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NATURAL ATTENUATION OF CHLORINATED ETHENES AT GROUND WATER/SURFACE WATER INTERFACE DRAFT ACTING AS FINAL NAS CECIL FIELD FL
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Natural Attenuation of Chlorinated Ethenes at a Ground Water/Surface Water Interface, Florida

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Abstract

Field and laboratory studies show that biodegradation of chlorinated ethenes is much more efficient at a ground water/surface water interface than in an adjacent shallow water-table aquifer. The aquifer lacks abundant anthropogenic or sedimentary organic matter and is characterized by Fe(III)- and sulfate-reducing conditions (H_2 concentrations ranging from 0.5 to 2.0 nM). This drives the reductive dechlorination of perchloroethene (PCE) and trichloroethene (TCE), but allows several isomers of dichloroethene (DCE) to persist in ground water and be transported to a discharge area in a nearby stream. Shallow wellpoints and passive diffusion samplers show that ground water within 50 cm of the sediment/water interface of the creek contains measurable concentrations (~10 to 50 µg/L) of DCE. However, passive diffusion samplers placed 5 cm from the sediment/water interface showed no measureable contamination. Laboratory studies indicated that biodegradation rates are roughly ten times higher in streambed sediments (~50% of [1,2-^{14}C] DCE recovered as $^{14}CO_2$ in 50 days) than aquifer sediments (~5% of [1,2-^{14}C] DCE recovered as $^{14}CO_2$ in 50 days). These relatively high biodegradation rates in streambed sediments are an important mechanism restricting contaminant transport to the stream water column, and are a significant component of the natural attenuation capacity of this hydrologic system.

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Introduction

Much of the risk to human health and the environment associated with chlorinated ethene-contaminated ground water is directly linked to the presence or absence of exposure pathways (Rifai et al., 1995). In the humid eastern United States, discharge to surface water bodies is the most common pathway for contaminated ground water to come into contact with human populations or ecosystems (Weaver et al., 1995). In order to rationally assess risks associated with such discharge, it is important to understand the behavior of chlorinated ethenes at ground water/surface water interfaces. This paper reports a combination of field and laboratory studies assessing the discharge of chlorinated ethene-contaminated ground water to a small stream in Florida. The results show that chlorinated ethene biodegradation is greatly enhanced in streambed sediments relative to aquifer sediments. Furthermore, the results show that, in this particular hydrologic system, these streambed biodegradation processes prevent significant contaminant transport from the aquifer to the sediment-water interface of the stream.

Materials and Methods

Geologic and hydrologic setting

The study site (Site 3) is a former drum disposal area located at the Naval Air Station (NAS), Cecil Field located near Jacksonville, Florida. The site is underlain predominantly by sands of marginal marine origin. Discontinuous layers of silty and clayey material also are present, but sandy material comprises most of the section to depths of about 25 m. The former drum disposal occupies a relatively high topographical area where vertically percolating precipitation recharges the underlying ground-water system. Ground water flows laterally away from the drum disposal area and discharges to surrounding creeks and wetlands. Site 3 is

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adjacent to Rowell Creek which receives outflow from Lake Fretwell and which acts as the discharge area for ground water that has flowed through contaminated sediments underlying the former drum disposal area (Fig. 1). Permanent monitoring wells at the site are screened at three different depths: A deep zone 20-25 m below land surface, an intermediate zone (10-15 m), and a shallow zone (5-10 m). Most of the contamination is present in the shallow zone of the flow system. The zone screened by a particular well is indicated in the well number as S (shallow), I (intermediate), or D (deep) (Fig. 1). In addition to permament monitoring wells, the area immediately adjacent to Rowell Creek was instrumented with shallow (0.5-1.5 m deep) temporary monitoring wells (Fig. 1). These wells were oriented to intercept ground-water flowlines as they converge on Rowell Creek.

Ground-water chemistry

Concentrations of the redox-sensitive parameters dissolved oxygen, ferrous iron, sulfide, and dissolved hydrogen (H_2) were determined in the field at the time of sampling. Each sampling well was purged until water-chemistry parameters stabilized. During sampling, each well was pumped at a rate of about 500 mL/min. Concentrations of dissolved oxygen were quantified using colorimetric methods, and ferrous iron and sulfide concentrations were quantified using spectrophotometric analysis (Hack Company, Loveland, Colorado). Concentrations of dissolved H_2 were measured using a gas-stripping procedure that has been previously described (Chapelle et al., 1995). Concentrations of dissolved methane and dissolved inorganic carbon (DIC) were measured by withdrawing 10 mls of water from the gas-sampling bulb through a syringe and injecting the water through a septa into a sealed 40-ml VOC vial. In the laboratory, the 10 mls of water was acidified. Concentrations of carbon dioxide and methane in the headspace gas were

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quantified by gas chromatography with thermal conductivity detection. Concentrations of chlorinated ethenes in ground-water were measured by placing 10 mL of water in a 20 mL VOC vial. In the laboratory, vials were heated to 80°C to drive VOCs into the headspace (Hewlett Packard model 7694 headspace analyzer), and chlorinated ethenes quantified by gas chromatography with flame ionization detection. Concentrations of dissolved sulfate and chloride were measured in the laboratory using ion chromatography with conductivity detection (Dionex).

Chemicals and Microcosm studies

Relative rates of microbial mineralization of 1,2 dichloroethene (1,2-DCE) were evaluated using radiolabled [1,2-^{14}C] DCE. A neat mixture of [1,2-^{14}C] DCE was obtained from Moravek Biochemicals, Inc. (Brea, California). This mixture consisted of 29% *trans* and 71% *cis* isomers. The radiochemical purity of the DCE mixture was determined by radiometric detection gas chromatography to be greater than 99.9%.

Microcosms consisted of 30 mL serum vials which were amended with 15 g of saturated aquifer or stream bed sediments (water content ~ 25 w/w) and sealed with teflon lined butyl rubber stopper/base trap assemblies. Aquifer sediments were collected from the water table (2 m depth) at a point approximately half-way between the source area and the creek side. Creek bed sediments were collected from the plume-ward side of the creek bed at a depth of 0.2 m. Microcosms were created with headspaces of air (aerobic treatments) or 100% helium (anaerobic treatments) and amended with 1.0 mL of anoxic, sterile disilled water (aerobic and methanogenic treatments) or 1.0 mL of an anoxic, sterile Fe-EDTA (Fe(III)-reducing treatments), or $MgSO_4$ (sulfate-reducing treatments). The final concentration of SO_4 and Fe-(EDTA was 1 mM. Killed controls were prepared in the same manner and autoclaved twice for 1 hour at 15 psi and 121°C.

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The absence of oxygen was confirmed in all anaerobic microcosms initially and at the end of the experiments by headspace analysis using thermal conductivity detection gas chromatography. The presence of oxygen in aerobic microcosms, and production of CH_4 in methanogenic treatments was confirmed in the same manner. Production of dissolved iron and sulfide was confirmed in Fe(III)-reducing and SO_4-reducing treatments by spectrophotometric analyses using colorimetric test kits (Hach Company, Loveland, Colorado).

Triplicate experminental microcosms and duplicate killed controls were prepared for each terminal electron accepting condition. The microcosms were pre-incubated 5 days to acclimate the indigenous microorganisms to the various electron acceptor amendments. To begin the experiments, approximately 50,000 DPM of [1,2-^{14}C] DCE was injected below the surface of the saturated sediments. Based on independently conducted headspace partitioning and sediment adsorption experiments, the initial dissolved substrate concentrations were about 5 μM DCE. To sample, the base traps of individual microcosms were rinsed with 0.5 mL of sterile distilled water and filled with 0.3 mls of 3 M KOH. After 24 hour collection period, the KOH was removed and the amount of trapped $^{14}CO_2$ was quantified by scintillation counting. Sediment microcosms were incubated in the dark at room temperature for a period of 50 days. $^{14}CO_2$ production was confirmed in select vials by addition of barium chloride as described previously (Davis and Carpenter, 1990). The fact that no radioactivity was detected in the base traps of sterile serum vials which contained radiolabled substrate but no sediment indicates that trapping of radiolabled DCE was not significant (less than 1%) in experimental microcosms. The $^{14}CO_2$ production data were corrected for the recovery efficiency of $H^{14}CO_3$. This recovery efficiency was quite consistent (52 ± 3 %) but relatively low due to the circum-neutral pH of the interstitial water and

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the non-sacrificial (i.e., the microcosms were not acidified) recovery method employed in this study.

Passive diffusion samplers

Passive diffusion samplers (Vroblesky et al., 1996) were used to detect chlorinated ethenes in streambed sediment pore water. Sampling streambed pore water for chlorinated ethenes or other contaminants is often problematic because pumping wellpoints screened near (within a few centimeters) a sediment/water interface can induce seepage of surface water. Passive diffusion samplers, which allow volatile constituents of ground water to pass through a membrane and accumulate in the gas phase, are one approach to more accurately sample water discharging to surface-water bodies (Vroblesky et al., 1996). Passive diffusion samplers were constructed by stretching two polyethylene membranes over the open end of a standard VOC vial and taping them in place with strapping tape. The vials were then taped to a wire survey flag and placed into streambed sediments for 48 hours. Laboratory tests have shown that passive diffusion samplers immersed in chlorinated ethene standards come into equilibrium in less than 24 hours. Immediately after retrieval, the soiled outer membrane was stripped away (leaving the inner membrane intact), and the VOC vial capped and sealed. The vials were then transported to the laboratory for analysis. Concentrations of chlorinated ethenes in the gas phase were analyzed by headspace gas chromatography with with flame ionization detection. The data are reported as aqueous concentrations of DCE isomers (μg/L of water) by applying Henry's Law. The dimensionless Henry's Law constants used in this study are 1,1-dichloroethene, 0.848; 1,2 *cis* dichloroethene, 0.121). Because of uncertainties associated with applying Henry's Law to these data, the reported aqueous concentrations should be considered estimates.

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Results

Redox conditions in the shallow aquifer

Concentrations of redox-sensitive solutes measured in ground water at Site 3 are shown in table 1, and concentrations of chlorinated ethenes are shown in table 2. The distribution of redox processes determined with data of table 1, using previously described methodology (Chapelle et al., 1995), are shown in figure 2. Near the drum disposal area (wells CF-3-13S, 14I, and 15D), ground water in the shallow part of the flow system is anoxic, contains relatively high concentrations of dissolved iron, and has dissolved hydrogen (H_2) concentrations (H_2 ~ 0.2 to 0.8 nM) in the range characteristic of Fe(III) reduction. The predominance of Fe(III) reduction in this zone is consistent with the lack of sulfate reduction as indicated by the presence of dissolved sulfate but the lack of significant dissolved sulfide. The deeper wells near the drum disposal areas are oxic. Further along the flowpath (wells CF-3-28D, 29D, 30DD), the ground water becomes uniformly anoxic with Fe(III)-reduction predominating in the shallower zones (H_2 0.2 to 0.8 nM) and sulfate reduction predominating in the deeper zone (H_2 1.0 to 4.0 nM). Near the discharge area (wells CF-3-31S and 32D) sulfate reduction and methanogenesis become the predominant redox processes (Fig. 2).

Contaminant transport to Rowell Creek

An initial survey using passive diffusion samplers to document the presence and absence chlorinated ethenes in the porewater of streambed sediments was performed in July, 1996. Duplicate diffusion samplers were placed specifically to maximize the chances of intercepting ground water discharging to the creek. Samplers were dug into the bank on the

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west side of the creek to depths of approximately 50 cm. The results of this initial survey are shown in Figure 3a. Positive hits for the 1,1-DCE, 1,2 *trans*-DCE, and 1,2 *cis* DCE were recorded in five locations. Only those locations where duplicate vials contained measurable DCE isomers are considered positive on figure 3a. Headspace concentrations (nanomoles per liter of headspace gas) and equivalent Henry's Law aqueous concentrations of these isomers (μg/L of water) are given in table 3. PCE, TCE, and VC were not detected in any of the vials. These results demonstrate that DCE isomers transported by flowing ground water are detectable in deeply buried diffusion samplers. These data are consistent with the presence of DCE isomers in ground water near the stream as documented with shallow temporary wellpoints (table 2). Ground water sampled from the shallow temporary wellpoints on the west bank of the stream contained DCE isomers, whereas ground water on the east bank of the stream lacked measureable DCE concentrations (table 2).

These data demonstrated that DCE-contaminated ground water was indeed reaching Rowell Creek. This raised the question as to whether DCE-contaminated ground water was actively discharging into Rowell Creek. To address this question, a sampling trip was made in February of 1997. The streambed on both banks of the creek, and on three traverses across the creek were extensively instrumented with diffusion samplers buried to a depth of 5 centimeters. In contrast to the July sampling event, none of the diffusion samplers indicated the presence of chlorinated ethenes in shallow creek bed sediments.

A final sampling event was carried out in March 1997. In this sampling event, diffusion samplers were simultaneously place in deep (50 centimeters) and shallow (5 centimeters) creek bed sediments. In this sampling event, DCE isomers were detected in two

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deep streambed sediments (Fig. 3c), but not in shallow streambed sediments. The lack of DCE isomers in ground-water discharging to Rowell Creek was also indicated by water samples collected with seepage meters (ABB Environmental Services, written communication, 1996).

Microcosm studies

Microcosm studies were performed on aquifer sediments and creek bed sediments in order to determine relative rates of mineralization under different terminal electron accepting conditions. [1,2-^{14}C]DCE was observed to mineralize to $^{14}CO_2$ in both aquifer sediment and streambed sediment microcosms (Fig 4). However, there were significant differences in rates of mineralization. In the aquifer sediment microcosms and under the Fe(III)- and sulfate-reducing conditions characteristic of the aquifer, [1,2-^{14}C] DCE mineralization was relatively inefficient, with about 7 % of the radiolabled DCE being recovered as $^{14}CO_2$ over 50 days. In contrast, under the partially aerobic conditions present in streambed sediments, particularly near the sediment/water interface, [1,2-^{14}C] DCE was relatively efficient, with approximately 70 % of the radiolabled DCE being recovered as $^{14}CO_2$ over 50 days. Under strictly anaerobic conditions, [1,2-^{14}C] DCE mineralization was much less efficient in streambed sediments (Fig. 4).

Discussion

It is well-established that reductive dechlorination of chlorinated ethenes is relatively efficient in highly reducing methanogenic environments (Vogel and McCarty, 1985; De Bruin et al., 1992), and that dechlorination becomes progressively less efficient in sulfate-reducing and Fe(III)-reducing environments (Vogel and McCarty, 1987). Similar behavior has been observed in ground-water systems (Chapelle, 1996). At Site 3, the hydrologic system is dominated by

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Fe(III) reduction and sulfate reduction. Under these ambient conditions, reductive dechlorination of highly oxidized PCE and TCE can be expected to proceed (DiStefano et al., 1991). However, reductive dechlorination of the more reduced DCE isomers should be less efficient (Vogel and McCarty, 1987). Because of inefficient DCE reduction to VC, and because VC has been shown to oxidize under Fe(III) reducing conditions (Bradley and Chapelle, 1996), the accumulation of VC in this hydrologic system would not be expected.

near the source or near the stream? DCE being degraded e. the stream?

The observed behavior of chlorinated ethenes in this ground-water system is largely consistent with these expectations. Near the former drum-disposal area, PCE and TCE are present in relatively high concentrations. As ground water moves along the flowpath, PCE and TCE disappear, the DCE isomers tend to persist, and VC is not observed. The redox conditions at this site (Fe(III) reduction and sulfate reduction) are sufficiently reduced to drive reductive dechlorination of the original contaminants PCE and TCE. However, conditions are not sufficiently reduced to drive efficient reductive dechlorination of the DCE isomers. This leads to the observed persistance of DCE in ground water, and contributes to DCE transport to Rowell Creek. Similar behavior has been observed in other predominantly Fe(III) reduction-dominated systems (Weidemeir et al, 1996).

While DCE is present in ground water near the creek, and while DCE can be detected in deeply buried (50 cm) diffusion samplers, DCE was not detected in shallow (5 cm) diffusion samplers near the sediment/water interface. These data suggest that, while DCE is actively transported to the creek by flowing ground water, biodegradation processes in the creek bed sediments and, possibly hydrodynamic dilution processes in the hyporheic zone, greatly attenuate contaminant concentrations. The importance of biodegradation processes is indicated

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by the microcosm experiments that show much more efficient biodegradation processes in streambed sediments than in aquifer sediments (Fig. 4). This is consistent with the common observation that the hyporheic zones of small streams exhibit high microbial activity (Hendricks, 1992). The importance of hydrodynamic dilution in the hyporheic zone is less easily evaluated. Hyporheic zones are highly dynamic environments where the depth of surface-water penetration into the underlying ground-water system--and thus the extent of ground water/surface water mixing--changes continually. The presence of dissolved oxygen in shallow ground water underlying the streambed (table 1) indicates a significant component of surface water/ground water mixing in this system. Such mixing serves both to enhance microbial degradation processes and to dilute discharging contaminants.

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The faster biodegradation rates observed in streambed sediments relative to aquifer "sediments" reflects differences in microbial processes between the two systems. Chlorinated ethenes are subject to three broad classes of biodegradation processes that include (1) reductive dechlorination (Vogel and McCarty, 1985; Freedman and Gossett, 1989; DeBruin et al., 1992; Dolfing and Beurskens, 1995), (2) direct oxidation (Davis and Carpenter, 1990; Bradley and Chapelle, 1996), and (3) cometabolism (Vogel et al., 1987; Gerritse et al. 1995; Bielefeldt et al., 1995). The aquifer sediments present at this site are relatively poor in sedimentary organic matter and are therefore not a highly reducing methanogenic system. The succession of redox processes from Fe(III) reduction to sulfate reduction suggests that reductive dechlorination of PCE and TCE will be relatively efficient, but that reduction of DCE isomers will be less efficient (Vogel et al., 1987; Pavlostathis and Zhuang, 1991). Because of the lack of methane or other petroleum hydrocarbon cosubstrates, cometabolism is not likely to be a significant

significant process in aquifer sediments (McCarty and Semprini, 1994).

In contrast, the creek bed sediments contain relatively high amounts of organic matter which supports a variety of microbial processes in the bed sediments including methanogenesis. Methanogenesis in streambed sediments is evident from the methane bubbles that cascade from the stream bed floor when disturbed. In addition, water produced from the temporary well points indicate that oxygen is transported into the streambed sediments from the overlying water column. This intersection of highly reducing and highly oxidizing environments promotes conditions favoring concomitant reduction, oxidation, and cometabolism of chlorinated ethenes (Gerritse et al., 1995; Moore et al., 1989; Phelps et al., 1991; Bielefeldt et al., 1995). Thus, the observation that biodegradation processes in streambed sediments are much more active than in aquifer sediments is consistent with current knowledge of chlorinated ethene biodegradation.

The observation that biodegradation of chlorinated ethenes in creek bed sediments can be much more efficient than in adjacent aquifer sediments has important implications for the assessment of natural attenuation processes. The efficiency of natural attenuation can be defined in terms of restricting contaminant transport from points of contact with humans or environmental receptors (Rafai et al., 1995). In the case of Site 3, natural attenuation processes in the ground-water system alone are not sufficient to prevent contaminant transport to Rowell Creek. However, the combination of natural attenuation (dispersion, dilution, biodegradation) in the aquifer and in the streambed sediments prevents measurable contaminant transport to the water column of Rowell Creek. While contaminant impacts on benthic communities in this system are possible, there appears to be little possibility of contaminant

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impacts on plants or animal populations beyond the sediment/water interface.

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Table 1.--Concentrations of redox sensitive solutes in ground water, Cecil Field Site 3.

Well number	Dissolved Oxygen (mg/L)	Fe(II) (mg/L)	Hydrogen sulfide (mg/L)	Hydrogen (nM)	Methane (mg/L)	DIC (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	pH (units)
A1	0.81	0.05	0.050	0.66	<0.05	54.8	2.43	3.77	6.68
A2	0.95	0.04	0.044	0.66	0.1	75.6	1.54	5.37	5.61
B1	0.72	0.11	<0.002	2.17	0.1	92.1	0.40	7.04	6.69
B2	3.14	<0.01	0.039	NA	0.1	90.0	0.32	7.00	6.92
B3	1.07	<0.01	0.031	0.67	<0.05	45.3	4.79	2.19	6.98
B4	1.67	0.18	0.072	1.91	<0.05	43.9	2.55	2.23	6.98
C1	NA	<0.01	0.039	NA	0.1	101.6	0.78	7.59	8.31
C2	1.95	<0.01	0.053	6.02	0.1	102.8	0.23	7.30	5.77
CF-3-13S	<0.1	5.7	0.003	0.57	0.2	138.4	7.59	11.21	6.56
CF-3-14I	1.69	0.62	0.063	2.43	<0.05	27.9	2.42	7.58	6.25
CF-3-15D	5.3	<0.01	0.003	9.69	<0.05	8.9	3.29	7.60	9.85
Cf-3-28S	<0.1	1.19	0.027	0.46	0.1	65.6	0.62	6.48	6.58
CF-3-29D	0.12	0.04	0.031	0.63	0.1	123.6	0.22	8.82	6.67
CF-3-30DD	<0.1	0.11	0.15	3.63	0.2	126.6	0.16	8.78	7.48
CF-3-31S	0.74	0.02	0.068	2.86	0.2	94.8	0.70	7.59	7.47
CF-3-32D	<0.1	0.01	0.030	4.87	0.1	143.0	0.45	10.30	6.86

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Table 2.--Concentrations of Chlorinated Ethenes in ground water, Cecil Field Site3, March 31, 1997

Well number	PCE	TCE	trans-1,2 DCE	cis-1,2 DCE	1,1-DCE	VC
A1	<1	<1	6.44	14.3	17.08	
A2	<1	<1	9.90	12.9	19.7	
B1	<1	<1	<1	58.6	62.6	<1
B2	<1	<1	<1	21.6	22.8	<1
B3	<1	<1	11.6	3.1	1.58	<1
B4	<1	<1	<1	<1	<1	<1
C1	<1	<1	<1	34.1	28.6	<1
C2	<1	<1	<1	39.6	33.1	<1
CF-3-13S	<1	1290 ± 31.1	<1	472 ± 73.7	468 ± 8.5	<
CF-3-14I	474	765	<1	<1	<1	<1
CF-3-15D	106	740	<1	<1	<1	<1
Cf-3-28S	<1	330	<1	83.4	168	<1
CF-3-29D	<1	<1	<1	<1	<1	<1
CF-3-30DD	<1	<1	<1	<1	<1	<1
CF-3-31S	<1	<1	<1	61.2	52.0	<1
CF-3-32D	<1	<1	<1	<1	<1	<1

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Table 3.--Concentrations of DCE isomers in streambed pore water calculated using Henry's Law and the results of heaspace concentrations measured in diffusion samplers, July 1996 sampling event.

Sample number (Fig. 2a)	1,1-DCE[1] (µg/L)	*cis* 1,2-DCE[1] (µg/L)
1	nd[2]	nd
2	nd	nd
3	nd	nd
4	2.9 ± 0.0	26.5 ± 6.5
5	nd	nd
6	nd	nd
7	nd	nd
8	nd	nd
9	1.1 ± 0.28	nd
10	nd	14.6 ± 3.3
11	63.4 ± 37.2	403 ± 55.9
12	nd	nd
13	8.2 ± 0.7	36.8 ± 0.1
14	12.3 ± 5.7	37.0 ± 2.0
15	nd	nd
16	nd	nd
17	nd	nd
18	nd	nd

[1]Aqueous concentration assuming Henry's Law partitioning between diffusion sampler headspace and pore water.
[2] not detected

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Figure Captions

Figure 1.--Map showing location of monitoring wells and approximate extent of ground-water contamination.

Figure 2.--Schematic diagram showing concentrations of dissolved hydrogen (nM) and the approximate distribution of redox processes, Site 3, Cecil Field.

Figure 3.--Location maps and results of diffusion sampler surveys.

Figure 4.--Recovery of [1,2-^{14}C]DCE radioactivity as $^{14}CO_2$ aquifer and streambed sediments after 50 days of microcosm incubation.

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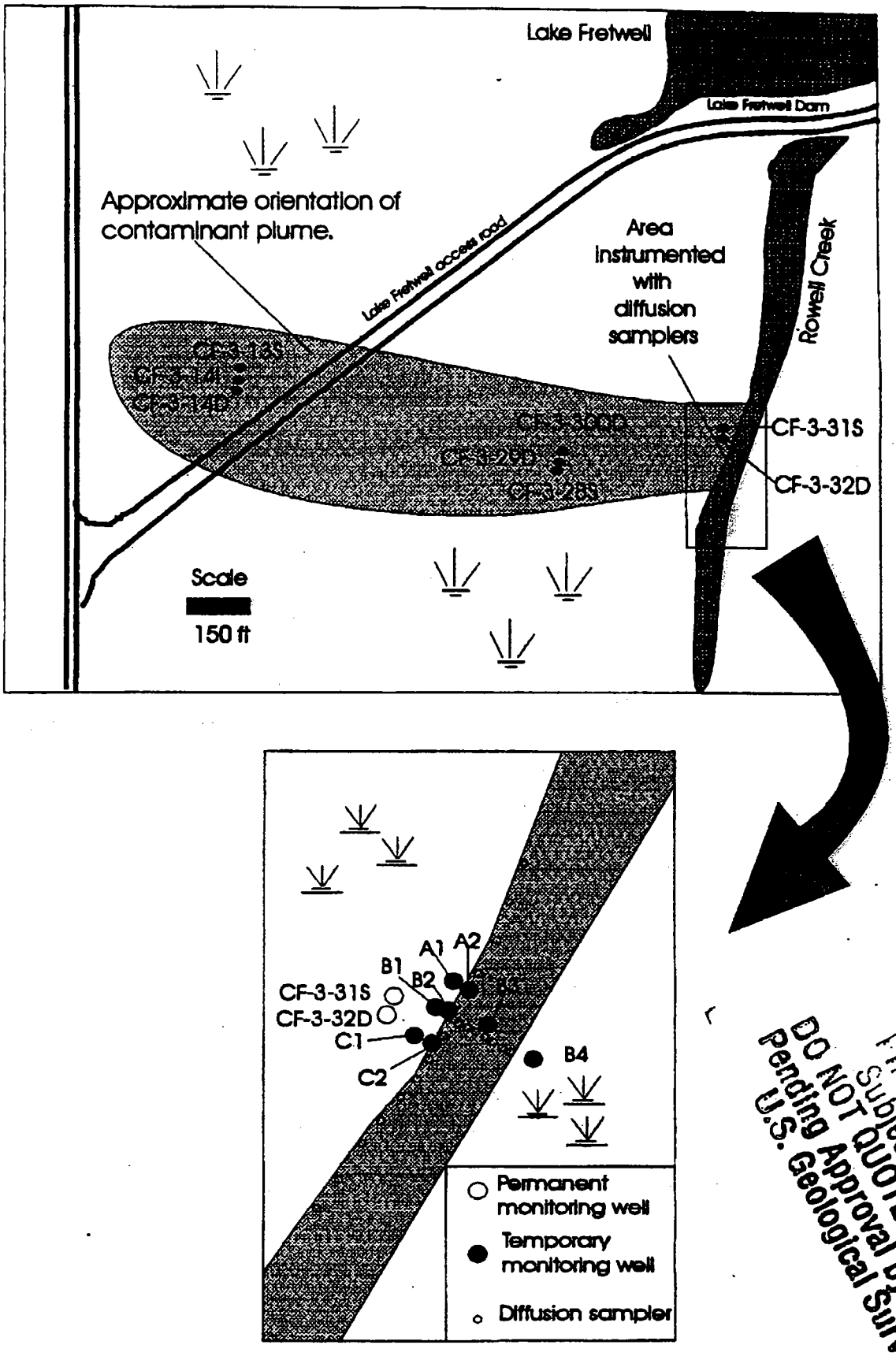

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Figure 1.--Map showing location of monitoring wells and approximate extent of ground water contaminantion..

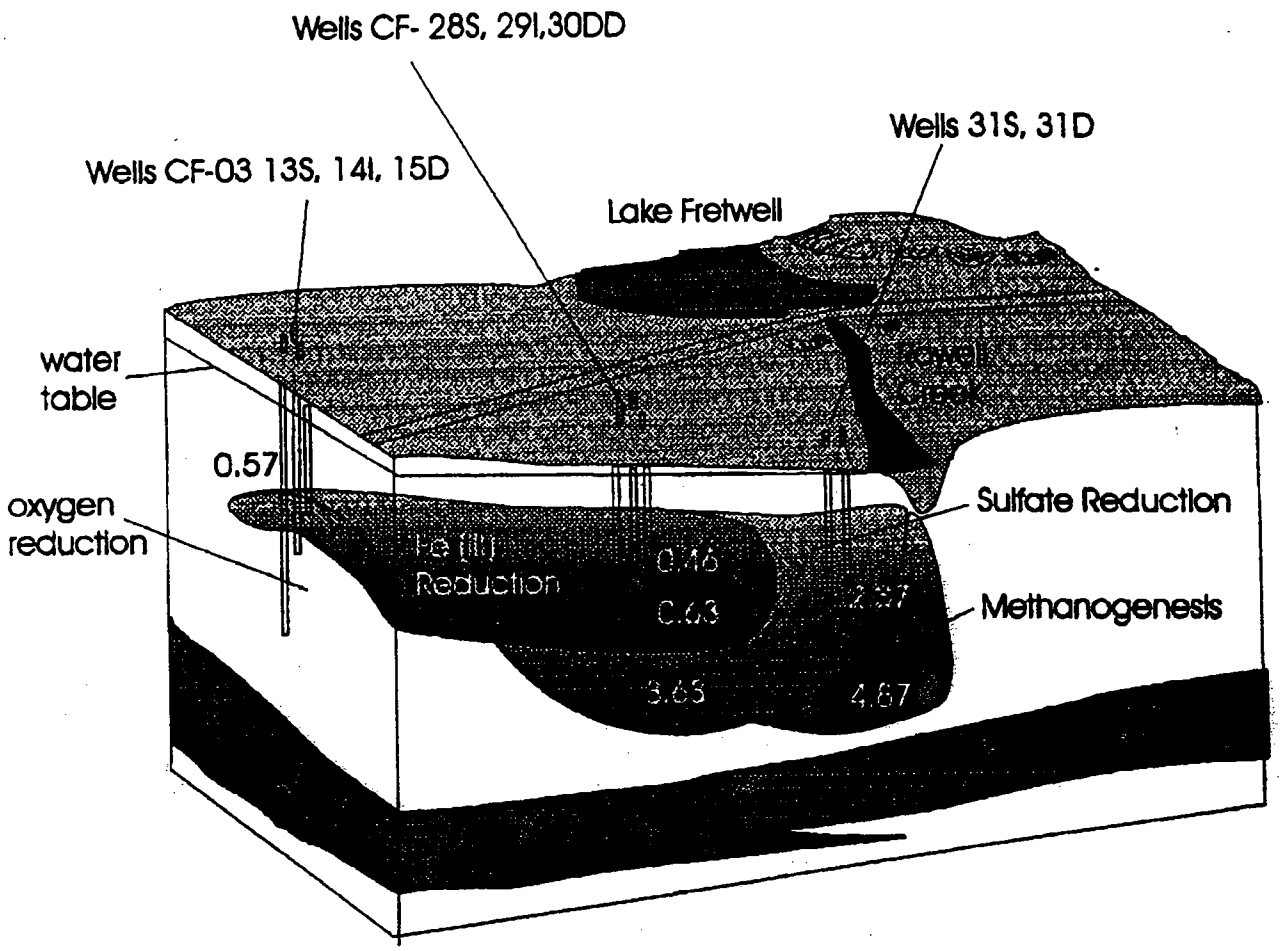

Figure 2.--Schematic diagram showing concentrations of dissolved hydrogen (nM) and the approximate distribution of redox processes, Site 3, Cecil Field.

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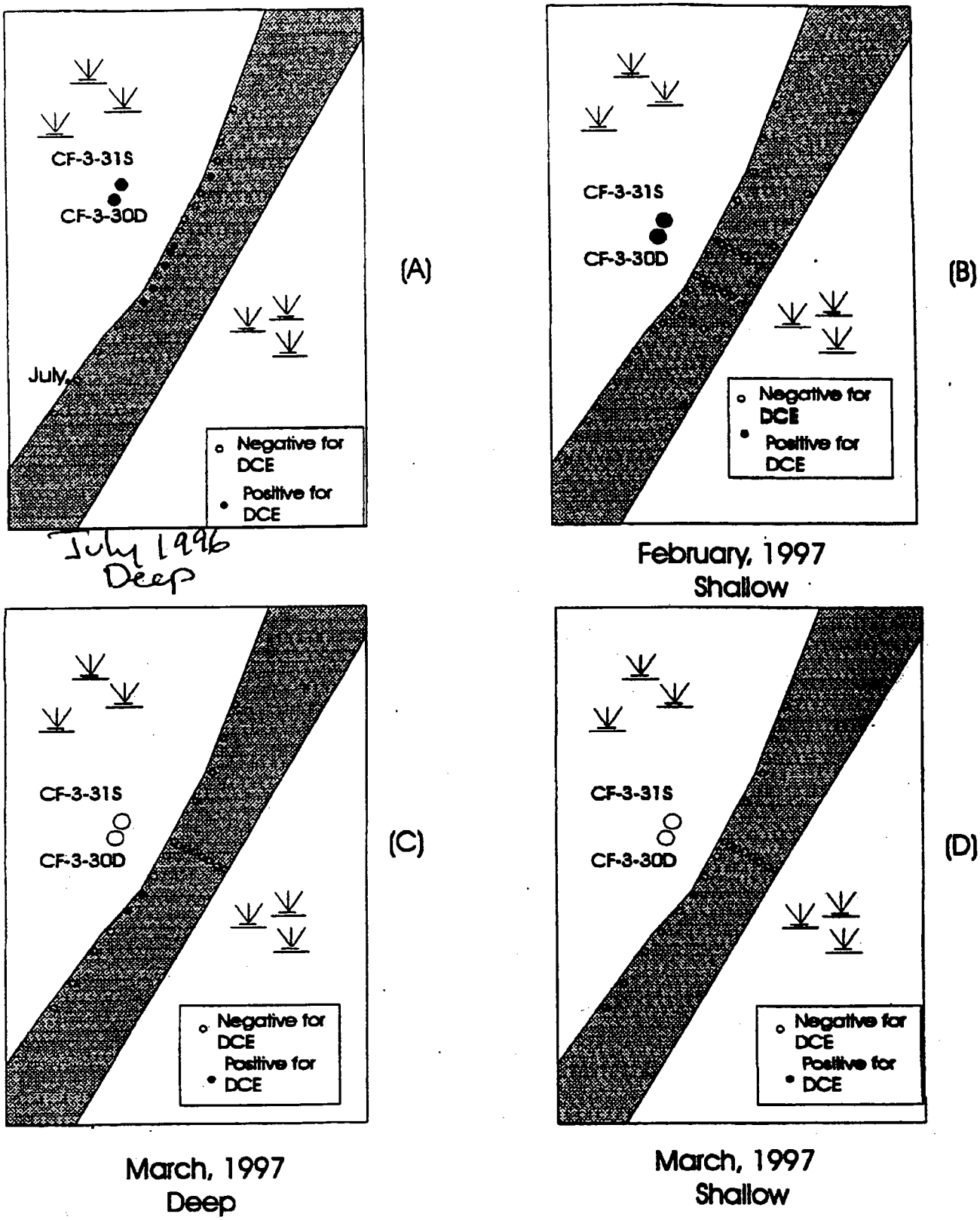

Fugure 3.--Location maps and results of diffusion sampler surveys.