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TRANSFORMATION OF CHLORINATED ORGANIC COMPOUNDS BY IRON AND MANGANESE POWDERS IN BUFFERED WATER AND IN LANDFILL LEACHATE

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ABSTRACT

Tetrachloroethylene was transformed by iron powder (4.1g/L) in oxygen-free, HEPES-buffered (pH 7) water at 50°C with a half-life of 20 days. The only products observed were the reactive intermediate, trichloroethylene, and ethene and ethane. 1,1,1-Trichloroethane, 1,1-dichloroethylene, and tetrachloroethylene were transformed by iron at room temperature in both autoclaved buffered water and in two non-autoclaved landfill leachates. The pattern and degree of removal were similar in all cases. Dichloromethane, 1,1-dichloroethane, and 1,4-dichlorobenzene were also tested, but were not removed from any of the systems. If manganese rather than iron was used, the substrates transformed depended upon the aqueous phase. Some biological transformations were seen in Leachate 2, but the activity was reduced by manganese and completely suppressed by iron.

INTRODUCTION

Several investigators *(1-6)* have described the dechlorination of organic compounds by metals such as iron. The reaction was usually reported as an undesirable increase in metal corrosion when chlorinated solvents were stored in steel containers or used to clean metal parts. Recently, however, researchers *(7-11)* have begun to explore the potential of using metal powders to treat water contaminated with chlorinated compounds.

In some cases, the reaction was shown to be a reductive dehalogenation in which the metal is the source of electrons (Eqn. 1; RX=halogenated hydrocarbon, M=metal). Matheson and Tratnyek *(11)* reported that carbon tetrachloride was partially transformed by iron to chloroform under anaerobic conditions, and Sweeny *(7)* showed that some of the substrates he investigated were reductively dehalogenated, although the products obtained depended upon the metal used. The stepwise reductive dehalogenation of PCE to ethene by iron in water is thermodynamically favorable *(based on reduction potentials for chlorinated species obtained from 12).*

In addition to the reaction with chlorinated substrates, some metals (such as iron) also react with water. In the absence of oxygen, iron reacts with protons to generate hydrogen and the ferrous ion (Eqn. 2); the reaction is slow at near-neutral or basic pH *(13)*. The reaction of manganese in anoxic water is analogous *(14)*.

$$RX + H^+ + 2e \rightarrow RH + X^-$$
$$M \rightarrow M^{2+} + 2e$$
$$RX + M + H^+ \rightarrow RH + M^{2+} + X^- \qquad \text{Eqn. 1}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad \text{Eqn. 2}$$

In the presence of anaerobic bacteria, biologically mediated reductive dehalogenation can occur *(15)*. The reaction products will depend upon the substrate, the types of bacteria present, and the availability of a carbon source, electron donors and acceptors, and nutrients. The effect of a metal on biological dehalogenation is difficult to predict. Conceivably, the metal may enhance the reaction by providing trace metals to the bacteria, or it may inhibit transformation because of toxicity. In addition, a metal may serve as an electron donor as demonstrated by Daniels *et. al. (16)* who showed that iron metal could serve as the sole source of electrons for reduction of carbon dioxide by methanogens. Hydrogen, produced by the reaction of metal and water, could provide electrons to some dechlorinating bacteria *(17)*. In our experiments, disappearance of substrate in the absence of metal and disappearance after a lag time were presumed to be indicators of biological transformation, though an unambiguous distinction between biological and abiotic transformation may be difficult to make. (A lag time is often seen in biological systems if the initial population of bacteria is small, or if synthesis of the appropriate enzymes must be induced.)

This paper reports that iron and manganese powders can transform some chlorinated organic compounds under anaerobic conditions. It focuses on the abiotic reaction of PCE with iron in buffered solution, and on an experiment designed to examine the ability of iron and manganese to transform halogenated hydrocarbons in leachate, a complex aqueous matrix. In the latter case, the reaction of 1,1,1-trichloroethane (TCA), 1,1-dichloroethylene (DCE), tetrachloroethylene (PCE), dichloromethane (DCM), 1,1-dichloroethane (DCA), and 1,4-dichlorobenzene (DCB) at room temperature in autoclaved buffered solution was compared to their reaction in two non-autoclaved leachates from two landfills. Because the leachates were not sterile, biological as well as chemical reactions were possible.

MECHANISTIC AND KINETIC MODELS

The general pathway hypothesized was a stepwise reductive dehalogenation (Eqn. 3, upper pathway) which may or may not continue until the substrate, RX_n, is completely dehalogenated. Possible side reactions which may occur with some substrates include dehydrohalogenation (RHC-CXR' $\rightarrow$ RC=CR' + HX) and dihalo-elimination (RXC=CXR' $\rightarrow$ RC$\equiv$CR' + $2X^-$). These and other potential modes of disappearance are combined in the lower pathway. The observed rate constant, k_{obs}, is given by $k_{obs} = k_1 + k_2$. The fraction of substrate transformed by reductive dehalogenation is, therefore, k_1/k_{obs}.

$$RX_n \xrightarrow{k_1} RHX_{n-1} \xrightarrow{k_a} RH_2X_{n-2} \xrightarrow{k_b} RH_3X_{n-3} \cdots$$
$$RX_n \xrightarrow{k_2} ?$$

Eqn. 3

The parameters k_1 and k_a can be estimated using equations and statistical procedures analogous to those developed by Kriegman-King and Reinhard *(18)* for intermediates formed during carbon tetrachloride transformation.

Assuming that both the appearance and disappearance of RHX_{n-1} are pseudo-first order processes, the concentration of RHX_{n-1} is

$$\frac{[RHX_{n-1}]}{[RX_n]_o} = \frac{k_1}{k_{obs} - k_a}\left[\exp(-k_a t) - \exp(-k_{obs} t)\right] \qquad \text{Eqn. 4}$$

Given $[RHX_{n-1}]$ and $[RX_n]$ as a function of time, k_{obs} can be calculated (see below) and k_1 and k_a can be fit to Eqn. 4 using the program SYSTAT 5.2 (Systat, Inc., Evanston, IL).

The experiments were designed such that the total moles of metal would be several orders of magnitude greater than the moles of chlorinated substrate to be transformed. However, heterogeneous reactions usually occur at specific sites on the surface, and the relative number of these sites (compared to the amount of substrate to be transformed) can not be determined from the mass of metal. If the number of surface sites is large compared to the amount of substrate to be transformed, and if the rate of transformation at the surface is rate limiting (i.e., mass transport of substrate to the metal surface is relatively fast) then the reaction should be pseudo-first order with respect to the substrate concentration. The rate law is, therefore,

$$[RX_n]/[RX_n]_o = \exp(-k_{obs} t) \qquad \text{Eqn. 5}$$

where $[RX_n]$ is the concentration at time, t, $[RX_n]_o$ is the initial concentration, and k_{obs} is the (initial) observed pseudo-first order rate constant. The half-life for a first order reaction is $t_{1/2} = (\ln 2)/k_{obs}$.

If, however, the surface site concentration on the metal is small compared to the concentration of substrate that may sorb, then the rate of reaction would be independent of the concentration of substrate. That is, the reaction would be zeroth order with respect to substrate, with the rate law given by

$$[RX_n] = [RX_n]_o - k^o_{obs} t \qquad \text{Eqn. 6}$$

where k^o_{obs} is the observed zeroth order rate constant. Both k_{obs} and k^o_{obs} are presumably proportional to the surface site concentration.

EXPERIMENTAL

HEPES Studies, 50°C. Experiments were conducted in 250mL glass bottles equipped with screw-cap Mininert™ valves. In a glovebox with a 90%N_2/10%H_2 atmosphere, the bottles were filled with 1-10g of 100-200 mesh iron powder (Johnson-Matthey) and 245mL of either Milli-Q™ water or 0.067-0.1M HEPES (N-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid]; Sigma Chemical) buffer, pH 7, which had been deoxygenated (by purging with N_2), autoclaved, and spiked with substrate (approx. 10μM). Controls containing no metal were also prepared. Analyses were performed either by withdrawing a 1.0mL aliquot from each bottle, extracting it into 1.0mL of pentane and analyzing the pentane by a gas chromatograph (GC) equipped with an electron capture detector (GC/ECD), or by analyzing the headspace via GC/flame ionization detection and either GC/ECD or GC/photoionziation detection. If aqueous samples were taken, the bottles were refilled with deoxygenated Milli-Q™ water in order to maintain a constant headspace volume. The bottles were then sealed in metallized plastic pouches (VWR Scientific, San Francisco, CA) to help ensure that the systems remained oxygen-free, and placed in a 50°C waterbath or stored on the bench top (~23°C). Chloride was measured by ion chromatography. In selected experiments substrate and products were measured in the headspace. In such cases, 120mL serum bottles equipped with Mininert valves were used, and filled with only 25mL of solution. ^{14}C was measured by liquid scintillation counting using a Packard 2500 TR/AB liquid scintillation analyzer.

HEPES Studies, room temperature. An experiment using six substrates and two metals was conducted. The substrates (approx. 5-10μM) were DCM, DCE, DCA, TCA, PCE, and DCB. The metals were iron and manganese. Three bottles were prepared: one contained no metal, one contained 5.0g (20g/L) iron (as above), and the third was filled with 2.5g (10g/L) of 100-200mesh manganese (Aldrich Chemical). Preparation and incubation were as described above except that the bottles were stored in the laboratory at room temperature (approximately 23±1°C). Substrate concentrations were determined by adding a 0.5mL aliquot to 1.0mL of 1M hydrochloric acid (to ensure that dissolved metals remained in solution), then analyzing the acidified samples by a purge-and-trap gas chromatograph equipped with a Hall detector. Analyses for Fe^{2+} and dissolved manganese were performed by UV/visible spectroscopy using a Ferrozine method *(19)* and potassium periodate method *(based on 20)* for iron and manganese, respectively. Assuming a 1.0mL sample size, the detection limit for iron was approximately 0.5mg/L, and that for manganese 7mg/L. The pH of each aqueous phase was measured initially with a pH meter. Due to limited sample size, subsequent measurements were made by placing a few drops of solution on tri-colored, 0.5-unit pH paper when the bottles were sampled.

Leachate Experiment. An experiment using two anaerobic leachates, L1 and L2, from two municipal landfills was prepared. Preparation, sampling and incubation were as described for the room temperature HEPES experiment, except that the two leachates were not autoclaved. No HEPES was added to the leachates.

RESULTS and DISCUSSION

HEPES Studies, 50°C

PCE disappeared in the presence of iron powder and HEPES buffer as shown in Figure 1a. (A and B refer to duplicate bottles.) The reaction was first order in PCE with an observed pseudo-first order rate constant, k_{obs}, of 0.049±0.010 day^{-1} and a half-life of 20±4 days. (All errors are reported as 95% confidence intervals.) A buffer was apparently necessary, since in unbuffered solution less than 30% of the PCE was transformed and reaction ceased within 10 days (data not shown). In a test with Milli-Q water and iron at 25°C, the pH rose from about 5.3 to 8.6 in three days suggesting that there may be a threshold pH, above which PCE transformation does not occur. The role of pH is not yet understood.

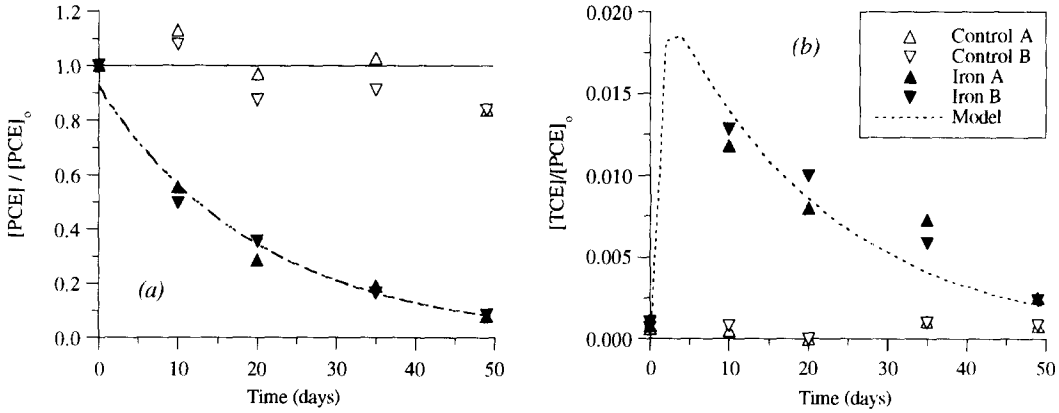


FIGURE 1. (a) Disappearance of PCE. (b) Appearance of TCE. Legend is the same for both figures. Dashed lines are fits to the data. Reaction conditions: 0.067M HEPES, pH 7, 4.1g/L iron, 50°C.

The only products observed were the reactive intermediate, trichloroethylene (TCE), whose apparent maximum concentration was typically less than two percent of the initial PCE concentration (Figure 1b), and ethene

and ethane. No other chlorinated ethenes or ethanes were detected. (The detection limit for each of these compounds was approximately 0.2μM, implying that they did not accumulate to greater than 2% of the initial PCE concentration.) Ethene and ethane appeared in an approximately 1.5:1 ratio. They typically accounted for between 15-25% of the mass balance, but did not account for all of the PCE lost. The mass balance obtained is shown in Figure 2.

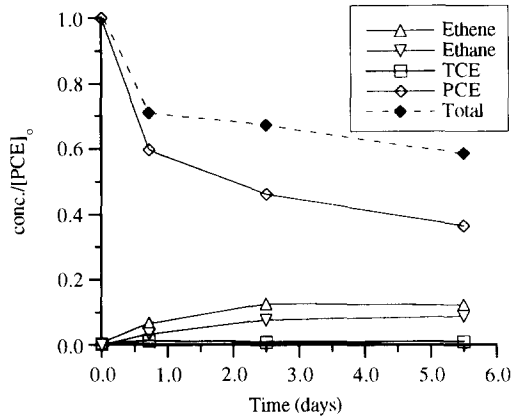
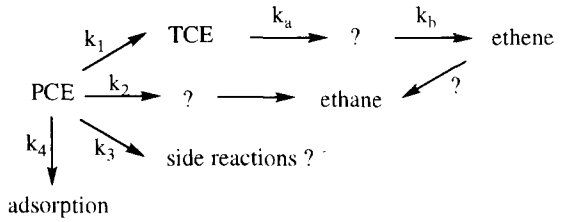


FIGURE 2. Mass Balance for PCE disappearance. "Total" refers to the sum of TCE, ethene and ethane produced and PCE remaining. Reaction conditions: 0.1M HEPES, pH 7, 160g/L iron 50°C.

Some of the unaccounted for material may have adsorbed onto the o-rings of the Mininert valve of the reaction bottle. In an experiment using ^{14}C-labeled TCE, which was presumed to react similarly to PCE, only 21% of the initial ^{14}C could be accounted for in the aqueous phase, headspace, and on the iron of the iron-containing bottles. A portion of the missing ^{14}C was eventually recovered as it slowly desorbed from the o-rings of the Mininert valve. It is not known whether the ^{14}C was due to TCE or to transformation products. No losses were seen in the controls containing no metal, suggesting a pressure dependent sorption effect.

Based on these observations, the reaction scheme in Eqn. 3 can be modified. Because TCE and ethene are transformation products of PCE, reductive dehalogenation is clearly taking place. However, ethane was also produced, though it is not known whether its source was an alternate dehalogenation pathway, or reduction of ethene. Some adsorption of either substrate or products seems likely. Other chemical pathways may also be occurring. These changes are depicted for PCE in Eqn. 7; note that k_{obs} is now given by $k_{obs} = k_1+k_2+k_3+k_4$.



Eqn. 7

Only a fraction of the PCE appeared to be transformed via reductive dehalogenation. Using $k_{obs} = 0.049$ day^{-1} and data from Figure 1b, k_1 and k_a were fit to Eqn. 4. (The model fit is shown as the dashed line in Figure 1b.) The results were k_1=0.024 day^{-1} and k_a=1.1day^{-1}, suggesting that 50% of the PCE was reductively

dehalogenated. The value of k_a was over an order of magnitude greater than the value (0.073±0.017 day^{-1}) obtained from an identical experiment using TCE as the substrate. This discrepancy may indicate that for TCE, which reacts faster than PCE, mass transfer limitations are significant.

Analysis of chloride (Figure 3a) showed that when ~99% of the PCE was removed, approximately two chloride ions were released per PCE transformed. This suggested either that partially dehalogenated products were formed, or that some of the chloride released complexed with iron. The initial rate of PCE disappearance was first order, but after Day 7 the rate slowed and deviated slightly from first order kinetics. This was confirmed by respiking the bottle with PCE at Day 21 (Figure 3b). The results indicate that although the rate of transformation slowed, the reaction continued. The cause of this apparent partial deactivation of iron is uncertain, but may have been related to a build up of oxides on the iron surface. In exploratory experiments, reciprocal shaking (200rpm, 0.5inch stroke length) prevented the deactivation without affecting the initial rate of PCE transformation (data not shown).

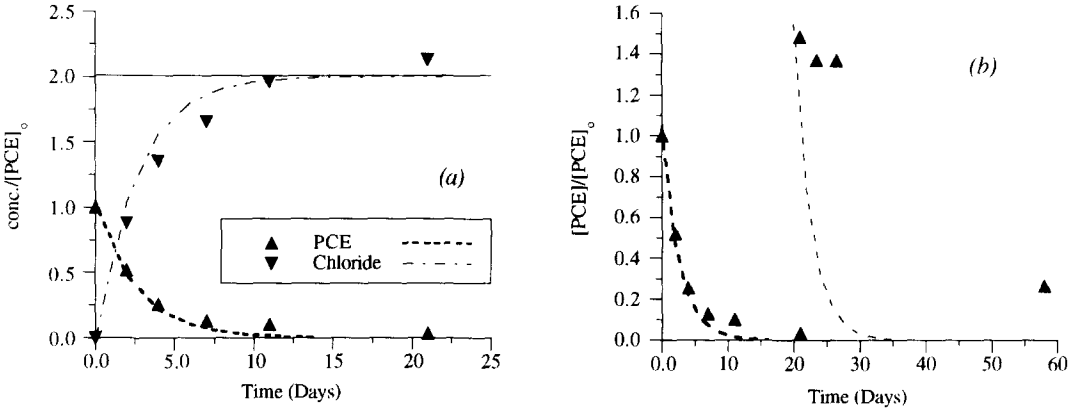


FIGURE 3. (a) Disappearance of PCE and appearance of chloride. (b) Disappearance of PCE including PCE respike at Day 21. 0.1M HEPES, pH 7, 50°C. Dashed lines are first order fits based on the initial (Day 0 to 7) rate constant for PCE disappearance..

HEPES Studies, Room Temperature

Of the six substrates tested, TCA, DCE, and PCE reacted both with iron and with manganese (Figure 4), while DCM, DCA, and DCB did not react with either metal. In the iron-containing experiment, TCA was completely transformed within 28 days. DCE and PCE were 80% and 55% removed, respectively, although the reaction ceased by Day 42. As expected from the 50°C experiment with PCE, the initial (Day 0 to Day 42) transformation rates were pseudo-first order. The initial rate constants and half-lives (obtained using only the Day 0 to Day 42 data) are listed in Table 1. The 95% confidence interval for the TCA rate was relatively large because only three data points could be used to obtain the fit.

In the manganese-containing experiment, the reactions of TCA, DCE and PCE also stopped or slowed dramatically by Day 28 to 42. In this experiment, however, both DCE and TCA were completely transformed, while only 80% of the PCE was removed. The data fit a zeroth order model better than a first order one, perhaps because manganese has fewer sites available for dechlorination than does iron. This difference may be due to inherently fewer active sites on manganese than on iron, or it may be due to greater competition between water and PCE for manganese active sites than for iron active sites. (Qualitative observations indicated that manganese reacted more rapidly with water than did iron.) The observed zeroth order rate constants in the manganese system were 0.13±0.07 $\mu Mday^{-1}$, 0.11±0.04 $\mu Mday^{-1}$, and 0.085±0.057 $\mu Mday^{-1}$ for TCA, DCE, and PCE, respectively.

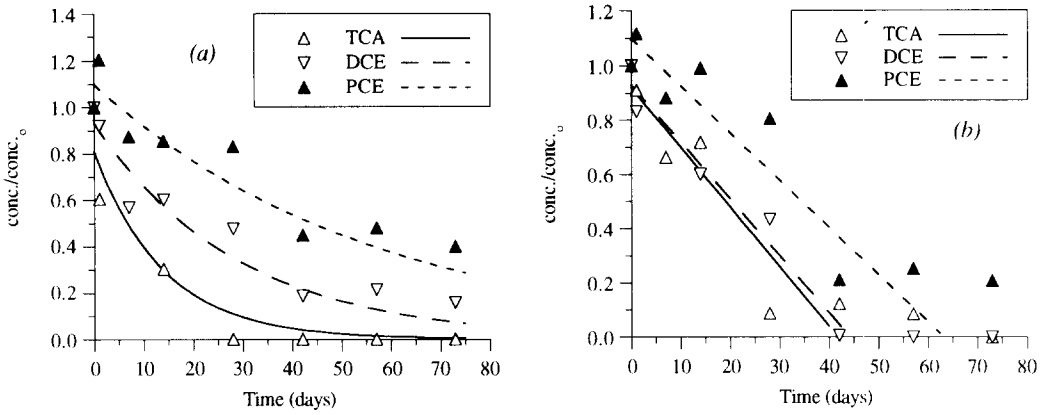


FIGURE 4. Comparison of room temperature HEPES experiment utilizing (a) 20g/L iron and (b) 10g/L manganese. Lines indicate first order and zeroth order fits for (a) and (b), respectively. DCM, DCA, and DCB did not react in these systems (data not shown).

TABLE 1. Initial Pseudo-First Order Rate Constants* and Half-lives* for the reaction of TCA, DCE, and PCE with Iron. All experiments conducted at room temperature using 20g/L iron.

	TCA		DCE		PCE	
	k_{obs}, day^{-1}	$t_{1/2}$, days	k_{obs}, day^{-1}	$t_{1/2}$, days	k_{obs}, day^{-1}	$t_{1/2}$, days
HEPES	0.07±0.3	10±40	0.035±0.016	20±9	0.018±0.012	38±25
Leachate 1	0.085±0.050	8.2±4.8	0.038±0.012	18±6	0.031±0.017	22±12
Leachate 2	0.095±0.008	7.3±0.6	0.034±0.011	20±6	0.024±0.007	28±8

* Values based on data before deactivation: Day 0 to Day 28 or 42. Error is reported as the 95% confidence interval.

The cause of the deactivation of the metals was not clear, but might have been due to a build-up of oxides caused by a lack of abrasion due to insufficient mixing, or to an increase in pH. In the iron experiment, pH rose from 7.2 at Day 0 to 7.5 by Day 28 and 8.5 by Day 57. In the manganese experiment it rose from 7.2 at Day 0 to 9.0 by Day 28. As discussed above, the reaction of PCE with iron ceased within 10 days if no buffer was used, though the effect of pH is not fully understood. It is not known why the iron was apparently completely deactivated in these experiments, but only partially deactivated in the experiment shown in Figure 3.

Leachate Experiment

Because the leachates were not sterilized prior to use, biological as well as chemical reactions could occur. Comparison of the reactivity of the two leachates in the absence of metal (Figure 5) indicated that biological transformation was not significant in L1, but may have been a major factor in L2; that is, in the former, none of the substrates was transformed, but in the latter, TCA, DCE, and PCE disappeared. All three compounds exhibited zeroth order kinetics with rate constants of 0.051±0.020μM day^{-1}, 0.042±0.012μM day^{-1}, and 0.043±0.028μM day^{-1} for TCA, DCE, and PCE, respectively.

When iron was added to the two leachates, the reactivity in both was similar to that seen for the room temperature HEPES experiment employing iron. (Compare Figure 4a and Figure 6.) Specifically, TCA was completely transformed, DCE and PCE were partially transformed, and the reaction apparently stopped after 28 days. The degree of DCE and PCE removal was similar in both the HEPES experiment and in the two leachates. The initial (Day 0 to Day 28) pseudo-first order rate constants for these three substrates are listed in Table 1. It must be noted

that although transformations in L2 in the absence of metal may have been biological, the transformations in the presence of iron appear to be abiotic. In addition, although the degree of removal of TCA and DCE was similar in L2 whether or not iron was used, the amount of PCE transformed was significantly less in the presence of iron than in its absence. Possibly the products of dissolution of iron or of impurities in the iron were toxic to the active microorganisms. The deactivation was probably not caused by an increase in pH. Although the pH rose from 7.7 to 9 in L1 and from 7.1 to 8.5 in L2 within the first seven days and was stable thereafter, the reaction stopped only after 28 days.

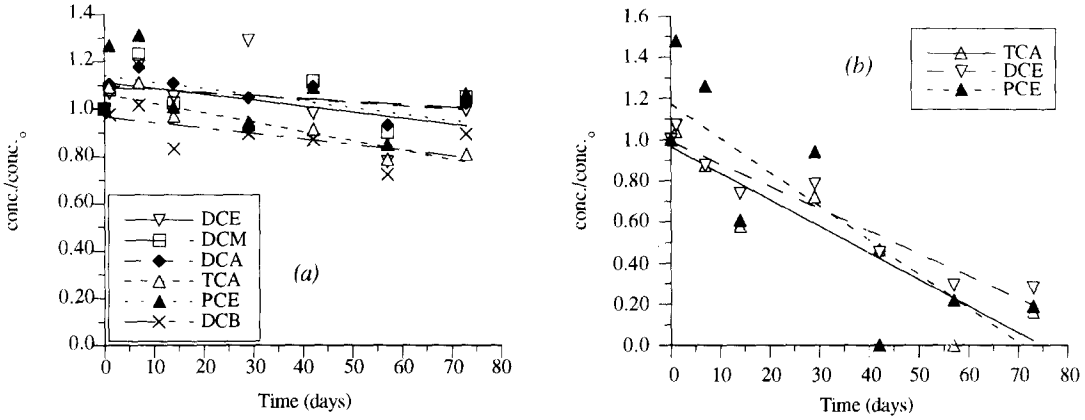


FIGURE 5. Comparison of leachate activity in the absence of metal. (a) Leachate 1. (b) Leachate 2. Lines indicate zeroth order fits. For clarity, only those substrates which reacted are shown in (b).

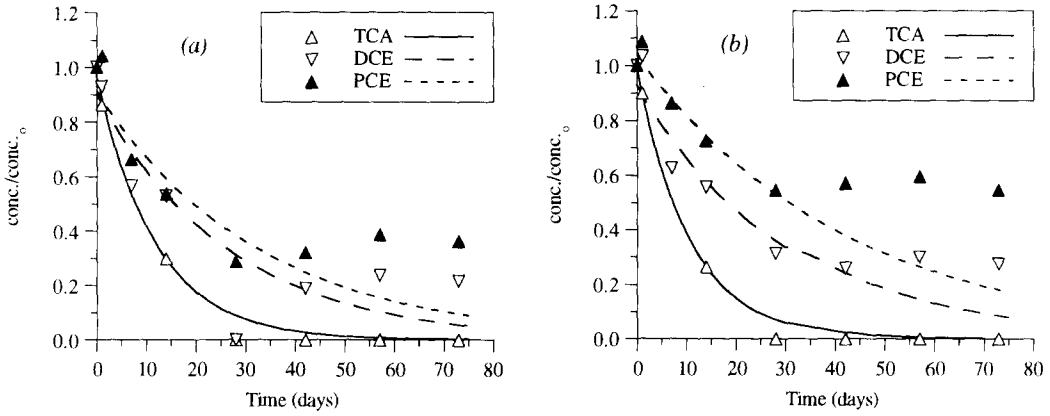


FIGURE 6. Comparison of reactivity in the presence of 20g/L iron. (a) Leachate 1. (b) Leachate 2. Lines indicate first order fits. DCM, DCA, and DCB did not react in these systems (data not shown).

The reactivity of the six substrates in the presence of manganese was similar in the two leachates (Figure 7.) Specifically, the concentration of TCA decreased, that of DCA increased, and DCM, DCE, and DCB did not react. PCE did not disappear from L1. PCE did disappear from L2, but only after a lag time of about 28 days, perhaps because the transformation was biological. The increase in DCA was not surprising since DCA is a hydrogenolysis product of TCA. The increased concentration of DCA accounted for about 85% of the TCA lost in L1 and for about

55% of the TCA transformed in L2. The rate of TCA disappearance and the rate of DCA appearance were apparently zeroth order; the rate constants are given in Table 2.

It is not known why the concentration of DCA did not increase in the HEPES experiment as it did in the leachate experiments, but differences in mechanism due to differences in pH (and, therefore, possibly manganese speciation and reactivity) is one possible explanation. Specifically, the pH fluctuated in the leachate experiments, but not in the HEPES experiment. In L1, the initial pH of 7.7 rose to 8.5, dropped to 7.5 then rose again to 9.0 over the 73 days of the experiment, while in L2 the pH increased from 7.1 to 8.5, decreased to 7.0, then rose to 8.5. In contrast, the pH of the HEPES system containing manganese steadily rose from 7.2 to 9.0 within 28 days then remained stable.

It is also not clear why DCE and PCE did not react abiotically with manganese when leachate was the aqueous phase as they did when HEPES buffer was the aqueous phase. Possibly the various anions or organic matter in the leachates reacted preferentially with the manganese, or pH adversely affected the speciation (and, therefore, the reactivity) of manganese.

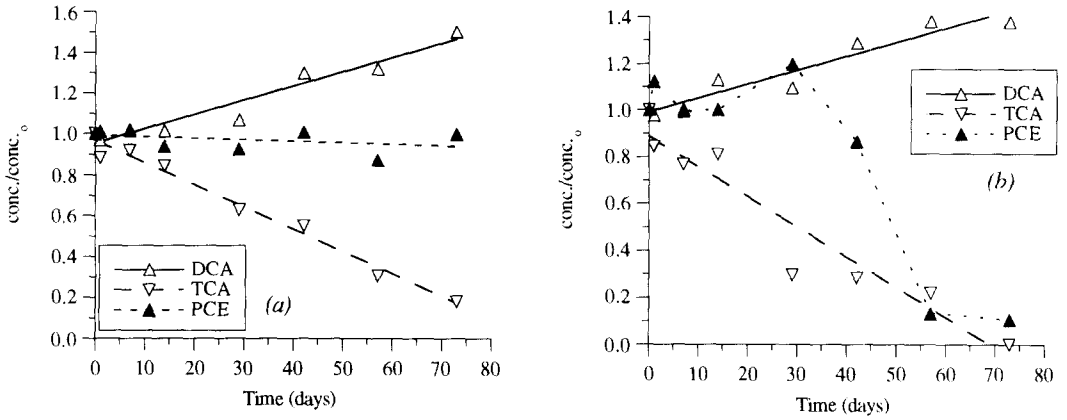


FIGURE 7. Comparison of reactivity in the presence of 10g/L manganese. (a) Leachate 1. (b) Leachate 2. Lines indicate zeroth order fits (except PCE in (b)). DCM, DCE, and DCB did not react in these systems (data not shown).

TABLE 2. Observed Zeroth Order Rate Constants* for the Reaction of TCA and DCA with Manganese. All experiments conducted at room temperature using 10g/L manganese.

	TCA, μMday^{-1}	DCA, μMday^{-1}
HEPES	0.13±0.07	0.006±0.002
Leachate 1	0.071±0.010	- 0.065±0.016
Leachate 2	0.076±0.025	- 0.054±0.015

* Error reported as 95% confidence interval.

CONCLUSIONS

PCE was transformed by iron powder in HEPES-buffered solution under abiotic, anaerobic conditions. The reaction was first order with respect to substrate with a half life of 20 days at 50°C using 4.1g/L iron. The only products were TCE, which was a reactive intermediate, and ethene and ethane, which together accounted for about 15-25% of the mass balance, but not for all of the PCE transformed. Chloride analysis showed that two chloride ions were removed per PCE transformed. Modeling suggested that 50% of the PCE reacted via reductive dehalogenation

(that is, through TCE as an intermediate) and 50% through other mechanisms. A recent experiment using ^{14}C-labeled TCE suggested that one such mechanism may be adsorption of substrate or products onto the o-rings of the Mininert valve bottle closures. This process appeared to occur only under pressure (in the presence of iron) and was not reflected in the data of the controls. A complete mass balance, relative rates of all five chlorinated ethenes, and the effect of parameters such as pH, should provide insight into additional mechanisms.

Partial iron deactivation was observed in some 50°C experiments. PCE transformation slowed (more than expected from the initial first order kinetics), but did not stop. The cause of deactivation is apparently related to mixing and possibly pH.

Of the six substrates tested in the buffered experiment at room temperature, three reacted: TCA, DCE, and PCE. TCA was completely transformed in the presence of iron, while the reactions of DCE and PCE stopped after 42 days. In the manganese experiment, both TCA and DCE were completely removed, though the rate of TCA reaction slowed after 28 days. PCE transformation stopped after 42 days. Considering only the initial (first 28-42days) rates of reaction, the kinetics of the iron experiment were apparently first order, while those of the manganese experiment were zeroth order. DCM, DCA, and DCB did not react.

Compared to the buffered experiment, the complex composition of the two leachates had little effect on the reactivity of the six substrates if iron was used, but did affect the reactivity if the metal was manganese. Specifically, in all three iron experiments TCA was completely removed, DCE and PCE transformation ceased after 28-42 days, and the initial rates of reaction were first order with respect to substrate. In the manganese experiments, however, TCA, DCE and PCE reacted in the buffered system, but only TCA was transformed in both leachates. The concentration of DCA, an apparent product of TCA transformation, increased in the leachate experiments using manganese, but, surprisingly, not in the buffered experiment using manganese.

Biological transformation, a potential factor in both leachates, was seen in L2 (but not in L1) as evidenced by the disappearance of TCA, DCE and PCE in the absence of metal. This biological activity was apparently suppressed when iron was added since the pattern and degree of substrate loss in L2 were the same as in the autoclaved HEPES experiment. When manganese was used PCE (but not DCE or TCA) was apparently biologically degraded, but only after a lag time of 28 days. The cause of the inhibitory effects of the two metals was unclear, but may have been due to possible toxicity of the dissolved metals or of pH changes.

The role of pH in these experiments was unclear. A buffer was needed to insure significant (>30%) and sustained reaction at 50°C, but the kinetics were not necessarily first-order throughout the experiment. In all three experiments with iron at room temperature, the transformations ceased abruptly by Day 28. While pH increased in these experiments, the value at the time of deactivation differed in all three cases. The potential application of these reactions for water treatment require further investigation.

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