F-102, in: T.C. Fox and H.V. Rectanus (Chairs). *Remediation of Chlorinated and Recalcitrant Compounds—2012.* Eighth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2012). ISBN 978-0-9819730-5-0, ©2012 Battelle Memorial Institute, Columbus, OH, **www.battelle.org/chlorcon**.

Anaerobic Degradation of Chlorinated Ethenes in a Low-pH, High-Sulfate, and Saline Environment

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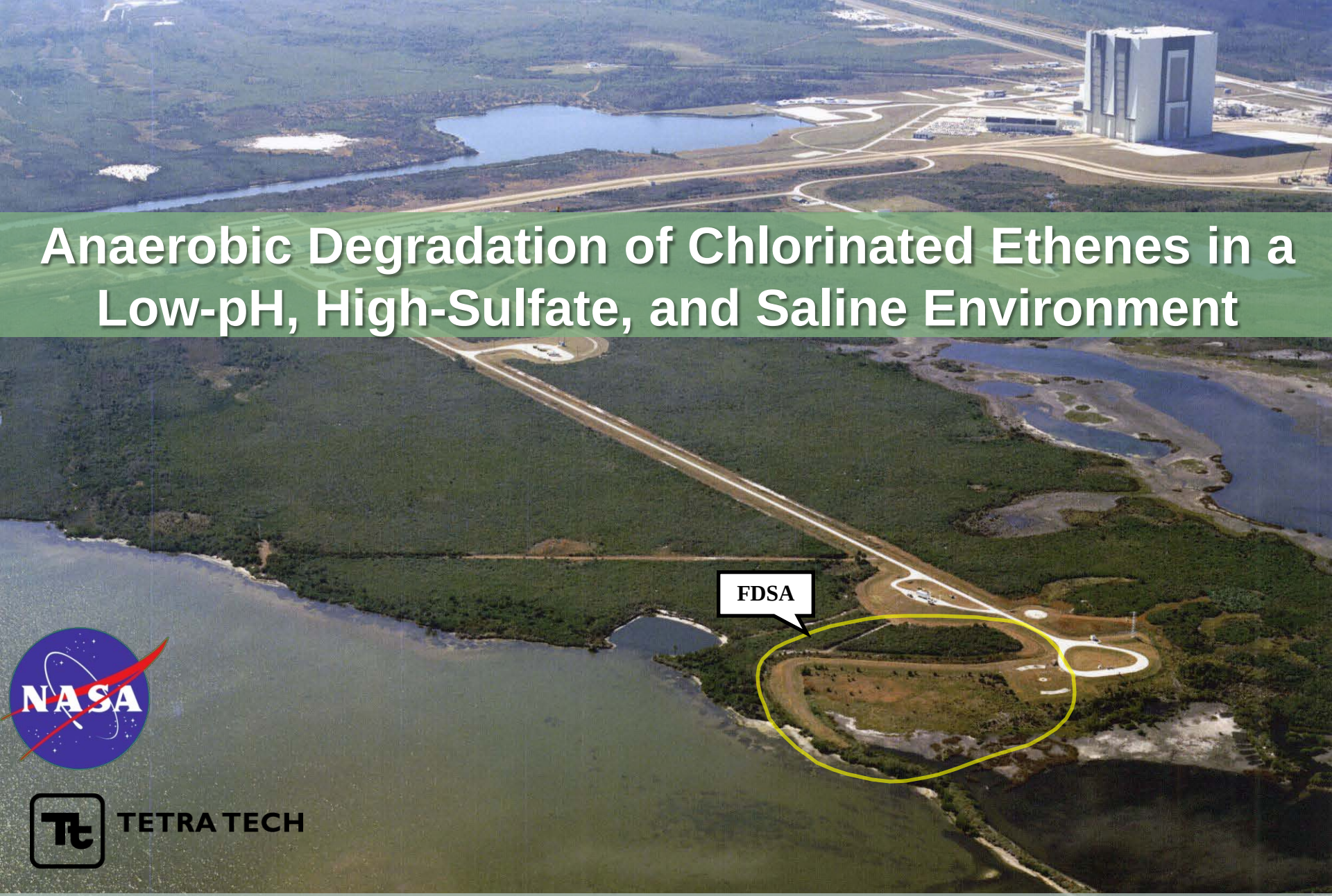
Background/Objectives. Implementing anaerobic biostimulation for chlorinated ethene degradation in groundwater with low pH and high sulfate and chloride levels can be challenging, even unsuccessful in many cases. An anaerobic biostimulation interim measure is currently under implementation and optimization at the NASA Former Drum Storage Area (FDSA) at Kennedy Space Center under these conditions. The site is situated in a remote area containing marshes and scrub-brush cover and is adjacent to a brackish surface water body classified as Outstanding Florida Water (OFW). Under this classification, no degradation of surface water may occur; therefore no detectable level of any contaminant is allowed. The horizontal extent of a chlorinated ethene plume is approaching the OFW, and an interim measure was implemented at the plume front via a biological treatment zone. The treatment zone consists of extraction and injection wells, electron donor addition, and a solar-powered recirculation system.

Approach/Activities. Data gathered during the first 6 months of interim measure activities indicated favorable trichloroethene and cis-1,2-dichloroethene reduction in plume front concentrations. Interestingly, vinyl chloride was not detected at treatment zone monitoring locations. Highly reducing conditions were created within the entire treatment zone as a result of electron donor addition and recirculation. Groundwater within the treatment zone was brackish with concentrations of sulfates and chlorides within a several grams per liter range. Stoichiometric parent/daughter relationships and site geochemistry suggest that degradation mechanisms were complex in nature compared to classic reductive dechlorination by the ethenogen *Dehalococoides spp.* (DHC). Populations of DHC were present, but activity is suspected to be fairly inhibited because chloride and sulfate levels, low pH , and iron and manganese may be limited for coprecipitation. Molecular biological tools (MBTs) indicated a robust consortia of varying microbial populations, primarily eubacteria, sulfate-reducing bacteria, methanogens, and DHC. Based on this information, a dynamic microcosm testing protocol was developed and will be executed to provide a better understanding of the degradation mechanisms operating at the site.

Results/Lessons Learned. The microcosm testing examined microbial electron donor competition, biological mechanisms, specialized bioaugmentation acclimation, and abiotic influences. As a result of microcosm testing, potential modifications currently under evaluation include specialized nutrient/vitamin supplementation, pH adjustment, and bioaugmentation with a low-pH and chloride-tolerant DHC strain. Additionally, the

feasibility of culturing indigenous microbial populations acclimated to the site's geochemical conditions is being considered.

Anaerobic Degradation of Chlorinated Ethenes in a Low-pH, High-Sulfate, and Saline Environment



NASA, Kennedy Space Center – *Michael J. Deliz, PG, Robert A. Kline, PE*

Tetra Tech - *Chris Hook, PE, Mark Jonnet, Boris Dynkin, PE, Chris Pike, PE*

Objectives

- Site overview
- IM pilot study summary
  - Design
  - Geochemical data
  - Biological data
  - Pilot study modifications
  - Contaminant data
- Path forward

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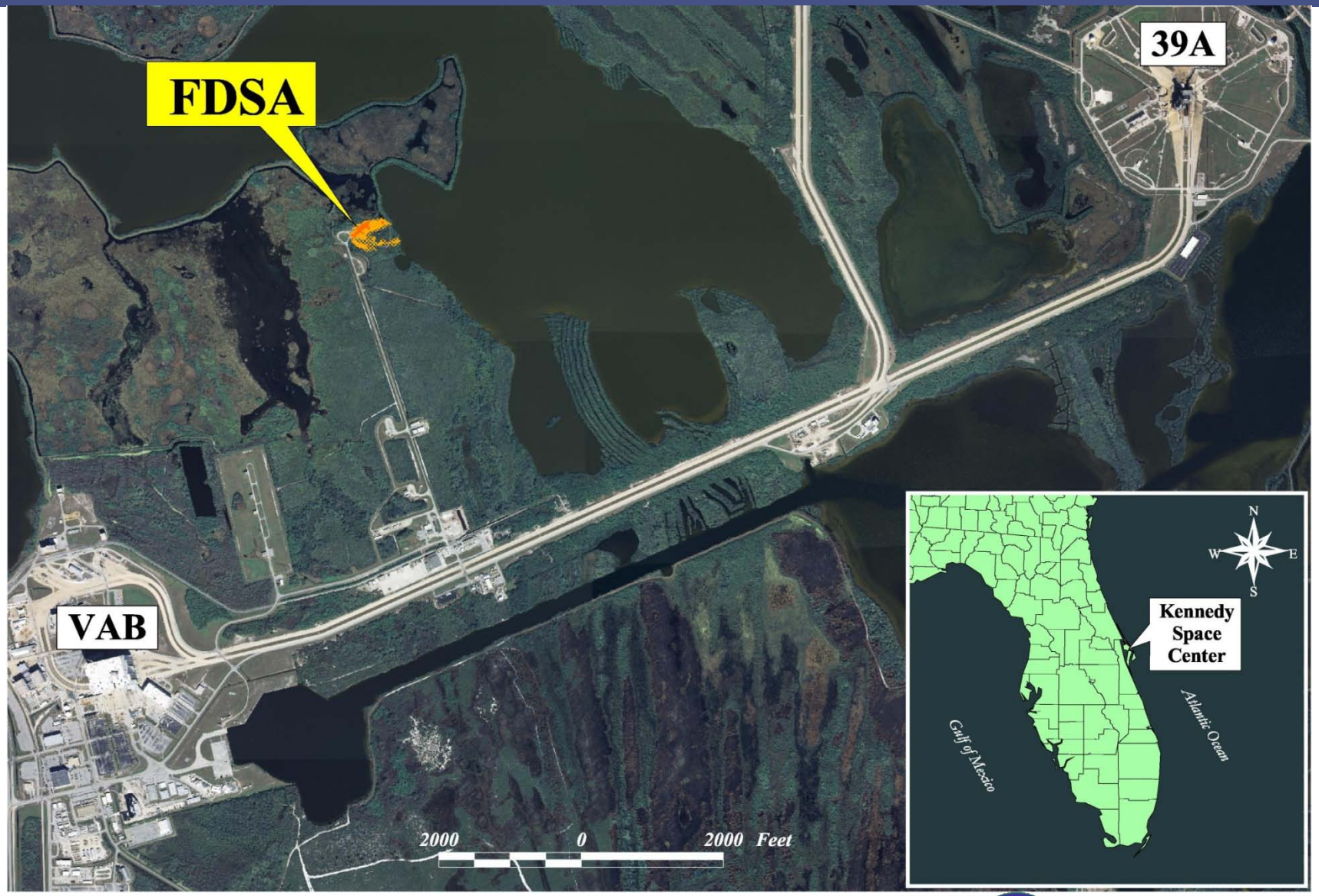
Site Location



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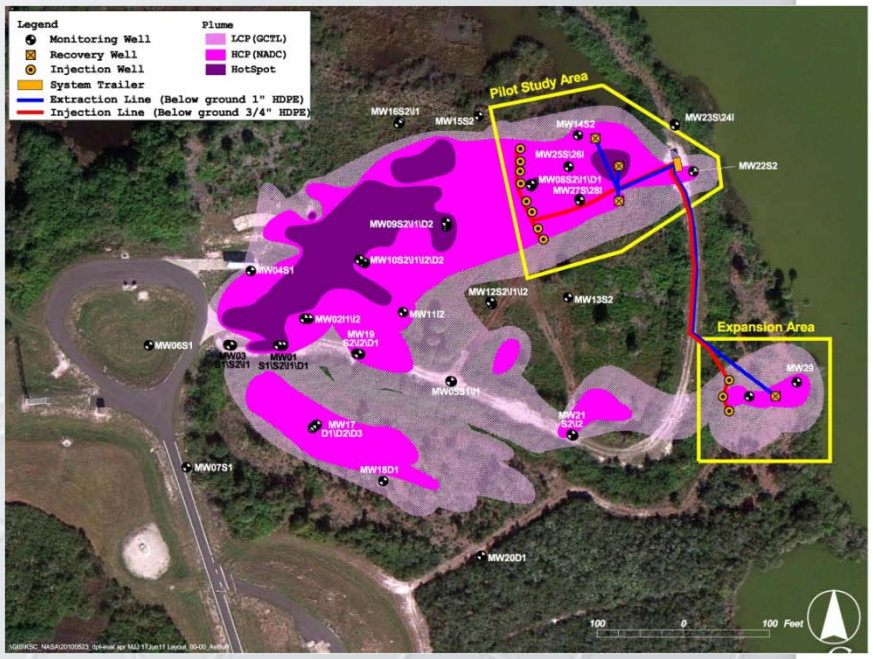
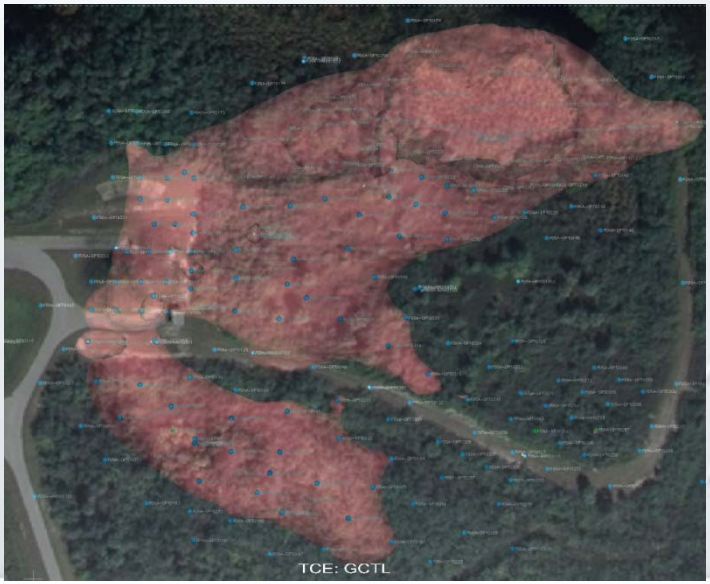
Pilot Study Introduction

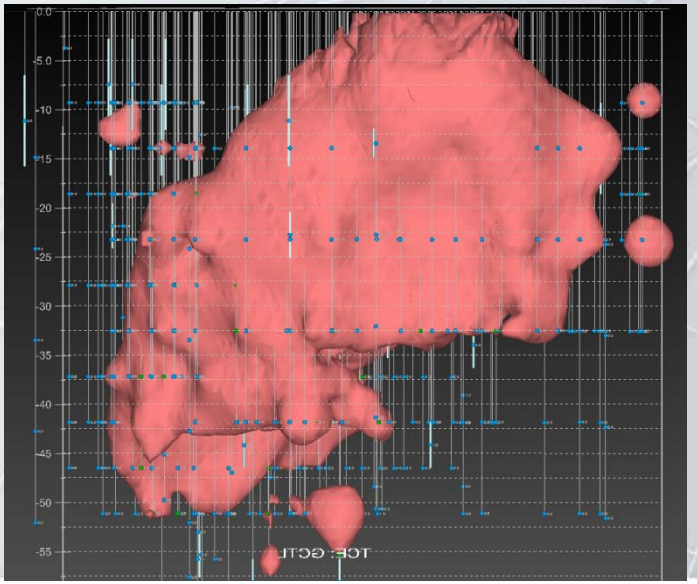
- ISB Pilot Study at Outstanding Florida Water (OFW) Area
- CMS prescribed remedy – DPT ISB
- Basis for future treatments
- Supplemental investigation fidelity resulted in changed site conditions
- Acceptable baseline biological and geochemical conditions
  - Low sulfate/sulfide
  - Low chloride
  - Neutral pH



Pilot Study Objectives

- Prevent discharge of CVOCs to OFW
- Create a zone of groundwater treatment as plume approaches OFW
- Collect data to determine the technology effectiveness
- Maintain continuous recirculation utilizing solar power
- Develop basis for expansion upgradient





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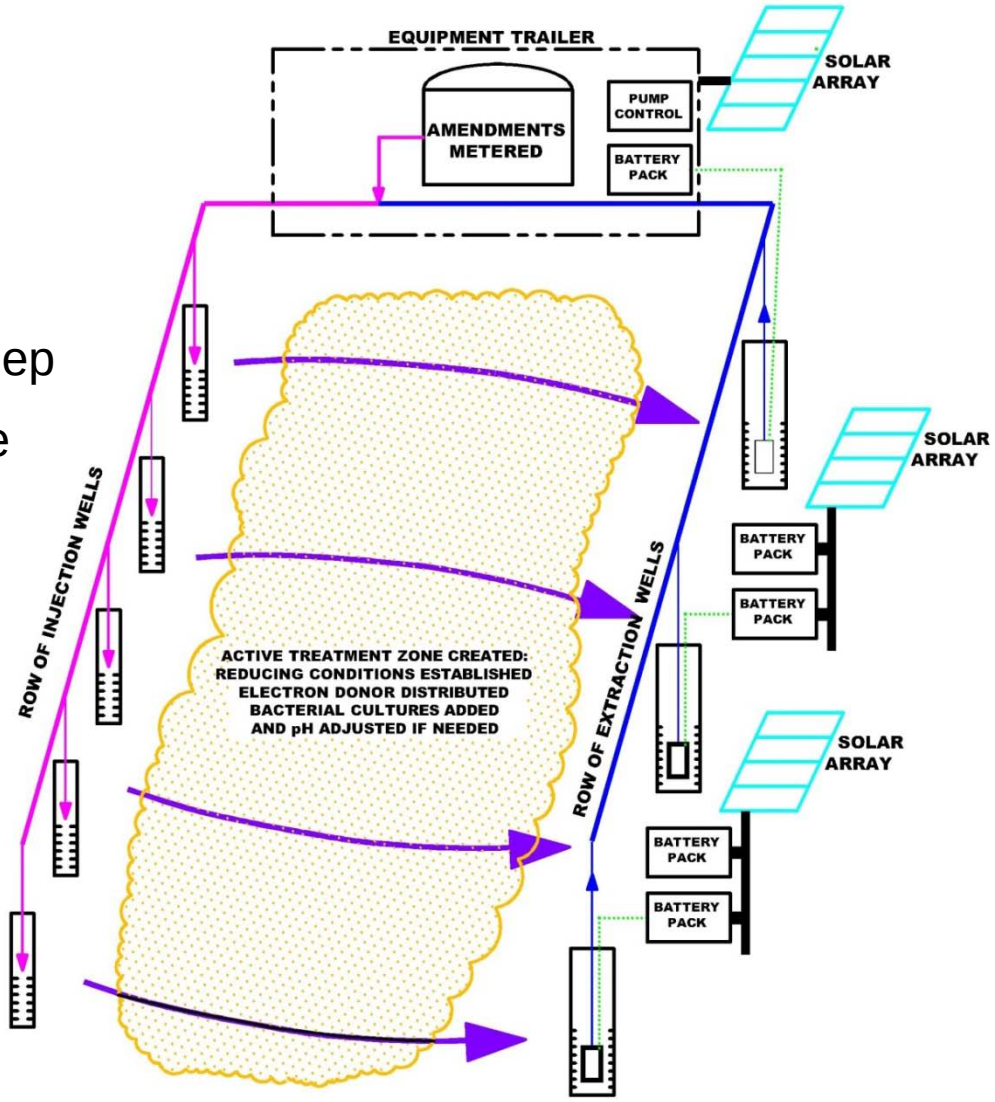
Pilot Study Design

- 3 recovery wells (3 gpm/well)
- 8 Injection wells (~1 gpm/well)
- Treatment zone:
  - ~150’ wide by ~100’ long by ~25’ deep
  - ~54 day pore volume exchange time
  - 24-hours operation via solar power
- Designed to allow use of different substrates and amendments
- Flexible manifold for active plume management
- Monitoring zones:
  - Shallow (5 – 15 feet bls)
  - Intermediate (15 to 25 feet bls)



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Pilot Study Equipment

System Trailer (view from South)

System Trailer (view from North East)

Substrate & Metering Pumps

System Stub-outs (view from West)

Manifolds & Metering Pumps

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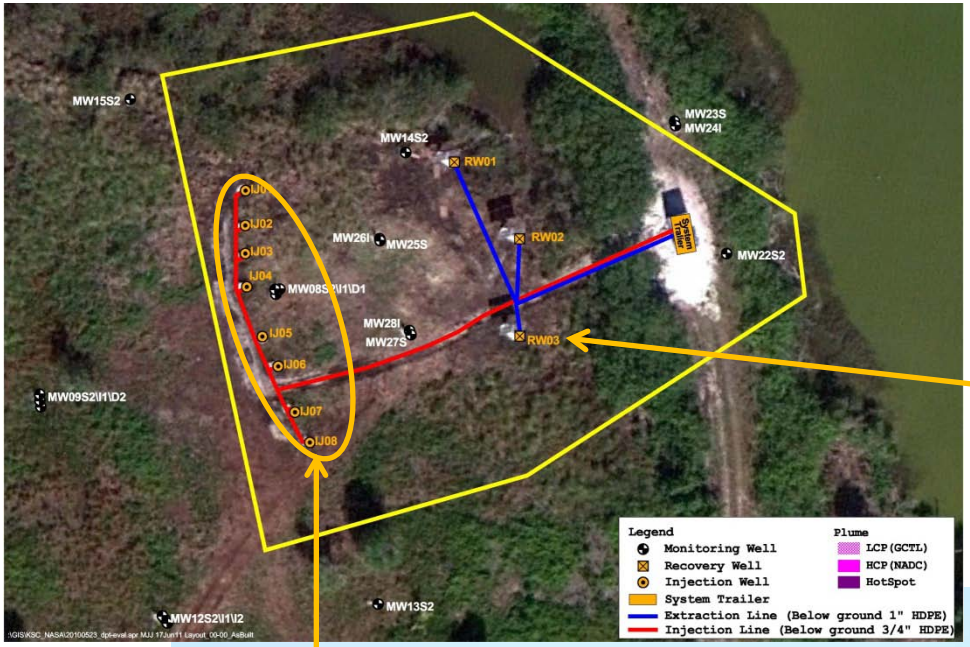
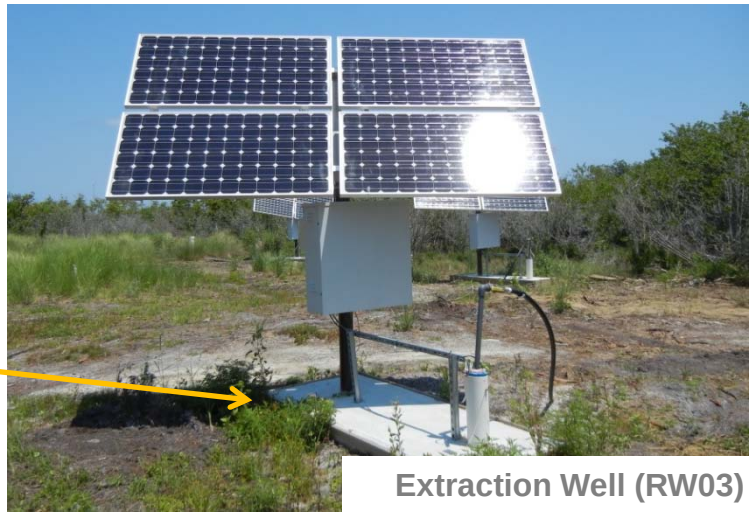
Pilot Study Injection/Extraction Layout

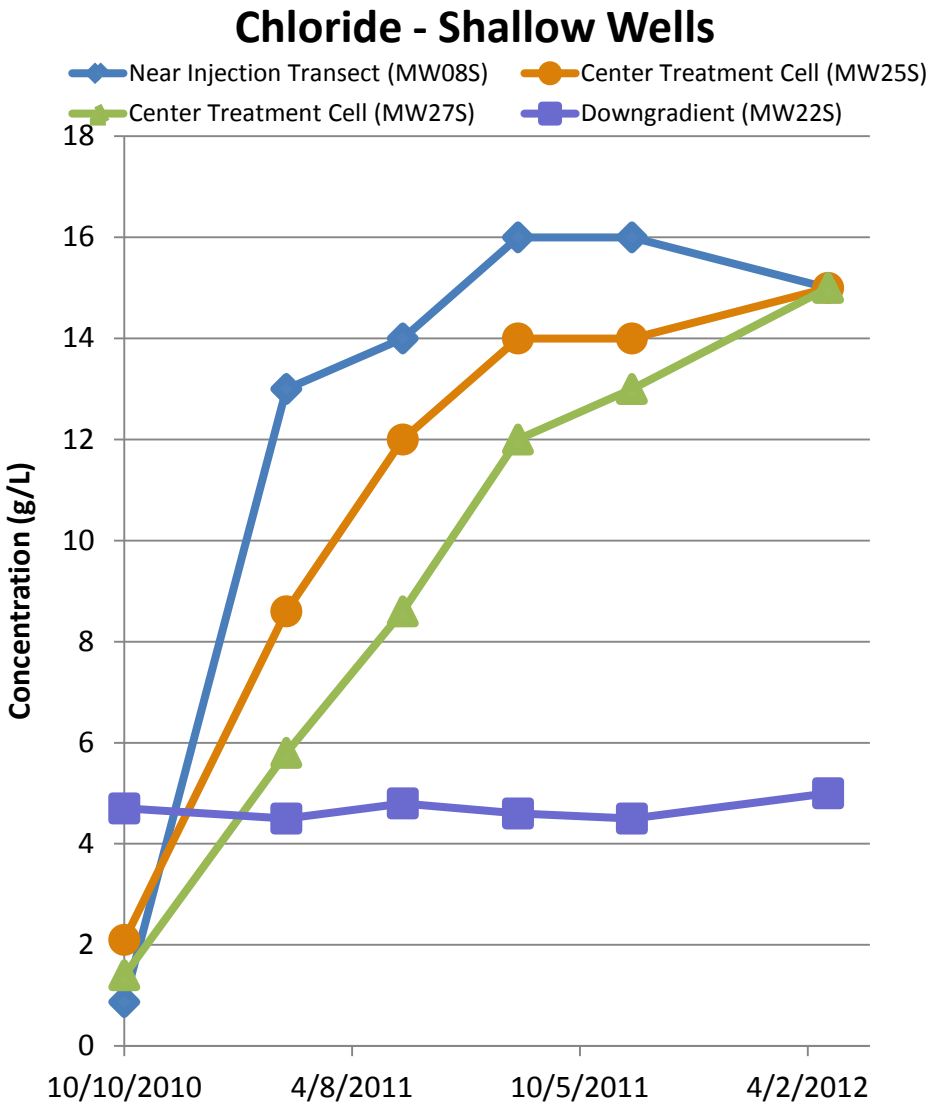


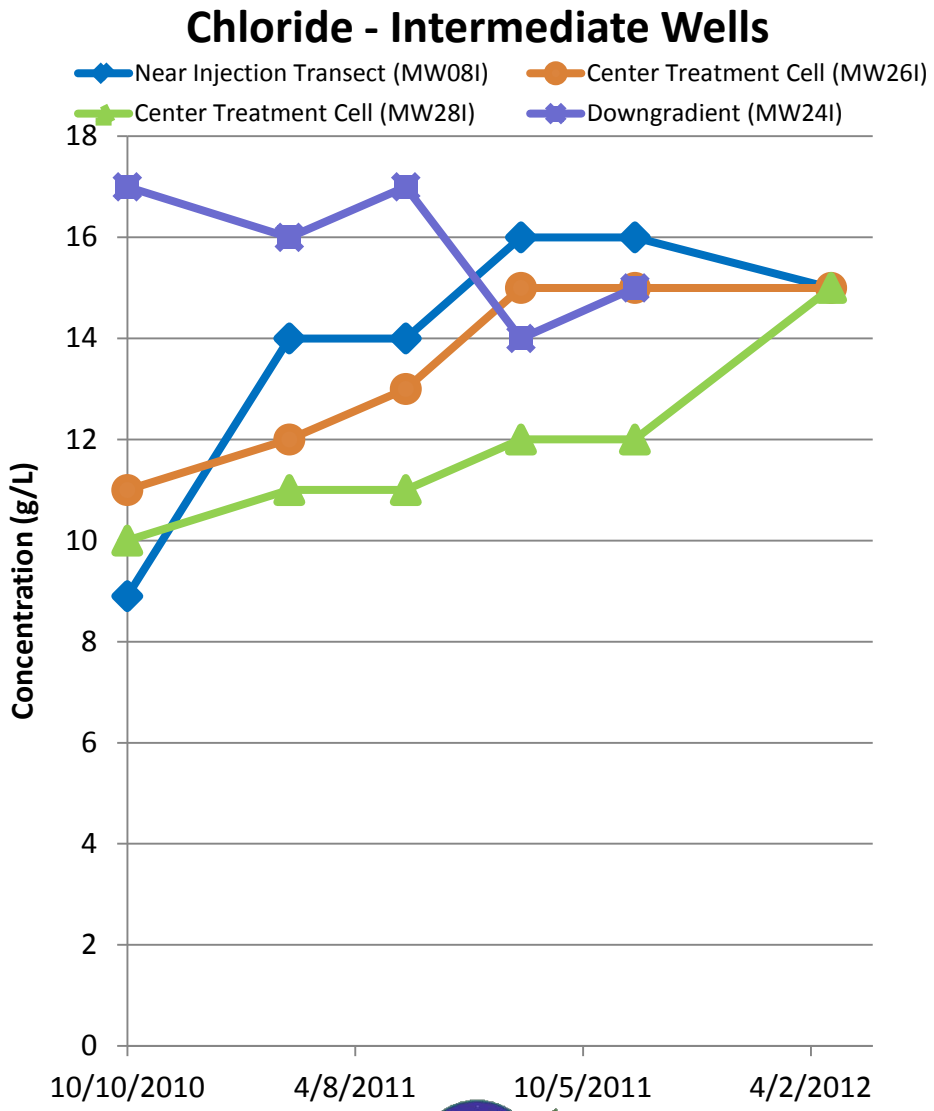


Extraction Well (RW03)

Injection Well Transect

Pilot Study Data - Chloride





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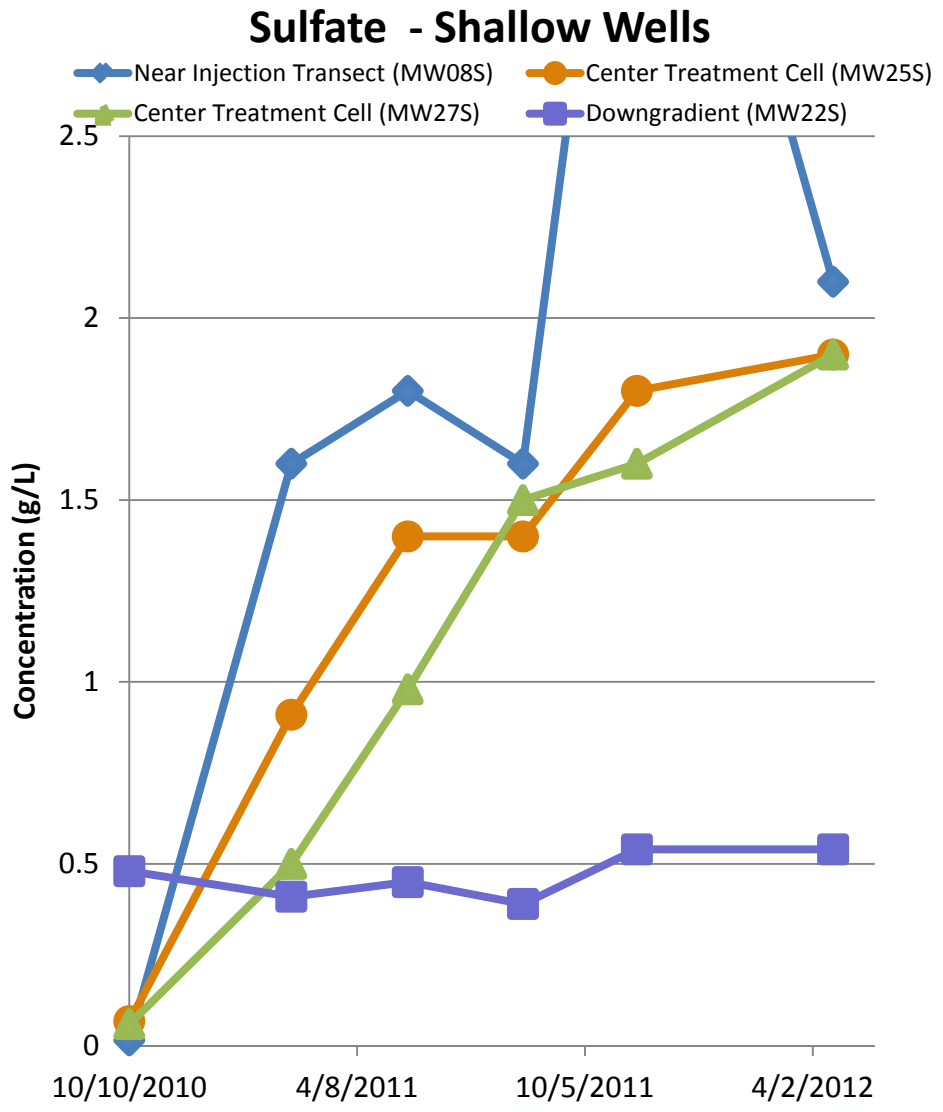
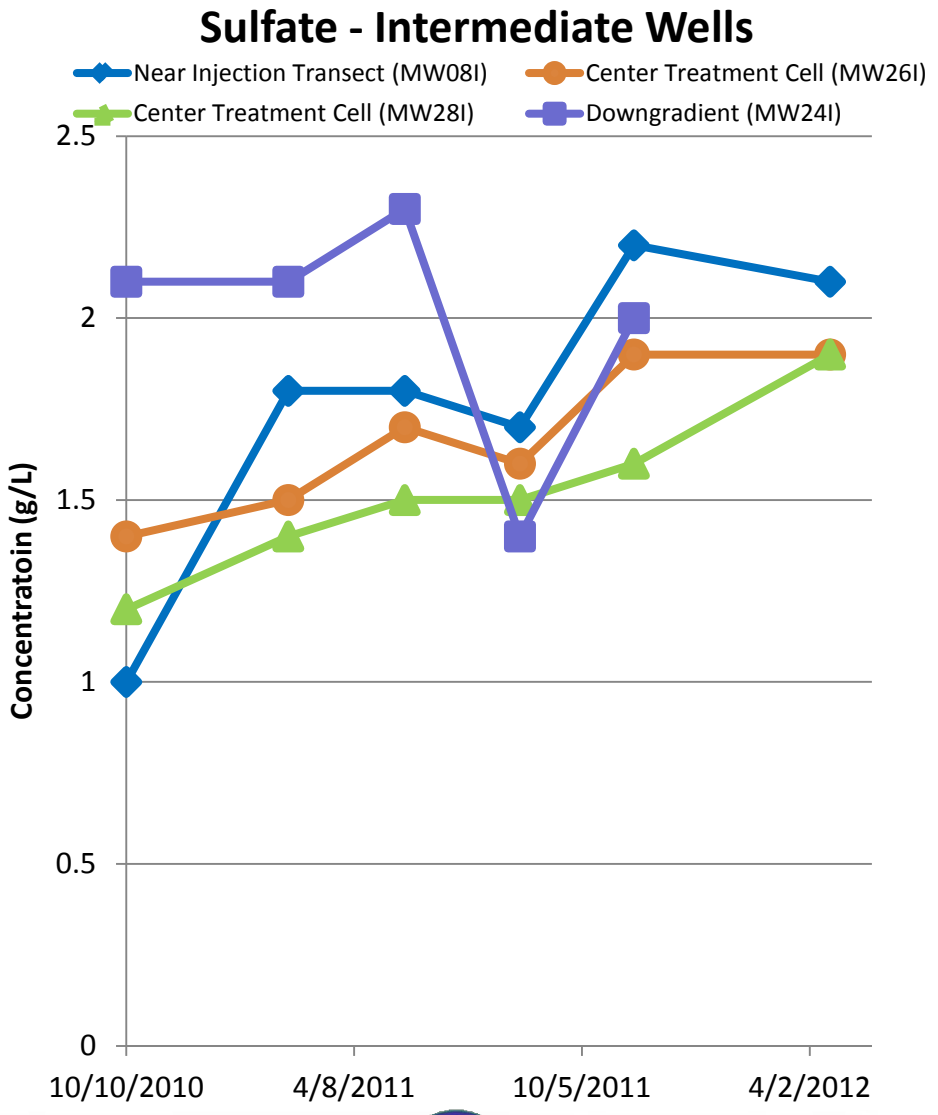
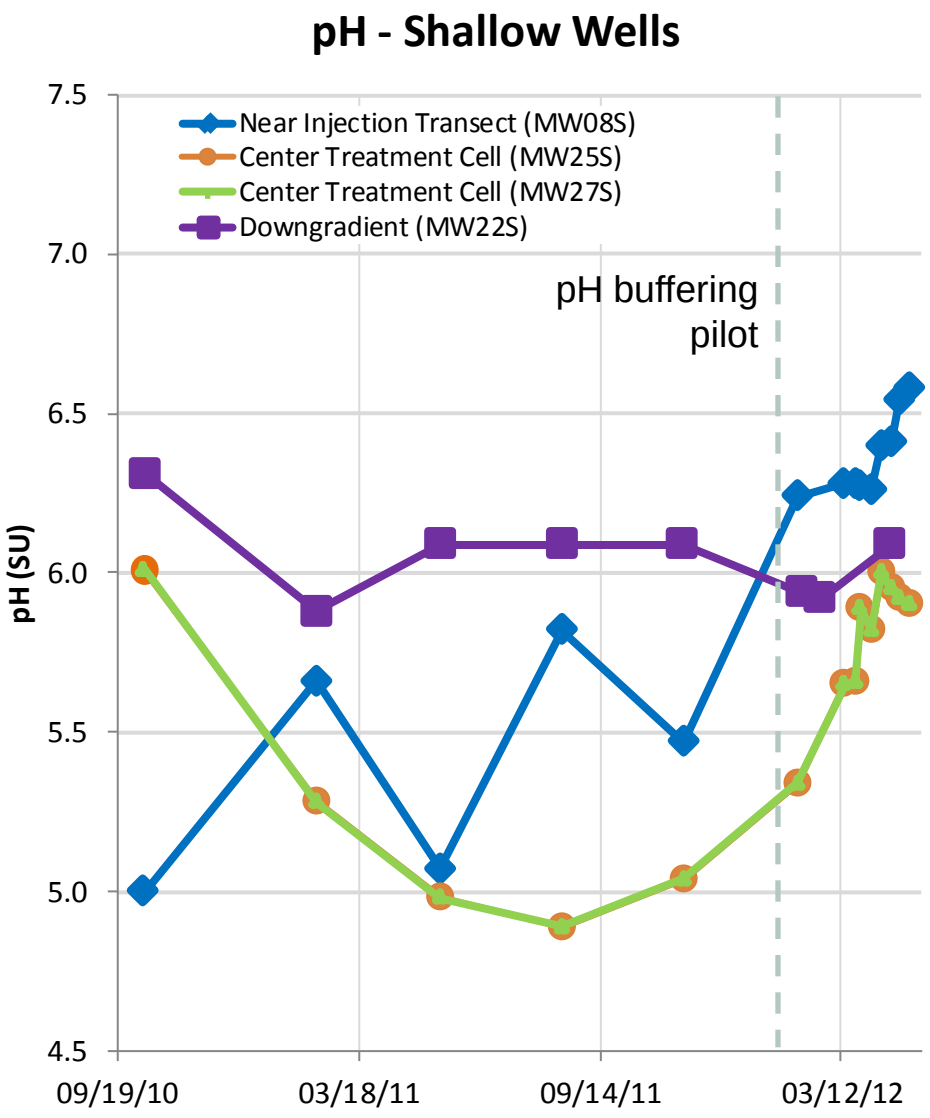
Pilot Study Data - Sulfate

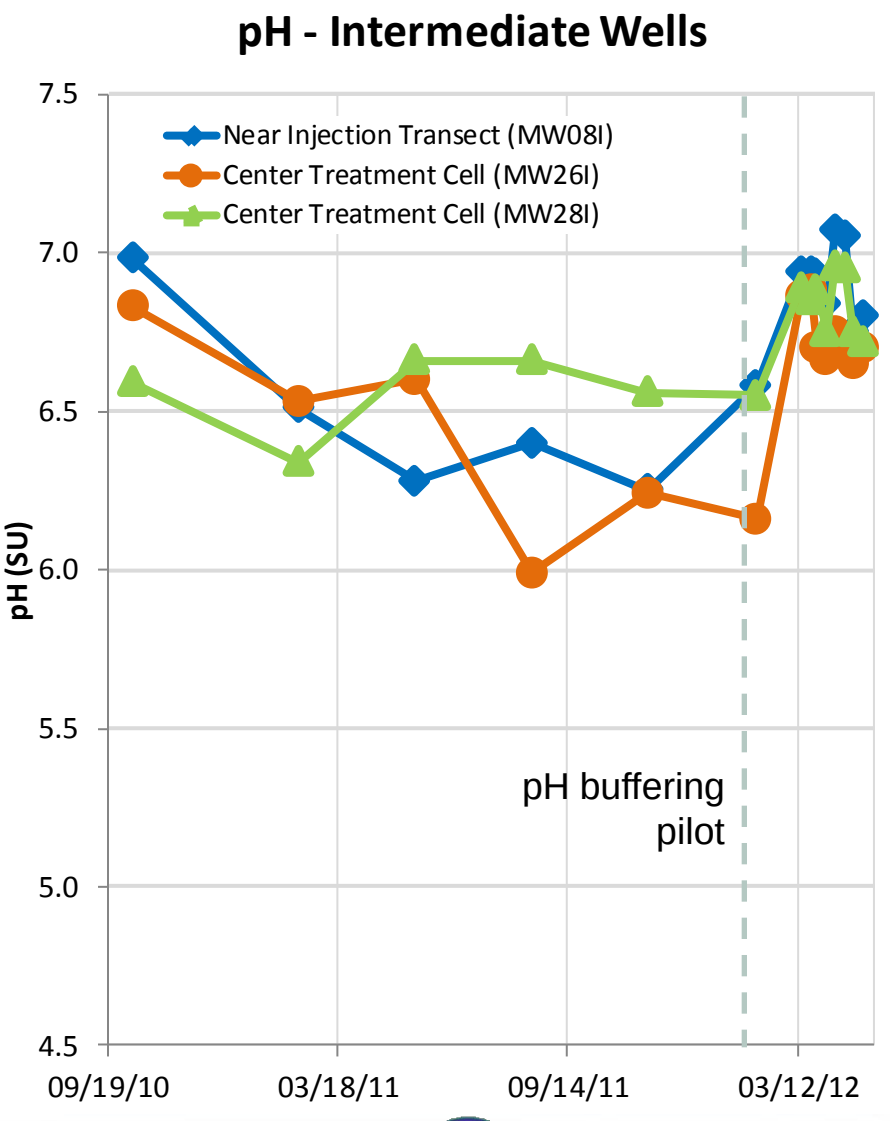




*Sulfide historically ranges from 40-100 mg/L (magnitudes <SO_3)

Pilot Study Data – pH





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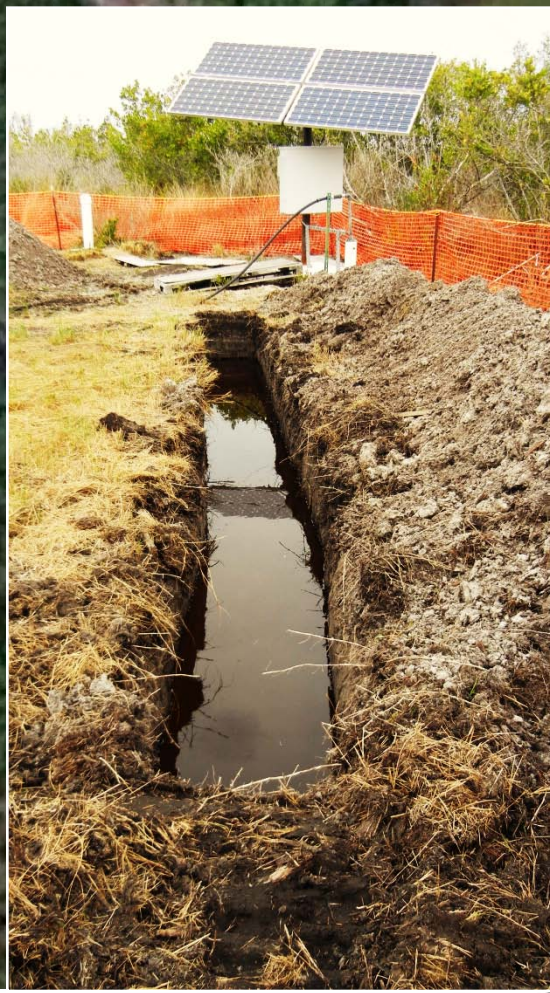
Passive Buffer Testing



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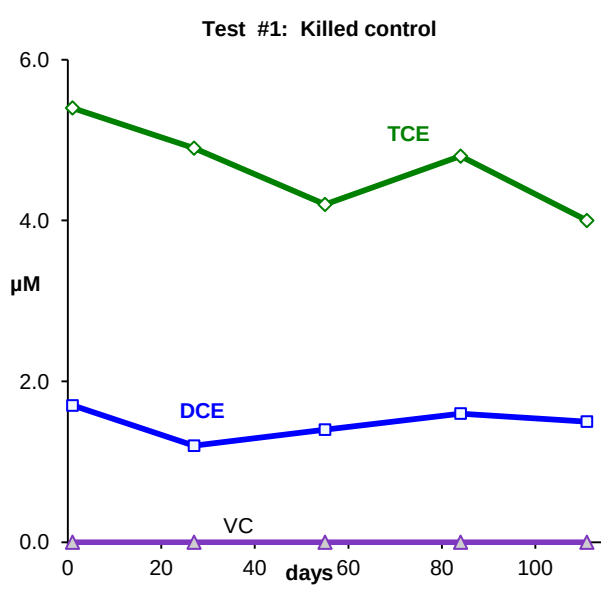
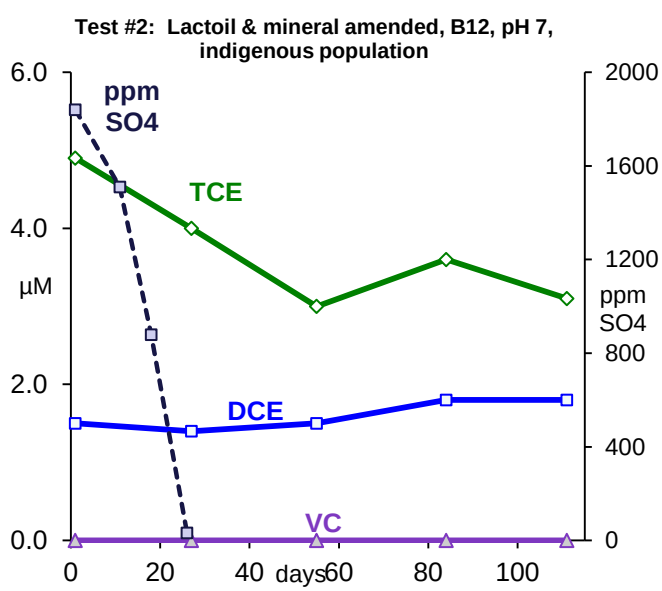
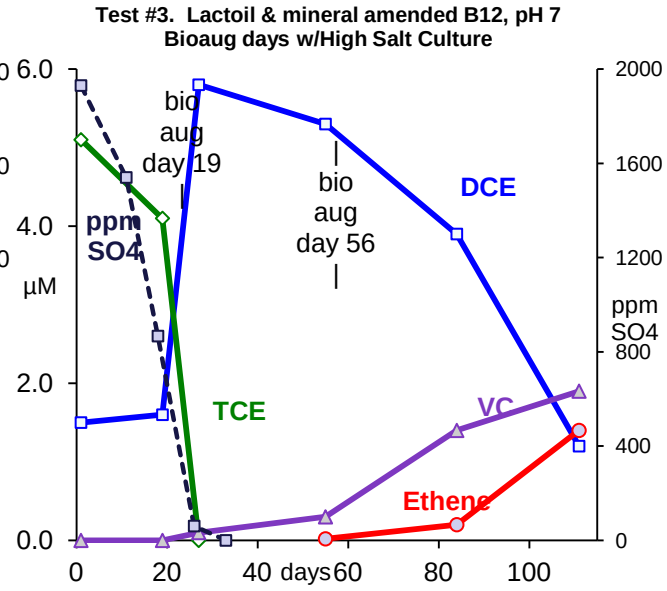
Additional Geochemical/Dissolved Gas Data

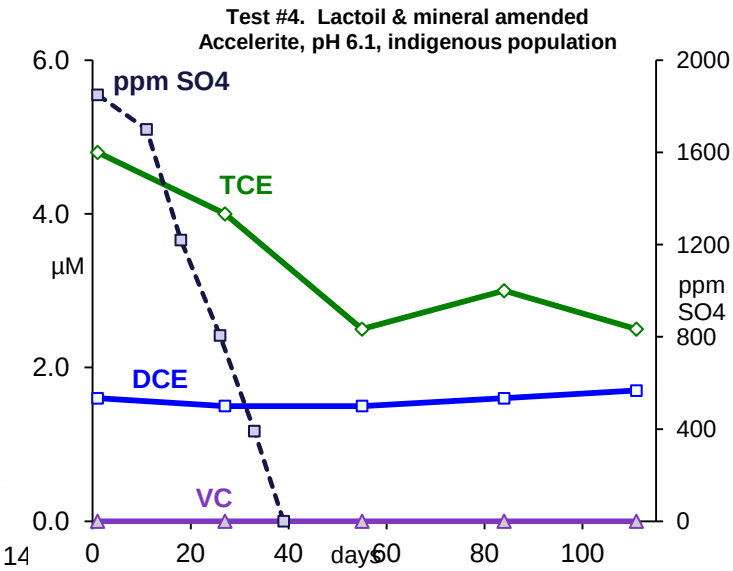
- ORP – ⁻200 to ⁻300 mV
- TOC – 20 mg/L (near injection) gradient down to 5 mg/L (near extraction)
- Alkalinity – 350 mg/L (site average)
- Acidity – 120 mg/L (site average)
- Dissolved iron (total) – 30 mg/L (site average)
  - Ferrous/ferric iron speciation variable spatially
- Dissolved Gases
  - Methane – 530 mg/L (site average)
  - Ethane – Generally ND
  - Ethene – Low/negligible detections
  - Carbon Dioxide – Initially 3 mg/L; now 234 mg/L (average)

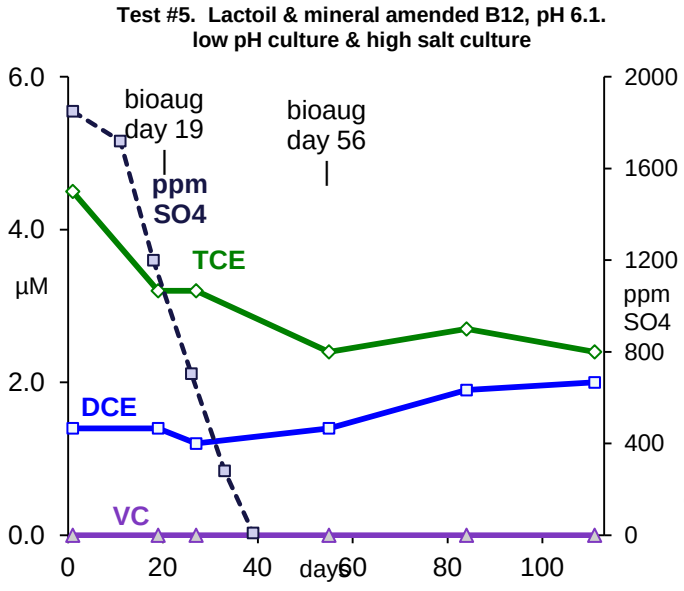
Microcosm Analysis











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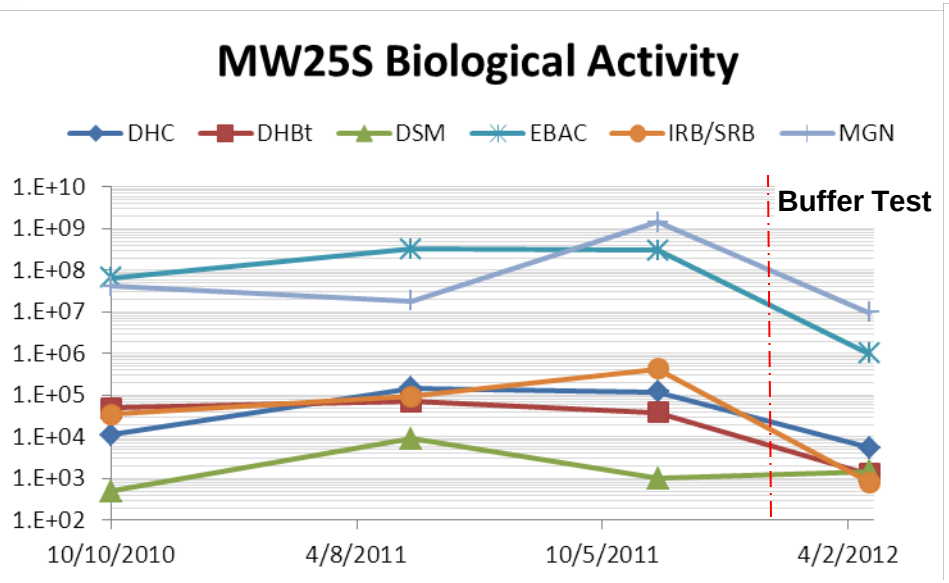
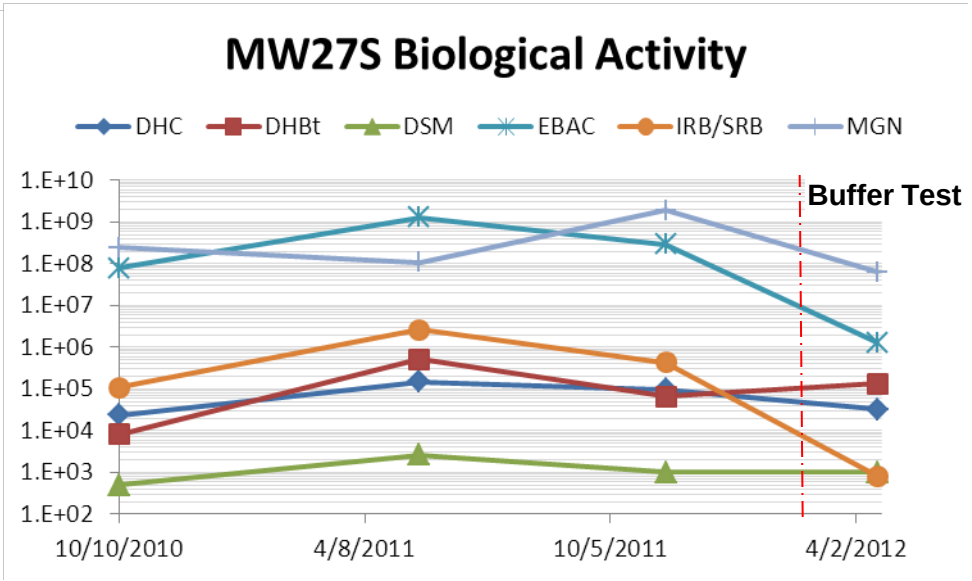
Biological Activity

- Complex mechanisms (e.g., cometabolism/beta-eliminations/etc.)
- $CaCO_3$ addition affected microbial activity (Feb 2012)
- Geochemical shifts from buffering affected IRB/SRB activity
  - Reduced competition from preferential sulfate reduction
- TCEr detected for the first time after buffering (substrate “pecking order”)
- VCr/BVC historically nondetect
- Sharp TCE concentration reductions; VC consistently detected for first time





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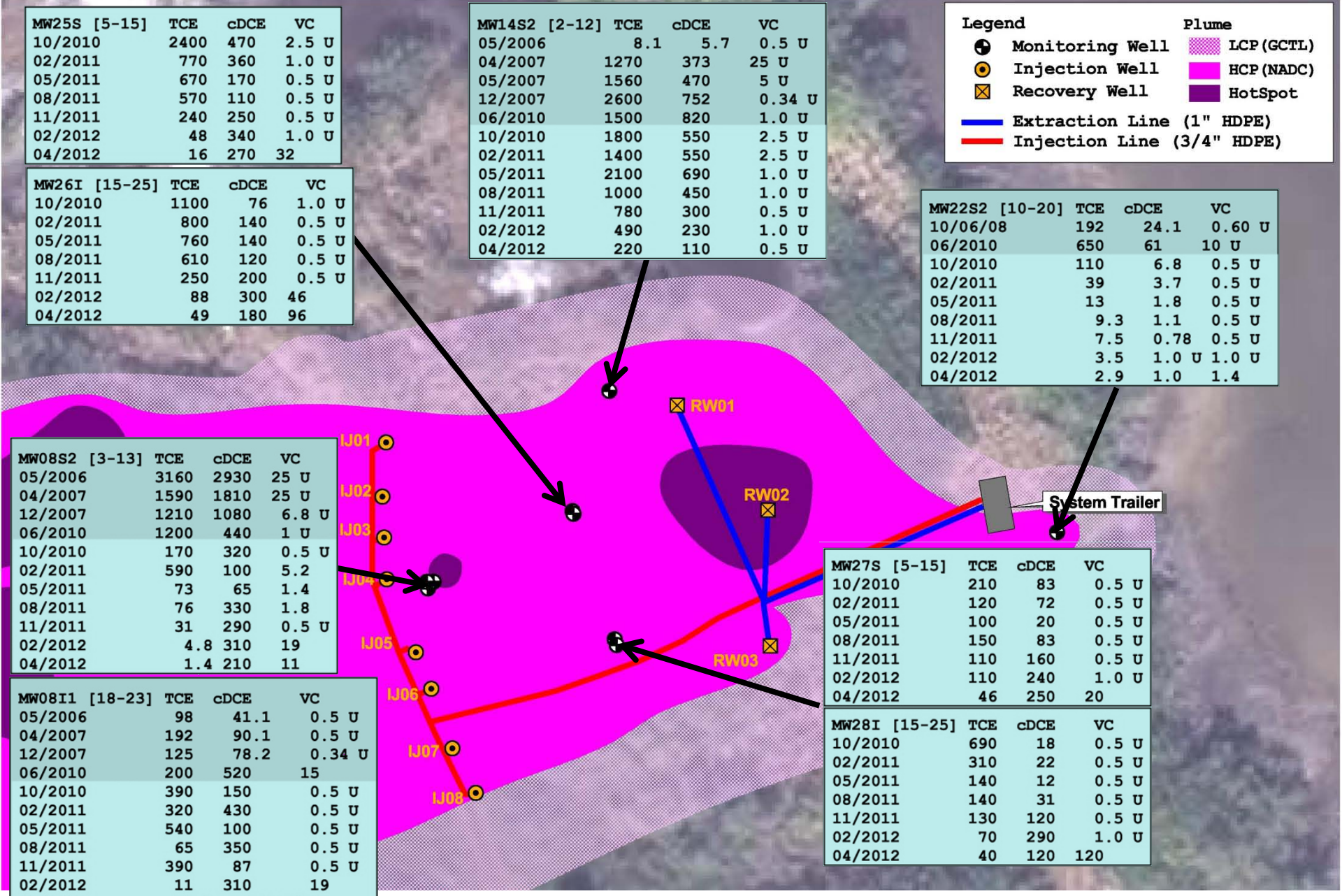

MW25S [5-15]	TCE	cDCE	VC
10/2010	2400	470	2.5 U
02/2011	770	360	1.0 U
05/2011	670	170	0.5 U
08/2011	570	110	0.5 U
11/2011	240	250	0.5 U
02/2012	48	340	1.0 U
04/2012	16	270	32

MW26I [15-25]	TCE	cDCE	VC
10/2010	1100	76	1.0 U
02/2011	800	140	0.5 U
05/2011	760	140	0.5 U
08/2011	610	120	0.5 U
11/2011	250	200	0.5 U
02/2012	88	300	46
04/2012	49	180	96

MW14S2 [2-12]	TCE	cDCE	VC
05/2006	8.1	5.7	0.5 U
04/2007	1270	373	25 U
05/2007	1560	470	5 U
12/2007	2600	752	0.34 U
06/2010	1500	820	1.0 U
10/2010	1800	550	2.5 U
02/2011	1400	550	2.5 U
05/2011	2100	690	1.0 U
08/2011	1000	450	1.0 U
11/2011	780	300	0.5 U
02/2012	490	230	1.0 U
04/2012	220	110	0.5 U

MW22S2 [10-20]	TCE	cDCE	VC
10/06/08	192	24.1	0.60 U
06/2010	650	61	10 U
10/2010	110	6.8	0.5 U
02/2011	39	3.7	0.5 U
05/2011	13	1.8	0.5 U
08/2011	9.3	1.1	0.5 U
11/2011	7.5	0.78	0.5 U
02/2012	3.5	1.0 U	1.0 U
04/2012	2.9	1.0	1.4

MW08S2 [3-13]	TCE	cDCE	VC
05/2006	3160	2930	25 U
04/2007	1590	1810	25 U
12/2007	1210	1080	6.8 U
06/2010	1200	440	1 U
10/2010	170	320	0.5 U
02/2011	590	100	5.2
05/2011	73	65	1.4
08/2011	76	330	1.8
11/2011	31	290	0.5 U
02/2012	4.8	310	19
04/2012	1.4	210	11

MW08I1 [18-23]	TCE	cDCE	VC
05/2006	98	41.1	0.5 U
04/2007	192	90.1	0.5 U
12/2007	125	78.2	0.34 U
06/2010	200	520	15
10/2010	390	150	0.5 U
02/2011	320	430	0.5 U
05/2011	540	100	0.5 U
08/2011	65	350	0.5 U
11/2011	390	87	0.5 U
02/2012	11	310	19
04/2012	1.7	5.9	210

MW27S [5-15]	TCE	cDCE	VC
10/2010	210	83	0.5 U
02/2011	120	72	0.5 U
05/2011	100	20	0.5 U
08/2011	150	83	0.5 U
11/2011	110	160	0.5 U
02/2012	110	240	1.0 U
04/2012	46	250	20

MW28I [15-25]	TCE	cDCE	VC
10/2010	690	18	0.5 U
02/2011	310	22	0.5 U
05/2011	140	12	0.5 U
08/2011	140	31	0.5 U
11/2011	130	120	0.5 U
02/2012	70	290	1.0 U
04/2012	40	120	120

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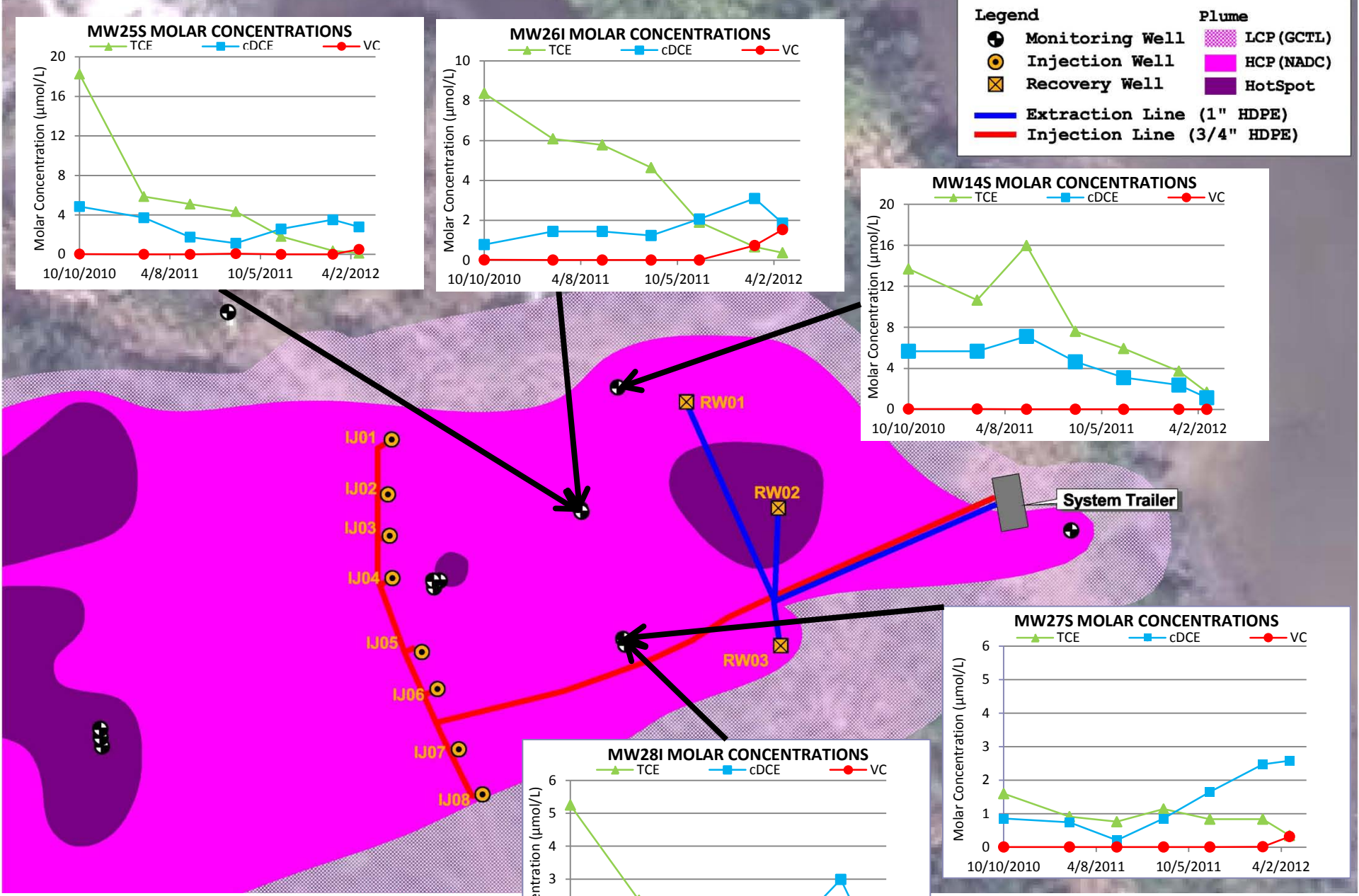

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Path Forward

- Continue to evaluate influence of $CaCO_3$ buffering
  - Consider integration into pilot study/IM
- Continue to monitor biological and geochemical parameters
  - Development of TCEr and VCr/BVC functional genes
  - Sulfate reduction and SRB activity
- Monitor degradation performance
- If functional genes not present, evaluate augmentation with chloride-tolerant culture from microcosm
- Pending additional data, expand upgradient as an IM

Acknowledgements

- NASA, Kennedy Space Center (site management lead)
- Tetra Tech (site assessment, CMS, pilot testing)
- BCI Laboratories (Microcosm Testing, Data Evaluation)
- Microbial Insights (CENSUS Analysis)
- JRW Remediation (Pilot Testing Support, Data Evaluation)