

TRANSPORT AND TRANSFORMATIONS OF CHLORINATED-SOLVENT CONTAMINATION IN A SAPROLITE AND FRACTURED ROCK AQUIFER NEAR A FORMER WASTEWATER-TREATMENT PLANT, GREENVILLE, SOUTH CAROLINA

By DON A. VROBLESKY, PAUL M. BRADLEY, JOHN W. LANE, JR., *and*
J. FREDERICK ROBERTSON

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BRUCE BABBITT, Secretary

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Gordon P. Eaton, Director

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For additional information write to:

District Chief
U.S. Geological Survey
Stephenson Center-Suite 129
720 Gracern Road
Columbia, South Carolina 29210-7651

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225-0286

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
Length		
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
foot per foot (ft/ft)	0.3048	meter per meter
mile (mi)	1.609	kilometer
Area		
foot squared per day (ft ² /d)	0.09294	meter squared per day
square mile (mi ²)	2.590	square kilometer
Flow		
foot per day (ft/d)	0.3048	meter per day
gallon per minute (gal/min)	0.06308	liter per second
gallon per day (gal/d)	0.003785	cubic meter per day
inches per year (in/yr)	25.4	millimeters per year
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:

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

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 (µg/L). Chemical concentration in air is expressed as nanomoles per liter (nM/L) or parts per million (ppm).

Biodegradation rate constant: In this report, first-order kinetics are used to describe the biodegradation rate of toluene. First-order rate constants (K) are expressed in units of percent of compound degraded per day (%d⁻¹). Because percent is dimensionless, this reduces to units of inverse days.

Other units used in report:

American Petroleum Institute units	API units
disintegrations per minute	DPM
gram	g
liter	L
megahertz	MHZ
micrograms	µg
micromoles	µM
micron	µm
microliter	µL
microliter per liter	µL/L
milligrams	mg
milliliter	mL
milliliter per minute	mL/min
millimole	mM
mole	M
nanomoles	nM

Abbreviations used in this report :

bls	below land surface
CO ₂	carbon dioxide
CVOC	chlorinated volatile organic compound
DCA	1,1-dichloroethane
DCE	cis 1,2-dichloroethene and trans 1,2-dichloroethene
DIC	dissolved inorganic carbon
DO	dissolved oxygen
Fe(II)	ferrous iron
Fe(III)	ferric iron
GC	gas chromatograph
H ₂	dissolved hydrogen
HgCl ₂	mercuric chloride
H ₂ O ₂	hydrogen peroxide
H ₂ S	hydrogen sulfide
ID	inside diameter
KOH	potassium hydroxide
MCL	maximum contaminant level
N	nitrogen
NO ₃	nitrate
OD	outside diameter
PCE	tetrachloroethene
psi	pounds per square inch
PVC	polyvinyl chloride
SCDHEC	South Carolina Department of Health and Environmental Control
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TEAP	terminal electron-accepting process
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride
VLF-EM	very low frequency electromagnetic
VOC	volatile organic compound
[1,2- ¹⁴ C]-VC	carbon-14 labeled vinyl chloride
¹⁴ C-CO ₂	carbon-14 labeled carbon dioxide
[1,2- ¹⁴ C]-ethene	carbon-14 labeled ethene

Transport and Transformations of Chlorinated-Solvent Contamination in a Saprolite and Fractured Rock Aquifer Near a Former Wastewater-Treatment Plant, Greenville, South Carolina

By Don A. Vroblesky, Paul M. Bradley, John W. Lane, Jr., and J. Frederick Robertson

Abstract

The transport and fate of chlorinated-ethene contamination was investigated in a fractured-rock aquifer downgradient from a wastewater-treatment plant at a gas-turbine manufacturing facility in Greenville, South Carolina. A vapor-diffusion-sampler technique, developed for this investigation, located fracture zones that discharged contaminated ground water to surface water. The distribution of chlorinated compounds and sulfate, comparison of borehole geophysical data, driller's logs, and the aquifer response to pumpage allowed subsurface contaminant-transport pathways to be delineated. The probable contaminant-transport pathway from the former aeration lagoon was southward. The probable pathway of contaminant transport from the former sludge lagoon was southward to and beneath Little Rocky Creek. South of the creek, the major pathway of contaminant transport appeared to be at a depth of approximately 80 to 107 feet below land surface. The contaminant-transport pathway from the former industrial lagoon was not readily discernible from existing data. A laboratory investigation, as well as examination of ground-water-chemistry data collected during this investigation and concentrations of chlorinated compounds collected during previous investigations, indicates that higher chlorinated compounds are

being degraded to lower-chlorinated compounds in the contaminated aquifer. The approaches used in this investigation, as well as the findings, have potential application to other fractured-rock aquifers contaminated by chlorinated ethenes.

INTRODUCTION

Chlorinated ethenes are among the most prevalent ground-water contaminants in the United States because of their extensive production and use as degreasing agents (Bouwer, 1994; McCarty and Semprini, 1994). The transport and fate of these contaminants in fractured-rock aquifers, however, remain poorly understood. In 1994, the U.S. Geological Survey (USGS) in cooperation with the South Carolina Department of Natural Resources - Water Resources Division, investigated these processes near a wastewater-treatment plant at a gas-turbine manufacturing facility in Greenville, S.C. The study area was a zone of ground-water contamination originating at the industrial wastewater-treatment plant and extending southward at least 1,200 ft. The site contained three unlined lagoons that received wastewater containing a variety of volatile organic compounds (VOC's) between 1987 and 1990 (Ede, 1992). Leakage from the lagoons resulted in ground-water contamination in the saprolitic and fractured-rock aquifers beneath and south of the wastewater-treatment plant (fig. 1). The ground-water contamination consisted primarily of

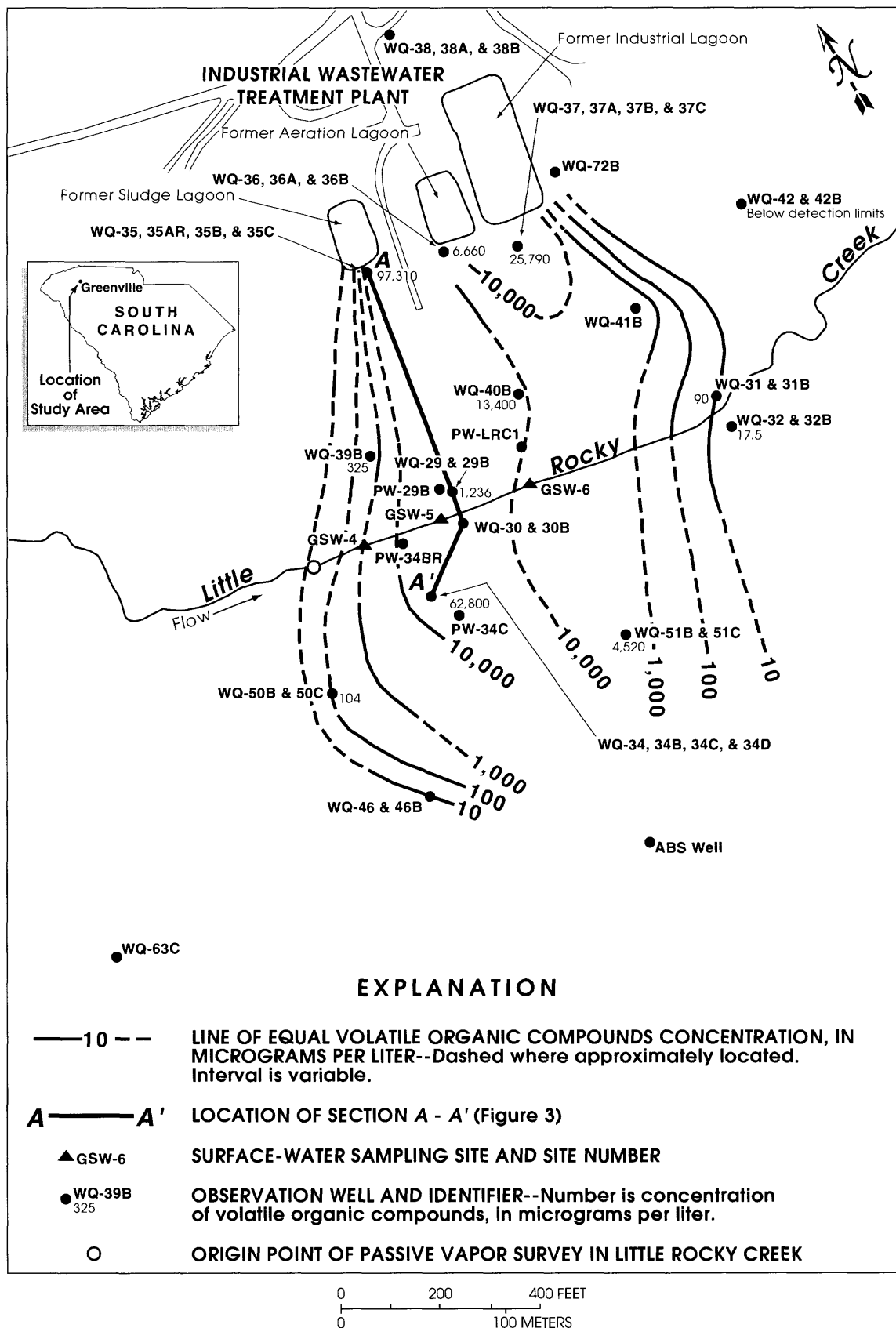


Figure 1. Location of study area, hydrogeologic section A-A', sampling locations, and distribution of dissolved chlorinated volatile organic compounds in ground water near a wastewater-treatment facility, Greenville, S.C., January 1994.

tetrachloroethene (PCE), trichloroethene (TCE), combined cis- and trans-1,2-dichloroethene (DCE), and vinyl chloride (VC). Because of the complexity of fractured-rock hydrology, limited information was available on specific contaminant-transport pathways and the potential for contaminant transformations at the site. The approaches used in this investigation, as well as the findings, have potential application to other fractured-rock aquifers contaminated by chlorinated ethenes.

Purpose and Scope

The purpose of this report is to document specific locations where contaminated ground water was discharging to surface water, identify pathways of ground-water flow in the fractured-rock aquifer, and show whether microbial processes in the aquifer contributed to the transformation of the chlorinated-hydrocarbon contamination. The scope of this report includes clarification of the geology and pathways of contaminant transport in the study area using borehole radar data and standard borehole geophysical logging techniques, as well as very low-frequency electromagnetic (VLF-EM) surveys from previous investigations. The results of a passive-vapor survey using vapor-diffusion samplers, a method developed for locating contaminant-bearing fractures discharging to local streams, are used to identify contaminant-discharge points in Little Rocky Creek. The report uses water-quality data collected during this investigation and VOC data from previous investigations to examine the potential for subsurface transformation of the contamination.

Description of Study Area

The study area is an industrial wastewater-treatment plant and the zone of ground-water contamination south of the plant in the Piedmont physiographic province near Greenville, S.C. The wastewater-treatment plant formerly contained three unlined lagoons: a sludge lagoon, an industrial lagoon, and an aeration lagoon. Observation wells near the facility include boreholes screened in the saprolite (designated with no alphanumeric suffix, that is WQ-34) and open to the shallow bedrock (designated with the suffix "B," as in WQ-34B) or deeper bedrock (designated with the suffix "C" or "D," as in WQ-34C). Boreholes designed to

operate as contaminant-extraction wells are designated by the prefix "PW," as in PW-34C.

The former lagoons are considered to be the probable sources of the ground-water contamination. Ground-water contamination from solvents in the lagoons extends at least 900 ft southward, as shown by the presence of chlorinated solvents in ground water at well WQ-51B (fig. 1) (Rust Environment and Infrastructure, 1995a).

Chlorinated solvents probably used in the area included TCE, PCE, DCE, TCA (1,1,1-trichloroethane), and methylene chloride (Sirrinc Environmental Consultants, 1991a; Ron Harper, General Electric Company, oral commun., 1996; W. Thomas Hyde, General Electric Company, oral commun., 1996). The former industrial lagoon contained chlorinated volatile organic compounds (CVOC's) and petroleum hydrocarbons (Sirrinc Environmental Consultants, 1991a). The former aeration lagoon received sewage sludge as well as water from the industrial lagoon (Sirrinc Environmental Consultants, 1991a). The former sludge lagoon received sludges from various areas and may have included PCE and TCA (Ron Harper, General Electric Company, oral commun., 1996).

Ground water downgradient from the lagoons flows through a shallow saprolite aquifer and an underlying fractured-rock aquifer. The saprolite is approximately 50 ft thick beneath the sludge lagoon and is hydraulically connected to the fractured-rock aquifer (Sirrinc Environmental Consultants, 1992). The bedrock in the area is dominantly biotite gneiss, although granite gneiss also has been reported (Koch, 1968; Sirrine Environmental Consultants, 1992). The saprolite aquifer is recharged by rainfall infiltration in upland areas, and ground water flows generally south-eastward beneath the wastewater-treatment area (fig. 2).

Little Rocky Creek (fig. 1), flows west to east, approximately 400 ft south of the wastewater-treatment plant and transects the ground-water contamination plume. The creek-bottom sediment is predominantly silty sand, but locally contains outcropping rock. The creek ranges in width from about 2 ft, in areas where flow is constricted by exposed rock, to about 14 ft. The depth of water in the thalweg of the creek ranges from about 0.2 to 4 ft.

The high densities (relative to water) of the leaked CVOC's probably allowed them to be transported downward through the saprolite aquifer and into the underlying fractured-rock aquifer. In

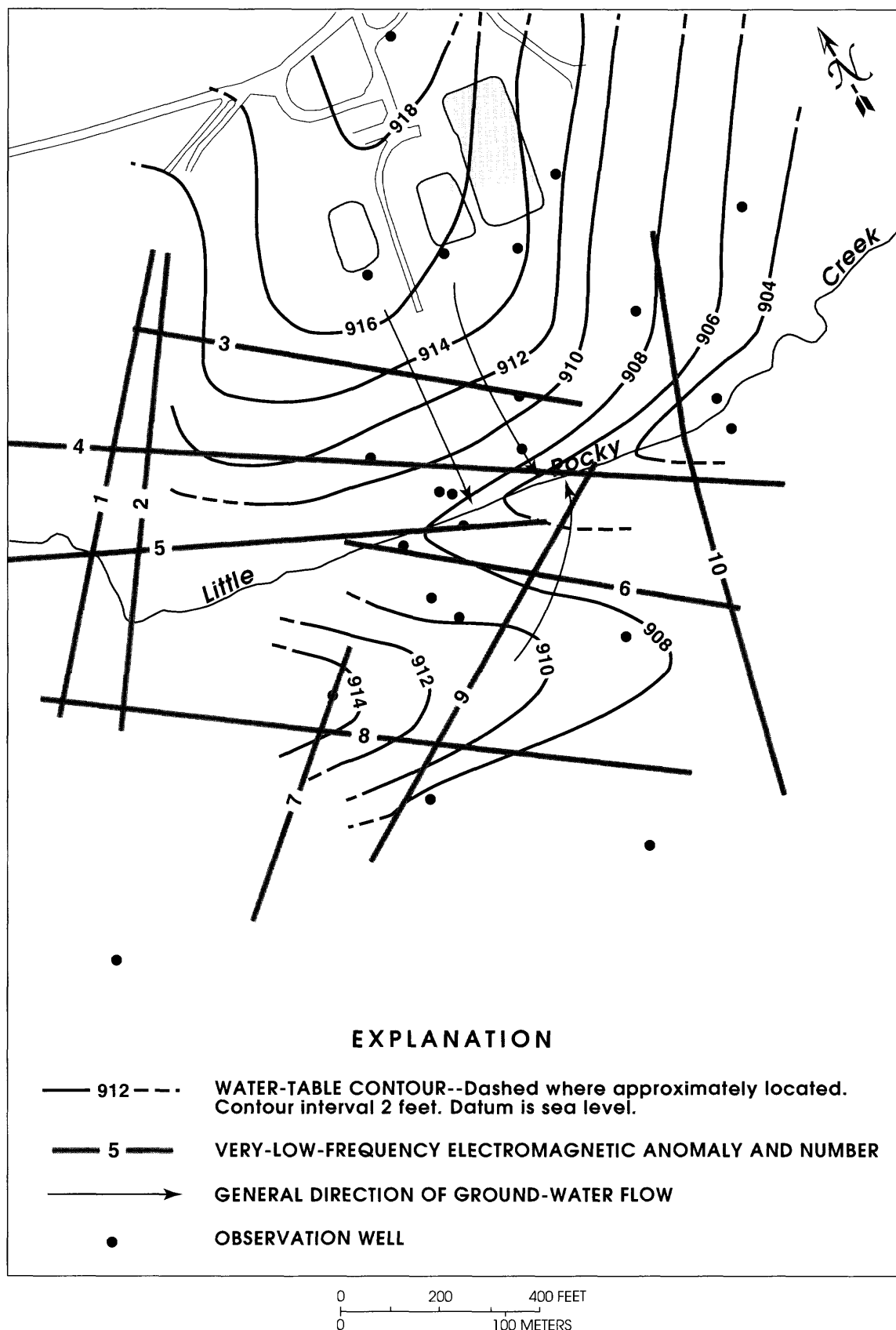


Figure 2. Very low-frequency electromagnetic anomalies and water-table elevation near a wastewater-treatment facility, Greenville, S.C., January 1994.

January 1994, concentrations of total VOC's in ground water exceeded 30,000 µg/L in the fractured-rock aquifer (wells WQ-34B and WQ-34C) approximately 150 ft south of Little Rocky Creek (fig. 1). At the same time, however, water in the overlying saprolite aquifer contained only 125 µg/L of VOC's (well WQ-34) (Rust Environment and Infrastructure, 1994a). The high concentrations in the fractured-rock aquifer indicate that transport through fractures is a major pathway for movement of dissolved VOC's at this site.

Previous Investigations

Water-level measurements made in 1994 implied that ground water in the deeper part of the fractured-rock aquifer discharged to Little Rocky Creek from both sides of the creek (Rust Environment and Infrastructure, 1994a). However, the presence of CVOC contamination at the WQ-34 and WQ-51 well clusters (fig. 1, table 1) (Rust Environment and Infrastructure, 1994a), on the opposite side of the creek from the wastewater-treatment plant, and the lack of contaminant sources south of these wells indicate that the contamination was transported beneath the creek (fig. 3). The lack of agreement between ground-water-flow directions determined from the potentiometric map and contaminant-transport pathways evidenced by contaminant distribution may be explained by the possibilities that either (1) contaminant transport followed pathways not reflected by 1994 water-level data or (2) complexities associated with hydrologic continuity among fractures prevented the water-level data from adequately representing ground-water flow in this fractured-rock aquifer. Analytical calculations implied that the water-level data did not adequately define the direction of ground-water flow (Stacy Sargent, Rust Environment and Infrastructure, written commun., 1996). The calculations showed that very little of the water volume discharging to the creek downgradient from the wastewater-treatment facility was derived from the fractured-rock aquifer, supporting the hypothesis that ground water in the fractured-rock aquifer flows beneath the creek.

Surface-water-sample analyses indicated that VOC contamination also discharged to Little Rocky Creek (Rust Environment and Infrastructure, 1993). In February 1993, VOC concentrations in surface water at sampling site GSW-4 (fig. 1) and at upstream sampling sites were less than 5 µg/L. However, the VOC concentrations were greater than 50 µg/L further

downstream at surface-water sampling sites GSW-5 and GSW-6.

In an effort to delineate the fractures controlling the site hydrogeology, a VLF-EM WADI survey was completed along 29 profiles covering 44,670 ft in the vicinity of the study area (Sirrine Environmental Consultants, 1991b). Military radio transmissions at various locations around the world generate VLF signals with a horizontal magnetic field that travel parallel to ground surface. When the signal encounters a low-resistivity zone, such as a water-filled fracture in host rock, a secondary electromagnetic field is generated. The WADI survey examined the distribution of these secondary fields. Reinterpretation of the WADI data (Vroblesky and others, 1996) showed linear VLF-EM anomalies transecting Little Rocky Creek in the contaminated area south of the wastewater-treatment plant (fig. 2).

Several factors indicate that the shallow hydrogeology of the site was influenced by fractures in bed-rock or relic fractures in saprolite. A ground-water depression in the shallow saprolite aquifer west of the wastewater-treatment plant aligned with VLF-EM anomalies 1 and 2 (Sirrine Environmental Consultants, 1992; Vroblesky and others, 1996). VLF-EM anomalies 1 and 2 crossed the creek in the vicinity of sharp changes in orientation of the creek. The orientation of the creek west of the plant (not shown in fig. 2) is approximately aligned with VLF-EM anomaly 4. These relations indicate that subsurface fractures may provide structural control of the creek bed (Sirrine Environmental Consultants, 1991b). Moreover, outcropping rock in Little Rocky Creek indicate the variability of saprolite thickness. Therefore, it is probable that fractures affect VOC transport and discharge to Little Rocky Creek south of the wastewater-treatment plant.

Methods

In general, ground-water sample collection and borehole geophysics were accomplished using standard methods. In addition, a new method to collect data on subsurface VOC's was devised for this investigation to locate areas where contaminated ground water was discharging to the creek. Specific methods used during this investigation are discussed in the following sections.

Table 1.--Construction data for selected observation wells, Greenville, S.C., (W. Thomas Hyde, General Electric Company, written commun., 1996)

[ft, feet; PVC, polyvinyl chloride; --, data not available; OH, open hole; SCN, slotted screen; SS, stainless steel; <, less than]

Well identification (fig. 1)	Casing material	Casing diameter (inches)	Total depth (ft below land surface)	Type of opening	Depth interval of open section (ft below land surface)	Land-surface elevation (ft above sea level)	Top of casing elevation (ft above sea level)
ABS-1	PVC	--	190.5	OH	--	--	934.26
PW-29B	PVC	6.00	73.7	OH	43.5 - 73.7	911.25	915.16
PW-34BR	PVC	6.00	92.0	OH	22.5 - 92.0	912.8	914.82
PW-34C	PVC	6.25	179.0	OH	37.5 - 179.0	924.09	925.66
PW-LRC1	PVC	5.76	63.3	OH	30.4 - 63.3	913.77	916.66
WQ-29	PVC	2.00	16.5	SCN	5.3 - 14.7	911.42	914.79
WQ-29B	PVC	4.00	63.4	OH	42.0 - 63.4	911.42	914.70
WQ-30	PVC	2.00	15.0	SCN	4.3 - 13.7	911.44	914.22
WQ-30B	PVC	4.00	55.8	OH	34.8 - 55.8	911.44	914.49
WQ-31	PVC	2.00	15.0	SCN	4.3 - 13.7	904.75	907.59
WQ-31B	PVC	4.00	57.8	OH	37.3 - 57.8	904.75	907.69
WQ-32	PVC	2.00	15.0	SCN	4.3 - 13.7	905.07	908.10
WQ-32B	PVC	4.00	63.6	OH	43.3 - 63.6	905.07	908.02
WQ-34	PVC	2.00	28.0	SCN	14.5 - 24.2	921.36	924.02
WQ-34B	PVC	4.00	59.0	OH	38.5 - 59.0	921.36	924.36
WQ-34C	SS	5.06	143.7	OH	98.7 - 143.7	921.34	923.34

Table 1.--Construction data for selected observation wells, Greenville, S.C., (W. Thomas Hyde, General Electric Company, written commun., 1996)--Continued

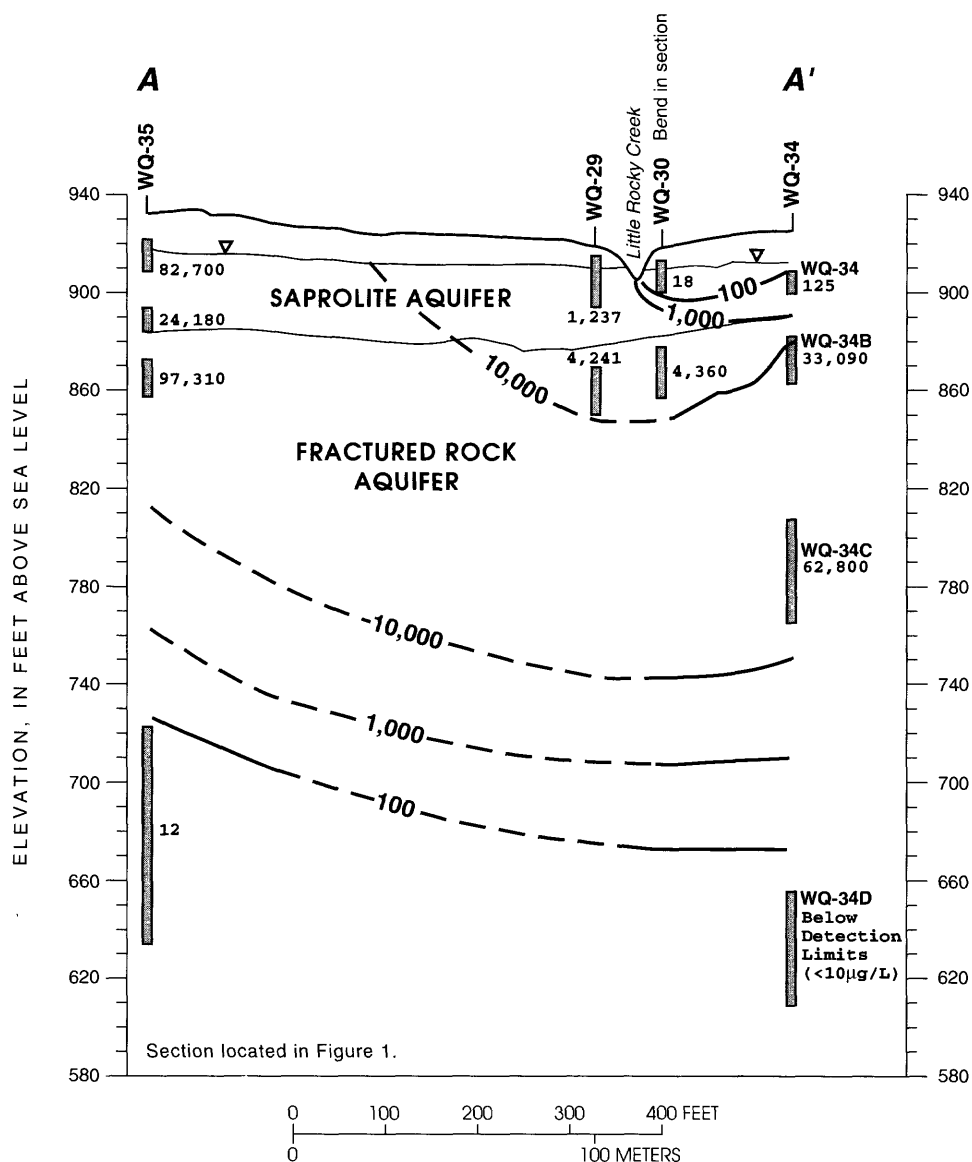
[ft, feet; PVC, polyvinyl chloride; --, data not available; OH, open hole; SCN, slotted screen; SS, stainless steel; <, less than]

Well identification (fig. 1)	Casing material	Casing diameter (inches)	Total depth (ft below land surface)	Type of opening	Depth interval of open section (ft below land surface)	Land-surface elevation (ft above sea level)	Top of casing elevation (ft above sea level)
WQ-34D	PVC	4.75	324.3	OH	258.4 - 324.3	921.19	923.95
WQ-35	SS	2.00	16.0	SCN	5.6 - 15.3	928.06	929.67
WQ-35AR	SS	2.00	42.5	SCN	32.1 - 41.8	927.75	930.68
WQ-35B	SS	4.00	72.3	OH	51.7 - 72.3	928.38	931.53
WQ-35C	SS	5.25	299.3	OH	202.5 - 299.3	927.02	929.31
WQ-36	SS	2.00	24.0	SCN	10.3 - 20.0	931.63	934.05
WQ-36A	SS	2.00	37.2	SCN	27.4 - 37.0	931.63	934.49
WQ-36B	SS	4.00	79.8	OH	44.6 - 79.8	931.63	934.52
WQ-37	SS	2.00	15.0	SCN	4.8 - 14.5	920.28	922.35
WQ-37A	SS	2.00	23.5	SCN	12.3 - 22.0	919.36	922.25
WQ-37B	SS	4.00	47.9	OH	27.9 - 47.9	919.65	921.73
WQ-37C	SS	5.00	180.8	OH	161.0 - 180.8	920.61	922.30
WQ-38	SS	2.00	29.7	SCN	19.5 - 29.2	941.26	943.97
WQ-38A	SS	2.00	52.3	SCN	42.2 - 51.9	941.17	944.10
WQ-38B	SS	4.00	77.4	OH	57.1 - 77.4	940.91	943.76
WQ-39B	PVC	4.00	61.6	OH	37.7 - 61.6	914.25	915.93
WQ-40B	PVC	4.00	58.9	OH	38.2 - 58.9	917.56	919.75

Table 1.--Construction data for selected observation wells, Greenville, S.C., (W. Thomas Hyde, General Electric Company, written commun., 1996)--Continued

[ft, feet; PVC, polyvinyl chloride; --, data not available; OH, open hole; SCN, slotted screen; SS, stainless steel; <, less than]

Well identification (fig. 1)	Casing material	Casing diameter (inches)	Total depth (ft below land surface)	Type of opening	Depth interval of open section (ft below land surface)	Land-surface elevation (ft above sea level)	Top of casing elevation (ft above sea level)
WQ-41B	PVC	4.00	66.4	OH	42.1 - 66.4	910.92	912.98
WQ-42	PVC	2.00	24.2	SCN	14.2 - 23.9	908.01	910.33
WQ-42B	PVC	4.00	70.5	OH	51.1 - 70.5	908.06	910.90
WQ-46	PVC	2.00	39.7	SCN	29.3 - 39.5	941.99	944.78
WQ-46B	PVC	4.00	119.8	OH	99.9 - 119.8	941.99	944.72
WQ-50B	PVC	4.75	165.0	OH	90.1 - 165.0	938.65	941.09
WQ-50C	PVC	4.75	331.0	OH	272.0 - 331.0	939.28	941.69
WQ-51B	PVC	4.75	90.5	OH	65.0 - 90.5	928.57	931.02
WQ-51C	PVC	<4.75	220.0	OH	165.0 - 220.0	928.82	931.40
WQ-58C	PVC	5.00	302.8	OH	159.2 - 302.8	952.81	953.84
WQ-63C	PVC	5.00	343.0	OH	260.0 - 343.0	944.80	946.97
WQ-72B	PVC	2.00	103.0	OH	52.0 - 103.0	922.3	924.24



EXPLANATION

- 100 — — LINE OF EQUAL CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN GROUND WATER—Interval, in micrograms per liter, variable as shown. Dashed where approximately located.
- ▽ — WATER TABLE
- ▮ 24,180 OPEN OR SCREENED INTERVAL AND CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN GROUND WATER, IN MICROGRAMS PER LITER

Figure 3. Hydrogeologic section A-A', near a wastewater-treatment facility, Greenville, S.C., January 1994.

Vapor-Diffusion Samplers

The approach used in this investigation to define areas where contaminated ground water was discharging to surface water involved the installation of vapor-diffusion samplers in the bottom sediment of Little Rocky Creek. The vapor-diffusion samplers consisted of 40-mL glass VOC vials enclosed in sealable polyethylene bags.

Preparation of the vapor-diffusion samplers involved placing an uncapped vial in a bag, removing excess air from the bag, and then sealing the bag. The vial was arranged in the bag so that a single 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). 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 threads around the opening of the tube. The VOC vial and bag were then placed inside another sealable polyethylene bag, and that bag was sealed using the same technique as the inner bag. 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 sand from bottle threads. The outer bag was removed after sample retrieval, immediately prior to capping the vials. Two individually wrapped VOC vials were placed in the same outer bag and sealed for sample replication. The vapor-diffusion samplers, which consisted of one or two uncapped 40-mL glass VOC vials enclosed in two sealable polyethylene bags, was attached to a wire survey flag prior to installation.

Vapor-diffusion samplers were installed by coring a hole approximately 1 ft deep using a hand auger in the bottom sediment of the creek. A vapor-diffusion sampler was placed in the hole, and the hole was backfilled with the sediment that was removed from the hole. Vapor-diffusion samplers were left in the bottom sediment for approximately 5 weeks, although previous work has shown that 1 day was a sufficient amount of time for benzene and toluene vapors to equilibrate across the polyethylene membrane (Vroblesky and others, 1992). In the upstream 210 ft of the bottom-sediment vapor survey (the vicinity of GSW-4 and GSW-5), the distance between sampling sites was about 5 ft. In general, vapor-diffusion samplers were separated by about 10 ft along the stream bottom.

The samplers were removed by gently pulling the wire survey flags, with the attached vapor-diffusion samplers, out of the bottom sediment. Immediately upon retrieval of each vapor-diffusion sampler from the bottom sediment, the outer polyethylene bag was cut open, leaving the inner polyethylene bag intact. The Teflon-septum-lined cap was screwed onto the vapor-diffusion sampler over the inner polyethylene bag (the single layer of polyethylene was between the glass vial and the cap).

The vapor-diffusion samplers were analyzed for VOC content within 48 hours of sample collection. Approximately 10 μ L of vapor was withdrawn through the cap using a 100- μ L gas-tight syringe and then flushed from the needle outside of the sampler. A 50- μ L vapor sample was slowly withdrawn and immediately analyzed on a Photovac 10S50 field gas chromatograph (GC). The GC was equipped with a column that provided little or no separation of chromatographic peaks, resulting in chromatographic peaks that can encompass a variety of volatile organic compounds. The GC was calibrated against a Scotty IV vapor standard (blend 2, mix number 4-6675-4EL) of mixed chlorinated organic compounds, at approximate concentrations of 1 ppm each, in nitrogen. The compounds in the mixture were cis-1,2-dichloroethene; 1,2-dibromomethane; 1,1-dichloroethane; 1,2-dichloroethane; PCE; TCA; VC; and vinylidene chloride. Because the VOC's detected in bottom-sediment vapors at this site were quantified relative to a mixed chlorinated organic compound standard, they are reported as relative concentrations of VOC's, in units of parts per million.

Vapor-diffusion samplers were retrieved from 117 sites south of the wastewater-treatment plant along an 871-ft traverse in Little Rocky Creek. The sample locations extended beyond the limits of known ground-water contamination. Most of the sampling locations were near the northern shoreline, but the eastern reach of the creek included a line of samplers along the center of the creek as well as near the northern shoreline.

Replicate samplers were installed and collected at 18 sites. The average precision of VOC concentrations in all 18 replicate samplers was 15 percent. The relative concentrations of VOC's detected differed by an average of 15 percent between respective replicates. The largest difference between respective replicates was 30 percent. At five of the sites, there was less than 5 percent difference between respective rep-

licates. Several vapor-diffusion samplers upstream and downstream from the area of known ground-water contamination contained no detectable VOC's (less than about 5 ppm), indicating that the strapping tape and polyethylene bag did not contribute VOC's to the samples.

To determine the amount of time that the capped vapor-diffusion samplers could be stored prior to analysis, 15 samplers were placed in a plastic container. The plastic container was flushed with the same mixed chlorinated organic compound vapor standard used to calibrate the GC and was then sealed, trapping the mixed vapor standard inside. After 16 hours, the plastic container was cut open, and the vapor-diffusion samplers were removed and capped.

Samples in each vapor-diffusion sampler were analyzed by extracting 50 μ L of vapor by syringe through the Teflon septum of the cap. Extraction and analysis of VOC's was done a total of four consecutive times for each collector. Total time elapsed during analysis of samples from each was about 5 to 10 minutes. Concentrations showed little variation between consecutive samples from the same vapor-diffusion sampler. The standard deviation of the concentrations

from each sampler varied from the respective average concentration by values ranging from 1.3 to 24 percent.

Vapor samples from three samplers were analyzed within 10 minutes of their removal from the plastic container. Samples from three additional samplers were analyzed 5.4 hours later. Similar analyses of samples from additional samplers were run at intervals of 21 hours, 54 hours, and 121 hours following removal from the plastic container. The data shown in figure 4, therefore, represent 12 analyses at each time point.

No loss of vapor from the capped vapor-diffusion samplers was detected within the range of the standard deviation of the analyses over 121 hours (fig. 4). Thus, once the samplers are retrieved and capped, they can be stored for at least 121 hours prior to analysis. Several vapor samples can be consecutively analyzed from each sampler with good replication over a period of several minutes, but substantial loss of vapor was observed after 33 hours from samplers having punctured septa after extraction of samples for analysis (fig. 4).

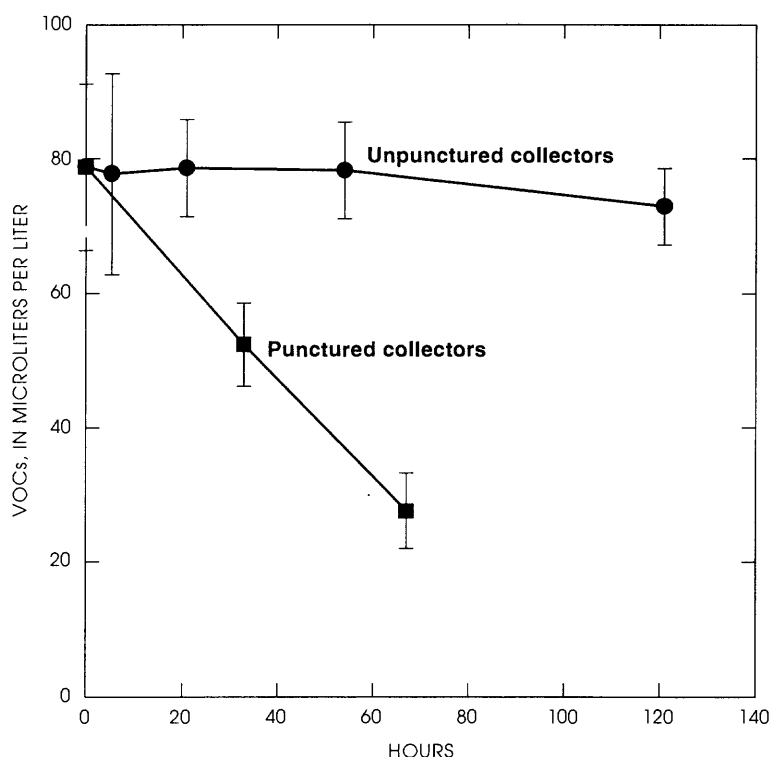


Figure 4. Changes in concentration of volatile organic compounds (VOCs) in vapor-diffusion samplers with time following capping of the collectors (bars represent standard deviations calculated for the samples).

Ground-Water Sample Collection and Analysis

All monitoring wells were purged of casing water prior to collecting ground-water samples. At least three casing volumes of water were removed from each well with either a Teflon bailer or a positive-displacement pump.

Ferrous iron [Fe(II)], dissolved oxygen (DO), pH, and water temperature were measured in the field. After well purging, the DO concentration in water from each well was determined by Winkler titration (Hach Company, 1983). Ferrous iron was analyzed using the Hach colorimeter/FerroZine method (Stookey, 1970).

Water samples for analysis of VOC's were collected by Rust Environment and Infrastructure. All sample bottles were capped with Teflon-lined bottle caps. The water samples for VOC's were analyzed using U.S. Environmental Protection Agency (USEPA) method 8240 (U.S. Environmental Protection Agency, 1986). Complete results of the VOC analyses are presented in Rust Environment and Infrastructure (1994a).

Methane and dissolved inorganic carbon (DIC) samples were collected by using a syringe to collect 5 mL of sample water and to inject it into sealed septated vials through a 0.45- μ m porous-membrane filter. The syringe and vials were rinsed with filtered sample water prior to sampling. The samples were packed in ice to minimize concentration changes by microbial activity. Methane was quantified by thermal-conductivity-detection gas chromatography. Dissolved methane concentrations were calculated using Henry's Law coefficients (Stumm and Morgan, 1981). The DIC samples were acidified in the laboratory with a 42.5 percent phosphoric acid solution, and DIC concentrations quantified by thermal-conductivity-detection gas chromatography. Because DIC samples were collected from headspace in the vials and gas chromatography attributes all carbon in this headspace to the DIC concentration, ambient air samples were collected and analyzed for carbon content to correct the DIC concentration for carbon present in the atmosphere.

Water samples for analysis of inorganic ions were collected in sample-rinsed polyethylene bottles after passing through a 0.45- μ m porous-membrane filter. The inorganic ion samples were packed in ice immediately following collection. The samples were analyzed for calcium (U.S. Environmental Protection Agency method 215.1), magnesium (U.S. Environmental Protection Agency method 242.1), sulfate

(U.S. Environmental Protection Agency method 375.4), and nitrate (U.S. Environmental Protection Agency method 352.1) (U.S. Environmental Protection Agency, 1983).

For quality control and assurance, duplicate samples were collected for at least 10 percent of the total number of wells sampled for each sample event. Duplicate samples not showing analytical agreement were reanalyzed when possible.

Ground-water hydrogen samples were collected by peristaltic pump 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 mL/min. The silicon tubing used in conjunction with the peristaltic pump was decontaminated by pumping approximately 1 L of deionized water through the system prior to sampling each well. The outside of the silicon tubing was rinsed with deionized water. 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 20 minutes of initiating the flow of water through the bulb), gas was extracted from the bulb using a gas-tight syringe. Dissolved hydrogen was measured on a gas chromatograph equipped with a reduction gas detector. The detection limit of this method varied between 0.1 and 0.5 nM. All dissolved hydrogen samples were collected as duplicates. Each duplicate was analyzed separately; however, hydrogen concentrations were reported as average values.

The use of hydrogen, 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), Vroblesky and Chapelle (1994). These studies indicated that dissolved hydrogen concentration ranges of 5 to 25 nM are characteristic of methanogenesis; 1 to 4 nM are characteristic of sulfate reduction; and 0.1 to 0.8 nM are characteristic of ferric iron [Fe(III)] reduction. Because hydrogen is an extremely transitory intermediate with a half-life of less than a minute (Conrad and others, 1987), it is a useful constituent for documenting predominant TEAP's. In this study, hydrogen concentrations were

used in conjunction with concentrations of other microbially active solutes to document the spatial and temporal variations in TEAP's.

Borehole Geophysics

Borehole geophysical methods used during this investigation included conventional and nonconventional (downhole radar) tools. In May 1994, televiewer, caliper, temperature, and heat-pulse-flow logs were run at wells PW-34C, WQ-34D, WQ-35B, WQ-35C, WQ-37B, WQ-37C, WQ-50C, WQ-51B, and WQ-51C (fig. 1). A natural gamma log was run at well PW-34C only. Heat-pulse flowmeter data are shown in appendix I, and geophysical logs obtained from selected wells are shown in appendix II.

Downhole radar measurements at single wells were obtained using a 60-megahertz (MHZ) RAMAC transmitter and directional receiver in late July 1994. The measurements were made in wells WQ-34D, WQ-46B, WQ-50C, WQ-51C, WQ-58C (not shown on figure 1), WQ-63C, WQ-72B, and the ABS well. In general, signal attenuation was high, restricting maximum penetration to approximately 75 ft from the well bore. Data processing included removal of direct-current offsets, application of linear and exponential gains, and band-pass filtering. The data analysis allowed estimation of the strike, dip, and projected borehole intersection depths of planar discontinuities, as well as the direction and distance to point-like discontinuities.

The borehole-radar attenuation with depth also was examined. Radar attenuation is a measurement of the peak to peak amplitude of the direct arrival radar pulse, in microvolts, from the transmitter to the receiver. The data are analogous to data obtained from a normal resistivity log, with the exception that the radar can be used in polyvinyl chloride (PVC)-cased or dry boreholes. Reflectors identified by single-hole borehole-radar surveys are shown in appendix III.

Cross-hole tomography from well PW-34C to well WQ-34D, allowed examination of the signal-attenuation fields between the wells. A 22-MHZ transmitting antenna was fixed at a location in one borehole, and a 22-MHZ nondirectional receiver was incrementally moved in the other borehole. After the receiver had been moved to all stations, the transmitter was moved one increment. The receiver again was moved to all stations, and the process was repeated until both the transmitter and receiver occupied all stations.

Microcosm Investigation of Vinyl Chloride Degradation

The ability of microorganisms indigenous to the saprolite aquifer underlying the site to mineralize VC under aerobic or Fe(III)-reducing conditions was evaluated in aquifer-sediment microcosms using [1,2-¹⁴C]-VC. Microcosm experiments were conducted using saprolite aquifer sediments collected near monitoring wells WQ-35 and WQ-36. Aquifer material was collected 2 to 5 ft below the water table at a depth of 20 to 25 ft below land surface (bls). Sediment samples were collected using a flame-sterilized, split-spoon sampler and stored in autoclaved jars. Samples were maintained at 4 degrees Celsius (°C) until initiation of microcosm studies.

Microcosms consisted of 20-mL serum vials that were amended with 5 g of saturated aquifer sediment and sealed with Teflon-lined butyl rubber stopper/base trap assemblies (Bradley and Chapelle, 1996). Microcosms were created with a headspace of air (aerobic treatments) or 100 percent helium (Fe(III)-reducing treatments) and amended with 0.5 mL of anoxic, sterile deionized water. Killed controls were prepared as described, amended with 0.5 mL of 50 mM mercuric chloride (HgCl₂) and autoclaved for 1 hour at 15 psi and 121 °C. Five live and triplicate killed controls were prepared for each treatment and each sediment. The microcosms were incubated for a 15-day acclimation period. Then, approximately 100,000 DPM radio-labeled vinyl chloride [(1,2-¹⁴C)-VC] were injected directly into the saturated sediment to minimize volatilization loss to the headspace to yield a final dissolved concentration of about 17 µM of VC. The purity of the radio-labeled VC (Du Pont, NEN Research Products, Boston, Mass.) was determined by radiometric detection-gas chromatography to be greater than 98 percent. Samples were collected by rinsing microcosm base traps with 0.5 mL of sterile deionized water and filling them with 0.3 mL of 3 M potassium hydroxide (KOH). After 12 hours, the KOH was removed and the amount of trapped radio-labeled carbon dioxide (¹⁴C-CO₂) was quantified by scintillation counting. Production of ¹⁴C-CO₂ was confirmed in selected vials using methods described previously (Davis and Carpenter, 1990). The fact that no radioactivity was detected in the base traps of sterile serum vials that contained radio-labeled VC but no sediment indicates that trapping of radio-labeled VC was not significant (less than 0.5 percent) in experimental microcosms. Microcosms were incubated in the dark,

and VC mineralization was monitored six times over a total incubation period of 166 days.

Rates of [1,2- ^{14}C]-VC mineralization were estimated by linearly regressing the percentage of ^{14}C recovered as $^{14}\text{C}\text{-CO}_2$ in base traps as a function of incubation time using a simple linear regression program (Jandel Scientific, 1992). Rates of [1,2- ^{14}C]-VC mineralization were considered insignificant in treatments where the final percentage recovery of ^{14}C was less than 2 percent [the purity of the (1,2- ^{14}C)-VC was 98.5 percent] or the slope of the linear regression was not statistically significant from zero ($p < 0.05$, Sigmatat, Jandel Scientific, 1992). Statistically significant differences between treatment mean rates of mineralization were determined by the Kruskal-Wallis one way ANOVA on ranks ($p < 0.05$).

TRANSPORT OF GROUND-WATER CONTAMINATION

Identification of contaminant-transport pathways was accomplished by integrating data from several aspects of this and previous investigations. The aspects included identifying areas of contaminated ground-water discharge to Little Rocky Creek, examining geochemical tracers of ground-water contamination, and examining borehole-geophysical data.

Discharge of Contaminated Ground Water to Little Rocky Creek

The vapor-diffusion samplers in the bottom sediment of Little Rocky Creek contained relative concentrations of VOC's ranging from less than 5 ppm to 980 ppm (table 2). The highest concentrations were between surface-water-sampling sites GSW-4 and GSW-5 (fig. 1). This reach was Area A (fig. 5), where the change from less than 7 $\mu\text{g/L}$ of total measured VOC's in surface water at GSW-4 to 300 $\mu\text{g/L}$ at GSW-5 during January 1994 (Rust Environment and Infrastructure, 1994a) indicated that contaminated ground water was discharging to surface water. Volatile organic compounds were not detected (less than 5 ppm) in passive-vapor collectors in the creek upstream from surface-water-sampling site GSW-4, where VOC's were not detected in surface water, and downstream from the area of known ground-water contamination (fig. 1). These data indicated that the passive-vapor survey using vapor-diffusion samplers was

capable of locating areas where contaminated ground water was being discharged from the aquifer to surface water.

Vapor extracted from a vapor-diffusion sampler in the reach of the creek between GSW-4 and GSW-5 was injected into the capillary column of the field GC to provide separation of individual compounds. The GC analysis tentatively identified TCE, PCE, VC, and 1,1-dichloroethane (DCA) as the major constituents of the VOC's beneath Little Rocky Creek. These compounds were known constituents of the ground-water contamination, and TCE and PCE were the dominant surface-water contaminants in that reach during January 1994 (Rust Environment and Infrastructure, 1994a). Thus, data from the vapor-diffusion samplers were not only useful for determining areas where ground water containing VOC contamination was discharging to Little Rocky Creek, but also for tentatively identifying specific VOC's being discharged.

Area A was also a site where VLF-EM anomalies crossed Little Rocky Creek or converged in or near the creek (fig. 5). Electromagnetic anomaly 5 crossed the creek at area A, and VLF-EM anomaly 6 crossed the creek near area A. Moreover, if VLF-EM anomaly 7 is extended northeastward, as represented by the dashed line in figure 5, it intersects VLF-EM anomalies 5 and 6 at area A near Little Rocky Creek.

The evidence for fracture control of ground-water and surface-water hydrology at this site implies that VOC contamination discharging to Little Rocky Creek south of the wastewater-treatment plant was derived dominantly from ground water flowing through fractures. The relation between relative concentrations of VOC's, areas of known VOC contamination in ground water and surface water, and VLF-EM anomalies indicates that the distribution of VOC's along Little Rocky Creek defined areas where contaminated ground water was discharging from a fracture-dominated ground-water flow system.

Additional confirmation of the ability of VOC samplers to locate VOC-contaminated fractures was seen during the installation of a contaminant-removal well (PW-34BR) near the creek, following completion of the VOC survey.

Based on results of the passive-vapor survey, a contaminant-removal well was installed about 15-ft south of Little Rocky Creek in an area adjacent to the zone of highest concentrations of VOC's in area A. While the borehole was being drilled using an air-rotary method through the bedrock, air bubbles were

Table 2.--Analysis of volatile organic compounds in bottom sediment beneath Little Rocky Creek derived from vapor-diffusion samplers, January 1994

[ft, feet; VOC's, volatile organic compounds; ppm, parts per million; <, less than; --, no data]

Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)
North side of Little Rocky Creek							
20	<5	191	183	356	27	597	17
47	<5	201	173	366	13	611	60
56	17	211	28	376	22	621	98
66	28	216	171	386	26	631	87
76	<5	231	90	391	30	641	26
86	<5	241	98	396	37	651	<5
91	<5	246	37	401	44	661	<5
96	<5	261	11	411	41	671	75
101	<5	266	42	416	59	680	<5
106	<5	271	9	421	65	689	9
116	31	276	45	431	101	711	21
121	31	281	94	436	109	721	20
126	171	286	53	441	<5	731	15
131	205	291	11	446	55	741	9
136	130	296	14	456	138	751	8
141	223	301	<5	461	111	761	13

Table 2.--Analysis of volatile organic compounds in bottom sediment beneath Little Rocky Creek derived from vapor-diffusion samplers, January 1994--Continued

[ft, feet; VOC's, volatile organic compounds; ppm, parts per million; <, less than; --, no data]

Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)	Distance downstream from origin point of creek survey (ft)	Relative concentration of VOC's (ppm)
146	139	306	15	465	<5	771	<5
151	160	311	<5	471	88	781	<5
156	396	316	<5	476	25	806	13
161	209	326	<5	500	17	811	<5
166	980	331	16	521	17	821	20
171	293	336	23	531	27	831	<5
176	252	341	11	541	18	851	<5
181	286	346	12	551	<5	863	<5
186	244	351	24	569	<5	871	<5
Center of Little Rocky Creek							
0	<5	126	209	156	370	196	244
10	<5	146	336	166	289	206	94
86	<5	151	204	176	220	216	24
116	6	--	--	186	273	221	44

observed rising from the bottom sediment of Little Rocky Creek in the zone of highest concentrations of VOC's in area A. Ground water from the well contained VOC's. These observations indicate that the well intersected a fracture zone that connected the contaminated aquifer to the stream in the zone of highest concentrations of VOC's. The data support the conclusion that the vapor-diffusion samplers were an effective tool for locating contaminated ground water.

Areas B and C (fig. 5) were additional reaches of the creek where locally elevated concentrations of VOC's were measured beneath the creek. Area B is near VLF-EM anomaly 4, and VLF-EM anomaly 9 intersects the creek adjacent to area C (fig. 5). As will be shown, Areas B and C probably represent additional areas where contaminated ground water was discharging from the fracture-controlled groundwater flow system.

Major Pathways of Subsurface-Contaminant Transport

The complex nature of ground-water flow in a fractured-rock aquifer causes difficulties in determination of major subsurface contaminant-transport pathways. Nevertheless, data from a variety of sources can be used to approximately locate probable transport pathways. These sources include data obtained from chemical analysis of ground water at various horizons, borehole and surface geophysics, and observations of transient phenomena (such as introducing air bubbles into the fractures) associated with well drilling and pumping.

Geochemical Tracers of Contaminant Transport

The areal distribution of ground-water contamination is an obvious source of data that can be used to approximately locate transport pathways. The potential for higher-chlorinated VOC's to dechlorinate to lower-chlorinated VOC's under some conditions, to sorb to aquifer material, and to be diluted along flow paths complicate definition of specific transport pathways from comparisons of individual CVOC distributions. However, other chemical species potentially can act as contaminant tracers. For example, at this site, sulfate concentrations were higher (greater than 100 mg/L) in parts of the aquifer down gradient from the former aeration lagoon at wells WQ-36, WQ-40B, WQ-41B, WQ-51B, and WQ-51C than in wells down-

gradient from the other lagoons (fig. 6, table 3). Sulfate concentrations in relatively uncontaminated areas or the area downgradient from the former sludge lagoon were less than 20 mg/L. Moreover, in the area of high sulfate concentration near the former aeration lagoon, the sulfate concentration decreased with depth (114 mg/L in WQ-36; 90 mg/L in WQ-36A, and 34 mg/L in WQ-36B). These data indicate that sulfate was introduced to the aquifer from the former aeration lagoon. The source of the sulfate is not known; however, sulfate can be a constituent of sewage (Metcalf and Eddy, Inc., 1991), which was a component of the waste discharged to the aeration lagoon.

The apparent introduction of sulfate at the former aeration lagoon provides a tracer to identify an approximate flow path from the lagoon. Some degree of caution must be used when sulfate is utilized as a tracer because it can be anaerobically depleted by sulfate-reducing microorganisms, and it can be a geochemically active ion. The presence of 359 mg/L of sulfate at well WQ-40B in ground water containing less than 1 mg/L of DO (November 1993), however, indicates that high concentrations of sulfate were locally persistent under low-oxygen conditions. The distribution of sulfate (fig. 6) implied that contaminants were transported from the former aeration lagoon southward through the areas intersected by the WQ-36 well cluster, well WQ-40B, and well WQ-51B (fig. 7).

The ground-water chemistry at the WQ-34 well cluster appeared to differ from the contaminated ground water from the aeration lagoon. The sulfate concentration measured during this investigation was within background concentrations (less than 5 to about 9 mg/L) at well WQ-34C (8.73 mg/L) and was slightly above background concentrations at well WQ-34B (20.8 mg/L) (fig. 6). The sulfate concentrations at both wells, however, were substantially lower than in the most contaminated water along the apparent flow-path from the former aeration lagoon (greater than 100 mg/L). This difference implied that the contamination at the WQ-34 well cluster did not originate from the former aeration lagoon.

Ground-water contamination at the WQ-34 well cluster contained sulfate concentrations similar to the sulfate concentrations found at WQ-35 well cluster (5 to 14.3 mg/L), adjacent to the former sludge lagoon. Because both the WQ-34 well cluster and the former sludge lagoon are slightly west of the

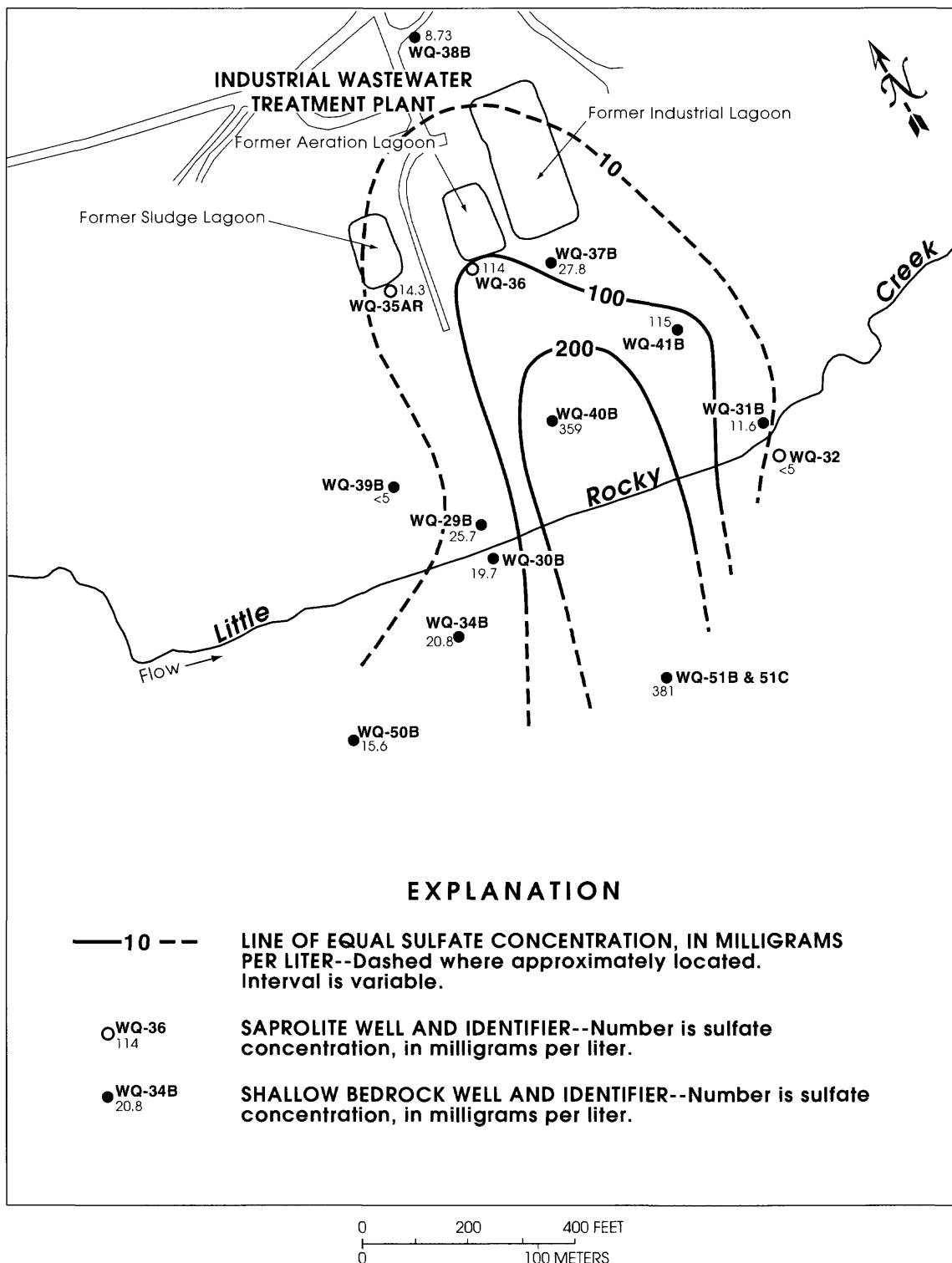


Figure 6. Distribution of sulfate (concentrations represent the value measured at a single well or the highest value at a well cluster) in the ground water south of the wastewater- treatment plant, November 1993.

Table 3. Concentrations of selected constituents measured in ground water downgradient from the wastewater-treatment facility, Greenville, S.C., November 1993

[DO, dissolved oxygen; Fe(II), ferrous iron; H₂, hydrogen; Ca, calcium; Mg, magnesium; NO₃, nitrate; SO₄, sulfate; CH₄, methane; DIC, dissolved inorganic carbon; --, data not available; <, less than; >, greater than; s.u., standard units; mg/L, milligrams per liter; µM, micromoles per liter; nM, nanomoles per liter; °C, degrees Celsius; *, data collected by Rust Environment and Infrastructure]

Site identifica- tion	Date	Tem- pera- ture (°C)	pH (s.u.)	DO (mg/L)	Fe(II) (mg/L)	H ₂ (nM)	Ca (mg/L)	Mg (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	CH ₄ (µM)	DIC (mg/L)
WQ-29B	11/03/93	15	6.9	<1	1.4	--	26.8	1.30	0.14	25.7	<1	69
WQ-30	11/01/93	--	5.0*	6.8	--	--	.36	.85	2.22	<5	<1	62
WQ-30B	11/02/93	15	8.1	<1	1.3	--	18.7	.85	.12	19.7	<1	62
WQ-31	11/03/93	17	5.6	3.52	.5	--	.48	.81	.65	<5	<1	99
WQ-31B	11/03/93	15.5	6.6	<1	1.1	2.5	13.7	1.60	.12	11.6	<1	57
WQ-32	11/01/93	--	--	>1	--	--	.38	12.30	1.13	<5	<1	71
WQ-34	11/01/93	--	5.0*	5.66	.6	--	.37	10.70	.88	<5	<1	66
WQ-34B	11/02/93	14.5	7.7	<1	.6	1.6	20.6	1.33	<1	20.8	<1	60
WQ-34C	11/01/93	--	6.6	<1	--	--	17.8	1.45	<1	8.73	<1	70
WQ-34D	11/09/93	15.5	10.1	1.75	.6	--	.47	.01	<1	<5	239	52
WQ-35AR	11/03/93	17	6.6	<1	5.7	1.2	.72	.76	.24	14.3	<1	79
WQ-35B	11/03/93	17	6.6	<1	6.2	1.8	.68	.77	.24	6.92	<1	88
WQ-35C	11/03/93	17.5	9.5	1.1	.5	--	.4	.01	<1	5.02	<1	71
WQ-36	11/02/93	14	5.8	2.1	.6	--	.64	.67	.22	114	47	202
WQ-36A	11/02/93	17	5.8	1.35	.4	--	1.89	.71	.57	89.6	37	199
WQ-36B	11/02/93	16	6.5	<1	1.9	--	24.4	2.05	.23	34.3	<1	129
WQ-37	11/04/93	14.5	6.1	<1	17.4	1.6	7.8	6.30	.55	9.73	489	424

Table 3. Concentrations of selected constituents measured in ground water downgradient from the wastewater-treatment facility, Greenville, S.C., November 1993--Continued

[DO, dissolved oxygen; Fe(II), ferrous iron; H₂, hydrogen; Ca, calcium; Mg, magnesium; NO₃, nitrate; SO₄, sulfate; CH₄, methane; DIC, dissolved inorganic carbon; --, data not available; <, less than; >, greater than; s.u., standard units; mg/L, milligrams per liter; µM, micromoles per liter; nM, nanomoles per liter; °C, degrees Celsius; *, data collected by Rust Environment and Infrastructure]

Site identifica- tion	Date	Tem- pera- ture (°C)	pH (s.u.)	DO (mg/L)	Fe(II) (mg/L)	H ₂ (nM)	Ca (mg/L)	Mg (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	CH ₄ (µM)	DIC (mg/L)
WQ-37A	11/04/93	17	6.2	<1	18.6	1.5	9.1	6.80	0.56	7.38	540	440
WQ-37B	11/03/93	15.5	6.3	1.99	1.4	--	35	8.90	<1	27.8	<1	175
WQ-37C	11/04/93	17	8.5	<1	1	--	11.7	.13	<1	11	<1	58
WQ-38A	11/01/93	--	5.2*	6.74	.6	--	<2	.37	.69	<5	<1	31
WQ-38B	11/01/93	--	6.8*	1	1	--	1.37	1.60	<1	8.73	<1	41
WQ-39B	11/09/93	13	7.0	1.84	.3	--	9.8	1.04	<1	<5	<1	60
WQ-40B	11/03/93	15.5	6.3	<1	1.1	--	138	3.85	<1	359	<1	62
WQ-41B	11/02/93	15	7.3	1.2	.9	--	62.5	.95	<1	115	<1	69
WQ-50B	11/02/93	15	10.3	1.13	.8	--	16.9	.50	<1	15.6	<1	23
WQ-50C	11/05/93	16.5	12.2	6.6	.4	--	370	.01	<1	5.3	<1	1
WQ-51B	11/04/93	16.5	8.3	1.32	.7	--	151	4.35	<1	381	<1	46
WQ-51C	11/04/93	16.5	7.9	<1	.6	--	72.5	1.48	<1	181	<1	47

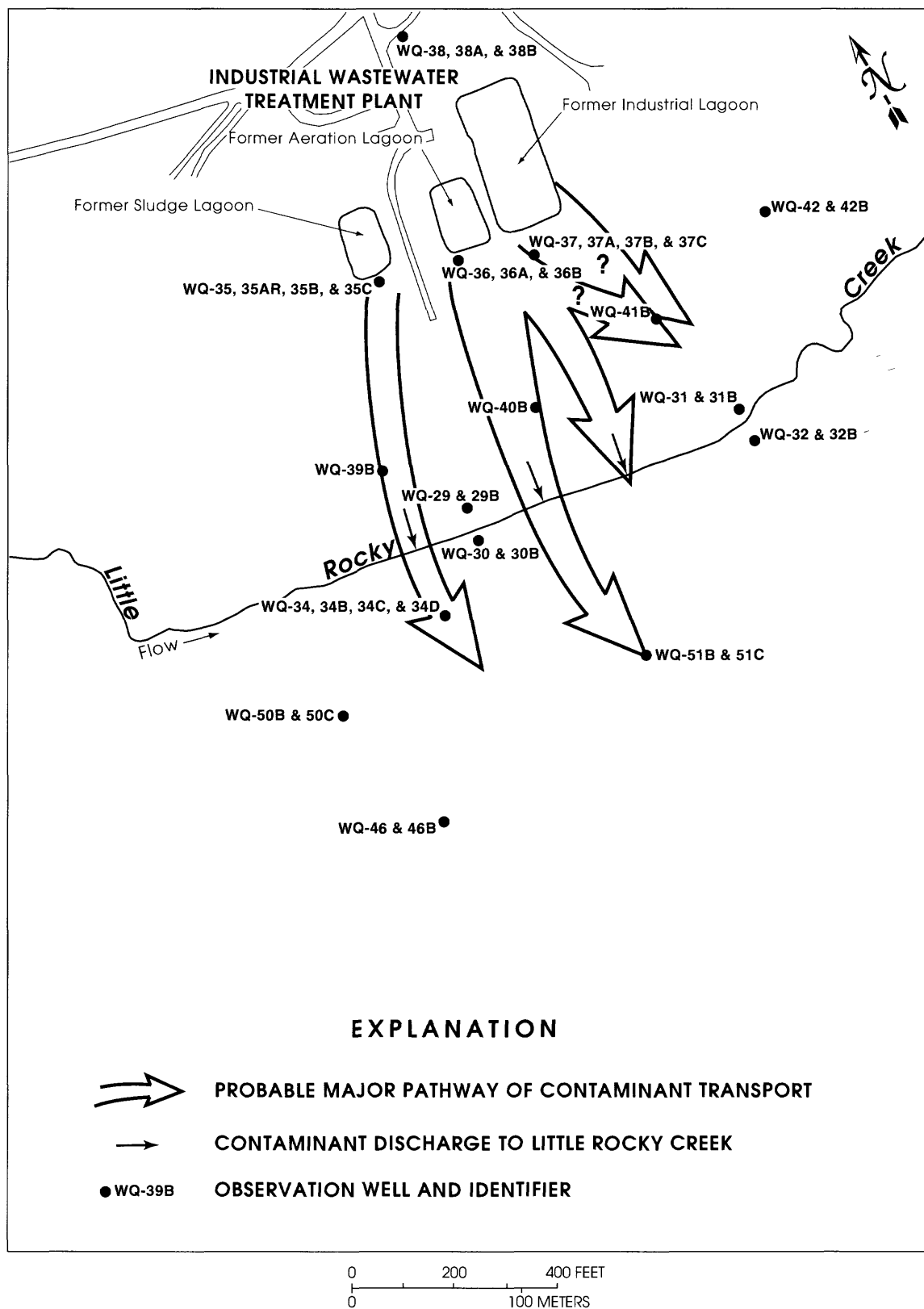


Figure 7. Probable major pathways of contaminant transport south of the wastewater-treatment plant, Greenville, S.C., January 1994.

contamination from the former aeration lagoon, the ground-water contamination at the WQ-34 well cluster probably was derived from the former sludge lagoon. Wells WQ-35B (near the former sludge lagoon), WQ-34B, and WQ-34C (south of Little Rocky Creek) contained concentrations of PCE at the mg/L level. The open sections of wells WQ-35B and WQ-34B are at approximately the same vertical horizon (elevations of about 856 to 876 and 862 to 883 ft, respectively) and well WQ-34C (near well WQ-34B) is slightly deeper (table 1). Thus, ground-water contamination at wells WQ-34B and WQ-34C probably was derived from the vicinity of well WQ-35B (fig. 7).

The contaminant-transport pathway from the former industrial lagoon is not readily discernible from existing data. Well WQ-41B, downgradient from the former industrial lagoon, was also downgradient from the former aeration lagoon (fig. 1). The presence of 115 mg/L of sulfate in ground water at well WQ-41B in November 1993 more closely resembled the sulfate concentrations near the former aeration lagoon (greater than 100 mg/L) than the sulfate concentrations near the former industrial lagoon (less than 30 mg/L). Thus, the ground water at well WQ-41B may represent a mixture of the two plumes (fig. 7). Alternatively, the downgradient part of the plume from the former industrial lagoon may be farther east than well WQ-41B or may have been depleted by contaminant-attenuation processes in the aquifer.

Fracture-Trace Analysis

Further information regarding contaminant-transport pathways downgradient from the wastewater-treatment facility was obtained from an examination of borehole data. The data included borehole radar, temperature, caliper, natural gamma, televiwer, and heat-pulse flowmeter logs from this investigation as well as examination of driller's logs from previous investigations. Although much of the data were obtained under hydraulic gradients induced by pumping wells, the flowpaths defined under stressed conditions sometimes can provide information on the probable pathways of contaminant transport under natural conditions.

The driller's log of well PW-34C showed major water-bearing fractures at depths of about 105 and 107 ft bls (Rust Environment and Infrastructure, 1993). A caliper log of the well obtained during this investigation also identified the fractures at elevations of about 817 and 819 ft relative to sea level (depth of about 108

and 106 ft below the top of the casing, respectively) (fig. 8), and acoustic televiwer logging showed the fractures to be nearly horizontal (fig. 9).

The significance of the fractures became clear after examining the borehole heat-pulse flowmeter tests and vertical temperature-profiling data. These data were obtained in May 1994 while a network of 8 pumping wells was in operation. The closest pumping wells to well PW-34C were wells PW-34BR (160 ft northward) and PW-29B (230 ft northeastward). The average pumping rates during May 1994 were 76 and 4 gal/min, respectively (Rust Environment and Infrastructure, 1995c). The heat-pulse flowmeter showed that 53.4 gal/min of water was entering well PW-34C at the base of the borehole and exiting the borehole through the two fractures at 105 and 107 ft bls. The temperature log showed that the water temperature sharply increased below about 107 ft bls and remained constant with continued depth (fig. 8), indicating the input of warmer water at the base of the borehole, rapid transport up the well bore, and discharge from the borehole at about 105 to 107 ft bls. It is also probable that additional water entered well PW-34C through the fractures at 105 and 107 ft bls along the southern side of the borehole, moved horizontally across the well bore, and discharged through the same fractures on the northern side, in response to pumpage north of the well.

Driller's logs and borehole-radar data provided information on the transport pathway of ground water after it exited well PW-34C. Cross-hole radar tomography between wells PW-34C and WQ-34D showed a zone of low radar-signal attenuation extending from the fractured horizon in well PW-34C to a zone in well WQ-34D between about 70 and 103 ft bls (fig. 8). The driller's log of well WQ-34D showed that the zone contained "high-yielding water-bearing fractures" (Rust Environment and Infrastructure, 1993), and the single-hole directional radar data in well WQ-34D indicated the presence of an apparent fracture at a depth of 81.6 ft oriented along the axis of the low radar-attenuation zone. These data not only imply that the low radar attenuation zone contained water-bearing fractures, but also that the fracture zone constituted a major pathway of water movement between well PW-34C and the WQ-34 well cluster.

The zone of water-bearing fractures and low radar-signal attenuation in well PW-34C corresponded to a zone described in the driller's log as "soft drilling"

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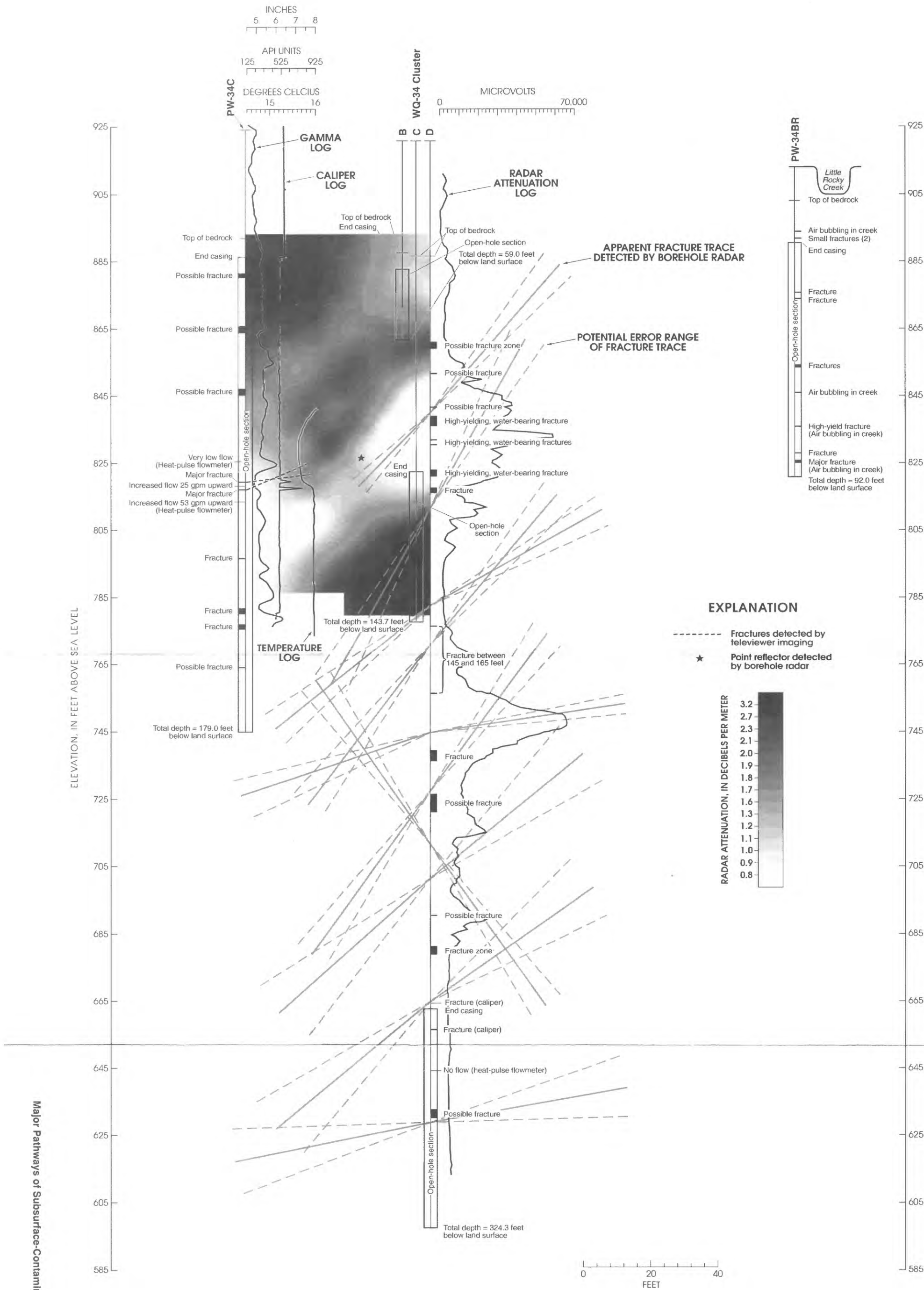


Figure 8. Fracture identification from boring logs (Rust Environment and Infrastructure, 1993; 1994b), geophysical data and interpretations (this investigation) at wells PW-34C, PW-34BR, and the WQ-34 well cluster, Greenville, S.C.

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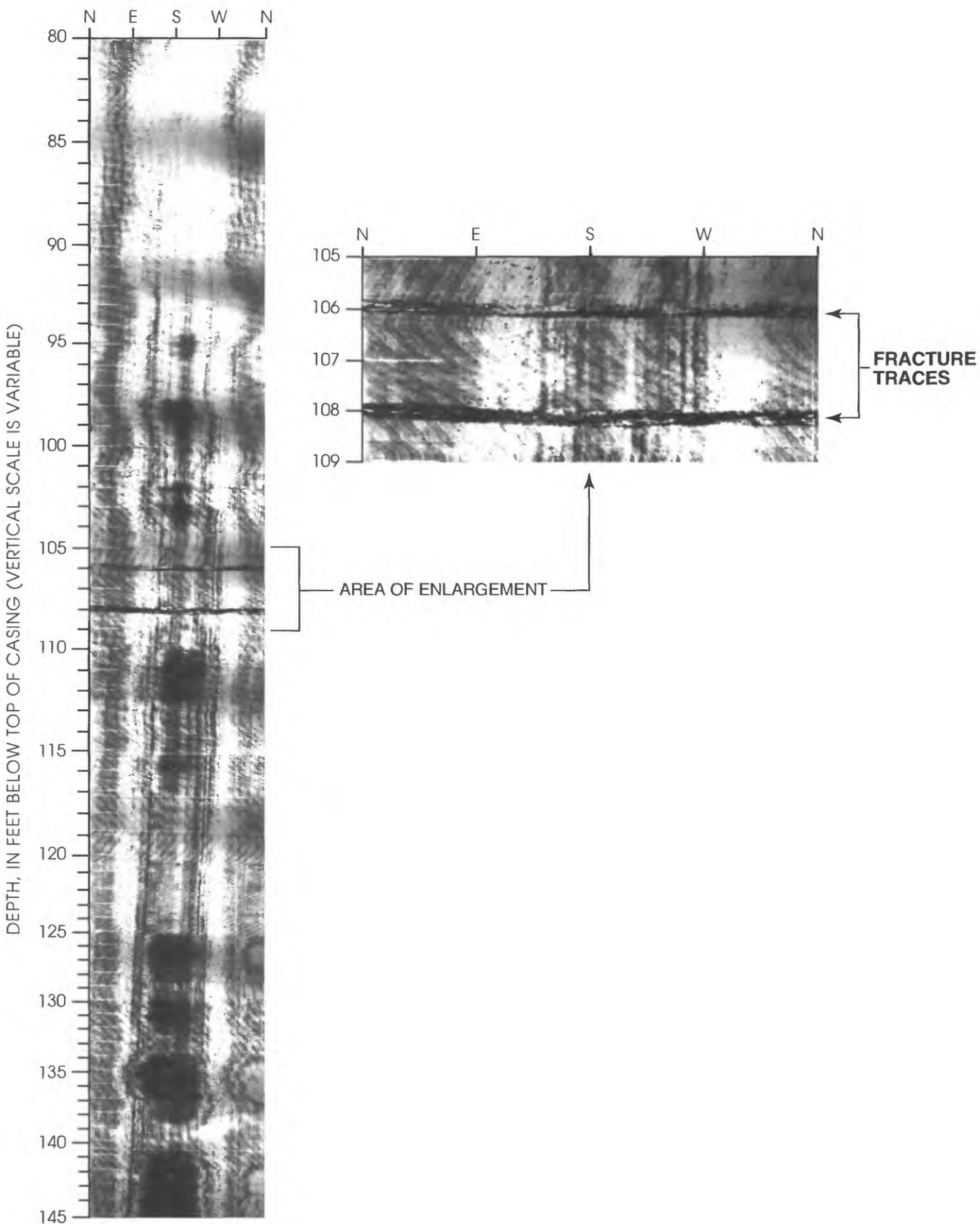


Figure 9. Borehole acoustic-televviewer image of monitoring well PW-34C, Greenville, S.C.

(Rust Environment and Infrastructure, 1993). Typically, reduced competency, increased weathering of rock, or increased water saturation is characterized by increased radar attenuation, measured as increased electrical resistivity (Lane and others, 1994). The apparent inverse relation at well PW-34C implied that despite the reduced competency and increased water content of the rock, the mineralogy may have imparted a relatively higher electrical resistivity to that horizon. Support for this hypothesis can be seen in the borehole natural-gamma log obtained in well PW-34C (fig. 8). In the zones of relatively higher radar-signal attenuation at well PW-34C, above and below the zone of relatively low signal attenuation, the natural-gamma readings were generally greater than 250 American Petroleum Institute (API) units. In the center of the high radar-attenuation zone at well PW-34C, however, the natural-gamma count decreased to 180 API units. The natural-gamma data implies that the fracture zone in PW-34C is characterized by a lower clay or biotite content than the adjacent high radar-attenuation zones. Because clays and biotite can decrease electrical resistivity, increasing radar attenuation, such mineralogy change could explain the radar data. An alternative explanation for the apparent inverse relation between competency and radar attenuation at well PW-34C is that because CVOC's are uncharged, their presence in that horizon may impart a relatively high electrical resistivity (low conductivity) to the material, causing lower radar attenuation. Because no water-quality samples were collected from the low radar-attenuation zones in either well PW-34C or the WQ-34 well cluster, this hypothesis cannot be adequately tested; however, the specific conductance of water from the nearest horizon (well WQ-34C) was slightly lower than water from the next shallower and next deeper horizons (Rust Environment and Infrastructure, 1994a).

These data strongly implied that pumpage at well PW-34BR induced movement of water into well PW-34C through the southern side of the borehole at about 105 and 107 ft bls and through the base of the borehole and that the water then exited the well through the northern side of the borehole at about 105 and 107 ft bls. The water then moved through fractures in the low radar-attenuation zone northward, passing well WQ-34D at a depth of between 70 to 103 ft bls.

Well WQ-34D was not open to the aquifer at the interval between 70 and 103 ft bls. Well WQ-34C,

adjacent to well WQ-34D, was open to the aquifer at 98.7 to 143.7 ft bls and was, therefore, slightly below the probable major pathway of ground-water movement. The data suggested that well WQ-34B was above the most contaminated horizon and that WQ-34C intercepted only part of the major pathway of contaminant transport.

The driller's log from well PW-34BR noted that air began bubbling from the bottom sediments in Little Rocky Creek as the air-rotary drilling tools were advanced in the borehole (Rust Environment and Infrastructure, 1994b). As the tools continued to advance, air bubbles from the drilling appeared in slightly different locations upstream and downstream along the axis of the creek. Eventually, water began to discharge from wells WQ-34C and PW-34C (Rust Environment and Infrastructure, 1994b). The air followed fracture zones and discharged to wells PW-34C and WQ-34C. The data also demonstrated that one or more steeply dipping fracture zones connected contaminated parts of the aquifer in well PW-34BR to Little Rocky Creek. The bubble discharge along the axis of the Little Rocky Creek and the linear morphology of creek south of the wastewater-treatment plant implies that the creek is aligned along a steeply dipping fracture zone.

Although specific pathways of water movement between wells WQ-34C and PW-34BR cannot be delineated with existing data, several lines of evidence suggest that more or less horizontal transport from well WQ-34C to PW-34BR occurred in response to pumpage at PW-34BR. Single-hole directional-radar data from well WQ-34D indicated that the apparent fracture at 81.6 ft bls, hypothesized to be a major pathway of water movement, dipped to the southwest at about 53° ($\pm 5^{\circ}$). The projected trace of the apparent fracture intercepted land surface between wells WQ-34C and PW-34BR; therefore, that anomaly could not be the sole pathway of water movement between wells PW-34BR and WQ-34C. The borehole radar and the driller's log of well WQ-34D, however, indicated that the rock unit was highly fractured. Moreover, near-horizontal fractures are sometimes not visible to directional-radar data. For example, some high yielding fractures in the zone of low radar attenuation were described in the driller's log (Rust Environment and Infrastructure, 1993) but were not identified as fractures in the directional-radar data. The presence of near-horizontal fractures at about the same horizon in well PW-34C (fig. 9) suggests that similar near-hori-

zontal fractures were present at the WQ-34 well cluster, approximately 55 ft away. The additional presence of high-angle fractures implied a high degree of connection among fracture zones. Thus, it is reasonable to assume approximately horizontal flow from the WQ-34 well cluster to well PW-34BR in response to pumpage.

The pathways of ground-water flow in response to pumpage at well PW-34BR can be used to gain an understanding of the probable pathways of contaminant transport prior to pumpage. The transmissive fracture zones identified during pumping stress were probable pathways of prepumping contaminant transport. Ground-water flow directions, however, would have been substantially different. Flow during operation of the ground-water pumping network was northward from well PW-34C and the WQ-34 well cluster to contaminant-extraction well PW-34BR. Prior to pumpage, the probable flow direction and direction of contaminant transport were southward through fracture zones between 70 to 103 ft bls at the WQ-34 well cluster (fig. 8) toward well PW-34C, where the major pathway of transport was the fracture zone between 105 and 107 ft bls.

Contamination also was present at a deeper horizon. During the period of pumpage-induced stress, samples collected by the USGS from the water moving up the borehole in the PW-34C well bore in October 1995 and January 1996 showed the presence of greater than 2,000 µg/L of TCE, with little change between the samplings. These data indicated that an additional body of contamination existed at a depth of about 179 ft (the total depth of the well). Although it is possible that such contamination was caused by previous downward vertical movement of contaminants through the well bore connecting the fractures at 105 and 107 ft bls to fractures at the base of the well, that scenario is not needed to account for the contaminant distribution. The single-hole directional-radar data from well WQ-34D indicate the presence of numerous radar anomalies interpreted as fractures dipping southward toward the contaminated horizon at the base of well PW-34C. These data indicated that numerous potential pathways of contaminant transport to that horizon are available for contaminant transport. Vertical continuity of fractures is further illustrated by the decrease in water levels at well WQ-34D, open at a depth of 258.4 to 324.3 ft bls, in response to pumpage at well PW-34BR, at a total depth of only 92 ft bls (Rust Environment and Infrastructure, 1995a).

The probable transport pathway from the former aeration lagoon also can be approximately located from fracture-trace analyses. For example, during air-rotary drilling of well WQ-51C, air bubbles and water began exiting the ground in a line trending approximately due north across Little Rocky Creek to the vicinity of well PW-LRC1 (W. Thomas Hyde, General Electric Company, oral commun., 1996). Air began bubbling from the bottom sediments in Little Rocky Creek at the intersection of the linear trend and the creek; however, the bubbles in the creek deviated from the linear trend and emanated from a broad area. The linear nature of the air and water release strongly suggests that the air followed a fracture across the creek. The broad zone of bubble-release in the creek is consistent with the observation that the straight reach of Little Rocky Creek south of the wastewater-treatment facility was aligned along the surface expression of a fracture zone.

The northward trending line of bubbles emanating from well WQ-51C closely coincided with a borehole-radar anomaly identified near well WQ-51C trending northward and dipping about 76 degrees west. The projected surface expression of these anomalies was approximately 25 ft and 57 ft west of the well. Although the anomalies did not appear to intersect the borehole, their proximity to the borehole implied indirect interconnection through fracture networks.

The area where the line of bubbles crossed Little Rocky Creek coincided approximately with Area B of the passive-vapor survey (fig. 5), where anomalously high concentrations of VOC's were detected in the vapor-diffusion samplers. The data implied that Area B was the surface expression of a northward-trending contaminant-bearing fracture zone connecting the former aeration lagoon to well WQ-51C. A northward oriented fracture would not be identifiable on a WADI survey at the facility because of the orientation of transmitting stations (Sirrinc Environmental Consultants, 1991b); therefore, it is not unusual that no WADI anomalies were reported along the linear bubble-release feature. Thus, considering that the geochemical data (discussed earlier) imply that the contamination at well WQ-51C was derived from the former aeration lagoon, the probable transport pathway from the former aeration lagoon was southward from the lagoon, beneath Little Rocky Creek at Area B, and southward toward the WQ-51 well cluster (fig. 7).

TRANSFORMATIONS OF GROUND-WATER CONTAMINATION

Chlorinated volatile organic ethanes and ethenes can be microbially degraded under both aerobic and anaerobic conditions; however, the potential for dechlorination under each condition depends on a variety of factors, including the number of chlorine substituents. The potential for reductive dechlorination decreases with the number of chlorine substituents, while the potential for microbial oxidation to yield CO₂ increases with decreasing number of chlorine substituents (Vogel, 1994; Vogel and others, 1987). Thus, biodegradation of higher-chlorinated VOC's is more efficient under anaerobic than aerobic conditions, while anaerobic reductive degradation of VC generally is considered slow and incomplete (Balapragada and others, 1995; Barrio-Lage and others, 1987; 1990; Bouwer, 1994; Carter and Jewell, 1993; De Bruin and others, 1992; DiStefano and others, 1991; Fennell and others, 1995; Freedman and Gossett, 1989; Maymo-Gatell and others, 1995; Odum and others, 1995; Vogel and McCarty, 1985). Under aerobic conditions, the transformations of higher-chlorinated compounds are generally the result of cometabolism, which is the fortuitous transformation of a compound by enzymes or cofactors produced by organisms for other purposes (Semprini and others, 1991). Aerobic oxidation of VC, however, has been reported by a number of investigators (Davis and Carpenter, 1990; Malachowsky and others, 1994; Phelps and others, 1991; Bradley and Chapelle, 1996).

It is clear that determination of the potential for CVOC transformation requires knowledge of whether aerobic or anaerobic metabolism dominates the microbial community. In addition, the specific anaerobic TEAP may play a role in CVOC transformation. Investigations have demonstrated anaerobic PCE degradation under methanogenic conditions (Vogel and McCarty, 1985; Vogel and others, 1987; Freedman and Gossett, 1989) and sulfate-reducing conditions (Cobb and Bouwer, 1991). Bradley and Chapelle (1996) demonstrated that oxidation of VC can be significant even under anaerobic aquifer conditions if a strong oxidant, such as Fe(III), is available to drive microbial degradation. Thus, determination of the predominant TEAP's can be used to determine whether conditions are favorable for CVOC transformations. The following discussion examines the distribution of predominant TEAP's south of the wastewater-treatment plant. Ratios among differing CVOC's are then used to

examine potential transformations of higher-chlorinated VOC's to lesser chlorinated VOC's in the aquifer downgradient from the facility, and the results of a laboratory investigation are used to examine the potential for VC transformation.

Distribution of Terminal Electron-Accepting Processes

The data collected during this investigation implied that the saprolite and fractured rock aquifers were aerobic prior to contamination. Dissolved oxygen (6 to 7 mg/L) occurred in uncontaminated ground water in the uncontaminated saprolite aquifer (WQ-30, WQ-38A) and lightly contaminated parts of the bed-rock aquifer (WQ-50C). Thus, aerobic metabolism was probably the predominant TEAP in most of the aquifer prior to contamination (table 3).

The lowest concentrations of DO were found in contaminated ground water. Dissolved-oxygen concentration was less than 1 mg/L at wells WQ-35AR and WQ-37A, containing 20,750 and 25,050 µg/L of VOC's, respectively (VOC data from Rust Environment and Infrastructure, 1994a), and in many of the contaminated wells. In addition, the dissolved-iron concentration was higher in ground water from many of the heavily contaminated areas relative to the lightly contaminated or uncontaminated areas. These data suggest that the depleted oxygen conditions were the result of the contamination and that iron reduction is or has been an active microbial process in the contaminated aquifer.

Although the anaerobic conditions appear to have been caused by ground-water contamination, the electronegative nature of PCE and TCE makes it unlikely that these compounds were the driving force contributing to DO depletion. It is more probable that aerobic oxidations of aliphatic or aromatic hydrocarbons that may have been associated with the wastewater provided a depletion mechanism for DO. Evidence for the presence of aromatic hydrocarbons can be seen in water-quality analyses from wells downgradient from the wastewater-treatment plant. In April 1992, the concentration of toluene in ground water was 59 µg/L at well WQ-37A, 24 µg/L at well WQ-37, 12 µg/L at well WQ-34B, and 8.8 µg/L at well WQ-37B (SEC Donohue, Inc., 1992). Biodegradation of toluene and other aromatic hydrocarbons can deplete the DO in contaminated ground water.

In parts of the aquifers that contained less than 1 mg/L of DO, the hydrogen concentrations were in the range characteristic of sulfate reduction (1 to 4 nM; Vroblesky and Chapelle, 1994). The hydrogen concentrations and the presence of sulfate at concentrations greater than 5 mg/L at the sites where hydrogen was measured imply that sulfate reduction was a dominant metabolic process in anaerobic parts of the ground water.

Field Evidence for Chlorinated Volatile Organic Compound Dechlorination

Examination of the potential for CVOC transformations in the aquifer is complicated by the possibility that a variety of chlorinated alkanes and alkenes were released at different times from the lagoons at the wastewater-treatment facility. Interpretations of changing CVOC ratios, however, are consistent with transformations of higher-chlorinated VOC's to lesser chlorinated VOC's in the aquifer downgradient from the facility. The following discussions concentrate on chlorinated ethenes, because chlorinated ethane concentrations downgradient from the wastewater-treatment facility were relatively low compared to chlorinated ethene concentrations.

Evidence of apparent dechlorination can be seen adjacent to the former aeration lagoon. The ratios of DCE to PCE or TCE in ground water at wells WQ-36 and WQ-36A generally increased with time between August 1991 and July 1993, strongly implying that DCE was being produced by reduction of PCE and TCE (table 4).

Evidence of apparent dechlorination along a flowpath away from the former aeration lagoon also is indicated by the TCE/PCE ratios in the aquifer. Examination of CVOC data along an apparent flowpath from the WQ-36 well cluster shows that the average TCE/PCE ratio increased as the contamination moved from the former aeration lagoon (table 4). The average ratio at the WQ-36 well cluster ranged from 0.44 to 0.6. Downgradient at well WQ-40B, the average TCE/PCE ratio increased to 0.83. Further downgradient, at wells WQ-51B and WQ-51C, the average ratio increased to 0.96 and 0.94, respectively. These data suggest that PCE was dehalogenating to TCE along the flowpath.

Following startup of the pumping-well network, the DCE/PCE ratio at observation wells WQ-51B and WQ-51C sharply increased (fig. 10). The increase in

ratio implied that water containing relatively low concentrations of CVOC's entered the observation wells during pumping of the extraction wells. There were two possible sources for the influx of this water. The first is that changes in ground-water flow direction, as a result of nearby pumping (Rust Environment and Infrastructure, 1995b), allowed water that had formerly moved past wells WQ-51B and WQ-51C to flow back toward these wells. In such a case, the increased ratio would have meant that the CVOC contamination continued to dechlorinate after moving downgradient past wells WQ-51B and WQ-51C. It was also possible, however, that the change in ground-water-flow direction allowed the downgradient edge of the contamination originating from the former industrial lagoon and having a high initial DCE/PCE ratio, to migrate towards wells WQ-51B and WQ-51C.

A similar comparison of ratios can be used to assess the potential biotransformation of ground-water contamination downgradient from the former sludge lagoon. The DCE/PCE, DCE/TCE, and TCE/PCE ratios and VC concentrations decreased with depth at well cluster WQ-35 (table 5), at the downgradient edge of the former sludge lagoon. These data indicate a predominance of lesser chlorinated compounds, or dechlorination breakdown products, in the saprolite aquifer and a predominance of higher-chlorinated compounds at depth. The probable explanation for this trend is that the primary initial contaminant was PCE. Because PCE is denser than water, the contamination could have migrated vertically downward in the aquifer. The ratios can then be explained by examining the distribution of DO. When well cluster WQ-35 was sampled by the USGS in November 1993, ground water at the shallowest well sampled (well WQ-35AR, screened 32.1 to 41.8 ft bls) was anaerobic. The intermediate depth well (WQ-35B, screened 52.3 to 72.3 ft bls) contained less than 1 mg/L of DO, and the deepest well sampled (WQ-35C, open 202.5 to 299.2 ft bls) was relatively uncontaminated and contained 1.1 mg/L of DO (table 3). The increasing amount of DO with depth indicates that the bulk of the PCE dechlorination would have taken place in the shallow part of the flow system, with less tendency to dechlorinate at depth, as reflected in the decrease in DCE/PCE, DCE/TCE, and TCE/PCE ratios.

The presence of substantial VC concentrations (greater than 1,000 µg/L) in the shallow ground water

Table 4. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former aeration lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; µg/L, micrograms per liter; -- data not available; J, result is detected below the reporting limit or is an estimate]

Site Identifi- cation	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/PCE	DCE/TCE	TCE/PCE	Average and (standard deviation) of TCE/PCE for period of record
WQ-36	08/21/91	19	32	90	23	9	<10	3.91	9.57	0.41	
	12/18/91	29	38	140	29	14	<10	4.83	10.00	.48	
	04/20/92	17	25	85	22	10	<10	3.86	8.50	.45	
	08/11/92	19	35	200	36	25	<10	5.56	8.00	.69	
	11/17/92	10	19	190	20	13	5.7J	9.50	14.62	.65	
	02/01/93	4J	10	89	6	5	<10	16.18	17.80	.91	
	05/12/93	15J	69	1,100	71	57	17J	15.49	19.30	.80	
	07/21/93	27J	180	3,100	220	140	<250	14.09	22.14	.64	
	11/02/93	30J	94	1,400	280	110	<100	5.00	12.73	.39	0.60 (0.17)
	08/21/91	170	160	910	170	81	<50	5.35	11.23	.48	
	12/18/91	130	120	660	130	66	<50	5.08	10.00	.51	
	04/20/92	81	120	600	110	66	<10	5.45	9.09	.60	
	08/11/92	63	120	910	100	73	<50	9.10	12.47	.73	
	11/17/92	52	110	900	130	71	22	6.92	12.68	.55	
WQ-36A	02/01/93	35J	89	860	230	70	<100	3.74	12.29	.30	
	05/12/93	54J	210	3,200	320	190	53J	10.00	16.84	.59	
	07/21/93	40J	250	4,200	380	190	<250	11.05	22.11	.50	
	11/02/93	55J	230	4,100	340	210	55J	12.06	19.52	.62	.54 (0.11)

Table 4. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former aeration lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; µg/L, micrograms per liter; -- data not available; J, result is detected below the reporting limit or is an estimate]

Site Identifi- cation	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/PCE	DCE/TCE	TCE/PCE	Average and (standard deviation) of TCE/PCE for period of record
WQ-36B	08/21/91	<100	180	2,700	360	180	<200	7.50	15.00	0.50	
	01/14/92	13	190	--	710	280	140	----	----	.39	
	04/20/92	10	<250	6,400	730	290	330	8.77	22.07	.40	
	08/19/92	<250	290	5,200	730	370	<500	7.12	14.05	.51	
	11/23/92	<120	140	2,400	380	220	41J	6.32	10.91	.58	
	02/01/93	<250	240J	4,900	1,300	350	150J	3.77	14.00	.27	
	05/12/93	<250	170J	4,100	470	210J	180J	8.72	19.52	.45	
	07/21/93	<120	160	3,800	430	160	<250	8.84	23.75	.37	
	11/02/93	<120	110J	2,700	460	210	81J	5.87	12.86	.46	0.44 (0.09)
	09/11/91	<5	<5	13	51	32	<10	.25	.41	.63	
	12/18/91	<50	75	1,600	940	600	<100	1.70	2.67	.64	
WQ-40B	04/15/92	9	18	300	45	28	<10	6.67	10.71	.62	
	08/18/92	28	54	840	130	77	<50	6.46	10.91	.59	
	11/16/92	15J	34	540	85	62	<50	6.35	8.71	.73	
	02/02/93	<120	86J	3,000	2,800	1,600	680	1.07	1.88	.57	
	05/12/93	<250	<250	1,800	3,900	3,300	370J	.46	.55	.85	
	07/21/93	<120	44J	1,800	2,800	2,300	250	.64	.78	.82	
	11/03/93	<250	<250	1,600	2,100	4,200	420J	.76	.38	2.00	.83 (0.42)

Table 4. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former aeration lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; µg/L, micrograms per liter; -- data not available; J, result is detected below the reporting limit or is an estimate]

Site Identifi- cation	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/PCE	DCE/TCE	TCE/PCE	Average and (standard deviation) of TCE/PCE for period of record
WQ-51B	02/11/93	<25	<25	180	740	770	<50	.24	.23	1.04	
	05/10/93	<50	<50	200	990	930	<100	.20	.22	.94	
	07/19/93	<25	<25	270	880	830	<50	.31	.33	.94	
	11/03/93	<120	<120	380	2,300	2,100	42J	.17	.18	.91	0.96 (0.05)
WQ-51C	12/18/92	<25	<25	79	1,200	1,100	<50	.07	.07	.92	
	02/10/93	<120	<120	220	2,200	2,600	<250	.10	.08	1.18	
	05/17/93	<250	<250	320	5,400	4,900	<500	.06	.07	.91	
	07/21/93	<120	<120	310	4,100	3,400	<250	.08	.09	.83	
	11/03/93	<120	<120	280	4,500	4,000	<250	.06	.07	.89	.95 (0.12)

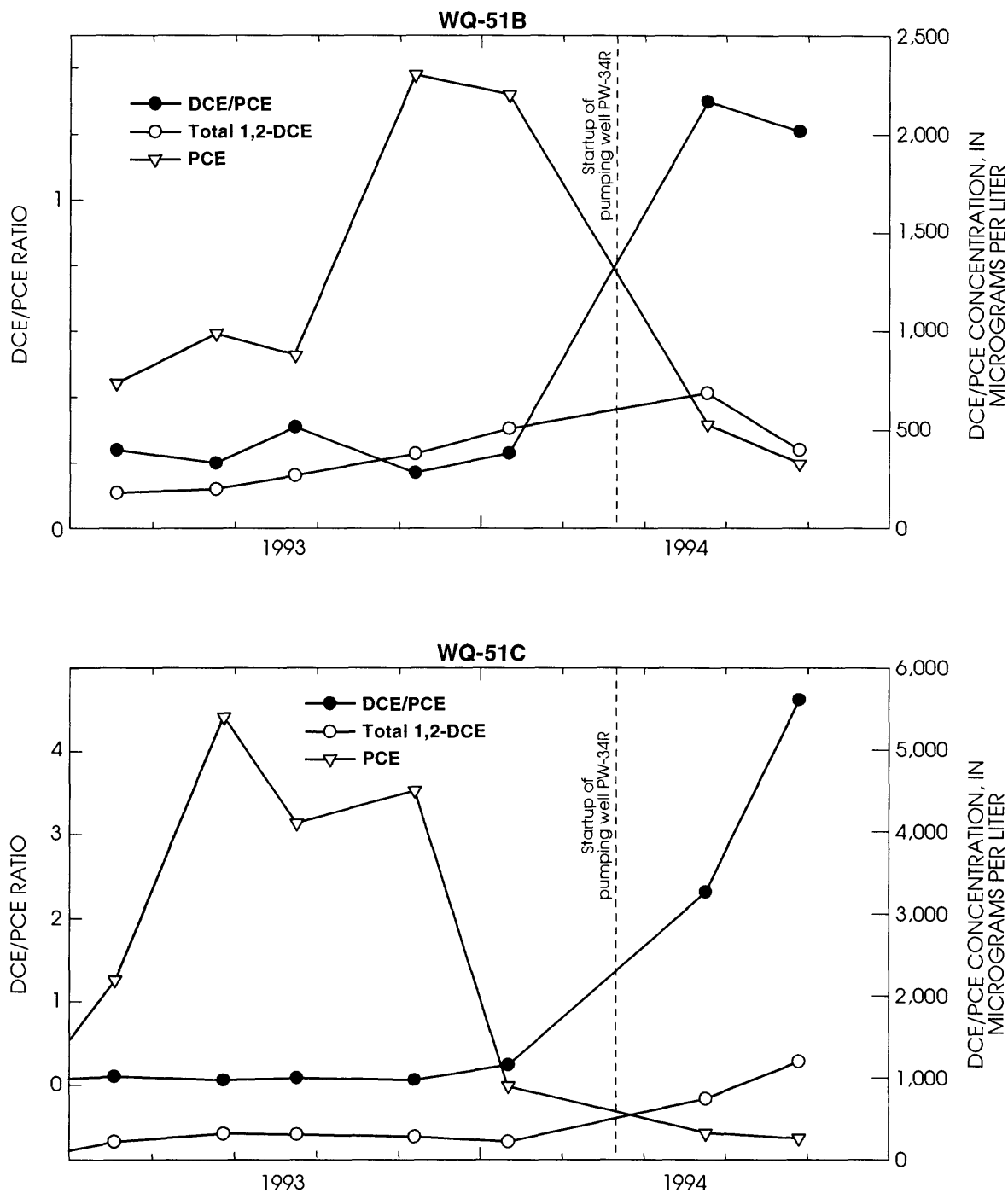


Figure 10. Changes in ratios and concentrations of total (cis + trans) 1,2-dichloroethene (DCE) and tetrachloroethene (concentration data from Rust Environment & Infrastructure electronic data base) at wells WQ-51B and WQ-51C, Greenville, S.C.

Table 5. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former sludge lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; ---, information not available; µg/L, micrograms per liter; <, less than; J, result is detected below the reporting limit or is an estimate]

Site identi- fication	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/ PCE	TCE/ PCE	Average and (standard deviation) of DCE/PCE for period of record	Average and (standard deviation) of DCE/TCE for period of record	Average and (standard deviation) of DCE/TCE for period of record
WQ-34	08/12/92	<5	<5	50	12	<5	28	4.17	---	---	---	---
	02/03/93	<5	<5	<5	1.3J	<5	<10	---	---	---	---	---
	05/10/93	<5	<5	<5	5.8	3.2J	<10	---	---	0.55	---	---
	07/20/93	<5	<5	1.9J	25	17	<10	.08	0.11	.68	---	---
	11/01/93	<5	<5	1.3J	18	12	<10	.07	.11	.67	1.44 (1.93)	0.11 (0)
	09/05/91	<170	<170	730	2,900	3,100	<380	.25	.24	1.07	---	---
WQ-34B	12/20/91	<190	<190	1,200	4,300	4,700	<330	.28	.26	1.09	---	---
	04/22/92	<5	15	1,200	3,300	1,700	12	.36	.71	.52	---	---
	08/12/92	<25	<25	1,600	4,400	4,100	<50	.36	.39	.93	---	---
	11/20/92	<250	<250	2,200	6,800	6,000	<500	.32	.37	.88	---	---
	02/02/93	<1,000	<1,000	2,500	16,000	11,000	<2,000	.16	.23	.69	---	---
	05/13/93	<1,000	<1,000	1,800	14,000	8,700	<2,000	.13	0.21	0.62	---	---
	07/20/93	<500	<500	1,900	19,000	10,000	<1,000	.10	.19	.53	---	---
	11/02/93	<500	<500	1,500	18,000	9,800	<1,000	.08	.15	.54	.23 (0.10)	.3 (0.16)
												.76 (0.22)

Table 5. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former sludge lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; ---, information not available; µg/L, micrograms per liter; <, less than; J, result is detected below the reporting limit or is an estimate]

Site identi- fication	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/ PCE	TCE/ PCE	Average and (standard deviation) of DCE/PCE for period of record	Average and (standard deviation) of DCE/TCE for period of record	Average and (standard deviation) of DCE/TCE for period of record
WQ-34C	06/04/92	<5	39	3,100	13,000	10,000	67	0.24	0.31	0.77		
	06/09/92	<5	65	3,500	24,000	17,000	38	.15	.21	.71		
	08/17/92	<500	<500	3,000	14,000	9,500	<1,000	.21	.32	.68		
	11/20/92	<500	<500	1,700	8,600	6,200	<1,000	.20	.27	.72		
	02/03/93	<1,200	<1,200	1,600	27,000	15,000	<2,500	.06	.11	.56		
	05/14/93	<1,200	<1,200	870	22,000	11,000	<2,500	.04	.08	.50		
	07/20/93	<1,000	<1,000	1,100	27,000	12,000	<2,000	.04	.09	.44		
	11/1/93	<120	50J	1,600	24,000	12,000	33J	.07	.13	.50	0.13 (0.08)	0.61 (0.12)
	08/21/91	<2,500	<2,500	52,000	10,000	32,000	<5,000	5.20	1.63	.20		
	12/18/91	<5,000	<5,000	72,000	10,000	54,000	<10,000	7.20	1.33	5.40		
WQ-35	04/20/92	<5,000	<5,000	110,000	17,000	69,000	13,000	6.47	1.59	4.06		
	08/10/92	2,500	<2,500	69,000	12,000	45,000	5,000	5.75	1.53	3.75		
	11/17/92	1,400	640	46,000	8,600	29,000	4,100	5.35	1.59	3.37		
	02/01/93	2,000J	760J	56,000	13,000	37,000	2,700J	4.31	1.51	2.85		
	05/10/93	2,100J	680J	66,000	16,000	46,000	1,200J	4.13	1.43	2.88		
	07/22/93	2,100J	720J	68,000	16,000	41,000	<5,000	4.25	1.66	2.56	5.33 (1.04)	3.51 (0.85)
											1.53 (0.1)	

Table 5. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former sludge lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; ----, information not available; µg/L, micrograms per liter; <, less than; J, result is detected below the reporting limit or is an estimate]

Site identi- fication	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/ PCE	TCE/ PCE	Average and (standard deviation) of DCE/PCE for period of record	Average and (standard deviation) of DCE/TCE for period of record	Average and (standard deviation) of DCE/TCE for period of record
WQ-35A	08/21/91	<1,000	<1,000	4,700	26,000	14,000	<2,000	.18	.34	.54		
	12/18/91	<1,000	<1,000	15,000	7,700	26,000	<2,000	1.95	.58	3.38		
	04/22/92	3,700	170	11,000	8,000	17,000	710	1.38	.65	2.13		
	08/11/92	110	30	1,900	17,000	6,400	96	.11	.30	.38		
	11/18/92	200J	68J	6,000	11,000	7,200	170J	.55	.83	.65	.83 (0.72)	.54 (0.2)
WQ-35AR	02/1/93	170J	<250	1,900	13,000	6,900	86J	.15	.28	.53		1.42 (1.17)
	05/10/93	<1,000	<1,000	1,200	15,000	5,700	<2,000	.08	.21	.38		
	07/22/93	130J	<500	1,200	14,000	5,400	<1,000	.09	.22	.39		
	11/03/93	140J	<500	1,300	13,000	6,300	<1,000	0.10	.21	0.48	.1 (0.03)	.23 (0.03)
	08/21/91	<2,500	<2,500	<2,500	64,000	21,000	<5,000	----	----	.33		.45 (0.06)
WQ-35B	01/14/92	620	<250	----	75,000	26,000	<500	----	----	.35		
	04/20/92	<2,500	<2,500	<2,500	82,000	26,000	<5,000	----	----	.32		
	08/11/92	<5,000	<5,000	<5,000	67,000	18,000	<10,000	----	----	.27		
	11/17/92	400J	<1,200	770J	46,000	16,000	<2,500	.02	.05	.35		
	02/01/93	280	<50	72	34,000	7,700	<100	<0.01	0.01	0.23		
	05/10/93	210J	<500	<500	46,000	9,200	<1,000	----	----	.20		
	07/22/93	<2,500	<2,500	<2,500	50,000	12,000	<5,000	----	----	.24		
	11/03/93	<2,500	<2,500	<2,500	50,000	13,000	<5,000	----	----	0.26	0.01 (0.01)	0.03 (0.02)
											0.28 (0.05)	

Table 5. Concentrations and ratios of selected chlorinated volatile organic compounds downgradient from the former sludge lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[TCA, 1,1,1-trichloroethane; DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; ----, information not available; µg/L, micrograms per liter; <, less than; J, result is detected below the reporting limit or is an estimate]

Site identifi- cation	Date	TCA (µg/L)	DCA (µg/L)	DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	DCE/ PCE	DCE/ TCE	TCE/ PCE	Average and (standard deviation) of	Average and (standard deviation) of	Average and (standard deviation) of
											DCE/PCE for period of record	DCE/TCE for period of record	DCE/TCE for period of record
WQ-35C	09/16/92	<5	<5	<5	29	14	<10	----	----	0.48			
	11/19/92	<5	<5	<5	3.2J	<5	<10	----	----	----			
	02/5/93	<5	<5	1.7J	9.9	3J	<10	0.17	0.57	.30			
	05/18/93	<5	<5	<5	1.2J	<5	<10	----	----	----			

near the lagoon (well WQ-35) provides evidence that vinyl chloride accumulation in ground water is a product of the degradation of higher-chlorinated ethenes. Vinyl chloride is a dechlorination product of chlorinated ethenes (Bouwer, 1994; Carter and Jewell, 1993; Freedman and Gossett, 1989; Maymo-Gatell and others, 1995; Odum and others, 1995) but is unlikely to ever have entered the waste stream as an initial contaminant at the facility (Sirrine Environmental Consultants, 1991a; Ron Harper, General Electric Company, oral commun., 1996; W. Thomas Hyde, General Electric Company, oral commun., 1996).

The vertical distribution of CVOC's at well cluster WQ-35 also could be related to the nature of the original contamination. If PCE, TCE, and DCE were all initial contaminants, the increasingly oxidized conditions with increasing depth may have allowed the less chlorinated solvents to be preferentially removed at greater depths, leaving the ground-water relatively enriched in PCE and, to a lesser extent, TCE. This explanation, involving the persistence of PCE with depth, however, cannot adequately explain the vertical distribution of CVOC's. Comparison of octanol-water partition coefficients indicates that PCE should exhibit a slight preferential sorption potential relative to TCE, and TCE should have a slightly greater tendency for sorption than DCE (Roy and Griffin, 1985; Gossett and others, 1983). Thus, if sorption were the dominant mechanism controlling the vertical distribution of CVOC's at well cluster WQ-35, then the vertical distribution of PCE, TCE, and DCE would be the reverse of the observed distribution. Moreover, the presence of VC strongly suggests dechlorination activity.

Because it is probable that the ground-water contamination at well cluster WQ-34 is derived from the former sludge lagoon (for reasons previously discussed), the potential for CVOC transformations along a flowpath can be examined by comparing CVOC ratios near the lagoon to ratios at the WQ-34 well cluster. The data show that the DCE/PCE, DCE/TCE, and TCE/PCE ratios increased from wells WQ-35B to WQ-34B and WQ-34C. These data imply that PCE was dechlorinating to TCE and DCE as it moved laterally through the aquifer.

The primary contaminants in the WQ-37 wells, downgradient from the former industrial lagoon, were VC and DCE, and DCA (SEC Donahue, Inc., 1992) (table 6). Because VC was probably not a initial contaminant, its presence indicates that it was derived

from CVOC dechlorination. The saprolite-aquifer chemistry at the former industrial lagoon is similar to conditions conducive to dechlorination of CVOC's; DO concentrations were less than 1 mg/L. Moreover, toluene was present (59 $\mu\text{g/L}$) at well WQ-37A and (24 $\mu\text{g/L}$) at well WQ-37 (SEC Donahue, 1992). Toluene has been shown to function as the primary substrate for biotransformation of TCE and three DCE isomers (Hopkins and McCarty, 1995) under aerobic conditions and as a suitable electron donor for the reductive dechlorination of PCE to DCE in anaerobic aquifer microcosms (Sewell and Gibson, 1991). Thus, it is possible that the presence of aromatic hydrocarbons, such as toluene, increased the potential for dechlorination of PCE and TCE by inducing microbial depletion of DO or by acting as electron donors for dechlorination processes. Similarly, the presence of DCA suggests the possibility of TCA dechlorination.

Laboratory Evidence for Vinyl Chloride Depletion

Significant VC mineralization was observed under aerobic conditions in sediments from sites near wells WQ-35 and WQ-36 (fig. 11). Mean rates of aerobic VC mineralization were 0.25 ± 0.09 percent d^{-1} and 0.12 ± 0.01 percent d^{-1} (\pm standard error) in the WQ-35 and WQ-36 microcosms, respectively. These results are consistent with previous reports of microbial utilization of VC as a primary substrate for growth and energy production under aerobic conditions (Hartmans and others, 1985; Hartmans and de Bont, 1992; McCarty and Semprini, 1994). The rates of aerobic VC mineralization observed in this study are comparable to those reported previously for aquifer samples (Davis and Carpenter, 1990), but less than rates of aerobic mineralization reported for VC acclimated cultures of *Rhodococcus* (Malachowsky and others, 1994; Phelps and others, 1991). Thus, the present results demonstrate that the microbial communities indigenous to the contaminated saprolite aquifer at the site are capable of VC mineralization under aerobic conditions (fig. 11A).

Anaerobic mineralization of VC also may be a viable mechanism for *in situ* remediation of VC-contaminated aquifers, if a sufficiently strong oxidant is available *in situ* to drive microbial metabolism. The results of the present study indicate that the microorganisms from the area near well WQ-36 are capable of

Table 6. Concentrations of selected chlorinated volatile organic compounds and toluene at the WQ-37 well cluster, downgradient from the former industrial lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93

[DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; µg/L, micrograms per liter; <, less than; ---, information not available; J, result is detected below the reporting limit or is an estimate]

Site identification	Date	DCA (µg/L)	Total DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	Toluene (µg/L)
WQ-37	08/22/91	470	3,300	<170	<170	3,200	<170
	12/18/91	1,000	17,000	<840	<840	23,000	<170
	04/20/92	<1,200	4,700	9.9	<5	21,000	24
	08/12/92	840	8,800	<500	<500	16,000	<500
	11/18/92	78	1,200	1.1J	<5	3,400	<5
	01/28/93	230	630	<100	<100	2,600	<100
	05/13/93	360	750	<25	<25	5,200	<25
	07/26/93	720	3,700	<120	<120	29,000	<120
	11/03/93	790	4,900	<250	<250	15,000	<250
WQ-37A	08/22/91	1,100	19,000	<840	<840	28,000	<840
	12/18/91	<1,200	20,000	<1,200	<1,200	26,000	<250
	04/20/92	1,200	20,000	<50	<50	58,000	59
	08/12/92	1,200	18,000	<500	<500	25,000	<500
	11/18/92	940	8,600	5	2.5J	22,000	25
	01/28/93	690	6,700	24J	<25	19,000	18J
	05/13/93	830	6,300	<250	<250	17,000	<250
	07/26/93	890	5,600	<250	<250	37,000	<250
	11/03/93	850	5,200	<250	<250	19,000	<250
WQ-37B	08/22/91	590	13,000	2,100	510	12,000	<500
	01/14/92	200	---	1,000	230	5,700	7.8
	04/20/92	370	10,000	680	190	9,400	8.8
	08/12/92	380	12,000	1,100	280	4,800	<50
	11/18/92	690	18,000	470	120	16,000	17

Table 6. Concentrations of selected chlorinated volatile organic compounds and toluene at the WQ-37 well cluster, downgradient from the former industrial lagoon, wastewater-treatment facility, Greenville, S.C., 1991-93--Continued

[DCA, 1,1-dichloroethane; DCE, cis and trans 1,2-dichloroethene; PCE, tetrachloroethene; TCE, trichloroethene; VC, vinyl chloride; µg/L, micrograms per liter; <, less than; ---, information not available; J, result is detected below the reporting limit or is an estimate]

Site Identification	Date	DCA (µg/L)	Total DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	VC (µg/L)	Toluene (µg/L)
WQ-37B	01/28/93	720	17,000	300	83	15,000	13J
	05/13/93	590	16,000	250J	<500	12,000	<500
	07/22/93	460J	13,000	240J	<500	9,600	<500
	11/03/93	350	8,300	510	120J	5,100	<250
WQ-37C	08/19/92	<100	130	2,100	860	<200	<100
	11/19/92	1.3J	110	2,300	760	<10	7.2
	01/29/93	1.3J	110	3,400	950	<10	10
	05/13/93	<250	130J	4,200	1,100	<500	<250
	07/22/93	<120	150	4,000	1,000	<250	<120
	11/03/93	<120	130	4,200	1,100	<250	<120

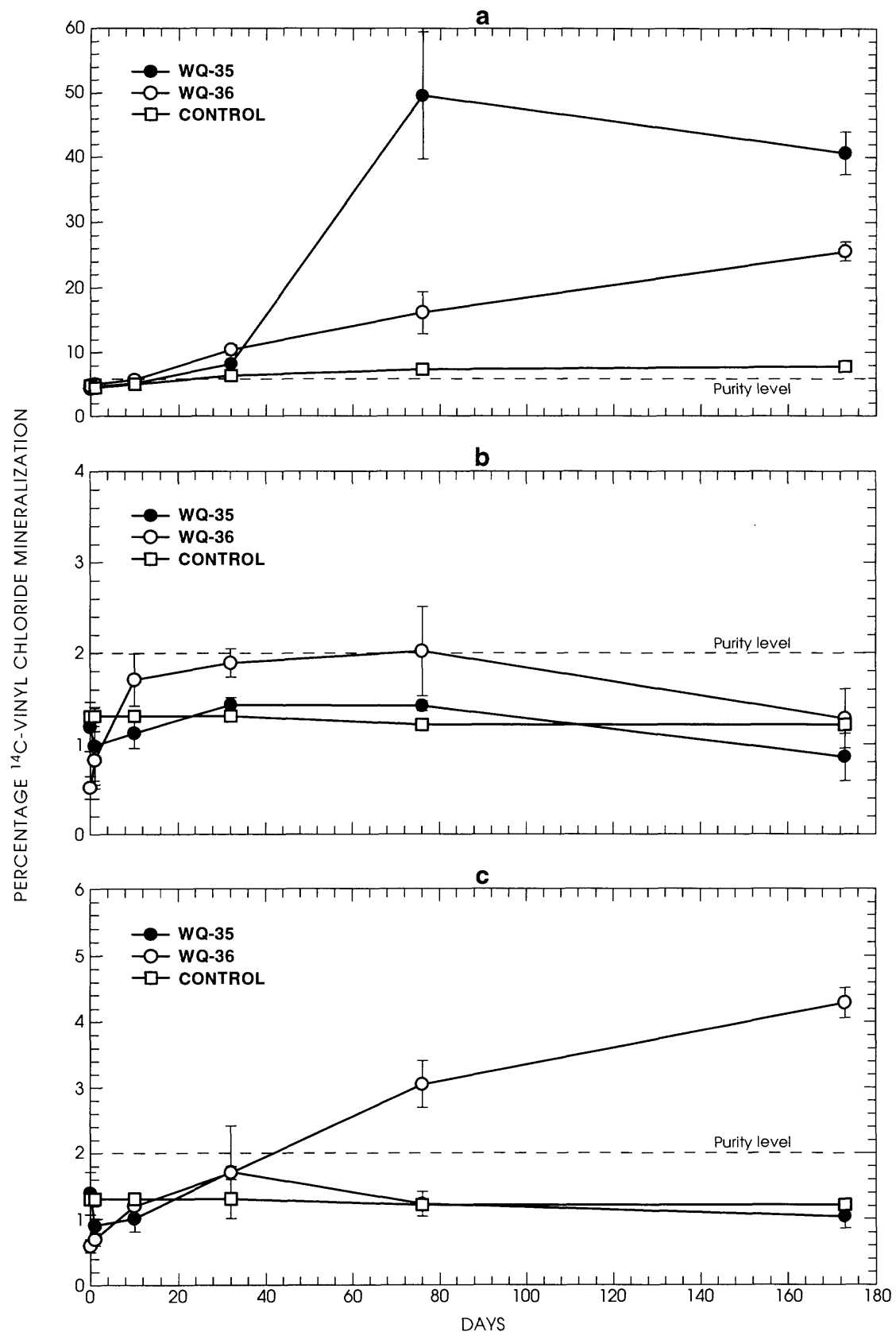


Figure 11. Percentage of mineralization of radio-labeled vinyl chloride to radio-labeled carbon dioxide in (a) aerobic, (b) unamended-anaerobic, and (c) iron (III)-reducing anaerobic microcosms containing aquifer sediments collected near well clusters WQ-35 and WQ-36, as mean (plus or minus standard deviation) for triplicate microcosms.

low but significant rates of anaerobic VC mineralization under Fe(III)-reducing conditions. No significant VC mineralization was observed in unamended anaerobic microcosms (fig. 11B). However, addition of Fe(III) in a bioavailable form resulted in a mineralization rate of 0.02 ± 0.00 percent d^{-1} in microcosms containing material near WQ-36 (fig. 11C). Even with amendment of bioavailable Fe(III), no significant mineralization was observed in WQ-35 microcosms. All VC mineralization observed in anaerobic microcosms could be attributed to biological activity, because no significant mineralization was observed in sterilized control microcosms. Use of a barium hydroxide precipitation protocol (Davis and Carpenter, 1990) on subsamples of trapping solution confirmed that the ^{14}C recovered in the microcosm base traps was ^{14}C - CO_2 and indicated that $[1,2-^{14}C]$ VC was oxidized to ^{14}C - CO_2 . No volatile organic compounds other than VC were detected in the sediment microcosms during the study. The close agreement between VC loss (data not shown) and ^{14}C - CO_2 recovery and the lack of detectable ethene in sediment microcosms strongly suggests that anaerobic VC mineralization involved direct oxidation to ^{14}C - CO_2 rather than an initial dechlorination to $[1,2-^{14}C]$ -ethene with subsequent oxidation to ^{14}C - CO_2 . Thus, these results provide direct evidence that anaerobic oxidation of VC can occur under Fe(III)-reducing conditions and suggest that in-situ biodegradation may be a significant mechanism for reduction of VC contamination in anaerobic zones of this and other study areas.

SUMMARY

In 1994, the U.S. Geological Survey in cooperation with the South Carolina Department of Natural Resources - Water Resources Division, investigated the transport and fate of chlorinated ethenes in saprolite and fractured rock aquifers. The study area was a wastewater-treatment plant in Greenville, S.C., with contaminated ground water. Chlorinated ethenes leaked from three unlined lagoons, contaminating the underlying saprolite and fractured-rock aquifers. Shallow ground-water contamination discharged to Little Rocky Creek, while deeper contamination moved beneath the creek southward.

A vapor-diffusion sampler technique, developed for this investigation, detected concentrations of VOC's in vapor as much as 980 ppm beneath Little Rocky Creek in an area where surface-water sampling

indicated discharge of VOC's from ground water to surface water. This area was also a site where very low-frequency electromagnetic anomalies (interpreted as fracture zones) intersected the creek or converged near the creek. Therefore, the technique also was able to locate fracture zones discharging contaminated ground water to surface water.

The distribution of sulfate in ground water allowed further delineation of contaminant-transport pathways. Relatively high concentrations of sulfate were introduced to the aquifer from the former aeration lagoon. The resulting distribution of sulfate implies that an approximate contaminant-transport path extended from the former aeration lagoon to the WQ-36 well cluster to well WQ-40B to well WQ-51C. Additional evidence to support this hypothesis was a northward trending line of air bubbles and water that began exiting the ground surface between well WQ-51C and the area near well PW-LRC1 during air-rotary drilling of well WQ-51C, and crossed Little Rocky Creek in the vicinity of area B of the passive-vapor survey. These data further suggest that area B was the surface expression of a contaminant-bearing fracture zone connecting the former aeration lagoon to well WQ-51C.

The contaminant-transport pathway from the former industrial lagoon is not readily discernible from existing data. Well WQ-41B, downgradient from the former industrial lagoon, was also downgradient from the former aeration lagoon. The presence of 115 mg/L of sulfate in ground water at well WQ-41B in November 1993 more closely resembles the sulfate concentrations near the former aeration lagoon (greater than 100 mg/L) than sulfate concentrations near the former industrial lagoon (less than 30 mg/L). Thus, the ground water at well WQ-41B may represent mixing of the two plumes. Alternatively, the downgradient part of the plume from the former industrial lagoon may be farther east than well WQ-41B or may have been depleted by contaminant-attenuation processes in the aquifer.

Borehole radar, temperature, caliper, natural gamma, heat-pulse flowmeter, and televiewer logs from this investigation, as well as driller's logs from previous investigations, showed the probable pathway of ground-water flow during pumping of well PW-34BR. In response to pumpage, ground water entered well PW-34C through the base of the borehole and through the southern side of the borehole from fractures at depths of about 105 and 107 ft bls. Water

exited the borehole along the northern side through the fractures at 105 and 107 ft bls. The water then moved northward through fractures, probably passing well WQ-34D at a depth of between 70 and 103 ft bls. The ground water then probably moved approximately horizontally to contaminant-extraction well PW-34BR.

The direction of ground-water flow in response to pumpage at well PW-34BR suggests probable pathways of contaminant transport prior to pumpage. The highly transmissive fracture zones identified during pumping stress were probable pathways of prepump contaminant transport. The flow directions, however, would have been substantially different. Flow during operation of the ground-water pumping network was northward from well PW-34C and the WQ-34 well cluster to contaminant-extraction well PW-34BR. Prior to pumpage, the probable contaminant transport direction was southward through fracture zones between 70 to 103 ft bls at the WQ-34 well cluster toward well PW-34C, where the major pathway of transport was the fracture zone between 105 and 107 ft bls. The areal and vertical location of the contamination at the WQ-34 well cluster; the relatively low sulfate concentration of the contamination; and the linear continuity between well PW-34C, the WQ-34 well cluster, well PW-34BR, and area A of the passive-vapor survey using vapor-diffusion samplers in Little Rocky Creek imply that the contamination in that area was derived from the former sludge lagoon.

An additional body of contamination was present at a horizon near the bottom of well PW-34C (a depth of about 179 ft bls). Although it is possible that such contamination was caused by downward vertical movement through the well bore connecting the fractures at 105 and 107 ft bls to fractures at the base of the well, that scenario is not needed to explain the contaminant distribution. The presence of numerous radar anomalies interpreted as fractures dipping southward toward the contaminated horizon at the base of well PW-34C indicated that several potential pathways of contaminant transport to that horizon were present for contaminant transport.

This investigation also examined ground-water-chemistry data collected during this and previous investigations to determine the potential for microbial degradation of the chlorinated ethenes in the aquifer. The data showed that contamination from the lagoons induced parts of the aquifer to become anaerobic, increasing the potential for reductive dechlorination of

the higher-chlorinated ethenes. Sulfate reduction became the predominant TEAP in much of the anaerobic ground water.

Examination of ratios between lower- and higher-chlorinated ethenes at individual wells strongly implied that PCE and TCE were degrading to DCE at the WQ-36 well cluster. The data further suggested that PCE was dechlorinating to TCE along a flowpath away from well WQ-36.

Similarly, the data suggested that ground-water contamination from the former sludge lagoon was degrading along a flowpath. Changes in ratios of compounds implied that PCE was dechlorinating to TCE between the WQ-35 and WQ-34 well clusters.

The predominance of VC, DCE, and DCA at the WQ-37 well cluster, downgradient from the former industrial lagoon, strongly implies that they were derived from dechlorination of higher-chlorinated ethanes and ethenes. Aquifer conditions in the shallow ground water near the former industrial lagoon were suitable for such solvent degradation. Dissolved-oxygen concentrations were less than 1 mg/L, and petroleum hydrocarbons were known to have constituted part of the waste stream. The ability of toluene to function as the primary substrate for biotransformation of TCE and DCE under aerobic conditions and as a suitable electron donor for the reductive dechlorination of PCE to DCE in anaerobic aquifer microcosms probably allowed extensive degradation of the more chlorinated ethenes and ethanes. The result was accumulation of the less chlorinated species, such as VC. A laboratory investigation using microcosms of sediment samples from the facility suggested that the native microbial population was capable of slow anaerobic VC mineralization under Fe(III)-reducing conditions and more rapid VC mineralization under aerobic conditions.

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APPENDIX I

Vertical flow measured with a heat-pulse flowmeter in selected wells, Greenville, S.C., May 10 - 13, 1994

Appendix I. Vertical flow measured with a heat-pulse flowmeter in selected wells, Greenville, S.C., May 10-13, 1994

[gal/min, gallons per minute; <, less than]

Well identification	Depth of measurements (feet below land surface)	Number of measurements	Standard deviation	Average flow (gal/min)	Direction of flow
PW-34C	98.4	8	0.12	0.02	downward
	105.4	5	2.48	26.57	upward
	110.4	9	.00	53.47	upward
WQ-27B	41.5	7	.04	.14	downward
	48.0	5	<.01	.08	upward
	52.0	8	.01	.09	upward
	57.0	6	.02	.02	upward
WQ-34D	256.3	7	.06	.03	upward
	277.3	9	.13	.01	downward
WQ-35B	53.0	4	.00	1.33	downward
	55.5	4	.04	1.55	downward
	62.0	5	.02	1.36	downward
	65.0	6	.00	1.33	downward
	71.0	6	.07	.68	downward
WQ-35C	213.0	8	.02	.03	upward
	247.0	6	.01	.02	upward
	254.0	7	<.01	.02	upward
	283.0	7	.01	.02	upward
	291.0	10	.01	.02	upward
WQ-37B	34.0	21	.05	.03	upward
	42.0	10	.02	.02	upward
WQ-37C	162.0	5	<.01	.02	upward
	165.7	4	<.01	.02	upward
	170.0	7	<.01	.02	upward

Appendix I. Vertical flow measured with a heat-pulse flowmeter in selected wells, Greenville, S.C.,
May 10-13, 1994--Continued

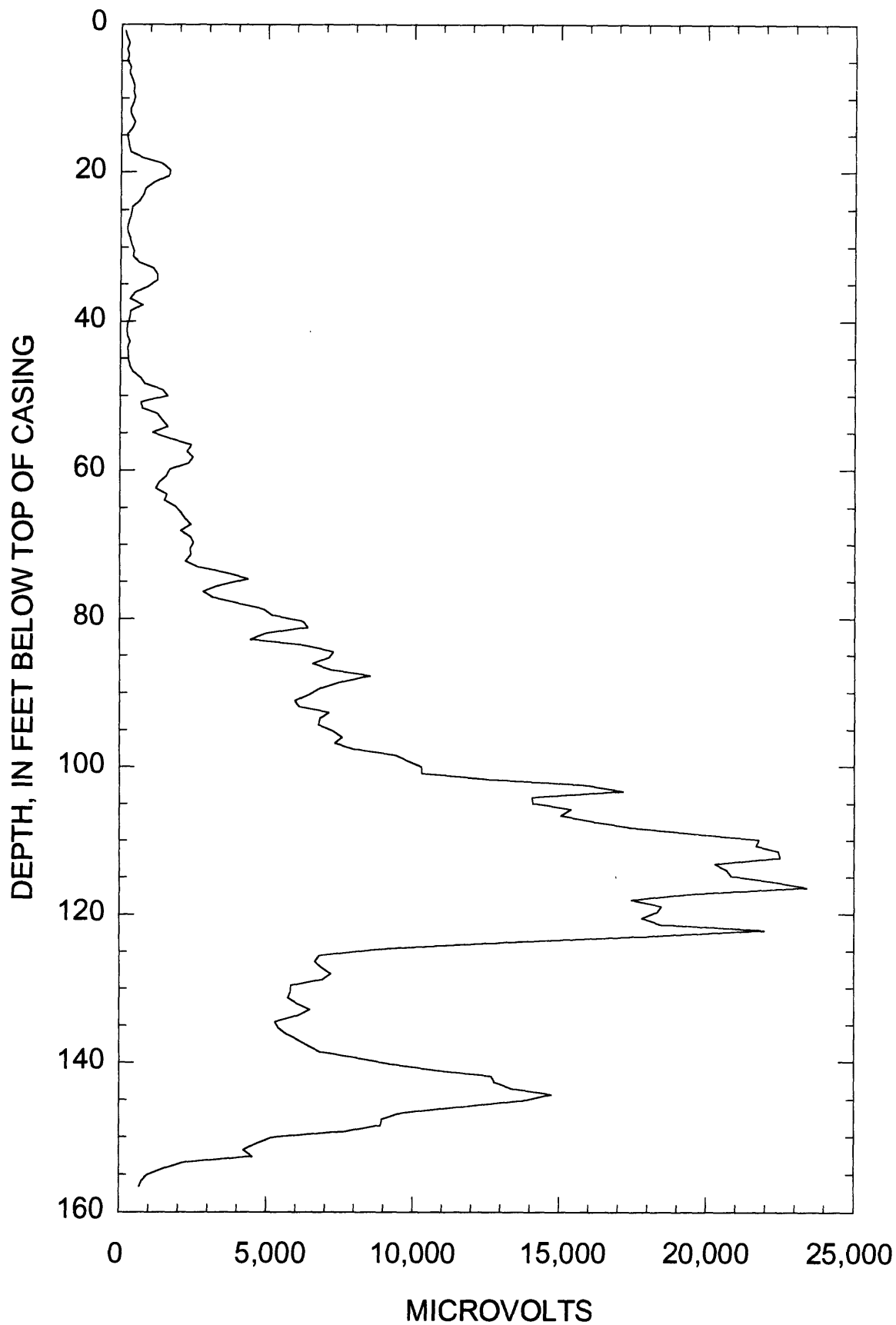
[gal/min, gallons per minute; <, less than]

Well identification	Depth of measure- ments (feet below land surface)	Number of measure- ments	Standard deviation	Average flow (gal/min)	Direction of flow
WQ-50C	275.0	8	0.02	0.01	upward
	320.0	8	.04	<.01	downward
WQ-51B	72.0	7	<.01	.02	upward
	88.0	6	<.01	.02	upward
WQ-51C	166.0	5	<.01	<.01	upward
	191.0	13	.07	.05	downward
	206.0	3	.00	<.01	downward
	218.0	9	.01	.03	upward

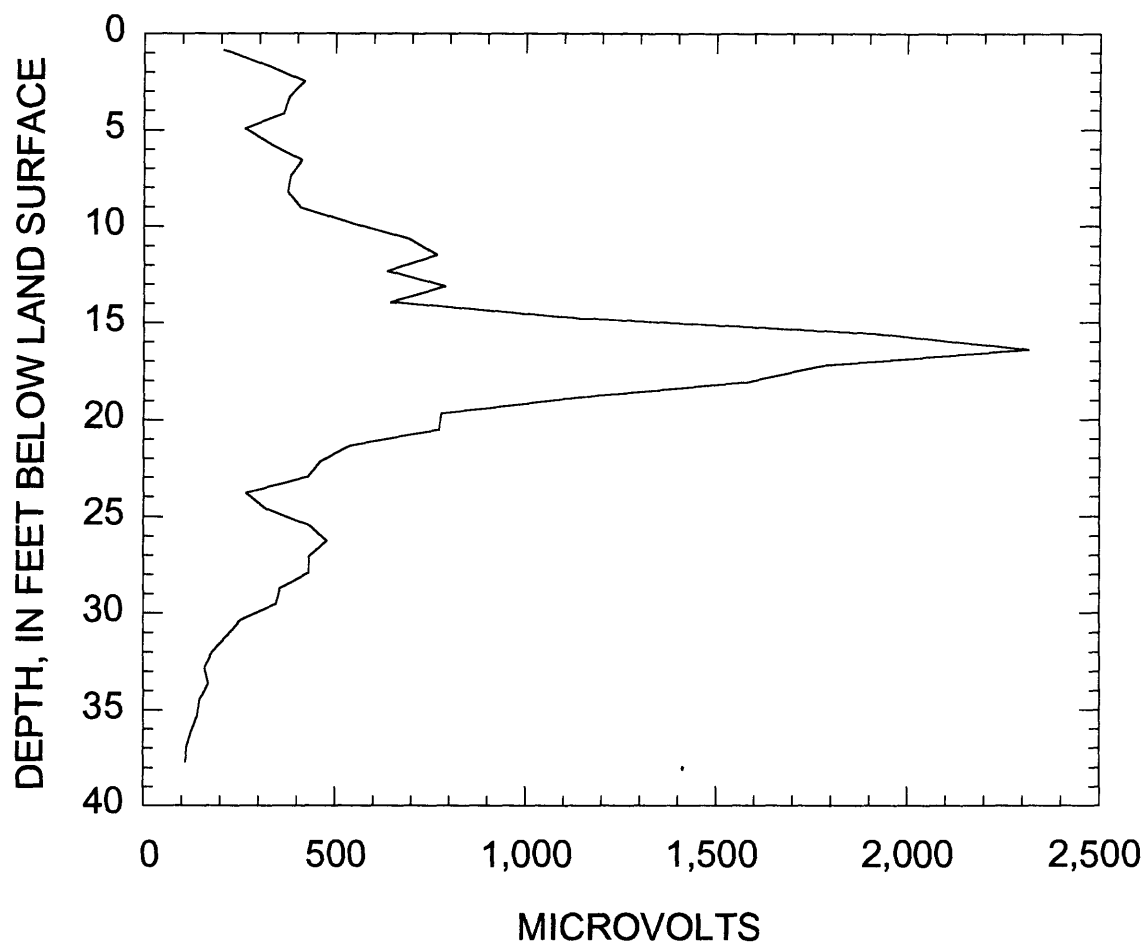
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APPENDIX II

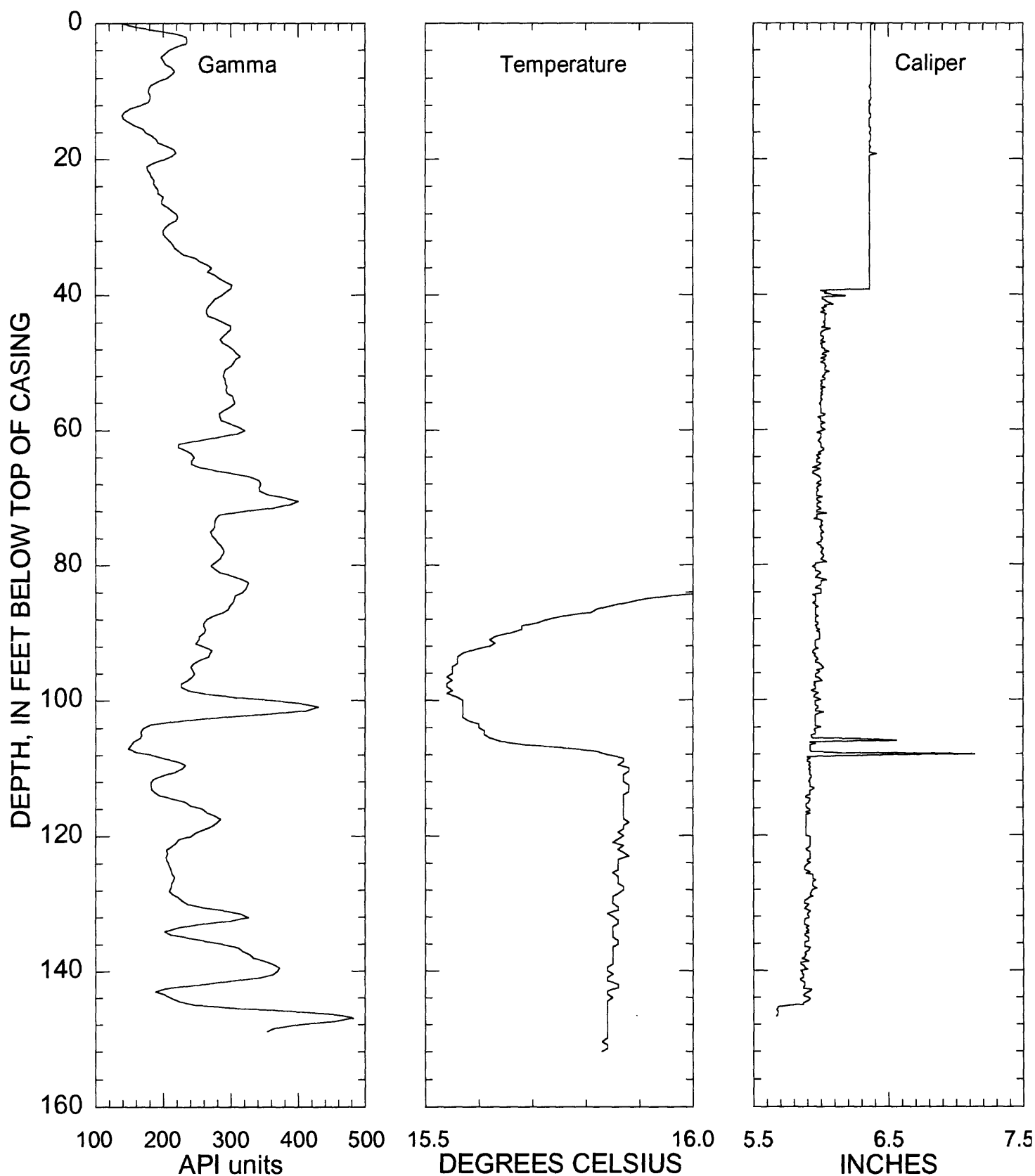
Plots of downhole geophysical logs obtained from selected wells, Greenville, S.C.



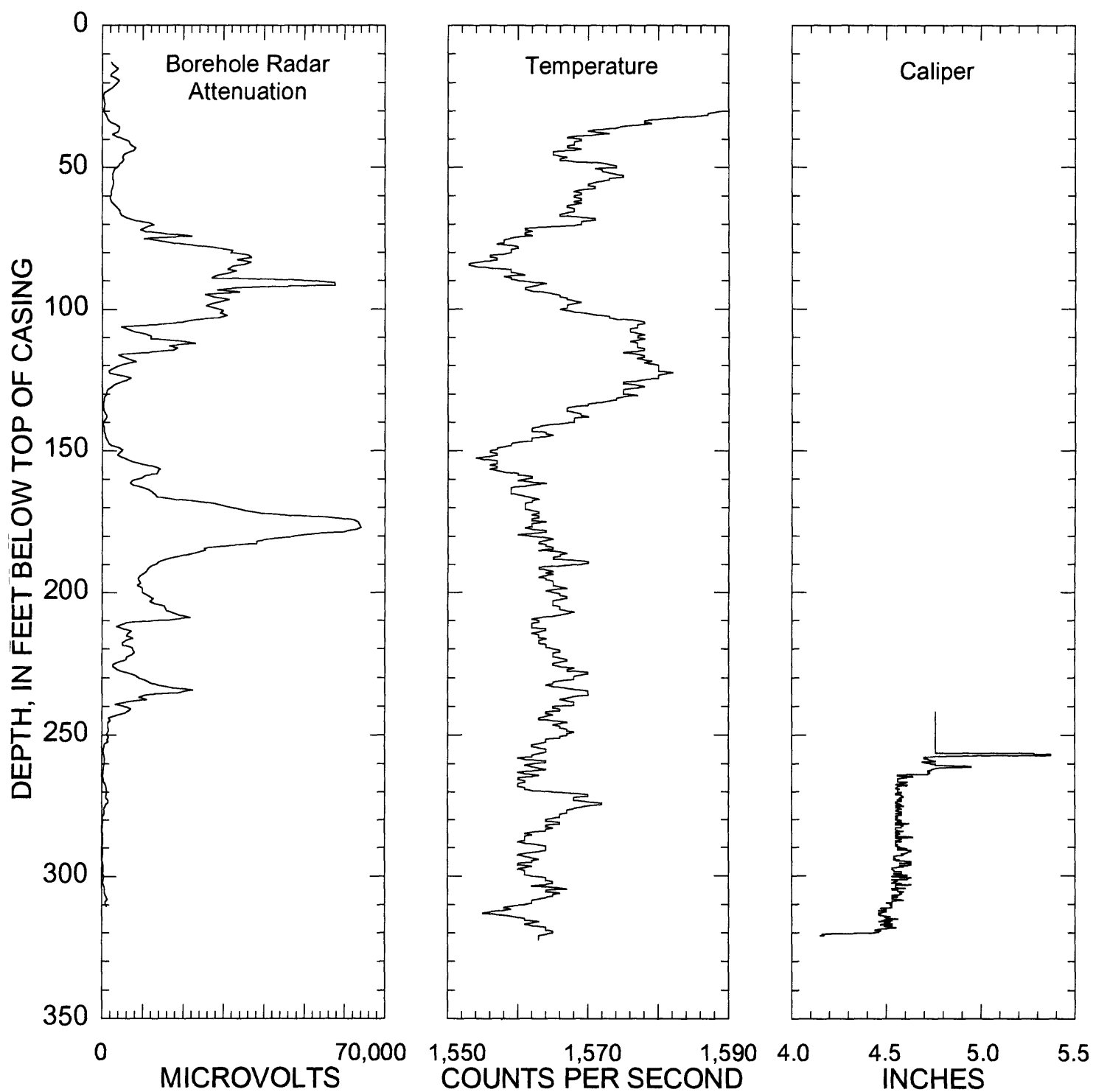
ABS Monitoring Well — Borehole Radar Attenuation — Greenville, S.C.



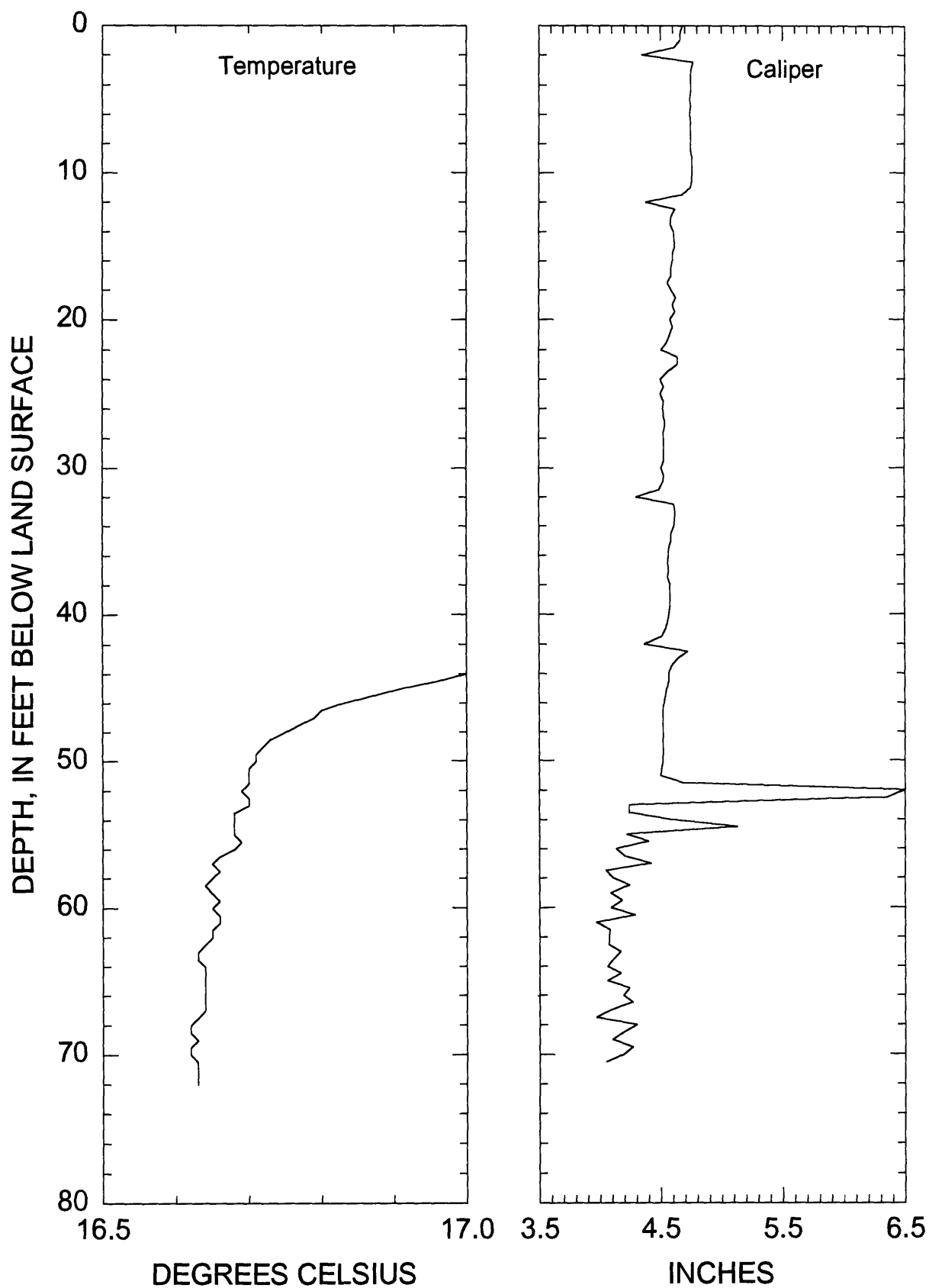
Monitoring Well P12BC — Borehole Radar Attenuation — Greenville, S.C.



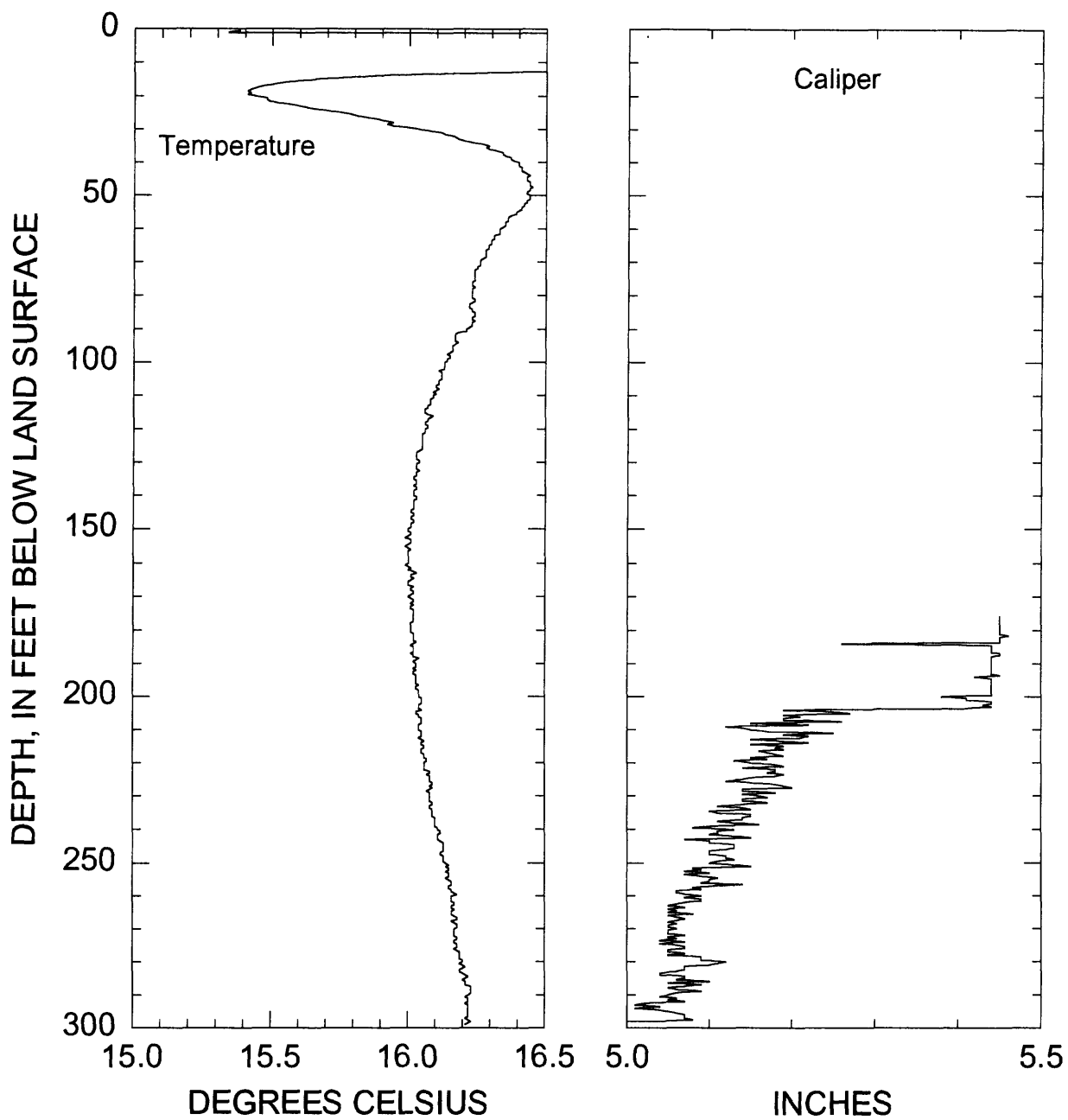
Monitoring Well PW-34C — Natural Gamma Log, Temperature Log, and Caliper Log — Greenville, S.C.



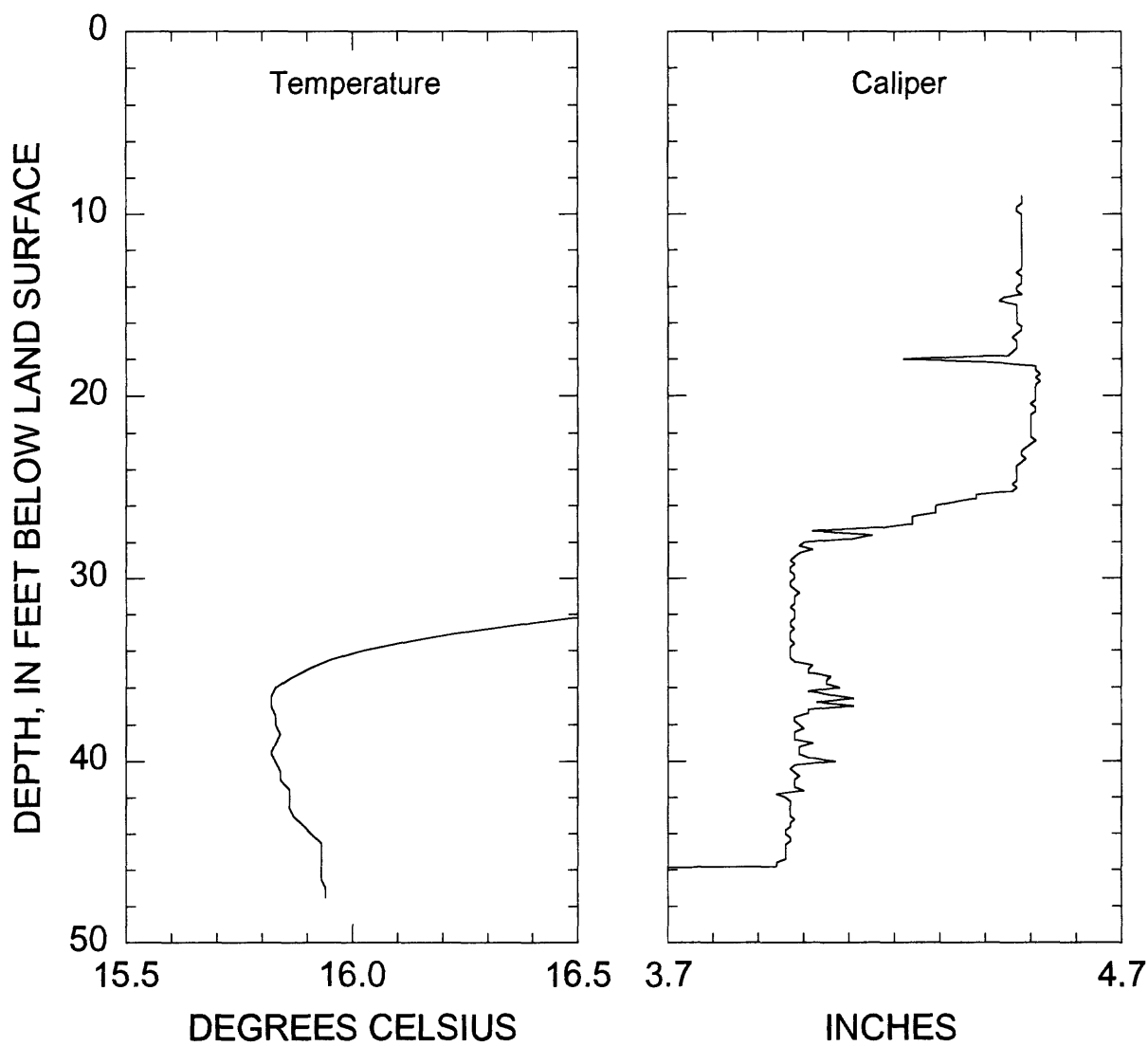
**Monitoring Well WQ-34D — Borehole Radar Attenuation, Temperature Log,
and Caliper Log — Greenville, S.C.**



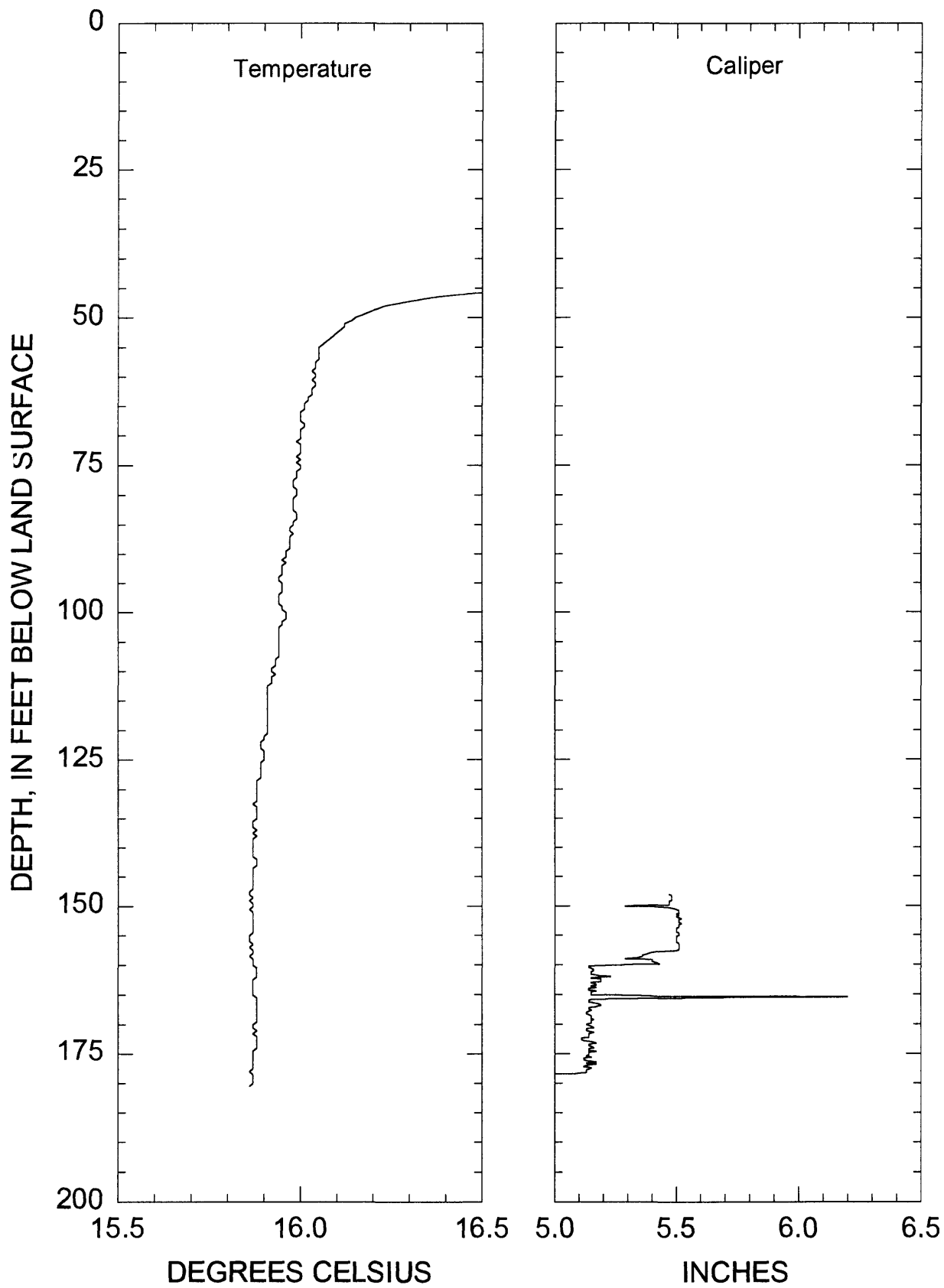
Monitoring Well WQ-35B — Temperature Log and Caliper Log — Greenville, S.C.



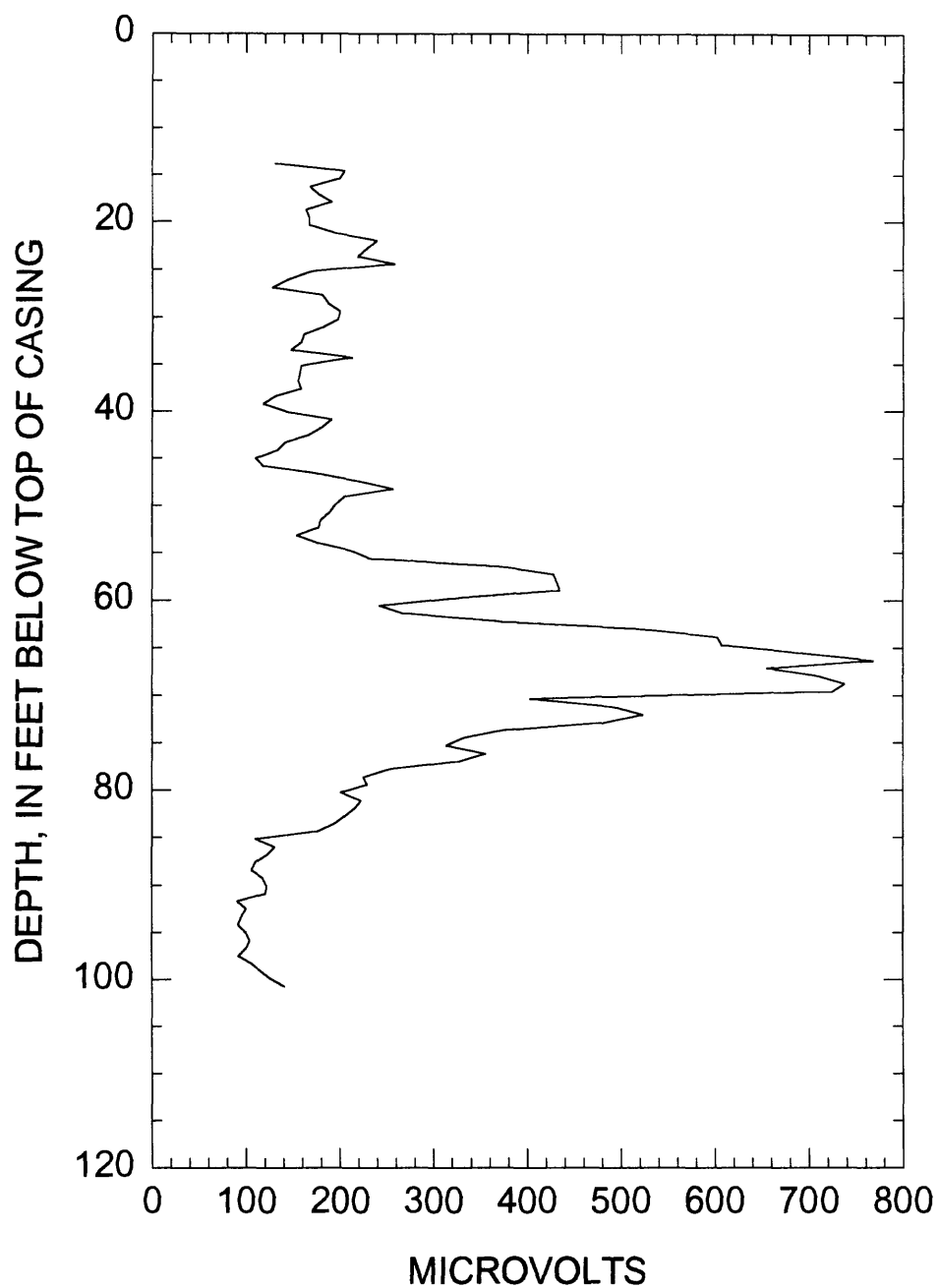
Monitoring Well WQ-35C — Temperature Log and Caliper Log — Greenville, S.C.



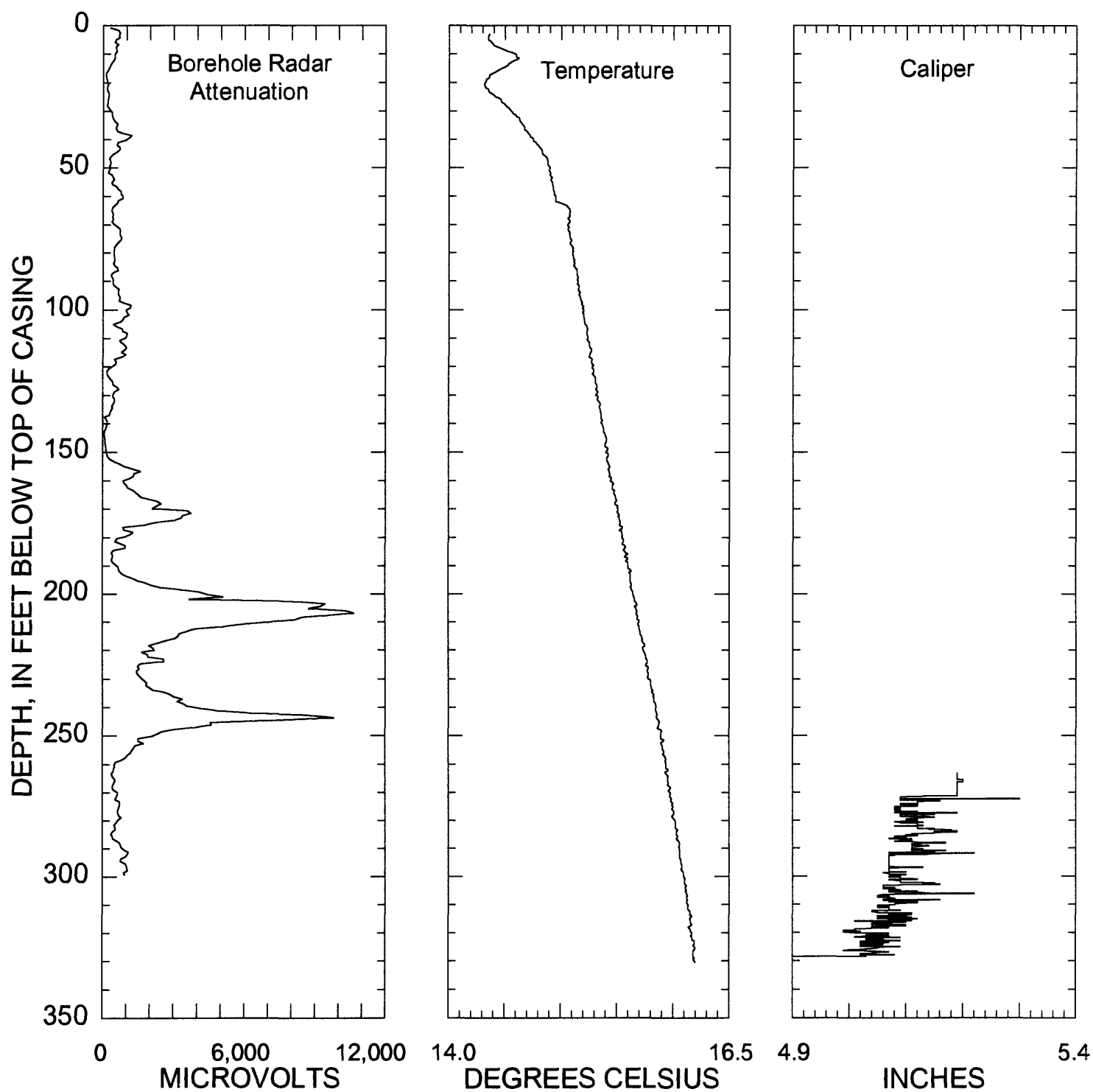
Monitoring Well WQ-37B — Temperature Log and Caliper Log — Greenville, S.C.



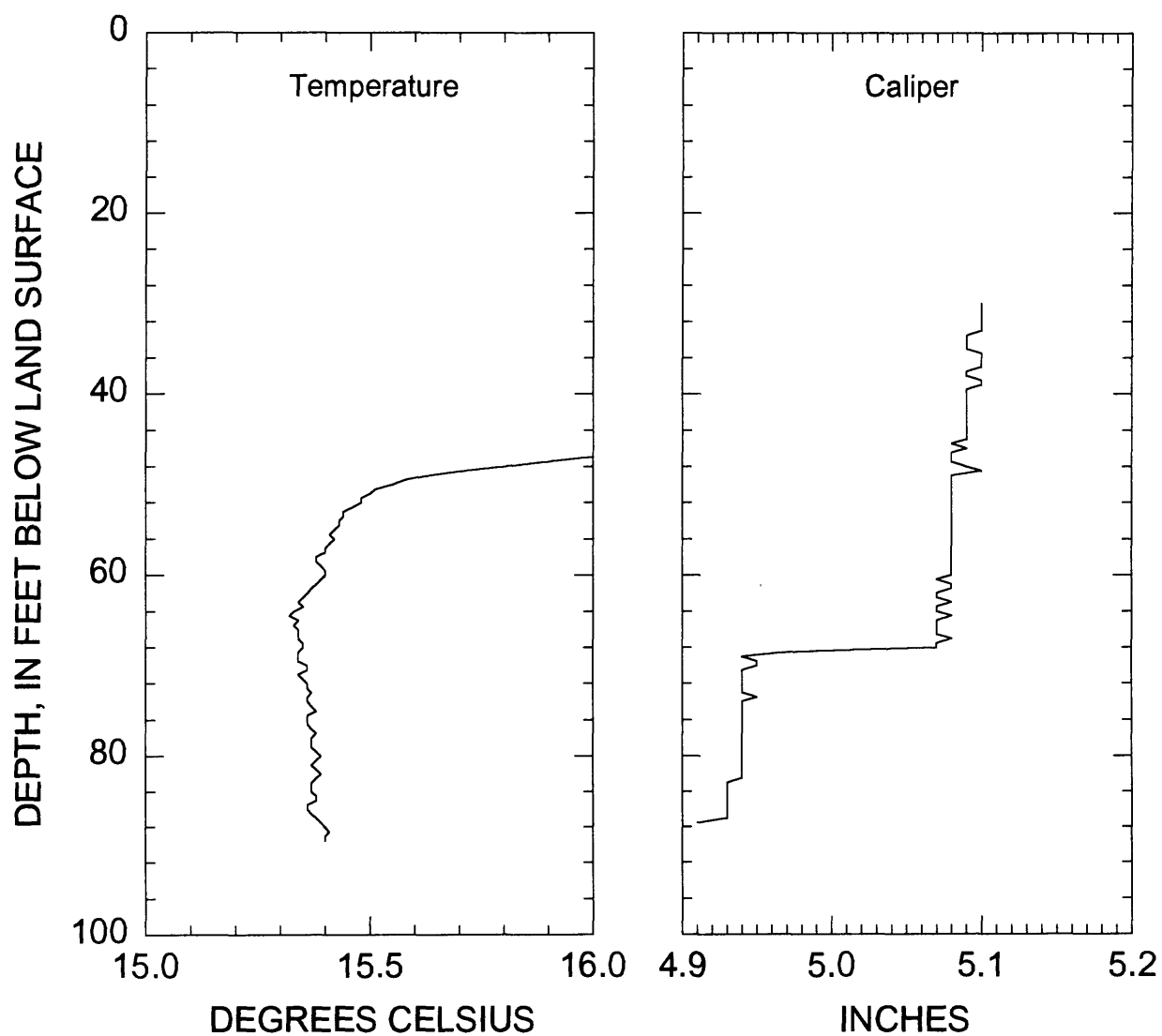
Monitoring Well WQ-37C — Temperature Log and Caliper Log — Greenville, S.C.



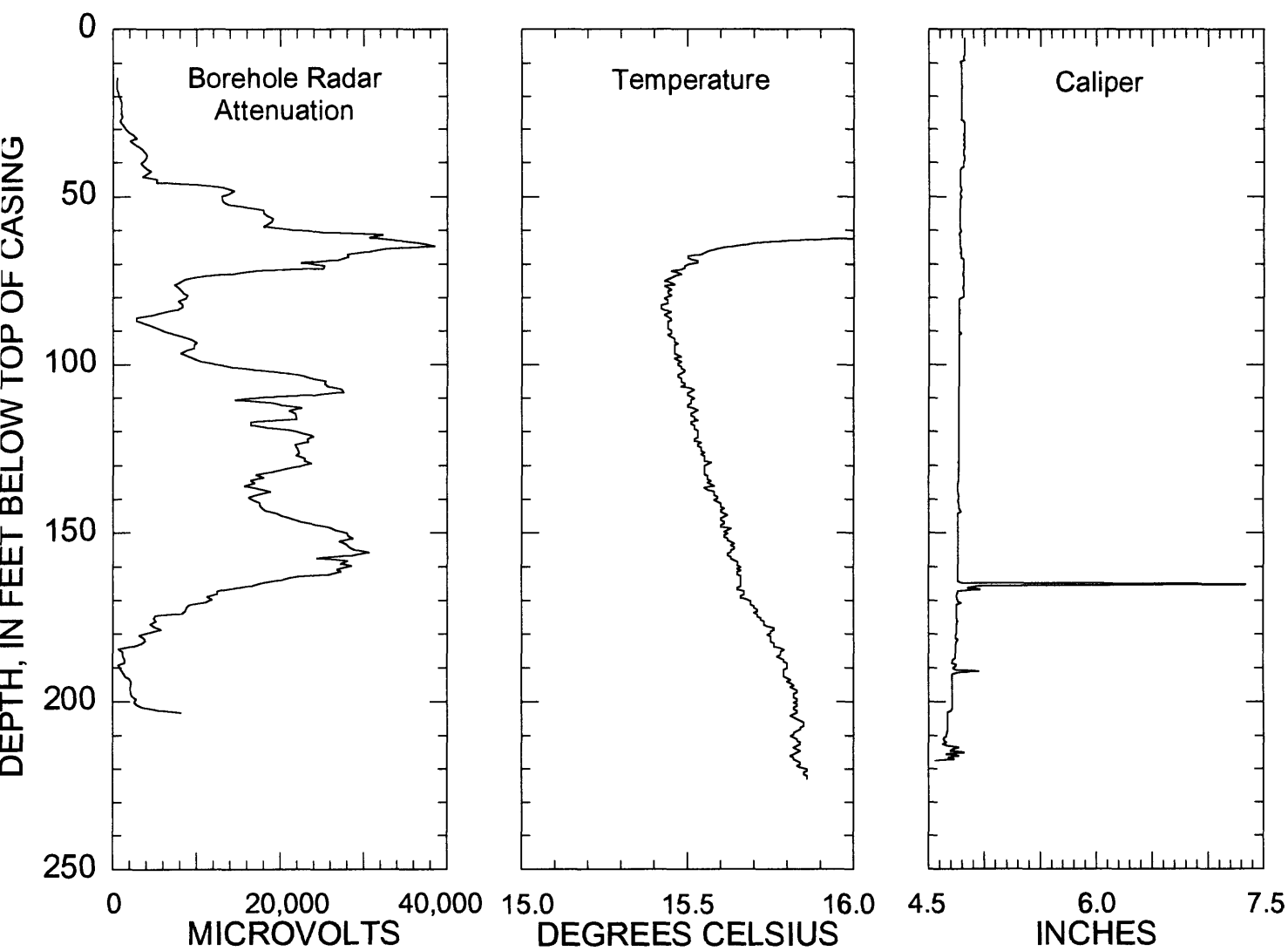
Monitoring Well WQ-46B — Borehole Radar Attenuation — Greenville, S.C.



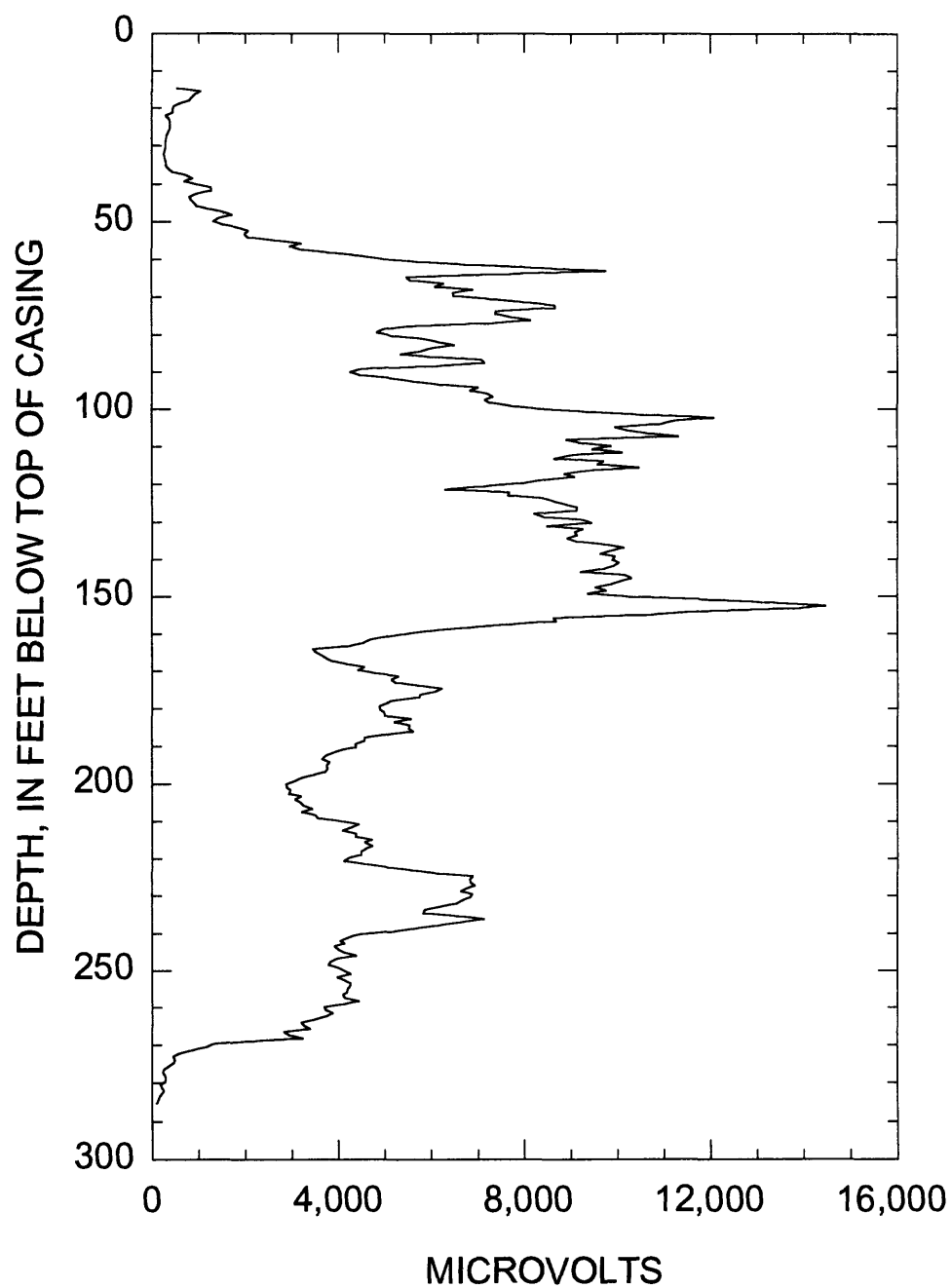
**Monitoring Well WQ-50C — Borehole Radar Attenuation, Temperature Log,
and Caliper Log — Greenville, S.C.**



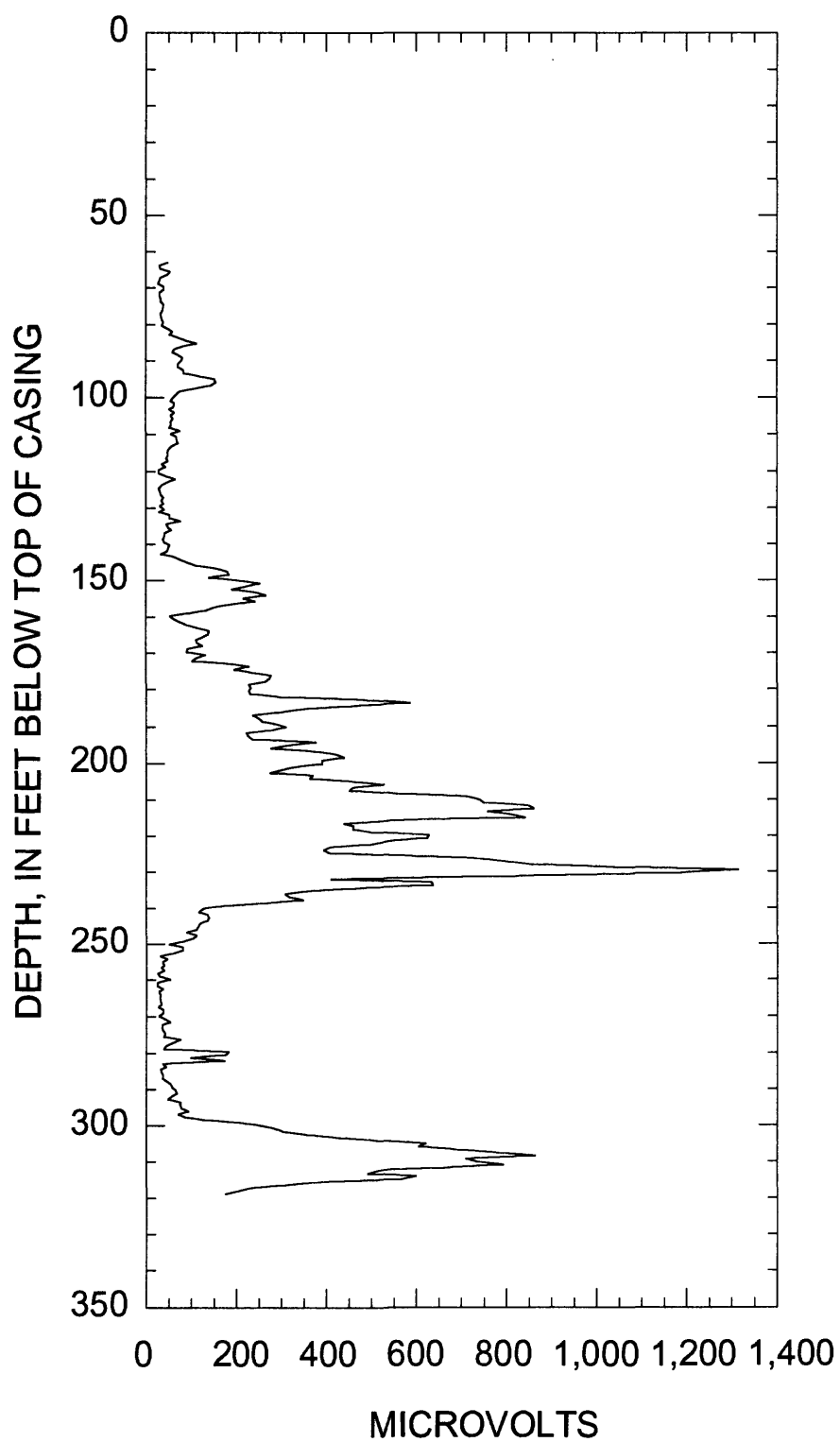
Monitoring Well WQ-51B — Temperature Log and Caliper Log — Greenville, S.C.



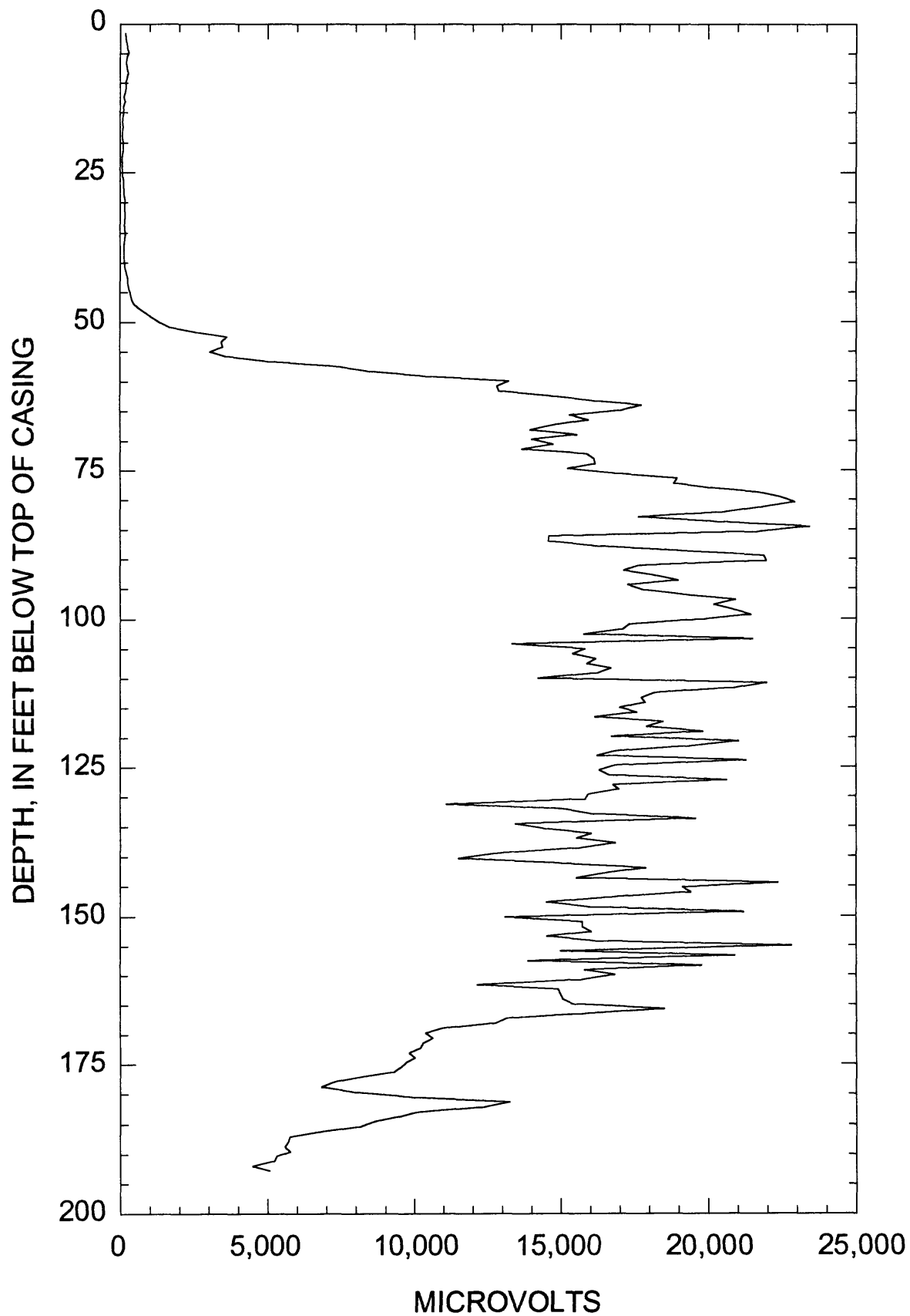
**Monitoring Well WQ-51C — Borehole Radar Attenuation, Temperature Log,
and Caliper Log — Greenville, S.C.**



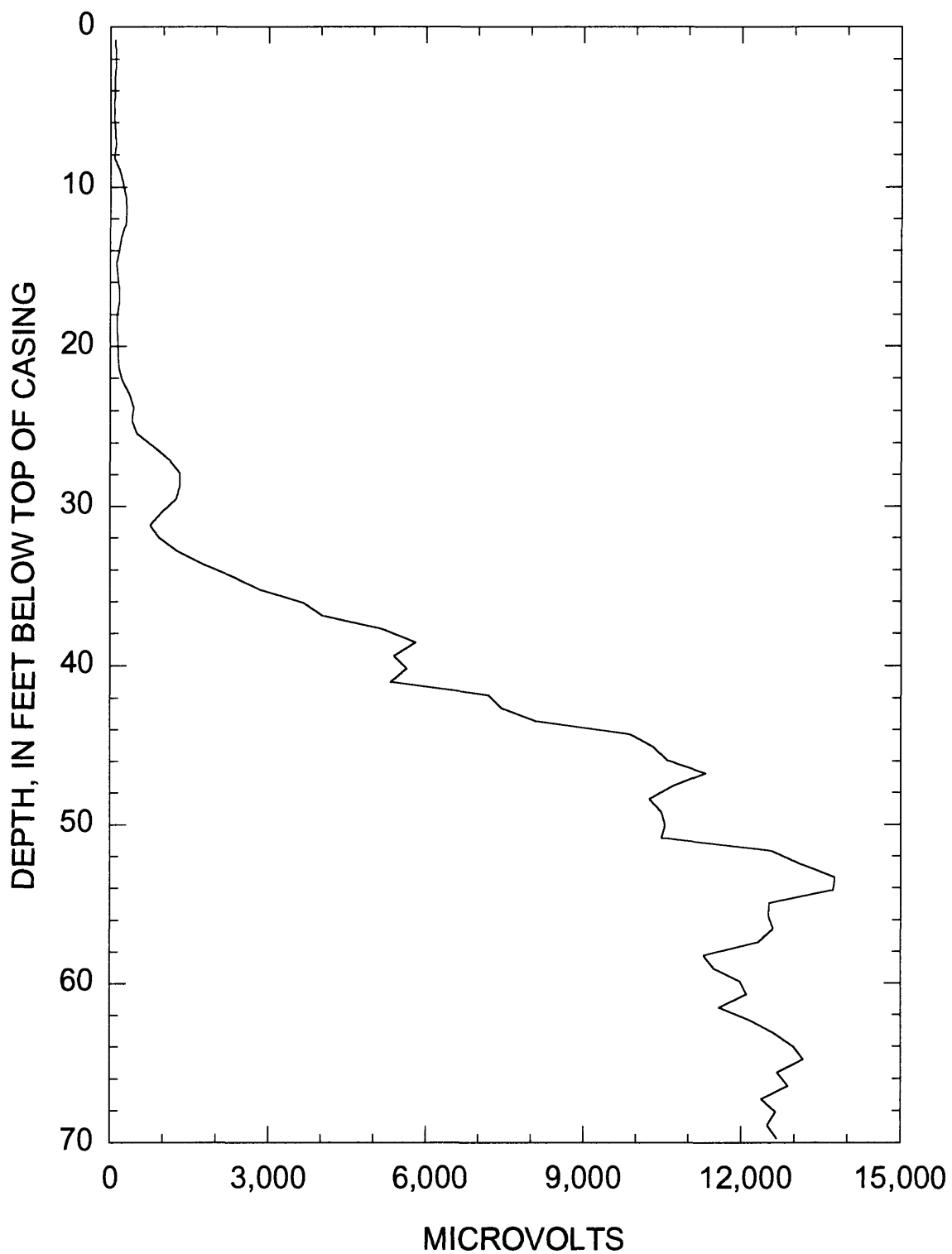
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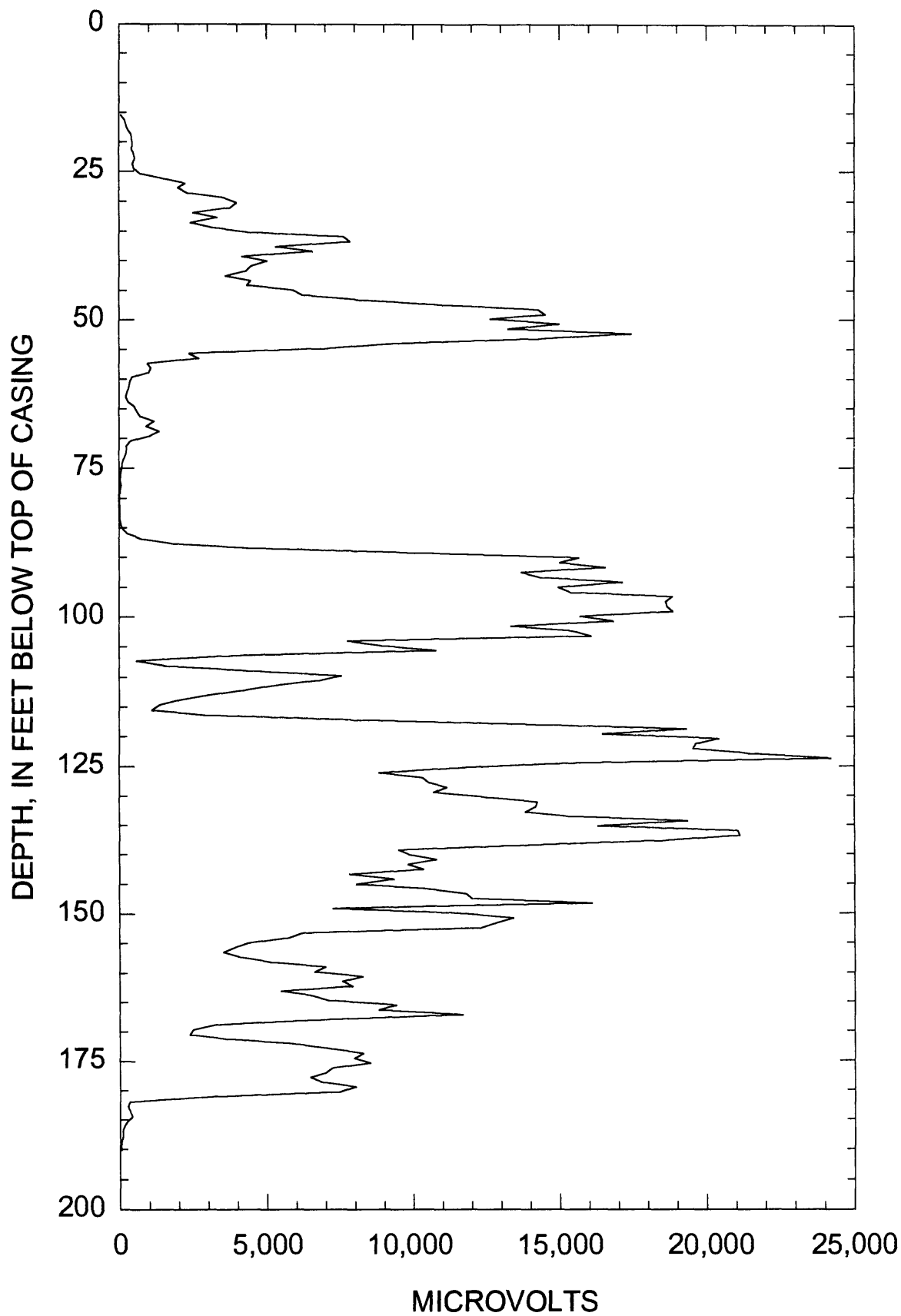
Monitoring Well WQ-63C — Borehole Radar Attenuation — Greenville, S.C.



Monitoring Well WQ-65C — Borehole Radar Attenuation — Greenville, S.C.



Monitoring Well WQ-72B — Borehole Radar Attenuation — Greenville, S.C.



Monitoring Well WQ-73C — Borehole Radar Attenuation — Greenville, S.C.

APPENDIX III

Reflectors identified by single-hole borehole-radar surveys, Greenville, S.C.,
July 26 through August 2, 1994

Appendix III. Reflectors identified by single-hole borehole-radar surveys, Greenville, South Carolina, July 26 through August 2, 1994

[Depths relative to top of casing; --, not applicable; ~, approximate; UI, uninterpretable]

Well number	Type of reflector	Projected borehole intersection depth (feet)	Distance from borehole (feet)	Dip angle ¹ (degrees)	Direction of strike or point reflector (azimuth from True North)
ABS	plane	89.9	--	~ horizontal	--
	plane	104.7	--	~ horizontal	--
	plane	132.9	--	53.1	155.9
	plane	157.5	--	33.5	135.9
	plane	192.6	--	58.0	125.9
	plane	229.3	--	47.0	85.9
	plane	290.0	--	69.1	UI
P12BC	plane	11.8	--	9.3	UI
	plane	50.2	--	~ horizontal	--
	plane	73.2	--	~ horizontal	--
WQ-34D	plane	84.3	--	52.8	115.9
	point	97.4	21.3	--	185.9
	plane	113.2	--	61.2	95.9
	plane	141.7	--	50.1	25.9
	plane	152.9	--	54.4	55.9
	plane	159.1	--	61.4	UI
	plane	179.1	--	43.7	5.9
	plane	196.9	--	53.8	85.9
	plane	211.9	--	55.1	255.9
	plane	222.5	--	43.6	55.9
	plane	259.2	--	43.3	45.9
	plane	295.2	--	11.6	55.9
	plane	394.4	--	76.9	275.9

Appendix III. Reflectors identified by single-hole borehole-radar surveys, Greenville, South Carolina, July 26 through August 2, 1994--Continued

[Depths relative to top of casing; --, not applicable; ~, approximate; UI, uninterpretable]

Well number	Type of reflector	Projected borehole intersection depth (feet)	Distance from borehole (feet)	Dip angle ¹ (degrees)	Direction of strike or point reflector (azimuth from True North)
WQ-46B	plane	6.6	--	~ horizontal	--
	plane	33.1	--	~ horizontal	--
	plane	73.8	--	~ horizontal	--
WQ-50C	plane	77.1	--	~ horizontal	--
	plane	107.6	--	35.1	155.9
	point	108.9	35.1	--	UI
	plane	135.5	--	33.5	105.9
	plane	157.2	--	~ horizontal	--
	plane	170.9	--	~ horizontal	--
	point	238.5	27.9	--	UI
	plane	253.0	--	40.3	35.9
	plane	276.3	--	~ horizontal	--
WQ-51C	plane	-28.5 ²	--	48.7	175.9
	plane	26.6	--	38.2	315.9
	plane	65.3	--	47.9	35.9
	plane	76.8	--	~ horizontal	--
	plane	79.7	--	44.6	245.9
	plane	96.8	--	28.4	115.9
	point	113.9	43.3	--	315.9
	point	114.8	29.9	--	315.9
	point	145.0	24.6	--	315.9
	plane	197.8	--	50.1	205.9
	plane	206.0	--	31.3	205.9
	plane	224.1	--	~ horizontal	--

Appendix III. Reflectors identified by single-hole borehole-radar surveys, Greenville, South Carolina, July 26 through August 2, 1994--Continued

[Depths relative to top of casing; --, not applicable; ~, approximate; UI, uninterpretable]

Well number	Type of reflector	Projected borehole intersection depth (feet)	Distance from borehole (feet)	Dip angle ¹ (degrees)	Direction of strike or point reflector (azimuth from True North)
WQ-58C	plane	229.7 ³	--	76.0	175.9
	plane	275.3	--	79.4	35.9
	plane	68.2	--	~ horizontal	--
	plane	92.2	--	45.5	125.9
	plane	110.9	--	33.8	125.9
	plane	131.6	--	37.2	75.9
	plan	139.8	--	~ horizontal	--
	plane	197.8	--	51.4	75.9
	plane	204.7	--	71.8	25.9
	plane	248.7	--	43.6	205.9
	plane	284.8	--	~ horizontal	--
	plane	295.0	--	~ horizontal	--
	plane	567.3	--	82.7	15.9
WQ-63C	plane	174.9	--	36.9	225.9
	plane	178.5	--	~ horizontal	--
	plane	189.3	--	59.4	35.9
	plane	193.9	--	~ horizontal	--
	plane	235.9	--	~ horizontal	--
	plane	258.9	--	~ horizontal	--
	plane	324.5	--	~ horizontal	--
WQ-65C	plane	74.2	--	~ horizontal	--
	plane	80.1	--	30.3	265.9
	plane	110.2	--	~ horizontal	--

Appendix III. Reflectors identified by single-hole borehole-radar surveys, Greenville, South Carolina, July 26 through August 2, 1994--Continued

[Depths relative to top of casing; --, not applicable; ~, approximate; UI, uninterpretable]

Well number	Type of reflector	Projected borehole intersection depth (feet)	Distance from borehole (feet)	Dip angle ¹ (degrees)	Direction of strike or point reflector (azimuth from True North)
WQ-72B	plane	116.5	--	~ horizontal	--
	plane	165.4	--	48.4	275.9
	plane	212.0	--	58.0	135.9
	plane	261.2	--	3.6	205.9
	plane	265.4	--	44.5	125.9
	plane	420.3	--	78.8	135.9
	plane	-6.9 ²	--	65.5	195.9
	plane	35.8	--	45.5	345.9
	point	77.1	97.8	--	165.9
	plane	80.1	--	~ horizontal	--
	point	86.9	72.2	--	165.9
	plane	124.3	--	28.4	15.9
	plane	133.2	--	20.5	15.9
WQ-73C	plane	75.5	--	~ horizontal	--
	plane	91.5	--	69.9	215.9
	plane	100.1	--	23.3	165.9
	plane	119.1	--	25.3	165.9
	plane	140.8	--	~ horizontal	--
	point	145.0	17.1	--	UI
	point	207.4	24.3	--	UI
	plane	215.2	--	32.7	145.9
	plane	303.2	--	39.1	135.9
	plane	305.1	--	49.9	135.9
	plane	342.2	--	30.2	335.9

Appendix III. Reflectors indentified by single-hole borehole-radar surveys, Greenville, South Carolina, July 26 through August 2, 1994--Continued

[Depths relative to top of casing; --, not applicable; ~, approximate; UI, uninterpretable]

Well number	Type of reflector	Projected borehole intersection depth (feet)	Distance from borehole (feet)	Dip angle¹ (degrees)	Direction of strike or point reflector (azimuth from True North)
	plane	346.1	--	67.5	115.9
	plane	366.5	--	37.6	135.9

¹Dip angles have an associated error range of plus or minus 10 degrees for angles between 0 and 50 degrees and plus or minus 5 degrees for angles between 50 and 90 degrees.

²Negative depth indicates that projected reflector intersection with the borehole is above land surface.

³Reflector probably extends no deeper than 108 feet, and therefore, is not thought to intersect borehole.