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Managing 1,4-Dioxane Contamination in Groundwater: The Role of Natural Attenuation

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GSI Environmental Inc.

25 YEARS OF ESTCP
SERDP • ESTCP SYMPOSIUM
2019 | Enhancing DoD's Mission Effectiveness

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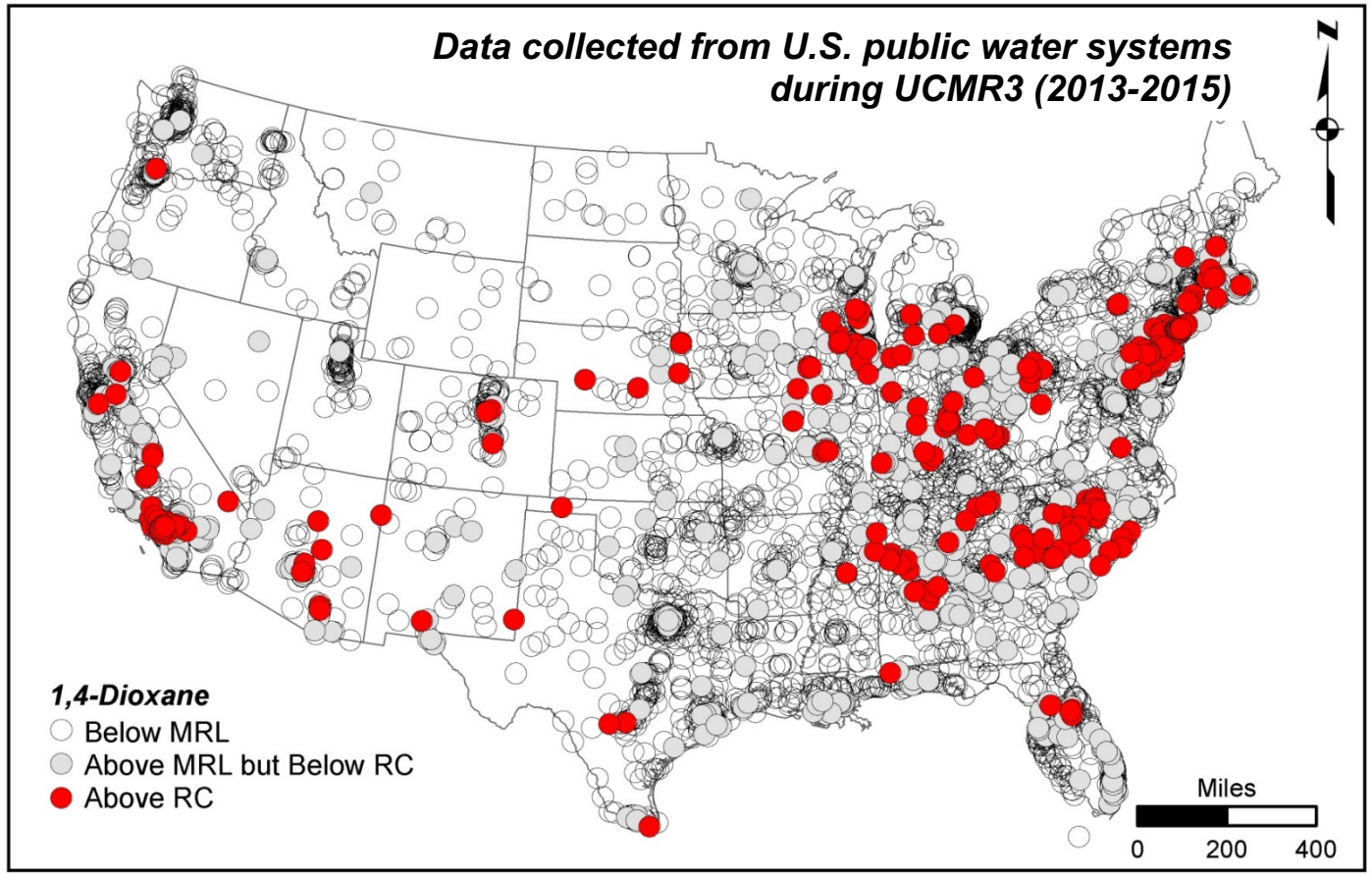
NAVFAC Naval Facilities Engineering Command ENGINEERING AND EXPEDITIONARY WARFARE CENTER

PROBLEM: *1,4-Dioxane is Widely-Occurring*



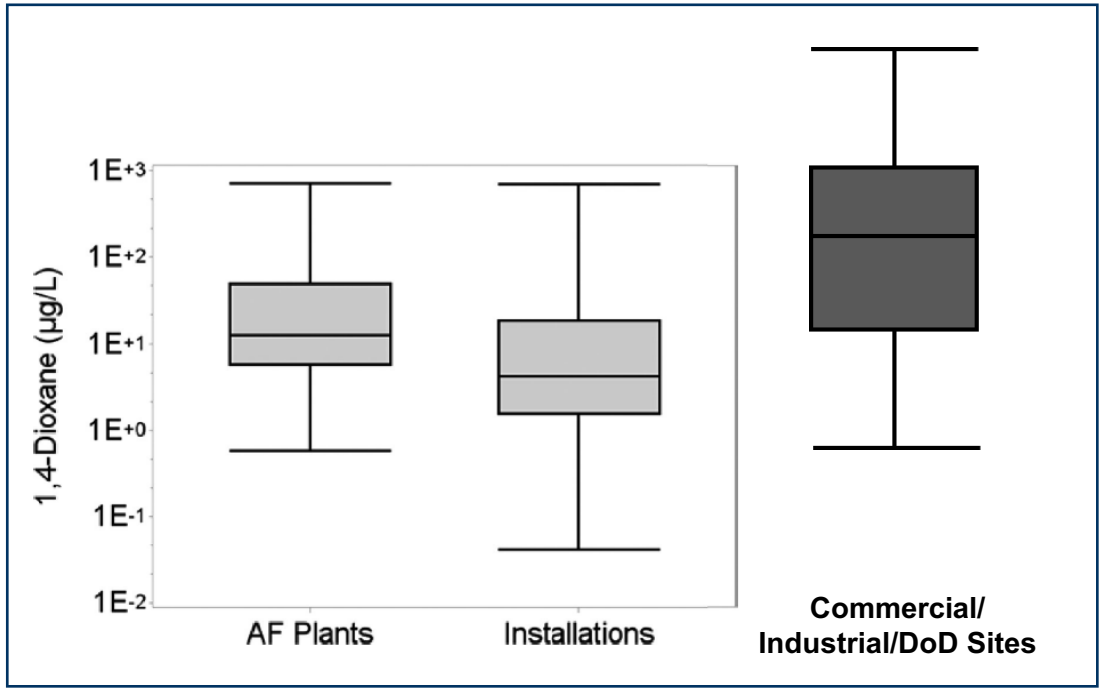
KEY POINTS

- **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 μg/L) in sample(s) from 7% of public water systems**

Source: Adamson, Pina, Cartwright, Rauch, Anderson, Mohr, and Connor, 2017, Science of the Total Environment

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

Distribution of Historical Maximum 1,4-D Concentrations



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

Source: Adamson, Anderson, Mahendra, et al., 2015; ES&T

- **1,4-D plumes are generally dilute**
  - **Particular concern at DoD sites (see chart)**
- **1,4-D sources are challenging to identify**
  - **Rapid dissolution and migration potential**
  - **Actual source may be 1,4-D diffusing out of lower-k zones (Adamson et al., 2016; SOTE)**
- **In situ treatment options for contaminated groundwater are limited**
  - **Many typical methods are likely to be ineffective or cost-prohibitive**

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HYPOTHESIS: *Monitored Natural Attenuation (MNA) May Be Best Approach at Some Sites*

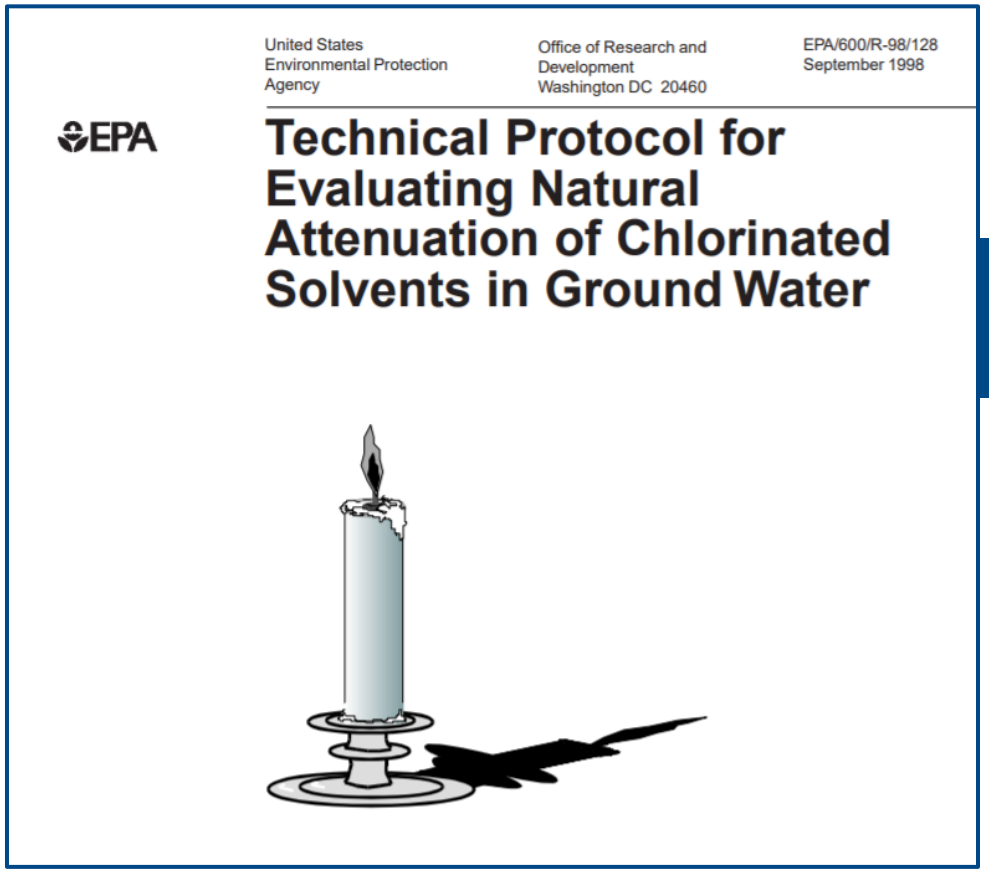
Feasibility of MNA for 1,4-D

1 **Evidence for attenuation of 1,4-dioxane at many (but not all) field sites**
(e.g., Adamson et al., 2015; Li et al., 2015; Gedalanga et al., 2016; da Silva et al., 2018)

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)

PROBLEM: *No Framework for Selecting MNA for 1,4-D and Many CVOCs*


United States Environmental Protection Agency

Office of Research and Development Washington DC 20460

EPA/600/R-98/128 September 1998

EPA

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

1,4-Dioxane and Chlorinated Ethanes (e.g., 1,1,1-TCA) are *not* included in original MNA protocol

Recent advances in "lines of evidence" can be used to support evaluation of MNA for these compounds

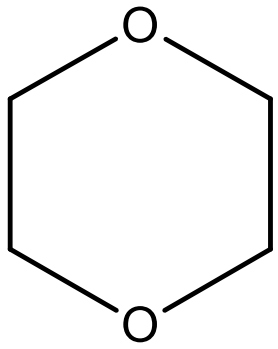
PROJECT OBJECTIVES:
Develop *1,4-Dioxane Attenuation Framework*

1. Develop and test a quantitative decision tool to evaluate MNA for 1,4-D and associated CVOCs

2. Validate ^{14}C-based assay (laboratory method) and other lines of evidence for attenuation (field sampling)

ESTCP

Project No. ER-201730



Search "Dioxane TCA natural attenuation" for project overview page

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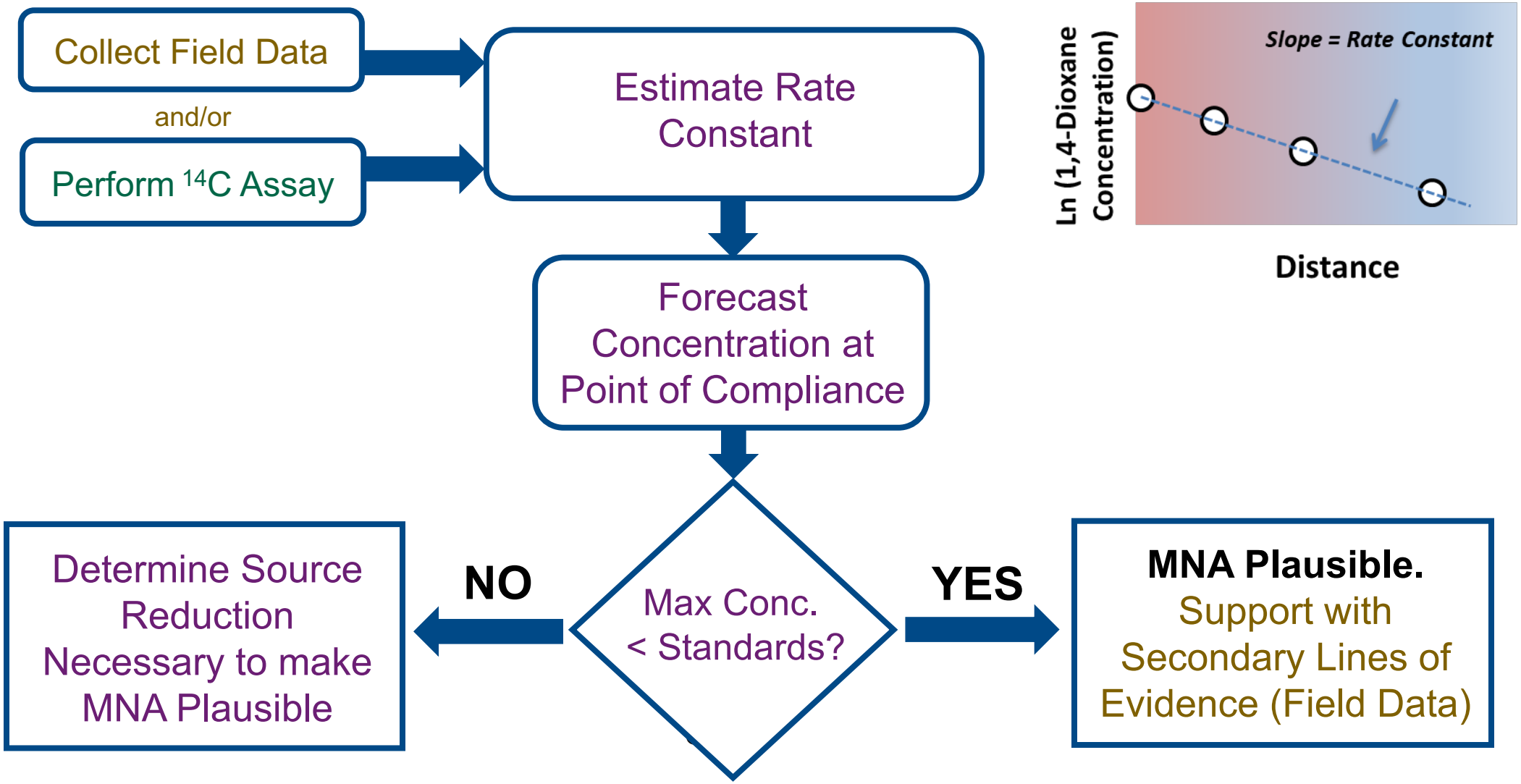
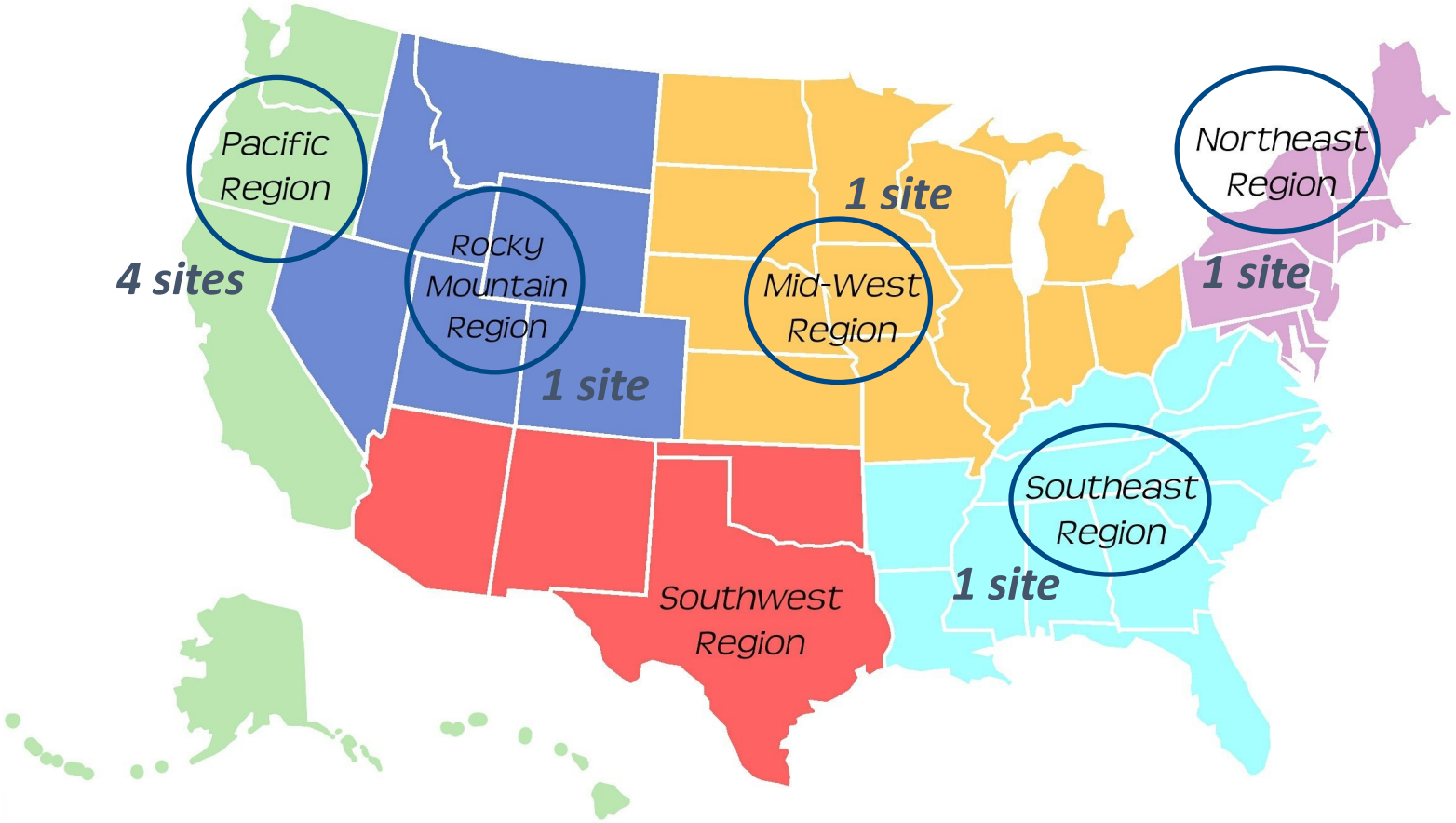
OVERVIEW OF DECISION PROCESS



PROJECT-SPECIFIC FIELD SAMPLING



OBJECTIVE:

Collect samples for ^{14}C assay and to evaluate several lines of evidence for attenuation

- Mix of DoD and commercial sites
- 6 sites sampled to-date
- 1 to 3 sites yet to be sampled
- Hoping to add more…

RESULTS TO-DATE: *What Positive Lines of Evidence for Attenuation Have Been Observed?*

Lines of Evidence

Site	C vs. Distance	Biomarkers	CSIA	^{14}C Assay
1				
2				
3				
4				
5				
6				

Legend:

- No Evidence
+ Low
++ Moderate
+++ Strong

1 to 3 additional sites yet to be sampled; partial data also collected at several other sites

RESULTS TO-DATE: *Why factors may have negatively influenced 1,4-D biodegradation?*

Site	High levels of CVOCs?	Low levels of Biomarkers	Absence of co-substrate?	Low DO?	Low levels of 1,4-D?
1	✓		✓	✓	
2		✓	✓	✓	✓
6		✓	✓	✓	✓
3				✓	
4			✓	✓	
5	✓		✓	✓	
7	✓	Not yet sampled	✓	✓	

Little or no ^{14}C-1,4-D degraded

^{14}C-1,4-D degraded in multiple locations

^{14}C-1,4-D assay not yet performed

RESULTS TO-DATE: *Compilation of Rate Constants from Various Studies*

Data Source	Type of Rate Constant	Range of Half-Lives (yr) (log-scale)
1,4-D Degrading Pure Cultures (CB1190 and ENV487 at 0.001 – 1 mg protein/L)	**Biodegradation Rate** (excludes non-destructive processes)	Median = 2.2 yr; 0.3 – 11
Multi-Site Survey (n = 22 sites + 131 wells w/ significant rates; Adamson, Anderson et al., 2015))	**Source Attenuation Rate** (includes non-destructive processes, excludes statistically non-significant rates)	Median = 3.6 yr; 0.3 – 14
Multi-Site Survey (n = 11 sites w/ C vs. d data)	**Bulk Attenuation Rate** (includes non-destructive processes)	Median = 164 yr; 0.4 – > 1000
^{14}C Assays from 7 sites (n = 13 well locations w/ significant rates)	**Biodegradation Rate** (excludes non-destructive processes, excludes statistically non-significant rates)	Median = 113 yr; 0.3 – 328

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KEY POINT: **These types of rates are generally most appropriate for modeling MNA, but broad range of values highlights site-specific nature of 1,4-D attenuation.**

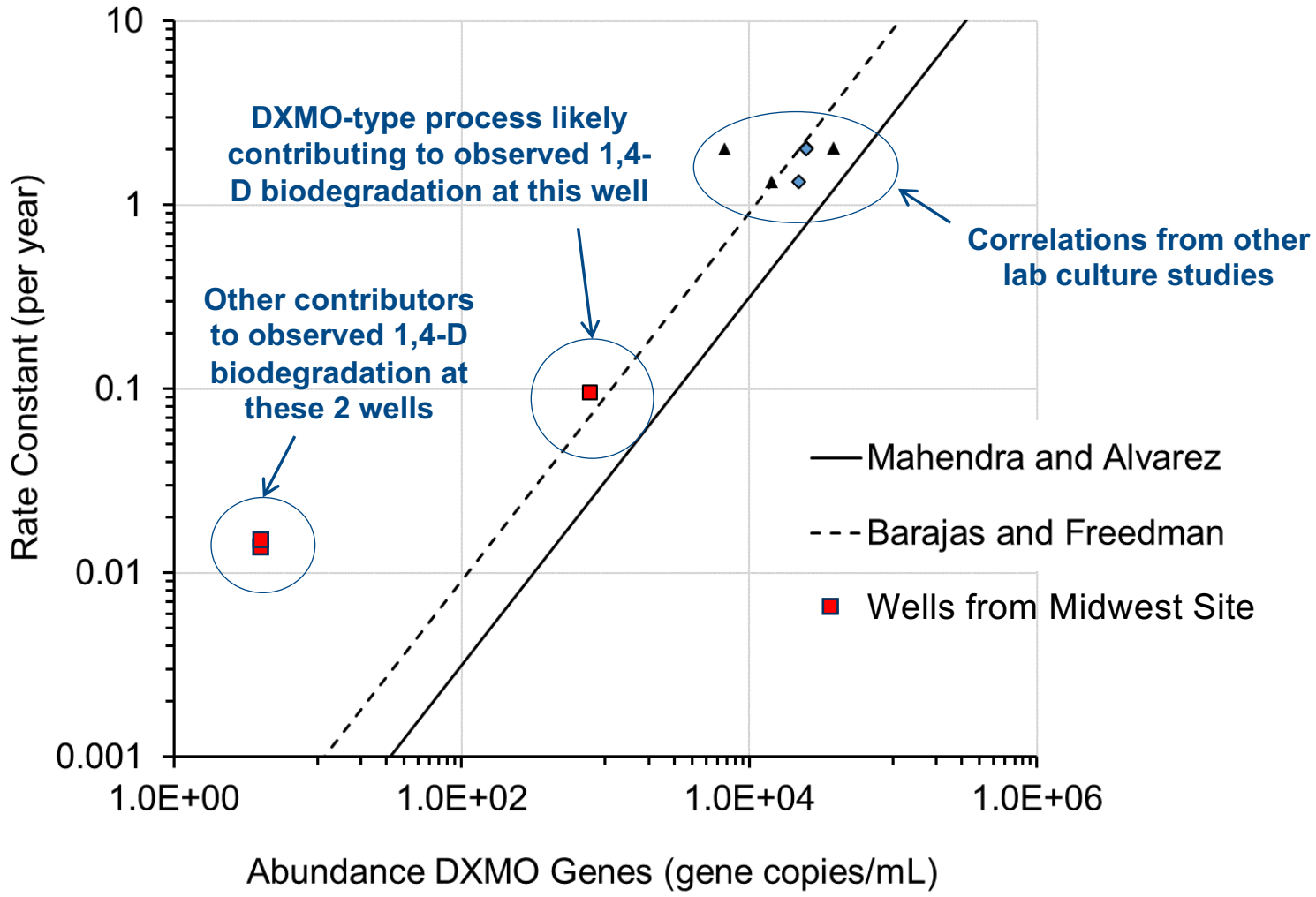
RESULTS TO-DATE:
How Should ^{14}C Assay Results Be Interpreted?

- Based on normal test procedures for ^{14}C assay, rate constants are likely to be conservative
  - Lack of solid-phase and/or nutrient supply may suppress rates
- One option is to use ^{14}C assay in step-wise approach

STEP 1 Run test using standard procedures as ***screening*** step

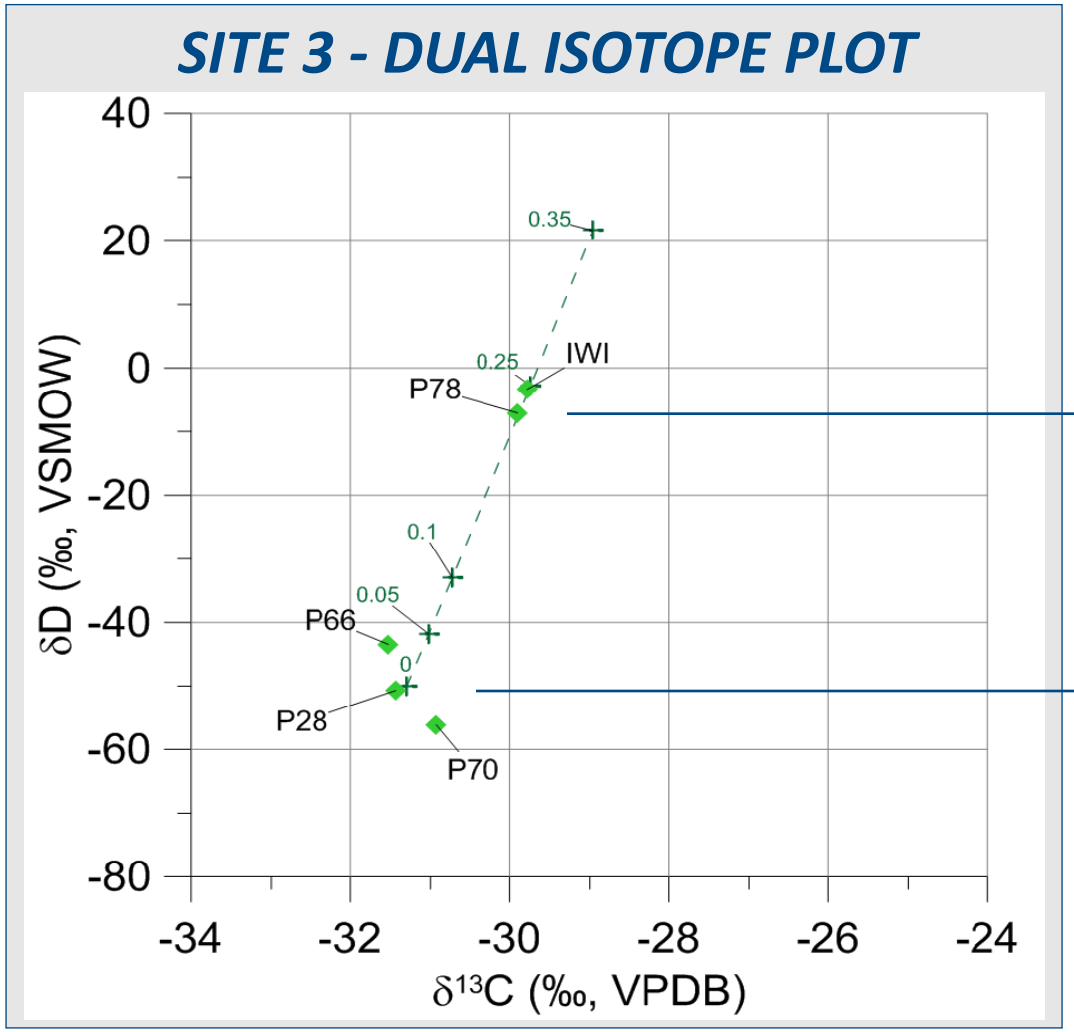
STEP 2 Perform follow test using soil and/or nutrients as ***validation*** step

RESULTS TO-DATE: *Other secondary lines of evidence for MNA to support rate estimates*



1. **Develop correlations between biomarkers and predicted rate constants**
2. **Plot site-specific rate constants to evaluate if identified biomarker is plausibly responsible for observed 1,4-D degradation**

RESULTS TO-DATE:
How Should CSIA Results Be Interpreted?



Site 3 Downgradient Wells:

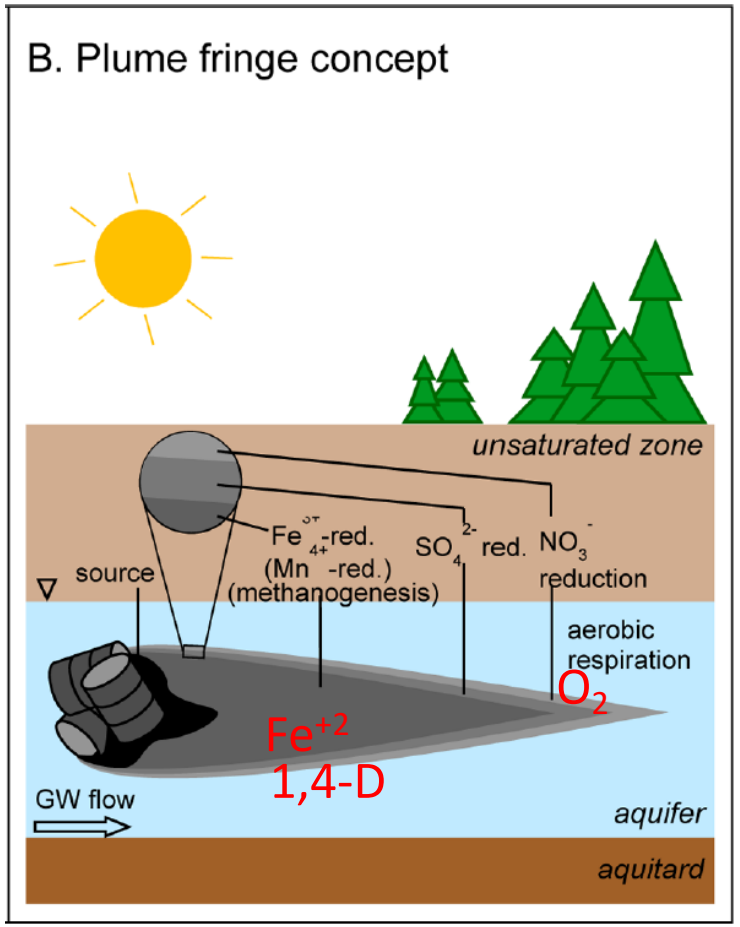
Extensive fractionation - reflects impact of attenuation along plume and pilot test

Site 3 Source/Mid-Plume Wells:

Little fractionation despite evidence of attenuation capacity (^{14}C assay, biomarkers) - presumably due to location and mixing with anaerobic groundwater (i.e., undegraded 1,4-D)

Data collected in collaboration with SERDP ER-2535 – Thanks to Peter Bennett, Katharine Morrison, and rest of team

RESULTS TO-DATE:
How Should CSIA Results Be Interpreted?



Why was no fractionation observed in some Site 3 wells?

- **Wells have a mix of O_2, and Fe^{+2}, meaning they almost certainly are producing blended samples of aerobic and anaerobic water.**
- **Lack of 1,4-D degradation in anaerobic portions masks fractionation occurring as a result of 1,4-D degradation in aerobic portions**
- **CSIA may yield false negatives and should be interpreted with other lines of evidence**

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Source: Meckenstock et al., 2015, Environ. Sci. Technol., 49, 7073-7081

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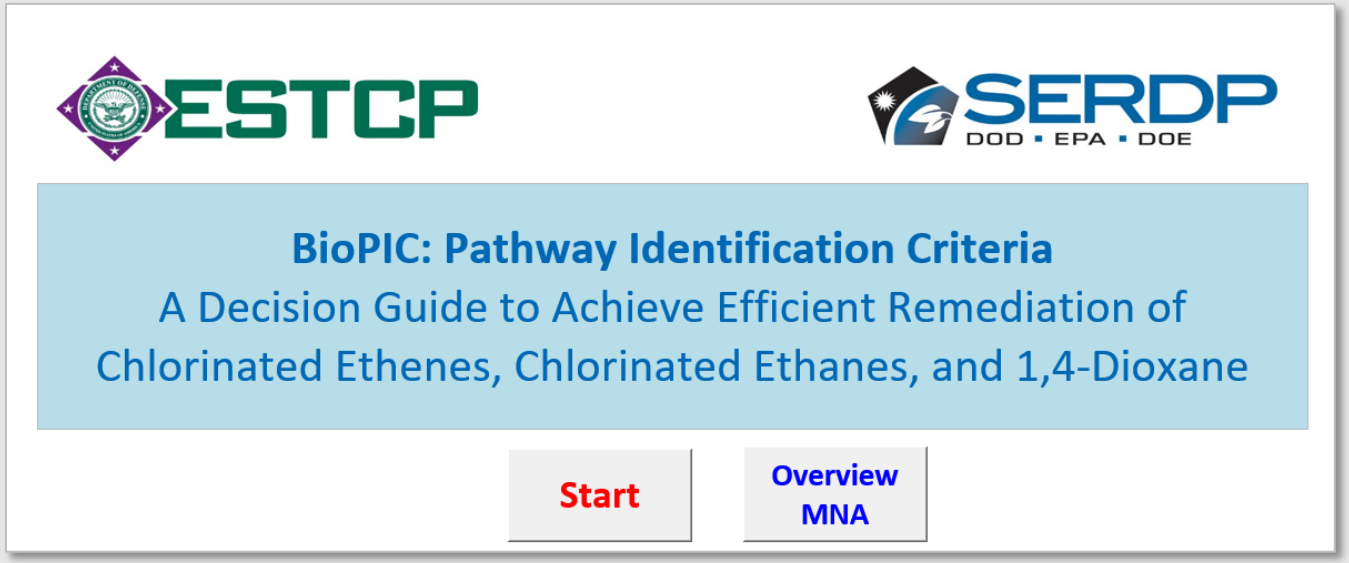
PROJECT DELIVERABLE



- Simple Excel-based spreadsheet
- Expands existing BioPic tool (which is for chlorinated ethenes)
- Includes “BIOCHLOR”-like rate constant estimator
- Expected in late 2020
- **Free!**

GOALS

1. Develop tool that walks through each step for remedy selection *(with focus on MNA)*
2. Provide guidance on how to collect data and interpret results

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KEY POINTS

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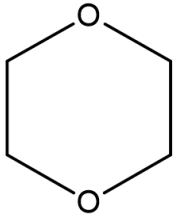
Project No. ER-201730



Search "Dioxane TCA natural attenuation" for project overview page

- **MNA should be evaluated as a potential long-term strategy for 1,4-D**
- **A robust ^{14}C laboratory method was developed and validated to determine 1,4-D degradation rates across many sites**
- **1,4-D biodegradation activity was confirmed at some—but not all–sites where attenuation was observed**
- **Interpretation of data shows benefit of additional lines of evidence to confirm actual degradation mechanisms at sites**
- **Data collected so far suggests that odds of observing 1,4-D biodegradation drops at sites with ≥ 3 of 5 key characteristics**
- **Tool to support evaluation of MNA of 1,4-D and "other" CVOCs will be available soon**

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BACK UP SLIDES

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