Occurrence, Fate, and Remediation of the Emerging Contaminant 1,2,3-Trichloropropane

Srinivasa Varadhan, Engineer, Sacramento
Eric Suchomel, Principal, San Francisco
Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

• Man-made compound
  - Formerly used as a chemical solvent and extraction agent
  - Chemical intermediate in the production of:
    - Other chemical intermediates
    - Agricultural fumigants
    - Specialty polymers and sealants

• Typically found at:
  - Ag-chem facilities, chemical manufacturing/storage facilities, military bases
  - Supply wells, particular those in agricultural areas (non-point sources)

• Classified as a likely or potential carcinogen to humans
  - EPA, US Health & Human Services, American Conference of Governmental Industrial Hygienists, NIOSH
  - Classified as a carcinogen by the State of California
Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

**Low Vapor Pressure & Henry’s Constant**

<table>
<thead>
<tr>
<th>Property</th>
<th>1,2,3-TCP</th>
<th>1,1,1-TCA</th>
<th>TCE</th>
<th>1,2-DCA</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure</td>
<td>3.1</td>
<td>133.4</td>
<td>131.5</td>
<td>387</td>
<td>Torr (mm Hg) @ 25° C</td>
</tr>
<tr>
<td>Henry’s Constant</td>
<td>2.3 – 3.4</td>
<td>167</td>
<td>93.7</td>
<td>11</td>
<td>$10^{-4}$ atm m$^3$ mole$^{-1}$ @ 25° C</td>
</tr>
<tr>
<td>Solubility</td>
<td>1.75</td>
<td>1.3</td>
<td>1.1</td>
<td>8.61</td>
<td>g/L @ 20° C</td>
</tr>
<tr>
<td>$K_{oc}$</td>
<td>51</td>
<td>152</td>
<td>126</td>
<td></td>
<td>mL/g</td>
</tr>
</tbody>
</table>

**Low Koc**

- Little retardation – may form long, straight groundwater plumes
- Compared to chlorinated ethenes and chlorinated ethanes, TCP is less likely to sorb to solid material or partition into the vapor phase.
<table>
<thead>
<tr>
<th>Regulatory Domain</th>
<th>Standards/Goals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Federal</td>
<td>USEPA tap water RSL is <strong>0.00075 µg/L</strong>&lt;br&gt;Listed on 2015 Draft Contaminant Candidate List 4 (CCL4)</td>
</tr>
<tr>
<td>California</td>
<td><strong>0.0007 µg/L</strong> Public Health Goal (est. 2009)&lt;br&gt;<strong>0.005 µg/L</strong> MCL (adopted 18 July 2017)</td>
</tr>
<tr>
<td>Hawaii</td>
<td>State MCL of <strong>0.6 µg/L</strong> (est. 2011)</td>
</tr>
<tr>
<td>Minnesota:</td>
<td>Health Risk Limits (HRL) (est. 2013):&lt;br&gt;<strong>0.003 µg/L</strong> Cancer HRL&lt;br&gt;<strong>0.7 µg/L</strong> Non-Cancer HRL</td>
</tr>
<tr>
<td>New Jersey</td>
<td><strong>0.03 µg/L</strong> Suggested MCL (est. 2009)</td>
</tr>
<tr>
<td>Other States?</td>
<td>Coming Soon?</td>
</tr>
</tbody>
</table>
Groundwater Remediation

- Groundwater ex situ treatment feasible but potentially costly
  - GAC effective, but long residence time required
  - Advanced oxidation processes may also be effective

- In situ remediation is most effective but not widely tested
  - Potentially costly for dilute plumes
  - Includes:
    - Biological Reduction (ISBR)
    - Chemical Oxidation (ISCO)
    - Chemical Reduction via Zero Valent Metals (ISCR)
1,2,3-TCP Degradation Pathway

2-chloro-2-propan-1-ol or 3-chloro-2-propen-1-ol

- HCl

2,3-dichloro-1-propane or (c/t) 1,3-dichloro-1-propene

- HCl

sequential hydrogenolysis products, possibly leading to additional elimination products

Note: Degradation products transient in water and rarely observed

Primary pathway observed for ISBR and ISCR

OH
H−C=CH
H H
allyl alcohol

allyl mercaptan, S-allyl mercaptocysteine, and allyl sulfides

Abiotic

Hydrolysis or Oxidation

1,2,3-trichloropropane

+[O]− Cl−

- 2Cl−

Reduction

in the presence of cysteine or sulfide
In Situ Biological Reduction (ISBR)

- **Since 2000** – Biostimulation at numerous sites; mixed results and unknown/unclear degradation mechanism and pathway
- **~2010** – Dihaloelimination of chlorinated propanes by *Dehalogenimonas* recognized (Bowman et al, 2012)
- **2014** – Commercially-available testing of *Dehalogenimonas* (Dhg) (SiREM’s Gene-Trac® Dhg) and discovery of Dhg in SiREM’s KB-1® Plus bioaugmentation culture
• Direct push injections of a slow-release electron donor (HRC™)
• Successful long-term reduction of TCP (and dichloropropane [DCP])
• Pilot led to full-scale implementation
• Understanding of remedial mechanisms remained unclear
• Recent Dhg testing inconclusive
  ▪ ~9 years after full-scale injections
In Situ Biological Reduction (ISBR)

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- **2014-Present** – Geosyntec/SiREM R&D to understand and develop ISBR for TCP remediation
  - Degradation pathway
  - KB-1®Plus inoculum size, culture acclimation, degradation rates
  - Evaluated practical concentration & pH ranges for effective ISBR
  - Mechanisms for degradation via biostimulation alone
- **2016-Present** – First field demonstration for bioaugmentation
Practical Ranges for Successful ISBR

- **pH Ranges**
  - Successful degradation at pH 5-9
  - Unsuccessful at pH 4
  - Optimal pH appears to be around 7-8

- **Concentration Ranges**
  - Degradation observed in laboratory from <10 to 10,000 ppb TCP
  - Optimal range observed 1,000 – 10,000 ppb
• Former agricultural chemical facility

<table>
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<tr>
<th>Constituent</th>
<th>Max Site Conc.</th>
<th>State Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,3-TCP</td>
<td>72 µg/L</td>
<td>0.005 µg/L (MCL)</td>
</tr>
<tr>
<td>1,2-DCP</td>
<td>680 µg/L</td>
<td>5 µg/L (MCL)</td>
</tr>
<tr>
<td>Nitrate (as N)</td>
<td>1,800 mg/L</td>
<td>10 mg/L (MCL)</td>
</tr>
<tr>
<td>Sulfate</td>
<td>415 mg/L</td>
<td>250 mg/L (Secondary MCL)</td>
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</table>

• Treatability study elements
  ▪ Biostimulation with lactate and emulsified vegetable oil (EVO)
  ▪ Bioaugmentation with KB-1®Plus

• Promising results with KB-1®Plus bioaugmentation

• Initiated pilot test in May 2016
• First-to-field bioaugmentation
• Injections - mid-May 2016
  ▪ EVO/lactate electron donor
  ▪ Bioaugmentation with KB-1®Plus
• Results
  ▪ Slow growth of Dhg population
  ▪ Degradation lag period ~ 6 months
In Situ Chemical Reduction via Zero Valent Metals

- **Since Mid-2000s** - Use of zero valent metals has been evaluated and applied at TCP sites (bench- and pilot-scale)
  - Zero valent metal formulations assessed for TCP remediation include Zero Valant Iron (ZVI), Zero Valant Zinc (ZVZ), proprietary mixtures of ZVI and other compounds (e.g., EHC®)
- **2014** - Geosyntec completed first field demonstration using ZVZ in conjunction with Navy and OHSU. Additional R&D pending under ESTCP grant.
Comparison of TCP Degradation by ZVI and ZVZ

Kinetics of TCP degradation by ZVZ and ZVI

Figure format

- Surface area normalized rate constant ($k_{SA}$) vs. mass normalized rate constant ($k_M$)
- Good for complex comparisons of kinetics
- Reactivity increases up and to the right

Observations

- Both ZVZ and ZVI produce relevant degradation rates, but ZVZ rates significantly faster than ZVI

Sarathy, Tratnyek, et al., 2010
• Field-scale column testing conducted
  - 25% Zn64 Dust/75% Sand
  - 33% Zn1210 Powder/67% Sand
  - 67% Zn1210 Powder/33% Sand
  - 100% Zn1210 Powder

• All Zn1210 columns met 1,2,3-TCP treatment goal
  - Treatment efficiency declined over 12 weeks of operation

• Hydrogen gas produced

• Effluent dissolved zinc (0.04 to 0.20 mg/L) was below secondary MCL (5 mg/L)
• Military facility located in Southern California
  ▪ 1,2,3-TCP present in source well at concentrations up to 10 µg/L, eventual remedial objective for 1,2,3-TCP expected to be 0.5 µg/L

• Pneumatic fracturing injections completed in July 2014 – injected ~14,000 pounds of Zn1210
  ▪ Main issues – surfacing, process challenges (pump plugging, etc.)
• TCP degradation by ZVZ ongoing over year of post-injection monitoring
• No observed impacts to groundwater flow or secondary water quality impacts
1,2,3-TCP is an emerging challenge
- Relatively high toxicity -> Low regulatory levels
- Degradation pathway not well understood until now

On-going advances in situ remediation provides more robust remedial technology alternatives for consideration
- ISBR parameters appear to be similar to chlorinated ethenes/ethanes
  - Potentially similar costs for implementation, with initial concentration considerations
- ISCR with ZVZ appears to be effective at low initial concentrations
  - Long-term validation of technology is ongoing
• Geosyntec Consultants
  • Melissa Schmitt, PE
  • Eric Suchomel, PhD, PE
  • Rula Deeb, PhD, PE

• SiREM
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  • Phil Dennis
  • Jennifer Webb

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