Establishing the Prevalence and Relative Rates of 1,4-Dioxane Natural Attenuation to Improve Remedy Evaluations

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GSI ENVIRONMENTAL

REMTEC & EMERGING CONTAMINANTS SUMMIT

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AGENDA / ACKNOWLEDGEMENTS

- Problem Statement(s)
- Project Objectives
- Site Descriptions and Approach
- Lines of Evidence for 1,4-Dioxane Degradation
- New Tools for Aiding Remedy Selection

ESTCP ER-201730
Project Completed in 2022

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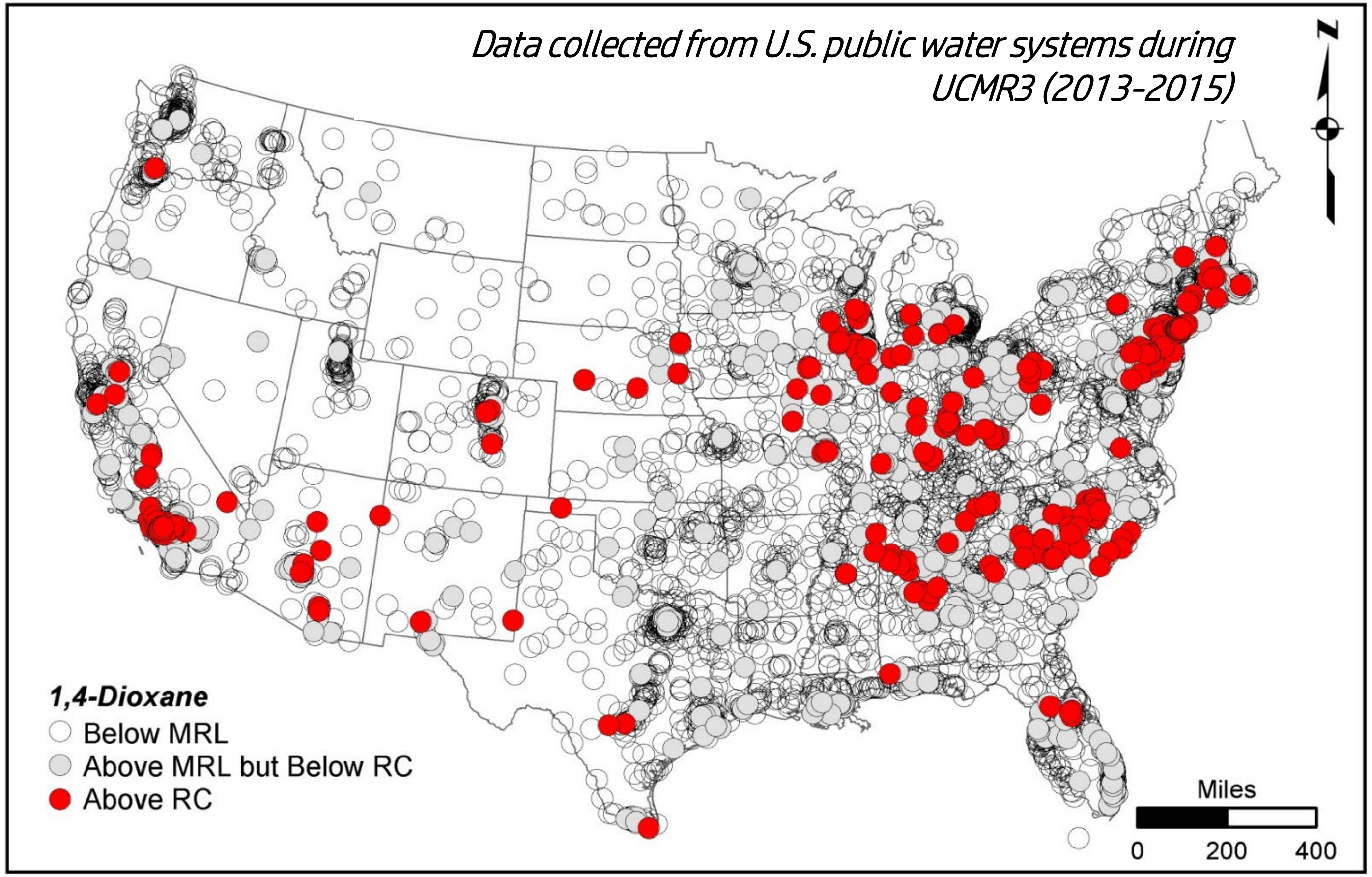
PROBLEM: 1,4-Dioxane is Widely Occurring

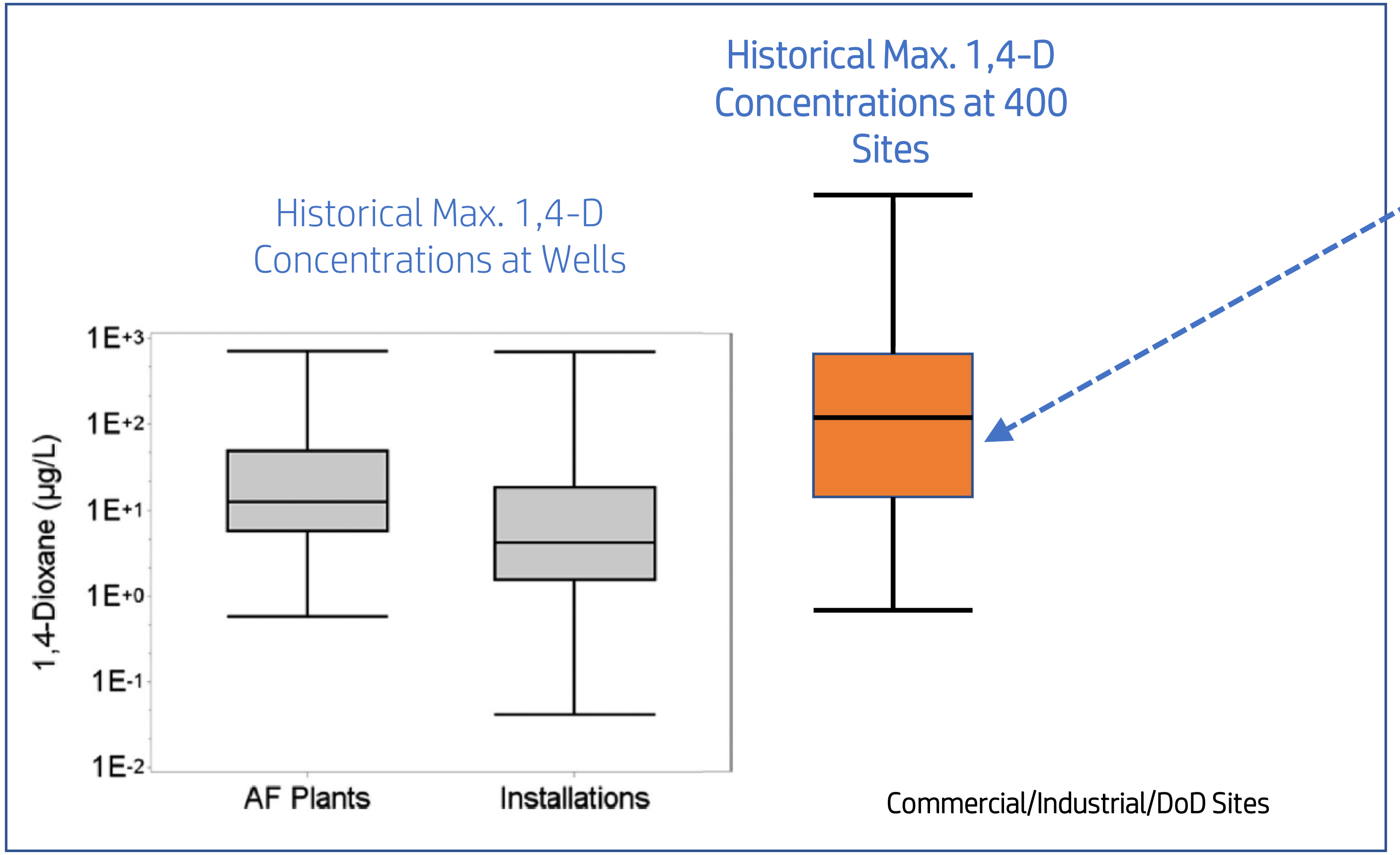


KEY POINTS

- 1,4-D detected above method reporting limit (MRL = 0.07 ug/L) in sample(s) from 21% of public water systems
- 1,4-D detected above health-based reference concentration (RC = 0.35 ug/L) in sample(s) from 7% of public water systems

Source: Adamson, Pina, Cartwright, Rauch, Anderson, Mohr, and Connor, 2017, *STOTEN*

PROBLEM: 1,4-Dioxane Sites are Challenging to Manage

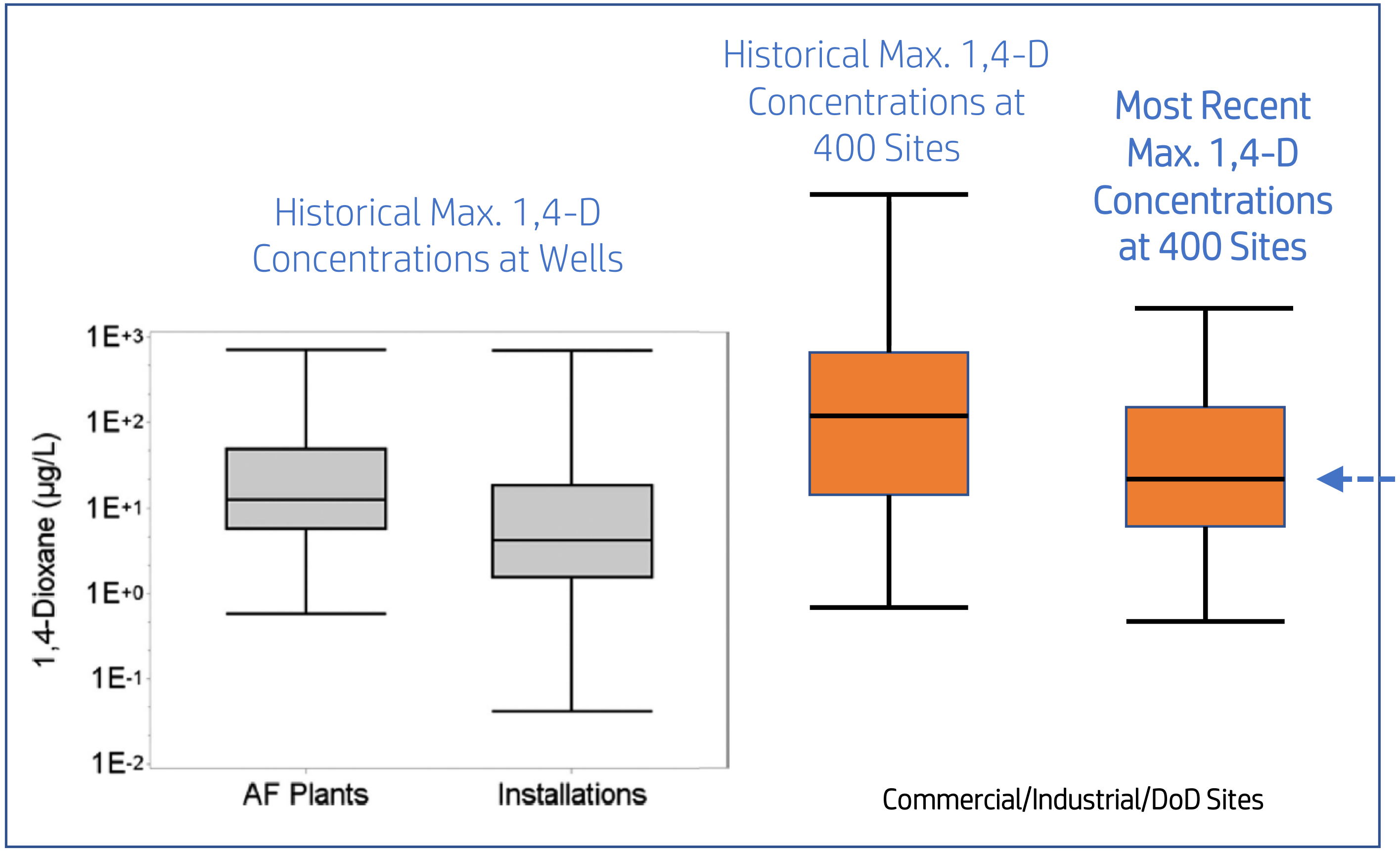


Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

Source: Adamson et al., 2015, *ES&T;* updated 2023 *(unpublished)*

- **1,4-D plumes are generally dilute**
  - Recent survey of 400 primarily commercial/industrial sites: median site had historical max. concentration of **110 µg/L**
- **1,4-D plumes are often diffuse with poorly defined "source areas"**
  - Similar concentrations throughout much of plume
- In situ remedial options are limited
  - Many typical methods are likely to be ineffective or cost-prohibitive

PROBLEM: 1,4-Dioxane Sites are Challenging to Manage



Source: Chiang, Anderson, Wilken, and Walecka-Hutchison, 2016, *Remediation*

Source: Adamson et al., 2015, *ES&T;* updated 2023 *(unpublished)*

- **Long-term management using Monitored Natural Attenuation (MNA) may be an option**
  - Requires understanding of relevant attenuation processes and associated rates
  - Median of the most recent max. detections at these same sites is **17 µg/L** (↓ from 110 µg/L historical max.)
  - "Attenuation" is likely occurring

PROBLEM: MNA May be Best Approach at Some Sites

Feasibility of MNA for 1,4-D

1. Evidence for attenuation of 1,4-D at field sites
   (e.g., Adamson et al., 2015; Li et al., 2015; Gedalanga et al., 2016; da Silva et al., 2018; Jackson et al., 2022)

2. Better understanding of 1,4-D behavior and distribution at contaminated sites
   (e.g., Adamson et al., 2014, 2016; Chiang et al., 2016; Karges et al., 2018)

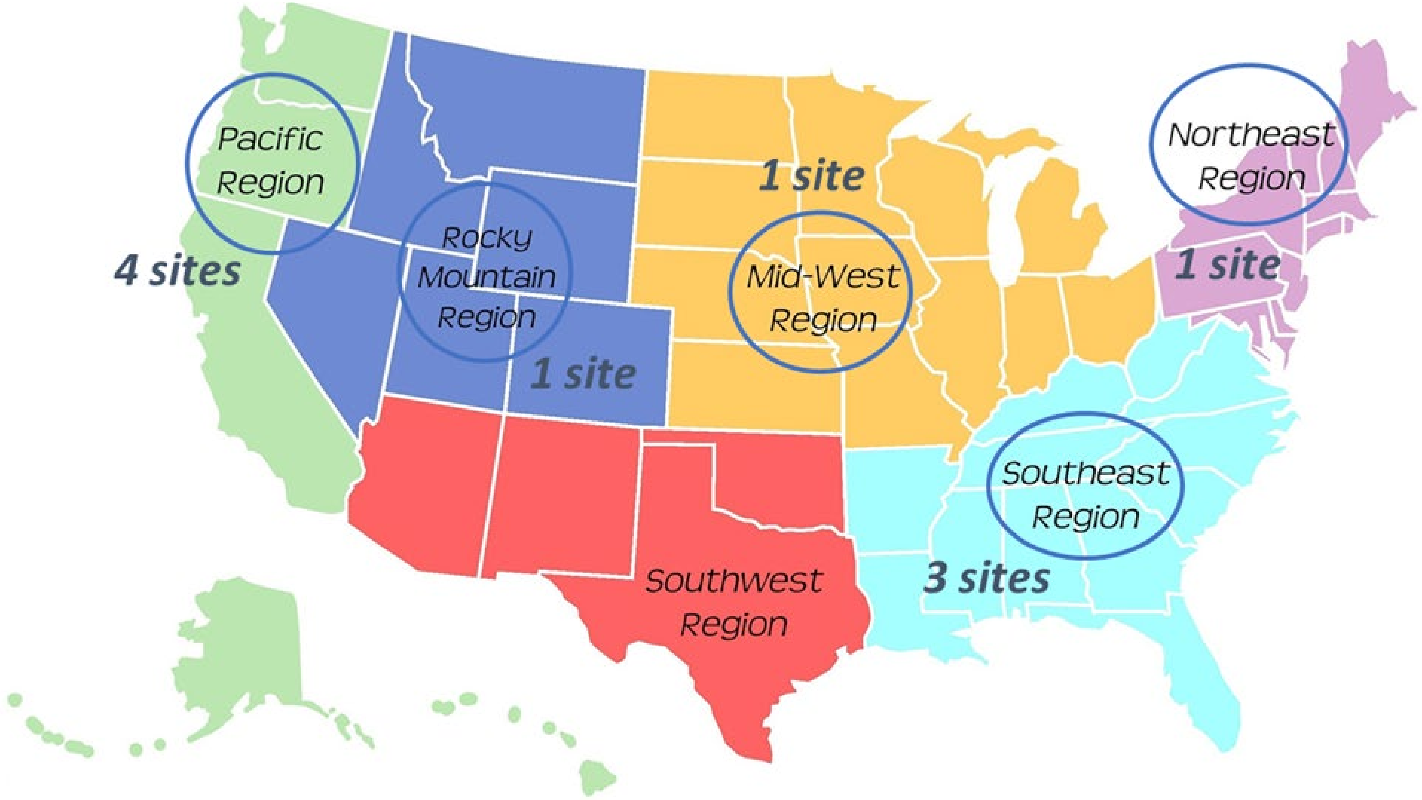
3. Improved forensic tools to support MNA evaluations
   (e.g., Gedalanga et al., 2016; Zhang et al., 2017; Bennett et al., 2018; Dang et al., 2018; Miao et al., 2021)

PROJECT OBJECTIVES

1. Demonstrate protocol for directly measuring rate constants for natural biodegradation of 1,4-Dioxane using ^{14}C-labeled 1,4-Dioxane
2. Develop decision framework to evaluate MNA as a remedy for 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 1,4-Dioxane
   - Develop F&T model (similar to BIOCHLOR) to estimate rate constants for these compounds
   - Build new version of BioPIC software that includes F&T model
3. Collect and evaluate various lines of evidence (LOEs) for MNA for 1,4-Dioxane
   - Specific focus on understanding prevalence, rates, and convergence between LOEs

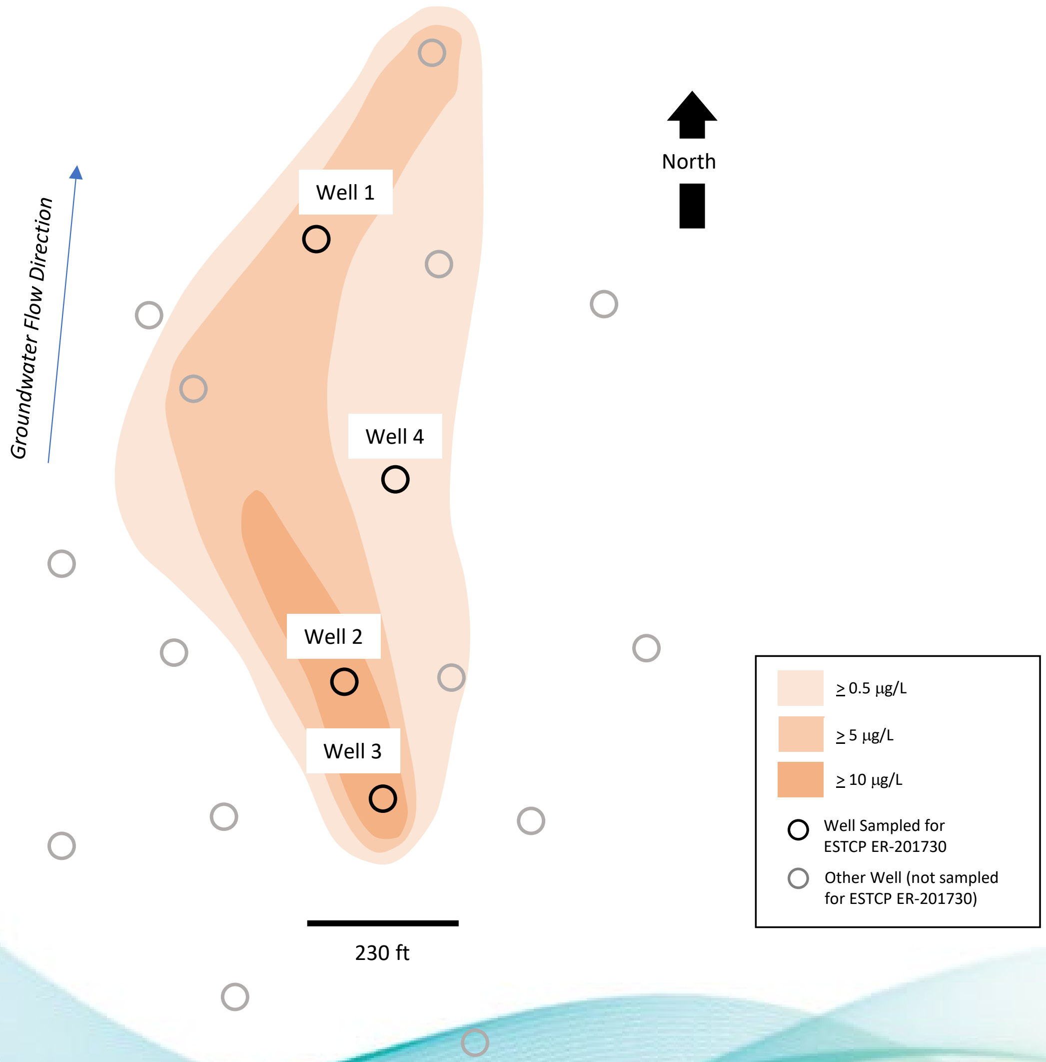
Focus of this talk

OVERVIEW OF TECHNICAL APPROACH



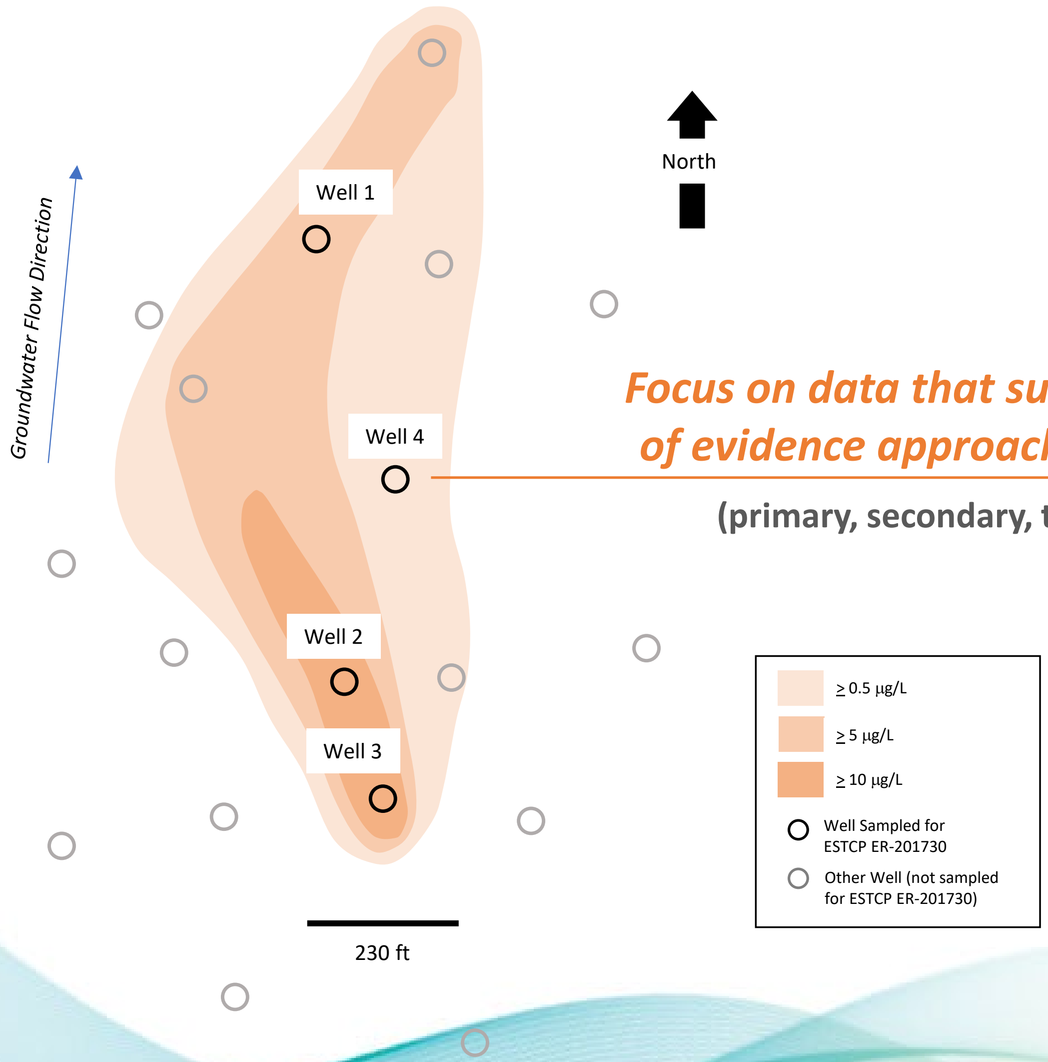
- 10 sites where data was collected
  - 8 DoD
  - 2 Industrial/ Commercial
- 1,4-dioxane present
  - Max at any site = 10,000 ug/L
  - Generally Max < 100 ug/L

OVERVIEW OF TECHNICAL APPROACH



- Collect groundwater samples from 4 or 5 existing monitoring wells along groundwater flow path

OVERVIEW OF TECHNICAL APPROACH



Focus on data that support lines of evidence approach for MNA

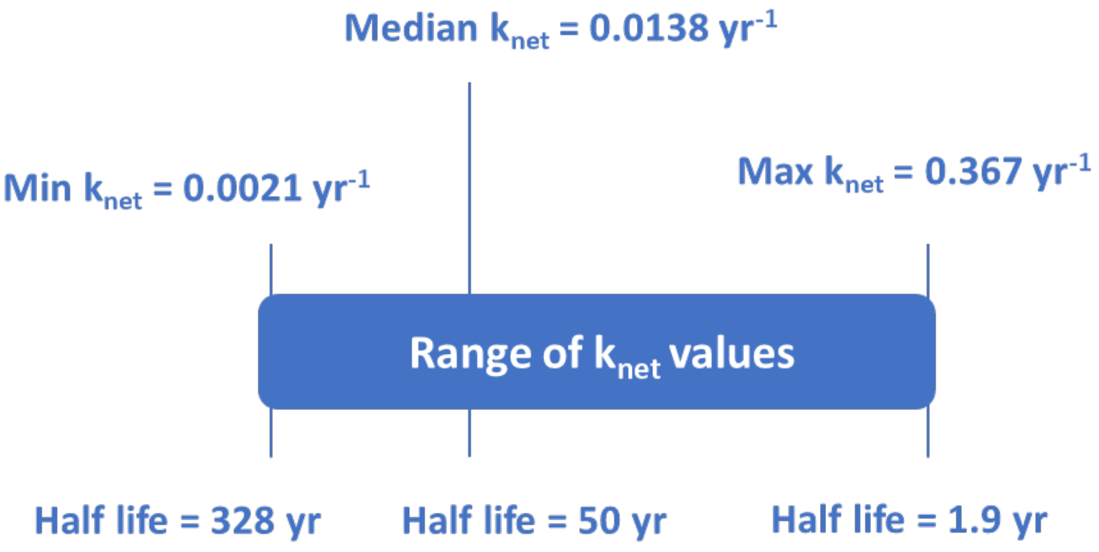
(primary, secondary, tertiary)

- Concentration vs. distance data, hydrogeologic parameters
  - Key for predicting degradation rates using F&T model
- Geochemical data (e.g., DO)
- CSIA data (δ^2H, δ^{13}C)
- Biomarkers for biodegradation (THFXO/DXMO, ALDH, possible cometabolic)
- ^{14}C-1,4-Dioxane Assay developed by Clemson

RESULTS: 1,4-Dioxane Degradation Rates from ^{14}C Assay

54 groundwater samples analyzed

- Statistically significant 1,4-D rate constant (k_{net}) obtained in 24 samples
- **At least 1 significant rate constant at 9 of 10 sites (i.e., 90% of all sites)**
  - 25 – 75% of locations at these sites had significant rate constant
- Collective results show that biodegradation of **1,4-dioxane is occurring at a relatively slow rate** when observed



k_{net} significant at 45% of sampled locations

Source: Ramos Garcia et al., 2022, *JHM;* Adamson et al., 2022, *JHM*

RESULTS: 1,4-Dioxane Degradation Rates from F&T Model

SERDP ESTCP

Development of a Quantitative Framework for Evaluating Natural Attenuation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 1,4-Dioxane in Groundwater

ER-201730

POINT OF CONTACT

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PRODUCTS

Final Report

ER-201730 Final Report.pdf

12/8/2022

Executive Summary

ER-201730 Executive Summary.pdf

5/4/2022

User's Guide

BioPIC User's Guide and Tool

ER-201730 BioPIC User's Guide and Tool.zip

1/16/2023

User's Guide

MNA Rate Constant Estimator User's Guide and Tool

ER-201730 MNA Rate Constant Estimator User's Guide and Tool.zip

1/16/2023

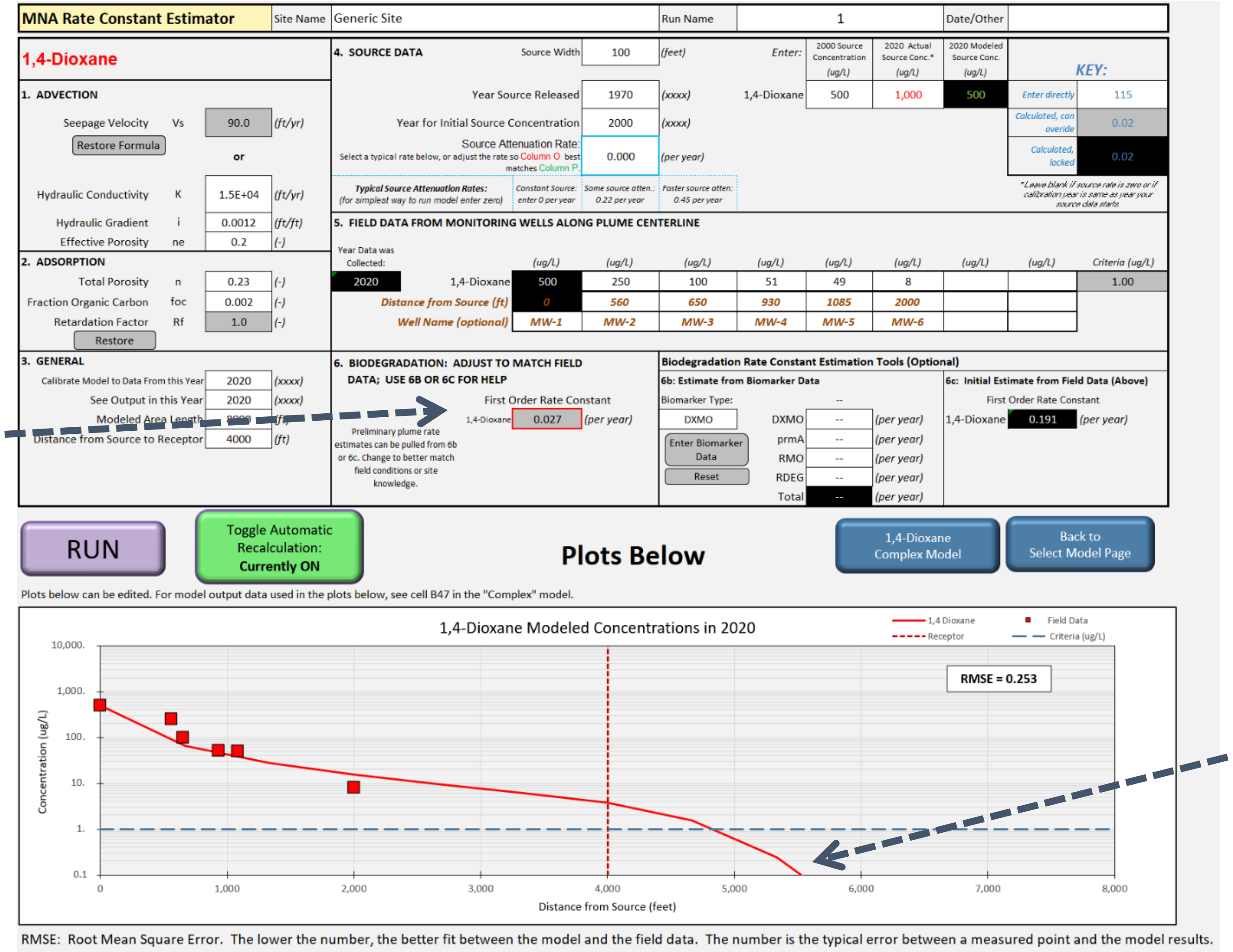
Free Excel-based modeling tool:

"MNA Rate Constant Estimator"

https://www.serdp-estcp.org/projects/details/bd9c56ae-002e-40fc-88cf-4a9c8566de93/er-201730-project-overview

RESULTS: 1,4-Dioxane Degradation Rates from F&T Model

MNA Rate Constant Estimator



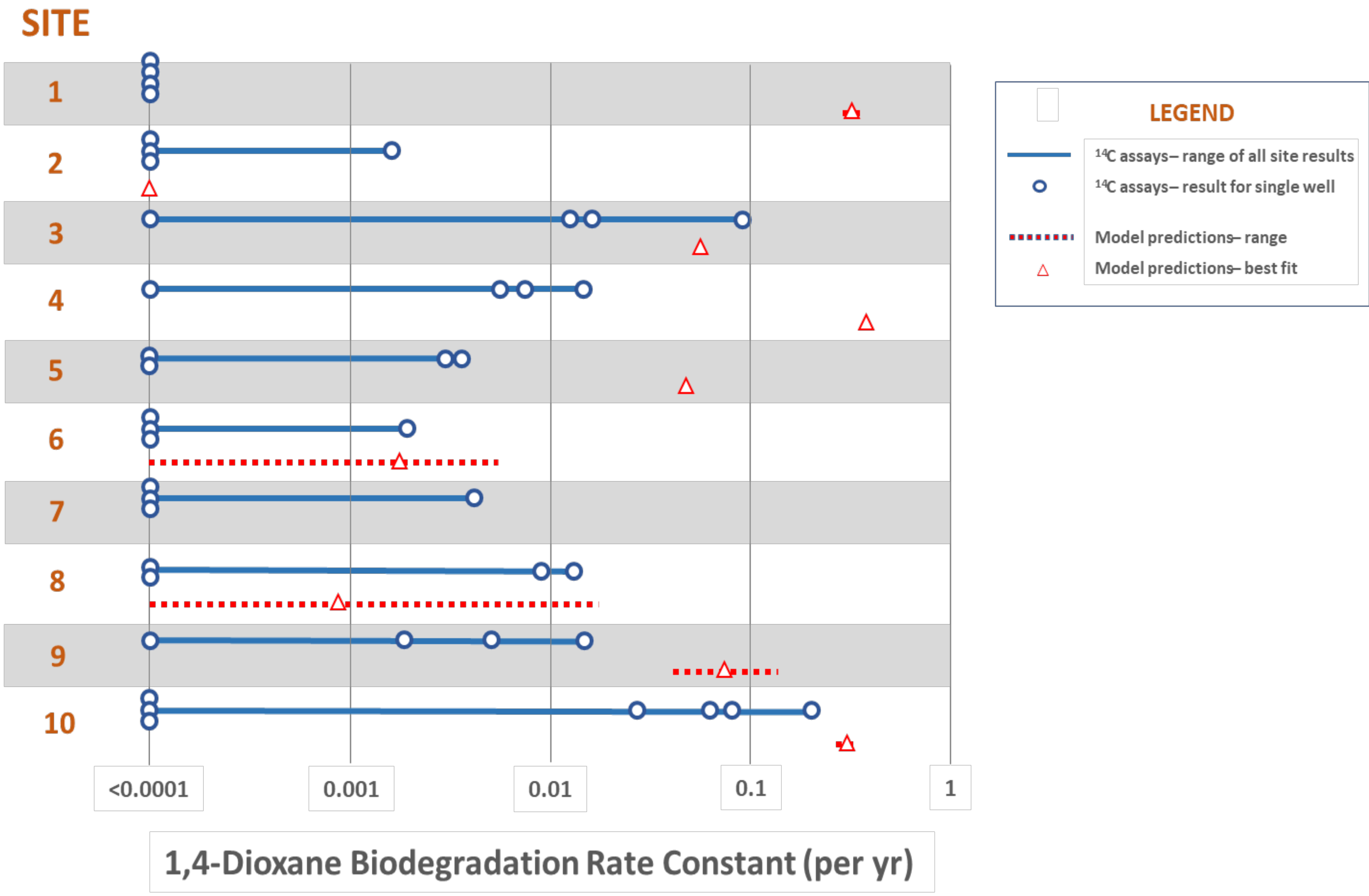
Intended Use #1: Determine appropriate rate constants for relevant natural degradation processes (by calibrating model with C vs d data)

Intended Use #2: Evaluate how far a dissolved plume will extend under natural attenuation scenario

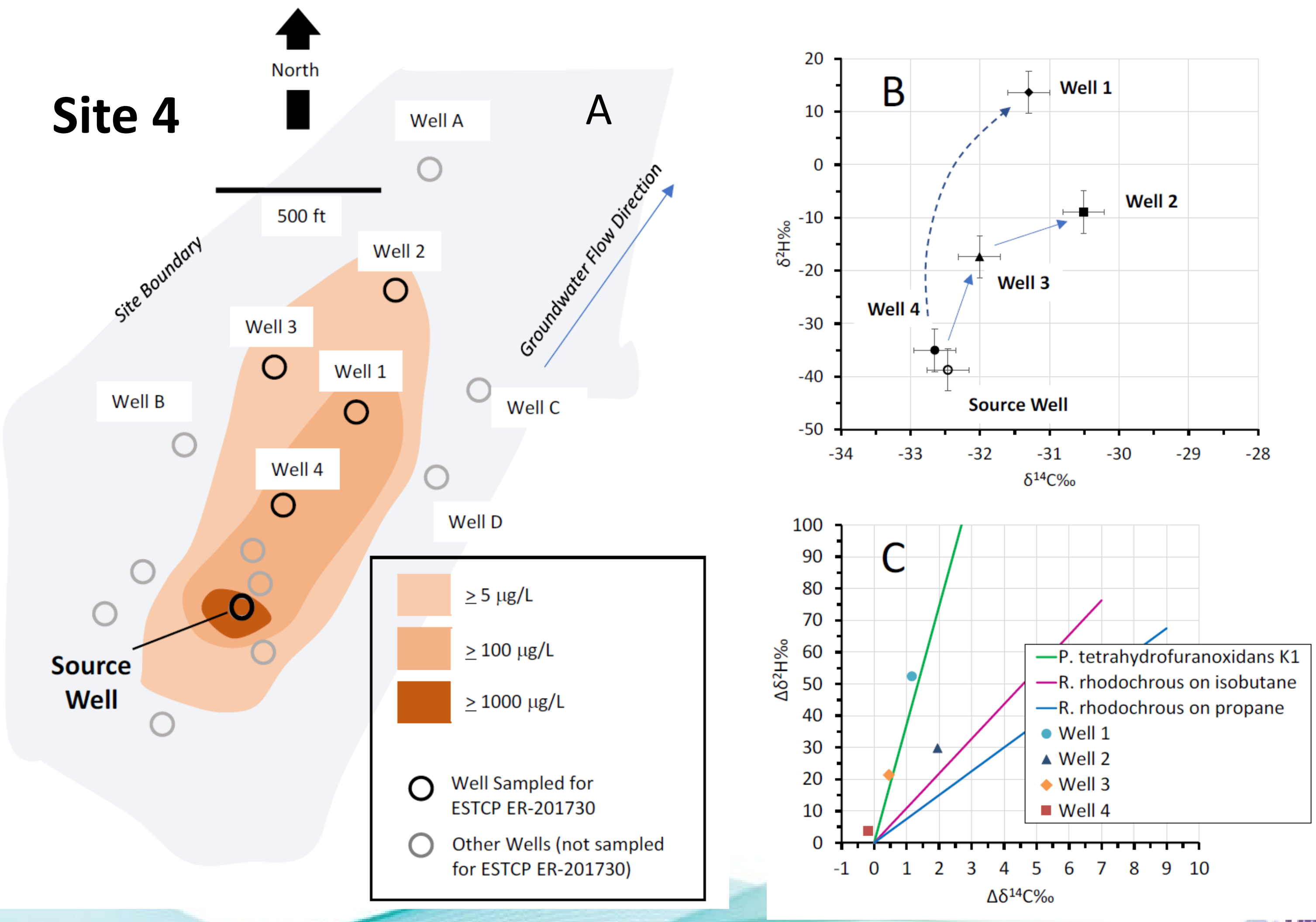
RESULTS: Comparison of 1,4-Dioxane Degradation Rates

- Model-predicted site-wide rates were typically **larger** than ^{14}C-derived rates
- Differences were not entirely unexpected

Source: Adamson et al., 2022, *JHM*



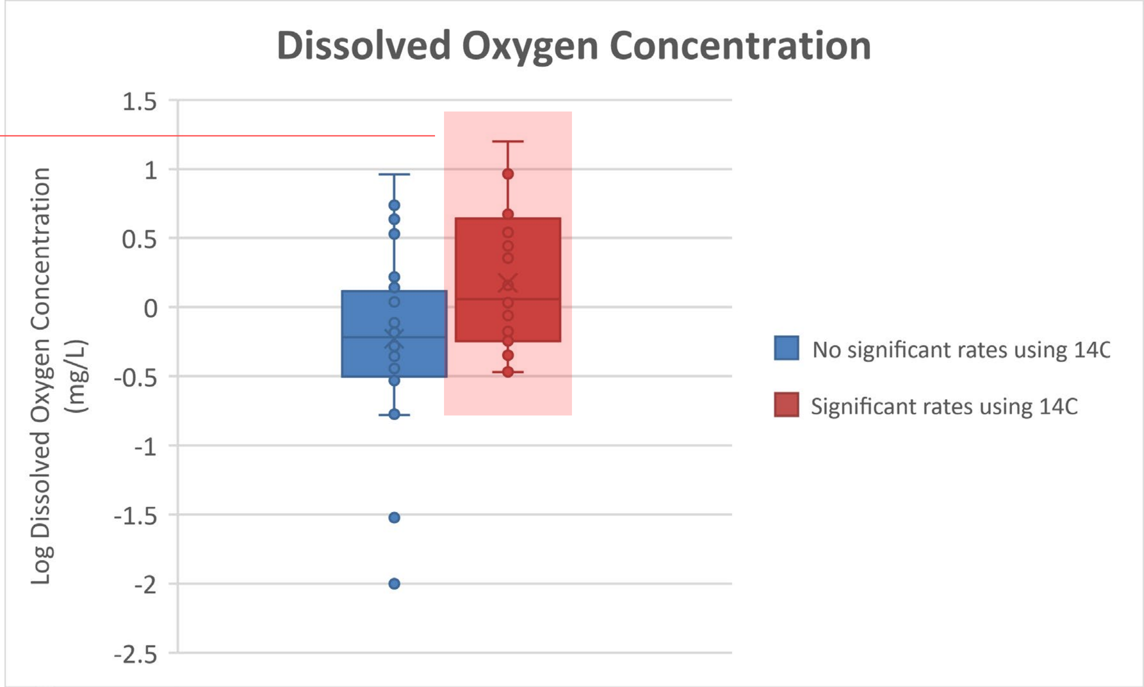
RESULTS: CSIA Data



- Well delineated 1,4-D plume (co-occurring w/ CVOCs) (Panel A)
- Strong evidence for isotope fractionation ($\delta^{13}C$ and $\delta^{2}H$ shift up and to the right) in downgradient wells (Panel B)
- Comparison using published isotope enrichment factors helps establish biological pathways for observed patterns (Panel C)
- *Evidence for 1,4-D degradation obtained at 7 of 9 study sites*

RESULTS: Influence of Geochemical Conditions

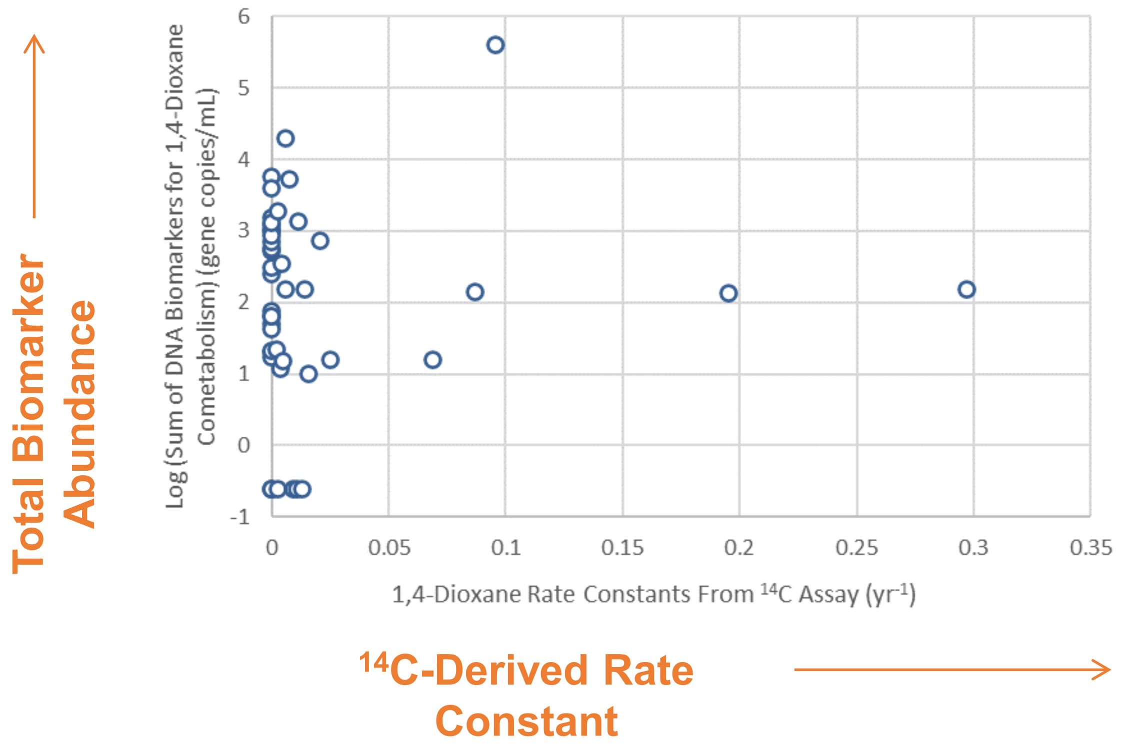
- Median DO (1.15 mg/L) was higher at wells with significant 1,4-D degradation than at wells where no rate could be obtained (0.61 mg/L) *(Wilcoxon Rank Sum test; p = 0.052)*
  - Consistent with more favorable conditions for aerobic biodegradation pathway for 1,4-D
  - Significant 1,4-D degradation was observed at several wells with < 1 mg/L DO (due to mixing w/in long-screened wells)



Source: Adamson et al., 2022, *JHM*

RESULTS: Biomarker Abundance

- Biomarkers for **direct metabolism of 1,4-D** were infrequently detected (< 10% of wells), so limited utility for predicting rate constants
- Possible biomarkers for **cometabolism** were detected more frequently (25% - 75% of wells, depending on biomarker), but no clear correlation with rate constants ***(see figure)***
- Alternate method based on lab-based kinetic parameters is included in MNA model (as “initial guess” during calibration), but generally underpredicted rate constant



RESULTS: Convergence Between Different LOEs for Degradation

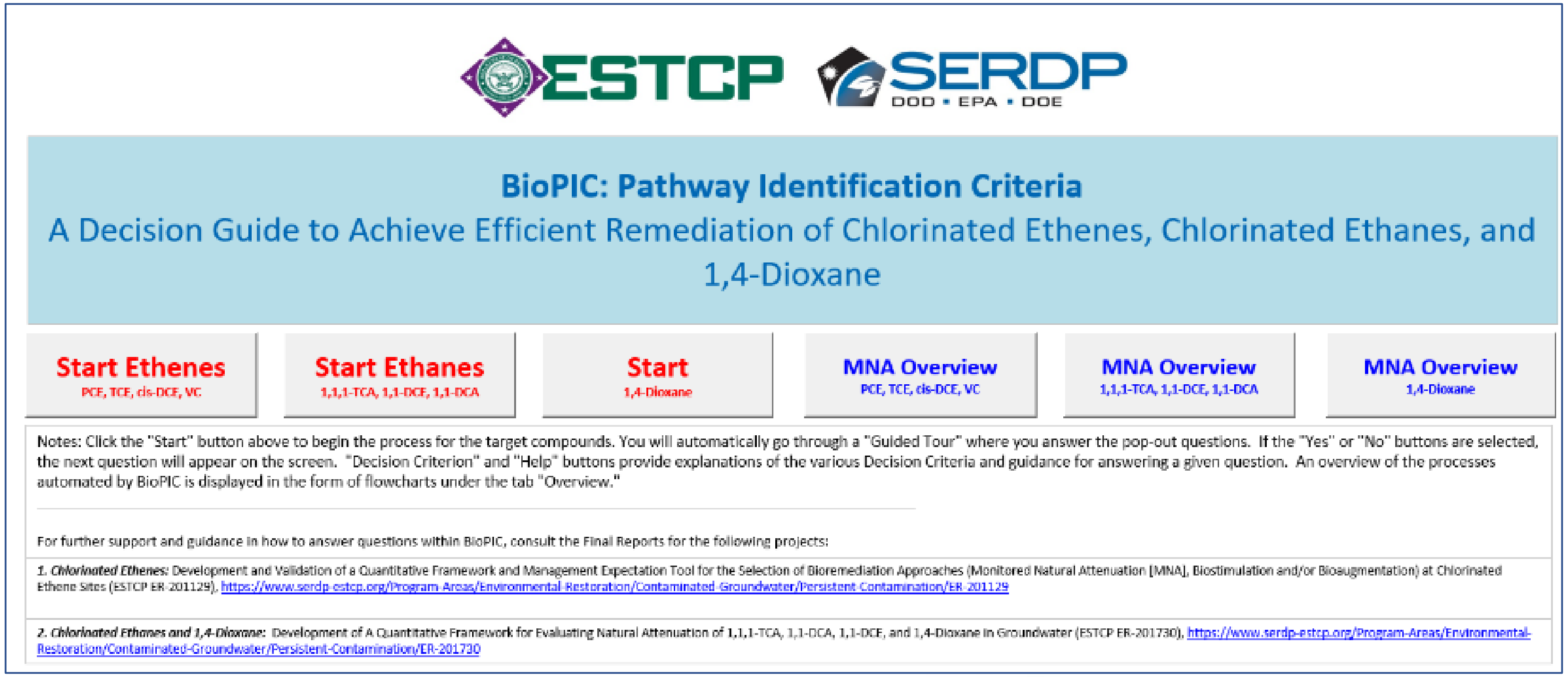
Site	1,4-dioxane concentrations decreasing with distance from source location?	1,4-dioxane biodegradation established using ^{14}C Assay?	Is 1,4-dioxane biodegrading based on model predictions?	Is model-predicted 1,4-dioxane rate constant consistent with rate constants from ^{14}C assay?	Are ^{2}H and/or ^{13}C enriched along the flow path?	Are geochemical conditions supportive of 1,4-dioxane biodegradation?	Are inhibitory CVOCs present at low levels and/or decreasing with time/distance?
1	YES	NO	YES	NO	YES	YES	NO
2	YES	YES (1 of 4 wells)	NO	NO	NO*	YES	YES
3	YES	YES (3 of 4 wells)	YES	YES	YES	YES	YES
4	YES	YES (3 of 4 wells)	YES	YES	YES	YES	YES
5	YES	YES (2 of 4 wells)	YES	NO	YES	YES	YES
6	YES	YES (1 of 4 wells)	YES	YES	YES	NO	YES
7	YES	YES (1 of 4 wells)	N/A	N/A	NO*	NO	NO
8	YES	YES (2 of 4 wells)	YES	YES	YES	YES	YES
9	YES	YES (3 of 4 wells)	YES	YES	YES	YES	YES
10	YES	YES (2 of 4 wells)	YES	YES	NO	NO	NO

- Widespread prevalence of 1,4-D degradation based on multiple LOEs
- Not all LOEs converged at all sites

Source: Adamson et al., 2022, *JHM*

NEW DECISION SUPPORT TOOLS FOR REMEDY SELECTION

1 **Updated BioPIC:** decision framework w/ new modules for 1,4-dioxane and chlorinated ethanes



plus...

2 **MNA Rate Constant Estimator:** new F&T model to support primary LOE

KEY TAKEAWAYS: 1,4-Dioxane Source Decay vs. Biodegradation

	Range of 1,4-D Half-Lives (yr) *(log-scale)*
1,4-D Degrading Pure Cultures *(Ramos-Garcia, Danko et al., 2022)*	*Median = 2.2 yr*; 0.3 – 11
Source Attenuation Rates *(n = 22 sites + 131 wells; Adamson et al., 2015)*	*Median = 3.6 yr*; 0.3 – 14
Site-Wide Biodegradation Rates *(n = 9 sites; Adamson et al., 2022)*	*Median = 9 yr*; 4.0 – > 1000
Well-Specific Biodegradation Rates *(n=18 wells; Adamson et al., 2022)*	*Median = 66 yr*; 1.9 – 328

- 1,4-D **source decay** can be rapid
- 1,4-D is biodegradable once it is in groundwater, but rates can be slow and activity is location-specific

KEY TAKEAWAYS: 1,4-Dioxane Biodegradation Prevalence

- Widespread prevalence of 1,4-D degradation capacity (90% of sites based on ^{14}C assay)
- Evidence for 1,4-D degradation capacity at monitoring locations/sites that are anoxic
- Widespread prevalence of *in situ* 1,4-D degradation (based on model predictions/isotope fractionation)
- Slow 1,4-D rates are common (may be an artifact of protocol)
- Lines of evidence for 1,4-D natural attenuation did not always converge
- Variability within sites was observed
- Lack of prevalence of direct biomarkers for 1,4-D degradation
- General lack of predictive power for biomarkers

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Establishing the prevalence and relative rates of 1,4-dioxane biodegradation in groundwater to improve remedy evaluations

David T. Adamson [a], John T. Wilson [b], David L. Freedman [c], Angel Alejandro Ramos-García [c], Carmen Lebrón [d], Anthony Danko [e]

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Volume 424, Part C, 15 February 2022, 127540

Evaluation of natural attenuation of 1,4-dioxane in groundwater using a ^{14}C assay

Ángel A. Ramos García [a], David T. Adamson [b], John T. Wilson [c], Carmen Lebrón [d], Anthony S. Danko [e], David L. Freedman [a]

Groundwater Monitoring & Remediation
NGWA The Groundwater Association
Communication

State of the Practice Worldwide: Development of a Quantitative Framework for Evaluating Natural Attenuation of 1,1,1-TCA, 1,1-DCA, 1,1-DCE, and 1,4-Dioxane in Groundwater

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