1,4-Dioxane Remediation - Where We Are, Where We're Going, and What We Need

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Outline

• The 1,4-Dioxane Work Group
• Where We Are (or why 1,4-dioxane is a difficult problem)
• Where We’re Going
• What We Need to Remediate 1,4-Dioxane in Groundwater
  • Microbial Diversity and Physiology
  • Field Data
  • Rates
  • Natural Attenuation
  • Creative Remedy Designs
  • Toxicity Review
The 1,4-Dioxane Work Group

• Collaborative project initiated by DuPont, Dow, RACER Trust, AECOM and Arcadis
• Academic Research funded by individual corporate entities
• 3 Technology exchange “summits” with researchers and practitioners
## Where We Are: 1,4-Dioxane Physicochemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>1,4-Dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Abstract Service (CAS) number</td>
<td>123-91-1</td>
</tr>
<tr>
<td>Physical description (physical state at room temperature)</td>
<td>Clear, flammable liquid with a faint, pleasant odor</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>88.11</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Miscible</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>11.8</td>
</tr>
<tr>
<td>Boiling point (°C) at 760 mm Hg</td>
<td>101.1</td>
</tr>
<tr>
<td>Vapor pressure at 25°C (mm Hg)</td>
<td>38.1</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.033</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log (K_{ow}))</td>
<td>-0.27</td>
</tr>
<tr>
<td>Organic carbon partition coefficient (log (K_{oc}))</td>
<td>1.23</td>
</tr>
<tr>
<td>Henry's law constant at 25°C (atm-m³/mol)</td>
<td>4.80 (\times) 10⁻³</td>
</tr>
</tbody>
</table>

- USEPA (2017) Technical Fact Sheet - 1,4 Dioxane EPA 505-F-17-011
Where We Are: 1,4-Dioxane as a Groundwater Issue

• History –
  • Often found with chlorinated solvents
  • Relatively short historical data sets for 1,4 dioxane
  • 1,4 dioxane potentially a cryptic groundwater constituent at many sites (often not analyzed)

• Understanding of plume behavior is developing:
  • Plumes are often relatively low concentration
  • Transport in low K zones can contribute to persistence
  • Evidence for natural attenuation of plumes

Where We Are: Remedies

• Current remedies are largely ex situ (AOP or sorption)
  • Difficult applications to dilute plumes
  • Low K zones can result in plume persistence
  • In situ applications are coming on line

• 1,4-dioxane is perceived as a poor candidate for natural attenuation (not true!):
  • Field evidence for attenuation of 1,4-dioxane plumes (Adamson, et al, 2017)
  • Biodegradation of 1,4-dioxane demonstrated in microcosms, mixed, and pure cultures (Mahendra et al, 2005; Li et al, 2015; da Silva et al, 2018)
  • Biomarkers for 1,4-dioxane degradation (Gedalanga et al, 2014)
Where We’re Going

• Dynamic regulatory environment
  • Trend towards decreasing guidance levels
  • Many sites could transition into non-compliance
  • Potential for re-opening sites and remedies

• Difficult for site owners to understand their true stake and plan accordingly
  • Based on co-occurrence with CVOCs there are many un-identified 1,4-dioxane sites out there. (Adamson, et al, 2017)

<table>
<thead>
<tr>
<th>State</th>
<th>Guideline (µg/L)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska</td>
<td>77</td>
<td>AL DEC 2016</td>
</tr>
<tr>
<td>California</td>
<td>1.0</td>
<td>Cal/EPA 2011</td>
</tr>
<tr>
<td>Colorado</td>
<td>0.35</td>
<td>CDPHE 2017</td>
</tr>
<tr>
<td>Connecticut</td>
<td>3.0</td>
<td>CTDPH 2013</td>
</tr>
<tr>
<td>Delaware</td>
<td>6.0</td>
<td>DE DNR 1999</td>
</tr>
<tr>
<td>Florida</td>
<td>3.2</td>
<td>FDEP 2005</td>
</tr>
<tr>
<td>Indiana</td>
<td>7.8</td>
<td>IDEM 2015</td>
</tr>
<tr>
<td>Maine</td>
<td>4.0</td>
<td>MEDEP 2016</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>0.3</td>
<td>MADEP 2004</td>
</tr>
<tr>
<td>Mississippi</td>
<td>6.09</td>
<td>MS DEQ 2002</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>0.25</td>
<td>NH DES 2011</td>
</tr>
<tr>
<td>New Jersey</td>
<td>0.4</td>
<td>NJDEP 2015</td>
</tr>
<tr>
<td>North Carolina</td>
<td>3.0</td>
<td>NCDENR 2015</td>
</tr>
<tr>
<td>Pennsylvania</td>
<td>6.4</td>
<td>PADEP 2011</td>
</tr>
<tr>
<td>Texas</td>
<td>9.1</td>
<td>TCEQ 2016</td>
</tr>
<tr>
<td>Vermont</td>
<td>3.0</td>
<td>VTDEP 2016</td>
</tr>
<tr>
<td>Washington</td>
<td>0.438</td>
<td>WA ECY 2015</td>
</tr>
<tr>
<td>West Virginia</td>
<td>6.1</td>
<td>WV DEP 2009</td>
</tr>
</tbody>
</table>

USEPA (2017) Technical Fact Sheet -1,4 Dioxane EPA 505-F-17-011
What We Need: Microbial Diversity

- **1,4-dioxane is absolutely biodegradable.**
- However, the full diversity of 1,4-dioxane biodegradation is not understood.
  - Aerobic biodegradation is well documented
    - Metabolic
    - Cometabolic
  - Anaerobic degradation has remained elusive
    - Absence of evidence is not evidence of absence

*New cultures = New possibilities for bioaugmentation approaches and new biomarkers*

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**The Principle of Infallibility** states: “It is probably not unscientific to suggest that somewhere or other some organism exists which can, under suitable conditions, oxidize any substance which is theoretically capable of being oxidized.”

E.F. Gale (1952)
What We Need: Understanding of 1,4-Dioxane Degrading Physiologies

• Have we gotten distracted by other systems and “charismatic microbial specialists” e.g. *Dehalococcoides*?

• Different physiologies may be better adapted to different conditions but balancing geochemistry may be difficult:
  • Metabolic (specialists) – high concentrations / source areas
  • Co-metabolic (accidental opportunists) – low concentrations / distal plume, but requires co-substrates

*Understanding the physiologies involved allows optimization of conditions for 1,4-dioxane degradation*
What We Need: Field Data

• Detailed long-term data sets on 1,4-dioxane plumes
  • Range of concentrations
  • Variety of co-contaminants
  • +/- source area treatments

• Including spatial resolution sufficient to:
  • Delineate plumes
  • Define oxic/anoxic boundaries and other geochemical regimes
  • Characterize geology and transport

• Microbial data
  • Community structure
  • Biomarkers

With better field data we can locate zones of 1,4-dioxane degradation.
What We Need: Quantification of In Situ Rates

• Generally dilute plumes make for generally low rates of degradation

• Can we tolerate low rates if we know the processes are operating?

In situ degradation rates allow informed choices about how and where to manage 1,4-dioxane plumes.
What We Need: Demonstration of Natural Attenuation Remedies

- Case Histories in both source areas and dilute plumes:
  - Field Data to showing shrinking Plume Trends
  - Demonstration of in situ 1,4-dioxane degradation Processes
    - Compound Stable Isotope Analysis (Pornwongthong, 2011; Wang, 2016)
    - Biomarkers (Gedalanga et al, 2014)
    - Degradation Rate Assays
- Geochemical data at the right level of detail at the right location

Understanding natural attenuation processes will inform the design of sustainable and protective engineered strategies.

Adamson et al, 2017
What We Need: Creative and Sustainable Treatment Strategies

- Promising results with combined chemical/physical/biological treatments:
  - Chemical treatments to address mixed source areas and provide oxygen downgradient
  - Electrolytic treatment of 1,4-dioxane and chlorinated solvents (Jasmann, et al 2017)
  - In situ microbially mediated Fenton’s reactions (Sekar and DiChristina, 2014)
  - Phytoremediation with bioaugmentation
  - Well head treatment
  - Selective pumping

When we control risk can we buy time to allow natural attenuation (including biodegradation) to work at slower rates?
What We Need: Toxicity Review

- EPA/OPPT Risk Evaluation of 1,4-dioxane currently in the scoping and problem formulation stage

- Points to review:
  - Mode of action
  - Threshold vs. non-threshold dose-response

Accurate risk assessments based on the most current data are necessary for selection of the best and most protective remedies.
Final Thoughts

• Potential for more 1,4-dioxane sites to need treatment in the future.

• Current active research programs are highly promising for improved treatment technologies and strategies including:
  • Demonstration of natural attenuation
  • Engineered biotreatments (biostimulation and/or bioaugmentation)
  • Treatment trains
  • Risk management while slow attenuation processes work

• Better characterization of biogeochemical conditions in plumes over time will inform the design of sustainable engineered remedies and selection of sites suitable for natural attenuation.
References


