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Degradation of 1,1,2,2-Tetrachloroethane in a Freshwater Tidal Wetland: Field and Laboratory Evidence

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Degradation reactions controlling the fate of 1,1,2,2-tetrachloroethane (PCA) in a freshwater tidal wetland that is a discharge area for a contaminated aquifer were investigated by a combined field and laboratory study. Samples from nested piezometers and porous-membrane sampling devices (peepers) showed that PCA concentrations decreased and that less chlorinated daughter products formed as the groundwater became increasingly reducing along upward flow paths through the wetland sediments. The cis and trans isomers of 1,2-dichloroethylene (12DCE) and vinyl chloride (VC) were the predominant daughter products detected from degradation of PCA in the field and in microcosms constructed under methanogenic conditions. Significantly lower ratios of *cis*-12DCE to *trans*-12DCE were produced by PCA degradation than by degradation of trichloroethylene, a common co-contaminant with PCA. 1,1,2-Trichloroethane (112TCA) and 1,2-dichloroethane (12DCA) occurred simultaneously with 12DCE, indicating simultaneous hydrogenolysis and dichloroelimination of PCA. From an initial PCA concentration of about 1.5 μmol/L, concentrations of PCA and its daughter products decreased to below detection within a 1.0-m vertical distance in the wetland sediments and within 34 days in the microcosms. The results indicate that natural attenuation of PCA through complete anaerobic biodegradation can occur in wetlands before sensitive surface water receptors are reached.

Introduction

Although 1,1,2,2-tetrachloroethane (PCA) is a relatively common groundwater contaminant, its fate in the environment is poorly understood. PCA was the first chlorinated solvent produced in large quantities before World War I but was later largely replaced by solvents that were thought to be less toxic (*1*). In addition to its use as a solvent for cellulose acetate, fat, waxes, greases, rubber, and sulfur, PCA was the major component of a decontaminating agent produced in the past by the U.S. military and was used in an organic solvent process to manufacture chemical-agent-resistant clothing (*2*). Reported industrial releases of PCA in the United States ranged from 44 000 lb in 1988 to 66 000 lb in 1991 (*1*). Use and improper disposal of PCA have resulted in groundwater contamination at several military bases (*3*) and other industrial sites (*1*). Although a drinking water standard has not been set for PCA, a low risk-based concentration of 0.05 μg/L has been established because of possible carcinogenic effects (4). Three types of degradation reactions are thought to be possible for PCA—hydrogenolysis, dichloroelimination, and dehydrochlorination (*5*) (Figure 1). Hydrogenolysis, which entails the sequential replacement of a chlorine atom by hydrogen in a reductive dechlorination reaction, is a common microbially mediated transformation for 1- and 2-carbon chlorinated aliphatics under anaerobic conditions. Hydrogenolysis of PCA could sequentially produce 1,1,2-trichloroethane (112TCA); 1,2-dichloroethane (12DCA); chloroethane; and finally, ethane as daughter products. Experiments with other highly chlorinated solvents such as trichloroethylene (TCE) have shown that hydrogenolysis rates tend to be greater under the highly reducing conditions associated with methanogenesis than under less reducing conditions (*6*).

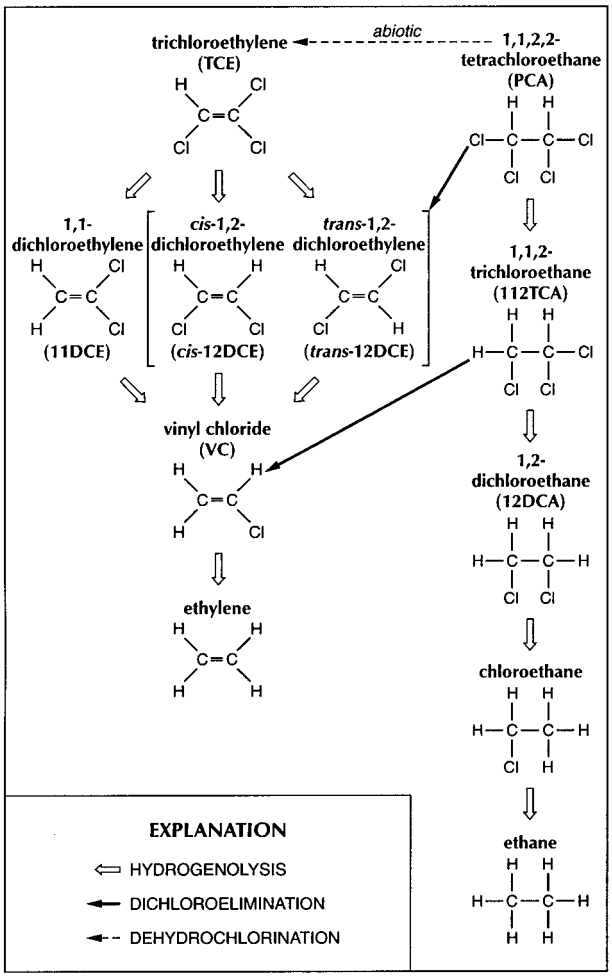

FIGURE 1. Anaerobic degradation pathways for PCA and TCE. [Modified from Chen et al. (*1*) and Vogel et al. (*5*).]

Dichloroelimination, which is another type of reductive dechlorination reaction, releases two adjacent chlorine atoms simultaneously, forming an alkene. Dichloroelimination of PCA can produce *cis*- and *trans*-1,2-dichloroethylene (*cis*- and *trans*-12DCE). Dichloroelimination is also a possible transformation pathway for 112TCA (a product of hydrogenolysis of PCA), producing vinyl chloride (VC) (*1, 5*). The third possible transformation pathway for PCA is production of TCE by dehydrochlorination, an abiotic elimination reaction.

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The occurrence and dominant pathways of in situ degradation of PCA in groundwater or soil are largely unknown. The few reported studies on PCA degradation are laboratory batch or column experiments that were constructed with anaerobic mineral medium or glass beads (*1, 7*). Methanogenic mixed cultures to seed these experiments were obtained from laboratory-scale municipal sludge digesters or wastewater filters. Another laboratory study was conducted using an abiotic aqueous mixture of transition metal coenzymes (*8*). While laboratory studies have helped to elucidate mechanisms by which PCA can be degraded, they provide little information on preferred PCA degradation pathways in groundwater or soil. The fact that field evidence of PCA degradation reactions has been lacking may be in part because TCE was frequently used and disposed of at the same sites as PCA. TCE can itself be a daughter product of PCA and can produce some of the same potential daughter compounds as PCA (Figure 1).

Both field and laboratory evidence of PCA degradation are reported in this paper for a freshwater tidal wetland that receives groundwater discharge from a contaminated sand aquifer. Degradation reactions controlling the fate of PCA were investigated by collecting biogeochemical data along a flow path where PCA is the primary parent contaminant and by conducting laboratory microcosm experiments using wetland sediment and groundwater from the site. These investigations were performed as part of a larger study to determine the major processes that naturally attenuate chlorinated volatile organic compounds (VOCs) in the wetland.

Materials and Methods

Field Site. The study site is located along the West Branch Canal Creek at Aberdeen Proving Ground (APG), an Army base in Maryland near the head of the Chesapeake Bay. Freshwater tidal wetlands surround much of West Branch Canal Creek. Release of waste products by spills, landfilling, and discharge to sewers during chemical manufacturing operations near the creek resulted in groundwater contamination (*2, 3*). Nested drive-point piezometers were installed in the wetland study area primarily along two transects (one is shown in Figure 2) on the eastern side of West Branch Canal Creek, where a previous study (*2*) had indicated a site of contaminated groundwater discharge. The transects are aligned perpendicular to the creek, along the general direction of groundwater flow in the aquifer. The contaminated aquifer, known as the Canal Creek aquifer, is about 12−14 m thick in the study area and consists mainly of medium- to coarse-grained sand and gravel. Wetland sediments that overlie the aquifer consist of two distinct layers that have a combined thickness of about 1.8 m along section C−C′ (Figure 2)—a lower unit of silty to sandy clay or clayey sand and an upper unit of peat mixed with variable amounts of clay and silt (*3*). Groundwater flow directions within the wetland area are predominantly upward. At low tide, water from the aquifer discharges through both the wetland and the channel sediments. At high tide, however, groundwater discharge is concentrated at a point about 9−15 m east of the creek channel (near nested piezometers WB-36 and WB-35 in Figure 2). The average linear groundwater flow velocity in the wetland sediments is estimated to be about 0.6 m/yr (*3*).

Groundwater Sampling and Analysis. For the purposes of this study, groundwater samples were collected during September−October 1995 from 25 piezometers that are located at six sites along section C−C′ (Figure 2). Samples were then collected from selected piezometers during March−April, June, and August 1996. The piezometers have 1.9-cm-diameter stainless steel casing and 15.2-cm-long stainless steel screens. An inner tube made of Teflon-lined polyethylene connects to the top of the screened interval, allowing withdrawal of samples that had minimum contact with the stainless steel. In addition, peepers that collect groundwater through diffusion were used to obtain water samples over 2.5-cm-depth intervals in the shallow wetland sediment at sites WB-34, WB-35, WB-36, and WB-37. Peepers were constructed of polycarbonate (Lexan) following the general design by Hesslein (*9*). The sample chambers were filled with deionized water, covered with a 0.2-μm polysulfone membrane (HT Tuffryn, Gelman Sciences, Ann Arbor, MI), and deoxygenated prior to installation (*3*).

Sampling and analytical procedures have been described elsewhere (*3*) and will be summarized here. Piezometers screened in the aquifer generally were purged and sampled using a peristaltic pump from which Tygon tubing was extended to directly above the piezometer screen. Because piezometers screened in the wetland sediments generally had low recovery rates, stainless steel bailers that had a bottom-discharge device were used for purging and sampling. Peepers were pushed vertically into the wetland sediment, allowed to equilibrate with surrounding porewater for approximately 3 weeks, and then removed from the sediment to withdraw samples.

For collection of VOCs, glass vials were filled with a slow steady stream of water from the sampling device to minimize aeration and were sealed with Teflon-lined caps. The analytical method used for VOCs is equivalent to the U.S. EPA Method 524.2 (*10*). Redox-sensitive constituents that were determined included dissolved oxygen, manganese, ferrous and ferric iron, ammonia, sulfide, and methane. Dissolved-oxygen concentrations were measured by use of a modified Winkler colorimetric method (*11*) for those piezometers that contained sufficient water. Samples collected for manganese analysis were filtered through 0.45-μm filters, acidified to pH less than 2.0, and analyzed using inductively coupled argon plasma spectroscopy. Samples for ferrous iron and total dissolved iron were filtered through 0.1-μm filters and analyzed by the colorimetric bipyridine technique (*11*). Sulfide and ammonia were determined in the field on unfiltered samples using colorimetric techniques from CHEMetrics (*3*). Methane was determined by collecting unfiltered water in sealed serum bottles and analyzing the headspace by gas chromatography with a flame ionization detector (*3, 11*).

Laboratory Experiments. During May−June 1996, microcosm experiments were conducted under methanogenic conditions to determine the degradation rate and pathways of PCA. Two sets of microcosms, one of which was a sterile control prepared with 1% by volume of formaldehyde, were amended with an initial (day 0) concentration of about 2.9 μmol/L of PCA (estimated from analysis of stock solution). Live and sterile microcosms that were amended with 3.0 μmol/L of TCE were constructed concurrently under the same conditions (*3*). An unamended live control was also prepared. Microcosms were constructed in 162-mL serum bottles using a 1.5:1 volumetric ratio of groundwater to wetland sediment. During the week prior to microcosm construction, groundwater from the upper peat unit was collected in 1-L glass bottles. Wetland sediment from the upper peat unit was collected from a depth of 0−25 cm below land surface and sieved to remove particles greater than 4.75 mm. Sieving and microcosm construction were done under a nitrogen atmosphere, and the bottles were then sealed with Teflon-lined rubber stoppers and aluminum crimp caps. Stock PCA and TCE solutions were made from neat chemicals (Supelco, Bellefonte, PA) and added to microcosms using gas-tight syringes. Microcosms were stored upside down in the dark at 19 °C, which was the approximate temperature of the wetland groundwater during the summer (*12*). Duplicate serum bottles were sacrificed at selected time intervals, and

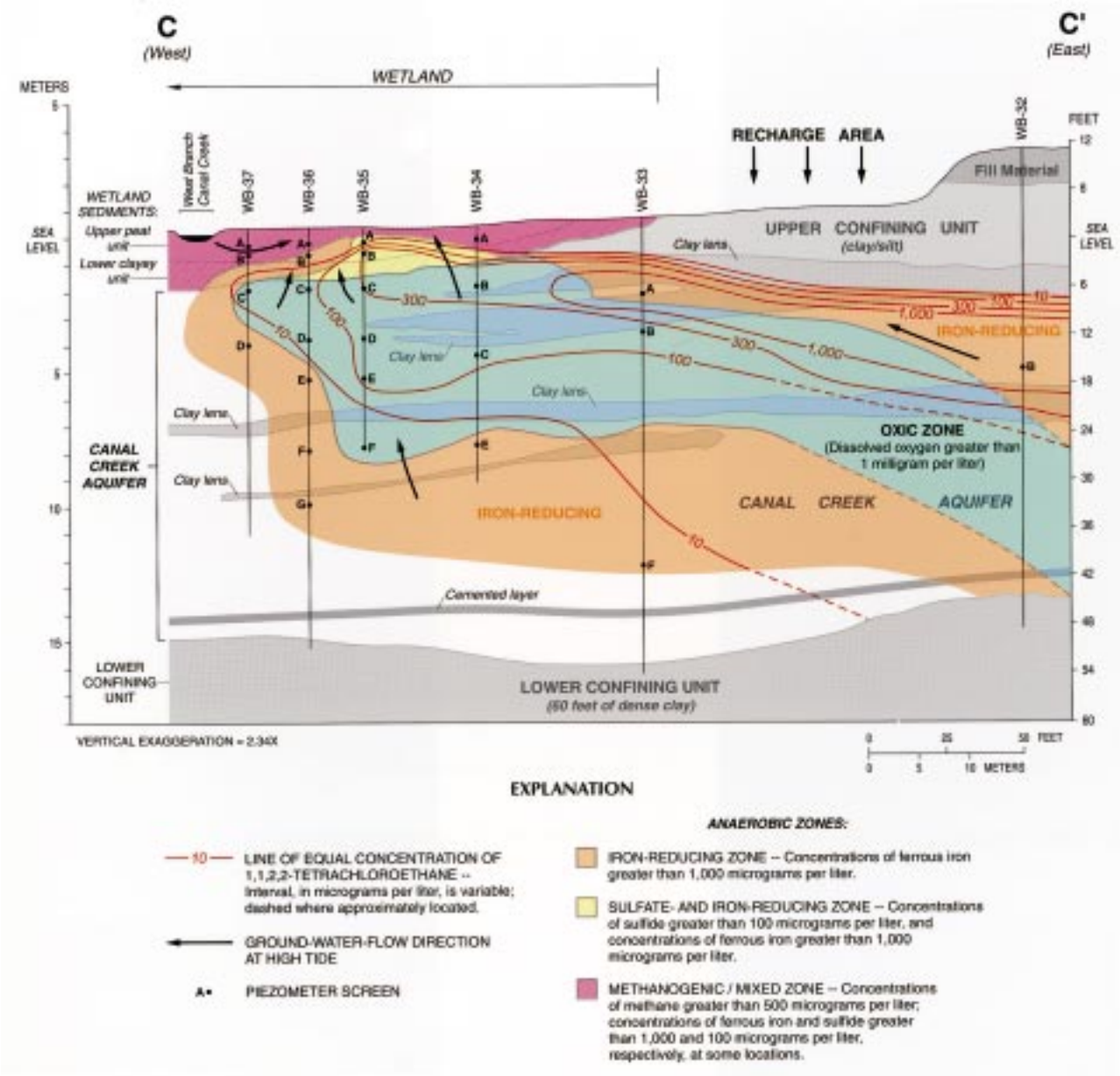

FIGURE 2. Section C−C′ showing the hydrogeology, locations of piezometer screens, distributions of PCA, and redox zones in groundwater, September−October 1995. Peepers were placed 0−0.6 m below land surface at sites WB-34, WB-35, WB-36, and WB-37.

the water was analyzed for VOCs and methane at an on-site laboratory as described above.

Results and Discussion

Field Evidence of PCA Degradation. PCA was the major contaminant in groundwater along section C−C′, occurring at concentrations greater than 1000 μg/L in the aquifer at the eastern edge of the wetland (sites WB-32 and WB-33 in Figure 2). The PCA plume is primarily in the shallow region of the aquifer and trends upward toward the wetland sediments, reflecting the upward groundwater flow directions. The maximum PCA concentration in the wetland porewater was measured at site WB-35, where groundwater discharge is focused at high tide. The PCA concentration was 300 μg/L (1.8 μmol/L) in water from WB-35B, which is screened near the base of the upper peat unit. PCA concentrations decreased along the upward direction of groundwater flow, however, to 1.5 μg/L in water from WB-35A, which is screened less than 0.30 m above WB-35B (Figure 2). Concentrations of PCA also were less than 1.5 μg/L in porewater from the wetland sediment at all other sites.

The upward decrease in PCA concentrations coincided with increasingly reducing conditions in the wetland sediments. The aquifer was primarily aerobic (dissolved-oxygen concentrations greater than 1.0 mg/L) (Figure 2). Iron-reducing conditions were indicated around the edges of the oxic zone by relatively high Fe(II) concentrations (greater than 1000 μg/L), although dissolved oxygen was sometimes detectable. Iron reduction or mixed sulfate and iron reduction seemed to be the major terminal electron-accepting processes near the base of the upper peat unit of the wetland sediments at two sites (WB-35 and WB-36 in Figure 2). Methanogenesis, however, was predominant in the upper 0−0.9 m of peat at these two sites and was also predominant elsewhere in the peat unit along section C−C′. The sites where iron- and sulfate-reducing zones were predominant in the lower part of the upper peat unit (WB-35 and WB-36) are where upward discharge from the aquifer is focused at high tide. This focused discharge probably causes a higher dissolved-oxygen flux from the aquifer and delays the onset of methanogenesis along the upward flow path through the wetland sediments at these sites as compared to other areas along section C−C′.

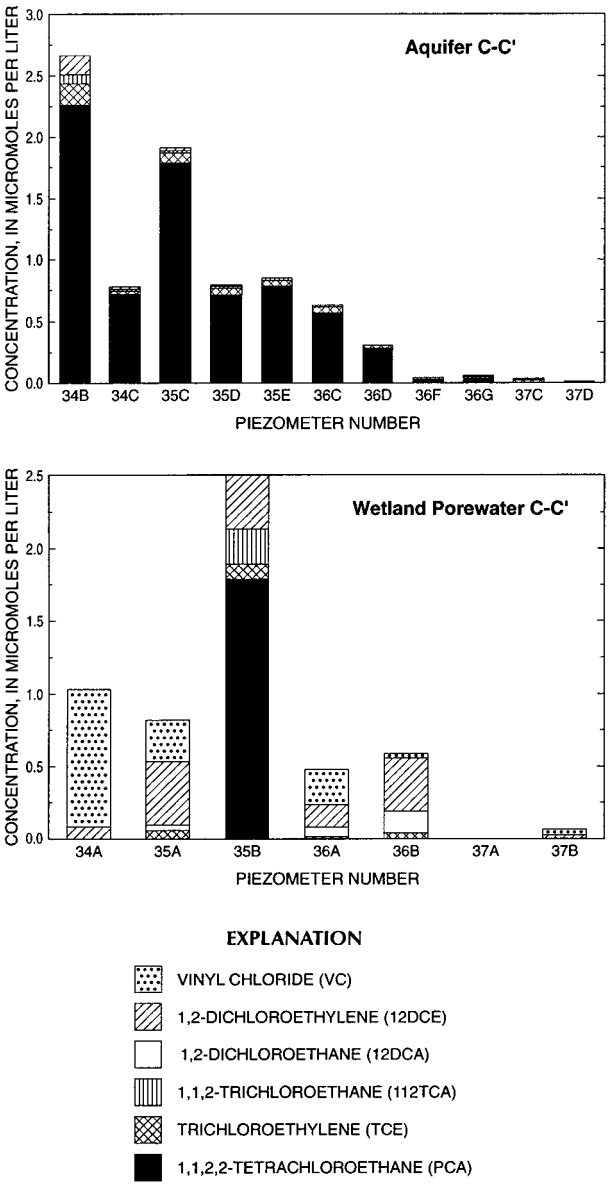

FIGURE 3. Concentrations of parent contaminants and their anaerobic daughter products in the aquifer and wetland porewater along section C−C′, September−October 1995.

The distributions of VOCs and redox constituents along C−C′ did not change substantially throughout the sampling periods in 1995 and 1996.

Concentrations of potential anaerobic daughter products of PCA were relatively high in the reducing environment of the wetland sediments, whereas their concentrations were low or undetectable in piezometers screened in the aquifer (Figure 3). The daughter products that were observed in the highest concentrations in most of the piezometers screened in the wetland sediment were 12DCE (total of *cis*- and *trans*-12DCE) and VC. 112TCA and 12DCA were detected in one and three piezometers, respectively, although concentrations generally were lower than those observed for 12DCE and VC. Because TCE concentrations were less than 3% of the PCA concentrations in water from the aquifer and wetland sediments along section C−C′, anaerobic biodegradation of TCE is not likely to be a significant source of the 12DCE or VC observed in the wetland porewater. The presence of 12DCE, VC, 112TCA, and 12DCA therefore indicates that PCA is being degraded through both dichloroelimination and hydrogenolysis pathways in the wetland sediment (Figure 1).

Porewater samples from the peepers give detailed vertical distributions of redox constituents, PCA, and potential PCA daughter products along the upward groundwater flow path through the thin upper peat unit (Figure 4). The concentration of 112TCA was a maximum at the base of the peat unit (piezometer WB-35B) and decreased to below detection levels at the deepest peeper sampling point, which was about 30 cm above the base of the peat unit. Concentrations of 12DCA and 12DCE increased as PCA concentrations decreased along the flow path, with the highest concentrations in the deepest peeper sample. 12DCE had concentrations more than five times higher than 12DCA and was present over a greater depth interval. Both the cis and trans isomers of 12DCE were observed in the porewater of the wetland sediments (Figure 4C).

Highly reducing conditions do not seem to be necessary for dichloroelimination or hydrogenolysis of PCA because the initial production of 12DCE and 112TCA was observed under iron-reducing conditions at piezometer WB-35B (Figure 4). Continued anaerobic degradation of these daughter products, however, may be dependent on the more reducing condition of methanogenesis. Concentrations of VC increased as 12DCE concentrations decreased along the flow path, reaching a maximum where methane concentrations reached 600 μmol/L (Figure 4). VC also appears to be a transient daughter product because concentrations rapidly decreased to below detection levels within the methanogenic zone along the flow path (Figure 4). The concomitant increase in VC and decrease in 12DCE concentrations indicate that hydrogenolysis of the 12DCE (produced from dichloroelimination of the PCA) to VC was occurring. Although dichloroelimination of the 112TCA could have produced some of the VC observed in the deepest peeper sampling points, concentrations of 112TCA were too low to account for the observed VC concentrations.

Laboratory Evidence of PCA Degradation. Rapid removal of PCA from solution was observed in the microcosm experiments under methanogenic conditions with wetland sediment and groundwater. Comparison of the decrease in PCA concentrations in the live microcosms to the sterile controls indicates that biodegradation is a significant removal mechanism, although abiotic processes were substantial during days 0−4 (Figure 5A). About 50% of the PCA that was added to the sterile and live microcosms at day 0 was lost within 24 h. Sorption to the organic-rich wetland sediments is probably the predominant cause of this abiotic loss of PCA in the microcosms, as was confirmed later by 24-h batch sorption experiments (*3*). After this initial period, however, concentrations of PCA decreased rapidly in the live microcosms, while concentrations in the sterile microcosms decreased substantially slower. PCA concentrations in the live microcosms were below detection by day 16. Production of daughter compounds in the live microcosms was significant as compared to the sterile microcosms, showing that biodegradation of PCA by microorganisms indigenous to the wetland sediments was occurring.

The predominant daughter products observed in the live PCA-amended microcosms were 12DCE and VC (Figure 5B). The 12DCE is most likely produced through dichloroelimination of PCA. Although PCA potentially could abiotically degrade to TCE, which could then degrade to 12DCE by hydrogenolysis (Figure 1), TCE concentrations were insignificant (less than 0.05 μmol/L) throughout the experiment. Dichloroelimination of PCA to produce 12DCE may not have been a strictly biotic reaction because the 12DCE isomers were the only daughter products observed in the sterile microcosms (Figure 5B). The great increase in 12DCE concentrations in the sterile microcosms after day 16, however, could indicate that the formaldehyde used to prepare the sterile microcosms did not maintain effective

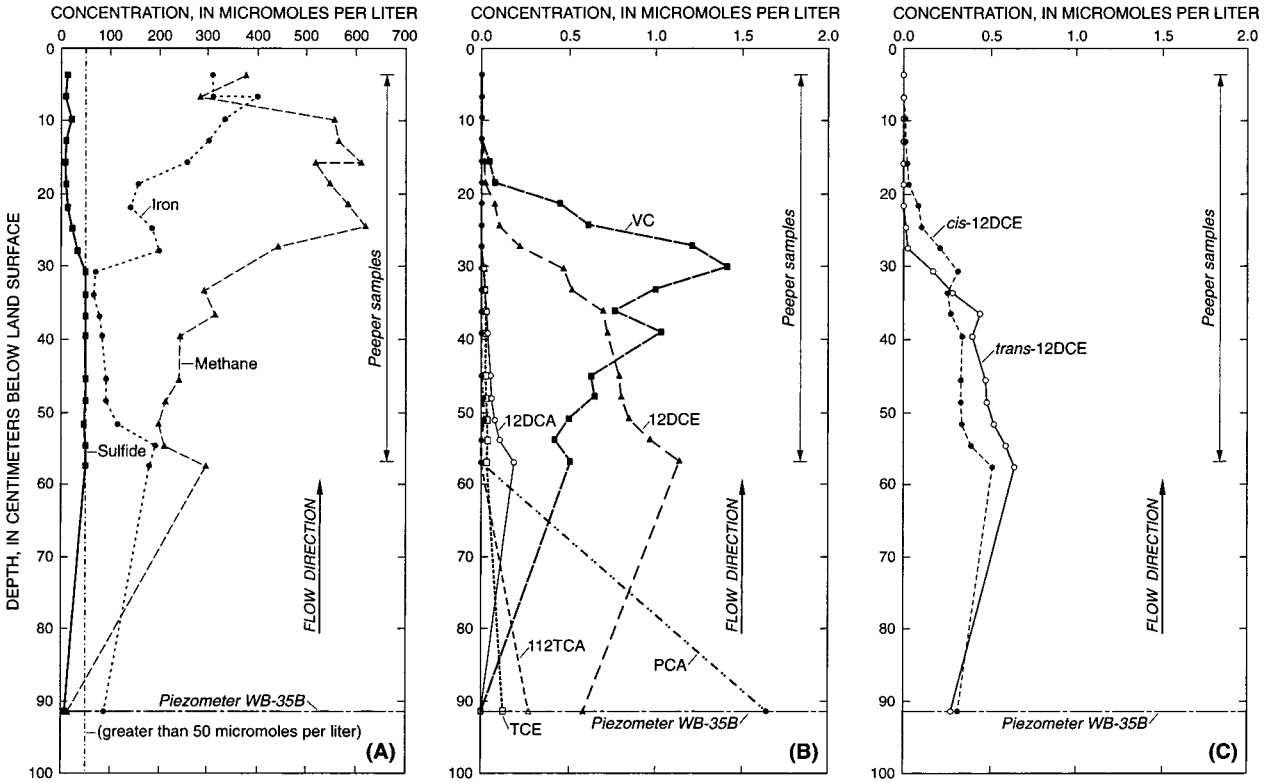

FIGURE 4. Vertical distribution of constituents in wetland porewater at site WB-35, June 1996: (A) ferrous iron, sulfide, and methane; (B) PCA, TCE, and the anaerobic daughter products 12DCE (total of the cis and trans isomers), VC, 112TCA, and 12DCA; (C) *cis*-12DCE and *trans*-12DCE. Sulfide concentrations >50 μmol/L were outside calibration range.

controls. The stable methane concentrations in the sterile microcosms show that methanogens remained inactive (Figure 6), but other microorganisms that favored the dichloroelimination pathway could have become active. Through day 16, concentrations of 12DCE in the sterile controls were less than about 50% of the 12DCE measured in the live microcosms.

Until day 12 in the live PCA-amended microcosms, *trans*-12DCE comprised up to 25% of the 12DCE (Figure 5C). In TCE-amended microcosms that were incubated under the same conditions as the PCA-amended microcosms, the trans isomer comprised less than 10% of the 12DCE (Figure 5D). Dichloroelimination of PCA, therefore, produced a greater proportion of the trans isomer than hydrogenolysis of TCE. The ratio of *cis*-12DCE to *trans*-12DCE produced from dichloroelimination of PCA in these microcosms with the wetland sediment and groundwater averaged 3.2:1, which is consistent with the fairly constant ratio of 2.4:1.0 found by Chen and others (*1*) in microcosm tests with municipal digester sludge. A laboratory study of the dechlorination of polychlorinated ethanes catalyzed by vitamin B_{12} (*8*), a biological coenzyme in anaerobic bacteria, yielded a lower ratio of *cis*-12DCE to *trans*-12DCE (1.7:1) than found in tests with the wetland sediment and municipal sludge.

The ratios of the 12DCE isomers changed after day 12 in the live PCA-amended microcosms as the concentrations of *cis*-12DCE began to decrease more rapidly than *trans*-12DCE (Figure 5C). On days 16 and 24, the *trans*-12DCE comprised about 50 and 75%, respectively, of the total 12DCE. This increased percentage of *trans*-12DCE probably resulted from faster degradation of the *cis*-12DCE as compared to *trans*-12DCE in the anaerobic microcosms; both isomers presumably were biodegraded to VC by hydrogenolysis. This observation is consistent with another microcosm study that showed faster hydrogenolysis of *cis*-12DCE than *trans*-12DCE (*1*) and could account for the fact that concentrations of *trans*-12DCE were slightly higher than *cis*-12DCE over a large part of the profile obtained with the peepers (Figure 4).

Production of 112TCA and 12DCA through hydrogenolysis of PCA also was observed in the PCA-amended microcosms (Figure 5B). Because VC, 112TCA, and 12DCA were not observed in the sterile microcosms amended with PCA, their production seems to be completely microbially mediated. The concentrations measured over time in the PCA-amended microcosms were consistent with the sequence of appearance and the relative concentrations of daughter products measured in porewater samples in the upward flow direction through the wetland sediments (Figures 4 and 5). Concentrations of 112TCA reached their peak and then decreased to below detection levels earlier than the other daughter products. The daughter product VC reached higher concentrations and peaked later than the other daughter products. This sequence and relative concentrations of the daughter products indicate that VC is produced by two mechanisms—dichloroelimination of the 112TCA and hydrogenolysis of the 12DCE.

The relative concentrations of daughter products that were observed from PCA degradation in these microcosms differ from concentrations reported by Chen et al. (*1*) in laboratory experiments with anaerobic municipal digester sludge. The cultures with digester sludge gave a higher percentage of TCE and a lower percentage of 112TCA and VC from PCA degradation than observed here. TCE comprised about 9−16% of the initial PCA added in four tests with sludge-seeded cultures that had high biomass and about 49% in diluted cultures with lower biomass (*1*). Abiotic dehydrochlorination, in addition to dichloroelimination and hydrogenolysis, was thus found to be important, especially in low biomass cultures (*1*). In contrast, TCE comprised less than 2% of the initial PCA in the microcosm experiments using wetland sediment. This difference in daughter products could result from differences in the microbial populations in the

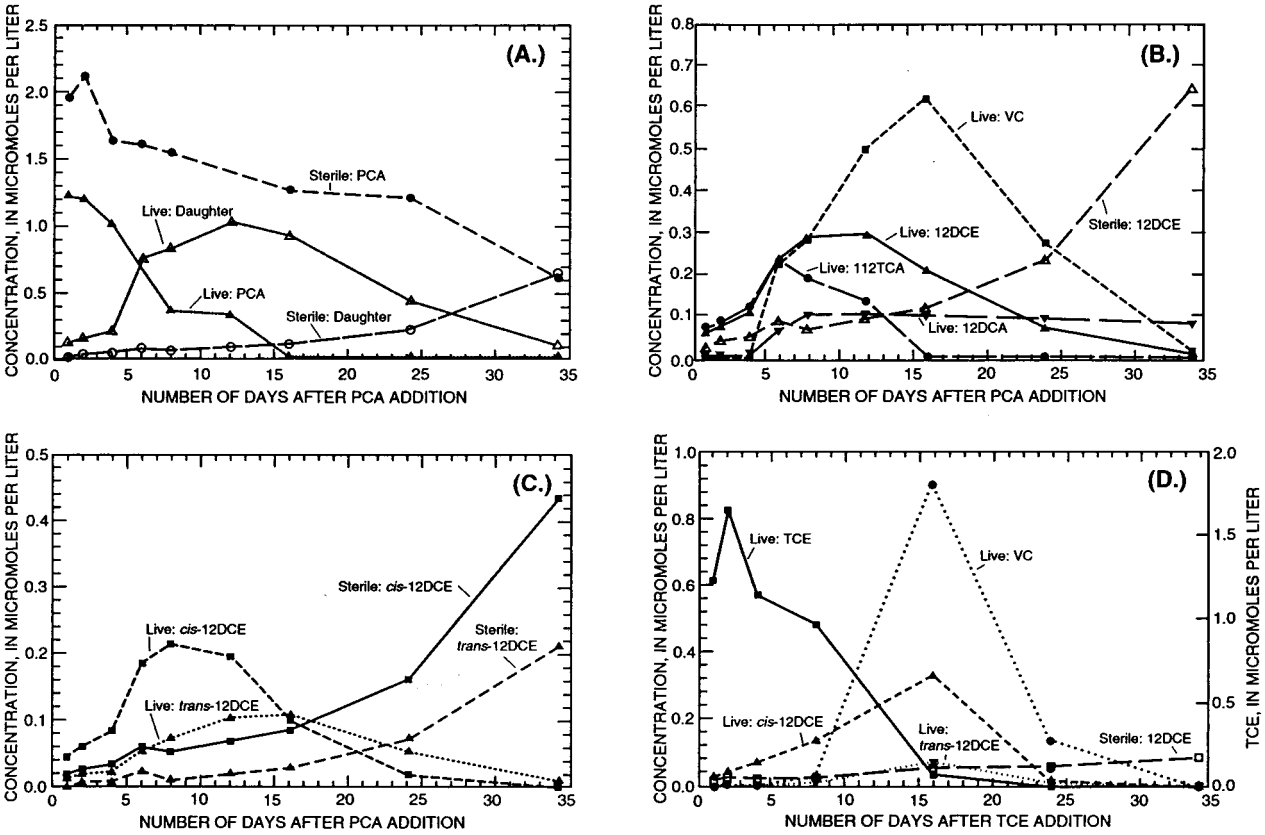

FIGURE 5. Degradation under methanogenic conditions in microcosms amended with 2.9 μmol/L of PCA or 3.0 μmol/L of TCE at day 0: (A) PCA and the sum of daughter products in the PCA-amended live microcosms and sterile controls; (B) daughter products 12DCE (total of the cis and trans isomers), VC, 112TCA, and 12DCA in the PCA-amended microcosms; (C) *cis*-12DCE and *trans*-12DCE in the PCA-amended microcosms; and (D) TCE and the daughter products *cis*-12DCE, *trans*-12DCE, and VC in the TCE-amended microcosms. The concentrations shown are the average measured in duplicate microcosms sacrificed at each time step.

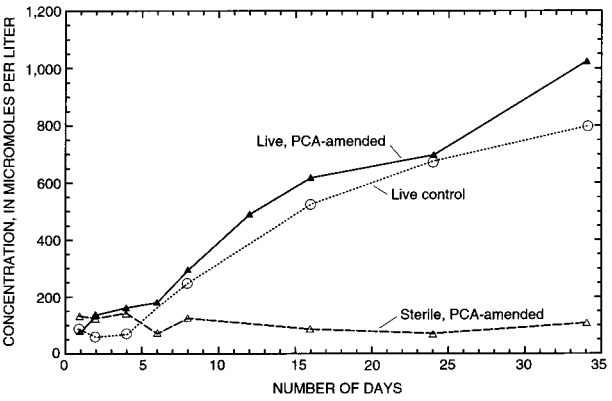

FIGURE 6. Methane concentrations in live and sterile microcosms amended with 2.9 μmol/L of PCA and in unamended live controls.

sludge and wetland sediment and from different acclimation times. The wetland sediment probably has been exposed to contaminated groundwater discharge for more than 20 years, whereas the sludge cultures may not have been exposed to PCA prior to the laboratory experiments. In addition, the initial PCA concentrations that were used by Chen et al. (*1*) were about 20 times higher than those used in the microcosms presented here. The abiotic dehydrochlorination may become a more significant degradation pathway at higher concentrations of PCA, possibly because toxicity effects could reduce the activity of the microorganisms. Concentrations of the daughter products in the microcosm experiments with wetland sediment decreased to below detection levels within 34 days, except low concentrations of 1,2-dichloroethane (less than 0.1 μmol/L) remained (Figure 5B). Chen et al. (*1*) did not observe complete degradation of the daughter products within 30−40-day microcosm test periods, but they began with much higher initial PCA concentrations.

Methane concentrations in the PCA-amended microcosms were approximately the same (within 20%) as in the live control, which was not amended with any VOCs (Figure 6). The natural methanogenic activity in the wetland sediments, therefore, was neither inhibited or stimulated by the presence of the added contaminant. This is not surprising because the micromolar concentration range of the contaminants is much less than the natural supply of organic substrates in the wetland sediments. The amount of methane produced in association with degradation of the VOCs therefore would be insignificant as compared to natural production rates.

Implications for Natural Attenuation. The percentages of each daughter product (based on the total concentration of daughter products) that were observed in the field on several sampling dates and in the laboratory microcosm experiments were very consistent (Table 1). These field and laboratory data clearly show that 12DCE (total of the cis and trans isomers) and VC are the predominant daughter products from degradation of PCA and that both dichloroelimination and hydrogenolysis of PCA occur in the anaerobic wetland sediments. Only one other study, which was conducted in the laboratory using anaerobic municipal sludge, reports evidence for both of these PCA degradation pathways (*1*). Recognition of these PCA degradation pathways is important because they produce some of the same daughter products (12DCE and VC) under anaerobic conditions as the common co-contaminant TCE. Hydrogenolysis of TCE has been shown to produce much higher proportions of the cis than the trans

TABLE 1. Percentage of Each Anaerobic Daughter Product in the Total Concentration of Daughter Products Observed in Wetland Porewater Samples and Anaerobic Microcosms[a]

sample	*cis*−12DCE	*trans*−12DCE	VC	112TCA	12DCA	TCE
porewater, October 1995	10	21	52	14	2.1	0.3
porewater, March 1996	11	18	42	21	4.3	2.9
porewater, June 1996	18	14	53	9.4	4.4	0.9
live microcosm	16	8.5	48	18	8.7	0.7

[a] To calculate percentages, maximum molar concentrations were used for each daughter product observed in porewater samples collected between depths of 0−1.0 m below land surface (from peepers and piezometers at site WB-35) and from the PCA-amended microcosm experiment.

isomer of 12DCE in several field and laboratory studies (for example, refs 13 and 14), and the results for TCE-amended microcosm that were constructed as part of the present study agree with this (Figure 5D). A common rule of thumb that has been stated is that if *cis*-12DCE comprises more than 80% of the 12DCE observed in groundwater, then the 12DCE resulted from hydrogenolysis of TCE rather than from a direct disposal source (*15*). The field and laboratory data presented here, however, indicate that this is invalid if PCA is present. Because dichloroelimination of PCA in the wetland sediment produced a substantially lower ratio of *cis*-12DCE to *trans*-12DCE (about 3.2:1) than was produced by hydrogenolysis of TCE (about 14:1), the isomer distribution could potentially assist in determining whether both TCE and PCA degradation are occurring at other sites. The effects of other factors besides degradation of PCA and TCE on the 12DCE isomer ratios in groundwater also have to be considered. The faster degradation of *cis*-12DCE as compared to *trans*-12DCE under methanogenic conditions (Figure 5C) can accentuate the difference in their concentrations and further lower the ratio of *cis*-12DCE to *trans*-12DCE in the groundwater. This is apparent when the field and laboratory data are compared. Concentrations of *trans*-12DCE in the wetland porewater were higher than *cis*-12DCE during two of the three sampling periods (Table 1), giving relative concentrations of the isomers that were similar to the period when degradation of the *cis*- and *trans*-12DCE occurred in the microcosms (Figure 5C). In a flowing system, sorption could increase the ratio of *cis*-12DCE to *trans*-12DCE, which is opposite the effect of anaerobic degradation of the 12DCE isomers, because sorption of *trans*-12DCE was higher than *cis*-12DCE in the wetland sediments in this study (*3*) and in sandy aquifer sediments in another study (*16*). The sediment−water distribution coefficient (K_d) was 2.4 for *trans*-12DCE and 1.8 for *cis*-12DCE in 24-h batch tests with the wetland sediments (*3*). The relative concentrations of *cis*-12DCE and *trans*-12DCE in the wetland porewater (Figure 4 and Table 1) are more consistent with anaerobic degradation of the 12DCE than sorption.

Understanding of PCA degradation pathways is necessary in determining whether natural attenuation or in situ bioremediation of PCA is a feasible groundwater remediation method. The decrease in concentrations of PCA and its daughter products to below detection levels within a 1.0-m vertical distance in the wetland sediments and within 34 days in the laboratory microcosms (Figures 4 and 5) indicates that natural attenuation is a feasible remediation method in the anaerobic wetland sediments. The feasibility of natural attenuation as a remediation method ultimately is determined by the fate of 12DCE and VC, toxic compounds that are the predominant and the most persistent daughter products. The fate of the 12DCE and VC is probably largely dependent on the redox conditions of the groundwater. Concentrations of VC began to decline in the porewater only when methane concentrations reached a maximum of 600 μmol/L (Figure 4). Similarly, concentrations of VC began to decline in the PCA-amended microcosms when methane concentrations reached about 600 μmol/L, although this was not the maximum methane concentration measured in the microcosms (Figures 5 and 6). This relation between VC and methane concentrations agrees with other studies that have shown that hydrogenolysis of 12DCE to VC and further reduction of VC to ethylene requires the extremely reducing conditions of methanogenesis. For example, Pavlostathis and Zhuang (*17*) and Bagley and Gossett (*18*) found that sulfate-reducing enrichment cultures could transform TCE to 12DCE by hydrogenolysis but that further dechlorination to VC and ethylene did not occur. In contrast, many laboratory and field studies have reported hydrogenolysis of TCE to VC and, in some cases, to ethylene and ethane, under methanogenic conditions (for example, refs *6, 13, 19, 20,* and *21*). Anaerobic oxidation of 12DCE and VC under iron-reducing conditions also has been shown *(22)*. Aerobic oxidation, especially through cometabolic degradation by methanotrophs, and volatilization are other possible attenuation mechanisms for the 12DCE and VC near land surface in the wetland. A decrease in methane concentrations in the wetland porewater that would be expected from methanotrophic activity or volatilization was not observed until depths of about 0.3−0.75 m below land surface, where VC concentrations were already below detection levels (Figure 4). The results of this study indicate that natural attenuation of PCA through complete anaerobic biodegradation can occur in wetlands before sensitive surface water receptors are reached and in similar environments, such as bottom sediments of streams or lakes and methanogenic zones in contaminant plumes.

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