IN-SITU BIOREMEDIATION OF 1,4-DIOXANE IN MIXED PLUME WITH METABOLIC BIOAUGMENTATION AND COMETABOLISM

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BATTELLE BIOSYMPOSIUM 2023

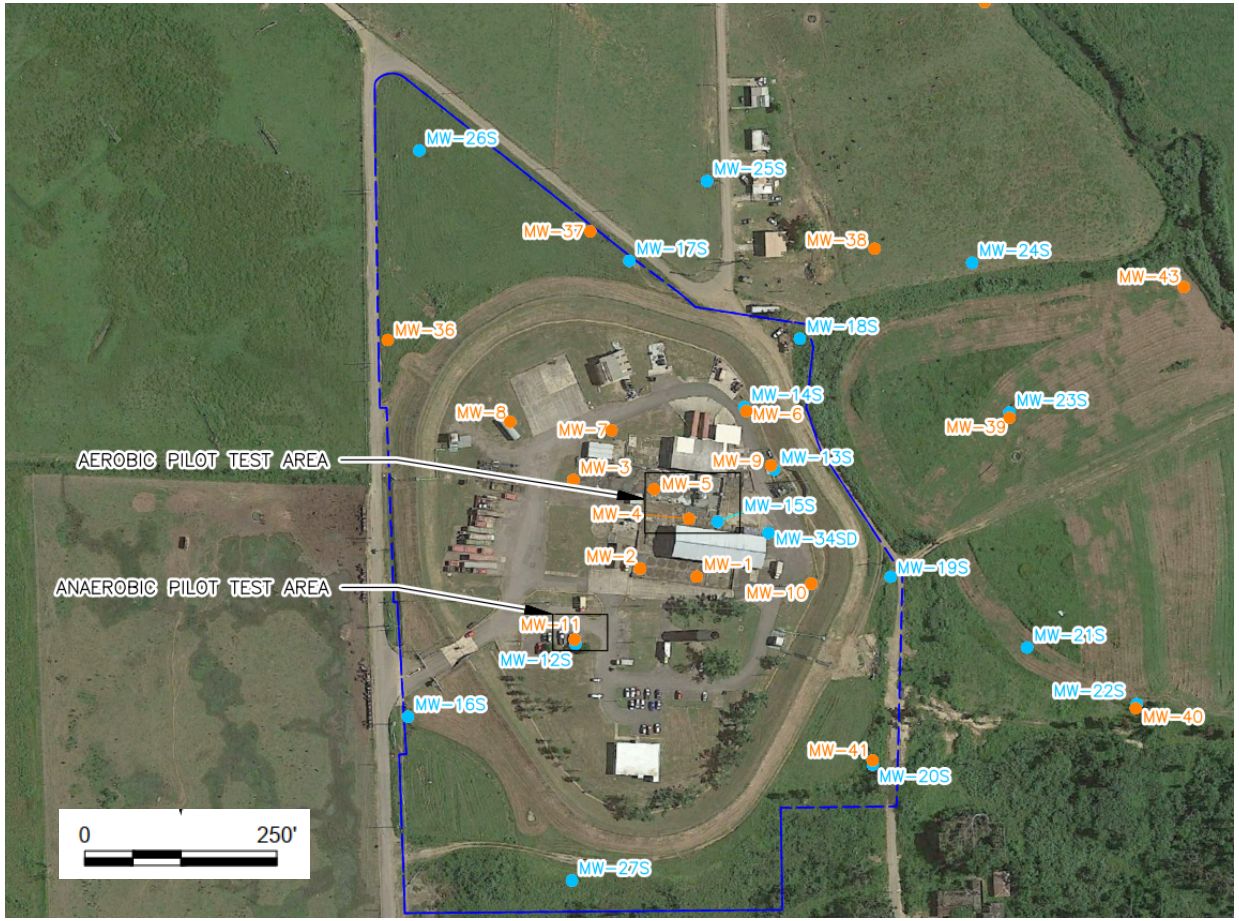
Trihydro

ACKNOWLEDGEMENT OF PROJECT TEAM

- Trihydro – Kyle McDonald, Mitch Olson, George Mathes, Kyle Power
- SiREM – Sandra Dworatzek, Phil Dennis, Ximena Druar, Jeff Roberts
- GeoEnviroTech – Rafael Diaz, Juan Negron
- Pace / PRS&T – Juan Redondo, Vincente Perez
- H2K Technologies – Mike Keilen

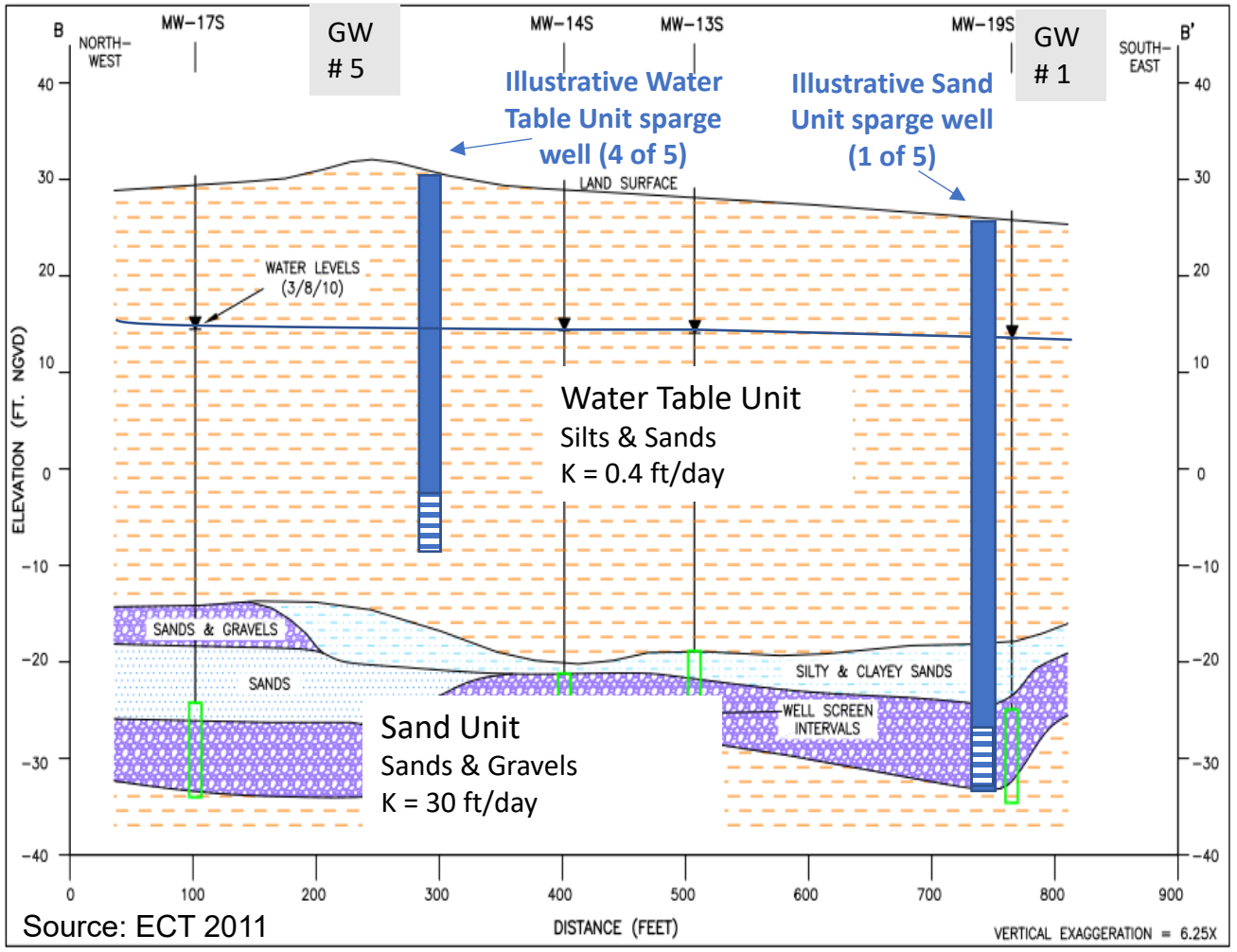
SITE BACKGROUND

- Northern Puerto Rico
- 1860s Sugar Mill
- 1970s Industrial
- 2008 Fire



SITE HYDROGEOLOGY

- Unconsolidated Alluvium
- Water Table Unit
  - 30 to 40 ft thickness
  - Silts & Sands
  - K = 0.4 ft/day
- Sand Unit
  - 5 to 15 ft thickness
  - Sand & Gravels
  - K = 30 ft/day

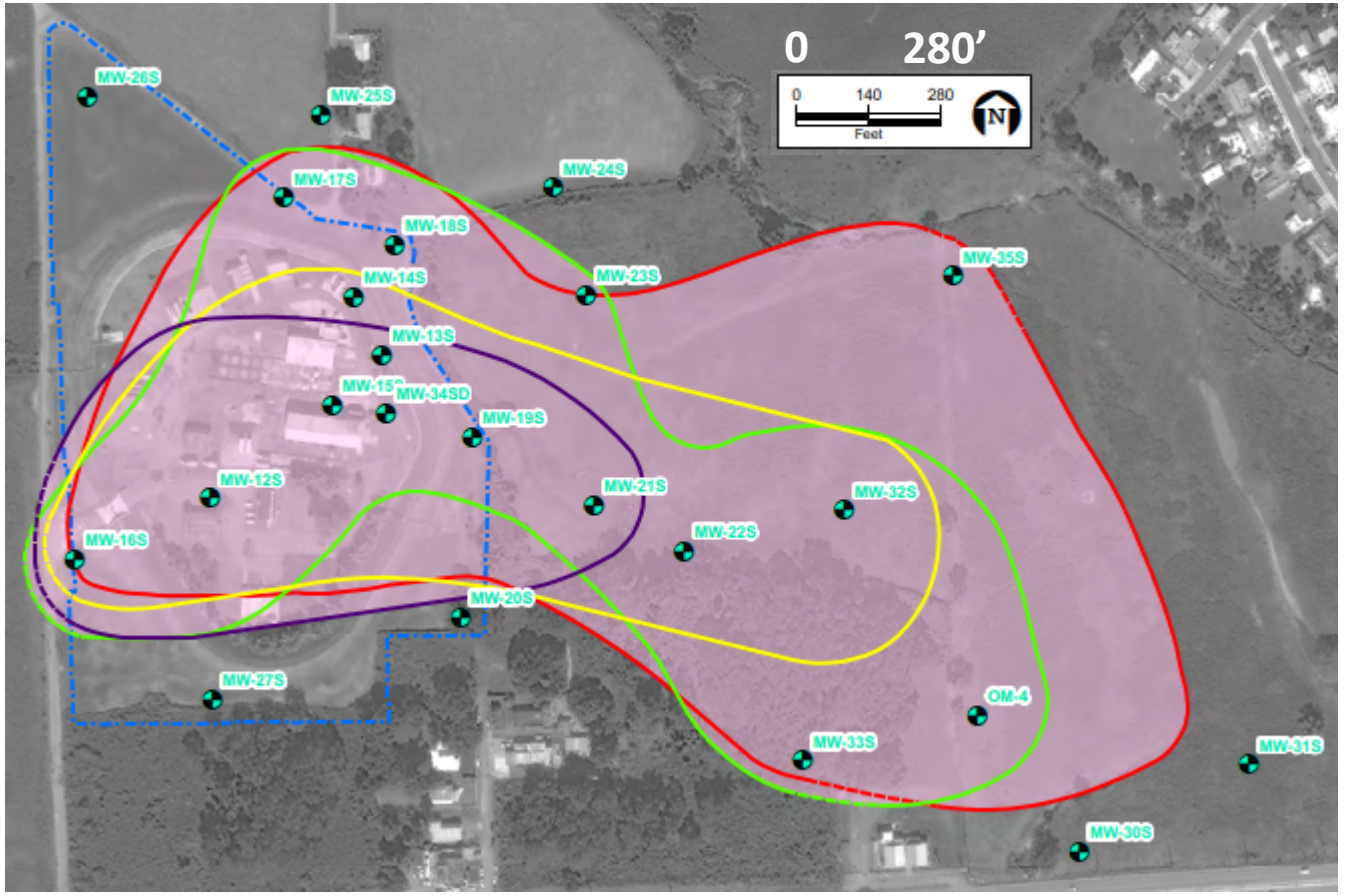


Source: ECT 2011

VOC AND 1,4-DIOXANE MAPS

Water Table (shallow)

Sand Unit (deeper)



Benzene Ethylbenzene Vinyl Chloride 1,2-DCA 1,4-Dioxane

BASELINE ANALYTICAL DATA

- Reducing conditions
  - Elevated iron
  - Reduced sulfate
  - Methane production
  - Anthropogenic carbon source

	Upgradient (Sand Unit) MW-26S	Source Area (Water Table Unit) MW-4	Source Area (Sand Unit) MW-15S
1,4-Dioxane	4	542	283
Benzene	ND	383	150
Toluene	ND	632	12
Ethylbenzene	ND	2,780	8
Xylenes, Total	ND	21,900	7
Trichloroethene	ND	ND	ND
cis-1,2-Dichloroethene	ND	16	0
Vinyl Chloride	ND	18	1
1,2-DCA	ND	ND	1.5
1,1-DCE	ND	ND	0.7
Carbon Tetrachloride	ND	ND	ND
Chloroform	ND	303	ND
Methylene Chloride	ND	ND	ND
Iron, Dissolved (mg/L)	ND	27	5.6
Sulfate (mg/L)	12.9	ND	ND
Methane (mg/L)	ND	2.2	2.1
Total Org. Carbon (mg/L)	1.2	98	14

units ug/L except as noted

BASELINE ANALYTICAL DATA

- TEX and chlorinated compounds attenuated under ambient conditions
- 1,4-dioxane and benzene partially attenuated

	Source Area (Water Table Unit) MW-4	Source Area (Sand Unit) MW-15S
1,4-Dioxane	542	283
Benzene	383	150
Toluene	632	12
Ethylbenzene	2,780	8
Xylenes, Total	21,900	7
Trichloroethene	ND	ND
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1,1-DCE	ND	0.7
Carbon Tetrachloride	ND	ND
Chloroform	303	ND
Methylene Chloride	ND	ND
Iron, Dissolved (mg/L)	27	5.6
Sulfate (mg/L)	ND	ND
Methane (mg/L)	2.2	2.1
Total Org. Carbon (mg/L)	98	14

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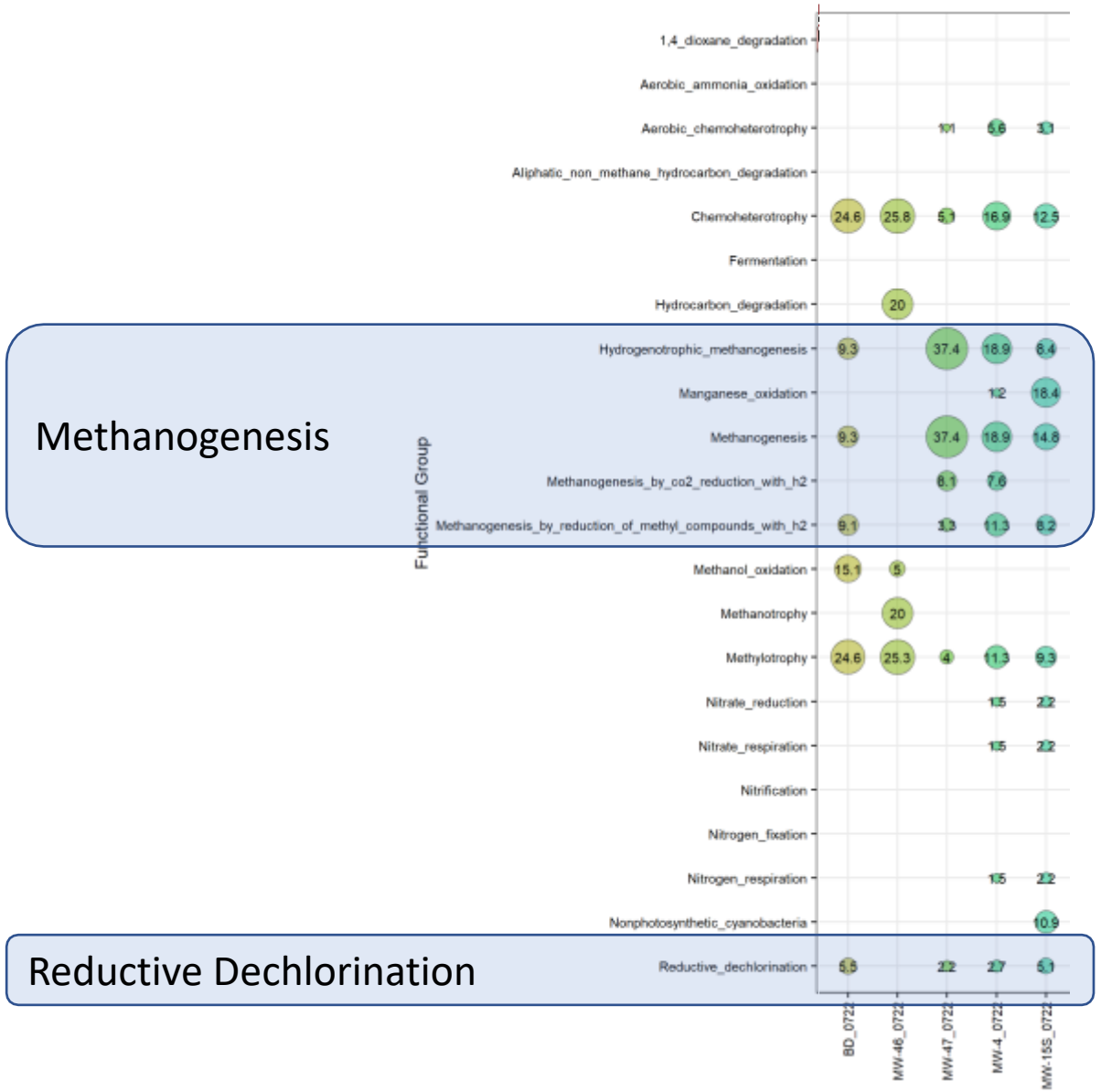
BASELINE MICROBIAL DATA

- Chlorinated solvent biomarkers at high concentrations (e.g., *DHC, DHG, DHB, DSB*)
- 1,4-Dioxane biomarkers not detected (ALDH, DXMO)
- Propane monooxygenase (PMO) detected at low levels
- Groundwater 27°C

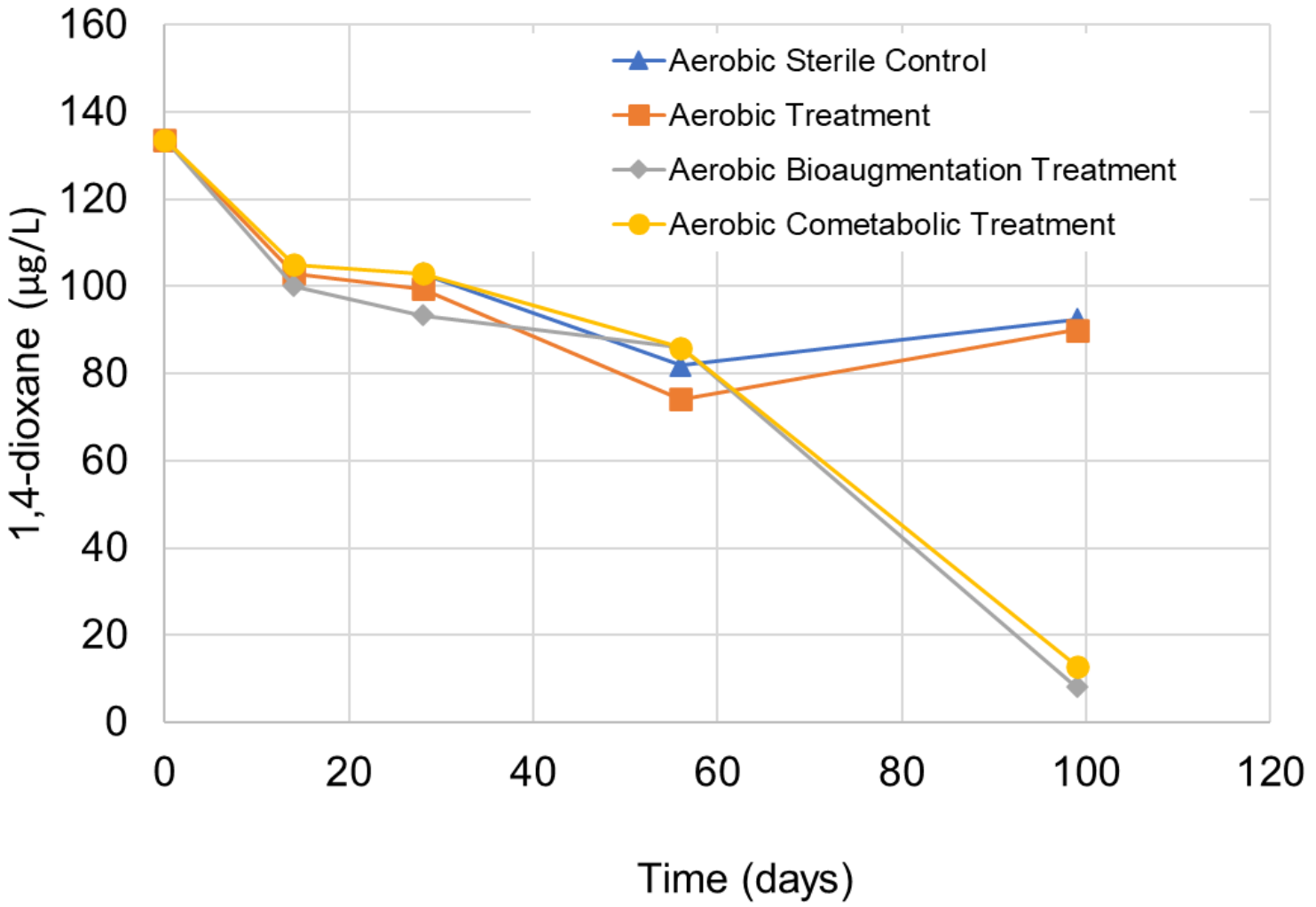


BENCH TESTING

- Performed by SiREM in Guelph
- 4 treatment sets
  - Sterile control
  - Aerobic (unamended)
  - Aerobic metabolism (DXO-88™)
  - Aerobic cometabolism (propane)
- Site soil and groundwater
- O2/propane/N2 ~weekly
- Monitored for 1,4-dioxane, DO, ORP, methane, propane

BENCH TESTING

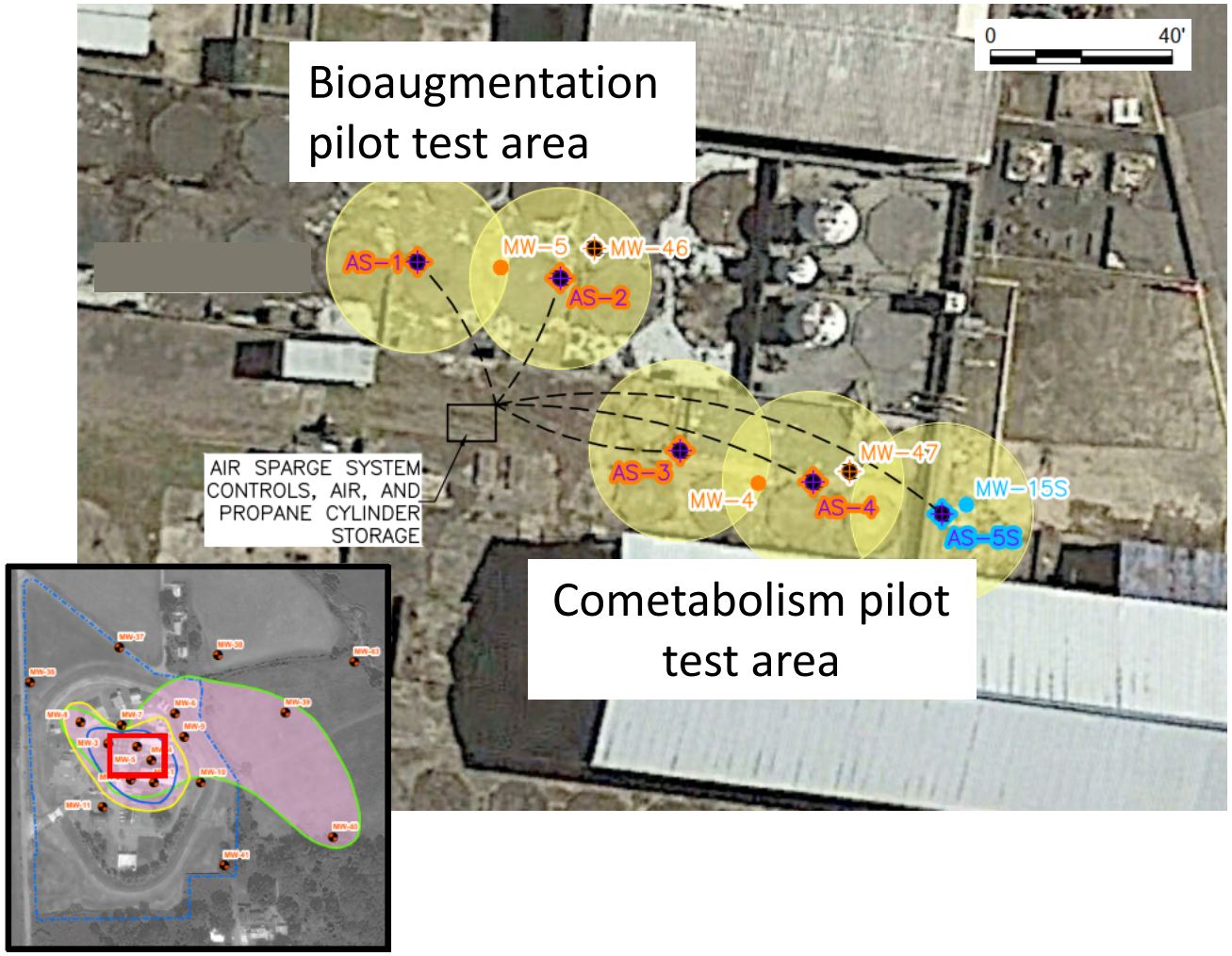
- 0-6 weeks: similar across the board
- 6-14 weeks: 90+% declines in DXO-88™ & propane treatments
- ORP, propane, methane data supported expected conditions
- Bioaug.: dxmB, ALDH, PMO peaked at 29 days
- Comet.: dxmB, PMO peaked at 100 days
- Conclusion: proceed to pilot with bioaug. and cometabolism



PILOT TEST - GOALS

- Evaluate/demonstrate treatment of 1,4-dioxane
- Assess effect on cVOCs
- Design parameters
  - ROI
  - Flow rates
  - Reagent dosing

PILOT TEST - IMPLEMENTATION



- Side-by-side aerobic treatment zones
- Common biosparge skid with telemetry
- Bioaugmentation with SiREM DXO-88™
- Cometabolism with propane

BIOSPARGE SYSTEM

- Flow: 3 to 7 scfm
- Pressure: 20 to 25 psi
- 30-minute pulses each well
- Remote monitoring/ control via telemetry

PROPANE ADDITION

- HD5 grade odorized propane
  - >90% propane, <5% propylene, <2.5% heavier hydrocarbon, and <0.0025% ethyl mercaptan (see Chu et. al 2018)
- 15% to 28% of LEL
- 0.4 lbs/well/day at comet. wells
- Pulsing to provide alternating conditions (growth vs. “hungry”)
- June to August 2022 only

DXO-88™ BIOAUGMENTATION

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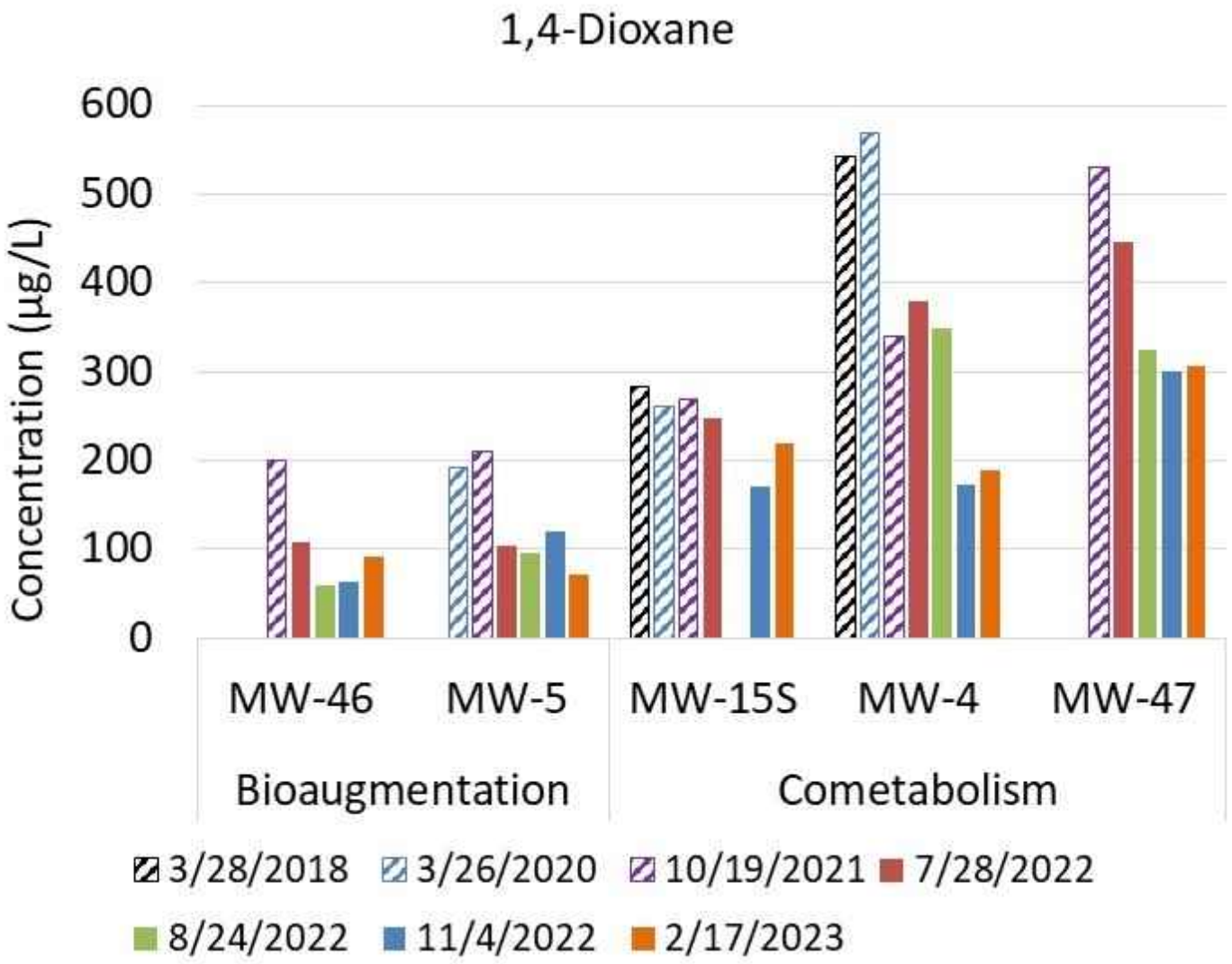
PERFORMANCE ASSESSMENT

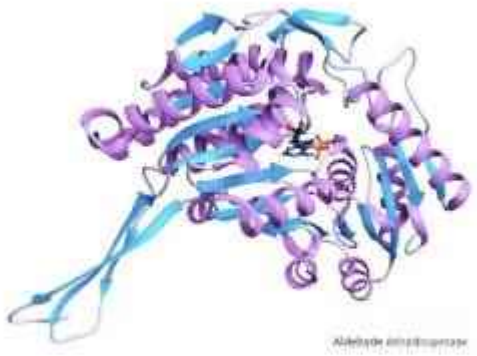
- 1,4-Dioxane
- Biomarkers
- CSIA
- VOCs

1,4-DIOXANE

- June 7, 2022 – Startup
- Aug 10, 2022 – Propane stopped
- Aug 19, 2022 – DXO-88™
- Sept 2022 – Offline for three weeks due to Fiona



BIOMARKERS qPCR



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	Date	dxmB gene (copies/L)	ALDH gene (copies/L)	PMO gene (copies/L)
MW-5	7/28/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-5	11/4/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-5	2/20/2023	U ($3x10^3$)	U ($3x10^3$)	U ($3x10^3$)
MW-46	7/28/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-46	11/4/2022	U ($3x10^3$)	U ($3x10^3$)	U ($3x10^3$)
MW-46	2/20/2023	U ($3x10^3$)	U ($3x10^3$)	U ($3x10^3$)
MW-4	7/28/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-4	11/4/2022	**$3X10^3$ J**	U ($5x10^3$)	**$7X10^4$**
MW-4	2/20/2023	U ($3x10^3$)	U ($3x10^3$)	**$1X10^4$**
MW-15S	7/28/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-15S	11/4/2022	U ($5x10^3$)	U ($5x10^3$)	**$5X10^4$**
MW-15S	2/20/2023	U ($3x10^3$)	U ($3x10^3$)	U ($3x10^3$)
MW-47	7/28/2022	U ($5x10^3$)	U ($5x10^3$)	U ($5x10^3$)
MW-47	11/4/2022	U ($3x10^3$)	U ($3x10^3$)	U ($2x10^3$)
MW-47	2/20/2023	U ($3x10^3$)	U ($3x10^3$)	**$1X10^4$**

BIOMARKERS NGS

- 1,000s of genetic sequences
- Species / genus names (not shown)
- **Functional groups >1%**

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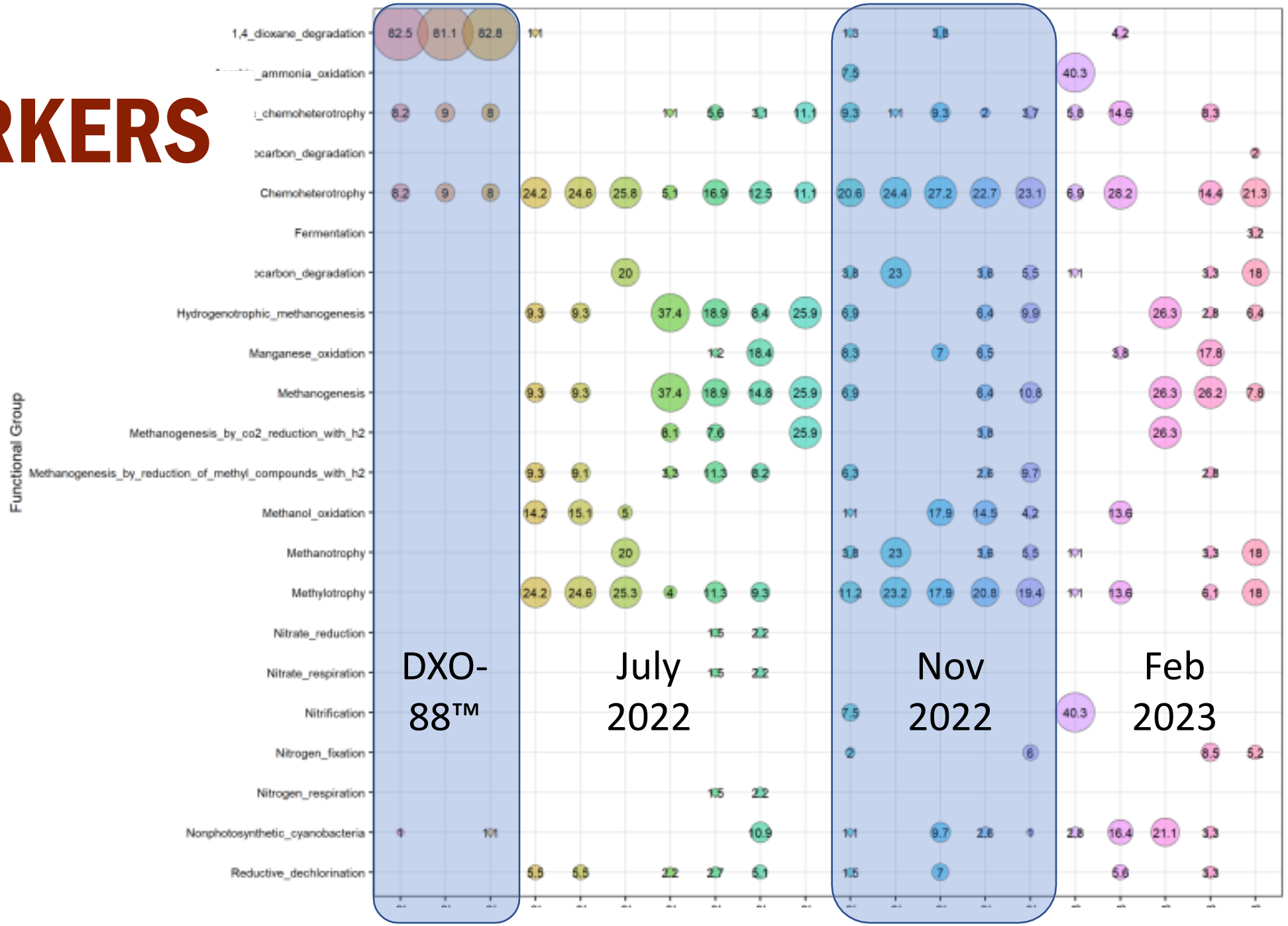
BIOMARKERS NGS

- Three time points
- DXO-88™ signature



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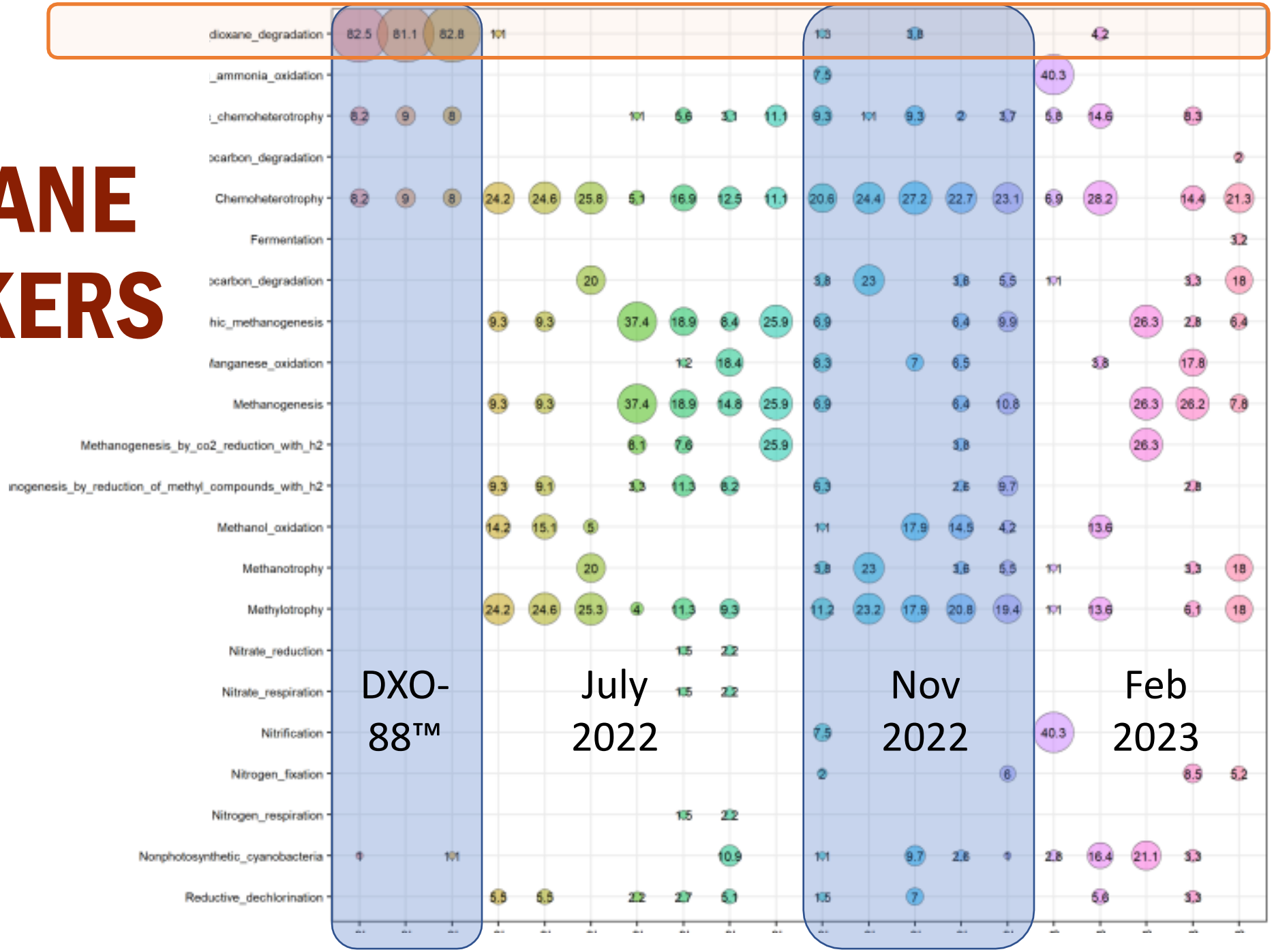
NGS 1,4-DIOXANE BIOMARKERS

- Very slight increase
- Baseline 1.1% in single sample
- 1.3% to 4.2%



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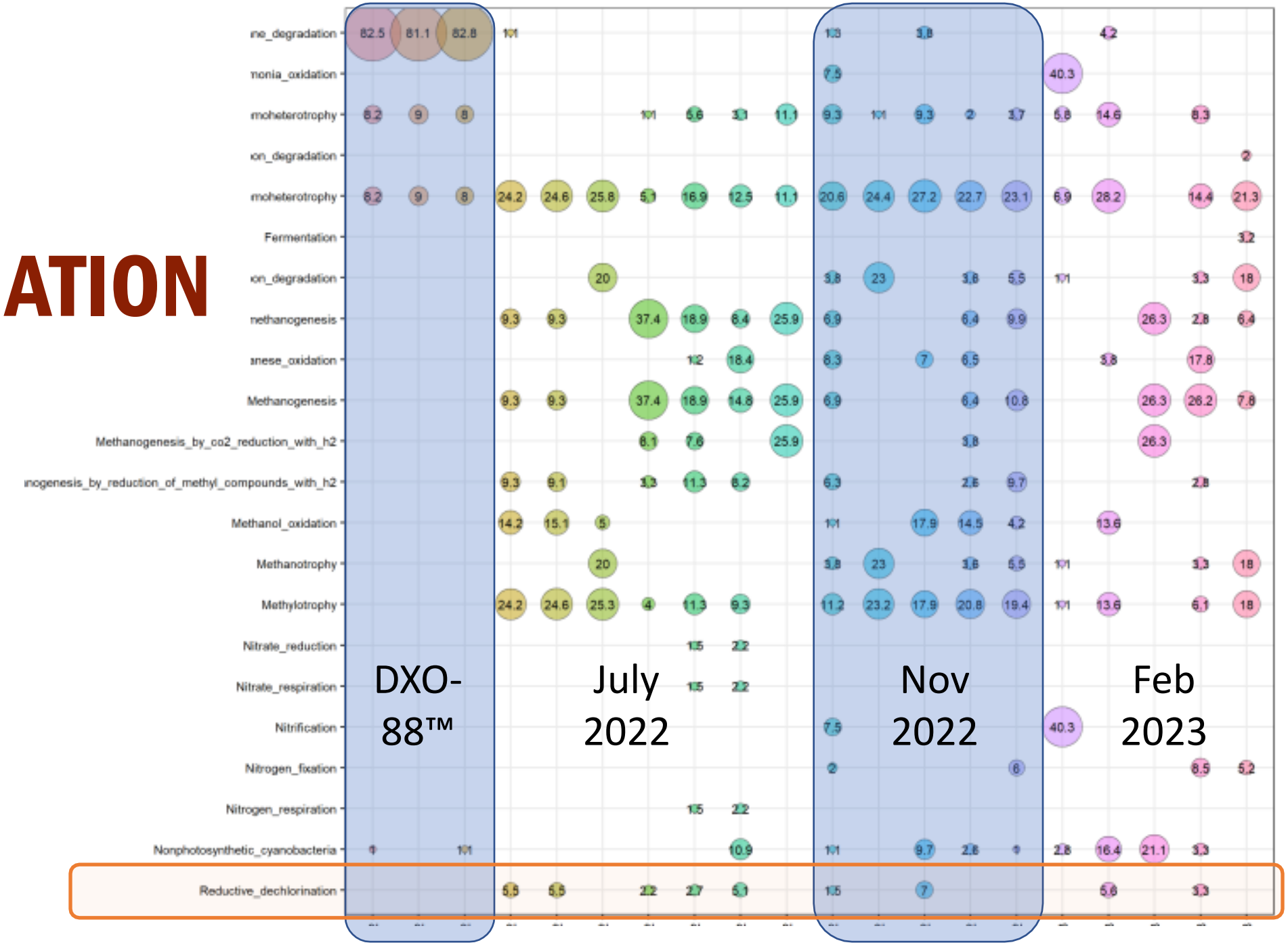
NGS REDUCTIVE DECHLORINATION

- Decreased abundance
- Still present



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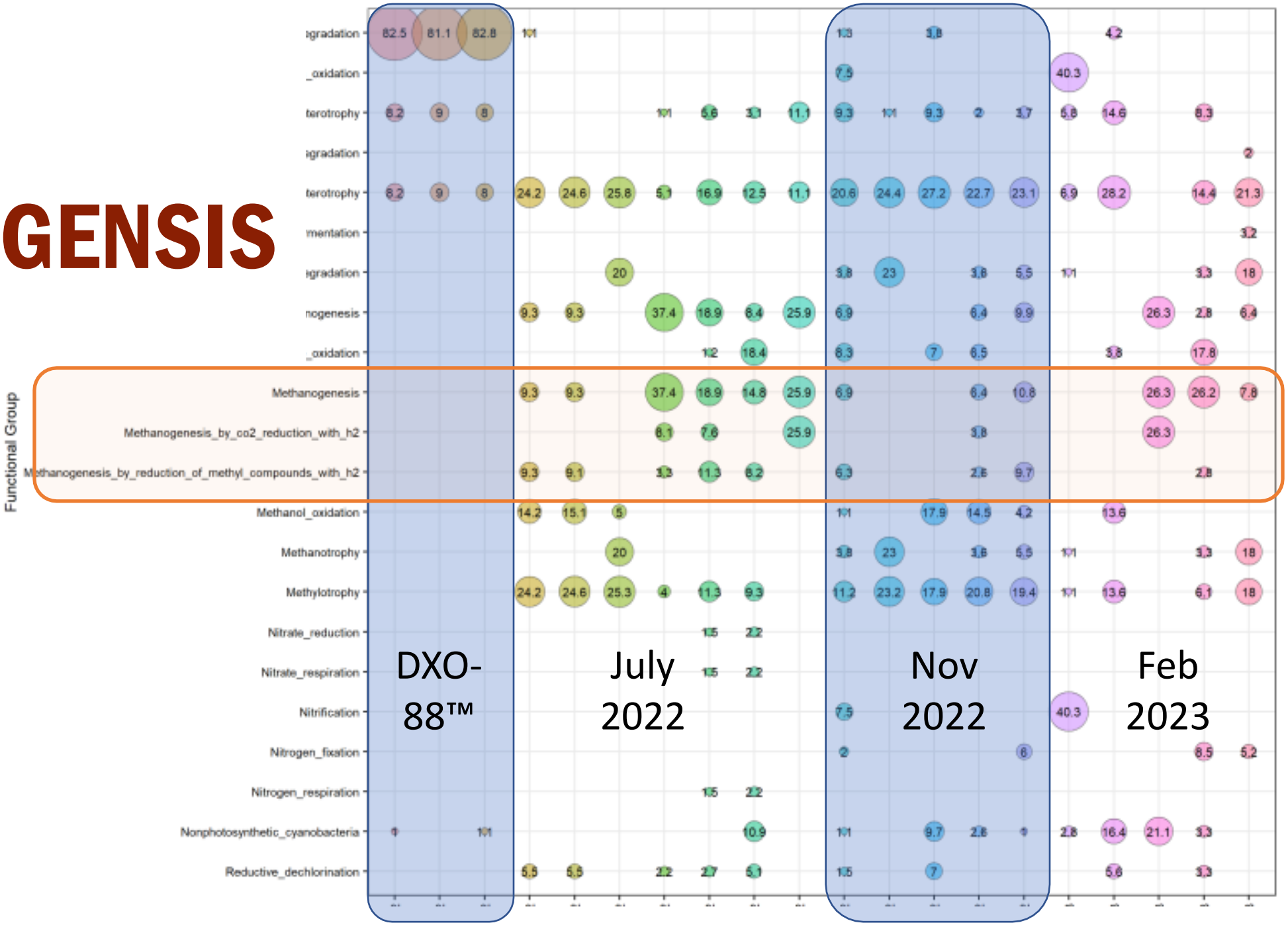
NGS METHANOGENSIS



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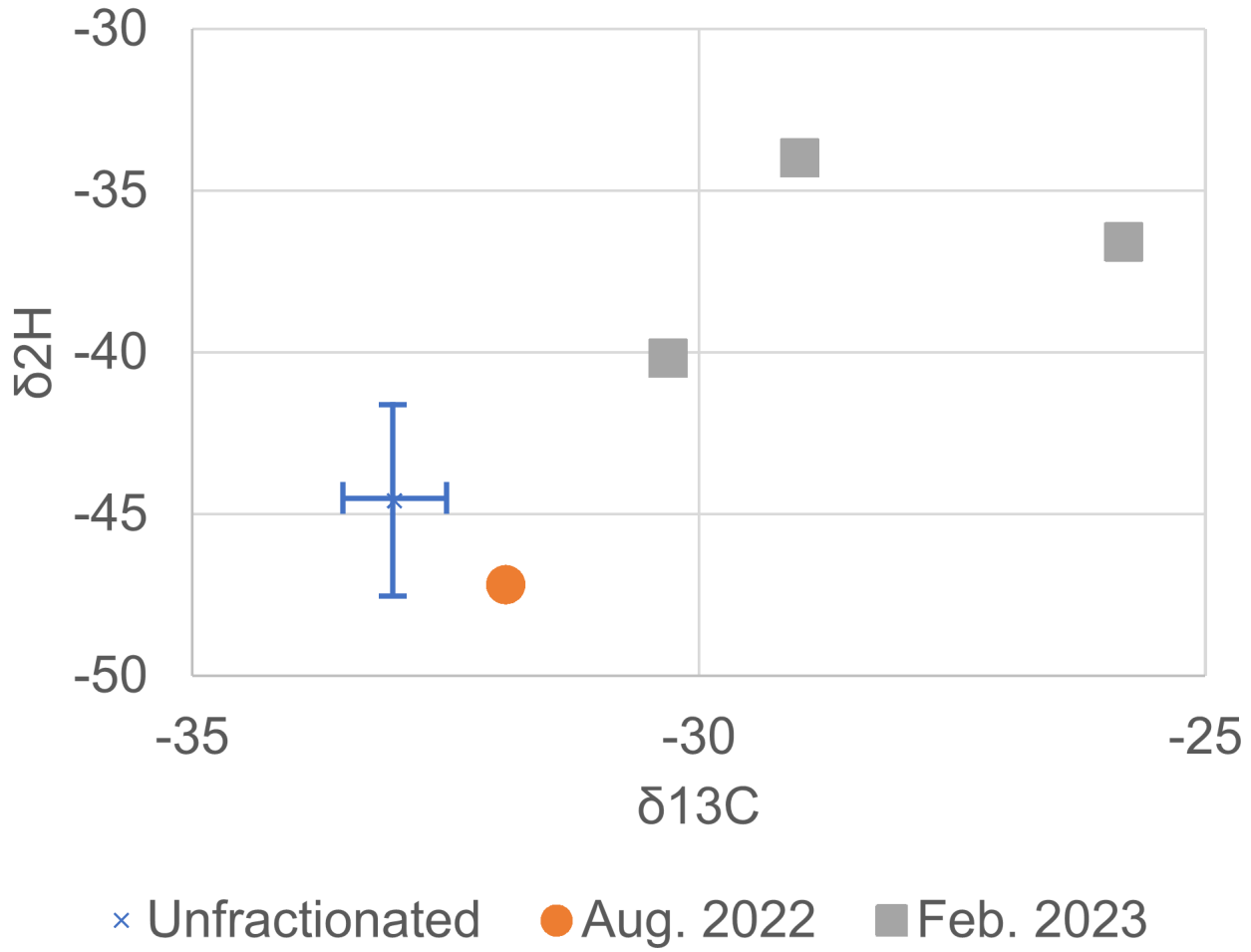
CSIA

- Hydrogen and carbon both show fractionation over time



Unfractionated range from Bennett *et al.* 2017 ER-2535

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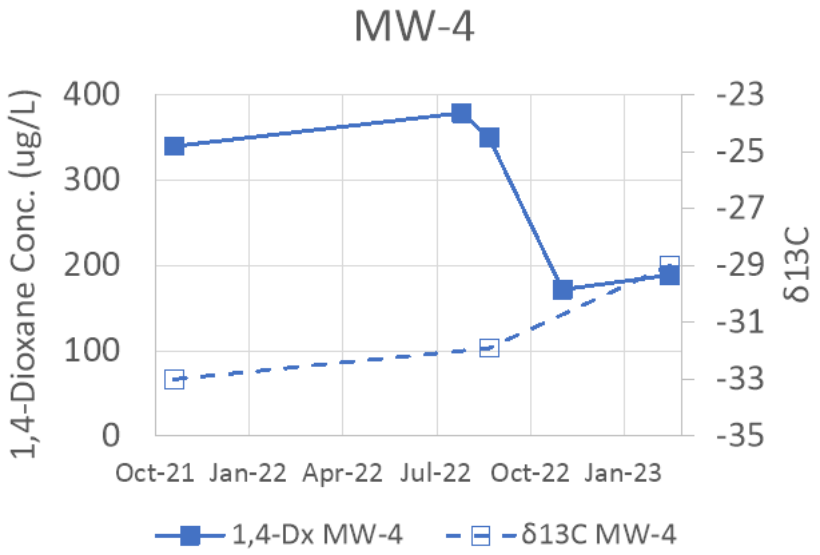
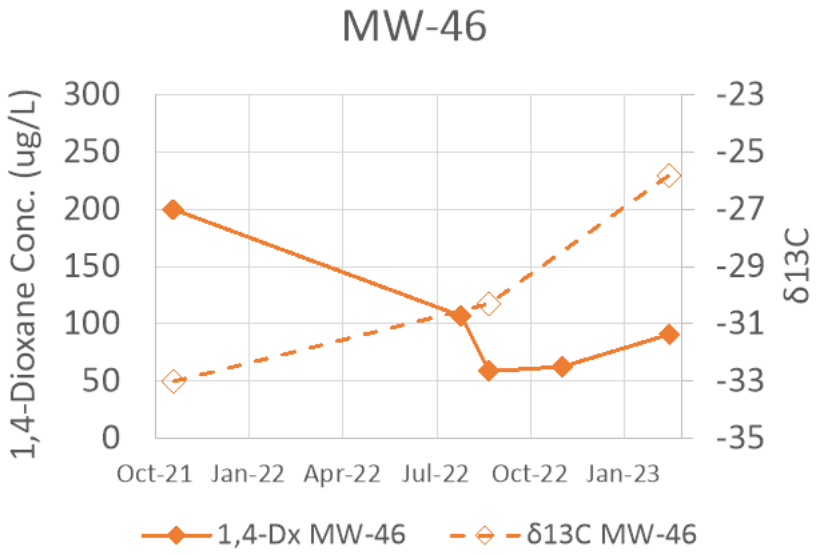
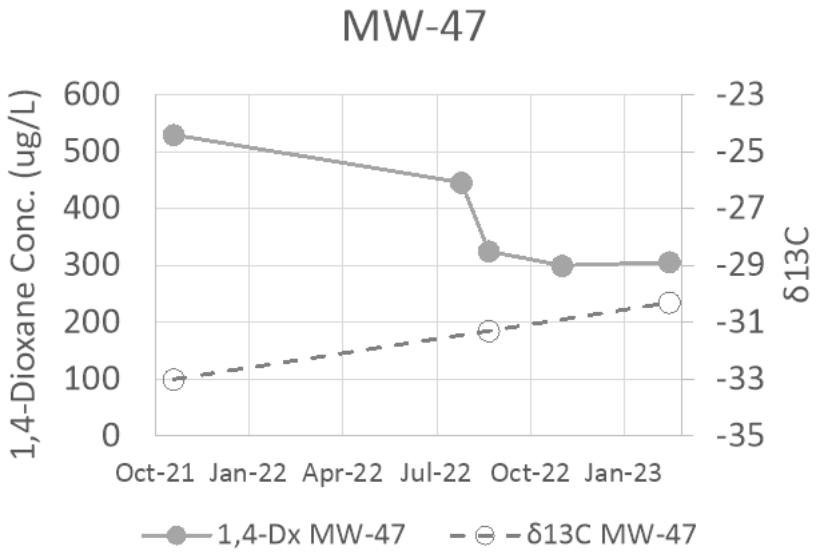
CSIA

- δ13C indicates degradation despite similar 1,4-dioxane concentrations







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Baseline values are literature estimates, not measured data
δ13C +/- 0.5$^{o}/_{oo}$ (Bennett *et al.* 2017 ER-2535)

CHLORINATED COMPOUNDS

- Concentrations of some chlorinated compounds have increased
- Changes due to perturbations in reductive dechlorination processes

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CONCLUSIONS

- 1,4-Dioxane concentrations reduced as result of pilot test
- Bioaugmentation culture successfully applied at field scale
- Difficult to discern bioaugmentation versus cometabolism
- Aerobic conditions have affected MNA processes

QUESTIONS / DISCUSSION

WHAT

WHY

WHERE

WHEN

WHO

HOW

Trihydro

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