

Prepared in cooperation with the U.S. Department of Energy



Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Water-Resources Investigations Report 99-4071

U.S. Department of the Interior

U.S. Geological Survey

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NATURAL ATTENUATION POTENTIAL OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN GROUND WATER, TNX FLOOD PLAIN, SAVANNAH RIVER SITE, SOUTH CAROLINA

By Don A. Vroblesky, Christopher T. Nietch, John F. Robertson, Paul M. Bradley, John Coates, and James T. Morris

U.S. GEOLOGICAL SURVEY Water-Resources Investigations Report 99-4071

Prepared in cooperation with the U.S. DEPARTMENT OF ENERGY

Columbia, South Carolina 1999

U.S. DEPARTMENT OF THE INTERIOR BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY

Charles C. Groat, Director

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CONTENTS

Abstract	1
Introduction	2
Methods	5
Well sampling	5
Ditch-bed pore-water sampling	5
Water-level measurements	8
Botanical studies	8
Field investigation	8
Laboratory investigation	10
Adsorption and biodegradation measurements	13
Hydrogeology	13
Ground-water quality	18
Natural attenuation potential of chlorinated volatile organic compounds	25
Botanical processes	25
Results of field botanical investigation	27
Results of laboratory botanical investigation	34
Adsorption	37
Microbiological processes	38
Influence of processes affecting the natural attenuation potential	39
Summary and conclusions	40
References	41

FIGURES

1-3.	Map	os showing:	
	1.	Location of study area, wells, soil borings, and seepage basins, TNX facility, Savannah River Site, S.C	3
	2.	Locations of diffusion samplers, ditch-bed piezometers, sediment samples, and observation wells,	
		TNX facility, Savannah River Site, S.C.	7
	3.	Location and identification numbers of test trees and selected observation wells on the Savannah	
		River flood plain, TNX facility, Savannah River Site, S.C.	9
4.	Sche	ematic diagram of mesocosm with baldcypress seedling	11
5-8.	Graj	phs showing:	
	5.	Evapotranspiration- and recharge-related water-table fluctuations at well TNX 16D	
		during June 1997, TNX facility, Savannah River Site, S.C.	14
	6.	Water levels measured at nested wells TIR 1L, TIR 1M, and TIR 1U, October 1996	
		to August 1997, TNX facility, Savannah River Site, S.C.	15
	7.	Water levels at the Savannah River, well TNX 10D, and well TNX 16D, October 1996 to	
		March 1998, TNX facility, Savannah River Site, S.C.	17
	8.	Concentrations of trichloroethene and cis-1,2-dichloroethene in water-to-vapor diffusion	
		samplers beneath the drainage ditch, August 25, 1997, TNX facility, Savannah River Site, S.C.	18
9-10.	Map	showing:	
	9.	Cis-1,2-dichloroethene concentrations in baldcypress trunks in January and February 1998	
		and in ground water during August 1997 and ground-water-flow directions, TNX	
		facility, Savannah River Site, S.C.	30
	10.	Trichloroethene concentrations in baldcypress trunks in January and February 1998, in ground	
		water at wells during May 1997 and 1996, and at the ditch-bed sampling point during August 1997	
		and ground-water-flow directions, TNX facility, Savannah River Site, S.C.	31

11-15. Graphs showing:

11.	Trichloroethene concentrations in cores at various heights along the trunk of tree 7	
	in July and August 1997, TNX facility, Savannah River Site, S.C.	34
12.	Average monthly water use by seedlings measured with Marriotte bottles and water use normalized	
	for seedling growth by dividing the mean stem basal area of all healthy seedlings into the average	
	monthly water use	34
13.	Trichloroethene removal from the rhizosphere of baldcypress seedlings as nanomoles per	
	minute through the above-ground portion of the plant and fractional trichloroethene loss	
	from carboy water during summer and winter	35
14.	Comparison of carbon dioxide exchange and trichloroethene flux from seedlings showing good	
	correlation in daytime and weak correlation in nighttime conditions, where negative values	
	represent net photosynthesis, or carbon dioxide consumption, and positive values represent	
	respiration, or net carbon dioxide production	37
15.	Percentage of initial head-space trichloroethene over time in microcosms of sediment from the	
	TNX flood plains, Savannah River Site, S.C.	38

TABLES

1.	Construction data for selected wells, upper and lower flood plains, TNX facility, Savannah River Site, S.C	4
2.	Comparison of volatile organic compound concentrations measured in well TIR 1U using	
	a water-to-water diffusion sampler and a submersible pump to obtain samples, TNX facility,	
	Savannah River Site, S.C., June 11, 1997	8
3.	Summary of the diffusion model for trichloroethene flux through internal air spaces within tree trunks	12
4.	Lithologic log of pilot hole near well TIR 1U, TNX upper flood plain, Savannah River Site, S.C.	13
5.	Differences in water-level measurements made inside and outside of ditch-bed piezometers	
	in the drainage ditch, TNX facility, Savannah River Site, S.C., May 23 and 27, 1997	15
6.	Water levels at selected wells in the upper and lower flood plains, TNX facility, Savannah River	
	Site, S.C., September 1996 to January 1998	16
7.	Concentrations of selected organic compounds in ground water from observation wells in the TNX	
	upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997	19
8.	Organic compounds analyzed but not detected in ground water from observation wells, TNX flood plain,	
	Savannah River Site, S.C., September 1996 to August 1997	21
9.	Concentrations of selected nitrogen compounds and dissolved solids in ground water	
	from observation wells in the TNX upper and lower flood plains, Savannah River Site, S.C.,	
	September 1996 to August 1997	22
10.	Comparison of cis-1,2-dichloroethene and trichloroethene concentrations obtained by using	
	water-to-water and water-to-vapor diffusion samplers, and a stainless-steel sampling point	
	beneath the drainage ditch, May to September 1997, TNX facility, Savannah River Site, S.C.	24
11.	Trichloroethene and cis-1,2-dichloroethene concentrations in water-to-vapor diffusion	
	samplers beneath the drainage ditch, TNX facility, Savannah River Site, S.C., August 1997	25
12.	Field-measured water-quality constituents and properties in ground water from observation wells	
	in the TNX upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997	26
13.	Concentrations of inorganic constituents in ground water from observation wells in the TNX upper	
	and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997	28
14.	Concentrations of cis-1,2-dichloroethene and trichloroethene in selected soil-gas diffusion	
	samplers, lower flood plain, TNX facility, Savannah River Site, S.C., March to April 1997	29
15.	Concentrations of cis-1,2-dichloroethene and trichloroethene vapor, expressed as nanomoles	
	of gas per liter of water, in tree cores from the TNX flood plain, Savannah River Site, S.C.,	
	January 1997 to February 1998	32
16.	Comparison among observed, estimated, and modeled trichloroethene removal by baldcypress seedlings	36
17.	Trichloroethene adsorption onto aquifer sediment from the upper and lower flood plains, TNX facility,	
	Savannah River Site, S.C.	37

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	Ву	To Obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi ²)	2.59	square kilometer
foot per day (ft/d)	0.3048	meter per day
foot squared per day (ft ² /d)	0.09294	meter squared per day
gallons per minute (gal/min)	0.06308	liters per second
gallons per day (gal/d)	0.003785	cubic meter per day
inches per year (in/yr)	25.4	millimeters per year
inches per week (in/week)	25.4	millimeters per week
	Volume	
gallon (gal)	3.785	liter

Temperature: In this report, temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

 $^{\circ}F = (9/5 \text{ x }^{\circ}C) + 32$

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration: In this report, chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (μ g/L).

Other units used in report:

cubic meters of atmosphere	m ³ atm/mol
per mole	
gram	g
liter	L
microgram	μg
micromole per liter	μM
micrometer	μm
microliter	μL
milligram	mg
milliliter	mL
milliliter per minute	mL/min
millimeter	mm
millimole per liter	mM
moles per liter	Μ
nanoliter per square centimeter of leaf surface per hour	nL/cm ² leaf surface/hr
nanomole per liter	nM
nanomoles of gas per liter of tree-core water	nmol/L
parts per million	ppm
pounds per square inch	psi

Abbreviations used in this report:

bls	- below land surface
СТ	- carbon tetrachloride
CO ₂	- carbon dioxide
¹⁴ CO ₂	- carbon-14 labeled carbon dioxide
[¹⁴ C]	- carbon-14 labeled
CVOC	- chlorinated volatile organic compound
<i>c</i> DCE	- cis-1,2-dichloroethene
DIC	- dissolved inorganic carbon
DO	- dissolved oxygen
FACT	- Flow and Contaminant Transport code
Fe(II)	- ferrous iron
Fe(III)	- ferric iron
GC	- gas chromatograph
H ₂	- dissolved hydrogen
H ₂ S	- hydrogen sulfide
m	- TCE loss-rate constant from mesocosm seedlings
MCL	- maximum contaminant level
NO ₃	- nitrate
PCE	- tetrachloroethene
PVC	- polyvinyl chloride
TCE	- trichloroethene
TEAP	- terminal electron-accepting process
USEPA	- U.S. Environmental Protection Agency
USGS	- U.S. Geological Survey
VC	- vinyl chloride
VOC	- volatile organic compound
WVD	- water-to-vapor diffusion sampler
WWD	- water-to-water diffusion sampler

Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

By Don A. Vroblesky¹, Christopher T. Nietch², John F. Robertson¹, Paul M. Bradley¹, John Coates³, and James T. Morris²

Abstract

The ability of naturally occurring processes to attenuate chlorinated volatile organic compounds (CVOC's) beneath the Savannah River flood plain at the TNX facility, Savannah River Site, South Carolina was examined for this investigation. The presence of CVOC's in flood-plain tree trunks indicated that the trees were removing contaminants from the ground water. Concentrations of CVOC's in tree trunks were used as an aid in mapping the shallow ground-water contamination. Mesocosm experiments of baldcypress showed that the seedlings were capable of removing substantial amounts of trichloroethene (TCE) (approximately 52 nanomoles per minute) from ground water during periods of active evapotranspiration and lower, but still significant, amounts (approximately 3 to 13 nanomoles per minute) during the winter when evapotranspiration was relatively inactive. The other naturally occurring potential contaminant-attenuation processes were less significant. The adsorption potential for chlorinated compounds was high in localized organicrich sediments of the lower flood plain, but was substantially lower in other tested areas. Bioreme-

Data collected during this investigation imply that approximately 200 micrograms per liter of TCE is discharged from ground water to a drainage ditch in the flood plain that drains into the Savannah River. Surface-water samples collected in August 1997, however, showed that TCE concentrations present in the drainage ditch water had decreased to undetectable levels 185 feet downstream, prior to discharging into the Savannah River. Water-level data imply that contaminated ground water can discharge upward from the eastern edge of the lower flood plain to the flood-stage Savannah River during times when the lower flood plain is inundated.

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diation potential of TCE may be present in localized areas of the lower flood plain, but probably is not significant in the upper flood-plain sediments. A conservative ground-water-flow and solutetransport model incorporating some of these processes implied that, despite the relatively high TCE removal rate by flood-plain trees, the groundwater flow is too fast to allow naturally occurring processes to prevent contaminant discharge to the Savannah River.

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INTRODUCTION

The TNX Area (fig. 1) is a former pilot-scale test facility for the Savannah River Technology Center, located approximately 0.25 mile (mi) east of the Savannah River, Savannah River Site (SRS), South Carolina. Wastewater potentially containing chlorinated volatile organic compounds (CVOC's) and other constituents from former operations was discharged to unlined basins. Observation wells were installed in 1984, and samples from the wells showed that CVOC contamination was present in the ground water and was moving westward beneath a forested flood plain toward the Savannah River. The source of the CVOC's is thought to be seepage from the unlined basins (Nichols, 1993).

The organic contaminants in ground water beneath the upper and lower flood plains consist primarily of trichloroethene (TCE), *cis*-1,2-dichloroethene (*c*DCE), and carbon tetrachloride (CT). The contamination also is characterized by nitrate concentrations above 45 mg/L (as nitrate) drinking-water limits established by the U.S. Environmental Protection Agency (USEPA) (1991).

The purpose of the investigation summarized in this report was to examine the processes influencing the natural attenuation potential of CVOC's in the aquifer beneath the forested flood plain between the TNX facility and the Savannah River (fig. 1) and to determine whether those processes are capable of preventing further contaminant transport. The natural attenuation potential of selected contaminants was evaluated using hydrologic, water-chemistry, microbial, and botanical data. Water-quality data collected by RCS Environmental Consultants were used in conjunction with water-quality data collected by the U.S. Geological Survey (USGS) at 11 wells to assist in the evaluation. The project was funded by the U.S. Department of Energy and was a cooperative effort by the USGS, the University of South Carolina, Southern Illinois University, and the Westinghouse Savannah River Company.

Land-surface topography is relatively flat in the vicinity of the source area. Between the source area and the river, topography slopes downward approximately 40 ft over a lateral distance of approximately 180 ft to a relatively flat-lying terrace, termed the upper flood plain in this investigation (fig. 1). The upper flood plain is approximately 550 ft wide. On the western side of the upper flood plain, the topography drops about 6 to 7 ft onto a relatively flat surface, termed the lower flood plain in this investigation. Topography in the lower flood plain gradually rises in a westward direction until

sharply dropping off to the Savannah River. Vegetation in the swamps of the flood plain consists primarily of baldcypress [*Taxodium distichum* (L) Rich.], tupelo (*Nyssa aquatica* L.), and sweetgum (*Liquidambar stryaciflua* L.). In drier parts of the flood plain, oak (*Quercus* spp.), loblolly pine (*Pinus taeda* L.), and sweetgum (*Liquidambar stryaciflua* L.) are dominant, with a relatively small population of baldcypress and sycamore (*Platanus occidentalis* L.).

The TNX area is underlain by shallow unconfined and partially confined sandy aquifers separated by discontinuous confining units (Nichols, 1993; Hamm, Aleman, and Shadday, 1997). The shallow system is separated from a deeper aquifer system by a confining unit at a depth of about 100 to 160 ft below land surface (Nichols, 1993). In downgradient areas, beneath the terrace and flood-plain deposits, the shallow aquifers appear to be hydraulically continuous. Depth to the water table beneath the flood plain ranges from the land surface to about 6 ft. The ground-water flow rate in the flood plain is approximately 1.5 ft/d (Hamm, Aleman, and Shadday, 1997).

An unlined drainage ditch typically discharges approximately 166 gal/min (measured at the outfall) of runoff and treated effluent from the TNX facility (fig. 1) (William Pidcoe, Westinghouse Savannah River Company, written commun., 1998). Water flows from the ditch outfall across terrace and flood-plain deposits consisting of organic detritus in some reaches and clay or sand in other reaches. Approximately 40 ft downstream from the outfall, surface water in the ditch contains less than 5 micrograms per liter (μ g/L) each of TCE and *c*DCE (William Pidcoe, Westinghouse Savannah River Company, written commun., 1998). The ditch empties into the Savannah River, approximately 1,000 ft downstream from the outfall.

Observation wells in the flood plain include both shallow drive points and drilled wells (fig. 1, table 1). The well nomenclature identifies various aspects of the well: a prefix of TIR indicates a well installed for this investigation; a prefix of TNX or TCM indicates a well installed for other investigations; and the suffixes of wells TIR 1L, TIR 1M, and TIR 1U indicates screened intervals in the lower, middle, and upper zones relative to the ground-water contamination, respectively. Drilling logs, geologic logs, geophysical logs, and other data related to the installation of observation wells for this investigation can be found in a summary report by Westinghouse Savannah River Company (1996).

2 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina





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 Table 1. Construction data for selected wells, upper and lower flood plains, TNX facility, Savan nah River Site, S.C. (William Pidcoe, Westinghouse Savannah River Company, written commun., 1998)

	Elevation of specified datum	Top of screen	Bottom of screen	Top of sand	Bottom of	Site coordinates, in ft		
Well identifier	(ft amsi)	(ft bls)	(ft bls)	pack (ft bls)	sand pack (ft bls)	Northing	Easting	
PH (pilot hole)	98.24 Ground surface	•				71048.2	16171.46	
TIR IU	99.48 Top of conc. pad 101.66 Top of PVC casing	7.5	9.5	5.2	13	71029	16170.9	
TIR 1M	99.56 Top of conc. pad 101.66 Top of PVC casing	13	15 11.2		20	71024.1	16169.8	
TIR 1L	99.72 Top of conc. pad 101.72 Top of PVC casing	32	34 27		40	71019.1	16169.33	
TIR 2	99.23 Top of conc. pad 101.28 Top of PVC casing	13	15	9	22.5	71068.7	16096.3	
TIR 3B	98.39 Top of conc pad 100.56 Top of PVC casing	12.9	14.9	14.9 9		71099.1	16522.9	
TNX 14D	92.1 Ground surface 92.8 Top of SS casing	4.3	6.3 °		·	70931.8	15971.1	
TNX 15D	92.5 Ground surface 93.1 Top of SS casing	4.6	6.6			71021.7	16002.2	
TNX 16D	92.7 Ground surface 93.4 Top of SS casing	4.6	6.6	·		71111.3	16012.2	
TNX 9D	101.7 Top of standpipe	6.3 below TOC	26.3 below TOC			70791.4	16145.7	
TNX 10D	102.3 Top of casing	5.3 below TOC	25.3 below TOC			70999.2	16166.6	
TCM 1	96.83 Ground surface 97.04 Top of concrete 99.21 Top of PVC	25.5	28	22.5		71151.6	16199.4	
TCM 2	96.67 Ground surface 97.26 Top of concrete 99.02 Top of PVC	2.82	22.82	1.5		71142.3	16199.7	
TCM 3	96.63 Ground surface 97.19 Top of concrete 99.41 Top of PVC	10.51	13.01	8.4		71134.9	16201.6	

[ft, feet; ft ams], feet above mean sea level; ft bls, feet below land surface; SS, stainless steel; PVC, polyvinyl chloride; conc., concrete; --- no data]

4 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

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METHODS

Established methods, as well as methods developed for this investigation, were used to assess the natural attenuation potential of chlorinated hydrocarbons. In general, the approach was to compare advective contaminant-transport processes to the processes affecting contaminant attenuation. Specific methods used during this investigation are discussed in the following sections.

Well Sampling

All monitoring wells were purged of casing water by using either a Teflon bailer or a positive-displacement pump prior to collecting water samples. At least three casing volumes of water were removed from each well until specific conductance and turbidity stabilized. After well purging, the dissolved oxygen (DO) concentration in water from each well was determined by Winkler titration (Hach Company, 1983). Ferrous iron [Fe(II)] concentration was measured in the field using the Hach colorimeter/FerroZine method (Stookey, 1970). Water temperature and pH in ground water were measured in the field.

Water samples for analysis of volatile organic compounds (VOC's) were collected at selected wells by RCS Environmental Services following established USEPA protocols. All sample bottles were capped with Teflon-lined bottle caps. The water samples for VOC's were analyzed using USEPA method 8240 (U.S. Environmental Protection Agency, 1986).

To determine methane and dissolved inorganic carbon (DIC) concentrations, a 5-milliliter (mL) water sample was collected using a clean syringe and injected into septated vials through a 0.45-micrometer (μ m) porous-membrane filter. The vials were rinsed with filtered sample water prior to sampling. The samples were stored on ice until analyzed. Methane was quantified by thermal-conductivity-detection gas chromatography. Dissolved methane concentrations were calculated using Henry's Law coefficients (Stumm and Morgan, 1996). The DIC samples were acidified in the laboratory with a 42.5 percent phosphoric acid solution, and DIC concentrations were quantified by thermal-conductivity-detection gas chromatography. Sample DIC concentrations were corrected for CO₂ present in sample-free blanks collected in the field.

Water samples for analysis of inorganic ions were collected in sample-rinsed polyethylene bottles

after passing through a 0.45-µm porous-membrane filter. The inorganic ion samples were packed in ice immediately following collection. The samples were analyzed for calcium (method 215.1), magnesium (method 242.1), sulfate (method 375.4), and nitrate (method 352.1) (U.S. Environmental Protection Agency, 1983). Anions were analyzed using ionexchange chromatography with chemical suppression [method 300.0 (U.S. Environmental Protection Agency, 1983)].

A ground-water hydrogen (H₂) sample was collected from well TIR 1L by using the bubble-strip method of Chapelle and McMahon (1991). A stream of water was pumped from the well through a gas-sampling bulb at an approximate rate of 600 milliliters per minute (mL/min). A bubble of nitrogen was injected into the bulb. Hydrogen and other soluble gases partitioned from the water into the bubble until equilibrium was achieved. Once equilibrium was achieved (less than 5 percent change in hydrogen concentration in 5 minutes, which typically occurred within 30 minutes of initiating the flow of water through the bulb), gas was extracted from the bulb by using a gas-tight syringe. Dissolved hydrogen was measured by using a gas chromatograph (GC) equipped with a reduction gas detector. The detection limit of this method ranged from 0.1 to 0.5 nanomoles per liter (nM). All H₂ samples were collected as duplicates.

The use of H_2 , a transient intermediate product of anaerobic microbial metabolism, as an indicator of predominant terminal electron-accepting processes (TEAP's) was introduced by Lovley and Goodwin (1988). This approach has been used to document the zonation of TEAP's in various systems by Chapelle and Lovley (1990, 1992), Chapelle and McMahon (1991), and Vroblesky and Chapelle (1994). These studies concluded that characteristic H_2 concentrations were 5 to 25 nM for methanogenesis; 1 to 4 nM for sulfate reduction; and 0.1 to 0.8 nM for ferric iron [Fe(III)] reduction. Because H_2 is an extremely transitory intermediate, with a half-life of less than a minute (Conrad and others, 1987), it is a useful constituent for characterizing the local predominant TEAP's.

Ditch-Bed Pore-Water Sampling

The method for VOC-sample collection in ditchbed sediments involved burying water-to-water diffusion (WWD) and water-to-vapor diffusion (WVD) samplers in the ditch-bed sediments. Each WWD sampler consisted of a 4-mil-thick (0.004 in.) polyethylene bag filled with approximately 100 mL of deionized water. The bags were made of 2-in.-wide lay-flat polyethylene sleeves. One end of the sleeve was heatsealed; the sleeve was filled with deionized water; and the second end of the sleeve was heat-sealed, leaving an elongated polyethylene bag containing deionized water with little or no head space. Although, the WWD sampler used in this investigation was smaller and lacked a Teflon stopcock, its design was otherwise similar to the downhole diffusion samplers used in a previous investigation (Vroblesky and Hyde, 1997) to successfully yield representative VOC samples in well water.

The polyethylene bag then was placed inside a stainless-steel screen for structural support. The screen was tubular, 1.5-in. (3.8 cm) in diameter and approximately 5 in. (12.7 cm) long. The bag was prevented from sliding out of the open ends of the screen by crossed wires. Similar results were obtained by using a 5 by 5 by 1.5 in. (12.7 by 12.7 by 3.8 cm) prism-shaped cage with vinyl-coated wire instead of the tubular stainless-steel screen.

Once the WWD sampler was prepared, it was attached to a wire survey flag and to a WVD sampler. The WVD samplers consisted of 20-mL empty, uncapped head-space vials enclosed in two polyethylene bags. Preparation of the WVD samplers involved placing a head-space vial in a polyethylene bag, removing excess air from the bag, and then sealing the bag. The vial was arranged in the bag so that one smooth layer of polyethylene tightly covered the opening of the vial, thereby creating a membrane permeable to VOC's but not to water (Vroblesky and others, 1991; 1996). Strapping tape was used around the outside of the bag to wrap the polyethylene firmly against the vial. Care was taken to ensure that no tape covered the opening of the tube or the lip around the opening of the vial. A previous investigation showed that the strapping tape and polyethylene bag did not contribute significant amounts of VOC's to the analyses (Vroblesky and others, 1996).

The vial and bag of the WVD sampler then were placed inside another sealable polyethylene bag. The second bag was sealed and taped as described above except that the polyethylene layer covering the vial opening was loose enough to be cut open without damaging the inner layer of polyethylene. The outer bag was used to reduce abrasion of the inner bag, to prevent residual carryover of contamination by keeping the inner bag from contacting contaminated soil, and to optimize the integrity of the bottle seal by eliminating sediment from the bottle lip. The outer bag covering the vial opening was removed immediately prior to capping the vials during sample retrieval. For sample replication, two individually wrapped head-space vials were placed in the same outer bag and sealed.

Installation of each WVD sampler was accomplished by using a coring hand auger or shovel to excavate a hole approximately 1 ft deep in the sediment. A WVD sampler was placed in the hole, and the hole was backfilled with the sediment that was removed from the hole. The WWD and attached WVD samplers were buried approximately 8 in. beneath the bed of the ditch at various locations. Site locations CB80U and CB5U were 80 ft and 5 ft, respectively, upstream from the embankment separating the upper and lower floodplain terraces (fig. 2). Site locations CB50D and CB110D were 50 ft and 110 ft, respectively, downstream from the embankment. Site location CB590D was at the mouth of the drainage ditch where it empties into the Savannah River.

The samplers were recovered after 8 days. Upon recovery, a second set of WWD and attached WVD samplers were installed in the same holes used for the first set of samplers. The second set of samplers was recovered after 4 days. Approximately 2 months later (July 17, 1997) a WWD and attached WVD sampler were buried in the ditch-bed sediment near site CB5U (fig. 2). After an equilibration period of 6 days, a surface-water grab-sample was collected from the diffusion-sampler site, and the diffusion samplers were recovered.

The WWD and WVD samplers were recovered by pulling the wire survey flags and attached samplers out of the ditch-bed sediment. Immediately upon removal, the outer polyethylene bag on the WVD sampler was cut open, and a Teflon-lined stopper was crimped onto the WVD sampler over the inner polyethylene bag.

Once the WVD sampler was capped, the WWD sampler was removed from the structural-support screen, cut open at one end, and the enclosed water was gently poured into pre-acidified (hydrochloric acid) 40-mL VOC vials. The vials were capped and inverted to ensure that no bubbles were present. The samples then were transported to a commercial laboratory for analysis using USEPA method 8260a. The lack of VOC detection at three sites indicates that the sampler-construction material did not contribute significant VOC concentrations to the samples.



Figure 2. Locations of diffusion samplers, ditch-bed piezometers, sediment samples, and observation wells, TNX facility, Savannah River Site, S.C.

Although the ability of the WWD samplers to collect a VOC sample in ambient water in wells has been demonstrated in a previous publication (Vroblesky and Hyde, 1997), a sampler also was tested in well water at the present study area to demonstrate transferability of the method to this site. Results of the samplers in well TIR 1U in June 1997 showed that the concentrations of TCE and CT measured in water from a diffusion sampler collected prior to well purging were approximately the same as concentrations in water collected with a positive-displacement submersible pump after slowly purging three casing volumes of water with the same pump (table 2). The WWD sampler, placed adjacent to the screened interval, had been in the well for 2 days prior to recovery.

Table 2. Comparison of volatile organic compoundconcentrations measured in well TIR 1U using a water-to-water diffusion sampler and a submersible pump to obtainsamples, TNX facility, Savannah River Site, S.C., June 11,1997

[TCE, trichloroethene; CT, carbon tetrachloride; μ g/L, micrograms per liter]

Sampling method	TCE (μg/L)	CT (μg/L)
Diffusion sampler	128	11.1
Submersible pump	101	8.4
Submersible pump replicate	123	8.1

The agreement between CVOC concentrations measured in water obtained from a WWD sampler in well TIR 1U and concentrations measured in water obtained by purging and sampling with a positive-displacement submersible pump shows that the diffusion sampler can be used to obtain concentrations of CVOC's representative of those in the surrounding ground water (table 2) at this site. WVD samplers were installed at 41 sites in the ditch bed, 22 sites in the upper flood plain, and 85 sites in the lower flood plain during March to June 1997 (fig. 2). The samplers were recovered after equilibration times ranging from 7 to 140 days.

Water-Level Measurements

Water-level measurements were made synoptically on a quarterly basis from September 1996 to August 1997 at selected wells in the TNX flood plain. Measurements were made using electrical water-level indicators. The measured depth-to-water then was converted to water-level elevation using surveyed elevations of measuring points or tops of casing (table 1).

Differences between water-stage level in the ditch and ground-water head below the drainage ditch (fig. 2) were measured using ditch-bed piezometers. The piezometers consisted of 1-in. (outer-diameter) steel pipe with a plug loosely fitted to one end. The plugged end of the pipe was driven 2 ft into the bottom sediment. At one location (site CB5U), an additional piezometer was driven to a depth of 4 ft. A rod then was inserted into the pipes and used to drive the loose plug approximately 1 in. further into the sediment, to ensure adequate communication with ground water beneath the ditch bed. The rod then was removed, leaving the pipe open at the bottom. After the piezometers were allowed to equilibrate for several hours, measurements were made from the top of the pipe to the water inside and outside of the pipe. Differences between the depth from the top of the piezometer to water levels measured inside and outside of the pipe provided information on locations of gaining reaches.

Botanical Studies

Botanical aspects of natural attenuation in the TNX flood plain were examined by using both field and laboratory studies. The field investigation consisted of headspace chemical analysis in vials containing tree cores collected from the site. The laboratory investigation consisted of examining TCE uptake and loss in baldcypress seedlings grown in controlled mesocosms.

Field Investigation

Cores were collected with an increment borer from 97 trees on the Savannah River upper and lower flood plains down-gradient from the TNX facility between January 1997 and February 1998 (fig. 3). The trees included 64 baldcypress, 5 tupelos, 12 loblolly pines, 3 sycamores, 6 oaks, and 7 sweetgums and were identified by consecutive numbers (fig. 3). Trees 11, 16, 17, and 53 were control oak, loblolly pine, sweetgum, and sycamore trees, respectively, collected from offsite areas not shown in figure 3.

Part of the area from which tree cores were collected contained ground water contaminated with TCE and cDCE. The tree cores used to delineate the areal extent of TCE and cDCE were collected from the northeastern (or upgradient) side of the respective tree. All cores used to examine areal distribution of contamination were collected from a height of approximately 5 ft above ground, except for tree 7a, which was

8 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina



Figure 3. Location and identification numbers of test trees and selected observation wells on the Savannah River flood plain, TNX facility, Savannah River Site, S.C.

collected from about 30 ft on August 11, 1997 and 9 ft on October 1, 1997, and trees 20a and 21a, which were collected from about 6 ft. Tree 7 branched into two trunks at a height of about 7 ft above ground. Tree 7a is the southern trunk of tree 7.

At selected trees, two replicate cores were collected approximately 1 in. horizontally from each other. The average concentration difference between replicate cores was 15.2 percent for TCE in six replicate pairs and 2.5 percent for *c*DCE in three replicate pairs.

Upon collection, the cores (approximately 2.5 in. in length) immediately were removed from the coring tools and placed in 20-mL head-space vials. Tefloncoated septum caps then were crimped onto the vials. The vials were heated at 40 degrees Celsius (°C) for 12 hours to vaporize volatile compounds in the cores. The vials then were cooled to room temperature, and a 100-microliter (μ L) sample of the head space was collected into a gas syringe. Gas samples were analyzed by photoionization detection on a Photovac 10S Plus gas chromatograph. Water content of the wood was determined by comparing wood weights before and after heat drying the cores. Concentrations are reported here as nanomoles of gas per liter of tree-core water (nmol/L). Statistical tests were done on concentrations based on core-water volume and the core dry weight and verified that the sample normalization procedure did not significantly affect the results.

At selected contaminated sites, ambient-air samples were collected from 5 ft above land surface adjacent to the trunks of several sampled trees by waving empty 20-mL glass vial in the air for several seconds. The ambient-air samples did not contain detectable concentrations, less than 10 nmol/L of TCE and less than 8 nmol/L of cDCE.

Laboratory Investigation

Controlled mesocosms were constructed to investigate TCE uptake and loss by baldcypress seedlings. The loss was monitored over both diel and seasonal cycles and compared to physiological parameters to quantify the relative importance of TCE-reduction mechanisms. Allometric relations between plant morphological and physiological parameters and rates of TCE transport also were examined.

Baldcypress was used as the test tree for the mesocosm experiments because it is the dominant tree species on the TNX flood plains. A total of 45 bare-root cypress seedlings purchased from the South Carolina Forestry Commission were planted in 5-gal (20 trees) or 2.8-gal (25 trees) glass carboy mesocosms. The mesocosms (fig. 4) were kept outside with full exposure to ambient conditions. Seedlings were planted on April 15, 1997 in a gravel/sand substrate. Water levels in the carboys were maintained above the substrate surface since the initial planting. A 0.25-percent Hoagland's nutrient solution (Epstein, 1972) was added monthly. At the end of the 1997 growing season the seedlings were an average height of 4.9 ft and had an average stem diameter of 0.08 ft.

Constant-head (Marriotte) bottles were attached to the carboys to serve as a mechanism for maintaining a constant water level and measuring seedling water use (Hussey and Odum, 1992) (fig. 4). The rate of water flow from the Marriotte bottle to the carboy is driven by the change in hydrostatic pressure in the carboy. Thus, water from the Marriotte bottle replaces water lost from the carboy by evapotranspiration. Seedling water use was monitored throughout the experiment from June to December 1997.

Measurements of TCE flux from seedlings in the mesocosms were conducted from August to December 1997. The September flux measurements were excluded due to hardware malfunction. Flux experiments (n=6 seedlings per month) were initiated by displacing 1 liter (L) of carboy water with water that had been mixed with 200 to 300 µL of TCE for small and large carboys, respectively. Dissolution of added TCE was not complete, and some amount of free product was present. Nominal soil pore-water TCE concentrations were 75 milligrams per liter (mg/L). The space between the neck of the carboy and the trunk of the seedling was sealed with closed-cell neoprene and silicone glue. Controls (four replicates) consisted of carboys with substrate, but in place of the seedling, a wooden dowel was sealed within the opening at the top of the carboy.

The amount of TCE flux through the plant was determined by a static-chamber technique. An air tight, clear polycarbonate (Lexan) chamber (80 L) was sealed over each mesocosm immediately prior to sampling. The chamber was outfitted with an environmental-control unit that maintained approximate ambient temperatures by recirculating cold water through a radiator. A sensor head mounted on the top of the chamber monitored photosynthetically-active radiation and chamber temperature. Two 12-volt fans mixed the chamber head space by drawing air from the top and blowing it across the heat exchanger at the bottom. Trichloroethene was



Figure 4. Schematic diagram of mesocosm with baldcypress seedling.

measured by drawing a sample of chamber air into a $100-\mu$ L glass syringe followed by immediate injection into the GC (Photovac 10S plus with a photoionization detection system) on site. The chamber air was sampled every 10 minutes for a 30-minute time series. The flux was computed from the slope of the linear regression of TCE concentration relative to time. The amount of TCE adsorption onto the chamber was assumed to be negligible. Flux through each of the dosed seedlings was determined twice on consecutive days, during the day and at night. Monthly day and night means were computed from a sample size of 12.

Exchange of carbon dioxide (CO_2) by the seedlings was measured concurrently with the TCE flux determination. The CO₂ gas concentration was quantified by pumping a fraction of the chamber head-space through an infrared gas analyzer (Licor 6200 portable photosynthesis system) in a closed system. The analyzer logged CO₂ concentration every 4 seconds over a 4-minute sampling interval. The CO₂ flux was computed by determining the slope of CO₂ concentration relative to time. Daytime flux values were calculated from measurements taken between 12:00 noon and 4:00 p.m., whereas the nighttime measurements were conducted between 8:00 p.m. and 3:00 a.m. depending on the season.

Experiments that quantified the loss rate of TCE from the rhizosphere were conducted on separate mesocosms (live seedling) in the winter (November 1997 to February 1998) and summer (June to August 1998). Loss from carboys containing dead, but still intact, seedlings also was determined in the summer. In these experiments, TCE-saturated water was added to previously drained carboys to prevent introduction of free-phase TCE.

The TCE concentration in the carboy water was sampled weekly (summer) to biweekly (winter) by collecting water from the outflow valve at the base of the carboy with a glass syringe (fig. 4). Sample water (0.5 mL) was injected into a 10-mL head-space vial, sealed immediately with a Teflon-coated butyl stopper, and crimped. Samples were stored at 5 °C until the experiment was completed. All samples from a given experiment were analyzed on the same date by GC analysis of the head-space gas. The TCE concentration in the sampled water was back calculated using Henry's law and a partition coefficient of 0.007 cubic meters of atmosphere per mol (m³ atm mol⁻¹)(Washington, 1996). Loss-rate constants (m) for TCE were computed for each experimental series by fitting an exponential model (C=be^{-mt}) to the observed concentrations (C). Controls for the experiments on TCE loss from rhizosphere water consisted of carboys with a severed stem glued in the opening in place of the live seed-ling. The severed stem, approximately 12 in. long, was positioned above the water level in the carboy.

Statistical analyses were performed with the SAS system software package (SAS Institute Inc., Cary, NC). Analyses of variance tests were performed on log-normalized values to evaluate differences in diel and monthly measurements of TCE flux and CO_2 exchange. Unless otherwise noted, data summaries give the arithmetic mean and 95 percent confidence interval. Means with overlapping error bars indicate no significant difference (p=0.05).

The observed TCE flux for small and large carboys did not differ significantly, nor were there significant differences between the size and mass of seedlings grown in the different sized carboys. Hence, small- and large-carboy flux measurements were pooled in the statistical calculations. Control carboys without seedlings had significant TCE flux only for the August measurements. In this case, the mean flux from the controls was subtracted from the seedling mean. For the rest of the year, the flux from controls could not be computed because of insignificant loss of TCE in the dead controls.

The potential for transfer of TCE from soil to the atmosphere as a gas within the plants was examined by using an analytical model of oxygen diffusion in roots (Armstrong, 1968) and was modified to account for TCE. The model assumes that a network of air spaces exists within the plant between roots and the stem. The modeling approach is shown in table 3.

Table 3. Summary of the diffusion model for trichloroethene flux through internal air spaces within tree trunks

1. Diffusion (D_f) of TCE (μ mol s⁻¹) from roots to the atmosphere:

$$D_f = \frac{1}{r_d} (C_r - C_a)$$

 C_r = TCE concentration in the gas phase of roots C_a = TCE concentration in the atmosphere

ii. r_d = The non-metabolic resistance of roots (Armstrong, 1978):

$$r_d = \frac{L}{TED_{corr}A}$$

- L= diffusive path length; 30 cm
- T= toruosity factor (Jenson and others, 1967); 0.75
- E = fractional porosity of root segment (Yu and others, 1969); 0.15
- A= stem cross-sectional area; 4 cm^2

iii. D_{corr}= vapor diffusivity corrected for temperature:

$$D_{corr} = D \left(\frac{T_A}{293}\right)^{1.75}$$

D= TCE vapor diffusion coefficient^{Ψ}; 0.096 cm² s⁻¹ T_A = ambient temperature (^oK)

iv. Gas phase TCE in roots $(C_r)^*$:

$$C_r = \frac{TCE_w}{(1/k_h) \times RT_s}$$

 TCE_w = TCE concentration in Carboy water R = universal gas constant

v. k_h = Henrys' law constant adjusted for temperature (Armstrong, 1978):

$$k_h = e^{-5594\left(\frac{1}{T_s}\right) + 14.244}$$

vi. T_s = sinusoidal approximation of carboy substrate temperature (Grosse and others, 1993):

$$T_s = \overline{T_A} + \Delta T_A e^{\frac{-z}{d}} \cos\left(\frac{2\pi t}{p} - \frac{z}{d}\right)$$

 T_A = ambient temperature (°C) z = depth; 30 cm t = time (hrs)

vii. d= damping depth:

$$d = \left(\frac{pK}{\pi H_c}\right)^{\frac{1}{2}}$$

p = period; 24 hrs

- K= thermal conductivity coefficient for wet soil (Hook and Scholtens, 1978);
 - 2160 J hr⁻¹ m⁻¹ °C⁻¹
- H_c = volumetric heat capacity for a moist sandy loam (Hook and Scholtens, 1978); $2x 10^6 \text{ J m}^{-3} \text{ o}\text{C}^{-1}$

ψ Four orders of magnitude greater than the solution diffusivity (Lee and Chrysipolous, 1995) as suggested in Jones (1992).

* We have assumed that the resistance to TCE flux into the gas space of roots is negligible.

12 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Adsorption and Biodegradation Measurements

Four sediment samples were used to determine the TCE adsorption rate and biodegradation rate. Sediment sample Sed-1 was obtained from about 7 ft below the water table in a bog that normally contained standing water in the lower flood plain (fig. 2). The remaining sediment samples, Sed-2, Sed-3, and Sed-4, were obtained immediately below the water table by hand augering. Sample Sed-2 was from a periodically flooded forest in the lower flood plain, sample Sed-3 was from an upland forest, and sample Sed-4 was from a periodically flooded part of the upper flood plain. The samples were chosen to represent a variety of environments present in the study area.

The adsorption coefficient for TCE was determined using a modification of the method described in Schwarzenbach and Westall (1981). Approximately 5 grams (g) of aquifer material collected from each of the four sediment-sampling sites was placed in 10-mL serum vials. The vials were filled with solutions containing uniformly labeled [¹⁴C] TCE at concentrations of 15 to 1,500 μ g/L TCE. Vials were sealed without airspace using Teflon-coated butyl rubber stoppers. Vials were prepared in duplicate for each sediment at each test concentration. The final volume of solution in the adsorption vials was 7.4 ± 0.1 mL. Adsorption vials were vigorously shaken for 5 minutes and allowed to stand overnight.

Final dissolved concentrations of $[^{14}C]$ TCE were determined by removing 1 mL of solution from each vial and quantifying radiolabelled solute by liquid scintillation counting. The difference between final dissolved concentrations observed in adsorption vials and the concentration in the source solutions was attributed to adsorption.

The biodegradation analysis involved setting up microcosms, treating them with TCE, and monitoring TCE loss with time. Sediment (15 g) from each sample was anaerobically weighed into 36-mL serum vials in an anaerobic chamber (Coy Laboratories, Michigan) with a head space of nitrogen and hydrogen gas mixture (95:5, vol/vol) and sealed with thick butyl rubber stoppers. On removal from the anaerobic chamber, the head space of each vial was purged with a gas stream of nitrogen and carbon dioxide mixture (95:5) to remove residual hydrogen gas. The vials were amended with 2.5 mL of sterile anoxic water and 100 mg/L of TCE. The bottles also were amended with 6.67 millimolar (mM) glucose from an anoxic sterile stock solution as an electron donor for TCE dechlorination. All vials were vortexed for 1 minute to mix the samples. All sediment incubations were at 25 °C in the dark. Heat-killed controls were prepared similarly to the test sediments and autoclaved at 121 °C for 1 hour on 3 consecutive days.

Concentrations of PCE, TCE, and cDCE in 0.2-mL head-space samples, taken in nitrogen-flushed syringes, were determined by using gas chromatography with flame ionization detection and compared against freshly prepared standards. The head-space sample was directly injected into a Shimadzu GC (GC14-A).

HYDROGEOLOGY

The unconfined aquifer horizontal hydraulic conductivity ranges from approximately 21 to 65 ft/d beneath the TNX facility and the flood plains (Nichols, 1993; Nichols and others, 1995; Phifer and others, 1995). Data from a pilot hole drilled for this investigation (Westinghouse Savannah River Company, 1996) showed that the sediments below the water table near well TIR 1U were predominantly sandy, except for clayey or sandy clay layers from 21.5 to 24.5 ft and from 54 to 64 (bottom of the boring) ft below land surface (table 4).

Table 4. Lithologic log of pilot hole near well TIR 1U, TNXupper flood plain, Savannah River Site, S.C. (modified fromWestinghouse Savannah River Company, 1996.

Depth to bottom of interval (ft below land sur- face)	Lithology
4	CLAYEY SILT, with fine- to medium- grained sand
21.5	SAND, fine- to coarse-grained, with pebbles below 12 ft and thin (0.2 ft) clay layers at about 20-21.5 ft
23	SANDY CLAY
24.5	CLAY
40	SAND, fine- to medium-grained, poorly sorted
49	SILTY SAND, sand is fine- to medium- grained, becoming coarse-grained below 46 ft
54	CLAY, dark gray
59.5	CLAYEY SAND, fine- to medium- grained, 15 to 25 percent clay
64	CLAY, dark gray, very hard
(bottom of boring)	

The shallow ground water beneath the TNX flood plains is derived dominantly from local precipitation infiltration. Ground water is recharged in upland areas (such as in the TNX facility) and discharges into the Savannah River, a drainage ditch crossing the upper and lower flood plains, and through seeps in the lower flood plain.

A major mechanism of ground-water discharge in the area is by evapotranspiration. Several studies in the Savannah River complex have examined evapotranspiration rates. Investigations at the SRS radiological burial ground (Hubbard and Emslie, 1984; Hubbard, 1986) estimated the evapotranspiration rate at about 30 in/yr, or about 64 percent of the estimated precipitation. The value was based on estimates from water balance of stream basins, climatic estimates, and water balance of lysimeters. The studies found that evapotranspiration was higher (about 40 in/yr) in areas having deep-rooted pines trees than in areas of bare soil or shallow-rooted grasses (Hubbard, 1986). Maximum evapotranspiration was during July.

A study approximately 7 mi from the TNX facility, between Upper Three Runs Creek, Four Mile Creek, and McQueen Branch, showed that the total potential evapotranspiration for November 1, 1982, to May 19, 1984, was 52.81 in. (Parizek and Root, 1986). For March 1, 1983, to March 31, 1984, the total potential evapotranspiration was 43.03 in. Weekly average potential evapotranspiration rates varied from approximately 0.3 inch per week (in/week) during January to approximately 1.5 to 1.8 in/week during July. The study was done in an area vegetated dominantly by evergreen (pine) trees.

These values probably approximate evapotranspiration values at the TNX area. The dominant species in contaminated areas of the TNX flood plain include loblolly pine, baldcypress, oak, and sweetgum trees. A study in west-central Florida showed that evapotranspiration varied among vegetation types, but the difference between annual evapotranspiration from a pine flatwood environment (42 in/yr) and a baldcypress swamp environment (38 in/yr) was relatively small (Bidlake and others, 1993). This consideration, coupled with the relatively high range of evapotranspiration values measured elsewhere in the SRS facility suggests that the values measured elsewhere in the SRS facility bracket the evapotranspiration values characteristic of the TNX flood plain.

The depth of the rhizosphere hydraulic influence beneath land surface at the TNX flood plain probably varies relative to the depth of ground water. Thus, it is practical to define the depth of the rhizosphere influence relative to the mean annual water level. During October 1996-October 1997, the ground-water levels in the TNX flood plain at well TNX 10D ranged from 92.08 ft to 95.6 ft above sea level, with a mean of 93.45 ft. Land surface datum is approximately between 92 and 93 ft above sea level in the lower flood plain and approximately 96 to 100 ft above sea level in much of the upper flood plain. During the periods of lowest ground-water levels, approximately 1.4 ft below the mean water level, continuous measurements showed diel water-level fluctuations indicative of active evapotranspiration (fig. 5). Thus, the depth of evapotranspirative influence extended to at least 1.4 ft below the mean water table, or at least approximately 8 ft below land surface, at well TNX 10D during 1997.

Qualitative indications of ground-water discharge to the drainage ditch (fig. 1) can be seen in data from ditch-bed piezometers (table 5). Water-level differences between the ditch stage and the underlying ground water, as measured in ditch-bed piezometers



Figure 5. Evapotranspiration- (small-scale changes) and recharge-related (large-scale changes) water-table fluctuations at well TNX 16D during June 1997, TNX facility, Savannah River Site, S.C.

14 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

open at 2 feet below the ditch base, indicate a larger upward hydraulic gradient beneath the ditch reach crossing the upper flood plain than in the ditch reach crossing the lower flood plain. Large water-level differences were measured at sites CB245U, CB80U, and CB5U (0.37 to 0.6 ft upward hydraulic gradient). In the lower flood plain during May 1997 (sites CB50D, CB110D, and CB200D), the water-level difference was 0.15 ft or less (table 5). These data imply a larger potential for ground-water discharge to the ditch crossing the upper flood plain than to the ditch crossing the lower flood plain.

The vertical hydraulic gradient in the upper flood plain varies. During periods of high ground-water levels, such as March to early May 1997, the net hydraulic gradient at wells TIR 1L, TIR 1M, and TIR 1U was upward (fig. 6). These data imply that the upper flood plain was at or near a ground-water discharge zone. Standing water in parts of the upper flood plain that did not appear to be related to rainfall runoff during this time provide supporting evidence that ground water was seeping out of the ground. However, during periods of low ground-water levels, such as November to December 1996 and June to August 1997, the hydraulic gradient at those wells was downward (fig. 6). These data imply that during periods of low ground-water levels, the upper flood plain functions as a local recharge area.

Table 5. Differences in water-level measurements madeinside and outside of ditch-bed piezometers in thedrainage ditch, TNX facility, Sa vannah River Site, S.C.,May 23 and 27, 1997

[Water-level difference is the depth from the top of the piezometer to water inside the piezometer minus the depth to water outside the piezometer. Negative numbers mean a net upward gradient. All piezometers were open at a depth of 2 ft below the ditch base, except piezometer CB5UB, which was open at a depth of 4 ft; ---, data not collected]

Site ID	Water-level difference on May 23, 1997 (feet)	Water-level difference on May 27, 1997 (feet)	Water-level difference on August 12, 1997 (feet)		
CB245U	-0.52	-0.59			
CB80U	-0.37	-0.41			
CB5U	-0.57	-0.6	-0.52		
CB5UB	-0.71	-0.77			
CB50D	-0.06	-0.15	-0.26		
CB110D	-0.04	-0.05			
CB200D	-0.09	-0.06			

The potential for ground-water discharge to the lower flood plain can be seen in the water-level data collected from wells TNX 15D and TNX 16D, in the lower flood plain (fig. 1). Water-level measurements at well TNX 15D showed that the ground-water level in the well was at land surface in September 1996 and was above land surface (elevation of 92.5 ft) during March, April, and part of May 1997 (table 6). The water level at well TNX 16D was above land surface (elevation of



Figure 6. Water levels measured at nested wells TIR 1L, TIR 1M, and TIR 1U, October 1996 to August 1997, TNX facility, Savannah River Site, S.C.

Table 6. Water levels at selected wells in the upper and lower flood plains, TNX facility, Savannah River Site, S.C.

 September 1996 to January 1998

[ft, feet; ft. amsl, feet above mean sea level; DTW, depth to water from datum; ---, not available]

WELL	DATE	TIME	DATUM	DTW	ALTI- TUDE	WELL	DATE	ТІМЕ	DATUM	DTW	ALTI- TUDE
			(ft amsl)	(ft)	(ft. amsi)				(it anisi)	(11)	(ft. amsl)
TCM 1	5/27/97		99.21	6.81	92.40	TIR 2	5/27/97		101.28	9.2	92.08
TCM 1	8/12/97	8:34	99.21	6.89	92.32	TIR 2	8/12/97	9:10	101.28	9.6	91.68
TCM 2	5/27/97		99.02	5.97	93.05	TIR 2	1/14/98		101.28	6.54	94.74
TCM 2	8/12/97	8:32	99.02	6.5	92.52	TIR 2	1/16/98	12:40	101.28	5.98	95.30
TCM 3	5/27/97		99.42	6.35	93.07	TIR 3B	9/11/96	10:17	100.57	4.05	96.52
TCM 3	8/12/97	8:30	99.42	6.86	92.56	TIR 3B	10/7/96	10:23	100.57	4.45	96.12
TIR 1L	9/11/96	9:55	101.72	7.92	93.80	TIR 3B	11/12/96	9:46	100.57	4.64	95.93
TIR 1L	10/7/96	9:55	101.72	8.4	93.32	TIR 3B	12/12/96	8:23	100.57	5.3	95.27
TIR 1L	11/12/96	8:54	101.72	8.7	93.02	TIR 3B	3/3/97		100.57	3.46	97.11
TIR 1L	12/12/96	8:28	101.72	8.95	92.77	TIR 3B	5/27/97		100.57	5.57	95.00
TIR 1L	3/3/97		101.72	6.28	95.44	TIR 3B	8/12/97	8:20	100.57	6.34	94.23
TIR 1L	3/18/97	15:17	101.72	7.31	94.41	TNX 13D	5/1/97	11:42	94.90	2.24	92.66
TIR 1L	3/25/97	12:36	101.72	7.87	93.85	TNX 14D	9/11/96	10:09	92.80	0.42	92.38
TIR 1L	4/3/97	9:53	101.72	8.01	93.71	TNX 14D	10/7/96	10:15	92.80	0.53	92.27
TIR 1L	5/1/97	10:29	101.72	7.57	94.15	TNX 14D	11/12/96	9:41	92.80	0.6	92.20
TIR 1L	5/27/97		101.72	9.3	92.42	TNX 14D	3/25/97	12:33	92.80	0.09	92.71
TIR 1L	8/12/97	8:45	101.72	9.5	92.22	TNX 14D	4/3/97	10:02	92.80	0.21	92.59
TIR 1M	9/11/96	10:00	101.66	8.25	93.41	TNX 14D	5/1/97	11:32	97.38	4.45	92.93
TIR 1M	10/7/96	10:01	101.66	8.43	93.23	TNX 15D	9/11/96	10:06	93.10	0.6	92.50
TIR 1M	11/12/96	8:53	101.66	8.54	93.12	TNX 15D	10/7/96	10:19	93.10	0.73	92.37
TIR 1M	12/12/96	8:25	101.66	8.8	92.86	TNX 15D	11/12/96	9:40	93.10	0.85	92.25
TIR 1M	3/3/97		101.66	67	94 96	TNX 15D	12/12/96	8:30	93.10	0.96	92.14
TIR 1M	3/18/97	15.15	101.66	7 51	94 15	TNX 15D	3/3/97		93.10		>93.1
TIR 1M	3/25/97	12:37	101.66	8	93.66	TNX 15D	3/18/97	15:12	97.66	4.46	93.20
TIR 1M	4/3/97	9.55	101.66	8 18	93 48	TNX 15D	3/25/97	12:31	97.66	4.87	92.79
TIR 1M	5/1/97	10.28	101.66	8.04	93.62	TNX 15D	4/3/97	10:04	97.66	5	92.66
TIR 1M	5/27/97		101.66	8 94	92 72	TNX 15D	5/1/97	10:32	97.66	4.7	92.96
TIR 1M	8/12/97	8.42	101.66	9 37	92.72	TNX 15D	5/27/97		97.66	5.71	91.95
TIR 111	9/11/96	10:05	101.60	8 1 5	93 46	TNX 15D	8/12/97	9:03	93.10	1.41	91.69
TIR 1U	10/7/96	10:03	101.61	84	93 21	TNX 16D	9/11/96	10:11	93.40	1.37	92.03
TIR 1U	11/12/96	8.52	101.01	8.5	93.11	TNX 16D	10/7/96	10:20	93.40	1.51	91.89
TIR 1U	12/12/96	8.26	101.01	8.5	93.11	TNX 16D	11/12/96	9:42	93.40	1.6	91.80
TIR IU	3/3/97	0.20	101.61	6.63	94 98	TNX 16D	12/12/96	8:32	93.40	1.7	91.70
TIR 11	3/18/97	15.14	101.61	7 46	94 15	TNX 16D	3/3/97		93.40	Flowing	>93.4
TIR 1U	3/25/97	12.38	101.01	7.93	93.68	TNX 16D	3/18/97	15:22	93.40	0.69	92.71
TIR 1U	1/3/07	0.56	101.01	8 12	03.00	TNX 16D	3/25/97	12.30	93 40	1 16	92 24
	5/1/07	10.27	101.01	0.12	73.47 03.63	TNX 16D	4/3/97	10.06	93.40	1.26	92.14
	5/1/9/	10:27	101.01	7.90 0.00	95.05	TNX 16D	5/1/97	10:00	97.28	4.62	92.66
	9/12/191	9.40	101.01	0.09	92.12	TNX 16D	5/27/97		97.20	5 77	91 51
	8/12/97	8:40	101.01	8.33	93.20	TNX 16D	8/12/07	0.06	93.40	2.77	01 18
TIK 2	9/11/90	10:03	101.28	8.02 9.79	92.00	TNX 16D	1/14/98	9.00	97.78	2.22	94 48
TIR 2	10///96	10:11	101.28	8.78	92.50	TNY 16D	1/16/08	12.36	07.28	2.0	0/ 03
TIK 2	11/12/90	9:00	101.28	8.9	92.38	TNX 18D	5/1/07	11.50	92.10	0.25	01.85
TIK 2	12/12/90	8:29	101.28	9.1	92.18	TNY 10D	5/1/07	11.01	97.10	4 11	03.17
TIK 2	5/5/9/	15.10	101.28	0.9	94.38	TNY 200	5/1/07	11.47	03 50	0.07	07 52
TIK 2	3/18/97	13:13	101.28	7.91	93.37		10/7/06	10.16	101 70	87	02.55 02.00
TIK 2	5/25/97	12:28	101.28	8.38	92.90		5/27/07	10.10	101.70	0.7	93.00
TIR 2	4/3/9/	9:59	101.28	8.55	92.73	TNY OD	9/12/17/ 9/12/07	0.00	101.70	9.07	92.03 02.20
TIR 2	5/1/97	10:25	101.28	8.25	93.03	11NA 9D	0/12/9/	9:00	101.70	7.3	92.20

16 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina 92.7 ft) during part of March 1997 (table 6). These data support the findings of earlier work (Nichols and others, 1995) indicating that part of the shallow groundwater-flow system discharges upward into the lower flood plain. Continuous water-level-recording data shows that ground-water levels in well TNX 16D were also above land surface during May and December 1997 and January through March 1998 (fig. 7). Moreover, the hydrographs show that the ground-water level at well TNX 16D was higher than the Savannah River stage even when the Savannah River was in flood conditions and the ground surface at well TNX 16D was under river water (fig. 7). These data suggest that during periods of high ground-water levels, shallow ground water discharges upward through the lower flood plain even when inundated by the Savannah River at flood stage.

Ground-water levels at well TNX 16D were more than 1 ft below land surface during July through November 1997 (fig. 7). During these times, the lower flood plain was dry except for a few isolated shallow pools. These observations indicate that ground-water discharge to the lower flood plain at those times was minimal or localized in low-lying zones. However, ground-water levels remained higher than surfacewater levels in the drainage ditch, indicating that the drainage ditch remained a ground-water-discharge zone during periods of low ground-water levels (table 5). Thus, both the lower flood plain and the drainage ditch function as ground-water discharge zones during periods of high ground-water levels (above land surface at the lower flood plain), while the influence of the drainage ditch as a discharge zone is larger than that of the lower flood plain during periods of low ground-water levels. The temporal variations in locations of ground-water-discharge zones imply a corresponding difference in directions of ground-water flow. During periods of low ground-water levels, ground-water-flow paths would be expected to converge more strongly toward the drainage ditch than during periods of high ground-water levels.



Figure 7. Water levels at the Savannah River (Jackson gage adjusted to TNX area), well TNX 10D, and well TNX 16D, October 1996 to April 1998, TNX facility, Savannah River Site, S.C.

GROUND-WATER QUALITY

The dominant VOC contaminants beneath the upper and lower flood plains downgradient from the TNX facility between September 1996 and August 1997 were TCE, cDCE, and CT. The maximum concentrations were 796, 55, and 94.3 μ g/L, respectively (table 7). These values are somewhat higher than those reported in previous investigations partly because the 2-ft long well screens used in this investigation allowed the contamination to be closely bracketed. Chloroform was present at some sites at concentrations near the detection limit (table 7). Analyses also were run for several other VOC's, but concentrations of these were below detection limits (table 8). Nitrate concentrations in the ground water exceeded the USEPA Maximum Contaminant Level (MCL) of 45 mg/L (10 mg/L as N) (U.S. Environmental Protection Agency, 1996). The highest detected nitrate concentration was 87.8 mg/L (19.5 mg/L as N) at well TIR 1U in August 1997. Nitrate concentrations exceeding MCL's also were measured in water from wells TCM 3, TIR 3B, TNX 15D, and TNX 16D (table 9).

Analyses of water obtained from WWD samplers beneath the ditch-bed sediment showed that up to 200 µg/L of TCE discharged to the drainage ditch (table 10). The close match between TCE concentrations obtained using the WWD samplers and concentrations obtained using adjacent stainless-steel sampling points open at the same horizon supports the validity of the WWD sampler data (table 10). Concentrations of TCE in ground water discharging to the drainage ditch were highest at, and upstream from, the edge of the embankment separating the upper and lower flood plain (table 11, fig. 8). The interpretation is consistent with piezometer data showing that area to be the reach with the largest upward hydraulic gradient (table 5). Numerical modeling simulations also suggest that this reach is an area of probable contaminated ground-water discharge (Hamm, Aleman, and Shadday, 1997). Trichloroethene and cDCE were not detectable in WVD samplers downstream from the embankment (fig. 8), indicating that contaminant discharge to the drainage ditch was minimal or absent in that reach.

Moreover, surface-water grab samples from the drainage ditch near the embankment separating the upper and lower flood plains contained 8.3 and 10 μ g/L of TCE on July 23 and August 18, 1997, respectively, while samples collected upstream near the outfall contained less than 5 μ g/L. These data provide



DISTANCE, IN FEET, UPSTREAM (+) AND DOWNSTREAM (-) FROM THE EMBANKMENT BETWEEN THE UPPER AND LOWER FLOOD PLAINS

Figure 8. Concentrations of trichloroethene and *cis*-1,2-dichloroethene in water-to-vapor diffusion samplers beneath the drainage ditch, August 25, 1997, TNX facility, Savannah River Site, S.C.

18 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Table 7. Concentrations of selected organic compounds in ground water from observation wells in the TNX upper and lowerflood plains, Savannah River Site, S.C., September 1996 to August 1997 (Bill Pidcoe, Westinghouse Savannah RiverCompany, unpub. dat a, 1996-97)

 $[\mu g/L, micrograms per liter; WA, Roy F. Weston, Inc.; <, less than; ---, not analyzed; >L, off-scale high; J, estimated quantity; GE, General Engineering Laboratories; QS, QST Environmental; V, laboratory blanks contaminated; Q, holding time exceeded; EX, Emax Laboratories, Inc.; R'following well identifiers indicates field replicates]$

Well	Sampla	Lab	Carbon	Chloroform	Total organia	Trichoroethene	ais 1.2 disbloresthere
identifier	date	coded	tetrachloride	(ua/L)	carbon (ug/L)	(μg/L)	cis-1,2-alchioroethene (μα/L)
TCM 1	05/27/07		<u>(μg/L)</u>		<1.000		
TCM 1	03/27/97	WΔ	()	<5	<1,000	35	5
TCM 2	05/27/07	WΔ	31	<5	<1,000	244	41
TCM 2	05/27/07	WA	20	<5	1 710	156	24
TCM 3	08/25/07	WA	13	6	2 020	136	27
	00/11/06	WA WA	15	-5	5,050	130	
TIR IL	10/09/11/90	WA WA	<5	<5	1,250	<5	
	10/08/96	WA	<5	<)	<1,000	<)	
TIR IL	11/12/96	WA	<)	<)	<1,000	<>	
TIR IL	12/12/96	WA	<5	<)	<1,000	<>	 ·
	12/12/96	WA	<>	<>>			
	12/12/96	WA	<>	<>		<>	
TIR IL	03/03/97	WA	<>>	<>>	<1,000	<>	
	05/2//9/	WA	<>>	<>		<>	
TIR IL	05/27/97	WA	<>	<>	<1,000	<>	
TIR IL	05/27/97	WA	<5	<5			
TIR 1L	08/25/97	WA	<5	<5	1,170	<5	<5
TIR 1LR	08/25/97	WA	<5	<5	1,370	<5	<5
TIR 1M	10/07/96	WA	<5	<5	<1,000	34	
TIR 1M	09/11/96	WA	<5	<5	<1,000	26	
TIR 1M	10/07/96	GE	6	<2	<1,000	39	
TIR 1M	10/07/96	WA	<5	<5			
TIR 1M	10/07/96	WA	5	<5		32	
TIR 1M	10/07/96	WA	5	<5	<1,000	34	
TIR 1M	11/12/96	WA	5	<5	<1,000	35	
TIR 1M	12/12/96	WA	5	<5	<1,000	38	
TIR 1M	03/03/97	WA	6	<5	<1.000	38	
TIR 1M	05/27/97	WA	8	<5	<1.000	48	
TIR 1M	08/25/97	WA	8	<5	1.170	47	8
TIR 1MR	10/07/96	GE	5	<2	<1.000	37	
TIR 1MR	10/07/96	GE			<1.000		
TIR 1U	09/11/96	WA	7	<5	<1 000	63	
TIR IU	10/07/96	WA	8.1	<5		74 J	
TIR IU	10/07/96	WA	91	<5	<1.000	68 I	
TIR IU	11/12/96	WA	7	<5	<1,000	70	
TIR IU	12/12/96	WA	7	<5	<1,000	80	
TIR IU	03/03/97	OS	ģ	~ 5	<1,000	82	
TIR IU	03/03/97	WA	9	<5	<1,000	89	
TIR IU	05/03/27	WΔ	6	<5	<1,000	82	
	08/25/07	WA	0 7	<5	<1,000	75	6
	03/03/07	05	0	~25	<1,000	83	0
	03/03/97	QS WA	9	<2.5	<1,000	85	
	00/11/06	WA WA	8 7	<	<1,000	8J 20	
	10/07/06	WA WA	12	<5	<1,000	59	
TIR 2	10/07/96	WA	12	<>	<1,000	54	
TIR 2	11/12/96	GE	14	<2	1,410 V	57	
TIR 2	11/12/96	GE	15	<2	<1,000	56	
TIR 2	11/12/96	WA	13	<5	2,240	56	
TIR 2	11/12/96	WA	13	<5	<1,000	55	
TIR 2	12/12/96	WA	15	<5	<1,000	60	
TIR 2	03/03/97	WA	24	<5	<1,000	78	
TIR 2	05/27/97	WA	15	<5	<1,000	73	
TIR 2	08/25/97	WA	19	<5	1,080	68	16
TIR 3B	09/11/96	WA	91	6	<1,000	796	

Table 7. Concentrations of selected organic compounds in ground water from observation wells in the TNX upper and low	er
flood plains, Savannah River Site, S.C., September 1996 to August 1997 (Bill Pidcoe, Westinghouse Savannah River	
Company, unpub. dat a, 1996-97)—Continued	

Well	Sample	Lab	Carbon tetrachloride	Chloroform	Total organic	Trichoroethene	cis-1,2-dichloroethene
identifier	date	coded	(μg/L)	(μg/L)	carbon (μg/L)	(µ 9/ Ľ)	(μ g/L)
TIR 3B	09/11/96	WA				>L	
TIR 3B	10/07/96	WA				627 J	
TIR 3B	10/07/96	WA	94.3 J	<5	<1,000	> L	
TIR 3B	11/12/96	WA	77	<5	<1,000	698	
TIR 3B	11/12/96	WA				> L	
TIR 3B	12/12/96	GE	79	6	<1,000	746	
TIR 3B	12/12/96	GE			<1,000		
TIR 3B	12/12/96	WA	83	<5	<1,000	> L	
TIR 3B	12/12/96	WA				717	
TIR 3B	03/03/97	WA	43	<5	<1,000	> L	
TIR 3B	03/03/97	WA			<1,000	480	
TIR 3B	05/27/97	WA				> L	
TIR 3B	05/27/97	WA	50	<5	<1,000	470	
TIR 3B	08/25/97	WA	58 J	<5	<1,000	> L	55 J
TIR 3BR	12/12/96	GE	68	5	<1,000	499 J,Q	
TIR 3BR	12/12/96	WA				> L	
TIR 3BR	12/12/96	WA	86	<5	<1,000	718	
TNX 9D	08/30/96	WA	<5	<5	<1,000	<5	
TNX 9D	09/11/96	WA	<5	<5	<1,000	<5	
TNX 9D	09/13/96	GE	<2	<2	2.050	<5	
TNX 9D	09/13/96	WA	<5	<5	<1.000	<5	
TNX 9D	10/07/96	WA	<5	<5	<1.000 0	<5	
TNX 9D	10/29/96	WA	<1	<1		<1	
TNX 9D	11/12/96	WA	<5	<1		<1	
TNX 9D	11/12/96	WA	<1	<5	<1.000	<5	
TNX 9D	11/21/96	WA	<5	<5	<1,000	~5	
TNX 9D	12/03/96	WΔ	<1	<1	<1,000	<1	
TNX 9D	12/12/96	WΔ	<5	<5	<1 000	<5	
TNY OD	05/27/97	FX	<5	<5	<10.000	<5	
TNY OD	05/27/07	WA	<5	<5	<1,000	<5	
TNY OD	05/27/07	WA	$\langle \rangle$	<5	<1,000		
TNY OD	08/25/07	WA	-5	~5	<1.000	-5	
TNX 9D	05/27/07	EV	<5	<5	<10,000	<5	
TNX 9DR	05/27/07	WA	<5	<5	<1,000	<	
TNX 9DR	00/12/06	CE	~	\sim	1,000	\sim	
TNA 9DR	09/13/90		<2	~5	-1,000	<2	
TINA 9DR	09/13/90	WA WA	<	<5	<1,000	25	
TNA ISD	09/11/90	WA WA	<5	<5	<1,000	21	
TNX ISD	10/07/06	WA	<5	<5	<1,000	20	
TINA ISD	10/07/96	WA	<5	<5	<1,000	29	
INX ISD	11/12/90	WA	<)	<)	<1,000	24	
TNX 15D	11/22/96	WA	<5	<5	<1,000	22	
TNX 15D	12/12/96	WA	<5	<5	<1,000	28	
TNX 15D	03/03/97	WA	<5	<5	<1,000	23	
TNX 15D	05/27/97	WA	<5	<5	<1,000	24	
TNX 15D	08/25/97	WA	<5	<5	<1,000	25	<5
TNX 16D	09/11/96	WA	<5	<5	<1,000	48	
TNX 16D	09/11/96	WA			<1,000		
TNX 16D	09/12/96	WA	<5	<5	<1,000	51	
TNX 16D	10/07/96	WA	<5	<5	<1,000	51	
TNX 16D	11/12/96	WA	<5	<5	1,010	46	
TNX 16D	11/25/96	WA	<5	<5	<1,000	38	
TNX 16D	12/12/96	WA	<5	<5	<1,000	46	
TNX 16D	03/03/97	WA	<5	<5	<1,000	45	
TNX 16D	05/27/97	WA	<5	<5	1,100	43	
TNX 16D	08/25/97	WA	<5	<5	1,170	36	<5

20 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina **Table 8.** Organic compounds analyzed but not detected in ground water from observation wells, TNX flood plain,Savannah River Site, S.C., September 1996 to August 1997

[µg/L, micrograms per liter]

Compound	Detection limit (µg/L)	Compound	Detection limit (µg/L)
1,1,1-Trichloroethane	5	cis-1,3-Dichloropropene	5
1,1,2,2-Tetrachloroethane	5	Dibromochloromethane	5
1,1,2-Trichloroethane	5	Ethylbenzene	5
1,1-Dichloroethane	5	Methyl bromide	10
1,1-Dichloroethylene	5	Methyl chloride	10
1,2-Dichloropropane	5	Methylene chloride ¹	5
2-Choroethyl vinyl ether	10	Tetrachloroethene	5
Benzene	5	Toluene	5
Bromodichloromethane	5	trans-1,2-Dichloroethene	5
Bromoform	5	trans-1,3-Dichloropropene	5
Chlorobenzene 5		Trichlorofluoromethane	5
Chloroethane	10	Vinyl chloride	10

¹Although some analyses for methylene chloride were greater than the detection limit methlene chloride also was present in laboratory blanks for those samples.

further evidence that contaminated ground water discharges to the drainage ditch. Once in the surface water, however, volatilization appears to be an effective removal mechanism for TCE. On August 18, 1997, a surface-water grab sample collected from site CB184D (fig. 2) in a reach that showed obvious downstream transport (no dilution from mixing with Savannah River water) contained less than 5 μ g/L of TCE.

The shallow ground water (less than about 25 ft below land surface) beneath the TNX upper flood plain is dominantly aerobic (table 12). At deeper wells, such as wells TIR 1L and TCM-1, the DO content was less than 1 mg/L, and sometimes less than 0.2 mg/L. These data imply that local recharge is sufficient to maintain aerobic conditions in the shallow part of the flow system. The DO concentrations in the deeper flow system (well TIR 1L) are lower than in the shallow system (table 12), probably as a result of microbial respiration or coprecipitation of oxygen as metal oxides. The high concentrations of sulfate (greater than 40 mg/L) in the deeper ground water at well TIR 1L (table 13) imply that methanogenic conditions do not predominate in ground water sampled by the wells. The data indicate that anaerobic conditions favorable to TCE reductive dechlorination do not occur in the most contaminated horizons.

The shallow ground water at wells TNX 15D and TNX 16D, in the lower flood plain, had lower DO con-

centrations (typically less than 1.5 mg/L) than the shallow ground water beneath the upper flood plain (typically greater than 4 mg/L) (table 12). These data imply that the ground water at wells TNX 15D and TNX 16D included water derived from upward movement of deeper, less oxygenated, ground water. The ground water at those wells contained increased concentrations of DO (greater than 3 mg/L) during March 1997 at a time when land surface at those wells was inundated by the flood stage of the Savannah River. It is unlikely that the sampled water at wells TNX 15D and TNX 16D during March 1997 represented leakage of Savannah River water along the well casing because the water levels in the wells were higher than the Savannah River stage, indicating a net upward hydraulic potential. It is more probable that the increased DO during March 1997 was caused by increased recharge from nearby rainfall infiltration.

Data from a series of WVD samplers placed along traverses in the upper and lower flood plains (fig. 2) implied that the distribution of TCE varied temporally. In April 1997, TCE was present in the shallow ground water (about 1 to 2 ft below the water table) at several locations along the downgradient edge of the low escarpment separating the upper and lower flood plains (table 14). By September 1997, TCE was not detected in diffusion samplers along that same traverse or along a traverse in the upper flood plain (fig. 2). A Table 9. Concentrations of selected nitrogen compounds and dissolved solids in ground water from observation wellsin the TNX upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997 (Bill Pidcoe,Westinghouse Savannah River Company, written commun., 1996-98)

N, nitrogen; $\mu g/L$, micrograms per liter; WA, Roy F. Weston, Inc.; ---, not analyzed; <, less than; J, estimated quantity; Q, holding time exceeded; V, laboratory blanks contaminated; GE, General Engineering Laboratories; QS, QST Environmental; EX, Emax Laboratories, Inc.; 'R' following well identifiers indicates field replicates]

Well identifier	Sample date	Lab code	Ammonia (μg/L)	Ammonia nitrogen (µg/L)	Nitrite as N (µg/L)	Nitrate as N (μg/L)	Dissolved solids (µg/L)
TCM 1	05/27/97	WA					59,000
TCM 1	08/25/97	WA	<122		<20	350 J,Q,V	
TCM 2	05/27/97	WA					71,000
TCM 2	08/25/97	WA	<122		<20	8,580 J,Q,V	
TCM 3	05/27/97	WA			·		114,000
TCM 3	08/25/97	WA	<122		<20 Q	12,400 J.O.V	
TIR 1L	09/11/96	WA	70 V		<50 O	<20	
TIR 1L	09/11/96	WA	75 V		`		
TIR 1L	10/08/96	WA	<50		<50 O	90	
TIR 1L	11/12/96	WA			<50		
TIR 1L	11/12/96	WA	<122		<50	184 V	
TIR 1L	12/12/96	WA			<50.0		
TIR 1L	12/12/96	WA	<122		<50	<20	
TIR 1L	03/03/97	WA	<122		<50 0	<20	
TIR 1L	05/27/97	WA	<122		<20 Q	105 LO V	90.000
TIR 1L	08/25/97	WA	<122		<20	59 I O V	
	08/25/97	WΔ	<122		<20	~20	-
TIR ILK	00/11/96	WΔ			\20	6 400	
TIR IM	09/11/90	WΔ	~50		<50.0	6 380	
	10/07/06	CE CE	<50	~50	<50 Q	~10	
TID 1M	10/07/06	WA	~50	<50	<50.0	6 450	
	10/07/90	WA WA	<50		<50 Q	6,450	
	10/07/90	WA	<50		<50 Q	0,200	
TIR IM TID 1M	10/07/90	WA WA	<50 160 V		<50 Q	 6 050 V	
TIR IM	11/12/90	WA	100 v		<50	0,930 V	
TIR IM	12/12/90	WA	<122		<50 Q	127 2 200 M	
TIR IM	03/03/97	WA	<122		<50 Q	3,290 V	
TIR IM	05/27/97	WA	<122		<20 Q	5,030 J,Q,V	
TIR IM	08/25/97	WA	<122		<20	7,700 J,Q,V	
TIR IMR	10/07/96	GE		<50	<125	6,140	
	10/07/96	GE		<50	<125	6,110	
TIR IU	09/11/96	WA	<50		<50 Q	16,600	
TIR IU	10/07/96	WA	<50		<50 Q	16,000	
TIR 10	11/12/96	WA	<122		<50	17,400 V	
TIR 1U	12/12/96	WA				17,400	
TIR 1U	12/12/96	WA	<122		<50 Q	17,400	
TIR 1U	03/03/97	QS		<50	<100 Q	14,700 J,Q	
TIR 1U	03/03/97	WA	<122		<50 Q	9,280 V	
TIR 1U	05/27/97	WA	<122		<20 Q	14,300 J,Q,V	109,000
TIR 1U	05/27/97	WA	<122				
TIR 1U	08/25/97	WA	<122		<20	19,500 J,Q,V	
TIR 1UR	03/03/97	QS		<50	<100 Q	14,900 J,Q	
TIR 1UR	03/03/97	WA	<122	<50	<50 Q	10,600 V	
TIR 2	09/11/96	WA	<50		<50 Q	4,350	
TIR 2	10/07/96	WA	<50 Q		<50	4,140	
TIR 2	11/12/96	GE		<50	2,040	3,690 J,Q	
TIR 2	11/12/96	GE		<50	2,690	3,680 J,Q	
TIR 2	11/12/96	GE			2,900	3,730 J,Q	
TIR 2	11/12/96	WA	<122		<50	3,940 V	
TIR 2	11/12/96	WA	<122		<50	3,780 V	
TIR 2	12/12/96	WA	<122		<50 O	<20	
TIR 2	03/03/97	WA	<122		<50 Q	2,100 V	

22 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina **Table 9.** Concentrations of selected nitrogen compounds and dissolved solids in ground water from observation wellsin the TNX upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997 (Bill Pidcoe,Westinghouse Savannah River Company, written commun., 1996-98)—Continued

		l ah	Ammonia	Ammonia	Nitrite as N	Nitrate as N	Dissolved solids
Well identifier	Sample date	code	(ug/L)	nitrogen	(u a/L)	(ug/L)	(u a/L)
			(~3/ -/	(μ g/L)	((+3)	(r·3·-/
TIR 2	08/25/97	WA	<122		<20	3,500 J,Q,V	
TIR 3B	09/11/96	WA	<50		<50 Q	10,400	
TIR 3B	10/07/96	WA	<50		<50 Q	9,320	
TIR 3B	11/12/96	WA	<122		<50	9,680 V	
TIR 3B	12/12/96	GE		<50	<5	9,510	
TIR 3B	12/12/96	GE		<50	<5	9,430	
TIR 3B	12/12/96	WA	<122		<50 Q	619	
TIR 3B	03/03/97	WA	<122		<50 Q	6,220 V	
TIR 3B	05/27/97	WA	<122		<20 Q	11,300 J,Q,V	79,000
TIR 3B	08/25/97	WA	<122		<20	11,700 J,Q,V	
TIR 3BR	12/12/96	GE		<50	<5	3,810	
TIR 3BR	12/12/96	WA	<122		<50 Q	514	
TNX 9D	08/30/96	WA			`	1	100.000
TNX 9D	09/11/96	WA			<50 O		
TNX 9D	09/11/96	WA	<50		<50 0	439	
TNX 9D	09/13/96	GE		<50	<50	1 030 1 0	
TNX 9D	09/13/96	WA	<50		~500	1,000 0,0	
TNX 9D	09/13/96	WΔ	<50		<50 Q	1,200	
TNY OD	10/07/06	WA	<50			712	
TNY OD	10/07/06	WA	<50		~50.0	715	
TNX 9D	10/07/90	WA	102 V		<50 Q	1 020 V	
TNA 9D	11/12/90	WA WA	195 v		<50	1,020 V	77.000
TNX 9D	11/21/90	WA					//,000
TNX 9D	12/12/96	WA	<122		<50 Q	<20	
INX 9D	05/27/97	EX		<100			20,000
TNX 9D	05/27/97	EX		<100			25,000
TNX 9D	05/27/97	WA					82,000
TNX 9D	05/27/97	WA	<122		<20 Q	1,370 J,Q,V	90,000
TNX 9D	08/25/97	WA	<122		<20	465 J,Q,V	
TNX 9DR	09/13/96	GE		<50			
TNX 9DR	09/13/96	GE		<50	<50 Q	976 J,Q	
TNX 9DR	09/13/96	WA	<50		<50 Q	1,240	
TNX 9DR	05/27/97	EX		<100			15,000
TNX 9DR	05/27/97	WA	<122		<20 Q	779 J,Q,V	85,000
TNX 15D	09/11/96	WA	<50		<50 Q	12,500	
TNX 15D	09/12/96	WA			`		129.000
TNX 15D	10/07/96	WA	<50		<50 O	11.500	,
TNX 15D	11/12/96	WA	<122		<50	11.800 V	
TNX 15D	11/22/96	WA					179.000 V
TNX 15D	12/12/96	WA	<122		<50.0	617	
TNX 15D	03/03/97	WA	<122		<50 Q	5 700 V	98.000
TNX 15D	05/27/97	WΔ	<122		<20 Q	9760 LO V	90,000
TNY 15D	05/27/07	W/A			120 Q	9,700 J,Q,V	<i>))</i> ,000
TNY 15D	09/25/07	WA WA	~122		-20	10 600 I O V	
TNX 15D	00/11/06		<122		<20	16,000 J,Q,V	
TNA 10D	09/11/90	WA	<30		<30 Q	10,000	
TINA TOD	09/12/90	WA					140,000
TNX I6D	10/07/96	WA	<50		<50 Q	15,100	
TNX 16D	11/12/96	WA	<122			13,500 V	
TNX 16D	11/12/96	WA	<122		<50	13,900 V	
TNX 16D	11/25/96	WA			·		126,000
TNX 16D	12/12/96	WA	<122		<50 Q	6,880	
TNX 16D	03/03/97	WA					100,000
TNX 16D	03/03/97	WA	<122		<50 Q	7,350 V	101,000
TNX 16D	05/27/97	WA	<122		<20 Q	12,400 J,Q,V	112,000
TNX 16D	08/25/97	WA	<122		<20	12,000 J,Q,V	

Ground-Water Quality 23

Table 10. Comparison of *cis*-1,2-dichloroethene and trichloroethene concentrations obtained by using water-to-water and water-to-vapor diffusion samplers, and a stainless-steel sampling point beneath the drainage ditch, May to September 1997, TNX facility, Savan nah River Site, S.C.

	Water-to-wa	ter diffusion	Stainle	ss-steel	Water-to-va	por diffusion
Site Location	sam	pler	samplii	ng point	san	npler
(fig 1)	<i>c</i> DCE	TCE	<i>c</i> DCE	TCE	CDCE	TCE
("g. ")	μ g/L in	μ g/L in	μ g/L in	μ g/L in	ppb as	ppb as
	water	water	water	water	vapor	vapor
	Test	1: Installed on	5/16/97 and Ro	emoved on 5/2.	3/97	
CB80u	6	200			230	13,020
CB5U	<5	58			90	2,150
CB5U rep	<5	59			110	2,620
CB50D	<5	<5			<20	<20
CB110D	<5	<5			<20	<20
CB590D	<5	<5			<20	<20
	Test	2: Installed on :	5/23/97 and R	emoved on 5/2'	7/97	
CB80U	<5	188			174	7,230
CB5U	15	156			900	9,190
CB5U rep	12	145			640	7,410
CB50D	<5	<5			<20	<20
CB110D	<5	<5			<20	<20
CB590D	<5	<5			<20	<20
	Tes	t 3: Installed on	9/9/97 and Re	moved on 9/17	/97	
CB5U	22.7	148	15.2	147	612	7,557
CB5U rep	27.3	· 141	12.6	131		

[cDCE, cis-1,2-dichloroethene; TCE, trichloroethene; $\mu g/L$, micrograms per liter; ppb, parts per billion; ---, analysis not done; rep, replicate sample; sites 1 and 6 were piezometer locations only, no samples were collected]

series of diffusion samplers placed at depths of 1.5, 3, 4, 5, and 6 ft below land surface between wells TNX 15D and TNX 16D also showed the presence of TCE during April 1997 (with higher concentrations at 6 ft below ground than at shallower horizons near the water table) and the absence of TCE during September 1997.

Further information regarding the distribution of ground-water contamination was derived by examining the VOC content of tree cores collected in the flood plain. *Cis*-1,2-dichloroethene was detected in cores from several baldcypress trees growing in the area of cDCE-contaminated ground water. The area where cDCE was detected in baldcypress trees (fig. 9) was along a ground-water-flow path from the former seepage basin (fig. 9) and the burying ground (fig. 1) and coincided with areas where cDCE was detected in ground water. The data strongly suggest that the cDCE in tree trunks is derived from the contaminated ground water originating from the direction of the former seep-

age basin and the burying ground.

Trichloroethene also was detected in baldcypress trunks growing in the area of TCE contaminated ground water downgradient from the former seepage basin (fig. 10) and the burying ground (fig. 1). Further, trichloroethene was present in leaves from trees growing in ground-water contaminated areas. The distribution of baldcypress containing TCE in xylem was more widespread than the distribution of baldcypress containing cDCE. Moreover, TCE also was detected in tree 78 (fig. 3) and the neighboring trees farther south than the flow path from the former seepage basin (fig. 10). These data suggest a second plume of TCE in the aquifer. Although no data were collected from well TNX 26D during 1997-98, 41 to 84 nmol/L of TCE was detected in ground water at the well during 1996 (William Pidcoe, Westinghouse Savannah River Company, written commun., 1998), supporting the hypothesis that the spatial distribution of TCE among baldcypress sam-

24 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina Table 11. Trichloroethene and cis-1,2-dichloroethene concentrationsin water-to-vapor diffusion samplers beneath the drainage ditch, TNXfacility, Savannah River Site, S.C., August 1997

[TCE, trichloroethene; *c*DCE, *cis*-1,2-dichloroethene; ppb, parts per billion; rep, replicate]

Somplor iden	Data	Dete	Dava	TCE	CDCE
tification	installed		elansed	(ppb as	(ppb as
			ciapoca	vapor)	vapor)
CB295D	4/9/97	8/25/97	138	<11	<11
CB245D	4/9/97	8/25/97	138	<11	<11
CB218D	4/9/97	8/25/97	138	<11	<11
CB200D	4/9/97	8/25/97	138	<11	<11
CB184D	4/9/97	8/25/97	138	<11	<11
CB170D	4/9/97	8/25/97	138	<11	<11
CB155D	4/9/97	8/25/97	138	<11	<11
CB140D	4/9/97	8/25/97	138	<11	<11
CB125D	4/9/97	8/25/97	138	<11	<11
CB110D	4/9/97	8/25/97	138	<11	<11
CB95D	4/9/97	8/25/97	138	<11	<11
CB80D	4/9/97	8/25/97	138	<11	<11
CB50D	4/9/97	8/25/97	138	<11	<11
CB35D	4/9/97	8/25/97	138	<11	<11
CB5U	4/9/97	8/25/97	138	160	13
CB20U	4/16/97	8/25/97	131	344	24
CB35U	4/16/97	8/25/97	131	163	<11
CB35U (rep)	4/16/97	8/25/97	131	179	<11
CB65U	4/16/97	8/25/97	131	140	<11
CB80U	4/16/97	8/25/97	131	123	<11
CB95U	4/16/97	8/25/97	131	71	<11
CB110U	4/16/97	8/25/97	131	<11	<11
CB125U	4/16/97	8/25/97	131	66	<11
CB140U	4/16/97	8/25/97	131	98	<11
CB155U	4/16/97	8/25/97	131	25	<11
CB166U	6/19/97	8/25/97	67	<11	<11
CB215U	4/16/97	8/25/97	131	<11	<11
CB230U	4/16/97	8/25/97	131	<11	<11
CB245U	4/7/97	8/25/97	140	<11	<11
CB245U (rep)	4/16/97	8/25/97	131	<11	<11
CB260U	4/17/97	8/25/97	130	<11	<11
CB275U	4/16/97	8/25/97	131	<11	<11
CB290U	4/16/97	8/25/97	131	<11	<11
CB325U	4/9/97	8/25/97	138	<11	<11
CB340U	4/16/97	8/25/97	131	<11	<11

pled across the area reflects the distribution of TCE in the shallow aquifer.

NATURAL ATTENUATION POTENTIAL OF CHLORINATED VOLATILE ORGANIC COMPOUNDS

A variety of processes were evaluated as part of this investigation to determine their potential to natu-

rally attenuate the ground-water contamination at the TNX facility. As will be shown, advective/ diffusive uptake of ground-water contaminants by flood-plain vegetation and adsorption onto organic-rich aquifer sediment remove a large amount of the shallow ground-water contamination. Biodegradation of trichloroethene does not appear to be an effective removal or attenuation process in the upper flood-plain sediments, although some biodegradation may occur in lower flood-plain sediments. However, a conservative ground-water solute-transport model suggests that the rapid ground-water flow rate beneath the flood plains transports the contaminants too quickly for these processes to prevent contaminant discharge to the Savannah River.

Botanical Processes

The use of vegetation to assist in aquifer remediation has received increasing attention for a variety of reasons. Plants can remove contaminants from the subsurface by direct uptake and degradation (Briggs and others, 1982; McCrady and others, 1987; Newman and others, 1997; Schnabel and others, 1997; Strand and others, 1995), evapotranspiration of volatile contaminants to the atmosphere (McFarlane and others, 1990; Newman and others, 1997; Tollsten and Muller, 1996), binding contaminants to plant tissue (Newman and others, 1997; Schnabel and others, 1997; Strand and others, 1995), enhancing microbial growth and contaminant biodegradation in the rhizosphere by transferring oxygen to the root zone (Anderson and Walton, 1989; Jordahl and others, 1997; Walton and Anderson, 1990), allowing aerobic mineralization of oxidizable organic compounds (Shimp and others, 1993), and releasing root exudates that bacteria can metabolize (Schnoor and others, 1995). Direct uptake of contaminants is controlled by a variety of factors, but, in general, moderately hydrophobic organic compounds (octanol-water coefficient, $\log K_{ow} = 0.5-3$), such as TCE and cDCE, readily enter vegetation evapotranspiration streams (Schnoor and others, 1995; Anderson and Walton, 1995).

Another biophysical process for mass transport that may be important for VOC's is diffusive transport through the air space of root and

 Table 12. Field-measured water-quality constituents and properties in ground water from observation wells in the TNX upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997

 $[mg/L, milligrams per liter; H_2S, hydrogen sulfide; nM, nanomolar = nanomoles per liter; su, standard units; C, Celsius; <math>\mu$ S/cm, microsiemens per centimeter; CaCO₃, calcium carbonate; NTU, nephelometric turbidity units; ---, not analyzed or recorded; >, greater than; values for pH, temperature, specific conductance, titrated alkalinity, and turbidity measured by RCS Environmental Services]

Well identifica- tion	Date	Time	Dissolved oxygen (mg/L)	Total sulfide as H ₂ S (mg/L)	Ferrous iron (mg/L)	Hydrogen (nM)	pH (su)	Tempera- ture (degrees C)	Specific conduc- tance (µS/cm)	Total alka- linity as CaCO ₃ (mg/L)	Turbid- ity (NTU)
TCM 1	05/27/97	1042	0.20	0.1	0.49	0.47	5.2	20	68	5	0.3
TCM 1	08/12/97	1015	<0.1	0.3	0.34	0.5	4.8	20	70	<1	0.3
TCM 1	08/25/97	1029	0.2	<0.1	0.31		5.4	20	58	5	1.4
TCM 2	05/27/97	1050	2.69				4.8	20	100	2	1.3
TCM 2	08/12/97	1036	>1				4.8	20	120	<1	1.3
TCM 2	08/25/97	1001	>1				5.2	20	120	8	0.8
TCM 3	05/27/97	1104	2.25				5.2	20	140	12	9.2
TCM 3	08/12/97	1053	>1				5.2	20	200	16	6.8
TCM 3	08/25/97	946	0.9				5.6	20	220	16	5.8
TIR 1L	09/11/96	1059	0.83	0.6	0.75	17	5.2	24	180	4	1.4
TIR 1L	10/07/96	1356	0.45	0.4	0.55	0.90	5.4	22	180		6.9
TIR 1L	11/12/96	1433	0.34	<0.1	0.23	1.0	5.0	23	160	1	0.9
TIR 1L	12/12/96	1230	0.34	0.5	0.49	3.1	4.8	25	150	1	0.6
TIR 1L	03/03/97	1500	Trace	<0.1	0.32		4.6	26	180	5	0.8
TIR 1L	05/27/97	1316	0.11	<0.1	0.27	0.70	5.0	21	120	3	1.5
TIR 1L	08/12/97	937	<0.1	<0.1	0.36	15.2	4.8	20	160	<1	0.7
TIR 1L	08/25/97	856	0.2	<0.1	0.38		5	19	120	5	3.7
TIR 1M	09/11/96	1201	6.44				5.2	24	100	2	2.2
TIR 1M	10/07/96	1117	6.30				4.8	22	100	1	0.2
TIR 1M	11/12/96	1411	5.81				5.0	22	100	1	0.3
TIR 1M	12/12/96	1254	>2				4.8	25	100	1	0.5
TIR 1M	03/03/97	1032	6.10				4.4	25	86	<1	0.5
TIR 1M	05/27/97	1255	5.96				4.4	22	86	<1	0.4
TIR 1M	08/12/97	932	>1				4	22	80	1	4.2
TIR 1M	08/25/97	906	>1				4.8	19	100	3	0.8
TIR 1U	09/11/96	1221	4.89				4.2	25	180	<1	2.7
TIR 1U	10/07/96	1300	4.24				4.4	23	180	<1	1.3
TIR 1U	11/12/96	1347	4.31				4.2	22	200	<1	0.9
TIR 1U	12/12/96	1318					4.2	25	200	<1	0.2
TIR IU	03/03/97	953	7.60				4.0	25	160	<1	2.4
TIR 1U	05/27/97	1329	4.00				4.4	20	180	<1	0.5
TIR 1U	08/12/97	923	>1				4.4	20	200	<1	7.3
TIR 1U	08/25/97	916	>1				4.4	19	200	5	0.3
TIR 2	09/11/96	1306	4.82				4.6	24	92	<1	4.2
TIR 2	10/07/96	1708	5.27		,		4.6	22	88	<1	0.5
TIR 2	11/12/96	1019	6.01				4.0	23	88	<1	0.5
TIR 2	12/12/96	1055	5.52				4.2	24	86	<1	0.6
TIR 2	03/03/97	1131	5.80				4.0	25	78	<1	1.3
TIR 2	05/27/97	1230	5 59				44	21	72	<1	03
TIR 2	08/12/97	1003	5.2				4	20	74	1	2.8
TIR 2	08/25/97	1036	>1				44	20	90	<1	2.0 4
TIR 3R	09/11/96	1524	4 35				48	20	80	<1	0.5
TIR 3B	10/07/96	1551	5.91				4.6	23	100	<1	0.5
TIR 3B	11/12/96	1252	5 22				4.0	23	120	<1	0.5
TIR 3B	12/12/96	1130	5 44				т.т Л Л	25	120	<1	0.5
TIR 2R	03/03/07	1338	5.64				7.7 3 8	25	100	~1	0.7
TIR 3B	05/27/07	05/	5 57				ΔΛ	10	100	~1	1.5
	08/12/07	1159	5 12				ч.ч ДЛ	20	140	<1 <1	0.4
TIR 2D	08/25/07	1216	5. 4 2				т.ч ДЛ	20	120	2	13.4
TNX 15D	09/11/96	1407	1 23				4.4	25	140	<1	14
111/11/1	5711170	1-107	1.20				4 .0	45	140	~1	1.4

26 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Table 12. Field-	measured water-quality	constituents and prop	perties in ground wat	ter from observation	wells in the TNX uppe	эr
and lower flood	plains, Savannah River	Site, S.C., Septembe	r 1996 to August 199	97—Continued		

Well identifica- tion	Date	Time	Dissolved oxygen (mg/L)	Total sulfide as H ₂ S (mg/L)	Ferrous iron (mg/L)	Hydrogen (nM)	pH (su)	Tempera- ture (degrees C)	Specific conduc- tance (µS/cm)	Total alka- linity as CaCO ₃ (mg/L)	Turbid- ity (NTU)
TNX 15D	10/07/96	1443	0.62	0.1	<0.1		4.6	22	160	<1	4.1
TNX 15D	11/12/96	1111	0.92				4.2	21	180	<1	0.8
TNX 15D	12/12/96	947	0.70				4.2	22	160	<1	0.6
TNX 15D	03/03/97	1221	3.47				4.0	25	160	<1	0.3
TNX 15D	05/27/97	1208	1.22				4.6	21	160	<1	0.8
TNX 15D	08/12/97	1033	0.6	0.2	<0.1		4.4	21	120	2	2.9
TNX 15D	08/25/97	1136	0.7	0.1	<0.1		4.6	20	146	8	3.4
TNX 16D	09/11/96	1430	0.69				4.4	22	180	<1	0.5
TNX 16D	10/07/96	1512	1.25				4.6	22	180	<1	0.6
TNX 16D	11/12/96	1142	0.75				4.2	24	200	<1	0.5
TNX 16D	12/12/96	1011	1.40				4.4	23	200	<1	0.8
TNX 16D	03/03/97	1159	3.70				4.0	25	140	<1	1.3
TNX 16D	05/27/97	1139	1.55				4.6	21	160	<1	0.2
TNX 16D	08/12/97	1103	1				4.6	21	140	2	4.3
TNX 16D	08/25/97	1201	0.5	<0.1	<0.1		4.8	20	180	3	1.6
TNX 9D	09/11/96	1612	0.26	0.3	0.39		4.6	24	100	1	1.7
TNX 9D	10/07/96	1625	0.52	0.3	0.36		5.2	22	120	4	1.6
TNX 9D	11/12/96	1507	0.50	0.4	0.32		5.0	23	120	1	0.4
TNX 9D	12/12/96	1359		<0.1	0.24		5.0	24	120	4	0.5
TNX 9D	05/27/97	1404	0.37	<0.1	0.45		5.0	21	120	3	0.6
TNX 9D	08/12/97	1313	0.5	0.4			4.6	20	98	2	5.4
TNX 9D	08/25/97	1249	0.5	<0.1	0.1		4.8	19	120	2	3.4

shoot tissue. The same pathway that transports atmospheric oxygen to root systems in flood-adapted wetland species also can act as a conduit for transport of soil gases to the atmosphere (Dacey, 1981). As a mechanism of methane transport, for example, flux through wetland plants can account for up to 95 percent of total gas emission in anaerobic, waterlogged sediment (Whiting and Chanton, 1992). In this investigation, laboratory and field investigations provide site-specific and species-specific data regarding contaminant uptake by trees.

Results of Field Botanical Investigation

All species of trees examined from areas of ground-water contamination showed evidence of TCE or *c*DCE in the trunks (table 15). Some species appeared to exhibit similar uptake potential. Examination of a cluster of baldcypress and tupelo (trees 19 to 24, 50 to 52, and 55) showed no significant differences in concentrations between the species. In January 1998, the TCE concentration in baldcypress 7 was approximately 2,000 to 3,000 nmol/L, and high concentrations of TCE also were found in nearby loblolly pines 12, 27, and 54 (1,742; 1,241; 1,324 nmol/L, respectively). Baldcypress 43 also contained similar TCE concentrations (296 nmol/L) to adjacent loblolly 42 (479 nmol/L).

Oaks, however, appeared to contain less TCE than adjacent baldcypress or loblolly pines. In September 1997, tree 11 (oak) contained less than 50 nmol/L of TCE, while a nearby loblolly pine (tree 12) contained 730 nmol/L of TCE, and a nearby baldcypress tree (tree 7) contained 3,180 nmol/L of TCE (table 15). Similarly, in January 1997, a different oak (tree 35) contained only 69 nmol/L of TCE, whereas loblolly pines on either side of tree 35 contained 2,263 (tree 34) and 479 (tree 42) nmol/L. Likewise, oak 13 contained less than 50 nmol/L of TCE while an adjacent loblolly (tree 32) contained 764 nmol/L of TCE. The pattern and consistency of the data imply that these findings are a function of tree-species differences.

Sweetgum also appeared to contain less TCE than loblolly pines. Sweetgums 14 and 33 contained less than 50 and 74 nmol/L of TCE, respectively, in January 1998, whereas loblolly pines on various sides of the sweetgums contained 764 nmol/L (tree 32), 2,263 nmol/L (tree 34), 308 nmol/L (tree 29), 318 nmol/L (tree 30), and 751 nmol/L (tree 31) (table 15).

Previous investigations also have noted differences in contaminant uptake and degradation among Table 13. Concentrations of inorganic constituents in ground water from observation wells in the TNX upper and lower flood plains, Savannah River Site, S.C., September 1996 to August 1997 (samples collected and analyzed by the USGS)

[Ca, calcium; Mg, magnesium; K, potassium; Na, sodium; Br, bromide; Cl, chloride; P, phosphorus; SO_4 , sulfate; DIC, dissolved inorganic carbon; CH_4 , methane; mg/L, milligrams per liter; <, less than; ---, not analyzed or recorded; \mathbb{R} ' following well identifiers indicates field replicate; SW, surface-water sample collected from flooded lower terrace]

Well	Date	Ca	Mg	К	Na	Br	CI	Р	SO4	DIC	CH4
identifier		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
TCM 1	05/27/97	6.92	1.17	1.26	5.72	0.04	3.07	< 0.02	21.69	49.3	<0.01
TCM 1	08/12/97	6.63	1.23	1.12	6.00	0.05	2.48	<0.02	15.06	40.7	<0.01
TCM 1	08/25/97					0.03	2.36	< 0.02	16.75	41.5	<0.01
TCM 2	05/27/97	4.38	1.59	0.98	12.39	0.04	3.51	< 0.02	5.50	73.1	<0.01
TCM 2	08/12/97	5.57	2.20	1.27	15.05	0.32	3.57	< 0.02	4.45	82.1	<0.01
TCM 2	08/25/97					0.04	3.45	< 0.02	4.02	69.5	<0.01
TCM 3	05/27/97	5.05	1.94	1.00	25.70	0.08	4.49	<0.02	10.69	113.2	<0.01
TCM 3	08/12/97	5.77	2.56	1.23	34.59	0.11	5.45	< 0.02	19.14	123.1	<0.01
TCM 3	08/25/97					0.09	5.27	< 0.02	18.37	124.1	<0.01
TIR 1L	09/11/96	18.71	2.81	1.95	27.02	0.25	4.34	< 0.02	77.62	48.0	<0.01
TIR 1L	10/07/96	21.56	3.53	1.94	26.50	0.28	4.37	< 0.02	60.40	57.4	<0.01
TIR 1L	11/12/96	18.25	1.76	1.45	18.25	0.26	4.84	< 0.02	53.58	86.3	<0.01
TIR 1L	12/12/96	12.26	1 74	1 48	18 24	0.23	4 68	<0.02	52.66	82.7	<0.01
TIR 11	03/03/97	16.30	2.16	1.78	20.92	0.25	4 61	<0.02	65 51	45.1	<0.01
TID 11	05/03/27	11.30	1 51	1.70	16.28	0.31	5.27	<0.02	13 87	78.8	<0.01
	09/12/19/	11.4	1.51	1.27	10.28	0.21	5.10	<0.02	50.07	76.6	<0.01
TIK IL	08/12/97	12.98	1.75	1.49	17.14	0.22	5.10	<0.02	12 66	70.0 64.2	<0.01
TIK IL	08/25/97					0.21	5.10	<0.02	43.00	04.2	<0.01
TIR IM	09/11/96	3.69	1.49	0.98	17.50	<0.01	4.90	<0.02	7.88	25.4	<0.01
TIR IM	10/07/96	5.32	2.18	0.97	19.71	<0.01	4.13	<0.02	7.59	46.4	<0.01
TIR 1M	11/12/96	15.63	0.95	0.77	15.63	0.05	4.14	<0.02	7.62	74.6	<0.01
TIR 1M	12/12/96	2.93	0.95	0.76	15.54	0.04	4.04	<0.02	7.55	73.8	<0.01
TIR 1M	03/03/97	2.87	0.91	0.68	12.93	0.05	3.71	<0.02	7.32	39.4	0.1
TIR 1M	05/27/97	2.88	0.85	0.67	12.22	0.04	3.75	<0.02	6.91	58.9	<0.01
TIR 1M	08/12/97	3.36	1.09	0.84	13.85	0.03	3.62	<0.02	5.47	56.0	<0.01
TIR 1M	08/25/97					0.04	3.51	<0.02	5.24	47.1	<0.01
TIR 1U	09/11/96	5.63	2.31	1.54	28.83	< 0.01	6.29	< 0.02	6.56	78.9	<0.01
TIR 1UR	09/11/96	5.67	2.30	1.54	28.74	< 0.01	6.48	< 0.02	6.61	72.6	<0.01
TIR 1U	10/07/96	7.63	3.29	1.73	34.25	< 0.01	5.42	< 0.02	6.28	83.9	<0.01
TIR 1UR	10/07/96	7.33	3.26	1.60	34.18	< 0.01	5.44	< 0.02	6.92	81.8	< 0.01
TIR 1U	11/12/96	26.70	1.93	1.38	26.70	0.10	5.20	0.05	6.47	89.9	<0.01
TIR 1UR	11/12/96	26.82	1.90	1.36	26.82	0.10	5.21	< 0.02	6.49	84.3	<0.01
TIR IU	12/12/96	5 77	1.99	1.37	27.51	0.10	5.06	< 0.02	6.49	83.1	<0.01
TIR IUR	12/12/96	5 28	1.89	1 36	27.46	0.09	5.05	<0.02	6 55	85.1	<0.01
TIR 1U	03/03/97	5.19	1.05	1 18	23.74	0.10	4 63	<0.02	7.00	40.1	01
	03/03/97	5 21	1.91	1.10	23.80	0.08	4 61	<0.02	6.98	46.3	0.1
TID 111	05/03/27	5.59	2.00	1.10	25.00	0.00	5.74	<0.02	8 11	60.3	<0.1 <0.01
	-05/27/97	5.00	2.00	1.24	20.03	0.11	5.74	<0.02	7 70	09.5	<0.01
	03/2//9/	J.29 6 01	2.10	1.19	25.07	0.10	5.10	<0.02	6.65	50.J	<0.01
	08/12/97	0.01	2.19	1.30	20.45	0.10	5.10	<0.02	0.05	69.0	<0.01
TIR IUR	08/12/97	6.10	2.18	1.40	26.46	0.13	5.14	<0.02	6.70	08.0	<0.01
TIR 1U	08/25/97					0.08	5.00	<0.02	6.47	67.6	<0.01
TIR 1UR	08/25/97					0.09	5.00	<0.02	6.46	67.3	<0.01
TIR 2	09/11/96	2.53	0.79	0.92	13.49	<0.01	4.58	<0.02	9.50	55.3	<0.01
TIR 2	10/07/96	3.69	1.70	1.23	15.40	<0.01	3.75	< 0.02	9.14	64.4	<0.01
TIR 2	11/12/96	11.84	0.56	0.75	11.84	0.04	3.65	< 0.02	8.21	36.0	<0.01
TIR 2	12/12/96	2.07	0.57	0.73	11.58	0.03	3.45	< 0.02	9.78	69.2	<0.01
TIR 2	03/03/97	2.89	0.83	0.75	10.23	0.04	3.25	< 0.02	11.74	34.4	<0.01
TIR 2	05/27/97	2.61	0.78	0.80	10.63	0.05	4.82	< 0.02	10.51	57.4	<0.01
TIR 2	08/12/97	2.34	0.71	0.77	9.56	0.04	3.48	< 0.02	8.22	53.6	<0.01
TIR 2	08/25/97					0.04	3.37	< 0.02	7.13	49.6	<0.01
TIR 3B	09/11/96	6.56	3.05	1.85	13.97	< 0.01	4.48	< 0.02	1.74	71.2	<0.01
TIR 3R	10/07/96	6 4 4	3.47	1.72	14.08	< 0.01	3.77	< 0.02	1.85	60.1	< 0.01
TIR 3B	11/12/96	13.04	2.48	1.59	13.04	0.04	4.03	0.06	1.56	66.0	< 0.01
			20					0.00	1.00	20.0	

28 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Table 1	13. Concentrations of inorganic constituents in ground water from observation wells in the TNX upper and lower floo	d
plains,	Savannah River Site, S.C., September 1996 to August 1997 (samples collected and analyzed by the	
USGS	Continued	

Well	Dete	Ca	Mg	ĸ	Na	Br	CI	P	SO4	DIC	CH4
identifier	Date	(mg/L)	(mg/Ĺ)	(mg/L)	(mg/L)						
TIR 3B	12/12/96	5.65	2.58	1.59	13.53	0.03	3.95	0.06	1.40	88.6	<0.01
TIR 3B	03/03/97	6.10	2.66	1.42	11.69	0.03	3.53	0.08	1.54	40.5	<0.01
TIR 3B	05/27/97	5.34	2.34	1.41	12.94	<0.01	4.48	0.07	2.02	70.4	<0.01
TIR 3B	08/12/97	6.38	2.82	1.50	13.39	0.04	3.41	< 0.02	1.52	60.5	<0.01
TIR 3B	08/25/97					0.03	3.24	< 0.02	1.28	49.7	<0.01
TNX 9D	09/11/96	10.51	1.85	1.42	14.13	0.25	7.13	< 0.02	28.22		<0.01
TNX 9D	10/07/96	13.89	2.90	1.54	16.69	0.26	6.27	< 0.02	28.21	70.7	<0.01
TNX 9D	11/12/96	13.17	1.59	1.28	13.17	0.25	6.45	< 0.02	25.29	72.3	<0.01
TNX 9D	12/12/96	9.39	1.58	1.22	13.39	0.24	6.22	< 0.02	24.54	109	<0.01
TNX 9D	05/27/97	10.82	1.79	1.27	11.98	0.28	8.84	< 0.02	26.83	80.0	<0.01
TNX 9D	08/12/97	10.62	1.68	1.34	11.42	0.25	8.18	< 0.02	26.89	79.6	<0.01
TNX 9D	08/25/97					0.24	8.25	<0.02	26.35		
TNX 15D	09/11/96	4.99	1.56	1.33	28.86	0.17	8.87	<0.02	8.35	60.4	<0.01
TNX 15D	10/07/96	7.45	2.43	1.34	30.20	0.34	7.33	< 0.02	9.26	93.1	<0.01
TNX 15D	11/12/96	24.22	1.30	1.16	24.21	0.34	7.85	< 0.02	8.29	121	<0.01
TNX 15D	12/12/96	5.49	1.31	1.17	24.49	0.34	7.87	< 0.02	8.29	112	<0.01
TNX 15D	03/03/97	4.37	1.23	1.08	22.22	0.21	7.24	< 0.02	8.80	58.5	0.1
TNX 15D	05/27/97	4.56	1.23	1.02	22.48	0.31	8.39	< 0.02	9.06	101.2	<0.01
TNX 15D	08/12/97	4.45	1.16	1.15	22.35	0.29	8.32	< 0.02	8.66	122.7	<0.01
TNX 15D	08/25/97					0.27	8.00	<0.02	8.19	87.5	<0.01
TNX 16D	09/11/96	4.01	1.66	1.02	34.04	0.09	8.89	<0.02	8.73	126.4	<0.01
TNX 16D	10/07/96	5.72	2.50	1.11	38.62	0.28	7.72	< 0.02	9.51	114	<0.01
TNX 16D	11/12/96	29.92	1.21	0.90	29.92	0.31	7.77	< 0.02	9.18	157	<0.01
TNX 16D	12/12/96	3.56	1.23	0.89	30.42	0.27	7.82	< 0.02	9.42	174	<0.01
TNX 16D	03/03/97	3.58	1.20	0.98	23.66	0.16	6.18	< 0.02	9.01	64.1	0.1
TNX 16D	05/27/97	3.27	1.12	0.77	27.45	0.23	8.23	< 0.02	12.17	109.5	<0.01
TNX 16D	08/12/97	2.81	1.03	0.78	26.57	0.25	7.81	< 0.02	10.69	123.9	<0.01
TNX 16D	08/25/97					0.26	7.74	< 0.02	10.28	110	<0.01
TNX SW	03/03/97	7.20	2.50	1.75	6.48	0.03	3.70	< 0.02	4.74		

Table 14. Concentrations of *cis*-1,2-dichloroethene and trichloroethene in selected soil-gas diffusion samplers, lower flood plain, TNX facility, S avannah River Site, S.C., March to April 1997

[WVD, water-to-vapor diffusion; *c*DCE, *cis*-1,2-dichloroethene; TCE, trichloroethene; $\mu g/L$, micrograms per liter; rep., replicate sample; rep2, replicate sample; <, less than]

WVD sampler	Date installed	Date recovered	Days elapsed	<i>с</i> DCE (µg/L)	TCE (μg/L)
FP50	3/18/97	3/25/97	7	19	272
FP50A	3/18/97	3/25/97	7	20	240
FP130	3/18/97	3/25/97	7	47	49
FP130A	3/18/97	3/25/97	7	29	11
FP265	3/18/97	3/25/97	7	88	193
FP265 rep.	3/18/97	3/25/97	7	95	182
FP265 rep2	3/18/97	3/25/97	7	76	179
FP150	3/18/97	4/3/97	15	<1	<1



Figure 9. *Cis*-1,2-dichloroethene concentrations in baldcypress trunks in January and February 1998 and in ground water during August 1997 and ground-water-flow directions (Hamm, Aleman, and Shadday, 1997), TNX facility, Savannah River Site, S.C.

30 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina



Figure 10. Trichloroethene concentrations in baldcypress trunks in January and February 1998, in ground water at wells during May 1997 and 1996 (well TNX26D only), and at the ditch-bed sampling point during August 1997 and ground-water-flow directions (Hamm, Aleman, and Shadday, 1997), TNX facility, Savannah River Site, S.C.

Table 15. Concentrations of *cis*-1,2-dichloroethene and trichloroethene vapor, expressed as nanomoles of gas per liter of water, in tree cores from the TNX flood plain, Savannah River Site, S.C, January 1997 to February 1998

[nd, analysis not done; nq, compound not quantified due to peak interferences; (), concentration in replicate core sample collected 25 mm laterally from original core sample; cyp, baldcypress (*Taxodium distichum* {L} Rich.); lob, loblolly pine (*Pinus taeda* L.); oak, oak (*Quercus* spp.); tup, tupelo (*Nyssa aquatica* L.); swe, sweet gum (*Liquidambar stryaciflua* L.); syc, sycamore (*Platanus occidentalis* L.); cDCE, cis-1,2-dichloroethene; TCE, trichloro-ethene]

Tree	Date	cDCE		Species	Tree	Date	cDCE	TCE (nmol/L)	Species
1	1/22/07	nd	<50 (<50)	SWA	13	1/30/08	<10	<50	oak
1	10/1/07	60	<20	SWC	14	0/0/07	<10	< <u>50</u>	owe
2	1/22/07	o0 nd	(725)	SWC	14	1/20/08	<10	~50	SWC
2	1/22/97	nd	933 (733) 180	cyp	14	0/0/07	<10	<50	ook
2	10/1/07	11u 55	220 (190)	cyp	15	0/0/07	<10	<50	lah
2	1/20/08	55	220 (180)	сур	10	919191	<10	<30	100
2	1/30/98	<10	370	сур	1/	919197	<10	-50	swe
3	1/22/97	nd	245 (380)	сур	18	919191	70	<50	oak
3	2/13/97	na	110	сур	18	1/10/98	90	<50	oak
3	10/1/9/	210	100	cyp	18	1/30/98	<10	<50	оак
3	1/16/98	<10	298	сур	19	1/14/98	47	780	сур
3	1/30/98	<10	<50	сур	20 a	1/14/98	18	119	сур
4	1/22/97	nd	410 (445)	сур	20 a	1/30/98	23	174	сур
5	2/13/97	nd	<50	сур	20	1/30/98	<10 (<10)	283 (248)	сур
5	8/11/97	<10	<50	cyp	21 a	1/14/98	66	1,021	tup
6	2/13/97	nd	<50	cyp	21 a	1/30/98	42	1,149	tup
7 a	8/11/97	61 (63)	35,040 (35,150)	cyp	21	1/30/98	56 (49)	1,469 (1,583)	tup
7 a	10/1/97	175 (176)	4,370 (4,350)	cyp	23	1/14/98	74	426	tup
7	7/23/97	225 (215)	8,590 (9,360)	cyp	24	1/14/98	23	1,033	tup
7	9/9/97	nq	3,180	сур	26	1/26/98	19	362	сур
7	1/30/98	24(17)(35)	2,093 (2,094)	cyp	26	1/30/98	26	457	сур
8	8/11/97	<10	(2,942)	swe	27	1/30/98	<10	1 241	loh
Q	8/11/07	<10	250 <50	oak	27	1/30/08	<10	-50	oak
0	0/0/07	<10	<50	oak	20	1/30/08	<10	308	loh
0	1/30/08	<10	<50	oak	30	1/30/98	<10	318	lob
2 10	0/0/07	<10	<50	Uak	21	1/20/09	<10	751	lob
10	0/0/07	<10	<50	swe	22	1/20/08	<10	751	lob
12	0/0/07	110	<30 730	lab	22	1/20/08	<10	704	100
12	1/20/09	<10 <10	1 740	lob	24	1/20/90	<10	2 262	lah
12	0/0/07	<10	1,742	loo	25	1/20/98	<10	2,203	look
15	1/20/09	40	<50	Oak	55 66	1/30/98	<10	09	Oak
20	1/30/98	<10	<30	syc	00	1/14/98	29	107	сур
31 20	1/30/98	<10	130	syc	00	1/20/98	25 (23)	244 (242)	сур
38	1/30/98	<10	106	сур	00	2/1//98	55 (55) =1	216 (212)	сур
39	1/30/98	<10	116	сур	67	1/14/98	71	351	сур
40	1/30/98	<10	118	lob	68	1/14/98	<10	<50	сур
41	1/30/98	<10	1,131	lob	69	1/14/98	<10 (<10)	310 (265)	cyp
42	1/30/98	<10	479	lob	70	1/14/98	<10 (<10)	<50 (<50)	сур
43	1/30/98	32	296	сур	71	1/14/98	<10	249	сур
43	2/17/98	33	153	cyp	71	1/16/98	<10	128	сур
44	1/30/98	11	824	cyp	72	1/14/98	<10	219	cyp
44	2/17/98	<10 (<10)	270 (229)	сур	72	1/16/98	<10	213	сур
45	1/30/98	54	310	сур	73	1/14/98	<10	71	сур
46	1/30/98	15	536	сур	73	1/16/98	<10	63	сур
47	1/30/98	<10	<50	swe	74	1/14/98	<10	78	сур
48	1/30/98	<10	<50	сур	74	1/16/98	<10	<50	cyp

32 Natural Attentuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Table	15.	Concentrations	s of <i>cis-</i>	1,2-dichloro	ethene and	trichloroeth	nene vapor,	expressed	d as nanon	noles of g	as per liter of
water,	in tr	ree cores from t	he TNX	flood plain,	Savannah	River Site,	S.C, Janua	ry 1997 to	February	1998—C	ontinued

Tree	Date	<i>c</i> DCE (nmol/L)	TCE (nmol/L)	Species	Tree	Date	<i>c</i> DCE (nmol/L)	TCE (nmol/L)	Species
49	1/30/98	<10	<50	сур	74	2/17/98	<10	<50	сур
50	1/30/98	12	415	сур	75	1/16/98	<10	<50	cyp
51	1/30/98	18	221	cyp	76	1/16/98	<10	<50	сур
52	1/30/98	25	430	cyp	77	1/16/98	<10	87	сур
53	1/30/98	<10	<50	syc	78	1/16/98	<10	409	сур
54	1/30/98	<10.	1,324	lob	78	1/26/98	<10 (<10)	418 (454)	сур
55	1/14/98	99	966	cyp	78	2/17/98	<10 (<10)	196 (245)	сур
56	1/14/98	125	242	cyp	79	1/16/98	<10	200	сур
57	1/16/98	<10	<50	сур	79	1/26/98	<10	120	сур
58	1/14/98	<10	<50	сур	80	1/16/98	<10	118	cyp
59	1/14/98	<10	<50	сур	80	1/26/98	<10	123	cyp
60	1/14/98	<10	<50	сур	81	1/16/98	<10	<50	сур
60	1/30/98	<10	<50	сур	81	1/26/98	<10	<50	cyp
61	1/14/98	<10	<50	tup	82	1/16/98	<10	<50	cyp
62	1/14/98	<10	<50	tup	82	1/26/98	<10	33	cyp
63	1/14/98	<10	<50	cyp	83	1/26/98	<10	<50	сур
64	1/14/98	<10	96	cyp	84	1/26/98	<10	<50	сур
65	1/14/98	<10	272	cyp	85	1/26/98	<10	<50	cyp
86	1/26/98	<10	<50	сур	93	2/17/98	<10	<50	сур
87	2/17/98	<10	<50	cyp	94	2/17/98	<10 (<10)	<50 (<50)	сур
88	2/17/98	<10	<50	сур	95	2/17/98	<10	<50	сур
89	2/17/98	<10	160	сур	96	2/17/98	<10	<50	cyp
90	2/17/98	<10	148	сур	97	2/17/98	<10	<50	cyp
91	2/17/98	<10	270	сур	98	2/17/98	<10	<50	сур
92	2/17/98	<10	<50	сур	99	2/17/98	<10	<50	сур

plant species. Selected chlorinated compounds have been found to be degraded faster in the rhizosphere soil of monocot species than dicot species (Shann and Boyle, 1994). Loblolly pines have been found to take up more TCE than grasses and legumes (Anderson and Walton, 1989). In this investigation, the concentration differences also may partly be a function of the waterconduction differences between species. Conifers (such as baldcypress and loblolly pine) conduct water through more than the outermost ring, whereas ringporous trees (such as oak) conduct nearly all of the water through the outermost growth ring (Ellmore and Ewers, 1986; Kozlowski and others, 1967). Thus, the higher concentrations detected in conifers relative to the oaks may be because the cores, being of approximately equal length, incorporated a proportionally greater amount of water-conducting xylem in conifers than in the ring-porous trees.

Examination of cores collected at various trunk heights of a baldcypress (tree 7) growing in an area of ground water contaminated with TCE showed that concentrations of TCE decreased significantly with increasing trunk height (p=0.001) (fig. 11), although *c*DCE concentrations did not (p=0.4) (data not shown). Tree 7 branched into two trunks at a height of 7 ft above ground. The two trunks are designated as southern (7a) and northern (7b). TCE concentrations along the southern trunk of tree 7 during July and August decreased by about 77 percent and 70 percent, respectively, from near the ground to a height of about 50 to 60 ft (fig. 11). The northern trunk of tree 7 showed an approximate 30 percent decrease in TCE concentrations over the same vertical distance in August 1997 (fig. 11).

The specific mechanism causing decreasing concentrations of TCE with increasing height in tree 7 (fig. 11) is not known. One possibility is that there is a loss mechanism for TCE along the transport pathway up the tree. Such a loss mechanism could be VOC volatilization followed by diffusion through the tree bark. The fact that water vapor is known to escape through the bark of trees, chiefly through lenticels (Kozlowski and Pallardy, 1997), is consistent with the loss of TCE through the tree bark. The Henry's law constant is slightly larger for TCE (0.227 unitless) than for cDCE



Figure 11. Trichloroethene concentrations in cores at various heights along the trunk of tree 7 (baldcypress) in July and August 1997, TNX facility, Savannah River Site, S.C.

(0.121 unitless), indicating that TCE has a slightly larger tendency to volatilize than *c*DCE (Washington, 1996). This explanation is consistent with findings from the mesocosm experiments showing that the trees continue to exude TCE even when evapotranspiration is reduced or absent. Additional possible explanations include TCE degradation or sorption within the trunk, the potential for spiral transport of fluids up the trunk (Kozlowski and others, 1967), or temporal changes in ground-water contaminant concentrations.

Although all of the cores collected for this analysis were from the northeastern side of each tree, selected trees were cored at various locations around the trunk to examine directional variability. Core data from different sides of individual trees showed concentration differences ranging from 44 to 92 percent for TCE and 6 to 90 percent for *c*DCE. The relatively good replication in cores collected 25 mm apart (15.5 percent for TCE and 2.5 percent for *c*DCE) indicates that the coring approach did not contribute significant inconsistencies to the data. The source of the directional variation is not known, but may be related to a variety of processes, such as injuries (Scholander and others, 1957), disease and insect damage (Kozlowski and others, 1962), gas embolisms (Clark and Gibbs, 1957), and variations in TCE concentration taken up by root systems on differing sides of the tree.

The sharp decline in ground-water levels and the diel fluctuations in the water table indicate that a substantial quantity of water and its associated contaminants is evapotranspired daily through the growing season. The presence of TCE in the wood even during January implies the possibility of diffusive TCE loss through the bark during non-growing seasons.

Results of Laboratory Botanical Investigation

Laboratory botanical investigations were initiated to better understand the potential for plants at the TNX flood plain to remove TCE from the shallow ground water. As will be shown, the results of investigations using mesocosms showed that baldcypress trees, a characteristic species in the TNX flood plains, are capable of advectively removing substantial amounts of ground-water TCE and that evapotranspirative processes are a major process controlling TCE uptake and loss in the trees. Contaminant removal by plants continued during periods of limited evapotranspiration, but at a reduced rate.

Water uptake was measured by monitoring water loss from the Marriotte bottles with live and dead seedlings. When seedling water use was normalized for seedling growth by dividing the basal stem cross-sectional area into the water flux, the data showed a significant decline in water use from August to December (fig. 12). The decline in water use coincides with the decrease in through-plant TCE flux from summer to winter (fig. 13). The large decrease in normalized water



Figure 12. Average monthly water use by seedlings measured with Marriotte bottles and water use normalized for seedling growth by dividing the mean stem basal area of all healthy seedlings into the average monthly water use.

34 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina



Figure 13. Trichloroethene removal from the rhizosphere of baldcypress seedlings as (a) nanomoles per minute through the above-ground portion of the plant and (b) fractional trichloroethene loss from carboy water during summer and winter.

use during September and October coincided with the onset of autumnal leaf-color change. Water use did not differ between those seedlings exposed to TCE and those that were not exposed. Predictions for aboveground TCE efflux based on the TCE loss rate from the rhizosphere (through-plant TCE flux estimated from decline in carboy water) agreed reasonably well with the direct flux (static-chamber) measurements (table 16).

Analysis of TCE efflux from the above-ground portion of cypress seedlings grown in the carboy mesocosms showed significantly higher daytime fluxes in August and October compared to November and December (fig. 13a). The daytime flux was substantially larger than the night-time flux during August and October (fig. 13a). The difference between daytime and night-time fluxes was less pronounced during November and December. In addition, TCE loss from carboy water was substantially higher in mesocosms containing live seedlings rather than dead seedlings (fig. 13b). Thus, plant evapotranspiration appears to be a major factor controlling TCE uptake and loss in baldcypress seedlings.

The water-conduction system of plants transports water from the rooting zone through the stem to the above-ground tissues. The physicochemical properties of TCE (log K_{ow} =2.53; Miller and Wasik, 1985) are such that TCE can be transported through the water-conducting network of xylem cells (Schnoor and others, 1995). A recent study has confirmed this mode of transport for TCE in a woody species by qualitative measurement of contaminant in bags placed over the leaves of hybrid poplar cultivars grown in a greenhouse (Newman and others, 1997).

A major control on evapotranspiration, as well as gas exchange, is the opening and closing of leaf stomata. To test the role of stomatal activity in TCE transport, simultaneous measurements of CO_2 exchange were made along with the TCE flux determinations. Uptake of CO_2 (negative values for CO_2 exchange) during the day across all months was positively correlated with TCE flux normalized for carboy TCE concentrations (fig 14a). However, there was no relation between CO_2 exchange and TCE flux at night (fig 14b). The data support the hypothesis that stomatal activity controls diel differences in TCE vapor flux by regulating the rate of water and gas transport through the plant.

The diel and seasonal variations in TCE flux from cypress seedlings that coincide with water use indicate that advective removal of ground-water contaminants by plants is most effective during periods of active evapotranspiration. The reduced effectiveness of this mechanism during night and winter should be considered when comparing the cost effectiveness of remediation strategies.

Despite the apparent influence on TCE efflux by evapotranspiration, significant TCE flux and carboywater loss was observed from live seedlings under nearzero water use in the winter (figs. 12 and 13) and from dead seedlings in the summer. These data suggest that TCE is transported through the plants even during periods when leaf evapotranspiration is minimal. One possible mechanism for this loss may be TCE transport by gas-phase diffusion through internal air spaces in the roots and stems. This mechanism is typical in floodadapted species as a means of significantly increasing the rhizosphere redox potential by transporting oxygen downward and out through the root system (Armstrong and Beckett, 1987; Grosse and others, 1993; Hook and Scholtens, 1978). The same pathway of interconnected airspace can serve as a mode of transport for soil gas to

[Root and stem tissue TCE is based on grams fresh weight. Numbers in parentheses are standard error of the mean; TCE, trichloroethene; -, not measured] Table 16. Comparison among observed, estimated, and modeled trichloroethene removal by baldcypress seedlings

			TCE con	centration					Throu	gh-plant TCE	flux (nmol/r	nin)
Measurement series	Condition	Initial carboy (µM)	Final carboy (µM)	Roots (nmol/g)	Stem (nmol/g)	Mean temp (°C)	Measured water use (cm ³ /hr)	Simulated carboy temp (°C)	Determined by static chamber	Esti- mated from TCE decline in carboy water	Esti- mated from mea- sured water use	Calcu- lated from diffusion model
Through-plant flux experiments:												
August-97	Day	79	·	·	·	34	30	26.9	52.1 (12.3)	25.7	38.5	4.4
	Night	83	,			18	24.6	25.1	31.9 (6.0)	26.9	33.1	3.9
October-7	Day	59	•			22	7.6	17.9	44.0 (9.2)	19.1	7.3	1.8
	Night	61	·		,	13	7.2	17	20.8 (5.7)	19.8	7.1	1.7
November-97	Day	63	ı	·	ı	16	3.8	12.5	14.9 (4.2)	5.1	3.9	1.1
	Night	70	ı	ı	ı	8	3.9	11.6	12.5 (4.9)	5.7	4.5	1.3
December-97	Day	87	ı	ı	ı	21	0.47	18.5	8.3 (5.8)	7.1	0.7	2.7
	Night	91	r	,	ı	14	0.34	17.6	4.1 (1.6)	7.3	0.5	2.6
Water loss experiments:												
Summer-Dead-98	ı	77	14	11.8 (4.8)	7.5 (3.0)	,	0	ı		6.0	0.0	4.2
Summer-Live-98	ı	80	13	2.7 (2.4)	0.7 (0.6)		ı	ı	ı	ı		
Winter-Live-97/98	ı	60	32	10.0 (1.0)	4.4 (2.1)	·			·	ı		•

36 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina



NIGHTTIME CARBON DIOXIDE EXCHANGE BETWEEN SEEDLINGS AND ATMOSPHERE, IN MILLILITERS PER LITER PER SECOND

Figure 14. Comparison of carbon dioxide exchange and trichloroethene flux from seedlings showing (a) good correlation in daytime and (b) weak correlation in nighttime conditions, where negative values represent net photosynthesis, or carbon dioxide consumption, and positive values represent respiration, or net carbon dioxide production.

the atmosphere. Diffusion of methane, for example, through the free space within the plant is significantly faster than diffusion through the soil column to the atmosphere (Thomas and others, 1996). Hence, the plant conduit for soil gas emission may be an important process in the removal rate of volatile organic contaminants in contact with the root system.

The potential for diffusive transport of TCE through the plant system was examined by comparing observed TCE fluxes to simulated diffusive fluxes obtained by using a diffusion model (table 3). The simulated diffusive TCE flux substantially differed from the observed TCE flux during the summer when evapotranspiration was advectively removing TCE from the subsurface. During December, however, the modelsimulated diffusive flux could account for approximately 64 percent of the observed TCE flux (table 16).

The comparison between the observed, estimated, and model-simulated fluxes of TCE (table 16) through baldcypress seedlings suggests that average water-use in the summer and diffusion during periods of dormancy may be useful for estimating contaminant transport through vegetation at the field site throughout the year. The average water loss of seedlings, scaled up to the basal area of trees in a southeastern flood plain (Mitsch and Gosselink, 1993), is consistent with estimates of evapotranspiration at the TNX flood plain (Hubbard, 1986).

Mesocosm experiments of baldcypress showed that the seedlings were capable of removing substantial amounts of TCE (approximately 52 nanomoles per minute) from ground water during periods of active evapotranspiration and lower, but still significant, amounts (approximately 4 to 15 nanomoles per minute) during the winter when evapotranspiration was relatively inactive.

Adsorption

Laboratory analysis of the aquifer sediment adsorption rates indicate that the organic-rich bog sediment of the lower flood plain, represented by sample Sed-1 (fig. 2), has a high potential to adsorb TCE from ground water (table 17). Thus, a substantial percentage of the TCE being transported through such zones probably will be removed from solution by sorption onto the organic-rich aquifer material. These zones, however,

Table 17. Trichloroethene adsorption onto aquifer sediment from the upper and lower flood plains, TNX facility, Savannah River Site, S.C.

[mL/g, milliliters per gram; L/kg, liters per kilogram; NA, not applicable]

Site number	Location of sediment sample	Adsorption (mL/g, or L/kg)	Standard deviation
Sed-1	Lower flood plain bog approximately 40 ft southeast of embankment between wells TNX 15D and TNX 16D	1.07	0.1
Sed-2	Lower flood plain in non-bog area approximately 140 ft southeast of well TNX 15D	0.59	0.06
Sed-3	Between wells TCM-3 and TIR 1U	0.15	0.003
Sed-4	Upland swamp half- way between wells TIR 3B and TIR 1U	<0.15	NA

appear to be associated with localized areas where standing water has allowed a thick buildup of finegrained organic detritus. The thickness of the finegrained organic detritus in the vicinity of sample Sed-1 (fig. 2) extends to at least 7 ft, as determined by hand augering.

In other areas of the flood plain, the adsorption potential was substantially less than at site Sed-1. The measured adsorption using sample Sed-2 (0.59 mL/g), obtained from a part of the lower flood plain where the sediment contained less organic detritus than at Sed-1 (fig. 2), was only about 55 percent of the absorption obtained using sample Sed-1 (table 17). The measured adsorption was less (0.15 mL/g) using sediment from the upper flood plain, and even less (<0.15 mL/g) using sample Sed-4 (table 17).

The data suggest that TCE in ground water at the facility will travel through the aquifer with relatively small amounts of adsorptive removal until it reaches

organic-rich zones in the lower flood plain. Adsorption will be a major TCE-removal mechanism for the part of the contamination moving into those organic-rich zones. In areas of the lower flood plain where organicrich zones are thin or absent, however, TCE adsorption will be reduced.

Microbiological Processes

The results of the microcosm experiments using sediment from sites Sed-2, Sed-3, and Sed-4 in the upper flood plain did not show evidence of significant TCE reductive dehalogenation (fig. 15). This conclusion is consistent with the apparent aerobic conditions present in much of the aquifer. It also is consistent with findings of a previous investigation in the nearby A/M area of the Savannah River Site, showing limited biodegradation potential for TCE (Brigmon and others, 1998).



Figure 15. Percentage of initial head-space trichloroethene over time in microcosms of sediment from the TNX flood plains, Savannah River Site, S.C.

38 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

Although the sediment from site Sed-1 also did not show significant variations in TCE head-space concentrations over time between the live and killed controls, this experiment may underestimate the actual dehalogenation rate. The high adsorptive potential of the anaerobic organic-rich sediment probably masked biological removal over the testing period (fig. 15). Thus, the organic-rich zones of the lower flood plain may exhibit dehalogenation potential. Dissolved oxygen content of the flood-plain ground water in downgradient parts of the lower flood plain were not investigated, but if aerobic conditions exist, then production of methane from organic-rich parts of the lower flood plain have the potential to support cometabolic aerobic metabolism of TCE. The data suggest that if TCE is being microbially degraded, then such degradation probably would be as reductive dehalogenation in localized organic-rich lower flood-plain sediments or as cometabolic aerobic degradation in possible oxygenated zones near the organic-rich lower flood-plain sediments.

Further evidence for limited biodegradation in upper flood-plain sediments can be seen in the distribution of CVOC's in flood-plain trees. Although TCE was present in trees at a variety of locations (fig. 10), cDCE was only present in trees down the hydraulic gradient from the former seepage basin (fig. 9) and the burying ground (fig. 1). If the cDCE observed in the trees was derived from TCE dechlorination in floodplain sediments, then some amount of cDCE should have been observed in other flood-plain trees containing TCE. The presence of cDCE only in a narrow area suggests that cDCE is not derived from reductive dechlorination within upper flood-plain sediments, but rather is derived from the source area as a primary contaminant or as a dechlorination product from the association of higher chlorinated compounds and oxidizable organic compounds probably codisposed with the chlorinated compounds.

Influence of Processes Affecting the Natural Attenuation Potential

As a test to determine whether the naturally occurring processes identified during this investigation were adequate to prevent further contaminant transport beneath the lower flood plain to the Savannah River, the Westinghouse Savannah River Company, in cooperation with the USGS, incorporated the processes into a ground-water-flow and solute-transport model. The subsurface Flow and Contaminant Transport (FACT) code (Hamm, Aleman, Flach, and Jones, 1997) was chosen to simulate ground-water flow at the TNX area and the adjacent Savannah River flood plain. The FACT code is a three-dimensional, finite element model designed to simulate steady-state and transient isothermal ground-water flow, moisture movement, and solute transport in variably saturated and fully saturated subsurface porous media. Modeling details can be found in a separate report (Aleman, 1998).

Five case scenarios were simulated. Each simulation involved the transient transport of TCE contaminant from residual TCE sources in the vadose zone located beneath the TNX proper area over the period from 1988 until the year 2028. The ending date of the simulation, 2028, was chosen to allow sufficient time for the TCE plume to reach discharge points. In all scenarios a recovery-well network was assumed to be operational from October 1996 until the end of the simulation.

Case 1 represented the base case, which closely resembled the model developed in a previous investigation (Hamm, Aleman, and Shadday, 1997). Modifications for this investigation included areally refining the mesh to a spacing of 50 ft by 50 ft, adding an additional material zone to simulate sediments in an upgradient area, adjusting the water-table surface, adjusting the pseudo-soil water retention properties to values consistent with other onsite ground-water models, and reducing the maximum recharge flux from 20 to 17 in/yr. Biodegradation was conservatively set to zero based on laboratory results from this investigation.

The remaining cases were modifications of the base case. In case 2, the base case was rerun adding sorption rates derived from this investigation and simulating the removal of the drainage ditch as a contaminant-discharge zone in the flood plain. The third scenario (case 3) was identical to case 2 except that evapotranspirative contaminant removal from the flood plain was included. This scenario, using an evapotranspiration rate of 30 in/yr below the water table, necessitated using a maximum recharge flux of 47 in/yr in the flood plain. Cases 4 and 5 were the same as cases 2 and 3, respectively, but without simulated removal of the drainage ditch.

The model used to evaluate the potential effects of naturally occurring attenuation processes can be considered as conservative, or an estimation of contaminant transport under conditions favoring maximum transport distance. These conditions included an estimate of recharge (47 in/yr) at the high end of the probable uncertainty range. Moreover, because of the lack of experimental evidence indicating reductive dehalogenation, biodegradation was not included as a loss mechanism in the simulations. This also is a conservative approach because it is probable that some degree of reductive dehalogenation occurs in localized organicrich anaerobic zones of the lower flood plain, and cometabolic TCE degradation may occur in possible aerobic zones near the organic-rich anaerobic zones.

Under the conservative simulated conditions, the model showed no significant influence on contaminant transport by naturally occurring attenuation processes. Moreover, model simulations showed that removal of the drainage ditch (simulating an engineered approach of redirecting surface drainage) allowed contaminants that formerly discharged to the drainage ditch to discharge directly to the Savannah River. Thus, within the uncertainty of the model simulations, the simulations imply that the ground-water flow [approximately 1.5 ft/d (Hamm, Aleman, and Shadday, 1997)] in the study area is too fast for naturally occurring attenuation processes to prevent contaminant discharge to the Savannah River.

SUMMARY AND CONCLUSIONS

Ground water is contaminated with CVOC's beneath the Savannah River flood plain at the TNX facility, Savannah River Site, South Carolina. Under a contract with the U.S. Department of Energy, the USGS, in cooperation with the University of South Carolina, Southern Illinois University, and the Westinghouse Savannah River Company, conducted an investigation to determine whether the naturally occurring contaminant-attenuation processes were adequate to prevent further transport of ground-water contaminants beneath the flood plain to the Savannah River. The investigation used established methods, as well as methods developed for this investigation. The methods developed for this investigation involved using GC analysis of tree cores to areally map CVOC's in ground water and using water-based diffusion samplers buried beneath the drainage ditch to determine the concentrations of CVOC's in ground water discharging to the drainage ditch.

Water-level measurements during 1996-97 indicate that the ground water discharged upward into the lower flood plain, even during periods when the Savannah River was at flood stage and the lower flood plain

was inundated. Because shallow ground-water contamination is present at the upgradient edge of the lower flood plain (well TNX 16D), it is highly probable that contaminants discharge upward into the flood-stage Savannah River. Diffusion samplers beneath the drainage ditch that extends from the upper flood plain to the Savannah River showed that at non-flood stage, approximately 58 to 200 μ g/L of TCE discharge from ground water to the drainage ditch. Concentrations of TCE in ground water discharging to the drainage ditch were highest at, and upstream from, the edge of the embankment. Thus, the drainage ditch provides a conduit for possible transport of ground-water contamination to the Savannah River. However, during a surfacewater sampling in August 1997, 10 µg/L of TCE was present in the drainage ditch near the embankment separating the upper and lower flood plains, while 184 ft downstream in water flowing toward the Savannah River, the concentrations had decreased to less than 5 µg/L. Thus, volatilization appears to have been adequate to remove the TCE from the drainage ditch water prior to discharging into the Savannah River.

A variety of naturally occurring contaminantattenuation processes were examined to determine the potential for those processes to mitigate the groundwater contamination. These processes included contaminant-removal by vegetation, adsorption onto aquifer sediments, and bioremediation.

The ability of trees to remove contamination at this site was examined because the ground-water contamination is shallow and in a forested area. It is clear from the usefulness of tree-core head-space analysis in mapping the TCE and cDCE contamination in ground water that the trees are capable of taking up these compounds from the ground water. The decrease in concentrations of these compounds up the trunk of a baldcypress at the site implies that there may be a contaminant-depletion mechanism for the volatile contaminants during advective transport up the tree trunks. To further quantify these effects, laboratory investigations were initiated involving baldcypress seedlings grown in mesocosms. The trees were found to be capable of removing substantial amounts of TCE (approximately 52 nanomoles per minute) from ground water during periods of active evapotranspiration. TCE-removal rates were lower during the winter when evapotranspiration was relatively inactive, but were still significant (approximately 4 to 15 nanomoles per minute).

Other natural processes examined showed lower attenuative potential than the plants. The adsorptive

40 Natural Attenuation Potential of Chlorinated Volatile Organic Compounds in Ground Water, TNX Flood Plain, Savannah River Site, South Carolina

potential of organic-rich sediment in the lower flood plain was high, but these areas are not extensive. In other areas of the flood plain, the adsorption potential was substantially less than at site Sed-1. The measured adsorption using sample Sed-2 (0.59 mL/g), obtained from a part of the lower flood plain where the sediment contained less organic detritus than at Sed-1, was only about 55 percent of the absorption obtained using sample Sed-1. The measured adsorption was less (0.15 mL/g) using sediment from the upper flood plain, and even less (<0.15 mL/g) using sample Sed-4. The data suggest that TCE in ground water at the facility will travel through the aquifer with a relatively small amount of adsorptive removal until it reaches organicrich zones in the lower flood plain. Adsorption will be a major TCE-removal mechanism for the part of the contamination moving into those organic-rich zones. In areas of the lower flood plain where organic-rich zones are thin or absent, however, TCE adsorption will be reduced.

Biodegradation by reductive dehalogenation does not appear to be an important attenuation process for CVOC's in the upper flood plain, as evidenced by the dominantly aerobic conditions in the aquifer. The high sorptive capacity of anaerobic organic-rich sediment from the lower flood plain made it difficult to quantify the biodegradation potential in a laboratory microcosm, but it is probable that the sediment has some potential for reductive dehalogenation. The potential for methane to be transported from the anaerobic organic-rich sediment to possible nearby aerobic zones implies the potential for aerobic cometabolic degradation of TCE as a removal mechanism.

To determine whether these processes were adequate to prevent further migration of the ground-water contamination, they were incorporated into a groundwater and solute-transport model. The model was run under conservative conditions, or conditions favoring maximum transport distance. These conditions included an estimate of recharge at the high end of the probable uncertainty range and a lack of simulated bioremediation potential. Under the simulated conditions, the model implied no significant influence on contaminant transport by naturally occurring attenuation processes. Moreover, model simulations showed that removal of the drainage ditch (simulating an engineered approach of redirecting surface drainage) allowed contaminants that formerly discharged to the drainage ditch to discharge directly to the Savannah River. Thus, within the uncertainty of the model simulations, the model implies that the ground-water flow in the study area (approximately 1.5 ft/d) is too fast for naturally occurring attenuation processes to prevent discharge of contaminants to the Savannah River.

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