# 1,4-Dioxane Treatment Technologies: What's New and What's Proven

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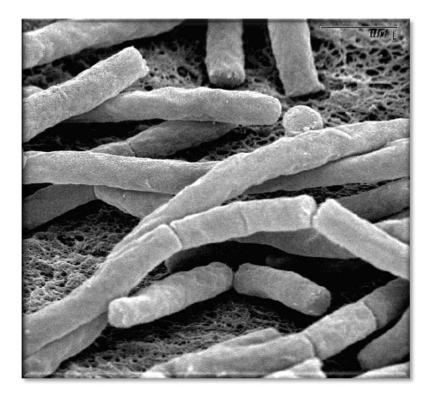




Delivering Sustainable Solutions to Complex Local Challenges, Worldwide Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies

## **Topics Covered**

- Introduction
- Chemistry
- Regulation
- Soil technologies (not covered)
- Water treatment technologies
  - Ex situ
  - In Situ
- Note that of Battelle platforms/posters: 1 soil XSVE, 1 MNA, 1 ISCO, 3 Phyto, 19 biodegradation!!!



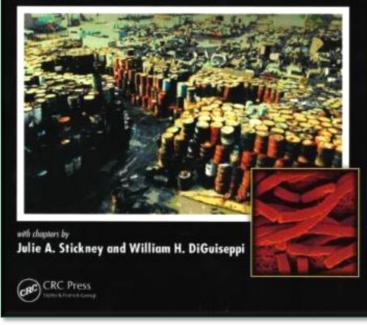
### 1,4-Dioxane Introduction

- Primarily used as a 1,1,1trichloroethane stabilizer (>95% of 1970's production)
- Commonly co-mingled with chlorinated volatile organic compounds and metals
- Hepatotoxic, neurotoxic, "Likely to be carcinogenic in humans"
- Low remediation goals:
  - US EPA tapwater Regional Screening Level 0.46 ug/L

#### ENVIRONMENTAL INVESTIGATION AND REMEDIATION

#### 1,4-DIOXANE AND OTHER SOLVENT STABILIZERS

Thomas K.G. Mohr

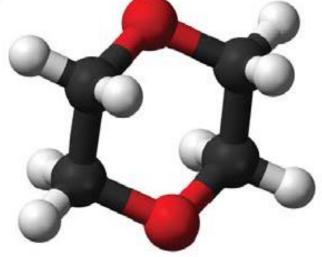


## Chemistry, Fate and Transport

- Formula:  $C_4H_8O_2$
- Synthetic cyclic ether
- Colorless, highly flammable liquid
- Miscible in water (infinite solubility)
- Migrates rapidly, sorbs minimally



- Diffuses into/through low permeability soils
- Results in large dilute plumes (<20 µg/L); few "source areas"</li>
- Many CVOC remedies (e.g., air sparge, GAC, ERD, KMnO4) are only marginally effective on 1,4-dioxane

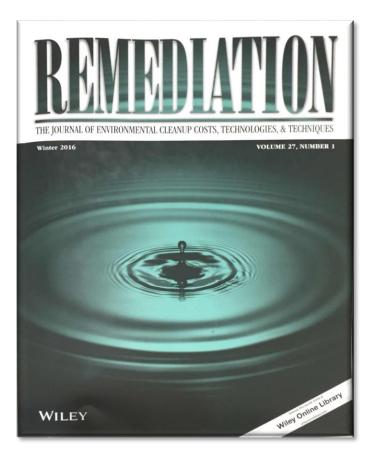


#### Representative US Regulations/Guidance

States	GW (µg/L)	Notes
New Hampshire	0.25	Reporting limit for all public water supplies
Massachusetts	0.3	Groundwater cleanup standard
New Jersey	0.4	Groundwater Quality Standard—October 2015
California	1	Notification level
Florida	3.2	Minimum criteria
Colorado	3.2	Drinking Water standard (proposed 0.35)
Michigan	7.2	Residential drinking water level
Illinois	7.7	Non- TACO (Tiered Approach to Corrective Action) Chemical
Texas	9.1	Residential Protective Concentration Level
New York	50	Drinking water standard
South Carolina	70	Drinking water health advisory

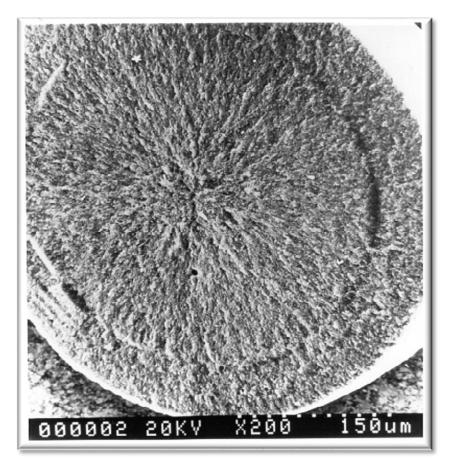
#### **Groundwater Remediation Technologies**

- Discussion is excerpted from Remediation Journal article (DiGuiseppi, Walecka-Hutchison, and Hatton, 2016)
- Ex Situ Technologies
  - Sorption
  - Advanced Oxidation
  - Biological Treatment
- In situ Technologies
  - Phytoremediation
  - Thermal
  - Chemical Oxidation
  - Biodegradation
  - Natural Attenuation



### Ex Situ - Sorption

- Granular activated carbon minimally effective
- CH2M tested several synthetic carbonaceous resins but found none to be effective
- DOW AMBERSORB 563<sup>TM</sup>
  - Demonstrated technology at multiple sites
  - Better than 99% removal rates
  - Applied up to 40,000 µg/L DX
  - Complex system engineering: regeneration, condensation, etc.
  - Cost competitive



Ambersorb 563 Bead, Woodard, 2016

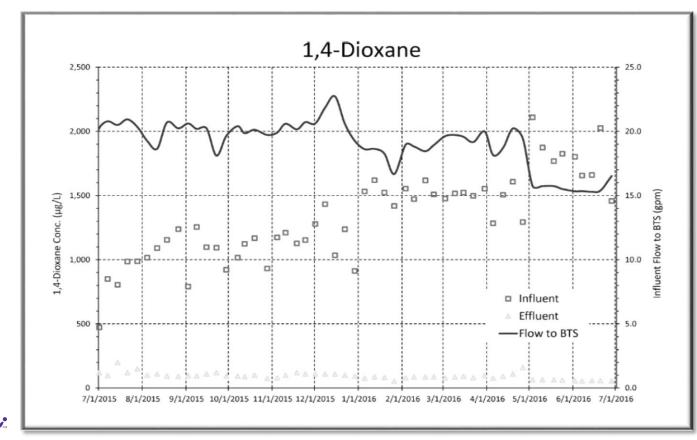
### Ex Situ – Advanced Oxidation

- Well demonstrated technologies at all flow rates (up to 7 MGD)
- UV-Peroxide (e.g., Rayox)
- Ozone Peroxide (e.g., HiPOx<sup>™</sup>)
- Relatively high capital cost, high O&M cost
- Removals of 99.9%, from >1,000 μg/L to <1 μg/L</li>
- Destructive approach, eliminates liability



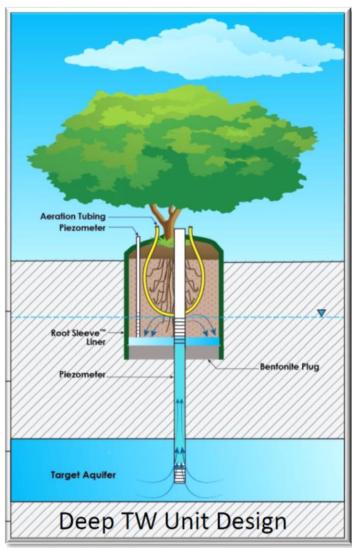
#### Ex Situ – Biological/Bioreactors

- Aerobic biodegradation demonstrated
- But: Inhibitors, co-contaminants, and concentration swings all can have an impact on effectiveness
- 90 to 98% removals achievable at high concentrations



Cordone, et al, 2016

#### Phytoremediation

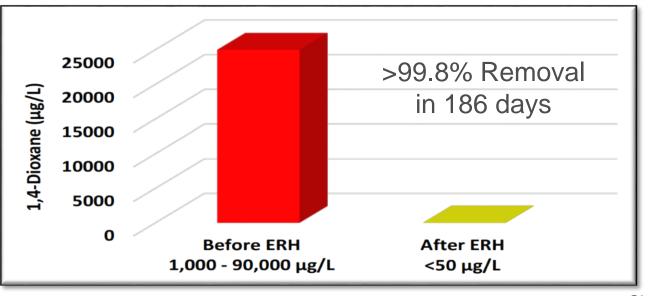


- Phytotranspiration process for DX well documented
- DX 7-day half-life in atmosphere; subject to oxidation
- Can be used for dewatering or containment (good for miscible 1,4-dioxane)
- Applied as engineered wetlands
- Treewell<sup>®</sup> application for deeper water successfully implemented

Gatliff, et al, 2013

### In Situ Thermal

- Electrical resistive heating (ERH)/Steam stripping
  - 1,4-Dioxane driven from soil with or after steam
  - High temperature improves stripping
  - Adsorbs to VGAC when "dry" (low relative humidity)
  - Demonstrated source area technology



Oberle, et al, 2015

### In Situ Chemical Oxidation

- Demonstrated in situ technology
- Drawbacks include:
  - Distribution of treatment materials
  - Secondary water quality (e.g., sulfate, manganese, ketones)
  - Potentially hazardous materials
- Utilizes oxidation reactions and radical reactions
- Oxidants include persulfate, permanganate, hydroxyl radicals
- Natural mineral activation of persulfate proven successful



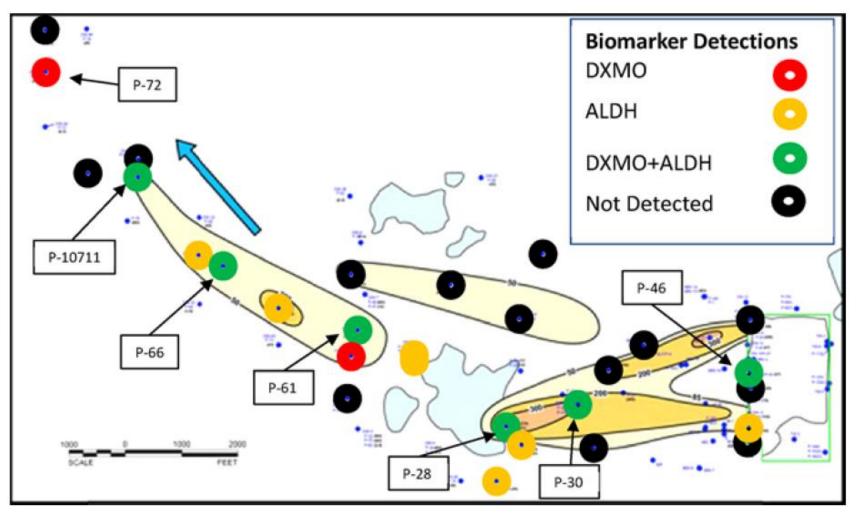
### Biodegradation

- Aerobic cometabolic or direct catabolic degradation
- Almost all the other talks in these two 1,4-dioxane sessions are about biodegradation!
- Microbiological tools (MBTs) developed by UCLA (Mahendra), Rice University (Alvarez/Li), others:
  - Bacterial communities
  - Enzymes: Dioxane monooxygenase, aldehyde dehydrogenase
  - Functional genes
  - Compound Specific Isotope Analysis (CSIA)
- MBTs now commercially available

#### **Monitored Natural Attenuation**

- DX-degrading bacteria found in many environments
- Occurrence of aerobic degradation likely widespread
- Example Study:
  - CH2M supported another consultant for an international pharmaceutical firm
  - Assessed MNA solution for long-term management
- Empirical data (trends, calibrated model, mass balance): indicated attenuation is occurring, mechanism undefined
- Worked with UCLA for 1,4-dioxane biomarker testing
  - Carbon Compound specific isotope analysis (CSIA) ineffective
  - Dioxane monooxygenase (DXMO)
  - Aldehyde dehydrogenase (ALDH)
- (Details in afternoon session)

#### DXMO/ALDH Results



Gedalanga, et al, 2016

## Remediation Technology Takeaways

- Solution, of course, depends on site characteristics
  - Concentrations
  - Hydrogeology
  - Co-contaminants, inhibitors (tetrahydrofuran, copper, trichloroethene)
  - Timeframe/remedial objectives
- Demonstrated Technologies:
  - High concentration source area removal: ISCO, thermal
  - Low concentration containment: **P&T with AOT/Sorption**
  - Low concentration extensive plume with long timeframe: aerobic biostimulation, MNA

Lots happening, new solutions being validated

# Thank you!

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