1,700	<25	320	<5	E12	E18	<5		<5

Date								Well	number						
sampled	BMW-1	BMW-2	BMW–3	BMW–3A	BMW-4	BMW–5	BMW-6A	BMW-7	BMWD–1	BMWD-2	BMWD–3	BMWD-4	BMWD–5	BMWD–6	BMWD-64
							trans-	1,2-Dichlord	oethene						
2/03/96	<5	<5	<5		<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
3/06/97	<5	<5	<5		<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	
6/01/97	<5	<5	<5		<5	<5	<5	<5	<5	<5	E1	<5	<5	<5	
9/01/97	<5	<5	<5		<5	<5	E3	<5	<5	<5	E1	<5	<5	<5	
2/01/97	E1	<5	<5		<5	<5	E3	<5	<5	<5	<5	<5	<5	<5	
3/01/98	<5	<5	<5		<5	<5	E3	<5		<5	<5	<5	<5	<5	
6/01/98	<5	<5	<5		<5	<5	5	<5	<5	<5	<5	<5	<5	<5	
9/01/98	<5	<5	<5		<5	<5	12	<5	E2	<5	E2	<5	<5	<5	
6/10/99	E2	<5			<5	<5	14	<5	E3	<5	<5	<5	<5	<5	
0/04/99	<5	<5		<5	<5	7	26	<5	<5	<5	<5	<5	<5	<5	
2/07/99	<5	<5		<5	<5	7	<5	<5	<5	<5	<5	<5	<5	<5	
4/14/00	2.4	<5		<5	<5	<10	14	<1	<5	<1	<5	<5	<1	<1	
9/27/00	E2	E1		E1	<5	5	16	<5	E4	<5	E1	<5	<5	<5	
3/05/01	<5	<5		<5	<5	E3	39	<5	E4	<5	<5	<5	<5	<5	
2/28/02	<25	<50		<25	<5	<50	E66	<25	<50	<5	<50	<50	<5		<5
							Ti	richloroethe	ene						
2/03/96	<5	9	E2		<5	13	20	<5	<5	<5	E2	<5	<5	<5	
3/06/97	<5	7	<5		<5	7	19	<5	<5	<5	<5	<5	<5	<5	
6/01/97	<5	9	E1		<5	9	23	<5	E2	<5	E3	<5	<5	<5	
9/01/97	<5	8	E2		<5	15	28	<5	16	<5	E4	<5	<5	<5	
2/01/97	E2	9	<5		<5	8	27	<5	20	<5	E2	<5	<5	<5	
3/01/98	<5	E4	E2		<5	E4	36	<5		<5	E2	<5	<5	<5	
6/01/98	<5	9	<5		<5	9	74	<5	51	<5	<5	<5	<5	<5	
9/01/98	<5	13	E2		<5	11	270	<5	61	<5	E4	<5	<5	<5	
6/10/99	E2	8			<5	<5	450	<5	61	<5	E2	E1	<5	<5	
0/04/99	<5	11		<5	<5	10	1,300	7	70	<5	<5	<5	6	<5	
2/07/99	E4	10		5	<5	10	950	<5	80	<5	<5	<5	<5	<5	
4/14/00	2.5	7.6		5.85	<5	<10	589	<5	89	1.4	<4.46	<5	<1	<1	
9/27/00	E4	7		5	<5	E3	560	<5	76	<5	E4	<5	<5	<5	
3/05/01	5	E4		5	<5	<5	1,000	<5	99	<5	5	E3	<5	<5	
2/28/02	E5	<50		<25	<5	<50	850	<25	160	<5	<50	<50	<5		<5

 Table 4.
 Historical analytical results for selected volatile organic compounds from well-water samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department of Environmental Quality—Continued

10

Date		Well number													
sampled	BMW-1	BMW-2	BMW–3	BMW-3A	BMW-4	BMW–5	BMW-6A	BMW-7	BMWD-1	BMWD-2	BMWD–3	BMWD-4	BMWD-5	BMWD–6	BMWD–6A
	Vinyl chloride														
12/03/96	<10	27	<10		<10	120	35	<10	<10	<10	<10	<10	<10	<10	
03/06/97	<10	25	<10		<10	180	35	<10	<10	<10	<10	<10	<10	<10	
06/01/97	<10	40	<10		<10	220	68	<10	<10	<10	<10	<10	<10	<10	
09/01/97	<10	33	<10		<10	140	58	<10	E8	<10	<10	<10	<10	<10	
12/01/97	17	100	<10		<10	630	120	<10	21	E3	<10	<10	<10	<10	
03/01/98	E3	E7	<10		<10	87	28	<10		<10	<10	<10	<10	<10	
06/01/98	<10	39	<10		<10	150	39	<10	15	<10	<10	<10	<10	<10	
09/01/98	<10	47	E1		<10	146	49	<10	15	<10	<10	<10	<10	<10	
06/10/99	E4	35			<10	110	60	<10	26	<10	<10	<10	<10	<10	
10/04/99	14	35		<10	<10	120	35	<10	17	<10	<10	<10	<10	<10	
12/07/99	12	22		<10	<10	100	35	<10	20	<10	<10	<10	<10	<10	
04/14/00	7.2	28.4		<10	<10	161	48	<10	17.64	2	<10	<10	<2	<2	
09/27/00	12	26		E2	<10	93	33	<10	24	<10	<10	<10	<10	<10	
03/05/01	15	9		<10	<10	75	36	<10	24	<10	<10	<10	<10	<10	
02/28/02	E23	67		<50	<10	E10	E61	<50	E31	<10	<100	<100	<10		<10

 Table 4.
 Historical analytical results for selected volatile organic compounds from well-water samples at the Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the Oklahoma Department of Environmental Quality—Continued

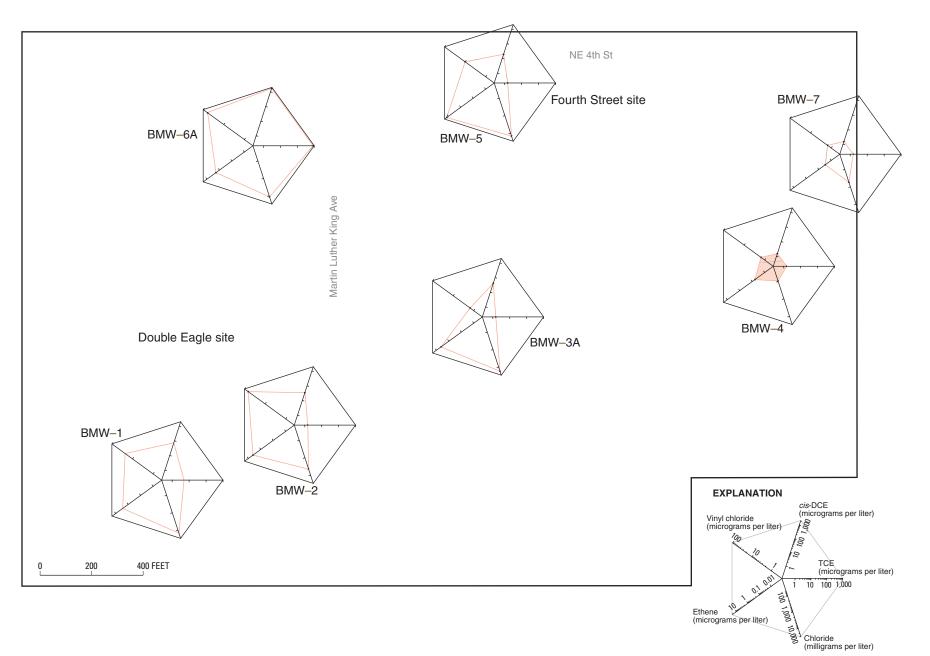
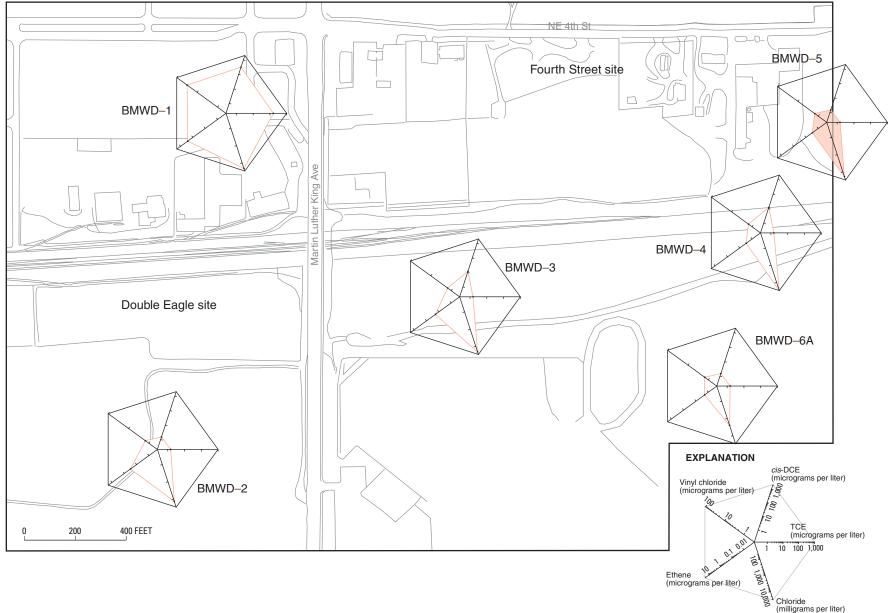


Figure 3a. Sequence diagrams showing concentrations of trichloroethene (TCE), *cis*-dichloroethene (*cis*-DCE), vinyl chloride, ethene, and chloride in the shallow zone of the Garber-Wellington aquifer, February 2002 (except ethene, December 2001).



Reductive Dechlorination of Chlorinated Ethenes Under Oxidation-Reduction Conditions

Figure 3b. Sequence diagrams showing concentrations of trichloroethene (TCE), cis-dichloroethene (cis-DCE), vinyl chloride, ethene, and chloride in the deep zone of the Garber-Wellington aquifer, February 2002.

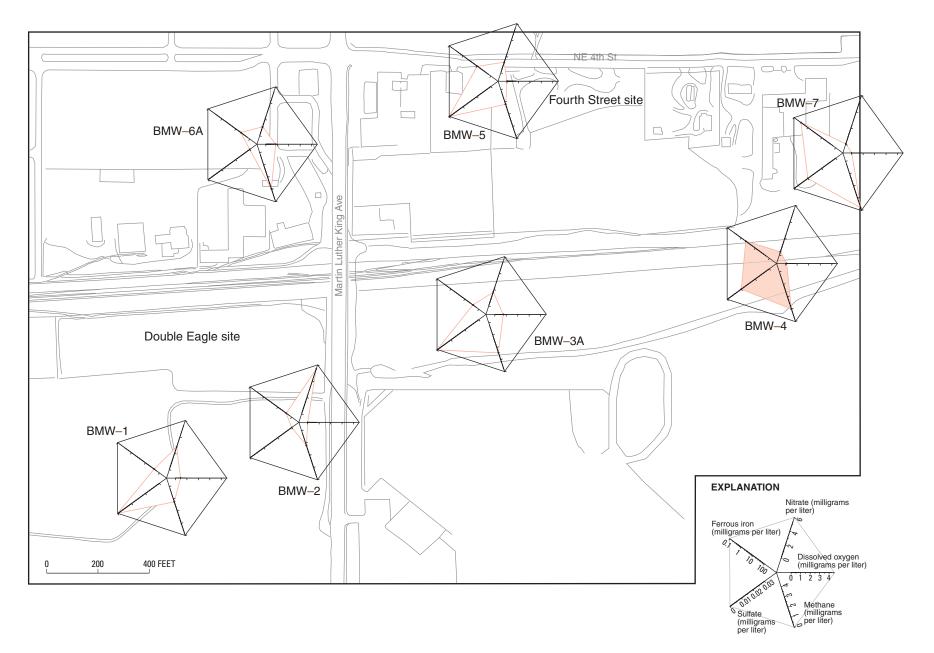


Figure 4a. Sequence diagrams showing concentrations of dissolved oxygen, nitrate, ferrous iron, sulfate, and methane in the shallow zone of the Garber-Wellington aquifer, December 2001.

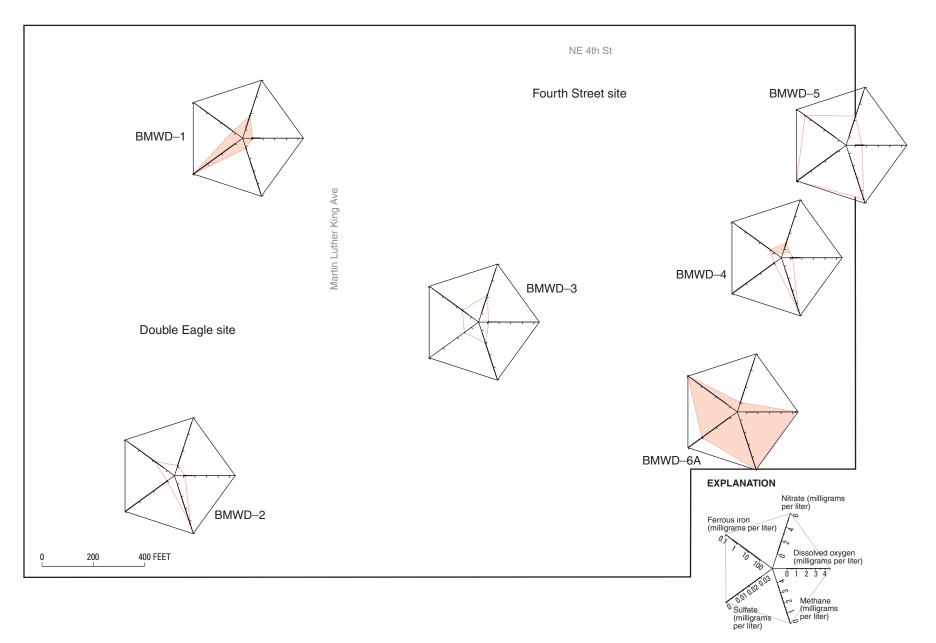


Figure 4b. Sequence diagrams showing concentrations of dissolved oxygen, nitrate, ferrous iron, sulfate, and methane in the deep zone of the Garber-Wellington aquifer, February–March 2002.

16 Reductive Dechlorination and Potentiometric Surfaces at Two Superfund Sites, Oklahoma City, Oklahoma

 Table 5.
 Analytical results for selected properties and inorganic constituents from well-water samples at the Double Eagle Refining

 Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the U.S. Geological

 Survey, December 2001 and February–March 2002

 $[\mu$ S/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; °C, degrees Celsius; ~, value is approximate (one or more dilutions were performed, thereby decreasing the reliability of the result); --, not analyzed; >, greater than]

Aquifer zone and well number (fig. 2)	Date sampled	Specific conduc- tance (µS/cm)	pH (standard units)	Alkalinity (mg/L as bicar- bonate)	Tem- per- ature (°C)	Dis- solved oxygen (mg/L)	Nitrate nitro- gen (mg/L)	Nitrite nitro- gen (mg/L)	Fer- rous iron (mg/L)	Total iron (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)
Shallow												
BMW-1	12/20/01	39,400	6.28	1,014	14.8	0.45	$^{1}2.8$	0	~42.2	~45.8	~1,600	0
BMW-2	12/19/01	14,900	6.41		14.1	0	¹ >5.5	0	~41.4	~43.2	~1,020	.03
BMW-3A	12/18/01	67,900	6.32	682.0	18.3	.75	1.7	0	² ~39.0	~36.0	~630	0
BMW-4	12/18/01	16,900	7.21	618.4	18.9	.10	.4	.020	2.09	3.08	~88.0	.01
BMW-5	12/19/01	66,300	6.56	829.6	17.4	.01	1.3	.010	~10.6	~18.1	~270	0
BMW-6A	12/20/01	38,000	6.57	609.6	12.9	.87	1.1	0	~22.7	~33.0	~330	.03
BMW-7	12/19/01	3,700	7.46	661.6	14.1	0	.1	.015	.32	.85	>80.0	.01
Deep												
BMWD-1	03/01/02	83,600	6.17	976.0	13.0	.07	$^{1}1.7$	0	~71.7	~72.3	~460	0
BMWD-2	03/01/02	37,200	6.41	680.0	13.9	.15	.3	.010	~13.0	~13.3	~380	.03
BMWD-3	03/01/02	162,000	5.81	348.0	12.8	.07	2.2	0	² ~23.5	~23.4	~140	0
BMWD-4	02/28/02	79,500	6.16	732.0	16.5	.20	.7	.040	~49.3	~51.5	~250	.03
BMWD-5	12/19/01	111,000	6.23	199.6	15.1	.10	1.8	.025	² 2.81	.66	~112	0
BMWD-5	02/22/02	114,000	5.98	205.2	13.7	.60	2.5	.025	.41	.47	~110	0
BMWD-6A	02/27/02	3,360	6.98	572.0	11.0	4.3	.2	.060	0	.04	45.0	.01

¹Nitrate sample was cloudy and showed little or no coloration, indicating an erroneously high result.

² Ferrous iron sample was cloudy, indicating an erroneously high result.

Ferrous Iron and Total Iron

Ferric iron (Fe^{+3}) is reduced to ferrous iron (Fe^{+2}) (table 5) by the reaction

$$CH_2O + 4Fe(OH)_3 + 7H^+ => 4Fe^{+2} + HCO_3^- + 10H_2O.$$
 (4)

Because of this process, an increase in ferrous iron concentration is expected where ferric iron reduction is occurring. Concentrations greater than about 1.00 mg/L indicate that iron reduction is probable (U.S. Environmental Protection Agency, 1999). Ferrous iron concentrations exceeded 1.00 mg/L in the majority of wells sampled. Concentrations were greater than 10 mg/L in samples from nine of the 13 wells.

Sulfate and Sulfide

Sulfate (SO₄) is reduced to sulfide (HS⁻) (table 5) during sulfate reduction as follows:

$$2CH_2O + SO_4^{-2} => HCO_3^{-2} + HS^{-} + CO_2 + H_2O.$$
 (5)

Because of this process, an increase in sulfide concentrations is expected where sulfate reduction is occurring. The low concentrations of sulfide (less than 0.05 mg/L in samples from all wells) (fig. 4; table 5), despite available sulfate (45.0 to about 1,600 mg/L in samples from wells) (table 5), indicate that sulfate reduction probably is not a key process in either zone of the Garber-Wellington aquifer.

Methane

During methanogenesis, either carbon dioxide (CO_2) is an electron acceptor and is reduced to methane (CH_4) (table 6) in the reaction

$$CO_2 + 4H_2 => CH_4 + 2H_2O,$$
 (6)

or acetic acid (CH₃COOH) is split to form carbon dioxide and methane in the reaction

$$CH_3COOH \Longrightarrow CH_4 + CO_2. \tag{7}$$

 Table 6.
 Analytical results for carbon dioxide, methane, ethane, and ethene from well-water samples at the Double Eagle Refining

 Superfund site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, collected by the U.S. Geological

 Survey, December 2001 and February–March 2002

Aquifer zone	Date	U.S. Geological	Survey analyses	Microseeps, Inc., analyses				
and well number (fig. 2)	sampled	Carbon dioxide	Methane	Methane	Ethane	Ethene		
Shallow								
BMW-1	12/20/01	615.9	2.75	2.63	0.07	< 0.01		
BMW-2	12/19/01	650.8	2.81	1.29	.02	<.01		
BMW-3A	12/18/01	348.8	1.56	1.03	.03	.02		
BMW-4	12/18/01	54.38	1.01	.69	<.01	<.01		
BMW-5	12/19/01	243.6	2.80	.98	.09	.01		
BMW-6A	12/20/01	126.9	1.04	1.48	.02	<.01		
BMW-7	12/19/01	46.99	.19	.11	<.01	<.01		
Deep								
BMWD-1	03/01/02	274.9	3.86	2.35	.03	<.01		
BMWD-2	03/01/02	130.8	.78	.32	.02	<.01		
BMWD-3	03/01/02	129.0	2.94	.65	.04	<.01		
BMWD-4	02/28/02	172.6	.45	.24	.03	<.01		
BMWD-5	12/19/01	73.59	.38					
BMWD-5	02/28/02	79.46	.32	.27	.02	<.01		
BMWD-6A	02/27/02	19.76	0	0	<.01	<.01		

[In milligrams per liter; <, less than; --, not analyzed]

Methanogenesis usually does not occur until DO, nitrate, and sulfate have been depleted (U.S. Environmental Protection Agency, 1999). The presence of methane in ground water is an indication of strongly reducing conditions that facilitate reductive dechlorination. Methane was detected in samples from all but one well (BMWD–6A) in USGS field analysis and Microseeps, Inc., laboratory analysis.

Potentiometric Surfaces

Salinity of ground water in the study area is large enough so that the water is of variable density. Thus measured heads in the wells (formation water heads) are lower than equivalent freshwater heads, and the difference between formation water head and freshwater head increases as density increases. Because the purpose of constructing potentiometric surfaces of the shallow and deep zones was to obtain directions of horizontal flow, and freshwater heads define horizontal hydraulic gradients, equivalent freshwater heads were used to construct the potentiometric surfaces. Equivalent freshwater heads were computed from measured pressure at the bottom of the screened interval of each well and the specific weight of freshwater at the prevailing ground-water temperature by applying the equation

$$h_f = p/\gamma_f, \tag{8}$$

- h_f = equivalent freshwater head above bottom of screened interval, in feet,
- p = pressure at the bottom of screened interval, in pounds per square inch, and

 $\gamma_{\rm f} = 0.4329$, the specific weight of freshwater at 65 degrees Fahrenheit, in pounds per square inch per foot.

The measured and computed data from wells used to construct the potentiometric surfaces are listed in table 7.

The potentiometric surface of the shallow zone of the Garber-Wellington aquifer (fig. 5) shows lines of equal freshwater head that range from 1,159 feet above NGVD 29 in the northeastern part of the study area to 1,152 feet above NGVD 29 in the northwestern part. In the eastern part of the study area, the lines indicate that ground water flowing from the north and south coalesces in a potentiometric trough, then moves westward and ultimately northwestward. In the western part of the study area, the lines indicate that ground water flows northwestward.

The potentiometric surface of the deep zone of the aquifer (fig. 6) shows lines of equal freshwater head that range from about 1,121 feet above NGVD 29 in the southeastern part of the study area to about 1,114 feet above NGVD 29 in the northwestern part. In the eastern part of the study area, the lines indicate that ground water generally flows northwestward; and in the western part of the study area, the lines indicate that ground water generally flows northward.

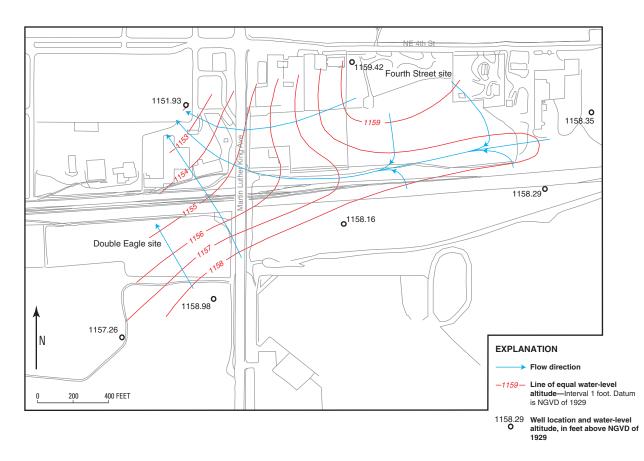


Figure 5. Potentiometric surface and flow directions in the shallow zone of the Garber-Wellington aquifer, Double Eagle Refining Superfund site and Fourth Street Abandoned Refinery Superfund site, December 2001.

Table 7. Measured and computed data from wells used to construct potentiometric surfaces at the Double Eagle Refining Superfund

 site and the Fourth Street Abandoned Refinery Superfund site, Oklahoma City, Oklahoma, December 2001 and February 2002

Aquifer zone and well number (fig. 2)	Date measured	Altitude of TOC (feet above NGVD 29)	Depth to water (feet below TOC)	Altitude of formation- water head (feet above NGVD 29)	Depth to pressure transducer ¹ (feet below TOC)	Altitude of pressure transducer (feet above NGVD 29)	Formation- water head (feet above pressure transducer)	Meas- ured pressure (lbs/in ²)	Equivalent freshwater head (feet above pressure transducer)	Altitude of equivalent freshwater head (feet above NGVD 29)
Shallow										
BMW-1	12/17/01	1,173.55	18.98	1,154.57	71.05	1,102.50	52.07	23.705	54.76	1,157.26
BMW-2	12/17/01	1,168.58	10.51	1,158.07	43.70	1,124.88	33.19	14.763	34.10	1,158.98
BMW-3A	12/17/01	1,171.97	16.87	1,155.10	61.80	1,110.17	44.93	20.774	47.99	1,158.16
BMW-4	12/17/01	1,171.88	14.46	1,157.42	47.10	1,124.78	32.64	14.505	33.51	1,158.29
BMW-5	12/17/01	1,170.41	12.87	1,157.54	47.31	1,123.10	34.44	15.723	36.32	1,159.42
BMW–6A	12/17/01	1,174.06	23.88	1,150.18	71.80	1,102.26	47.92	21.500	49.67	1,151.93
BMW-7	12/17/01	1,169.30	11.67	1,157.63	45.30	1,124.00	33.63	14.872	34.35	1,158.35
Deep										
BMWD-1	02/25/02	1,174.02	66.5	1,107.52	150.0	1,024.02	83.50	38.840	89.72	1,113.74
BMWD-2	02/25/02	1,178.11	65.15	1,112.96	145.0	1,033.11	79.85	36.128	83.46	1,116.57
BMWD-3	02/25/02	1,171.16	61.93	1,109.23	157	1,014.16	95.07	43.556	100.61	1,114.77
BMWD-4	02/25/02	1,172.29	64.37	1,107.92	150.0	1,022.29	85.63	41.303	95.41	1,117.70
BMWD-5	02/25/02	1,168.69	58.26	1,110.43	150.0	1,018.69	91.74	42.173	97.42	1,116.11
BMWD-6A	02/25/02	1,175.33	55.77	1,119.56	145.9	1,029.43	90.13	39.977	92.35	1,121.78

¹ Transducer positioned as close as possible to bottom of screened interval.

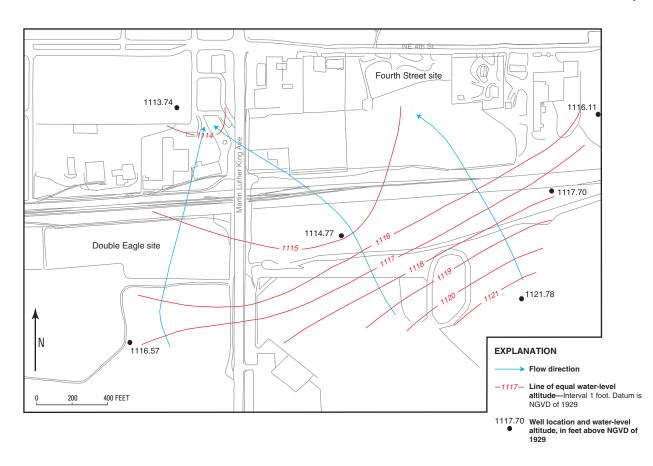


Figure 6. Potentiometric surface and flow directions in the deep zone of the Garber-Wellington aquifer, Double Eagle Refining Superfund site and Fourth Street Abandoned Refinery Superfund site, February 2002.

Summary

The Double Eagle Refining Superfund site and the Fourth Street Abandoned Refinery Superfund site are in northeast Oklahoma City, Okla., adjacent to one another. The Double Eagle facility became a Superfund site on the basis of contamination from lead and volatile organic compounds (VOCs); the Fourth Street facility became a Superfund site on the basis of VOCs, pesticides, and acid-base neutral compounds. The study documented in this report, supported by an interagency agreement between the U.S. Geological Survey and the U.S. Environmental Protection Agency, was done to investigate whether reductive dechlorination of chlorinated ethenes under redox conditions is occurring in two zones of the Garber-Wellington aquifer (shallow zone 30-60 to 75 feet below land surface, deep zone 75 to 160 feet below land surface) at the sites; and to construct potentiometric surfaces of the two water-yielding zones in the aquifer to determine the directions of ground-water flow at the sites. The assessment of reductive dechlorination was made using data from 13 water samples from 13 wells (seven in the shallow zone, six in the deep zone). Water-quality data for this study were collected and analyzed by the U.S. Geological Survey and the Oklahoma Department of Environmental

Quality or their contractor in December 2001 and February-March 2002. Because salinity of ground water at the sites is large enough so that the water is of variable density, the potentiometric surfaces were constructed from measured pressures (converted to hydraulic heads) at the bottoms of the 13 wells.

The presence in some wells of intermediate products of reductive dechlorination, dichloroethene and vinyl chloride, is an indication that reductive dechlorination of trichloroethene is occurring. Dissolved oxygen concentrations were in the anaerobic range (less than 0.50 mg/L) in the majority of wells sampled, an indication that consumption of dissolved oxygen likely had occurred in the oxygen-reducing microbial process associated with reductive dechlorination. Low concentrations of both nitrate and nitrite nitrogen (generally less than 2.0 and 0.06 mg/L, respectively, in samples) indicate that nitrate reduction probably is not a key process in either the shallow or deep zones of the Garber-Wellington aquifer. Concentrations of ferrous iron greater than 1.00 mg/L in the majority of wells sampled indicate that iron reduction is probable. Low concentrations of sulfide (less than 0.05 mg/L in samples from all wells) indicate that sulfate reduction probably is not a key process in either zone. The presence of methane in ground water is an indication of strongly reducing conditions that facilitate reductive

20 Reductive Dechlorination and Potentiometric Surfaces at Two Superfund Sites, Oklahoma City, Oklahoma

dechlorination. Methane was detected in samples from all but one well.

The potentiometric surface of the shallow zone of the Garber-Wellington aquifer shows that in the eastern part of the study area, ground water flowing from the north and south coalesces in a potentiometric trough, then moves westward and ultimately northwestward. In the western part of the study area, ground water flows northwestward.

The potentiometric surface of the deep zone of the aquifer shows that in the eastern part of the study area, ground water generally flows northwestward; and in the western part of the study area, ground water generally flows northward.

References Cited

- American Public Health Association, 1992, Standard methods for the examination of water and wastewater including bottom sediments and sludges: New York, American Public Health Association, American Water Works Association, Water Pollution Control Federation [jointly published].
- Bradley, P.M., and Chapelle, F.H., 1998, Microbial mineralization of VC and DCE under different terminal electron accepting conditions: Anaerobe, v. 4, p. 81–87.
- Carr, J.E., and Marcher, M.V., 1977, A preliminary appraisal of the Garber-Wellington aquifer, southern Logan and northern Oklahoma Counties, Oklahoma: U.S. Geological Survey Open-File Report 77–278, 23 p.
- Chapelle, F.H., 1996, Identifying redox conditions that favor the natural attenuation of chlorinated ethenes in contaminated ground-water systems, *in* Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, Dallas, Tex., 1996, Proceedings: U.S. Environmental Protection Agency, EPA/540/R–96–509, p. 17–20.

- Ecology and Environment, Inc., 1988, Final report for expanded site investigation, Double Eagle Refinery site: Lancaster, N.Y., contractor report submitted to U.S. Environmental Protection Agency, Region 6, [variously paged].
- Fluor Daniel, Inc., 1993, Groundwater operable unit final remedial investigation report Double Eagle superfund site WA #31–6LB1: Aliso Viejo, Calif., contractor report submitted to U.S. Environmental Protection Agency, Region 6, [variously paged].

Gilbert, T.W., Behymer, T.D., and Castaneda, H.B., 1982, Determination of dissolved oxygen in natural and wastewaters: American Laboratory, American Society for Testing and Materials ASTM D 888-87, p. 119–134.

HACH Co., 1989, Water analysis handbook: Loveland, Colo., 691 p.

Suarez, M.P., and Rifai, H.S., 1999, Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater: Bioremediation Journal, v. 3, no. 4, p. 337–362.

- U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Washington, D.C., Office of Research and Development, EPA/600/4–79–020.
- U.S. Environmental Protection Agency, 1999, The technical protocol for evaluating natural attenuation of chlorinated solvents in ground water: Cincinnati, Ohio, Office of Research and Development, EPA/600/R–98/128, [variously paged].
- U.S. Environmental Protection Agency, 2001a, Double Eagle Refinery Company Oklahoma EPA ID# OKD007188717: Dallas, U.S. Environmental Protection Agency, Region 6, 7 p.
- U.S. Environmental Protection Agency, 2001b, Fourth Street abandoned refinery Oklahoma EPA ID# OKD980696470: Dallas, U.S. Environmental Protection Agency, Region 6, 6 p.