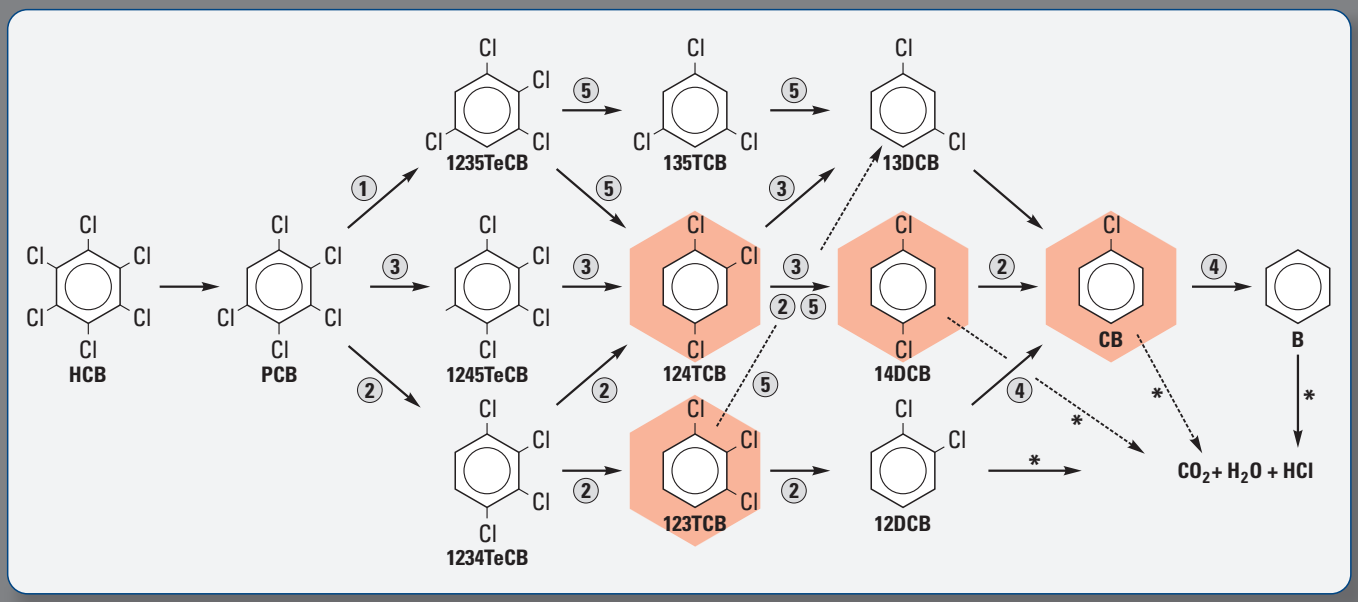
Prepared in cooperation with the
U.S. Environmental Protection Agency

Hydrogeologic Characterization and Assessment of Bioremediation of Chlorinated Benzenes and Benzene in Wetland Areas, Standard Chlorine of Delaware, Inc. Superfund Site, New Castle County, Delaware, 2009–12



Scientific Investigations Report 2014–5140

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

Cover. Diagram showing possible degradation pathways for chlorobenzenes. Refer to figure 2 for explanation.

Hydrogeologic Characterization and Assessment of Bioremediation of Chlorinated Benzenes and Benzene in Wetland Areas, Standard Chlorine of Delaware, Inc. Superfund Site, New Castle County, Delaware, 2009–12

By Michelle M. Lorah, Charles W. Walker, Anna C. Baker, Jessica A. Teunis, Emily H. Majcher, Michael J. Brayton, Jeff P. Raffensperger, and Isabelle M. Cozzarelli

Prepared in cooperation with the
U.S. Environmental Protection Agency

Scientific Investigations Report 2014–5140

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit http://www.usgs.gov or call 1-888-ASK-USGS

For an overview of USGS information products, including maps, imagery, and publications, visit http://www.usgs.gov/pubprod

To order this and other USGS information products, visit http://store.usgs.gov

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

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

Suggested citation:
Lorah, M.M., Walker, C.W., Baker, A.C., Teunis, J.A., Majcher, E.H., Brayton, M.J., Raffensperger, J.P., and Cozzarelli, I.M, 2014, Hydrogeologic characterization and assessment of bioremediation of chlorinated benzenes and benzene in wetland areas, Standard Chlorine of Delaware, Inc. Superfund Site, New Castle County, Delaware, 2009–12: U.S. Geological Survey Scientific Investigations Report 2014–5140, 89 p., *http://dx.doi.org/10.3133/sir20145140*.

ISSN 2328-031X (print)
ISSN 2328-0328 (online)
ISBN 978-1-4113-3848-7

Contents

Abstract 1
Introduction 2
Purpose and Scope 4
Description of Study Area 4
Regional and Site Hydrogeologic Setting 5
Summary of Contamination Extent and Wetland Remedial Alternatives 6
Background on Degradation Pathways 7
Methods of Data Collection and Analysis 8
Monitoring Network 8
Hydrogeologic Data 11
Water-Level Measurements 16
Slug Tests 16
Calculations of Hydraulic Gradient, Specific Discharge, and Linear Velocity 17
Groundwater and Surface-Water Geochemical Data 18
Sample Collection 18
Chemical Analysis 19
Data Quality 20
Experiments to Assess Bioremediation 21
In Situ Microcosms 21
Laboratory Bioreactors 22
Hydrogeologic Characterization 24
Lithology of the Study Area 25
Groundwater Hydraulic-Head Distribution and Flow Direction 26
Hydraulic Conductivity 31
Groundwater Discharge and Velocity 31
Effect of Tidal Fluctuation in Red Lion Creek 35
Groundwater Discharge to Red Lion Creek 36
Geochemical Characterization 38
Distribution of Volatile Organic Compounds 38
Spatial Distribution 38
Temporal Distribution 42
Distribution of Redox-Sensitive and Other Geochemical Constituents 43
Spatial Distribution 43
Temporal Distribution 47
Dense Non-Aqueous Phase Liquid (DNAPL) Extent 50
Previous Dense Non-Aqueous Phase Liquid (DNAPL) Investigations 50
Updated Dense Non-Aqueous Phase Liquid (DNAPL) Site Conceptual Model 52
Columbia and Potomac Aquifers 53
Wetland Porewater 54
Source Assessment for Wetland Study Area 55
Columbia Aquifer and Overland Spills as Sources of Contamination 55
Sediment as a Source of Contamination 58
Natural and Enhanced Biodegradation of Chlorinated Benzenes and Benzene 59
Evidence from Field Sampling Results 59
In Situ Microcosms 62
Microbial Communities in the Wetland Sediment 66
Laboratory Bioreactor Experiments 69
Summary and Conclusions 82
Acknowledgments 83
References Cited 84

Figures

1. Maps showing location of Standard Chlorine of Delaware, Inc. Superfund Site (SCD), New Castle County, Delaware 3
2. Diagram showing possible degradation pathways for chlorobenzenes 9
3. Maps showing *(A)* monitoring network and locations of hydrogeologic sections in the wetland study area, and *(B)* sampling locations in the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 10
4. Schematic diagram of Bio-Trap (Microbial Insights, Rockford, Tennessee) sampler used for *in situ* microcosms 21
5. Diagram of the anaerobic bioreactor system and sampling locations 24
6. Cross section showing hydrogeology and locations of monitoring wells and drive-point piezometers along section A–A′, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 26
7. Cross section showing hydrogeology and locations of monitoring wells and drive-point piezometers along section B–B′, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 27
8. Map showing groundwater altitude (in meters above mean sea level) in the Columbia aquifer, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 28
9. Map showing groundwater altitude (in meters above mean sea level) in the wetland sediments, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 29
10. Graph showing water-level altitudes of Red Lion Creek and selected drive-point piezometers and daily total precipitation, July 2008–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 30
11. Cross section showing head distributions and groundwater-flow direction in section A–A′, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 32
12. Cross section showing head distributions and groundwater-flow direction in section B–B′, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 33
13. Hydrograph showing water-level altitudes at selected wetland-aquifer pairs and other drive-point piezometers screened in the Columbia aquifer, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 35
14. Map showing location of Red Lion Creek watershed, U.S. Geological Survey streamgage 01482298 (Red Lion Creek near Red Lion, Delaware), U.S. Geological Survey stage gage 01482320 at River Road Bridge, and the watersheds used to estimate discharge to tidal Red Lion Creek 37
15. Maps showing distribution of volatile organic compounds from passive diffusion bags deployed in the wetland sediments in the study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, *(A)* March 2011, and *(B)* October–December 2011 39
16. Graphs showing molar composition of volatile organic compounds and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) in passive diffusion bag samples collected from the northwest and northeast wetland areas during *(A, B)* March 2011, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 41
17. Graphs showing vertical distributions of volatile organic compounds (VOCs) from peepers in the northwest and northeast wetland areas *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 42

18. Graphs showing temporal changes in molar composition of volatile organic compounds and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) at site 8 in the northwest wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 43
19. Graphs showing temporal changes in molar composition of volatile organic compounds and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) at site 6 in the northeast wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, October 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 44
20. Boxplots showing distributions of pH in the wetland study area *(A)* March 2011, and *(B)* October–December 2011 synoptic sampling results, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware....45
21. Graphs showing distributions of chloride, sulfate, ammonia, sulfide, methane, and ferrous iron in passive diffusion bag (PDB) samples of wetland groundwater collected in the nothwest and northeast areas in *(A, B)* March 2011, and *(C, D)* October 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 46
22. Graphs showing spatial distribution of nonvolatile dissolved organic carbon (NVDOC) in passive diffusion bag (PDB) samples of the wetland groundwater collected in *(A)* northwest, and *(B)* northeast wetland areas in October 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 47
23. Graphs showing vertical distributions of chloride concentrations in peepers from the northwest and northeast wetland areas in *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 48
24. Graphs showing vertical distributions of sulfate concentrations in peepers from the northwest and northeast wetland areas in *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 49
25. Graphs showing temporal changes in *(A)* chloride and *(B)* sulfate for selected sites in the wetland study area, July 2009–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 50
26. Graphs showing temporal changes in concentrations of chloride and redox-sensitive constituents at site 8 in the northwest wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 51
27. Graphs showing temporal changes in concentrations of chloride and redox-sensitive constituents at site 6 in the northeast wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 52
28. Graph showing reduction in total volatile organic compound concentrations in monitoring wells along the wetland-upland boundary after the installation of the barrier wall, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 53
29. Map showing potential current (2012) distribution of dense non-aqueous phase liquids (DNAPLs) in the Columbia aquifer, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 54

30. Map showing potential current (2012) distribution of dense non-aqueous phase liquids (DNAPLs) in the wetland porewater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, on the basis of computed concentrations that exceed 1 percent of the compound's solubility 55
31. Graphs showing comparison of molar composition (in percent) of water samples from aquifer monitoring wells in *(A)* 1993 and 2004, and *(B)* 2004 and 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 56
32. Graph showing comparison of molar composition (in percent) in the Columbia aquifer immediately below the wetland sediments and wetland porewater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, 2012 57
33. Graph showing comparison of volatile organic compound molar ratios (micromolar/micromolar) in the Columbia aquifer and wetland porewater for the 1986 spill compounds (1,4-dichlorobenzene/1,2,4-trichlorobenzene+ 1,2,3-trichlorobenzene), Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, 2012 58
34. Graphs showing comparison of *(A)* molar composition (in percent) and *(B)* molar ratios (micromolar/micromolar) in the Columbia and Potomac aquifers, using average concentrations from 2011–12, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 59
35. Graphs showing *(A)* molar composition of volatile organic compounds (VOCs), and *(B)* concentrations of redox-sensitive constituents in standard *in situ* microcosms (MNA, monitored natural attenuation treatment; Lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009 63
36. Graph showing molar composition of volatile organic compounds (VOCs) in standard *in situ* microcosms (MNA, monitored natural attenuation treatment; Lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at four sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010 63
37. Graphs showing *(A)* removal of ^{13}C-chlorobenzene, *(B)* incorporation of ^{13}C in dissolved inorganic carbon (DIC) and phospholipid fatty acid (PLFA) biomass, and *(C)* enrichment of ^{13}C in the PLFA biomass in the ^{13}C-chlorobenzene amended *in situ* microcosms (MNA, monitored natural attenuation; WBC-2, bioaugmented treatment) deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009 64
38. Graphs showing *(A)* incorporation of ^{13}C in dissolved inorganic carbon (DIC) and phospholipid fatty acid (PLFA) biomass, and *(B)* enrichment of ^{13}C in the PLFA biomass in the ^{13}C-chlorobenzene amended *in situ* microcosms (MNA, monitored natural attenuation; Lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at three sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010 65
39. Graph showing microbial populations determined by quantitative polymerase chain reaction (qPCR) analysis of wetland sediment collected at sites DP-9 and DP-6 and in the control (MNA, monitored natural attenuation) *in situ* microcosm deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009 68

40. Graph showing microbial community composition determined from analysis of the chemical structures of phospholipid fatty acid (PLFA) in wetland sediment collected at sites DP-9 and DP-6 and in the control (MNA, monitored natural attenuation) *in situ* microcosm deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009 68
41. Graphs showing amount of *(A)* total Eubacteria, and *(B) Dehalococcoides* species determined by quantitative polymerase chain reaction (qPCR) analysis of samples from standard and monochlorobenzene (^{13}C-CB) or 1,4-dichlorobenzene (^{13}C-DCB) *in situ* microcosms (MNA, monitored natural attenuation treatment; Lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at four sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010 70
42. Concentrations of total chlorobenzene compounds and benzene (total CBs+benzene), naturally input from the wetland groundwater, and amended 1,1,2,2-tetrachloroethane (TeCA) and its anaerobic daughter products in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture 71
43. Graphs showing pH measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture 72
44. Graphs showing oxidation-reduction potentials (ORPs) in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture 73
45. Graphs showing sulfate concentrations measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture 74
46. Sulfate and methane concentrations measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture 75
47. Boxplots showing percent removals of *(A)* 1,2,3-trichlorobenzene (123TCB), *(B)* 1,2,4-trichlorobenzene (124TCB), *(C)* 1,4-dichlorobenzene (14DCB), *(D)* 1,3-dichlorobenzene (13DCB), *(E)* 1,2-dichlorobenzene (12DCB), *(F)* chlorobenzene, and *(G)* benzene that were calculated from inflow and outflow concentrations under anaerobic and aerobic conditions in bioreactors C, D, and E 77
48. Boxplots showing hydraulic residence time in bioreactors C, D, and E 78
49. Graphs showing concentrations of chlorobenzene compounds and benzene measured under anaerobic conditions (except in bioreactor C on August 13, 2012) at sampling ports along flowpaths through bioreactors C, D, and E on selected sampling dates 79

Tables

1. Summary of significant fate and transport properties of contaminants in wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 8
2. Monitoring network for the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 12
3. Groundwater sampling and site events that may have influenced sampling results in the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 15
4. *In situ* microcosm treatments deployed from October 20–December 16, 2009 and from October 26–December 14, 2010 at selected wetland sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 22
5. Description of phospholipid fatty acid (PLFA) structural groups that are used to describe microbial community composition on the basis of fatty acid biosynthesis 23
6. Calculated vertical gradients from selected drive-point piezometer pairs in the Columbia aquifer and wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 31
7. Maximum and minimum estimates of hydraulic conductivity calculated from slug tests conducted at selected drive-point piezometers in the Columbia aquifer and wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 34
8. Variation in vertical specific discharge and linear velocity of groundwater from the Columbia aquifer through wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 34
9. Spatial variation in lateral groundwater specific discharge and linear velocity of groundwater at Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 34
10. Area and measured or estimated annual mean discharge for subwatersheds in the Red Lion Creek watershed, and estimated groundwater discharge to tidal Red Lion Creek 38
11. Concentrations of selected inorganic constituents measured in groundwater samples collected with passive diffusion bags from upland monitoring wells, October 2011 49
12. Concentrations of chloride and sulfate measured in 2008 in drive-point piezometers screened in the Columbia aquifer near the upland-wetland boundary east of the Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 50
13. Traveltime of selected site contaminants in groundwater along a flowpath 57
14. Comparison of calculated and measured porewater volatile organic compound concentrations 60
15. Concentrations of redox-sensitive constituents and volatile fatty acids measured in samples from *in situ* microcosms deployed from October 20–December 16, 2009 and from October 26–December 14, 2010 at selected wetland sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware 66
16. Amount of ^{13}C incorporation into phospholipid fatty acid (PLFA) biomass and dissolved inorganic carbon (DIC) measured in *in situ* microcosms that were preloaded with ^{13}C-labeled 1,4-dichlorobenzene or benzene and deployed from October 26–December 14, 2010 at selected wetland sites 67
17. Summary of microbial species identified using denaturing gradient gel electrophoresis (DGGE) analysis of samplers from the monitored natural attenuation (MNA) and lactate/chitin biostimulated treatments of *in situ* microcosms deployed from October–December 2010 69

Conversion Factors and Datums

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
	Area	
square meter (m^2)	0.0002471	acre
square kilometer (km^2)	247.1	acre
square meter (m^2)	10.76	square foot (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
cubic kilometer (km^3)	0.2399	cubic mile (mi^3)
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
	Flow rate	
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)
cubic meter per year (m^3/yr)	0.000811	acre-foot per year (acre-ft/yr)
meter per second (m/s)	3.281	foot per second (ft/s)
meter per minute (m/min)	3.281	foot per minute (ft/min)
meter per hour (m/hr)	3.281	foot per hour (ft/hr)
meter per day (m/d)	3.281	foot per day (ft/d)
meter per year (m/yr)	3.281	foot per year ft/yr)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
cubic meter per day (m^3/d)	35.31	cubic foot per day (ft^3/d)
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m^3/d)	264.2	gallon per day (gal/d)
cubic meter per day per square kilometer [(m^3/d)/km^2]	684.28	gallon per day per square mile [(gal/d)/mi^2]
cubic meter per second (m^3/s)	22.83	million gallons per day (Mgal/d)
cubic meter per day per square kilometer [(m^3/d)/km^2]	0.0006844	million gallons per day per square mile [(Mgal/d)/mi^2]
cubic meter per hour (m^3/h)	39.37	inch per hour (in/h)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
	Pressure	
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
kilopascal (kPa)	0.01	bar
kilopascal (kPa)	0.2961	inch of mercury at 60 °F (in Hg)
kilopascal (kPa)	0.1450	pound-force per inch (lbf/in)
kilopascal (kPa)	20.88	pound per square foot (lb/ft^2)
kilopascal (kPa)	0.1450	pound per square inch (lb/ft^2)

Multiply	By	To obtain
	Density	
kilogram per cubic meter (kg/m^3)	0.06242	pound per cubic foot (lb/ft^3)
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
	Hydraulic conductivity	
meter per day (m/d)	3.281	foot per day (ft/d)
	Hydraulic gradient	
meter per kilometer (m/km)	5.27983	foot per mile (ft/mi)
	Transmissivity	
meter squared per day (m^2/d)	10.76	foot squared per day (ft^2/d)

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

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

Hydrogeologic Characterization and Assessment of Bioremediation of Chlorinated Benzenes and Benzene in Wetland Areas, Standard Chlorine of Delaware, Inc. Superfund Site, New Castle County, Delaware, 2009–12

By Michelle M. Lorah[1], Charles W. Walker[1], Anna C. Baker[1], Jessica A. Teunis[1], Emily H. Majcher[2], Michael J. Brayton[1], Jeff P. Raffensperger[1], and Isabelle M. Cozzarelli[1]

Abstract

Wetlands at the Standard Chlorine of Delaware, Inc. Superfund Site (SCD) in New Castle County, Delaware, are affected by contamination with chlorobenzenes and benzene from past waste storage and disposal, spills, leaks, and contaminated groundwater discharge. In cooperation with the U.S. Environmental Protection Agency, the U.S. Geological Survey began an investigation in June 2009 to characterize the hydrogeology and geochemistry in the wetlands and assess the feasibility of monitored natural attenuation and enhanced bioremediation as remedial strategies. Groundwater flow in the wetland study area is predominantly vertically upward in the wetland sediments and the underlying aquifer, and groundwater discharge accounts for a minimum of 47 percent of the total discharge for the subwatershed of tidal Red Lion Creek. Thus, groundwater transport of contaminants to surface water could be significant. The major contaminants detected in groundwater in the wetland study area included benzene, monochlorobenzene, and tri- and di-chlorobenzenes. Shallow wetland groundwater in the northwest part of the wetland study area was characterized by high concentrations of total chlorinated benzenes and benzene (maximum about 75,000 micrograms per liter [µg/L]), low pH, and high chloride. In the northeast part of the wetland study area, wetland groundwater had low to moderate concentrations of total chlorinated benzenes and benzene (generally not greater than 10,000 µg/L), moderate pH, and high sulfate concentrations. Concentrations in the groundwater in excess of 1 percent of the solubility of the individual chlorinated benzenes indicate that a contaminant source is present in the wetland sediments as dense nonaqueous phase liquids (DNAPLs). Consistently higher contaminant concentrations in the shallow wetland groundwater than deeper in the wetland sediments or the aquifer also indicate a continued source in the wetland sediments, which could include dissolution of DNAPLs and desorption from the sediments.

When highly reducing, methanogenic, or sulfate-reducing conditions existed in the wetland groundwater, molar composition of the volatile organic compounds (VOCs) showed that chlorobenzene and benzene were predominant, indicating biodegradation of the chlorinated benzenes through reductive dechlorination pathways. Temporal changes in redox conditions between 2009 and 2011–12 have shifted the locations in the wetland study area where reductive dechlorination is evident. Microbial community analyses of sediment showed relatively high cell numbers and diversity of populations (*Dehalococcoides*, *Dehalobacter*, *Desulfitobacterium*, and *Geobacter*) that are known to contain species capable of reductive dechlorination, confirming groundwater geochemistry evidence of the occurrence of reductive dechlorination. Natural attenuation was not sufficient, however, to reduce total VOC concentrations along upward groundwater flowpaths in the wetland sediments, most likely due to the additional source of contaminants in the upper sediments. *In situ* microcosms that were unamended except for the addition of ^{13}C-labeled contaminants in some treatments, confirmed that the native microbial community was able to biodegrade the higher chlorinated benzenes through reductive dechlorination and that 1,2-dichlorobenzene, chlorobenzene, and benzene could be degraded to carbon dioxide through oxidation pathways. Microcosms that were bioaugmented with the anaerobic dechlorinating consortium WBC-2 and deployed in the wetland sediments showed reductive dechlorination of tri-, di-, and monochlorobenzene, and ^{13}C-chlorobenzene treatments showed complete degradation of chlorobenzene to carbon dioxide under anaerobic conditions.

[1] U.S. Geological Survey.

[2] Cherokee Nation Technology Solutions.

Experiments with a continuous flow, fixed-film bioreactor seeded with native microorganisms in groundwater from the wetland area showed both aerobic and anaerobic biodegradation of dichlorobenzenes, monochlorobenzene, and benzene, although monochlorobenzene and benzene degradation rates decreased under anaerobic conditions compared to aerobic conditions. In two bioreactors with established biofilms of WBC-2, percent removals of all chlorinated benzene compounds (medians of 86 to 94 percent) under anaerobic conditions were as high as those observed for the bioreactors seeded only with native microorganisms from the site groundwater, and benzene removal was greater in the WBC-2 bioaugmented bioreactors. The high percent removals in the WBC-2 bioreactors without the need for an acclimation period indicates that the same dechlorinators are involved in the chlorinated benzene degradation as those for the chlorinated ethanes and ethenes that the culture was developed to degrade. The ability of the WBC-2 culture to completely reduce the chlorinated benzenes and benzene, even in the presence of high sulfate and sulfide concentrations, is unique for known dechlorinating cultures. The availability of the established culture WBC-2, as well as the ability of the native wetland microbial community to degrade the site contaminants under anaerobic and aerobic conditions, provides flexibility in considering bioremediation options for the wetland areas at SCD.

Introduction

Major releases of chlorinated benzenes and benzene occurred at the Standard Chlorine of Delaware, Inc. Superfund Site (SCD) in New Castle County, Delaware, from 1966–2002, resulting in contamination of the groundwater underlying the site and the wetlands surrounding Red Lion Creek (fig. 1). The U.S. Environmental Protection Agency (EPA) issued a Record of Decision (ROD) for SCD in 1995 that included an interim action for containment of groundwater and treatment for soils and sediments either by bioremediation or thermal desorption. Predominant contaminants identified at the site include 1,2,3-trichlorobenzene (123TCB), 1,2,4-trichlorobenzene (124TCB), 1,3,5-trichlorobenzene (135TCB), 1,2-dichlorobenzene (12DCB), 1,3-dichlorobenzene (13DCB), 1,4-dichlorobenzene (14DCB), chlorobenzene (also referred to as monochlorobenzene) (CB), and benzene (U.S. Environmental Protection Agency, 2011). Although installation of a groundwater interception and treatment system has been completed around the main industrial area of the SCD (designated by the barrier wall in fig. 1), wetland and sediment areas impacted by contaminated groundwater discharge and past surficial spills remain outside this barrier wall. Implementation of *in situ* bioremediation was identified for the wetland areas under the selected remediation alternative for the SCD during the Feasibility Study, and a laboratory treatability investigation of bioremediation of wetland sediments was completed in 1993 (Roy F. Weston, Inc., 1993a). This feasibility investigation, however, was inconclusive on the potential bioremediation technologies that could be used to enhance degradation and their effectiveness in the wetland areas (U.S. Environmental Protection Agency, 1993), and the contingency remedy of low temperature thermal desorption was considered instead (Black & Veatch, 2003; HydroGeoLogic, Inc., 2009). The extremely high estimated cost of a thermal remedy and the recognition of advances in bioremediation since 1993 (Black & Veatch, 2003; HydroGeoLogic, Inc., 2009) led to the decision to reinvestigate the potential of bioremediation for the SCD wetland areas. In cooperation with EPA, the U.S. Geological Survey (USGS) expanded its ongoing Potomac aquifer investigation at the site (Degnan and Brayton, 2010) and began a preliminary investigation in June 2009 of the feasibility of monitored natural attenuation or of combined natural attenuation and enhanced bioremediation as remedial strategies for the contaminated wetland areas.

Biodegradation is recognized as the key destructive process for successful use of monitored natural attenuation as a groundwater remediation method for organic contaminants (U.S. Environmental Protection Agency, 1998). An understanding of the native microbial communities and their possible degradation mechanisms can also be applied in engineered bioremediation solutions that can lead to more complete or rapid biodegradation at a site than through a monitored natural attenuation remedy (Lovley, 2003). Bioremediation techniques can be divided into two general categories—biostimulation, which involves the addition of electron acceptors or donors (usually an organic carbon donor for anaerobic degradation), nutrients, or other compounds that have been determined to stimulate the activity of microorganisms naturally present at the site, and bioaugmentation, which involves the addition of bacteria known to degrade the contaminants of interest. Bioaugmentation can be applied to increase the population size, and thus degradation capacity, of bacteria already present at the site or to add contaminant-degrading bacteria that were not present.

Since the bioremediation treatability investigation was conducted with the wetland sediments in 1993 for the SCD, substantial progress has been made in the understanding of biodegradation processes for chlorinated solvents, including chlorinated benzenes, and the microorganisms involved, as well as in hydrogeologic investigation and bioremediation technologies applicable to wetland areas (Lorah and Olsen, 1999a, b; Kassenga and others, 2003; Lorah and others, 2007; Lorah, Majcher, and others, 2008; Majcher and others, 2007, 2009; Braeckevelt and others, 2008; Imfeld and others, 2008). Both aerobic and anaerobic degradation processes have been identified for chlorinated benzenes (Ramanand and others, 1993; Adrian and others, 2007; Field and Sierra-Alvarez, 2008). In general, higher chlorinated benzenes such as 124TCB are degraded more readily under anaerobic conditions by reductive dehalogenation reactions, whereas DCBs and especially CB are degraded more readily by aerobic bacteria through an oxidation reaction. One of the most frequent problems with bioremediation of groundwater contaminated

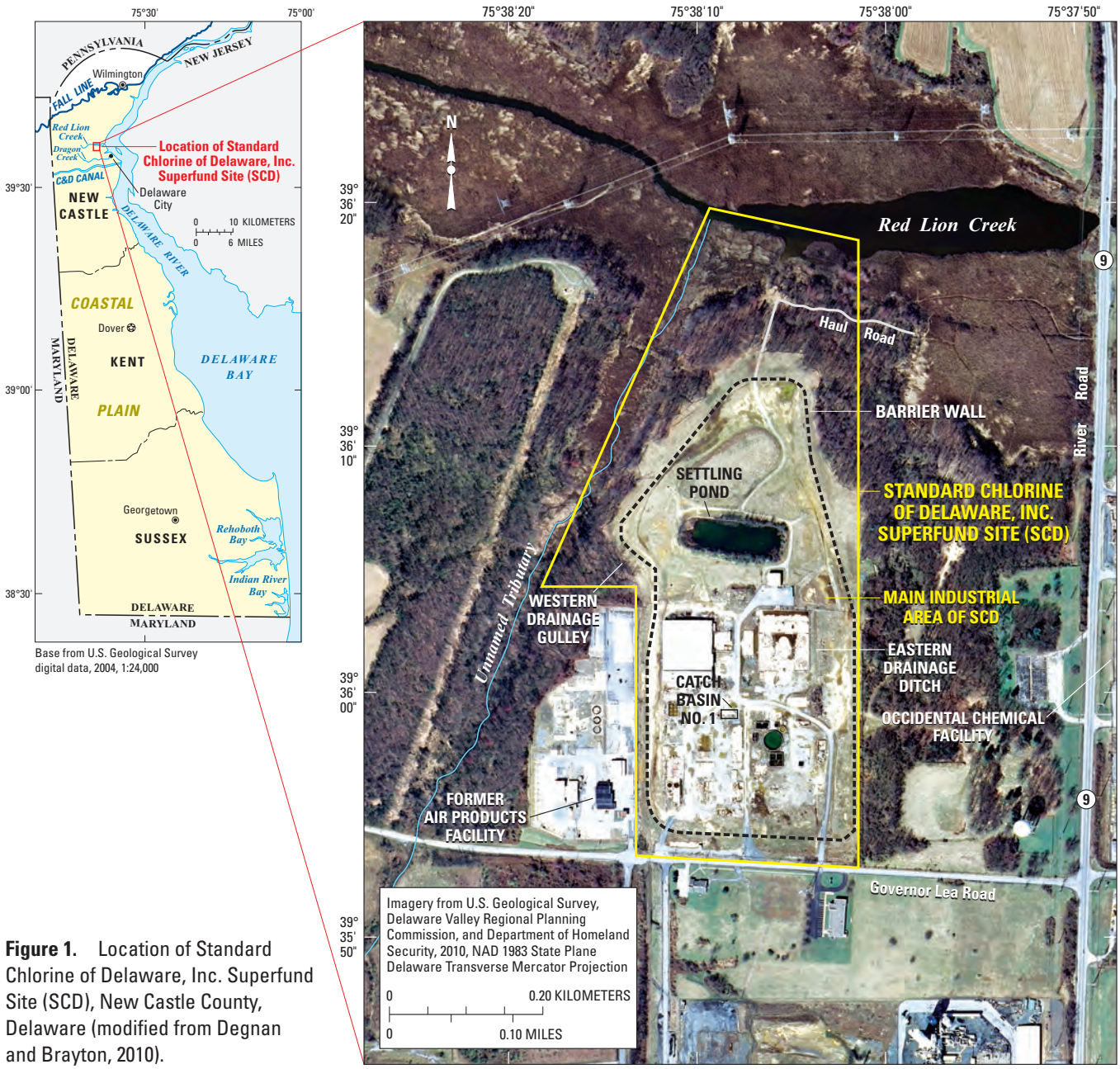


Figure 1. Location of Standard Chlorine of Delaware, Inc. Superfund Site (SCD), New Castle County, Delaware (modified from Degnan and Brayton, 2010).

with chlorinated benzenes has been the incomplete degradation of higher chlorinated benzenes to CB and the typical recalcitrance of CB under anaerobic conditions (Field and Sierra-Alvarez, 2008; Fung and others, 2009). Reductive dehalogenation of DCBs to CB and of CB to benzene has been reported primarily in laboratory studies (Fung and others, 2009), although a few field studies, including a wetland study, have recently reported evidence of anaerobic degradation of CB (Kaschl and others, 2005; Kästner and others, 2006; Braeckevelt and others, 2008). Because of the abundance of organic carbon substrates and the influence of wetland plants, which transport oxygen to the sediment through their roots, wetland sediments typically contain a high diversity of redox zones and microbial populations that can support a variety of contaminant degradation pathways (Amon and others, 2007; Lorah and others, 1997). Anaerobic and aerobic degradation reactions have been shown to occur in the same wetland sediment for chlorinated ethenes (Lorah and others, 2001) and for CB (Braeckevelt and others, 2007; Braeckevelt and others, 2008).

Anaerobic degradation of chlorinated benzenes occurs by reductive dechlorination, the same process identified for chlorinated ethenes and chlorinated ethanes, such as trichloroethene and tetrachloroethane, respectively. In fact,

many of the anaerobic bacteria that have been identified as able to degrade chlorinated benzenes are in the same genera (such as *Dehalococcoides*, *Dehalobacter*, and *Desulfitobacterium*) that have been extensively studied for reductive dechlorination of the chlorinated ethenes and ethanes (Hölscher and others, 2003). For example, *Dehalococcoides* sp. strain CBDB1 has been shown to derive energy from dechlorination of 123TCB, 124TCB, all tetrachlorobenzene isomers, pentachlorobenzene, and hexachlorobenezene, as well as polychlorinated dibenzodioxins (Bunge and others, 2003; Adrian and others, 2007). Although reductive dehalogenation of DCBs has been observed, no specific bacteria that derive energy from this reaction have been identified (Fung and others, 2009). Even though several anaerobic microbial cultures are commercially available for degradation of chlorinated ethenes and ethanes, none are currently available for degradation of chlorinated benzenes.

The USGS wetland study at SCD includes two major objectives: (1) wetland characterization, including determination of the hydrogeology and the distributions of groundwater contaminants and other geochemical constituents, and (2) determination of biodegradation processes naturally occurring in the wetland sediment and the effects of amendments to enhance biodegradation, including biostimulation and bioaugmentation. An anaerobic consortium, called WBC-2, that was developed by the USGS from wetland sediment at a site in Maryland to degrade chlorinated ethanes and ethenes, was used for bioaugmentation testing in this study. WBC-2 contains several *Dehalococcoides* strains, including CBDB1, as well as *Dehalobacter*, *Acetobacteria*, and *Bacteroidetes* species that have been identified by others in chlorobenzene degrading communities (Geosyntec Consultants Inc., 2006; Lorah and others, 2008, Lorah and others, 2012). This report describes the results of field and laboratory investigations that occurred between 2009–12 for the ongoing wetland study at the SCD. The goal of the wetland study was to assist the EPA in identifying an effective remedial strategy for the contaminated wetland areas. Bioremediation can be a cost-effective strategy with the potential for *in situ* applications that would have minimum adverse impact on the wetland ecosystem.

Purpose and Scope

The purpose of this report is to provide a hydrogeologic and geochemical characterization of the wetland study area and to assess the evidence for natural and enhanced biodegradation of chlorinated benzenes and benzene in the SCD wetland area from field and laboratory investigations conducted in 2009–12. The hydrogeologic characterization includes description of the lithology of the wetland sediments from sediment cores, evaluation of head distributions and groundwater-flow directions from synoptic and continuous water-level measurements in piezometers, and calculation of groundwater-flow velocities using head distributions and estimates of hydraulic conductivities from slug tests. In addition, a preliminary estimate of the groundwater discharge rate to Red Lion Creek was made to assess the potential significance of groundwater on contaminant transport to surface water. The geochemical characterization includes evaluation of the distributions of volatile organic compounds (VOCs) and of redox-sensitive and other geochemical constituents in the wetland groundwater using samples collected from passive diffusion samplers and piezometers. Samples collected during synoptic sampling of many sites across the wetland were used to assess areal distributions of constituents, whereas samples collected monthly at selected sites were used to assess temporal changes in the wetland geochemistry.

Field and laboratory studies were used to obtain evidence of natural or enhanced biodegradation processes. For field investigations, ratios of parent and potential daughter VOCs in different areas of the wetland were calculated with geochemical data from piezometers and 1.22-meter (m; 4-feet [ft])-long peepers (porous diffusion samplers with 22 rows of sampling ports) and compared to ratios observed in upland wells and sediment samples that were indicative of the contaminant sources. *In situ* microcosms that included treatments to evaluate monitored natural attenuation, biostimulation with organic donor, and bioaugmentation with WBC-2 also were used to provide field evidence of biodegradation. Microbial community analysis of samples collected from the *in situ* microcosms and the wetland sediment provided distributions of possible microbial species involved in contaminant degradation. Anaerobic bioreactors, operated under flow-through conditions with varying amendments, were used to provide laboratory evidence of natural and enhanced biodegradation processes by comparing reactors seeded with WBC-2 to a control bioreactor seeded only with native microorganisms derived from the inflow of site groundwater.

Description of Study Area

The area of the USGS wetland study at SCD is composed of wetlands in the northern extent of the SCD boundary along the southern border of Red Lion Creek, as well as wetlands that extend along the northern border of Red Lion Creek, primarily north of the installed barrier wall and east of the unnamed tributary of Red Lion Creek (fig. 1). In order to more fully understand factors that contribute to the geochemistry and hydrogeology of the wetlands, a part of the bordering uplands were included in the study area, particularly along Haul Road (fig. 1). The USGS study area is entirely contained within the boundaries of the SCD and largely contained within what was referred to as the “eastern wetlands” in the Remedial Approach to Wetlands investigation conducted in 2009 (HydroGeoLogic, Inc., 2009). The SCD is a 0.26 square kilometer (km^2) former chemical manufacturing facility bounded to the north by Red Lion Creek, to the east by Occidental Chemical Corporation (and Delaware Route 9), to the west by the former Air Products, Inc. and an unnamed tributary of Red Lion Creek, and to the south by Governor Lea Road (fig. 1).

Environmental responses, investigations, and remedial actions have been ongoing at the SCD since 1981, and it was placed on the EPA National Priority List in 1987.

Subsurface contamination is a result of on-site production of chlorinated benzenes in the central-upland part of the SCD from 1966–2002. A variety of chlorinated benzenes (CB, 14DCB, 12DCB, and lesser amounts of 13DCB, 123TCB, and 124TCB) were produced by combining (through reaction and distillation) chlorine and benzene, which were purchased from adjacent industrial facilities and stored and disposed at the SCD until closure in 2002. Numerous spills and long-term leaks contributed to subsurface contamination that has extended spatially to the wetland study area and Red Lion Creek.

Regional and Site Hydrogeologic Setting

Three distinct lithologic formations are predominant in the vicinity of the SCD—coarse to medium sands and gravels of the Quaternary Columbia Formation, followed by marine fine silt and clay of the Upper Cretaceous Merchantville Formation, and then alternating layers of clay, silt, and fine to medium sand of the Cretaceous Potomac Formation (Ramsey, 2005). Pleistocene erosion due to lowering of sea level resulted in downcutting of rivers into the Potomac Formation. These channels were refilled with undifferentiated sediments (sand, gravel, and clay) of the Columbia Group (Phillips, 1987). Holocene sediments overlying the Columbia also are present as marsh deposits and consist of black to dark grey organic rich silty clay with beds of peat ranging in thickness between 0.3 and 12 m (Ramsey, 2005).

The water-table aquifer in the Columbia Formation (referred to herein informally as the Columbia aquifer) is 12–23 m thick locally, discontinuous, and infrequently used for small domestic water supplies (Roy F. Weston, Inc., 1992). Groundwater in the water-table aquifer is recharged by precipitation and generally discharges to bordering wetlands and surface-water features. The depth to water ranges from about 6.1 m below land surface in the uplands to near land surface in the wetlands, which have an elevation close to mean sea level. At the SCD, the direction of flow for shallow groundwater is generally from south to north. Deeper groundwater is present in confined and semi-confined aquifers that vary in thickness and spatial extent. Historical long-term water use has led to a documented regional cone of depression that affects all levels of the Potomac aquifer (Martin, 1984) and water levels within various Potomac aquifer sands can vary depending on production well demands. Increases in salinity in the Potomac aquifer also have been documented due to the strong influence of production wells on flow direction. Vertical flow gradients of the deeper flow system in the area are consistently downward from the Columbia to the Potomac aquifer, and downward between sand layers within the Potomac Formation (Martin, 1984).

The Merchantville Formation clay, stratigraphically beneath the Columbia aquifer, was initially thought to be a nearly continuous impermeable layer that prevented contamination from migrating deeper at the site. This conclusion was partially drawn from the lack of water-level response in Columbia wells to an aquifer test conducted in 1990 (Roy F. Weston, Inc., 1992). Further investigations indicated that the clay is discontinuous and that holes may have been eroded through the clay by paleochannels prior to and during the deposition of the Columbia Formation (Roy F. Weston, Inc., 1992; Degnan and Brayton, 2010).

Flow from the upland part of the SCD to the USGS study area is impeded by an approximately 1-m-thick soil-bentonite containment barrier wall that extends up to 22 m below land surface. This barrier wall was installed in 2007 to prevent migration of contaminants from the upland part of the site downgradient toward Red Lion Creek (U.S. Environmental Protection Agency, 2011) in compliance with the ROD (U.S. Environmental Protection Agency, 1995a). The barrier wall was installed into the confining units of the Merchantville clay and (or) upper Potomac sequences, although these units have been demonstrated to be laterally variable in thickness and, in the case of the Merchantville, discontinuous in the vicinity of the site.

Groundwater withdrawals from the Potomac aquifer for industrial and public supply use occur within 5 kilometers (km) of the SCD. Public supply use is typically 0.011 cubic meters per second (m^3/s), or 0.25 million gallons per day (Mgal/d), whereas aggregate industrial withdrawal by the Delaware City Refining Company (DCRC) is typically 0.24 m^3/s (5.5 Mgal/d) (Doug Rambo, Delaware Department of Natural Resources and Environmental Control, written commun., 2013). Water-level declines up to 61 m below sea level have been documented in parts of the Potomac aquifer since industrial withdrawals began in the 1950s (Martin, 1984). Most of the decline near the SCD is due to long-term sustained use by the DCRC. No impact on the shallow flow system in the Columbia aquifer has been observed from industrial pumping; however, lower head values in the Potomac aquifer relative to the Columbia aquifer have enhanced a vertically downward groundwater gradient in the deeper flow system of the Columbia aquifer. Historically, aggregate groundwater use by the refinery has been fairly constant, however, production wells were inactive during an ownership transition period from May 2010 to January 2011. During this period, selected wells were occasionally pumped to ensure that the pumps remained in good working condition, with only very limited withdrawals to support plant maintenance (Rebecca Gudgeon, DCRC, oral commun., 2011). Industrial groundwater withdrawal wells located closest to the SCD (wells P-6A, P-5B, and R-15) typically pump a combined 0.044 m^3/s during normal operation. These wells were operated in limited capacity from December 2009 to May 2010, pumping less than 378 cubic meters per day (m^3/d) from when the plant was idled until January 2011. A groundwater recovery was observed during this period with a corresponding reduction in the magnitude of the vertically downward gradients.

Surface runoff at the SCD moves generally north into Red Lion Creek, or into small streams feeding the creek. Shallow groundwater discharges to the creek and to wetland areas surrounding the creek. Water from Red Lion Creek drains during low tide through a tide control structure located approximately 0.8 km downstream from Delaware State Route 9. Starting in the late 1950s, the creek was no longer subject to tidal influence because gates on the tide control structure closed during high tide to prevent water from entering from the Delaware River (Mickowski, 1986). However, the creek and wetlands of the SCD have been tidally flooded periodically since the 1950s, including during the 1986 spill discussed below. Despite several attempts at repair, the tide control structure is currently (June 2014) not functioning and approximately one-third of the wetlands are submerged under high tide conditions.

Summary of Contamination Extent and Wetland Remedial Alternatives

Industrial activities at the SCD resulted in extensive contamination of groundwater, soils, and sediments that has been documented over the last 30 years (Roy F. Weston, Inc., 1993a, Black & Veatch, 2007; HydroGeoLogic, Inc., 2009; Christopher Wolfe, HydroGeoLogic, Inc., written. commun., 2012) and led to required interim and final remedial actions, as specified in the site ROD (U.S. Environmental Protection Agency, 1995a; 2011). Subsurface contamination at the SCD is likely the result of leaks and several spills of chlorinated benzenes, including a leaking catch basin that was discovered and repaired in 1976, a spill of 5,000 gallons of CB in 1981, and a much larger spill of 400,000 gallons of 14DCB and 169,000 gallons of TCBs in 1986 (U.S. Environmental Protection Agency, 1995a). In addition to the known compounds released in spills, previous studies have detected hexachlorobenzne (HCB) and tetrachlorobenzenes (TeCBs) as compounds of concern in soil and sediment at the site (U.S. Environmental Protection Agency, 1995a). All of the known contaminant releases were upgradient of the wetland study area. The CB that was spilled in 1981 was the result of an overflowing railroad tanker. Spill contents traveled along the railroad tracks and entered the drainage gully, which led to Red Lion Creek (Standard Chlorine of Delaware, Inc., 1982). Booms and dams were placed to prevent migration of CB to Red Lion Creek, and soils and sediments were excavated in the vicinity of the unnamed tributary. However, further investigation determined that the creek was impacted with chlorinated benzenes, and contamination was found in site groundwater and creek bottom sediments (Standard Chlorine of Delaware, Inc., 1982). In the case of the 1986 spill, the wetlands were directly impacted by released product because the spill occurred during high tide and resulted in a “fan” of product being swept into the wetlands and along the southern bank of Red Lion Creek (Roy F. Weston, Inc., 1988). Similar to the 1981 spill, product also traveled along the unnamed tributary to Red Lion Creek (first through the western drainage gully) and entered the wetlands to the west of the USGS study area and along its western boundary. Remedial actions conducted after the 1986 spill included the construction of booms and an earthen dike in the vicinity of the drainage gully to prevent tidal influence during manual removal of solid product along the tributary. Chemical product also was recovered along the southern bank of Red Lion Creek and in the wetlands (Roy F. Weston, Inc., 1988). During removal activities, a geotextile filter fence was installed at the mouth of the wetlands in an attempt to prevent any further mobilization of solidified spill products to the creek (Roy F. Weston, Inc., 1988). The tidally influenced wetlands between the earthen dike and filter fence proved particularly challenging for product recovery. Dredging operations were conducted in this area, but were abandoned after it was determined that no additional removal could be performed without damaging the root mass of the wetland (Roy F. Weston, Inc., 1988).

Estimates of contaminant extent have been made based on numerous investigations dating from the years immediately following the first major spill until the present (Roy F. Weston, Inc., 1993a; U.S. Environmental Protection Agency, 1995a; Black & Veatch, 2005, 2007; HydroGeoLogic, Inc., 2009; Christopher Wolfe, HydroGeoLogic, Inc., written commun., 2012). Most investigations have focused on the Columbia aquifer; however, some sampling has been conducted more recently at the SCD in the Potomac aquifer (Black & Veatch, 2005, 2007; Christopher Wolfe, HydroGeoLogic, Inc., written commun., 2012) and the wetland sediments (HydroGeoLogic, Inc., 2009). Based on these investigations, contamination was documented in the Columbia aquifer as a large plume containing numerous chlorinated benzene compounds plus benzene, extending across a large part of the SCD from the central area where the spills occurred to the southern boundary of the creek (U.S. Environmental Protection Agency, 1995a). The interim action for groundwater specified in the 1995 ROD (U.S. Environmental Protection Agency, 1995a) of a containment barrier wall and recovery and treatment system was reported to be operating as designed to prevent continued migration of potential dense nonaqueous phase liquids (DNAPLs) (U.S. Environmental Protection Agency, 2011). In addition to the interim remedy, a final remedy for contaminated groundwater and impacted soil and sediment was required in the ROD for SCD (U.S. Environmental Protection Agency, 1995a, 2004). Biological treatment of SCD soils and sediment was selected as the preferred remedy (U.S. Environmental Protection Agency, 1995a); however, treatability testing had not demonstrated bioremediation to be a viable method at the time the ROD was approved (Roy F. Weston, Inc., 1993b).

Although spill contaminants were known to impact the wetlands bordering Red Lion Creek, sampling and evaluation of remedial alternatives was not conducted in this part of the SCD until 2008. In 2008, HydroGeoLogic, Inc. conducted an investigation of wetland sediments and evaluated potential remedial actions compatible with the wetlands (HydroGeoLogic, Inc., 2009) in order to fulfill the

requirements of the ROD. In what was called the "western wetlands" or the area to the west of the unnamed tributary to Red Lion Creek, particularly north of the containment dike, total concentrations of chlorinated benzenes and benzene in the sediment ranged from 800 milligrams per kilogram (mg/kg) to 14,000 mg/kg (HydroGeoLogic, Inc., 2009). South of the dike, the maximum concentration in sediment was near 400 mg/kg (HydroGeoLogic, Inc., 2009). In the "eastern wetlands" or the area to the east of the unnamed tributary, concentrations were typically not detected to an order of magnitude less than the concentrations in the western wetlands south of the containment berm, particularly in the easternmost samples (HydroGeoLogic, Inc., 2009). However, one sample (EW-07), which is from a site in the USGS study area, had a concentration greater than 2,000 mg/kg (HydroGeoLogic, Inc., 2009). Contamination was greater in the surficial sediment samples (0–15 centimeters or cm) collected in the "eastern wetlands" than in deeper (15–30 cm) samples collected at the same location (HydroGeoLogic, Inc., 2009).

In situ treatment of the contaminants in the wetland is advantageous due to the difficulty in operating large machinery and excavating in the soft sediment, sensitive environment. Following the inconclusive bioremediation treatability study, other treatment alternatives were evaluated for the wetlands, including *in situ* chemical oxidation using laboratory tests and a pilot field test (HydroGeoLogic, Inc., 2009). Whereas some oxidants tested resulted in mass reductions of chlorinated benzenes and benzene in areas where the oxidant was mixed with sediment in the field test, secondary water-quality effects (such as increases in certain metals) were observed and no downgradient effect from the oxidant addition was noted (HydroGeoLogic, Inc., 2009). Other *in situ* alternatives including bioremediation, phytoremediation, and *in situ* capping were suggested as possible components of a remedy, given the advances in these technologies over the last 10 years (HydroGeoLogic, Inc., 2009).

Background on Degradation Pathways

Most of the chlorinated benzenes present at the SCD, particularly the higher chlorinated compounds, have a high affinity for the solid phase in soils and sediments and low solubility in porewater as shown by their chemical properties (table 1). Notably, low aqueous solubilities and relatively high partitioning coefficients for organic carbon (table 1) may indicate that aquifer and organic-rich wetland sediments act as a reservoir and ongoing source of contamination to groundwater and porewater. Despite the persistent nature of the various chlorinated benzenes spilled and detected at the SCD, this class of compounds is considered to be a candidate for natural attenuation given the reported aerobic and anaerobic biodegradation of compounds from HCB through CB (Spain, 1997). The preferential degradation of higher chlorinated benzenes in anaerobic environments and lesser chlorinated benzenes in aerobic environments (Field and Sierra-Alvarez, 2008) indicates that wetlands could provide a unique environment for complete degradation of chlorinated benzenes. Wetland sediments commonly provide predominantly anaerobic conditions in the subsurface while oxygen delivery to the root zone permits aerobic processes to occur in conjunction with anaerobic processes (Lorah and others, 2001; Amon and others, 2007; Braeckevelt and others, 2007, 2008). This section summarizes the aerobic and anaerobic pathways of all the SCD chlorinated benzenes, including CB, DCBs,TCBs, TeCBs, and HCB.

Aerobic degradation has been widely reported (Spain, 1997) particularly for TeCBs and all lesser chlorinated benzenes (Rapp and Gabriel-Jurgens, 2003; Field and Sierra-Alvarez, 2008). The mechanism of biodegradation occurs primarily through oxidation dechlorination by microbial deoxygenase enzymes, producing short-lived chlorocatechol intermediates and end products of carbon dioxide (CO_2), water, and hydrochloric acid (Potrawfke and others, 1998; Field and Sierra-Alvarez, 2008). Complete mineralization (transformation to CO_2) of chlorinated benzenes has been demonstrated primarily in laboratory studies based on inorganic chloride release, oxygen uptake, and $^{14}CO_2$ release from labeled contaminants (studies summarized in Field and Sierra-Alvarez, 2008). Due to the increased solubility of the lesser chlorinated benzenes and thus increased availability to microorganisms, aerobic degradation rates are more rapid for these compounds compared to anaerobic degradation. Depending on the microorganisms that are present, biodegradation may be cometabolic, or the direct use of chlorinated benzenes as a sole energy source may occur (Field and Sierra-Alvarez, 2008). Whereas the majority of wetland sediments are anaerobic at depth, aerobic degradation pathways are significant in wetland sediments like those found at the SCD, particularly in the root zone and during transport of precipitation downward into shallow wetland sediments (Lin, 2003).

Anaerobic biodegradation through reductive dechlorination has been reported for HCB (Ramanand and others, 1993; Nowak and others, 1996) through CB (Fung and others, 2009) and to benzene by mixed cultures (fig. 2). Dechlorination will proceed through both cometabolic and dehalorespiration mechanisms, which dictate preferential pathways of degradation (Field and Sierra-Alvarez, 2008). The microbial strain CBDB1, a close relative of the *Dehalococcoides ethogenes* strain known to degrade tetrachloroethene and trichloroethene, was the first isolated bacterium that was shown to derive energy through the reductive dechlorination of chlorinated benzenes (dehalorespiration mechanism) (Adrian and others, 2000). CBDB1 can dechlorinate TeCB and TCB to various DCB isomers (Adrian and others, 2000). After the isolation of this first strain, other *Dehalococcoides* spp. and *Chloroflexi* spp. also have been shown to degrade higher chlorinated benzenes by dehalorespiration to various DCB isomers but not completely to benzene (Adrian and others, 2000; Nelson and others, 2011). Anaerobic reductive dechlorination of these reduced products, the DCB isomers, will proceed under both methanogenic and sulfate-reducing conditions (Field and Sierra-Alvarez, 2008; Nelson and others, 2011). Preferential

Table 1. Summary of significant fate and transport properties of contaminants in wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Vp, vapor pressure; S, solubility; Calc. Sscl, calculated super-cooled solubility; NAPL, nonaqueous phase liquid; Csat, saturated concentration; KH, Henry's Law Constant; Kow, octanol-water partioning coefficient; Koc, organic carbon partitioning coefficient; g/mol, grams/mole; mm Hg, millimeters mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; atm-m^3/mol, atmospheres-meters cubed per mole; L/kg; liter per kilogram; %, percent]

Compound	Molecular mass (g/mol)	Mean Vp[1] (mm Hg)	Median Vp[1] (mm Hg)	Mean aqueous S[1] (mg/L)	Median aqueous S[1] (mg/L)	Van-Noort[2] Calc. Sscl (mg/L)	Chiou[3] Calc. Sscl (mg/L)	Cohen and Mercer[4] effective solubility (mg/L)	NAPL interaction or presence 1% Csat (µg/L)	Mean KH[1] (atm-m^3/mol)	Median KH[1] (atm-m^3/mol)	Mean Log Kow[1]	Median Log Kow[1]	Mean log Koc[1]	Median log Koc[1]
Benzene	78.11	94.8	94.8	1,770	1,770				17,500	5.57E-03	5.57E-03	2.13	2.13	1.85	1.85
Chlorobenzene	112.6	11.30	11.85	446	472				4,460	3.53E-03	3.65E-03	2.89	2.84	2.24	2.25
1,2-Dichlorobenzene	147	1.31	1.38	132	156				1,560	1.82E-03	1.91E-03	3.41	3.42	3.09	2.89
1,3-Dichlorobenzene	147	2.15	2.15	121	124				1,250	3.20E-03	3.20E-03	3.48	3.51	3.19	2.75
1,4-Dichlorobenzene	147	1.38	1.70	66	76.4	173	137.2	102	1,020	2.28E-03	2.43E-03	3.42	3.44	2.64	2.79
1,2,3-Trichlorobenzene	181.4	0.17	0.17	15	15.1	46	169.3	10.5	105	2.13E-03	2.13E-03	4.05	4.05	4.52	4.20
1,2,4-Trichlorobenzene	181.4	0.39	0.39	131	49			8.7	88	2.39E-03	1.42E-03	4.00	4.02	4.20	4.18

[1] Malcolm and others, 2004; Agency for Toxic Substances and Disease Registry, 2012; Toxnet, 2013, U.S. Environmental Protection Agency, 1996.

[2] VanNoort, 2009.

[3] Chiou and others, 1986.

[4] Cohen and Mercer, 1993.

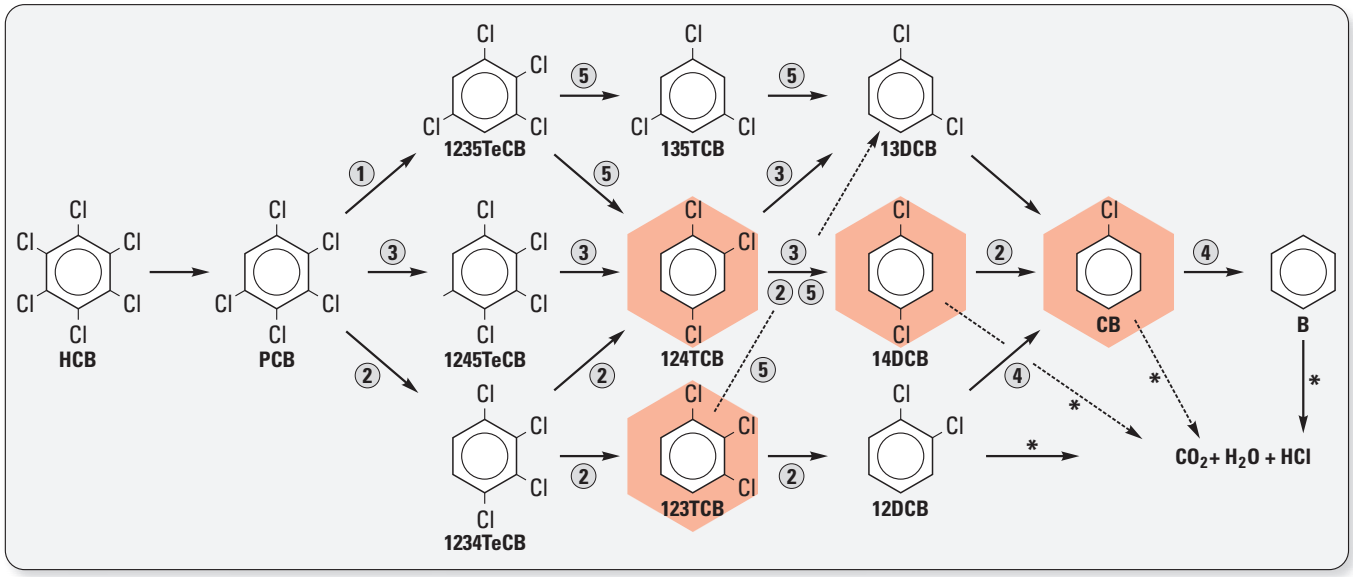
pathways and rates of anaerobic biodegradation vary, with the more highly chlorinated compounds degrading most rapidly, and particular isomers of TCBs and DCBs degrading more rapidly than others on the basis of their structures (fig. 2). The anaerobic degradation rate of CB is slowest, and production of benzene from CB has been verified only recently (Fung and others, 2009), attributable largely to *Dehalobacter* spp. (Nelson and others, 2011). Anaerobic biodegradation of benzene can occur under conditions ranging from iron-reducing to methanogenic (Lovley, 2000), but proceeds more rapidly under aerobic conditions. In wetlands, an increased abundance of organic acids and increased rates of biodegradation of chlorinated benzenes have been observed in the presence of wetland plants (such as *Typha*) (Lin, 2003).

Methods of Data Collection and Analysis

From 2009–12, an investigation was performed in the wetland study area at the SCD to characterize the hydrogeology and geochemistry of the wetland groundwater and to assess the evidence for natural and enhanced biodegradation of chlorinated benzenes and benzene. A monitoring network consisting of both conventional piezometer and passive diffusion-based devices was used to characterize wetland porewater and groundwater in the underlying aquifers. The following sections describe the methods used to characterize groundwater hydrogeology and geochemistry in the wetland and to conduct *in situ* microcosm and bench-scale bioreactor testing to assess the potential for biodegradation of chlorinated benzenes and benzene in the groundwater.

Monitoring Network

The groundwater monitoring network in the study area included existing and newly installed drive-point piezometers, existing monitoring wells, and several types of passive diffusion samplers, including low density polyethylene (LDPE) and dialysis passive diffusion bags (PDBs) and porous membrane samplers (peepers) (fig. 3). Data collected from the entire SCD monitoring network were used for hydrogeologic analysis (fig. 3a), whereas the sampling network included only selected sites close to the wetland study area (fig. 3b, table 2). The groundwater sampling network included previously installed monitoring wells (designated with the prefix "MW") in the upland area, shallow drive-point piezometers near the upland-wetland



EXPLANATION

Compounds

HCB	hexachlorobenzene	**13DCB**	1,3-dichlorobenzene
PCB	pentachlorobenzene	**14DCB**	1,4-dichlorobenzene
1235TeCB	1,2,3,5-tetrachlorobenzene	**12DCB**	1,2-dichlorobenzene
1245TeCB	1,2,4,5-tetrachlorobenzene	**CB**	chlorobenzene
1234TeCB	1,2,3,4-tetrachlorobenzene	**B**	benzene
135TCB	1,3,5-trichlorobenzene	**CO_2**	carbon dioxide
124TCB	1,2,4-trichlorobenzene	**H_2O**	water
123TCB	1,2,3-trichlorobenzene	**HCl**	hydrochloric acid

Known site spill compounds from 1981 and 1986.

Pathways reported previously in the following references:

1. Middledorp and others, 1997; Masunaga and others, 1996
2. Ramanand and others, 1993; Nowak and others, 1996
3. Lin, 2003
4. Nelson and others, 2011 (*Dehalobacter species* responsible for dehalorespiration.)
5. Adrian and others, 2000 (Strain *CBDB1* responsible for dehalorespiration.)

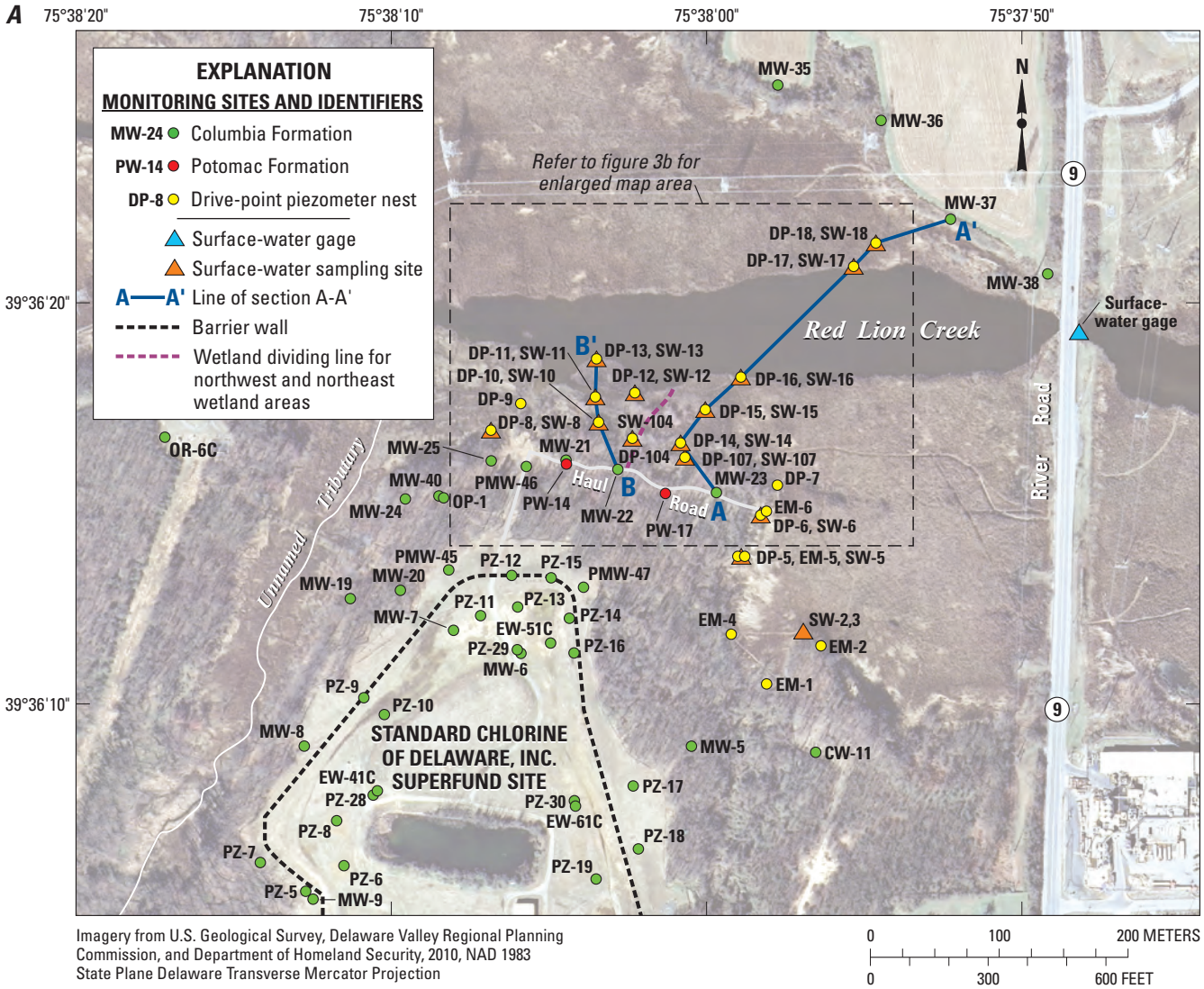
* Can also proceed via aerobic degradation.

Figure 2. Diagram showing possible degradation pathways for chlorobenzenes (modified from Field and Sierra-Alvarez, 2008).

boundary installed in 2008–09 prior to this wetland study (designated with the prefix "EM"), and 11 piezometer sites installed between April and December 2011 as part of the wetland study (table 2; fig. 3).

The "MW" wells, which are screened in the shallow Columbia aquifer (fig. 3a, table 2),were installed in the late 1990s to delineate contamination north of the industrial part of the SCD and continue to be sampled by HydroGeoLogic, Inc. as part of the biannual sampling (Christopher Wolfe, HydroGeoLogic, Inc., written. commun., 2012). The five "EM" drive-point piezometer sites were installed as part of the USGS Potomac Aquifer Study to investigate potential groundwater discharge to the wetlands (fig. 3a, table 2). These drive-point piezometers, mostly screened in the Columbia aquifer, were constructed with 5.08-cm-diameter stainless steel casing and a 30.5-cm-long slotted screen (0.025 cm). It should be noted that polyvinyl chloride (PVC) piezometers (with a 1.90-cm diameter) also were installed prior to this study at sites 7, 8, and 9, but were not used for the wetland study (and thus are not shown in table 2); these sites were utilized only for passive diffusion samplers and a newly installed piezometer at site 8 (DP-8A) (table 2; figs. 3a, b).

Most of the new piezometers installed for the wetland study were placed along expected groundwater flowpaths (transects) toward the southern bank of Red Lion Creek. (fig. 3a). The western transect consisted of drive-point piezometers (DP) at sites 10, 11, and 13. The eastern transect consisted of drive-point piezometer nests at sites 14, 15, and 16. Additional new piezometers were installed at sites near the upland-wetland boundary (sites 8, 104, 107, 6, 5); at an observed seep area in the wetland (site 12); and on the northern bank of Red Lion Creek (sites 17 and 18). These transect sites generally consist of one or more shallow drive-point piezometers screened within the wetland sediment and one drive point screened just below the wetland sediment in the Columbia aquifer. The initial drive points screened in the shallow wetland sediment, labeled "S," were installed in May 2011 and constructed of 1.9-cm-diameter PVC casing and a 15.2-cm-long screen made out of high density polyethylene filter with a pore size of 60 microns (table 2). Later in 2011, the "A" and "AA" drive-point piezometers were installed in



Imagery from U.S. Geological Survey, Delaware Valley Regional Planning Commission, and Department of Homeland Security, 2010, NAD 1983 State Plane Delaware Transverse Mercator Projection

0 100 200 METERS

0 300 600 FEET

Figure 3. *(A)* Monitoring network and locations of hydrogeologic sections in the wetland study area, and *(B)* sampling locations in the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

the wetland sediments for water sampling and collection of continuous water-level data, respectively. The "A" and "AA" drive-point piezometers were constructed of 5.1-cm-diameter PVC with a 15.2-cm-long, 0.025-cm slotted screen. The "B" drive-point piezometers, most of which were screened in the Columbia aquifer, were constructed of 5.1-cm-diameter 304 stainless steel casing and a 30.5-cm- or 22.9-cm-long slotted screen (0.025 cm). Because the wetland sediment thickness varied across the site, the bottom of the screens ranged from 0.55 m to 0.98 m below land surface for the "A," "AA," and "S" drive points and from 2.3 m to 10.1 m below land surface for the B drive points (table 2).

Additional shallow "A" drive-point piezometers also were installed for water-quality and hydrologic sampling at sites 8, 104, 107, 6, and 5 near the edge of the wetland-upland boundary. These piezometers were constructed of 5.1-cm-diameter PVC with a 30.5-cm-long slotted screen (0.025 cm). Drive point DP-6AA with a 15.2-cm-long screened interval also was installed at site 6 to collect continuous water-level data.

Several types of passive-diffusion based samplers were included in the monitoring network for this investigation. Peepers, installed at selected sites in July 2009, September 2011, and November 2011 (table 3), are passive-diffusion samplers with closely spaced sampling cells to capture changes in redox conditions and water quality at a single location across a range of depths (Lorah and others, 1997; Spencer and others 2002). The 122-cm-long peepers used in this study were constructed of thick acrylic plastic with 22 equally spaced rows of sample cells, each cell holding approximately 22 milliliters (mL) of water. Both sides of the sample cells were overlain with 0.2-micrometer (µm) polysulfone filter paper, held in

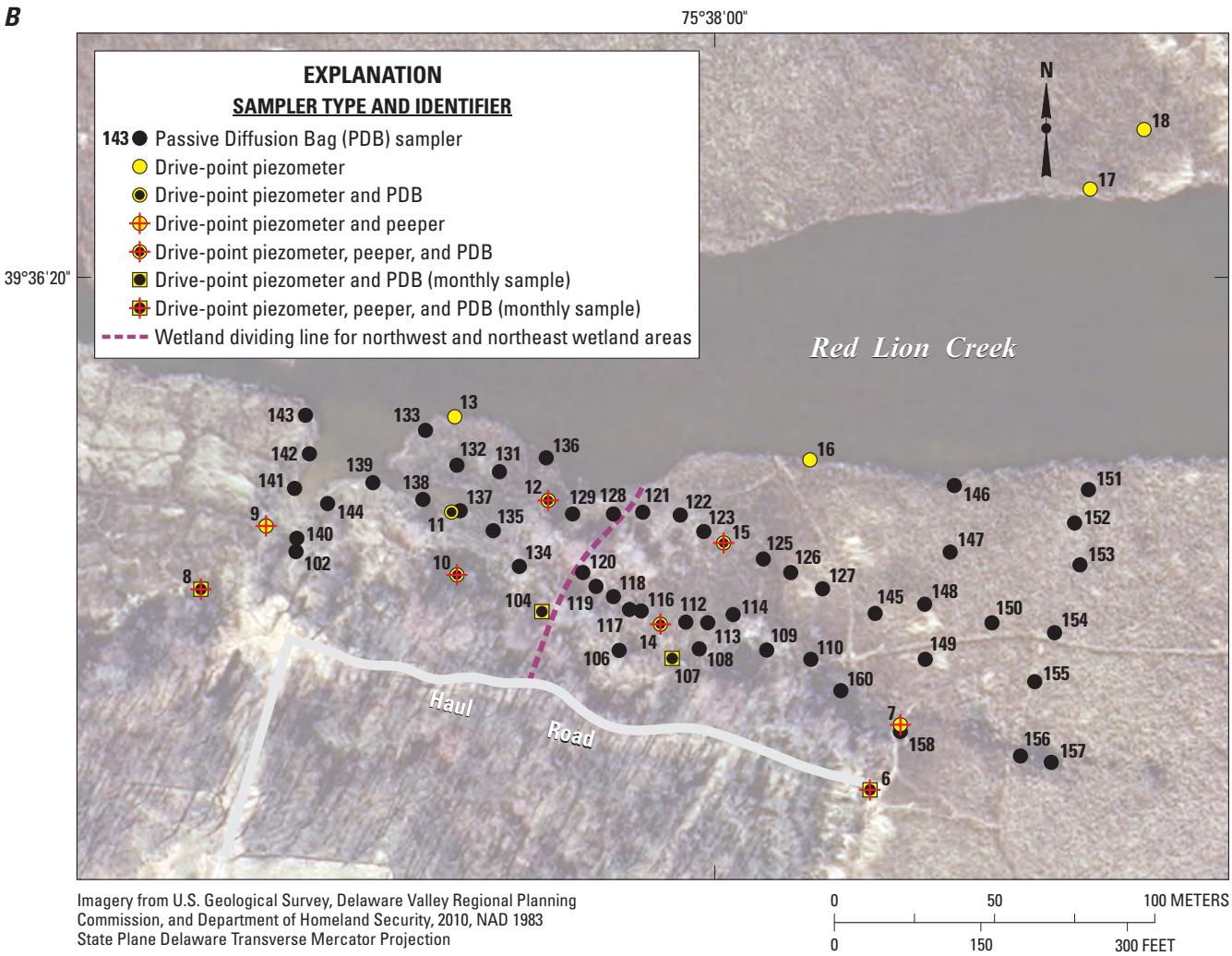


Figure 3. *(A)* Monitoring network and locations of hydrogeologic sections in the wetland study area, and *(B)* sampling locations in the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.—Continued

place by thin acrylic plastic frames. The peepers were installed just below the land surface and allowed to equilibrate with the adjacent porewater for a minimum of 2 weeks.

PDBs, constructed of either LDPE tubing or dialysis membrane tubing to obtain samples for different analyses, have been shown to be an effective way to characterize wetland groundwater (Vroblesky, 2001; Ehlke and others, 2004; Majcher and others, 2007). PDBs installed directly in the wetland sediment were used as a relatively rapid method to obtain a large number of groundwater samples across a broad area of the wetland, allowing spatial characterization and determination of locations for piezometer installation. The LDPE PDBs were constructed of heat-sealed, LDPE plastic that was filled with deionized water. The dialysis PDBs were constructed from regenerated cellulose tubing with a molecular weight cutoff (MWCO) of 8,000 Daltons that was filled with deionized water and closed with cable ties. The dialysis tubing was pretreated by the manufacturer to remove any trace amounts of hydrogen sulfide and metals and was rinsed thoroughly before use in order to remove any remaining preservatives. Before installation, the LDPE and dialysis PDBs were purged with nitrogen for at least 12 hours to displace any dissolved oxygen within the bags. Both PDBs were placed in the saturated wetland sediments, approximately 20–40 cm below land surface, in adjacent mesh stainless steel screens attached to PVC rods to mark the location.

Hydrogeologic Data

Hydrogeologic data were collected from across the wetland study area in order to gain a clearer understanding of groundwater flow and groundwater/surface-water interactions within the wetland area of the SCD. Data collected from parts of the SCD outside of the wetland study area as part of a broader site monitoring network also were used in parts of this

Table 2. Monitoring network for the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[NAD83, horizontal coordinate information referenced to North American Datum of 1983; NGVD29, vertical elevation referenced to National Geodetic Vertical Datum of 1929; MP, reference elevation of measuring point referenced to land surface; als, above land surface; bls, below land surface; casing material: PVC, polyvinyl chloride; SS, stainless steel; CS, carbon steel; sampler type: PP, peristaltic pump; PDB, passive diffusion bag; PS, pumped syringe from well tubing; NC, not collected; N/A, not applicable; m, meters; in., inches; ° ' ", degrees, minutes, seconds]

Site name	Site identification number	Construction date	Latitude (NAD83)	Longitude (NAD83)	Land surface (m above NGVD29)	MP height (m als)	Well depth (m bls)	Screened depth (m bls)	Geologic unit[1]	Casing material	Casing diam-eter (in.)	Sampler type	Continuous record
Drive-point piezometers													
EM-1S	393610075375902	5/7/2008	39°36'10.35"	75°37'58.07"	1.19	0.78	1.25	0.94-1.25	Wetland sediments	SS	2	PP	NC
EM-1D	393610075375901	5/7/2008	39°36'10.35"	75°37'58.07"	1.14	1.24	3.05	2.85-3.15	Wetland sediments	SS	2	PP	NC
EM-2S	393611075375602	5/7/2008	39°36'11.27"	75°37'56.32"	0.18	0.85	1.15	0.85-1.15	Columbia Formation	SS	2	PP	NC
EM-2D	393611075375601	5/7/2008	39°36'11.27"	75°37'56.32"	0.11	1.08	3.05	2.68-2.99	Columbia Formation	SS	2	PP	06/09-05/12
EM-4D	393612075375901	8/25/2008	39°36'11.57"	75°37'59.23"	1.02	0.61	2.86	2.56-2.86	Columbia Formation	SS	2	PP	NC
DP-5A	393614075375802	5/3/2012	39°36'13.50"	75°37'58.91"	0.44	0.75	0.76	0.52-0.67	Columbia aquifer—Wetland sediments interface	PVC	2	PDB, PS	NC
EM-5D	393614075375801	8/25/2008	39°36'13.50"	75°37'58.91"	0.47	0.97	3.10	2.79-3.10	Columbia Formation	SS	2	PP, PS, PP	NC
DP-6A	393615075375805	5/11/2011	39°36'14.62"	75°37'58.15"	0.22	0.73	0.73	0.43-0.73	Wetland sediments	PVC	2	PDB, PS	NC
DP-6AA	393615075375804	12/13/2011	39°36'14.62"	75°37'58.15"	0.23	1.30	0.76	0.61-0.76	Wetland sediments	PVC	2	NC	12/11-11/12
EM-6S	393615075375801	8/25/2008	39°36'14.53"	75°37'58.28"	0.35	0.69	1.27	0.97-1.27	Columbia aquifer—Wetland sediments interface	SS	2	PDB, PP	NC
EM-6D	393615075375802	8/25/2008	39°36'14.53"	75°37'58.28"	0.38	0.82	3.34	3.03-3.34	Columbia Formation	SS	2	PDB, PP	NC
DP-8A	393616075380701	5/11/2011	39°36'16.66"	75°38'06.9"	-0.03	0.50	0.66	0.37-0.67	Wetland sediments	PVC	2	PDB, PS	NC
DP-10S	393617075380405	6/15/2011	39°36'16.80"	75°38'03.55"	0.35	1.05	0.62	0.46-0.61	Wetland sediments	PVC	0.75	PP	NC
DP-10A	393617075380407	12/13/2011	39°36'16.80"	75°38'03.55"	0.34	1.12	0.70	0.55-0.70	Wetland sediments	PVC	2	PS	NC
DP-10AA	393617075380403	11/16/2011	39°36'16.80"	75°38'03.55"	0.35	1.22	0.73	0.58-0.73	Wetland sediments	PVC	2	NC	01/12-10/12
DP-10B	393617075380402	4/27/2011	39°36'16.80"	75°38'03.55"	0.37	1.07	3.32	3.02-3.32	Columbia Formation	SS	2	PP	06/11-11/12
DP-11S	393617075380406	6/15/2011	39°36'17.45"	75°38'03.64"	-0.17	1.13	0.55	0.40-0.55	Wetland sediments	PVC	0.75	PP	NC
DP-11A	393617075380404	11/16/2011	39°36'17.45"	75°38'03.64"	-0.06	1.08	0.75	0.61-0.76	Wetland sediments	PVC	2	PDB, PP	N/A
DP-11B	393617075380401	4/27/2011	39°36'17.45"	75°38'03.64"	-0.13	1.01	4.30	3.99-4.30	Columbia Formation	SS	2	PDB, PP	06/11-11/12
DP-12S	393618075380204	6/15/2011	39°36'17.55"	75°38'02.37"	-0.31	1.04	0.55	0.40-0.55	Wetland sediments	PVC	0.75	PP	NC
DP-12AA	393618075380202	11/16/2011	39°36'17.55"	75°38'02.37"	-0.33	1.71	0.79	0.64-0.79	Wetland sediments	PVC	2	NC	12/11-11/12
DP-12A	393618075380203	12/13/2011	39°36'17.55"	75°38'02.37"	-0.26	1.48	0.98	0.82-0.98	Wetland sediments	PVC	2	PP, PS	NC
DP-12B	393618075380201	4/27/2011	39°36'17.55"	75°38'02.37"	-0.30	1.47	3.69	3.38-3.69	Columbia Formation	SS	2	PP	NC
DP-13S	393618075380403	6/15/2011	39°36'18.40"	75°38'03.60"	-0.34	1.09	0.59	0.43-0.58	Wetland sediments	PVC	0.75	PP	NC

Table 2. Monitoring network for the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.—Continued

[NAD83, horizontal coordinate information referenced to North American Datum of 1983; NGVD29, vertical elevation referenced to National Geodetic Vertical Datum of 1929; MP, reference elevation of measuring point referenced to land surface; als, above land surface; bls, below land surface; casing material: PVC, polyvinyl chloride; SS, stainless steel; CS, carbon steel; sampler type: PP, peristaltic pump; PDB, passive diffusion bag; PS, pumped syringe from well tubing; NC, not collected; N/A, not applicable; m, meters; in., inches; ° ' ", degrees, minutes, seconds]

Site name	Site identification number	Construction date	Latitude (NAD83)	Longitude (NAD83)	Land surface (m above NGVD29)	MP height (m als)	Well depth (m bls)	Screened depth (m bls)	Geologic unit[1]	Casing material	Casing diameter (in.)	Sampler type	Continuous record
DP-13A	393618075380402	11/16/2011	39°36'18.40"	75°38'03.60"	-0.32	1.07	0.77	0.61-0.76	Wetland sediments	PVC	2	NC	NC
DP-13B	393618075380401	5/11/2011	39°36'18.40"	75°38'03.60"	-0.31	1.19	5.67	5.36-5.67	Columbia Formation	SS	2	PP, PDB	06/11-02/13
DP-14S	393616075380103	6/15/2011	39°36'16.30"	75°38'00.89"	0.37	1.07	0.58	0.43-0.58	Wetland sediments	PVC	0.75	PP, PDB	NC
DP-14A	393616075380102	11/16/2011	39°36'16.30"	75°38'00.89"	0.37	1.07	0.74	0.58-0.73	Wetland sediments	PVC	2	PDB	NC
DP-14B	393616075380101	6/15/2011	39°36'16.30"	75°38'00.89"	0.43	1.16	3.96	3.66-3.96	Columbia Formation	SS	2	NC	11/11-11/12
DP-15S	393617075380004	6/15/2011	39°36'17.12"	75°38'00.08"	0.02	1.09	0.59	0.43-0.58	Wetland sediments	PVC	0.75	PP	NC
DP-15A	393617075380003	12/13/2011	39°36'17.12"	75°38'00.08"	0.06	1.00	0.80	0.64-0.79	Wetland sediments	PVC	2	PDB, PS	NC
DP-15AA	393617075380002	11/16/2011	39°36'17.12"	75°38'00.08"	0.07	1.14	0.85	0.70-0.85	Wetland sediments	PVC	2	NC	12/11-01/13
DP-15B	393617075380001	6/15/2011	39°36'17.12"	75°38'00.08"	0.04	1.07	4.15	3.84-4.15	Columbia Formation	SS	2	PP, PDB	6/11-02/13
DP-16S	393618075375903	6/15/2011	39°36'17.96"	75°37'58.95"	-0.37	1.09	0.60	0.43-0.58	Wetland sediments	PVC	0.75	PP	NC
DP-16AA	393618075375902	11/16/2011	39°36'17.96"	75°37'58.95"	-0.32	1.80	0.85	0.70-0.85	Wetland sediments	PVC	2	NC	11/11-11/13
DP-16A	393618075375904	1/18/2012	39°36'17.96"	75°37'58.95"	-0.36	1.46	0.98	0.82-0.98	Wetland sediments	PVC	2	PDB	NC
DP-16B	393618075375901	6/15/2011	39°36'17.96"	75°37'58.95"	-0.31	1.53	10.15	9.85-10.15	Wetland sediments	SS	2	PP, PDB	12/11-02/13
DP-17A	393620075375502	11/16/2011	39°36'20.87"	75°37'53.38"	-0.31	1.12	0.70	0.55-0.70	Wetland sediments	PVC	2	PDB, PS	NC
DP-17B	393620075375501	11/15/2011	39°36'20.87"	75°37'53.38"	-0.26	1.43	5.36	5.06-5.36	Columbia Formation	SS	2	PDB, PP	12/11-02/13
DP-18AA	393621075375503	5/24/2012	39°36'21.47"	75°37'52.75"	0.23	0.74	0.83	0.59-0.75	Wetland sediments	PVC	2	PS	NC
DP-18B	393621075375501	12/13/2011	39°36'21.47"	75°37'52.75"	0.23	0.52	2.29	2.06-2.29	Columbia Formation	SS	2	PDB	NC
DP-104A	393616075380201	5/11/2011	39°36'16.42"	75°38'02.44"	0.39	0.40	0.75	0.46-0.76	Wetland sediments	PVC	2	PDB, PS	NC
DP-107A	393615075380001	5/11/2011	39°36'15.96"	75°38'00.74"	0.42	0.45	0.59	0.27-0.58	Wetland sediments	PVC	2	PDB, PS	NC
Monitoring wells													
MW-21	393616075380502	11/10/1995	39°36'15.86"	75°38'04.58"	2.26	0.67	6.10	3.05-6.10	Columbia Formation	CS	2	PDB	NC
MW-22	393616075380202	11/10/1995	39°36'15.65"	75°38'02.92"	2.04	0.58	5.03	1.98-5.03	Columbia Formation	CS	2	PDB	NC
MW-23	393615075375901	12/27/1995	39°36'15.08"	75°37'59.73"	2.09	0.73	7.92	4.88-7.92	Columbia Formation	CS	2	PDB	NC
MW-24	393614075380901	10/7/1999	39°36'14.91"	75°38'09.76"	4.36	0.83	11.43	8.38-11.43	Columbia Formation	CS	4	NC	NC
MW-25	393616075380601	10/5/1999	39°36'15.86"	75°38'07.02"	3.39	0.70	9.51	6.46-9.51	Columbia Formation	CS	4	PDB	NC
MW-36	393624075375401	10/1/1999	39°36'24.35"	75°37'54.42"	4.62	0.96	16.46	13.41-16.46	Columbia Formation	CS	4	NC	NC
MW-37	393622075375203	5/25/2001	39°36'21.89"	75°37'52.19"	1.25	0.59	15.24	9.14-15.24	Columbia Formation	CS	4	NC	NC
MW-38	393620075374801	5/29/2001	39°36'20.53"	75°37'49.03"	1.62	0.57	15.24	9.14-15.24	Columbia Formation	CS	4	NC	NC

Table 2. Monitoring network for the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.—Continued

[NAD83, horizontal coordinate information referenced to North American Datum of 1983; NGVD29, vertical elevation referenced to National Geodetic Vertical Datum of 1929; MP, reference elevation of measuring point referenced to land surface; als, above land surface; bls, below land surface; casing material: PVC, polyvinyl chloride; SS, stainless steel; CS, carbon steel; sampler type: PP, peristaltic pump; PDB, passive diffusion bag; PS, pumped syringe from well tubing; NC, not collected; N/A, not applicable; m, meters; in., inches; ° ’ ”, degrees, minutes, seconds]

Site name	Site identification number	Construction date	Latitude (NAD83)	Longitude (NAD83)	Land surface (m above NGVD29)	MP height (m als)	Well depth (m bls)	Screened depth (m bls)	Geologic unit[1]	Casing material	Casing diam-eter (in.)	Sampler type	Continuous record
Surface-water sampling sites													
SW-02	393611075375603	5/7/2008	39°36’21.47”	75°37’56.90”	-0.50	1.42	N/A	N/A	N/A	N/A	N/A	NC	06/09-08/10
SW-06AA	393615075375806	12/13/2011	39°36’14.62”	75°37’58.15”	0.23	1.30	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-08A	393617075380702	5/11/2011	39°36’16.66”	75°38’06.9”	-0.03	0.50	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-104A	393616075380203	5/11/2011	39°36’16.42”	75°38’02.44”	0.39	0.40	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-107A	393616075380105	5/11/2011	39°36’15.96”	75°38’00.74”	0.42	0.45	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-10B	393617075380408	4/27/2011	39°36’16.8”	75°38’03.55”	0.37	1.07	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-11B	393617075380409	4/27/2011	39°36’17.45”	75°38’03.64”	-0.13	1.01	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-12B	393618075380205	4/27/2011	39°36’17.55”	75°38’02.37”	-0.30	1.47	N/A	N/A	N/A	N/A	N/A	PP	NC
SW-13B	393618075380404	5/11/2011	39°36’18.40”	75°38’03.60”	-0.31	1.19	N/A	N/A	N/A	N/A	N/A	PP	NC
SW-14B	393616075380104	6/15/2011	39°36’16.30”	75°38’00.89”	0.43	1.16	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-15B	393617075380006	6/15/2011	39°36’17.12”	75°38’00.08”	0.04	1.07	N/A	N/A	N/A	N/A	N/A	NC	NC
SW-16B	393618075375905	6/15/2011	39°36’17.96”	75°37’58.95”	-0.31	1.53	N/A	N/A	N/A	N/A	N/A	PP	NC
SW-17B	393620075375503	11/15/2011	39°36’20.87”	75°37’53.38”	-0.26	1.43	N/A	N/A	N/A	N/A	N/A	PP	NC
SW-18B	393621075375403	12/13/2011	39°36’21.47”	75°37’52.75”	0.23	0.52	N/A	N/A	N/A	N/A	N/A	NC	NC

[1] Wetland sediments: most commonly described as Marsh Deposits (Qm) that are structureless to finely laminated, black to dark gray, organic-rich silty clay with some peat beds.

Columbia Formation (Qcl): Yellow to reddish-brown, fine to coarse sand, typically cross-bedded, with some gravel at base of unit. Scattered beds of clayey silt common, often overlying medium to coarse sand.

From Ramsey, 2005.

Table 3. Groundwater sampling and site events that may have influenced sampling results in the wetland study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[LDPE, low density polyethylene; dialysis, dialysis membrane; PDBs, passive-diffusion bags; DCRC, Delaware City Refining Company]

Sample type	Sample locations or sites	Sampling dates
Barrier wall installed in 2007		
Peepers	6, 7, 8, 9	July 2009
In Situ microcosms	6, 9	October–December 2009
DCRC limited pumping starting December 2009 and stopped in May 2010		
LDPE PDBs (in sediment)	8, 102, 103, 104, 106, 107, 108, 109, 110, 7, 6, 14, 15, 112, 113, 114, 116, 117, 118, 119, 120, 131, 121, 122, 123, 125, 126, 127	September 2010
LDPE and dialysis PDBs (in sediment)	8, 102, 103, 104, 107, 110, 6, 114, 14, 119, 121, 15, 113, 117, 126, 130	October 2010
LDPE and dialysis PDBs	8, 104, 107, 112, 7, 6, 116, 123, 125; 128, 129, 12, 131, 132, 133, 134, 135, 136, 11, 138, 139, 140, 144, 141, 142, 143	April 2011
LDPE and dialysis PDBs (in drive-point piezometers)	DP-6A, DP-8A, DP-104A, DP-107A	Monthly beginning July 2011–January 2012
Hurricane Irene, August 28, 2011, and damage to tide control structure		
LDPE and dialysis PDBs (in sediment and drive-point piezometers)	Existing PDB sites + DP-10B, DP-11B, DP-13B, DP-14B, DP-15B, MW-21, MW-22, MW-23, MW-25, EM-6D, EM-6S	October 2011
Peepers	10, 12, 14, 15	October 2011
LDPE and dialysis PDBs (in sediment and drive-point piezometers)	145*–160*, 6, 8, 17, DP-6A, DP-8A, DP-104A, DP-107A, DP-17B, EM-6D, EM-6S	December 2011
Peepers	6, 8	December 2011
DCRC pumping resumes January 2011		
LDPE and dialysis PDBs/purge and recover	DP-6A, DP-8A, DP-104A, DP-107A	Monthly beginning February 2012–May 2012
LDPE and dialysis PDBs (in sediment for comparison to PDBs placed in drive-point piezometers)	DP-6A, DP-8A, DP-104A, DP-107A	March 2012
Purge and recover for A piezometers, peristaltic pump for B piezometers	DP-6A, DP-8A, DP-104A, DP-107A, DP-5A, DP-17A, DP-18AA, DP-10B, DP-15B, SW-13, SW-17	May 2012
Purge and recover for A piezometers, peristaltic pump for B piezometers	DP-6A, DP-8A, DP-104A, DP-107A, DP-5A, DP-17A, DP-18AA, DP-10B, DP-15B, SW-13, SW-17, DP-10A, DP-15A, DP-12A, DP-12B	July 2012–August 2012

* Only LDPE PDBs installed.

analysis. Data collected for hydrologic interpretation included water-level measurements for determination of groundwater hydraulic head, flow direction and rates, and slug tests to approximate hydraulic conductivity. Measured gradients and hydraulic conductivities were used to calculate specific discharge and average linear velocity of groundwater.

Water-Level Measurements

Water-level measurements were made in the wetland study area and across the SCD in order to determine groundwater-flow directions and rates and to monitor for changes in the flow system that could result from seasonal fluctuations, pumping in the Potomac regional water-supply aquifer, and tidal influence following damage sustained by the tide control structure on Red Lion Creek. Water-level measurements were used to construct groundwater head maps, hydrographs, and cross-sectional flow diagrams. Vertical and lateral flows within the Columbia aquifer and surficial wetland sediments were examined individually, and vertical flow between the two units was analyzed.

Water levels in the drive-point piezometers and monitoring wells were measured during monthly synoptic assessments and during sampling events (table 3) to monitor any seasonal variations within the aquifer and the porewater in the wetland sediments. Monthly synoptic measurements were coordinated with HydroGeoLogic, Inc. to obtain wetland and upland measurements in the SCD area; USGS and HydroGeoLogic, Inc. staff measured water levels in wells outside of the wetland area, whereas USGS measured water levels in the piezometers within the wetland area. The water levels were measured from the measuring point with electronic tapes graduated to 0.30 cm. The altitude of the measuring points is given relative to the National Geodetic Vertical Datum of 1929 (NGVD 29) and was determined using a digital level to an accuracy of 0.61cm for all sites except DP-18AA. Water levels in surface water, denoted as “SW,” were measured at a cluster from the “B” drive point measuring point at all sites except site 6, which referenced DP-6AA. All water-level data were entered and stored in the USGS National Water Information System (NWIS) database. Once in the database, the water levels were normalized to altitudes, allowing them to be compared across the study area.

Continuous water-level data were collected to provide information about shallow groundwater response to seasonal changes, tidal effects, groundwater withdrawals, and groundwater recharge events. Pressure transducers were installed at the Red Lion Creek tide gage and in 12 drive-point piezometers, consisting of 5 shallow “AA” piezometers and 7 deeper “B” piezometers (table 2), to provide coverage along both transects and at the wetland boundary. The pressure transducers were installed in the piezometers between June 2011 and December 2011 with a period of record ranging from 12 to 19 months. The range of the pressure transducers was 5 to 15 pounds per square inch gage (psig), and the water levels interpreted from readings of pressure were accurate to 0.1 percent. The pressure transducers recorded the water-level altitudes every 15 minutes, and the data were stored in NWIS. The calibration of the transducers was checked during the monthly water-level synoptic assessments and any drift or datum corrections were applied in NWIS.

Slug Tests

Slug tests were conducted at four drive-point piezometer nests in the wetland study area in order to approximate hydraulic conductivity of the hydrologic units. Tests were performed on piezometers screened in wetland sediments (DP-6A, DP-11A, DP-12AA), and in the Columbia aquifer (EM-6D, DP-11B, DP-12B, DP-15B), representing both the east and west sides of the wetland study area during two different time periods. Tests were conducted at the DP-11, DP-12, and DP-15 drive-point piezometer nests during the winter 2011–12 field season, whereas tests at EM-6D and DP-6A were conducted during the winter of 2013. A test was initiated at DP-15A but was terminated prior to completion because of an extremely slow response to the artificially induced change in hydraulic head.

Slug tests were performed by inducing an artificial change in hydraulic head and measuring the time taken for a water level to return to its static condition. A Troll 700 (In Situ, Inc.) pressure transducer was placed in the piezometer following an initial static water-level measurement, and was used to collect water-level data at a logarithmic time scale during the test. Induced change in hydraulic head was accomplished in two ways depending on the formation in which the drive-point piezometer was screened. For drive-point piezometers screened in shallow wetland sediments, bail tests and slug tests were accomplished using deionized water (Freeze and Cherry, 1979, p. 339). Drive-point piezometers were bailed for rising head tests, and a slug of deionized water was injected for falling head tests. These tests were done in sequence at each drive-point piezometer. At DP-11A and DP-12A, a falling head test was conducted first by adding 1 liter (L) of deionized water to the drive-point piezometer and recording the return to static water level. Three subsequent rising head tests were completed by removing approximately 340 mL of water from the drive-point piezometer using a PVC bailer, which was 4.1 cm in diameter and 30 cm in length. For DP-6A, the bailer (approximately 340 mL) was used in place of the initial 1-L slug of deionized water. First, the bailer was inserted into the drive point and the water level was allowed to equilibrate; then it was removed, bailing approximately 340 mL of native water from the drive-point piezometer, and the return to static conditions was monitored. Once static water level was regained, the full bailer was replaced, and the return to static conditions was again monitored. Two sequences of these tests were conducted at DP-6A. At drive-point piezometers screened in the Columbia aquifer, at least three sequences of rising and falling head slug tests were conducted using a PVC cylindrical slug, which was 2.86 cm in diameter and

152 cm in length. All data were collected using WinSitu software (In Situ, Inc.).

Slug test data were analyzed and hydraulic conductivities were computed using the Bouwer-Rice method (Fetter 2001, p. 197–200). These estimates of hydraulic conductivity were then used to determine approximate groundwater discharge rates for given drive-point piezometers.

Calculations of Hydraulic Gradient, Specific Discharge, and Linear Velocity

Groundwater altitudes collected within the wetland study area were used to determine hydraulic gradients (flow directions). Hydraulic conductivities derived by slug test analysis for selected points were used in conjunction with these gradients to compute specific discharge (Darcian velocity) and average linear velocity in the wetland and Columbia aquifer in the wetland study area. Hydraulic gradient, specific discharge (v), and average linear velocity (V) were calculated in both the lateral and vertical directions.

Vertical gradients were calculated for drive-point piezometer pairs at sites EM-1, EM-2, EM-5, EM-6, DP-10, DP-11, DP-12, DP-13, DP-14, DP-15, and DP-16. At each of these pairs, the vertical gradient was calculated between wells screened in the Columbia aquifer and wetland sediments, except for EM-1, where both wells were screened in wetland sediments, and EM-2 and EM-5, where both wells were screened in the Columbia aquifer or at the interface of the Columbia aquifer and wetland sediments, respectively. Lateral hydraulic gradients were calculated by estimating the change in hydraulic head (estimated from mapped potentiometric surface contours) and dividing this difference by the difference between these contours along transects where drive-point piezometers were installed.

Lateral specific discharge (Darcian velocity) was calculated using the following equation (Fetter, 2001, p. 82):

$$v = -K\left(dh / dl\right) \tag{1}$$

where

K = hydraulic conductivity;
dh = the change in hydraulic head between points; and
dl = the lateral distance between points.

Estimates of vertical groundwater discharge were calculated across the interface between wetland sediments and the Columbia aquifer, which have differing hydraulic conductivities. In order to represent the thickness of each unit through which groundwater discharge is estimated, a weighted hydraulic conductivity was used. Thus, the equation for specific discharge was modified:

$$v = -K_w\left(dh / dz\right) \tag{2}$$

where

K_w = weighted hydraulic conductivity;
dh = the change in hydraulic head between points; and
dz = the vertical distance between screen midpoints.

Weighted hydraulic conductivity was calculated using the equation (Freeze and Cherry, 1979, p. 34):

$$K_w = \left(d_1 + d_2\right) / \left(\left(d_1 / K_1\right) + \left(d_2 / K_2\right)\right) \tag{3}$$

where

K_w = weighted hydraulic conductivity;
d_1 = the distance between the screen midpoint of the piezometer screened in wetland sediments and the interface between the wetland sediments and the Columbia aquifer at that piezometer;
d_2 = the distance between the midpoint of the screen in the Columbia aquifer and the wetland sediment interface;
K_1 = the hydraulic conductivity of wetland sediments at the given piezometer; and
K_2 = the hydraulic conductivity of the Columbia aquifer at the given piezometer.

Average linear groundwater velocity was calculated using the following equation (Fetter 2001, p. 125):

$$V = \left(-Kdh / dl * n_e\right) \text{ for lateral velocity} \tag{4}$$

and a modified version of Fetter's average linear groundwater velocity for the vertical direction:

$$V = \left(-K_w dh / dl * n_e\right) \text{ for vertical velocity} \tag{5}$$

where

K = hydraulic conductivity;
K_w = weighted hydraulic conductivity;
dh = the change in hydraulic head between points;
dl = the lateral distance between points; and
n_e = the effective porosity of the unit through which groundwater is traveling (dimensionless).

Estimates of effective porosity of the wetland sediments and the underlying aquifer sediments at the SCD were drawn from previous studies conducted in similar wetland environments. For wetland sediments, an effective porosity of 0.4 was used based on computations conducted for groundwater velocity in a similar environment (Lorah and others, 1997; Mitsch and Gosselink, 1993). Soil cores were collected at four drive-point piezometer nest locations (EM/DP-6, DP-8,

DP-104, DP-107) within the SCD wetland study area and analyzed for carbon content resulting in a range of 0.19 to 24.2 percent carbon. For groundwater velocity estimates for the Columbia aquifer, an effective porosity of 0.3 was used (Domenico and Schwartz, 1990). This effective porosity also was used for calculations of vertical velocity, which were made across the wetland sediments interface and included both Columbia sands and wetland sediments consisting of clay, silt, and organic matter.

Groundwater and Surface-Water Geochemical Data

Groundwater and surface-water samples collected between July 2009 and August 2012 are summarized in table 3. Sample collection began with only four sites in July 2009 and then expanded spatially and temporally to characterize the wetland geochemistry. Sample collection and methods of analysis and data quality are discussed below.

Sample Collection

An initial assessment of the wetland groundwater chemistry began in 2009 with a detailed vertical characterization of the shallow wetland sediments using peepers at four sites (table 3). Large scale synoptic and recurring monthly sampling events then were used to determine the spatial extent of contamination and capture any seasonal variation in the geochemistry of the wetland and aquifer groundwater (table 3). Because of the ease of installation and sampling, peepers and PDBs were initially installed in the sediments, allowing more sampling sites in the wetland area with minimal infrastructure before installation of the piezometers. LDPE PDBs were used to obtain samples for VOCs and dissolved gas analyses, and dialysis membrane PDBs were used to obtain samples for all other constituents and field parameters. Usage of either one or both of these diffusion samplers are referred to simply as PDBs for the remainder of this report, although table 3 notes specific sampler types that were used for each sampling event. PDBs were used to obtain samples by direct push into the sediment and also to obtain downhole samples from drive-point piezometers and wells. For downhole sampling, PDBs were placed inside a polyethylene mesh tubing with stainless steel weights and suspended within or slightly above the screened interval with braided nylon cord. All PDBs were allowed to equilibrate for a minimum 2-week period before removal for sample collection.

In July 2009, peepers at sites 6, 7, 8, and 9 were sampled for VOCs, ferrous iron, chloride, nitrate, and ammonia. In September 2010, PDBs for the collection of VOC and methane samples were installed in the ground along three parallel transects: one extending from site 8 to site 6, along the edge of the wetlands and two shorter transects in the eastern part of the wetland (table 3). The synoptic sampling event in October 2010 was a resampling of selected sites using in-ground PDBs and included samples for VOCs, methane, sulfate, chloride, pH, and specific conductance (table 3). Multiple sets of PDBs also were installed at some sites (6, 8, 15, 121, 104, and 114) to assess spatial geochemical variability and assist in selecting sites for *in situ* microcosm experiments. During the April 2011 synoptic sampling event, PDBs were installed at existing sites and at new sites that extended the two northern transects to the west (table 3). In July 2011, PDBs were used to sample newly installed piezometers DP-10B, 11B, 12B, 13B, and 15B by suspending them within or slightly above the screened interval.

The largest sampling event began in October 2011 and continued through December 2011, collectively referred to as the October–December 2011 sampling event in this report. PDBs were installed in the sediment at most pre-established sites and at new sites; peepers were installed at six sites; and selected drive-point piezometers and monitoring wells were sampled by suspending PDBs within or slightly above the screened interval (table 3). All PDBs were sampled for VOCs, dissolved gases, ferrous iron, total iron, sulfide, anions, cations, ammonia, pH, and specific conductance, however only VOCs and dissolved gases were sampled from the PDBs installed in the sediment at new sites 145 to 158 and site 160 (fig. 3b). Peepers were sampled for VOCs, dissolved gases, ferrous iron, sulfide, anions, cations, and ammonia.

Monthly samples collected from July 2011 through August 2012 are included in this report (table 3). Starting in July 2011, monthly sampling occurred at sites 6, 8, 104, and 107 in the “A” depth piezometers to determine if groundwater and porewater geochemistry varied seasonally. At each site and event, samples were typically collected for analysis of VOCs, dissolved gases, ferrous iron, total iron, sulfide, anions, cations, ammonia, pH, and specific conductance. From July 2011 to January 2012, monthly sampling was conducted by suspending PDBs downhole. Beginning in February 2012, the drive-point piezometers screened within the wetland sediments were sampled by the purge and recover method, which involved purging with a dedicated bailer and then sampling the next day with dedicated Teflon tubing, a three-way stopcock, and a syringe. Sampling was conducted after ensuring that the water level had recovered at least 75 percent. In May 2012, the monthly sampling was expanded to include DP-5A, DP-17A, DP-18AA, DP-10B, DP-15B, SW-13, and SW-17 and expanded again in July 2012 to include DP-10A, DP-15A, DP-12A, and DP-12B.

Nearly all piezometers were fully recovered within 24 hours except DP-104A, which sometimes required 2 days to recover. The tubing was placed near the bottom of the piezometer while sampling but within the screened interval to decrease the turbidity of the purge water and prevent filter loading. Throughout sample collection, a three-way stopcock was used to maintain positive pressure within the tubing in between syringe volumes. All filtered samples were collected with a rinsed Pall Acrodisc® 0.2-µm Supor® membrane syringe filter and a 10-mL syringe.

A change in sample collection method (downhole PDBs to purge and recover sampling; see table 3) was implemented in the shallow wetland piezometers due to results of direct comparisons of in-well PDBs, sediment PDBs, and purge and recover samples. These comparisons indicated that in-well PDBs may generally underestimate VOCs and, to a lesser extent, methane, sulfide and ferrous iron concentrations in porewater compared to both sediment PDBs and purge and recover samples. Particularly at elevated concentrations (greater than 10 milligrams per liter [mg/L] of VOCs), the disparity between in-well and sediment PDBs was apparent. It is possible groundwater passively entering screened intervals in shallow drive-point piezometers was dominated more by deeper porewater (where results generally showed lower VOC concentrations, as discussed later in the Distribution of Volatile Organic Compounds section) or were less directly impacted by contaminant sources in nearby sediment. Nonetheless, direct comparisons of the purge and recover sampling method to the PDB methods resulted in an order of magnitude concentration difference between the sediment and in-well PDBs at some sites, although good agreement was observed at others. To eliminate this potential bias, further samples were collected using the purge and recover method.

Drive-point piezometers screened in the Columbia aquifer were sampled with a peristaltic pump fitted with dedicated Teflon and CFlex© tubing, a three-way stopcock, and a syringe. The piezometers were purged and sampled using the methods described by the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). The pump intake was placed within the screened interval and the piezometer was purged of a minimum of three casing volumes at a pump rate that allowed the water level to remain stable. Field parameters, including pH, water temperature, specific conductance, and sometimes turbidity were recorded every 5 minutes. Once the field parameters were stable for 25 minutes, the piezometer was sampled with a syringe.

The surface-water samples were collected using a peristaltic pump fitted with dedicated Teflon and C-Flex® tubing, a three-way stopcock, and a syringe. The intake tubing was placed within the center one-third of the water column and held in position with a permanently installed PVC pipe. Use of the pipe ensured the samples were consistently collected at the same location and prevented suspension of bottom sediments. The sample was collected after the tubing had been rinsed with native water a minimum of 10 tubing volumes and the field parameters were stable.

Chemical Analysis

Water temperature, specific conductance, and pH were measured with a Hach HQ 40d multi-parameter meter with a standard conductivity probe and gel-filled pH probe. Turbidity was determined using a Hach 2100Q turbidity meter calibrated with Hach StablCal® standards. All meters were calibrated daily as described in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated).

Methane, ethane, and ethene samples were collected by injecting 2 to 5 mL of raw sample water into a weighed, sealed, nitrogen purged, serum bottle filled with at least .035 grams (g) of trisodium phosphate (TSP), a preservative (Majcher and others, 2007). The samples were stored on ice or in a refrigerator until the headspace was analyzed on a HP 7890 gas chromatograph with a flame ionization detector (GC-FID) located at the USGS Maryland-Delaware-DC Water Science Center (MD-DE-DC WSC) (Spencer and others, 2002).

VOC analyses were conducted at the USGS MD-DE-DC WSC Research lab on a purge and trap gas chromatograph with a mass spectrometer (GC-MS) and a headspace autosampler. A modified purge and trap method that combines components of EPA methods 524.2 (U.S. Environmental Protection Agency, 1995) and 8260C (U.S. Environmental Protection Agency, 2006) was implemented on the GC-MS with modifications outlined in Majcher and others (2007) and the addition of selected chlorinated benzenes to the analyte list. The GC-MS is equipped with an OI Analytical 4560 sample concentrator and an OI Analytical 4552 headspace autosampler. The modified method enabled low volume samples to be analyzed. VOC samples were collected in the field in 8-mL borosilicate glass vials with Teflon septa with no headspace and stored on ice or in a refrigerator until processed.

Total and ferrous iron concentrations were determined using the colorimetric bipyridine method (Baedecker and Cozzarelli, 1992) after filtering the samples using a 2-µm membrane syringe filter and diluting them by a factor of 10 with deionized water. The appropriate reagents were added at sample collection to induce the color change and fixed in the field with sodium acetate. The samples were stored chilled until analyzed on a Hach DR 2800™ spectrophotometer reading at a wave length of 520 nanometers.

Ammonia, nitrate, and sulfate samples were analyzed in the field or mobile lab using Hach TNTplus™ vials and analyzed immediately after collection on a Hach DR 2800™ spectrophotometer (Hach Company, 2007). Sulfide samples were collected and analyzed immediately in the field or mobile lab using the methylene blue method (Hach Company, 2007) and also analyzed on the spectrophotometer. To ensure that the sample concentrations fell within the range determined by the manufacturer, samples were diluted with deionized water, or multiple test kits covering different concentration ranges were used if possible. Samples were filtered with a 0.2-µm membrane syringe filter if the sample was visibly turbid, except for sulfide samples. Sulfide samples were not filtered because of sulfide's high potential for volatilization and oxidation. For each lot of test kit vials or reagents, the calibration of the spectrophotometer was confirmed with standards purchased from Hach Company.

Samples for analysis of nonvolatile dissolved organic carbon (NVDOC) were filtered with a 0.2-µm membrane syringe filter into 4-mL baked amber vials with Teflon septa.

The samples were acidified to a pH below 2 with high purity hydrochloric acid in the field. The samples were stored chilled until analyzed at the USGS Research Laboratory, Reston, Virginia. The NVDOC samples were measured using a Shimadzu TOC-Vcsn Total Organic Analyzer and the 680 degrees Celsius (°C)-combustion catalytic oxidation method modified from EPA Method 415.3 (U.S. Environmental Protection Agency, 2009).

Before August 2011, chloride concentrations were determined by the mercuric nitrate method using the Hach Digital Titrator (Hach Company, 2006) at the USGS MD-DE-DC WSC laboratory. The samples were collected raw, stored in 40-mL amber glass vials with Teflon septa, and chilled until processed. After August 2011, anion samples, including chloride, were filtered using a 0.2-µm membrane syringe filter and stored in a rinsed 15-mL high density polyethylene bottle. The samples were stored chilled and then analyzed at the USGS Reston laboratory using a Dionex 120 Ion Chromatograph with an ED50 Electrochemical detector. The AS14 anion-exchange column was used for the separation of the anions chloride, bromide, nitrate, phosphate, and sulfate, meeting the performance requirements specified in EPA Method 300.0 (A) (U.S. Environmental Protection Agency, 1993).

Data Quality

The quality of the groundwater data collected was determined based on quality-control data obtained from blanks and duplicate samples. Inadvertent cross-contamination of water-quality samples was minimized by using either new or dedicated tubing, syringes, and other sampling supplies for all piezometer samples that were collected by the syringe or peristaltic pump sampling methods, and for withdrawal of samples from PDBs and peepers. Equipment blanks were collected for about 10 percent of the total number of samples during a sampling event by running deionized water through clean tubing and syringes and collecting it as a sample to evaluate potential contamination from equipment. For each sampling event, a set of blank PDBs was sampled after preparing and purging with nitrogen gas and before deployment in the field; the deionized water used to fill the peepers also was analyzed as an equipment blank. In addition, trip blanks for VOC analysis were collected during each sampling event by filling vials with deionized water and keeping them with the groundwater samples collected at the site to evaluate the potential for cross-contamination during transport and storage until analyses were performed. Duplicate samples were collected by sequential or concurrent filling of vials during piezometer sampling with the syringe or peristaltic pump. Duplicate samples were not collected from peepers or PDBs due to the limited amount of sample available.

An analysis of a total of 24 blanks collected during this study indicated that concentrations of chlorinated benzenes and benzene were generally less than 1 microgram per liter (µg/L). One blank sample had sample concentrations of CB, 14DCB, and 12DCB between 1 and 2 µg/L, which is negligible given the high concentrations observed at the site.

Sequential duplicate samples were used to estimate measurement precision for analyses of chlorinated benzenes and benzene. Relative sample difference (RSD) of duplicate sample measurements for a given constituent provides an indication of general precision. The RSD for each constituent was computed as follows:

$$RSD_i = ABS\left[\left[\left(X_2 - X_1\right) / \left(Mean\left(X_1 + X_2\right)\right)\right]\right] * 100 \qquad (6)$$

where

RSD_i = the relative sample difference for a given constituent X and the ith duplicate pair (i = 1, 2, 3 or 4), expressed in percent;

ABS = the absolute value of the entire subsequent calculation;

$X_2–X_1$ = the difference in measurements between first sample collected (X_1) and the second sample (X_2) collected sequentially after X_1; and

$Mean\ (X_1+X_2)$ = the value used to normalize their difference for comparative purposes.

A total of 18 duplicate samples were collected from the following drive-point piezometers: DP-15A, DP-15B, DP-12A, DP-12B, DP-10B, DP-107A, and DP-104A. The overall average RSD (benzene and chlorinated benzenes) for the 18 duplicates included in this analysis was 10 percent. Concentrations for samples included in this analysis ranged from below detection to over 12,000 µg/L. Average RSD values ranged from 6.5 percent for 12DCB to 13.6 percent for 124TCB. A total of 6 out of 133 individual RSD values were excluded from these calculations as extreme outliers, possibly due to compound misidentification.

RSDs of duplicate sample pairs also were calculated for field parameters and other geochemical constituents. Specific conductance and pH had an average RSD of less than 1 percent. Ammonia, ferrous iron, and sulfide had average RSDs of 20 percent or lower based on 13, 11, and 14 duplicate pairs, respectively. Total iron had an average RSD of 23 percent, based on 11 duplicate pairs. Based on 38 duplicate pairs, NVDOC, chloride and sulfate measurements had average RSD values of 18, 3, and 12 percent, respectively. Methane analyses had an average RSD of 10 percent, based on 26 duplicate pairs.

Several analyses (less than 5) for benzene and chlorinated benzenes were completed outside of the recommended hold time, which is 2 weeks (monthly samples taken during January, February, April, May, and July of 2012; and the October 2011 synoptic event). Typically, the hold time was not longer than 3 weeks, however, an additional experiment was designed to determine if longer hold times affected the concentrations of contaminants in the sample. The RSD between the initial and first week measurements were under 15 percent,

except for benzene, 12DCB and 124TCB, which had RSDs of 21, 16, and 20 percent, respectively. However, subsequent differences between week one and week five were all under 10 percent. For VOC analyses, analytical precision of 30 percent is considered acceptable.

The measurement precision among the different constituents was taken into consideration for the interpretation of this report. However, with the wide range of concentrations found in the study area, the RSDs are within acceptable limits to describe patterns in the occurrence and distribution of constituents in the groundwater at the SCD.

Experiments to Assess Bioremediation

In Situ Microcosms

In situ microcosms allow assessment of bioremediation potential under field conditions, including natural groundwater flow rates, and with native microbial populations. The *in situ* microcosms utilized for field assessment of biodegradation of the chlorobenzene compounds and benzene at the SCD are Bio-Trap units (Microbial Insights, Rockford, Tennessee) contained in a 35.6-cm (14-inch [in.])-long, 3.18-cm (1.25-in.)-diameter screened (10 slot) PVC section, along with other customized passive diffusion samplers to collect groundwater for chemical analyses (fig. 4). Bio-Traps contain small beads, called Bio-Sep beads, made of a non-reactive, high-surface-area carbon material that provides a surface for attachment and subsequent collection of the native subsurface microorganisms (White and others, 2003; Peacock and others, 2004; Geyer and others, 2005; Weiss and Cozzarelli, 2008; Burns and others, 2013). The Bio-Sep beads also can be preloaded with amendments, including bioaugmentation cultures and ^{13}C-labeled contaminants, to assess specific issues, such as the efficiency of natural biodegradation compared to enhanced bioremediation and the relative rate of contaminant degradation.

The *in situ* microcosms were pushed directly into the wetland sediment, with each PVC unit containing one treatment and separated from other treatments pushed to the same depth by a lateral distance of about 25 cm. In October 2009, three sets of *in situ* microcosm devices were deployed for 8 weeks at two sites, 6 and 9 (fig. 3), to evaluate natural attenuation (unamended device), biostimulation (device amended with lactate and chitin as an electron donor), and bioaugmentation (device amended with lactate, chitin, and the WBC-2 culture) (fig. 4; table 4). Two additional *in situ* microcosms, a natural attenuation treatment and a bioaugmented treatment, were constructed with an additional microbial sampler containing Bio-Sep beads pre-loaded with ^{13}C-labeled monochlorobenzene and deployed at site EM-6. The ^{13}C-labeled Bio-Traps were used to evaluate degradation of the contaminant by loss of the ^{13}C-labeled contaminant over the incubation period and incorporation of ^{13}C from the labeled monochlorobenzene in

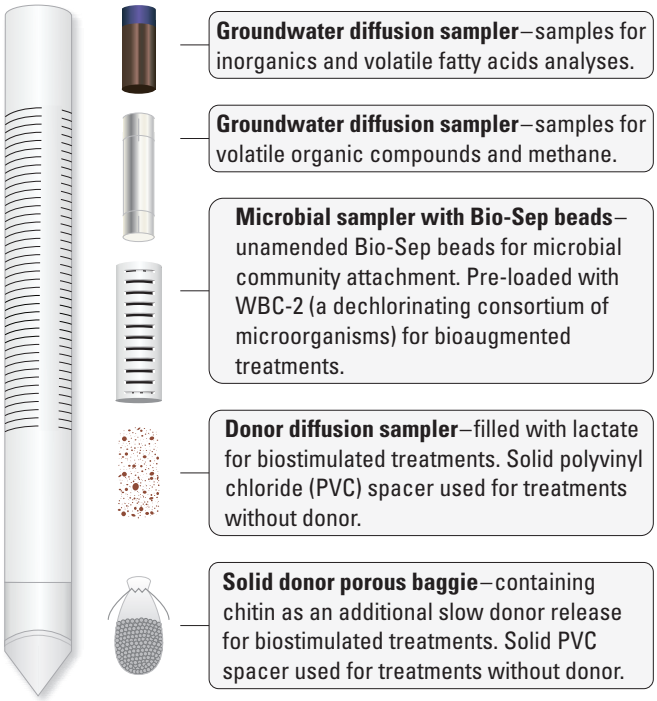


Figure 4. Schematic diagram of Bio-Trap (Microbial Insights, Rockford, Tennessee) sampler used for *in situ* microcosms.

dissolved inorganic carbon (DIC, reported as carbon dioxide, CO_2) and in phospholipid fatty acid (PLFA). The presence of ^{13}C in DIC indicates mineralization of the labeled contaminant. PLFA is a primary component of the membrane of all living cells and decomposes quickly upon death; thus, ^{13}C incorporation in PLFA provides a measurement of contaminant utilization for growth by living biomass. In October 2010, a total of 36 *in situ* microcosms were deployed for 7 weeks at four sites, including two sites that were the same or near those used for testing in 2009 (sites 6, 8, 104, and 107 in fig. 3; table 4). Treatment sets (unamended, biostimulated, and bioaugmented) at all sites included control microcosms that were not amended with ^{13}C compounds and sets amended with ^{13}C-labeled contaminants (table 4). ^{13}C-14DCB treatments were deployed at all four sites, and ^{13}C-CB treatment sets were deployed at three sites with a ^{13}C-benzene treatment set deployed instead at the fourth site. Screens of the microcosm devices were placed in the wetland sediment at a depth of 25 to 56 cm below land surface in 2009 and 2010.

Upon retrieval of the *in situ* microcosms, groundwater diffusion samplers for collection of VOCs, anions (sulfate, chloride, nitrate, and phosphate), and volatile fatty acids were sealed with Teflon-lined caps and placed in coolers for transport to the laboratories. VOCs were analyzed in the USGS MD-DE-DC WSC laboratory as described above for groundwater sampling, whereas anions and volatile fatty acids were sent to Microbial Insights for analysis by ion chromatography. Groundwater diffusion samplers for the

Table 4. *In situ* microcosm treatments deployed from October 20–December 16, 2009 and from October 26–December 14, 2010 at selected wetland sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Treatments included MNA, monitored natural attenuation (control); lactate/chitin, donor addition for biostimulation; and WBC-2, West Branch Consortium-2, for bioaugmentation; WBC-2 treatment also contained added lactate/chitin; --, no treatment deployed]

Original site name	Site number	Sample date	Control treatments	^{13}C-labeled treatments		
				^{13}C-Chlorobenzene	^{13}C-1,4-Dichlorobenzene	^{13}C-Benzene
PDB-10-28	DP-6	12-16-09	MNA	MNA	--	--
PDB-10-29	DP-6	12-16-09	Lactate/chitin	Lactate/chitin	--	--
PDB-10-30	DP-6	12-16-09	WBC-2	WBC-2	--	--
	DP-9	12-16-09	MNA	--	--	--
	DP-9	12-16-09	Lactate/chitin	--	--	--
	DP-9	12-16-09	WBC-2	--	--	--
PDB-01-01	DP-8	12-14-10	MNA	MNA	MNA	--
PDB-01-02	DP-8	12-14-10	Lactate/chitin	Lactate/chitin	Lactate/chitin	--
PDB-01-03	DP-8	12-14-10	WBC-2	WBC-2	WBC-2	--
PDB-04-10	DP-104	12-14-10	MNA	MNA	MNA	--
PDB-04-11	DP-104	12-14-10	Lactate/chitin	Lactate/chitin	Lactate/chitin	--
PDB-04-12	DP-104	12-14-10	WBC-2	WBC-2	WBC-2	--
PDB-07-19	DP-107	12-14-10	MNA	MNA	MNA	--
PDB-07-20	DP-107	12-14-10	Lactate/chitin	Lactate/chitin	Lactate/chitin	--
PDB-07-21	DP-107	12-14-10	WBC-2	WBC-2	WBC-2	--
PDB-10-28	DP-6	12-14-10	MNA	--	MNA	MNA
PDB-10-29	DP-6	12-14-10	Lactate/chitin	--	Lactate/chitin	Lactate/chitin
PDB-10-30	DP-6	12-14-10	WBC-2	--	WBC-2	WBC-2

redox-sensitive constituents ammonia, ferrous iron, and sulfide were sealed without headspace in VOC vials with Teflon-lined caps; samples were analyzed by using colorimetric methods (as described in the Geochemical Data section above) either immediately in the field or within 24 hours of collection at the USGS MD-DE-DC WSC laboratory. Methane, ethane, and ethene analyses by GC/FID were conducted by Microbial Insights for the 2009 microcosms and at the USGS MD-DE-DC WSC laboratory for the 2010 microcosms.

The Bio-Traps from the *in situ* microcosms were immediately placed in zippered bags and sent to Microbial Insights for microbial community and ^{13}C analyses using methods detailed in Burns and others (2013). Microbial genetic analyses included quantitative polymerase chain reaction (qPCR) analysis for total eubacteria and for specific target populations known to be involved in anaerobic degradation of chlorinated solvents. Although these target population tests originally were developed specifically for evaluation of reductive dechlorination of chlorinated ethenes and ethanes, several of the target populations also have been shown to be involved in reductive dechlorination of chlorobenzene compounds. General composition of the microbial communities present in the *in situ* microcosms was obtained by analysis of the PLFA structural groups (table 5). Microbial populations colonizing the *in situ* microcosms deployed in 2010 also were analyzed using denaturing gradient gel electrophoresis (DGGE) and excising selected bands for sequencing and identification. During the 2009 *in situ* microcosm retrieval, wetland sediment samples were collected from depths of 12.7 cm and 27.9 cm below land surface at the two microcosm sites and sent to Microbial Insights for analysis of microbial communities by qPCR and PLFA structure for comparison to the Bio-Trap samplers. Isotope analyses included the amount of ^{13}C-labeled contaminant, $^{13}C\text{-}CO_2$, and ^{13}C-PLFA in the microcosms after incubation compared to quantities measured before the Bio-Traps were deployed.

Laboratory Bioreactors

Three bench scale, static bed bioreactor systems were operated in an on-site trailer for the wetland study (a diagram of one bioreactor system is shown in figure 5). Two bioreactor systems were seeded with WBC-2 (“D” and “E”), and a third bioreactor was seeded only with bacteria derived from the site groundwater pumped through the bioreactor (“C,” or control bioreactor). The D and E bioreactors were previously

Table 5. Description of phospholipid fatty acid (PLFA) structural groups that are used to describe microbial community composition on the basis of fatty acid biosynthesis.

PLFA sructural group	Community classification	Description
Polyenoics	Eukaryotes	Found in eukaryotes such as fungi, protozoa, algae, higher plants, and animals; includes scavengers that will prey on contaminant-utilizing bacteria.
Normal Saturated (Nsats)	General	Found in all organisms. High proportions indicate a low diversity in microbial populations.
Mid-Chain Branched Daturated (MidBrSats)	Actinomycetes	High G+C gram-positive cell membrane structure common in sulfate-reducing bacteria and Actinobacteria.
Branched Monoenoic (BrMonos)	Anaerobic metal reducers	Found in the cell membranes of micro-aerophiles and anaerobes; often associated with anaerobic sulfate and iron-reducing bacteria.
Monoenoic (Monos)	Proteobacteria	One of the largest groups of bacteria (gram negative bacteria) and represents a wide variety of aerobes and anaerobes, including the majority of bacteria that utilize hydrocarbons.
Terminally Branched Saturated (TerBrSats)	Firmicutes	Indicative of presence of anaerobic fermenting bacteria (mainly *Clostridia* and *Bacteriodes*), which are important for breakdown of organic substrates to a form utilized by bacteria during reductive dechlorination.

bioaugmented with 1 L of WBC-2 microbial consortium and had viable populations of the consortium established during operation for a previous USGS-Geosyntec collaborative study to assess biodegradation of chlorinated ethanes and ethenes (Geosyntec Consultants, 2012).

The bioreactor systems each consisted of a groundwater equalization/mixing tank, three 1-L PVC vessels filled with a high-surface area polypropylene support matrix for biofilm growth, and an effluent (waste) tank (fig. 5). Water was pumped to the first reactor vessel with a peristaltic pump, equipped with Viton tubing. Effluent from the first vessel was transported by gravity to the second and third vessels and finally to the effluent tank. Two sample ports were located on each vessel, and samples also were collected from the groundwater equalization and effluent tanks. An argon gas blanket was maintained in the headspace of each bioreactor vessel by delivering a slow, continuous flow of argon to the top of each bioreactor vessel from a compressed gas cylinder. Because argon has a density greater than air, it would sink and expel air from the top of the bioreactor to help keep the system anaerobic. Operation of the three bioreactors began in March–April 2012, with the bioaugmented D and control C bioreactors receiving groundwater inflow from piezometer DP-15B and the bioaugmented E bioreactor receiving groundwater from piezometer DP-10B. These piezometers, selected on the basis of contaminant concentrations and ease of pumping, were located within the wetland area but screened at shallow depths in the aquifer underlying the wetland sediments (table 2, fig. 3). The bioreactors were operated through the end of October 2012, with varying amendments during selected periods to evaluate factors affecting biodegradation of the chlorobenzene compounds and benzene present in the influent groundwater.

Operational maintenance was performed several times a week and involved refilling the groundwater equalization tank and maintaining the peristaltic pumps and associated tubing. The equalization tank was filled with a combination of the influent groundwater from DP-10B or DP-15B, nutrients, electron donor, and a pH buffer to support microbial growth and anaerobic degradation of the contaminants. A combination of ammonia chloride and potassium phosphate were used as the nutrient stock solution, with optimal concentrations of 3 mg/L (as N) and 0.3 mg/L (as P), respectively. A mixture of lactate and corn syrup was added to provide electron donors; donor concentrations were monitored by measuring the chemical oxygen demand (COD) with desired concentrations of 300 mg/L in the influent and about 50–100 mg/L remaining in the waste. Sodium bicarbonate ($NaHCO_3$) was used as a buffer to adjust the pH of the influent water to about 7.0. To evaluate the activity of WBC-2 compared to the native microbial community in the bioreactors, the bioreactors were amended with the main VOC that WBC-2 was developed to degrade, 1,1,2,2-tetrachloroethane (TeCA), for a period of about 80 days in addition to the site contaminants. Site contaminants were delivered throughout the bioreactor experiment only from those naturally present in the site groundwater used to fill the inflow tanks, and concentrations varied with changes in the groundwater at the piezometer sites during the experiment and with VOC losses during groundwater pumping, transport, and filling of the influent tanks and during the holding time in the tanks. The flow rate for all of the bioreactors ranged from

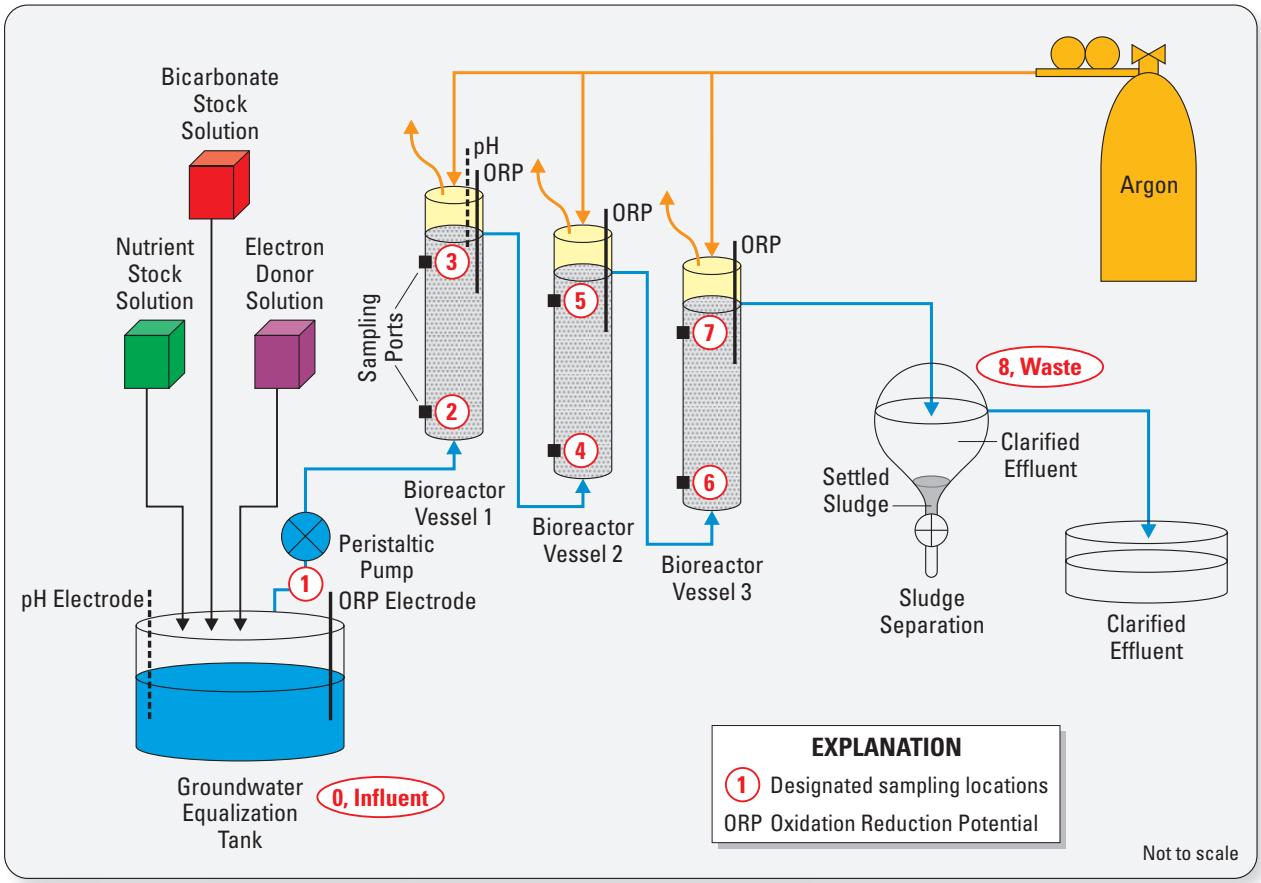


Figure 5. Diagram of the anaerobic bioreactor system and sampling locations.

1 and 3 milliliters per minute (mL/min) with a measurement precision of 0.1 mL/min.

Samples were taken from various ports in the vessels and from the influent and waste tanks several times a week and analyzed for VOCs, methane, ammonia, reactive phosphate, sulfate, sulfide, pH, and oxidation-reduction potential (ORP). VOCs and methane were analyzed in the USGS MD-DE-DC WSC laboratory, as explained for the groundwater sampling. Duplicate VOC samples were taken sequentially from one sampling port throughout the experiments to obtain 33 pairs of duplicates. Average RSDs for the duplicate pairs ranged from 7.2 to 15 percent for all VOCs analyzed, except for trichloroethene (one of the daughter products of TeCA), which was 20 percent. COD samples were collected in 8-mL borosilicate vials and processed in the USGS MD-DE-DC WSC laboratory using Hach TNTplus™ vials and analyzed on a Hach DR 2800™ spectrophotometer (Hach Company, 2007). Ammonia, phosphate, sulfate, and sulfide also were analyzed using Hach test kits and a spectrophotometer but were processed on-site immediately after sample collection. The pH was measured with a Hach HQ 40d multi-parameter meter with a standard gel-filled pH probe that was calibrated daily with pH 4 and 7 buffers. The ORP was measured with a Hach ORP Pocket Pal Tester™ in millivolts (mV). The calibration of the ORP tester was confirmed monthly with GLI, International's +200 mV ORP Reference Solution (Hach Company, Loveland, Colorado).

Hydrogeologic Characterization

In order to assess the distribution, migration, and potential for degradation of contaminants in the wetland study area at the SCD, an understanding of the hydrogeologic context for contaminant transport is critical. Prior to this study, the understanding of the hydrology of the SCD was limited to the uplands. The following section provides this hydrogeologic context by presenting the lithology of the wetland study area at the SCD, analysis of groundwater-flow directions and rates in the wetland and underlying Columbia aquifer, and an estimate of groundwater flux to Red Lion Creek.

Lithology of the Study Area

The lithology of the USGS wetland study area at the SCD was assessed using core logs from drive-point piezometers that were installed by USGS staff as part of this study and from previously installed wells along the wetland-upland boundary of the wetland study area along Haul Road (fig. 3; Black & Veatch, 2007). The upland-wetland boundary occurs at the primary change in slope south of Haul Road and parallel to Red Lion Creek (fig. 3b). Boring logs recorded as part of this study provide descriptions of wetland sediments and the Columbia Formation within the wetland study area, and provide a more detailed characterization of wetland sediments in the vicinity of Red Lion Creek. Lithology is shown along two transects through the wetland study area—transect A–A′, which extends to the northeast from the east side of Haul Road in the upland area and across Red Lion Creek, and transect B–B′, which extends to the northwest from the west side of Haul Road in the upland area to the south edge of Red Lion Creek (figs. 3a, 6, 7). Descriptions of regional stratigraphy from the Delaware Geological Survey (Ramsey, 2007) and site-specific stratigraphy from Black & Veatch (2007) also were used to describe the Columbia aquifer and the underlying Merchantville and Potomac Formations.

Wetland sediments at the SCD can be grouped into two stratigraphic units, an upper organic-rich unit consisting of root mass and organic matter in a mineral matrix of silt and (or) clay, and a basal unit consisting of clay, silt, and fine-grained sand. The upper, organic-rich unit is typically dark brown to black with scattered grey clay layers, with a median carbon content of 7.7 percent and a maximum carbon content of 24.2 percent. Carbon content was measured in sediment cores collected from the upper 0.44 to 0.6 m of wetland sediments near the upland-wetland boundary. Organic carbon content may be higher in the thick organic units adjacent to Red Lion Creek, but was not quantified. The lithology of the basal wetland sediment unit varies laterally and includes interfingering lenses of grey to tan and brown clay with fractions of silt and (or) sand, and lenses that are predominantly tan to brown silt with fractions of clay. Orange or reddish tan clay, silty clay, sandy clay, and clayey sand have been noted along transect B–B′ at drive-point piezometer nests DP-10, DP-11 and DP-13 (fig. 7), as well as in sand and clayey sand units along transect A–A′ at drive-point piezometer DP-15B, and on the north side of the creek at drive-point piezometers DP-17B and DP-18B (fig. 6).

Wetland sediments vary laterally in thickness. Transect A–A′ shows a profile of an incised channel, with lenses of clay along the creek banks and predominantly silt and organic fill in the channel center (fig. 6). Wetland sediments have been estimated to extend to greater than 10 m below land surface at DP-16B, however, further data collection would help to define the interface between wetland sediments and the Columbia aquifer in this area (fig. 6). Transect B–B′ shows upper organic-rich wetland sediments deepening from the upland-wetland boundary toward the creek to greater than 2 m thick. This organic-rich unit is underlain by silty clay, clay and sandy clay up to 2 m thick (DP-11B, fig. 7). The combined thickness of upper organic rich and basal fine-grained mineral wetland sediment units along this transect is as much as 5.2 m at the edge of Red Lion Creek at DP-13B (fig. 7). Wetland sediments on site are underlain by the Columbia Formation.

The Columbia Formation has been described as a fine- to medium-grained feldspathic quartz sand, which is typically yellow to reddish-brown in color, and with varying amounts of gravel and intermittent layers of tan to reddish grey, clayey silt (Ramsey, 2007). Upper units of the Columbia Formation have been reported to contain grey to red-brown silt and very fine sand underlain by medium to coarse sand, whereas the base of the unit contains quartz and chert gravel beds with cobble and boulder-sized clasts of sandstone, siltstone, shale, pegmatite, schist and amphibolite (Ramsey, 2007). This formation is thought to have been formed as a result of fluvial deposition of glacial outwash filling an eroded, non-planar topographic surface (Ramsey, 2007). Previous investigations have shown that this unit ranges from approximately 2.5 to 25 m in thickness at SCD, and is capped by wetland sediments in the vicinity of Red Lion Creek (Black &Veatch, 2007). Boring logs from drive-point piezometers installed in the wetland study area describe the Columbia aquifer as a brown to orange-brown, medium to coarse, poorly sorted, angular to sub-angular sand and gravel with fine to coarse sand. The Columbia sands have silty (DP-11B) and clayey (DP-13B) layers along transect B–B′ (fig. 7), and a gravel layer that is greater than 1 m thick is noted at DP-15B along transect A–A′ (fig. 6). Well logs from previously installed wells in the upland part of the study area give similar descriptions for the Columbia Formation (Black & Veatch, 2007). The Columbia Formation is underlain by the low permeability Merchantville Formation, and in areas where the Merchantville is absent, is underlain by low permeability beds of the upper Potomac Formation (Black & Veatch, 2007).

Drive-point piezometers did not extend into the Merchantville or Potomac Formations, but they are described here to frame the regional geology. The Merchantville in the area of the SCD has been described as a grey to green-grey glauconitic micaceous clay to silty or sandy clay (Black & Veatch, 2007). At the SCD, the unit has been reported to have a maximum thickness of 6.7 m and an average thickness of 3.1 m where present, but has been found to be laterally discontinuous. The Merchantville Formation has been considered to be a confining unit regionally, separating the surficial Columbia aquifer from the Potomac aquifer. However, numerous studies in the vicinity of the SCD have described absence of the Merchantville in boring logs, erosion of the Merchantville prior to deposition of the Columbia aquifer, and hydraulic connection between the Columbia and Potomac aquifers (Black & Veatch, 2007). Black & Veatch reported in their 2007 Final Remedial Investigation Report that the Merchantville Formation was either missing or could not be distinguished from the upper Potomac Formation in nearly half of boring logs evaluated from SCD (Black & Veatch, 2007).

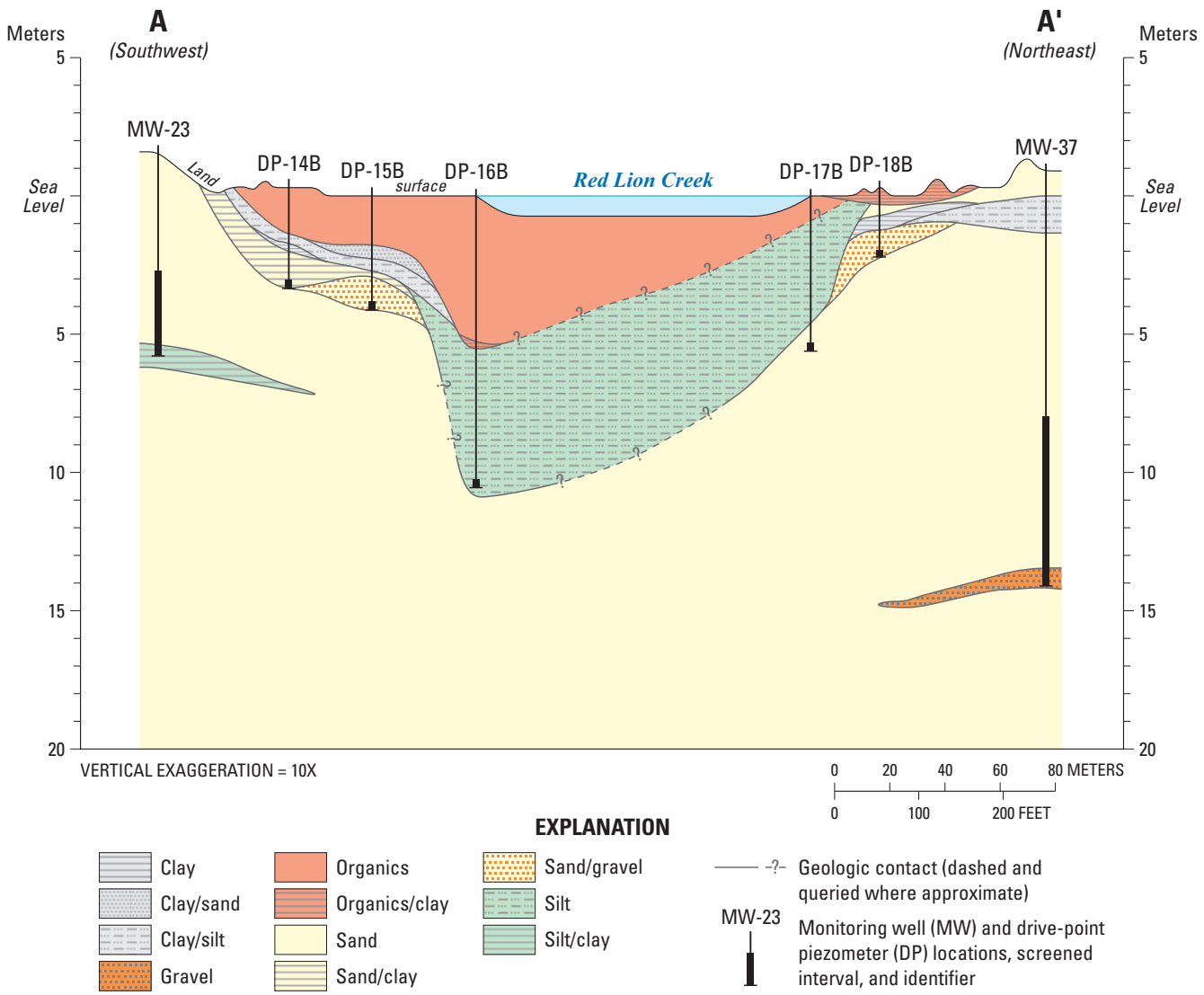


Figure 6. Hydrogeology and locations of monitoring wells and drive-point piezometers along section A–A′, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

The Potomac Formation consists of red, grey, pink, and white silty clay and clayey silt, interbedded with very fine to medium sand units of fluvial deposition (Ramsey, 2005). The top of the Potomac at SCD consists of predominantly clayey sediments, which may have eroded into paleochannels (Black & Veatch, 2007).

Groundwater Hydraulic-Head Distribution and Flow Direction

Potentiometric surface maps for the Columbia aquifer and the wetland sediments were constructed for five dates between June 22, 2011 and September 30, 2012 in order to examine changes in flow direction and hydraulic gradient that could result from seasonality or in response to changing hydrologic conditions. Potentiometric surface maps for the Columbia aquifer and the wetland sediments are shown in figures 8 and 9, respectively for August 8, 2012, which is considered representative of “normal” precipitation and hydraulic head conditions, with 10 cm total precipitation during the preceding month and active photosynthesis. Little to no temporal variations in flow direction in the Columbia aquifer and minimal variation in flow direction in the shallow wetland sediments were observed compared to this period of “normal” conditions, although other dates included extreme events (fig. 10):

1. June 22, 2011—relatively dry conditions, preceding month had 3.8 cm total precipitation during a period of high photosynthetic activity; date also precedes Hurricane Irene and Tropical Storm Lee;

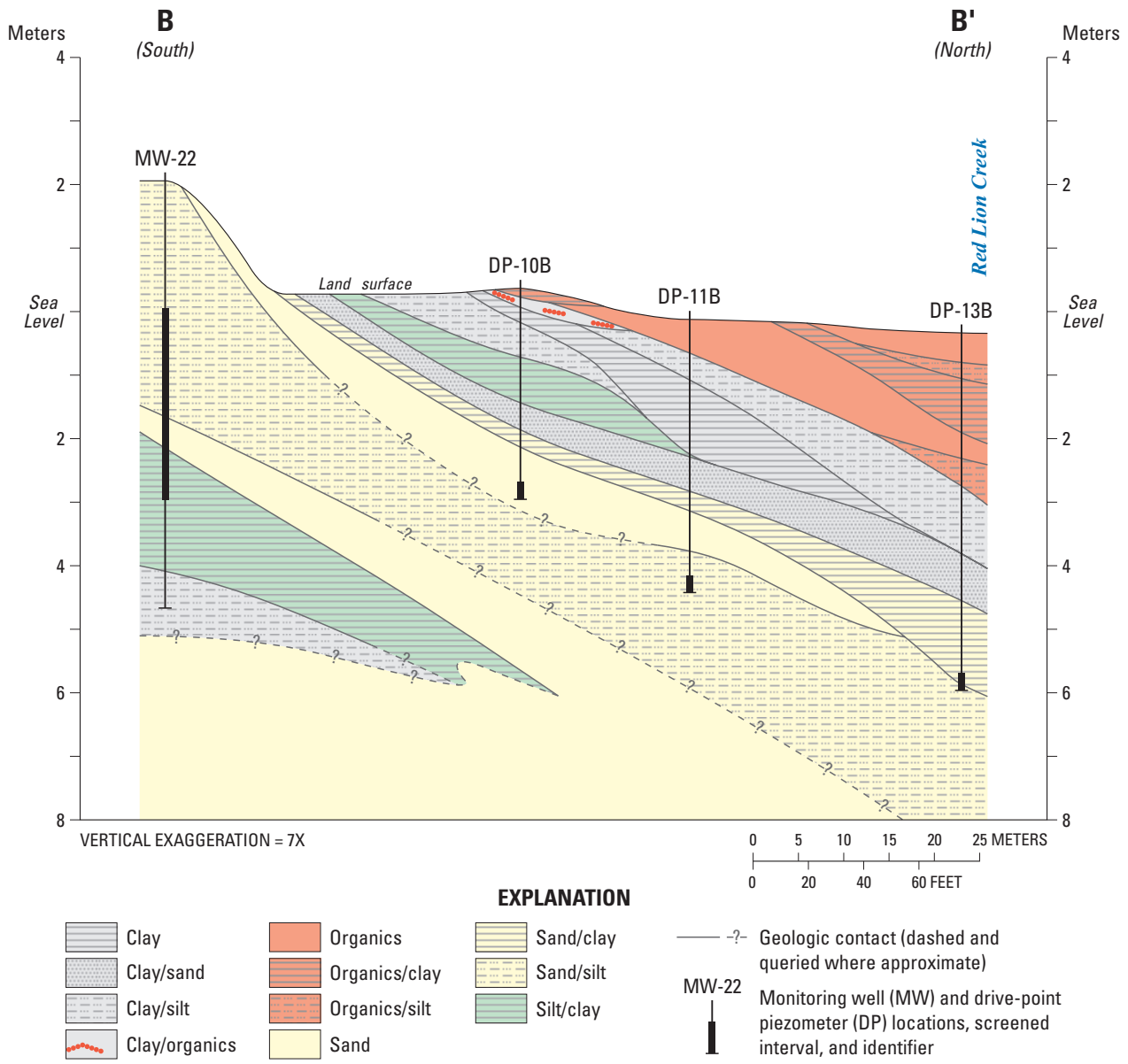


Figure 7. Hydrogeology and locations of monitoring wells and drive-point piezometers along section B–B′, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

2. September 14, 2011—very wet conditions, preceding month had 41 cm total precipitation; date is immediately following Hurricane Irene and Tropical Storm Lee and potential damage to the tide control structure on Red Lion Creek;

3. December 8, 2011—high moisture conditions, preceding month had 16 cm total precipitation and this date immediately follows a storm during a period of minimal photosynthetic activity; this is a very high point in the hydrographs for nearly all of the drive-point piezometers in the SCD wetland study area;

4. February 16, 2012—relatively dry period, preceding month had a total of 5 cm of total precipitation, during a period of low photosynthetic activity.

Hydraulic head distributions measured across the SCD showed that lateral flow in the Columbia aquifer is toward Red Lion Creek on both its north and south sides (fig. 8), which is consistent with previous studies of flow direction at the SCD (Black & Veatch, 2007). Although flow generally follows topography, the containment barrier installed in 2007 surrounding the developed part of SCD produces an artificially low gradient north of the upland-wetland boundary (fig. 8).

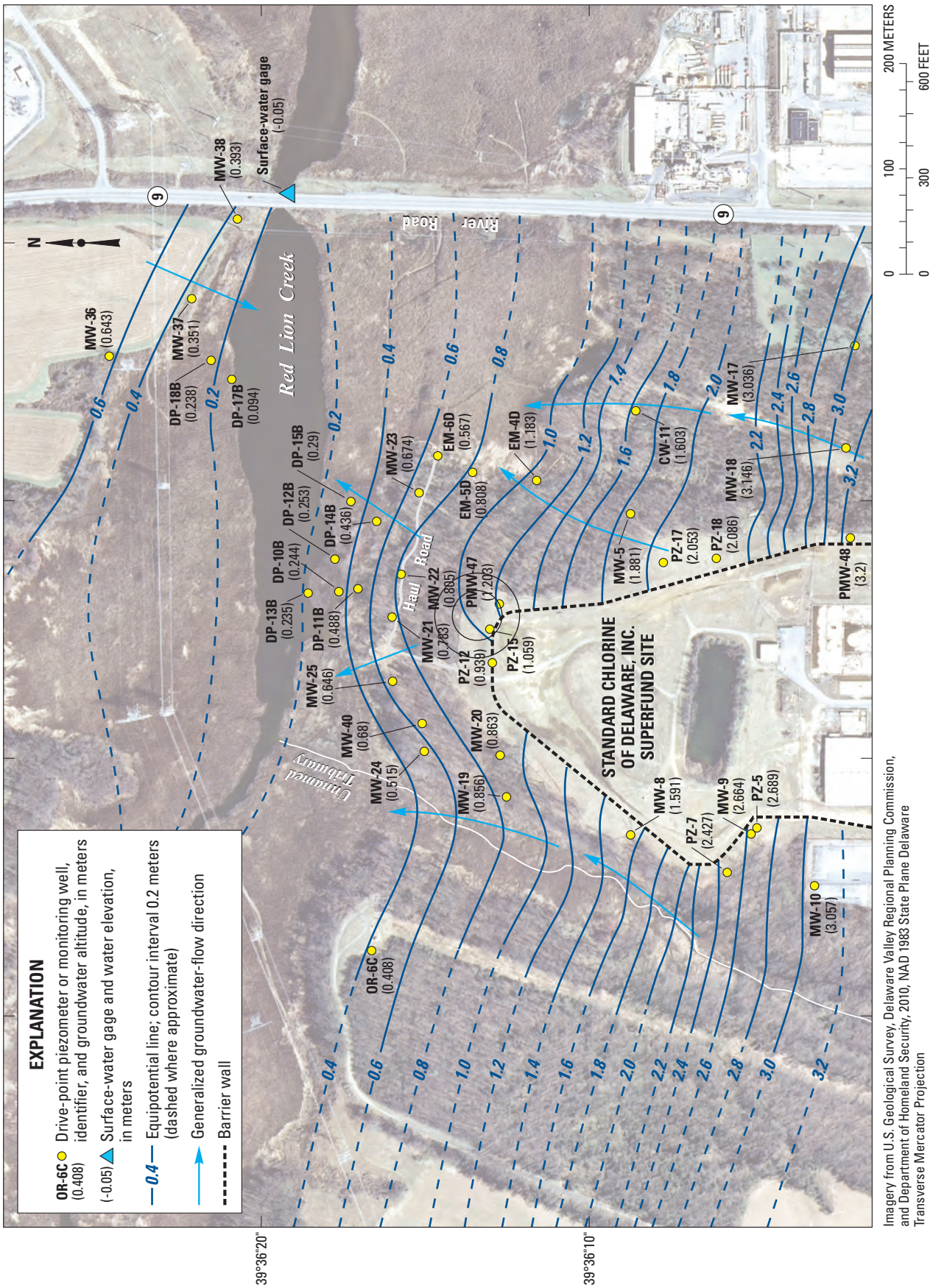


Figure 8. Groundwater altitude (in meters above mean sea level) in the Columbia aquifer, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

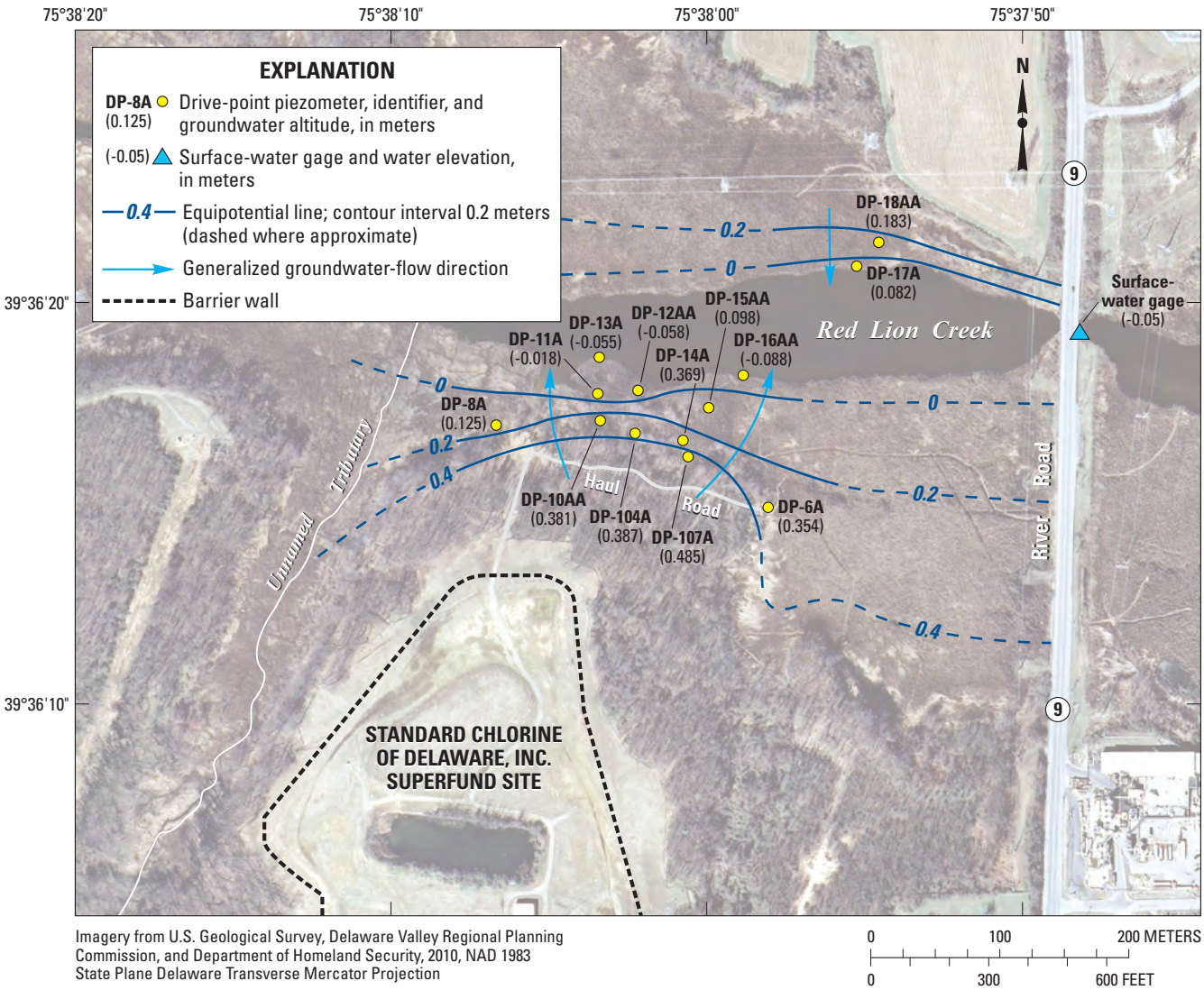


Figure 9. Groundwater altitude (in meters above mean sea level) in the wetland sediments, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

On the south side of Red Lion Creek, north of the barrier wall and within the wetland study area, lateral groundwater flow radiates generally out into the wetland about a flow divide between sites 12 and 15. Flow on the east side of this boundary is slightly toward the northeast, and flow on the west side of the boundary is slightly to the northwest (fig. 8).

Wetland sediments at the SCD are present in the low-lying fringe of Red Lion Creek, with less than 1 m of topographic variation from the boundary of the wetland to open water on Red Lion Creek. Though topographic variation in this area is very shallow, lateral groundwater flow in the wetland sediments reflects the topography near the upland-wetland boundary and is generally toward Red Lion Creek (fig. 9). Near the creek, where the thickness of wetland sediments increases, hydraulic head in the wetland sediments is very close to that of the creek, and the influence of lateral movement of groundwater is muted by upward components of flow (fig. 9).

Although groundwater-flow directions in the Columbia aquifer and wetland sediments were quite similar, the distribution of lateral hydraulic gradient differed between the units. Lateral hydraulic gradients in the Columbia aquifer were calculated using the head map constructed from water levels measured on August 8, 2012, and were fairly consistent from east to west (fig. 8). A gradient of 0.006 meters per meter (m/m) to the north/northeast was calculated along transect A–A′ on the eastern side of the wetland flow divide, and a gradient of 0.0068 m/m to the north/northwest was calculated along B–B′ on the west side of the wetland. This is consistent with the previously reported average gradient of groundwater in the Columbia aquifer of approximately 0.005 feet per feet (ft/ft) (or m/m) to the north/northeast (Black & Veatch, 2005).

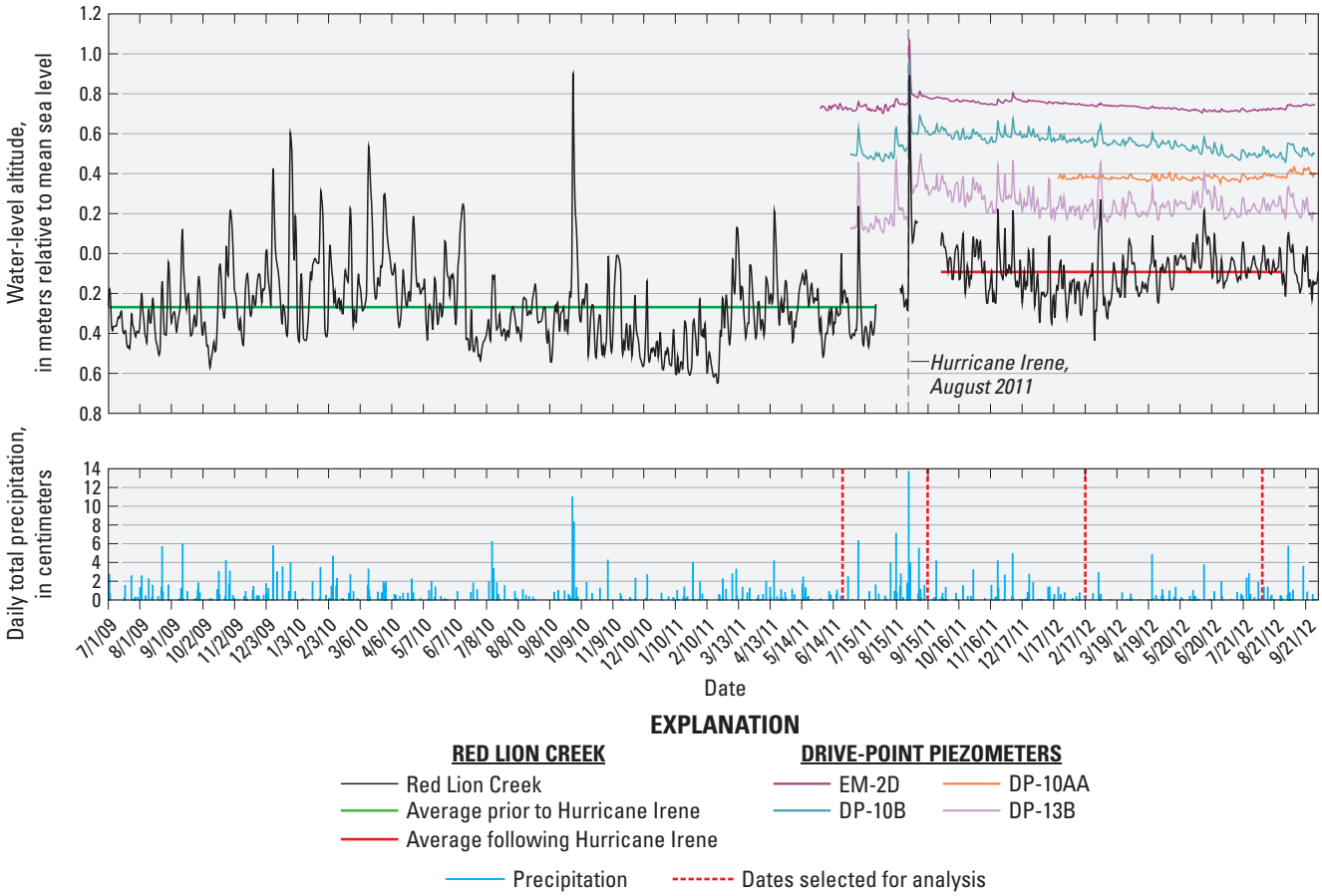


Figure 10. Water-level altitudes of Red Lion Creek and selected drive-point piezometers and daily total precipitation, July 2008–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

Lateral gradients were calculated using a groundwater head map from the same date for wetland sediments, and these lateral gradients showed greater variation from east to west than those calculated for the Columbia aquifer (fig. 9). Gradients were steeper in wetland sediments along transect B–B′ (0.013 m/m) on the west side of the flow divide than along A–A′ (0.007 m/m) on the east side. Lateral gradients calculated from piezometer to piezometer in both the Columbia aquifer and wetland sediments varied with proximity to the upland boundary with the wetland, with gradients more than an order of magnitude greater near the upland-wetland boundary than those observed between piezometers located closer to the creek (data on file at the MD-DE-DC WSC). This is due in part to the strong component of upward vertical groundwater discharge that was observed near the creek.

Upward vertical flow of groundwater between the Columbia aquifer and overlying wetland sediments was apparent at most locations where groundwater heads were measured across the wetland study area. Of the drive-point piezometers installed in the wetland study area, only two showed variation between groundwater recharge and discharge conditions (vertically upward and downward gradients, respectively). Alternating gradients were observed at the EM-1 and DP-14 drive-point clusters, whereas all other sites showed consistent vertically upward gradients (table 6). The magnitude of upward discharge of groundwater in the wetland showed only small variation seasonally and spatially, ranging from -0.01 m/m to -0.16 m/m for selected dates in 2011 and 2012 (table 6). Site DP-12, which is located at the boundary between the wetland and open water on Red Lion Creek, had the largest vertically upward hydraulic gradients site-wide for the dates that were evaluated. In contrast, the smallest gradient was observed at site EM-1 (-0.01 m/m), which is the southernmost drive-point piezometer and farthest from the creek of the sites that were evaluated.

Overall, the magnitude of lateral and vertical hydraulic gradients supports the conceptual model for groundwater flow to Red Lion Creek in the wetland study area, which is laterally toward the creek from the north and south and vertically upward through the wetland sediments. Cross-sectional flow diagrams constructed for transects A–A′ (fig. 11) and B–B′ (fig. 12) show that flow is lateral from the south and north and becomes increasingly vertical with proximity to the creek center.

Table 6. Calculated vertical gradients from selected drive-point piezometer pairs in the Columbia aquifer and wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Negative gradient values indicate vertically upward discharge, whereas positive gradients indicate vertically downward movement of groundwater. See table 2 for piezometer site information; --, no data]

Site identification number	Drive-point pair	Geologic unit	2011				2012		
			June	July	Sept.	Dec.	Jan.	Feb.	Aug.
EM-1	1S–1D	Wetland sediment—Wetland sediment	--	0.03	-0.01	-0.05	-0.00	-0.00	0.05
EM-2	2S–2D	Columbia aquifer—Columbia aquifer	-0.04	-0.04	-0.05	-0.05	-0.05	--	-0.04
EM-5	5A–5D	Columbia aquifer/Wetland sediment interface—Columbia aquifer	--	--	--	--	--	--	-0.12
EM/DP-6	6S–6D	Columbia aquifer/Wetland sediment interface—Columbia aquifer	-0.11	-0.10	-0.11	-0.12	--	-0.11	-0.09
	6A–6D	Wetland sediment—Columbia aquifer	-0.12	-0.10	-0.12	-0.15	--	-0.11	-0.09
DP-10	10S–10B	Wetland sediment—Columbia aquifer	-0.04	-0.04	--	--	-0.07	-0.07	--
	10AA–10B	Wetland sediment—Columbia aquifer	--	--	--	-0.12	-0.08	-0.07	-0.04
DP-11	11S–11B	Wetland sediment—Columbia aquifer	-0.10	-0.09	-0.09	-0.05	-0.10	-0.10	--
	11A–11B	Wetland sediment—Columbia aquifer	--	--	--	-0.06	-0.11	-0.10	-0.07
DP-12	12S–12B	Wetland sediment—Columbia aquifer	-0.15	--	--	-0.11	-0.15	-0.13	--
	12AA–12B	Wetland sediment—Columbia aquifer	--	--	--	-0.11	-0.16	-0.16	-0.11
DP-13	13S–13B	Wetland sediment—Columbia aquifer	-0.10	-0.12	-0.06	-0.04	-0.08	-0.09	--
	13A–13B	Wetland sediment—Columbia aquifer	--	--	--	-0.05	-0.09	-0.07	-0.06
DP-14	14S–14B	Wetland sediment—Columbia aquifer	--	--	--	-0.08	0.01	0.00	--
	14A–14B	Wetland sediment—Columbia aquifer	--	--	--	-0.11	--	-0.06	-0.02
DP-15	15S–15B	Wetland sediment—Columbia aquifer	-0.04	-0.05	--	-0.06	-0.05	-0.04	--
	15AA–15B	Wetland sediment—Columbia aquifer	--	--	--	-0.07	-0.07	-0.06	-0.06
DP-16	16S–16B	Wetland sediment—Wetland sediment	--	--	--	-0.05	-0.05	-0.06	--
	16A–16B	Wetland sediment—Wetland sediment	--	--	--	--	-0.08	-0.07	-0.05
DP-17	17A–17B	Wetland sediment—Columbia aquifer	--	--	--	--	-0.07	-0.06	-0.04
DP-18	18AA–18B	Wetland sediment—Columbia aquifer	--	--	--	--	--	--	-0.06

Hydraulic Conductivity

Hydraulic conductivity was measured by conducting slug tests at four drive-point piezometer nests in the wetland study area for use in determining rates of groundwater discharge. Hydraulic conductivity was generally higher in the Columbia aquifer compared to the wetland sediments, although measurements from both hydrologic units were within two orders of magnitude (table 7). Previous studies of hydraulic properties of wetland sediment in a similar Coastal Plain setting in Maryland showed hydraulic conductivity estimates ranging from 0.0003 to 0.04 feet per day (ft/d) in peat-dominated sediments and 0.0008 to 0.04 ft/d in clay-dominated wetland soils (Lorah and others, 1997). Slug tests were performed where responses to induced gradient were measureable; therefore, these estimates of hydraulic conductivity within the SCD wetland study area may be biased slightly high. However, estimates of hydraulic conductivity are within the range of values reported for non-peat wetland soils to moderately to slightly decomposed, northern peatland sediments (Mitsch and Gosselink, 1993). A slug test was initiated at DP-15A but was abandoned due to slow recovery, which likely would have produced an orders-of-magnitude smaller hydraulic conductivity value for surrounding wetland sediments compared to the other sites tested.

Groundwater Discharge and Velocity

Because most drive-point piezometer nests were screened in the Columbia aquifer and wetland sediments, rates of vertical groundwater discharge were estimated using weighted values of hydraulic conductivity and vertical gradients calculated

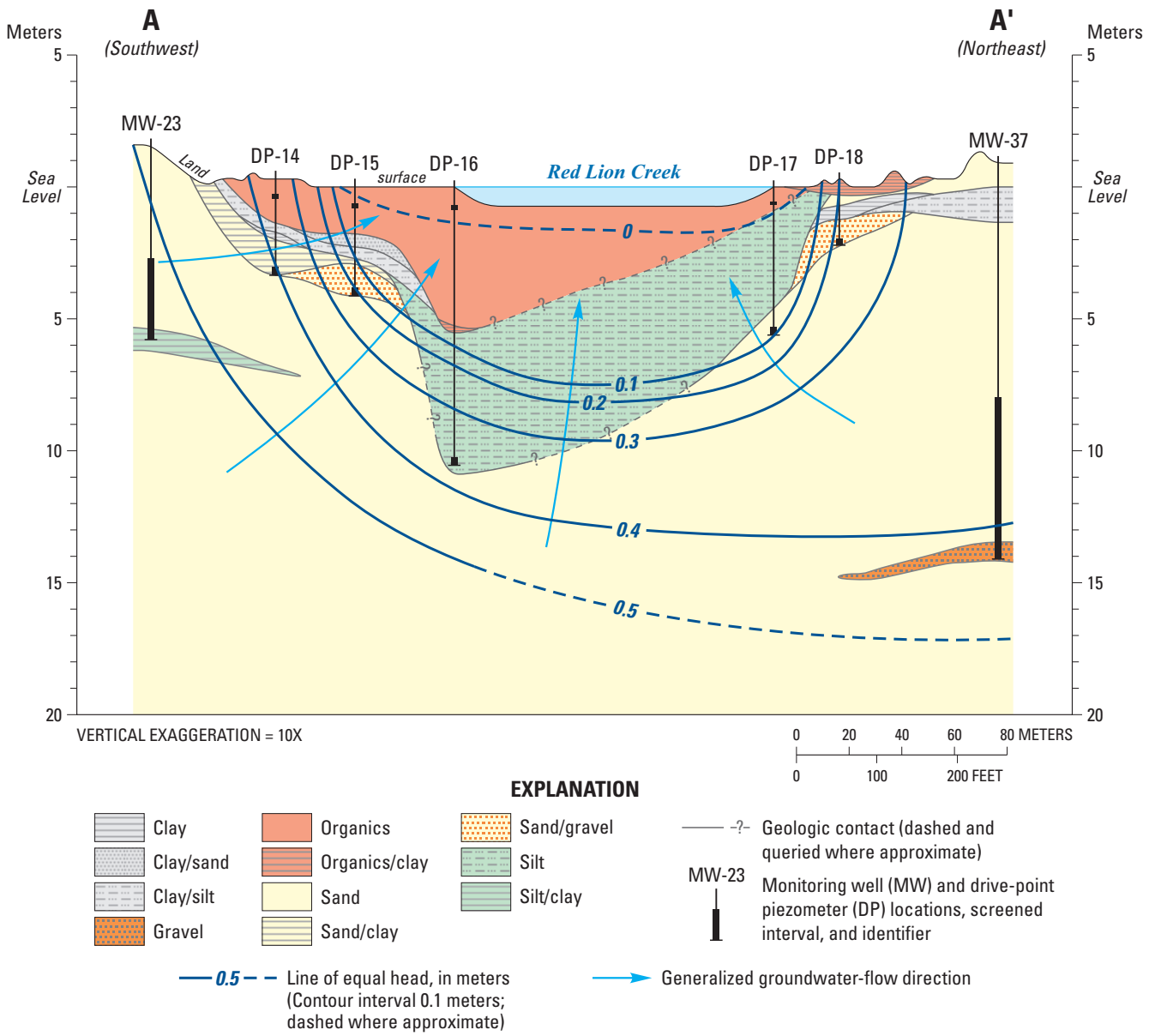


Figure 11. Head distributions and groundwater-flow direction in section A–A′, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

between these two hydrologic units at drive-point piezometer nests for which hydraulic conductivity values were available (table 7). Vertical specific discharge (Darcian velocity) was calculated using equation 1, and vertical linear velocity was calculated using equation 5 (table 8). Both the arithmetic and geometric means were calculated and the generally close agreement of the two means, for most sites, indicate that the data for the different variables (hydraulic gradient and hydraulic conductivity) generally did not contain extreme ranges that dominate the weighting. Results of these analyses showed a maximum specific discharge rate of 118 meters per year (m/yr) from the Columbia aquifer through the wetland sediments in the wetland study area (table 8). Groundwater discharge is spatially variable in the wetland study area, with minimal rates of discharge near the upland-wetland boundary at site EM/DP-6 (table 8). This site is on the southeast side of the upland-wetland boundary and set farther south of open water on Red Lion Creek than the other sites for which discharge was calculated. The greatest rates of discharge were obtained at site DP-15, where the piezometer screened within the Columbia aquifer (DP-15B) is in a gravel dominated part of the formation. It should be noted that hydraulic conductivity values for wetland sediments measured at DP-6A were used for this estimate of vertical discharge rather than those measured at DP-15A because the slug test at DP-15A had to be terminated prior to completion.

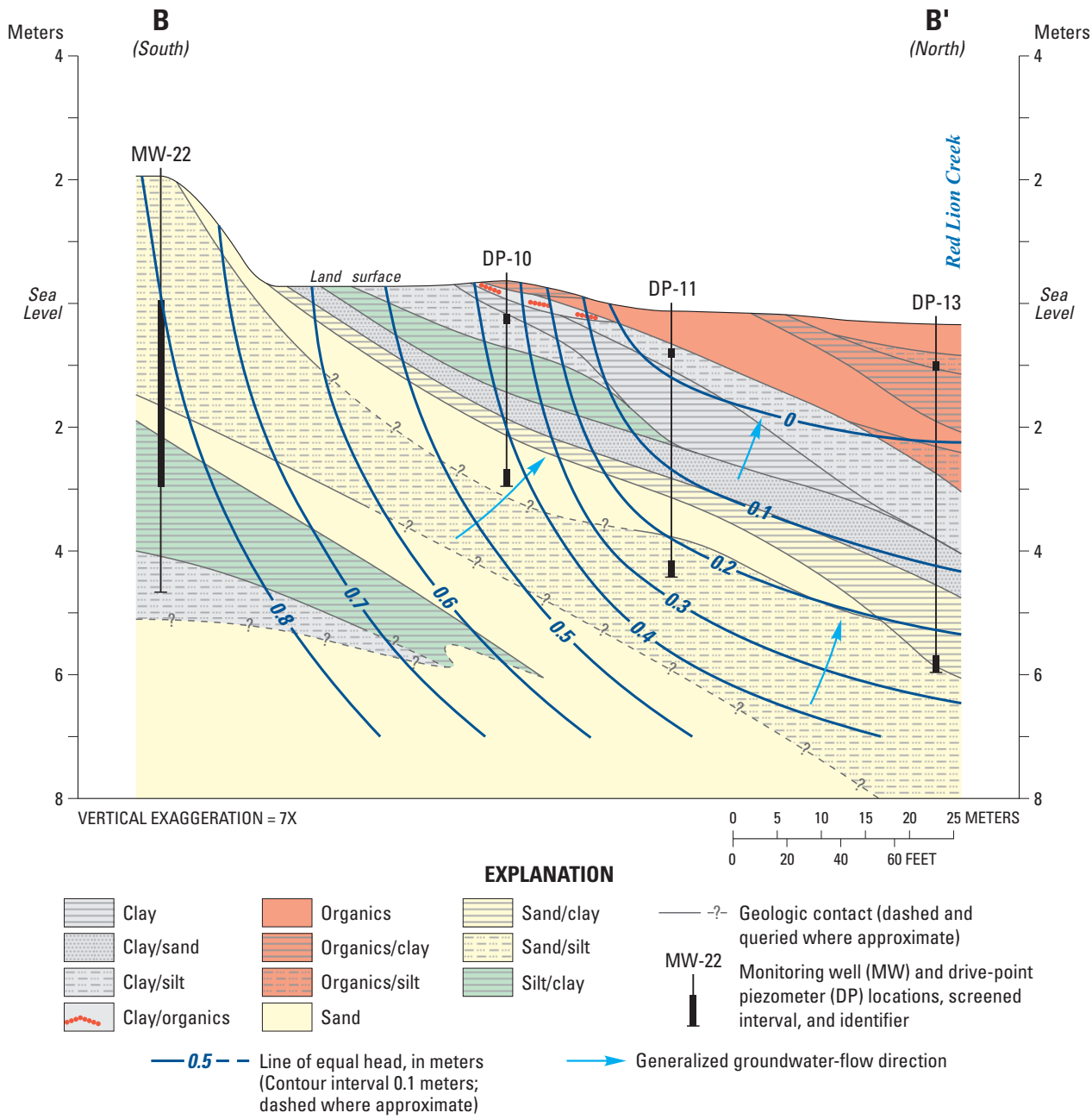


Figure 12. Head distributions and groundwater-flow direction in section B–B′, August 8, 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

Rates of lateral groundwater discharge through the Columbia aquifer and wetland sediments along transects A–A′ and B–B′ at the SCD also were estimated using slug test derived hydraulic conductivity and gradients obtained from groundwater head maps (table 9). The maximum lateral groundwater velocity in the Columbia aquifer was 151 m/yr toward Red Lion Creek along transect A–A’, whereas the highest rate in the wetland sediments was an order of magnitude less. Maximum lateral linear velocities of 3.9 m/yr to 13.8 m/yr were estimated for the wetland sediments, with higher rates along transect B–B′ than A–A′, which was expected based on the spatial variation in hydraulic gradient. Groundwater velocity in the Columbia aquifer, however, was greater along A–A′ than B–B′. This variation in velocity is mostly due to an elevated hydraulic conductivity measured at DP-15B (on transect A–A′) compared to other estimates of hydraulic conductivity in the Columbia aquifer (table 7), and was not caused by a spatial difference in gradient.

When comparing lateral and vertical linear groundwater velocity, flow in the wetland is predominantly vertical along

Table 7. Maximum and minimum estimates of hydraulic conductivity calculated from slug tests conducted at selected drive-point piezometers in the Columbia aquifer and wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[K, hydraulic conductivity; NM, not measured; ft/d, feet per day; m/d, meters per day; max, maximum; min, minimum]

Site identification number	Columbia aquifer			Wetland sediments		
	Drive-point identification number	K (ft/d)	K (m/d)	Drive-point identification number	K (ft/d)	K (m/d)
DP-11 Max	DP-11B	7.80	2.38	DP-11A	5.30	1.62
DP-11 Min	DP-11B	5.50	1.68	DP-11A	4.20	1.28
DP-12 Max	DP-12B	7.30	2.23	DP-12AA	1.40	0.43
DP-12 Min	DP-12B	4.40	1.34	DP-12AA	1.00	0.30
EM/DP-6 Max	EM-6D	14.00	4.27	DP-6A	1.50	0.46
EM/DP-6 Min	EM-6D	10.00	3.05	DP-6A	0.83	0.25
DP-15 Max	DP-15B	68.00	20.73	DP-15A	NM	NM
DP-15 Min	DP-15B	40.00	12.19	DP-15A	NM	NM
	Max measured–Columbia	68.00	20.73	Max measured–wetland	5.30	1.62
	Min measured–Columbia	4.40	1.34	Min measured–wetland	0.88	0.27

Table 8. Variation in vertical specific discharge and linear velocity of groundwater from the Columbia aquifer through wetland sediments, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Hydraulic gradients calculated from water levels collected in June and September 2011 (except for DP-12 and DP-15), February and August 2012; maximum and minimum calculated hydraulic conductivities used; effective porosity of 0.3 used for linear velocity calculation; m/yr, meters per year]

Location	Maximum specific discharge range (m/yr)	Arithmetic mean specific discharge (m/yr)	Geometric mean specific discharge (m/yr)	Median specific discharge (m/yr)	Maximum linear velocity range (m/yr)	Arithmetic mean linear velocity (m/yr)	Geometric mean linear velocity (m/yr)	Median linear velocity (m/yr)
DP-6	15–43	27.2	18.6	25.0	48–143	90.7	86.0	83.2
DP-11	36–78	57.8	56.2	56.5	121–261	193	187	188
DP-12	27–62	41.4	39.9	40.9	91–205	138	134	137
DP-15	12–118	55.9	39.7	42.5	39–393	186	132	142

Table 9. Spatial variation in lateral groundwater specific discharge and linear velocity of groundwater at Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Calculated using groundwater head gradients measured on August 8, 2012 and maximum, minimum, and mean values of hydraulic conductivity from DP-15B and EM-6D for the Columbia aquifer along transect A–A', DP-11B and DP-12B for the Columbia aquifer along transect B–B', DP-6A for wetland sediments along transect B–B', and DP-11A and DP-12AA for wetland sediments along transect B–B'; m/yr, meters per year]

Hydrologic unit	Transect	Maximum specific discharge (m/yr)	Minimum specific discharge (m/yr)	Mean specific discharge (m/yr)	Maximum linear velocity (m/yr)	Minimum linear velocity (m/yr)	Mean linear velocity (m/yr)
Columbia aquifer	A–A'	45	7	20	151	22	67
	B–B'	6	3	4	20	11	15
Wetland sediments	A–A'	1.2	0.6	1.0	3.9	2.1	3.2
	B–B'	4.1	0.8	2.3	13.8	2.6	7.8

both transects A–A′ and B–B′ (tables 8 and 9). Maximum vertical groundwater velocity through the Columbia aquifer and wetland sediments along transect B–B′ was 261 m/yr at DP-11 (table 8), whereas the highest lateral velocity along this transect was within the Columbia aquifer (20 m/yr, table 9). Along transect A–A′, maximum vertical groundwater velocity was 393 m/yr (at DP-15), whereas lateral groundwater velocities were less than half the vertical estimate, with a maximum of 151 m/yr in the Columbia aquifer, and only 3.9 m/yr in the wetland sediments. Although maximum rates of lateral groundwater movement along A–A′ may be biased slightly high due to the lack of hydraulic conductivity data from DP-15A, estimates of vertical flow are generally biased low because they are calculated between the higher conductivity Columbia aquifer and the lower conductivity wetland sediments. Overall, comparisons of lateral to vertical rates of groundwater velocity show that vertical discharge predominates in the wetland near Red Lion Creek (tables 8 and 9).

Effect of Tidal Fluctuation in Red Lion Creek

Tidal fluctuation along Red Lion Creek has been minimized since the installation of a tide control structure downstream of the SCD, when it has operated as designed. Previous investigations indicated that with the tide gate open, Red Lion Creek exhibited a tidal range of 1.29 m, whereas the Delaware River showed fluctuations of 0.87 m (Black & Veatch, 2005). Hydrographs from Red Lion Creek and drive-point piezometers in the wetland study area indicate that the tide gate may have been damaged during Hurricane Irene and Tropical Storm Lee in late August and early September of 2011, resulting in consistent inundation of the wetland study area at the SCD and increased tidal influence upon both creek stage and groundwater altitude at the SCD after these storm events. Evaluation of the continuous creek stage data from Red Lion Creek between August 28, 2008 and August 28, 2012 showed that the average creek stage increased from an elevation of -0.27 m above mean sea level to -0.09 m above mean sea level following Hurricane Irene (fig. 10). Continuous water-level data collected at the gage on Red Lion Creek and at several drive-point piezometers installed in the wetland study area at the SCD prior to the major storms during fall 2011 showed little to no indication of tidal influence (data on file at the MD-DE-DC WSC), whereas hydrographs following these storms show a distinctly tidal signature at Red Lion Creek in both drive-point piezometers screened in the Columbia aquifer and in some wells screened in shallow wetland sediments (fig. 13). In both the Columbia aquifer and wetland sediments, the magnitude of the tidal signature varies with proximity to Red Lion Creek and the material in which the given piezometer is screened. Response to tidal fluctuation in the Columbia aquifer is the least evident at EM-2D, which is positioned on the southeast edge of the upland part of the wetland study area, and is the farthest from Red Lion Creek of the drive-point piezometers instrumented for continuous water-level data collection (fig. 13). Drive-point piezometers located closer to the

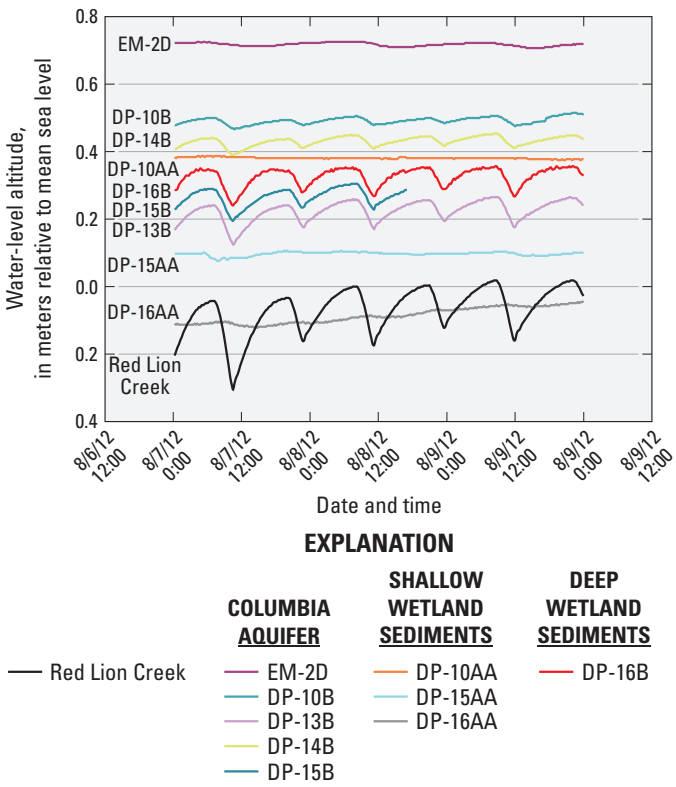


Figure 13. Water-level altitudes at selected wetland-aquifer pairs and other drive-point piezometers screened in the Columbia aquifer, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

creek, such as DP-11B, DP-13B, DP-15B and DP-17B more closely reflect the fluctuation in elevation of Red Lion Creek than those located closer to the upland part of the study area, such as DP-10B and DP-14B (fig 13). In the wetland sediments, no response to tidal fluctuation was seen at DP-10AA, DP-15AA or DP-16AA, but DP-12AA, which was screened in shallow wetland sediments, and DP-16B, which is screened in much deeper wetland sediments, showed fluctuations which very closely mimic that of the creek (all except DP-12AA shown in fig. 13).

A potential combined effect of the increase in tidal influence on Red Lion Creek and variation in hydraulic properties of the material underlying the creek is the cyclical reversal of head gradients, which would result in fluctuation between groundwater recharge and discharge at points in the wetland along Red Lion Creek. This fluctuating condition would occur if the range of head fluctuation in a more hydraulically conductive unit was large enough to overlap the range of a less hydraulically conductive unit, changing which well has higher hydraulic head throughout the course of a tidal cycle. Paired drive points (one screened in the Columbia aquifer and one in the wetland sediments) at three locations were instrumented for continuous water-level data collection in order to

determine whether tidal influence was significant enough to reverse head gradients and subsequent recharge and discharge conditions. Hydrographs from these pairs showed little to no response to tidal fluctuation at points screened in shallow wetland sediments (DP-10AA, DP-15AA, and DP-16AA) but showed a distinct tidal signature at points screened in the Columbia aquifer (DP-10B and DP-15B) and the deepest wetland sediments (DP-16B) (fig.13). The range of fluctuation in water levels in the more responsive wells, however, is not large enough to cause hydraulic head in the wetland sediments to be higher than those observed in the Columbia aquifer, and thus, despite tidal influence, gradients remain vertically up throughout the tidal cycle (fig. 13). This indicates that groundwater discharge to Red Lion Creek is not reversed despite tidal influence on Red Lion Creek and groundwater altitudes in the wetland study area. Consistent vertically upward discharge of groundwater (or, flux, described in the following section) from the wetland sediments to Red Lion Creek contributes to the transport of contaminants from the groundwater system to surface water at the SCD.

Groundwater Discharge to Red Lion Creek

In order to assess the potential significance of groundwater discharge to tidal Red Lion Creek, a comparison was made between vertical groundwater flux estimates (see previous section) integrated over the area of the tidal creek and an estimate of total discharge from the watershed draining to tidal Red Lion Creek (fig. 14). The goal was to determine, within reasonable limits given the absence of a detailed water budget, the percentage of the net recharge that may be discharging to the tidal creek and wetland.

During this study, no streamgage was active in the watershed that could provide data on discharge, though stage data were collected at River Road Road bridge on Red Lion Creek near the wetland study area (data available online for stage gage 01482320 at *http://waterdata.usgs.gov/de/nwis/sw)* (fig. 14). A previously active streamgage (station 01482298, Red Lion Creek near Red Lion, Delaware), upstream of the study area (fig. 14), provided measurements of annual mean discharge for water years 1979–81 of 5.27, 3.71, and 1.85 cubic feet per second (ft^3/s). The average annual discharge for those years, 3.61 ft^3/s (3,220,000 cubic meters per year [m^3/yr]), was used in this analysis, although the data do indicate substantial variation from year to year. The annual mean discharge measured at the gage represents the sum of surface and groundwater runoff, although groundwater runoff (base flow) is likely to be the biggest contributor in the relatively flat and permeable materials of the surficial aquifer in a Coastal Plain setting (Bachman and others, 1998). Assuming no change in storage within the watershed on an annual basis, annual mean discharge should be balanced by net recharge (precipitation minus evapotranspiration). Therefore, annual mean discharge represents an upper limit on recharge to the groundwater system in a watershed.

The drainage-area ratio method was used to estimate annual mean discharge for the ungaged subwatershed draining to tidal Red Lion Creek, based on the average annual mean discharge at the Red Lion Creek streamgage. The drainage-area ratio method is a technique that statistically transfers streamflow information from one location to another on the basis of the drainage areas of the two locations. The method is algebraically simple and is fairly straightforward to implement (Asquith and others, 2006). The method is expressed mathematically as:

$$Y = X\left(\frac{A_Y}{A_X}\right)^{\alpha} \tag{7}$$

where

Y = the streamflow for the ungaged location;

X = the streamflow at a streamflow-gaging station;

A_Y = the drainage area for the ungaged location; and

A_X = the drainage area for the streamflow-gaging station.

Although the exponent α may take on a range of values depending on the particular flow duration (seasonal, monthly, storm peaks) being estimated (Doheny and Fisher, 2000; Emerson and others, 2005), its value is approximately equal to 1 at an annual average time scale, and therefore the drainage-area ratio method is a direct proration of flow based on streamflow per unit area.

In order to apply the method, the watershed above the streamgage, as well as the watersheds above tidal Red Lion Creek (point A in fig. 14) and the River Road bridge below tidal Red Lion Creek (point B in fig. 14), were delineated using 30-m Digital Elevation Model (DEM) data. The contributing area between points A and B is referred to as the subwatershed draining to tidal Red Lion Creek. The areas for these watersheds are listed in table 10. Applying the drainage-area ratio method based on the average mean annual discharge at the gage and the areas determined for the different watersheds results in estimates of annual discharge for each of the watersheds (table 10). The estimate for the subwatershed draining to tidal Red Lion Creek was 795,000 m^3/yr, and represents the expected increase in discharge between points A and B, and an upper limit on potential groundwater discharge to the wetland.

The groundwater discharge to tidal Red Lion Creek was estimated using calculated vertical specific discharge values from the nested piezometer sites with hydraulic conductivity values and the area of the tidal creek estimated from aerial photography (table 10). Using a minimum value of 12 m/yr for the range in vertical specific discharge (table 8) results in a calculated groundwater discharge to the tidal creek of 372,000 m^3/yr, or 47 percent of the estimated total discharge for the subwatershed. Using a minimum value of 18.6 m/yr for the geometric mean vertical specific discharge (table 8) results in a calculated groundwater discharge to the tidal creek

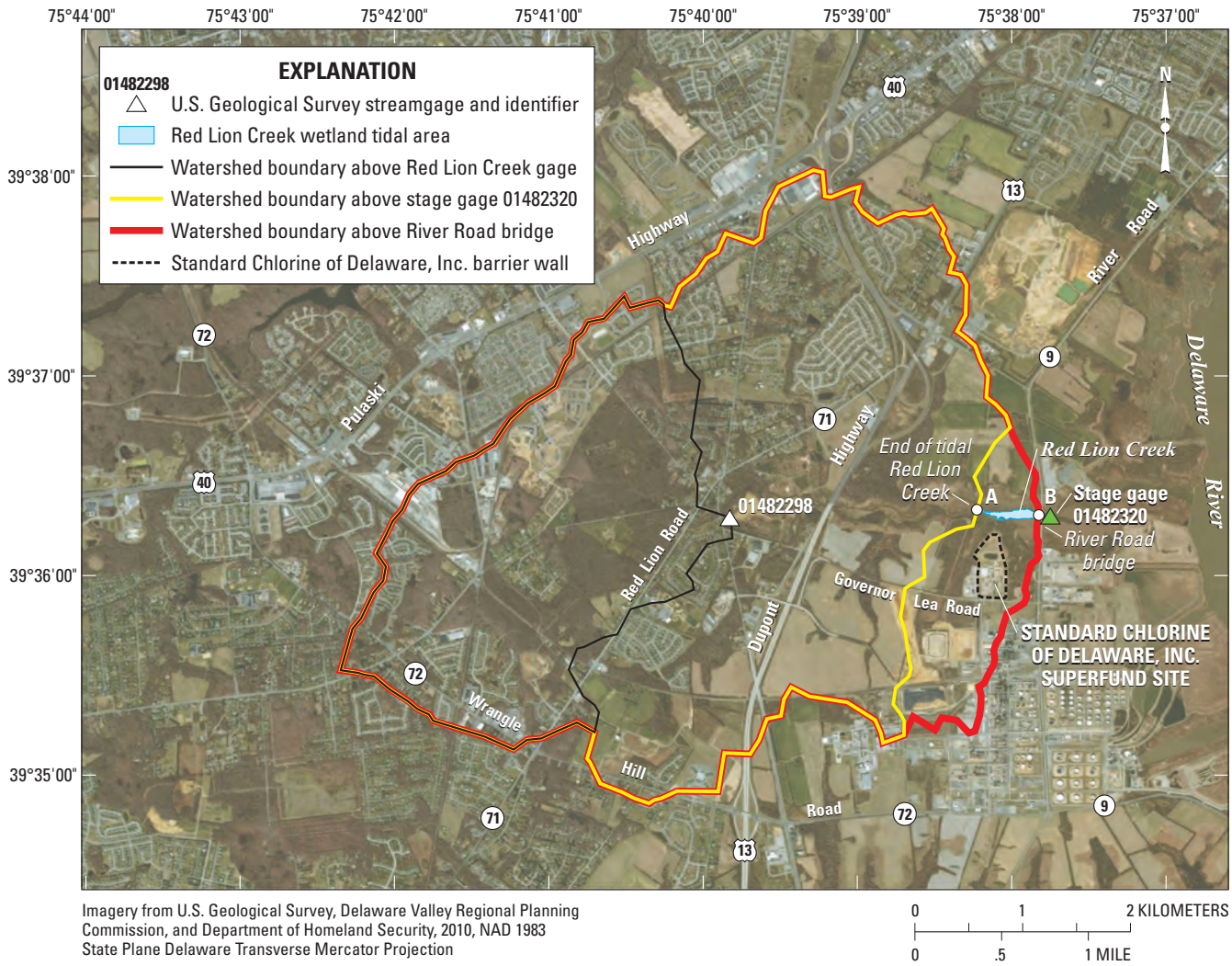


Figure 14. Location of Red Lion Creek watershed, U.S. Geological Survey streamgage 01482298 (Red Lion Creek near Red Lion, Delaware), U.S. Geological Survey stage gage 01482320 at River Road Bridge, and the watersheds used to estimate discharge to tidal Red Lion Creek.

of 576,600 m^3/yr, or about 72 percent of the estimated total discharge for the subwatershed. Minimum values for specific discharge were chosen partly to reflect the possible bias in hydraulic conductivity values based on slug tests that were more likely to be successful in more permeable locations, and partly to provide conservative estimates.

These estimates, with some limitations, indicate that at least half of the net recharge to the subwatershed of tidal Red Lion Creek is discharging as groundwater to the tidal creek and wetland. The estimates of 47 to 72 percent represent lower limits, as minimum vertical specific discharge ranges and means were chosen for the tidal creek. These estimates are similar, however, to base-flow estimates recently reported for Coastal Plain streams in Maryland, Delaware, and Virginia using chemical hydrograph separation techniques (Sanford and others, 2012). Base-flow estimates by Sanford and others (2012) ranged from more than 50 percent to more than 90 percent of measured streamflow.

The calculated volumetric groundwater fluxes (372,000 to 576,600 m^3/yr) to Red Lion Creek were based on the area of the tidal creek only and do not include the surrounding wetland that is likely receiving groundwater discharge (based on observed vertical hydraulic head gradients). Using a larger discharge area or higher value of vertical specific discharge would result in an even greater calculated groundwater contribution to the wetland. The large estimated volume of groundwater discharge to Red Lion Creek indicates that groundwater transport of contaminants to Red Lion Creek could be significant.

Geochemical Characterization

Geochemical characterization of the groundwater in the wetland study area, in conjunction with an understanding of the hydrogeology, is critical to evaluate possible contaminant source locations and the potential effectiveness of natural attenuation and other remedial alternatives. Distributions and types of VOCs and redox-sensitive constituents (nitrate, ammonia, sulfate, sulfide, iron, and methane) present in groundwater in the wetland sediments in the study area are discussed here for samples collected between July 2009 and August 2012. Other geochemical constituents, including chloride and NVDOC, that help characterize contaminant sources and natural attenuation also are presented. Spatial distribution of geochemical constituents is described aerially using PDB results and vertically using piezometer and peeper results from synoptic sampling events; temporal changes in the wetland geochemistry are assessed using results from monthly sampling of selected sites from July 2011–August 2012, combined with results from earlier samples collected from these sites. Distributions of geochemical constituents are detailed in this section, but their implications for contaminant sources and natural attenuation, respectively, are discussed further in later sections on DNAPL extent and assessment of biodegradation.

Distribution of Volatile Organic Compounds

The major VOCs detected in groundwater in the wetland study area were consistent with those reported previously for aquifer contamination in the upland area at SCD and for sediment samples from the wetland area, including benzene and six chlorobenzene compounds—123TCB, 124TCB, 12DCB, 13DCB, 14DCB; and CB (Black & Veatch, 2007). The sum of these major VOCs are collectively referred to as total chlorobenzene compounds and benzene, or CBs+benzene, in this report. Other VOCs detected in the wetland groundwater relatively frequently (more than 5 samples of the 60 PDB and piezometer samples collected in the October-December 2011 synoptic event) included chloroform, toluene, and 1,2,3-trichloropropane (data on file at USGS MD-DE-DC WSC, Baltimore, Maryland). These constituents were detected only at sites where chlorinated benzenes and benzene also were detected and are not discussed in this report.

Spatial Distribution

The distributions of CBs+benzene contamination varied widely throughout the wetland study area south of Red Lion Creek, as shown by results from PDBs deployed at a depth of approximately 20 to 40 cm below ground surface in March 2011 and October–December 2011 (fig. 15). Based on differences seen in both geochemical and hydrogeologic observations, results were separated into two geographic areas of the wetlands, northwest and northeast. The line between the two areas is shown in figure 15 and corresponds approximately with the flow divide observed in the wetland groundwater (fig. 8). Two sites, DP-17 and DP-18, in the wetland area on the northern bank of Red Lion Creek (table 2, fig. 3) had low concentrations of CBs+benzene, with maximum concentrations in the shallow wetland groundwater and Columbia aquifer, respectively, of 50 and 20 µg/L. There were no detections of CBs+benzene in MW-37, which is screened in the Columbia aquifer and is the site farthest north of Red Lion Creek that was sampled (fig. 3). Results for sites north of Red Lion Creek are not included in the discussion below; additional investigation would be needed to determine the source of observed low concentrations (such as groundwater transport from sources south of the creek or from contaminated sediments in the creek channel or along the northern bank).

CBs+benzene concentrations ranged from 36 µg/L at site 125 in the northeast wetland area to over 64,000 µg/L at site 141 in the northwest area for the March 2011 sampling event. CBs+benzene concentration ranges were similar in the larger October–December 2011 synoptic sampling event

Table 10. Area and measured or estimated annual mean discharge for subwatersheds in the Red Lion Creek watershed, and estimated groundwater discharge to tidal Red Lion Creek.

[km^2, square kilometers; m/yr, meters per year; m^3/yr, cubic meters per year]

	Area (km^2)	Discharge (m/yr)	Discharge (m^3/yr)
Red Lion Creek, mean measured discharge, 1979–81	8.13	0.396	3,220,000
Watershed above tidal Red Lion Creek, estimated	21.06	0.396	8,350,000
Watershed above River Road bridge, estimated	23.06	0.396	9,150,000
Subwatershed including tidal Red Lion Creek, estimated	2.01	0.396	795,000
Tidal Red Lion Creek, based on minimum value for maximum estimated vertical specific discharge	0.031	12.0	372,000
Tidal Red Lion Creek, based on minimum geometric mean estimated vertical specific discharge	0.031	18.6	576,000

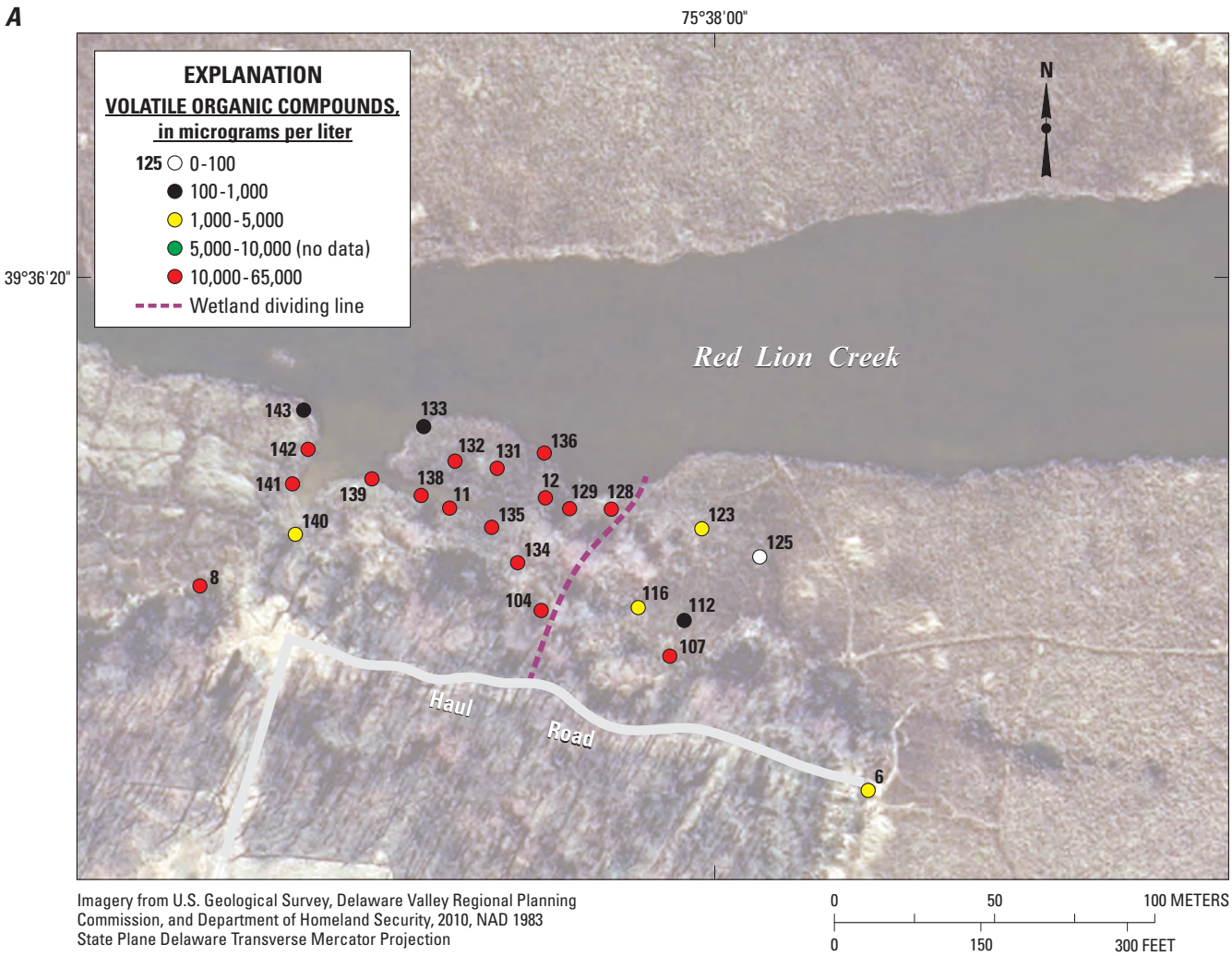


Figure 15. Distribution of volatile organic compounds from passive diffusion bags deployed in the wetland sediments in the study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, *(A)* March 2011, and *(B)* October–December 2011.

compared to March 2011, with a minimum of 1 µg/L at site 151 in the northeast wetland area to over 44,000 µg/L at site 8 in the northwest wetland area. In general, the northeast wetland area had lower concentrations of CBs+benzene than those observed in the northwest wetland area for both of the synoptic sampling events.

The higher concentrations of CBs+benzene in the northwest area of the wetland than those in the northeast wetland are consistent with the flowpath of the major release, 400,000 gallons of dichlorobenzenes and 169,000 gallons of trichlorobenzenes, documented in 1986 (U.S. Environmental Protection Agency, 1995a). During that release, the majority of chemicals flowed from the center of the site northwest to the unnamed tributary, which flows into Red Lion Creek, resulting in DNAPL contamination in the wetland sediment (see section on DNAPL extent). Although the majority of sites in the northeast part of the wetland had much lower concentrations, there were localized areas of moderate contamination, mainly along the boundary between the wetland and upland.

The wetland sediment lithology may also affect the distribution of contamination in the wetland study area. Shallow clay lenses are prevalent in the northwest area of the wetland, compared to more organic-rich, marsh-like sediments in the northeast area (figs. 6 and 7). The shallow clay layers may cause areas of more concentrated groundwater flow to the surface in the northwest wetland area, yielding higher concentrations of CBs+benzene. However, concentrations of CBs+benzene were consistently less than 10 µg/L at sites 145 through 157, which are the sites farthest from the upland and from the path of the1986 major release (fig. 15b). Many of the sampling locations in the northeast wetland are on a thick mat-like upper wetland sediment unit, rich in organic matter and roots from *Phragmites*, with a lithology thought to be similar to that observed at site 16 (fig. 7). Diffuse groundwater flow through this mat-like wetland sediment may result in lower

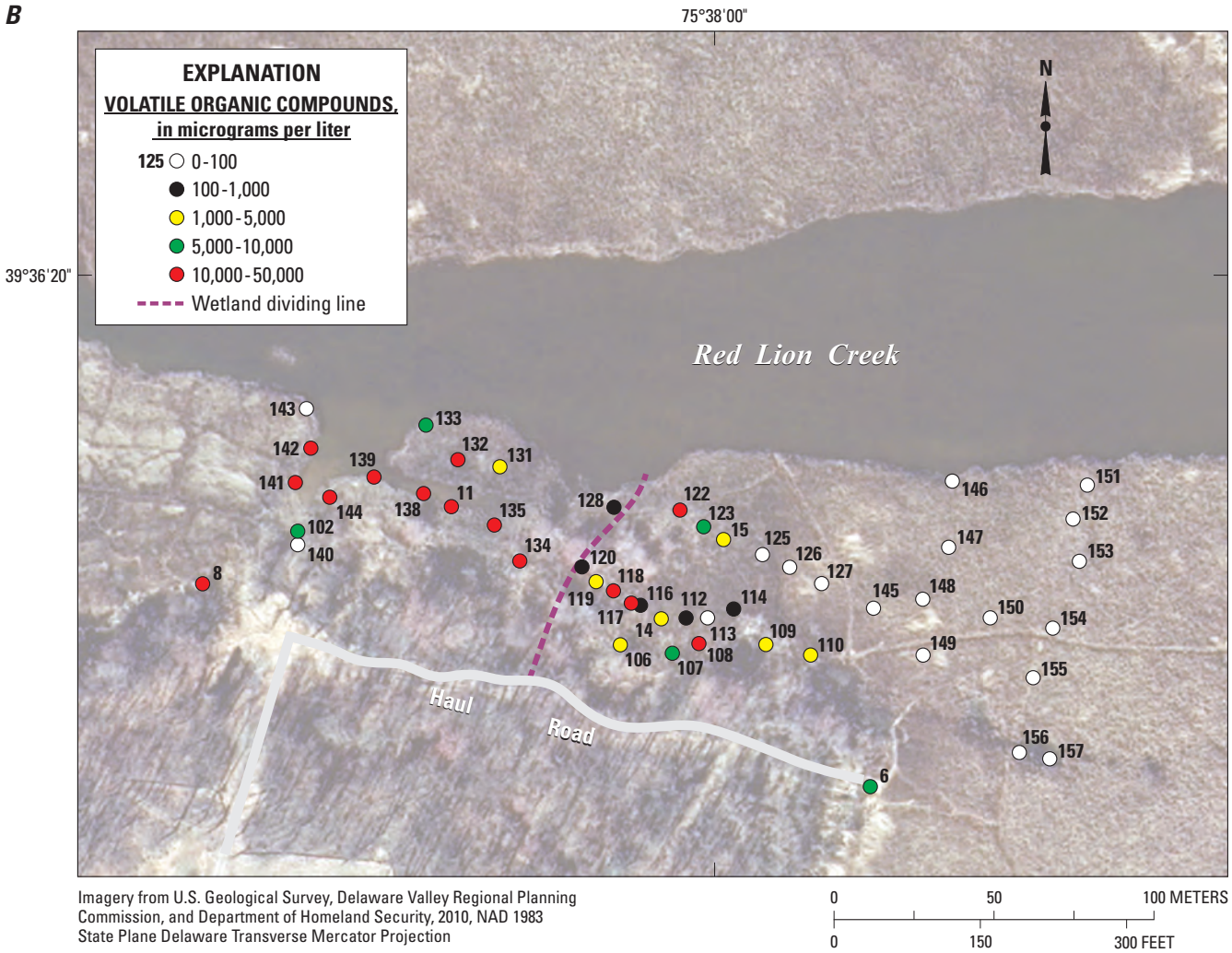


Figure 15. Distribution of volatile organic compounds from passive diffusion bags deployed in the wetland sediments in the study area, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, *(A)* March 2011, and *(B)* October–December 2011. —Continued

contaminant concentrations because of dilution and longer residence time for physical, chemical, and biological contaminant attenuation processes.

The October–December 2011 PDB sampling results indicated that the concentrations of CBs+benzene were significantly ($p<0.001$, Mann-Whitney Rank Sum Test, Non-Parametric) greater in the northwest wetland area than in the northeast wetland area, with median concentrations of 16,600 µg/L and 114 µg/L, respectively (figs. 16c, d). However, of the individual compounds measured, CB and TCB isomers were the only compounds to have a significantly ($p<0.01$) different molar percentage between the northwest and northeast wetland areas in the October 2011 PDBs (fig. 16). Note that molar compositions are shown in figure 16 for all samples with total CBs+benzene that had concentration greater than 10 µg/L; thus, sites 145–157, sampled in December 2011, are not shown. CB was the predominant VOC in PDB samples from the northeast wetland area with a median of 69 molar percent, compared to a median of 35 molar percent in samples from the northwest wetland area. Concentrations of the TCB isomers were relatively low compared to the other chlorinated benzenes, as might be expected from their lower solubility (table 1), but the median molar percentage of 0.33 percent was greater in the northwest wetland area than in the northeast wetland area (median 0 percent). The sum of the three DCB isomers were the predominant VOCs in most samples from the northwest wetland area in October 2011 (figs. 16c, d), with a median molar percentage of 50 percent compared to 24 percent in samples from the northeast wetland area, although the difference was not statistically significant ($p = 0.178$). Statistics were not calculated for the March 2011 synoptic sampling event (figs. 16a, b) because of the limited number of samples collected in the northeast wetland area.

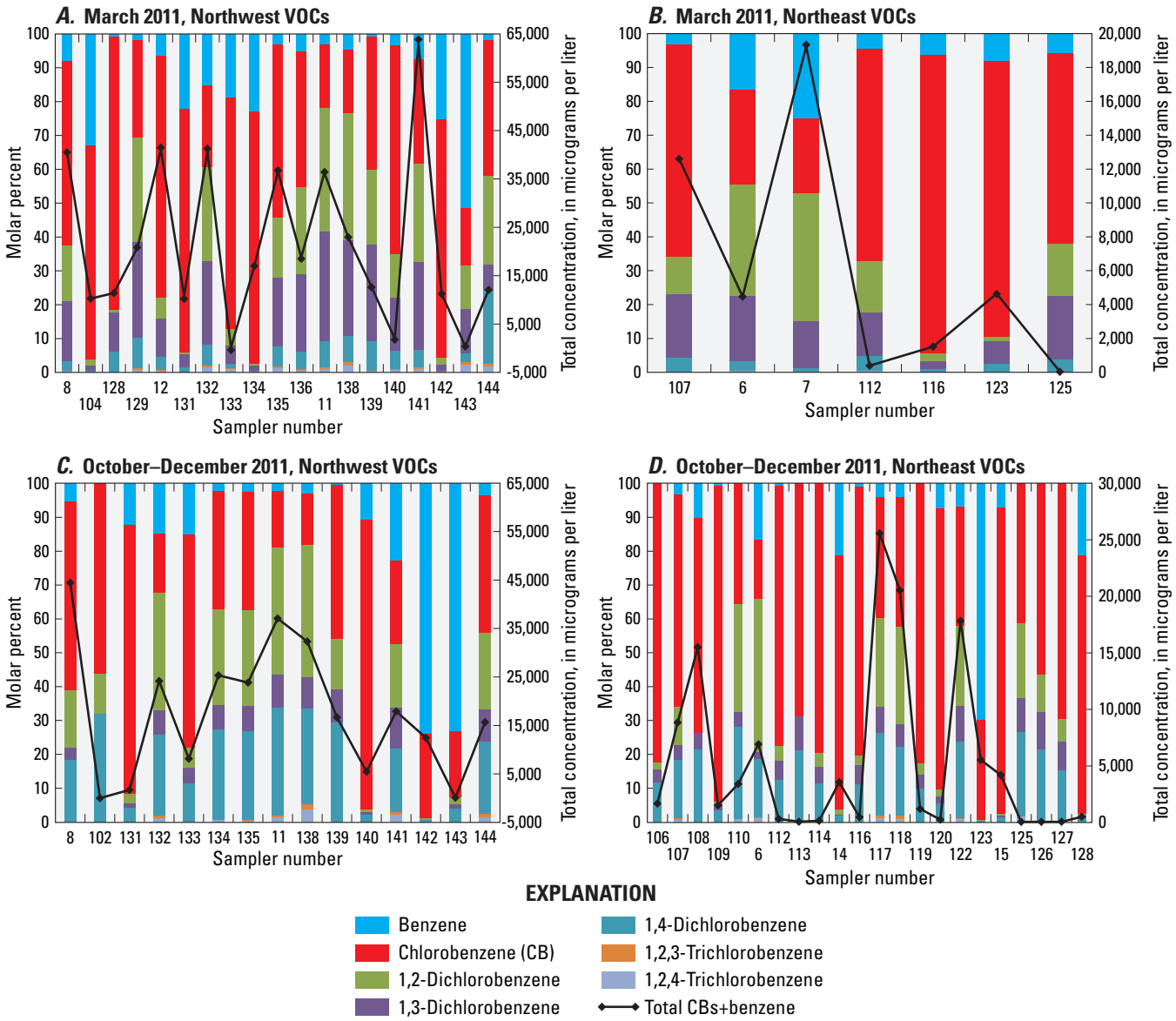


Figure 16. Molar composition of volatile organic compounds (VOCs) and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) in passive diffusion bag samples collected from the northwest and northeast wetland areas during *(A, B)* March 2011, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

Fine-scale vertical delineation of VOCs from peeper sampling in 2009 and 2011 showed that concentrations of CBs+benzene were generally highest in the upper 40–50 cm of wetland sediment in both the northwest and northeast areas (fig. 17). Two exceptions to this pattern occurred in the peepers at sites 9 and 10 in the northwest wetland area, where CBs+benzene concentrations were nearly uniform with depth. In peepers in the northwest area, concentrations of CBs+benzene were greater than 10,000 µg/L at practically all depths sampled and reached a maximum concentration of about 75,000 µg/L (figs. 17a, c). As observed in the PDB samples, generally lower concentrations of VOCs occurred in the peepers in the northeast area compared to the northwest area, although concentrations were higher than 10,000 µg/L at sites 7 and 15 in the upper 50 cm. For peeper sites where deeper piezometer data were also available, the vertical distributions showed that VOC concentrations at greater depth in the peepers (more than 50 cm deep) were lower than in the underlying groundwater sampled from piezometers, except at site 14 (figs. 17b-d). These vertical distributions indicate that another source of VOCs is present in the shallow wetland sediments in addition to upward groundwater discharge from the contaminant plume in the deeper wetland sediments and underlying aquifer. The individual VOCs that make up the

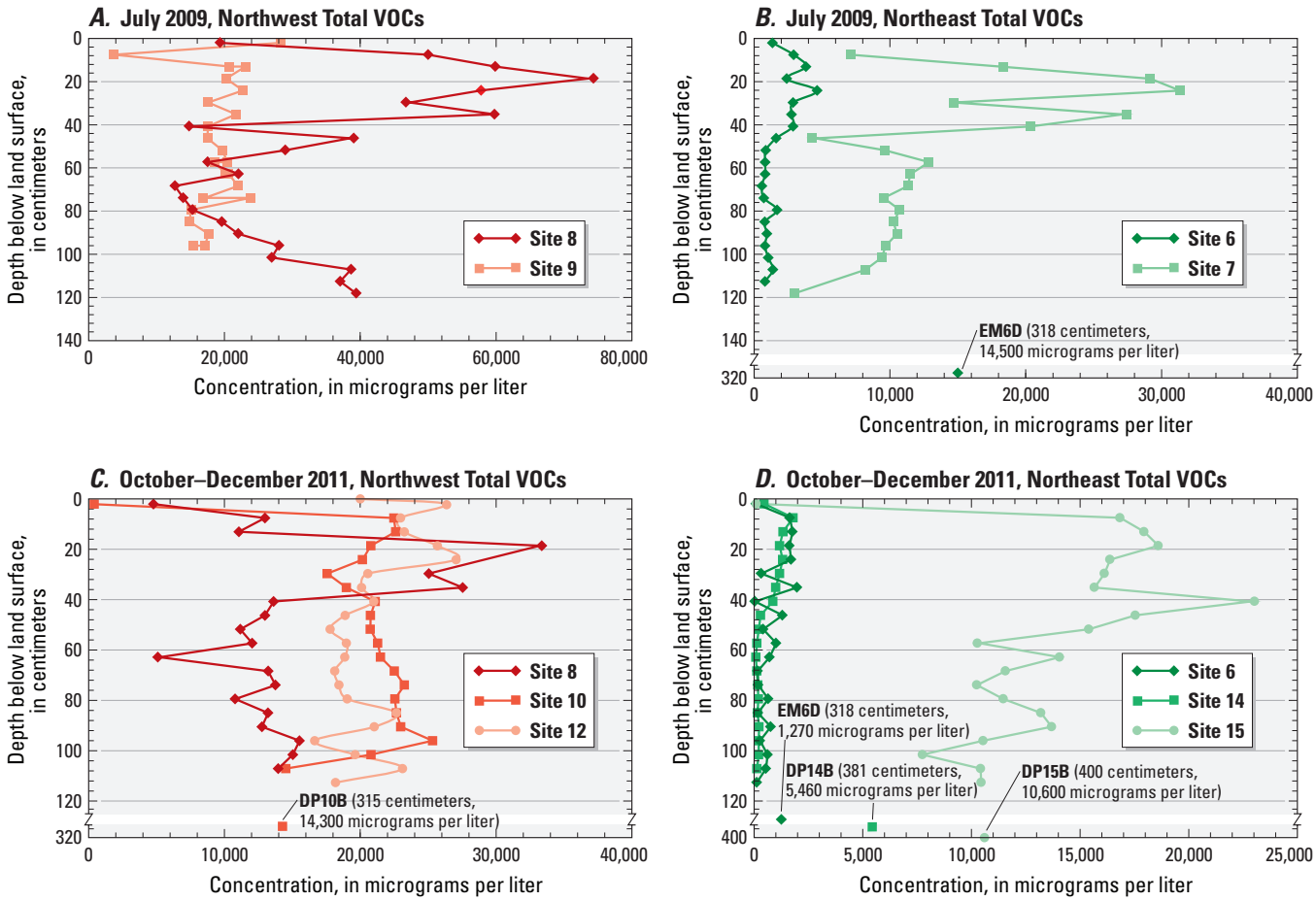


Figure 17. Vertical distributions of volatile organic compounds (VOCs) from peepers in the northwest and northeast wetland areas *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

total CBs+benzene observed in the wetland groundwater also differed between the northwest and northeast wetland areas, although these VOC compositions varied temporally and are discussed in the next section on Temporal Distribution.

Temporal Distribution

Sites 8 and 6 that were used for peepers, PDB synoptics, and monthly sampling provided the best temporal data from the wetland groundwater (figs. 18 and 19). The molar composition of the VOCs varied greatly between the July 2009 and December 2011 peeper sampling events at site DP8 in the northwest area (figs. 18a, b). In the July 2009 peeper at site 8, CB and benzene comprised over 90 percent of the VOC composition in the wetland groundwater along the entire approximately 120-cm-long profile. Peeper samples from nearby site 9 in July 2009 showed similar molar VOC compositions with about 80 percent comprised of CB and benzene (data on file, USGS MD-DE-DC WSC). In contrast, the VOC composition in peeper samples from site 8 in December 2011 showed substantially lower percentages of CB and benzene and higher percentages of the DCB isomers (12DCB, 13DCB, and 14DCB) than those observed in 2009. Monthly sampling results in 2011–12 for DP8A, which is screened at site 8 deeper in the wetland sediment (370–670 cm) than the zone sampled with the peepers, were consistent with the VOC composition observed in the December 2011 peeper and remained consistent throughout the year, although the total concentrations of CBs+benzene varied between about 12,000 and 58,000 µg/L (fig. 18c). The trichlorobenzene isomers 123TCB and 124TCB made up an insignificant percentage of the high concentrations of total VOCs in the wetland groundwater at site 8 during all sampling periods (fig. 18).

In the northeast area at site 6, the VOC composition in July 2009 differed greatly from the VOC composition observed at site 8, with a substantially higher percentage of 12DCB and lower percentages of CB and benzene (figs. 18a and 19a). In 2011–12, the VOC compositions in wetland groundwater at sites 6 and 8 were similar, however, with the three DCB isomers generally making up 50 percent or more of the total VOCs (figs. 18b, c and 19b, c). The TCB isomers

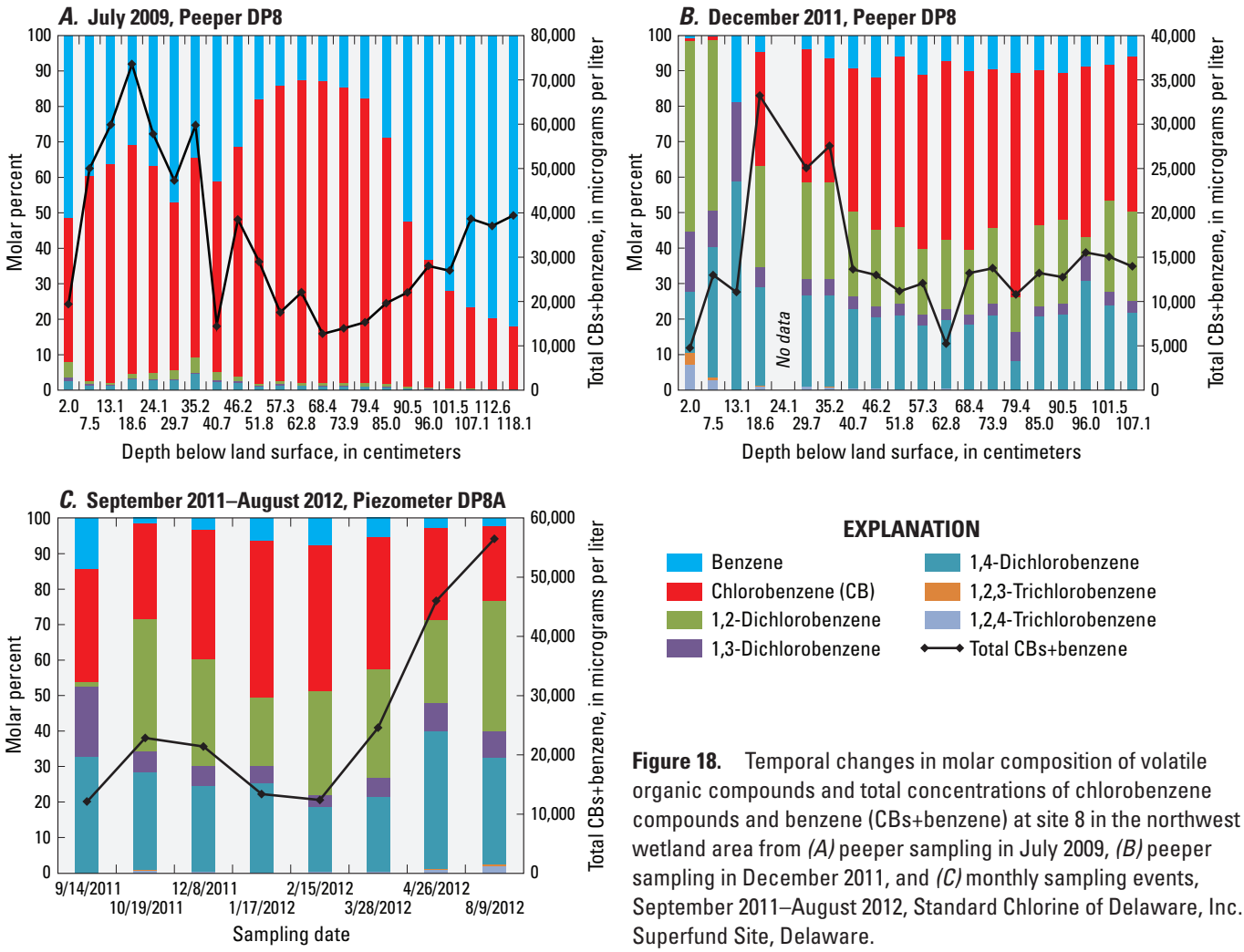


Figure 18. Temporal changes in molar composition of volatile organic compounds and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) at site 8 in the northwest wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

were a significant percentage of the total VOC concentrations observed at site 6 when total CBs+benzene concentrations were relatively low, such as in the deep peeper samples (about 68 to 113 cm below land surface) in December 2011 (fig. 19b) and in the 2011–12 monthly samples (fig. 19c).

Because 2009–12 temporal data were only collected from a few sites in the wetland, it is difficult to determine if the changes at sites 8 and 6 are representative of changes across the northwest and northeast wetland areas. The synoptic PDB sampling in October 2011 indicates that the VOC composition observed at site 8 was consistent with most of the sites sampled in the northwest area (fig. 16c). In the northeast area, many of the sites had a predominantly higher percentage of CB than the percentage observed at site 6, although at least six other sites in October 2011 had a similar VOC composition to the one observed at site 6 (fig. 16d). The peeper at site 6 in December 2011 did have a relatively high percentage of CB and benzene in the upper 24 cm of wetland sediment (fig. 19b), indicating that variability with depth may account for some of the variability observed at different sites across the wetland area.

Distribution of Redox-Sensitive and Other Geochemical Constituents

In addition to measuring VOCs, geochemical constituents were measured during the sampling events between 2009 and 2012, although the suite of constituents varied with the amount of sample available from the sampling device (table 3). Selected constituents are discussed here to describe the redox conditions of the groundwater and the general differences observed between the northwest and northeast wetland areas. Inorganic constituents, except methane, and NVDOC were measured from PDBs constructed of dialysis membrane and placed at the same location as the PDBs sampled for VOCs and methane.

Spatial Distribution

The primary inorganic constituents in the wetland groundwater that showed distinct differences between the northwest and northeast wetland areas during all sampling

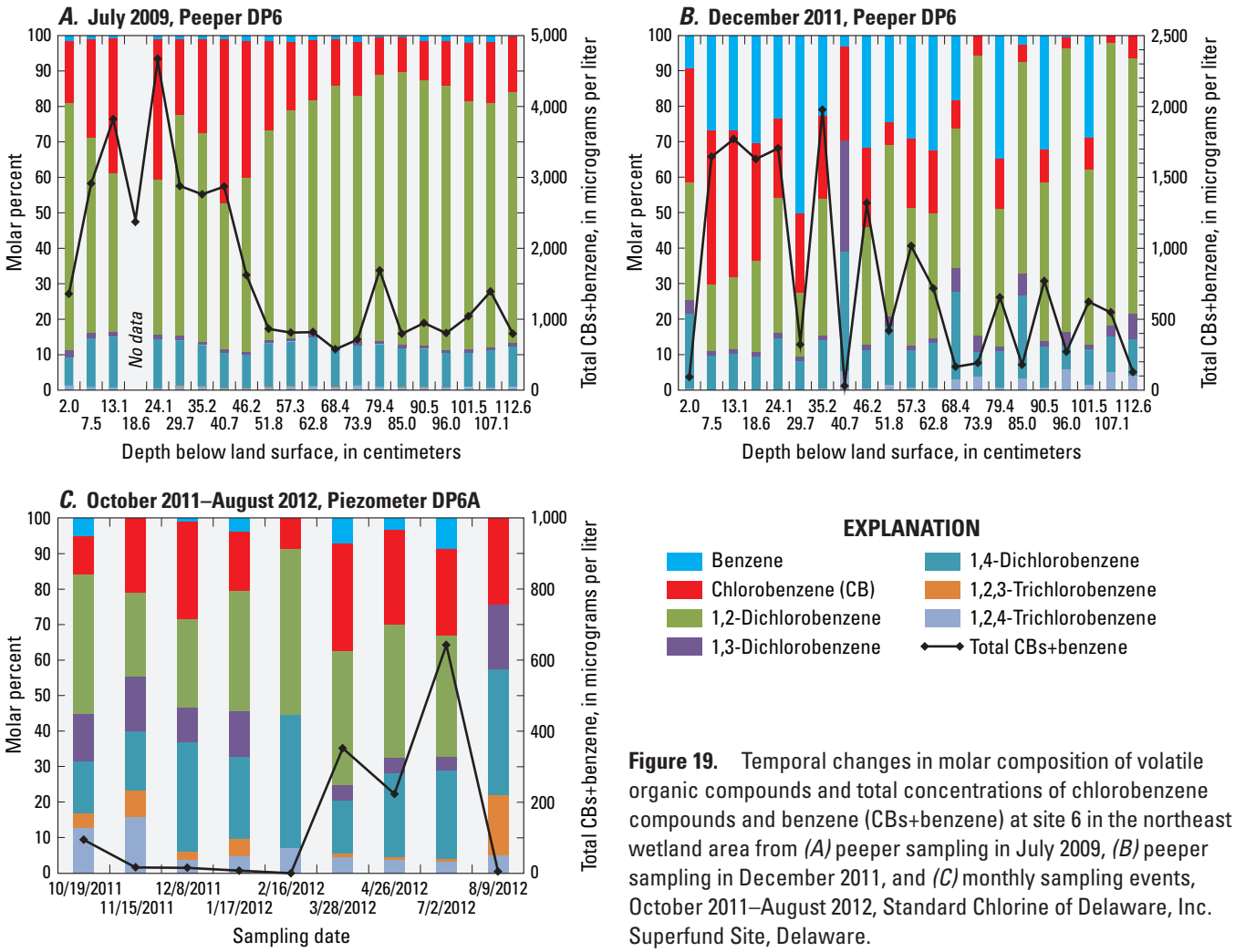


Figure 19. Temporal changes in molar composition of volatile organic compounds and total concentrations of chlorobenzene compounds and benzene (CBs+benzene) at site 6 in the northeast wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, October 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

events were pH, chloride, sulfate and sulfide (figs. 20 and 21). The pH of the wetland groundwater measured in the northeast area was significantly higher ($p = 0.043$, March 2011; $p = 0.003$, October 2011) than the pH measured in the northwest area for both synoptic sampling events in 2011. Median pH values for the two synoptic sampling events were 5.8 and 6.1 in the northeast wetland area and 4.5 and 5.2 in the northwest wetland area (fig. 20). The lowest pH (3.6) was measured at site 141 in the northwest wetland area, whereas the highest pH (6.8) was measured at site 127 in the northeast area.

In addition to chlorinated benzenes and benzene releases, the study area was affected by at least two acid spills (Black & Veatch, 2007). Hydrochloric acid (HCl) was part of the major release of 1986 and primarily affected the northwest wetland area, whereas a sulfuric acid spill from the oil refinery affected the groundwater flowing from the Columbia aquifer to the northeast wetland area. Despite both areas of the wetland experiencing strong acid spills, the lower median pH and higher concentrations of CBs+benzene in the northwest area indicate a more concentrated flow of contamination through the wetland sediments than in the northeast wetland area, where the median pH was higher and concentrations of CBs+benzene were lower. Reductive dechlorination of the chlorinated benzenes (fig. 2) in the more highly contaminated northwest wetland area also may have generated additional HCl and contributed to the lower pH compared to the pH in the northeast wetland area.

The northeast wetland groundwater had significantly higher concentrations of sulfate and sulfide (October 2011, $p<0.01$) than the concentrations measured in the northwest wetland area. During the October 2011 sampling event, the highest concentration of sulfate (1,090 mg/L) was found at site 6 in the northeast wetland area, and the lowest concentration of sulfate (0.42 mg/L) was observed at site 135 in the northwest wetland area. The anion sulfate is the conjugate base of sulfuric acid, and sulfide can be produced from sulfate reduction in oxygen-depleted environments. Thus, the higher sulfate and sulfide in the northeast wetland groundwater compared to the northwest wetland groundwater provides evidence of the effect of the sulfuric acid spill. Because the sulfate reduction reaction utilizes hydrogen ions and thus can increase the pH of a solution, this reaction may be contributing to the higher

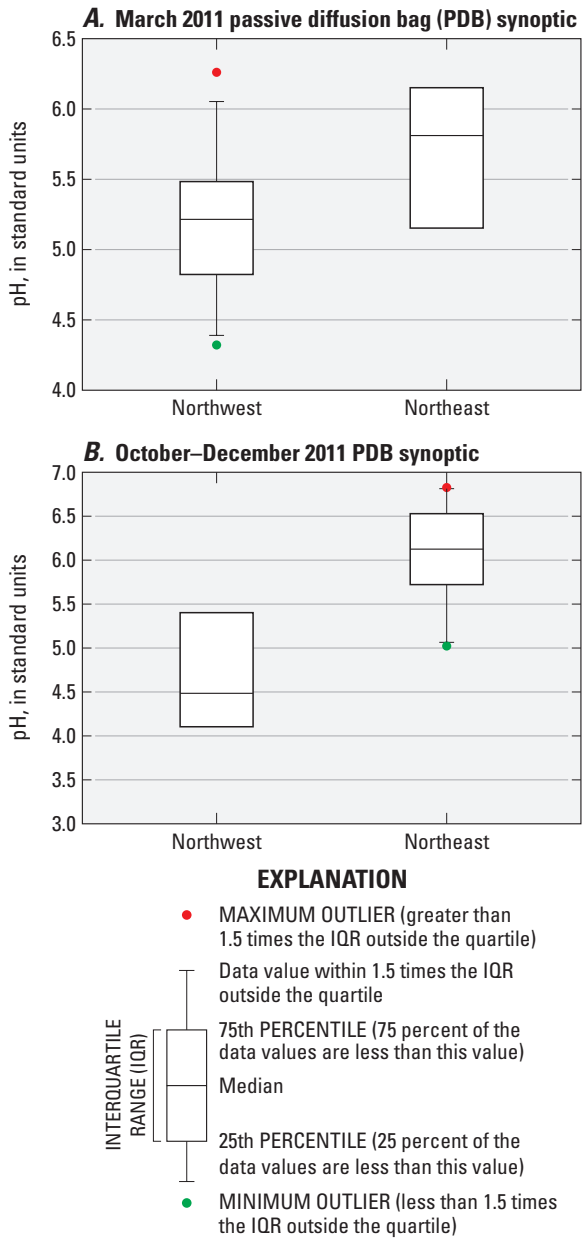


Figure 20. Boxplots showing distributions of pH in the wetland study area *(A)* March 2011, and *(B)* October–December 2011 synoptic sampling results, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

pH observed in the northeast wetland area compared to the northwest area.

Concentrations of chloride were significantly higher ($p = 0.003$) in the northwest wetland area than in the northeast wetland area during the October 2011. Site 132 in the northwest wetland area had the highest measured concentration of chloride (171 mg/L), whereas site 110 in the northeast area had the lowest measured concentration of chloride (27 mg/L). The chloride anion is the conjugate base of HCl and could have resulted from the HCl spill. Another possible source of chloride at this site is from the reductive dechlorination of the chlorinated benzenes.

Other redox-sensitive constituents, in addition to sulfate and sulfide, that were predominant in the wetland groundwater at many sites included ferrous iron and methane (fig. 21), but concentrations of these constituents were not statistically significant different between the northwest and northeast wetland areas in the March and October 2011 PDB samples. The presence of ferrous iron indicates moderately reducing conditions, whereas the presence of methane indicates highly reducing conditions. Wetland sediments are commonly anaerobic, and the distribution of these additional redox-sensitive constituents does not appear to be related to the groundwater contamination. Ammonia concentrations were typically low or undetectable in the wetland groundwater (fig. 21). During October 2011, the highest concentration (19.1 mg/L) of aqueous phase methane was found at site 142 in the northwest wetland area. The lowest concentrations, under 1 mg/L, were observed at numerous sites in both the northwest and northeast wetland areas. Similar to the methane results in the March and October 2011 samples, several localized areas within the wetland had relatively high concentrations of ferrous and total dissolved iron (greater than 5 mg/L), whereas the majority of areas had low concentrations (approximately 1 mg/L). On average, 90 percent of the total dissolved iron measured was ferrous iron, which is the reduced form of iron.

The distribution of NVDOC, measured during the October 2011 PDB sampling, was variable and not statistically significant based on geographic position (fig. 22). Because the analytical method for organic carbon excluded volatile carbon compounds, the presence of chlorinated benzenes and benzene contamination or other VOCs should not have affected the NVDOC distribution. Instead, the NVDOC distribution reflected the presence of natural organic carbon in the groundwater that can support microbial reduction of metals and sulfate in addition to the reductive dechlorination of the chlorinated benzenes. The northeast wetland area had an average NVDOC concentration of 56 mg/L, whereas the northwest wetland area had an average concentration of 14 mg/L. Both the highest (436 mg/L) and lowest (1.6 mg/L) NVDOC concentrations were found in the northeast wetland area (sites 108 and 6, respectively). Site 108, which had the maximum NVDOC concentration, also had elevated concentrations of ferrous iron, sulfide, and methane compared to other wetland sites.

Vertical distributions of chloride and sulfate in the July 2009 peepers were consistent with the results of the 2011 PDB and piezometer sampling, showing substantially higher concentrations of chloride and lower concentrations of sulfate in the wetland groundwater at all depths in the northwest area than those observed in the northeast area (figs. 23 and 24). In peepers sampled in October–December 2011, however, chloride concentrations in the peepers in both the northwest and northeast areas had similar maximum concentrations, ranging from 122–223 mg/L in the northwest area peepers and from

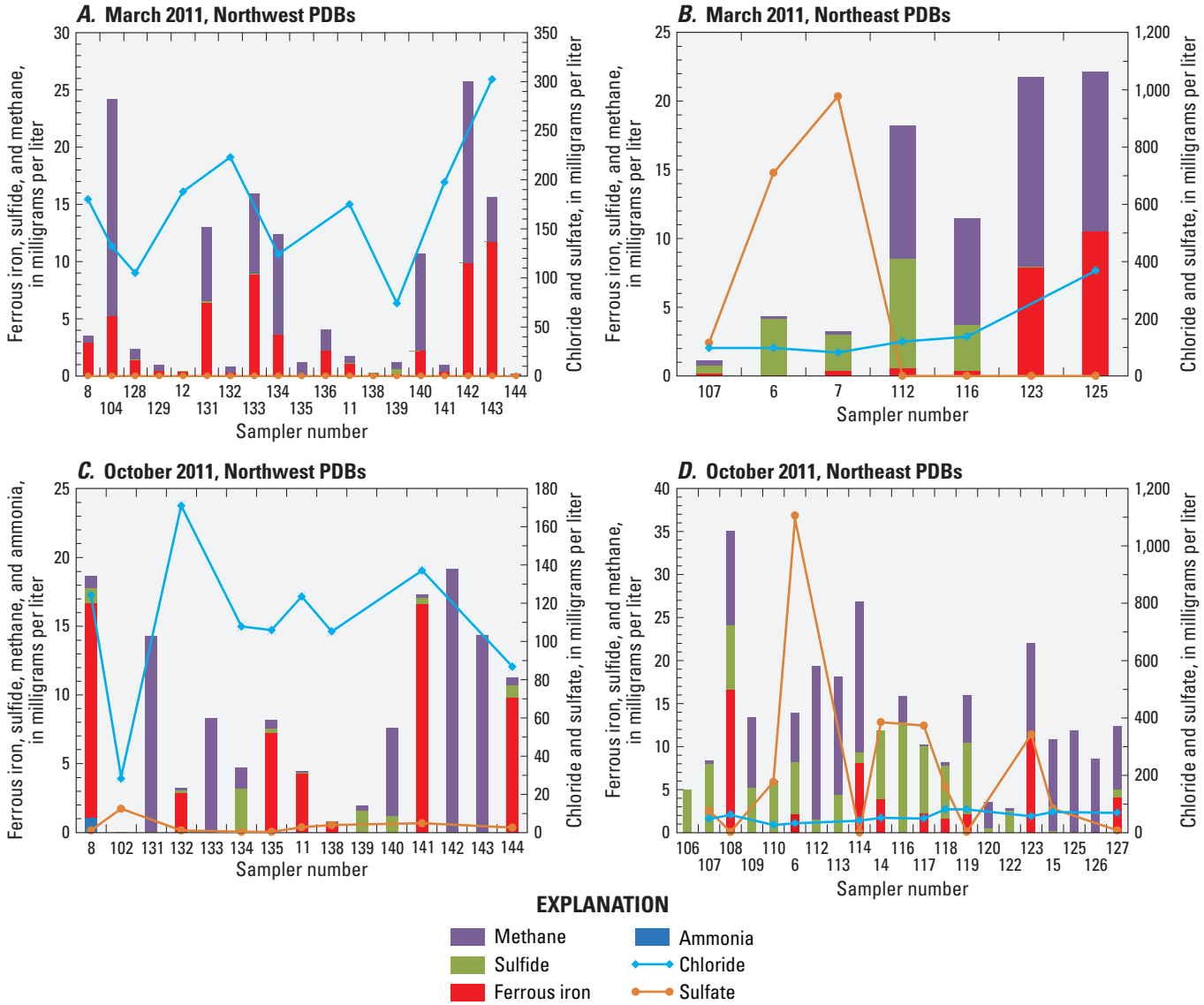


Figure 21. Distributions of chloride, sulfate, ammonia, sulfide, methane, and ferrous iron in passive diffusion bag (PDB) samples of wetland groundwater collected in the nothwest and northeast areas in *(A, B)* March 2011, and *(C, D)* October 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

150–180 mg/L in the northeast area peepers (figs. 23c, d). Minimum chloride concentrations were lower in the northeast peepers (40–50 mg/L) than those sampled in the northwest area (80–112 mg/L). Groundwater chloride concentrations from the only peeper in the northwest wetland where a deeper groundwater sample from a piezometer was also available (site 10) were nearly uniform with depth and similar to the concentration in the underlying groundwater of the Columbia aquifer (fig. 23c). In the northeast wetland area, however, the chloride concentrations in all three peepers reached concentrations two to five times greater than those observed in the deeper groundwater from piezometer samples (fig. 23d). Maximum chloride concentrations in the peeper samples from both wetland areas were more than three times as high as chloride concentrations in the surface-water samples. Thus, vertical distributions of chloride indicate another source of chloride in the shallow wetland porewater besides surface-water infiltration or upward discharge of contaminated groundwater, as was also observed from vertical distributions of the VOCs (fig. 17). Surface-water infiltration may instead act to dilute shallow groundwater concentrations in the wetland at some sites where chloride concentrations in the peeper samples decrease near land surface.

Sulfate concentrations at each peeper site in 2009 and 2011 were relatively uniform with depth, except in the upper 20 cm below land surface where the greatest change in sulfate concentrations occurred (fig. 24). In the northwestern peeper sites where sulfate was low, the highest sulfate concentrations

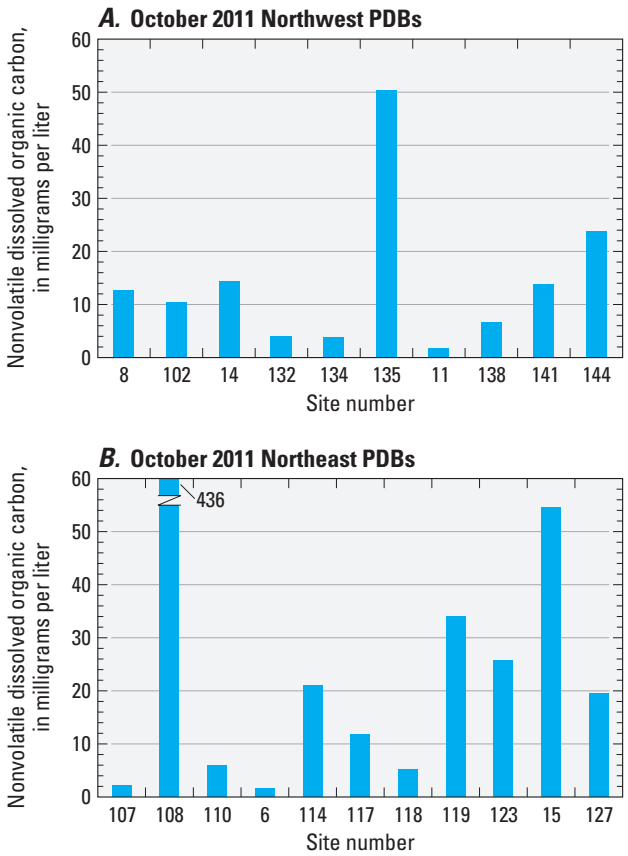


Figure 22. Spatial distribution of nonvolatile dissolved organic carbon (NVDOC) in passive diffusion bag (PDB) samples of the wetland groundwater collected in *(A)* northwest, and *(B)* northeast wetland areas in October 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

occurred in this upper 20-cm zone and were similar to surface-water concentrations (available in 2011), indicating surface-water infiltration. In contrast, wetland groundwater concentrations of sulfate were 10 to 50 times greater than surface-water concentrations in peepers in the northeast wetland area. The equal or higher sulfate concentrations at piezometers screened deeper than the peeper samples at the same sites indicate that groundwater discharge from the Columbia aquifer provides a source for the high sulfate. Upland monitoring wells MW22 and MW23, screened in the Columbia aquifer near the wetland boundary in the northeast area, had higher sulfate concentrations than monitoring wells in the northwest area (MW21, MW25; table 11). In addition, previous samples collected from drive-point piezometers along the eastern wetland-upland boundary also showed high sulfate concentrations, ranging from 180 to 2,490 mg/L, that were attributed to a sulfuric acid spill at the oil refinery (table 12). Other redox-sensitive constituents in addition to sulfate showed temporal as well as spatial variations in the wetland groundwater and are discussed in the next section.

Temporal Distribution

Although limited data collection occurred during the early stages of this study, large changes in concentrations of some geochemical constituents were apparent in both areas of the wetland from July 2009 to March 2011, compared to relatively stable concentrations of constituents observed during monthly sampling from August 2011–August 2012 (fig. 25). Chloride and sulfate concentrations in the shallow wetland groundwater at two sites—8 in the northwest wetland area and 6 in the northeast wetland area—that were consistently sampled during 2009–12 reflect these changes (fig. 25). To construct figure 25, concentrations in peeper samples were averaged over their 120-cm-depth range to compare with PDB samples (depths of 20 to 40 cm) before installation of DP-6A and DP-8A and the piezometer samples from DP-6A and DP-8A (screens at about 40 to 70 cm below land surface; table 2). Chloride concentrations at site 8 in the northwest decreased substantially from about 350 to 180 mg/L in July 2009–March 2011, and then remained relatively low (between 100–125 mg/L) during August 2011–12. Sulfate concentrations at site 6 increased from about 300 to 1,400 mg/L between July 2009 and December 2010 but then decreased again, returning to around 300–400 mg/L by the end of the 2012 sampling period (fig. 25).

Although sulfate concentrations showed greater temporal variability than chloride concentrations at these sites, sulfate concentrations were consistently a factor of 10 or more higher at site 6 in the northeast than observed at site 8 in the northwest (fig. 25). In contrast, chloride concentrations at the two sites were similar in August 2011–12 (fig. 25a), as noted previously in the peepers (figs. 23c, d). It is possible that the decline in chloride concentrations in the northwest wetland area observed between July 2009 and March 2011 is due to the installation of the barrier wall in 2007 that removed a source of chloride from groundwater flow from the Columbia aquifer to wetland sediments in the northwest area. Because the high sulfate source is believed to be from the sulfuric acid spill at the oil refinery, which is outside this barrier wall, sulfate concentrations in groundwater discharging to the northeast wetland area would not be affected by the barrier wall; thus, sulfate concentrations remained high in the northeast area, whereas chloride concentrations decreased in the northwest area.

Substantial changes in concentrations of redox-sensitive constituents occurred in the wetland porewater in both the northwest and northeast areas between 2009–12 (figs. 26 and 27). Although a predominance of ferrous iron indicated that iron reduction was the predominant redox process at site 8 in the northwest during each sampling period, ferrous iron concentrations were about a factor of 10 higher in the July 2009 peeper samples than peeper samples from other sampling periods at this site (fig. 26). In addition, high methane concentrations at site 8 during July 2009, which peaked at nearly 10 mg/L between depths of 62–79 cm below land surface, indicated mixed iron reducing-methanogenic conditions. In

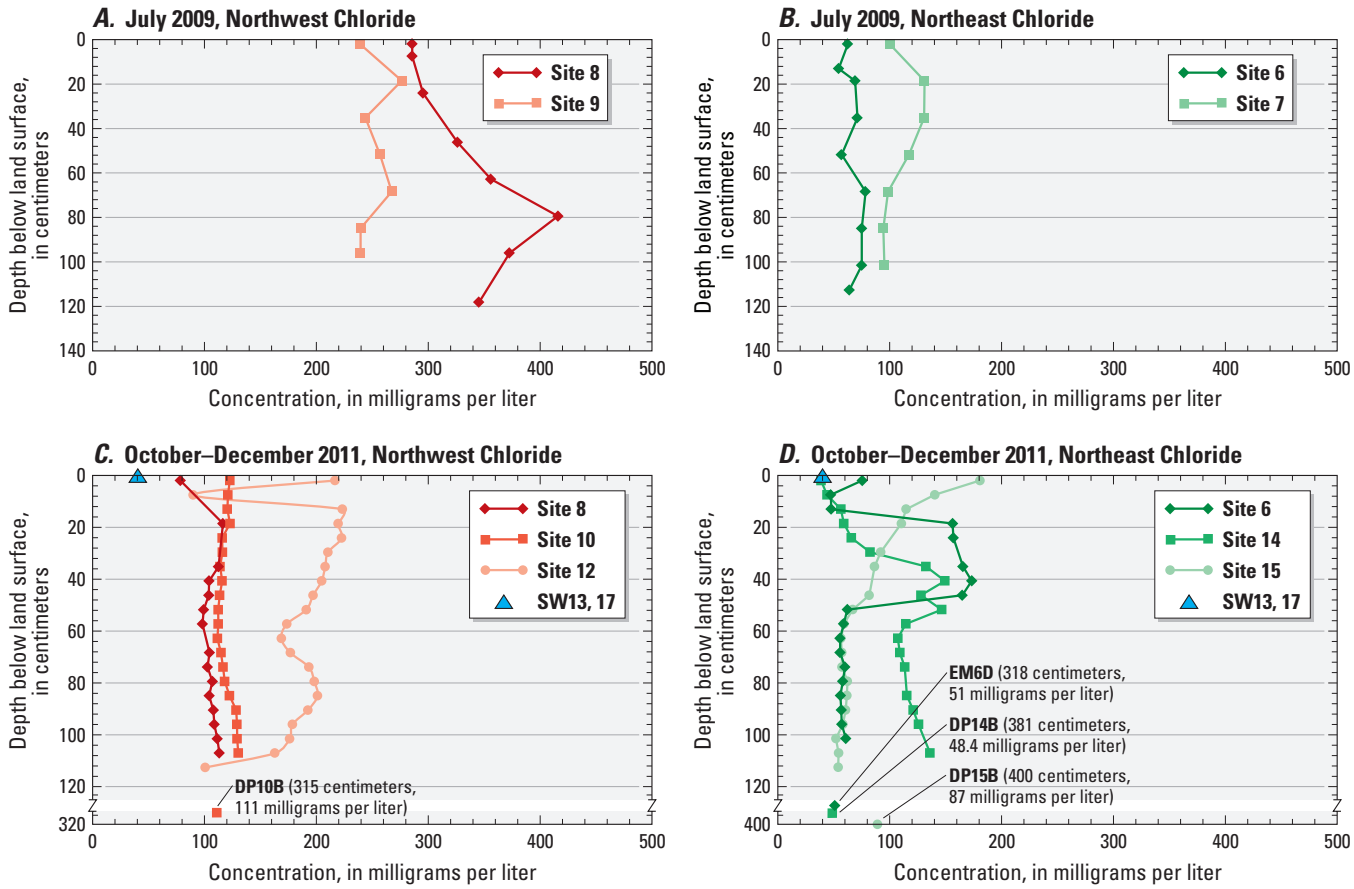


Figure 23. Vertical distributions of chloride concentrations in peepers from the northwest and northeast wetland areas in *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

December 2011, methane concentrations were generally less than 0.040 mg/L at all depths in the peeper sampled at site 8, and in conjunction with the low ferrous iron concentrations, indicate a shift to less reducing conditions (fig. 26b). Although temperature decreases in the winter can lead to lower methanogenic activity, ferrous iron and methane concentrations also were low or undetectable during monthly sampling events from September 2011 to August 2012 at DP-8A (fig. 26c). Other northwest sites sampled with peepers in October 2011, sites 10 and 12, also showed low or nondetectable methane concentrations (data on file, USGS MD-DE-DC WSC).

In contrast, the peeper samples from site 6 in the northeast had sulfide concentrations that were up to three to four times higher in December 2011 than in July 2009, indicating a shift to more reducing conditions (figs. 27a, b). Peeper samples at site 6 in December 2011 had the highest concentrations of reduced iron and sulfide in the upper 20 cm of wetland sediment, whereas the July 2009 samples showed only slightly reducing conditions in this upper zone (total concentrations of reduced species less than 1 mg/L). Other peepers sampled in the northeast wetland area in October 2011 (sites 14 and 15) had high sulfide concentrations in the upper 60 cm, with maximum sulfide concentrations of 12 and 16 mg/L (data on file, USGS MD-DE-DC WSC). The sulfide concentrations in peeper samples from October-December 2011 were consistent with the significantly higher sulfide concentrations observed in PDB samples from the northeast wetland area in October 2011 than those in the northwest area (fig. 21). Methane concentrations also were high (about 8 to 34 mg/L) in the upper 60 cm of sediment in the northeast peepers sampled in October 2011 (data on file, USGS MD-DE-DC WSC). It should be noted however, that monthly samples from DP-6A showed low concentrations of reduced constituents in 2011–12. This apparent discrepancy may be due to the preferential sampling of deeper groundwater with the piezometers (screened 43–73 cm below land surface) where conditions were less reducing than at shallower depths in the wetland sediment, as indicated by the peeper profile at site 6 in December 2011 (fig. 27b).

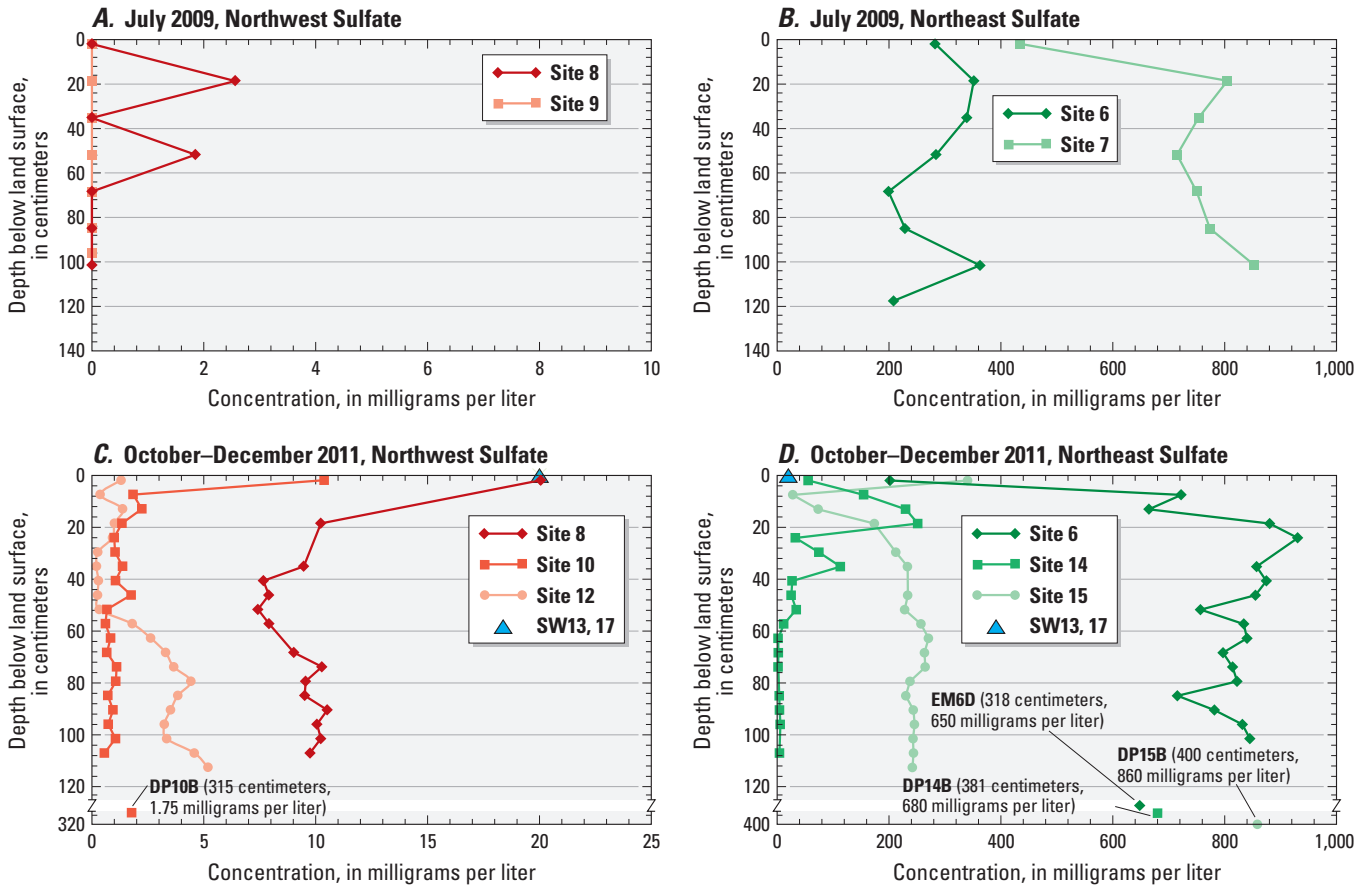


Figure 24. Vertical distributions of sulfate concentrations in peepers from the northwest and northeast wetland areas in *(A, B)* July 2009, and *(C, D)* October–December 2011, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

Table 11. Concentrations of selected inorganic constituents measured in groundwater samples collected with passive diffusion bags from upland monitoring wells, October 2011.

[cm, centimeters; mg/L, milligrams per liter; <, less than]

Well name	Sample date	Depth (cm)	pH (standard units)	Chloride (mg/L)	Sulfate, as SO_4 (mg/L)	Ammonia, as N (mg/L)	Ferrous iron, as Fe (mg/L)	Total dissolved iron (mg/L)	Sulfide, as S (mg/L)	Methane (mg/L)
MW-25	10/26/2011	736.2	5.05	255	0.25	0.35	5.39	5.53	0.018	<.027
MW-21	10/26/2011	404.6	5.80	83.9	35.2	0.34	5.42	5.53	0.006	<.027
MW-22	10/26/2011	349.8	5.11	76.8	320	0.10	0	0.06	<.005	0.073
MW-23	10/26/2011	626.7	6.92	36.3	122	0.37	15.9	15.59	<.005	<.027

Table 12. Concentrations of chloride and sulfate measured in 2008 in drive-point piezometers screened in the Columbia aquifer near the upland-wetland boundary east of the Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Samples analyzed by the U.S. Geological Survey National Water Quality Laboratory; mg/L, milligrams per liter; dup, duplicate]

Well name	Sample date	Chloride (mg/L)	Sulfate (mg/L)
EM-1D	6/12/2008	102	462
EM-2D	6/12/2008	61.0	2,450
EM-2D (dup)	6/12/2008	61.3	2,490
EM-5D	9/16/2008	55.1	180
EM-6D	9/16/2008	75.3	637
EM-6D (dup)	9/16/2008	74.6	636

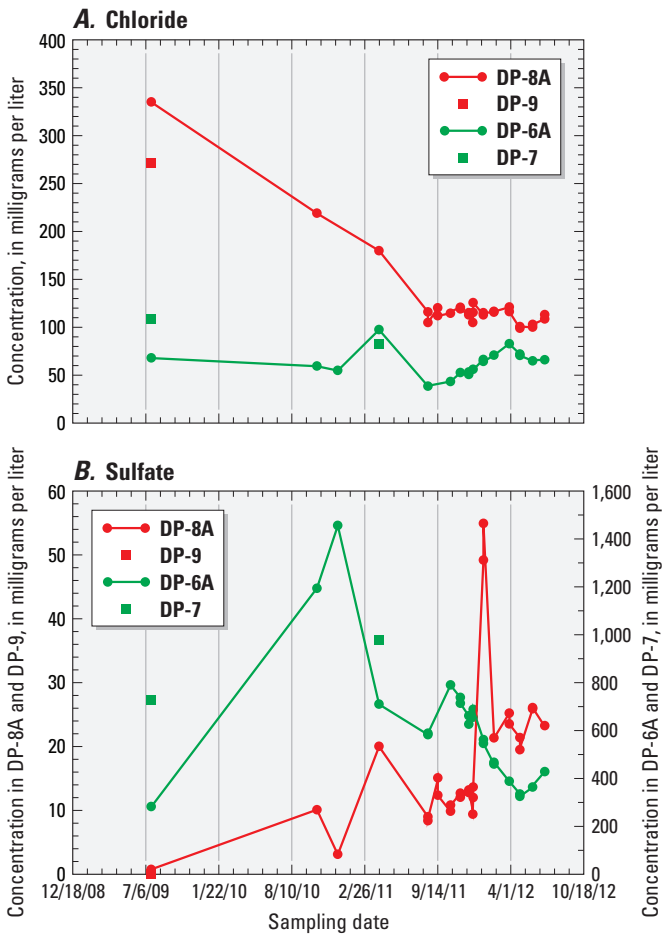


Figure 25. Temporal changes in *(A)* chloride and *(B)* sulfate for selected sites in the wetland study area, July 2009–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

Dense Non-Aqueous Phase Liquid (DNAPL) Extent

The chlorinated hydrocarbon contaminants that spilled and were detected in the subsurface environment at the SCD can be characterized as DNAPLs (denser than water), whereas benzene is a light non-aqueous phase liquid (LNAPL) [less dense than water]. Previous reports and calculations made with data collected for this study showed evidence only of DNAPLs, not LNAPLs. Because DNAPLs have a different density than water, they behave uniquely in the subsurface environment depending on the route of entry, mixture of contaminants present in the DNAPL, and subsurface conditions (Cohen and Mercer, 1993). These properties allow them to migrate as a separate phase over long distances and to great depths away from their point of entry into the subsurface (Kueper and Davies, 2009). The presence and transport of DNAPLs is critical to the understanding of a contaminated site and ultimately the selected remediation, because their behavior and transport is different than the behavior of dissolved contaminants. In addition, DNAPLs may persist for centuries as a source of groundwater contamination, stored in the aquifer as dispersed droplets or pools along contacts of low permeability sediment layers and in low permeability sediment from matrix diffusion (Cohen and Mercer, 1993; Kueper and Davies, 2009). Failure to understand the extent of DNAPLs can result in the expansion of contamination during either characterization or remediation activities (Cohen and Mercer, 1993). The following sections summarize past DNAPL characterization efforts at the SCD and provide an updated conceptual model for DNAPL extent in the subsurface using data collected during this study, in conjunction with other recent data collected in the wetland and the Columbia and Potomac aquifers.

Previous Dense Non-Aqueous Phase Liquid (DNAPL) Investigations

The presence of DNAPL has been reported within the Columbia aquifer for 25 years, starting with early investigations of the SCD. Quarterly sampling of monitoring wells in the late 1980s through the early 1990s consistently showed free product in some previous monitoring and recovery wells including TW-5, TW-28, TW-32, RW-2, and RW-5 (Roy F. Weston, Inc., 1993a) that are all located within the current barrier wall area, within and to the west of the main industrial area of the site, and near the settling pond (fig. 1). Laboratory reports indicate that DNAPL was visible as a thin layer of film at the base of the sample (Roy F. Weston, Inc., 1993a) collected from these wells. Similarly, early investigations conducted by the SCD (Conestoga Rovers Associates, 2000) indicated the likely presence of DNAPL (by the use of Sudan dye tests with soil samples) in the central industrial part of SCD (near previous monitoring well TW-30). On the basis of these initial results, possible DNAPL migration and extent was

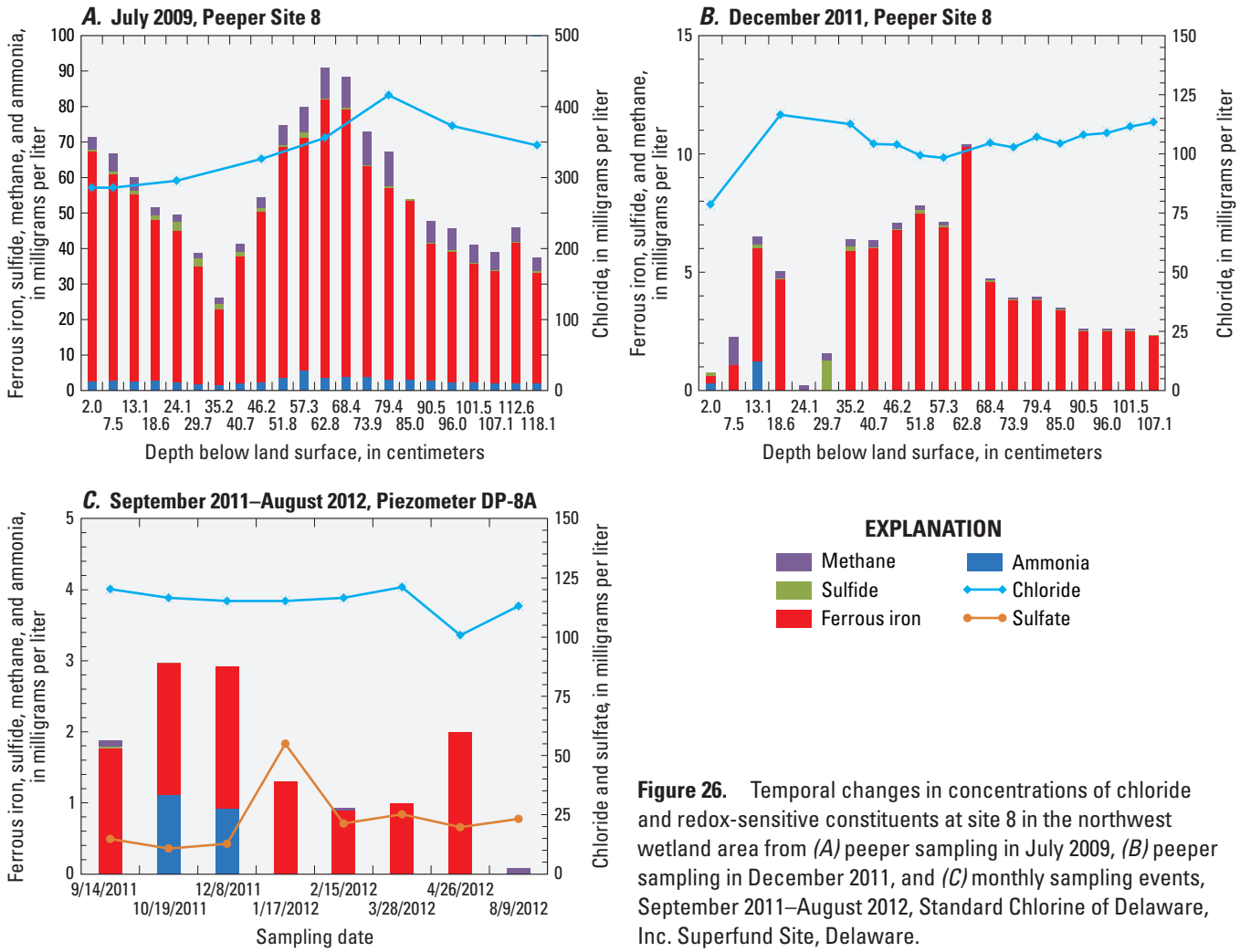


Figure 26. Temporal changes in concentrations of chloride and redox-sensitive constituents at site 8 in the northwest wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

included in the 1993 feasibility study (Roy F. Weston, Inc., 1993a) and the 1995 ROD (U.S. Environmental Protection Agency, 1995a). The 1993 feasibility study estimated that the extent (based on effective solubility estimates with groundwater concentrations) extended beyond the barrier wall slightly to the west and included three monitoring points in the wetland near Red Lion Creek that were screened in the Columbia aquifer (U.S. Environmental Protection Agency, 1995). When these reports were published, the extent was estimated to be limited to the Columbia aquifer with migration interrupted by the underlying confining unit (Merchantville clay). Any migration within the Columbia aquifer was estimated to be toward the center of the SCD (Roy F. Weston, Inc., 1993a). Subsequent investigations have identified dissolved phase contaminants in the Upper Potomac aquifer underlying this confining layer (Merchantville/Upper Potomac clay) (Christopher Wolfe, HydroGeoLogic, Inc., written commun., 2012), although to date, no evidence of DNAPL migration into the Lower Potomac aquifer has been reported.

In preparation for the design and construction of the barrier wall and in keeping with directives outlined in the 1995 ROD to limit and contain the migration of DNAPL, additional work was conducted in 2002 to aid in identifying potential DNAPL pools (by use of Membrane Interface Probe [MIP]/Electrical Conductivity [EC] screening), the extent of contamination, and the continuity of the clay layer underlying the contaminated Columbia aquifer (Black & Veatch, 2005). Extensive contamination was reported based on the MIP screening results (Black & Veatch, 2005); however, no additional spatial resolution of DNAPL pools was reported. EC results from the MIP/EC screening yielded locations for groundwater sampling and possible DNAPL identification (using FLUTe liners). Staining of the FLUTe liners installed at three locations in the central industrial part of SCD (out of the five tested) showed the presence of DNAPL in the range of 15.2–18.3 m (5–60 ft) below land surface in the Columbia aquifer (Black & Veatch, 2005).

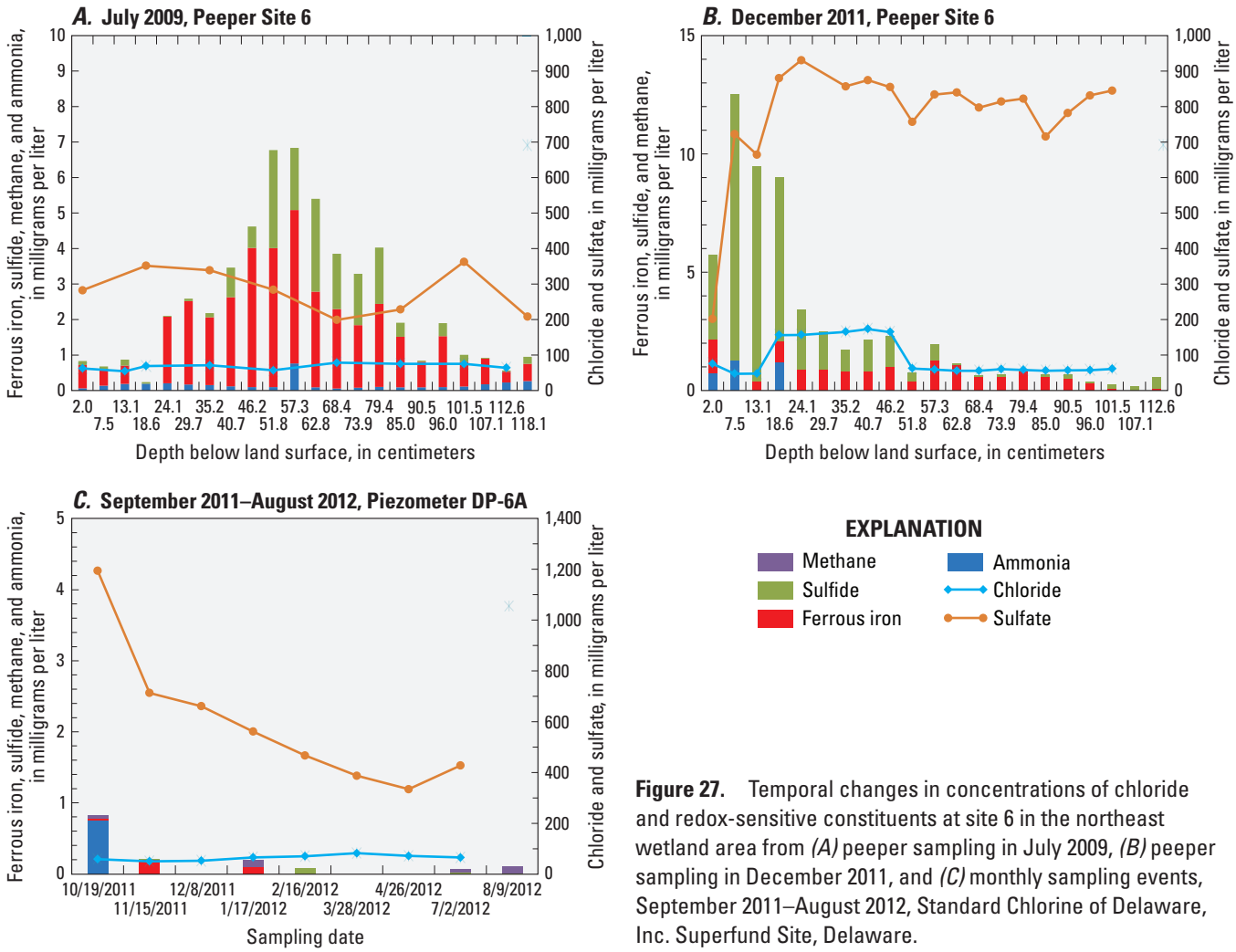


Figure 27. Temporal changes in concentrations of chloride and redox-sensitive constituents at site 6 in the northeast wetland area from *(A)* peeper sampling in July 2009, *(B)* peeper sampling in December 2011, and *(C)* monthly sampling events, September 2011–August 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

During this investigation, the EPA installed DNAPL recovery systems at recovery wells RW-2 (to the north of the settling basin) and RW-5 (at the western boundary of the existing barrier wall near the Air Products facility) in an attempt to remove product (Black & Veatch, 2005). Although some DNAPL was recovered, recharge was reported to be extremely slow; therefore, long-term recovery by this method was not considered to be cost-effective (Black & Veatch, 2005).

Following the installation of the barrier wall, which was designed to contain the majority of known DNAPL extent, no subsequent DNAPL investigations have been conducted and no additional DNAPL areas have been identified. Review of the interim action (U.S. Environmental Protection Agency, 2011) indicates that the barrier wall in combination with pumping is performing as designed.

Updated Dense Non-Aqueous Phase Liquid (DNAPL) Site Conceptual Model

Although the barrier wall was designed to hydraulically contain most DNAPL from the SCD industrial area in the Columbia aquifer, the design report acknowledged that DNAPL may extend beyond the wall (Black & Veatch, 2005). Possible locations for this DNAPL underlie or are within the USGS wetland study area where high tide resulted in the fanning of contaminants into the wetland. Since minimal investigations of the wetland porewater and underlying groundwater from the Columbia and Potomac aquifers have been conducted until this study, an update to the DNAPL site conceptual model is provided.

Dissolved and DNAPL phase contamination in the wetland may originate from various sources: (1) DNAPL resulting from overland flow from the 1986 spill that reached the wetlands, (2) subsequent product removal efforts that may have caused possible migration downward from the surface, and (3) long-term upward migration of dissolved contaminants into the wetland porewater due to vertical discharge from the Columbia aquifer that was contaminated from various waste disposal activities, leaks, and spills over the period of industrial operation. In addition, desorption of contaminants from highly organic wetland sediments may act as a secondary source.

The likelihood of DNAPL contact with site groundwater or the actual presence of DNAPL in groundwater was estimated based on a calculated threshold concentration (C) of 1 percent of the solubility, S_i, (or effective solubility, C_i, in the case of 14DCB, 123TCB, and 124TCB) of a given compound (table 1).

$$C > C_i * (0.01) \tag{8}$$

Where spill contents were known, the effective solubility, C_i, was calculated using Raoult's Law (Kueper and Davies, 2009), where m_i is the mole fraction of compound in the 1986 spill and S_i is the single-component solubility:

$$C_i = m_i S_i \tag{9}$$

In the case of 14DCB and 123TCB, the super-cooled solubilities were used in these calculations because these compounds are solids at steady state (VanNoort, 2009). Using the super-cooled solubility increases the calculated solubility of the compounds by about a factor of 2 (table 1), thus making the estimate of DNAPL presence more conservative.

Columbia and Potomac Aquifers

Following the installation of the barrier wall, total VOC concentrations in the Columbia aquifer in the vicinity of the wetland (along the upgradient boundary at Haul Road) have decreased between 60 and 90 percent, as determined from quarterly monitoring reports (fig. 28). Despite this decrease, currently much of the Columbia aquifer upgradient of and underlying the USGS wetland study area is indicative of continued interaction with or the presence of DNAPL, based on the percent of solubility of the concentrations present in groundwater (fig. 29), and may serve as a possible contaminant source to the wetlands. Whereas 1 percent was used to indicate possible DNAPL extent, maximum concentrations of individual compounds in 2011–12 indicated a range of 2 (13DCB at MW-21) to over 40 (123TCB at MW-25) percent solubility of individual compounds present in site groundwater. Total VOC concentrations in groundwater wells within the barrier wall near its northern extent were some of the highest

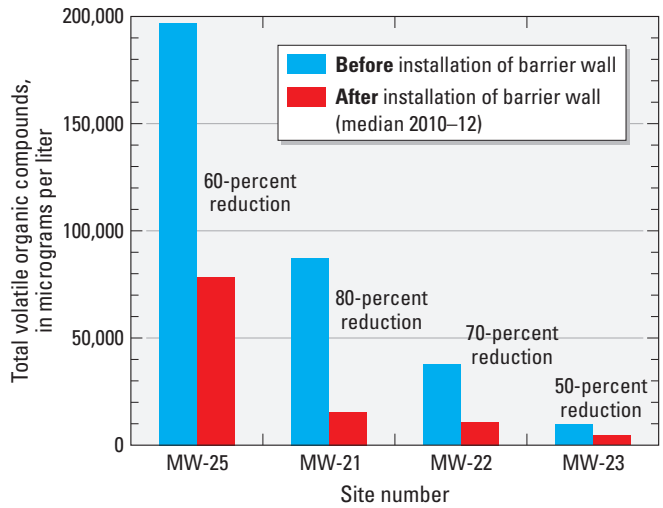


Figure 28. Reduction in total volatile organic compound concentrations in monitoring wells along the wetland-upland boundary after the installation of the barrier wall, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

detections currently identified in the Columbia aquifer, ranging from 100–145 mg/L (wells PZ29 and PZ11). Wells immediately north-northwest of the barrier wall boundary and just upgradient from the wetland study area contained total VOCs in the range of 75–90 mg/L (MW-25, PMW-45, and MW-24). Moving spatially from west to east toward MW-23, total concentrations declined by an order of magnitude and fewer compounds had concentrations that are indicative of DNAPL presence (fig. 29). As was the case with the Columbia aquifer, wells screened in the Potomac aquifer north of the barrier wall near the wetland-upland boundary were indicative of DNAPL presence or contact for all chlorinated benzenes present at the site (wells PW-14 and PW-17; fig. 29). The magnitude of concentration in these Potomac wells averaged about 60 mg/L (Christopher Wolfe, HydroGeoLogic, Inc., written commun., 2012).

Groundwater concentrations of VOCs from drive-point piezometers screened immediately below the wetland sediments in the Columbia aquifer differed in the northwest and northeast parts of the USGS wetland study area. Concentrations in wells located in the northwest wetland area are indicative of DNAPL (mainly for 14DCB, 12TCB, and 124TCB), and total VOC concentrations ranged from 10 to 14 mg/L (fig. 29). In the northeast wetland area, the overall magnitude of groundwater concentrations in the Columbia aquifer was considerably less, resulting in no exceedances of 1 percent of the solubility in this region (fig. 29). The spatial distribution of the DNAPL extent in the Columbia aquifer may indicate lateral migration from the central part of the SCD downgradient towards the wetland (fig. 8). Contaminant transport from the western drainage gully (fig. 1) may have had additional impact on the aquifer, particularly along the western boundary.

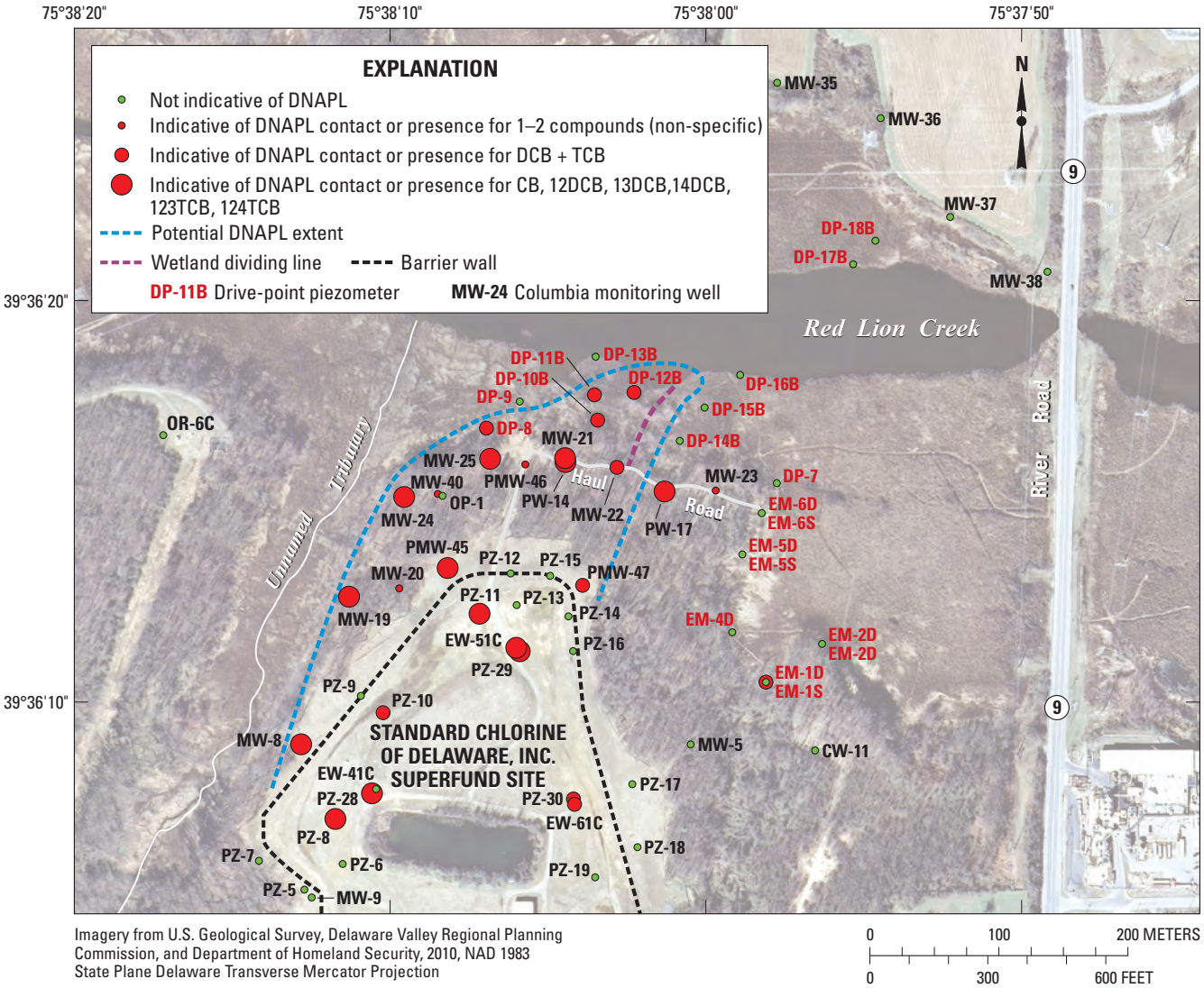


Figure 29. Potential current (2012) distribution of dense non-aqueous phase liquids (DNAPLs) in the Columbia aquifer, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware. (DCB, dichlorobenzene; TCB, trichlorobenzene; CB, chlorobenzene; 12DCB, 1,2-dichlorobenzene; 13DCB, 1,3-dichlorobenzene; 1,4-DCB, 1,4-dichlorobenzene; 123TCB, 1,2,3-trichlorobenzene; 124TCB, 1,2,4-trichlorobenzene.)

Wetland Porewater

Results from the current study showed that groundwater in the overlying wetland sediments also had concentrations in the range of DNAPL contact or presence (fig. 30). The impacted wetland area is not spatially consistent with the footprint of potential DNAPL in the aquifer, and differences between the northwest and northeast areas are not as apparent. Possible DNAPL presence or contact extends farther east compared to the footprint in the Columbia aquifer (figs. 29, 30). The area of impact is more spatially extensive, and in some cases, concentrations in shallow wetland groundwater are higher than concentrations in the immediately underlying aquifer. This increase may be a result of overland contamination in the wetland due to the 1986 spill, as was also noted from the vertical distributions of contaminants observed in the wetland groundwater in the peepers (fig. 17). Although the possibility of redistribution of contaminants due to the damaged tide control gate and current increased flooding of the wetland sediments cannot be ruled out, peeper samples collected in 2009 before the storm damage to the tide control structure (August 2011) showed the same general increase in VOC concentrations in the wetland groundwater near land surface (upper 40–50 cm) as observed in peeper samples collected in October–December 2011 (fig. 17).

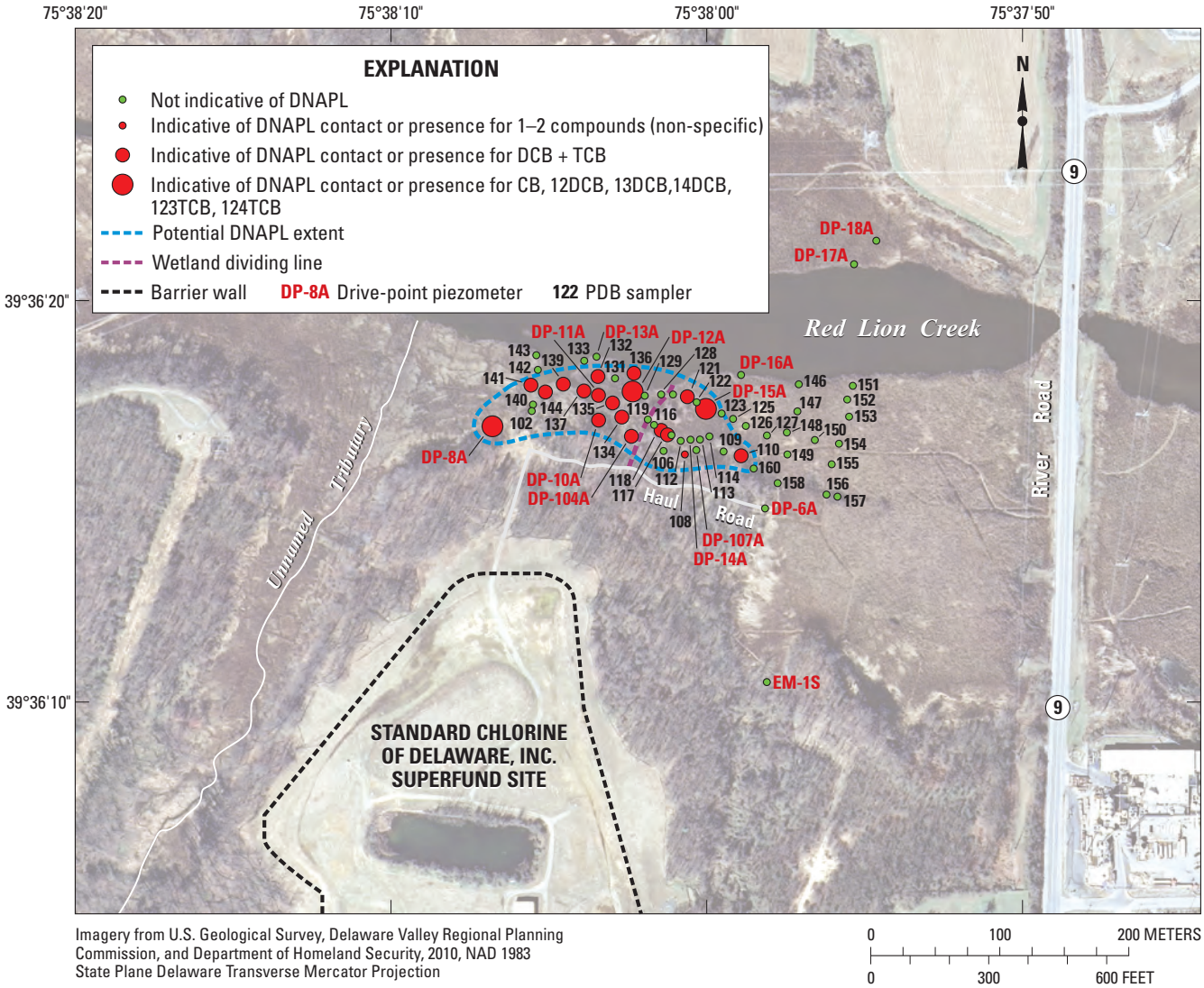


Figure 30. Potential current (2012) distribution of dense non-aqueous phase liquids (DNAPLs) in the wetland porewater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, on the basis of computed concentrations that exceed 1 percent of the compound's solubility. (DCB, dichlorobenzene; TCB, trichlorobenzene; CB, chlorobenzene; 12DCB, 1,2-dichlorobenzene; 13DCB, 1,3-dichlorobenzene; 1,4-DCB, 1,4-dichlorobenzene; 123TCB, 1,2,3-trichlorobenzene; 124TCB, 1,2,4-trichlorobenzene.)

Source Assessment for Wetland Study Area

An attempt was made to discern more about the contribution of possible sources of contamination to the USGS wetland study area (formerly referred to as the eastern wetlands in HydroGeoLogic, Inc., 2009) because this is critical in selecting and implementing a final remedy at the wetland area of the SCD. Molar composition, molar ratios, and total molar concentrations in groundwater samples collected from the aquifers and wetland groundwater were compared over time and in space to infer more about the transport of the contaminants and their possible origins.

Columbia Aquifer and Overland Spills as Sources of Contamination

In order to assess possible contributions of the contaminants from the aquifer to the wetland, an analysis of contaminant transport in the aquifer was conducted. Monitoring wells north of the spill areas (TW-49, MW-6, and MW-7) spaced approximately 61 m apart along the flowpath towards the wetland study area (MW-25) were used to compare VOC composition over time and distance (fig. 31a). Molar composition of these wells in 1993 and 2004 were dominated by CB and benzene, which was unexpected because the largest spill

(569,000 gallons in 1986) mostly contained 14DCB and TCBs. CB and benzene were components of the relatively small 1981 spill (5,000 gallons) and are the most soluble of the VOCs at the site. Similar total VOC concentrations and molar profiles were observed in the wells in 1993 and 2004 (fig. 31a). There was little downgradient change over time to indicate that, prior to the installation of the barrier wall, contaminant mass may have migrated in groundwater to Haul Road at the upland boundary, particularly groundwater in contact with CB DNAPL from the 1981 spill. To evaluate this possible migration to the upland-wetland boundary, travel-times of specific compounds were estimated using assumptions of bulk sediment properties and chemical properties to calculate a retardation factor, R,

$$R = 1 + \left(p_b / n_e\right) * K_d \tag{10}$$

where

p_b = average bulk density of medium sand or 1.59 grams per cubic centimeter (g/cm^3);

n_e = effective porosity of 0.3 (Domenico and Schwartz, 1990); and

K_d = the distribution coefficient (f_{oc}*K_{oc}), where f_{oc} is the fraction of organic carbon in the sediment, and K_{oc} is the organic carbon partitioning coefficient (table 1).

Organic carbon content analyses of sediment core samples collected at a depth of 6 m near the wetland-upland boundary gave a median f_{oc} of 0.003.

To estimate traveltime, T, over a given distance, L, 61 to 122 m

$$T = L / V_c \tag{11}$$

and contaminant (such as CB) velocity, V_c,

$$V_c = v / R \tag{12}$$

where

v = average linear velocity in the central part of the site, 255 meters per year (836 feet per year [ft/yr], Black & Veatch, 2007).

Calculated traveltimes of CB and 14DCB in groundwater between wells TW-49 and MW-7 and MW-25 were less than the sampling time difference of 11 years shown in figure 31, whereas the traveltime of 124TCB exceeded 11 years (table 13). These traveltimes indicate that CB (and therefore benzene as well) and 14DCB could theoretically have traveled in groundwater to the wetland boundary (and beyond) in this 11-year timeframe. However, given the more than an order of magnitude greater estimated traveltime for 124TCB than

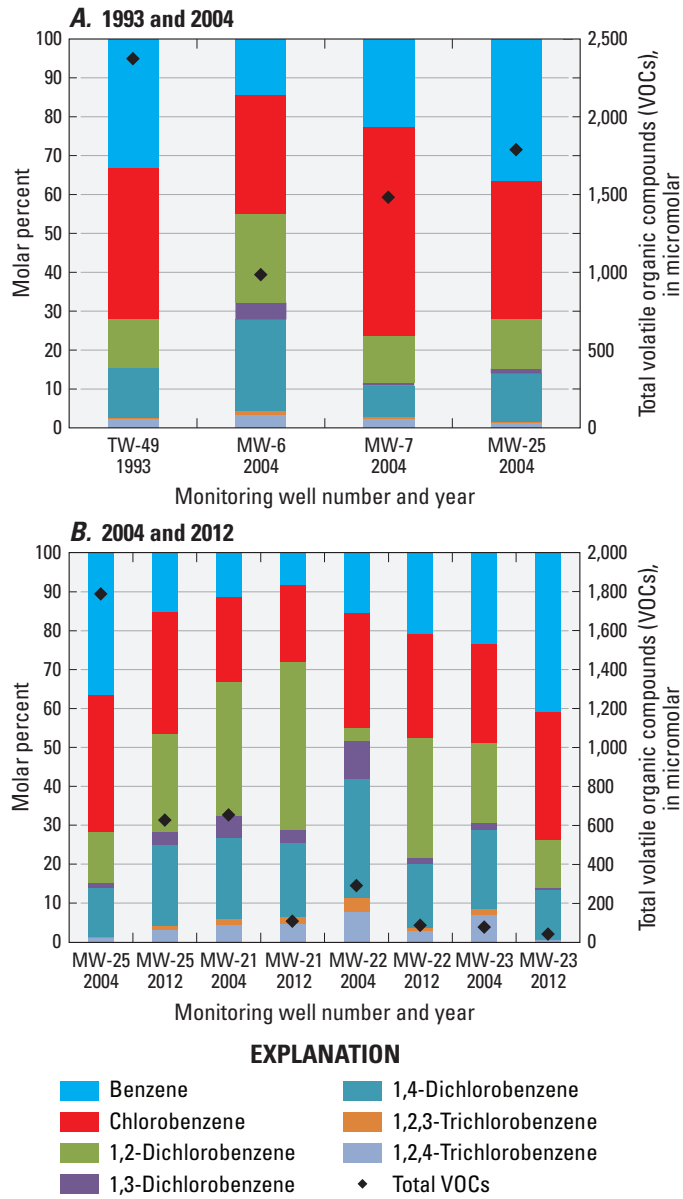


Figure 31. Comparison of molar composition (in percent) of water samples from aquifer monitoring wells in *(A)* 1993 and 2004, and *(B)* 2004 and 2012, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

for CB and 14DCB, it is unlikely that 124TCB (and therefore 123TCB, since these compounds were spilled together in 1986) traveled in groundwater to the wetland boundary. Instead, these compounds may originate from sources nearer to the wetland as opposed to flow-through sources in the main part of the site. This analysis is consistent with previous discussions of possible sources north of the barrier wall (Black & Veatch, 2005).

Concentrations in relatively shallow monitoring wells along Haul Road were compared before and after the barrier wall was installed (fig. 31, 2004 data from Black & Veatch,

Table 13. Traveltime of selected site contaminants in groundwater along a flowpath.

[CB, chlorobenzene; 14DCB, 1,4-dichlorobenzene; 124TCB, 1,2,4-trichlorobenzene]

Site compound	Calculated R[1]	Calculated T[2] (years) to travel between TW-49 and MW-7	Calculated T[2] (years) to travel between TW-49 and MW-25
CB	3.8	1	2
14DCB	7.9	2	4
124TCB	251	60	120

[1] $R = 1 + (p_b / n_e)*K_d$, where R is retardation factor, p_b is dry bulk density, n_e is effective porosity, and K_d is the retardation or distribution coefficient.

[2] $T = L/V_c$, where $V_c = v/R$, T is time, L is distance traveled, V_c is contaminant velocity, and v is linear horizontal velocity.

2007; Christopher Wolfe, HydroGeoLogic, Inc., written commun., 2012). As previously discussed (see figure 28), the barrier wall installation resulted in a reduction in overall concentrations in these wells. In 2012, there were clear differences between wells upgradient (south) of the northwest and northeast wetland areas (fig. 31). Upgradient of the northwest area (wells MW-25 and MW-21), there is a decreased predominance of CB and an increased predominance of 12DCB in the VOC molar composition between 2004 and 2012 (fig. 31). This pattern is less apparent moving from west to east where overall VOC concentrations declined, but the easternmost well MW-23 instead had an increase in the predominance of CB and benzene in 2012 compared to 2001 (fig. 31b). An increase in the molar percent of TCBs between 2004 and 2012 also was apparent in the western wells MW-25 and MW-21, whereas the opposite pattern was observed again in the easternmost well (MW-23, fig. 31b). In the northwest area, the decrease in the percentage of CB may be due to the presence of the barrier wall, installed immediately upgradient in 2007, interrupting a primary source of CB flowing toward the wetland in the aquifer. The simultaneous increase in the molar percent of other less soluble, non-spill compounds, such as 12DCB and the TCBs, may simply reflect their relative increased contribution to the overall VOC composition with the decline in CB, or they may reflect the relative increased importance of DNAPL sources outside the barrier wall on the VOC composition in the aquifer. The decline in chloride concentrations observed in the groundwater in the northwest wetland area between 2009 and 2011 (fig. 25) supports the possibility of the barrier wall at least partly interrupting transport from a source upgradient of the wall. The increased molar percentages of CB and benzene in the northeast wetland (MW-23) also may be attributable to contaminant degradation, given the simultaneous reduction in other higher chlorinated benzene compounds and overall concentrations (fig. 31b). The possible effects of degradation on VOC composition is discussed in more detail in the Natural and Enhanced Biodegradation section.

Both similarities and differences between the northwest and northeast wetland areas were apparent in the piezometer pairs screened in the Columbia aquifer and wetland sediments (fig. 32). For 2012, data in the Columbia aquifer in the northwest wetlands and parts of the northeast wetland were consistent and only averaged concentrations from representative sites are shown (sites 10 and 12 in the northwest area and site 15 in the northeast area, fig. 32). Site 6 was included in this analysis, but due to large variability in concentrations between sampling events, data were not averaged and are not shown. Compared to the upland boundary wells in 2012 (fig. 31), total VOC concentrations in groundwater from piezometers screened in the aquifer immediately below the wetland sediments were slightly lower (fig. 32). Molar composition of groundwater from piezometers closer to Red Lion Creek, DP-12B and DP-15B, differed from the upland boundary wells and from DP-10B, which is slightly upgradient of DP-12B, with decreased proportions of 12DCB and 124TCB and increased proportions of 13DCB and 123TCB (fig. 32). With decreasing depth, concentrations of VOCs increased in the wetland sediments nearest to the creek (DP-12B and DP-15B), and another shift in molar composition was observed (fig. 32). To better evaluate contaminant sources to the aquifer and the overlying wetland sediments, molar ratios, R_s, reflective of the 1986 spill compounds were calculated:

$$R_s = (14DCB) / (123TCB + 124TCB) \tag{13}$$

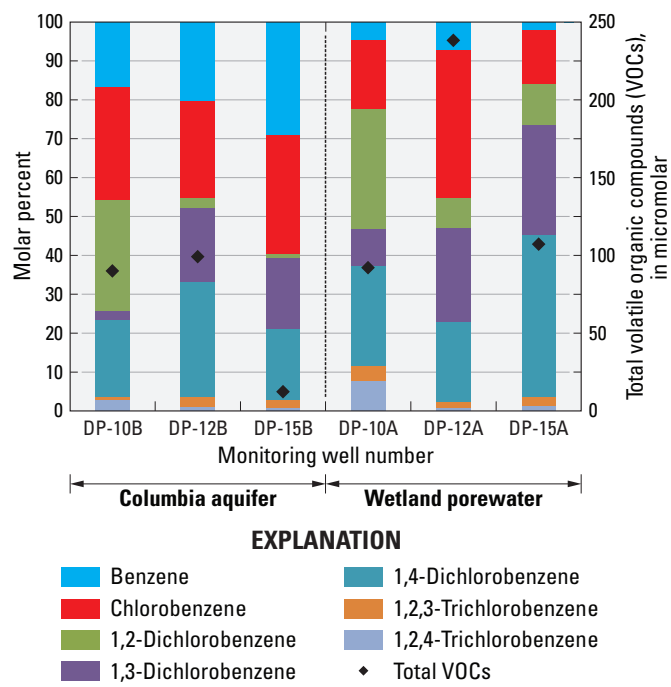


Figure 32. Comparison of molar composition (in percent) in the Columbia aquifer immediately below the wetland sediments and wetland porewater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, 2012.

The R_s calculated from the reported composition of the 1986 spill is 2.9. The R_s values calculated for the shallow Columbia aquifer were slightly higher than the 1986 spill composition and were fairly consistent, ranging from 4.0 at a site located immediately upgradient of the wetland boundary (MW-22) and between 4.5 to 5.8 at sites within the wetland area (fig. 33). In contrast, the R_s values of groundwater from the overlying wetland sediment were highly variable, ranging from about 2.1 to 8.8 (fig. 33). The 1986 spill molar ratio indicates that the deep (Columbia aquifer) and shallow wetland groundwater contamination differ from one another, likely due to mixing of different sources in the wetland groundwater and the effects of biodegradation and other natural attenuation processes (fig. 33). The greater variability in R_s is consistent with the change in molar compositions of the VOCs (fig. 32) in the wetland groundwater compared to the Columbia aquifer and indicates the complexity of processes that could affect the contaminant distribution in the wetland. A similar, limited analysis was used to evaluate possible common sources of contamination in the Potomac aquifer near the wetland compared to the Columbia aquifer or wetland groundwater. The total VOC concentrations in groundwater from the Potomac aquifer wells were similar to those detected in the Columbia aquifer at MW-25 and only slightly lower than concentrations measured inside the barrier wall (PZ-29) (fig. 34a). Groundwater samples from both the Potomac and Columbia aquifers indicated that about half of the molar mass is made up of CB and benzene (similar to the older profile from inside the barrier wall). However, some differences in the molar composition of the VOCs were found between the Columbia and Potomac aquifers. 123TCB and 13DCB were more dominant in the groundwater in the Potomac aquifer than in the Columbia aquifer, whereas 124TCB and 12DCB were more dominant in the Columbia aquifer (fig. 34a). Nonetheless, calculated source ratios (based on the 1986 spill, equation 13) between the Potomac aquifer and Columbia aquifer wells were similar (fig. 34b). It is possible that contamination in both aquifers resulted from the same contaminant source containing a mixture of 123TCB and 124TCB, but microbial degradation of the contaminants over time occurred through different pathways, leading to differing predominances in the TCB and DCB isomers.

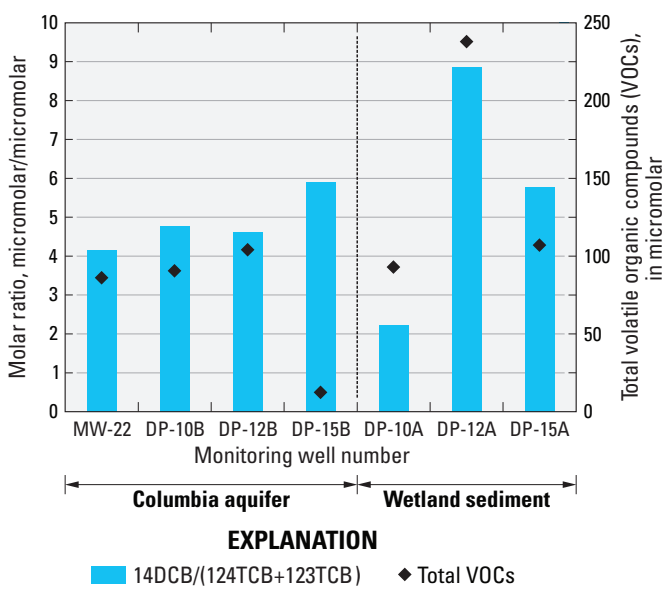


Figure 33. Comparison of volatile organic compound molar ratios (micromolar/micromolar) in the Columbia aquifer and wetland porewater for the 1986 spill compounds (1,4-dichlorobenzene/1,2,4-trichlorobenzene+ 1,2,3-trichlorobenzene), Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, 2012. (14DCB, 1,4-dichlorobenzene; 124TCB, 1,2,4-trichlorobenzene; 123TCB, 1,2,3-trichlorobenzene.)

Sediment as a Source of Contamination

In addition to the possible presence of contaminants as DNAPL or in contact with DNAPL, a long-term, secondary contaminant source to groundwater in the wetland may be the wetland sediments themselves due to desorption. The relatively low solubility and high affinity of the chlorinated benzenes for the solid phase (table 1) indicate that sorption and desorption are dominant processes in the wetland sediment. Simple theoretical calculations were conducted to estimate the equilibrium desorption of contaminants into groundwater. These calculated groundwater concentrations were compared to measured groundwater concentrations from USGS PDB sampling sites in the wetland sediments. Theoretical or predicted concentrations (C_{pred}) in groundwater were calculated using the f_{oc} of the sediments (USGS determined), average organic carbon partitioning coefficient (K_{oc}, table 1), and sediment concentrations (C_{sed}) from the shallow sampling depth detailed in the previous Wetland Remedial Approach study (HydroGeoLogic, Inc., 2009) according to the following formula.

$$C_{pred} = \left(K_{oc} * f_{oc}\right) / C_{sed} \tag{14}$$

The predicted concentrations compare fairly well to measured concentrations in the wetland porewater, particularly for the higher chlorinated compounds (table 14). In the case of CB and 14DCB (both of which were spill compounds and also possible anaerobic degradation products of higher chlorinated benzenes) the predicted concentrations were greater than the actual measured concentrations by a factor of about 2. Reasonable agreement of predicted and actual measured concentrations may indicate a large amount of sorbed mass in the sediments (near capacity). Gomez-Hermosillo and others (2006) reported that at very high concentrations of DCBs and TCBs in wetland porewater when the sorption capacity of the sediment is reached, desorption is largely linear for the chlorinated benzenes. In cases where concentrations are not

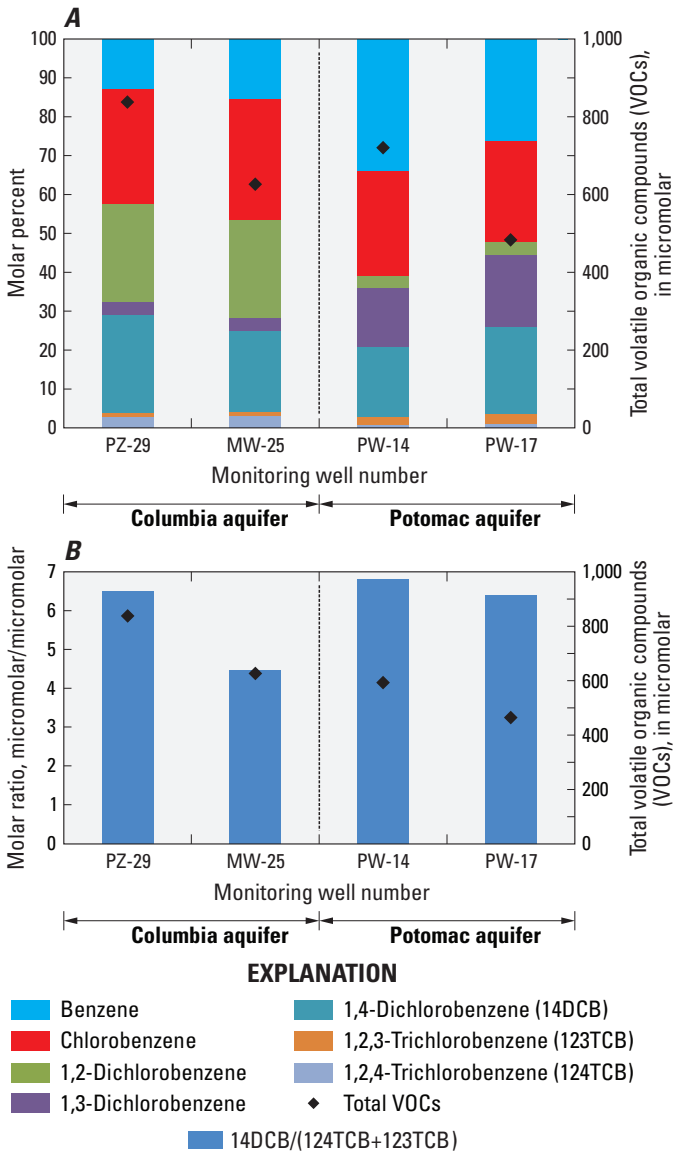


Figure 34. Comparison of *(A)* molar composition (in percent) and *(B)* molar ratios (micromolar/micromolar) in the Columbia and Potomac aquifers, using average concentrations from 2011–12, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

as significant, previous studies have reported between 30 and 62 percent of CB to be relatively resistant to desorption (Shin, 2000) and up to 95 percent of DCBs and TCBs present in a "slow desorption fraction" (ten Hulscher and others, 1997). This desorption resistance can result in the over-prediction of porewater concentrations using equilibrium partitioning. The relatively good agreement for high concentrations of chlorinated benzenes at SCD may indicate that equilibrium partitioning could be used to estimate sediment concentrations using measured groundwater concentrations, particularly in the western wetland in an effort to target additional sediment sample collection.

Natural and Enhanced Biodegradation of Chlorinated Benzenes and Benzene

An understanding of biodegradation processes of site contaminants is critical for evaluating the feasibility of monitored natural attenuation or engineered bioremediation as part of the site remedial action. Defining biodegradation processes at SCD is complicated by the fact that contaminants used, stored, and released at the site include metabolites of the anaerobic degradation pathways; thus, for example, the presence of CB does not necessarily indicate that reductive dechlorination has occurred (fig. 2). In addition, aerobic degradation pathways produce only the ubiquitous end products of CO_2, chloride, and water, or short-lived metabolites that could not be analyzed. Spatial and temporal variability in contaminant concentrations and the effect of possible abiotic processes, such as volatilization or evapotranspiration, also affect interpretation of field concentration data for biodegradation processes. To compensate for these complexities, a dual field and experimental approach was utilized and is discussed below, including evaluation of field geochemical data, field microcosms experiments under native (untreated) and stimulated conditions, and bench-scale experiments with bioreactors using site groundwater.

Evidence from Field Sampling Results

To evaluate biodegradation on the basis of field results, the molar VOC compositions of the water samples collected between 2009–12 were used in conjunction with knowledge of the redox conditions in the water, as indicated by the relative concentrations of the redox-sensitive constituents (figs. 16–19 and 26–27). The molar compositions, rather than the individual VOC concentrations, can indicate production or removal of compounds despite the complication of possible metabolites, such as DCBs and CB, also being source (parent) contaminants at this site. Comparison of the VOC molar compositions in the wetland groundwater to the upland and wetland sediment sources assists in determining the occurrence and extent of biodegradation. Molar compositions of water samples from wells screened in the Columbia aquifer in upland source areas did indicate a change before and after installation of the barrier wall in the northwest compared to the northeast areas; however, the greater variability in the VOC compositions and calculated molar ratios, R_s (reflective of the 1986 spill compounds), in the wetland groundwater indicates that processes such as reductive dechlorination may be occurring to a greater extent in the wetland sediments (fig. 33).

Compared to source VOC compositions, anaerobic degradation by reductive dechlorination would be expected to produce a higher molar percentage of the less chlorinated compounds, CB and benzene (fig. 2). Highly reducing conditions, such as methanogenesis compared to nitrate-reducing conditions, are most favorable for complete reductive

Table 14. Comparison of calculated and measured porewater volatile organic compound concentrations.

[foc, fraction organic carbon; Csed, concentration in sediment; Cgw pred, predicted concentration in groundwater; µg/kg, micrograms per kilogram; µg/L, micrograms per liter; B, benzene; CB, chlorobenzene; 12DCB, 1,2-dichlorobenzene; 13DCB, 1,3-dichlorobenzene; 14DCB, 1,4-dichlorobenzene; 123TCB, 1,2,3-trichlorobenzene; 124TCB, 1,2,4-trichlorobenzene; --, no data; <, less than]

Sediment identifier[1]	Location	foc	Csed (µg/kg) B	Cgw pred (µg/L) B	Cgw actual (µg/L) B	Csed (µg/kg) CB	Cgw pred (µg/L) CB	Cgw actual (µg/L) CB	Csed (µg/kg) 12DCB	Cgw pred (µg/L) 12DCB	Cgw actual (µg/L) 12DCB	Csed (µg/kg) 13DCB	Cgw pred (µg/L) 13DCB	Cgw actual (µg/L) 13DCB
EW-07A	In vicinity of DP12, site 128	0.071	0	0	1,382	230,000	18,646	9,509	630,000	7,145	7,007	240,000	2,203	2,922
EW-04A	South of Site 6	0.071	23	5	<5	15,000	1,216	1,203	11,000	125	45	2,200	20	75
EW-05A	In vicinity of site 158	0.071	0	0	5	5,100	413	1,227	2,700	31	6,999	1,400	13	198

Sediment identifier[1]	Location	foc	Csed (µg/kg) 14DCB	Cgw pred (µg/L) 14DCB	Cgw actual (µg/L) 14DCB	Csed (µg/kg) 123TCB	Cgw pred (µg/L) 123TCB	Cgw actual (µg/L) 123TCB	Csed (µg/kg) 124TCB	Cgw pred (µg/L) 124TCB	Cgw actual (µg/L) 124TCB
EW-07A	In vicinity of DP12, site 128	0.071	560,000	18,089	9,604	130,000	566	263	340,000	305	553
EW-04A	South of site 6	0.071	12,000	388	226	51	0	<5	73	0	<5
EW-05A	In vicinity of site 158	0.071	4,900	158	2,621	--	--	4	--	--	62

[1] Identification from HydroGeoLogic, Inc., 2009.

dechlorination. When the peeper profiles from July 2009 showed highly reducing methanogenic conditions in the wetland groundwater at northwest site 8 compared to weaker reducing conditions (no detected methane and factor of 10 lower ferrous iron concentration) at northeast site 6 (figs. 26a, 27a), the VOC compositions at northwest site 8 showed a correspondingly higher percentage of CB and benzene compared to the northeast site (figs. 18a, 19a). The molar percentages of greater than 90 percent for CB and benzene combined indicate that TCBs and DCBs were being almost completely reduced through reductive dechlorination in the northwest wetland groundwater at site 8 in July 2009. Similar differences in redox conditions and VOC compositions at other peeper sites in July 2009 (site 9 in the northwest and site 7 in the northeast) gave evidence of similar extensive reductive dechlorination in the northwest compared to the northeast wetland study areas (data on file, USGS MD-DE-DC WSC). Chloride concentrations, which increase with chlorine released during each reductive dechlorination reaction, can provide another indication of the occurrence of this degradation process. Although chloride was high throughout the peeper profile at site 8 in July 2009 (and at other northwest sites, probably from the HCl spill), a distinct increase in chloride was observed between depths of about 46 and 90 cm below land surface, corresponding to the depth over which the highest methane concentrations and lowest total CBs+benzene were observed (figs. 18a, 26a).

Peeper results in 2011 showed a change in reducing conditions and associated change in the extent of reductive dechlorination at the northwest sites compared to the northeast sites. With a change to more moderate reducing conditions at site 8 in 2011, less benzene and more DCBs made up the molar VOC composition than those observed at this northwest site in 2009, indicating that reductive dechlorination was less complete in 2011. Molar VOC compositions across the wetland area from the PDB samples collected in 2011 also indicated that reductive dechlorination was less extensive in the northwest area than than in the northeast area. Temporal monitoring showed a continuation of the redox and VOC molar compositions observed in 2011 through August 2012. Thus, the change to more moderate reducing conditions and less extensive reductive dechlorination that was observed in the December 2011 peeper at site 8 compared to July 2009 does not appear to be due to a short-term seasonal effect of lower temperatures on microbial activity. The opposite trend was observed in the peeper at site 6 in 2011 compared to 2009, with sulfide concentrations increasing and more extensive reductive dechlorination indicated by the higher percentage of CB and benzene in the upper approximately 60 cm of wetland sediment (figs. 18b, 26b). These peeper results were consistent with results for the northwest and northeast wetland areas collectively from the PDB sampling in October 2011. Overall, the significantly higher sulfide concentrations in the northeast area indicated more favorable reducing conditions for reductive dechlorination in the wetland groundwater in the northeast area than in the northwest area in October 2011, and CB was the predominant VOC in PDB samples from the northeast wetland area (median of 69 molar percent) compared to samples from the northwest wetland area (median of 35 molar percent).

Volatilization/evapotranspiration and aerobic biodegradation could also affect the molar VOC composition in the wetland groundwater but both of these processes would be expected to preferentially remove the lighter (less chlorinated) compounds (Field and Sierra-Alvarez, 2008). Thus, volatilization and aerobic biodegradation would result in a decrease in the molar percentages of benzene and the lower chlorinated compounds, such as CB, in contrast to the effect of anaerobic reductive dechlorination. Some of the PDB samples and near-surface peeper samples with very low total VOC concentrations and high percentages of TCBs and DCBs could be indicative of these processes, such as samples from the 2.0- and 7.5-cm depth in the December 2011 peeper at site 8 (fig. 18b).

There are several possible causes of the changes observed between 2009 and 2011, including natural temporal changes in groundwater-flow conditions and geochemistry in the wetland area or induced changes from the installation of the barrier wall, industrial pumping effects, or the inoperative tide control structure. Because longer term data are not available for the wetland area, it is not possible to fully evaluate the most likely cause. However, the decrease in chloride concentrations in the northwest wetland area (fig. 25) and results of the 2009 and 2010 *in situ* microcosms (see the following section) indicate that the change occurred before October 2010, which is before the problem with the tide control structure began (August 2011). Industrial pumping for the DCRC was stopped from May 2010 to January 2011 and possibly affected groundwater-flow conditions and wetland geochemistry between the July 2009 and October 2010 sampling in the wetland, but monthly groundwater sampling after January 2011 when pumping resumed indicated little change in wetland geochemistry (figs. 18c, 25, 26c). If the decreased chloride concentrations in the northwest wetland area were caused by the barrier wall decreasing or eliminating the contribution from a source behind the wall, it is possible that other constituents associated with this source acted to generate more highly reducing conditions in the Columbia aquifer discharging to the northwest wetland area, and contributed to the onset of highly methanogenic conditions observed in the 2009 wetland groundwater. The addition of selected redox constituents and chloride to the current monitoring plan for the upland area near the wetland boundary, and the addition of piezometers within the wetland area to this monitoring network would assist in determining the effect of the barrier wall on the wetland geochemistry, contaminant sources, and biodegradation.

Except for limited near-surface decreases that could be due to volatilization or aerobic degradation, it is important to note that total VOC concentrations did not decrease substantially along upward groundwater-flow gradients in the peeper profiles, even when the molar compositions indicate substantial reductive dechlorination was occurring. This is probably due to the additional source of VOCs in the upper wetland

sediments, present as DNAPL or sorbed to the sediment, that was evident throughout much of the northwest wetland area and part of the northeast wetland area (fig. 30). The presence of this source and its continued dissolution/desorption is indicated by the increased concentrations between depths of approximately 15 to 40 cm below land surface in many of the peepers (fig. 17). At site 8 in July 2009 and site 6 in December 2011, reductive dechlorination apparently occurred at a sufficient rate to degrade contaminant input from this additional source, however, because the percentages of higher chlorinated compounds—DCBs and TCBs—did not increase along upward groundwater-flow gradients in the peeper profiles. In parts of the northeast wetland area where DNAPL presence was not evident (fig. 30) and concentrations of VOCs in PDBs were low or undetectable (fig. 16), natural attenuation may be occurring to completion within the shallow wetland groundwater. However, groundwater samples from deeper than about 50 cm in the wetland sediments or aquifer were not collected and would be needed to determine whether contamination is present at these sites. Achieving more complete dechlorination of the chlorinated benzenes and removal of benzene, either by slowing groundwater-flow rates or enhancing degradation rates, would be necessary for a bioremediation remedy where DNAPL presence is still evident.

In Situ Microcosms

In situ microcosms provided evidence under field conditions of the potential for biodegradation by the native microbial community in the wetland, with or without stimulation by addition of electron donors to support reductive dechlorination, and of the potential for biodegradation by a bioaugmented microbial consortium, WBC-2. Three microcosm treatment types were deployed at each site—a monitored natural attenuation treatment (referred to as the MNA treatment) that had no added amendments, a biostimulated treatment that was amended with lactate and chitin as donors for reductive dechlorination (lactate/chitin treatment), and a bioaugmented treatment amended with lactate/chitin and WBC-2 (WBC-2 treatment). The molar compositions of VOCs and redox conditions in the three standard (no ^{13}C label) treatments and the results of stable isotope probing for the ^{13}C-labeled treatments are discussed for *in situ* microcosms incubated during October–December 2009 and October-December 2010 (figs. 35–38; tables 15–16). Although *in situ* microcosms were deployed at sites 6 and 9 in October–December 2009, only site 6 results are presented here because VOC concentrations and compositions in the three standard treatments at site 9 gave inconclusive evidence of biodegradation and ^{13}C-labeled treatments were not performed at this site in 2009.

The MNA microcosm at site 6 in October–December 2009 had a relatively high percentage of combined TCBs and DCBs (greater than 60 percent), indicating a relatively low extent of naturally occurring reductive dechlorination of the VOCs (fig. 35). The aerobic or mildly reducing conditions in the MNA treatment, indicated by the high sulfate concentrations and low or undetectable concentrations of ammonium, ferrous iron, sulfide, and methane, were not conducive for reductive dechlorination of the chlorinated benzenes at site 6 in October–November 2009. The MNA microcosm results (screen depth of 26–50 cm below land surface) were consistent with the results from the peeper sampled at site 6 in July 2009 (figs. 19a, 27a). The high sulfide concentrations in the lactate/chitin treatment compared to the MNA treatment showed that sulfate-reducing conditions were stimulated by the added donor, although sulfate concentrations and the molar composition of the VOCs showed little change. Addition of WBC-2 and lactate/chitin, however, generated more highly reducing conditions than those observed in the MNA or lactate/chitin treatments, as shown by the complete removal of sulfate and increased sulfide production. A concomitant increase in the molar percentage of CB and benzene (collectively about 90 percent of the total VOCs) occurred in the WBC-2 treatment compared to the MNA or lactate/chitin treatments, indicating an increase in reductive dechlorination of the higher chlorinated benzenes and CB with bioaugmentation (fig. 35a). The decrease in total VOC concentrations indicates complete degradation of VOCs in the bioaugmented treatment compared to the MNA or lactate/chitin treatments (fig. 35a).

The standard (no ^{13}C label) *in situ* microcosms deployed in 2010 were variable for the four sites (fig. 36). Site 6 showed very little difference between the three treatments, unlike the 2009 *in situ* microcosm results. The MNA treatment at site 6, however, indicated that reductive dechlorination was naturally more extensive at this site in 2010 than in 2009, even though the aerobic to mildly reducing conditions observed in the MNA treatment in 2010 were similar to the conditions in the 2009 MNA treatment (table 15). The molar percentage of CB and benzene together was about 60 percent in the MNA treatment in 2010, compared to about 30 percent in 2009. Thus, the *in situ* microcosm results for VOCs at site 6 in 2010 are consistent with the VOC molar compositions observed in the peeper installed at this site in 2011, when more highly reducing conditions were observed in the peeper compared to 2009 (figs. 19b, c; 27b, c).

Of the four sites where microcosms were deployed in 2010, *in situ* microcosms at northwestern site 8 showed the greatest difference between the MNA and biostimulated treatments, where total VOC concentrations decreased by more than 50 percent and the percentage of CB and benzene approximately doubled in the lactate/chitin biostimulated treatment. These changes in VOC concentration and composition are consistent with stimulation of more extensive reductive dechlorination due to the stimulation of more highly reducing conditions, as evidenced by high methane concentration in the lactate/chitin treatment at DP-8 (table 15). The addition of WBC-2 at site 8 did not substantially stimulate reductive dechlorination compared to the lactate/chitin treatment, indicating that the native microbial population at this site contained dechlorinators. These experimental results are consistent with the fact that reductive dechlorination appeared

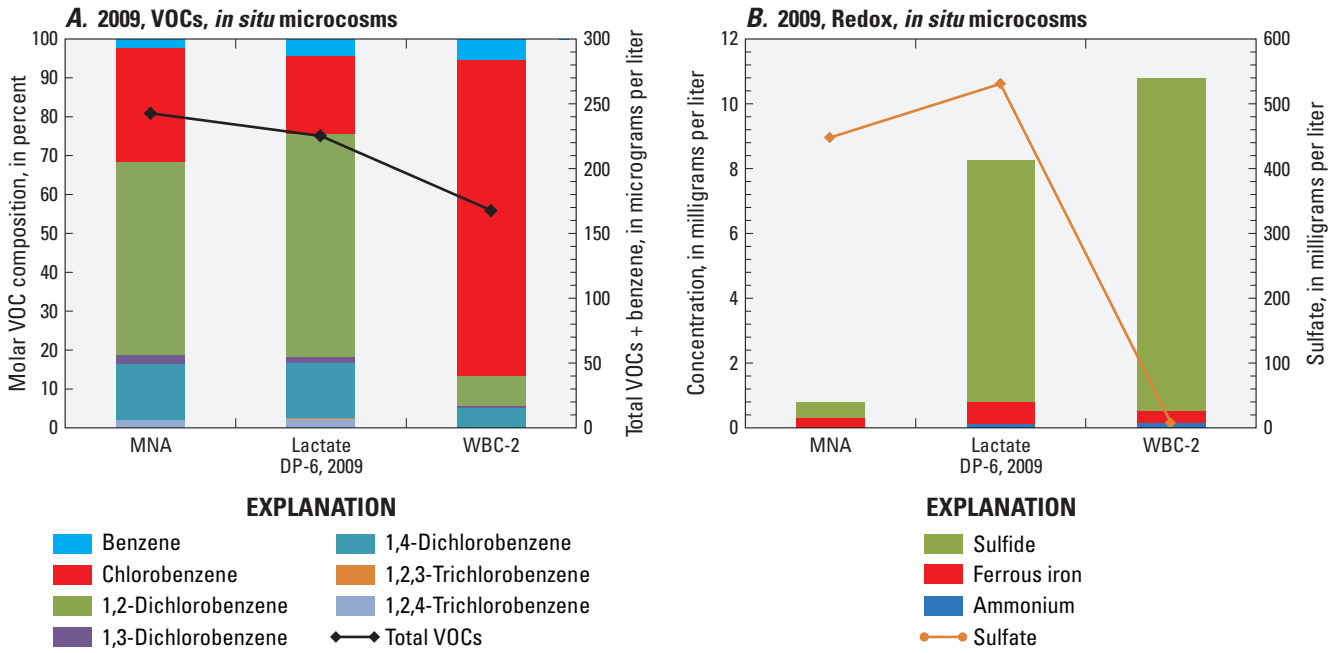


Figure 35. *(A)* Molar composition of volatile organic compounds (VOCs), and *(B)* concentrations of redox-sensitive constituents in standard *in situ* microcosms (MNA, monitored natural attenuation treatment; lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009. [Note that methane was not detected.]

to be naturally extensive at site 9 and nearby site 8 in 2009, when highly reducing methanogenic conditions were naturally present (figs. 18a, 26a). The *in situ* microcosm results for sites 6, 8, and 9 also indicate that the changes observed in the peepers between July 2009 and December 2011 may have occurred by October–November 2010.

Although the standard *in situ* microcosms indicated that reductive dechlorination was producing CB and benzene at some sites under natural or stimulated conditions, the ultimate fate of these intermediate compounds could not be determined from these tests and instead required the use of the ^{13}C-labeled treatments. *In situ* microcosms amended with ^{13}C-CB provided direct, quantitative evidence of CB removal in the MNA and WBC-2 bioaugmented treatments at site 6 in 2009 (fig. 37a). Compared to predeployment measurements of the amount of ^{13}C-CB placed on the Bio-Sep beads, CB decreased by 66–69 percent in the MNA and WBC-2 treatments over the 57-day incubation period in the wetland sediments, giving calculated first-order rate constants of 0.02 per day for both treatments. Although CB degradation rates were similar for the two treatments, the different redox conditions and distribution of ^{13}C in microbial biomass (PLFA) and DIC, which would primarily be CO_2, indicated that different degradation pathways occurred in the MNA and WBC-2 treatments (fig. 37). Not all redox-sensitive constituents were measured in the ^{13}C-CB treatments, but sulfate concentrations of 426 and 11 mg/L, respectively in the MNA and WBC-2 treatments with ^{13}C-CB at site 6 indicated similar redox conditions as those observed in the respective

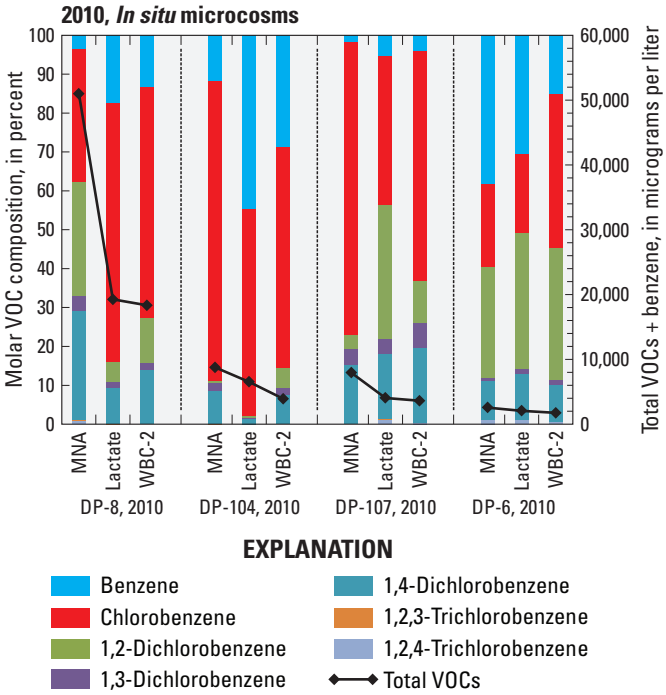


Figure 36. Molar composition of volatile organic compounds (VOCs) in standard *in situ* microcosms (MNA, monitored natural attenuation treatment; lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at four sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010.

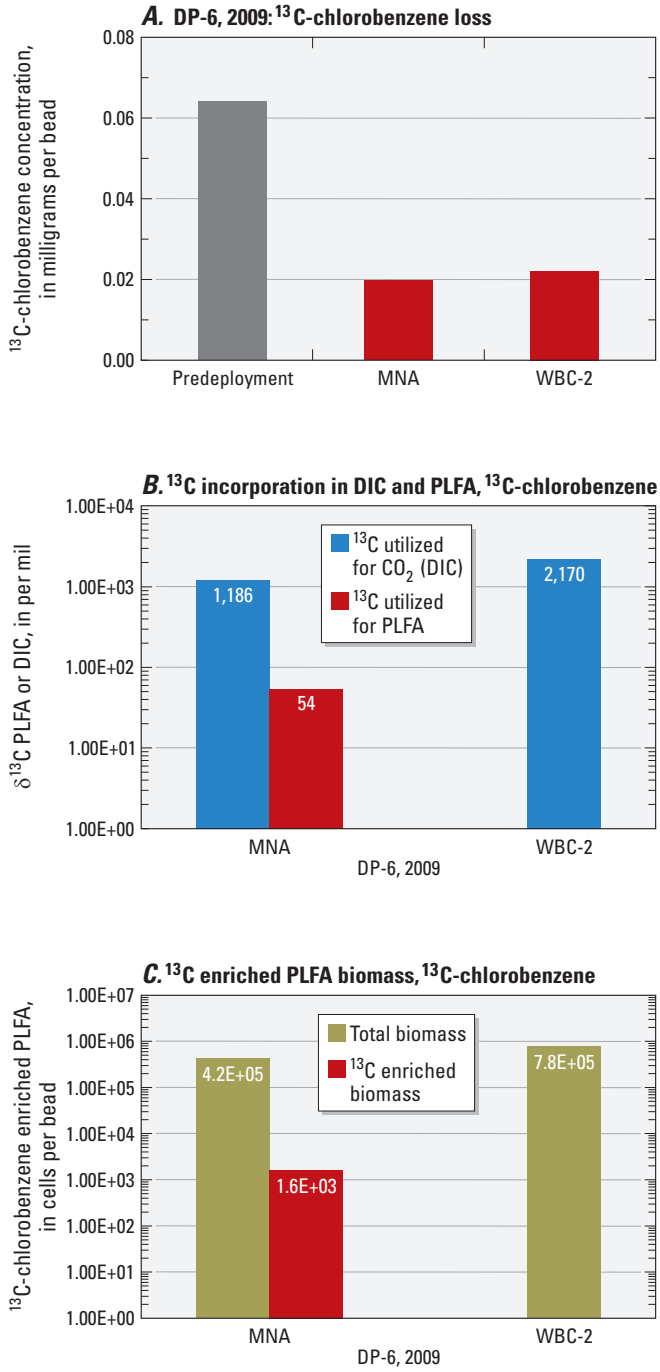


Figure 37. *(A)* Removal of ^{13}C-chlorobenzene, *(B)* incorporation of ^{13}C in dissolved inorganic carbon (DIC) and phospholipid fatty acid (PLFA) biomass, and *(C)* enrichment of ^{13}C in the PLFA biomass in the ^{13}C-chlorobenzene amended *in situ* microcosms (MNA, monitored natural attenuation; WBC-2, bioaugmented treatment) deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009.

standard microcosm treatments (fig. 35b). Both the MNA and WBC-2 treatments showed incorporation of ^{13}C into DIC (or CO_2), which can be produced as an end product through aerobic or anaerobic degradation pathways of the CB and indicates use of the contaminant for cellular energy. Only the MNA treatment with ^{13}C-CB showed incorporation of ^{13}C in the microbial biomass measured on the beads, indicating that some microorganisms were utilizing the carbon as a source for cellular material through oxidative degradation pathways (figs. 37b, c). In reductive dechlorination, the chlorinated contaminant is utilized as an energy source (electron acceptor) but not as a carbon source for cellular growth (Vogel and others, 1987). Previous studies have shown that CB is susceptible to aerobic degradation through oxidation, and the high sulfate concentrations and low or undetectable concentrations of the reduced species ammonium, ferrous iron, sulfide, and methane support the possibility of dissolved oxygen availability in the wetland sediment for aerobic oxidation to occur in the MNA treatment (fig. 35b). Anaerobic (rather than aerobic) oxidation of CB is not known to occur; although anaerobic oxidation has been reported previously for other chlorinated VOCs. Recent studies indicate that oxidation under apparent anaerobic conditions may actually occur by aerobic oxidation under microaerophilic conditions, and not by oxidation by anaerobic bacteria (Bradley and Chapelle, 2011).

The high percent removal of ^{13}C-CB and production of ^{13}C-DIC in the WBC-2 treatment at site 6 under sulfate-reducing conditions (figs. 35 and 37a, b) is significant because few field studies have reported evidence of anaerobic degradation of monochlorobenzene to either benzene or completely to CO_2 (Fung and others, 2009). In the MNA treatment, it also is possible that some of the CB was initially reduced to benzene and the benzene was oxidized to CO_2, although redox conditions were not conducive to reductive dechlorination in this treatment. All three of the ^{13}C-CB *in situ* microcosms deployed in 2010 also showed ^{13}C incorporation in DIC, indicating that the native microbial population in both the northwest and northeast wetland areas are capable of complete degradation of CB (fig. 38a). The average δ^{13}DIC for the the MNA treatments at the 2010 sites was 1,420 per mil, which was similar to the δ^{13}DIC of 1,190 per mil measured for the MNA treatment in 2009. Incorporation of ^{13}C in the PLFA of the biomass also was observed in the MNA treatments with ^{13}C-CB at all three sites in 2010, although the δ^{13}-PLFA values (8 to 176 per mil) were substantially lower than those observed for δ^{13}DIC. The amount of PLFA biomass enriched with ^{13}C was two orders of magnitude lower than the total biomass measured (fig. 38b). It is significant, however, that a low amount of oxidation of CB (or the anaerobic metabolite, benzene) and incorporation into the biomass was possible in the wetland area even where methane concentrations indicated highly reducing conditions, especially at site 104 (table 15). Macropores, especially along root channels, in the wetland sediment may allow low amounts of oxygen into the wetland sediment to support oxidation of the CB even where bulk water concentrations of redox-sensitive constituents indicate nominally reducing conditions.

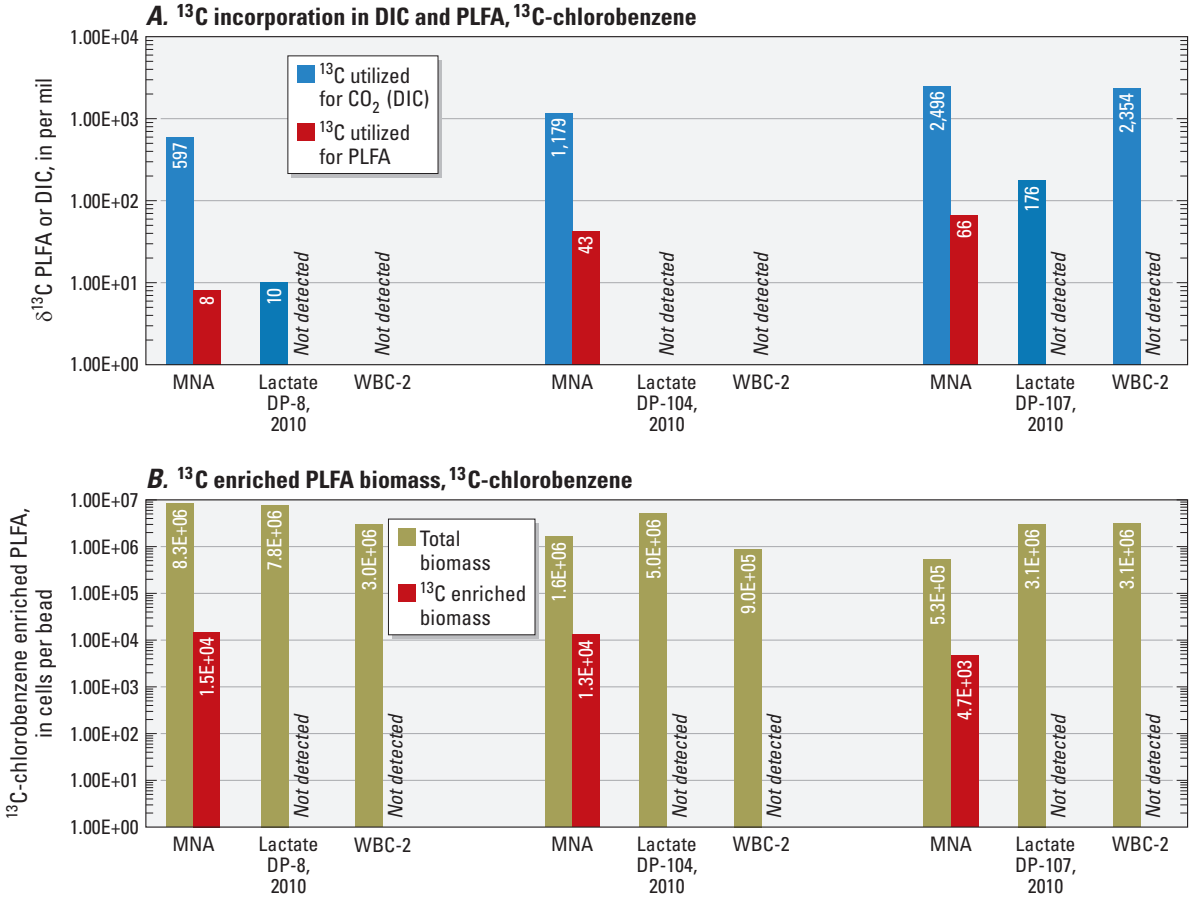


Figure 38. *(A)* Incorporation of ^{13}C in dissolved inorganic carbon (DIC) and phospholipid fatty acid (PLFA) biomass, and *(B)* enrichment of ^{13}C in the PLFA biomass in the ^{13}C-chlorobenzene amended *in situ* microcosms (MNA, monitored natural attenuation; lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at three sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010.

Oxygen transport to the wetland sediments would be expected to be greater during the growing season, when the wetland plants actively transport oxygen to their roots, compared to the December–October period of microcosm deployment. For the lactate/chitin and WBC-2 treatments amended with ^{13}C-CB in 2010, incorporation into ^{13}DIC was observed at some sites, but not into the biomass (fig. 38a).

Natural, complete breakdown of 14DCB to CO_2 was shown in the MNA treatments with ^{13}C-14DCB microcosms at two of the four sites tested in 2010, sites 107 and 104, which are in or near the northeast wetland area (table 16). Aerobic to mildly reducing conditions that were conducive for aerobic oxidation of the 14DCB were naturally present (MNA treatment) at site 6 during 2010, similar to the conditions observed in 2009. However, site 107 showed more highly reducing conditions than site 6 in 2010, with low sulfate concentrations and relatively high sulfide and methane (table 15). The $\delta^{13}DIC$ values in the ^{13}C-14DCB microcosms were an order of magnitude lower than those observed for the MNA treatments amended with ^{13}C-CB, which may indicate a slower complete degradation rate for 14DCB to DIC than observed for CB under these site conditions (table 16, fig. 38a). Oxidation rates of chlorinated VOCs generally decrease with an increasing number of chlorines (Field and Sierra-Alvarez, 2008). No ^{13}DIC was measured in the lactate/chitin or WBC-2 treatments amended with ^{13}C-14DCB, although this does not preclude the possibility that 14DCB was degraded to benzene through reductive dechlorination, because carbon isotope ratios of intermediate metabolites could not be analyzed.

In situ microcosms amended with ^{13}C-benzene were only deployed at site 6 in 2010, and these showed complete mineralization to ^{13}DIC in the MNA, lactate/chitin, and WBC-2 treatments (table 16). The $\delta^{13}DIC$ measured in the MNA treatment amended with ^{13}C-benzene was substantially greater than the $\delta^{13}DIC$ measured in the other ^{13}C-benzene treatments, or in the 14DCB or CB ^{13}C-labeled microcosms, indicating a relatively rapid complete breakdown of benzene under natural conditions at the site. Incorporation of ^{13}C into

Table 15. Concentrations of redox-sensitive constituents and volatile fatty acids measured in samples from *in situ* microcosms deployed from October 20–December 16, 2009 and from October 26–December 14, 2010 at selected wetland sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware.

[Units for redox-sensitive constituents are milligrams per liter, and units for volatile fatty acids are micrograms per liter. Ferrous iron, sulfide, and methane analyzed by U.S. Geological Survey (Baltimore, Md.), and all other constituents analyzed by Microbial Insights (Rockford, Tenn.). Treatments included monitored natural attenuation (MNA), (control); lactate/chitin, donor addition for biostimulation; and WBC-2, West Branch Consortium-2, for bioaugmentation; WBC-2 treatment also contained added lactate/chitin; <, less than, NS, not sampled (broken bottle)]

Wetland area	Site number	Sample date	Treatment	Redox-sensitive constituents					Volatile fatty acids			
				Nitrate, as Nitrogen	Sulfate, as SO_4	Ferrous Iron, as Fe	Sulfide, as S	Methane	Lactate	Acetate	Propionate	Pyruvate
Northwest	DP-8	12-14-10	MNA	<0.10	3.1	1.8	0.00	0.031	<0.39	40	7.8	5.1
	DP-8	12-14-10	Lactate/chitin	<0.10	<0.73	31	0.09	7.95	1.6	660	910	<0.69
	DP-8	12-14-10	WBC-2	NS	NS	NS	NS	1.11	NS	NS	NS	NS
Northwest	DP-104	12-14-10	MNA	<0.10	5.3	7.4	0.00	8.28	4.9	380	2.3	<0.69
	DP-104	12-14-10	Lactate/chitin	<0.10	4.5	2.4	0.00	6.85	4,800	360	26	<6.9
	DP-104	12-14-10	WBC-2	2.7	118	40	0.86	4.44	340	5,950	11,600	11
Northeast	DP-107	12-14-10	MNA	<0.10	8.6	0.87	0.4	0.82	2.7	130	0.8	<0.69
	DP-107	12-14-10	Lactate/chitin	<0.10	1.5	1.4	1.2	0.57	<0.78	850	1,360	1.1
	DP-107	12-14-10	WBC-2	<0.10	<0.73	0.58	0.65	0.45	<0.78	650	1,030	<0.14
Northeast	DP-6	12-14-10	MNA	<0.10	1,460	1.1	0.00	0.024	0.47	1.70	4.7	6.2
	DP-6	12-14-10	Lactate/chitin	<0.10	248	2.6	5.2	0.50	1,300	1,210	1,530	<0.14
	DP-6	12-14-10	WBC-2	<0.10	129	<0.50	6.6	0.97	1.2	250	280	<0.69
Northeast	DP-6	12-16-09	MNA	<0.10	448	0.28	0.49	<0.040	<0.39	<0.54	<0.31	5.0
	DP-6	12-16-09	Lactate/chitin	<0.10	531	0.69	7.5	<0.040	<0.39	27	21	6.0
	DP-6	12-16-09	WBC-2	<0.10	7.5	0.37	10	<0.040	<0.39	<0.54	<0.31	<0.69

biomass was not observed for the ^{13}C-benzene treatments at site 6 (table 16). This is surprising because benzene is known to be easily oxidized by many microorganisms under aerobic conditions, and the natural (MNA) conditions at this site in December 2010 indicated fairly oxidizing conditions (table 15). Anaerobic oxidation of benzene can occur under a wide range of anaerobic conditions but generally at a slower rate than aerobic oxidation.

Microbial Communities in the Wetland Sediment

Microbial communities in the wetland sediment were determined by direct analysis of sediment samples collected from sites 6 and 9 when the *in situ* microcosms were removed during December 2009 (figs. 39, 40). Cores were collected about 0.5 m laterally from the *in situ* microcosms and at two depths, one of which was near the top of the screened interval of the microcosms, to allow comparison to the microbial samples collected from the microcosms. Microbial communities were analyzed only in the *in situ* microcosm samples from site 6 at this time. Microorganisms that colonize Bio-Sep beads from groundwater flowing through the *in situ* microcosms over the incubation period are generally considered representative of the community in the surrounding sediment (Peacock and others, 2004; North and others, 2012). Because many microorganisms prefer to attach to surfaces, the microcosm samplers can detect microorganisms that may not be detected by sampling the groundwater and may provide more representative community analyses than those obtained by sampling the groundwater (Peacock and others, 2004; North and others, 2012). Microbial analyses performed in 2009 included qPCR determination of total eubacteria, which includes all bacteria except for methanogens and other archaebacteria, and of specific genera of bacteria that are known to have species capable

Table 16. Amount of ^{13}C incorporation into phospholipid fatty acid (PLFA) biomass and dissolved inorganic carbon (DIC) measured in *in situ* microcosms that were preloaded with ^{13}C-labeled 1,4-dichlorobenzene or benzene and deployed from October 26–December 14, 2010 at selected wetland sites.

[All constituents analyzed by Microbial Insights (Rockford, Tenn.). Treatments included monitored natural attenuation (MNA), (control); lactate/chitin, donor addition for biostimulation; and WBC-2, West Branch Consortium-2, for bioaugmentation; WBC-2 treatment also contained added lactate/chitin; ND, not detected; total biomass is given as a cell equivalent based on the total amount of phospholipid fatty acids (PLFAs) extracted from a sample and includes bacterial and eukaryotic biomass]

Wetland area	Site number	Sample date	Treatment	Total biomass (cells per bead)	^{13}C enriched biomass PLFA (cells per bead)	^{13}C in biomass, as average δ ^{13}C-PLFA (per mil)	^{13}C in DIC, δ ^{13}C-DIC (per mil)
^{13}C-Dichlorobenzene							
Northwest	DP-8	12-14-10	MNA	4.54E+6	ND	ND	-11
	DP-8	12-14-10	Lactate/chitin	5.58E+6	ND	ND	-11
	DP-8	12-14-10	WBC-2	5.43E+6	ND	ND	-10
Northwest	DP-104	12-14-10	MNA	2.00E+6	ND	ND	-17
	DP-104	12-14-10	Lactate/chitin	1.56E+6	ND	ND	-11
	DP-104	12-14-10	WBC-2	1.84E+6	ND	ND	-14
Northeast	DP-107	12-14-10	MNA	3.75E+6	ND	ND	129
	DP-107	12-14-10	Lactate/chitin	3.73E+6	ND	ND	-11
	DP-107	12-14-10	WBC-2	4.58E+6	ND	ND	-15
Northeast	DP-6	12-14-10	MNA	7.21E+6	ND	ND	286
	DP-6	12-14-10	Lactate/chitin	7.59E+6	ND	ND	-12
	DP-6	12-14-10	WBC-2	5.30E+6	ND	ND	-18
^{13}C-Benzene							
Northeast	DP-6	12-14-10	MNA	4.10E+6	ND	ND	10,110
	DP-6	12-14-10	Lactate/chitin	6.01E+6	ND	ND	61
	DP-6	12-14-10	WBC-2	4.53E+6	ND	ND	244

of reductive dechlorination of chlorinated VOCs, including *Dehalococcoides*, *Dehalobacter*, and *Desulfitobacterium* species. Only total eubacteria and *Dehalococcoides* species were determined by qPCR for the *in situ* microcosm samples collected in 2010 (fig. 41), but other microbial species, including *Geobacter*, that also are capable of reductive dechlorination of chlorinated VOCs were identified using DGGE analysis (table 17). In addition, the general microbial community composition was evaluated from PLFA structural groups during 2009 and 2010 (table 5; fig. 40).

The population density of total eubacteria in the *in situ* microcosm MNA treatment at site 6 in 2009 was about 10 times lower than the population densities measured at two depths in the wetland sediment at the same site (fig. 39). Populations of *Dehalococcoides* and *Desulfitobacterium* species also were lower in the *in situ* microcosm MNA treatment than in the wetland sediment at 6, although *Dehalobacter* populations were similar (fig. 39). At both sites, the populations of total eubacteria and dechlorinating species were very similar in sediment samples from the two different depths, indicating uniformity with depth. Vertical variability cannot be discounted as a factor in the lower populations observed in the *in situ* microcosm sample, however, because the screened interval of the *in situ* microcosm extends about 20 cm below the deepest sediment sample collected. With the greater number of MNA *in situ* microcosms deployed in 2010 (including standard and ^{13}C-labeled treatments), spatial variability in the native microbial populations was apparent at each site (fig. 41). Total eubacteria population levels commonly differed by a factor of 10 among the three MNA treatments deployed at each of the sites in 2010, and total *Dehalococcoides* populations varied from less than 1,000 cells per bead to to slightly more than 10,000 cells per bead at two of the sites. The PLFA structural analysis of the sediment and MNA microcosm sample in 2009 indicated similar microbial community compositions, with Firmicutes (fermenting bacteria) and Proteobacteria (gram negative bacteria) the most dominant groups. Overall, comparison of the sediment and *in situ* microcosm samples indicates that the microcosms provided microbial samples

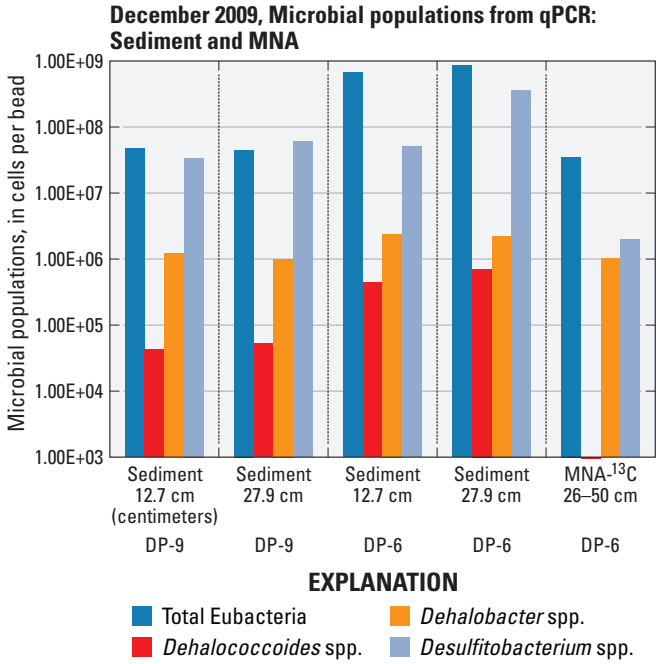


Figure 39. Microbial populations determined by quantitative polymerase chain reaction (qPCR) analysis of wetland sediment collected at sites DP-9 and DP-6 and in the control (MNA, monitored natural attenuation) *in situ* microcosm deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009.

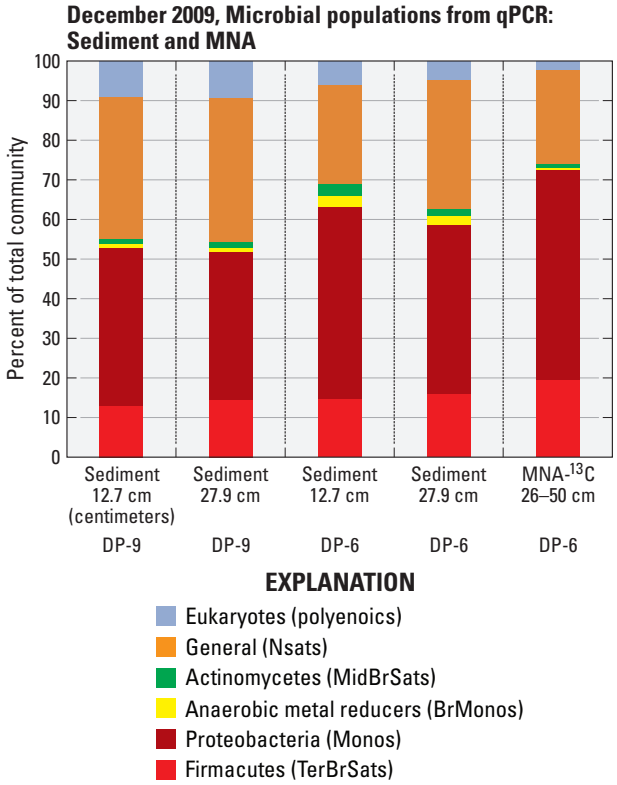


Figure 40. Microbial community composition determined from analysis of the chemical structures of phospholipid fatty acid (PLFA) in wetland sediment collected at sites DP-9 and DP-6 and in the control (MNA, monitored natural attenuation) *in situ* microcosm deployed in the wetland sediment at site DP-6, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 20–December 16, 2009. (See table 5 for descriptions of PLFA structural groups.)

that are representative of the native populations in the wetland sediment.

The relatively high cell numbers and diversity of populations (*Dehalococcoides*, *Dehalobacter*, *Desulfitobacterium*, and *Geobacter*) known to contain species capable of reductive dechlorination of VOCs indicates a high natural dechlorination potential in the wetland sediment at the SCD, confirming the geochemical evidence from peeper and other groundwater samplers and from the *in situ* microcosms. Relatively high total eubacteria population densities were found even at sites where high VOC concentrations were indicative of DNAPL presence (sites 8, 104, 107 in fig. 30). VOC concentrations at site 8 were substantially higher than those at the other sites but showed similar eubacteria population levels (figs. 36, 41a). *Dehalococcoides* population levels were lower in the MNA microcosms from two of the sites, 8 and 104, that had VOC concentrations indicative of DNAPL presence, although stimulation with lactate/chitin resulted in measurable increases in *Dehalococcoides* levels (fig. 41b). Both sites 8 and 104 are located in the northwest wetland area where the low pH may have inhibited bacterial growth and dechlorination activity (Zhuang and Pavlostathis, 1995; Schaefer and others, 2010). Besides providing donor for reductive dechlorination, the added lactate/chitin in the biostimulated microcosms provided pH buffering that could have stimulated growth of the dechlorinating species. The biostimulated treatments also had higher *Dehalococcoides* population levels than the MNA treatments in several of the *in situ* microcosms placed at the northeast sites 107 and 6 . Although the pH in the northeast wetland area was higher than the pH in the northwest wetland area, pH levels across the wetland were lower than the near neutral (7.0) optimum pH range for growth of several known dechlorinating *Dehalococcoides* and *Desulfitobacterium* species (Suyama and others, 2001; Tas and others, 2010). All *in situ* microcosms bioaugmented with WBC-2 showed similar *Dehalococcoides* population levels, indicating similar survival in the wetland porewater with varying VOC contaminant concentrations, including the areas where DNAPL presence was indicated (figs. 30, 41b).

Laboratory Bioreactor Experiments

Testing conducted with three flow-through bioreactors from March–October 2012 provided further evidence that both the natural wetland microbial community and the WBC-2 culture are capable of biodegrading the chlorinated benzenes and benzene at the SCD. A substantial decrease in concentrations between the inflow ("tank" sample) and the outflow ("waste" sample) throughout the tests was observed in the three bioreactors (fig. 42). Near-neutral pH and anaerobic conditions, characterized by negative ORPs, were initially established in all three bioreactors (figs. 43 and 44). The "C," or control bioreactor, which was seeded only with bacteria that colonized the bioreactor matrix from the inflow water from well DP-15B, can be compared to bioreactor "D," which received the same groundwater from well DP-15B but contained a well-established biofilm of WBC-2 on the matrix. The "E" bioreactor also was pre-established with WBC-2 but received groundwater from well DP-10B, which had higher total concentrations of CBs+benzene and lower concentrations of sulfate than the input water from well DP-15B (figs. 42 and 45). Amendments to bioreactor C, including the amounts of bicarbonate as a buffer, nutrients, and carbon donor, were altered during the testing period to evaluate the factors controlling biodegradation, whereas these amendments were kept about the same until near the end of testing in the D bioreactor and throughout the entire testing in the E bioreactor (fig. 42). TeCA, the primary VOC that WBC-2 was developed to degrade, was added as a co-contaminant to all bioreactors beginning in August 2012 to assist in evaluating the activity of WBC-2 and its importance relative to the native microbial communities in degrading the chlorinated benzenes in the D and E bioreactors (fig. 42). The geochemical changes resulting from these amendments and their effects on biodegradation are discussed below.

Microbial species that are capable of reductive dechlorination of chorinated VOCs generally are strict anaerobes, and WBC-2 performs most efficiently under anaerobic conditions, although it tolerates some oxygen exposure. The chlorinated benzenes and benzene in the study area also are highly susceptible to oxidative degradation pathways by aerobic bacteria. Sequential anaerobic and aerobic conditions were tested in the C bioreactor because results of the *in situ* microcosms indicated that degradation of the chlorinated benzenes, especially CB, could be occurring by both anaerobic and aerobic bacteria in the wetland sediment. Amendment with excess amounts of soluble organic donors (corn syrup and lactate) was used to generate and maintain anaerobic conditions in the bioreactors, and the donor amendments were stopped to try to generate aerobic conditions. From April to mid-June 2012 when the three bioreactors received the same donor amendments, ORPs were around -300 mV in all bioreactor cells and outflows, indicating that similar reducing conditions that are favorable for reductive dechlorination of the chlorinated benzenes had been established. Concentrations of sulfate, sulfide, and methane, however, indicated that conditions were less reducing in the C bioreactor than in the D and E bioreactors during this period (figs. 45 and 46). Sulfate concentrations only decreased about 10 to 15 percent in the outflow (waste) from the C bioreactor compared to the input concentrations in the tank. Sulfide

Table 17. Summary of microbial species identified using denaturing gradient gel electrophoresis (DGGE) analysis of samplers from the monitored natural attenuation (MNA) and lactate/chitin biostimulated treatments of *in situ* microcosms deployed from October–December 2010.

Site	Treatment	***Clostridium* species** (Obligately anaerobic fermentors; some species reduce metals)	***Caldiscericum* species** (Obligately anaerobic, chemoheterotrophic thermophiles that can reduce sulfur compounds)	***Geobacter* species** (Anaerobic iron-reducing bacteria; some capable of reductive dechlorination of chlorinated volatile organic compounds)	***Pelobacter* species** (Strict anaerobes that can oxidize organic substrates with ferric ion and sulfur as electron acceptors)	***Desulfitobacterium* species** (Anaerobic sulfate-reducing bacteria; may reduce heavy metals)
DP-8	MNA	X	X	X		
	Lactate			X	X	
DP-104	MNA	X		X		
	Lactate					
DP-107	MNA		X			X
	Lactate		X			
DP-6	MNA		X			
	Lactate		X			

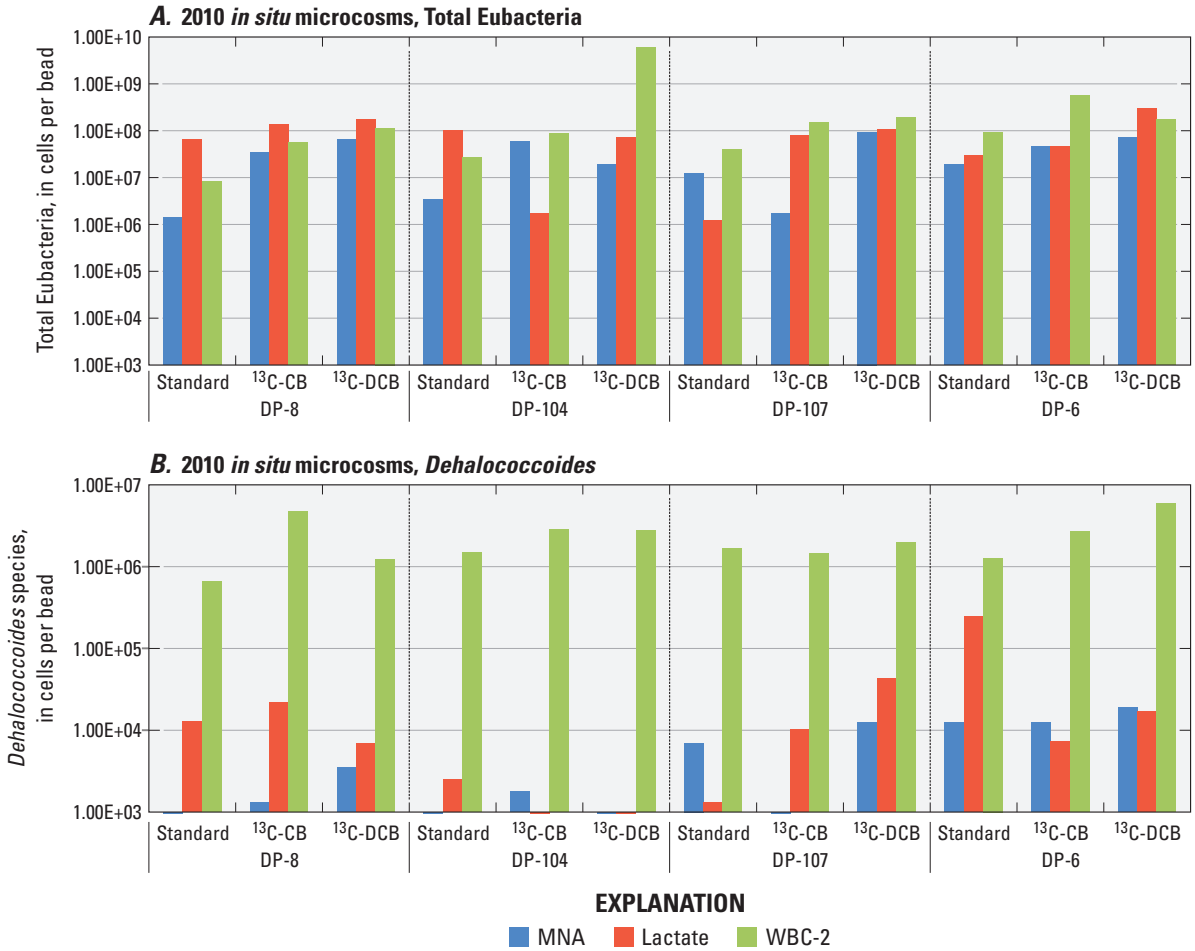


Figure 41. Amount of *(A)* total Eubacteria, and *(B) Dehalococcoides* species determined by quantitative polymerase chain reaction (qPCR) analysis of samples from standard and monochlorobenzene (^{13}C-CB) or 1,4-dichlorobenzene (^{13}C-DCB) *in situ* microcosms (MNA, monitored natural attenuation treatment; lactate, lactate/chitin biostimulated treatment; WBC-2, bioaugmented treatment) deployed in the wetland sediment at four sites, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, October 26–December 14, 2010.

concentrations increased to 25–35 mg/L in the C bioreactor during this initial anaerobic period but increased to more than 80 mg/L in the D bioreactor over the same period (figs. 46a, b). Methane concentrations were below detection levels in the C bioreactor in the few samples that were analyzed before donor amendments were stopped on June 14, 2012; however, concentrations were about 9 mg/L in the D bioreactor. Thus, the well-established WBC-2 biofilm in the D bioreactor apparently had a greater population density of sulfate-reducing and methanogenic bacteria than in the C bioreactor and rapidly generated highly reducing conditions, despite the high inflow sulfate concentrations. The similarly high sulfide and methane production in the E and D bioreactors is indicative of the similar WBC-2 community in each (figs. 46b, c).

When the organic donor and other amendments to the C reactor were stopped between June 14 and August 24, 2012, ORP increased to +200 mV in the C bioreactor cells by June 20, 2012, and then remained between + 100 and -100 mV through August 25, 2012, indicating aerobic to mildly reducing conditions (fig. 44a). Sulfide and methane were not detectable during this period in the C bioreactor (fig. 46a). The D and E bioreactors maintained anaerobic conditions with the same organic donor amendments during the June 20–August 24 period, but donor amendments were stopped in the D bioreactor, as well as in the C bioreactor again, for a 2-week period in October 2012. When donor amendments were stopped in October 2012, ORPs quickly increased to about +100 to +200 mV in the C bioreactor and to about -100 to +50 mV in the D bioreactor. Sulfate concentrations did not decrease and sulfide was not produced during groundwater flow through either the C or D bioreactors during this 2-week aerobic period in October 2012.

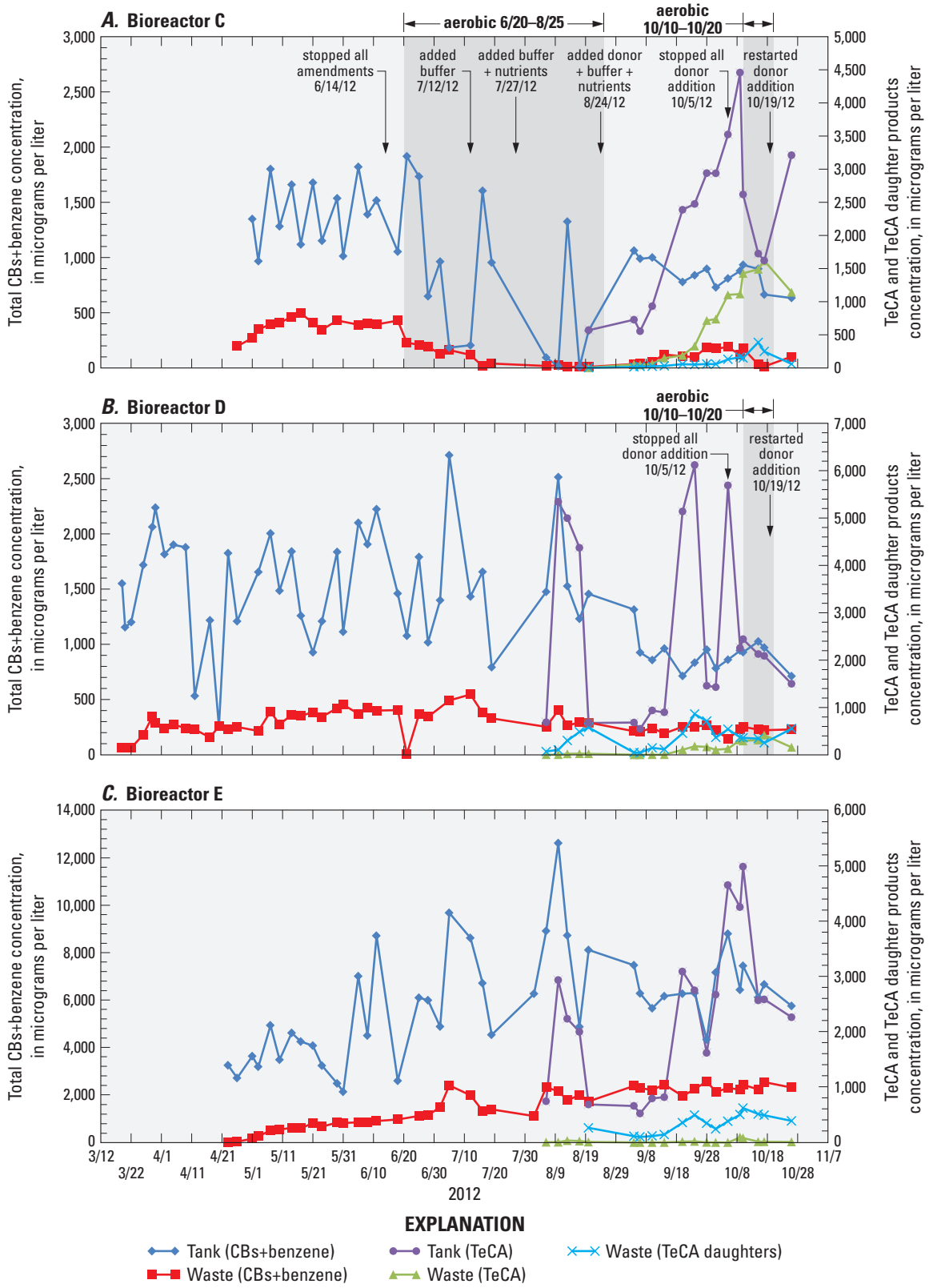


Figure 42. Concentrations of total chlorobenzene compounds and benzene (total CBs+benzene), naturally input from the wetland groundwater, and amended 1,1,2,2-tetrachloroethane (TeCA) and its anaerobic daughter products in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture.

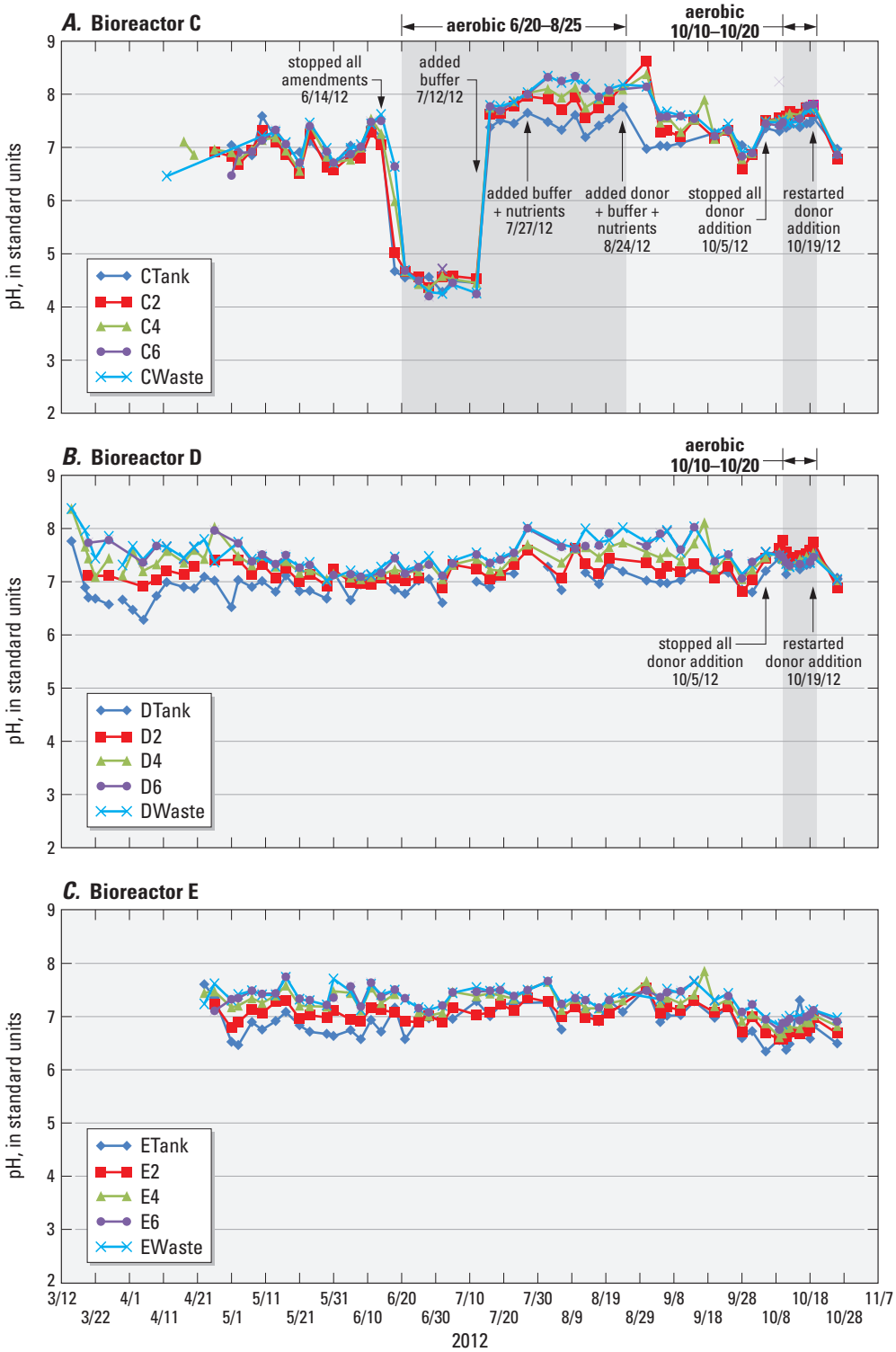


Figure 43. pH measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture.

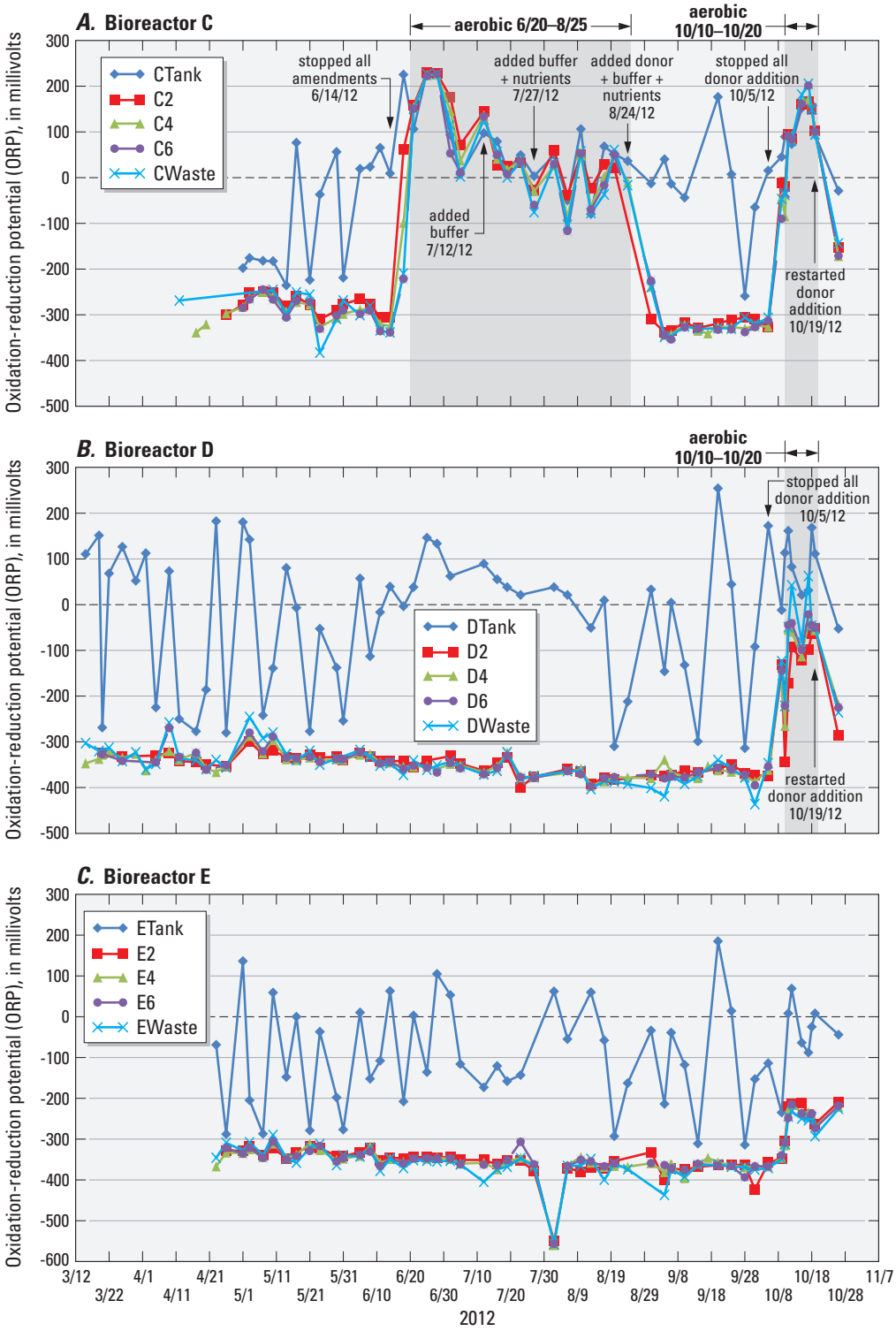


Figure 44. Oxidation-reduction potentials (ORPs) in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture.

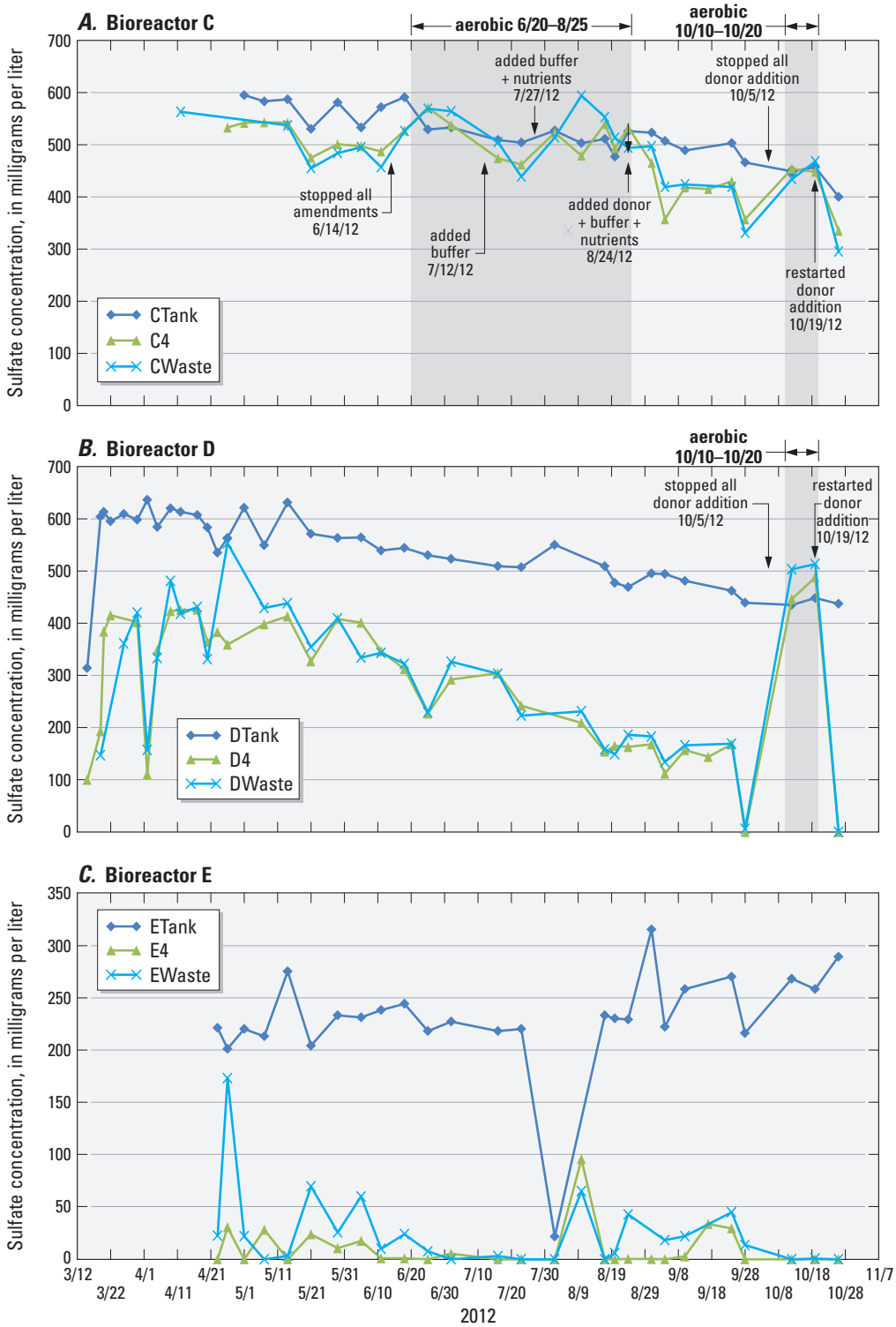


Figure 45. Sulfate concentrations measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture.

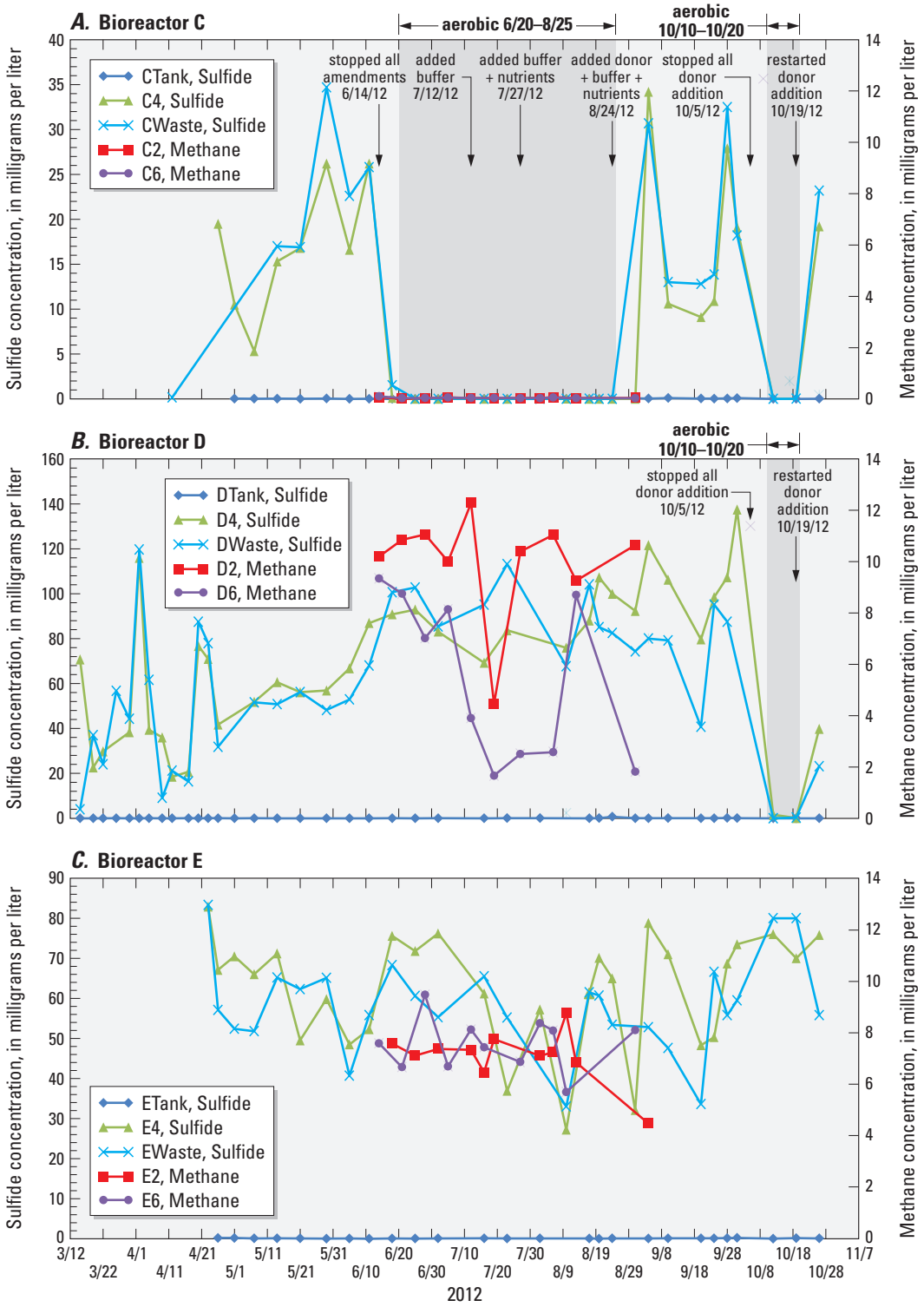


Figure 46. Sulfate and methane concentrations measured in *(A)* bioreactor C, which was seeded only with native microorganisms from the site groundwater, Standard Chlorine of Delaware, Inc. Superfund Site, Delaware, and in bioreactors *(B)* D, and *(C)* E, which were pre-established with the WBC-2 anaerobic culture.

The percent removals of each chlorinated benzene compound and benzene during transport through the bioreactors were calculated using the difference in concentrations measured in the tank and waste on each sampling date (fig. 42) and compared for the three bioreactors, separating the anaerobic (donor amended) and aerobic (donor unamended) periods for the C and D bioreactors (fig. 47). The calculated percent removals from the inflow and outflow concentrations indicated the amount of each contaminant degraded during the time of transport (residence time) through each bioreactor. Residence times were maintained within a relatively narrow range during the March–October 2012 period of operation, with median residence times between 37 and 41 hours in the bioreactors (fig. 48). The percent removals under anaerobic conditions for the three bioreactors showed a general pattern of decreasing removal rates with a decreasing number of chlorine atoms in the compounds, which is consistent with the relative reductive dechlorination rates reported for chlorinated benzenes (Field and Sierra-Alvarez, 2008). During the anaerobic periods, median percent removals of 123TCB, 124TCB, 14DCB, and 13DCB were equally high for the native (C) bioreactor and WBC-2 bioaugmented (D and E) bioreactors, with median percent removals ranging from 86 to 94 percent (figs. 47a, b, c, d). The percent removal for the dichlorobenzene isomer 12DCB, however, was substantially lower in the bioaugmented bioreactors (medians of 76 percent in bioreactors D and E) than in the native C bioreactor (median of 88 percent) (fig. 47e). This differs from previous studies of chlorinated benzenes that have shown 13DCB anaerobic degradation rates to be the slowest of the DCB isomers (Field and Sierra-Alvarez, 2008; Nelson and others, 2011). CB removal in the C and D bioreactors was similar (medians of 79 and 80 percent, respectively) and higher than observed in the E bioaugmented bioreactor (median of 73 percent) (fig. 47f). Of all the site contaminants in the groundwater input to the bioreactors, only benzene removal was substantially higher in the bioaugmented bioreactors (medians of 79 and 72 percent in D and E, respectively) than in the native C bioreactor (median 65 percent) under anaerobic conditions (fig. 47g).

Under the aerobic/mildly reducing conditions in the C and D bioreactors when the organic donor amendments were stopped, the most substantial differences compared to strongly anaerobic conditions in the respective bioreactors were the higher percent removals in the native C bioreactor for CB (median 96 percent) and benzene (median 99 percent) (fig. 47). Slightly lower percent removals in the bioaugmented D bioreactor for 123TCB (median 82 percent), 124TCB (median 82 percent), 14DCB (median 75 percent), and 13DCB (median 74 percent) also were measured during this aerobic/mildly reducing period rather than during strongly anaerobic conditions (fig. 47). The increased removal of CB and benzene from the C bioreactor under aerobic conditions actually began in the tank inflow concentrations, which commonly were nearly the same as the outflow concentrations from the bioreactor during the longer aerobic period from June 20–August 25, 2012 (fig. 44a). The rapid removal of chlorinated benzenes and benzene from the tank occurred under the natural acidic conditions of the wetland groundwater, which was observed early during this period because pH buffer amendment also was stopped, and was also observed under the near neutral pH conditions that resulted when pH buffer amendment resumed (figs. 42, 43). These results have important implications for both natural attenuation in the wetland and the potential application of bioremediation—the native aerobic microorganisms that can degrade the chlorinated benzenes could be active in the wetland under the range of pH conditions observed in the groundwater (fig. 20), and stimulation of aerobic degradation, either using an *in situ* or *ex situ* engineered bioremediation method, would not require the addition of pH buffer. The percent removal calculations for the aerobic period were conservative because only sampling dates when detectable concentrations of VOCs remained in the tank could be used. These results support the evidence from the *in situ* microcosms and incorporation of ^{13}C-CB in microbial biomass that bacteria capable of oxidation of CB are present in the wetland groundwater (figs. 37, 38). Biodegradation of benzene and and DCBs under aerobic or mildly reducing conditions also is supported by the bioreactor and *in situ* microcosm results.

Resumption of organic donor addition to the C bioreactor on August 24, 2012 resulted in a rapid (within a week) return to -300 mV ORP and production of sulfide (figs. 44a, 46a). The prolonged aerobic period did not negatively impact the resumption of anaerobic degradation of the chlorinated benzenes and benzene by the native bacteria in the C bioreactor, indicating that an active, anaerobic degrading microbial community had become established in the bioreactor cells and was able to become active again with the addition of organic donor (fig. 42a).

Degradation of the chlorinated benzenes and benzene in the C, D, and E bioreactors commenced without any lag and then improved over time under anaerobic conditions in the D bioreactor (figs. 42 and 49). Concentrations measured at different sampling ports in the bioreactors for selected sampling dates are shown in figure 49. The concentration profiles show that degradation shifted over time in the D bioreactor to principally occur in the first bioreactor cell (before sampling port D2 in figs. 49e-h); about 50 percent or more of each compound was left by port D2 on May 14, 2012, whereas only about 2 to 30 percent of each compound was left by port D2 on June 5, 2012 and later sampling dates. This improvement in biodegradation indicates that a substantial population of microorganisms capable of degradation of the chlorinated benzenes and benzene was present in the WBC-2 biofilm and grew over time. Similarly, degradation of chlorinated benzenes and benzene in the E bioreactor commenced without a lag and improved over time under anaerobic conditions until nearly the end of its operation (figs. 49i-l); the decline in removal near the end may have been caused by toxicity effects from the higher VOC concentrations in this bioreactor. Although the long period of aerobic conditions in the C bioreactor between July–August 2012 most likely slowed the development of an anaerobic degrading community, concentration profiles in the

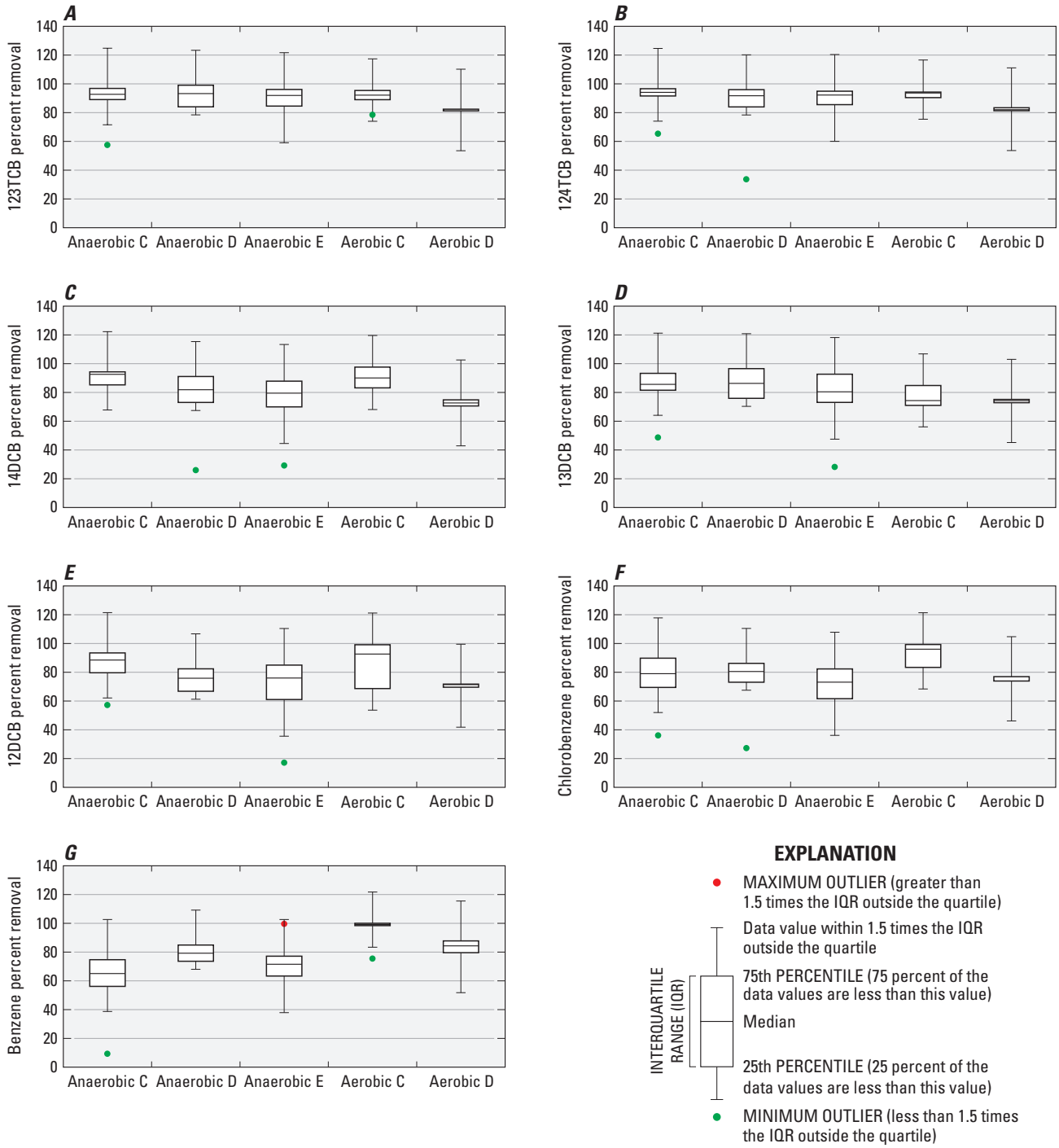


Figure 47. Boxplots showing percent removals of *(A)* 1,2,3-trichlorobenzene (123TCB), *(B)* 1,2,4-trichlorobenzene (124TCB), *(C)* 1,4-dichlorobenzene (14DCB), *(D)* 1,3-dichlorobenzene (13DCB), *(E)* 1,2-dichlorobenzene (12DCB), *(F)* chlorobenzene, and *(G)* benzene that were calculated from inflow and outflow concentrations under anaerobic and aerobic conditions in bioreactors C, D, and E.

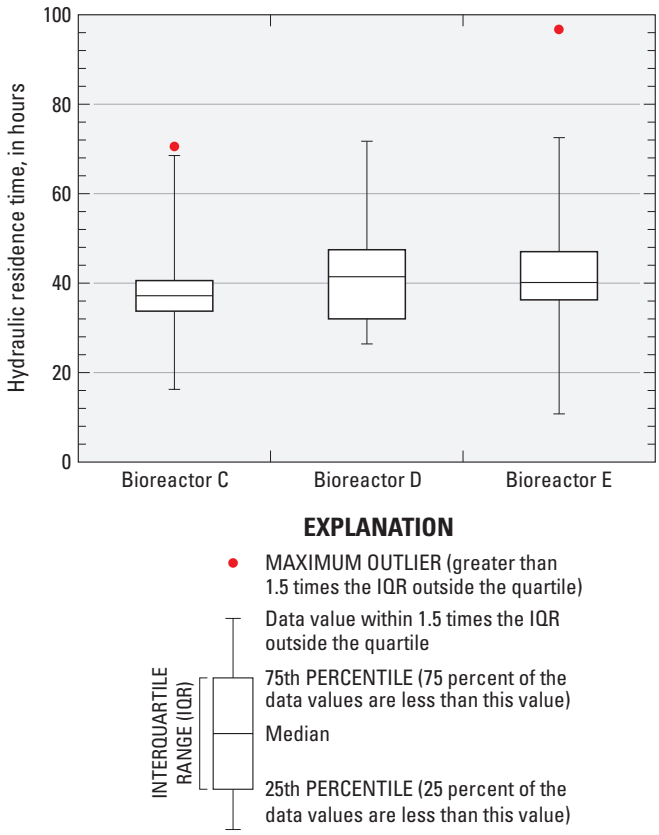


Figure 48. Boxplots showing hydraulic residence time in bioreactors C, D, and E.

C bioreactor under the initial anaerobic conditions from May–June 2012 indicate a slower development of the anaerobic degrading community than that observed in the D bioreactor (figs. 49a, b, e, f). About 40 to 60 percent of the chlorinated benzenes and benzene remained at port C2 on the June 5, 2012 sampling date compared to the 2 to 30 percent observed in the D bioreactor. Thus, although native bacteria, introduced with the site groundwater, may have grown over time in the WBC-2 bioaugmented bioreactors, it does not appear that they were primarily responsible for the observed degradation of chlorinated benzenes and benzene in the D and E bioreactors.

The different responses of the C bioreactor to aerobic conditions and to the addition of TeCA compared to the responses of the D and E bioreactors also indicate that the native C bioreactor and the WBC-2 bioaugmented bioreactors continued to have distinct microbial populations throughout their operation (fig. 42). Because the well-established WBC-2 populations in the D and E bioreactors would not be expected to contain microorganisms capable of degradation of chlorinated benzenes and benzene under aerobic conditions, a decline in the degradation of these compounds would be expected, and was observed. The negative impact on percent removals of chlorinated benzenes in the D bioreactor under aerobic conditions was minimal, however, probably because reducing conditions could be maintained in deeper layers of the WBC-2 biofilm during the relatively short (2-week) period that donor addition was stopped and ORPs increased. During this 2-week aerobic/mildly reducing period in October, TeCA removal did not change significantly in the WBC-2 bioaugmented D reactor, but it did stop rapidly in the native C bioreactor, as shown by the nearly equal concentrations of TeCA in the bioreactor inflow and outflow (fig. 42a). Thus, although degradation of the chlorinated benzenes and benzene occurred under both anaerobic and aerobic conditions by the native site bacteria in the C bioreactor, TeCA degradation required anaerobic conditions. The bioreactor results are consistent with the microbial community analyses that showed the presence of the same dechlorinating populations in the wetland sediment and groundwater from the site as those in WBC-2, but with lower population densities.

The generally greater than 70 percent removal of all chlorinated benzenes and benzene in the WBC-2 bioreactors was similar to the percent removals achieved for TeCA and its anaerobic degradation products, which included both chlorinated ethanes and chlorinated ethenes (Lorah and Olsen 1999a; Lorah and others, 2008). The relatively high percent removals without the need for an acclimation period for chlorinated aromatic compounds that WBC-2 had not previously been exposed to during culturing or fed during maintenance indicates that the same dechlorinators are involved as those that are involved in the degradation of the chlorinated ethanes and ethenes. The complete anaerobic degradation of tri-, di-, and monochlorobenzene to benzene and further degradation of the benzene demonstrated in the WBC-2 bioreactors has been reported for only one other bioaugmentation laboratory test, in which a previously enriched methanogenic, benzene-degrading culture was combined with an anaerobic CB-degrading culture (Liang and others, 2013). The ability of the WBC-2 culture to reduce the chlorinated VOCs in the presence of high sulfate concentrations (figs. 45b, c), which typically inhibits reductive dechlorination by acting as a competing electron acceptor with the chlorinated contaminants, and in the presence of high sulfide concentrations (figs. 46b, c), which typically have a toxicity effect on a wide range of bacteria (Maillacheruvu and Parkin, 1996; Parsons Infrastructure & Technology Group, Inc., 2010), is unique. The availability of a culture that has already been developed to a sediment-free form with dense populations of chlorinated aromatic dechlorinators, as well as the ability of the native wetland microbial community to degrade the site contaminants, provides flexibility in considering bioremediation options for the SCD wetland areas. The laboratory experiments for this study, however, were designed only to provide evidence of the occurrence of natural and enhanced biodegradation of the chlorinated benzenes at the site and to provide preliminary information on the degradation pathways and controlling factors. Additional studies would be needed to determine the best methods to utilize these degradation pathways in a remediation design and to optimize the degradation.

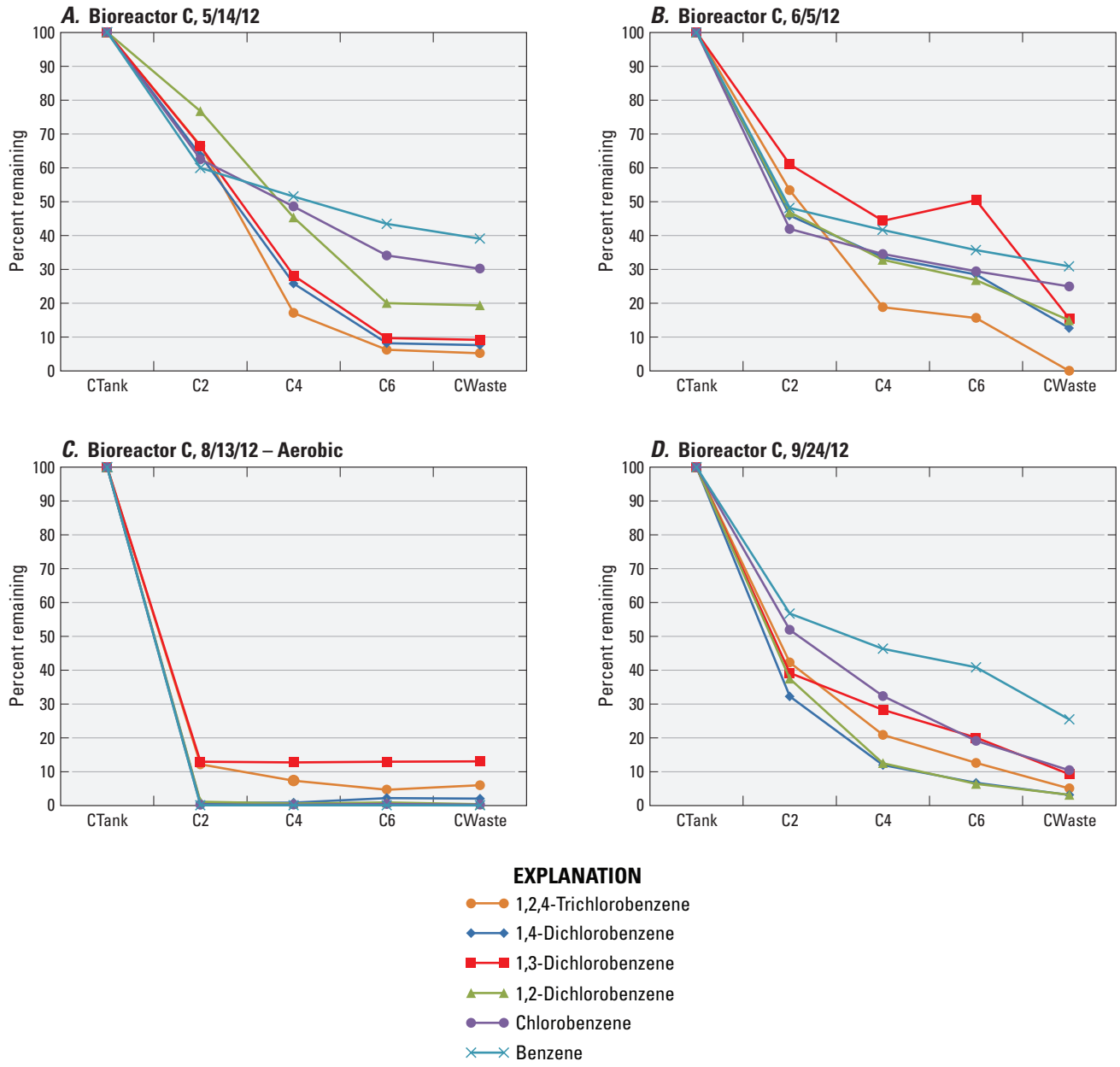


Figure 49. Concentrations of chlorobenzene compounds and benzene measured under anaerobic conditions (except in bioreactor C on August 13, 2012) at sampling ports along flowpaths through bioreactors C, D, and E on selected sampling dates.

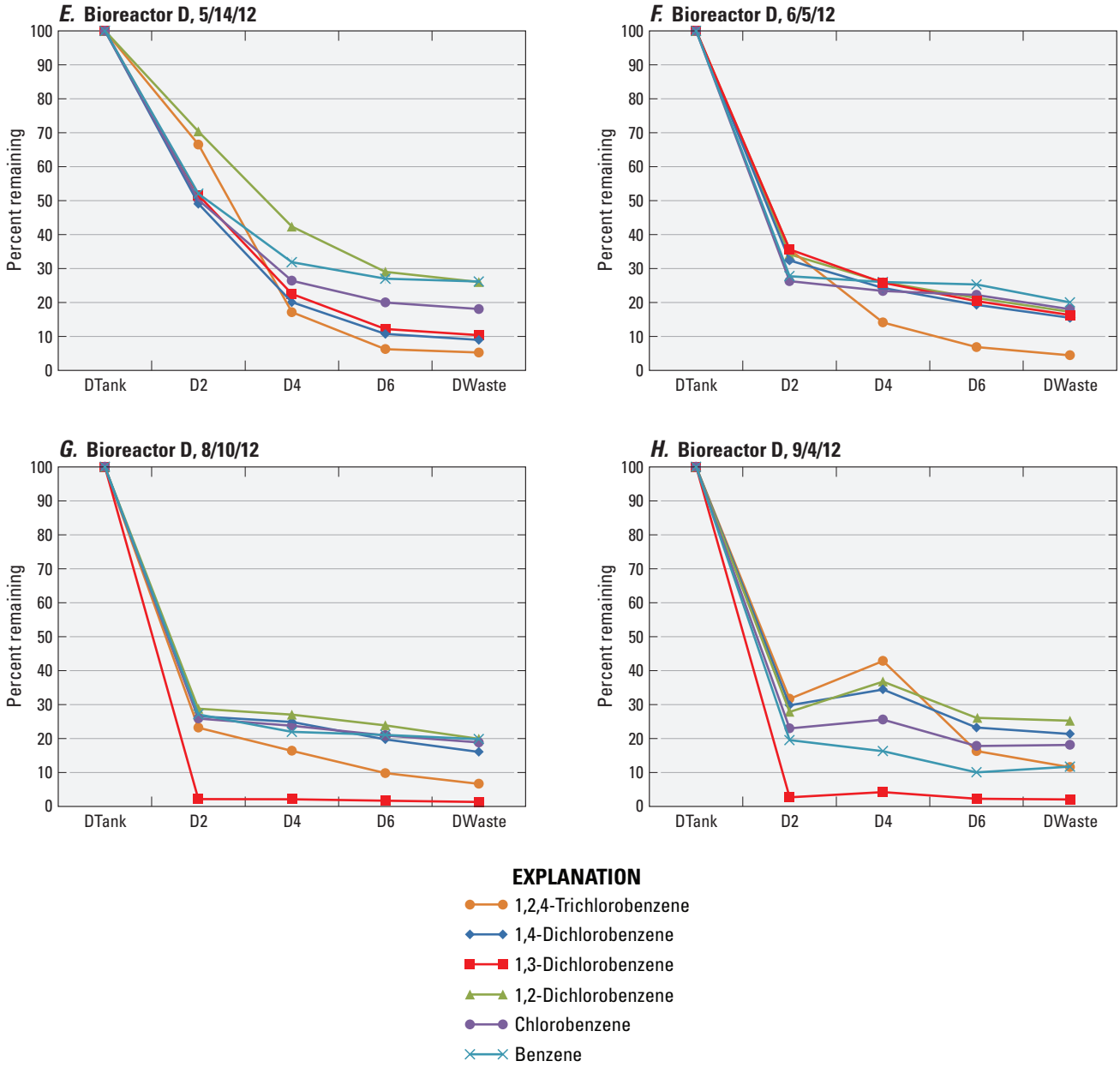


Figure 49. Concentrations of chlorobenzene compounds and benzene measured under anaerobic conditions (except in bioreactor C on August 13, 2012) at sampling ports along flowpaths through bioreactors C, D, and E on selected sampling dates.—Continued

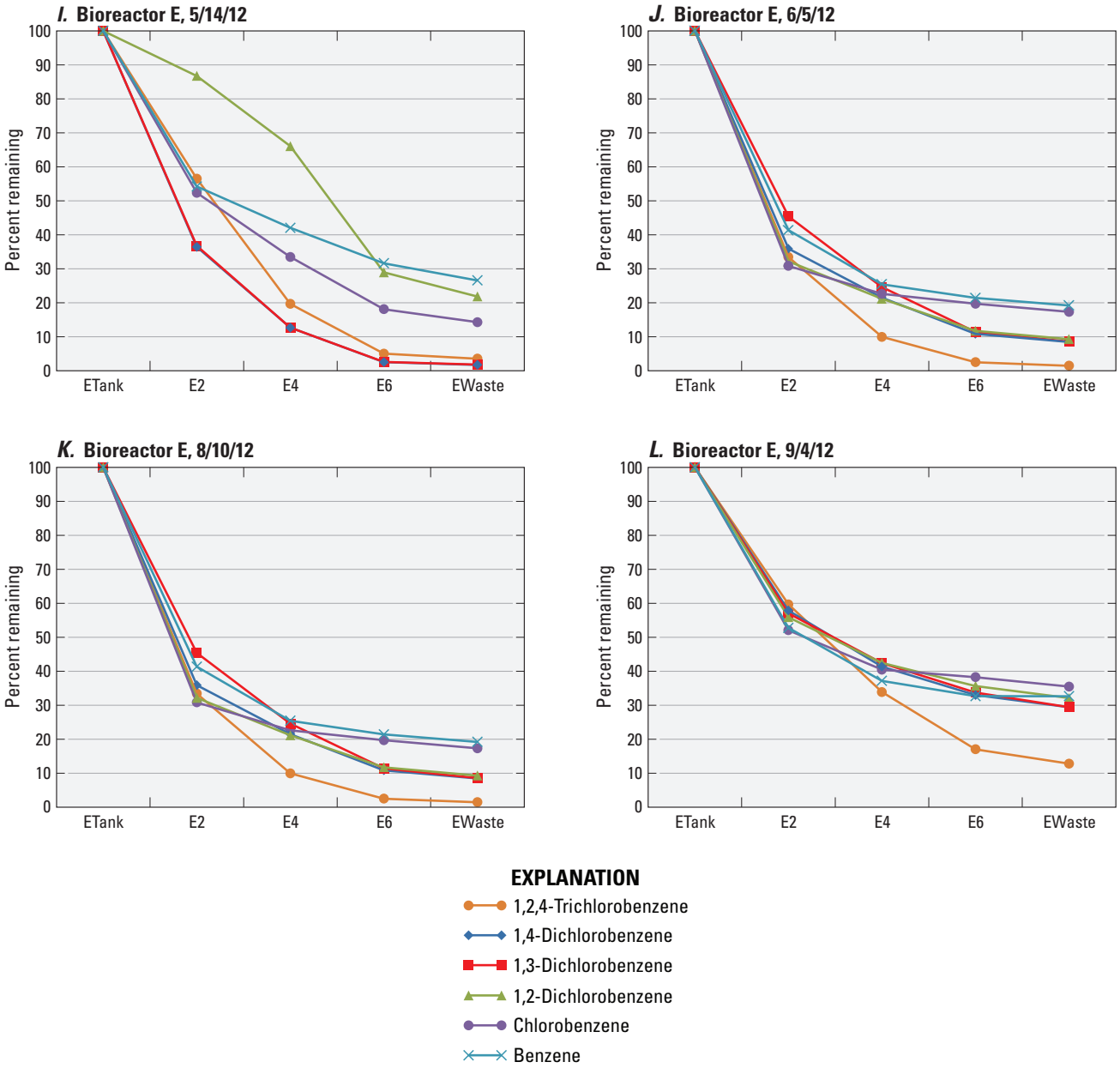


Figure 49. Concentrations of chlorobenzene compounds and benzene measured under anaerobic conditions (except in bioreactor C on August 13, 2012) at sampling ports along flowpaths through bioreactors C, D, and E on selected sampling dates.—Continued

Summary and Conclusions

Wetland areas north of an industrial facility that operated from 1966–2002 at the Standard Chlorine of Delaware, Inc. Superfund Site (SCD) in New Castle County, Delaware, are affected by contamination with chlorobenzenes and benzene from past waste storage and disposal, spills, leaks, and contaminated groundwater discharge. Prior to this study, the understanding of the hydrology of the SCD was limited to the uplands. In cooperation with the U.S. Environmental Protection Agency (EPA), the U.S. Geological Survey (USGS) began an investigation in June 2009 to provide a hydrogeologic and geochemical characterization of the wetland study area and to assess the feasibility of monitored natural attenuation or of combined natural attenuation and enhanced bioremediation as remedial strategies for the contaminated wetland areas. This assessment included a field and experimental approach, with measurement of water levels, collection of groundwater samples using passive diffusion samplers and piezometers, *in situ* microcosms deployed directly in the wetland sediment, microbial community analyses, and tests with flow-through anaerobic bioreactors seeded with either the native microbes or a bioaugmented dechlorinating culture, WBC-2.

Wetland sediments at SCD are present in the low-lying fringe of Red Lion Creek, with less than 1 meter (m) of topographic variation from the boundary of the wetland to open water on Red Lion Creek. Wetland sediments at SCD can be grouped into two stratigraphic units—an upper organic rich unit consisting of root mass and organic matter in a mineral matrix of silt and (or) clay, and a basal unit consisting of clay, silt and fine-grained sand. Wetland sediments generally are between 5 and 10 m thick in the study area but are estimated to extend to greater than 10 m at one site. Further data collection would help to define the interface between wetland sediments and the underlying Columbia aquifer. Groundwater flow in the wetland area is predominantly vertically upward in the wetland sediments and the Columbia aquifer, with lateral velocities less than half the estimated vertical flow velocities. Groundwater discharge accounts for an estimated minimum of 47 percent of the total discharge for the subwatershed of tidal Red Lion Creek at the site. Thus, groundwater transport to shallow creek sediments and surface water is most likely a significant transport mechanism for contaminants to ecological receptors, requiring treatment of both sediments and groundwater in the wetland and Red Lion Creek.

The major contaminants detected in groundwater in the wetland study area included benzene and six chlorinated benzenes—1,2,3- and 1,2,4-trichlorobenzene (123TCB and 124TCB); 1,2-, 1,3-, and 1,4-dichlorobenzene (12DCB, 13DCB, and 14DCB); and chlorobenzene (CB). Shallow wetland groundwater in the northwest area was characterized by high concentrations of total chlorinated benzenes and benzene (with a maximum concentration of about 75,000 micrograms per liter or µg/L), low pH (median 4.5 to 5.2), high chloride concentrations, and low or undetectable sulfate concentrations. In the northeast area, wetland groundwater had low to moderate concentrations of total chlorinated benzenes and benzene (generally not greater than 10,000 µg/L), moderate pH (median 5.8 to 6.1), and high sulfate concentrations (200–1,000 milligrams per liter or mg/L) as a result of a sulfuric acid spill. Concentrations in excess of 1 percent of the solubility of the individual chlorinated benzenes remain in the groundwater in the wetland sediments and aquifer, indicating that sources of dense nonaqueous phase liquids (DNAPLs) remain outside the subsurface barrier constructed around the main industrial facility. The consistently higher contaminant concentrations detected in the shallow wetland groundwater than in groundwater deeper in the wetland sediments or the Columbia aquifer also indicate a continued source in the wetland sediments, either as DNAPLs or compounds sorbed to the sediments, or both. Decreasing chloride concentrations in the shallow groundwater in the northwest wetland area from 2009–11 may have resulted from an interruption of a contaminant source from behind the barrier wall after its construction in 2007; however, volatile organic compound (VOC) concentrations indicative of DNAPL presence remain outside the barrier wall.

When highly reducing conditions (methanogenic or sulfate-reducing) existed in the wetland groundwater, molar ratios of the VOCs showed that CB and benzene were predominant, compared to higher percentages of TCBs and DCBs under weaker reducing conditions, and indicated that biodegradation of the chlorinated benzenes was occurring through reductive dechlorination pathways. In July 2009, reductive dechlorination was evident in the groundwater in the northwest wetland area but not the northeast area; however, a change in redox conditions in the wetland reversed this pattern, with groundwater in the northeast wetland area showing greater evidence of reductive dechlorination in 2011–12. Total VOC concentrations did not decrease substantially along upward groundwater flowpaths in the wetland sediment, even when the molar compositions indicated substantial reductive dechlorination, most likely due to the additional source of VOCs in the upper wetland sediments. Natural attenuation alone, therefore, is not sufficient to remove the VOCs from the wetland groundwater where these sources are present in the wetland sediment.

The changes in the wetland geochemistry observed between 2009 and 2011 were most likely due to alterations in groundwater flow and geochemistry from the Columbia aquifer after the installation of the barrier wall in 2007, although induced changes from industrial pumping and tidal fluctuations with an inoperative tide control structure also may have been contributing factors. The addition of selected redox constituents and chloride to the current monitoring plan for the upland area near the wetland boundary, and the inclusion of piezometers within the wetland area to this monitoring plan would assist in determining the effect of the barrier wall on the wetland geochemistry, contaminant sources, and biodegradation.

Unamended and WBC-2 bioaugmented microcosms (deployed during 2009 and 2010 at two to four sites in the wetland sediments) confirmed that the native microbial community and WBC-2, respectively, were able to biodegrade the higher chlorinated benzenes through reductive dechlorination. Both the unamended and WBC-2 treatments showed incorporation of ^{13}C-labeled CB into dissolved inorganic carbon (predominantly carbon dioxide), which can be produced as an end product through aerobic or anaerobic degradation pathways and indicates use of the contaminant for cellular energy. Only the unamended treatments with ^{13}C-labeled CB, however, showed incorporation of ^{13}C into the microbial biomass (measured as the amount of phospholipid fatty acids), indicating that microorganisms were utilizing the carbon as a source for cellular material through oxidative degradation pathways. This apparently aerobic degradation pathway for CB was evident in all the unamended microcosms under a wide range of measured redox conditions. Natural, complete breakdown of ^{13}C-labeled 14DCB and benzene to carbon dioxide was also measured in unamended microcosms. The relative amounts of ^{13}C incorporation in carbon dioxide in these *in situ* microcosms indicated that dichlorobenzene degradation was slowest and benzene degradation was fastest by the native microbial community, which is consistent with the expected order of degradation rates by aerobic oxidation pathways. Microbial community analyses of samples from the *in situ* microcosms and from the wetland sediment, however, showed relatively high cell numbers (10^3 to 10^5 cells per bead) and diversity of populations (*Dehalococcoides*, *Dehalobacter*, *Desulfitobacterium*, and *Geobacter*) that are known to contain species capable of reductive dechlorination of VOCs. Thus, a high natural reductive dechlorination potential at the site also was apparent, consistent with evidence from molar composition of the contaminants observed under highly reducing conditions in the wetland groundwater.

Experiments with a continuous flow, fixed-film bioreactor seeded with native microorganisms in groundwater from the wetland area showed both aerobic and anaerobic biodegradation of dichlorobenzenes, monochlorobenzene, and benzene, although monochlorobenzene and benzene degradation rates decreased under anaerobic conditions compared to aerobic conditions. In two bioreactors with established biofilms of WBC-2 that also operated with inflow of site groundwater, generally greater than 70 percent removal of all chlorinated benzene compounds and benzene were removed under mixed sulfate-reducing and mixed sulfate-reducing/methanogenic conditions. During anaerobic operation, median percent removals of all chlorinated benzene compounds were equally high for the native and WBC-2 bioaugmented bioreactors, with median percent removals ranging from 86 to 94 percent. Benzene removal was greater in the WBC-2 bioaugmented bioreactors than in the bioreactor seeded only with site groundwater. The relatively high percent removals without the need for an acclimation period for the chlorinated aromatic compounds that WBC-2 had not previously been exposed to during culturing or maintenance indicates that the same dechlorinators are involved as those in the degradation of the chlorinated ethanes and ethenes that the culture was developed to degrade. The ability of the WBC-2 culture to completely reduce the chlorinated benzenes and benzene, even in the presence of high sulfate concentrations and high sulfide concentrations, is unique for known bioaugmentation cultures.

Both field and laboratory investigations provide evidence that biodegradation is active in the wetland and can be enhanced under anaerobic conditions by bioaugmentation with the dechlorinating culture WBC-2. The availability of a culture that has already been developed to a sediment-free form with dense populations of dechlorinators, as well as the ability of the native wetland microbial community to degrade the site contaminants, provides a range of possible bioremediation options for the wetland areas at the SCD. Further investigation and testing would be needed, however, to evaluate the most appropriate bioremediation methods, or combination of methods, for implementation in the different wetland areas. The laboratory and field tests for the current study were designed only to provide preliminary information on degradation pathways and controlling factors. Additional studies would be needed to determine the best methods to utilize these degradation pathways in a remediation design and to optimize the degradation, taking into consideration the continued source of contaminants in areas of the wetland and aquifer in their DNAPL form.

Acknowledgments

The authors thank the following agencies and people for their contributions to this study. EPA, Region III, provided management and logistical support; the efforts of Hilary Thornton and Brad White are gratefully acknowledged. The authors thank Duane Graves with Geosyntec Consultants (Knoxville, Tennessee) and SiREM Laboratory (Guelph, Ontario, Canada) for their continued maintenance of WBC-2 and support under our USGS-Geosyntec Cooperative Research and Development Agreement (CRADA). WBC-2 culture and anaerobic medium used in all laboratory and field tests reported here were provided by SiREM with the assistance of Jennifer Webb. The following USGS personnel also are thanked for laboratory and field assistance throughout this study: Mastin Mount and Melody Flinchbaugh for VOC and methane analyses; Roberto Cruz, Luke Myers, and Jessica Thompson for hydrogeologic measurements, field and experiment sampling, and database support. We also thank Andrew Reid (currently at the University of Rhode Island) and Elizabeth Shipley for assistance with sampling preparation, laboratory analyses, and data management. Special thanks are extended to Jeanne Jaeschke (USGS) for providing chemical analyses of major ions and dissolved organic carbon.

References Cited

Adrian, Lorenz, Rahnenführer, Jan, Gobom, Johan, and Hölscher, Tina, 2007, Identification of a chlorobenzene reductive dehalogenase in *Dehalococcoides* sp. Strain CBDB1: Applied and Environmental Microbiology, v. 73, no. 23, p. 7,717–7,724, accessed May 20, 2014, at *http://dx.doi.org/10.1128%2FAEM.01649-07*.

Adrian, Lorenz, Szewzyk, Ulrich, Wecke, Jörg, and Görisch, Helmut, 2000, Bacterial dehalorespiration with chlorinated benzenes: Nature, v. 408, p. 580–583, accessed June 1, 2014, at DOI:10.1038/35046063.

Amon, J.P., Agrawal, Abinash, Shelley, M.L., Opperman, B.C., Enright, M.P., Clemmer, N.D., Slusser, Thomas, Lach, Jason, Sobolewski, Teresa, Gruner, William, and Entingh, A.C., 2007, Development of a wetland constructed for the treatment of groundwater contaminated by chlorinated ethenes: Ecological Engineering, v. 30, p. 51–66, accessed May 20, 2014, at DOI:10.1016/j.ecoleng.2007.01.008.

Agency for Toxic Substances and Disease Registry (ATSDR), 2013, Toxicological profiles for chlorobenzene, dichlorobenzenes, and trichlorobenzenes, accessed March 18, 2013, at *http://www.atsdr.cdc.gov/substances/index.asp*.

Asquith, W.H., Roussel, M.C., and Vrabel, Joseph, 2006, Statewide analysis of the drainage-area ratio method for 34 streamflow percentile ranges in Texas: U.S. Geological Survey Scientific Investigations Report 2006–5286, 34 p., accessed May 20, 2014, at *http://pubs.usgs.gov/sir/2006/5286/*.

Bachman, L.J., Lindsey, Bruce, Brakebill, John, and Powars, D.S., 1998, Ground-water discharge and base-flow nitrate loads of nontidal streams, and their relation to a hydrogeomorphic classification of the Chesapeake Bay watershed, Middle Atlantic Coast: U.S. Geological Survey Water-Resources Investigations Report 98–4059, 71 p., accessed May 20, 2014, at *http://pubs.usgs.gov/wri/wri98-4059/*.

Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents in contaminated groundwater, *in* Lesage, S., and Jackson, R.E., eds., Groundwater contamination and analysis at hazardous waste sites: New York, Marcel Dekker, p. 425–461.

Black & Veatch, 2003, Soil/sediment design comparison study, Standard Chlorine of Delaware Site, New Castle County, Delaware: Black & Veatch Special Projects Corporation, June 2003.

Black & Veatch, 2005, Final (100%) groundwater basis of design/design criteria report, Volume 1, Interim groundwater remedy remedial design, Standard Chlorine of Delaware Site, New Castle County, Delaware: Black & Veatch Special Projects Corporation, September 2005, [variously paged].

Black & Veatch, 2007, Final remedial investigation report, Volumes 1–3, Standard Chlorine of Delaware Site, New Castle County, Delaware: Black & Veatch Project No. 047123.0109, Prepared for U.S. Environmental Protection Agency, Region III, Philadelphia, Pennsylvania, August 2007, [variously paged].

Bradley, P.M., and Chapelle, F.H., 2011, Microbial mineralization of dichloroethene and vinyl chloride under hypoxic conditions: Groundwater Monitoring and Remediation, v. 31, no. 4, p. 39–49, accessed May 20, 2014, at DOI:10.1111/j.1745-6592.2011.01339.x.

Braeckevelt, Mareike, Mirschel, Gabriele, Wiessner, Arndt, Rueckert, Michael, Reiche, Nils, Vogt, Carsten, Schultz, Andrea, Paschke, Heidrun, Kuschk, Peter, and Kaestner, Matthias, 2008, Treatment of chlorobenzene-contaminated groundwater in a pilot-scale constructed wetland: Ecological Engineering v. 33, no. 1, p. 45–53, accessed May 20, 2014, at DOI:10.1016/j.ecoleng.2008.02.002.

Braeckevelt, Mareike, Rokadia, Hemal, Imfeld, Gwenaël, Stelzer, Nicole, Paschke, Heidrun, Kuschk, Peter, Kästner, Matthias, Richnow, Hans, H.-H., and Weber, Stefanie, 2007, Assessment of in situ biodegradation of monochlorobenzene in contaminated groundwater treated in a constructed wetland: Environmental Pollution, v. 148, no. 2, p. 428–437, accessed May 20, 2014, at *http://dx.doi.org/10.1016/j.envpol.2006.12.008*.

Bunge, Michael, Adrian, Lorenz, Kraus, Angelika, Opel, Matthias, Lorenz, W.G., Andreesen, J.R., Görisch, Helmut, and Lechner, Ute, 2003, Reductive dehalogenation of chlorinated dioxins by an anaerobic bacterium: Nature, v. 421, no. 6921, p. 357–360, accessed June 1, 2014, at DOI:10.1038/nature01237.

Burns, Matt, Sublette, K.L., Sobieraj, James, Ogles, Dora, and Koenigsberg, Stephen, 2013, Concurrent and complete anaerobic reduction and microaerophilic degradation of mono-, di-, and trichlorobenzenes: Remediation Journal, v. 23, no. 3, p. 37–53, accessed May 20, 2014, at DOI: 10.1002/rem.21356.

Chiou, C.T., Malcolm, R.L., Brinton, T.I., and Kile, D.E., 1986, Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids: Environmental Science & Technology, v. 20, no. 5, p. 502–508, accessed May 20, 2014, at DOI: 10.1021/es00147a010.

Cohen, R.M, and Mercer, J.M., 1993, DNAPL site evaluation, EPA/600/R-93/022: Robert S. Kerr Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Ada, Oklahoma, February 1993, [variously paged], accessed June 20, 2014, at *http://www.clu-in.org/download/contaminantfocus/dnapl/600r93022.pdf*.

Conestoga Rovers Associates, 2000, Remedial design investigation and preliminary design report for interim groundwater remediation program, Standard Chlorine of Delaware Site: prepared for U.S. Environmental Protection Agency, Region III, Philadelphia, Pennsylvania, March 2000, [variously paged].

Degnan, J.R., and Brayton, M.J., 2010, Preliminary investigation of paleochannels and groundwater specific conductance using direct-current resistivity and surface-wave seismic geophysical surveys at the Standard Chlorine of Delaware, Inc., Superfund Site, Delaware City, Delaware, 2008: U.S. Geological Survey Open-File Report 2010–1058, 27 p., accessed May 20, 2014, at *http://pubs.usgs.gov/of/2010/1058/*.

Doheny, E.J., and Fisher, G.T., 2000, Estimated flood frequency and corresponding water-surface elevations at the confluence of the Potomac and Shenandoah Rivers, Harpers Ferry, West Virginia: U.S. Geological Survey Open-File Report 00–461, [variously paged], accessed May 20, 2014, at *http://md.water.usgs.gov/publications/ofr-00-461/report_nofig.html* [online only].

Domenico, P.A, and Schwartz, F.W., 1990, Physical and chemical hydrogeology: New York, John Wiley & Sons, 824 p.

Ehlke, T.A., Imbrigiotta, T.E., and Dale, J.M., 2004, Laboratory comparison of polyethylene and dialysis membrane diffusion samplers: Groundwater Monitoring and Remediation, v. 24, no. 1, p. 53–59, accessed May 20, 2014, at DOI: 10.1111/j.1745-6592.2004.tb00704.x.

Emerson, D.G., Vecchia, A.V., and Dahl, A.L., 2005, Evaluation of drainage-area ratio method used to estimate streamflow for the Red River of the North Basin, North Dakota and Minnesota: U.S. Geological Survey Scientific Investigations Report 2005–5017, 13 p., accessed May 20, 2014, at *http://pubs.usgs.gov/sir/2005/5017/* [online only].

Fetter, C.W., 2001, Applied hydrogeology (4th ed.): Upper Saddle River, New Jersey, Prentice Hall, 598 p.

Field, J.A., and Sierra-Alvarez, Reyes, 2008, Microbial degradation of chlorinated benzenes: Biodegradation, v. 19, p. 463–480, accessed May 20, 2014, at DOI 10.1007/s10532-007-9155-1.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, New Jersey, Prentice Hall, 604 p.

Fung, J.M., Weisenstein, B.P., Mack, E.E., Vidumsky, J.E., Ei, T.A., and Zinder, S.H., 2009, Reductive dehalogenation of dichlorobenzenes and monochlorobenzene to benzene in microcosms: Environmental Science & Technology, v. 43, no. 7, p. 2,302–2,307, accessed May 20, 2014, at DOI: 10.1021/es802131d.

Geosyntec Consultants, Inc., 2006, Final report: West Branch Canal Creek, microbial consortium growth and characterization: Knoxville, Tenessee, Geosyntec Consultants, Report Number GA060547, 133 p.

Geosyntec Consultants, Inc., 2012, Anaerobic bioreactor evaluation for groundwater treatment at Canal Creek and Old O-Field, Aberdeen Proving Ground, Maryland: Knoxville, Tennessee, Geosyntec Consultants, prepared for contract number GS-10F-0106M, [variously paged].

Geyer, R., Peacock, A.D., Miltner, A., Richnow, H.-H., White, D.C., Sublette, K.L., and Kästner, M., 2005, In situ assessment of biodegradation potential using biotraps amended with ^{13}C-labeled benzene or toluene: Environmental Science & Technology, v. 39, no. 13, p. 4,983–4,989, accessed May 24, 2014, at DOI: 10.1021/es048037x.

Gomez-Hermosillo, Cesar, Pardue, J.H., and Reible, D.D., 2006, Wetland plant uptake of desorption-resistant organic compounds from sediments: Environmental Science & Technology, v. 40, no. 10, p. 3,229–3,236, accessed May 24, 2014, at DOI: 10.1021/es051341l.

Hach Company, 2006, Digital titrator manual, Model 16900, for all digital titrator test kits (24th ed.): Loveland, Colorado, Hach Company, 196 p.

Hach Company, 2007, DR 2800 spectrophotometer procedures manual (2d ed.): Loveland, Colorado, Hach Company, 814 p.

Hölscher, Tina, Gorisch, Helmut, and Adrian, Lorenz, 2003, Reductive dehalogenation of chlorobenzene congeners in cell extracts of *Dehalococcoides* sp. Strain CBDB1: Applied and Environmental Microbiology, v. 69, no. 5, p. 2,999–3,001, accessed May 24, 2014, at DOI: 10.1128/AEM.69.5.2999-3001.2003.

HydroGeoLogic, Inc. (HGL.), 2009, Wetlands remedial approach and pilot study summary report, Standard Chlorine of Delaware Site, New Castle, Delaware, February 2009, [variously paged].

Imfeld, Gwenaël, Aragonés, C.E., Zeiger, Simone, von Eckstädt, C.V., Paschke, Heidrun, Trabitzsch, Ralf, Weiss, Holger, and Richnow, H.H., 2008, Tracking in situ biodegradation of 1,2-dichloroethenes in a model wetland: Environmental Science & Technology, v. 42, no. 21, p. 7,924–7,930, accessed May 24, 2014, at DOI: 10.1021/es8014277.

Kaschl, Arno, Vogt, Carsten, Uhlig, Sylvia, Nijenhuis, Ivonne, Weiss, Holger, Kästner, Matthias, and Richnow, H.H., 2005, Isotopic fractionation indicates anaerobic monochlorobenzene biodegradation: Environmental Toxicology and Chemistry, v. 24, no. 6, p. 1,315–1,324, accessed June 1, 2014, at DOI: 10.1897/04-321R.1.

Kassenga, G.R., Pardue, J.H., Blair, Steve, and Ferraro, Tom, 2003, Treatment of chlorinated volatile organic compounds in upflow wetland mesocosms: Ecological Engineering v. 19, no. 5, p. 305–323, accessed May 27, 2014, at *http://dx.doi.org/10.1016/S0925-8574(02)00122-2*.

Kästner M., Fischer, A., Nijenhuis, I., Geyer, R., Stelzer, N., Bombach, P., Tebbe, C.C., and Richnow, H.H., 2006, Assessment of microbial in situ activity in contaminated aquifers: Engineering in Life Sciences, v. 6, no. 3, p. 234–251, accessed May 28, 2014, at DOI: 10.1002/elsc.200620125.

Kueper, B.H., and Davies, K.L., 2009, Ground water issue: Assessment and delineation of DNAPL source zones at hazardous waste sites: Cincinnati, Ohio, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, EPA 600-R-09-119, 20 p., accessed June 20, 2014, at *http://nepis.epa.gov/Exe/ZyPDF.cgi/P1006Y98.PDF?Dockey=P1006Y98.PDF*.

Liang, Xiaoming, Devine, C.E., Nelson, Jennifer, Lollar, B.S., Zinder, Stephen, and Edwards, E.A., 2013, Anaerobic conversion of chlorobenzene and benzene to CH_4 and CO_2 in bioaugmented microcosms: Environmental Science & Technology, v. 47, no. 5, p. 2,378–2,385, accessed May 27, 2014, at DOI: 10.1021/es3043092.

Lin, L., 2003, Dechlorination of 1,2,3,4-tetrachlorobenzene in organic matter- and mineral-dominated soils and effects of Typha Latifolia roots: Baton Rouge, Louisiana, Louisiana State University Department of Civil Engineering, Master's Thesis, May 2003, 124 p.

Lorah, M.M., Dyer, L.J., and Burris, D.R., 2007, Anaerobic biodegradation and hydrogeochemical controls on natural attenuation of trichloroethene in an inland forested wetland: Bioremediation Journal, v. 11, no. 2, p. 85–102, accessed May 27, 2014, at DOI:10.1080/10889860701429294.

Lorah, M.M., Jones, E.J., and Voytek, M.A., 2012, Anaerobic microbial composition and methods of using same: United States Patent No. 8,105,808 B2, January 31, 2012.

Lorah, M.M., Majcher, E.H., Jones, E.J., and Voytek, M.A., 2008, Microbial consortia development and microcosm and column experiments for enhanced bioremediation of chlorinated volatile organic compounds, West Branch Canal Creek wetland area, Aberdeen Proving Ground, Maryland: U.S. Geological Survey Scientific Investigations Report 2007–5165, accessed May 27, 2014, at *http://pubs.usgs.gov/sir/2007/5165/*.

Lorah, M.M., and Olsen, L.D., 1999a, Degradation of 1,1,2,2-tetrachloroethane in a freshwater tidal wetland: Field and laboratory evidence: Environmental Science & Technology, v. 33, no. 2, p. 227–234, accessed May 27, 2014, at DOI: 10.1021/es980503t.

Lorah, M.M., and Olsen, L.D., 1999b, Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland: Field evidence of anaerobic biodegradation: Water Resources Research, v. 35, no. 12, p. 3,811–3,827, accessed May 27, 2014, at DOI:10.1029/1999WR900116.

Lorah, M.M., Olsen, L.D., Capone, D.G., and Baker, J.E., 2001, Biodegradation of trichloroethylene and its anaerobic daughter products in freshwater wetland sediments: Bioremediation Journal, v. 5, no. 2, p. 101–118, accessed May 27, 2014, at DOI:10.1080/20018891079221.

Lorah, M.M., Olsen, L.D., Smith, B.L., Johnson, M.A., and Fleck, W.B., 1997, Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland, Aberdeen Proving Ground, Maryland: U.S. Geological Survey Water-Resources Investigations Report 97–4171, 95 p., accessed May 27, 2014, at *http://pubs.usgs.gov/wri/wri97-4171/wrir-97-4171.pdf*.

Lorah, M.M., Vogler, E.T., Dennis, P., Graves, D., and Gallegos, J., 2008, Laboratory and in situ tests for bioremediation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by the dechlorinating consortium WBC-2, Remediation of Chlorinated and Recalcitrant Compounds: Proceedings of the Sixth International Conference, Monterey, California, May 19–22, 2008, Battelle, Columbus, Ohio.

Lovley, D.R., 2000, Anaerobic benzene degradation: Biodegradation, v. 11, nos. 2–3, p. 107–116, accessed June 2, 2014, at DOI: 10.1023/A:1011191220463.

Lovley, D.R., 2003, Cleaning up with genomics: applying molecular biology to bioremediation: Nature Reviews Microbiology, v. 1, p. 35–44, accessed May 27, 2014, at DOI:10.1038/nrmicro731.

Maillacheruvu, K.Y., and Parkin, G.F., 1996, Kinetics of growth, substrate utilization and sulfide toxicity for propionate, acetate, and hydrogen utilizers in anaerobic systems: Water Environment Research, v. 68, no. 7, p. 1,099–1,106, accessed June 2, 2014, at *http://www.jstor.org/stable/25044818*.

Majcher, E.H., Lorah, M.M., Phelan, D.J., and McGinty, A.L., 2009, Design and performance of an enhanced bioremediation pilot test in a tidal wetland seep, West Branch Canal Creek, Aberdeen Proving Ground, Maryland: U.S. Geological Scientific Investigations Report 2009–5112, 70 p. plus appendixes, accessed May 28, 2014, at *http://pubs.usgs.gov/sir/2009/5112/*.

Majcher, E.H., Phelan, D.J., Lorah, M.M., and McGinty, A.L., 2007, Characterization of preferential ground-water seepage from a chlorinated hydrocarbon-contaminated aquifer to West Branch Canal Creek, Aberdeen Proving Ground, Maryland, 2002–04: U.S. Geological Survey Scientific Investigations Report 2006–5233, 59 p. plus appendixes, accessed May 28, 2014, at *http://pubs.usgs.gov/sir/2006/5233/*.

Malcolm, H.M., Howe, P.D. and Dobson, S., 2004, Chlorobenzenes other than hexachlorobenzene: environmental aspects: Geneva, Switzerland, World Health Organization, Concise International Assessment Document 60, 58 p.

Martin, M.M., 1984, Simulated ground-water flow in the Potomac aquifers, New Castle County, Delaware: U.S. Geological Survey Water-Resources Investigations Report 84–4007, 85 p., accessed May 28, 2014, at *http://pubs.er.usgs.gov/publication/wri844007*.

Masunaga, Shigeki, Susarla, Sridhar and Yonezawa, Yoshitaka, 1996, Dechlorination of chlorobenzenes in anaerobic estuarine sediment: Water Science and Technology, v. 33, no. 6, p. 173–180, accessed May 28, 2014, at *http://www.iwaponline.com/wst/03306/wst033060173.htm*.

Mickowski, Richard, 1986, Tidegate Study for New Castle County, DE, New Castle Conservation District.

Middledorp, P.J.M, deWolf, J., Zehnder, A.J.B., and Schraa, G., 1997, Enrichment and properties of a 1,2,4-trichlorobenzene-dechlorinating methanogenic microbial consortium: Applied and Environmental Microbiology, v. 63, no. 4, p. 1,225–1,229.

Mitsch, W.J., and Gosselink, J.G., 1993, Wetlands (2d ed.): New York, John Wiley & Sons, 722 p.

Nelson, J.L., Fung, J.M., Cadillo-Quiroz, Hinsby, Cheng, Xu, and Zinder, S.H., 2011, A role for *Dehalobacter* spp. in the reductive dehalogenation of dichlorobenzenes and monochlorobenzene: Environmental Science & Technology, v. 45, no. 16, p. 6,806–6,813, accessed May 28, 2014, at DOI: 10.1021/es200480k.

North, K.P., Mackay, D.M., Annable, M.D., Sublette, K.L., Davis, Greg, Holland, R.B., Petersen, Daniel, and Scow, K.M., 2012, An *ex situ* evaluation of TBA- and MTBE-baited bio-traps: Water Research, v. 46, no. 12, p. 3,879–3,888, accessed May 28, 2014, at *http://dx.doi.org/10.1016/j.watres.2012.04.029*.

Nowak, J., Kirsch, N.H., Hegemann, W., and Stann, H.J., 1996, Total reductive dechlorination of chlorobenzenes to benzene by a methanogenic mixed culture enriched from Saale River sediment: Applied Microbiology and Biotechnology, v. 45, no. 5, p. 700–709.

Parsons Infrastructure & Technology Group, Inc. (Parsons), 2010, Final technology demonstration report: Loading rates and impacts of substrate delivery for enhanced anaerobic bioremediation: Arlington, Virginia, prepared for Environmental Security Technology Certification Program (ESTCP) (ESTCP Project ER-0627).

Peacock, A.D., Chang, Y.J., Istok, J.D., Krumholz, L., Geyer, R., Kinsall, B., Watson, D., Sublette, K.L., and White, D.C., 2004, Utilization of microbial biofilms as monitors of bioremediation: Microbial Ecology, v. 47, no. 3, p. 284–292, accessed May 29, 2014, at DOI 10.1007/s00248-003-1024-9.

Phillips, S.W., 1987, Hydrogeology, degradation of ground-water quality, and simulation of infiltration from the Delaware River into the Potomac aquifers, northern Delaware: U.S. Geological Survey Water-Resources Investigations Report 87–4185, 86 p., accessed May 28, 2014, at *http://pubs.er.usgs.gov/publication/wri874185*.

Potrawfke, Thomas, Timmis, K.N., and Wittich, R.-M., 1998, Degradation of 1,2,3,4-tetrachlorobenzene by *Pseudomonas chloroaphis* RW71: Applied and Environmental Microbiology, v. 64, no. 10, p. 3,798–3,806, accessed June 2, 2014, at *http://aem.asm.org/content/64/10/3798.full*.

Ramanand, K., Balba, M.T., and Duffy, J., 1993, Reductive dehalogenation of chlorinated benzenes and toluenes under methanogenic conditions: Applied and Environmental Microbiology, v. 59, no. 10, p. 3,266–3,272, accessed June 2, 2014, at *http://aem.asm.org/content/59/10/3266.abstract*.

Ramsey, K.W., 2005, Geologic map of New Castle County, Delaware: Delaware Geological Survey Geologic Map Series No. 13, accessed April 29, 2013, at *http://www.dgs.udel.edu/sites/dgs.udel.edu/files/publications/geomap13.pdf*.

Ramsey, K.W., 2007, Geologic map of Kent County, Delaware: Delaware Geological Survey Geologic Map Series No. 14, accessed April 29, 2013, at *http://www.dgs.udel.edu/sites/dgs.udel.edu/files/publications/DeGeoMap14.pdf*.

Rapp, Peter, and Gabriel-Jürgens, L.H.E., 2003, Degradation of alkanes and highly chlorinated benzenes, and production of biosurfactants, by a psychrophilic Rhodococcus sp. and genetic characterization of its chlorobenzene dioxygenase: Microbiology, v. 149, no. 10, p. 2,879–2,890, accessed May 28, 2014, at DOI: 10.1099/mic.0.26188-0.

Roy F. Weston, Inc., 1988, Report on response and cleanup efforts of a 5 January 1986 chlorobenzene spill, April 1988: [variously paged].

Roy F. Weston, Inc., 1992, Remedial investigation report for the Standard Chlorine of Delaware, Inc. Site, Delaware City, Delaware: [variously paged].

Roy F. Weston, Inc., 1993a, Feasibility study report for the Standard Chlorine of Delaware, Inc. Site, Delaware City, Delaware, May 1993: [variously paged].

Roy F. Weston, Inc., 1993b, Feasibility study addendum, Standard Chlorine of Delaware, Inc., Delaware City, Delaware, September 1993: [variously paged].

Sanford, W.E., Nelms, D.L., Pope, J.P., and Selnick, D.L., 2012, Quantifying components of the hydrologic cycle in Virginia using chemical hydrograph separation and multiple regression analysis: U.S. Geological Survey Scientific Investigations Report 2011–5198, 152 p., accessed May 28, 2014, at *http://pubs.usgs.gov/sir/2011/5198/*.

Schaefer, C.E., Lippincott, D.R., and Steffan, R.J., 2010, Field-scale evaluation of bioaugmentation dosage for treating chlorinated ethenes: Groundwater Monitoring and Remediation, v. 30, no. 3, p. 113–124, accessed May 28, 2014, at DOI:10.1111/j.1745-6592.2010.01297.x.

Shin, W.S., 2000, Desorption-resistance of chlorobenzene and phenanthrene in wetland peat soils: Environmental Engineering Research, v. 5, no. 1, p. 23–33.

Spain, Jim, 1997, Synthetic chemicals with potential for natural attenuation: Bioremediation Journal, v. 1, no. 1, p. 1–9, accessed May 28, 2014, at DOI:10.1080/10889869709351313.

Spencer, T.A., Phelan, D.J, Olsen, L.D, and Lorah, M.M., 2002, Ground-water and surface-water quality data for the West Branch Canal Creek area, Aberdeen Proving Ground, Maryland, November 1999–May 2001: U.S. Geological Survey Open-File Report 01–420, 301 p., accessed at *http://pubs.usgs.gov/of/2001/ofr01-420/pdf/ofr-01-420.pdf*.

Standard Chlorine of Delaware, Inc., 1982, Preliminary assessment, site inspection and sampling, September 1982: [variously paged].

Suyama, Akiko, Iwakiri, Ryo, Kai, Keiichirou, Tokunaga, Takashi, Sera, Nobuyuki, and Furukawa, Kensuke, 2001, Isolation and characterization of *Desulfitobacterium sp.* strain Y51 capable of efficient dehalogenation of tetrachloroethane and polychloroethanes: Bioscience, Biotechnology, and Biochemistry, v. 65, no. 7, p. 1,474–1,481, accessed May 28, 2014, at DOI:10.1271/bbb.65.1474.

Tas, Neslihan, van Eekert, M.H.A., De Vos, W.M., and Smidt, Hauke, 2010, The little bacteria that can—diversity, genomics and ecophysiology of '*Dehalococcoides*' spp. in contaminated environments: Microbial Biotechnology, v. 3, no. 4, p. 389–402, accessed May 28, 2014, at DOI: 10.1111/j.1751-7915.2009.00147.x.

ten Hulscher, Th.E.M, VanNoort, P.C.M., and van der Velde, L.E., 1997, Equilibrium partitioning theory overestimates chlorobenzene concentrations in sediment porewater from lake Ketelmeer, the Netherlands: Chemosphere, v. 35, no. 10, p. 2,331–2,344, accessed May 28, 2014, at *http://dx.doi.org/10.1016/S0045-6535(97)00311-1*.

Toxnet, 2013, Hazardous substances data base profiles, accessed March 19, 2013, at *http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB*.

U.S. Environmental Protection Agency (EPA), 1993, Memorandum AR308544S, technical review of bioremediation treatability testing program summary—Review, Standard Chlorine Site (93-RO3-001), October 8, 1993.

U.S. Environmental Protection Agency (EPA), 1995a, Record of Decision, Standard Chlorine of Delaware, Inc., Delaware City, Delaware: EPA/ROD/RO3-95/193, March 1995, [variously paged], accessed June 20, 2014, at *http://nepis.epa.gov/*.

U.S. Environmental Protection Agency (EPA), 1995b, Method 524.2: Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry: U.S. Environmental Protection Agency, Revision 4.1., 47 p., accessed March 14, 2013, at *http://www.epa.gov/sam/pdfs/EPA-524.2.pdf*.

U.S. Environmental Protection Agency (EPA), 1996, Attachment C—Chemical properties for SSL development, *in* Technical background document for soil screening guidance: EPA/540/R-95/128, July 1996, 7 p.

U.S. Environmental Protection Agency (EPA), 1998, Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water: Washington, D.C., Office of Research and Development, EPA/600/R-98/128, accessed June 20, 2014, at *http://nepis.epa.gov/*.

U.S. Environmental Protection Agency (EPA), 2004, Amendment no. 1 to the 1995 Record of Decision for the Standard Chlorine of Delaware Inc. Superfund Site Operable Units one and two, New Castle County, Delaware, September 2004, [variously paged].

U.S Environmental Protection Agency (EPA), 2006, Method 8260C (SW-846): Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS): U.S. Environmental Protection Agency, Revision 3, 92 p., accessed March 14, 2013, at *http://www.epa.gov/sam/pdfs/EPA-8260c.pdf*.

U.S Environmental Protection Agency (EPA), 2009, Method 415.3: Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water: U.S. Environmental Protection Agency, Revision 1.2, EPA/600/R-09/122, 56 p., accessed September 17, 2014, at *http://www.epa.gov/microbes/documents/Method%20415_3_Rev1_2_Final.pdf*.

U.S. Environmental Protection Agency (EPA), 2011, First five-year review report for Standard Chlorine of Delaware, Inc. Site, New Castle County, Delaware: Philadelphia, Pennsylvania, U.S. Environmental Protection Agency, Region III, [variously paged], accessed June 20, 2014, at *http://www.epa.gov/reg3hwmd/npl/DED041212473/fyreview/SCD_5YR_Final.pdf.*

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, accessed May 30, 2014, at *http://pubs.water.usgs.gov/twri9A*.

VanNoort, P.C.M., 2009, Estimation of amorphous organic carbon/water partition coefficients, subcooled liquid aqueous solubilities, and n-octanol/water partition coefficients of nonpolar chlorinated aromatic compounds from chlorine fragment constants: Chemosphere, v. 74, no. 8, p. 1,024–1,030, accessed June 20, 2014, at DOI: 10.1016/j.chemosphere.2008.11.002.

Vogel, T.M., Criddle, C.S., and McCarty, P.L., 1987, Transformations of halogenated aliphatic compounds: Environmental Science & Technology, v. 21, no. 8, p. 722–736, accessed May 30, 2014, at DOI: 10.1021/es00162a001.

Vroblesky, D.A., 2001, User's guide for polyethylene-based passive diffusion bag samplers to obtain volatile organic compound concentrations in wells. Part 1, Deployment, recovery, data interpretation, and quality control and assurance: U.S. Geological Survey Water-Resources Investigations Report 2001–4060, 18 p., accessed May 30, 2014, at *http://pubs.er.usgs.gov/publication/wri014060*.

Weiss, J.V., and Cozzarelli, I.M., 2008, Biodegradation in contaminated aquifers: Incorporating microbial/molecular methods: Ground Water, v. 46, no. 2, p. 305–322, accessed May 30, 2014, at DOI: 10.1111/j.1745-6584.2007.00409.x.

White D.C., Gouffon J.S., Peacock A.D., Geyer, Roland, Biernacki, Anita, Davis, G.A., Pryor, Marsha, Tabacco, M.B., and Sublette K.L., 2003, Forensic analysis by comprehensive rapid detection of pathogens and contamination concentrated in biofilms in drinking water systems for water resource protection and management: Environmental Forensics, v. 4, p. 63–74, accessed June 3, 2014, at DOI: 10.1080/15275920390186967.

Zhuang, Ping, and Pavlostathis, S.G., 1995, Effect of temperature, pH and electron donor on the microbial reductive dechlorination of chloroalkenes: Chemosphere, v. 31, no. 6, p. 3,537–3,548, accessed June 3, 2014 at *http://dx.doi.org/10.1016/0045-6535(95)00204-L*.

Prepared by USGS West Trenton Publishing Service Center.
Edited by Valerie M. Gaine.
Graphics and layout by Timothy W. Auer.

For additional information, contact:
Director, MD-DE-DC Water Science Center
U.S. Geological Survey
5522 Research Park Drive
Baltimore, MD 21228

or visit our Web site at:
http://md.water.usgs.gov

Lorah, M.M., and others—**Hydrogeologic Characterization and Bioremediation of Chlorinated Benzenes in Wetland Areas, SCD Superfund Site, Del., 2009–12**—Scientific Investigations Report 2014–5140

ISBN 978-1-4113-3848-7

ISSN 2328-031X (print)
ISSN 2328-0328 (online)
http://dx.doi.org/10.3133/sir20145140

Printed on recycled paper