♻EPA

Project Summary

Abiotic Reductive Dechlorination of Carbon Tetrachloride and Hexachloroethane by Environmental Reductants

Martin Reinhard, Gary P. Curtis, and Michelle R. Kriegman

The transformation rates of hexachloroethane (HCA) and carbon tetrachloride (CTET) have been measured in model systems representing the ground water environment and in slurries of fractionated Borden aquifer material. This report summarizes research conducted to identify the environmental factors which affect the abiotic (chemical) transformation rates of HCA and CTET in systems consisting of minerals and Borden aquifer material under both aerobic and anaerobic conditions The mineral systems studied consisted of both homogeneous solutions containing soluble environmental reductants and heterogeneous systems containing well characterized solids representative of mineral phases in aquifers. The following soluble reductants were used: bisulfide (HS⁻), L-cysteine, and ferrous iron complexes. Reaction rates were compared with those measured in heterogeneous systems containing biotite, vermiculite, pyrite, marcasite, or 13X zeolite and one of the dissolved reductants. Heterogeneous reaction rates were at least an order of magnitude faster than the homogeneous rates. The reductive dechlorination of hexachloroethane (HCA) to form tetrachloroethene (PCE) has been studied in the presence of aquifer material excavated from the aerobic sandy Borden aquifer. Studies with magnetically separated fractions of the aquifer material indicated that the fraction consisting of quartz, feldspars, and carbonates accounted for most of the reactivity. Studies with the acid and base pretreated quartz, feldspar, and carbonates fraction suggested that the electron donor was associated with organic matter in the aquifer solids. The addition of 20 mg/l humic acids to 0.5 mN ferrous sulfate or 0.5 mM sodium sulfide increased the rate of the reduction reaction by a factor of 15 and 7, respectively. These results suggest that the abiotic reduction reactions may be closely coupled to microbially produced reductants such as ferrous iron and sulfide.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Reductive transformations are important processes that influence the fate and mobility of certain organic pollutants in aqueous environments. In particular, in sediment-water systems, halogenated aliphatic compounds may be reductively dehalogenated to form products that may be more mobile in the environment and of either greater or lesser environmental concern. The electron donors that have been speculated to participate in these

reduction reactions in sediment-water systems include microorganisms, reduced iron complexes such as iron porphyrins, reduced iron minerals and hydroquinone functional groups in humic acid. However, the electron donor in these reduction reactions has not been identified.

The report is focused on reactions with carbon tetrachloride (CTET) and hexachloroethane (HCA), two relatively reactive substrates. HCA was selected as a model compound to investigate the properties of the electron donor of an aquifer material with respect to the reductive dechlorination because it reacts quantitatively to perchloroethene (PCE). CTET transformation was studied in model systems because it is a common environmental contaminant and is susceptible to a wider range of transformations. The purpose of this work was to further characterize the abiotic reduction of chlorinated hydrocarbons and to investigate the nature of the electron donor in natural sediment systems. The 74-125 μm size fraction of Borden sand was used as the natural aquifer material. In addition, the reactivity of possible electron donors was studied in heterogeneous model systems consisting of zeolites, sheet silicates, and iron sulfides.

The reductive transformation of HCA can be described by the following reaction:

$$\frac{1}{2}C_2Cl_6 + e^- = \frac{1}{2}C_2Cl_4 + Cl^- \quad (1)$$
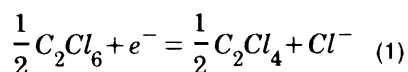
Two electrons per mole of HCA are required for this half reaction. CTET can undergo hydrogenolysis to form chloroform according to the reaction:

$$\frac{1}{2}CCl_4 + \frac{1}{2}H^+ +$$

$$e^- = \frac{1}{2}CHCl_3 + \frac{1}{2}Cl^- \quad (2)$$
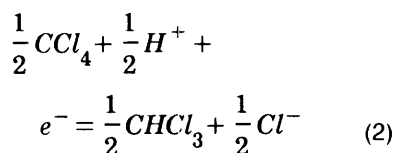
where the proton is transferred from proton donors such as aqueous H_2O or surface coordinated H_2O. In aquatic environments, the electron donors required to balance such half reactions typically involve the elements carbon, nitrogen, oxygen, sulfur, iron or manganese. For Borden aquifer material, which was used in this study, it was assumed that the electron donor was associated with the solid aquifer material. Soluble reduced forms of iron, manganese, sulfur or nitrogen were not

detected in ground water from the Borden site. The dissolved organic carbon content was less than 0.7mg/L

Calculations based on published reduction potentials or thermodynamic data showed that HCA and CTET should be spontaneously reduced by a range of environmental reductants including ferrous iron and manganese (II) minerals, humic and fulvic acids, and hydrogen sulfide. A table of redox potentials and their references are contained in the report. Some potentially important sources of ferrous iron in an aerobic aquifer include iron-bearing silicates such as biotite, hornblende, and clay minerals or iron oxides such as ilmenite or magnetite. In humic and fulvic acids, the nature of the reducing site is poorly understood due to the structural complexity and heterogeneity of these materials. It has been proposed that the electron transfer site involves functional groups such as hydroquinones or the semiquinone radicals where the semiquinone radicals are the intermediates in the reversible oxidation and reduction with quinone groups present in the humic acid.

Transformation studies with natural reference minerals, such as biotite, vermiculite, pyrite, and marcasite were conducted to see if ferrous iron in minerals could act as an electron donor to reduce the HCA and CTET. Because it would be difficult to distinguish surface transformation and mineral dissolution with subsequent transformation, systems with a synthetic mineral, 13X zeolite, were studied. 13X zeolite is an aluminosilicate with a three-dimensional cagelike pore structure which can readily exchange divalent cations, such as ferrous iron. Its hydrophilic pores allow the exchange of iron while sorbing hydrophobic haloaliphatics only weakly. This system was used as a model for ferrous iron bearing silicates, such as biotite, which contain Fe^{2+} within an aluminosilicate lattice. Zeolite experiments with ferrous iron and thiol group containing reductants allowed investigation of surface catalyzed transformations of haloaliphatics.

Experimental Methods

The work with Borden sand focused on a single size fraction with a nominal diameter range of 74 - 125 μm (U.S. Mesh 120-200). In previous studies this fraction was observed to react rapidly relative to other size fractions. The 74 - 125 μm fraction was further separated nondestructively with a magnetic mineral

separator. Magnetic mineral separation separates minerals on the basis of their magnetic susceptibility which correlates with the ferrous iron content of the mineral. Experimental results with these fractions were compared with results obtained with reference minerals. The most reactive fraction obtained by magnetic separation was treated with acid and base to investigate the properties of the electron donor with respect to treatment with acid and base. Finally, the influence of added reducing agents on the transformation rate of HCA was investigated.

All transformation experiments were conducted in flame-sealed glass ampules to prevent losses of the haloaliphatics and entrance of oxygen to the experimental systems over the time scale of the experiments (weeks to months). To minimize oxidation in the autoclave, the sediment or mineral-filled ampules were sterilized under a nitrogen atmosphere. The procedure for autoclaving under nitrogen is explained in the report. After autoclaving, ampules were placed in a glove box with a 90%N_2/10%H_2 atmosphere and were filled with a synthetic ground water or Tris buffer that was cold-sterilized with 0.2 μm polysulfone membrane filter. In the case of humic acids, an aliquot of the pH 3 humic acid extract was neutralized to pH 6.0 with NaOH and diluted with a 2.5 mM pH 5.8 phthalate buffer to give a final concentration of 20 and 40 mg/l of dissolved organic carbon (DOC). The solution was filter sterilized with a 0.2 μm nylon filter and then directly added to autoclaved ampules.

Sealed ampules were held in the dark in 50°C (±0.1°C) water bath for the duration of the experiment. Samples were regularly removed from the bath, manually mixed and returned to the bath within five minutes. At each sampling time, duplicate ampules for each experimental condition were removed from the constant temperature bath, centrifuged, extracted and analyzed for CTET or HCA and their products using a gas chromatograph equipped with an electron capture detector.

Results

Mineral Studies

Table 1 summarizes the overall rate constants (k'_{obs}) and calculated half-lives for the disappearance of HCA in homogeneous solution with and without 4 mM HS⁻; and in heterogeneous systems with biotite and vermiculite, with and

2

without HS⁻ added. The experiments were conducted at 50°C and pH 7.5 - 8. In the absence of HS⁻, HCA slowly reacted with biotite and vermiculite to form PCE. In the presence of HS⁻ the transformation rate was greatly increased (Figure 1). Similarly, Table 1 also includes k'_{obs} at 50°C for CTET disappearance in homogeneous solution with 4 mM HS⁻ and in heterogeneous systems with HS and biotite or vermiculite. Due to the slow rate of transformation of HCA at 50°C in water and in mineral systems with biotite and vermiculite (no bisulfide), the analogous rates for CTET were not measured. In experiments conducted with pyrite and marcasite, CTET was transformed very rapidly, indicating that clean iron sulfide surfaces are very reactive toward haloaliphatic compounds. These reactions support a heterogeneous mechanism because iron sulfides are extremely insoluble (with the $pK_{so} = 18.1$ for FeS). In bisulfide (Table 1) or ferrous iron (Table 2) solutions, CTET reacted much slower than in the pyrite or marcasite systems, but faster than in aqueous solution containing no reductant. In all cases, only 10-15% of the CTET reacted to form chloroform. These data clearly demonstrate that bisulfide in conjunction with solid surfaces may significantly increase the transformation rate of HCA and CTET.

To investigate the effect of an aluminosilicate structure with and without Fe^{2+}, studies with 13X zeolite were conducted. In Table 2, disappearance rates of CTET and H⁺, cysteine, or ferrous iron in homogeneous solution were compared to the same systems with 13X zeolite added. The iron concentration varied from 10^{-4}M to 10^{-3}M. In the homogeneous case where the total iron concentration was 1 mM, an iron oxyhydroxide precipitate formed. In the presence of the zeolite or when $[Fe^{2+}]_{aq}$ = 10^{-4}M, no precipitation was observed. As shown in Table 2, the system with the iron oxyhydroxide precipitate reacted much faster than the zeolite/iron systems or the 0.1 mM Fe(II) system. Interestingly, when an iron oxyhydroxide precipitate was present, the reaction with CTET was very fast (a half-life of 2 days). These studies suggest that a ferrous iron precipitate can act as an electron donor. However, the 13X zeolite structure apparently inhibited electron transfer from Fe^{2+} sorbed within the aluminosilicate structure to the organic substrate.

To test the reactivity of thio-compounds in the presence of mineral surfaces, experiments were conducted with bisulfide or cysteine and 13X zeolite. The reaction rate in cysteine/CTET systems was much faster in the presence of zeolite than in homogeneous solution. For the reactions of CTET with bisulfide and 13X zeolite, the presence of zeolite greatly enhanced the reaction rate, as observed with cysteine. The transformation rate with cysteine was faster than HS⁻ (even though the initial sulfide concentration was slightly higher than the cysteine concentration), possibly due to differences in the complexation of cysteine and HS⁻ with zeolite. These experiments suggest that mineral surfaces can act as catalysts for electron transfer reactions between haloaliphatics and environmental reductants (such as bisulfide), even if the mineral surfaces themselves are not redox active.

Aquifer Material Studies

Borden Sand Fractions

The fractions isolated by the Frantz magnetic separator are listed in Table 3 along with the extractable ferrous iron, the total extractable manganese and the organic carbon fraction (f_{oc}). The results show that the mineral fraction consisting of quartz, feldspars and carbonates accounted for the majority of transformation (data not shown). It is also clear from Table 3 that this fraction accounts for nearly 75% w/w of the unfractionated parent sample and also contains the majority of the extractable ferrous iron, total manganese and organic carbon. Therefore, the reactivity is in the fraction containing the highest concentration of the potential redox active elements but it is not possible to suggest which element plays the most significant role.

The fractions that consisted primarily of the iron bearing silicates and oxides isolated from the aquifer material, showed only a small capability to transform the HCA to PCE with the possible exception of the fraction containing predominantly ilmenite. This low relative reactivity can be attributed to the small amount of each of the individual fractions used and possibly due to a low specific surface area.

Acid and Base Extracted Fractions

The sample containing the quartz, carbonate, and feldspars was further investigated by conducting transformation studies after pretreating the minerals with either strong acid to dissolve the carbonate minerals or strong base to extract the humic acids. Each of the treated fractions was analyzed for extractable Fe^{2+} and for the f_{oc}. As expected, the extractable iron was considerably depleted in the two samples pretreated with acid while the base pretreatment decreased the f_{oc} of the fractions. The f_{oc} was reduced slightly by the base extraction and was considerably increased if the base extraction was preceded by the acid pretreatment. Presumably the organic matter that was incorporated in carbonaceous rock fragments became soluble after removal of the carbonaceous rock matrix.

The capability of the quartz, carbonate and feldspar fraction to reduce HCA to PCE was tested after carbonate dissolution with 5N HCl, humic acid extraction with 1N NaOH, and humic acid reprecipitation after carbonate dissolution. The data indicate that the electron donor is insoluble in acid and soluble in base which corresponds closely with the solubility behavior of humic acids with respect to pH. The amount of PCE formed was the greatest in the fraction that contained the largest f_{oc} and was the least in the sample with the least f_{oc}. Conversely, the amount of PCE formed was inversely related to the extractable iron concentrations. Therefore, these results suggest the participation of humic acids in the reduction of HCA.

Humic Acid Systems

The results of the transformation studies in the presence of humic acids are summarized in Table 4. In all cases, the total mass of HCA that disappeared could be accounted for as PCE with the exception of the samples that contained the humics plus the sulfide where approximately 10 percent of the added haloaliphatic could not be accounted for after two half-lives. For samples containing HS⁻, the data used in the regression were limited to samples from the first half-life of the reaction where a mass balance was observed.

The observed rate constants are summarized in Table 4. No disappearance of HCA nor formation of PCE was observed when the humic acids extracted from the aquifer materials were investigated in the absence of an added reductant. This experiment was repeated with double the initial concentration of the humic acids and with Suwannee River humic acids obtained from the IHSS. In all three cases no transformation of HCA was detected after 10 days as indicated by the rate constants reported in Table 4

Table 1 Observed Rate Constants for HCA and CTET Disappearance Temp = 50°C, pH = 7.7, [Tris(hydroxymethyl)aminomethane (Tris buffer)] = 0.01M, [Na₂S•9H₂O] = 4mM, $[CTET]_{initial}$ = 1 μm, $[HCA]_{initial}$ = 1 μm)

Experiment Name	k'_{obs} (days⁻¹)	$t_{1/2}$ (days)[a]
HCA	0.0019	290-520
HCA, Biotite[b]	0.0036	150-270
HCA, Vermiculite[b]	0.0121	41-98
HCA, HS	0.0463	9.4-37
HCA, Biotite, HS	1.0614	0.49-0.70
HCA, Vermiculite, HS	1.531	0.38-0.57
CTET	0.0018	380
CTET, HS	0.0102	69-1600
CTET, Biotite, HS	0.1541	4.2-4.9
CTET, Vermiculite, HS	0.2409	2.7-3.0
CTET, Pyrite[c]	1.586	0.17-0.71
CTET, Marcasite[d]	0.8185	0.69-1.0

[a]95% Confidence Interval around k'_{obs}.
[b]Solids concentration for biotite and vermiculite experiments was 38.5 g/L.
[c]Solids concentration for pyrite experiment was 18.1 g/L.
[d]Solids concentration for marcasite experiment was 17.3 g/L.
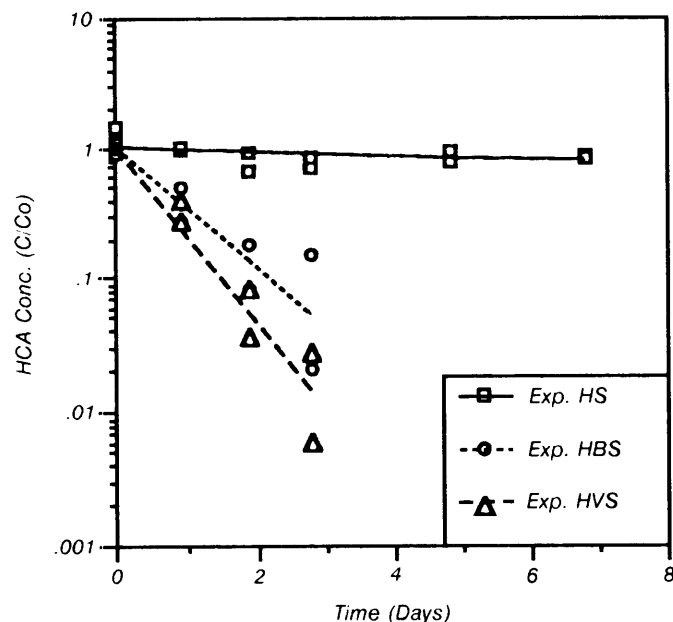
Figure 1. HCA transformation in the presence of HS-, biotite (38.5 g/L) and vermiculite (38.5 g/L) at 50°C where H = HCA, S = bisulfide, B = biotite, V = vermiculite.

that are statistically indistinguishable from zero.

When equal molar amounts of the various reductants were added to humic acid solutions containing 20 mg/l DOC, the conversion of HCA to PCE depended strongly on the reductant added. As a control, the transformation of HCA to PCE by the reductants was studied without humic acid added. The reductants were added in excess quantities relative to the initial HCA concentration, and the

Table 2. Observed Rate Constants for Disappearance of CTET (Temp = 50°C, [Tris] = 0.01 M, [Fe(II)]total = 0.1 or 1 mM, [L-cysteine] = 1 mM, [Na₂S•9H₂O] = 2-4 mM, [CTET]initial = 1 μM

Experiment Name	k'_{obs} (days⁻¹)	$t_{1/2}$ (days)
CTET, 0.1mM Fe(II)	0.0066	69-216
CTET, Zeol., 0.1mM Fe(II)	0.0026	81-∞[a]
CTET, 1mM Fe(II)(ppt)[b]	0.3023	2.0-2.6
CTET, Zeol., 1mM Fe(II)[c]	0.0014	250-∞[a]
CTET, Cysteine	0.0108	45-114
CTET, Zeolite, Cysteine	0.1375	4.1-5.2
CTET, 4 mM HS	0.0052	69-1600
CTET, Zeolite, 2 mM HS	0.0389	13-26

[a]Upper limit of the half-life is infinity because the 95% confidence interval around k'_{obs} encompasses zero.
[b]Iron oxyhydroxide precipitate.
[c]Solids concentration for zeolite experiments was 9.5 g/L.

Table 3. Characteristics of Fractions Isolated from the 74-125 μm Size Fraction of the Borden Aquifer Material

Mineralogy	Mass, %	Extractable Fe(II) (μg/g)	Extractable Mn (T) (μg/g)	f_{oc} (% gC/g)
Quartz, Feldspars & Carbonates	74.6	184 ± 19	35 ± 2	0.013 ± 0.001
Ferrodolomite	1.5	1808 ± 50	210 ± 32	0.073 ± 0.032
Hornblende	15.3	64 ± 17	7 ± 5	0.012 ± 0.001
Ilmenite	4.7	79 ± 13	n.d.[a]	0.011 ± 0.001
Garnet	3.3	62 ± 5	n.d.	0.006 ± 0.005
Magnetite	0.3	61 ± 7	12 ± 6	0.020 ± 0.007
Calculated Total	100.	180	30.3	0.014
Unfractionated Materials		203 ± 15	34 ± 5	0.015 ± 0.002

[a]Not detected.

reactivity of the reductants increased with the trend: Fe²⁺ < hydroxylamine hydrochloride < HS⁻. For hydroxylamine hydrochloride, the addition of humic acid had an insignificant effect on the transformation rate, however. In contrast, the humic-Fe²⁺ system reacted 15 times faster than with Fe²⁺ alone and humic acids increased the rate in the presence of HS⁻ by a factor of seven which corresponds to half lives of 78 and 25 hours, respectively, as indicated in Table 4. The direct comparison between humics with either Fe²⁺ or HS⁻ is not possible due to the different pH in these two experiments but clearly the rate was higher in both cases in the presence of the humic acids. Experiments with humic acid plus 0.5 mM FeCl₃ indicated that only a small amount of reaction occurred relative to the case of ferrous iron. Although the ferric hydroxide precipitated under the conditions of the experiments the results nevertheless suggest that the

iron must be added in the reduced form in order to form a reactive humic acid.

The k_{obs} of the reaction between a 1 mM solution of reduced 2,6-anthrahydroquinone-disulfonic acid (AHQDS) and HCA at pH 6.8 is also listed in Table 4. Apparently, the reduced quinone groups of AHQDS, which are assumed to model the significant redox properties of humic acids, quantitatively reduce HCA to PCE.

Discussion

Reduction by Minerals

In homogeneous solution there was an absence of significant reaction between the haloaliphatics and HS⁻, suggesting that the reaction with HS⁻ is heterogeneous. Although the exact mechanism is not known, the following three processes may be considered:

1) HS⁻ can regenerate Fe(II) sites (which may react with a sorbed haloaliphatic substrate), as shown in the reaction:

$$2[Fe^{3+},(n-1)M^+]_{mineral} + 2HS^- + 2M^+ \rightarrow HSSH + 2[Fe^{2+},nM^+]_{mineral},$$
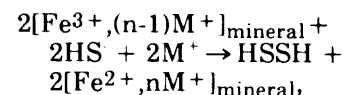
where HSSH is a polysulfide which can become further oxidized to sulfate and M⁺ is a cation removed from the solution to maintain a charge balance;

2) HS⁻ can transfer electrons to the haloatiphatic via a surface reaction which does not include ferrous iron according to the reaction:

$$2[HS^-]_{adsorbed} + HCA \rightarrow [HSSH]_{adsorbed} + PCE + 2Cl^-;$$
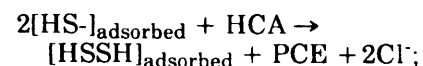
and 3) HS⁻ can react with ferrous iron which has dissolved from the minerals to form an iron sulfide precipitate. This precipitate can act as an electron donor

Table 4. Observed Rate Constants for the Transformation of HCA to PCE in Humic-Reductant Systems

System[a]	N[b]	pH	% Recovered	$k_{obs}(h^{-1}) \times 10^{-3}$	R^2
Humic Acids	7	6.0	100 ± 5	-0.0005 ± 0.0008	0.01
Humic Acids (40 mg/l DOC)	6	5.9	100 ± 1	0.0005 ± 0.0006	0.002
IHSS Suwannee River Humic Acids	8	5.6	102 ± 2	0.10 ± 0.05	0.52
$NH_2OH \bullet HCl$	6	5.4	102 ± 6	1.7 ± 0.1	0.99
Fe^{2+}	7	5.8	98 ± 4	0.59 ± 0.05	0.97
HS^-	7	8.7	93 ± 7	3.74 ± 0.7	0.85
Humic Acids + $NH_2OH \bullet HCL$	5	5.4	103 ± 4	1.84 ± 0.03	0.99
Humic Acids + Fe^{2+}	7	5.8	95 ± 7	8.92 ± 1.4	0.90
Humic Acids + $FeCl_3$	10	5.6	97 ± 4	0.36 ± 0.05	0.88
Humic Acids + HS^-	10	8.7	90 ± 5	27.0 ± 6.0	0.76
2,6-Anthrahydroquinone disulfonate	6	6.7	101 ± 7	0.27 ± 0.02	0.97

[a]Humic acids used were extracted from the Borden aquifer material and were present at 20 mg/L except as noted. All reductants and $FeCl_3$ were present at 0.5 mM.
[b]N = the number of samples used in the regression.

as was shown for ferric iron. From the results of the sheet silicate experiments described above, the presence of biotite or vermiculite, with or without bisulfide, increases the degradation rate of HCA and CTET. However, the data are insufficient to show that the reactions are truly heterogeneous because it is conceivable that the minerals are dissolving and the solutes formed are reacting with the haloaliphatics in solution.

The zeolite experiments were conducted to investigate if the sheet silicate reactions could be heterogeneous and to determine which environmental reductants are reactive in heterogeneous systems. As indicated by the experiment with the iron precipitate, ferrous iron can act as an electron donor to transform CTET. However, in the zeolite systems, ferrous iron was not reactive. Because of the hydrophilicity of the zeolite pores, it is likely that the zeolite is excluding CTET but sorbing Fe^{2+} within the zeolite structure, thereby inhibiting the electron transfer between Fe^{2+} and CTET. Assuming the zeolites are an adequate model of the sheet silicates, ferrous iron/zeolite systems may have been reactive over longer-time scales as was evident in the biotite and vermiculite systems in the absence of bisulfide. Since the thiol groups, bisulfide and cysteine, were both an order of magnitude more reactive in the presence of the zeolite surface than in solution, we can conclude that the heterogeneous transformation of CTET is more favorable. Consequently, it is possible that adsorbed bisulfide could be the electron donor in the sheet silicate systems described above (process 2).

The reactivity of CTET and iron sulfides was studied because sulfide minerals are very common in reducing environments. Both pyrite and marcasite were much more reactive than either ferrous iron or sulfide in homogeneous solution. Due to the low solubility of iron sulfides, the disappearance of CTET could not be accounted for in a homogeneous reaction. These results suggest that in the abovementioned sulfide/sheet silicate systems, a reactive iron sulfide precipitate might be forming and reacting with CTET (process 3).

In summary, the results of the mineral systems show that heterogeneous transformation of haloaliphatics is much more favorable than homogeneous transformation. Once the temperature dependence of the rates is determined, the data can be extrapolated to environmentally relevant temperatures. It is likely that these rates will be significant compared with time scales of ground water transport.

Influence of Reductants on Humic Acid

The humic acid extracted from the aquifer solids exhibited the capability to reduce HCA only after a reductant was added to the system, and even then, the reactivity depended on the reductant added. HS^- was the most effective in forming a reactive humic acid followed by Fe^{2+} while the hydroxylamine hydrochloride was ineffective as indicated in Table 4. It is plausible to assume that the Fe^{2+} or HS^- reduces a reactive site in the humic acid which in turn reduces

HCA more rapidly than the original reductant. Due to the structural complexity and heterogeneity of the humic acids, there may be several different types of reactive sites in humic acids that could be capable of reducing a halocarbon.

The observation that Fe^{2+} and the HS^- both increased the rate of reduction of HCA, but $NH_2OH \bullet HCl$ did not, is consistent with the different reactions between these three reagents and the quinone groups in humic acid. Fe^{2+} in aqueous solution rapidly reduces 1,4-benzoquinone to hydroquinone. This reduction of quinones to form hydroquinones by Fe^{2+} has been used to quantify the number of quinone groups in humic acid. Sulfide also reduces quinone groups in simple laboratory systems, and it is reasonable to assume that HS^- in aqueous solution will also reduce quinone groups in humic acid. In contrast, hydroxylamine reacts with carbonyl groups by nucleophilic addition to form the corresponding oxime. This reaction has been used to determine the total carbonyl content, which includes quinone groups plus the unconjugated carbonyl groups, of humic acids.

From this evidence, it is inferred that the hydroquinone groups in humic acids could play a central role in the reduction of HCA in these systems. This inference is supported by our observation that HCA is reduced in model systems by AHQDS. If the hydroquinone groups in humic acid are oxidized back to the original quinone group by HCA, then the humic acids would be acting as a catalyst for the reduction of HCA by Fe^{2+} or HS^-. The quinone/hydroquinone couple is

reversibly oxidized and reduced in coenzyme Q which participates in electron transport system in many biological systems and there is also evidence that humic acids can be reversibly oxidized and reduced as well.

The results from this work suggest that humic acids may be playing the unusual role in these systems as both a sorbent and a reactant. The results in Table 4 clearly indicate that humic acids increase the rate of reductive dehalogenation of HCA by Fe^{2+} and HS^-. In addition, organic matter associated with the aquifer solids, which includes humic acids, is widely accepted as being the dominant sorbent for hydrophobic organic compounds in aqueous solution. Therefore, the rate of disappearance of HCA in aquatic systems containing humic acids is likely to be enhanced because the humic acids (1) concentrate the HCA in sorbed state and (2) accelerate the reduction of HCA by Fe^{2+} and HS^-.

The observation that both Fe^{2+} and HS^- were both reactive, particularly in the presence of humic acids, is relevant to environmental systems since both Fe^{2+} and HS^- are often microbially produced in anoxic environments and therefore the reduction of HCA could be directly coupled to the microbial production of reductants such as Fe^{2+} and HS^-. Unlike typical biotransformations, where it is often assumed that sorbed compounds are unavailable for transformation, transformations involving humics may be favored by the concentrating effect of sorption to organic matter. In ground water environments with organic carbon concentrations as low 0.03%, as for the Borden aquifer, 80% of the HCA would be sorbed to the solid. Since the rates of sorption and desorption have been reported to be very slow for compounds similar to HCA, slow transformation reactions in the sorbed state may become significant relative to microbiological transformations. This coupled sorption/reduction reaction is probably most significant for the highly halogenated compounds since these compounds sorb more strongly and are expected to be reduced more rapidly.

Summary and Conclusions

Environmental factors which affect the abiotic fate of chlorinated hydrocarbon compounds under simulated ground water conditions have been studied. Specifically, the capability of fractionated Borden aquifer material, humic acid, and commercially available reference minerals to promote the transformation of HCA and CTET with and without

environmental reductants present was investigated. HS^-, L-cysteine and Fe^{2+} were used as environmental reductants. Reference minerals studied included 13X zeolite, sheet silicates (biotite and vermiculite) and iron sulfides (pyrite and marcasite).

In the studies involving reference minerals, the rate of disappearance of CTET and HCA was first order with respect to substrate concentration. The addition of sodium sulfide or L-cysteine to the experimental systems made the reactions much more reactive. The sheet silicate surfaces increased the transformation rate of CTET and HCA by approximately an order of magnitude. The iron sulfides, pyrite and marcasite, increased the reaction rate with CTET by two orders of magnitude above the rate with bisulfide or ferrous iron in solution. Although reaction rates were only measured at 50°C, the rates were fast enough such that when they are extrapolated to environmentally relevant temperatures, the transformation rates will still be appreciable, relative to ground water residence times.

For studying the reactivity of natural aquifer material, HCA was used as a test oxidant and magnetically isolated mineral fractions of Borden aquifer material. The fraction containing the majority of the organic matter and extractable iron and manganese was the most reactive fraction. Other fractions containing iron bearing minerals such as ilmenite, biotite, hornblende and magnetite were also reactive although to a lower degree. Humic acid extracted from the sediment was capable of reducing HCA only after a reductant was added and even then the reactivity depended on the reductant added. Specifically, addition of sulfide or ferrous iron increased the reactivity of the humic acids whereas hydroxylamine had no significant accelerating effect.

Based on experiments with AHQDS as a model compound, it is proposed that hydroquinone functions in the humic acid are responsible for at least part of the observed transformation of HCA. These groups are apparently reduced by Fe^{2+} and HS^- and are, in turn, apparently oxidized back to the quinones by the HCA. Humic acids in soil systems are suggested to play the role of a catalyst as they alternate between the oxidized and reduced states. The ultimate electron donor in the Borden sediment remains poorly understood, however. It is hypothesized that Fe^{2+} present in the aquifer is responsible for the reduction of the humic acids which then reduce the HCA. The finding that Fe^{2+} and HS^- both

increase the rate of the reductive dechlorination of HCA mediated by humic acids represents a direct link between abiotic reactions and microbially produced reductants.

Recommendations

This report shows that humic acid and mineral surfaces can promote the transformation of HCA and CTET, two perchlorinated alkanes. Although the study has been limited to these two substrates and to only a few reducing agents, it seems reasonable to propose that the transformation rate of a broad range of substrates may be accelerated in these systems and that other reductants, natural or synthetic, may be effective too. Decontamination of soils contaminated with chlorinated hydrocarbon compounds using chemical reductants could be feasible if the reductants can be brought in contact with the soil and if their activity within the soil matrix could be maintained. However, the transformation reactions must be understood at the mechanistic level and the effect of environmental variables on rates and product formation must be understood before efficient treatment schemes can be devised.

Chemical treatment may have several advantages over biological alternatives: (1) biological processes are generally more difficult to control than chemical ones; (2) it may be applicable at high concentrations which are toxic to microorganisms; (3) it may not depend on desorption of the contaminant which tends to be slow for hydrophobic compounds and which tends to be a rate limiting factor for bioremediation. Accordingly, the recommendations are to:
(1) develop detailed mechanistic models for mineral surface promoted transformations of chlorinated hydrocarbon compounds;
(2) develop empirical rate laws for reductive dechlorination reactions with humic acids representative of variable redox states; and
(3) study the effect of natural solid matrices on the transformation rates.
Clearly, in most natural settings, a complex interlay between chemical and biological phenomena may occur. Once a detailed picture of the chemical processes is obtained, such phenomena may be addressed.

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

EPA/600/S2-90/040