In Situ Chemical Oxidation and Bioremediation of Oil Across a Louisiana Beach Profile

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Presentation Outline

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- ✓ Site Description
- ✓ Project Objectives
- ✓ Remediation Approach & Methods
- ✓ Results & Discussion
- ✓ Summary & Next Steps

Fourchon Beach, Louisiana

2010 Deepwater Horizon Shoreline Oiling

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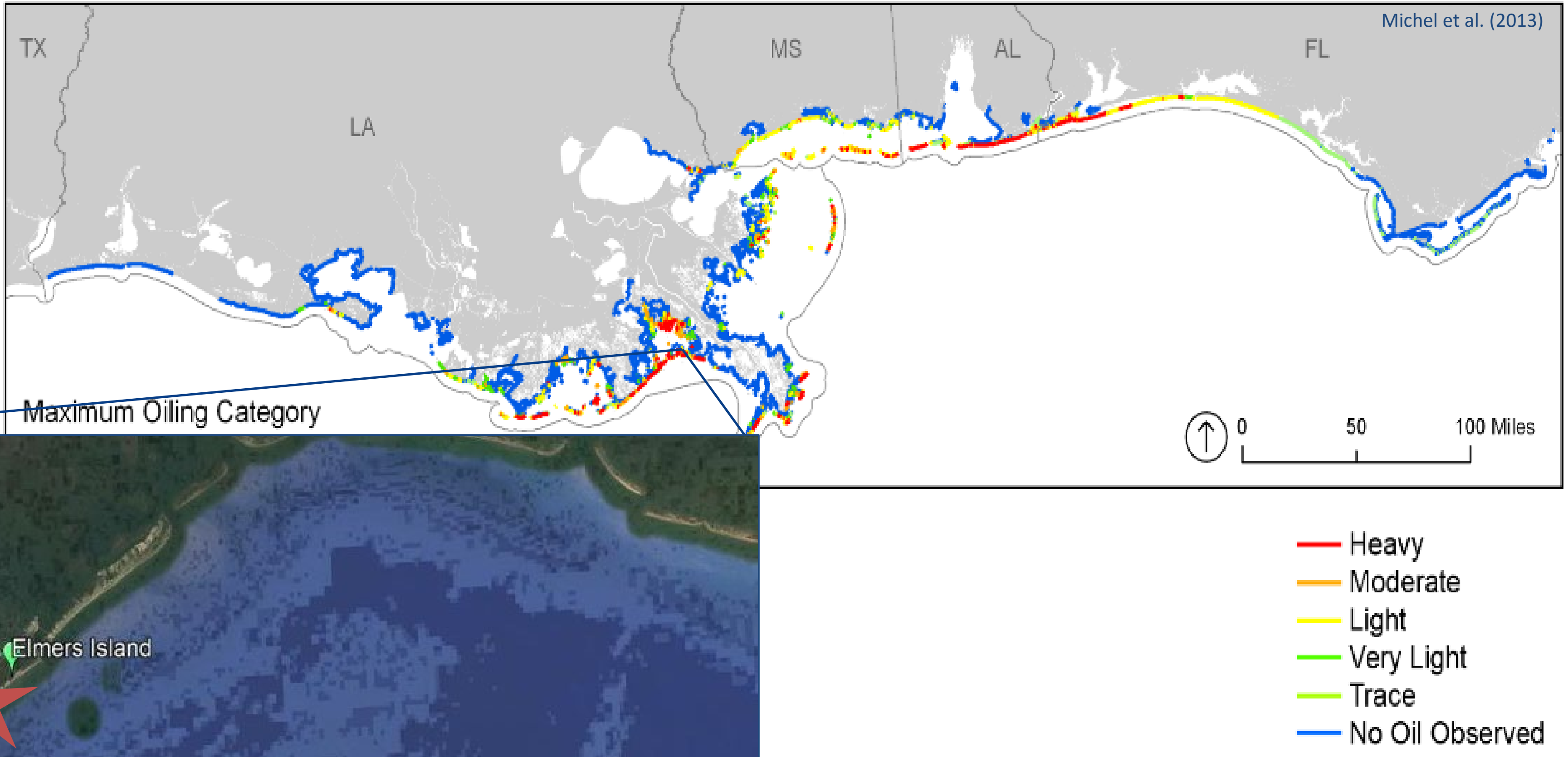

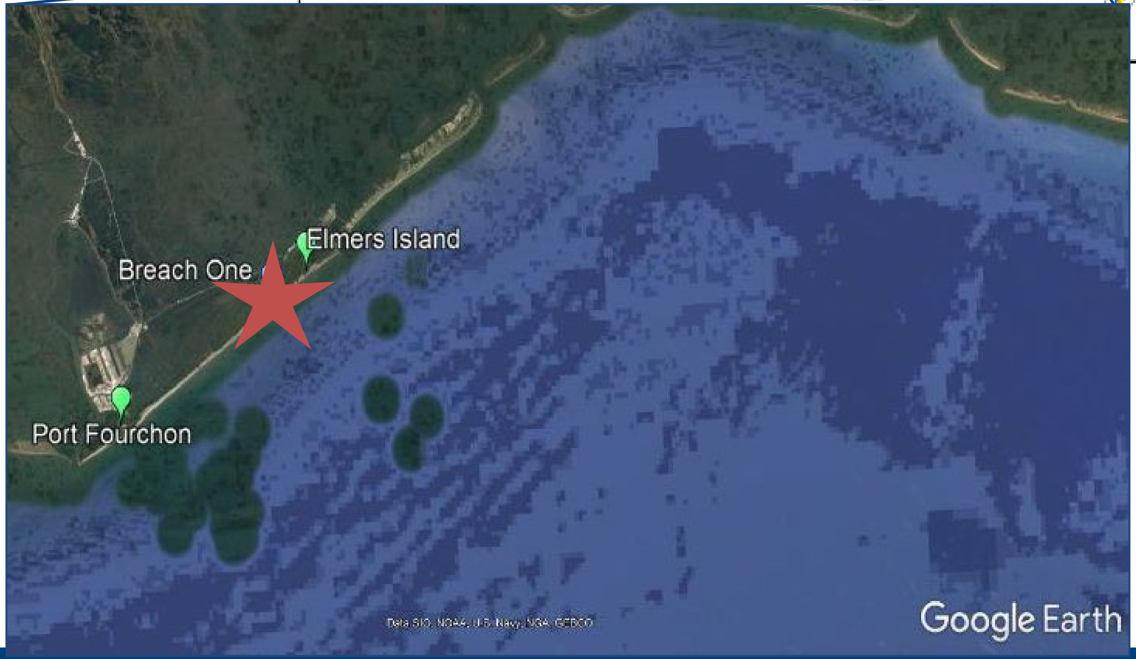

Site Description
Breach One


May 11, 2010


May 21, 2010


May 22, 2010


July 2010

Site Description

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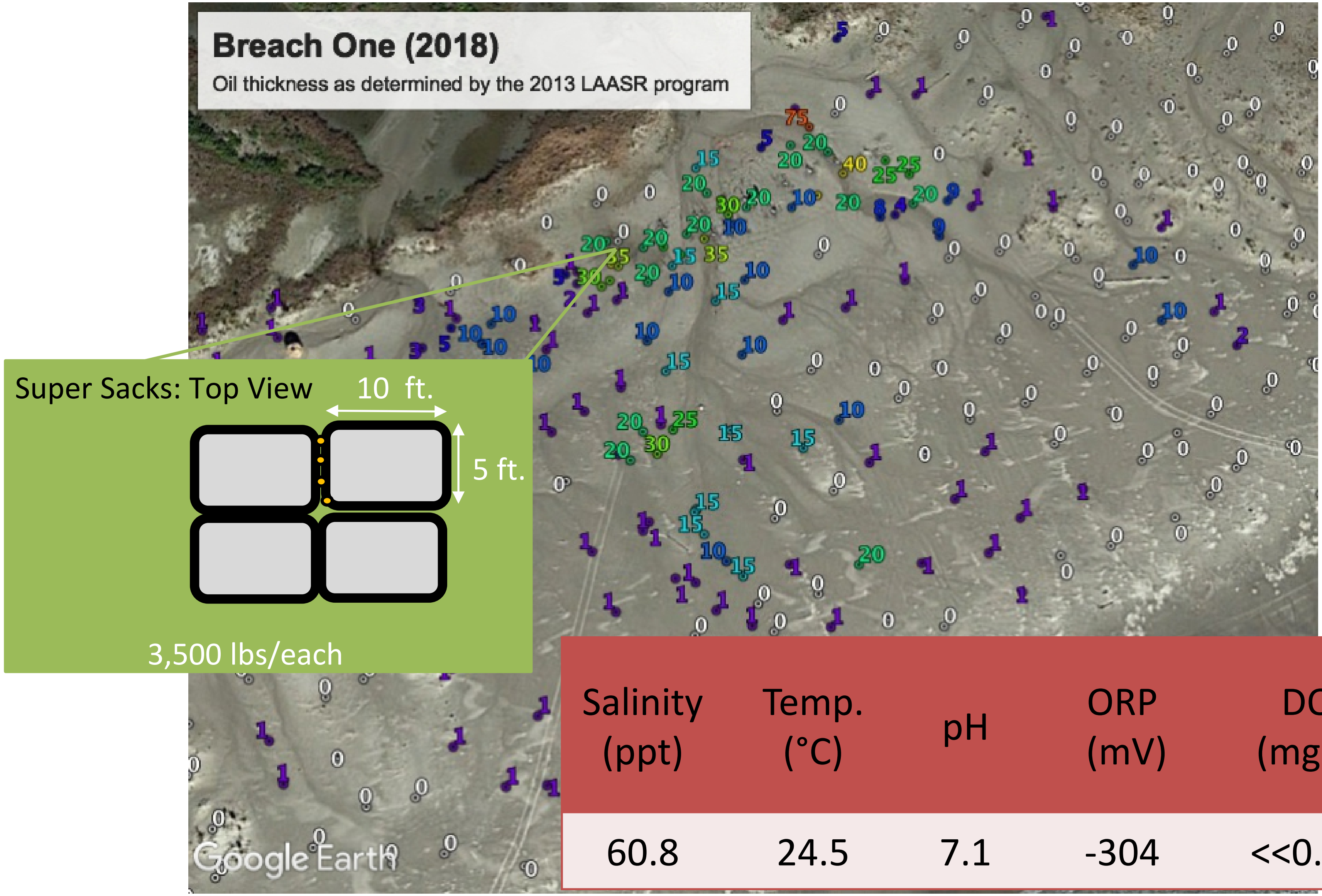
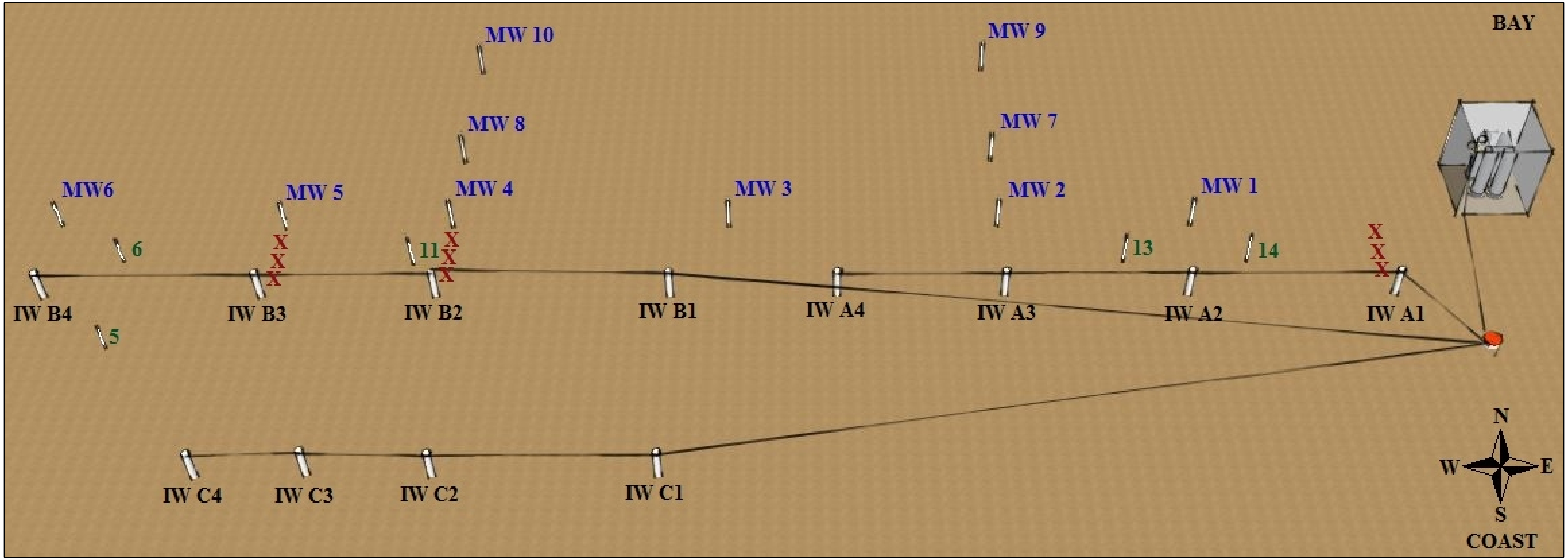


Salinity (ppt)	Temp. (°C)	pH	ORP (mV)	DO (mg/L)	Sulfide (mg/L)	Ferrous Iron (mg/L)
60.8	24.5	7.1	-304	<<0.02	312	0.80

Previous Research at Breach One
O_2 Biostimulation



Research Objectives

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Breach 1 Remedial Strategy: Enhance degradation of buried oil through combination of *in situ* chemical oxidation (ISCO) and enhanced aerobic bioremediation with oxygen release compound (ORC)

- Assess efficacy of overcoming intrinsic O_2 demand with chemical oxidation to prepare environment for ORC addition
- Investigate extent of direct degradation via chemical pre-oxidation and determine distribution of residual oil
- Evaluate impact of chemical pre-treatment on groundwater chemistry and subsequent biodegradation; determine alterations to microbial population

(1) Chemical Oxidation with Persulfate

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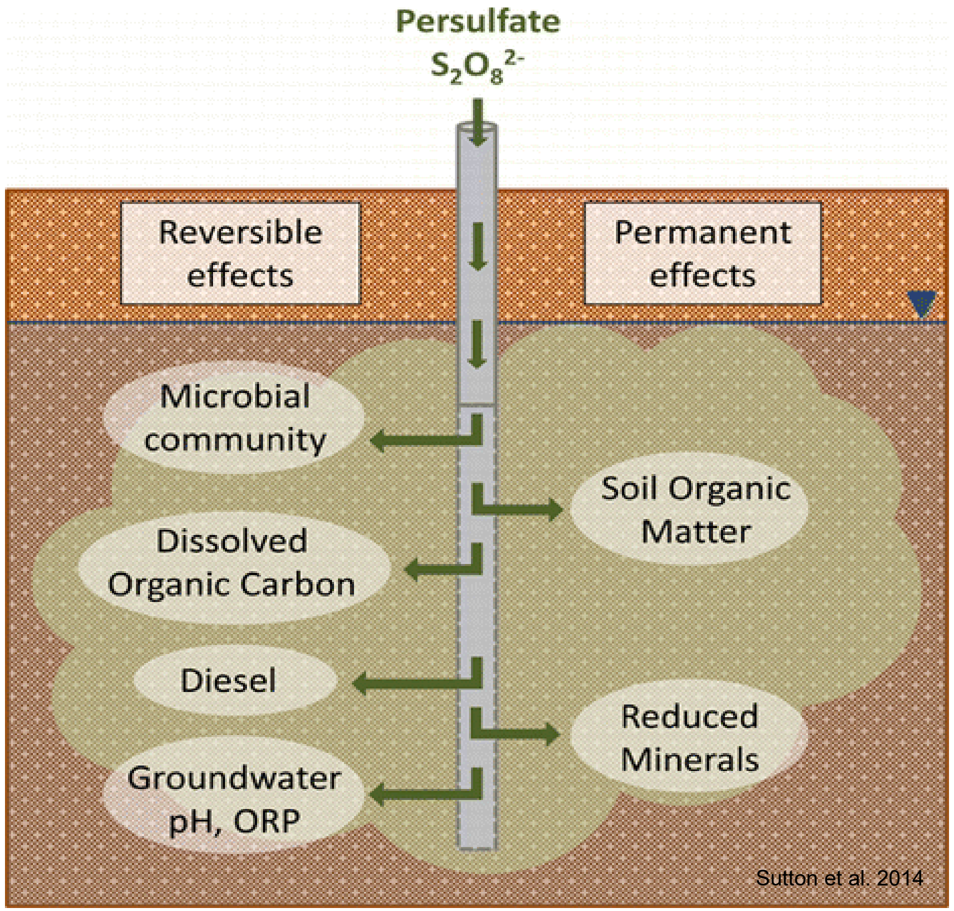
$$Na_2S_2O_8 \leftrightarrow S_2O_8^{2-}$$

$$S_2O_8^{2-} + 2e- \rightarrow 2SO_4^{2-}$$

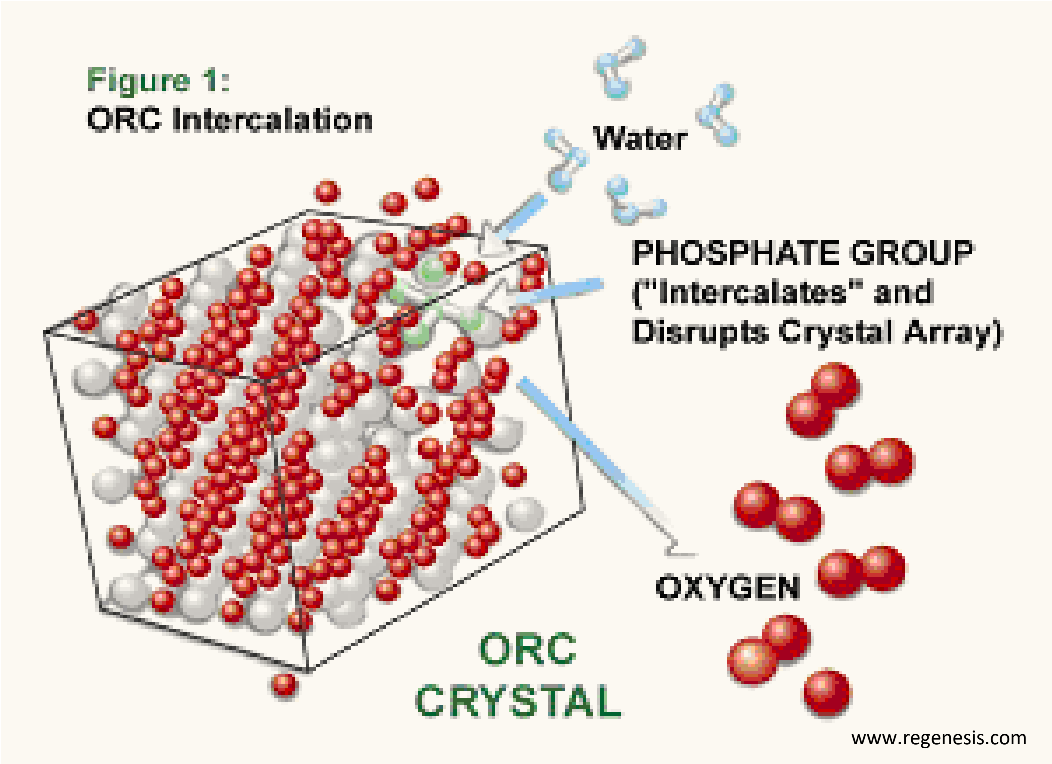
$$S_2O_8^{2-} + 2e- \rightarrow SO_4^{2-} + SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + OH- \rightarrow SO_4^{2-} + OH^{\bullet}$$

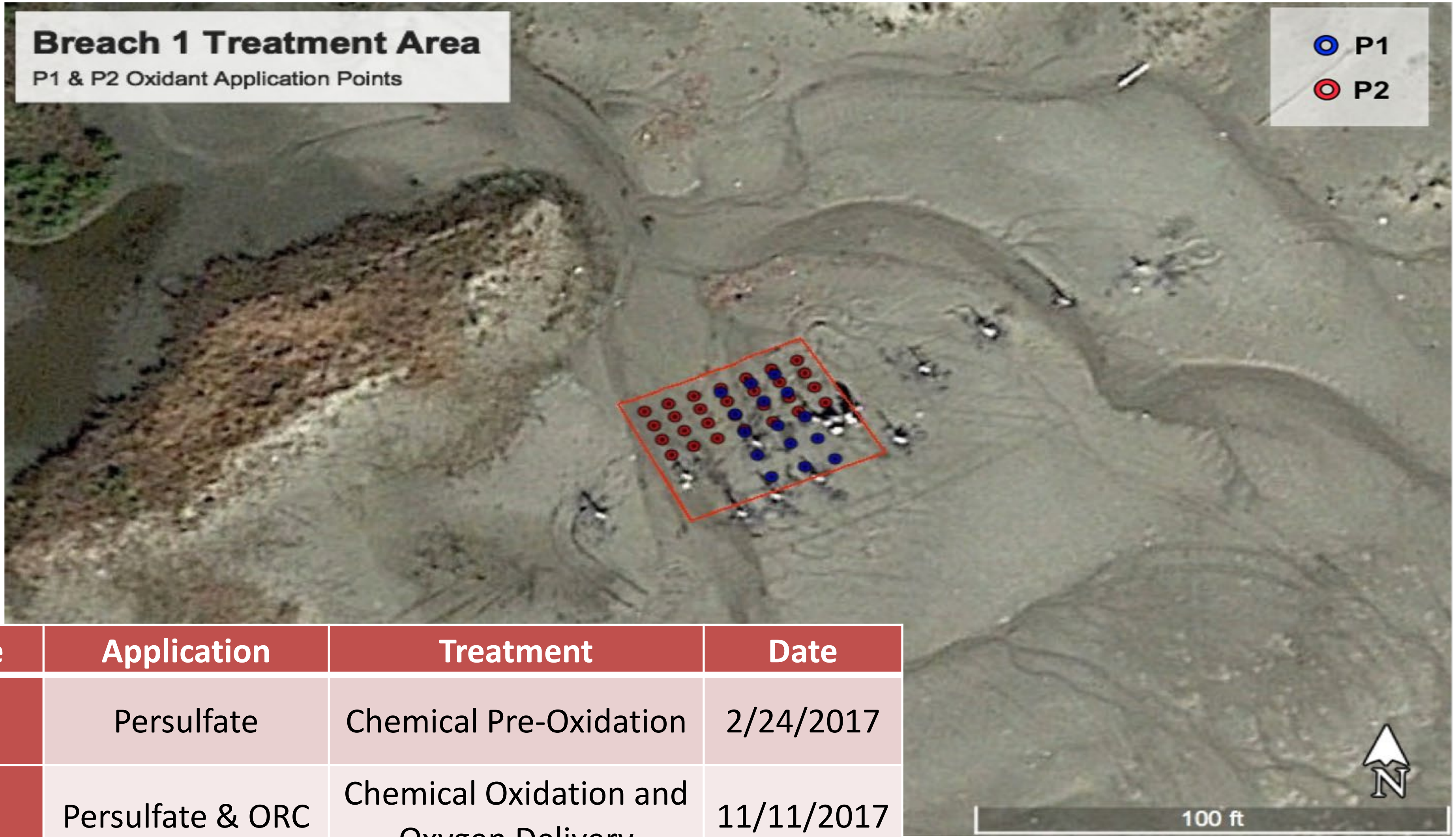


(2) Oxygen Delivery with ORC

- Enhanced aerobic bioremediation of a wide variety of organic contaminants
- Calcium oxy-hydroxide based proprietary material
- Controlled release of molecular oxygen
- Low operation and maintenance costs



Treatment Phases & Application



Phase	Application	Treatment	Date
P1	Persulfate	Chemical Pre-Oxidation	2/24/2017
P2	Persulfate & ORC	Chemical Oxidation and Oxygen Delivery	11/11/2017

Groundwater Monitoring

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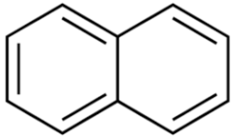
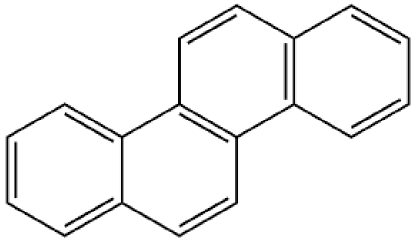
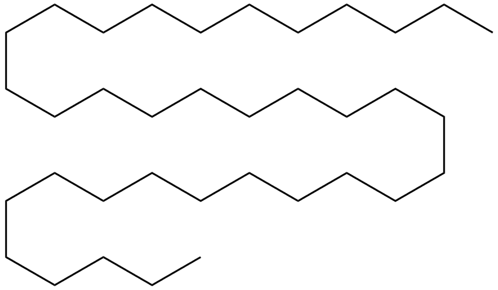
Sediment Analysis





Polycyclic Aromatic Hydrocarbons (PAHs)				
Naphthalene	**Flourene**	**Phenanthrene**	**Dibenzothiophene**	**Chrysene**
C1-naphthalene (C1-N)	C1-flourene (C1-F)	C1-phenanthrenes (C1-P)	C1-dibenzothiophenes (C1-D)	C1-chrysene (C1-C)
C2-naphthalene (C2-N)	C2-flourene (C2-F)	C2-phenanthrenes (C2-P)	C2-dibenzothiophenes (C2-D)	C2-chrysene (C2-C)
C3-naphthalene (C3-N)	C3-flourene (C3-F	C3-phenanthrenes (C3-P)	C3-dibenzothiophenes (C3-D)	C3-chrysene (C3-C)
C4-naphthalene (C4-N)		C4-phenanthrenes (C4-P)	C4-dibenzothiophenes (C4-D)	

n-alkanes (ALKs)	
Light	**Heavy**
decane (C_{10})	docosane (C_{22})
undecane (C_{11})	n-tetracosane (C_{24})
dodecane (C_{12})	n-hexacosane (C_{26})
tridecane (C_{13})	n-octacosane (C_{28})
tetradecane (C_{14})	n-tricontane (C_{30})
pentadecane (C_{15})	n-dotricontane (C_{32})
hexadecane (C_{16})	n-hexatriacontane(C_{36})
heptadecane(C_{17})	
octadecane (C_{18})	
n-eicosane (C_{20})	



Microbial Characterization

- Genomic DNA isolation and extraction of sediment
- PCR amplification of 16S rRNA gene fragments
- Next generation sequencing on MiSeq Illumina Platform
- Sequences aligned to SILVA database
- OTU based cluster analysis (97% threshold)

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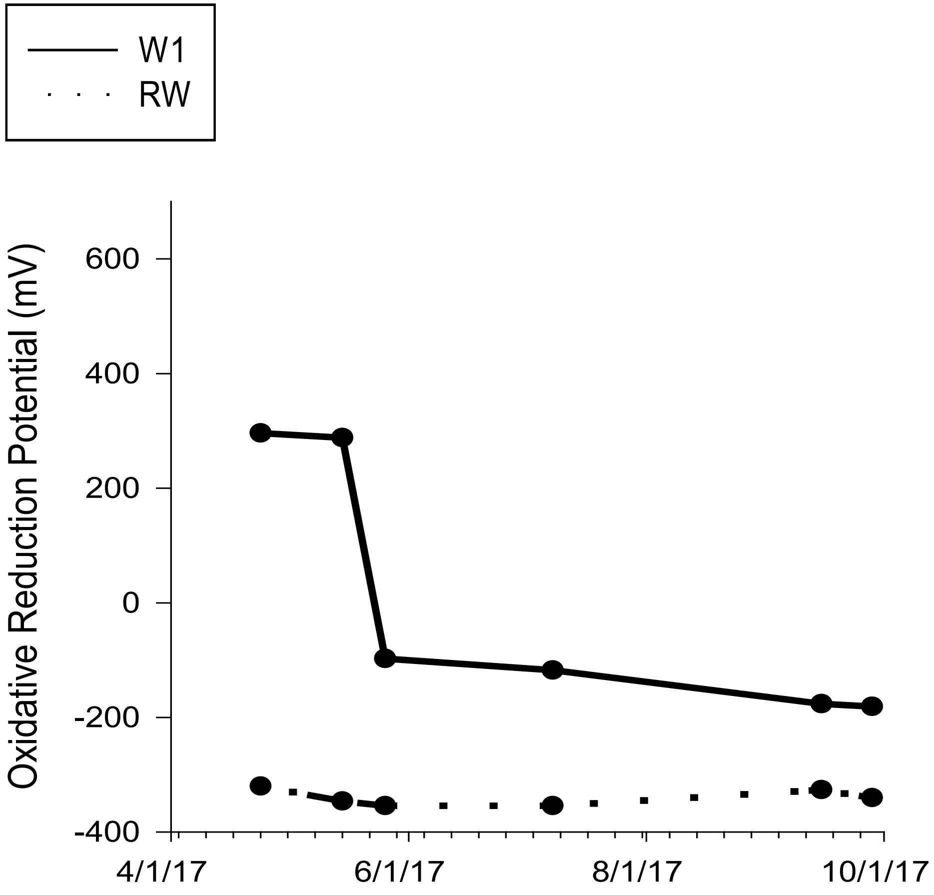
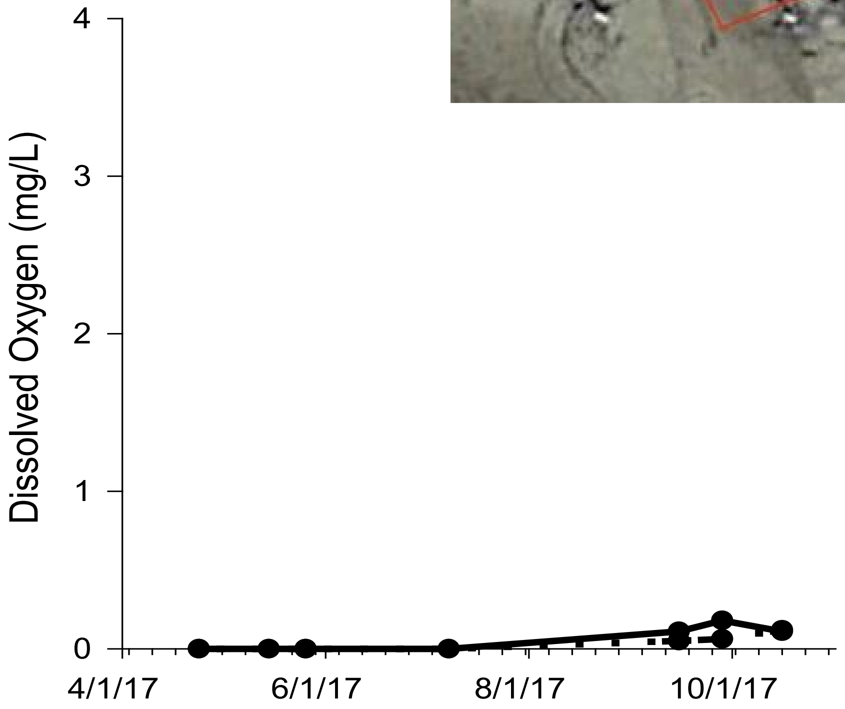
POST-P1 Results
Groundwater





POST-P1 Results
PAH Degradation & Distribution

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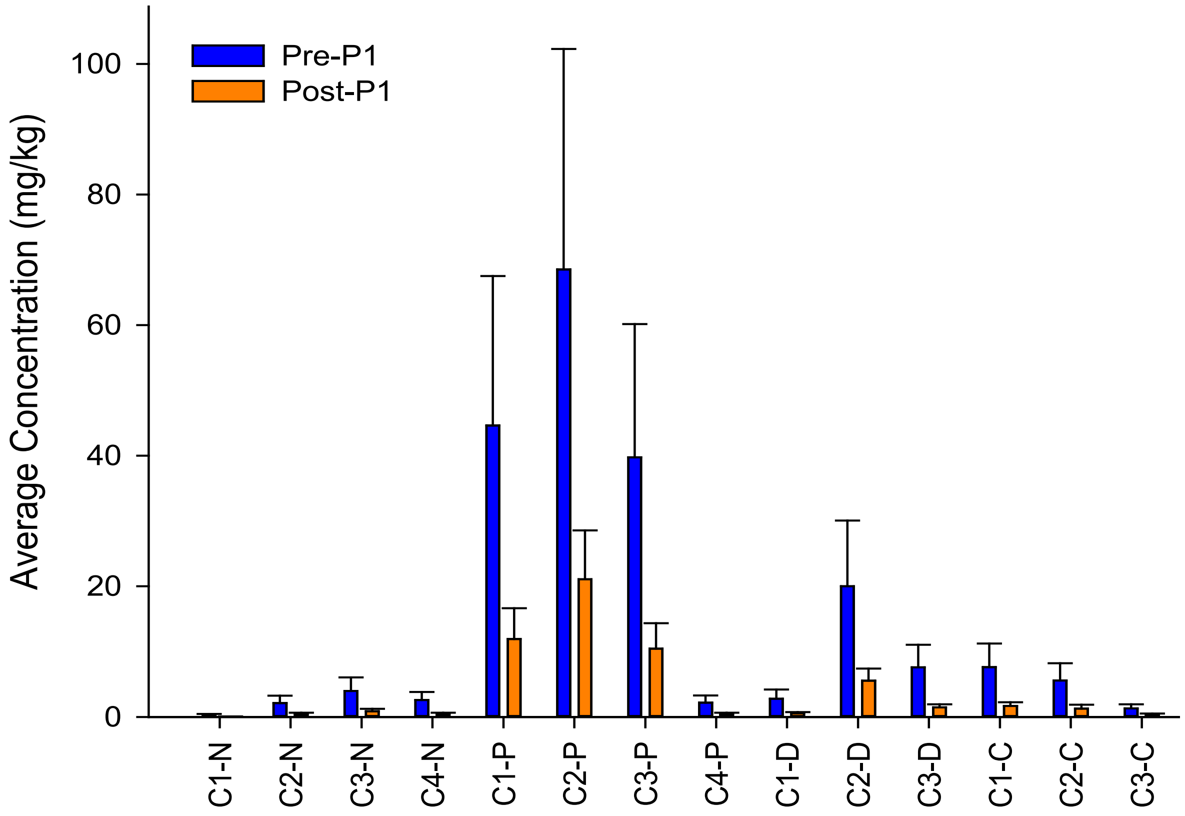
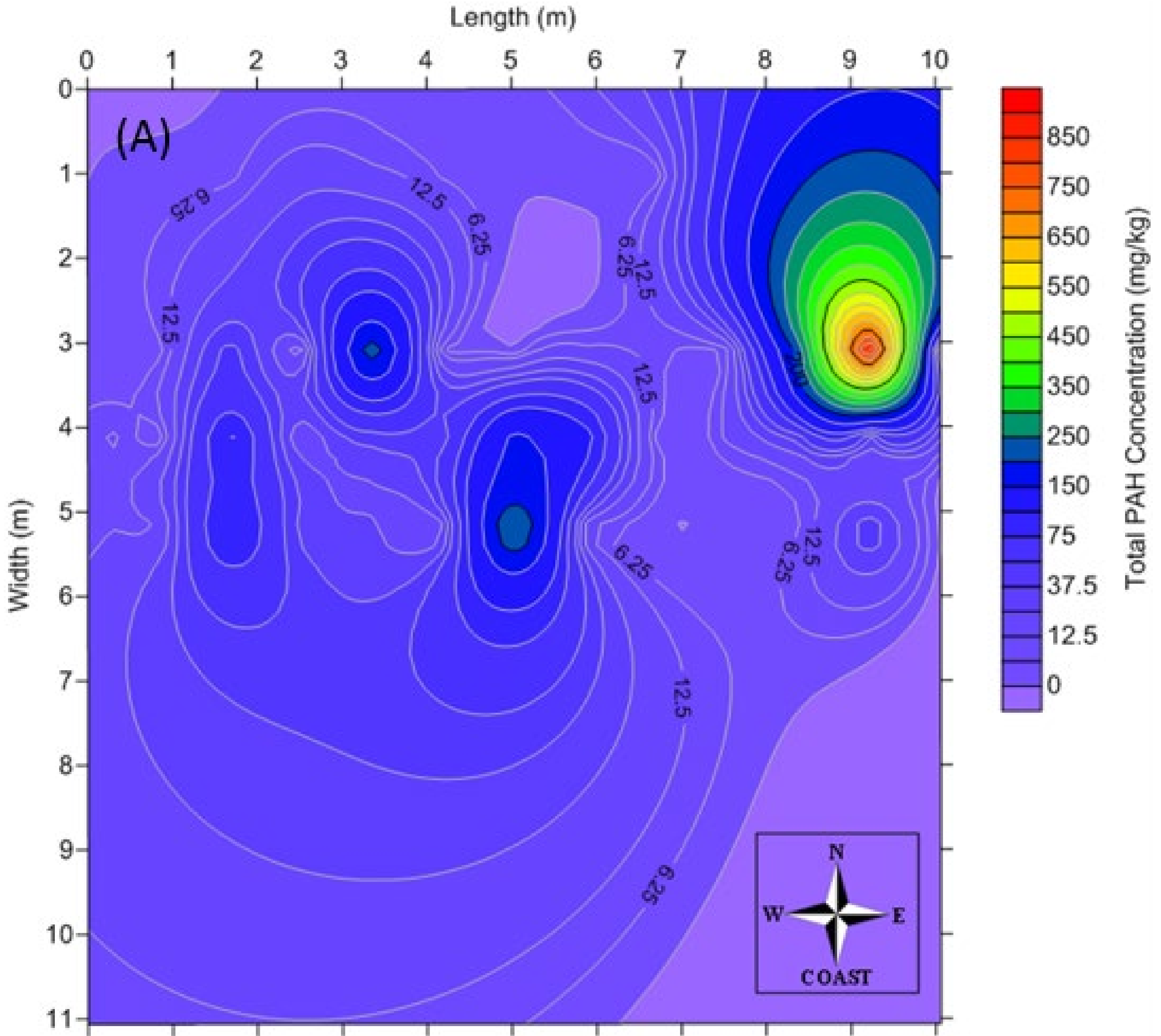


Phase	Total PAH Range (mg/kg)	Total PAH Mean ± s.e. (mg/kg)
Pre-P1	3.00 – 1,714	256 ± 126
Post-P1	0.65 – 1,052	65.4 ± 24.2



POST-P1 Results
ALK Degradation & Distribution

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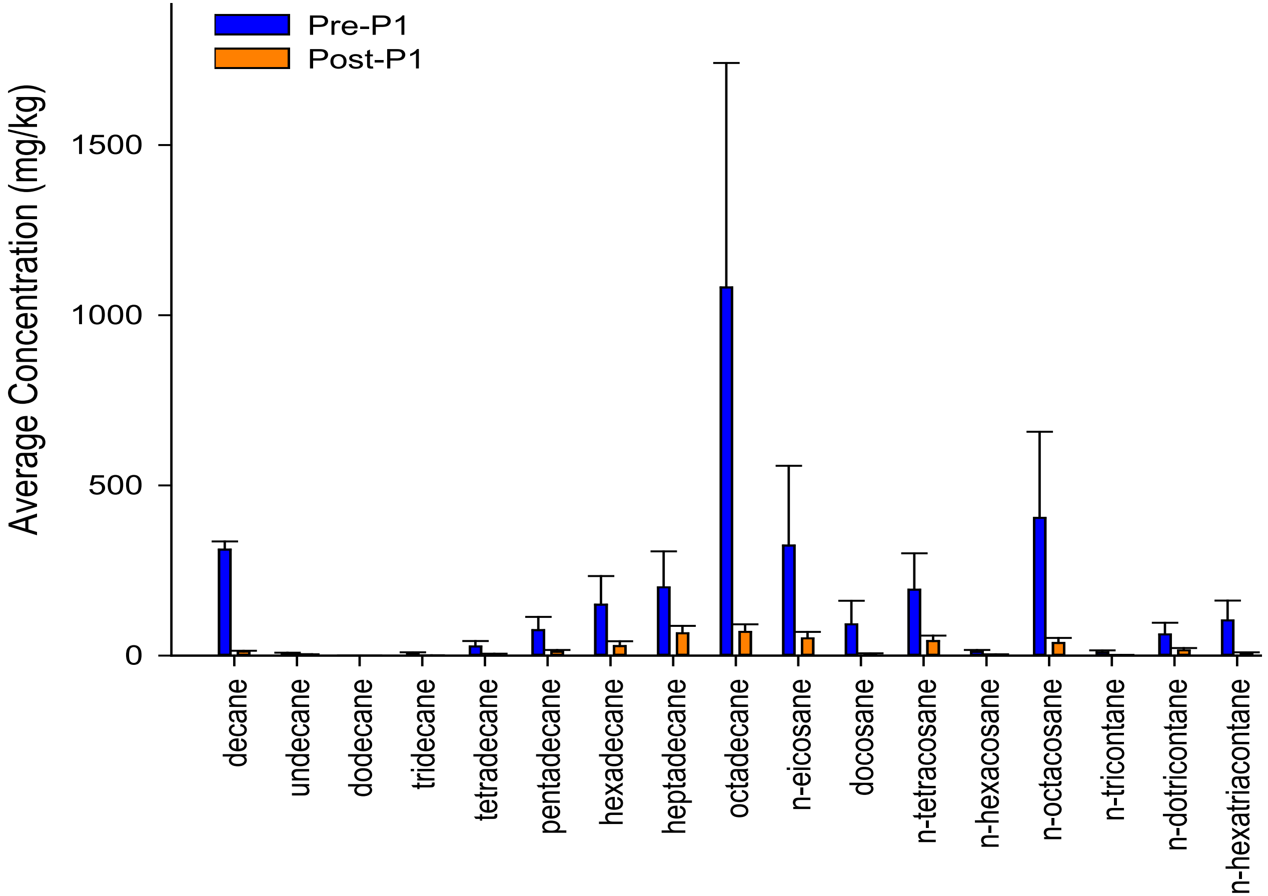

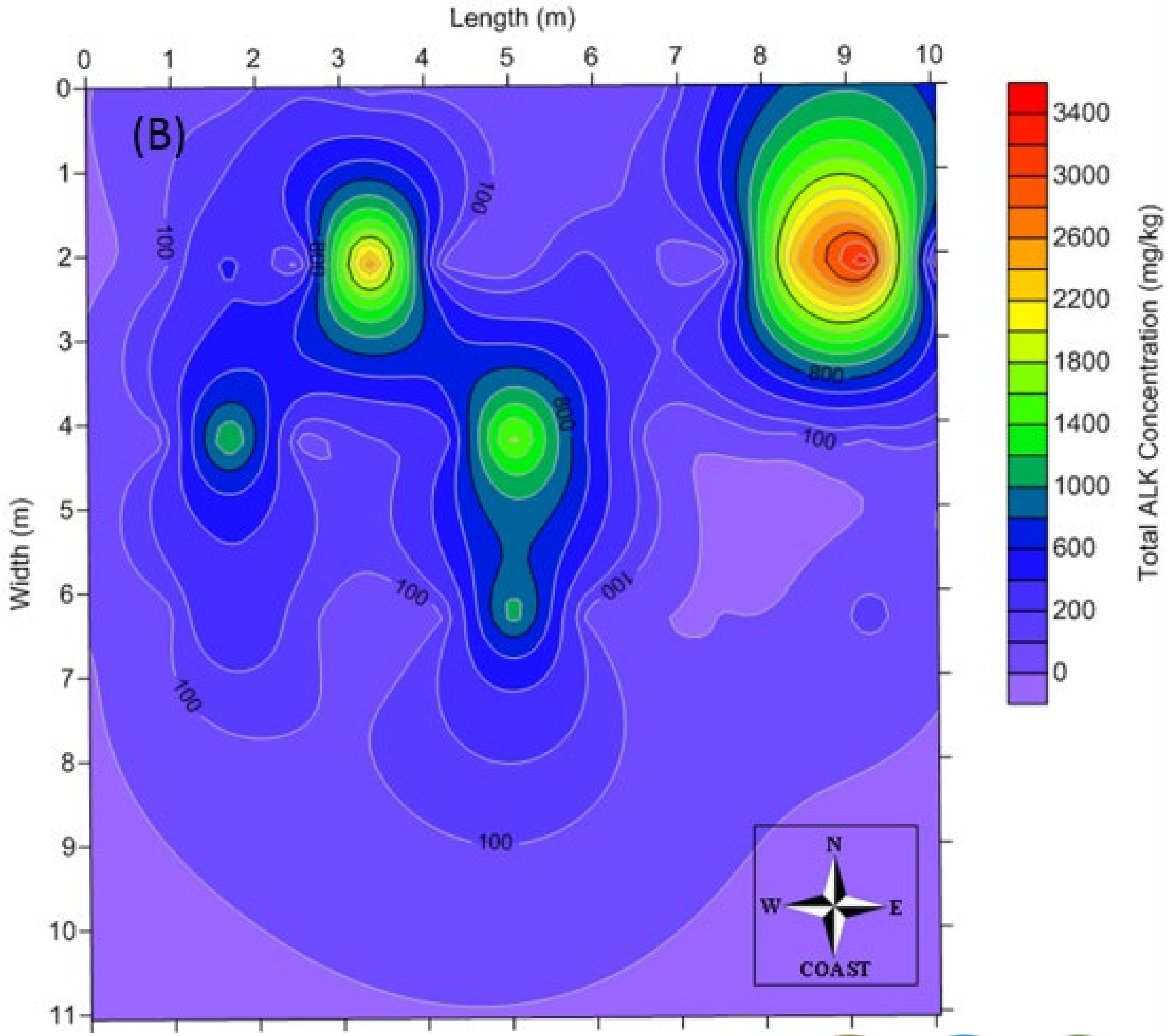

Phase	Total ALK Range (mg/kg)	Total ALK Mean ± s.e. (mg/kg)
Pre-P1	235 – 27,922	3,064 ± 1,672
Post-P1	2.11 – 3,394	357 ± 110

POST-P1 Results
Microbial Community

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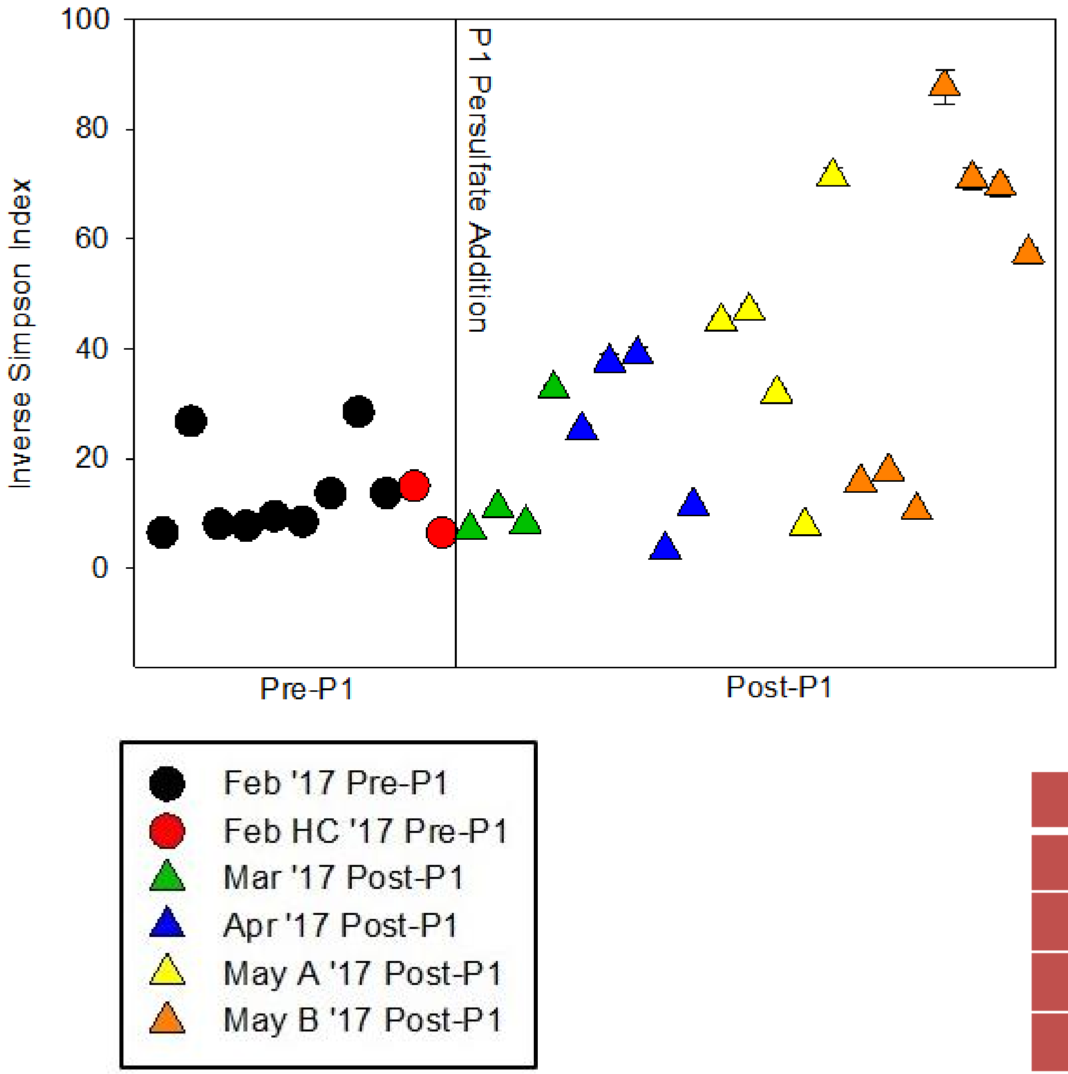
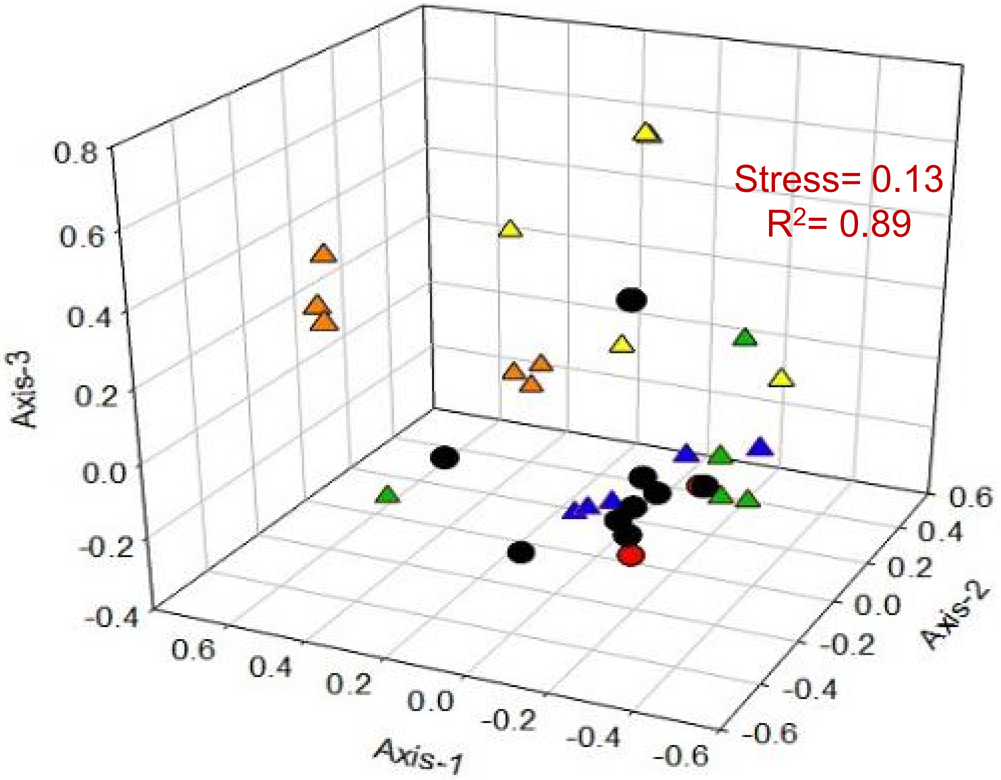
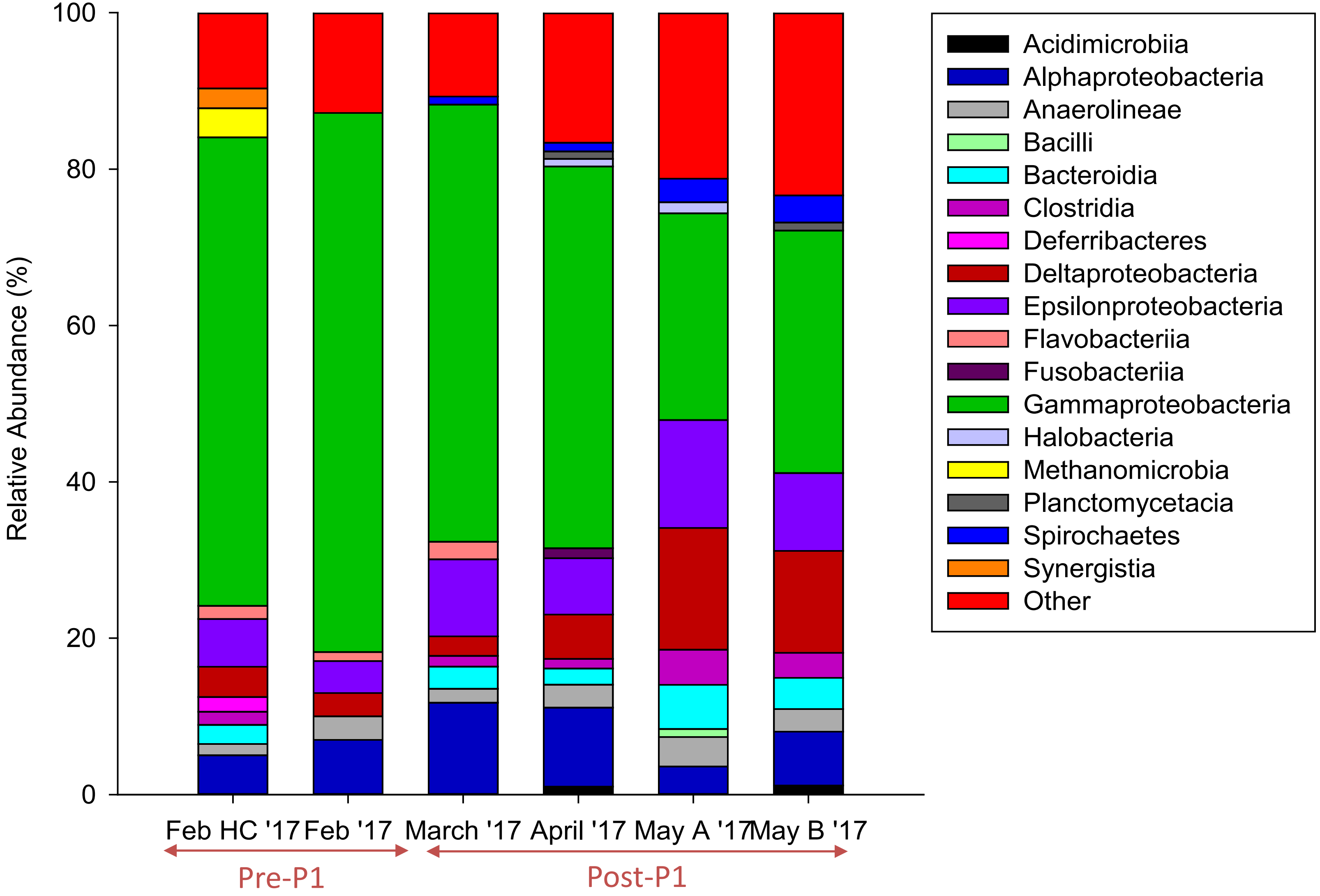




Comparison	AMOVA p-value
Feb Pre-P1 vs. Mar Post-P1	0.01
Feb Pre-P1 vs. Apr Post-P1	0.04
Feb Pre-P1 vs. May A Post-P1	0.001
Feb Pre-P1 vs. May B Post-P1	0.001

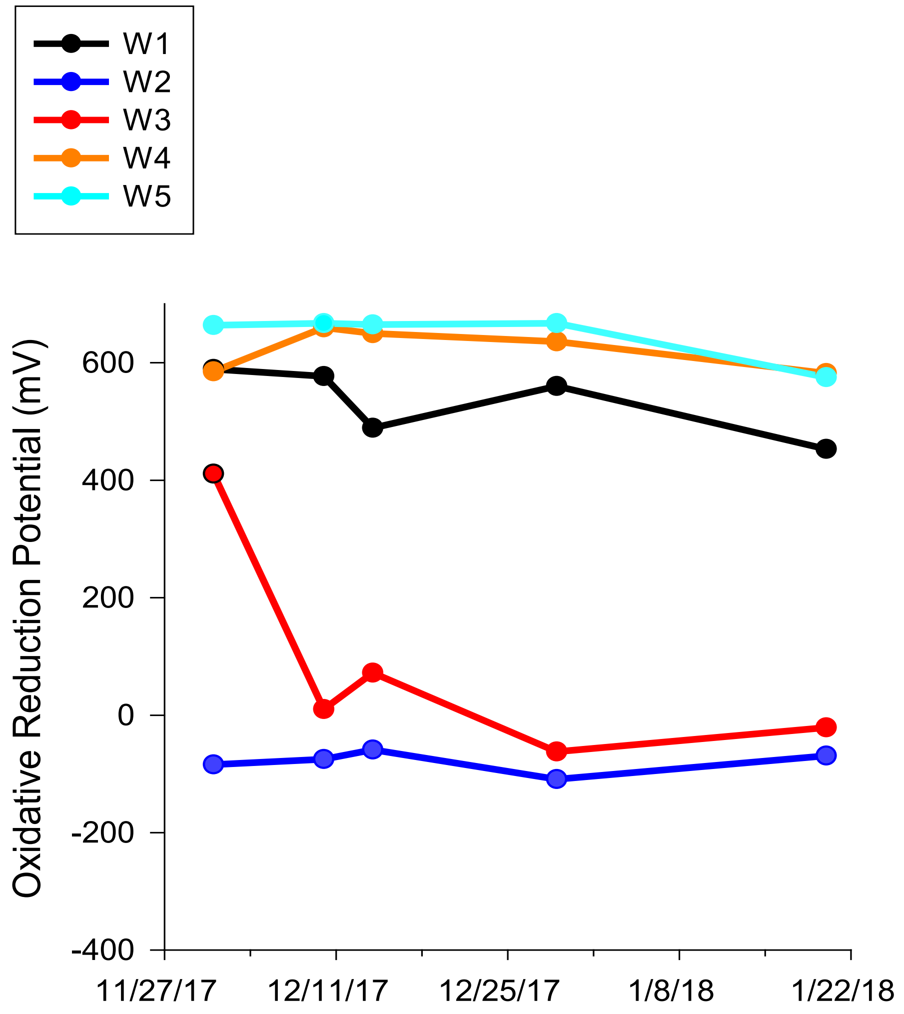
POST-P1 Results
Microbial Characterization

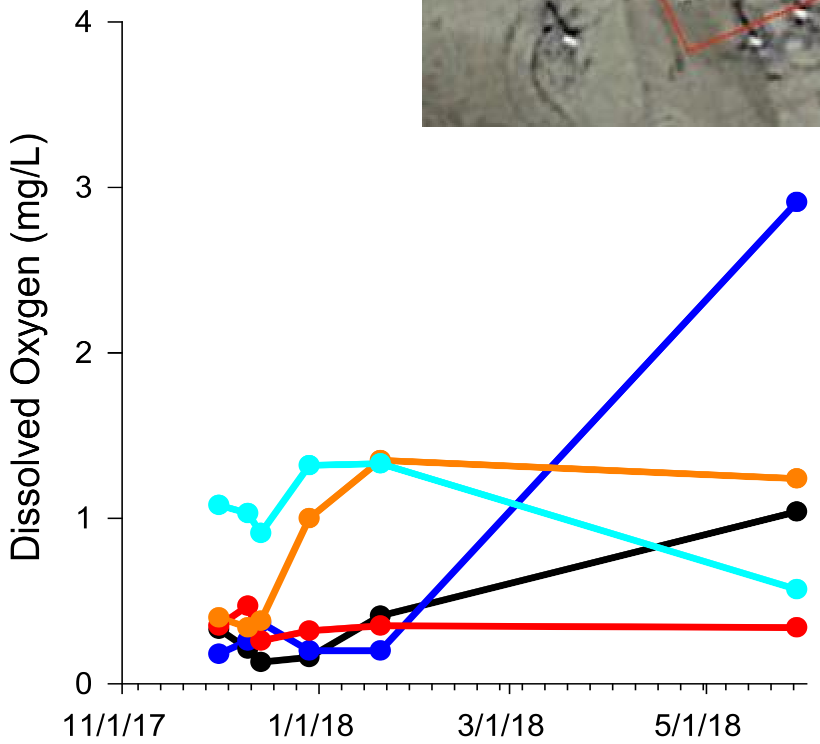


POST-P1 Results
Lefse Analysis

Identification	Abundance (%)					
	Pre-P1		Post-P1			
	Feb HC	Feb	March	April	May-A	May-B
Alcanivorax	4.1E-01	2.0	10	1.3	7.2E-02	5.1E-01
Desulfosalsimonas	4.0E-02	6.2E-04	5.0E-02	1.6E-01	1.4	9.7E-01
Halanaerobium	4.7E-01	5.8E-02	8.0E-02	1.1E-01	2.2	1.4
Halomonadaceae	3.8	2.0	3.9E-01	6.4E-01	6.6E-01	5.2E-01
Halomonas	2.0E-01	3.3E-02	5.0E-03	2.0E-03	6.0E-03	7.1E-03
Idiomarina	1.8	8.9E-01	2.8	2.2	2.1E-01	1.8E-01
Marinobacter	40	33	27	27	11	5.8
Methylohalobius	2.5E-02	9.4E-04	1.0E-02	2.0E-03	2.0	6.3E-01
Porticoccus	1.9E-01	1.2	5.1E-01	1.5E-01	8.0E-03	1.6E-02
Rhodobacteraceae	2.7	3.4	7.5	4.7	1.5	1.4
Sediminimonas	9.5E-02	1.9E-01	1.0	2.0E-03	1.5E-01	2.2E-01
Spirochaeta	5.2E-01	5.5E-01	8.6E-01	2.4E-01	2.5	2.7
Sulfurimonas	5.7	3.3	8.5	3.6E-01	8.9	8.3
Sulfurovum	1.0E-01	7.4E-01	1.8E-01	1.1	2.1E-01	1.7
Thiomicrospira	4.5	1.9	4.8	6.1	8.3	4.6
Thermovirga	2.1	3.3E-02	1.3E-02	1.2E-02	1.6E-01	6.4E-02

POST-P2 Results
Groundwater





Results

Oxygen Demand Study

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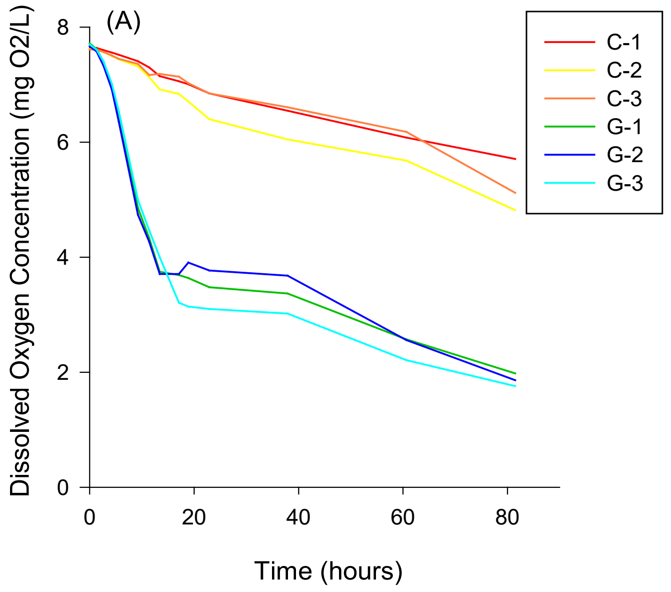
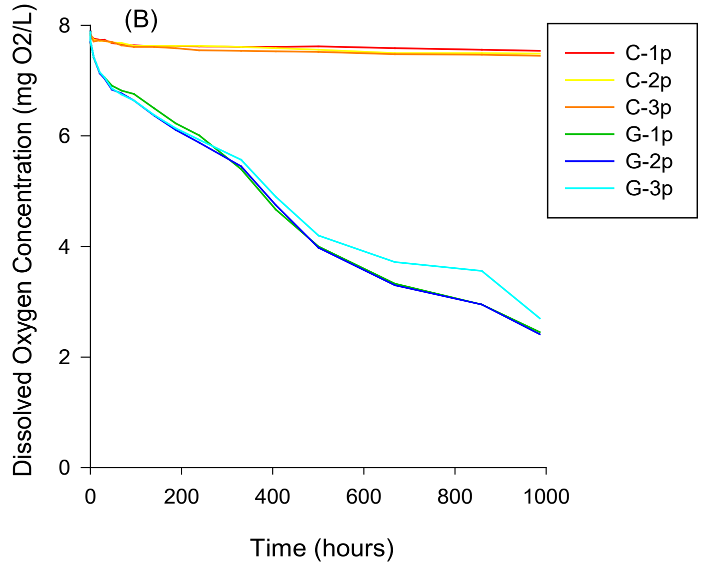
UNTREATED



TREATED



Sample	Treatment	O_2 Demand ($mg\ O_2/L\text{-}hr$)	R^2
Control (C)	Untreated	0.029	0.967
	Treated	0.00037	0.795
Groundwater (G)	Untreated	0.319	0.965
		0.0271	0.939
	Treated	0.00530	0.962

Treatment	Ferrous Iron (mg/L)	Sulfide (mg/L)
Untreated	0.0901 ± 0.02	64.6 ± 0.80
Treated	0.00672 ± 0.01	N.D.

Summary of Results

- Oxidation of reduced chemical species represent major oxygen sinks in intrinsically reducing subsurface environments; can affect aerobic bioremediation outcomes
- Chemical oxidation phase decreased concentrations of PAH/ALK and allowed for more efficient addition of applied oxygen to be used in aerobic bioremediation phase
- Perturbation of microbial community after P1 but increase in diversity after 3 months and increased O_2 levels after P2

Next Steps: Determine impact on microbial community post-P2 and monitor aerobic bioremediation phase

Acknowledgements

Funding provided by GOMRI and the Edward J. Wisner Donation

GULF OF MEXICO RESEARCH INITIATIVE

Edward J Wisner Donation,
New Orleans, LA