What We Know and What We Need to Know to Establish Biodegradation of 1,4-Dioxane

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1,4-Dioxane: Another Forever Chemical?

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Research Paper

The first quantitative investigation of compounds generated from PFAS, PFAS-containing aqueous film-forming foams and commercial fluorosurfactants in pyrolytic processes

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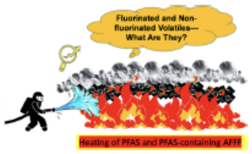
HIGHLIGHTS

- Compounds emitted from PFAS-relevant commercial products and PFAS upon pyrolysis.
- Approximately 30 non-fluorinated compounds were detected at 200–500 °C.
- 1,4-Dioxane was emitted from multiple heated AFFF and fluorosurfactant samples.
- Perfluoroheptene (C_7F_{14}) thermally decomposed at temperatures as low as 200 °C.
- Most of these compounds were not detected at 890 °C.

GRAPHICAL ABSTRACT



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POLLUTION

1,4-Dioxane: Another forever chemical plagues drinking-water utilities

Highly miscible in water, the likely carcinogen is challenging to remove

by Cheryl Hogue

November 8, 2020 | A version of this story appeared in Volume 98, Issue 43

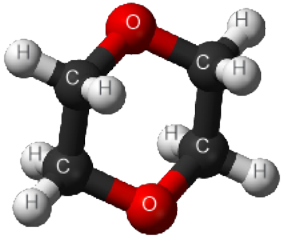
1,4-Dioxane gets around.

It's on laboratory shelves, a reagent familiar to bench scientists. Some drugmakers use it to purify pharmaceutical ingredients. Filter makers employ it to create tiny pores in membranes. The chemical's commercial heyday was in the second half of the 20th century, when it stabilized chlorinated solvents used for metal degreasing.

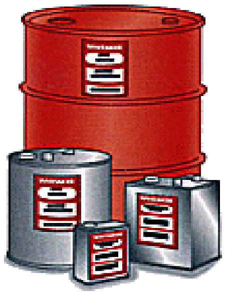
Since then, the chemical's reputation has dimmed.

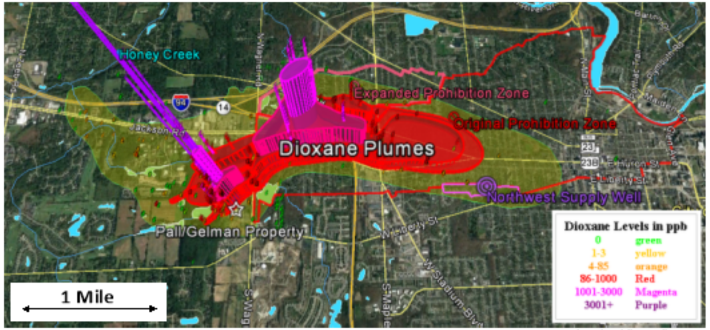
In toxicity studies, laboratory rodents given 1,4-dioxane in their drinking water developed liver cancer. The US National Toxicology Program classifies the synthetic compound as "reasonably anticipated to be a human carcinogen." Likewise, the US Environmental Protection Agency deems this synthetic chemical a likely carcinogen. In addition, 1,4-dioxane doesn't readily biodegrade in the environment, the EPA says.

1,4-Dioxane (DX) in the Environment



- Sources
  - Stabilizer for 1,1,1-trichloroethane (1,1,1-TCA)
  - Paint strippers, dyes, greases, varnishes, waxes
  - Impurity in detergents, antifreeze, cosmetics, deodorants, shampoos
- Enters groundwater through improper storage, handling, and disposal
- High solubility + moderate adsorption + chemical stability => challenging to remove from water





Source: National Public Radio 2018

(Mohr, Stickney, and DiGuiseppi, 2010)
(EPA, Scope of the Risk Evaluation for 1,4-Dioxane, 2017)

1,4-Dioxane Regulatory Framework

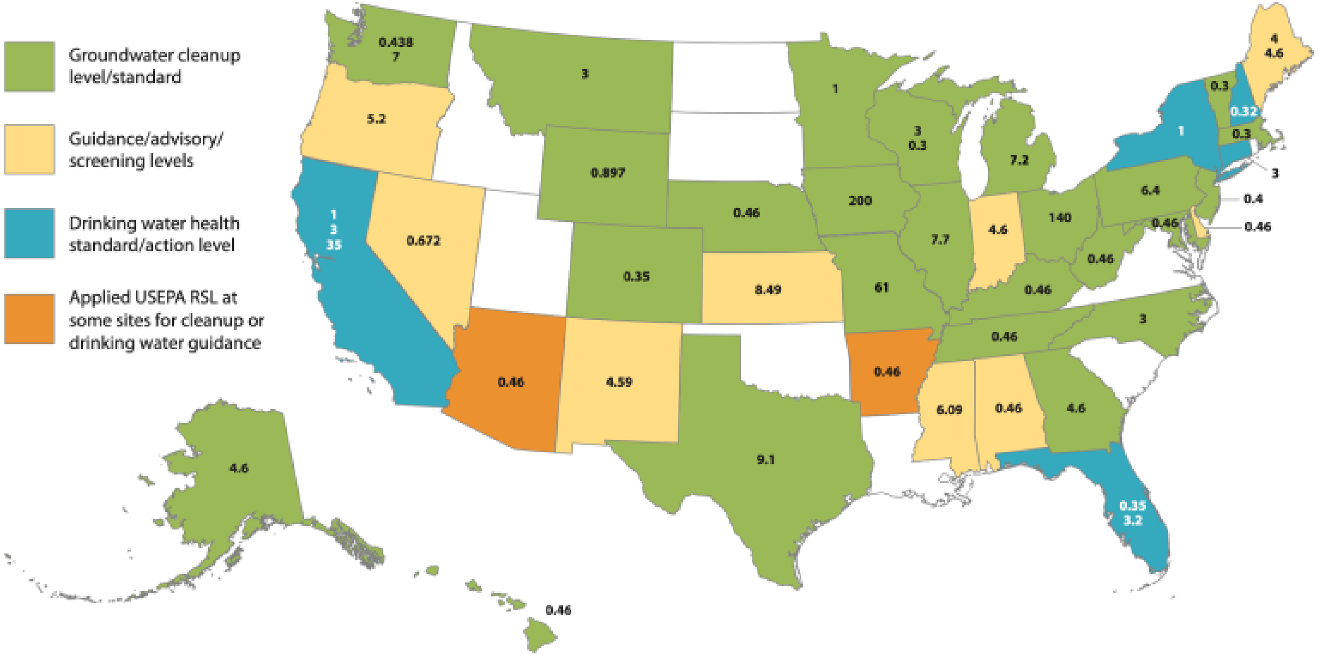
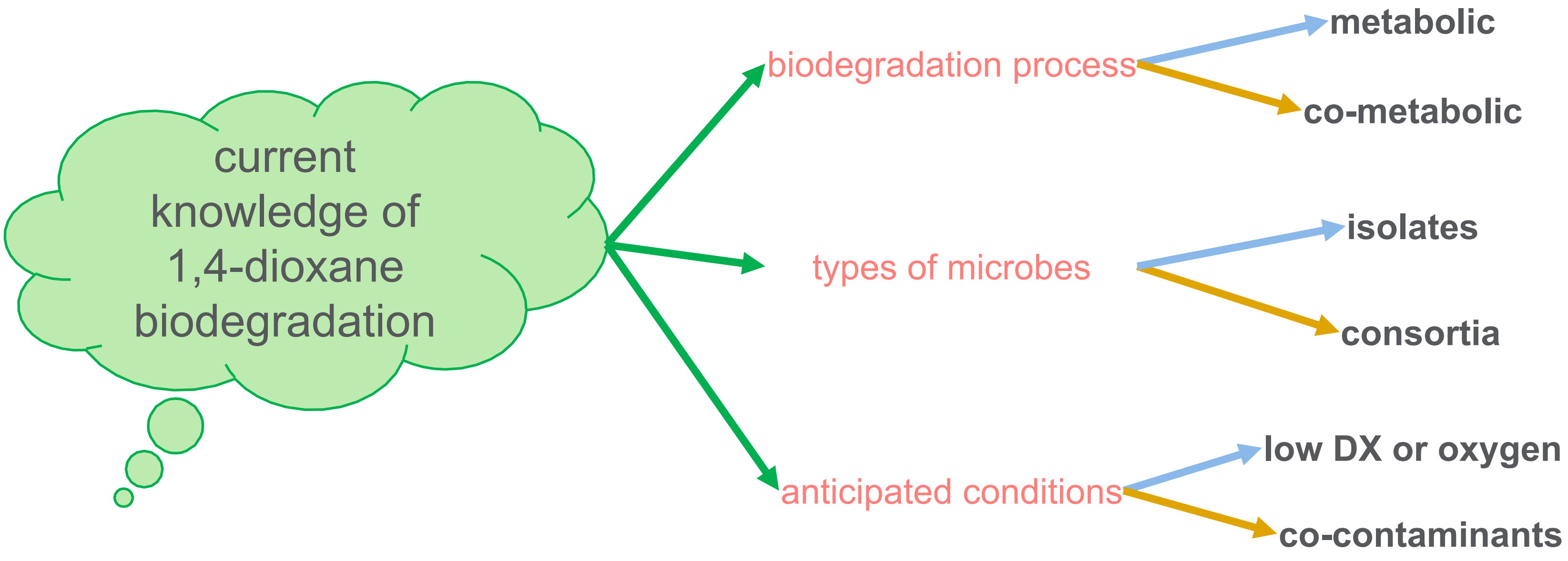


Figure 1. 1,4-Dioxane state regulatory values for drinking water and groundwater in micrograms per liter (µg/L). (RSL: regional screening level; USEPA: U.S. Environmental Protection Agency.)

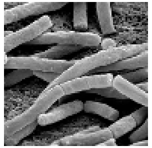
ITRC 2021

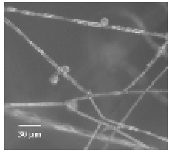
1,4-Dioxane Biodegradation in the Environment



Mounting Evidence of DX Biodegradation

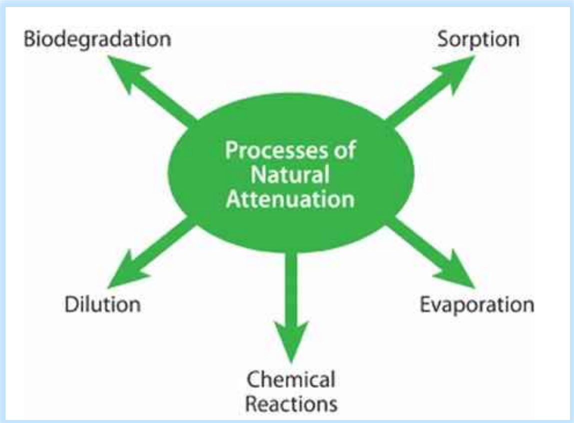
- **pure cultures**
  - aerobic bacteria
  - aerobic fungi





- **mixed communities** in industrial sludge
- **co-metabolism** induced by hydrocarbons
  - tetrahydrofuran
  - methane
  - ethene
  - propene
  - toluene
- **treatment trains**
  - abiotic-biotic

- **field efforts**
  - biostimulation
  - bioaugmentation
- **natural attenuation** in groundwater
  - limited evidence



Assimilative v. Co-Metabolic Biodegradation

Pros:

- no other substrates required
- accumulation of toxic byproducts less likely

Cons:

- specific microbes required
- minimum growth-supporting concentration

***Pseudonocardia dioxanivorans* CB1190**
{DX is mineralized}

electron donor: $C_4H_8O_2 + 6H_2O \rightarrow 4CO_2 + 20e^- + 20H^+$
electron acceptor: $5O_2 + 20H^+ + 20e^- \rightarrow 10H_2O$
biosynthesis: $C_5H_7O_2N$

***Mycobacterium dioxanotrophicus* PH-06**
{HEAA terminal product}

electron donor: $C_3H_8 + 6H_2O \rightarrow 3CO_2 + 20e^- + 20H^+$
electron acceptor: $5O_2 + 20H^+ + 20e^- \rightarrow 10H_2O$

co-substrate: $C_4H_8O_2 + 2H_2O \rightarrow C_4H_8O_4 + 4e^- + 4H^+$
electron acceptor: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
biosynthesis: none

Pros:

- concentration-independent
- can degrade co-contaminants

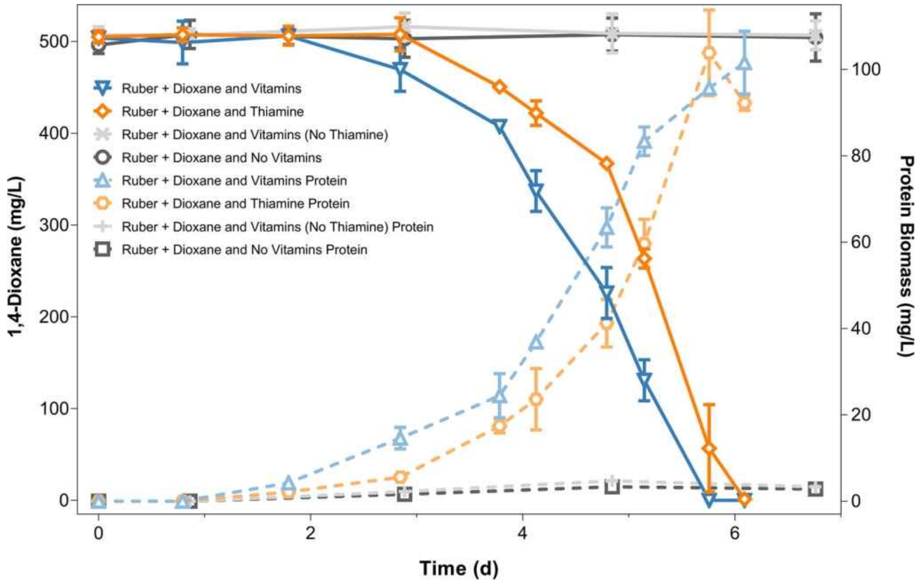
Cons:

- requires other substrates
- incomplete degradation; maybe toxic intermediates

Mahendra et al. 2007; Deng et al. 2018

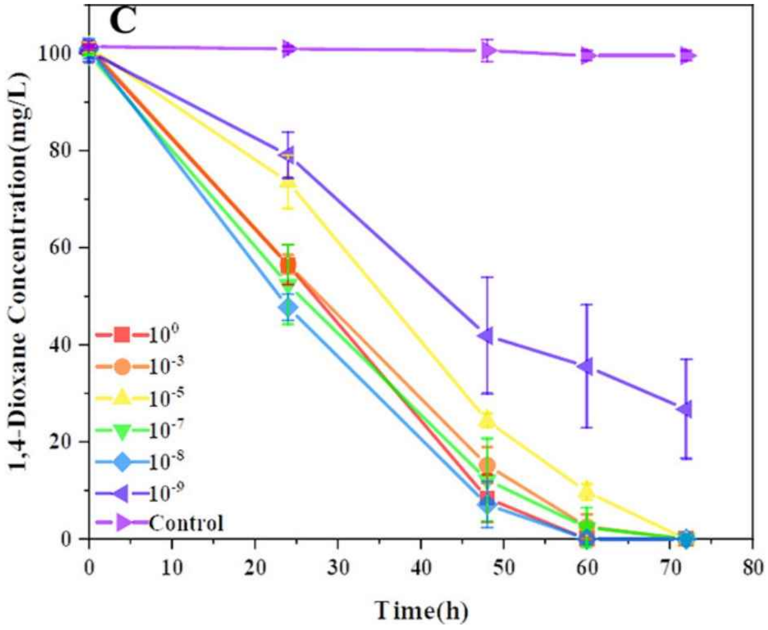
DX Degradation by Isolates v. Consortia

Pure culture
***Rhodococcus ruber* Strain 219**



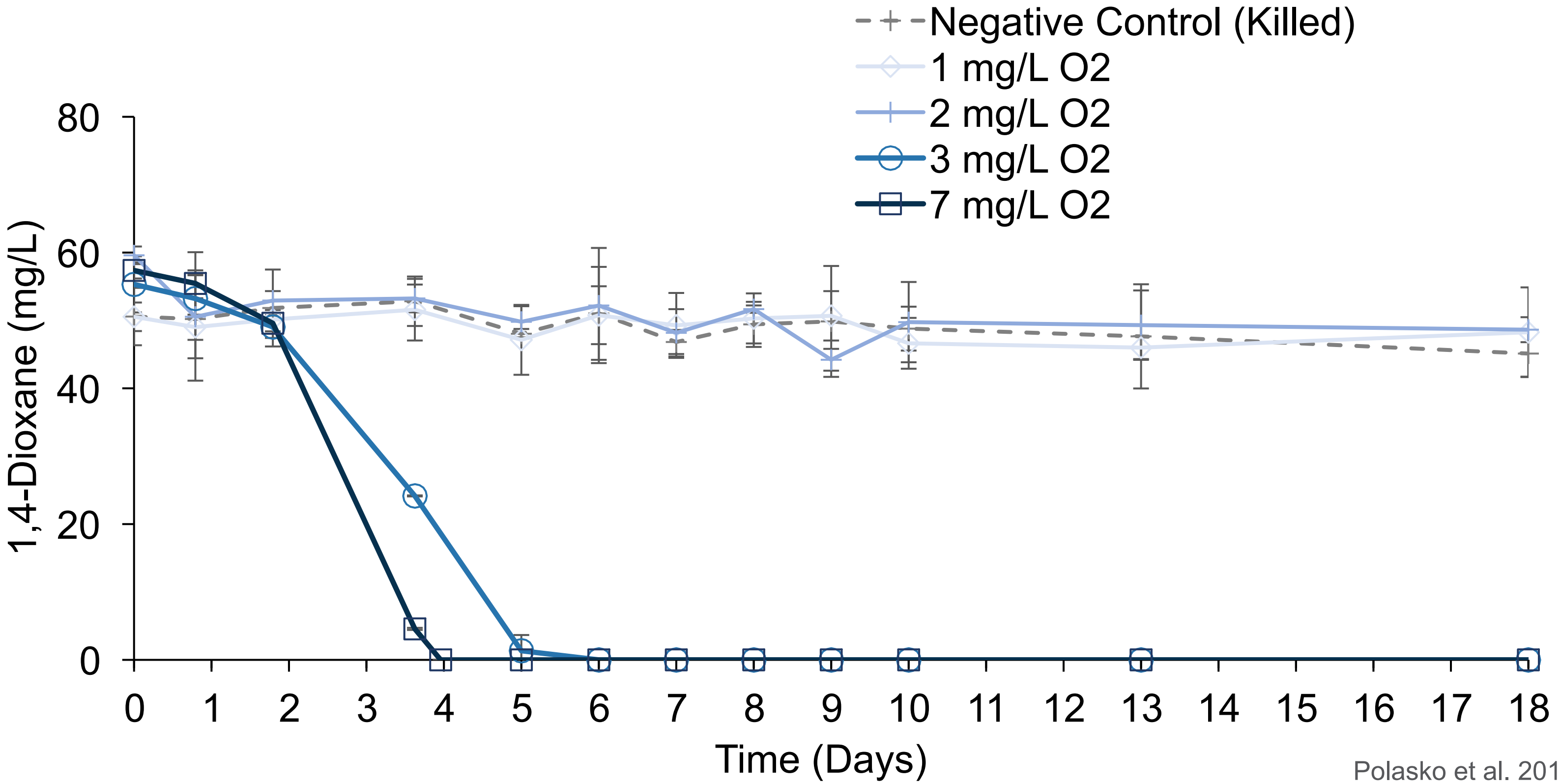
Simmer et al. 2021

Microbial consortium
containing *Shinella yambaruensis*



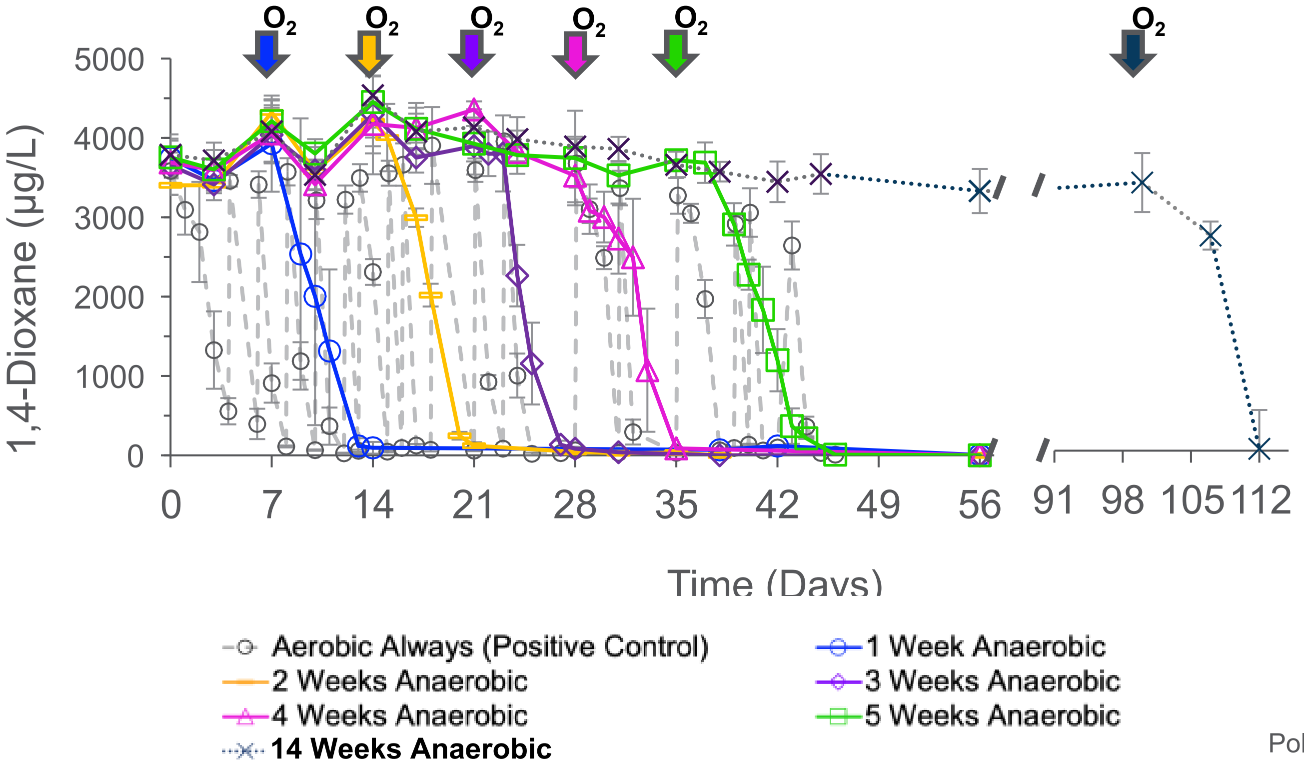
Tian et al. 2023

CB1190 Degrades DX in the Presence of Only ~3 mg/L O_2



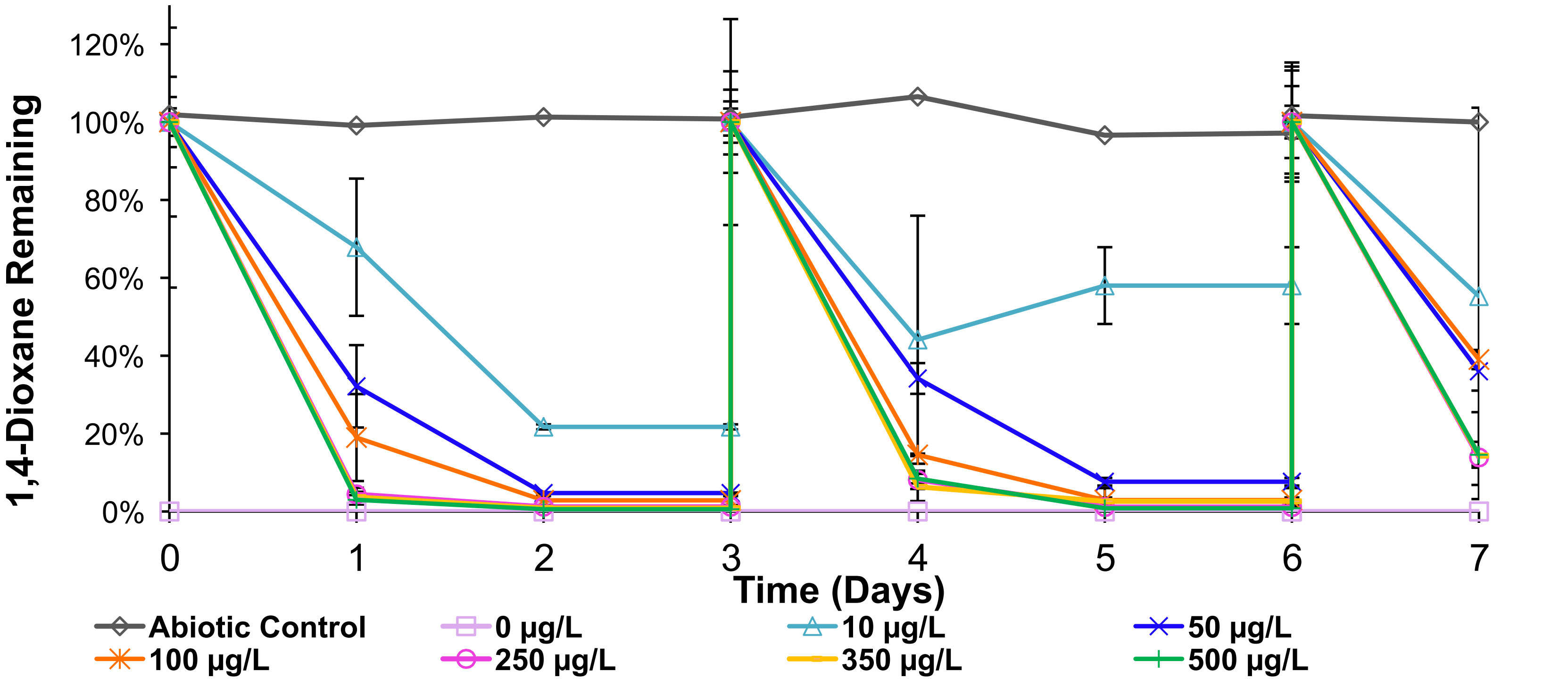
Polasko et al. 2018

CB1190 Degrades DX after 100 Days Anaerobic Incubation



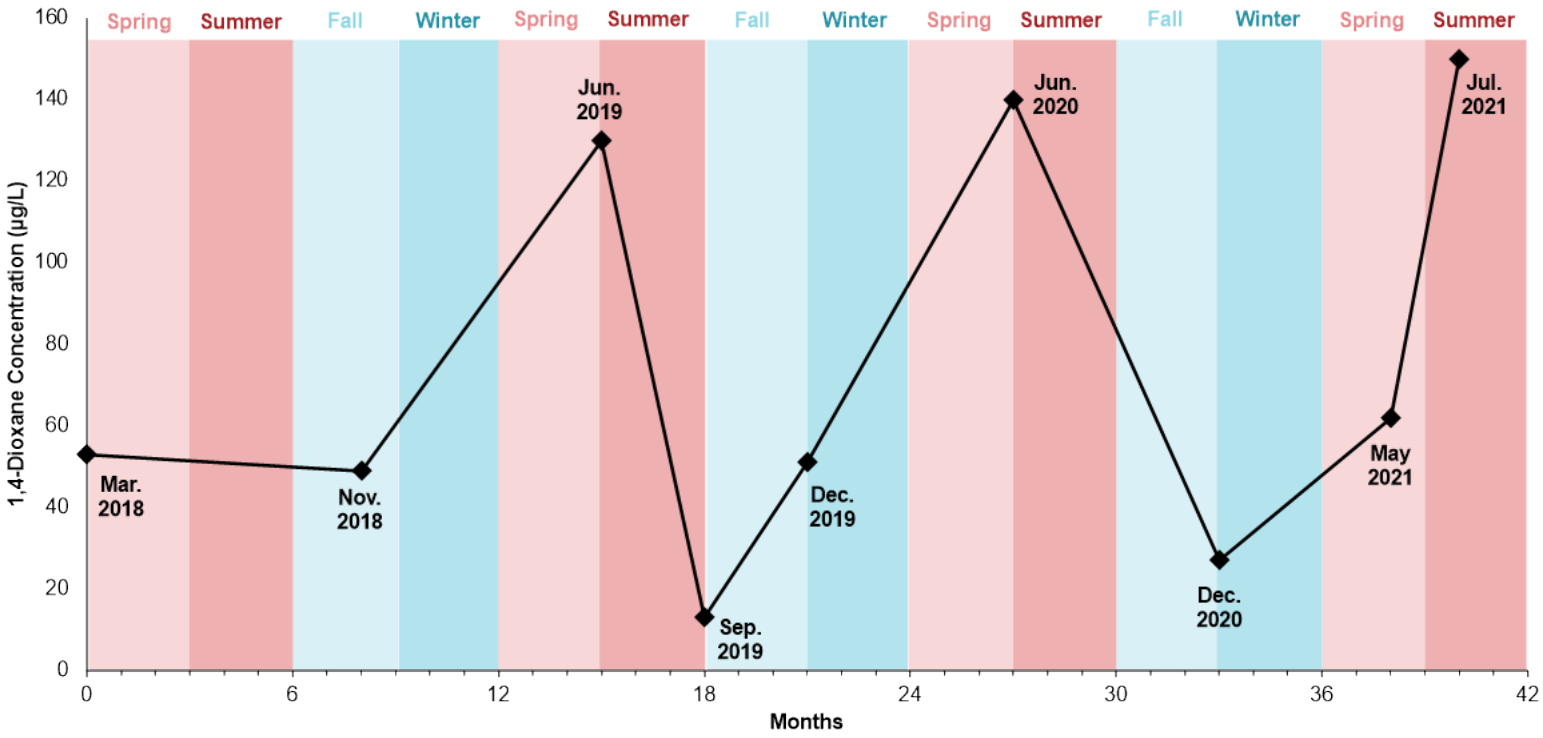
Polasko et al. 2018

CB1190 continuously biodegrades low DX concentrations



Pornwongthong, PhD Dissertation, UCLA 2014

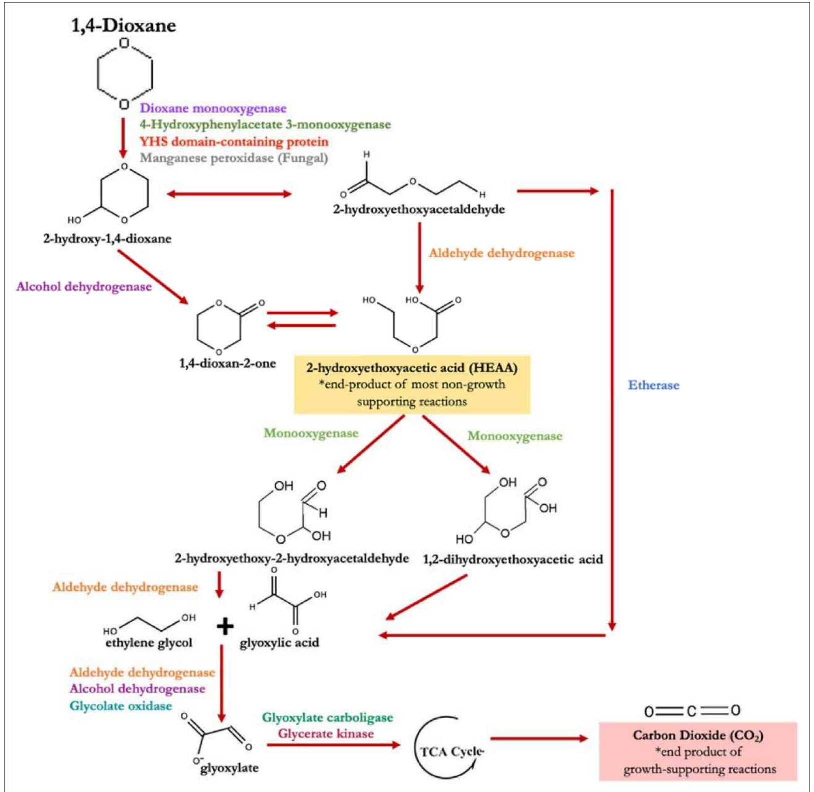
Natural Attenuation of DX in Warmer Months



1,4-dioxane impacted groundwater downgradient from landfill site

Kwok et al. (in preparation)

Biomarker Genes to Identify DX Degradation

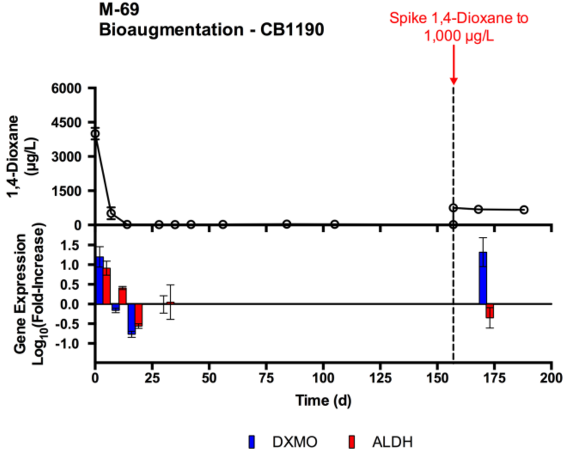


Current Opinion in Environmental Science & Health

dxmB – codes for dioxane monooxygenase (DXMO), which initiates 1,4-dioxane degradation

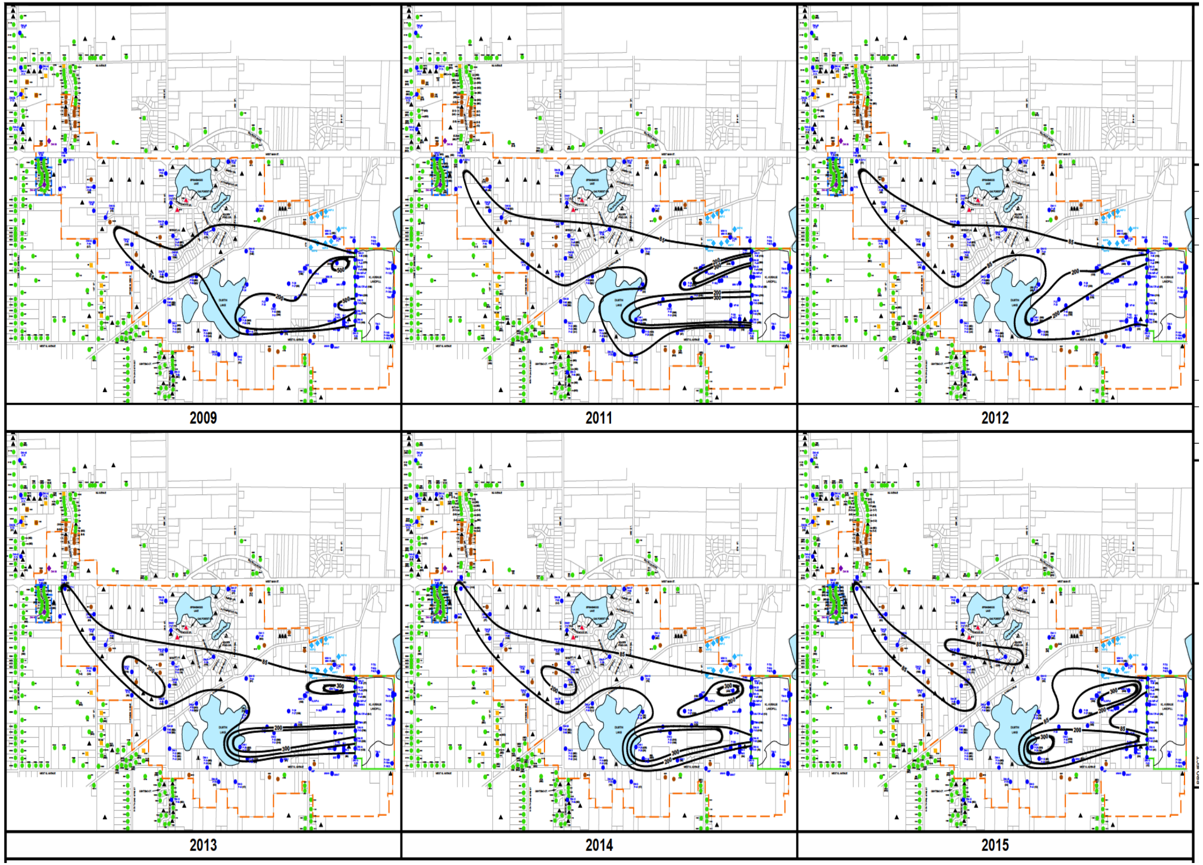
aldH – codes for aldehyde dehydrogenase, which degrades intermediates in the 1,4-dioxane degradation pathway

dxmB responds to 1,4-dioxane presence;
aldH responds to 1,4-dioxane degradation



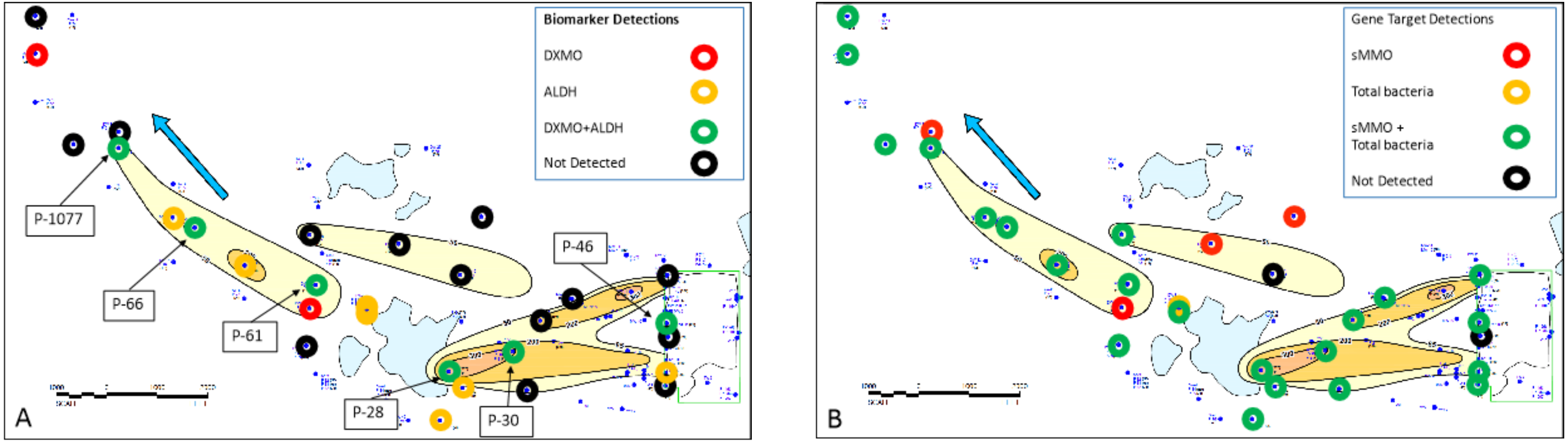
Ramos et al. 2022; Gedalanga et al. 2014

Observed Shrinking of a DX Plume over 6 Years



Gedalanga et al. 2016

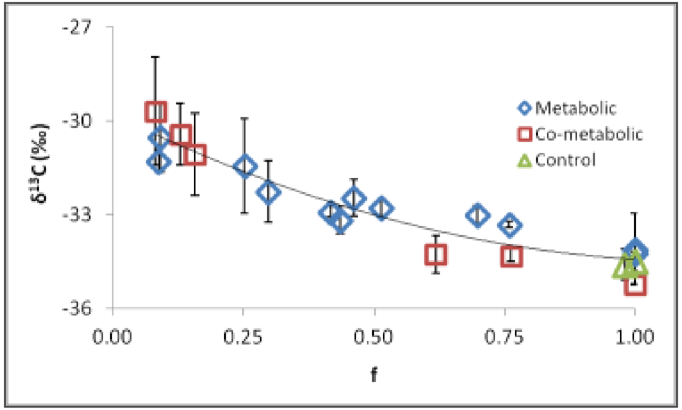
Biomarkers to Validate DX Natural Attenuation

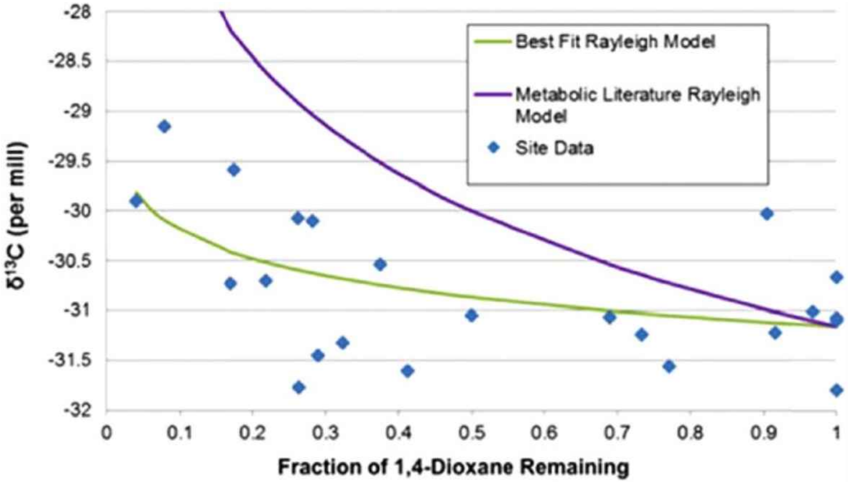


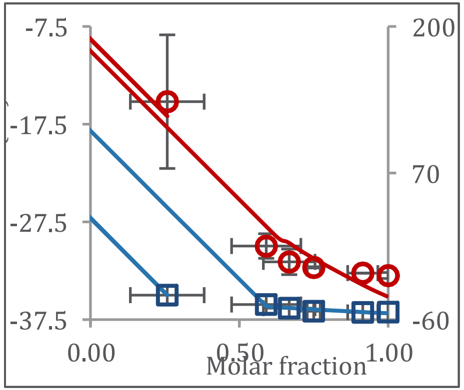
- Confirmed natural attenuation of DX in shrinking plume at a landfill site
- Detected of biomarker genes (*dxmB*, *aldH*, ***smmO***) indicated DX **metabolic** and potential **co-metabolic** degradation

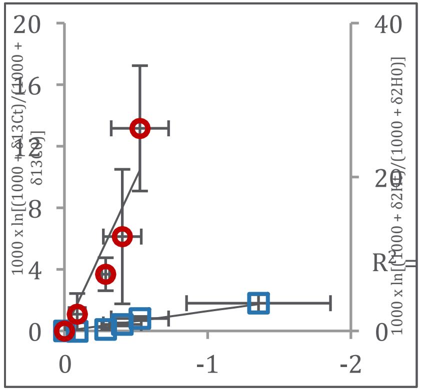
Gedalanga et al. 2016

Stable Isotopic Shifts During DX Biodegradation







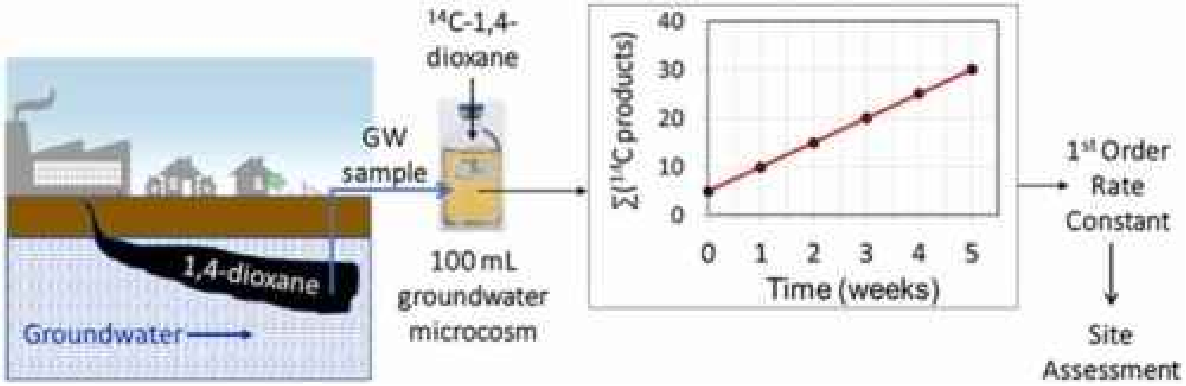


$^{13}C/^{12}C$ and $^{2}H/^{1}H$ isotope ratios of residual DX increase as it is aerobically biodegraded.

Small enrichment of ^{13}C isotope leads to the difficulty in interpretation of field data.

Pornwongthong et al. 2014; Gedalanga et al. 2016

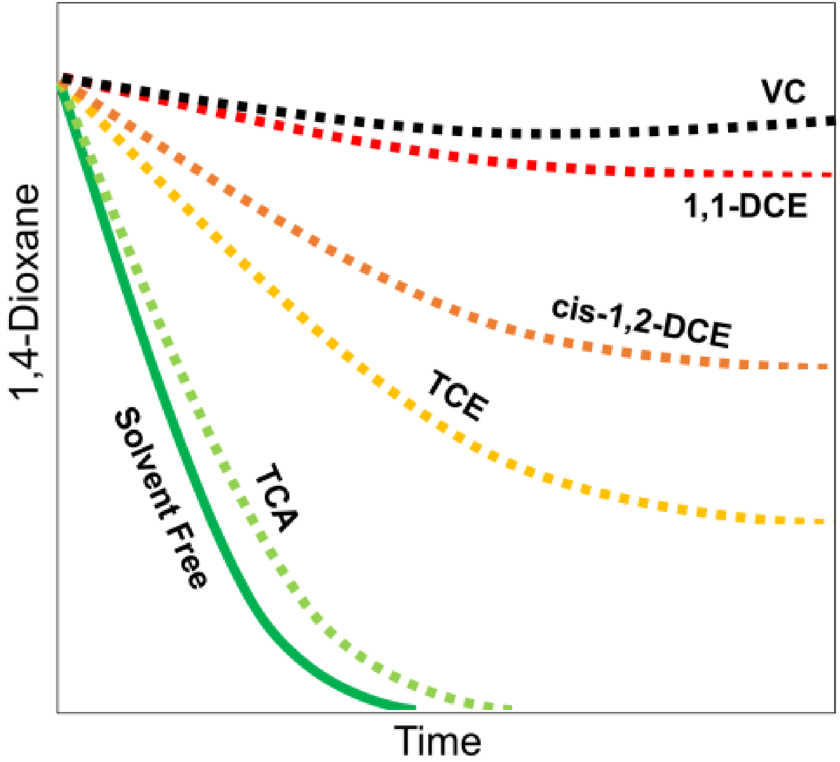
^{14}C Assay for 1,4-Dioxane Natural Attenuation



Ramos García et al. 2022

- ^{14}C assay developed to determine rate constants for natural attenuation of DX in groundwater
- validated with DX-metabolizing and co-metabolizing aerobic bacteria
- rate constants as low as 0.0021 yr^{-1}, but increased with added nutrients

DX Degradation in the Presence of CVOCs



- CVOCs slow down DX biodegradation by *Pseudonocardia dioxanivorans* CB1190, and some cultures capable of 1,4-dioxane cometabolism

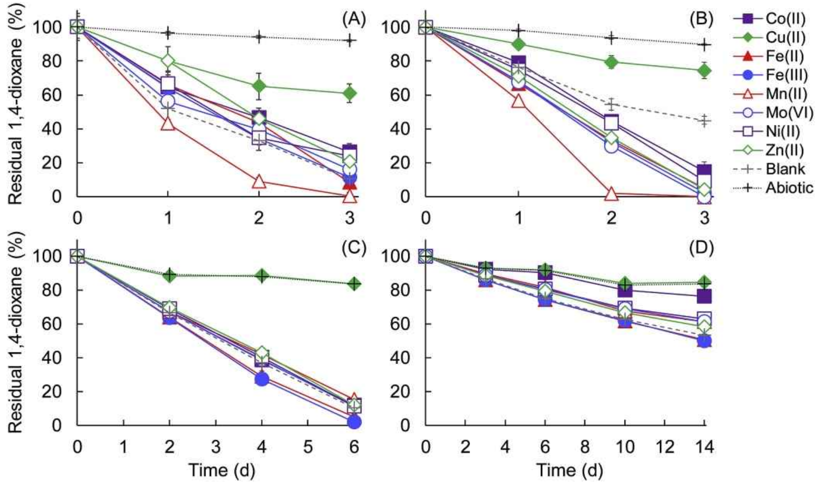
- Inhibitory effects from highest to lowest:

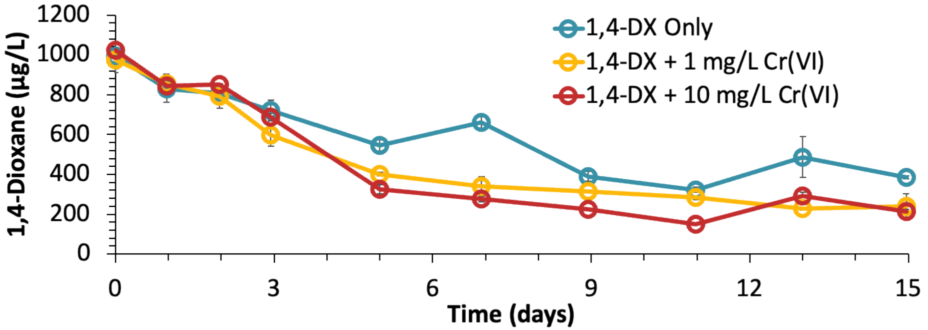
VC > 1,1-DCE > *cis*-1,2-DCE > TCE > 1,1,1-TCA

- CB1190 can grow on VC and cDCE with or without DX

Zhang et al. 2016; Polasko & Miao et al. 2021

DX Biodegradation in the Presence of Metals



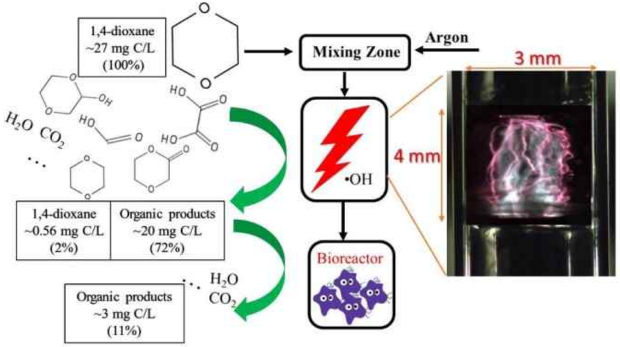


- DX biodegradation by *Pseudonocardia* sp. D17 (A), *Pseudonocardia* sp. N23 (B), *Mycobacterium* sp. D6 (C), and *Rhodococcus aetherivorans* JCM 14343 (D) in presence of various metals 2 mg-metal/L
- Cu(II) was most inhibitory
- Little to no inhibition of DX biodegradation by Cr (VI)
- Role of exopolysaccharides in mitigating heavy metal effects

Johnson, et al. 2019; Inoue et al. 2020

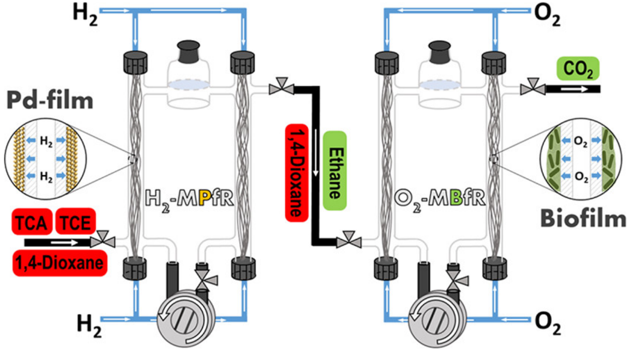
Treatment Trains for DX (and CVOC) Degradation

Non-thermal plasma/biodegradation



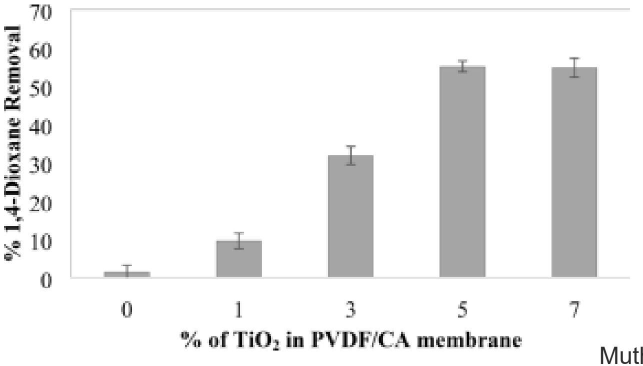
Xiong et al. 2019

H_2-based membrane palladium-film reactor/O_2-based membrane biofilm reactor



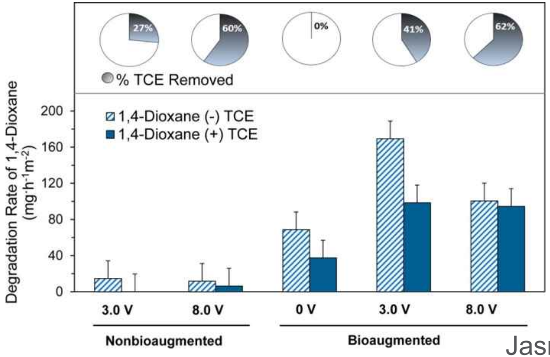
Luo et al., 2021

TiO_2/electrospun membranes



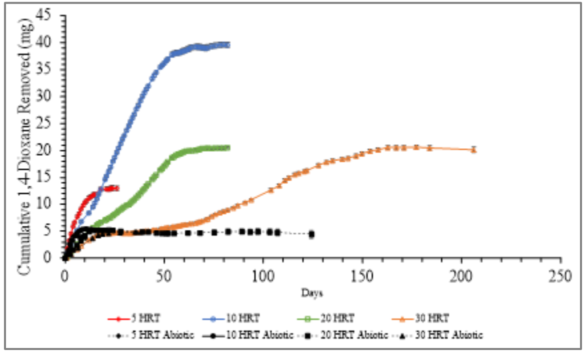
Muthu Kumar et al., 2021

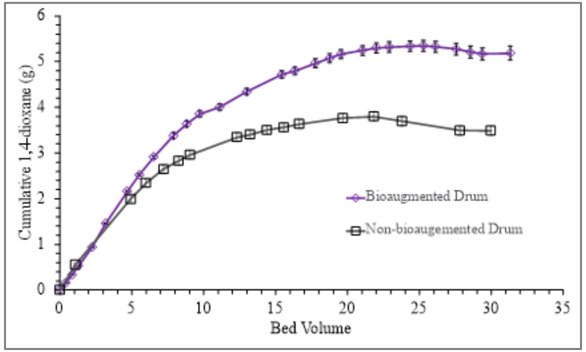
Combined electro-biodegradation



Jasmann et al. 2017

DX Treatment Trains: BioGAC

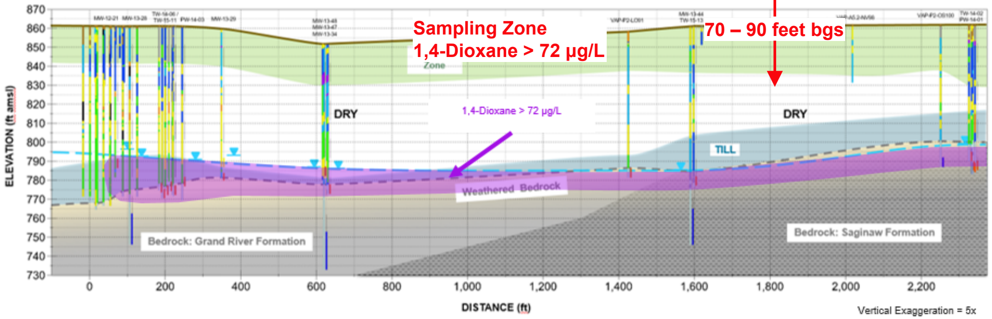




- BioGAC can remove **50% - 800%** more DX than non-augmented GAC
- Low H_2O_2 doses (≤0.001% w/v) maintained aerobic conditions
- BioGAC mitigates the inhibition concerns of CVOCs on DX aerobic biodegradation by CB1190
- GAC sorption reversibility → $$ ☠
- BioGAC sorption regeneration → $
- Field demonstration yielded 50% less DX removal compared to controlled laboratory columns

Ngo, Johnson et al. in prep

Bioremediation Comparison and Optimization



Condition	Day 0 - 90	Day 90 – 150 w/ N&P	Day 90 – 150 w/o N&P
Autoclaved control			
Biostimulation with Oxygen			
Biostimulation with Propane			
Bioaugmentation with ENV425			
Bioaugmentation with CB1190			

Pseudonocardia dioxanivorans CB1190

Rhodococcus ruber ENV425

Phase I

Spargability of weathered bedrock

Air Sparge Only Test

Determine spargability and optimal well placement field testing

Phase II

Proof of concept biodegradation lab studies

Lab Proof of Concept

Understand processes and response to changing conditions in a controlled environment

Phase III

Proof of concept biodegradation field studies

Propane Biosparge and Bioreactor Tests

Determine if biosparge and/or bioreactors are capable of biodegrading 1,4-dioxane at the site

Phase IV

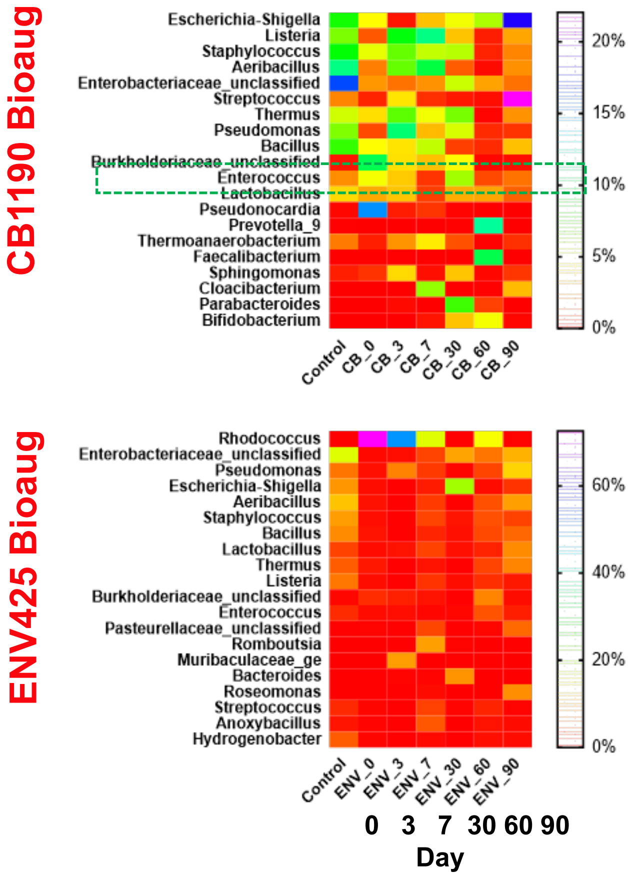
Pre-design testing with enhancements

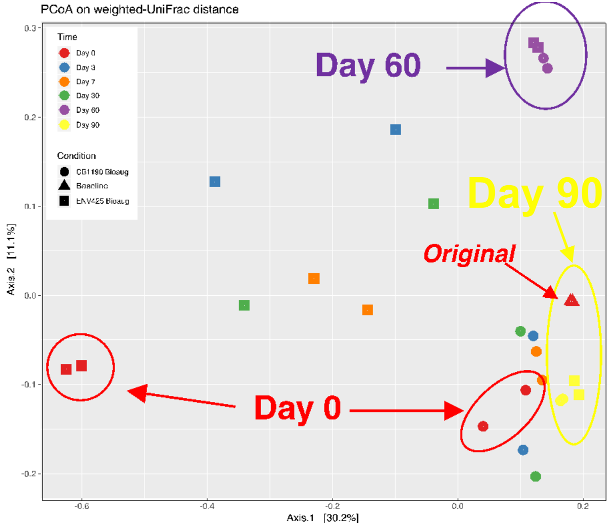
Pre-Design Test

Incorporate field/lab findings. Vet conceptual design assumptions and assess realistic treatment expectations

Hosrt et al., 2019; Miao et al., 2021a

Bench and Pilot Test with Microbial Functions

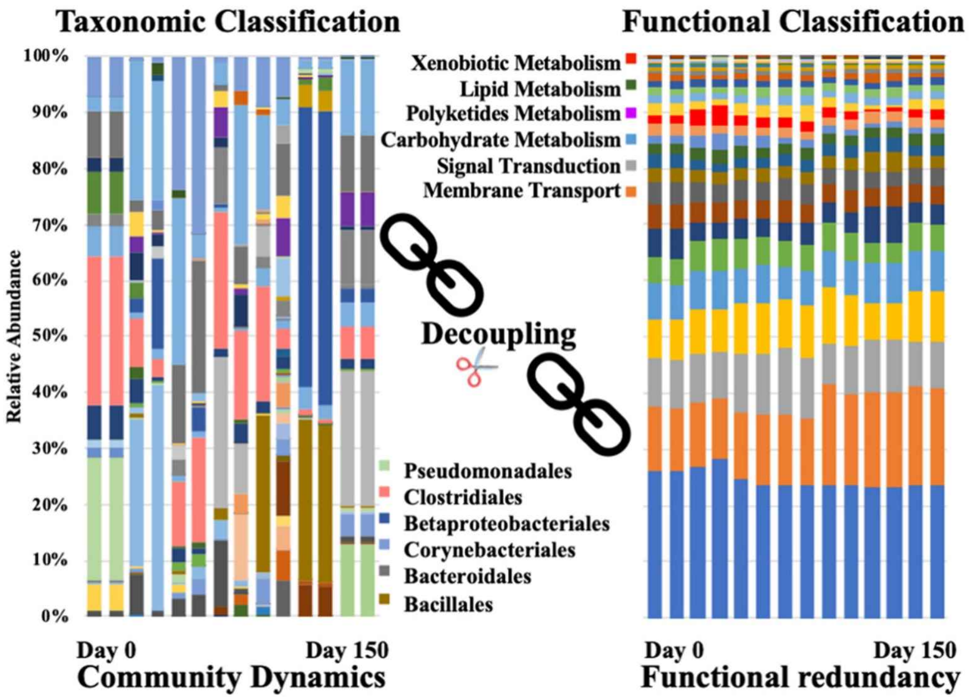




- Bioaugmentation with CB1190 and ENV425 resulted in rapid 1,4-dioxane biodegradation, but were eventually outcompeted by native microbes.
- Typically, bioaugmentation will have immediate effect on 1,4-dioxane biodegradation rates, while biostimulation will result in longer lasting biodegradation.

Hosrt et al., 2019; Miao et al., 2021a

Decoupling between Function and Community



- Abundance of biomarker genes is useful for indicating biodegradation potential; expression is better for forecasting rates.
- Microbes responsible for biodegradation of specific compounds don't need to be a large fraction of the population.
- Even though the microbial community composition changes, functional redundancy ensures stable microbiomes and biogeochemical processes.

Hosrt et al., 2019; Miao et al., 2021a

Summary and Significance

WHAT WE KNOW

- DX biodegradation is possible
- low DX and O_2 concentrations not necessarily limiting
- molecular and isotopic monitoring tools are available
- treatment trains are effective
- DX degradation may be inhibited by co-contaminants

WHAT WE NEED TO KNOW / DO

- identify more organisms, enzymes, and pathways relevant to DX degradation
- characterize and control biogeochemical conditions and co-contaminants
- understand microbial community structures and functions
- integrate multi-omics site data into predictive models

Thanks to $ponsors and Collaborators

NSF

Air Force Civil Engineer Center

SERDP
DOD · EPA · DOE

Pfizer

NAVFAC

Colorado State University

Geosyntec

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