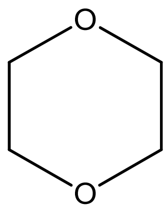
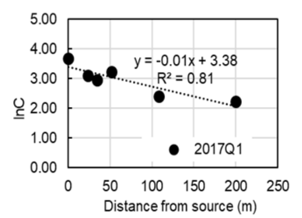
DEVELOPMENT OF A QUANTITATIVE FRAMEWORK FOR EVALUATING NATURAL ATTENUATION OF 1,4-DIOXANE, 1,1,1-TCA, 1,1-DCA, AND 1,1-DCE





GSI ENVIRONMENTAL

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PROJECT TEAM

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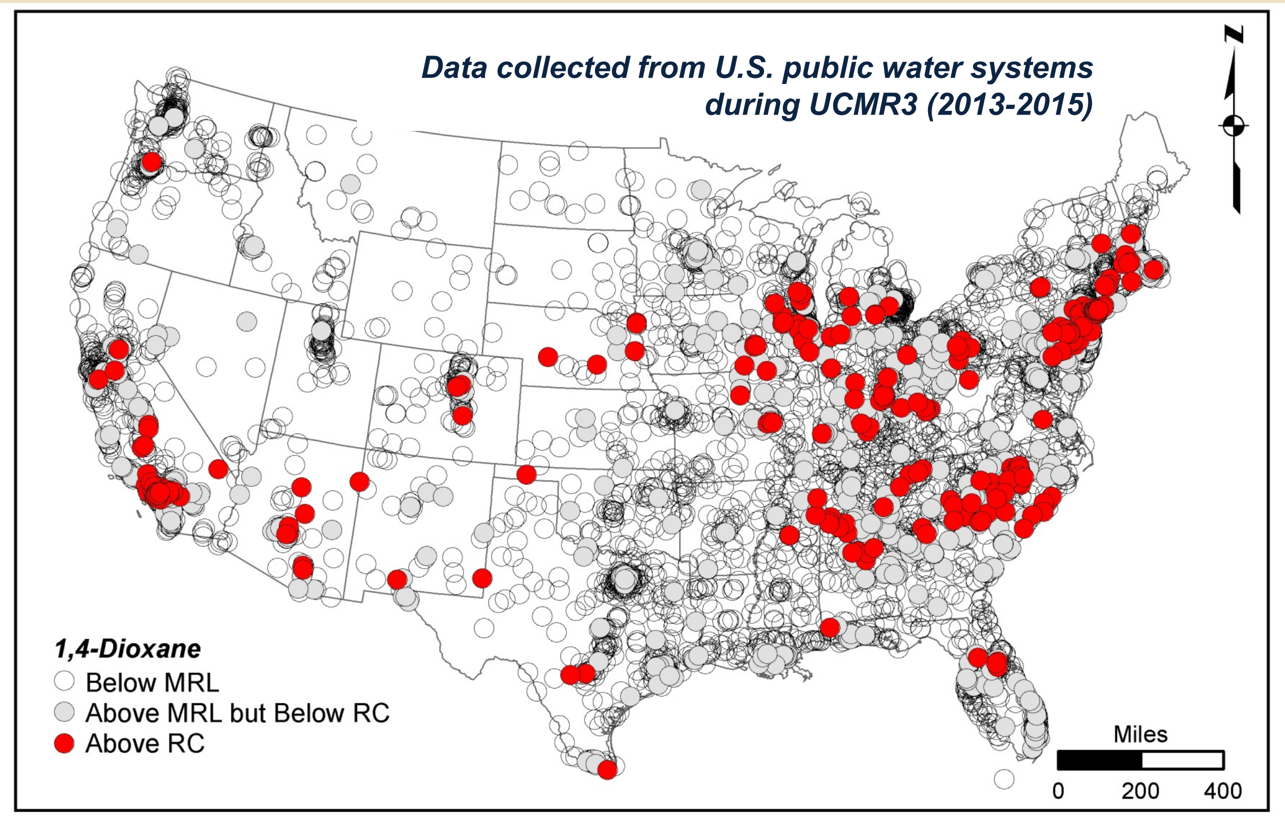
PROBLEM #1: *1,4-Dioxane is widely occurring*



KEY POINTS

- **1,4-D detected in 21% of samples collected**
- **Slightly higher occurrence in GW sources than SW, but GW has higher concentrations**
- **In many cases, sources are either unrecognized or poorly-addressed**

Source: Adamson, Pina, Cartwright, Rauch, Anderson, Mohr, and Connor, 2017, Science of the Total Environment, 596-597: 236-245

PROBLEM #2:
Our understanding of 1,4-dioxane attenuation is still evolving

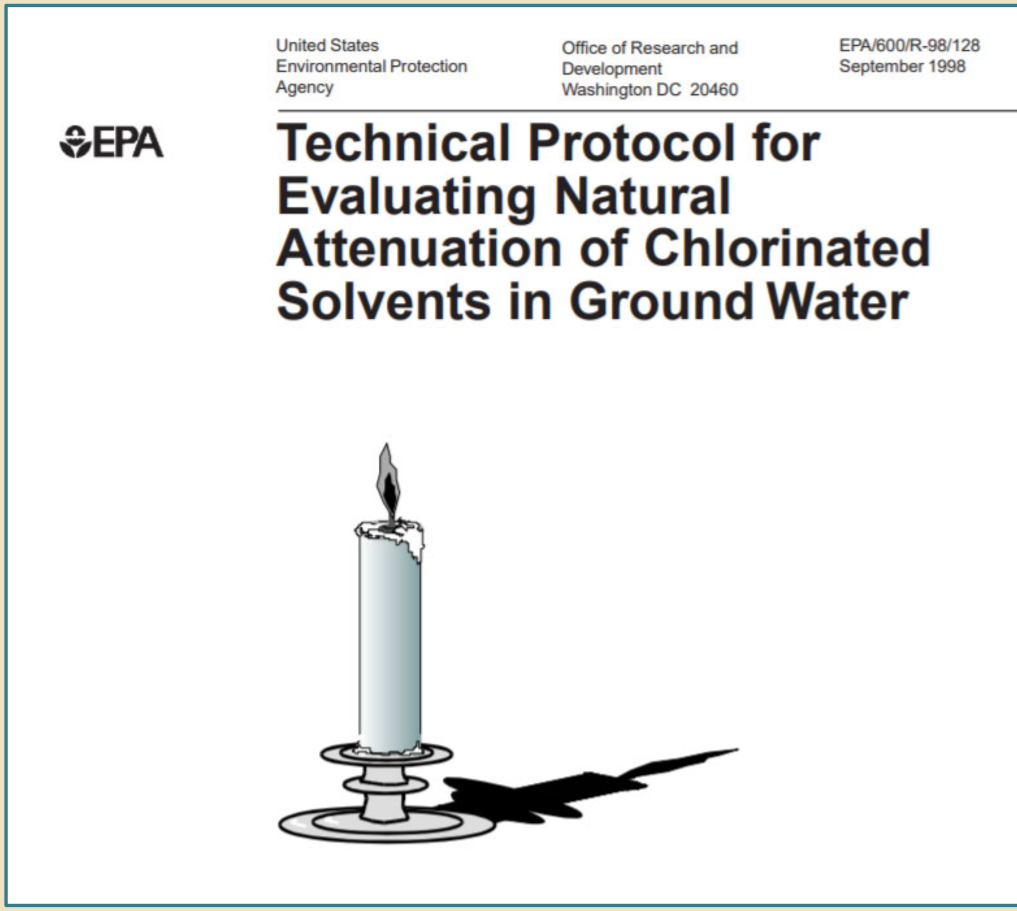
Evidence for attenuation of 1,4-dioxane at many (but not all) field sites
(e.g., Adamson et al., 2015; Li et al., 2015; Gedalanga et al., 2016; da Silva et al., 2018)

Presence of CVOCs (particularly 1,1-DCE) can inhibit 1,4-dioxane biodegradation
(e.g., Mahendra and Alvarez-Cohen, 2006; Zhang et al., 2016)

Direct or indirect evidence for 1,4-dioxane attenuation at field sites where CVOC attenuation is occurring
(e.g., Adamson et al., 2015; Chu et al., 2018; Dang et al., 2018)

Identification of pure or mixed cultures that can degrade both 1,4-dioxane and CVOCs
(e.g., Deng et al., 2018; Polasko et al., 2018)

PROBLEM #3:
No framework for selecting MNA for 1,4-Dioxane 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

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

2. **Validate ^{14}C-based laboratory assay and other lines of evidence for attenuation**

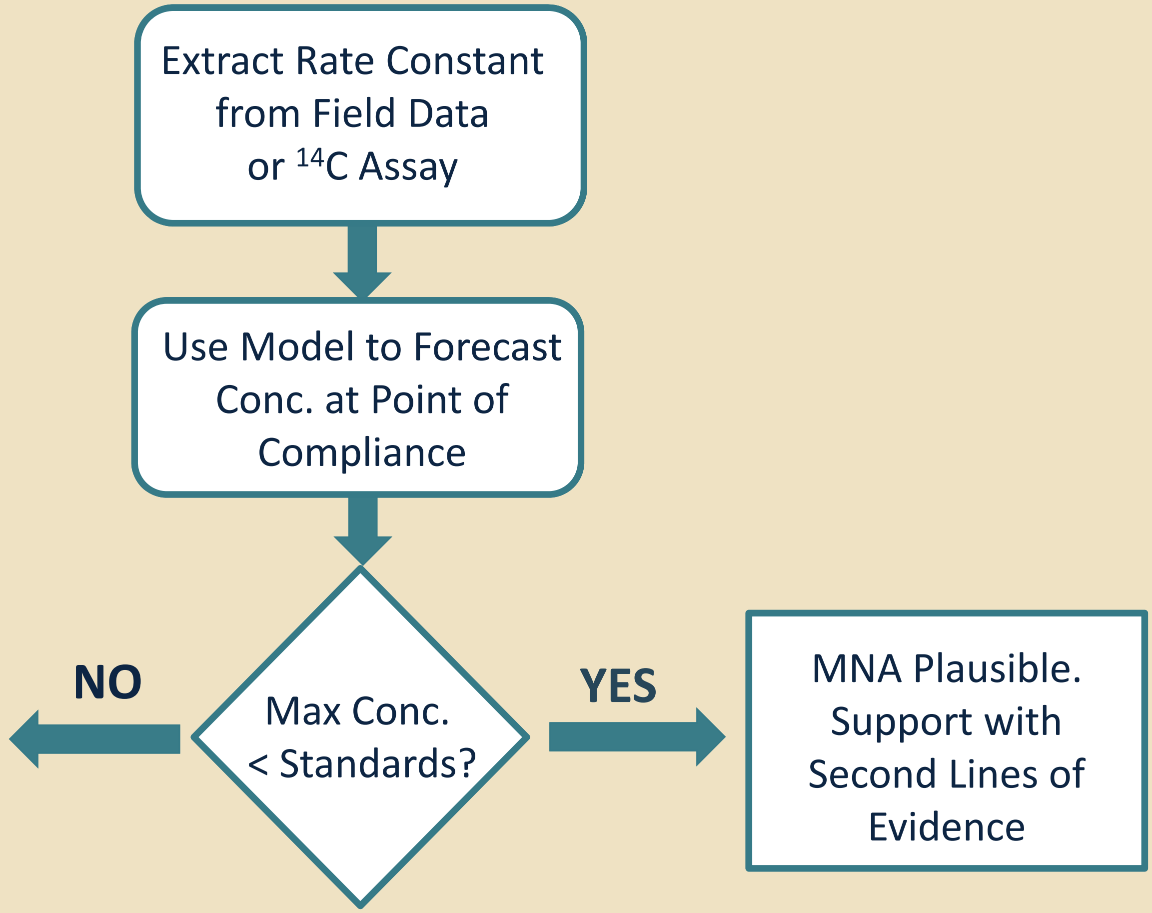
ESTCP

Project No. ER-201730

OVERVIEW OF DECISION FRAMEWORK

GOAL:

Develop tool that will walk RPMs through process for evaluating MNA for 1,4-D and associated CVOCs

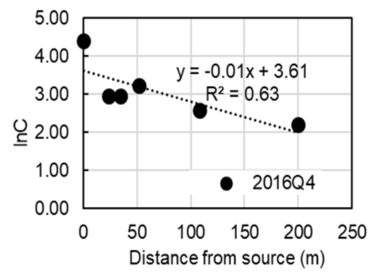


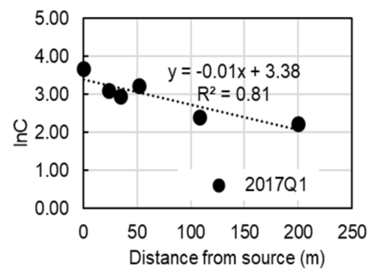
DESKTOP EVALUATION OF RATE CONSTANTS FOR 1,4-DIOXANE

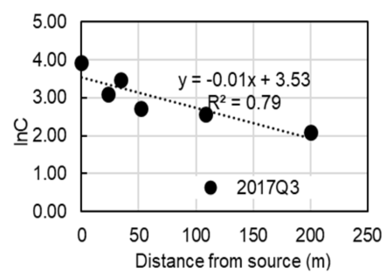
OBJECTIVE:
Establish range for 1,4-D rate constants by estimating values at many sites

1 *Plot concentration vs. distance in direction of groundwater flow*

Can plot data from multiple events







2 *Multiply slope of regression line(s) by groundwater seepage velocity =*

BULK ATTENUATION RATE CONSTANT FOR 1,4-D

DESKTOP EVALUATION OF RATE CONSTANTS FOR 1,4-DIOXANE

Results of Preliminary Evaluation (11 sites)

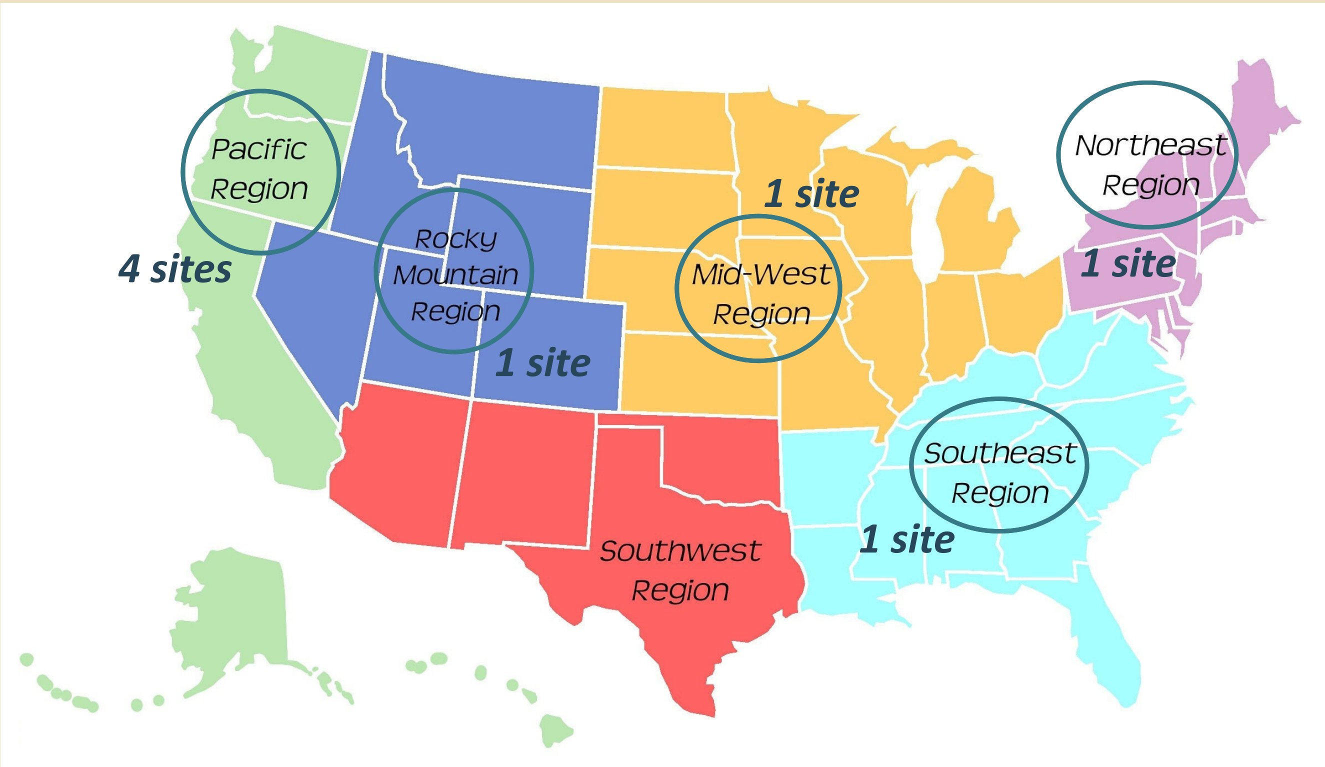
Site ID	# of Monitoring Events	1,4-Dioxane Bulk Attenuation Rate (yr^{-1})		Half-life (yr)		Distance between source and goal concentration of 1 µg/L (m)	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
6	3	1.8846	0.4592	**0.4**	0.1	831	103
7	2	1.4529	0.1378	**0.5**	0.0	85	3
1	3	0.2095	0.0246	**3.3**	0.4	531	37
10	1	0.6657	--	**10**	--	1356	--
9	4	0.0724	0.0146	**54**	10	178	35
4	5	0.0387	0.0040	**171**	65	119	45
11	5	0.0419	0.0079	**184**	53	62	18
3	3	0.0110	0.0035	**683**	122	146	26
2	13	0.0007	0.0002	**1047**	265	4074	1264
8	3	0.0002	0.0001	**24458**	7812	91	29
5	8	0.0003	0.0001	**25324**	18680	94	69

NEXT STEPS: Add sites, refine estimates using a BIOCHLOR-type tool (to account for non-destructive processes)

KEY POINTS ABOUT RATES

- Significant variability observed ***between*** sites (4 orders of magnitude)
- Limited variability observed ***within*** individual sites (generally < 30% difference between rates estimated from different monitoring events)

FIELD SAMPLING: *Where are we looking?*



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
- 2 to 3 sites yet to be sampled
- Hoping to add more…

FIELD SAMPLING: *What are we looking for?*

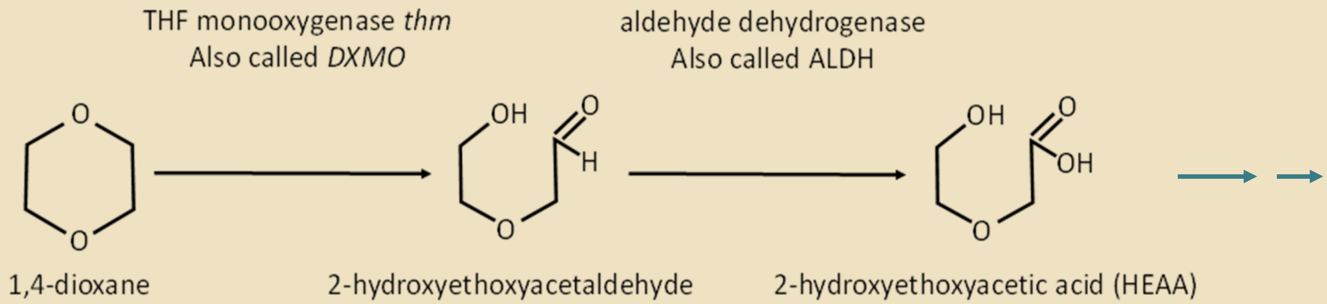
- **Single mobilization per site**
- **4 to 5 wells per site**
  - **Biomarkers for 1,4-D and cVOC degradation**
    - **DHB, DCA, DXMO, ALDH, sMMO, RMO, RDEG, PHE, SCAM**
  - **DO, Fe(II), pH, Temperature, Conductivity, ORP**
  - **Stable isotopes (^{13}C, ^{2}H) for 1,4-D**
    - **Completed in coordination with ER-2535 (PI: Bennett)**
  - **Samples for ^{14}C-Assay of 1,4-D biodegradation at Clemson**

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

^{14}C ASSAY TO ASSESS BIODEGRADATION OF 1,4-DIOXANE

What if you need direct evidence of aerobic biodegradation based on product formation and an estimate of the rate?

- ***KEY ISSUE:*** **Aerobic biodegradation of 1,4-dioxane yields CO_2, biomass, and possibly soluble intermediates; *how to document the product formation?***



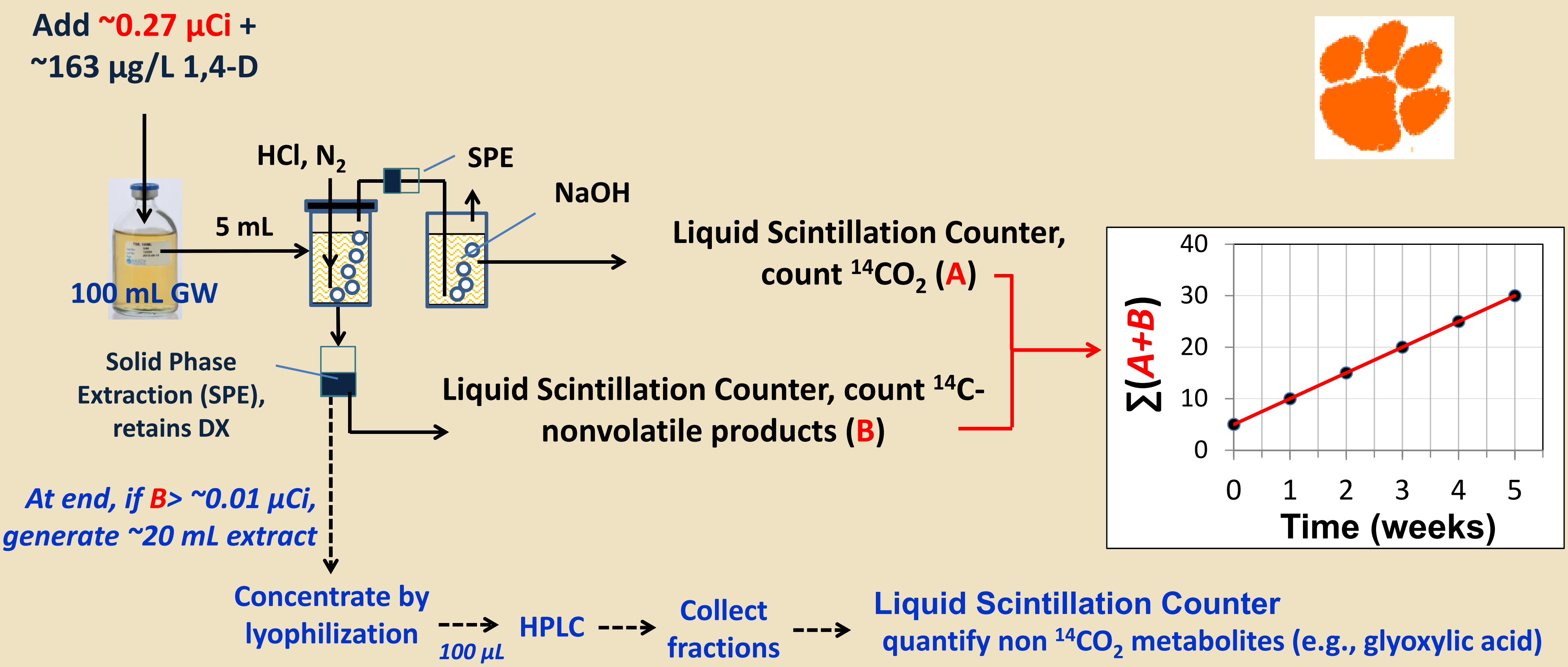
(Difficult to quantify using standard analyses)

CO_2

Biomass

Other soluble intermediates?

^{14}C ASSAY TO ASSESS BIODEGRADATION OF 1,4-DIOXANE

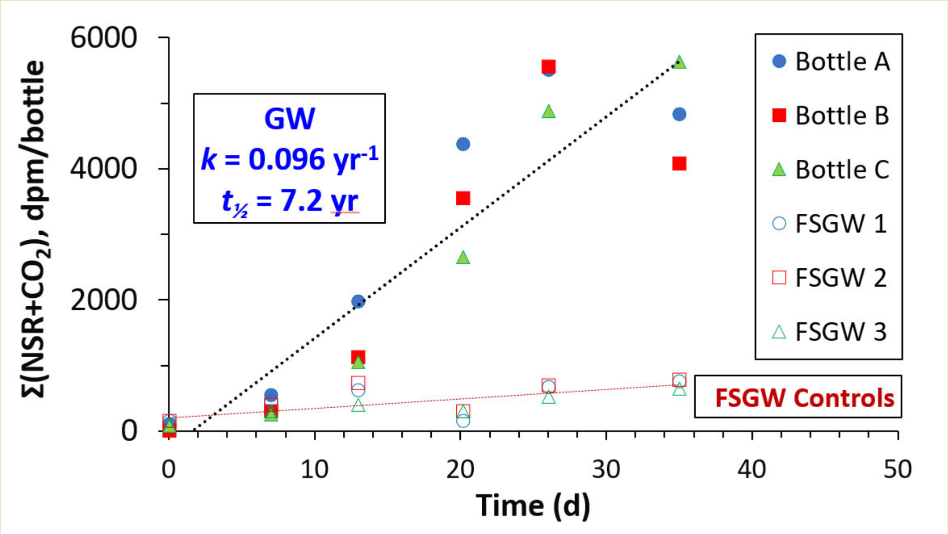


^{14}C ASSAY TO ASSESS BIODEGRADATION OF 1,4-DIOXANE

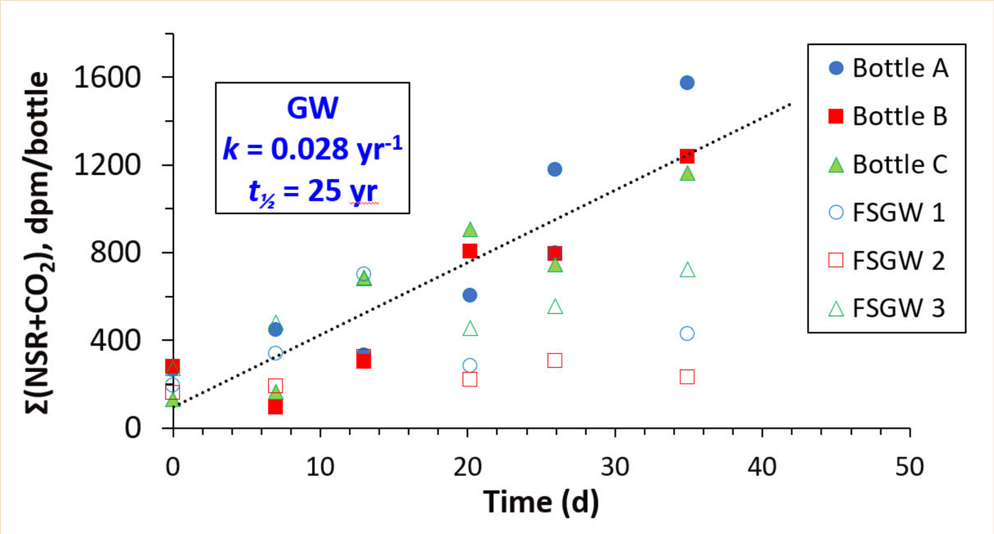
EXAMPLE: Site #3

3 of 5 wells demonstrated measurable 1,4-D degradation activity

Well #4 – IW1



Well #5 – P70



RESULTS TO-DATE: *Summary*

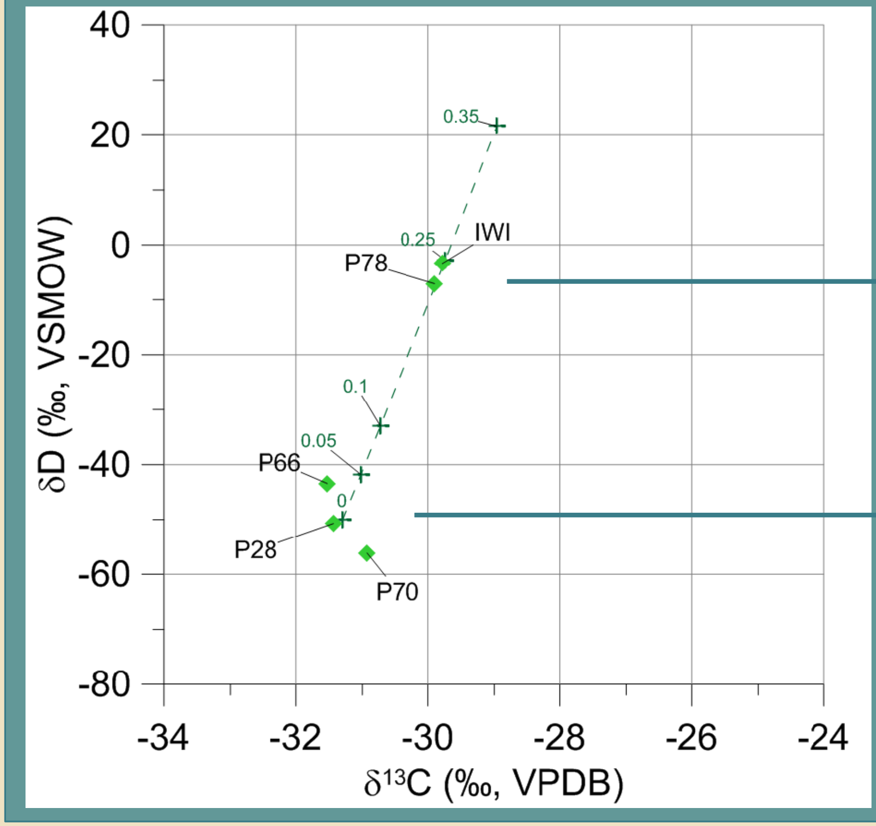
Site	C vs. Distance	Biomarkers	CSIA	^{14}C Assay
	Positive Evidence for 1,4-D Natural Attenuation?			
1				
2				
3				
4				
5				
6				

1 to 3 additional sites yet to be sampled

-
+
++

RESULTS TO-DATE: *Site #3 Example*

DUAL ISOTOPE PLOT:



Downgradient Wells:

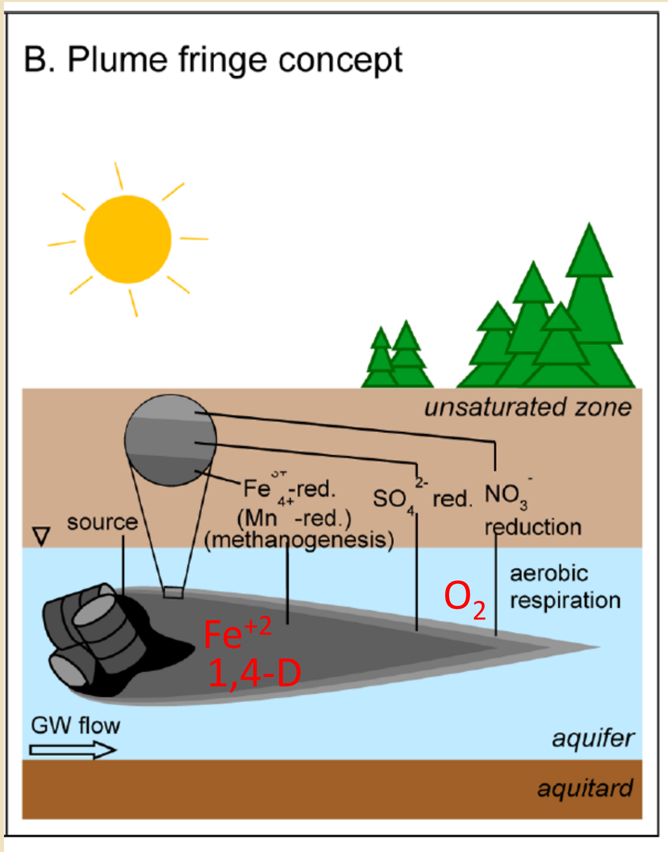
Extensive fractionation - reflects impact of <u>attenuation along plume</u> and <u>pilot test</u>

Source/Mid-Plume Wells:

Little fractionation despite evidence of attenuation capacity (^{14}C assay, biomarkers) - presumably due to <u>location</u> and <u>mixing with anaerobic groundwater</u> (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: *Site #3 Example*



Why was there no fractionation in some 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**

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

RESULTS TO-DATE: *Summary*

Site	High levels of CVOCs?	Low levels of Biomarkers	Absence of co-substrate?	Low DO?	Low levels of 1,4-D?
1	✓		✓	✓	
2		✓	✓		✓
5	✓		✓	✓	
6		✓	✓		✓
3					
4			✓	✓	

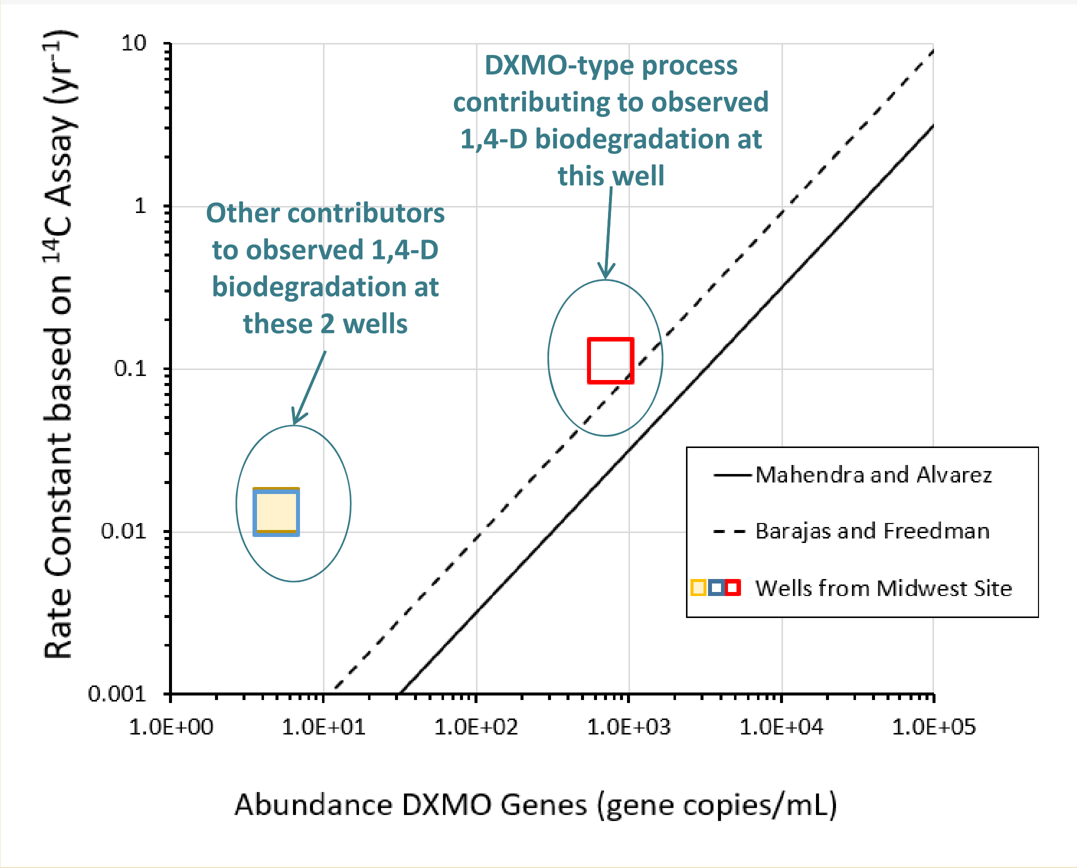
^{14}C-1,4-D degraded (sites 3 and 4)

Why a lack of 1,4-D biodegradation at several sites?

- **Several possible factors identified**
- **1,4-D biodegradation is not ubiquitous**

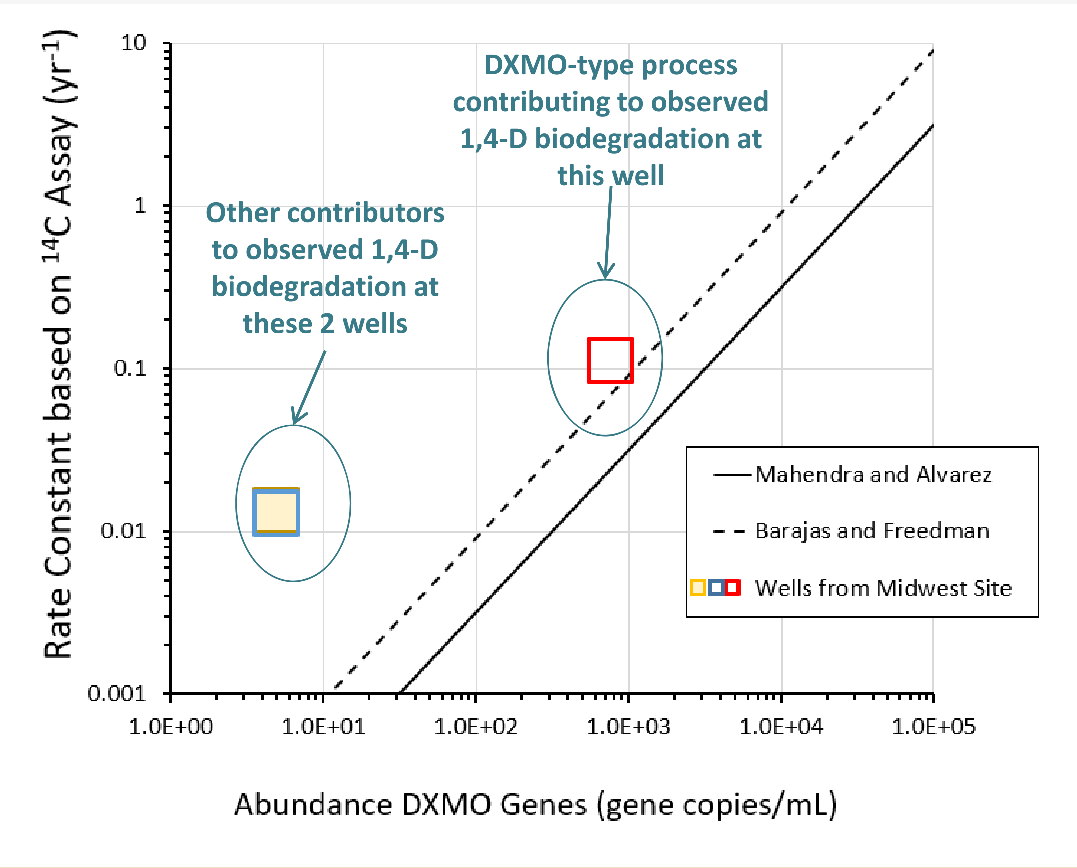
END PRODUCTS: *Integrated Decision Tool*

- **Modify BIOCHLOR to get rate constants for 1,4-dioxane**
- **Develop lines of evidence to validate rate constants:**
  - **Build a data base comparing qPCR markers to field-scale rate constants and ^{14}C assay rate constants at benchmark sites**



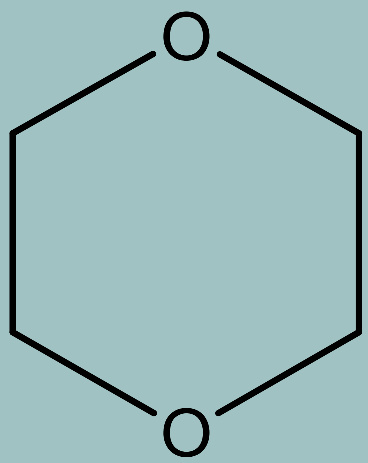
END PRODUCTS: *Integrated Decision Tool (continued)*

- **Separate decision matrices will be developed for degradation pathways for:**
  - **1,4-Dioxane, and**
  - **1,1,1-TCA and degradation products**
- **Develop an easy-to-use Excel-based spreadsheet application (BioPIC with TCA/Dioxane).**



KEY POINTS

1,4-Dioxane



- 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
  - e.g., lack of isotope fractionation may reflect mixed redox conditions
- Data collected so far suggests that odds of observing 1,4-D biodegradation drops at sites with $\geq$ 3 of 5 key characteristics
- Tool to support evaluation of MNA of 1,4-D and "other" CVOCs will be available soon