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) biodegradation 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 well defined
  3. Range in isotopic composition of 1,4-D sources is not well described
  4. Interpretation of CSIA at a variety of field sites lacking

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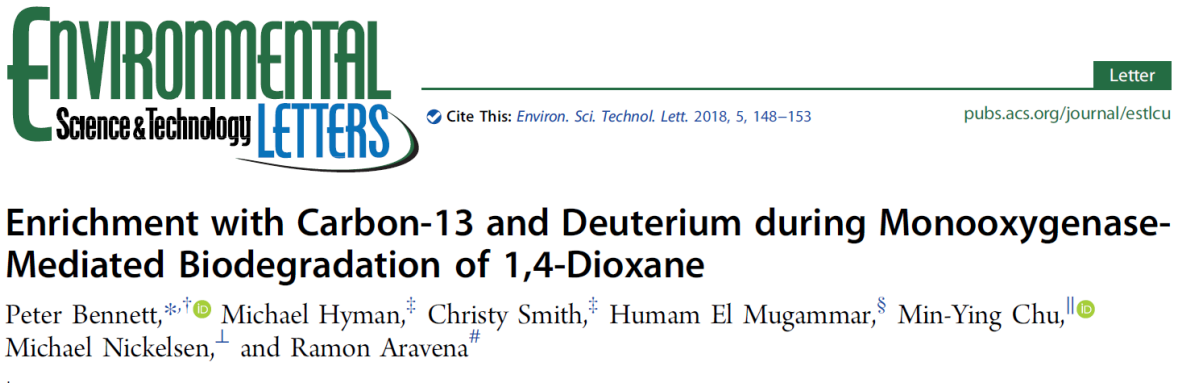
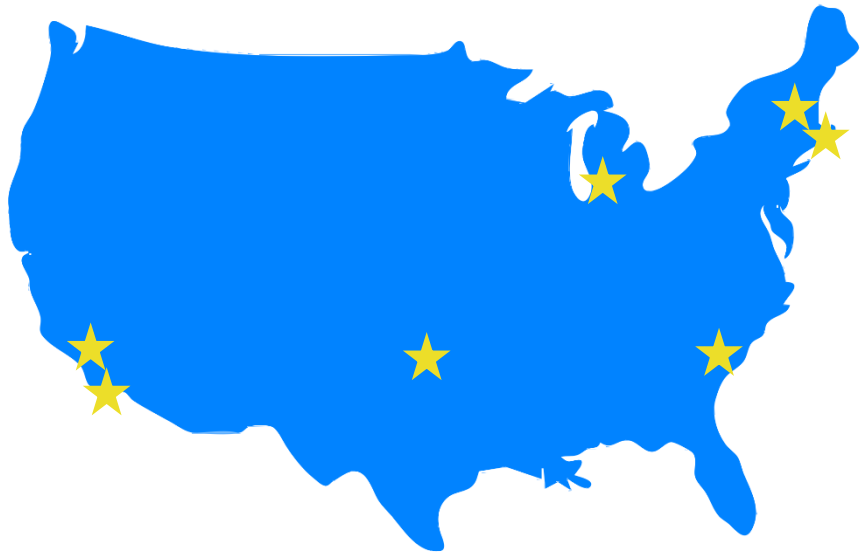
Phase I

- Phase I focus:
  1. Development of analytical method to perform CSIA on 1,4-D down to ~1-10 µg/L
  2. Determination of enrichment factors (ε) of 1,4-D for different microbial cultures



Phase II

- Phase II focuses on further development:
  1. Expand the database of isotopic composition of 1,4-D sources
  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

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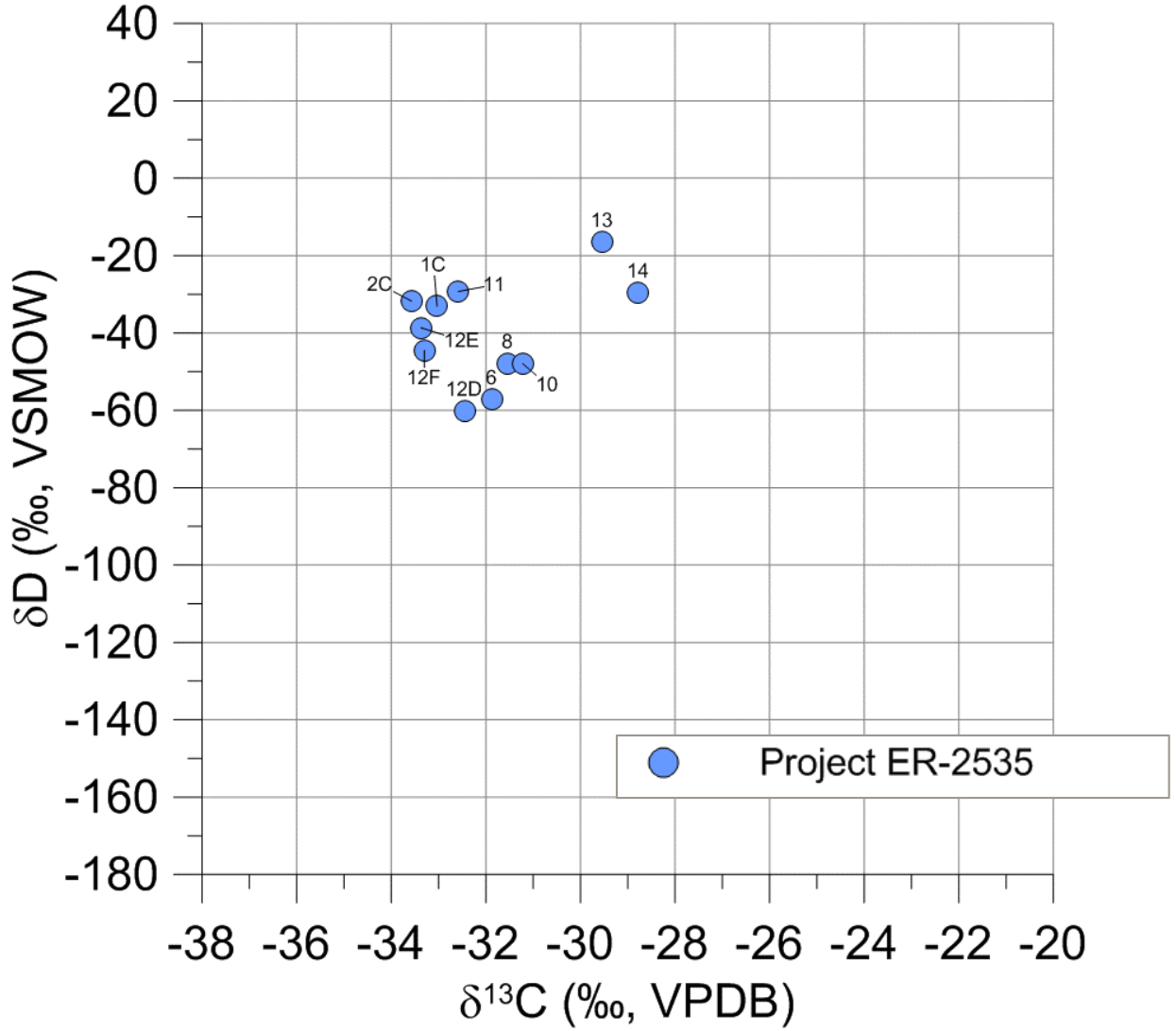
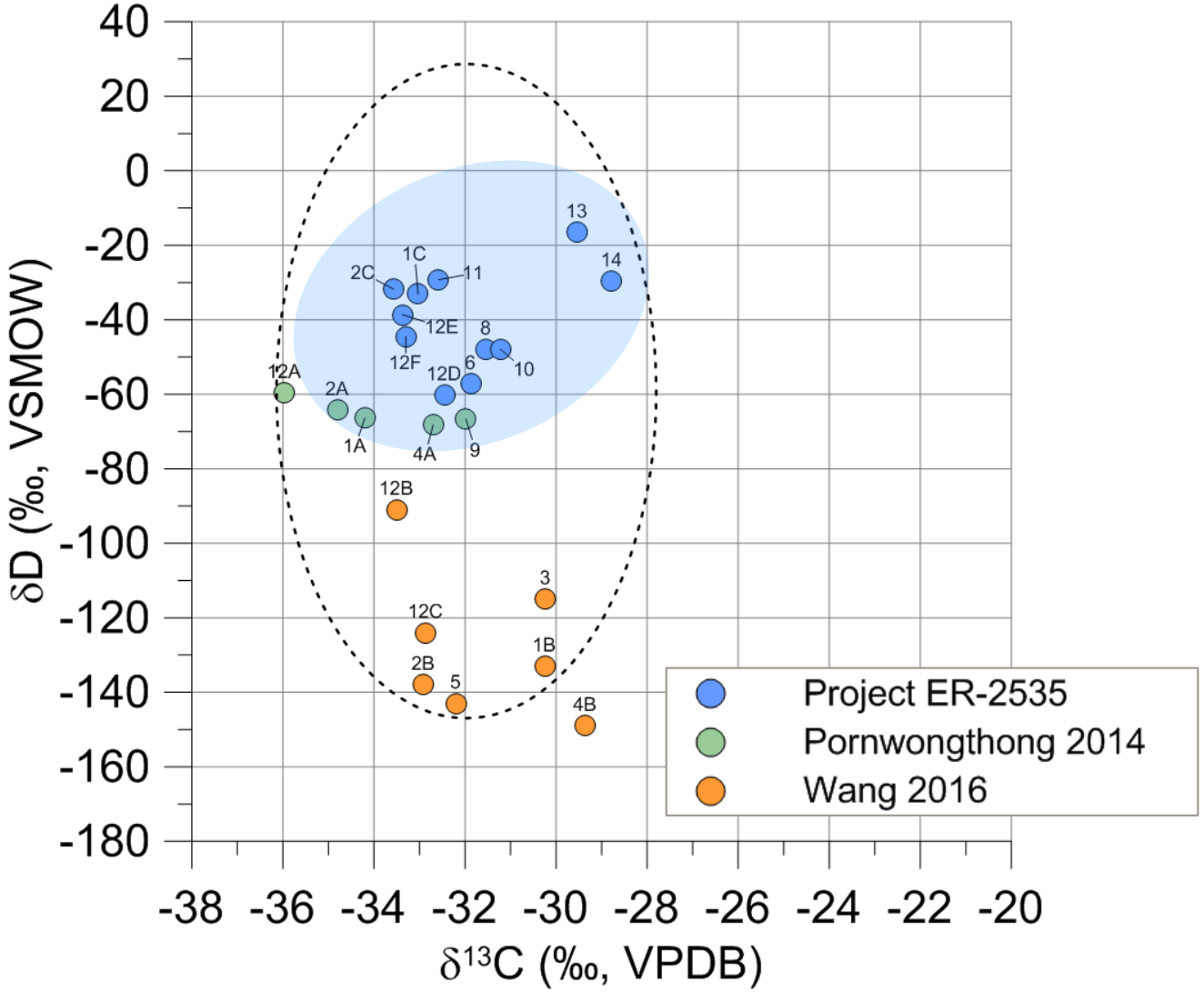
Source isotopic composition



No.	Manufacturer	δ13C ‰	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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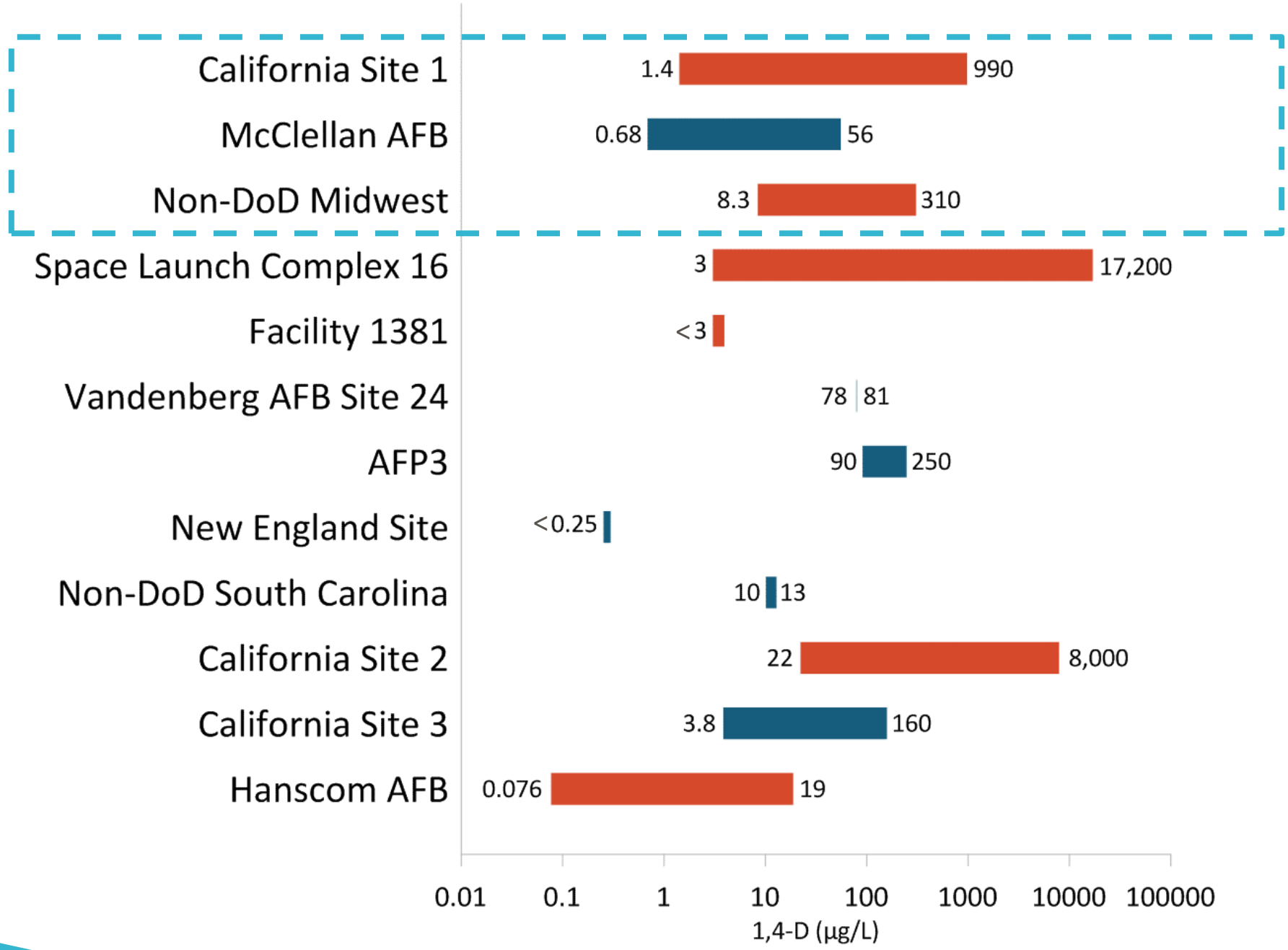
Pornwongthong, P., 2014. Stable isotopic and molecular biological tools to validate bio-degradation of 1,4-dioxane, Ph.D. thesis, UCLA.

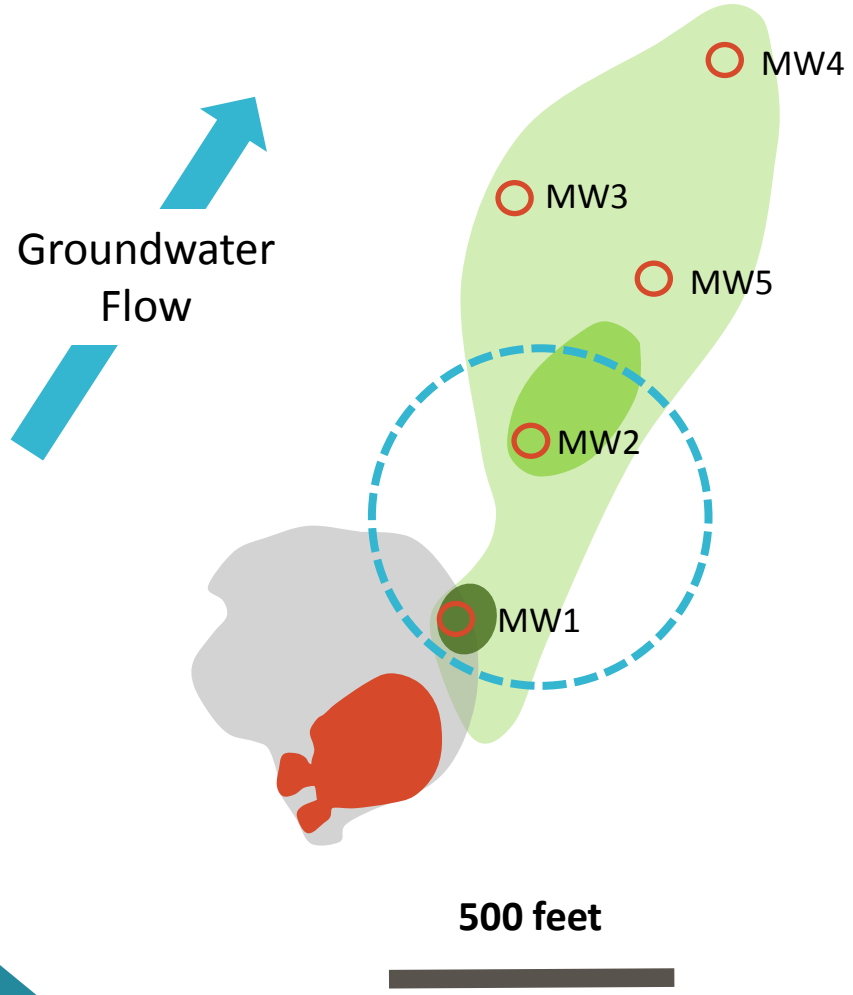
Wang, Y., 2016. Breakthrough in 2D-CSIA technology for 1,4-dioxane, Remediation, p.61-70.

Case studies

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


California Site 1
1.4
990
McClellan AFB
0.68
56
Non-DoD Midwest
8.3
310
Space Launch Complex 16
3
17,200
Facility 1381
<3
Vandenberg AFB Site 24
78
81
AFP3
90
250
New England Site
<0.25
Non-DoD South Carolina
10
13
California Site 2
22
8,000
California Site 3
3.8
160
Hanscom AFB
0.076
19
0.01
0.1
1
10
100
1000
10000
100000
1,4-D (µg/L)
Anaerobic
Aerobic

California Site 1



1,4-D and 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

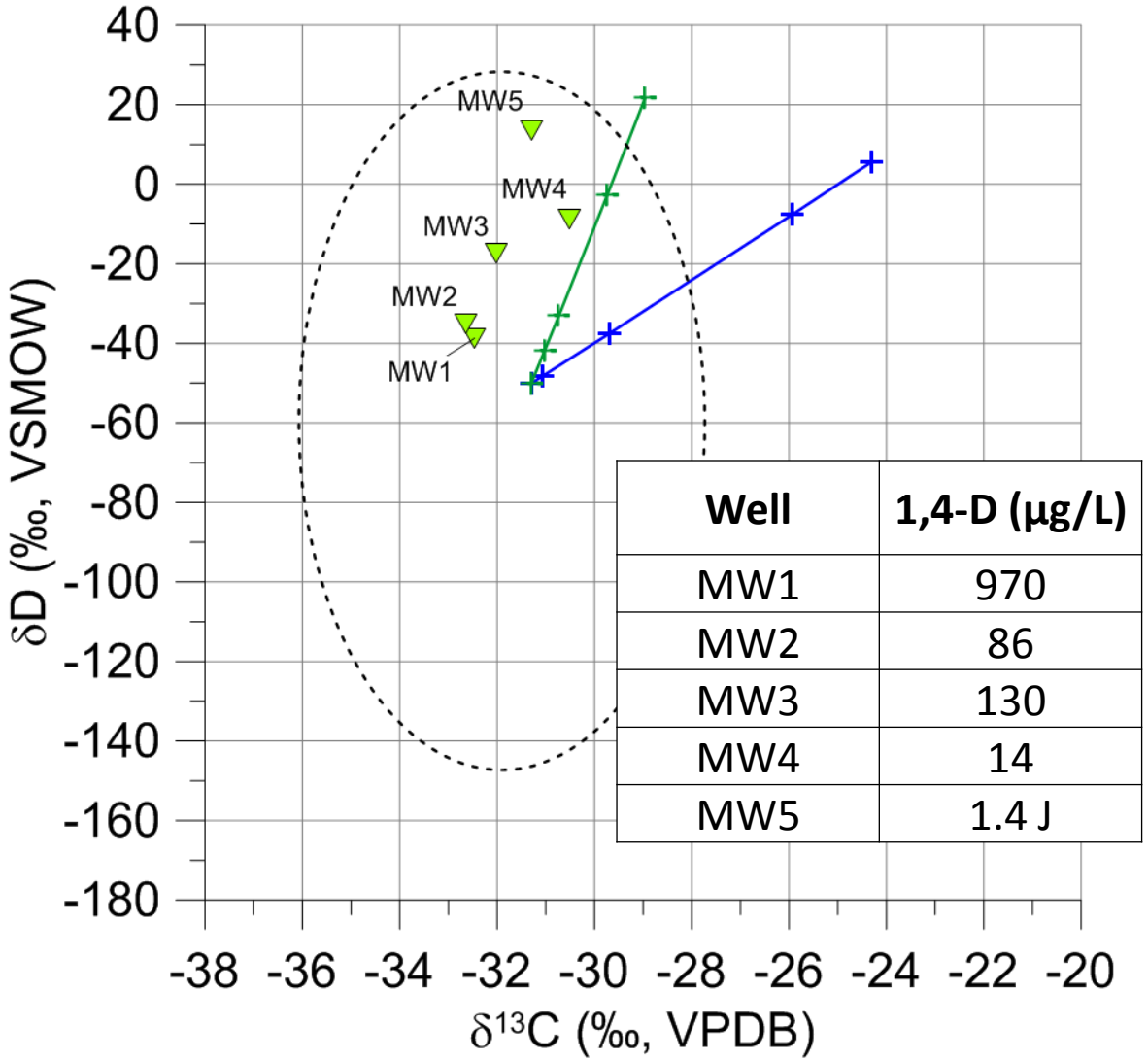
NAPL with TCE

NAPL w/o TCE

North

California Site 1

- Rayleigh degradation curves:
  - THF-grown culture
  - Propane-grown culture
- Fractionation not that great given concentration decrease
- Dual isotope trend indicates biodegradation

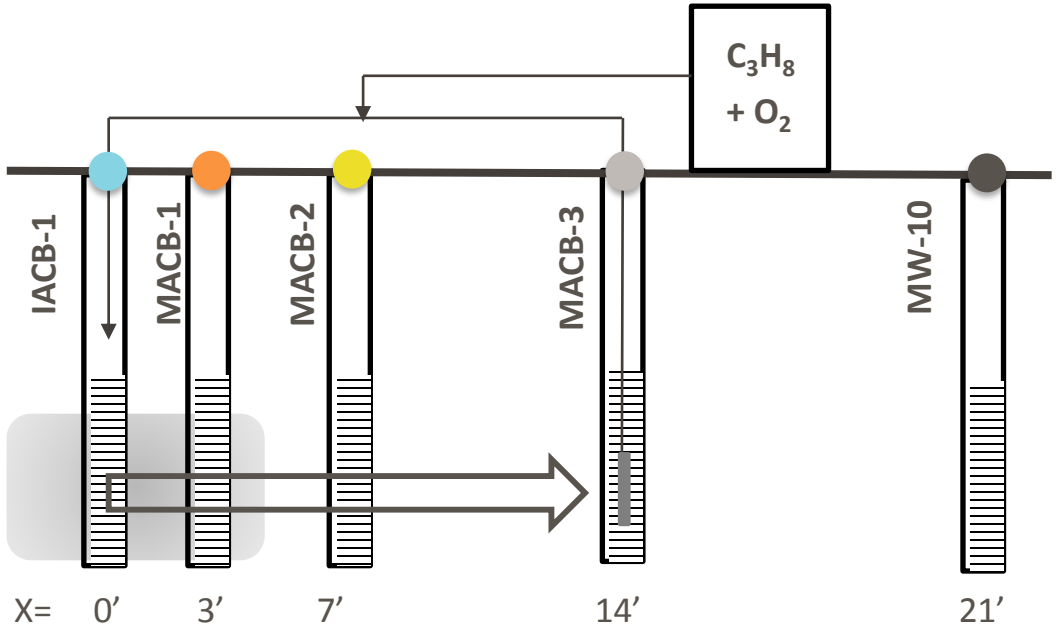


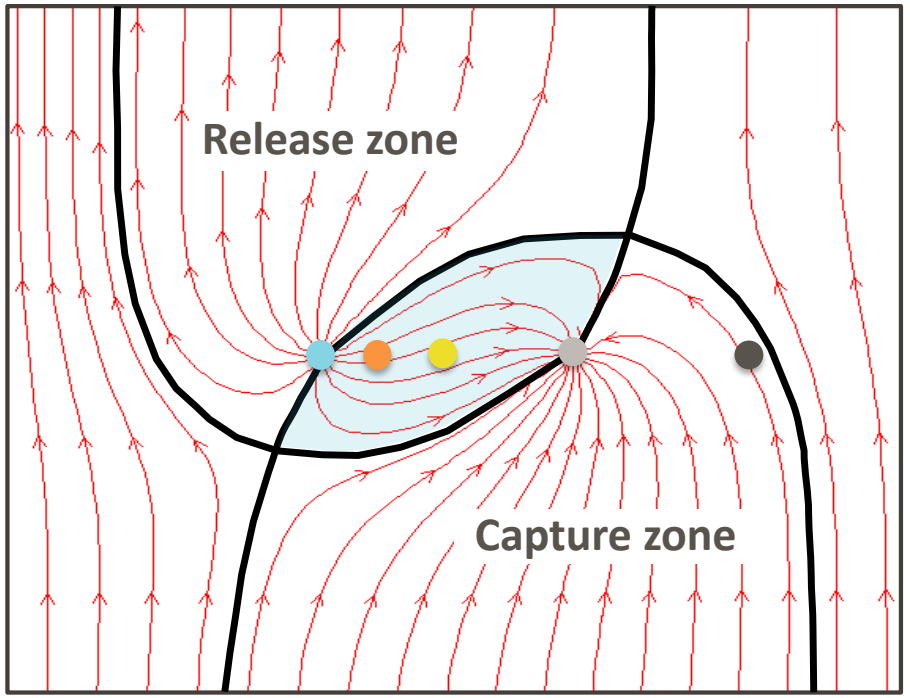
Well	1,4-D (µg/L)
MW1	970
MW2	86
MW3	130
MW4	14
MW5	1.4 J

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

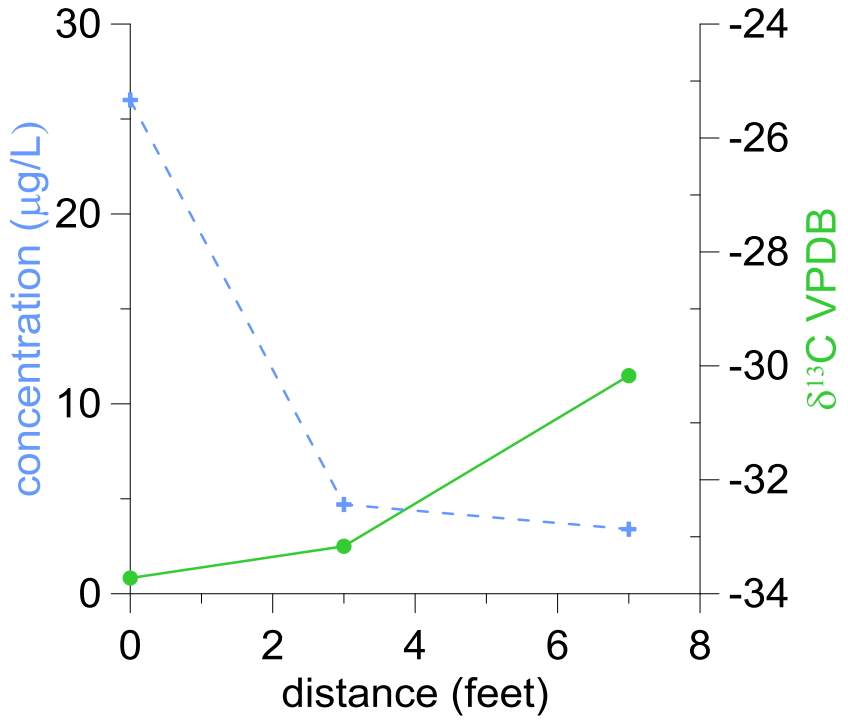
- Maintenance depot 1939-2001 with waste pits and trenches
- Recirculation with propane and oxygen created an in situ bioreactor
- Propane and oxygen injection began Oct 2015





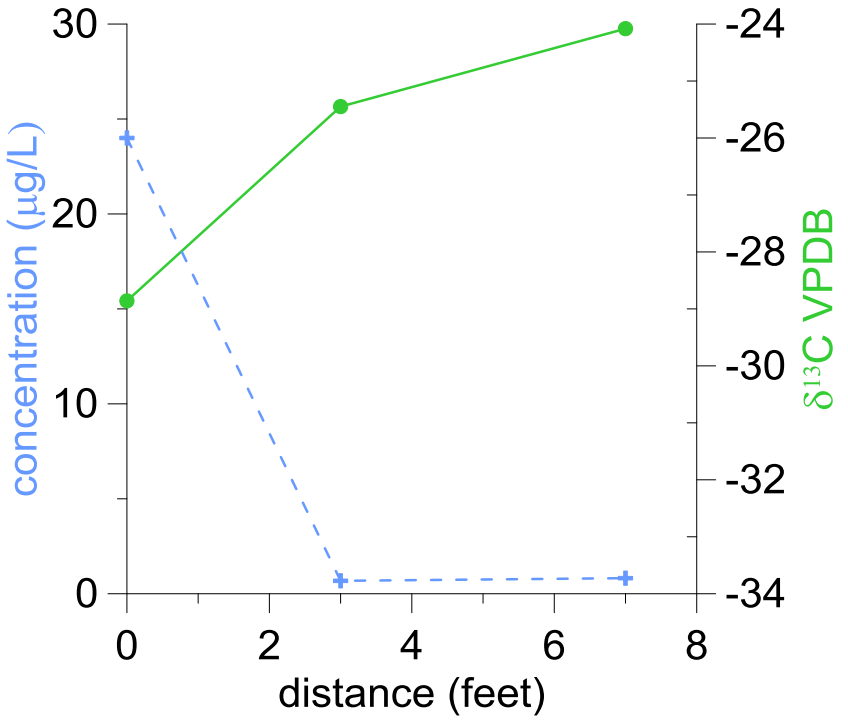
Enrichment in $\delta^{13}C$ in samples from treatment zone

December 2015



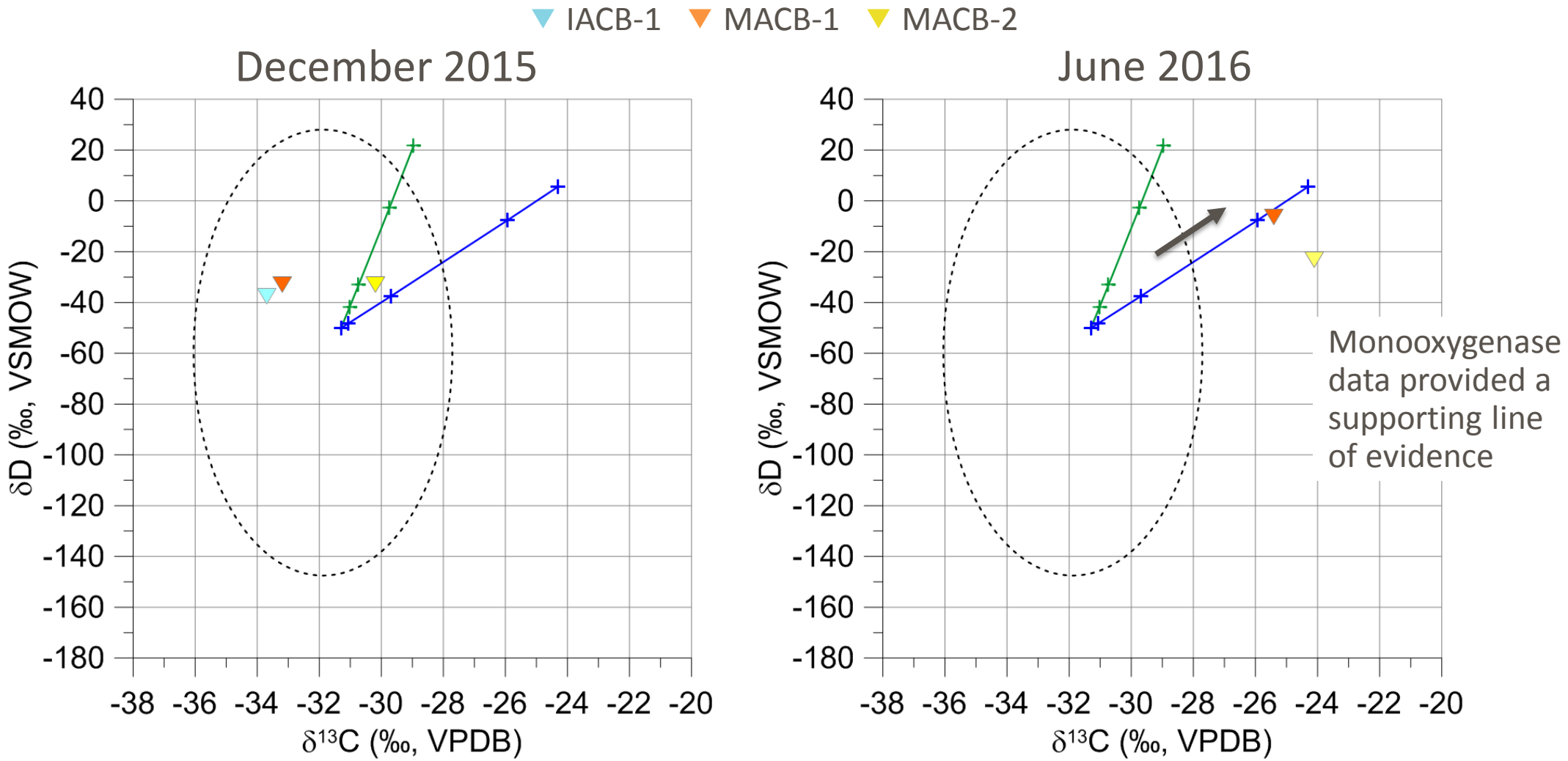
IACB-1 MACB-1 MACB-2

June 2016



IACB-1 MACB-1 MACB-2

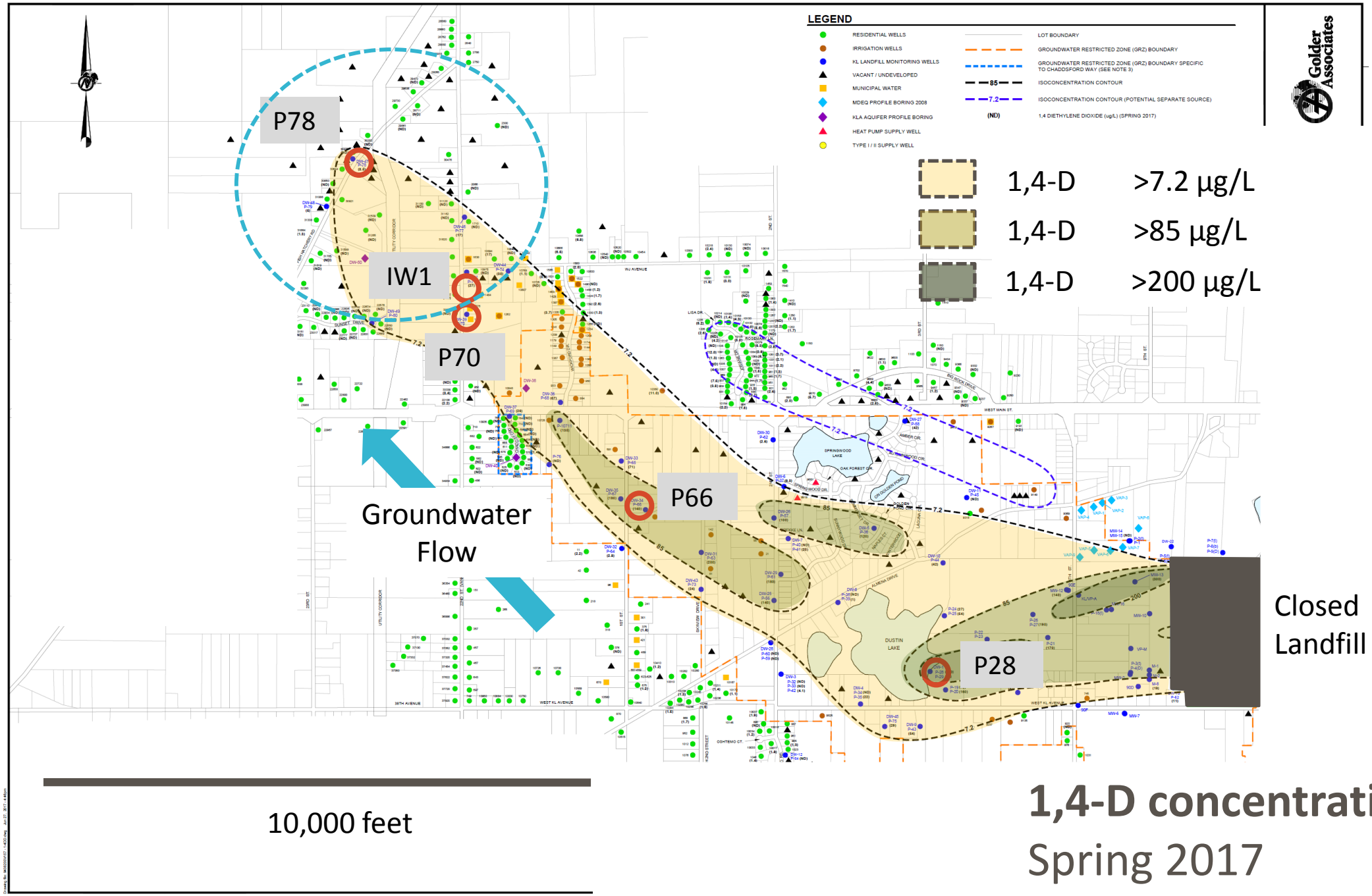
Dual isotope plots from treatment zone



Monooxygenase data provided a supporting line of evidence

Non-DoD Midwest site

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

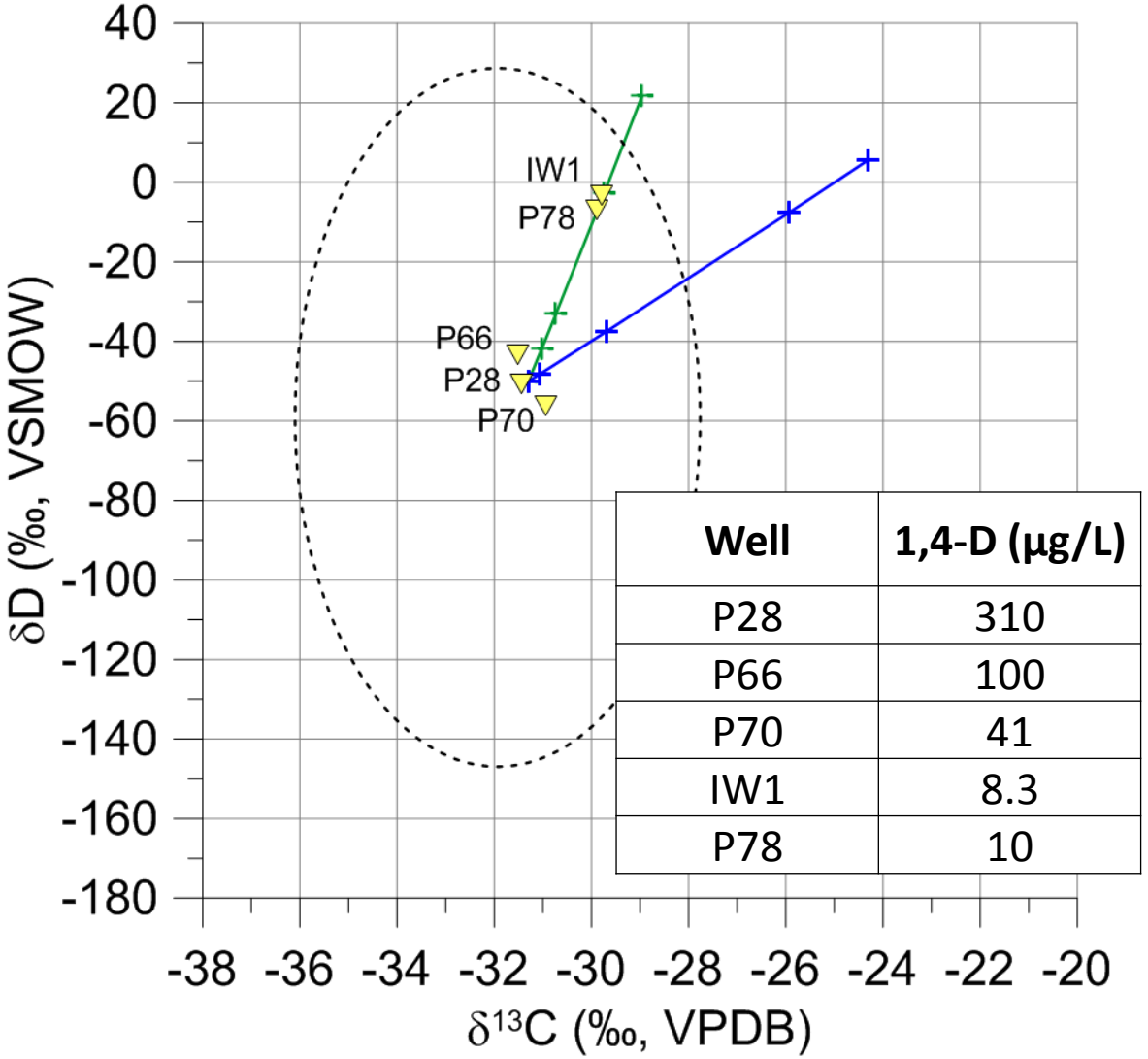


1,4-D concentrations

Spring 2017

Midwest site

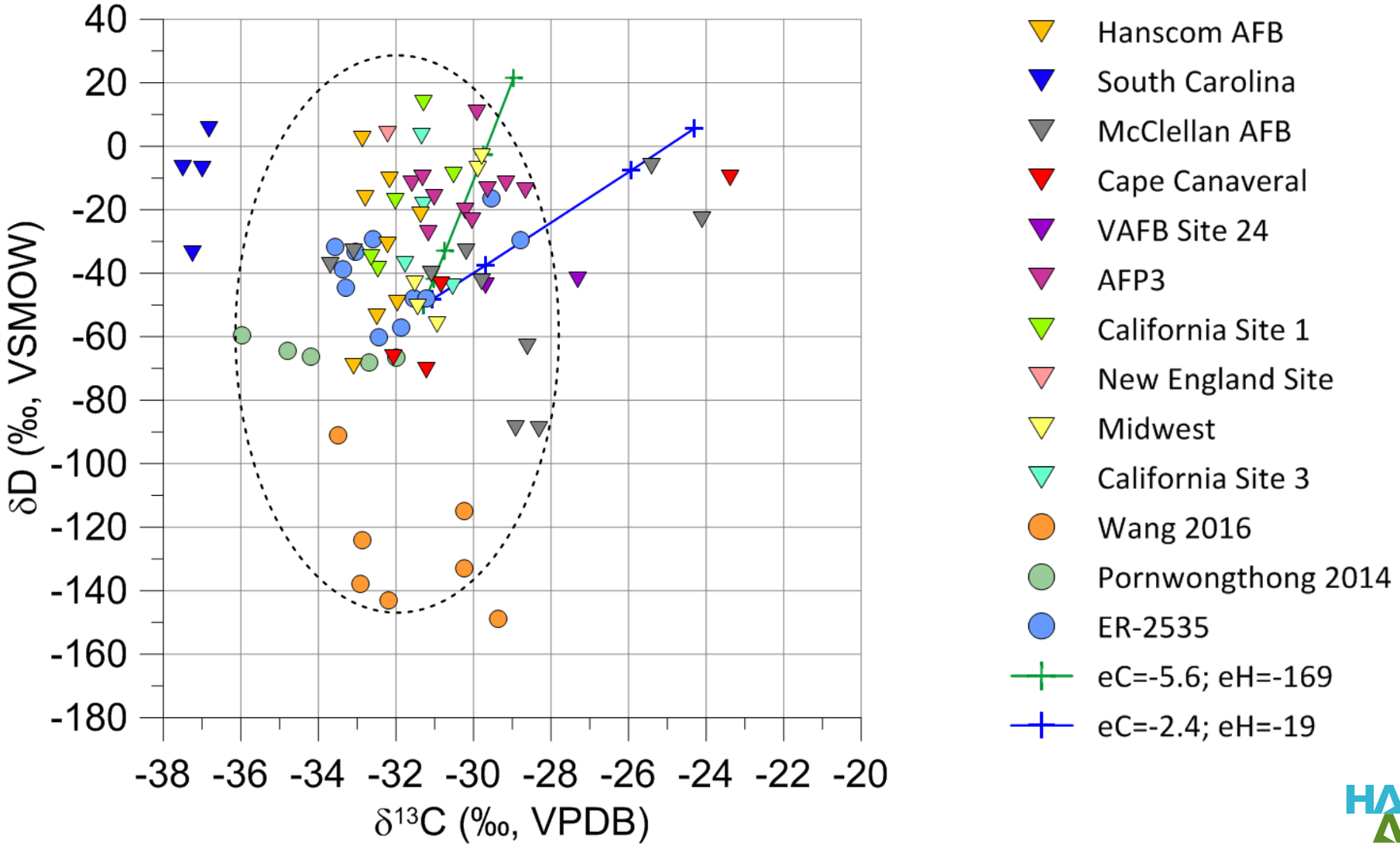
- Extensive fractionation at injection well IW1 and leading edge of plume P78
- Upgradient locations consistent with 1,4-D source
- THF-grown culture



Well	1,4-D (µg/L)
P28	310
P66	100
P70	41
IW1	8.3
P78	10

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

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 successful CSIA field implementation:
  - Demonstrate enrichment in both $\delta^{13}C$ and δD
  - Multiple samples needed to demonstrate degradation
  - Analyze samples at or near the source
- Natural attenuation assessments should be supported by multiple lines of evidence
  - Analysis of monooxygenase biomarkers is valuable supporting information

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What we need to learn:

- 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

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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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