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Thermal Activation of Contaminant Degradation

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ABSTRACT: Thermal treatment technology has been used to treat contaminated soils since the mid 1980s. The applications has progressed from desorbtion to, more recently, thermal degradation. Recent laboratory studies have shown that a number of chlorinated solvents will thermally degrade at temperatures as low as 50^{o}C. Of particular interest are trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,1-trichloroethane (1,1,1-TCA). The degradation reactions appear to be surface catalyzed. The results of this research suggest that thermal degradation may be a viable treatment technology in and of itself.

INTRODUCTION

Thermal treatment technology has been used to treat contaminated soils since the mid 1980s. The technology was first applied to treat excavated soils via low temperature process was based on increasing the vapor pressure of volatile organics with increasing temperature. Thermal technology was next applied in situ (Dev, 1986), with the focus again on volatilization. As in-situ thermal remediation technologies developed, the focus initially was on enhanced recovery based on changes in the chemical or physical properties of the contaminant in response to heating, such as volatilization, (Figure 1). Chemical transformations, though postulated for natural attenuation (Vogel, 1987), were, with the exception of hydrolysis, not considered as thermal remediation pathways. Hydrolysis was considered a major pathway, for 1,1,1-TCA (Gerkens, 1989). Through the 1990s much of the focus of development was on in situ heating methods instead of on identifying pathways; the thought being that physical removal of liquids and gases were the principal treatment processes involved in thermal treatment.

Increased Volatility

Reduced Viscosity

(Slightly) Increased Solubility

Mixture of Water and Contaminants boil at lower temperature than normal contaminant boiling point

Increased hydrolysis rates

Thermal processes less affected by heterogeneity

FIGURE 1. Beneficial effects of increased temperature.

In the late 1990s, the focus of the development of thermal technology began to shift towards a more mechanistic approach. There was an increased focus on destructive processes driven by the application of thermal treatment to low-volatility contaminants, such as creosote at the Visalia Pole Yard (Davis, 1997). Steam was initially applied at Visalia to mobilize and recover free product. However, it was discovered that the steam also promoted the oxidation of the PAHs. The process was termed "hydrous pyrolysis/oxidation (HPO)" (Leif, 1997). HPO is a direct oxidation reaction yielding carbon dioxide as the product. A second destructive process also discovered at this time was thermophilic biodegradation. Thermophiles are aerobic bacteria that thrive at elevated temperatures and are capable of the rapid degradation of hydrocarbons.

Groundwater results from six-phase heating projects have demonstrated that a range of volatile organic compounds will thermally degrade at temperatures of 50–80°C (Heath, 2001). The loss of these compounds was due to hydrolysis or other chemical reactions and not simple volatilization.

More recently, RF heating was applied to a fractured bedrock aquifer for the purpose of promoting the hydrolysis and dehydrohalogenation of 1,1,1-TCA (Brody, 2004). After nine months of treatment at 50°C, the TCA was reduced by more than 80%.

Several key questions in the continued development of thermal treatment technology are (1) the response of many common VOCs to elevated temperatures, and (2) can thermal degradation be enhanced by a controlled program of heating? The first question focuses on which VOCs degrade and which are stable. The second question is at which temperature(s) does thermal degradation occur for a given compound?

METHODOLOGY

Sealed 40 mL VOA bottles were used for the studies. A stock solution containing a mixture of VOCs was added to the VOA bottles to give a concentration of 10,000 to 20,000 µg/L of each of the compounds studied. The VOAs were filled so that there was no headspace. A “Time = 0” VOA, or a control was also run. A mixture of chloroethenes, chloroethanes, chloromethanes, chlorobenzenes, and BTEX compounds was studied. The VOAs were placed in an incubator set at the appropriate temperature. After the desired time, the VOAs were removed from the incubator, allowed to cool, and analyzed for residual VOCs by Purge & Trap GCMS.

Two sets of experiments were run. In the first set, the temperature was varied but the time was not. The VOAs were analyzed after 20 days. The temperatures studied were 20, 35, 45, and 55°C. The 20°C experiments serve as a control, all of the VOCs which were spiked are considered stable at 20°C. Therefore, any losses observed at 20°C may be considered to be due to volatilization and/or handling. In the second set of experiments, the VOAs were heated to 45°C and analyzed at one, two, and four weeks. A VOA was sacrificed at each time point. Three sub-conditions were run. In the first, only spiked DI water was used. In the second, sand was added to the spiked DI water to test for surface catalysis effects. The third subset consisted of DI water spiked with a single, select compound. The results are discussed in reference to the initial concentration as measured in a “time-zero” test bottle.

All the results are expressed as percent loss versus a control or an initial level. The concentrations were converted to milli-moles per liter, by dividing the concentration by the molecular weight. This “normalizes” the data making it easier to compare between compounds.

RESULTS AND DISCUSSION

As will be discussed, significant losses were observed for a number of the compounds studied. Before the results are discussed, an important question needs to be answered, “What proof is there that the loss was due to degradation and not volatile loss through the septum of the VOA?”

Validity of Results. If the losses are due to leakage of VOCs through the septum, then there should be a strong correlation between the percent loss observed and the vapor pressure of the compound. Table 1 provides an analysis of the percent loss (relative to the 20^{o}C concentrations after 20 days) and the vapor pressures of the various VOCs. The nine VOCs with the highest vapor pressures are listed in Table 1a. The correlation between the percent loss observed and the vapor pressure of these nine VOCs was very low: 0.42 at 35^{o}C, 0.14 at 45^{o}C, and 0.12 at 55^{o}C. If volatile loss (leakage) were a significant factor, one would expect the correlation between vapor pressure and percent loss to increase with increasing temperature since vapor pressure increases with increasing temperature.

Methylene chloride, chloroform, 1,1-DCA, 1,2-DCA, and 1,1,2-TCA were the five VOCs that consistently had the lowest % loss (Table 1b.). These VOCs appear to be non-degradable at the temperatures studied. A correlation between the vapor pressure of these five compounds and their percent loss does show that the small loss observed was probably due to volatile leakage through the septum. The correlations were 0.82 at 35^{o}C, 0.79 at 45^{o}C, and 0.78 at 55^{o}C. Based on these results, one may conclude that there is a slow leakage of volatile compounds through the septum. The percent loss for the most volatile of the non-degradable VOCs can be used for a threshold value to assess whether

TABLE 1. Analysis of percent loss and. vapor pressure for 14 VOCs.

Table 1a: Correlation between VP and % Loss

	VP	% Loss @ Temperature		
		35°C	45°C	55°C
1,1-Dichloroethene	495.0	24.1	39.2	61.7
Methylene Chloride (DCM)	350.0	6.8	11.7	21.2
t-1,2-Dichloroethene	265.0	39.9	64.0	84.4
1,1-Dichloroethane	234.0	4.8	11.4	19.0
c-1,2-Dichloroethene	200.0	12.4	23.1	36.9
Chloroform (CF)	160.0	5.1	12.5	20.8
1,1,1-Trichloroethane	100.0	16.9	61.6	97.6
Benzene	95.0	7.4	16.8	29.6
1,2-Dichloroethane	87.0	3.6	7.9	16.0
Correlation: High VP vs % Loss		0.41	0.14	0.12

Table 1b: Examination of VP effect on Non-Degradable VOCs ("Bottom 5")

	VP	% Loss @ Temperature		
		35°C	45°C	55°C
Methylene Chloride (DCM)	350.0	6.8	11.7	21.2
Chloroform (CF)	160.0	5.1	12.5	20.8
1,1-Dichloroethane	234.0	4.8	11.4	19.0
1,2-Dichloroethane	87.0	3.6	7.9	16.0
1,1,2-Trichloroethane	19.0	-4.3	2.0	3.4
Correlation: % Loss - "Bottom 5" vs VP		0.82	0.78	0.79

thermal degradation is occurring. Methylene Chloride is the most volatile of the non-degradable VOCs. It has a vapor pressure of 350 mm Hg at 20^{o}C. At 35^{o}C, the percent loss was 6.8%; at 45^{o}C, 11.7%; and at 55^{o}C, 21.2%. It should be noted that thermal degradation of DCM may also be occurring; it has been reported from field data. However it is not possible to quantify how much of the loss of DCM is due to volatile leakage and how much is due to thermal degradation. For the purposes of discussion of the results of the studies presented in this paper, it will be assumed that all of the loss for the non-degradable VOCs is due to volatile leakage. Therefore, any loss observed for a VOC that is greater than the percent loss observed for DCM will be considered a valid indication of thermal degradation.

Effect of Temperature on the Extent of Degradation. Table 2 and Figure 2 summarize the results. The VOCs are listed in decreasing order of the percent loss for each temperature. The "Bottom 5" VOCs (discussed above) are highlighted in gray. Any percent loss greater than the percent loss observed for these VOCs is considered a valid indication of thermal degradation. This value is a "threshold" value. The threshold is 6.8% at 35^{o}C, 12.5% at 45^{o}C, and 21.2% at 55^{o}C (see Figure 2).

Several observations can be made from these data. First, there is a wide range of VOCs that thermally degrade. Sixteen of the twenty-one compounds studied showed evidence of degradation. Second, a number of VOCs show degradation loss greater than 75% at 55^{o}C in 20 days. These include 1,1,1-TCA, PCE, 1,2,4-trichlorobenzene, trans-1,2-DCE, TCE, and 1,3-Dichlorobenzene. Third, the order of the VOCs, based on their percent loss, does not change significantly with increasing temperature. The only exception to this observation is 1,1,1-TCA, which shows a marked increase in percent

TABLE 2. Loss compared to concentration at 20°C, 20 days reaction.
Results listed in decreasing order of percent loss.

Temperature	35°C		45°C		55°C
Tetrachloroethene	52.7	Tetrachloroethene	78.9	1,1,1-Trichloroethane	97.6
t-1,2-Dichloroethene	39.9	1,2,4-Trichlorobenzene	74.3	Tetrachloroethene	95.0
1,2,4-Trichlorobenzene	35.9	t-1,2-Dichloroethene	64.0	1,2,4-Trichlorobenzene	91.7
1,3-Dichlorobenzene	33.6	1,1,1-Trichloroethane	61.6	t-1,2-Dichloroethene	84.4
Trichloroethene	27.0	1,3-Dichlorobenzene	61.5	1,3-Dichlorobenzene	83.2
1,1-Dichloroethene	24.1	Trichloroethene	54.1	Trichloroethene	76.9
m,p-Xylene	21.4	m,p-Xylene	45.4	m,p-Xylene	67.8
1,1,1-Trichloroethane	16.9	1,1-Dichloroethene	39.2	1,1-Dichloroethene	61.7
Ethylbenzene	16.8	Ethylbenzene	38.9	Ethylbenzene	61.0
Chlorobenzene	13.7	1,2-Dichlorobenzene	35.2	1,2-Dichlorobenzene	54.3
1,2-Dichlorobenzene	13.3	Chlorobenzene	33.6	Chlorobenzene	53.1
c-1,2-Dichloroethene	12.4	o-Xylene	29.4	o-Xylene	48.5
o-Xylene	10.8	Toluene	28.8	Toluene	48.4
Toluene	9.7	c-1,2-Dichloroethene	23.1	Carbon Tetrachloride	37.5
Benzene	7.4	Carbon Tetrachloride	19.0	c-1,2-Dichloroethene	36.9
Carbon Tetrachloride (CT)	7.0	Benzene	16.8	Benzene	29.6
Methylene Chloride (DCM)	6.8	Chloroform	12.5	Methylene Chloride	21.2
Chloroform (CF)	5.1	Methylene Chloride	11.7	Chloroform	20.8
1,1-Dichloroethane	4.8	1,1-Dichloroethane	11.4	1,1-Dichloroethane	19.0
1,2-Dichloroethane	3.6	1,2-Dichloroethane	7.9	1,2-Dichloroethane	16.0
1,1,2-Trichloroethane	-4.3	1,1,2-Trichloroethane	2.0	1,1,2-Trichloroethane	3.4

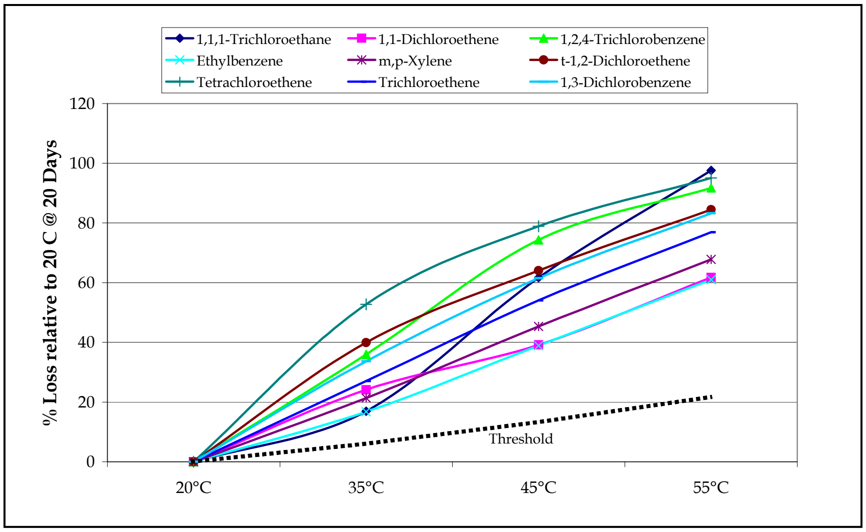


FIGURE 2. Percent loss as a function of temperature.

loss with increasing temperature. At 35^{o}C, 1,1,1-TCA has a percent loss of 16.9 and its rank is eighth; at 45^{o}C, the percent loss is 61.6% and its rank is fourth, and at 55^{o}C the percent loss is 97.6%, and its rank is first. As shown on Figure 2, 1,1,1-TCA and 1,2,4-TCB is the only VOC that shows a change in its relative ranking in terms of percent loss. This suggests that 1,1,1-TCA and 1,2,4-TCB may degrade by a different mechanism(s) than the other VOCs.

Loss over Time at Constant Temperature. Table 3 presents the data for the percent loss of the target VOCs compared to their initial concentration, at 45^{o}C over a four-week period. The results listed in Table 3 are for a water-only study. The results are listed in decreasing order of the percent loss. The "bottom 5" are highlighted in grey. Any loss greater than the maximum 6.7% loss observed for these non-degradable VOCs is a valid indication of thermal degradation.

TABLE 3. Percent loss at 45°C, aqueous phase, no sand.

Water	1 week		2 week		4 week
1,1,1-trichloroethane	31.6	tetrachloroethene	57.9	tetrachloroethene	80.5
tetrachloroethene	31.6	trans-1,2-dichloroethene	52.0	1,1,1-trichloroethane	74.7
1,2,4-trichlorobenzene	24.1	1,2,4-trichlorobenzene	51.9	1,2,4-trichlorobenzene	60.8
trans-1,2-dichloroethene	24.0	1,1,1-trichloroethane	47.4	trans-1,2-dichloroethene	60.0
1,3-dichlorobenzene	23.1	1,3-dichlorobenzene	41.5	1,3-dichlorobenzene	57.7
trichloroethene	17.4	trichloroethene	39.1	trichloroethene	56.5
m,p-xylene	14.9	m,p-xylene	29.7	m,p-xylene	47.3
toluene	14.3	toluene	21.4	ethylbenzene	36.4
ethylbenzene	14.3	ethylbenzene	21.4	chlorobenzene	33.3
1,2-dichlorobenzene	11.1	1,1-dichloroethene	18.1	1,1-dichloroethene	29.2
chlorobenzene	11.1	1,2-dichlorobenzene	16.7	1,2-dichlorobenzene	22.2
o-xylene	9.1	chlorobenzene	16.7	toluene	21.4
cis-1,2-dichloroethene	8.3	o-xylene	13.6	carbon tetrachloride	20.8
carbon tetrachloride	8.3	cis-1,2-dichloroethene	8.3	o-xylene	18.2
1,1-dichloroethene	8.3	carbon tetrachloride	8.3	cis-1,2-dichloroethene	16.7
benzene	7.1	benzene	7.1	benzene	7.1
methylene chloride	6.7	methylene chloride	6.7	methylene chloride	6.7
1,1-dichloroethane	5.6	1,1,2-trichloroethane	5.7	chloroform	4.5
1,2-dichloroethane	4.3	1,2-dichloroethane	4.3	1,2-dichloroethane	4.3
chloroform	0.0	1,1-dichloroethane	0.0	1,1-dichloroethane	-5.6
1,1,2-trichloroethane	-2.9	chloroform	0.0	1,1,2-trichloroethane	-5.7
Median	11.1	Median	16.7	Median	22.2

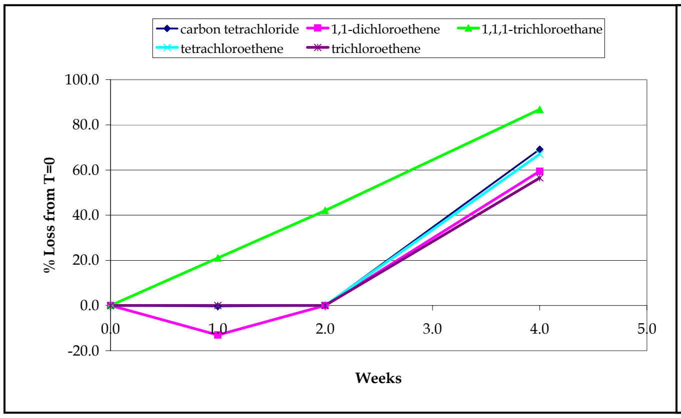
The five VOCs that had the highest loss after 4 weeks were tetrachloroethene (PCE); 1,1,1-TCA; 1,2,4-trichlorobenzene, trans-1,2-dichloroethene, and 1,3-dichlorobenzene. The five VOCs that show the greatest increase in percent loss (based on the ratio of the four week results to the 1 week results) over the four week period are tetrachloroethene (2.6, ratio 4 Wk:1 Wk), chlorobenzene (3.0), m,p-xylene (3.2), trichloroethene (3.3), and 1,1-dichloroethene (3.5).

Effect of Surface Area on Thermal Degradation. A second set of experiments were conducted with the mixture of VOCs at 45^{o}C in which sand was added to the VOAs to determine if there was any surface-catalysis of the thermal degradation reactions. Table 4 presents the data for the percent loss of the target VOCs compared to their initial concentration, at 45^{o}C over a four-week period. The results are listed in decreasing order of the percent loss. The “bottom 5” are highlighted in grey. Any loss greater than the maximum 22.7% loss (at 4 weeks) observed for these non-degradable VOCs is a valid indication of thermal degradation. One interesting observation from this data is that, with the exception of 1,1,1-TCA, there appears to be a significant lag phase in the degradation of these VOCs; there was virtually no loss observed at one and two weeks. This lag phase, while unusual, is not without precedence. A lag phase has been observed previously for thermally activated persulfate oxidation (Bruell, 2001) with soil present, while the aqueous phase reaction showed no lag phase. This is pictured in Figure 3, which shows the percent loss over four weeks for the five VOCs with the greatest percent loss. The 1,1,1-TCA shows a steady loss over time.

Once the lag phase is over, the other VOCs show a very substantial degradation. One other interesting observation is that the level of 1,1-DCE shows a net increase at 1 week compared to its initial level. 1,1-DCE is produced from 1,1,1-TCA by dehydrohalogenation, the loss of HCl. Since 1,1,1-TCA does not have a lag phase and produces 1,1-DCE from the beginning, 1,1-DCE shows a net accumulation during its lag phase.

TABLE 4. Percent loss at 45°C; sand added.

Water & Sand	1week		2 week		4 week
1,1,1-trichloroethane	21.1	1,1,1-trichloroethane	42.1	1,1,1-trichloroethane	86.8
1,1,2-trichloroethane	5.6	trans-1,2-dichloroethene	8.7	carbon tetrachloride	69.2
1,2-dichlorobenzene	0.0	1,2,4-trichlorobenzene	1.4	tetrachloroethene	67.1
toluene	0.0	1,1,2-trichloroethane	0.0	1,1-dichloroethene	59.4
chlorobenzene	0.0	1,2-dichloroethane	0.0	trans-1,2-dichloroethene	56.5
1,3-dichlorobenzene	0.0	1,2-dichlorobenzene	0.0	trichloroethene	50.0
ethylbenzene	0.0	toluene	0.0	ethylbenzene	42.9
trichloroethene	0.0	chlorobenzene	0.0	m,p-xylene	41.4
trans-1,2-dichloroethene	0.0	1,3-dichlorobenzene	0.0	1,3-dichlorobenzene	35.0
carbon tetrachloride	-4.2	ethylbenzene	0.0	benzene	28.6
1,2,4-trichlorobenzene	-4.3	trichloroethene	0.0	o-xylene	28.6
1,2-dichloroethane	-4.3	tetrachloroethene	0.0	1,1-dichloroethane	27.8
chloroform	-4.5	carbon tetrachloride	-4.2	chlorobenzene	27.8
1,1-dichloroethane	-5.6	chloroform	-4.5	toluene	26.2
m,p-xylene	-5.7	1,1-dichloroethane	-5.6	1,2,4-trichlorobenzene	25.7
tetrachloroethene	-5.9	methylene chloride	-7.1	cis-1,2-dichloroethene	24.2
methylene chloride	-7.1	benzene	-7.1	chloroform	22.7
benzene	-7.1	m,p-xylene	-7.1	1,2-dichlorobenzene	16.7
cis-1,2-dichloroethene	-8.3	cis-1,2-dichloroethene	-8.3	1,2-dichloroethane	13.0
o-xylene	-9.5	o-xylene	-9.5	methylene chloride	7.1
1,1-dichloroethene	-13.0	1,1-dichloroethene	-18.8	1,1,2-trichloroethane	-19.4
Median	-4.3	Median	0.0	Median	28.6



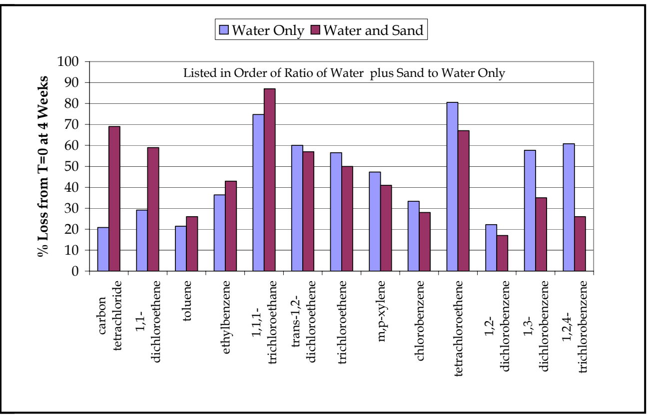


FIGURE 3. Percent degradation over time; sand present.

FIGURE 4. Effect of added sand on degradation.

Figure 4 compares the percent loss observed between the initial concentration and that after four weeks for the target VOCs under two conditions—(1) with water only and (2) with sand added. The VOCs are organized left to right in decreasing order of the ratio between percent loss when water and sand are present and that when only sand is present. Two VOCs, carbon tetrachloride and 1,1-DCE, show very substantial differences (increases) between the percent loss when sand is present and that when sand is not present. Three other VOCs—toluene; ethylbenzene, and 1,1,1-TCA—show moderate increases. The rest of the VOCs show decreases. For most of those the decrease is slight, but for four it is significant— tetrachloroethene , the two dichlorobenzenes (1,2- and 1,3-), and 1,2,4-trichlorobenzene. These results suggest that there is a variety of degradation mechanisms and that there is a surface effect for some of the VOCs.

Single Compound Study. As a follow-up to the degradation study at 45°C, individual VOCs were monitored over four weeks. The purpose of this study was to determine if any other VOCs were formed by the thermal degradation. The other studies were conducted with a mixture of 21 different VOCs. It is difficult to determine if there is any transformation of a VOC into a different VOC—for example, PCE thermally degrading to TCE. Table 5 presents data for six VOCs—PCE, TCE, 1,1,1-TCA, cis-1,2-DCE, trans-1,2-DCE, and 1,3-dichlorobenzene. The test bottles were analyzed at 1, 2, and 4 weeks using GCMS. As can be seen from the data, no VOCs other than the parent compound were detected for any of the VOCs studied other than 1,1,1-TCA. (With 1,1,1-TCA degradation, 1,1-DCE was formed. That amount of 1,1-DCE formed represents about 10% of the original 1,1,1-TCA molar concentration.) Table 5 also provides the percent loss relative to initial concentrations for each of the VOCs in the VOC mixture. With the exception of cis-1,2-DCE, there were good agreements between the percent-loss results for the single compound and those for the VOC mixture. Thus, it may be concluded that there is no synergistic effect due to the presence of other VOCs. This study suggests that, with the exception of 1,1,1-TCA, the likely mechanism is hydrolysis, which forms small carboxylic acids such as acetic acid and ultimately carbon dioxide.

TABLE 5. Thermal degradation of single compounds.

VOC Added	Condition	% Loss at			Compound(s) Detected - GCMS
		1 week	2 week	4 week	
Trichloroethene	*Single VOC*	12	32	68	trichloroethene
	VOC Mix	17	39	57	
Tetrachloroethene	*Single VOC*	36	50	81	tetrachloroethene
	VOC Mix	32	58	81	
1,1,1-Trichloroethane	*Single VOC*	21	42	71	1,1,1-trichloroethane
	% Formed	6	10	12	1,1-dichloroethene
	VOC Mix	32	47	75	
t-1,2-Dichloroethene	*Single VOC*	31	42	100	trans-1,2-dichloroethene
	VOC Mix	24	52	60	
c-1,2-Dichloroethene	*Single VOC*	13	6	66	cis-1,2-dichloroethene
	VOC Mix	8	8	17	
1,3-Dichlorobenzene	*Single VOC*	28	48	74	1,3-dichlorobenzene
	VOC Mix	23	42	58	

Degradation Mechanisms. The data strongly support the applicability of thermal degradation to a wide range of VOCs, both chlorinated and non-chlorinated. The question is, what are the mechanisms that would account for the widespread response to heat? There are basically three types of reactions that are possible—oxidation, reduction, and no-electron-transfer reactions such as hydrolysis, dehydrohalogenation (loss of HCl) (Vogel, 1987).

In the laboratory studies conducted, the amount of oxidant (dissolved oxygen) was limited. There were no reductants present. As a result, the most likely mechanism was hydrolysis. Hydrolysis has been studied as a ubiquitous mechanism for the degradation of a wide range of VOCs (Washington, 1995). Most of the chlorinated solvents hydrolyze to acetic acid. Other reactions such as dehydrohalogenation, loss of HCL, may also play a role in thermal degradation. Dehydrohalogenation is a primary degradation mechanism for 1,1,1-TCA yielding 1,1-DCE. It may occur for other chlorinated compounds such as 1,2-DCA and 1,1-DCA, yielding vinyl chloride, which rapidly hydrolyzes. For the non-chlorinated aromatics, hydrolysis most likely yields low molecular weight carboxylic acids (2 to 4 carbons) such as adipic acid, oxalic acid, and acetic acid. Other degradation mechanisms such as oxidation or reduction can occur at elevated temperatures, using dissolved oxygen or oxidized minerals, such as iron.

CONCLUSIONS

The laboratory studies discussed above demonstrate that thermal degradation is an important degradation pathway for groundwater remediation. Several conclusions can be drawn from the data presented.

1. Thermal degradation occurs for a wide variety VOCs: both chlorinated and non-chlorinated.
2. Thermal degradation occurs at relatively modest temperatures.
3. The response to thermal degradation is highly varied. The VOCs most susceptible to thermal degradation are 1,1,1-TCA; carbon tetrachloride; 1,1-DCE; PCE; 1,3-dichlorobenzene; 1,2,4-trichlorobenzene; and TCE. The VOCs most resistant to thermal degradation are chloroform; 1,1-DCA; 1,2-DCA; methylene chloride; and 1,1,2-TCA.

4. Surface catalysis appears to be important for several VOCs: 1,1-DCE and carbon tetrachloride in particular.
5. The mechanisms of degradation are not well understood. Hydrolysis appears to be the most likely mechanism.

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