APPROACHES FOR EVALUATING NATURAL ATTENUATION OF 1,4-DIOXANE

October 13, 2016

RemTech™ Banff, Alberta, Canada

Overview

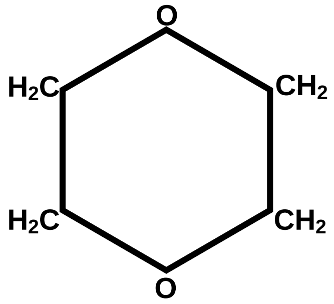
- 1,4-Dioxane as an Emerging Contaminant
- Monitored Natural Attenuation of 1,4-Dioxane
- Advanced Characterization Approaches
  1. High resolution hydrostratigraphy/mass flux approach
  2. Microbial toolkit
- Case Studies
  1. Source mass and transport.
  2. High resolution characterization and advanced microbial tools
  3. Lesson learned
- Summary and Conclusions

1,4-Dioxane as an Emerging Contaminant

Emerging contaminant: Any synthetic or naturally occurring substance that is not commonly monitored in the environment, but has the potential to enter the environment and cause known or suspected adverse effects

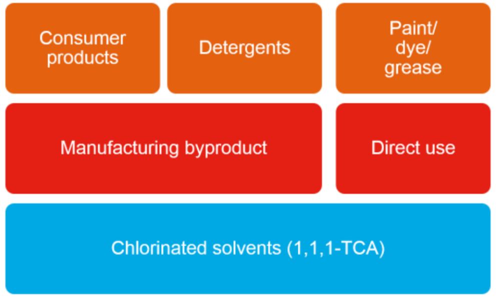
1,4-Dioxane

- Highly soluble and stable in water
- Does not readily adsorb to organic material
- Can be stored by saturation of the static pore fraction



1,4-Dioxane
(Dioxane)

1,4-Dioxane: A potential health risk in water



Common stabilizer for chlorinated solvents

50 µg/L in soap/water mix

85 mg/kg

6.5-24 mg/kg

Byproduct from detergent production

Main ingredient: cellulose acetate membrane production

Likely human carcinogen

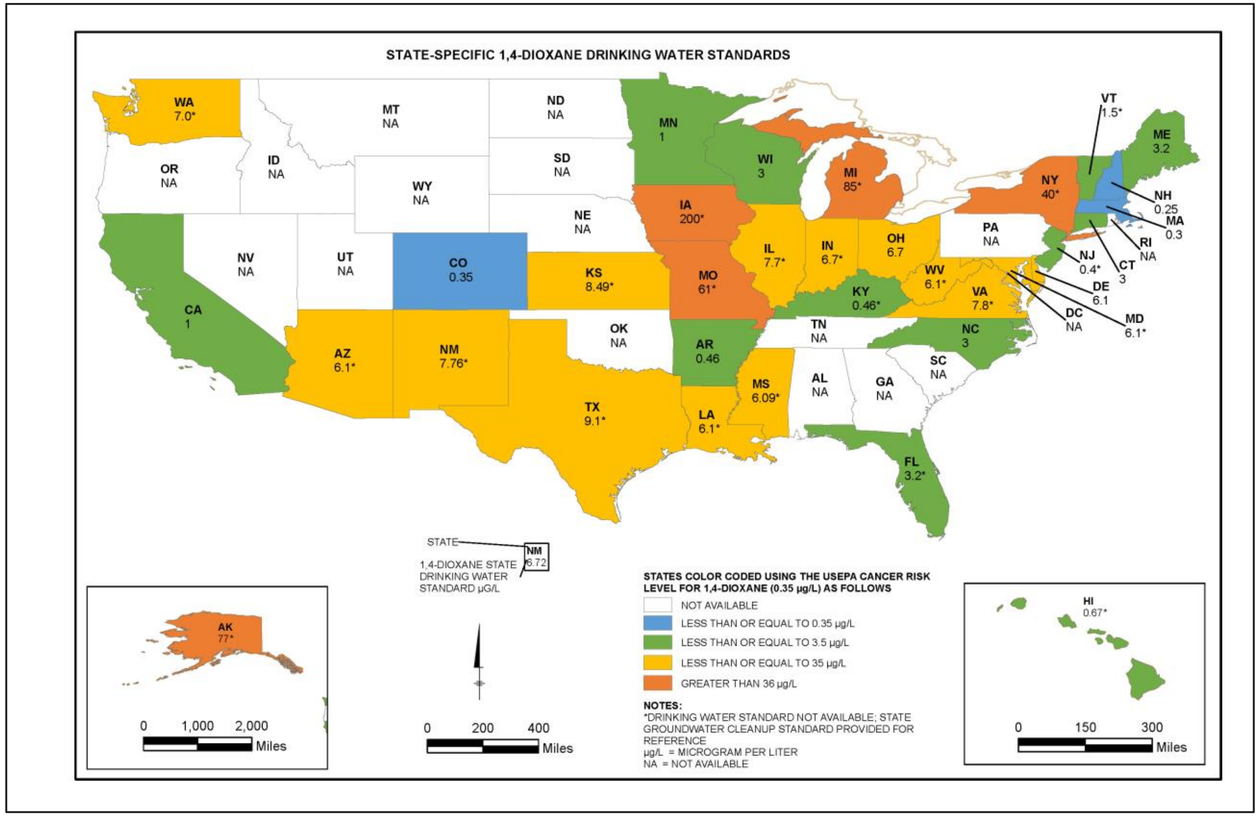
- Short-term exposure: nausea, drowsiness, headache, and irritation of the eyes
- Chronic exposure: dermatitis, eczema, drying and cracking of skin, as well as liver and kidney damage
- U.S. risk-based drinking water heath advisory level of 200 µg/L

Detected in ~20% of public water supplies in the United States, ~7% exceed health-based standards.

Standards by State in the United States

- No federal MCL; many states do not have standards

- 30+ states with drinking water or groundwater standards
  - Many <1 µg/L
  - Some have recently dropped to lower levels near analytical limits



More questions than answers:

- Are there enough studies done to establish basis for standard?
- Does science support the regulations? If it did, would we expect less variability in standard setting?
- Does fear of being wrong drive process?
- How long is too long to wait for science?

Management Strategies: Modest

Reacting to…

- Regulatory pressure
- Potential health risk
- Reputational risk

Appropriate when…

- No state regulations in place
- No human exposure risk
- Project goals include long-term strategies

Drawbacks…

- Causes a sense of urgency
- Requires resources immediately
- Options may be limited due to limited data

A modest approach may be appropriate in some cases, but not the status quo

Management Strategies: Proactive

Proactively…

- Evaluating sites within portfolio
- Determining presence of 1,4-dioxane when TCA/11DCE are present
- Collecting data sets over time

Appropriate when…

- Several sites are managed
- Sites in different states are managed
- Reputation is a concern
- Project goals necessitate site closure

Benefits…

- Understand risk within the portfolio; allocate resources accordingly
- Collect data in advance of regulatory pressure
- Build long-term data set for decision making (e.g., MNA)
- Optimize existing remedies

A proactive approach can provide more exit strategies in the long run

1,4-Dioxane Treatment Options

In-situ

- Chemical oxidation (ISCO)
- Natural attenuation/Bioremediation
- Thermal
- Extreme soil vapor extraction (XSVE)

Ex-situ/ Drinking Water

- Advanced oxidation processes (AOPs)
- Specialized synthetic media
- Bioreactor

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Air stripping
GAC

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Monitored Natural Attenuation of 1,4-Dioxane

Why Monitored Natural Attenuation?

Health & Safety	• No chemical handling or concentrate disposal • No mechanical hazards
Cost	• ~20% of cost of AOP over 10 years • After mechanism confirmation, monitoring cost optimized
Sustainability	• Efficient for large, dilute plumes • Low energy intensity • Compatible with site operations and remediation activities
Efficacy	• Lines of evidence demonstration

Basis for Approach: U.S. EPA's Three Tiers

1. Clear trend of decreasing mass or concentrations over time (e.g., statistical trend analysis)
2. Indirect evidence of attenuation mechanisms (e.g., assessment of geochemical & hydrological conditions)
3. Direct evidence of attenuation mechanisms (e.g., environmental molecular diagnostic tools [MBT, CSIA])

ARCADIS Design & Consultancy for natural and built assets

Lines of Evidence: A Path to Success

Conceptual Site Model
- Source
- Transport (mass-flux)
- Commingled COCs

Risk Assessment
- Receptors
- Distance and Timeframes

Attenuation Demonstration
- Stable to Shrinking Plume (requires data over time)
- Isotopic Shift (cutting edge)

Attenuation Mechanism
- Geochemical Conditions
- Microbial Community and Activity
- Physical Attenuation

Appropriate Monitoring
- Optimized Locations
- Optimized Parameters

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Advanced Characterization Approaches

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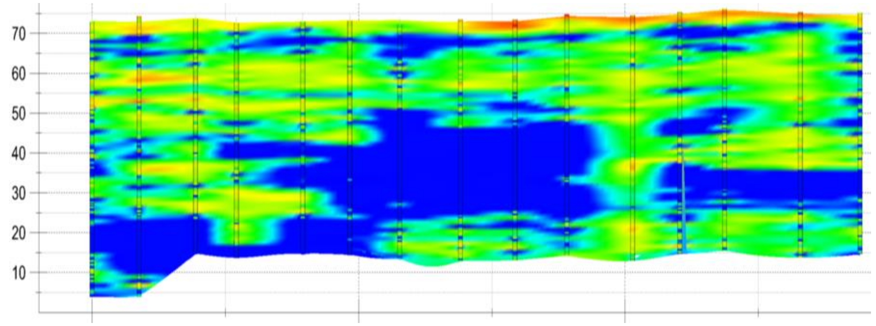
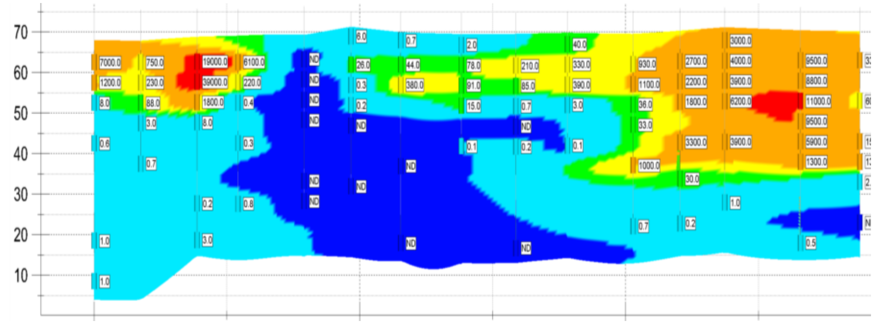
- Microbial toolkit

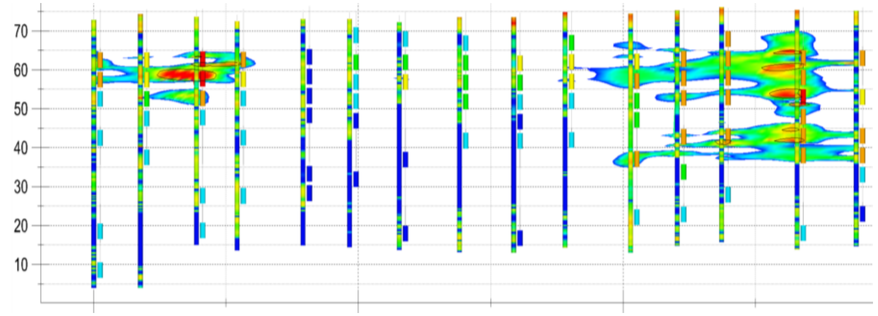
Value of High Resolution Characterization



HYDRAULIC CONDUCTIVITY



CONCENTRATION PROFILES



RELATIVE FLUX

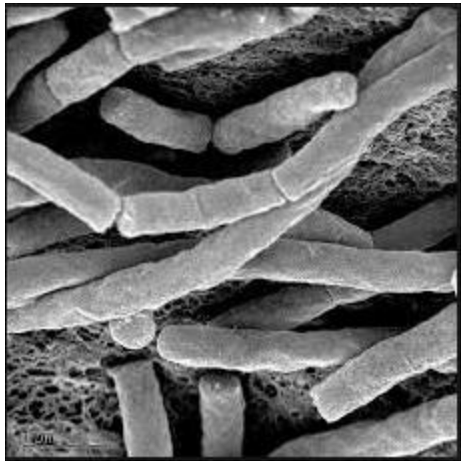
- Start with aquifer properties
  - ✓ Hydraulic Profiling Tool (HPT)
  - ✓ Cone Penetrometer Test (CPT)
- Layer on concentration information
  - ✓ Vertical Aquifer Profiling (VAP) samples
  - ✓ Whole soil data
- Visualize mass flux
  - ✓ Passive flux meters
  - ✓ 2D and 3D

>90% of contaminants often flow in <10% of aquifer volume

Biodegradation: Metabolism vs. Cometabolism

Metabolism: the goal is to produce energy

1,4-Dioxane → Carbon Dioxide

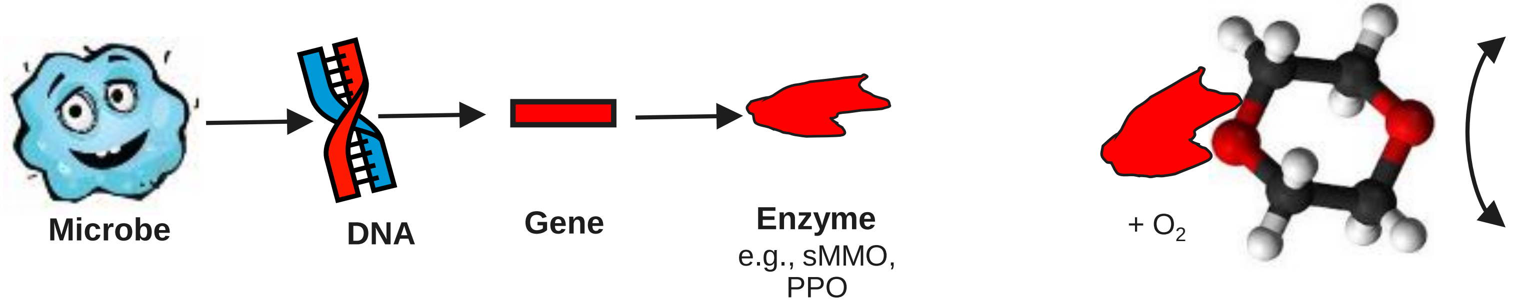


Oxygen → Water

(http://bacmap.wishartlab.com/organisms/1305)

Cometabolism: a fortuitous side reaction

Primary substrate e.g., methane, propane, toluene, THF → Energy



Carbon Dioxide ↔ Water

Assessing Biodegradation Mechanism

- Are the right microbes present?
  - Previously identified 1,4-dioxane degraders
  - Based on DNA surveys
- Do they have what they need to grow?
  - Primary substrates, comfortable conditions
- Are they expressing the enzymes needed?
  - mRNA for key functional genes
  - Particularly important for cometabolism

Metabolism

- Substrates: 1,4-Dioxane and DO
- Genes: DXMO and ALDH

Cometabolism

- Substrates: Methane, propane, or toluene and DO
- Genes: SMMO, PPO, RMO/RDEG

Knowledge of processes and analytical methods are rapidly evolving

Case Studies

1. Where is the source mass? Where does transport occur?
2. High resolution characterization provides powerful insight; advanced microbial tools build a case for cometabolic 1,4-dioxane biodegradation
3. Lesson learned: multiple lines of evidence are needed for methane-linked cometabolism

Case Studies

1. Where is the source mass? Where does transport occur?

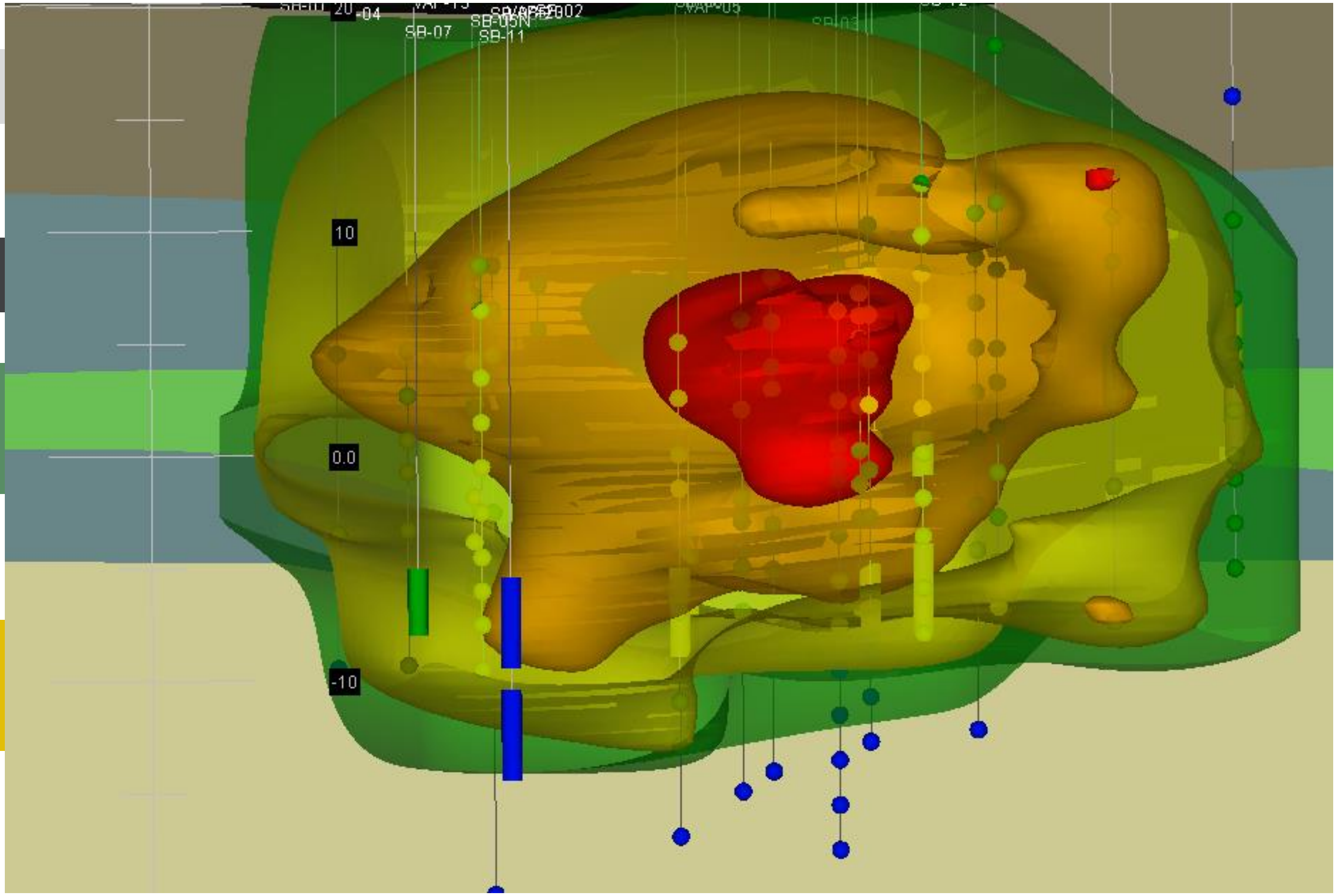
Where is the 1,4-Dioxane Source Mass?

Surface deposits

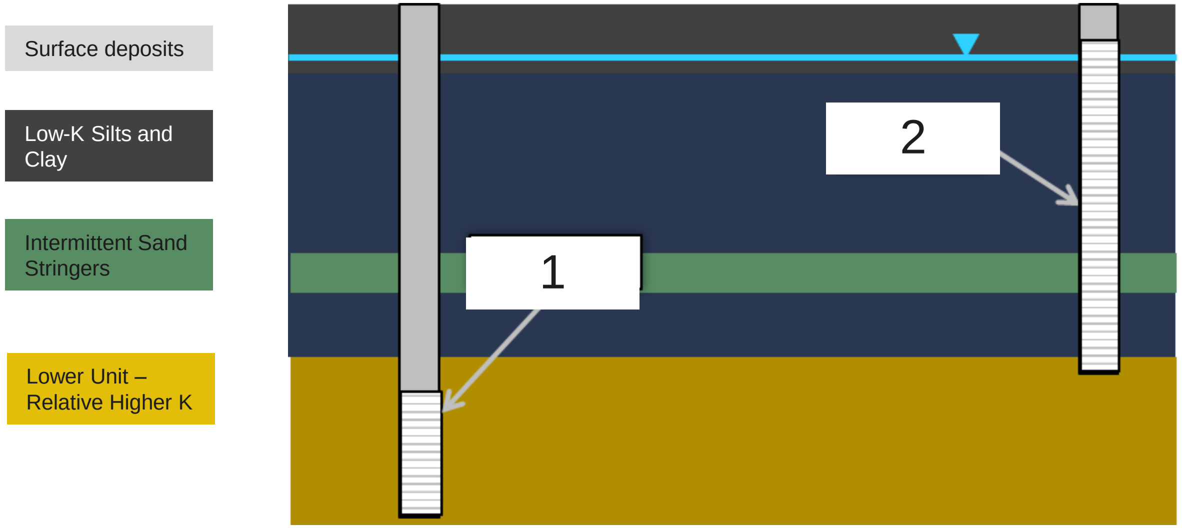
Low-K Silts and Clay

Intermittent Sand Stringers

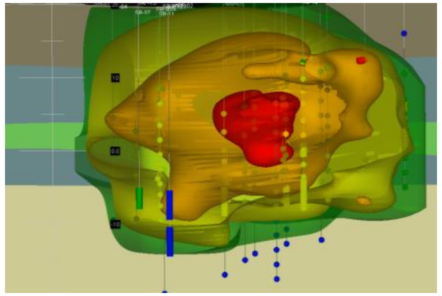
Lower Unit – Relative Higher K

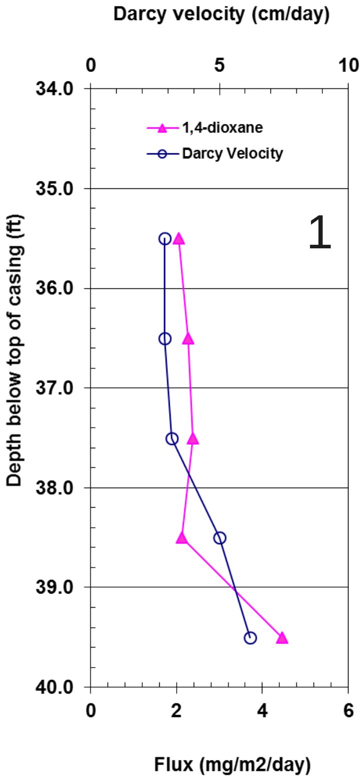


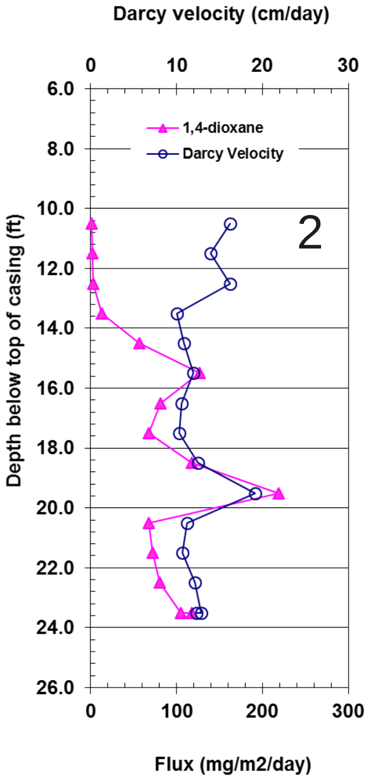
Where Does Transport Occur?



Mass Flux = Permeability x Gradient x Concentration







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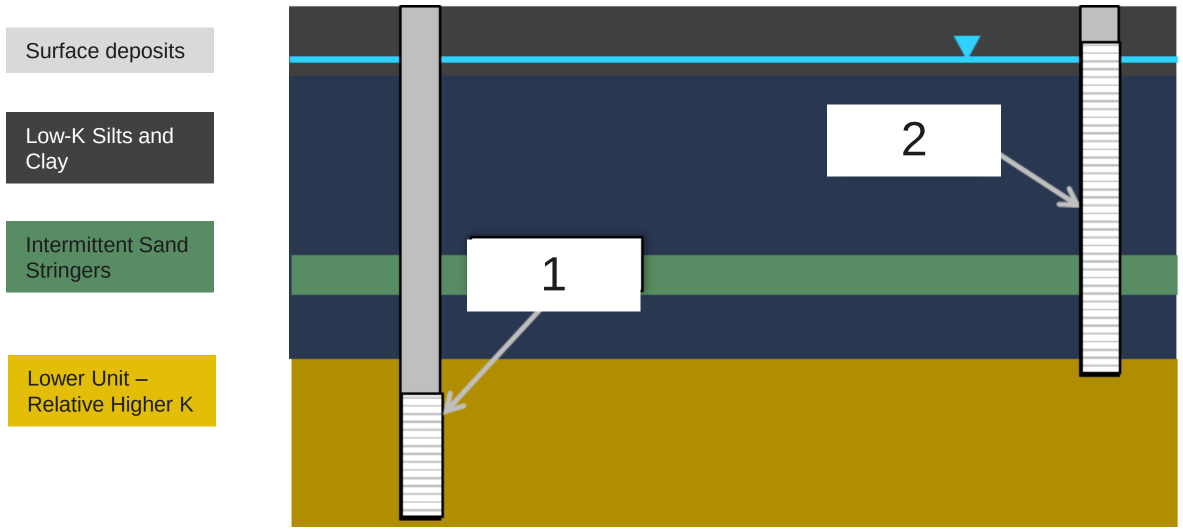

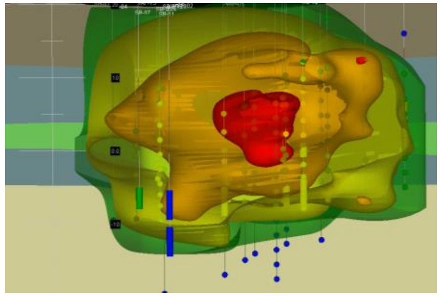

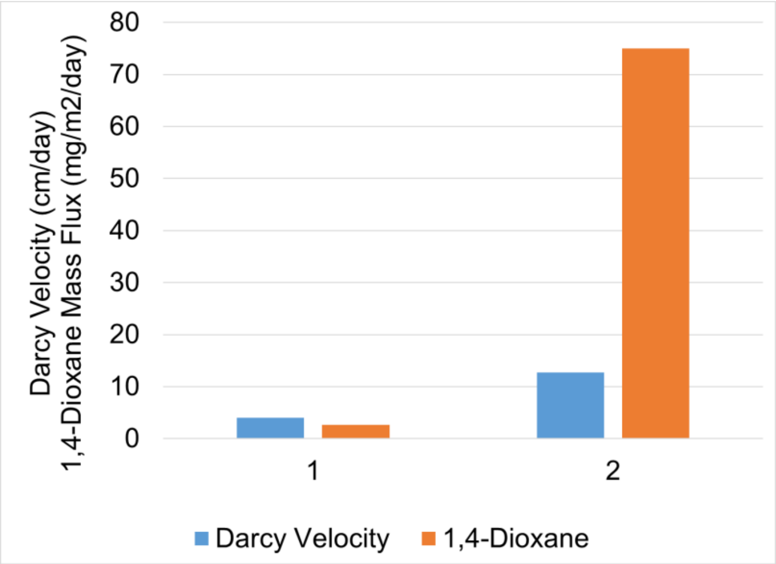

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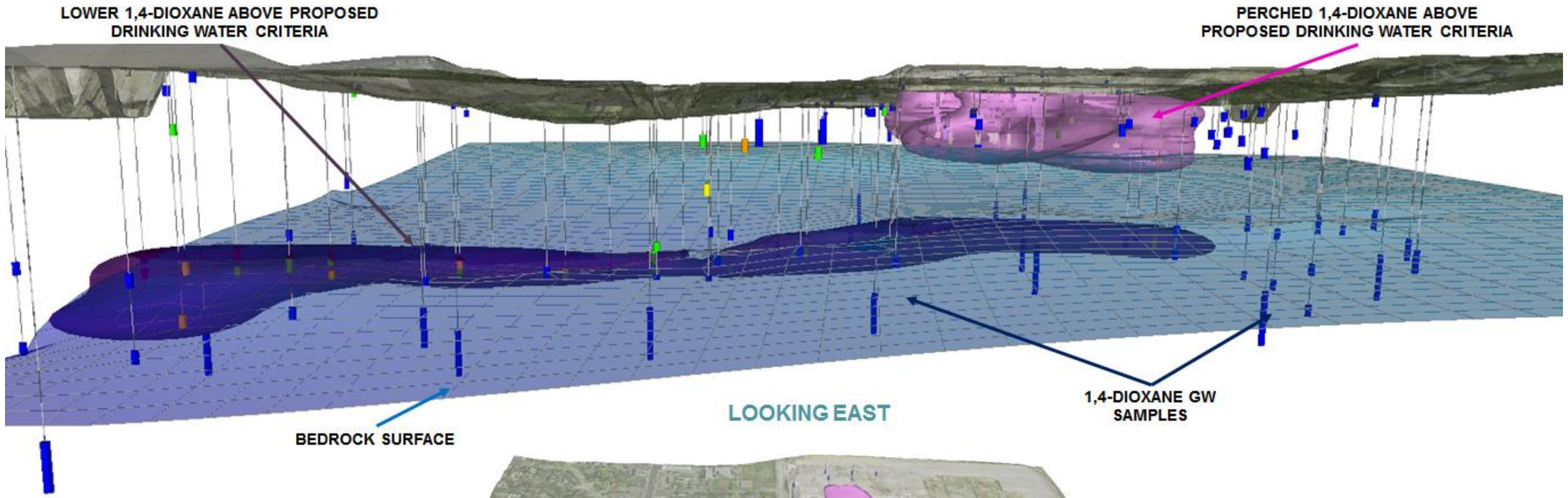
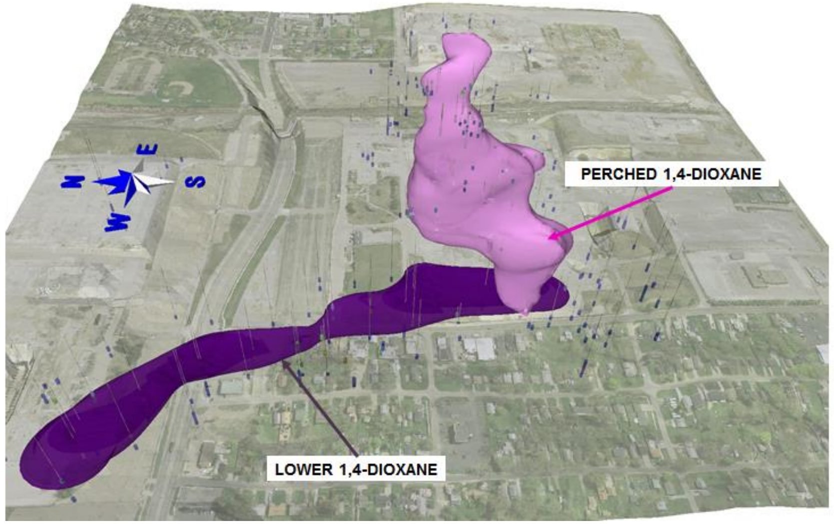
Understanding where 1,4-dioxane is and where it is going leads to appropriate treatment. Here that means ISCO and MNA combined.

Case Studies

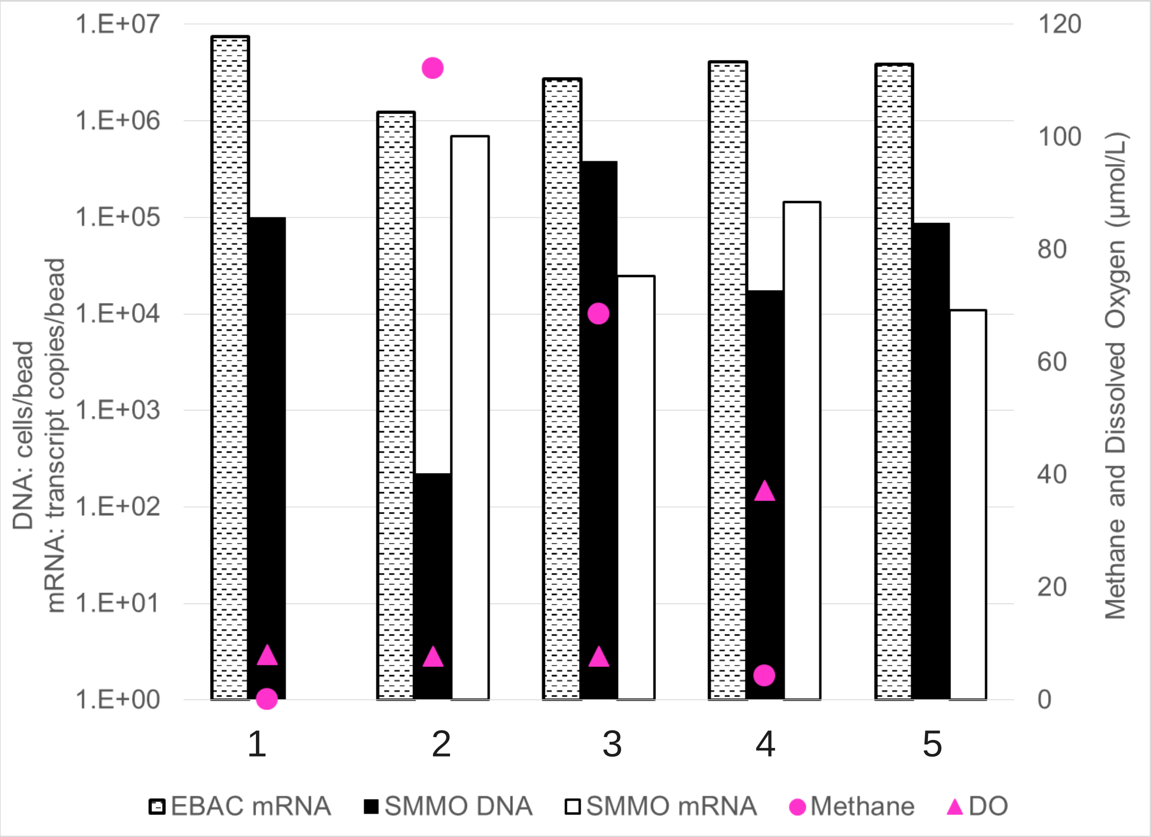
2. High resolution characterization provides powerful insight; advanced microbial tools build a case for cometabolic 1,4-dioxane biodegradation

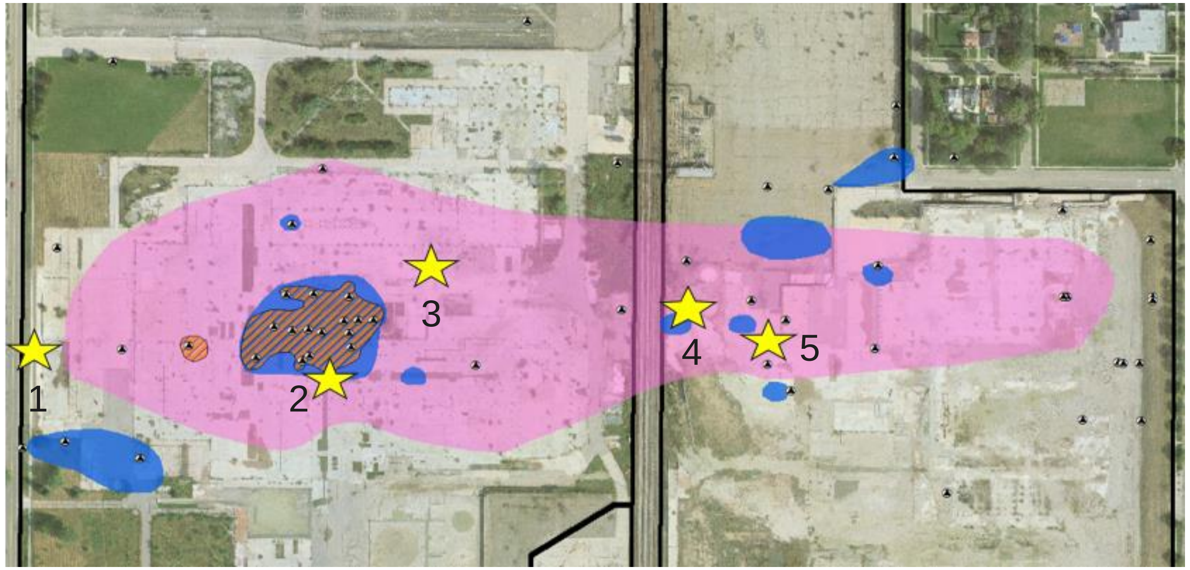
High Resolution Characterization - Powerful Insight into Plume Behavior



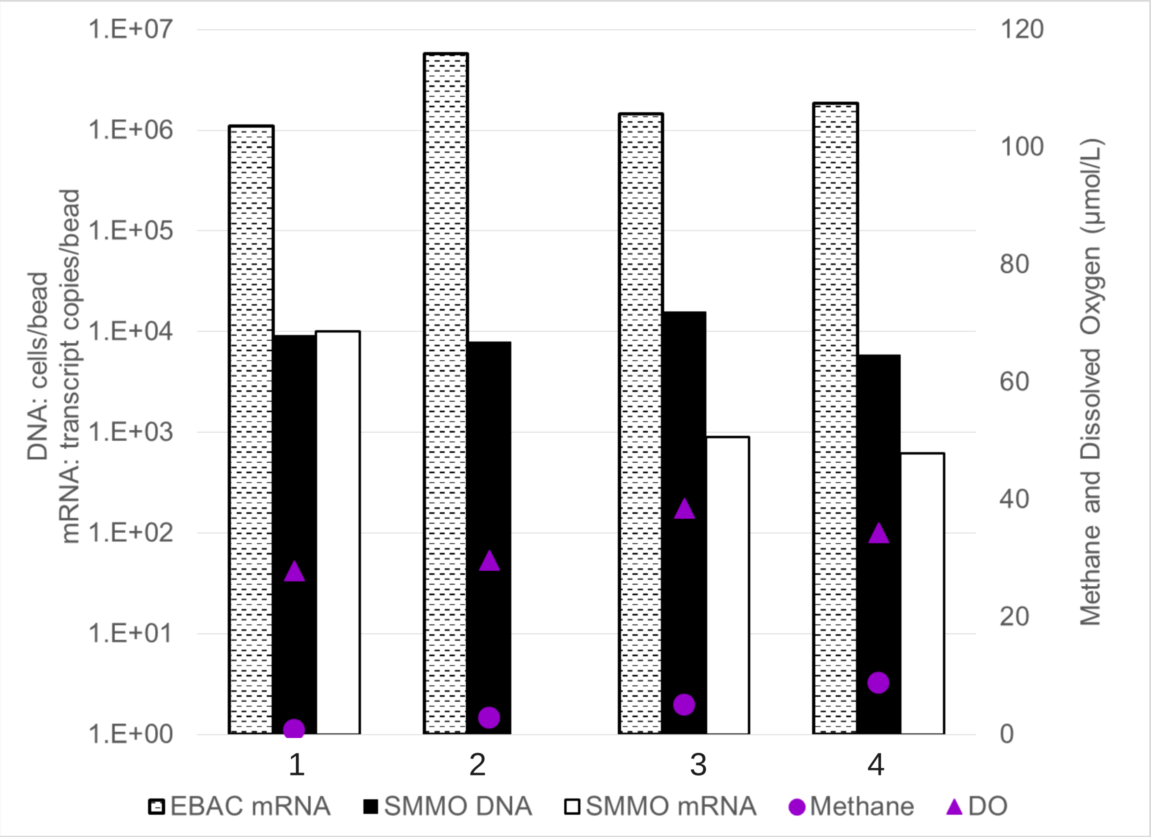


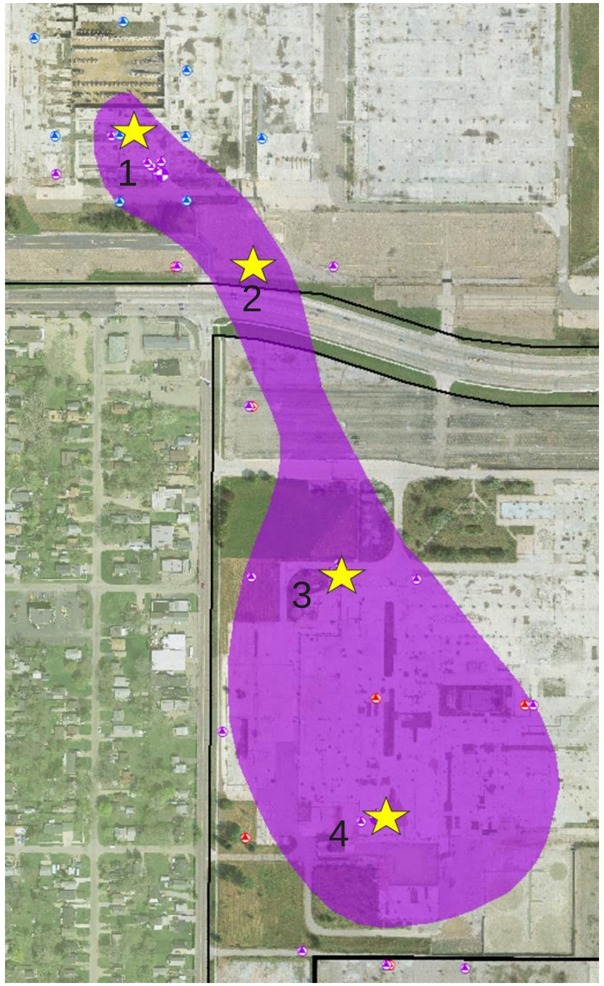
Upper Plume – Methane-linked Cometabolism





Lower Plume – Methane-linked Cometabolism

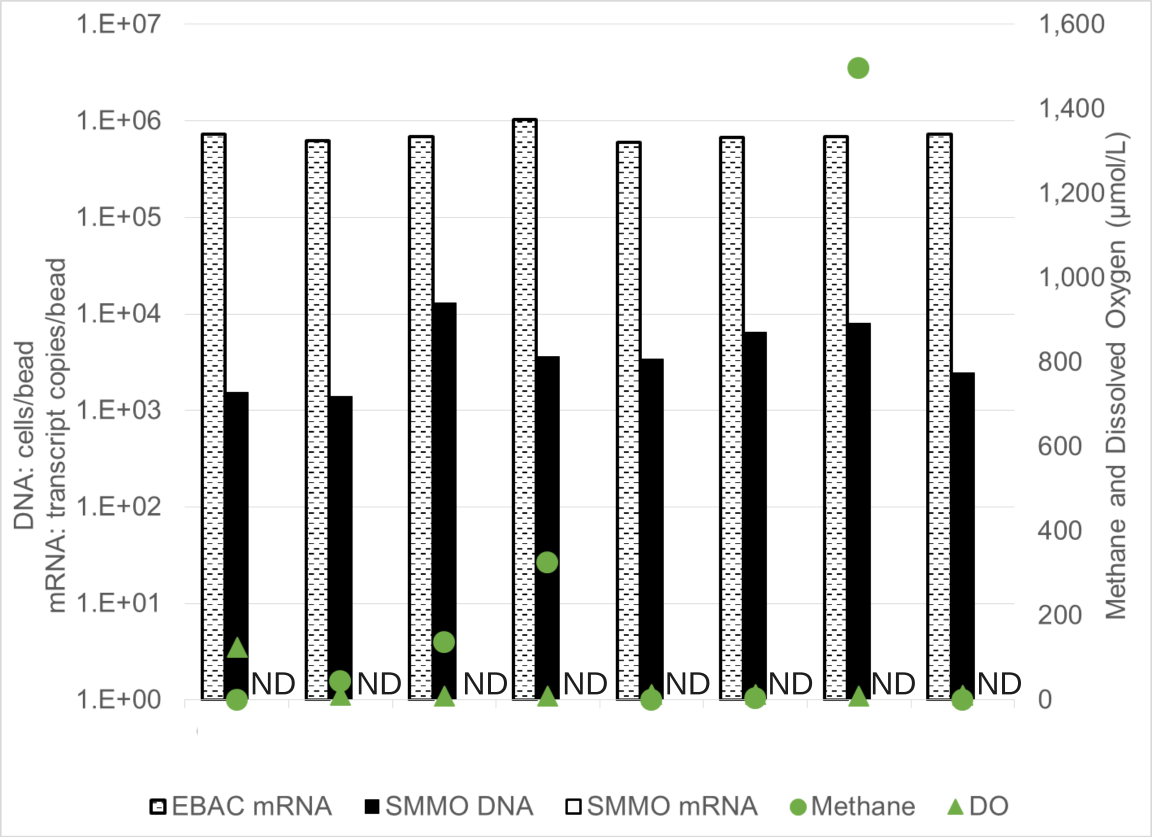


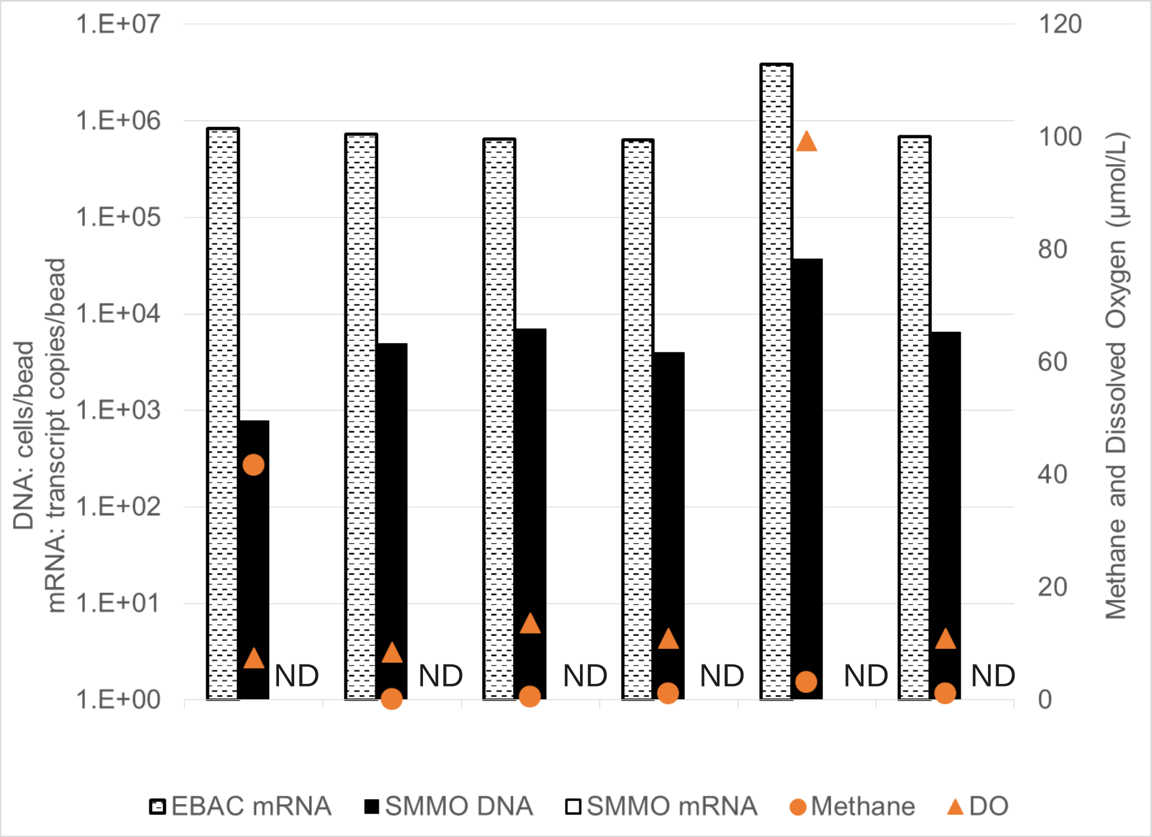


Case Studies

3. Lesson learned: multiple lines of evidence are needed for methane-linked cometabolism

Presence of SMMO Doesn't Prove Activity





Summary and Conclusions

- 1,4-Dioxane is an emerging contaminant
- A proactive management approach can be advantageous
- Monitored natural attenuation provides an attractive remedial alternative
- Advanced characterization approaches provide evidence needed to support a monitored natural attenuation approach
  - Understanding where mass is and where it is going is key
  - Microbial biodegradation is a viable remediation process
    - Requires multiple lines of evidence,
    - Nuanced understanding of cometabolic processes for demonstration