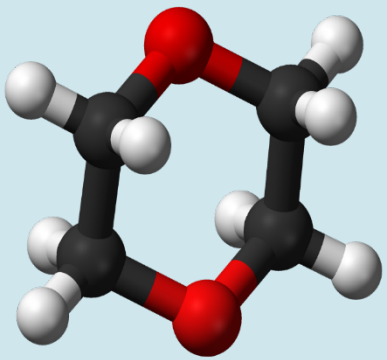

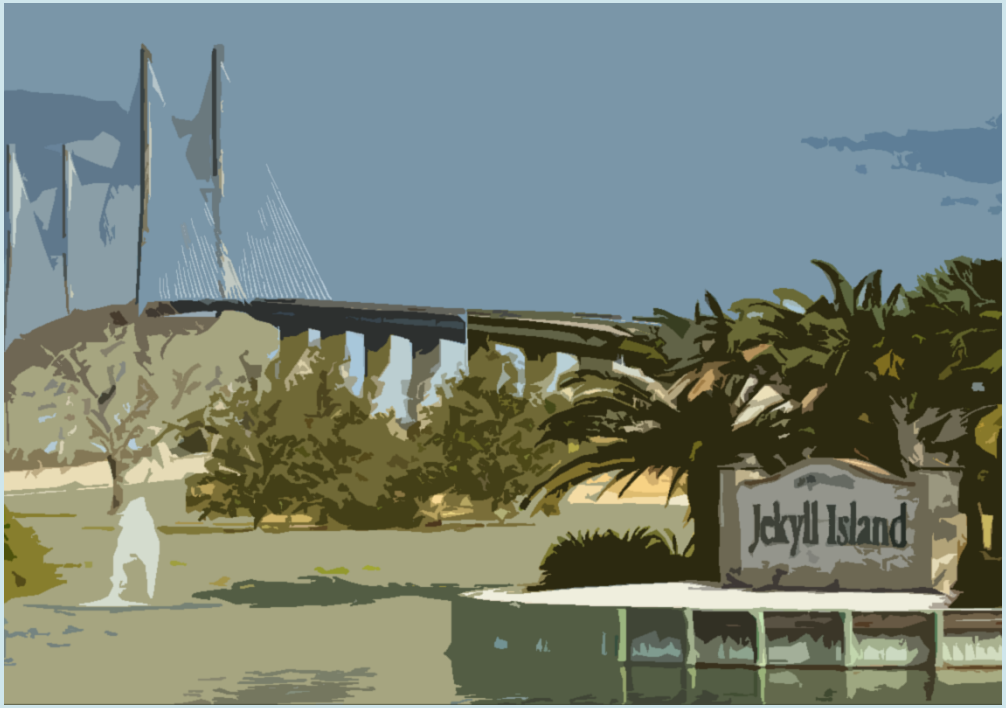

1,4-Dioxane: Multiple Lines of Evidence to Evaluate Intrinsic Biodegradation

11th Annual Georgia Environmental Conference

August 24-26, 2016, Jekyll Island, Georgia

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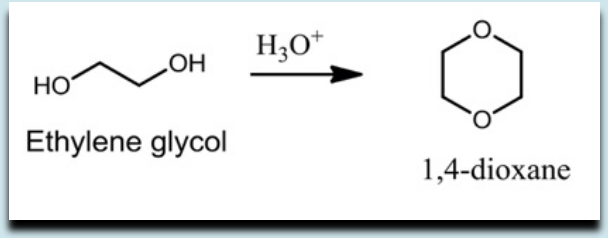
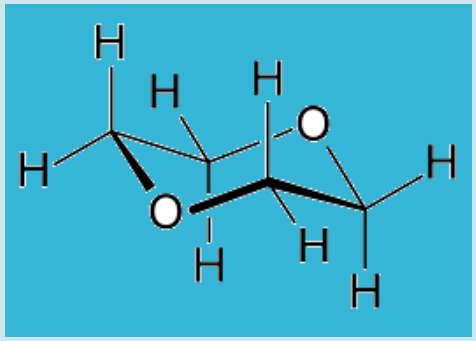
Outline of Discussion

- 1,4-Dioxane…What, How, Where and Why?
- Regulatory Status
- Site Conceptual Model
- OSWER Directive on Using MNA and MLOE Framework
- MLOE Evaluation
  - Source and Plume Mass Estimates
  - Temporal and Spatial Trends
  - Spatial Distributions
  - Geochemical Biodegradation Indicator Parameters
  - Fate and Transport Modeling
  - Compound Specific Isotope Analyses
  - Biomarker Analyses
- Conclusions
- Acknowledgements

1,4-Dioxane – What is it?





- First produced commercially in 1929; largest demand 1950-1960 to stabilize methyl chloroform (Mohr et al, 2010)
- Produced when ethylene glycol is heated and reacted with a strong acid catalyst
- Cyclic ether (C4H8O2) – highly stable ring
- Clear, flammable, potentially explosive liquid
- Specific gravity – 1.033 at 20ºC
- Boiling point - 101ºC
- Miscible in water and hydrophilic (remains in dissolved-phase)
- Very low Henry's Law Constant of 4.88 x 10-6 (atm-m3/mol)
- 1,4-Diethylene Dioxide, *para*-Dioxane, Diethylene Ether, 1,4-D

1,4-Dioxane – How is used?

- Stabilize chlorinated solvents – e.g., 1,1,1-TCA
- Paint strippers, wood glue, brake cleaning fluids
- Aircraft deicing fluid
- Antifreeze production byproduct
- Pesticides
- Personal-care products
  - Shampoos
  - Detergents (pre-2013 Tide contained 85 ppm)
  - Baby hair and body washes

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www.midwestgeo.com

Direct Uses of 1,4-Dioxane and its Occurrence in By-products: Surfactant Examples, 2010

Detergents	mg/kg
Tide Laundry Detergent	85**
Ivory Snow Laundry Detergent	31
Tide Free Laundry Detergent	29**
Purex Laundry Detergent	25
Gain 2X Ultra Laundry Detergent	21
Cheer BrightCLEAN Detergent	20
Era 2X Ultra Laundry Detergent	14
Planet Ultra Liquid Detergent	6.1
Arm & Hammer Laundry Detergent	5
Wisk 2X Ultra Laundry Detergent	3.9
Clorox Green Works Natural	<0.2
Ecos Laundry Detergent	<0.2
Sun Burst Laundry Detergent	<0.2

Shampoos	mg/kg
Clairol Herbal Essence Body Envy	24
Aura Cacia Natural Aromatherapy Bubble Bath	14.9
Clairol Herbal Essences "Long Term Relationship Shampoo for Long Hair"	14
Clairol Herbal Essence Drama	10
Gerber Grins & Giggles Gentle & Mild Aloe Vera Baby Shampoo	8.4
Healthy Times "Baby's Herbal Garden Pansy Flower" Shampoo	8.2
Sea-Chi Organics Shampoo	7.5
Pantene Pro-V Shampoo	6.5
Others	
Dial Antibacterial Hand Soap	18
Disney "*Clean as Can Bee*" Body Wash	8.8
Sesame Street Bubble Bath	7.4

More info at www.1-4dioxane.com

Source: David Stehman, March 8th, 2010

1,4-Dioxane in consumer products as an impurity of ethoxylated surfactants (*ppm*)

Contaminants of Concern Webinar Series

Slide 10

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1,4-Dioxane – Where is it in the Environment?

- Not readily in air - low volatility
- Not readily in soil vapor – breaks down
- Not readily in soil – very low sorption
- Primarily in surface water and groundwater

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1,4-Dioxane – Why is it in the Environment?

- Waste disposal sites
- Leaking landfills
- Household septic systems
  - Personal care and household products
- WWTP:
  - Release to surface water
  - Land farmed sludge
- Pesticide application

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Regulatory Status

- USEPA finalized the human health risk profile for 1,4-D in 2010
- No MCL as of 2016
- Listed on the Unregulated Contaminant Monitoring Rule (UCMR 3) for monitoring public water systems (PWSs) 2012
  - MRL = 0.07 µg/L
  - B2 human carcinogen
  - USEPA 10^{-4} lifetime cancer risk = 0.3 mg/L or 0.003 µg/L
- Some states are defaulting to the USEPA Region IX RSL – 0.67 µg/L
- Criteria are changing and vary by State – Georgia = 70 µg/L

Table 1 - Regulatory Guidelines for 1,4-Dioxane in Water

State	Guideline	Concentration (ug/L)
California	Notification Level	1
Colorado	Drinking Water Standard	3.2
Connecticut	Action Level	3
Maine	Maximum Exposure Guideline	4
Massachusetts	Guideline	0.3
New Hampshire	Proposed Risk-Based Remediation Value	3
New York Dept. of Health	Drinking Water Standard	50
South Carolina	Drinking Water Health Advisory	70

2014 Water Research Foundation – 14-Dioxane White Paper

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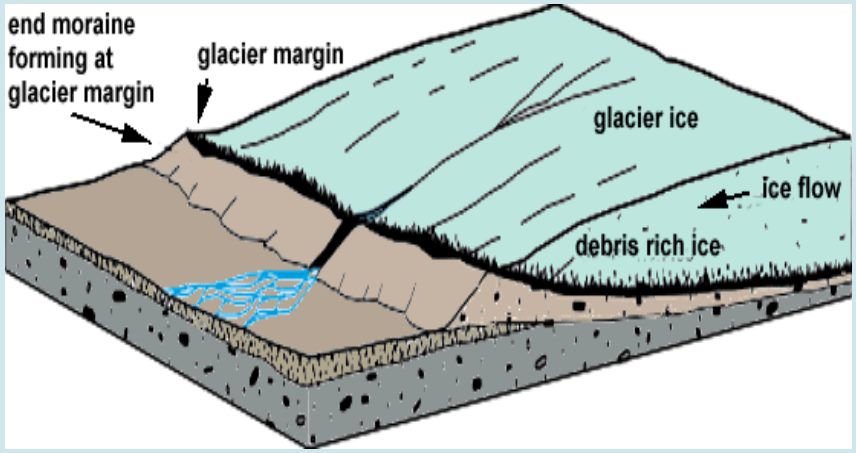
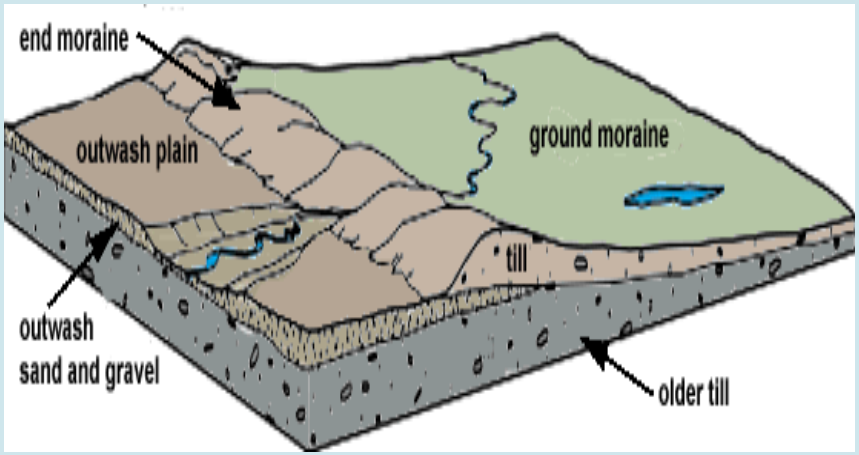
Conceptual Site Model

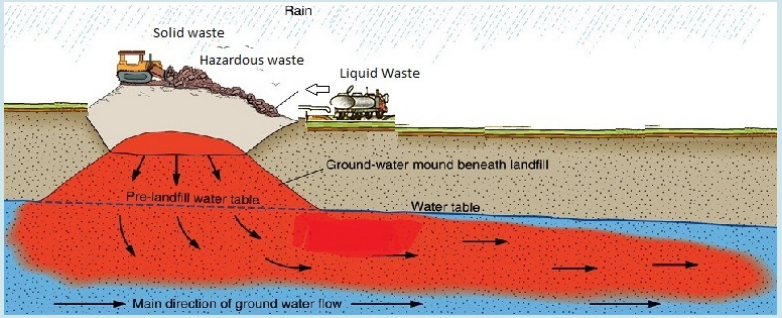
- Former landfill in the Midwestern US that accepted industrial waste form 1968 to 1979
- Underlain by thick glacial outwash deposits – sands and gravels interbedded by till and lacustrine clay [similar to Coastal Plain]
- Aquifer(s) are unconfined to semi-unconfined and the average advective flow velocity is approximately 1.0 ft/day





Conceptual Site Model

- A large dilute plume comprised of 1,4-D (up to 420 µg/L) and THF (up to 340 µg/L)
- A main plume is 90-150 feet thick thinning to less than 50 feet beyond approximately 10,000 feet downgradient



- Source control consists of low-perm cap with active gas collection
- Long-time monitoring of extensive network of test wells has provided an understanding of chemical and geochemical conditions changing over time

OSWER Directive on MNA and MLOE Framework

OSWER Directive on using MNA

- Historical site data demonstrating decreasing trends
- Hydrogeological and geochemical data that indirectly support natural contaminant removal processes
- Microcosm studies for direct support of specific removal mechanisms

Multiple Lines of Evidence (MLOE) Approach

- Source and plume mass estimates
- Spatial distribution analyses
- Trend and regression analyses
- Compound Stable Isotope Analysis
- Fate and Transport Modeling
- Biomarker analyses

Development of a MLOE framework to evaluate the intrinsic biodegradation potential for 1,4-D is vital to implementing management strategies at groundwater sites impacted by 1,4-D

Source Plume Mass Estimates

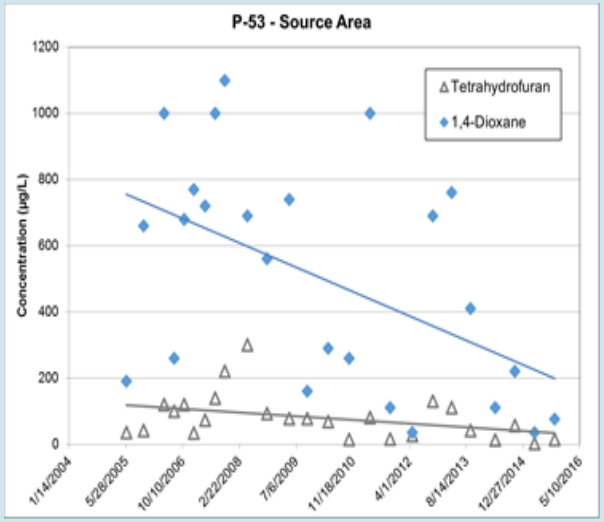
- Source and plume mass estimates were conducted using Environmental Visualization System/Mining Visualization System (EVS/MVS) calibrated to time series distributions of 1,4-D and THF
- Results indicate substantial decreases in source and downgradient mass of both 1,4-D and THF

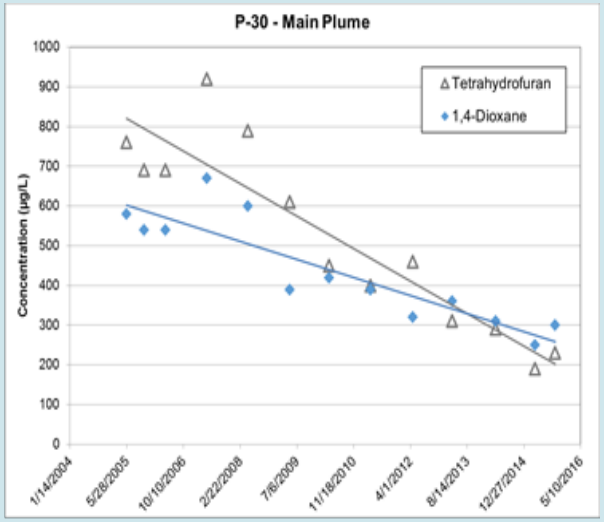
Compound	%Reduction (kg) Near Source Mass (2002 to 2015)	%Reduction (kg) Total Plume Mass (2002 to 2015)
Benzene	95%	74%
THF	99%	80%
1,4-DD	82%	38%

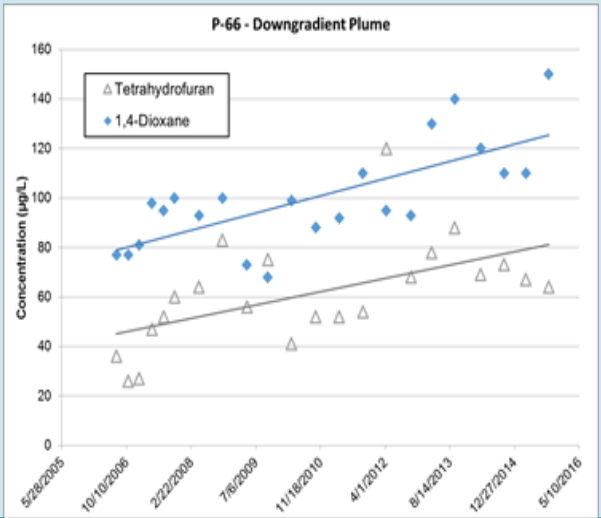
- Correlation between the collapse of the THF plume (<100 µg/L) and the accelerated contraction of the 1,4-D plume
- Temporal tend analyses and spatial changes indicate natural degradation of both compounds is occurring within source and downgradient

Temporal and Spatial Trends

- Trend analyses indicate declining source concentrations since 2004
- 1,4-D concentrations are:
  - Decreasing or stable in 92% of the test wells between landfill and shallow lake (2010 to 2015) and;
  - Decreasing or stable in 88% of the test well downgradient of the lake (2013 to 2015)







1,4-Dioxane and THF groundwater concentration trends in source and downgradient plume areas.

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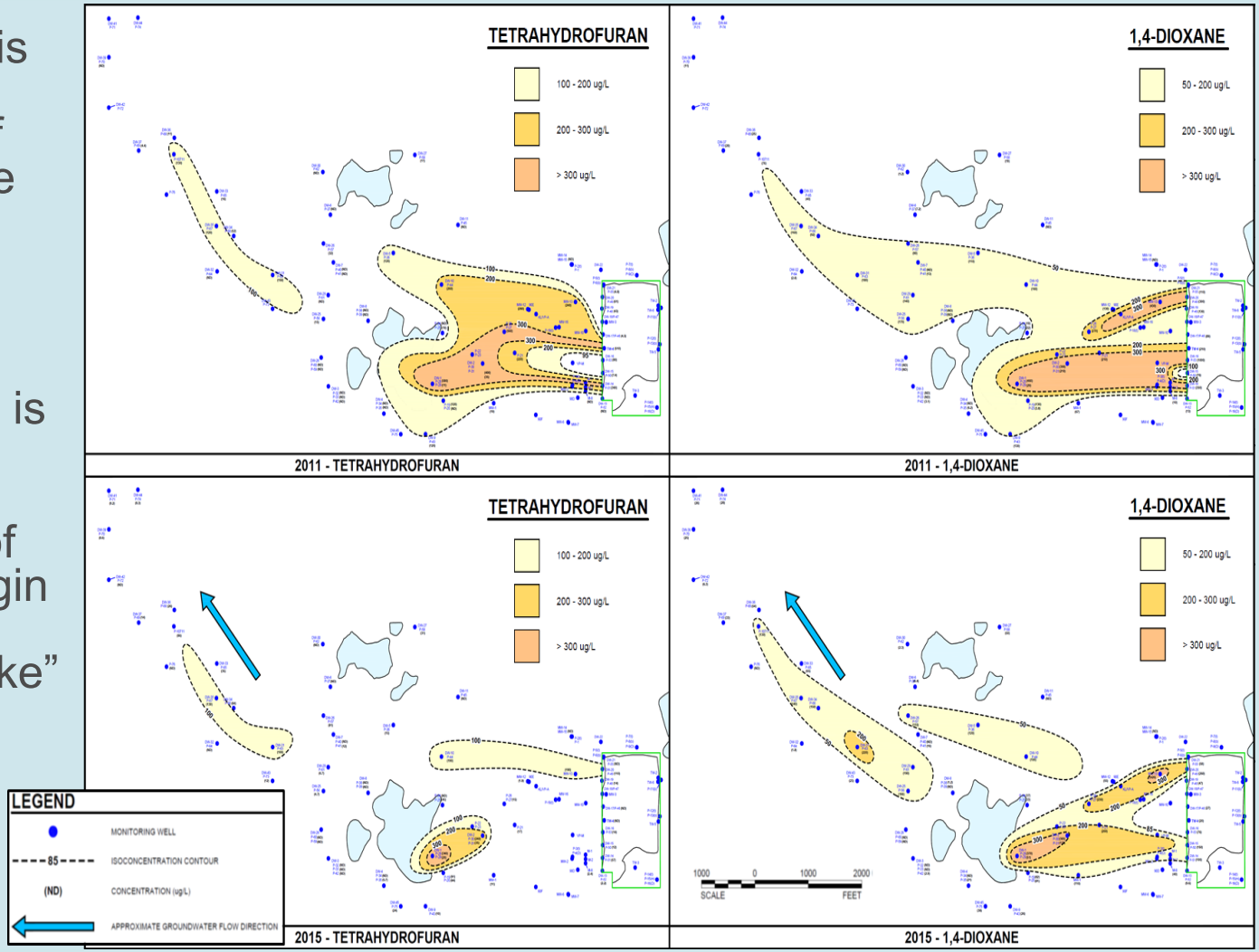
1,4-D and THF Spatial Distributions (2011 to 2015)

- Isopleth analysis confirms the lateral extent of the 1,4-D plume has decreased significantly between 2011 and 2015
- 1,4-D depletion is also occurring immediately downgradient of the landfill margin evidenced by isolated “slug-like” plumes



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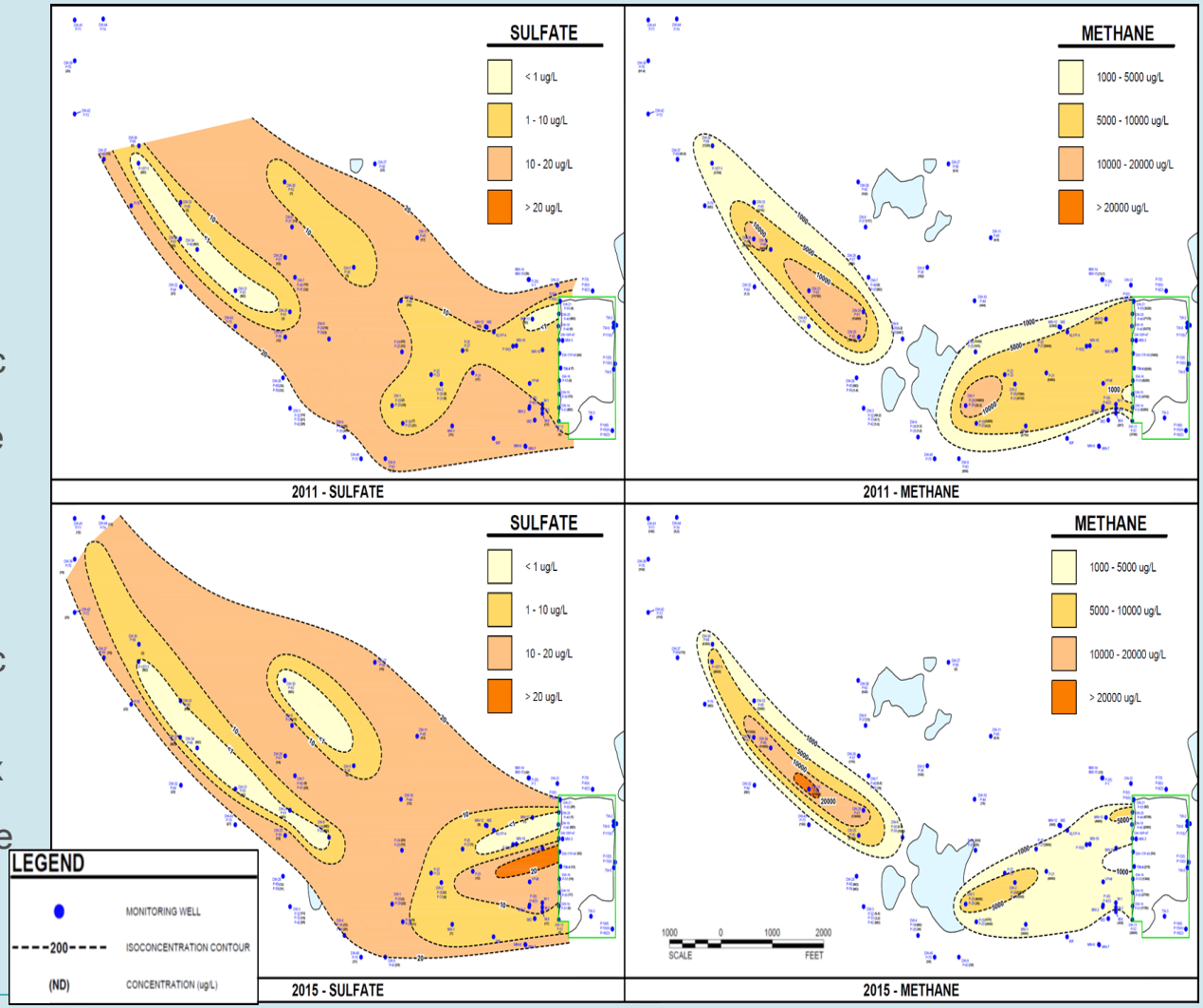
Geochemical Biodegradation Attenuation Parameters

- Evaluation of geochemical parameters indicate 2 generalized areas within the plume with distinctive geochemical conditions
- **Source Area:**
  - Groundwater immediately downgradient of landfill is dominated by sulfate-reducing and methanogenic conditions
  - This area is becoming more aerobic with rebounding sulfate and decreasing methane levels
- **Downgradient Plume Area:**
  - Also dominated by sulfate-reducing and methanogenic conditions
  - Has a more narrow areal extent with significant redox gradient (reducing to oxidizing), continuing sulfate depletion and increasing methane levels



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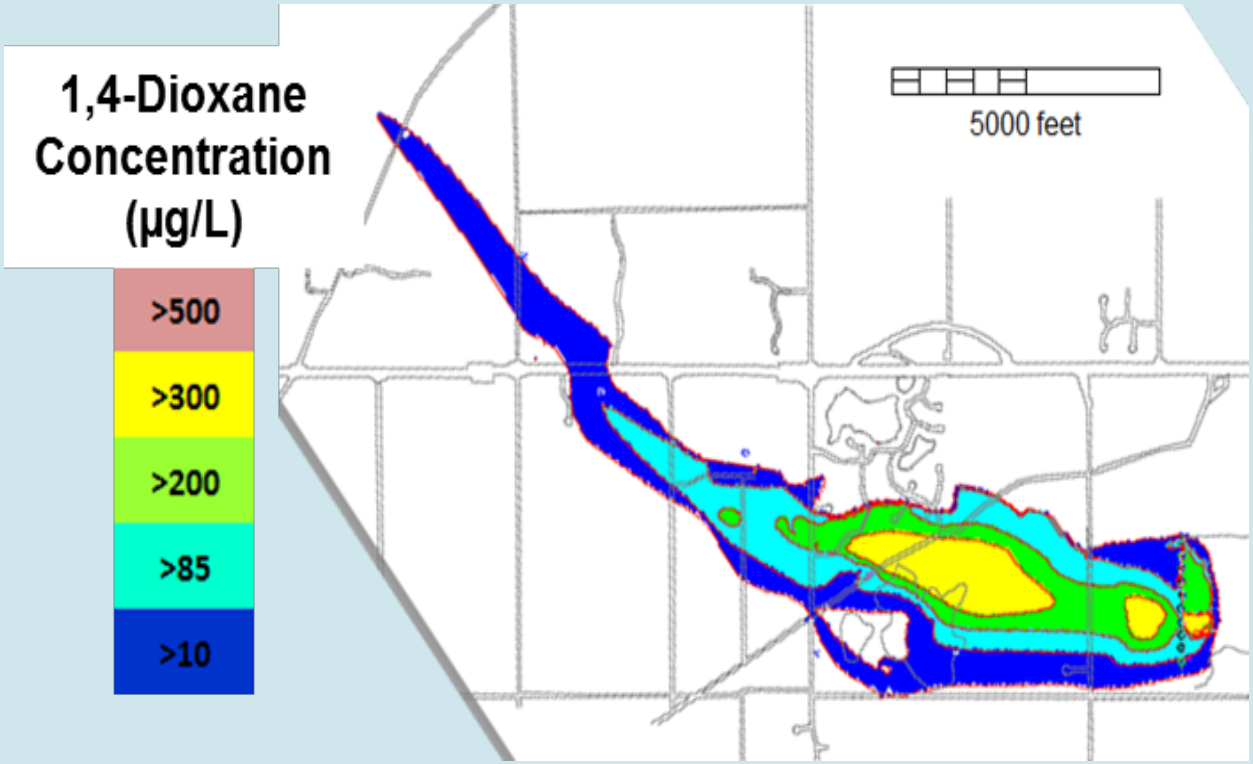
Fate and Transport Model Simulation

- MODFLOW with MT3DMS were used to simulate the fate and transport of 1,4-Dioxane
- Model calibrated to historic hydrogeologic and chemical data
- Base scenario for transport used varying 1,4-Dioxane concentrations (3 time periods [TP]) at 3 areas of the landfill.
- Solute transport was calibrated to the 2015 dataset with biodegradation simulated using first-order decay kinetics (half-life for 1,4-Dioxane set to 3,500 days)

Time Period	TP-1	TP-2	TP-3
Year	1970 - 1980	1980-2006	2006-2014
Concentration (ppb), South Area	3500	1500	500
Concentration (ppb), Central Area	1200	900	300
Concentration (ppb), North Area	1000	800	600

Fate and Transport Model Simulation

- Simulation of the base scenario showed reasonable match to the observed plume core and distribution of 1,4-D
- Dispersion and dilution only simulations did not match 2015 plume extent or concentrations
- Adding the 1,4-D biodegradation process substantially improved model calibration
- Results suggest intrinsic biodegradation is occurring within the groundwater plume



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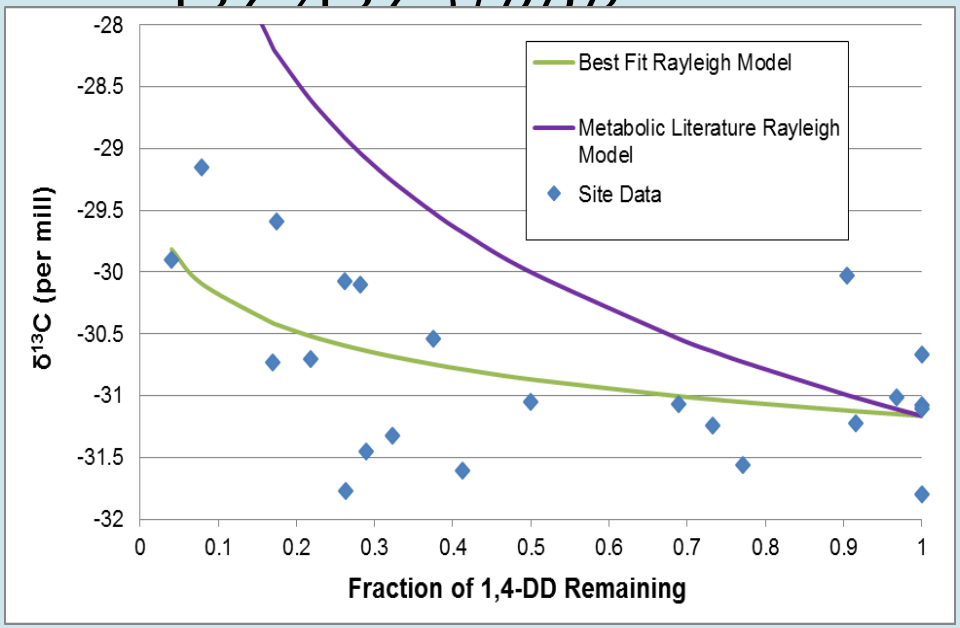
CSIA and Molecular Characterization

- Isotopic fractionation of the 1,4-D ranged from -29.15% to -31.80% with the higher values $\delta^{13}C$ indicating 1,4-D biodegradation processes are likely occurring.
- Site data fit to a Rayleigh model compared the enrichment factor to literature values by Pornwongthong et al., 2011
- A clear trend shows $\delta^{13}C$ values increase with decreasing fractionation (i.e., increasing attenuation) of 1,4-D, indicative of biodegradation by the intrinsic microbial community

$$\delta 13C = ((13C/13C)\downarrow sample/(13C/13C)\downarrow PDB$$

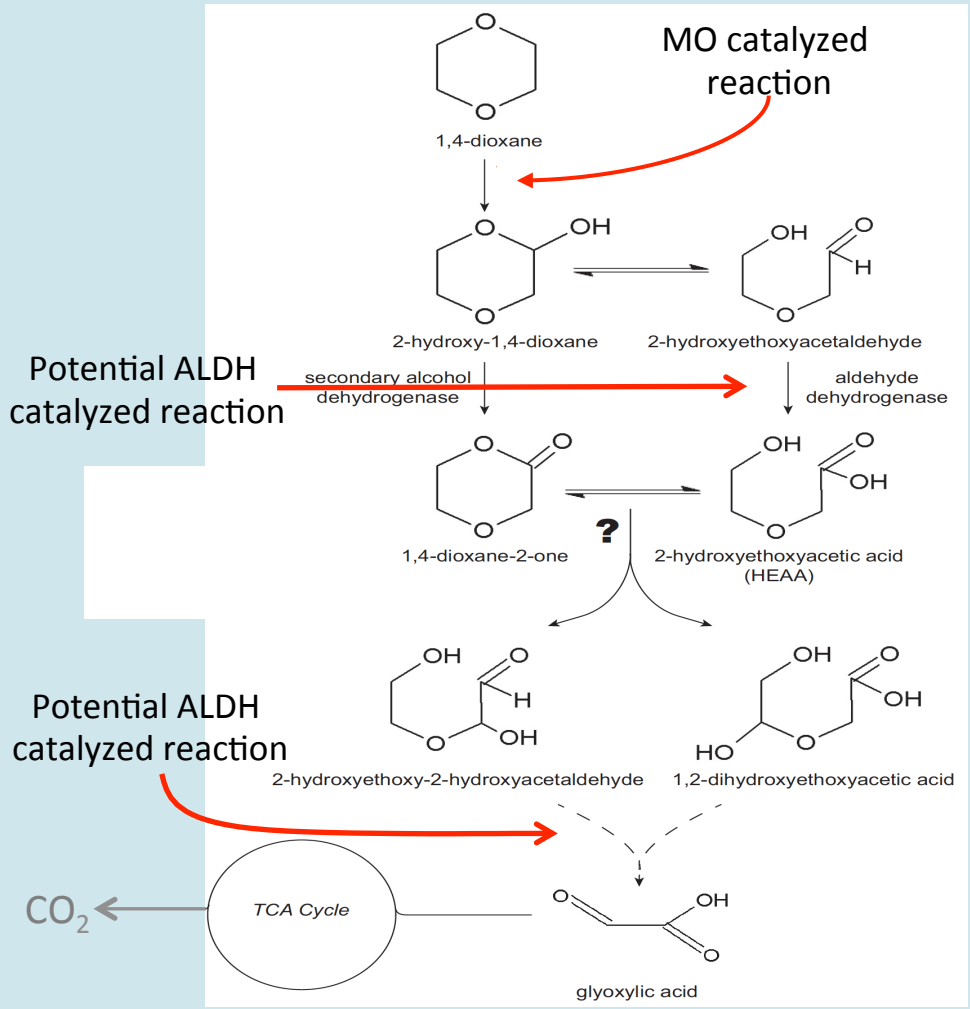


CSIA results for laboratory pure culture (purple; (Pornwongthong et al., 2011; Pornwongthong et al., In review)) and site-specific (green) biodegradation of 1,4-dioxane.

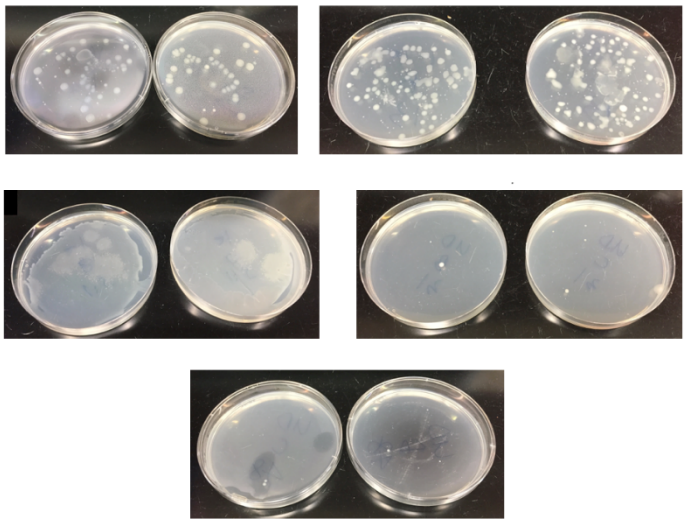
Cometabolic Degradation Pathway for 1,4-Dioxane

- Cometabolic degradation pathways are catalyzed by methane (sMMO), propane, phenol, THF and toluene monooxygenases
- sMMO oxidizing methane with O_2 fortuitously degraded 1,4-D (Mahendra & Alvarez-Cohen, 2006)
- DXMO and ALDH have been established as biomarkers for 1,4-D (Gedalanga et al., 2014; Li et al., 2014)

1,4-Dioxane aerobic degradation pathway (Grostern et al., 2012; Mahendra et al., 2007). Similar pathway was reported for both metabolic and cometabolic processes, resulting in nearly complete mineralization.

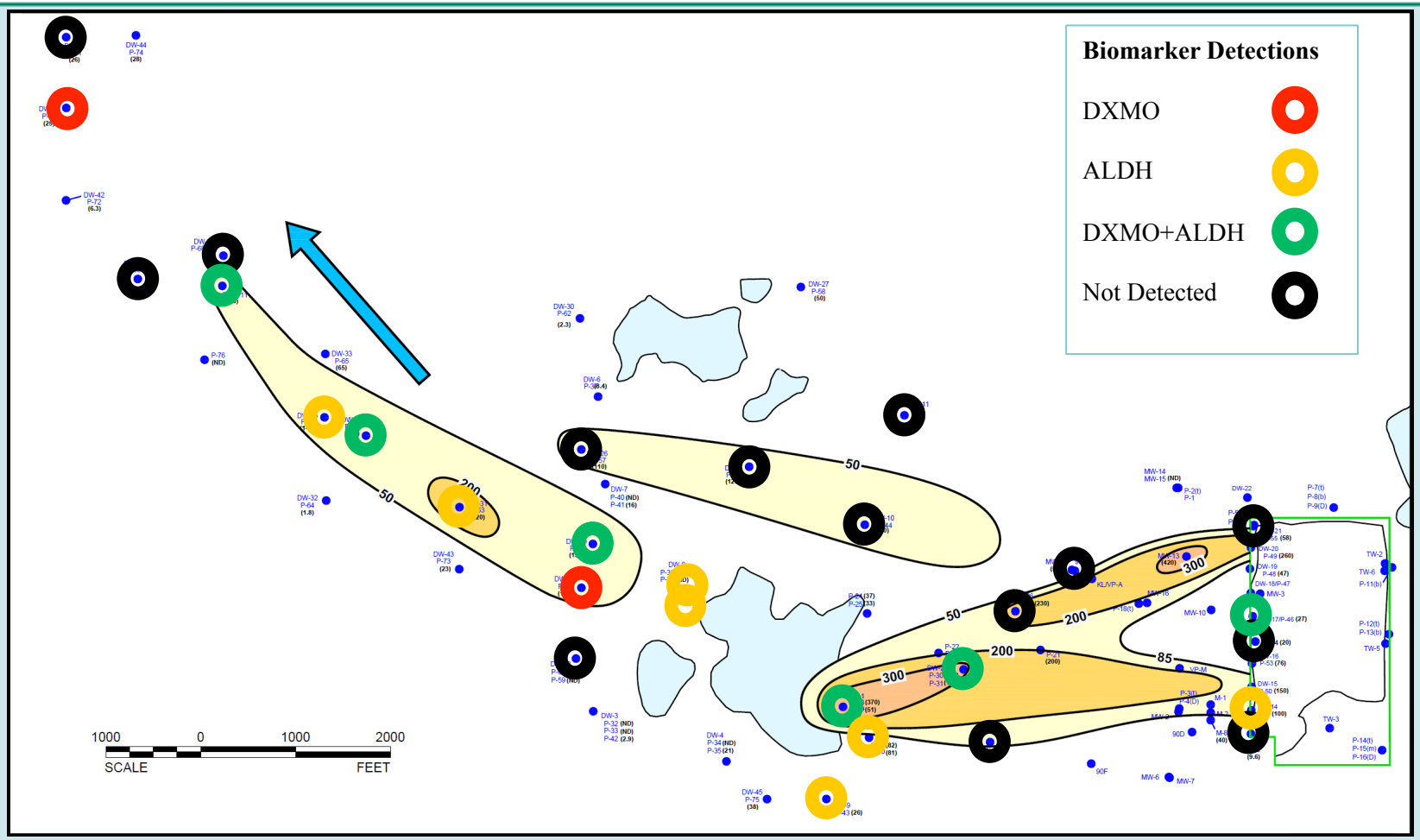


Biomarkers – DXMO and ALDH



- DXMO and ALDH quantified using quantitative polymerase chain reaction (qPCR)
- DXMO and/or ALDH were observed in 15 test wells 93% of which were located with the plume with elevated 1,4-D
- 83% of samples positive for both DXMO and ALDH were from areas of the plume were 1,4-D was >50 µg/L
- Absence of 1,4-D biomarkers in test wells with <50 µg/L – anomalous – 57% of wells lacking biomarkers
- No false positives in test wells with elevated 1,4-D with biomarkers present

DXMO and ALDH Biomarkers Distribution



DXMO and ALDH biomarker detections track well within the 1,4-dioxane plume.

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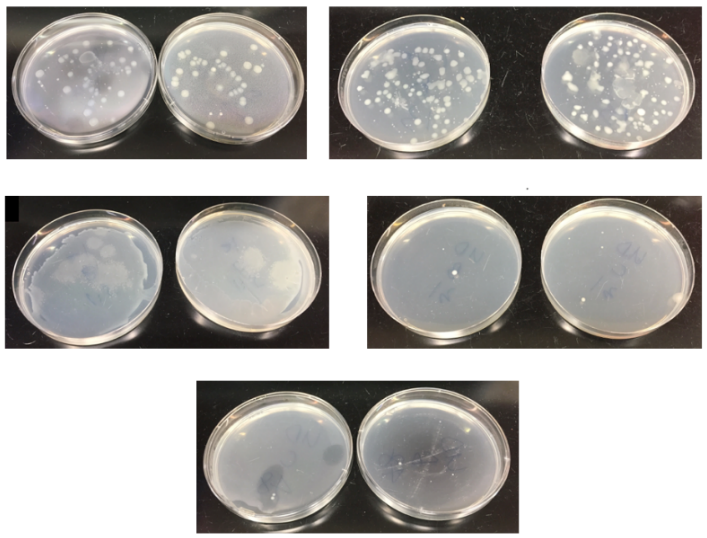
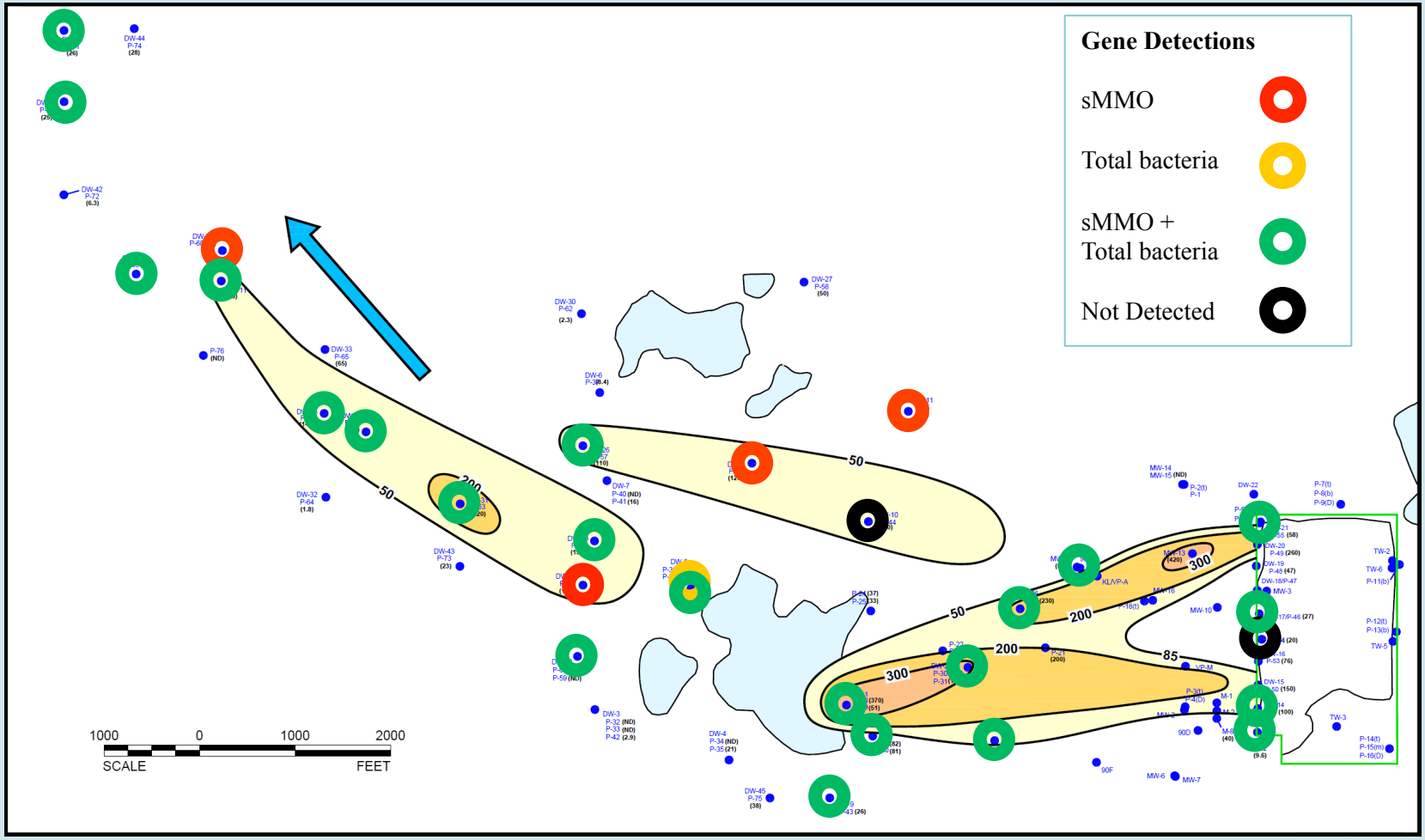
Biomarkers – sMMO and RNA



- sMMO and RNA were present across the site and highly prevalent in test wells; 90% positive detections
- Results for total RNA and sMMO indicate high concentration of bacteria in samples ranging from 1.9×10^4 to 8.6×10^6
- 75% of test wells with 1,4-D concentrations were >50 µg/L were positive for sMMO

sMMO and Total Bacteria



Presence of sMMO and total bacteria in a 1,4-dioxane contaminated aquifer are independent of the 1,4-dioxane plume.

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Acknowledgements

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