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Transformations of 1,1,2,2-Tetrachloroethane under Methanogenic Conditions

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Abiotic and biotic transformations of 1,1,2,2-tetrachloroethane (TeCA) under methanogenic conditions were studied. TeCA degradation started without lag with municipal digester sludge. 1,1,2-Trichloroethane (1,1,2-TCA), *trans*-1,2-dichloroethene (tDCE), and *cis*-1,2-dichloroethene (cDCE) were products of biotic transformation, while trichloroethene (TCE) resulted from abiotic degradation. TCE was further transformed to cDCE, vinyl chloride (VC), and ethene. Ethene, VC, and tDCE were the persistent products of TeCA transformations. With the same municipal digester sludge culture, 1,1,2-TCA was removed and converted to 1,2-dichloroethane (1,2-DCA) and VC. 1,2-DCA partially degraded, resulting in chloroethane and ethene formation. Reductive dechlorination, dichloroelimination, and dehydrochlorination simultaneously took place during the degradation of TeCA. Dichloroelimination and dehydrochlorination played important roles in the removal of TeCA and 1,1,2-TCA under methanogenic conditions.

Introduction

1,1,2,2-Tetrachloroethane (TeCA) was the first chlorinated hydrocarbon solvent produced in large quantities before World War I (*1*). It was used as a solvent for cellulose acetate, fat, waxes, greases, rubber, and sulfur. In a few cases, TeCA is used as a carrier or reaction solvent in manufacturing processes for other chemicals and as an analytical reagent for polymers (*1*).

TeCA was largely replaced by less toxic solvents after World War II. TeCA release in the United States varied from 44 thousand pounds in 1988 to 66 thousand pounds in 1991 (*2*). TeCA as a principal contaminant along with trichloroethene (TCE), *trans*-1,2-dichloroethene (tDCE), *cis*-1,2-dichloroethene (cDCE), vinyl chloride (VC), 1,1,2-trichloroethane (1,1,2-TCA), and tetrachloroethene (PCE), contaminates an aquifer that supplies water for residential and industrial use for the city of Tacoma, WA (*3*). TeCA concentrations measured in this aquifer are up to 5 mg/L.

While little information about TeCA transformation in groundwater is available, reductive dechlorination, dehydrochlorination, and dichloroelimination are three possible reactions in TeCA transformations (*4*).

Reductive dechlorination or reductive hydrogenolysis is a common transformation of 1- and 2-carbon chlorinated aliphatics under methanogenic conditions (*4, 5*). 1,1,1-Trichloroethane (1,1,1-TCA), for example, is converted to 1,1-dichloroethane (1,1-DCA) (*6*), and PCE is successively converted to TCE, cDCE, VC, and ethene (*11*). Each reductive dechlorination is a two-electron transfer reaction.

Dehydrochlorination has been seen, for example, in the abiotic conversion of pentachloroethane to PCE (*7*) and 1,1,1-TCA conversion to 1,1-DCE (*6*). Dehydrochlorination is not a redox reaction.

Bouwer and McCarty (*5*) suggested 1,1,2-TCA as an intermediate of TeCA transformation in continuous-flow column experiments and TCE as an intermediate in a batch experiment under methanogenic conditions. Those transformations are a reductive dechlorination and a dehydrochlorination, respectively.

Dihaloelimination is a two-electron transfer reaction. Thompson et al. (*8*) reported reductive dichloroelimination of 1,1,2-TCA and TeCA by hepatic microsomes from rat liver, with VC and both tDCE and cDCE as metabolites. Reductive dichloroelimination of hexa- and pentachloroethane by microsomal cytochrome P450 was studied by Nastainczyk et al. (*9*, *10*). The main products of the *in vitro* metabolism of hexa- and pentachloroethane were PCE (99.5%) and TCE (96%), respectively, with minor amounts of pentachloroethane (0.5%) and TeCA (4%) via reductive dechlorination.

Dihaloelimination has also been observed under partially aerobic conditions (*11*). With cytochrome P-450$_{CAM}$ as a primary catalyst, dichloroelimination of hexa-, penta-, and 1,1,1,2-tetrachloroethane were catalyzed, and the products were PCE, TCE, and 1,1-DCE, respectively; no reaction was observed with TeCA. Significant rates of these reactions were observed at 5% oxygen concentration.

Schanke and Wackett (*12*) reported TeCA degradation by transition-metal coenzymes. cDCE (53%), tDCE (29%), VC (14%), ethylene (1%), and traces of 1,1,2-TCA were the products from this abiotic transformation with vitamin B_{12} and titanium(III) citrate. Both dechlorination and dichloroelimination had occurred; the major route of degradation was reductive dihaloelimination.

Both abiotic and biotic transformations of TeCA under methanogenic conditions are poorly understood. TeCA, 1,1,2-TCA, and 1,2-DCA transformations under methanogenic conditions are studied in order to better understand the origin and fate of contaminants found at the site in Tacoma and to develop possible bioremediation approaches.

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Materials and Methods

Test Chemicals. The compounds used in this study were TeCA (99%), 1,1,2-TCA (98%), 1,2-DCA (99%), TCE (99%), cDCE (97%), and tDCE (98%) (Aldrich Chemical Company, Inc., Milwaukee, WI). VC and chloroethane were obtained as standard solutions in methanol from Supelco Inc. (Supelco Park, Bellefonte, PA). Standard gases included carbon dioxide and methane (20% nitrogen and 30% carbon dioxide in methane, Airco Special gases, Vancouver, WA), and ethene (Matheson, East Rutherford, NJ).

Saturated stock solutions of TeCA, 1,1,2-TCA, and 1,2-DCA were used in all experiments. The concentration of stock solutions were 2960, 4420, and 8520 mg/L, respectively.

Culture Media. Reduced anaerobic mineral medium (RAMM) (*13*) was used in all experiments. The medium was autoclaved and subsequently boiled while purged with oxygen-free nitrogen that had been passed through a copper column at 300 °C. $NaHCO_3$ (1.2 g/L) and $Na_2S{\cdot}9H_2O$ (5 mg/L) were added to the media after cooling. Resazurin was used as the redox indicator. Serum bottles with 160 mL volume were used. Organic-free water used in selected controls was prepared as follows: tap water was passed through a mixed bed ion-exchange column, then a reverse osmosis membrane, and finally a granular activated carbon column.

Source of Organisms. Anaerobic sludge from a laboratory-scale municipal sludge digester was used as the initial seed material. This digester had been fed primary and waste-activated sludge spiked with chlorinated compounds, including PCBs (Aroclor 1254), pentachlorophenol, 1,2,4-trichlorobenzene, PCE, and carbon tetrachloride. It was operated at 35 °C, pH 7, with a retention time of 25 days for 21 months. The suspended solids concentration was 20 g/L total suspended solids with 11 g/L volatile suspended solids (VSS). The concentration used in all the bottle tests except tests with diluted biomass was 1.5−2.5 g/L VSS.

The 5.0 mL of PCE and cDCE dechlorinating enrichments (*14*) were added to TeCA bottles before the third and fourth spikings of TeCA and the subsequent tests with 1,1,2-TCA and 1,2-DCA. The enrichments were from the PCE and cDCE batch transformation tests in which complete dechlorination of PCE and cDCE, producing VC and ethene as the main products, had been observed. Those enrichments had also been developed from the sludge digester by repetitive spikings with lactate and 100 μmol/L PCE or cDCE for 4 months (*14*).

Analytical Methods. Chlorinated compounds were analyzed by gas chromatography (Perkin-Elmer 8700) attached to a purge & trap system (Tekmar ALS-LSC). A Restek Rt_x 502.2, 0.53 mm i.d. wide bore capillary column was used to separate the chlorinated compounds which were then analyzed with an electrolytic conductivity (Model 1000 Hall) detector. The column was held isothermal for 5 min at 35 °C, followed by a ramp rate of 8 °C/min until it reaches 199 °C, and then held isothermal for 2 min. The carrier gas (helium) had a flow rate of 14 mL/min.

Gas composition (CH_4 and CO_2) was analyzed by gas chromatography (Carle Series 100 AGC), using a Hayesep Q (Supelco) 6-ft packed column and a thermal conductivity detector. The column was held isothermal at 60 °C. The carrier gas (helium) flow rate was 30 mL/min.

Ethane and ethene were measured using a gas chromatograph (5830A GC, Hewlett Packard) equipped with Hayesep Q (Supelco) 6-ft packed column and a flame ionization detector. The column was held isothermal at 80 °C, and the carrier gas (N_2) flow rate was 50 mL/min.

Chlorinated compounds were measured in liquid-phase samples. The total quantities in bottles were calculated using the volume of the liquid and gas phases and the Henry's law constant for each compound. Henry's constants for the compounds are as follows (*15*, *16*): TeCA, 0.019; 1,1,2-TCA, 0.049; 1,2-DCA, 0.045; TCE, 0.59; cDCE, 0.22; tDCE, 0.55; VC, 1.42; C_2H_4, 8.77; and C_2H_6, 20.5. Ethene and ethane were measured in the gas phase because of their large Henry's constants. Total amounts were calculated in an analogous way.

Experimental Design. To understand the biological pathways, batch bottle tests were used in a series of tests with different compounds, refeedings, and respikings. Bottle bioassay procedures followed those described by Shelton and Tiedje (*13*), Owen et al. (*17*), and those used in our laboratory (*18*). The sludge from the laboratory digester (30 mL each bottle) and RAMM media (130 mL each bottle) were used. Sludge seed and RAMM were dispensed into each bottle while purging with N_2 and CO_2. Bottles were sealed with butyl rubber stoppers and sealed with an aluminum crimp cap. Sterile syringes and needles were used for feeding lactate and chlorinated compounds. The bottles were incubated at 35 °C on a shaker at 150 rpm.

Gas production and gas composition were periodically analyzed. Gas production was measured by displacement using a glass syringe at atmospheric pressure. Chlorinated compounds, ethene, and ethane were measured daily during the first week and then every 2−3 days.

Lactic acid was used as the sole carbon source and fed once a week. It was neutralized to pH 7 by sodium hydroxide and diluted 10 times before feeding. Lactate was added to give an initial concentration of 720 μmol/L and again at each refeeding.

TeCA Degradation Experiments. TeCA degradation was tested in a sludge seeded culture that was fed TeCA four times over about 4 months. This culture was also used in tests with 1,1,2-TCA and 1,2-DCA. Before each TeCA respiking, the duplicate bottles were purged with N_2 and CO_2. The TeCA concentration fed was about 60 μmol/L in the first spiking, 70 μmol/L in the second spiking, 80 μmol/L in the third spiking, and 105 μmol/L in the fourth and following spikings. Similar concentrations were used for killed and blank controls.

Killed controls, containing the same medium, seed, lactate, and TeCA, were made by both autoclaving and adding 4% formaldehyde. Blank controls (mineral media) were made with reduced RAMM and Na_2S or titanium(III) citrate but without inocula.

Abiotic Tests with TeCA. In order to understand abiotic transformations of TeCA under anaerobic conditions, reduced cell-free extracts were prepared. A sonicator (8893-MT Sonicator, Cole-Parmer Instrument Cop., Chicago, IL) was used to disrupt the samples for the laboratory digester culture. The cells were sonicated 20 min, removed to a refrigerated centrifuge kept at 5 °C, centrifuged at 5000 rpm for 20 min, and then further processed by filtration through a 0.45-μm membrane filter (Millipore). Procedures except centrifugation were carried out in an anaerobic glovebox. The filtered media was dispensed to the replicate bottles, which contained either RAMM (with Na_2S, 500 mg/L), RAMM [with titanium(III) citrate, 2 mmol/L], RAMM (without reducing agent), or unreduced organic-free water,

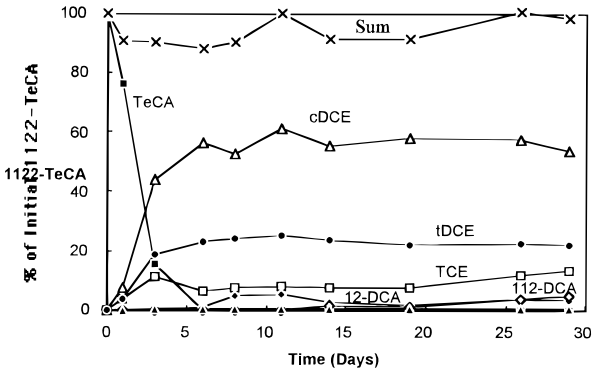


FIGURE 1. TeCA transformation under anaerobic conditions during second spiking test (TeCA initial concentration: 61 μmol/L).

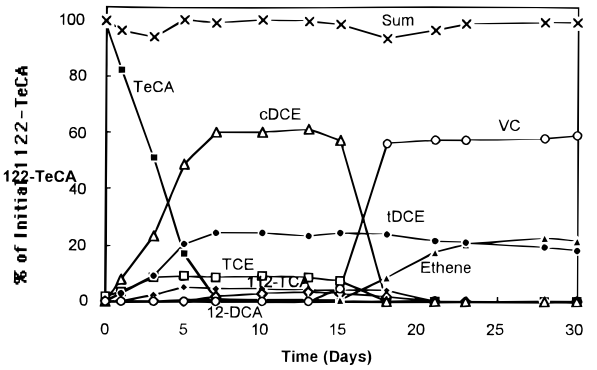


FIGURE 2. TeCA transformation under anaerobic conditions during the fourth spiking test (TeCA initial concentration: 106 μmol/L).

TABLE 1

Distribution of Products in the First and Second Spiking Tests

	compound (%)[a]						
spiking	1,1,2-TCA	1,2-DCA	TCE	tDCE	cDCE	ethane	ethene
first[b]	3.2	1.3	16.5	21.4	51.6	0.3	0.6
second[c]	3.1	1.4	9.1	22.6	54.8	0.3	0.8

[a] Based on percentage of initial TeCA fed. [b] Mean values between day 6 and day 17 for first spiking. [c] Mean values between day 6 and day 19 for second spiking.

TABLE 2

Distribution of Products in the Third and Fourth Spiking Tests

	compound (%)[a]						
spiking	1,1,2-TCA	1,2-DCA	TCE	tDCE	cDCE	ethane	ethene
third[b]	5.3	1.9	15.1	20.1	51.7	0.2	0.1
fourth[c]	4.2	0.5	8.7	25.4	61.4	0.5	0.3

[a] Results based on percentage of TeCA fed. [b] Mean value between day 3 and day 10 for third spiking. [c] Mean value between day 7 and day 13 for fourth spiking.

respectively. Finally, TeCA stock solution was added to each bottle. The initial TeCA feed was about 50 μmol/L. All bottles were kept at 35 °C and shaken. Bottles with live cells from the same source, killed controls, and blank controls were also prepared. The cell free extract added to the bottles was derived from digester culture representing about 1.1 g/L VSS.

1,1,2-TCA Transformation Experiments. To study 1,1,2-TCA transformations under anaerobic conditions, 1,1,2-TCA was fed to different bottles at about 15 μmol/L. A live cell bottle with inocula from a TeCA bottle after the fourth spiking, RAMM media, and Na_2S as the reducing agent was fed once a week with lactate at 720 μmol/L. A second bottle was abiotic, containing sonicated, filtered, biological media with titanium(III) citrate as the reducing agent. A third bottle was a blank control with RAMM and Na_2S without live cells or sonicated biological media. The initial cell concentration in live cell bottles or used for cell-free extract was 1.1 g/L VSS.

1,2-DCA Transformation Experiments. Bottle experiments with 20−25 μmol/L 1,2-DCA were similar to those for 1,1,2-TCA. They were made with anaerobic live cells, reduced cell-free extract, and a blank control.

Results

Biotic Transformations of TeCA. TeCA removal in the first and second spikings occurred without lag (Figure 1). TCE, cDCE, and tDCE were formed simultaneously during the first six days. Much smaller amounts of 1,1,2-TCA and 1,2-DCA appeared later. The five products persisted in the first two spiking tests for at least 4 weeks. Traces of ethene were seen in the gas phase. The typical composition of metabolites after TeCA had disappeared is shown in Table 1 for the first and second tests. TCE was the only product formed in killed controls, amounting to about 5% of initial TeCA during the 30-day test period. No transformations were seen in the blank control.

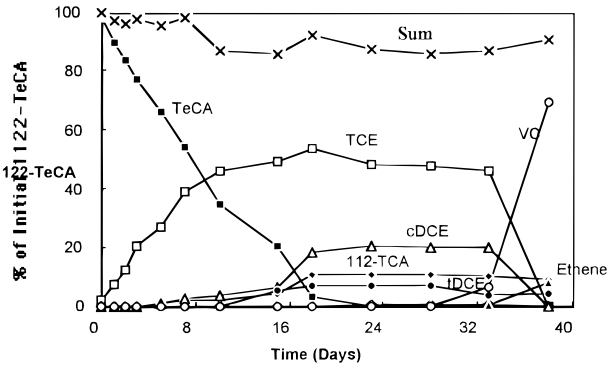


FIGURE 3. TeCA transformation under anaerobic conditions with diluted culture (110 mg/L VSS from TeCA culture after the fourth spiking test. TeCA initial concentration: 105 μmol/L).

In the third and subsequent spikings, after the addition of inocula from PCE and cDCE enrichments, the transformation pattern for the first 12 days (Figure 2) was similar to that for the first two tests. 1,1,2-TCA and 1,2-DCA appeared earlier than in the earlier tests. The distribution of products during their stable periods, shown in Table 2, was very similar to the first two spikings (Table 1). TCE and cDCE removal began after about a 10-day lag; VC and ethene appeared between day 15 and day 18. 1,1,2-TCA and 1,2-DCA were not detected after day 21. Ethene, VC, and tDCE still remained after 30 days. The mass balance of 2-carbon compounds during all test periods was above 90%.

In order to understand the role of seed quantity, a test was carried out with a 10% diluted culture following the fourth TeCA spiking (Figure 3). Test conditions were the same as for the preceding tests. TeCA was removed again without lag but at a rate about one-third of that with the concentrated inocula. TCE was the main product and the only product until day 7. cDCE and tDCE appeared after day 5 and day 15, respectively. 11,2-DCA was formed in

TABLE 3

Distribution of Products in the TeCA Spiking with 10% Diluted Culture[a]

	compound (%)[a]						
	1,1,2-TCA	1,2-DCA	TCE	tDCE	cDCE	ethane	ethene
distribution[b]	10.5	0.37	48.9	7.06	19.7	0.0	0.3

[a] Data based on percentage of TeCA fed. [b] Mean values between day 17 and day 33.

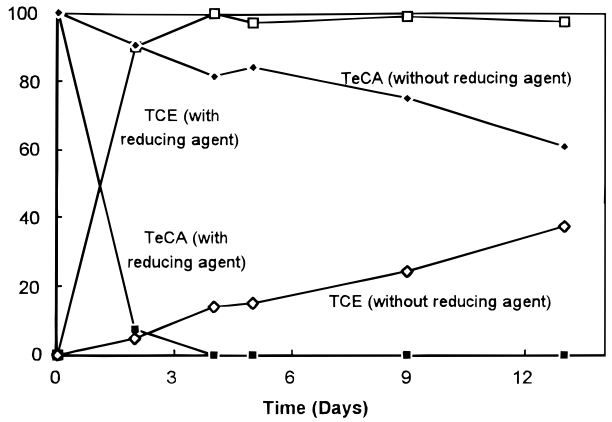


FIGURE 4. TeCA abiotic transformation under anaerobic conditions with cell free extract, with and without titanium(III) citrate (TeCA initial concentration: 50 μmol/L).

small amounts after day 5, but 1,2-DCA remained below 0.5% in all the experiments. TCE, cDCE, tDCE, and 1,1,2-TCA remained stable between day 17 and day 33, but the product distribution was not the same as in previous tests. TCE was predominant, and 1,1,2-TCA was present in larger amounts and persisted longer. cDCE and tDCE were present in similar proportion relative to each other, but in smaller amounts relative to the other products (Table 3). TCE and cDCE were further transformed to VC and ethene by day 38.

Abiotic Transformations of TeCA. Abiotic transformation of TeCA with and without titanium(III) citrate resulted in TCE formation in all bottles, including control bottles. The rate of conversion, however, depended strongly on the experimental conditions. The transformation with cell-free extract in the presence or absence of titanium(III) citrate shows that the rate depends strongly on the presence of the reducing agent and that conversion to TCE, the sole product, is stoichiometric (Figure 4). Organic-free water bottles had the lowest conversion (2.5 μmol L^{-1} d^{-1}), and cell-free extract with titanium(III) citrate had the highest rate (12.5 μmol L^{-1} d^{-1}). The abiotic transformation rate of TeCA had the following order (based on TeCA removal or TCE formation): cell-free extract with titanium(III) citrate > killed controls with titanium(III) citrate > live cells with Na_2S > killed controls without reducing agent ≥ blank controls with titanium(III) citrate ≥ blank controls without reducing agent > cell free extracts without reducing agent > unreduced organic-free water. The results indicate that TeCA was converted to TCE by abiotic dehydrochlorination, and this dehydrochlorination partially takes place in nonreduced conditions (*11*).

1,1,2-TCA and 1,2-DCA Transformations. 1,1,2-TCA was transformed to VC, 1,2-DCA, and traces of ethene by

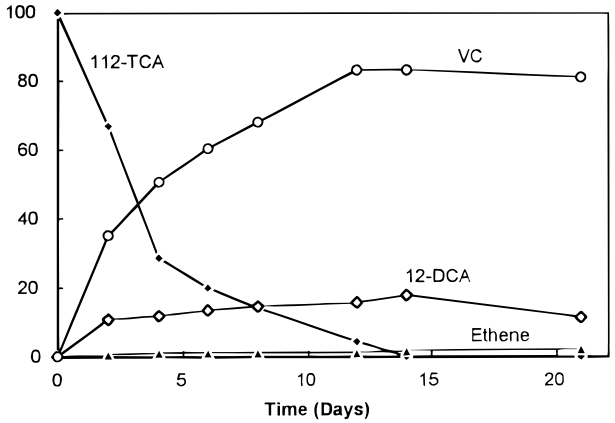


FIGURE 5. 1,1,2-TCA transformation under anaerobic conditions. The seed was from TeCA feed culture after the fourth TeCA spiking test. Lactate was the only carbon source, and Na_2S was used as the reducing agent. The initial concentration of 1,1,2-TCA was 16.2 μmol/L.

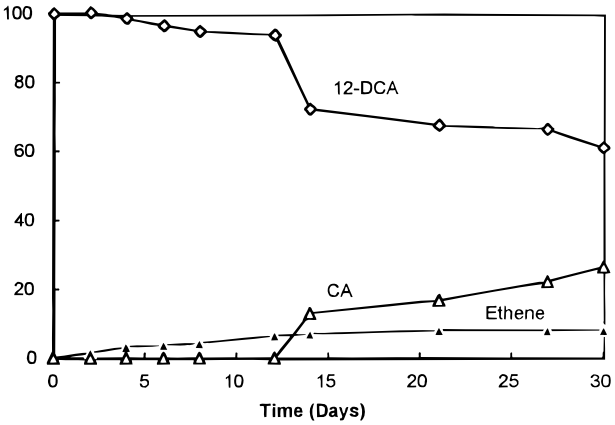


FIGURE 6. 1,2-DCA transformation under anaerobic conditions. The seed was from TeCA feed culture after the fourth TeCA spiking test. Lactate was the only carbon source, and Na_2S was used as the reducing agent. The initial concentration of 1,2-DCA was 25.4 μmol/L.

live cells under methanogenic conditions (Figure 5). 1,1,2-TCA was simultaneously converted to 1,2-DCA (20%) by dechlorination and to VC (80%) by dichloroelimination with no lag time. Ethene was formed by reductive dechlorination of VC or by further dichloroelimination of 1,2-DCA. Less than 3% was converted to ethene. Since both VC and 1,2-DCA decrease slightly, the predominant precursor is not clear. No transformation was seen with reduced cell-free extract, blank controls, and killed controls.

1,2-DCA was partially transformed under methanogenic conditions (Figure 6) in tests conducted along with 1,1,2-TCA test. Transformation of 1,2-DCA was much slower than for TeCA and 1,1,2-TCA. Chloroethane was detected after 14 days. Chloroethane (20%) and ethene (10%) resulted from reductive dechlorination and dichloroelimination of 1,2-DCA, respectively. No transformation products were measured in reduced cell-free extract, killed controls, or blank controls, although the total loss of 1,2-DCA was about 15% in those bottles.

Discussion

Reductive dechlorination, dehydrochlorination, and dichloroelimination are common transformations in the degradation of polychlorinated alkanes under methanogenic

conditions. This study shows that all three reactions take place simultaneously with TeCA under methanogenic conditions; dehydrochlorination and dichloroelimination are more important in the initial degradation of TeCA and 1,1,2-TCA; 1,2-DCA and other intermediates are mainly degraded by reductive dechlorination.

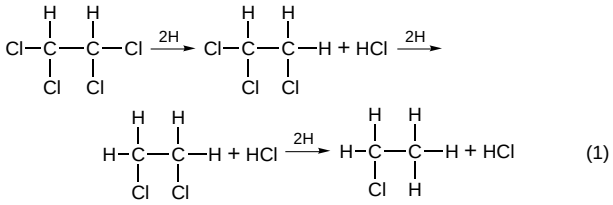
Reductive dechlorination is often the predominant degradation path for chlorinated organics in anaerobic environments. Reductive dechlorination of TCE has been seen with enrichment cultures and with abiotic conditions (*19*−*21*). In all cases, cDCE is the predominant initial product, which can be further transformed to VC and to ethene. tDCE is also reductively dehalogenated in some of these studies, but at a much slower rate than cDCE. Reductive dechlorination of TCE and cDCE was observed in this study only after inoculation with PCE and cDCE transforming enrichments. Transformation started about 10 days after TeCA had disappeared and TCE and cDCE had reached maximum levels. Dechlorination proceeded rapidly to VC, but VC was only partially converted to ethene. Reductive dechlorination was also observed for TeCA, 1,1,2-DCA, and 1,2-DCA. Reductive dechlorination of TeCA was observed in a test prior to the addition of the PCE and cDCE enrichment; 1,1,2-TCA and 1,2-DCA were dechlorinated only after inoculation with PCE and cDCE enrichments. Each of the reductive dechlorinations seen in this study occurred only with live cells. Killed controls, reduced blanks, and reduced cell-free extract from a methanogenic culture did not catalyze reductive dechlorination.

Dehydrochlorination, which is not a redox reaction, is a common abiotic reaction. 1,1-DCE from 1,1,1-TCA dehydrochlorination has been reported under abiotic conditions without live cells (*22*), and pentachloroethane is dehydrochlorinated to PCE (*7*). In this study, TCE is the only product of TeCA dehydrochlorination in reduced cell-free extract, reduced killed controls, and reduced blank controls. No abiotic transformations of 1,1,2-TCA and 1,2-DCA occurred in reduced cell-free extract, in killed controls, or in reduced blank controls.

Dichloroelimination is commonly seen with highly chlorinated compounds (*8*−*12*). Abiotic transformation of hexachloroethane, pentachloroethane, and 1,1,1,2-tetrachloroethane and 1,1,2-TCA is reported by dichloroelimination to PCE, TCE, 1,1-DCE, and VC, respectively (*8*−*12*). In our study, dichloroelimination occurred only with live cells, not with reduced cell-free extract, killed controls, or reduced blanks. Dichloroelimination transformed a major part of TeCA to cDCE and tDCE in a fairly constant ratio of 2.4:1.0, respectively. Schanke and Wackett (*12*) observed the same products at a similar ratio (5:3) but formed abiotically with vitamin B_{12} and titanium(III) citrate. In our study, the relative amount of dichloroelimination (cDCE and tDCE) compared to dehydrochlorination (TCE) decreases when the seed biomass concentration decreased. 1,1,2-TCA and 1,2-DCA were degraded via both dichloroelimination and dechlorination under methanogenic conditions.

Seven products were seen in TeCA transformations by three different dechlorinating reactions. In a complex methanogenic community that had not previously been exposed to TeCA, TeCA removal was rapid, without lag, and was complete.

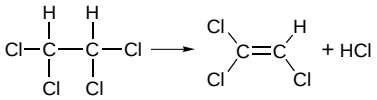
Reductive dechlorination of TeCA resulted in 1,1,2-TCA and 1,2-DCA, which was dehalogenated to CA in separate tests (eq 1). This transformation pathway required live cells;



(1)

however, it was relatively insignificant quantitatively, since 1,1,2-TCA and 1,2-DCA totaled no more than 5% of the initial TeCA. CA was formed slowly from 1,2-DCA. After about 3 weeks, CA could no longer be detected in the TeCA-spiked bottles. Small quantities of ethane were observed in some tests but could not be clearly linked to dehalogenation of CA.

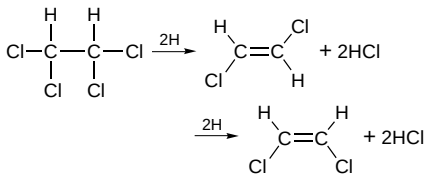
Dehydrochlorination of TeCA resulted in the production of TCE (eq 2). This reaction was seen with live cells, with



(2)

reduced cell-free extract, and at a slower rate with reduced mineral media. TCE was a minor product (8% of TeCA) in tests with a high biomass concentration. With diluted seed, the fraction of TCE increased to 47% (see Figure 4 and Table 3). This was the only dehydrochlorination reaction.

Dichloroelimination products, cDCE and tDCE, were formed simultaneously from TeCA (eq 3). They were the



(3)

major products seen with high biomass, respectively 60% and 25% of the original TeCA. The cDCE to tDCE ratio of about 2.4 was stable in successive spikings of the undiluted and the diluted culture. cDCE is usually the primary product of reductive dechlorination of TCE. However, simultaneous formation of cDCE and tDCE without sign of TCE removal and the long periods when TCE and cDCE were present together at stable levels both indicate that dichloroelimination of TeCA rather than reductive dechlorination is the predominant reaction leading to DCE formation.

Dichloroeliminations of 1,1,2-DCA to VC and possibly 1,2-DCA to ethene were also observed. Dichloroelimination was seen only with live cells, not with reduced cell-free extracts, reduced killed controls, or reduced mineral media.

Further reductive dechlorination of TCE and cDCE was seen only after inoculation with PCE and cDCE enrichments. VC was rapidly formed and then subsequently partially transformed to ethene. tDCE was transformed at an insignificant rate.

Figure 7 summarizes the reactions and products observed in this study. In four instances, light lines indicate likely reactions that could not be confirmed because of very small amounts of the products or because more than one pathway leading to the product is possible. Some of these transformations are consistent with the contaminants that occur in groundwater at the Tacoma site. Analysis of groundwater from an extraction well at the site shows that

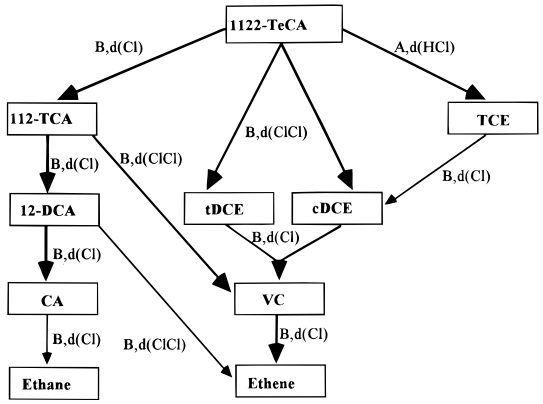


FIGURE 7. Probable pathway of biotic and abiotic transformations of 1,1,2,2-tetrachloroethane under methanogenic conditions. Abbreviations: A, abiotic transformation; B, biotic transformation; d(HCl), dehydrochlorination; d(ClCl), dichloroelimination; d(Cl), reductive dechlorination.

TeCA, 1,1,2-TCA, TCE, cDCE, tDCE, VC, and PCE are present at concentrations of 31, 0.5, 9.3, 7.2, 6.8, 1.9, and 0.5 μmol/L, respectively. Since 1,1,2-TCA and TCE are the dechlorination and dehydrochlorination products of TeCA, respectively, cDCE and tDCE are found in TeCA dichloroelimination, VC can be formed by reductive dechlorination, and all these compounds were observed in this study, it is possible that at the site they all are from the transformation of TeCA. Only PCE, which is present at a low concentration (0.5 μmol/L), was not observed as a transformation product of TeCA in this study.

Most of the contaminants seen in the extraction well were biotransformed in our study with only VC and tDCE persisting for more than 30 days. Furthermore, VC and tDCE have been reductively dechlorinated in tests by others. It is possible that complete transformation of TeCA to ethene and ethane could occur with *in situ* anaerobic bioremediation or in biological treatment of extracted contaminated water.

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