Applying compound-specific isotope analysis to sites with low concentrations of 1,4-dioxane

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Motivation for this work

- Little is known about 1,4-dioxane (1,4-D) degradation at field sites
- SERDP-funded project in response to Statement of Need for cost-effective diagnostic methods for natural attenuation
- CSIA is uniquely powerful method for demonstrating biodegradation in the field, BUT:
  1. 1,4-D concentrations <100 µg/L are too low for conventional CSIA methods
  2. Variety of enrichment factors for 1,4-D are not defined
  3. Range in isotopic composition of source 1,4-D is not well described
  4. Interpretation of CSIA at a variety of field sites lacking

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Phase I

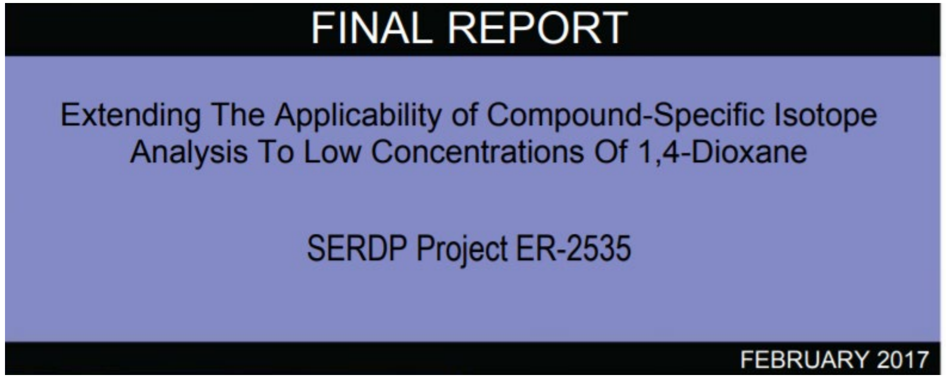
- Phase I focus:

1. Development of method to perform CSIA on low concentrations of 1,4-D

   $\delta^{13}C$ ~ 1 µg/L

   δD ~ 10 µg/L

2. Determination of enrichment factors (ε) of 1,4-D for different microbial cultures

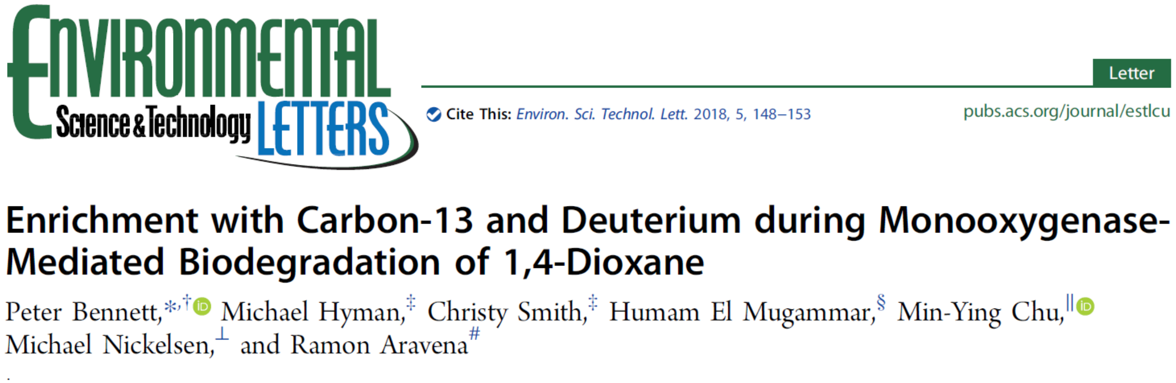


FINAL REPORT

Extending The Applicability of Compound-Specific Isotope Analysis To Low Concentrations Of 1,4-Dioxane

SERDP Project ER-2535

FEBRUARY 2017



Environmental Science & Technology LETTERS

Letter

Cite This: *Environ. Sci. Technol. Lett.* 2018, 5, 148−153

pubs.acs.org/journal/estlcu

Enrichment with Carbon-13 and Deuterium during Monooxygenase-Mediated Biodegradation of 1,4-Dioxane

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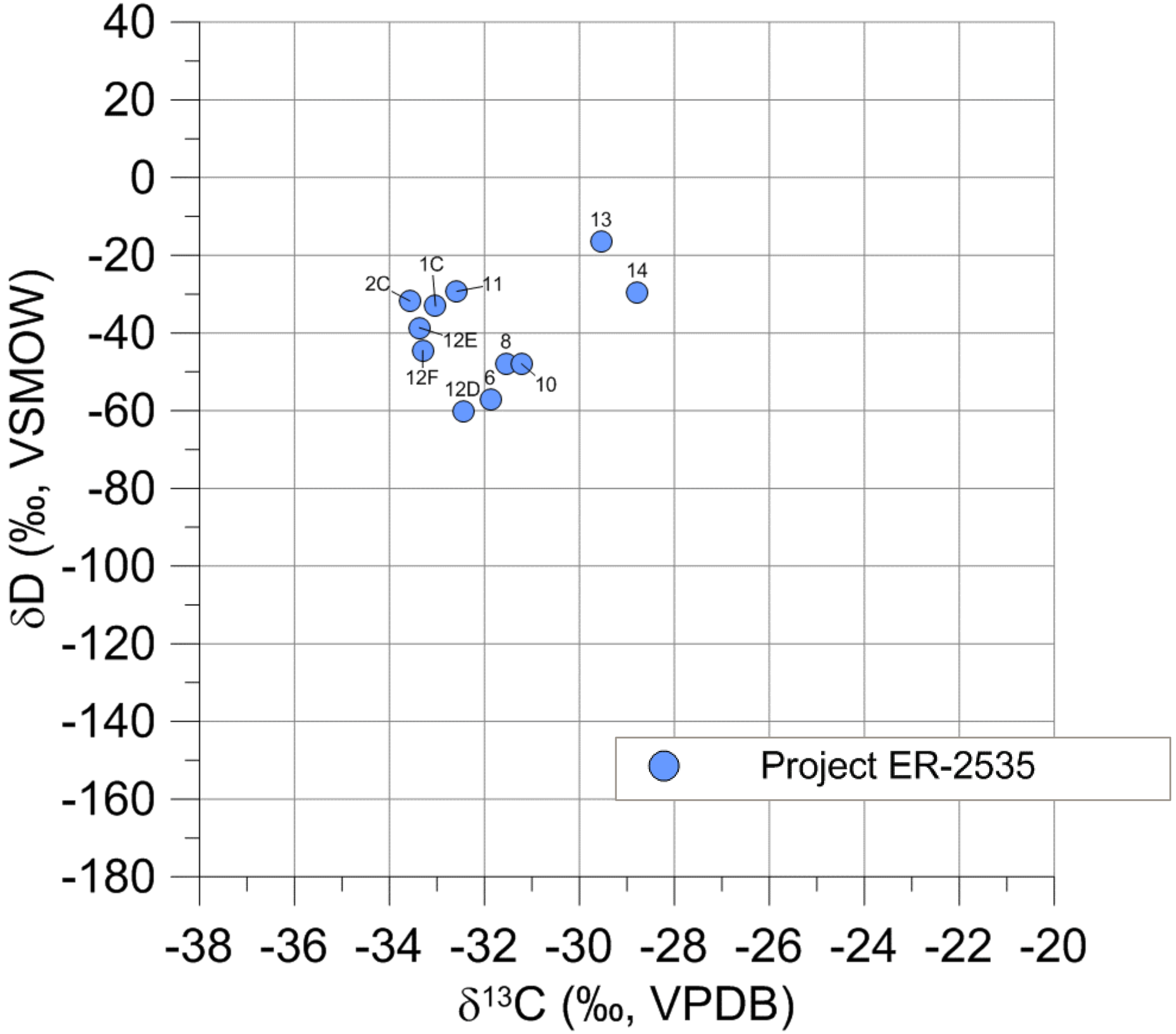
Phase II

- Phase II focuses on further development:
  1. Expand the database of source 1,4-D isotopic compositions
  2. Add at least six additional case studies at field sites

Isotopic composition of 1,4-dioxane sources

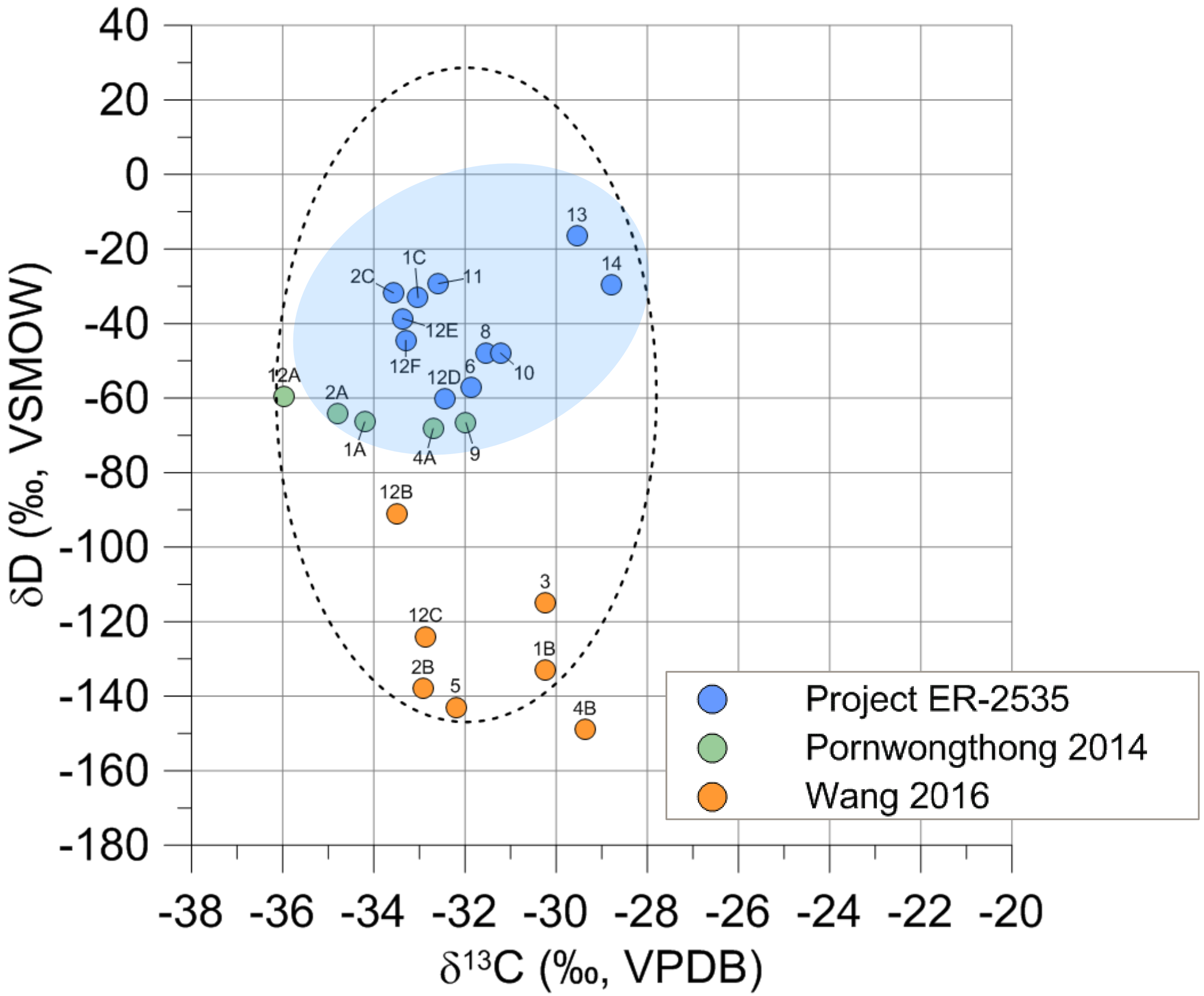
- Analyzed 11 different neat 1,4-D sources from various manufacturers, bringing total to 23
- Methodology
  - Used two different methods: EA-IRMS and GC-IRMS
  - Results identical when purity was >99.5%
  - GC-IRMS results shown along with results published by others

Source isotopic composition



No.	Manufacturer	$\delta^{13}C$ ‰	δD ‰	Reference
1A	Acros Organics	-34.2	-66	Pornwongthong, 2014
1B		-30.3	-133	Wang, 2016
1C		-33.0	-33	SERDP ER-2535, Phase II
2A	Alfa Aesar	-34.8	-64	Pornwongthong, 2014
2B		-32.9	-138	Wang, 2016
2C		-33.6	-32	SERDP ER-2535, Phase II
3	EMD 2013	-30.2	-115	Wang, 2016
4A	Fisher Scientific	-32.7	-68	Pornwongthong, 2014
4B		-29.4	-149	Wang, 2016
5	Fluka 2014	-32.2	-143	Wang, 2016
6	Honeywell	-31.9	-57	SERDP ER-2535, Phase II
8	J.T.Baker	-31.5	-48	SERDP ER-2535, Phase II
9	Mallinckrodt	-32.0	-67	Pornwongthong, 2014
10	Molecular Dimensions	-31.2	-48	SERDP ER-2535, Phase II
11	Restek	-32.6	-29	SERDP ER-2535, Phase II
12A	Sigma-Aldrich	-36.0	-60	Pornwongthong, 2014
12B		-33.5	-91	Wang, 2016
12C		-32.9	-124	Wang, 2016
12D		-32.5	-60	SERDP ER-2535, Phase II
12E		-33.4	-39	SERDP ER-2535, Phase II
12F		-33.3	-45	SERDP ER-2535, Phase I
13	TCI America	-29.5	-17	SERDP ER-2535, Phase II
14	Ultra Scientific	-28.8	-30	SERDP ER-2535, Phase II

Source isotopic composition database



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Pornwongthong, P., 2014. Stable isotopic and molecular biological tools to validate bio-degradation of 1,4-dioxane, Ph.D. thesis, UCLA.

Wang, Y., 2016. Breakthrough in 2D-CSIA technology for 1,4-dioxane, Remediation, p.61-70.

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Case studies

Eight additional sites analyzed in Phase II, for total of 12

All case studies

Site	Location	Redox conditions	Biostim.?	1,4-D (µg/L)	
				Min.	Max.
McClellan AFB	Sacramento, CA	Aerobic	Yes	0.68	56
Space Launch Complex 16	Cape Canaveral, FL	Anaerobic	No	<3.0	17,200
Facility 1381	Cape Canaveral, FL	Anaerobic	No	all <3.0	
Vandenberg AFB Site 24	Lompoc, CA	Aerobic	Yes	78	81
AFP3	Tulsa, OK	Aerobic	Yes	90	250
JBCC, Ashumet Valley	Buzzards Bay, MA	Aerobic	No	all <0.25	
NASNI OU-19/20	San Diego, CA	Anaerobic	Yes	1.4	990
Non-DoD	Midwest	Anaerobic/Aerobic	Yes	8.3	310
Non-DoD	South Carolina	Aerobic	No	10	13
NASNI OU-11	San Diego, CA	Anaerobic	No	22	>8,000
MCB Camp Pendleton	Oceanside, CA	Aerobic	Yes	3.8	160
Hanscom AFB	Lincoln, MA	Aerobic	No	0.076	19

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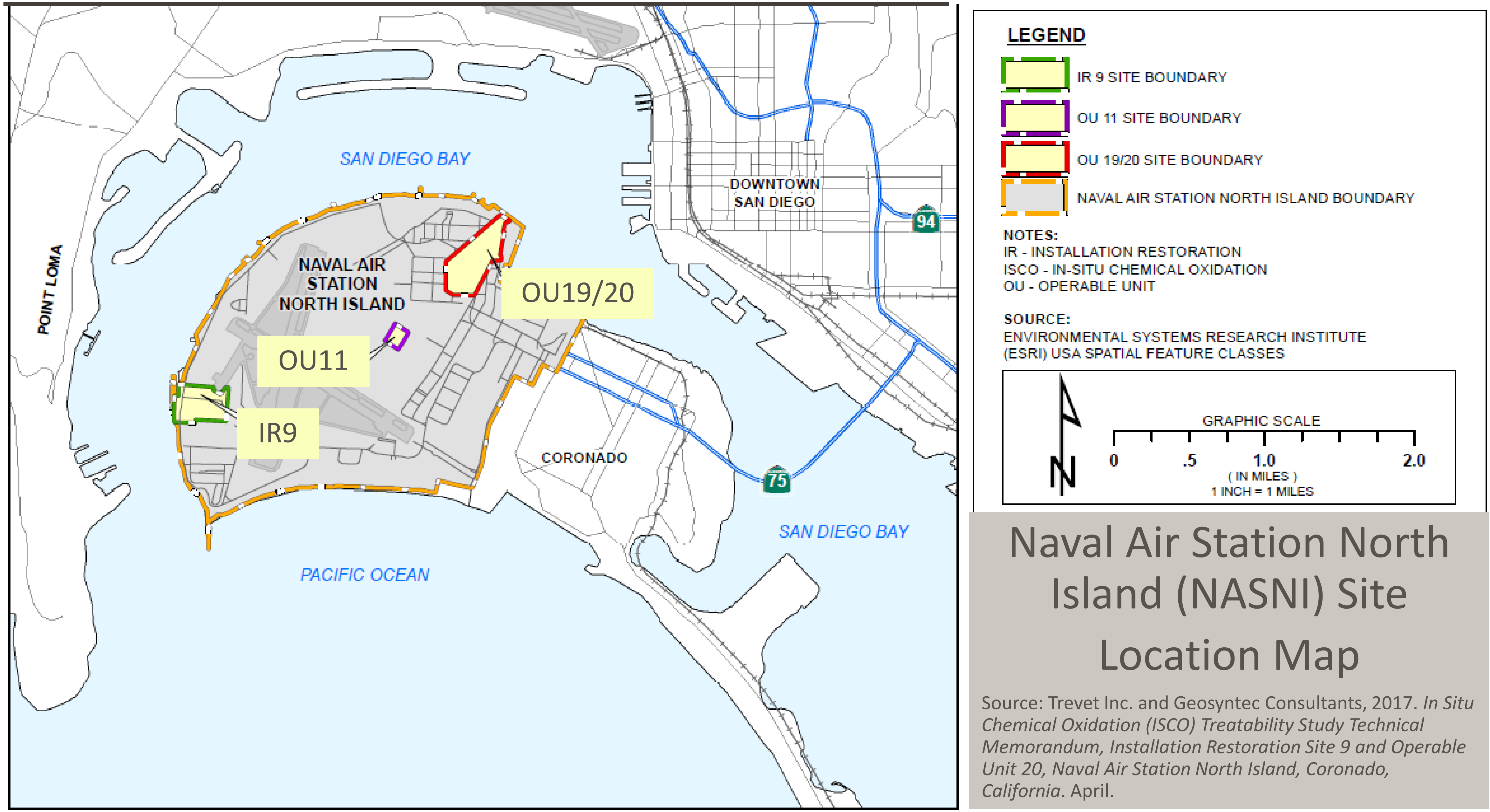
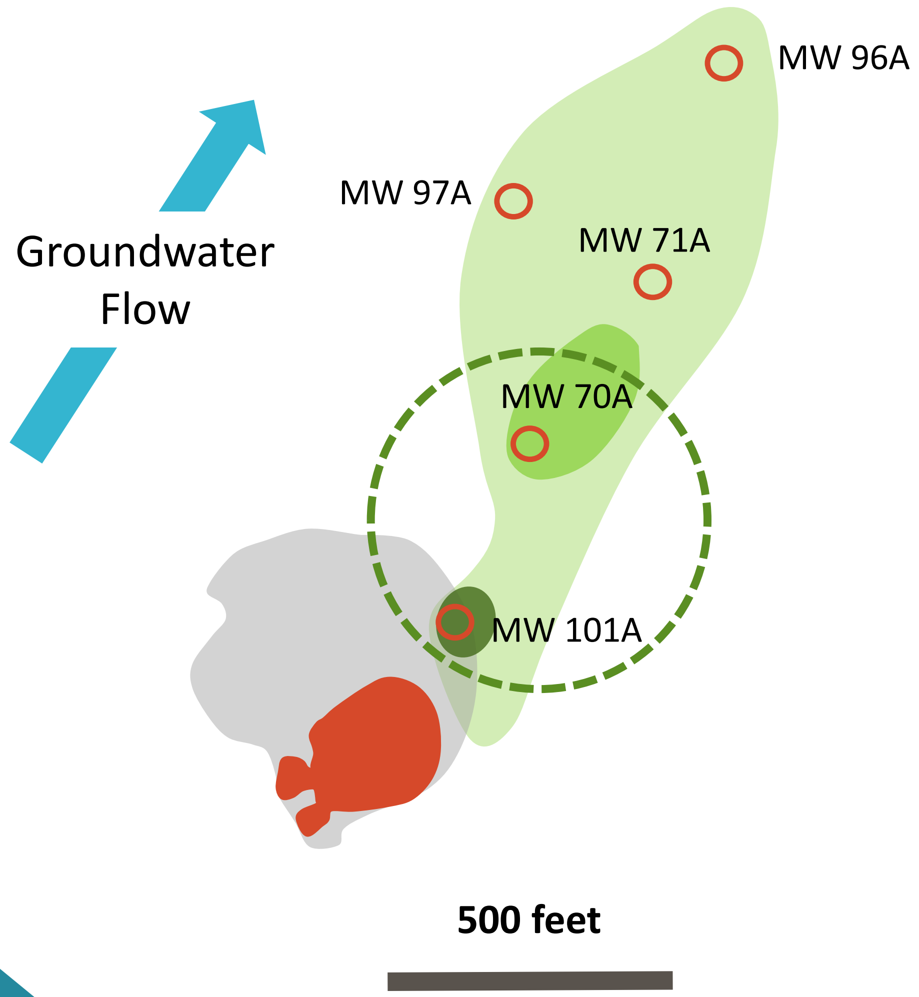


Naval Air Station North Island (NASNI) Site Location Map

Source: Trevet Inc. and Geosyntec Consultants, 2017. *In Situ Chemical Oxidation (ISCO) Treatability Study Technical Memorandum, Installation Restoration Site 9 and Operable Unit 20, Naval Air Station North Island, Coronado, California*. April.

NASNI OU-19/20



OU 19: LNAPL (JP-4, Stoddard solvent, TCE)
OU 20: Chloroethene plume with Cr (VI)

Anaerobic with possible shallow aerobic zones

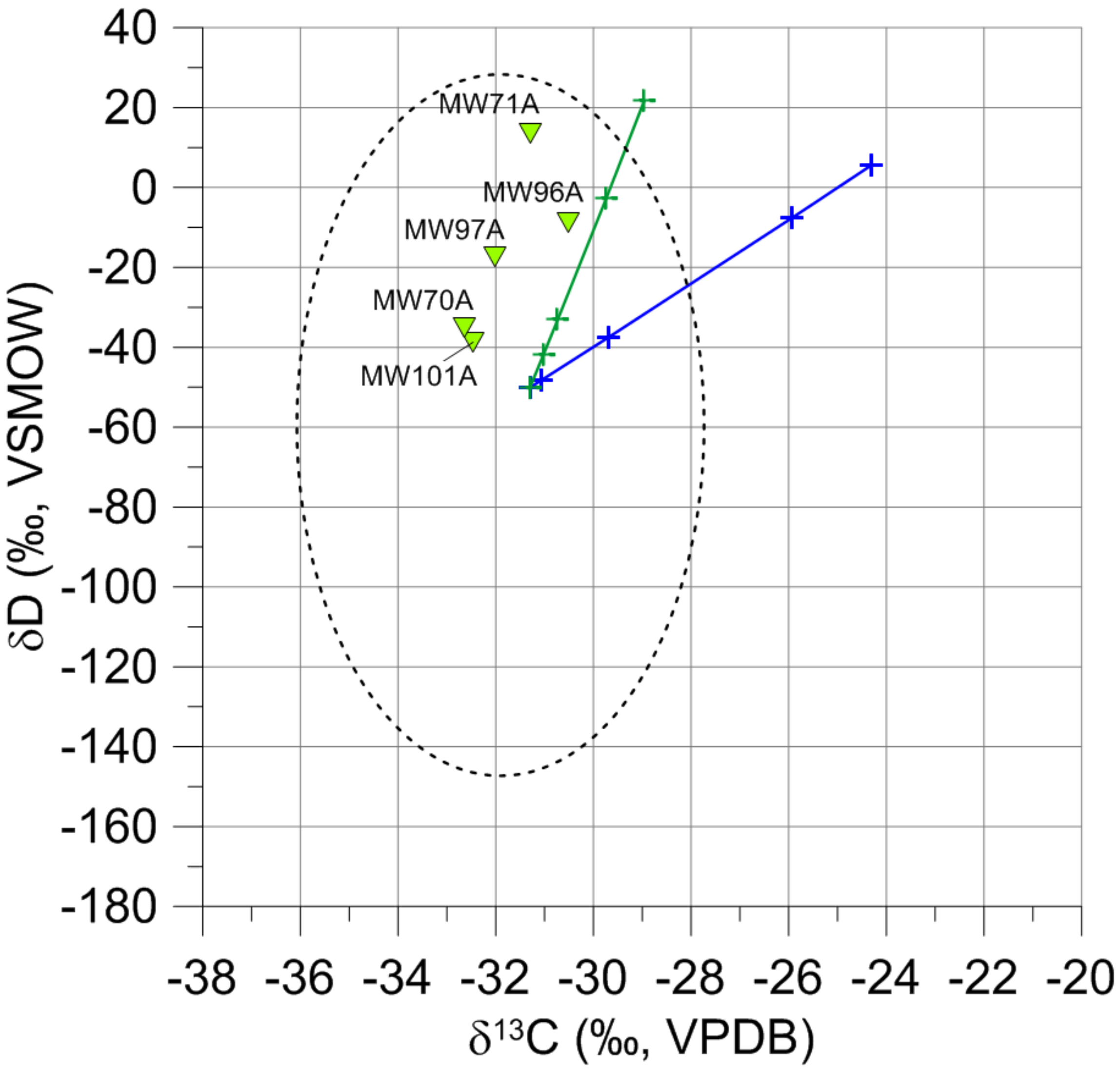
	1,4-D	>10 µg/L
	1,4-D	>100 µg/L
	1,4-D	>1000 µg/L
	NAPL with TCE	
	NAPL w/o TCE	

North

NASNI OU-19/20

- Rayleigh degradation curves:
  - THF-grown culture
  - Propane-grown culture

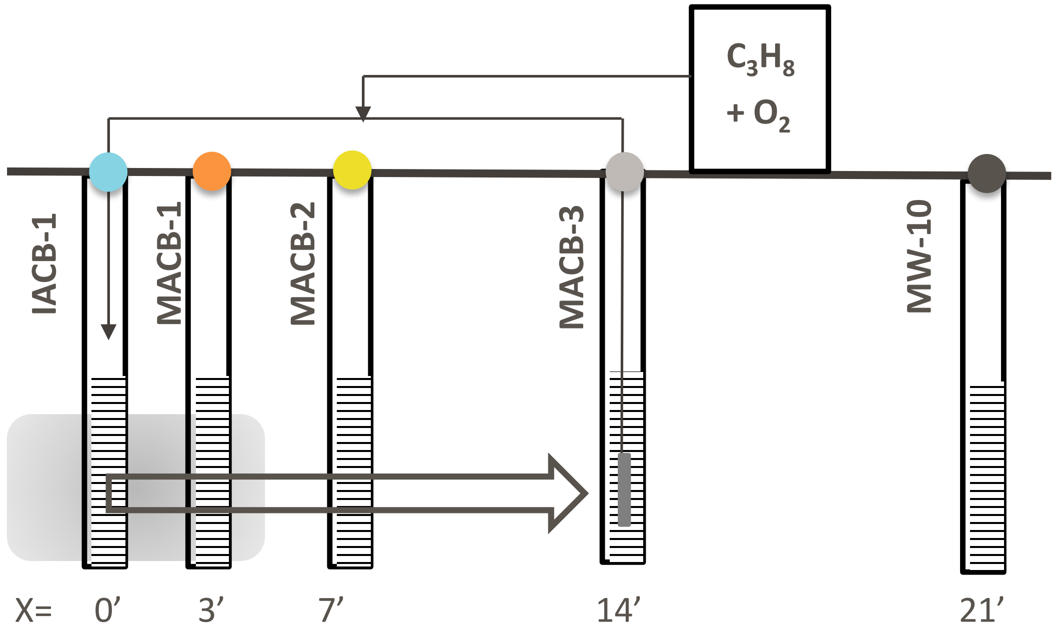
Well	1,4-D (µg/L)
MW101A	970
MW70A	86
MW71A	1.4 J
MW97A	130
MW96A	14

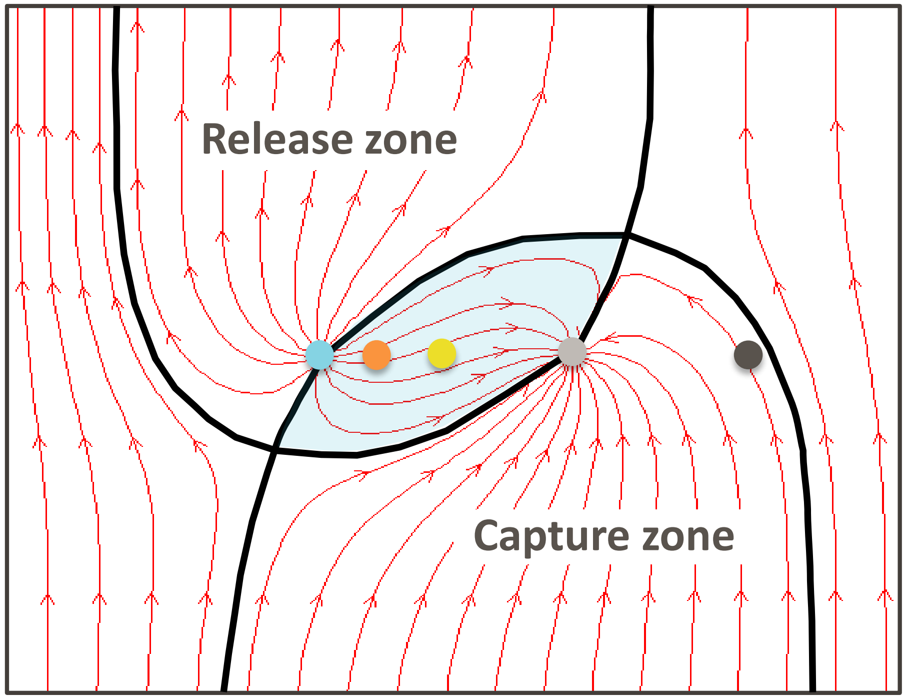


Bennett et. al., 2018. Enrichment with Carbon-13 and Deuterium during Monooxygenase-Mediated Biodegradation of 1,4-Dioxane. Environmental Science & Technology Letters 5(3): 148-153

McClellan AFB aerobic cometabolic biodegradation pilot

- Recirculation with propane and oxygen created an in-situ bioreactor
- Propane and oxygen injection began Oct 2015





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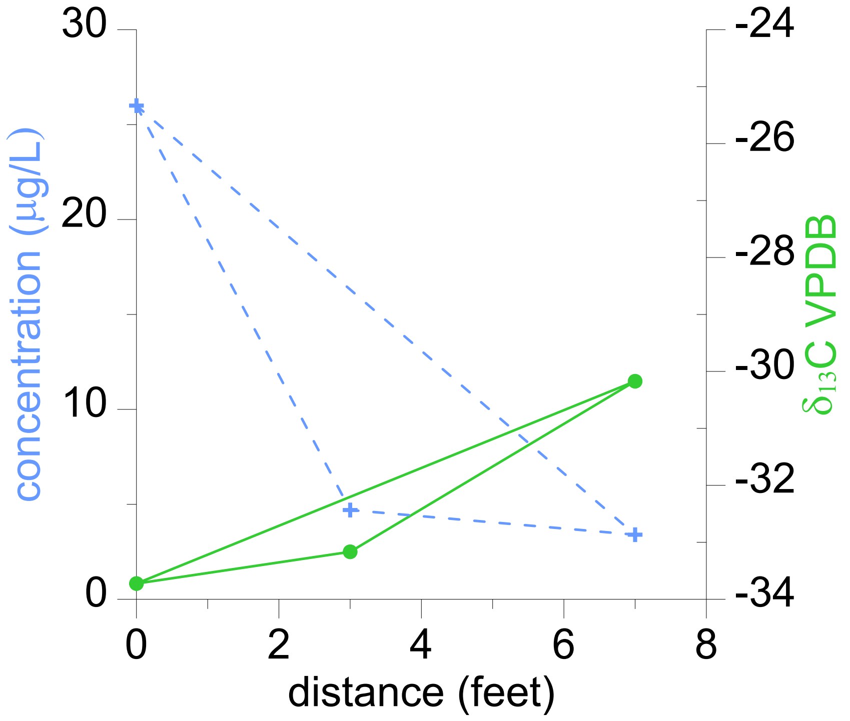
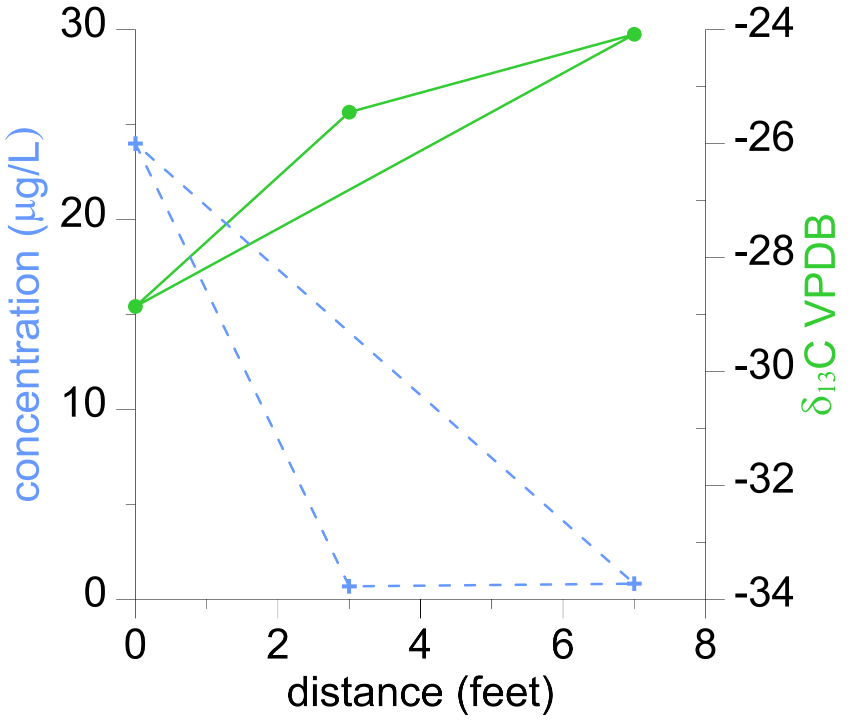
Enrichment in ^{13}C in samples from treatment zone

December 2015



IACB-1 MACB-1 MACB-2

June 2016



IACB-1 MACB-1 MACB-2

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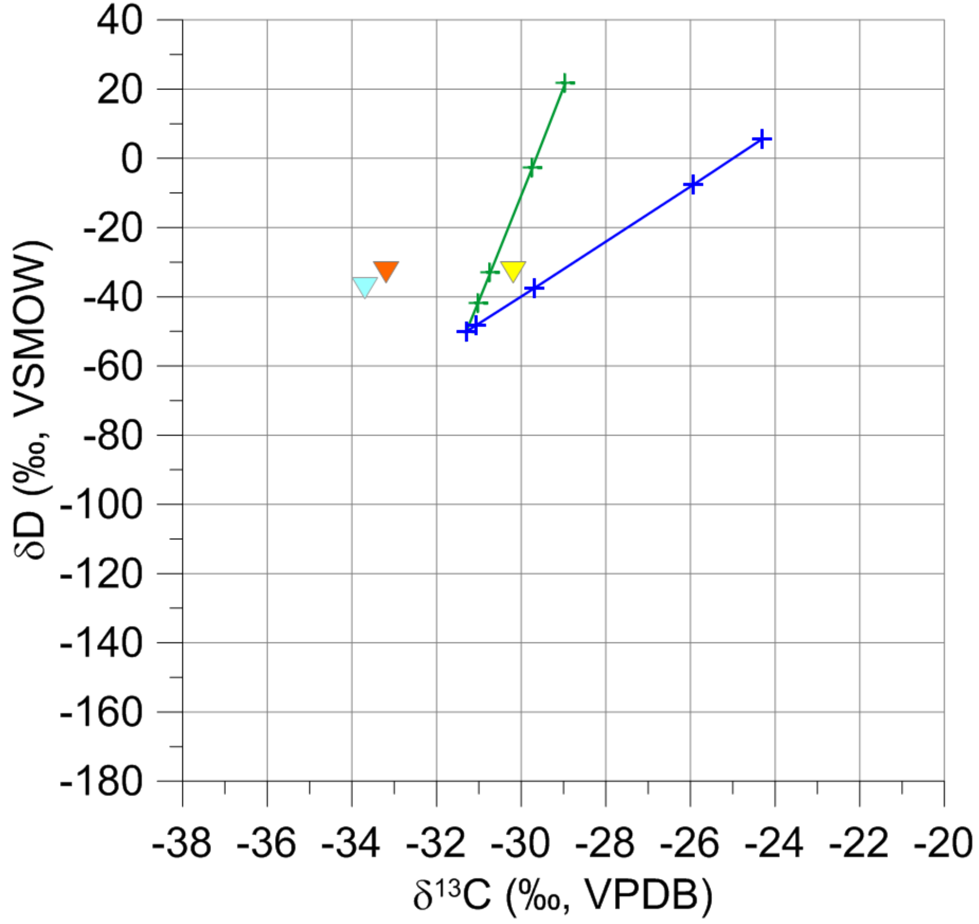
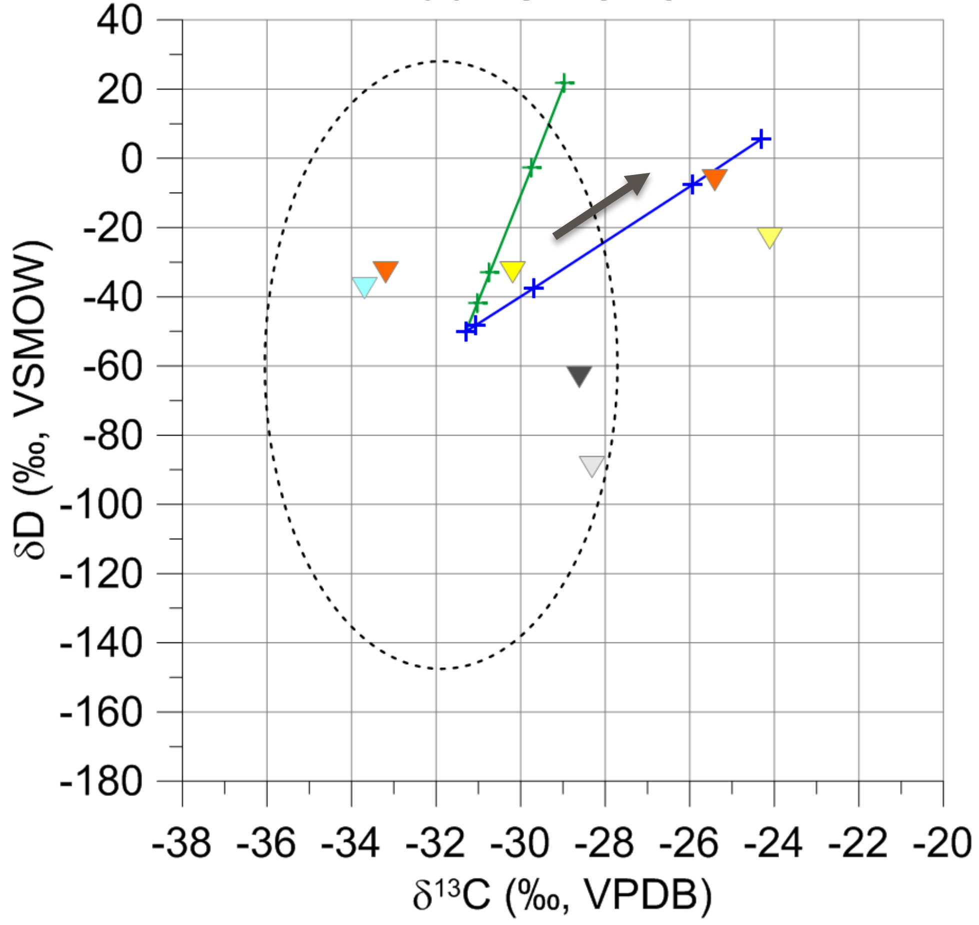
Dual isotope plots from treatment zone

▯ IACB-1 ▯ MACB-1 ▯ MACB-2 ▯ MACB-3 ▯ MW-10

December 2015



June 2016



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Non-DoD Midwest site

- Landfill accepted industrial waste 1968-1979
- THF is a co-contaminant
- Treatment with injected groundwater infused with oxygen and propane for ~four months prior to sampling

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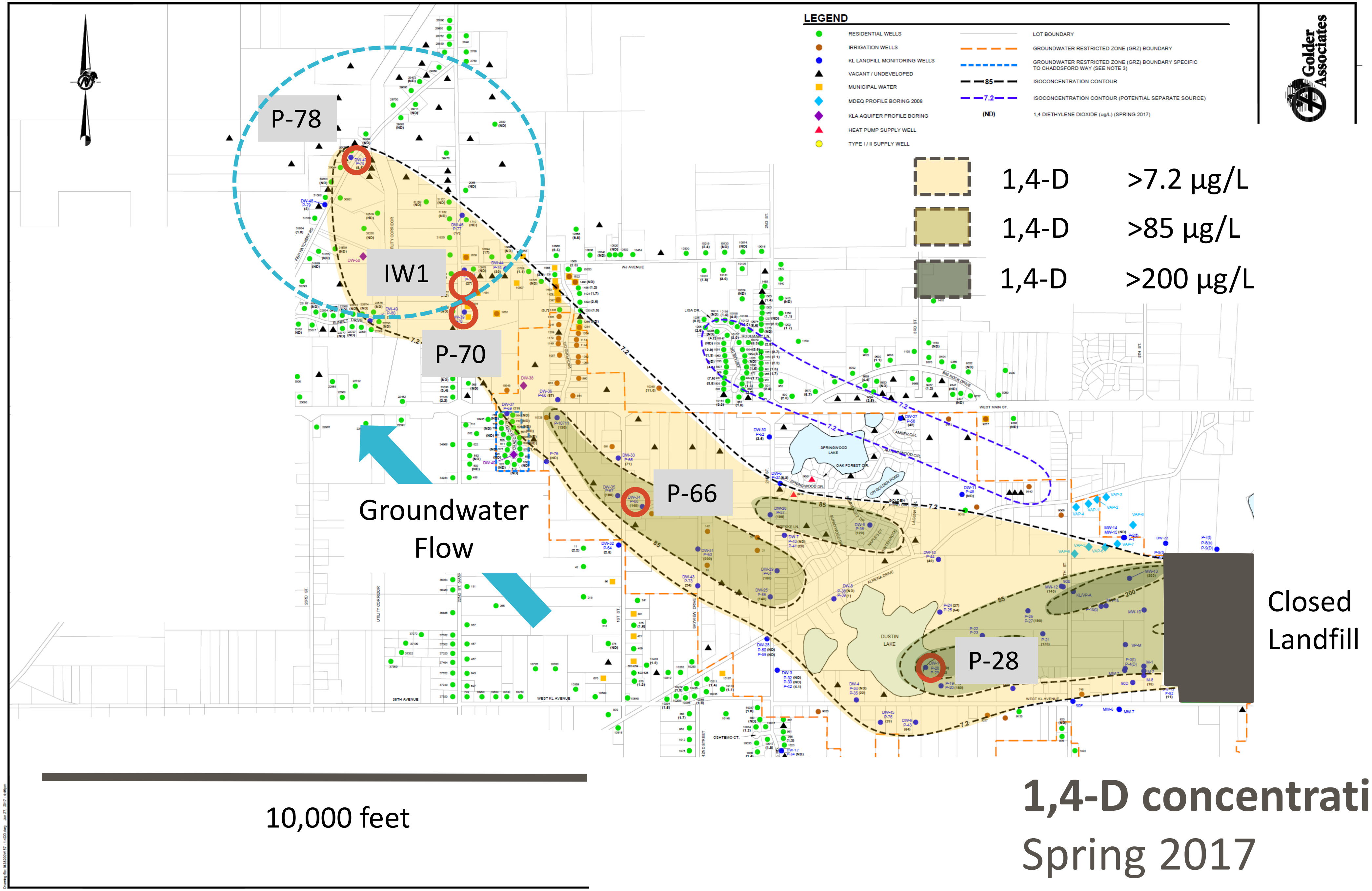
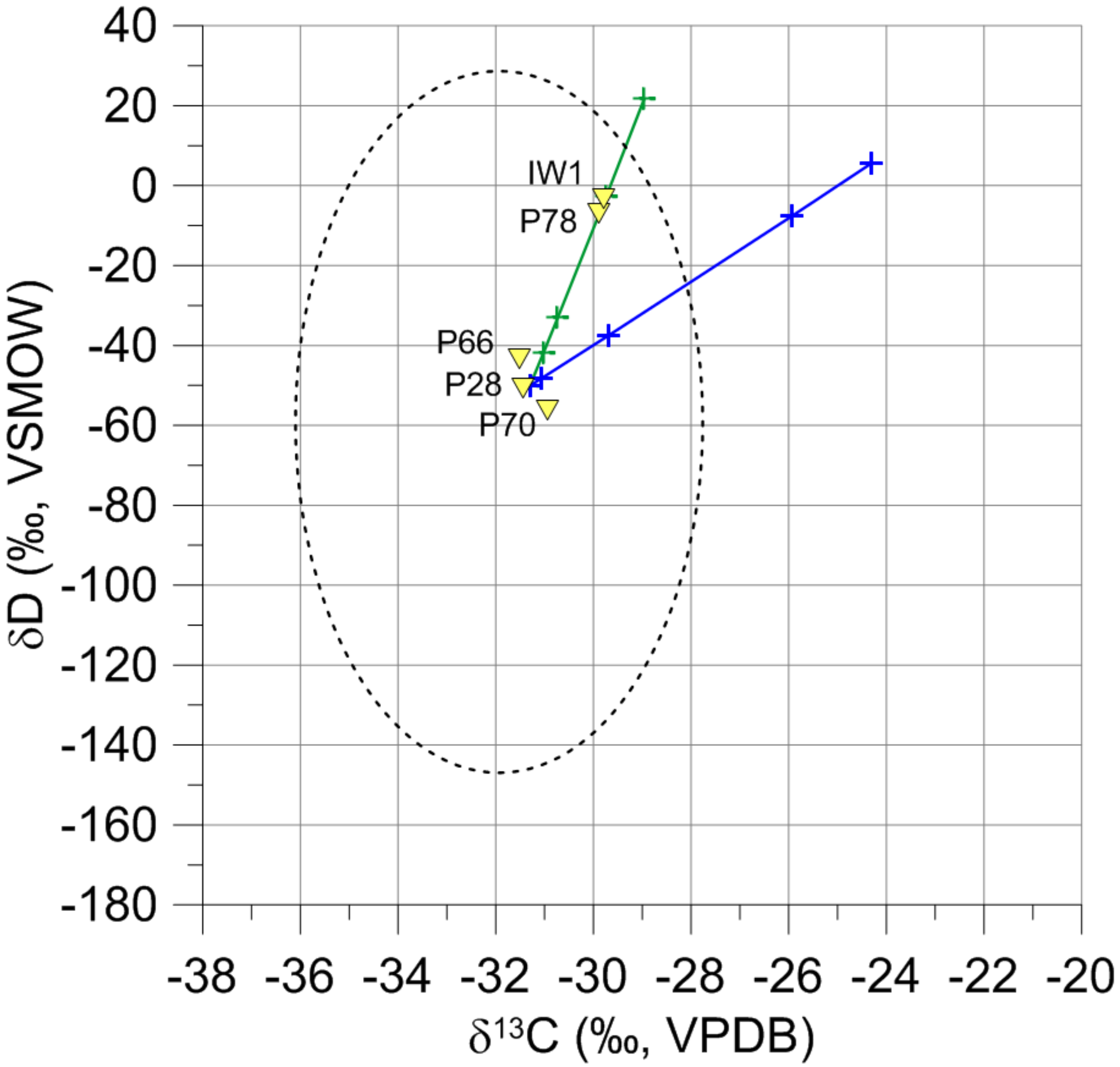


1,4-D concentrations
Spring 2017

Midwest site

- Extensive fractionation at injection well IW1 and leading edge of plume P78
- Other locations consistent with 1,4-D source
- THF-grown culture



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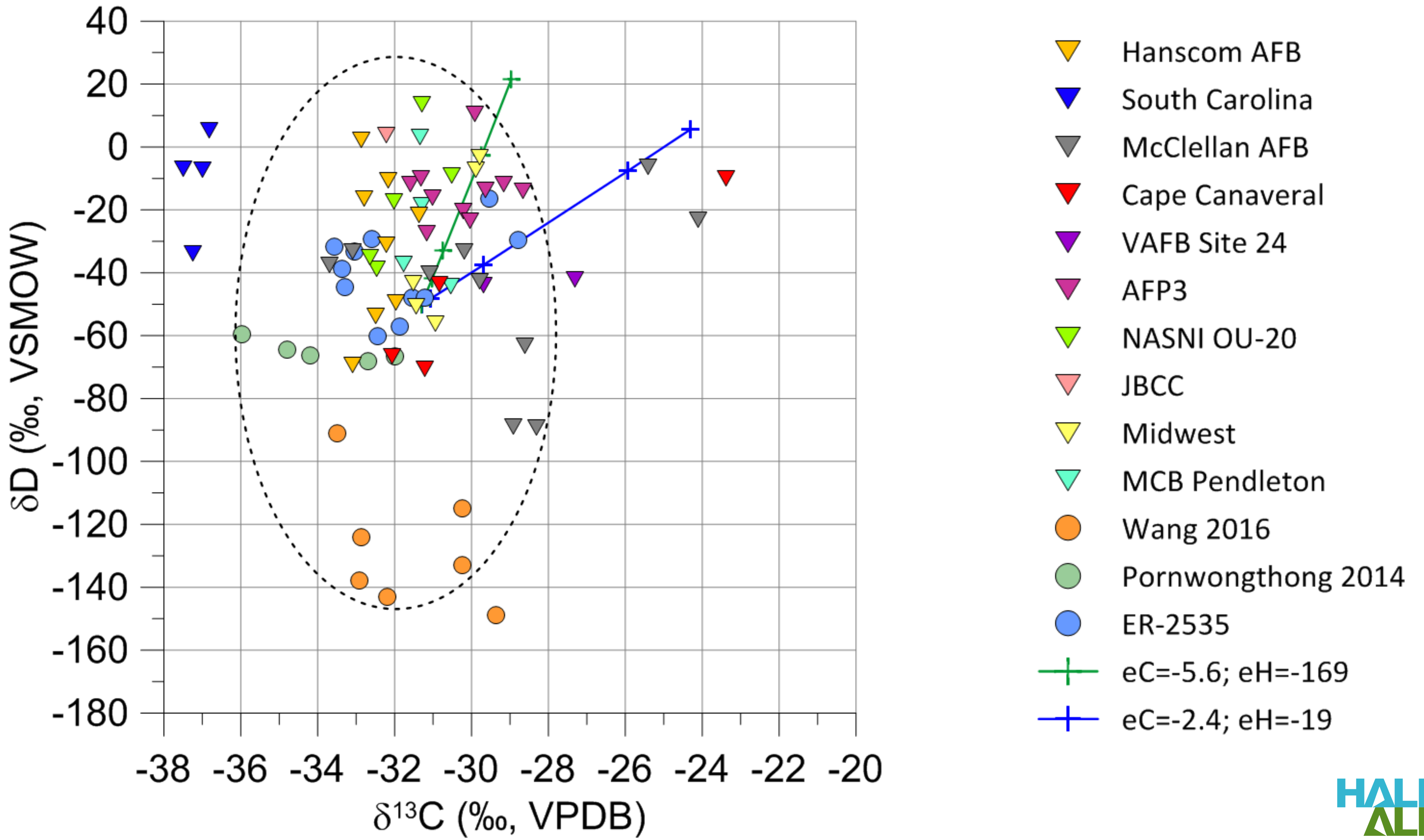
Isotopic composition of 1,4-dioxane: Source and groundwater samples



What we've learned:

- High variability in 1,4-D sources → high variability in groundwater
- For field implementation:
  - Demonstrate enrichment in both $\delta^{13}C$ and δD
  - Many samples likely needed to demonstrate degradation
- Natural attenuation assessments should be supported by multiple lines of evidence
  - Analysis of monooxygenase biomarkers is valuable supporting information

What we need to learn:

- Other factors potentially affecting isotopic composition of 1,4-D require further study (e.g., evaporation, pH, etc.)
- 2D enrichment factors for other microbes, e.g., CB1190
- Characterization of natural degradation and isotopic enrichment under anaerobic conditions

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Field site sampling collaborators

- ESTCP Project 201730: **Tony Danko** (NAVFAC), **Dave Adamson** (GSI Environmental, Inc.), and **John Wilson** (Scissortail Environmental Solutions LLC)
- Hanscom AFB: **Kinshuk Shroff**, Versar
- AFP3: **Rebecca Mora**, AECOM

Acknowledgements

- SERDP Grant ER-2535 (Bennett): CSIA method development
- SERDP Grant ER-2303 (Hyman): Degradation reactions performed at NCSU
- NSERC Discovery Grant (Aravena): CSIA of 1,4-D in samples from degradation reactions
- AFCEC FA8903-13-C0002 (Chu): Field Demonstration at Former McClellan AFB
- Dr. Andrea Leeson and Cara Patton at SERDP
- Dr. Hunter Anderson at AFCEC
- In-kind support from ECT2 (Nickelsen and Schmitz)

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Thank you!

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