7. Organics: Solvents

- US Solvent Occurrence (NAWQA)
- Review of Biodegradation Processes
- CS-10 plume, MMR, Cape Cod, MA
- Kings Bay, GA, Landfill site
- Plattsburgh, NY, Air Force Base
- Assessment of 55 VOCs, collected from ~2,400 domestic and ~1,100 public wells.
- About 20% of ground water contained one or more of 55 VOCs, at an assessment level of 0.2 μg/L.
- VOC concentrations and total VOC concentrations generally were low (< 1 μg/L).
- 90% of the total analyzed VOCs in samples were < 1 μg/L.
Most frequently detected VOCs

- 42 VOCs were detected in aquifer samples, only 15 occurred in 1% or more of the samples.

- These include:
  7 solvents (PCE, TCE), 4 trihalomethanes (THM), 2 refrigerants, 1 gasoline oxygenate (MTBE), and 1 gasoline hydrocarbon (Toluene).

<table>
<thead>
<tr>
<th>Compound name</th>
<th>VOC group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>Perchloroethene</td>
<td>solvent</td>
</tr>
<tr>
<td>Methyl \textit{tert}-butyl ether</td>
<td>gasoline oxygenate</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>solvent</td>
</tr>
<tr>
<td>Toluene</td>
<td>gasoline hydrocarbon</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>refrigerant</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>solvent</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>solvent</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>refrigerant</td>
</tr>
<tr>
<td>Bromoform</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>\textit{trans}-1,2-Dichloroethene</td>
<td>solvent</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>solvent</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>solvent</td>
</tr>
</tbody>
</table>
- Twelve (12) VOCs were detected in more than 1 percent of the samples, and 3 other VOCs at slightly less than 1 percent.
- VOC detection frequencies were larger at an assessment level of 0.02 μg/L than at an assessment level of 0.2 μg/L.
Concentrations for the 15 most frequently detected VOCs ranged from about 0.002 to about 350 μg/L; most were less than about 1 μg/L. PCE and TCE have MCLs of 5 μg/L.
- PCE, TCE, Methylene Chloride, and Vinyl Chloride were all solvents found at concentrations levels that exceeded a human health standard.
- Detection of the most frequently detected VOCs were greater in samples from public wells than from domestic wells (at 0.2 μg/L).
- Mixtures of 2 or more of the 55 VOCs were found in about 13 percent of the public well samples—more than three times greater than in domestic well samples.
VOC concentrations at potential human-health concern in public well samples occurred predominantly in the highly populated areas of southern California and the Northeast US.

Solvents accounted for about 85 percent of these concentrations.
MTBE, a gasoline oxygenate, was one of the most frequently detected VOC in samples from domestic and public wells.

- Detection of MTBE is likely due to higher solubility, lower sorption, and greater persistence in ground water relative to other hydrocarbons.

- Production of MTBE increased markedly from 1985 to about 1999, however, because of concerns about the occurrence of MTBE in water supplies, it has since declined.

**Figure 29.** The annual production rate of methyl tert-butyl ether (MTBE) in the United States generally has increased until 1999, but has since decreased.
Figure 30. Most detections of methyl tert-butyl ether (MTBE) are in the highly populated New England and Mid-Atlantic States.\textsuperscript{(15,113)}
Explaining VOC contamination in aquifers is complex—VOC occurrence is determined not only by sources but also by natural and anthropogenic factors that affect the transport and fate of VOCs in aquifers.

<table>
<thead>
<tr>
<th>Factors most commonly associated with VOCs in aquifers</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Septic systems</td>
</tr>
<tr>
<td>• Urban land</td>
</tr>
<tr>
<td>• Resource Conservation and Recovery Act (RCRA) hazardous-waste facilities</td>
</tr>
<tr>
<td>• Gasoline storage and release sites</td>
</tr>
<tr>
<td>• Climatic conditions</td>
</tr>
<tr>
<td>• Hydric (anoxic) soils</td>
</tr>
<tr>
<td>• <strong>Dissolved oxygen in ground water</strong></td>
</tr>
<tr>
<td>• Type of well</td>
</tr>
<tr>
<td>• Depth to top of well screen</td>
</tr>
</tbody>
</table>
Some VOCs (TCA, chloroform, and PCE), were detected more frequently in oxic ground water than in anoxic ground water. Other VOCs, (methylene chloride and chloromethane), were more frequently detected in anoxic ground water.

Figure 10. The occurrence of most VOCs was dependent on dissolved-oxygen conditions in ground water at an assessment level of 0.02 microgram per liter.
- Ratios of PCE to TCE were three times larger in oxic ground water compared to anoxic groundwater.

* PCE was detected in about 13 percent of samples from oxic ground water, but in only about 6 percent of samples from anoxic groundwater.
VOC Production rates don't fully explain VOC detection frequencies, for example, total fuel hydrocarbon production is much greater than other classes of VOCs (note log scale!).
Figure 23. Production of most solvents in the United States began declining as early as the 1970s.\textsuperscript{(3, 89, 90)}
During biodegradation, contaminants can serve as electron donors (e.g., benzene, DCE, VC) or as electron acceptors (e.g. PCE, TCE, DCE, VC) for microbial respiration, a process that yields energy for metabolism and growth.
Reductive Microbial Degradation:

- Chloroethene compounds display a considerable reaction variability under different (varying) reduction-oxidation (redox) conditions.

- The most frequently occurring two-solvent mixture at contamination sites, PCE–TCE, probably represents the degradation of PCE to TCE.

- PCE and TCE are highly oxidized compounds that readily degrade anaerobically (reductive dechlorination), in which chlorine is sequentially replaced by hydrogen to yield dichloroethylene (DCE) and vinyl chloride (VC).
In reductive dechlorination of PCE, a chlorine atom is replaced by a hydrogen atom, producing TCE; this reaction is mediated by microbes under anoxic conditions.

(Zorgorski, 2006)
- PCE, with four chlorine atoms, is a stronger oxidant than all of the naturally occurring TEA species found in groundwater systems, except for O_2 (and NO_3?).
- Thus, PCE readily undergoes reductive dechlorination to TCE, except in aerobic aquifers.
- Reductive dechlorination of TCE to cis-DCE occurs under Fe(III)-reducing conditions and in more strongly reducing environments.
- Reductive dechlorination of cis-DCE to yield VC appears to be favored under SO_4-reducing and methanogenic conditions.
- So, the tendency of chloroethene compounds to undergo reductive dechlorination appears to decrease with the number of chlorine substituents.
- DCE occurs in groundwater primarily as the result of in-situ microbial degradation (reduction) of TCE. 
- *Cis* is the predominant product of TCE reduction under in situ groundwater conditions, *trans*-DCE is less commonly observed; 1,1-DCE is primarily a transformation product of trichloroethane (TCA). 
- *Cis*-DCE and 1,1-DCE currently have EPA drinking water MCLs of 70 μg/L and 7 μg/L, respectively. 
- VC contamination of ground-water results primarily from microbial reduction of DCE and TCA under anaerobic conditions, is a known carcinogen, a EPA priority pollutant, and has a drinking water MCL of 2 μg/L. 
- High dissolved concentrations of VC in ground water, however, have occurred due to releases from PVC manufacturing operations.
Figure 2. Ecological succession of electron-accepting processes and sequential production of final products. PCE, tetrachloroethene; TCE, trichloroethene; DCE, dichloroethene; VC, vinyl chloride.

McMahon & Chapelle, 2008
- Vinyl chloride is a relatively reduced compound with limited inclination to undergo further reduction, and microbial reductive dechlorination of VC is dependent on the dissolved VC concentration and likely to be inefficient under low VC concentrations.
- Reductive dechlorination of VC to the non-chlorinated product, ethene, is characteristically slow in situ and generally associated with highly reducing, methanogenic conditions.
- Hence, PCE and TCE contamination often leads to the production and accumulation of reduced daughter products (cis-DCE and VC).
- Reductive dechlorination of chloroethene contaminants is common in anaerobic groundwater systems, but the efficiency of chloroethene reductive dechlorination is highly variable under field conditions.
Summary

The following **practical conclusions** can be made about **reductive dechlorination** as a mechanism for *in situ* remediation of chloroethene contaminants in groundwater systems.

1. **Reductive dechlorination** is common in anaerobic **groundwater systems** and is likely the primary mechanism for *in situ* biotransformation of the parent compounds, PCE and TCE.
2. In practice, the efficiency of chloroethene reductive dechlorination appears to decrease with decreasing chlorine number.

3. Thus, accumulation and persistence of the principal daughter products, cis-DCE and VC, are commonly observed in chloroethene contaminated groundwater systems under anaerobic conditions, and reductive dechlorination of VC to ethene generally is viewed as inefficient except under highly reducing methanogenic conditions.
Oxidative Microbial Degradation of Chloroethenes

- Aerobic co-metabolism of chloroethenes requires the presence of oxygen and a primary carbon substrate (e.g. methane) to initiate and maintain the production of a suitable oxygenase.
- For example, TCE contamination in aerobic aquifers can biodegrade by methanotrophic microorganisms when methane is present in sufficient quantity to support methanotrophic activity.
- Because methane and oxygen do not typically co-occur in ground-water systems, methanotrophic oxidation of chloroethenes is unlikely under natural circumstances.
- The requirement for both oxic conditions and high co-substrate concentrations can be avoided, if the chloroethene contaminant can serve as a primary substrate during biodegradation.
- The tendency of chloroethene compounds to undergo oxidation increases with decreasing number of chlorine substituents.
- Therefore, neither PCE nor TCE have been shown to serve as primary substrates for aerobic microbial degradation, except in aerobic co-metabolism conditions.
- In contrast, aerobic microbial degradation of DCE and VC as primary substrates has been shown.
# Conclusions on Microbial Oxidation of Chloroethenes

## Table 2
The relative efficiency of chloroethene biodegradation via microbial reductive dechlorination (RD) or microbial oxidation (MO) as a function of in situ Red-Ox conditions

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Mechanism</th>
<th>Predominant Terminal Electron Accepting Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$O_2$</td>
</tr>
<tr>
<td>PCE</td>
<td>RD</td>
<td>—$^a$</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>Fair$^b$</td>
</tr>
<tr>
<td>TCE</td>
<td>RD</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>Good$^b$</td>
</tr>
<tr>
<td>$o$-DCE</td>
<td>RD</td>
<td>Poor</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>Excellent</td>
</tr>
<tr>
<td>VC</td>
<td>RD</td>
<td>Poor</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

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$^a$ Indicates no evidence for this process under this Red-Ox condition.

$^b$ Aerobic cometabolism only.

$^c$ Associated with humic-acids reduction not methanogenic activity.
BOMARC Missile Site:
Source of Chemical Spill-10 Plume

Case Study: CS-10 MMR
Cape Cod, MA

http://en.wikipedia.org/wiki/BOMARC
Joint Base Cape Cod (MMR)
Chemical Spill-10 Plume
Pump and Treat Remediation Systems
2006
Results of detailed sampling of TCE hot-spot

Concentrations in head space air in ppb air-water concentrations approximately 20:1 for volatile organic compounds
Case Study: Kings Bay (GA) landfill site

Contaminant (solvents) plume and monitoring wells

Chapelle, 2003
Upper unconfined (marine) sand, Middle organic-rich confining bed, and Lower confined (aeolian) sand; recharge is ~14 in/yr; GW velocity is about 50 ft/yr, flow is to the west.
Redox Chemistry in the Kings Bay Plume

Note: no measurable DO
Concentrations of chlorinated ethenes along the flowpath of the Kings Bay plume
Vinyl Chloride Concentrations in the Kings Bay Plume, 1998
Figure 2. Variation in dissolved concentrations of VC (µM; triangles) and O₂ (mg/L; squares and circles) observed at NSB Kings Bay in USGS 4 (black symbols) and USGS 8 (red symbols) during 2002 to 2007. Top of gray area indicates the dissolved oxygen minimum detection limit (MDL = 0.05 mg/L). Ethene was detected infrequently and only at the MDL (= 0.3 µM). Ethane was not detected (MDL = 0.3 µM).
Model Estimated values for PCE, TCE, cis-DCE, and VC

Ranges of biodegradation rate constants

<table>
<thead>
<tr>
<th>Chlorinated Ethene</th>
<th>Range of estimated k (d⁻¹) values</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>0.02 - 0.005</td>
</tr>
<tr>
<td>TCE</td>
<td>0.02 - 0.005</td>
</tr>
<tr>
<td>cis-DCE</td>
<td>0.04 - 0.01</td>
</tr>
<tr>
<td>VC</td>
<td>0.04 - 0.01</td>
</tr>
</tbody>
</table>
Conclusions

- The Kings Bay Landfill ground-water redox conditions grades from sulfate reduction to Fe(III)-reduction.

- In the zone of sulfate reduction, PCE and TCE are rapidly dechlorinated to cis-DCE and VC.

- In the Fe(III)-reducing zone, cis-DCE and VC are oxidized to carbon dioxide and chloride.

- Despite this natural attenuation capacity, ground water containing concentrations of chlorinated ethenes higher than regulatory limits leaves the site, and migrates to a nearby point of compliance, and thus required active remediation.
Natural Attenuation of Chlorinated Aliphatic Hydrocarbons at Plattsburgh Air Force Base, New York

By Todd H. Wiedemeier, John T. Wilson and Donald H. Kampbell

- A fire training area (Site FT-002) on the Air Base was contaminated with a mixture of chlorinated solvents and fuel hydrocarbons
- Ground water contaminants include TCE, cis-1,2-DCE, vinyl chloride, and BTEX
- Site is underlain by glacial sands, clays, and till; and carbonate bedrock
- Ground-water flow at the site is to the southeast, at an average rate of 0.39 ft/d.
The average hydraulic conductivity for the site is 11.6 ft/day. Effective porosity was assumed to be 0.30. Average ground-water velocity for the unconfined sand aquifer is 0.39 ft/day, about 142 feet per year.
Approximate distribution of light nonaqueous-phase liquid (LNAPL) at the site. LNAPL is a mixture of jet fuel and waste solvents that partitions BTEX and TCE to groundwater. Predominant chlorinated solvent is TCE.
- The dissolved BTEX plume extends approximately 2,000 feet downgradient and is not expanding, indicating biodegradation of BTEX.
- Areas of elevated BTEX concentrations correlate with areas of depleted dissolved oxygen, nitrate, and sulfate. **Background values in red.**
Dissolved TCE, DCE, and vinyl chloride currently extend approximately 4,000 feet downgradient from FT-002. Concentrations of TCE, DCE, and vinyl chloride were as high as 25 mg/L, 51 mg/L, and 1.5 mg/L. Data for the site show that the solvent plumes are at steady-state and are no longer expanding. Background chloride is about 2 mg/L.
Distribution of metabolic byproducts (iron(II), methane) produced by microbially-mediated redox reactions. Elevated BTEX concentrations correlate with areas with elevated iron(II) and methane. Background concentrations (in red) suggest that iron(III) reduction and methanogenesis are biodegrading fuel hydrocarbons at the site. Low pE correspond to areas of biologically mediated oxidation-reduction reactions.
First-order biodegradation rates for Plattsburgh AFB site

### Table 3. Approximate First-Order Biodegradation Rate Constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Correction Method</th>
<th>A - B (0 to 970 feet 1/year)</th>
<th>B - C (970 to 1,240 feet 1/year)</th>
<th>C - E (1,240 to 2,560 feet 1/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>Chloride</td>
<td>1.27</td>
<td>0.23</td>
<td>-0.30</td>
</tr>
<tr>
<td>TMB</td>
<td></td>
<td>1.20</td>
<td>0.52</td>
<td>NA</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.24</td>
<td>0.38</td>
<td>-0.30</td>
</tr>
<tr>
<td>DCE</td>
<td>Chloride</td>
<td>0.06</td>
<td>0.60</td>
<td>0.07</td>
</tr>
<tr>
<td>TMB</td>
<td></td>
<td>0.00</td>
<td>0.90</td>
<td>NA</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.03</td>
<td>0.75</td>
<td>0.07</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>Chloride</td>
<td>0.00</td>
<td>0.14</td>
<td>0.47</td>
</tr>
<tr>
<td>TMB</td>
<td></td>
<td>0.00</td>
<td>0.43</td>
<td>NA</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.00</td>
<td>0.29</td>
<td>0.47</td>
</tr>
<tr>
<td>BTEX</td>
<td>Chloride</td>
<td>0.13</td>
<td>0.30</td>
<td>0.39</td>
</tr>
<tr>
<td>TMB</td>
<td></td>
<td>0.06</td>
<td>0.60</td>
<td>NA</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.10</td>
<td>0.45</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Note: Letters Refer to Locations On the Site map
Chlorinated solvent plumes can exhibit three types of behavior (I-III) depending on
1. amount of solvent,
2. amount of biologically available organic carbon (i.e. substrate),
3. the distribution and concentration of natural electron acceptors (TEAs), and
4. the types of electron acceptors being used (alternate TEAs).
Type 1 Behavior

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and this substrate drives reductive dechlorination. For natural attenuation of a plume exhibiting Type 1 behavior the following questions should be addressed:

1. Is the substrate supply adequate for microbial reduction of the chlorinated organic compounds? That is, will they degrade all of the chlorinated aliphatic hydrocarbons (TEA) before they run out of electron donors?

2. What are the concentrations and distributions of competing TEAs (e.g. DO, nitrate, iron(III), sulfate)?

Type 1 behavior can result in the rapid and extensive degradation of the highly chlorinated solvents such as PCE, TCE, and DCE.
Type 2 Behavior

Type 2 behavior dominates in areas that are characterized by high concentrations of biologically available native organic carbon. This natural carbon source drives reductive dechlorination (i.e., is the primary substrate for microorganism growth). Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon content) this type of behavior can also result in rapid degradation of chlorinated solvents.
Type 3 Behavior

Type 3 behavior dominates in areas that are characterized by low concentrations of native and/or anthropogenic carbon and by higher DO (concentrations greater than 1.0 milligrams per liter). Under these aerobic conditions, reductive dechlorination will not occur; thus, there is no removal of PCE, TCE, and DCE. The most significant natural attenuation mechanisms for these compounds is advection, dispersion, and sorption. However, vinyl chloride can be rapidly oxidized under these conditions.
Plattsburgh Air Force Base, NY, exhibits Type 1 behavior in the source area, and Type 3 behavior down gradient from the source.
Figure 7. Plot of TCE, DCE, and ethene versus distance down-gradient.
Conclusions: Plattsburgh AFB

-Near the source the plume exhibits Type 1 behavior. TCE is being reductively dechlorinated to cis-DCE and vinyl chloride. Average calculated first order biodegradation rate constants in this zone are as high as 1.24/yr for TCE, and 0.75/yr for DCE.

-At about 1,500 feet downgradient from the source, the plume reverts to Type 3 behavior. Dissolved oxygen concentrations are on the order of 0.5 mg/L. Average calculated rate constants in this zone are 0.07/yr for DCE and 0.47/yr for vinyl chloride. Vinyl chloride likely is being oxidized via a combination of Fe$^{3+}$ reduction and aerobic respiration.
Summary

- The NAWQA solvent survey indicated solvents are among the most widespread contaminants in US GWs.

- A review indicated PCE and TCE degradation will typically occur under reducing conditions, with DCE and VC as daughter products.

- Typically DCE and VC require aerobic degradation.

- The field studies at Kings Bay, GA, landfill site and the Plattsburgh (NY) Air Force Base indicated both similarities and differences in the pattern and rates of solvent degradation.
Next:

Metals
(Zn, Cd, Cr, As, Pb, Hg)