NAVFAC
Naval Facilities Engineering Command
SOUTHWEST

Who Says Chlorinated Solvents Can't Biodegrade in the Presence of High Sulfate in Marine Sediments?

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What Does the Literature Say about Sulfate & Dechlorination?

1. “Dechlorination can be inhibited or might occur very slowly when sulfate is present” (Mazur and Jones 2001; Hoelen and Reinhard 2004)

2. “Sulfate- reducing bacteria (SRB) [may] compete with dechlorinators for available hydrogen” (McCarty 1997; Mazur and Jones 2001)

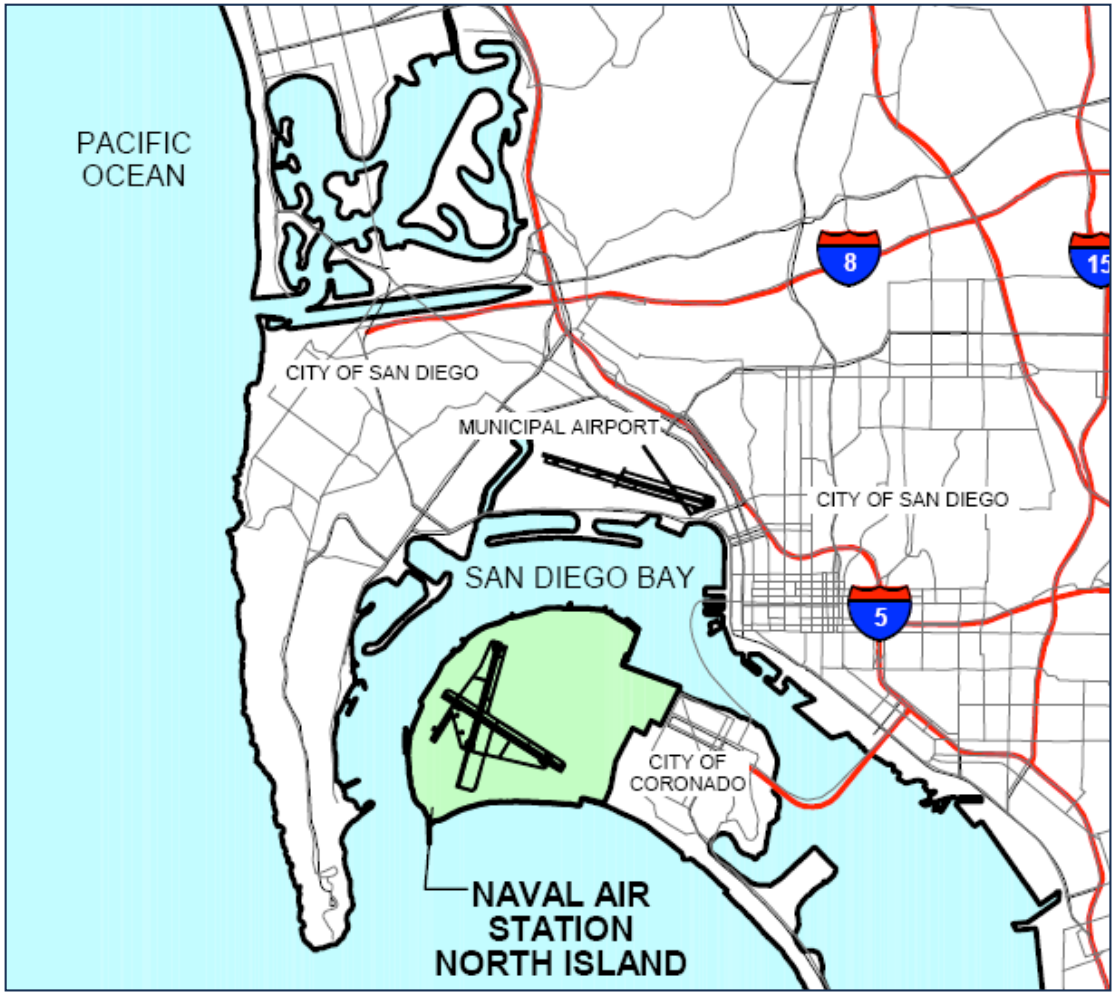
3. “5.0 mM sulfide [170 mg/L] shut down [TCE] dechlorination activity, but no inhibition was observed at 1 mM [34 mg/L]” (He et al. 2005).

4. TCE “dechlorination was not affected by the addition of sulfate (up to 10 mM [960 mg/L])” (He et al. 2005)

5. “This study demonstrates that sulfide rather than sulfate exhibits inhibitory effects on the dechlorination and growth of *D. mccartyi*” (Mao et al. 2017)”

Site Background

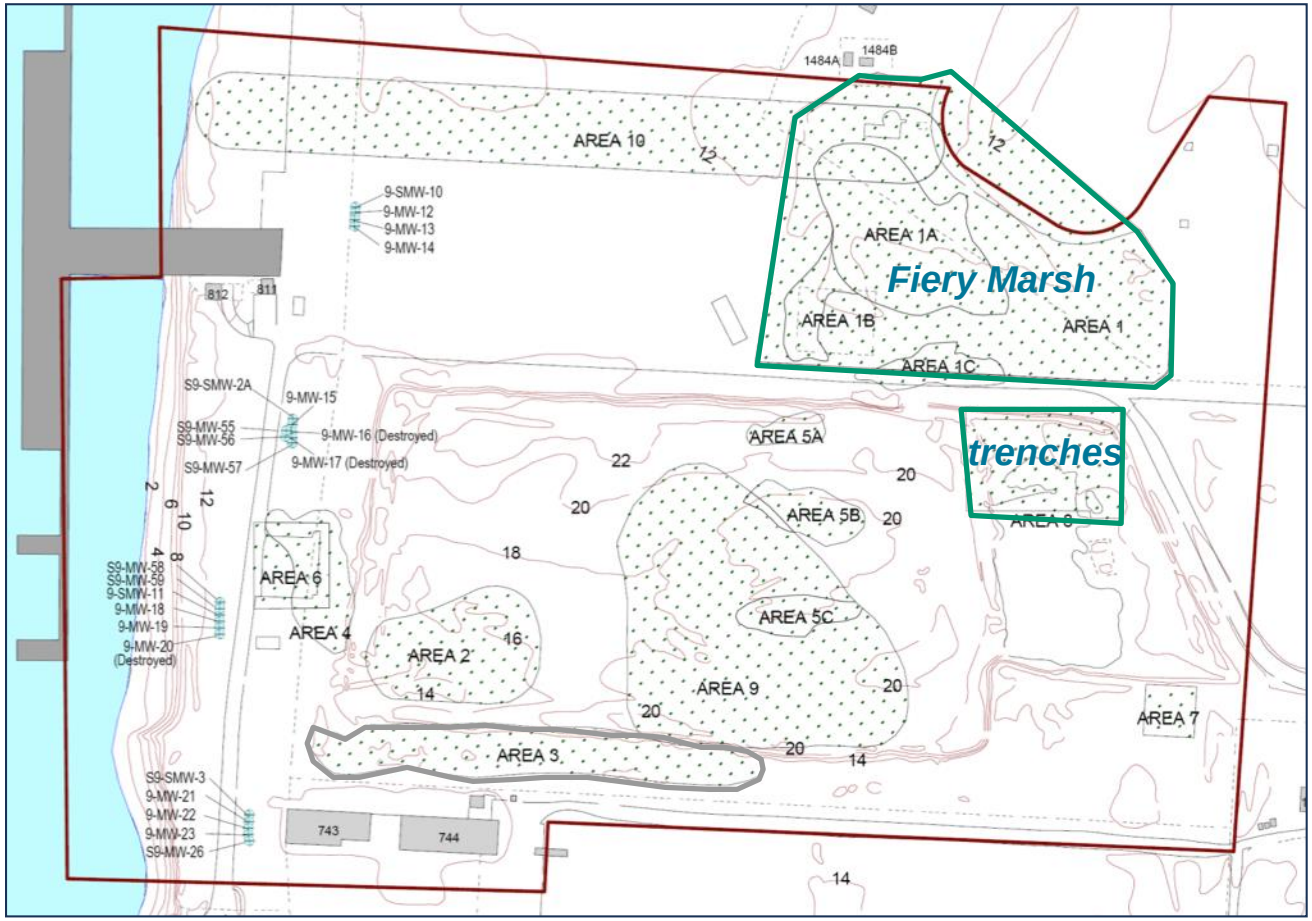
Naval Air Station North Island Location – Coronado, California



IR Site 9, Naval Air Station North Island Coronado California

IR Site 9

Contamination Source Areas

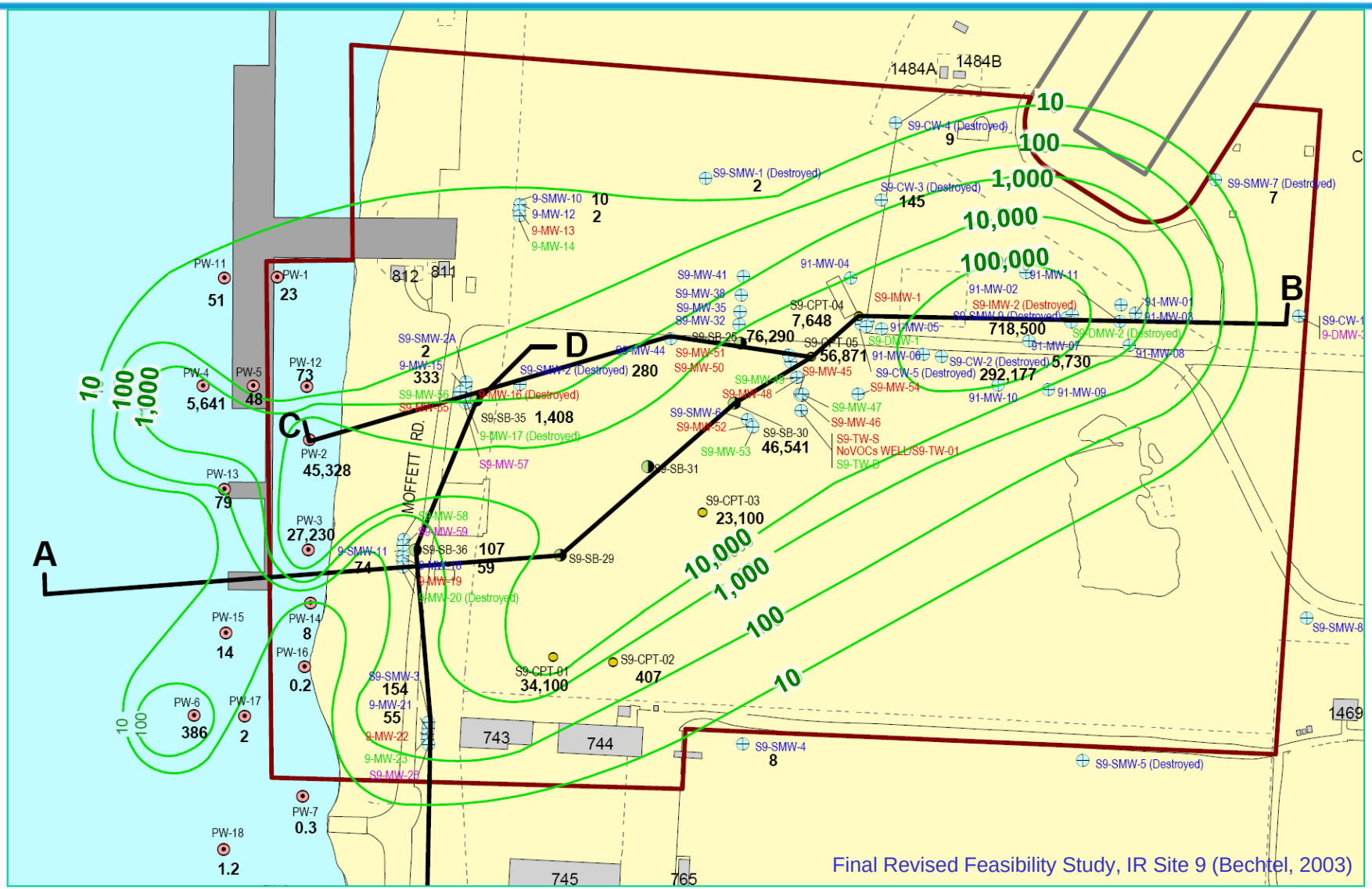


Final Revised Feasibility Study, IR Site 9 (Bechtel, 2003)

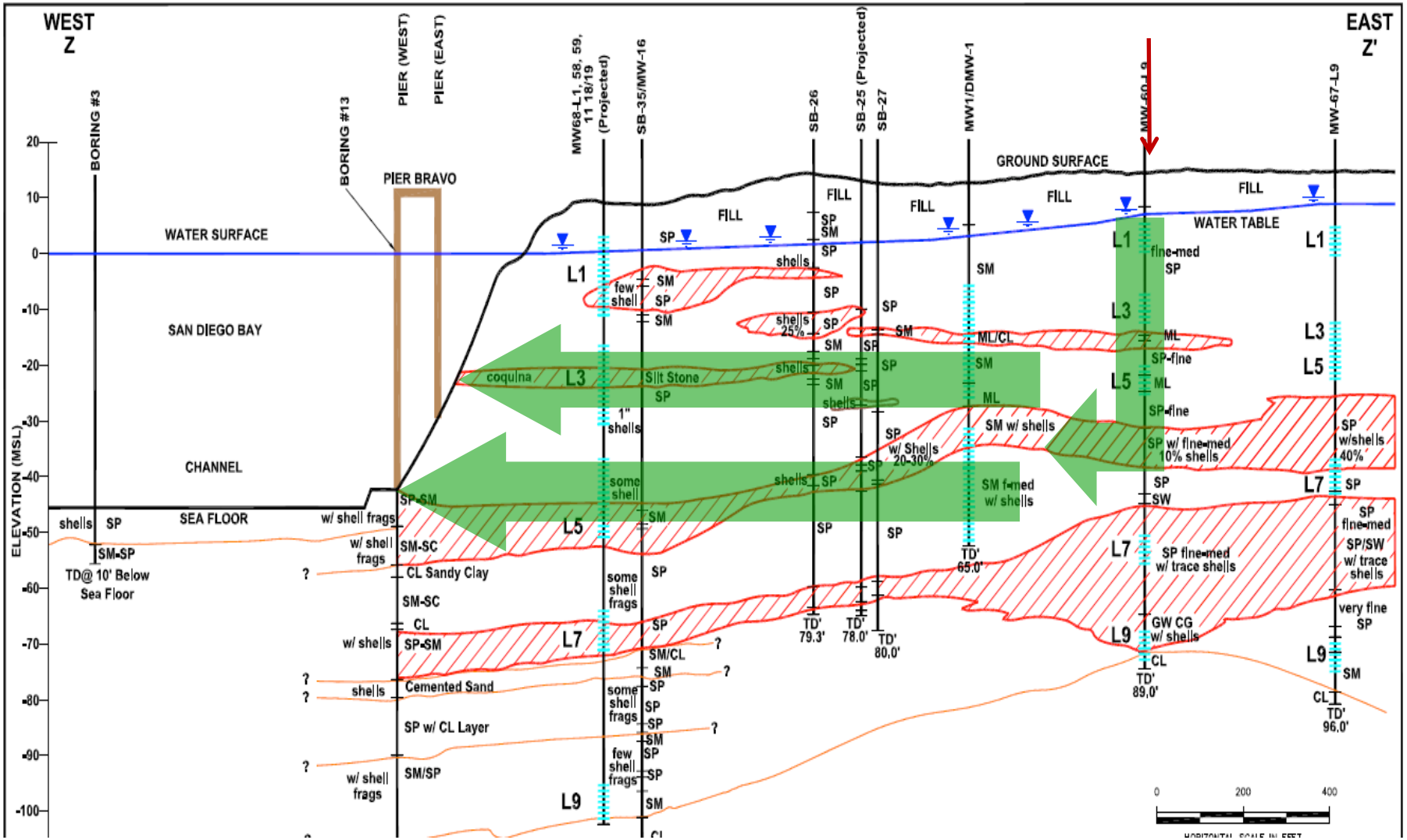
1940s - 1970s

- 8 to 32 million gallons waste disposed
  - fuels
  - solvents
  - degreasers
  - paints
  - plating wastes

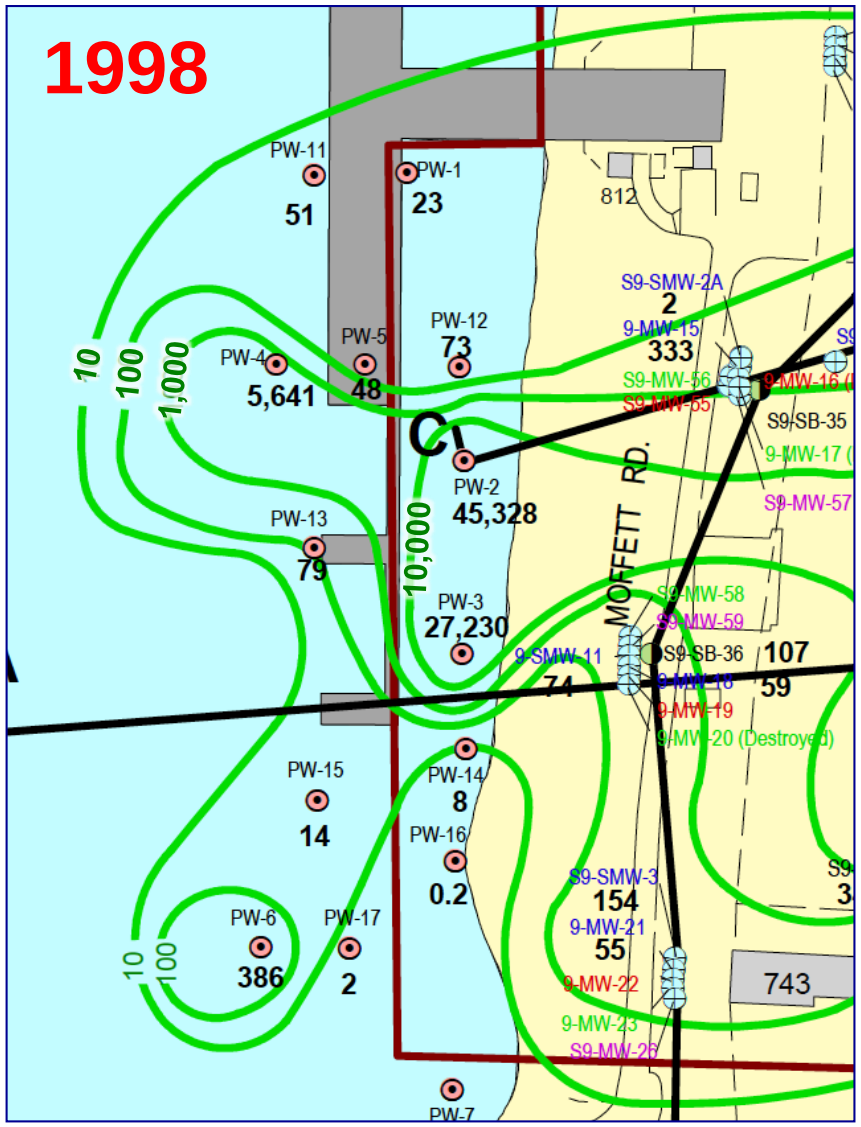
Conceptual Site Model – Total VOCs in Shallow Groundwater (µg/L), 1998

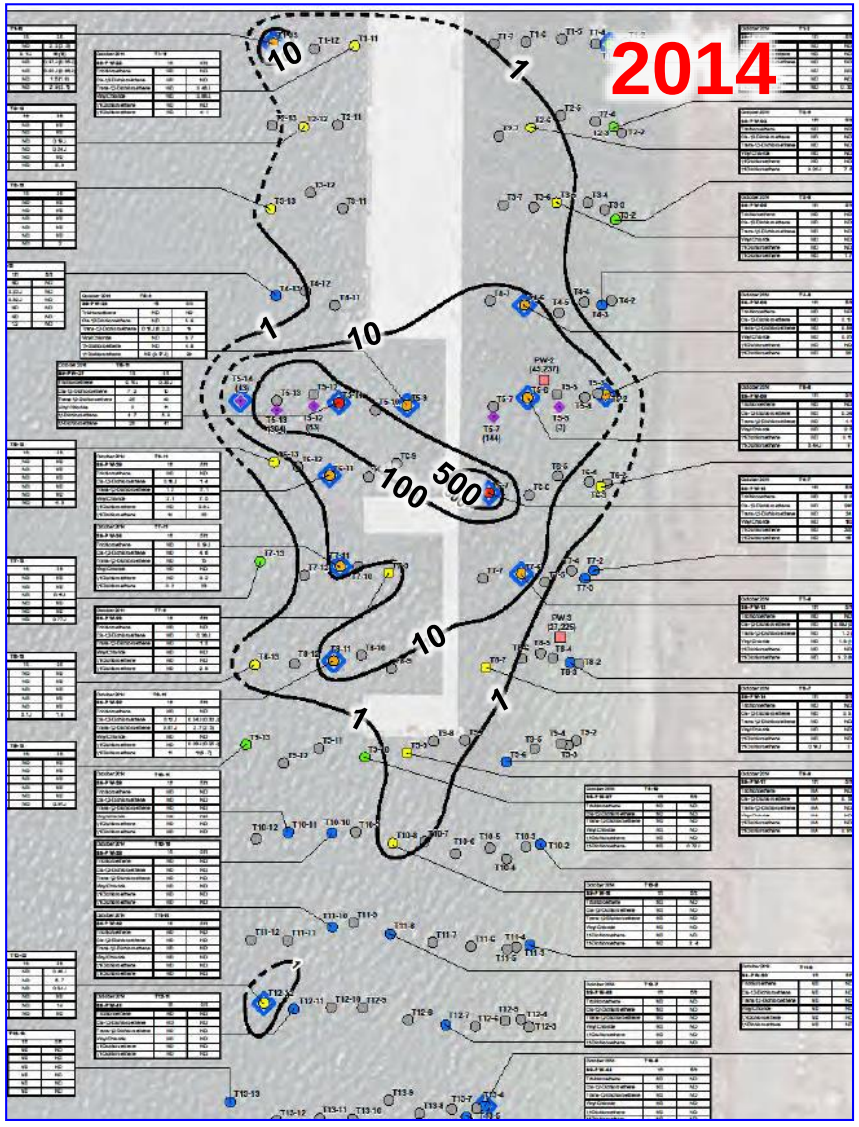


IR Site 9 – Hydrogeologic Cross Section



CVOCs in Offshore Porewater, 5-ft Depth 1998 vs. 2014





Study Objectives and Investigation Approach

Study Objectives

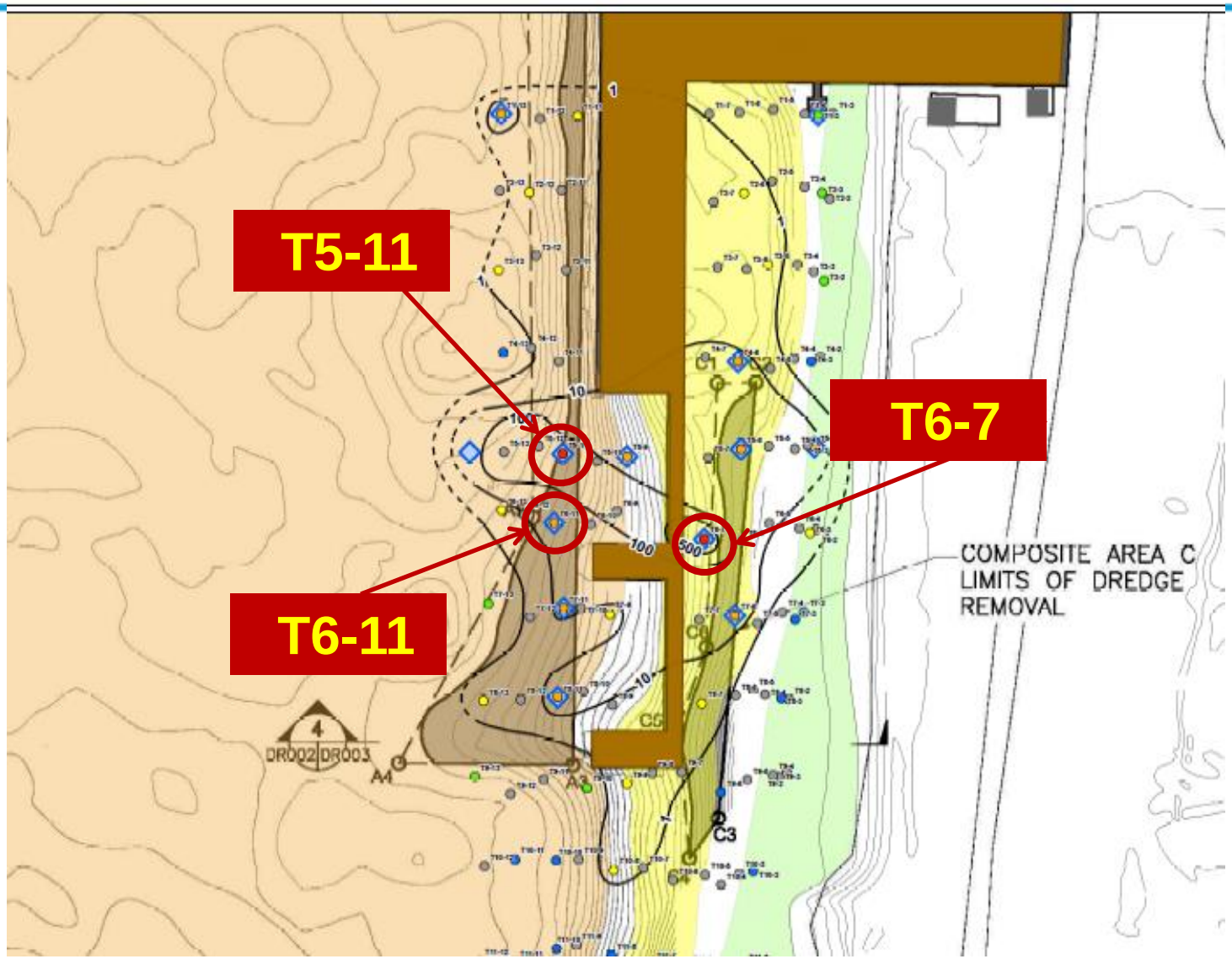
Evaluate:

1. role of natural biological and abiotic degradation in contributing to reduction in CVOC concentrations in offshore porewater
2. Occurrence of dechlorinating and sulfate-reducing bacteria in marine sediments at Site 9
3. Potential interference by sulfate in biological dechlorination
4. Supply of natural organic carbon in marine sediments to support biological dechlorination
5. Occurrence of Fe(II)-bearing reductants in sediments
    - magnetite
    - FeS
    - biotite

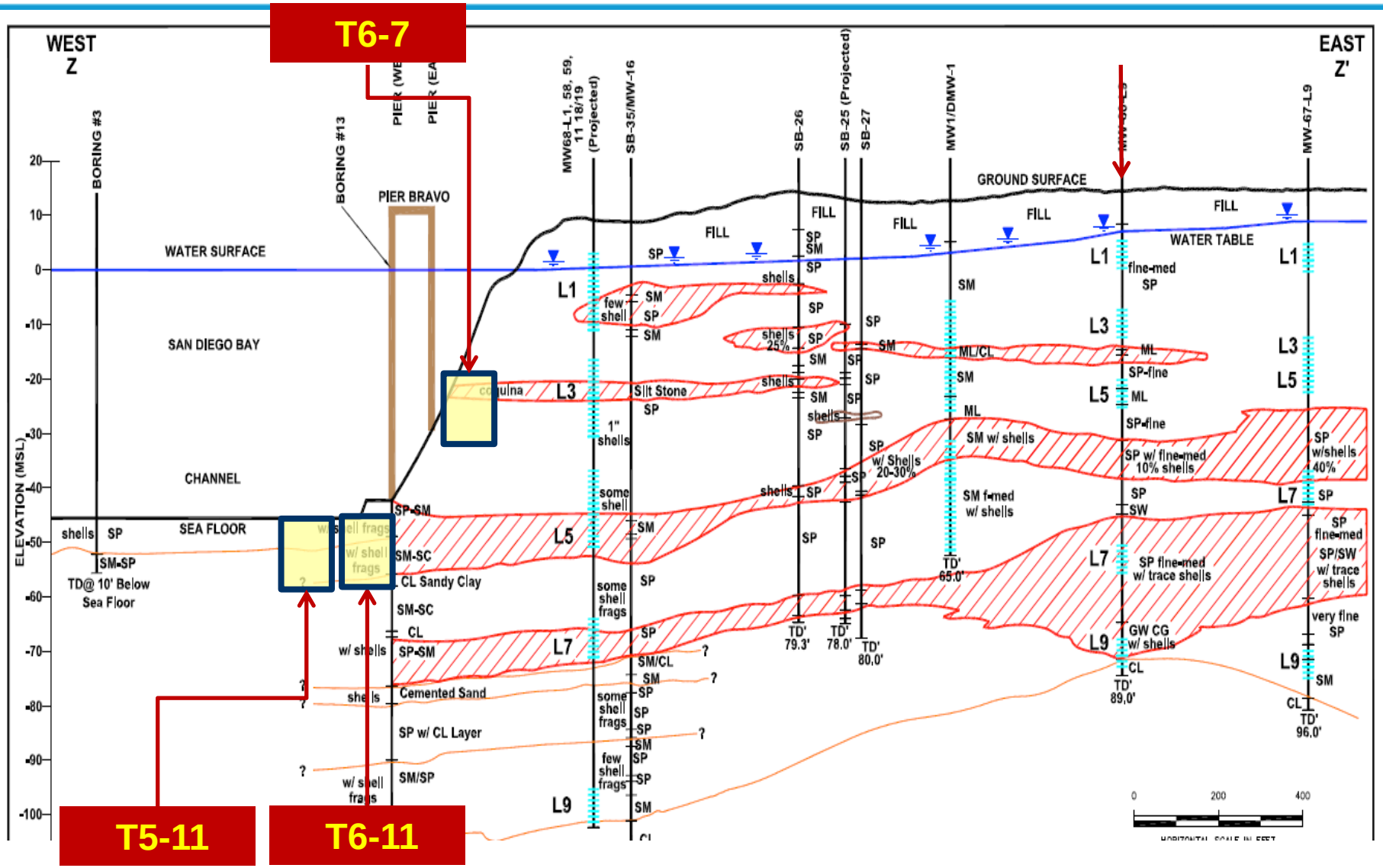
Investigation Approach

- ✓ Multiple lines of evidence
- ✓ Three sediment sampling locations representing a **range of VOC concentrations** from within plume discharge zone
  - ➢ High VOC concentrations => T5-11
  - ➢ Middle VOC concentrations => T6-7
  - ➢ Low VOC concentrations => T6-11
- ✓ At each location, collect porewater + sediment core from **three depths (1-foot, 5-foot, and 8-foot)**
- ✓ Measure natural degradation in **laboratory microcosms**
- ✓ Collect **CSIA** samples upland and offshore to screen for ^{13}C enrichment in CVOCs

Offshore Sampling Locations – IR Site 9



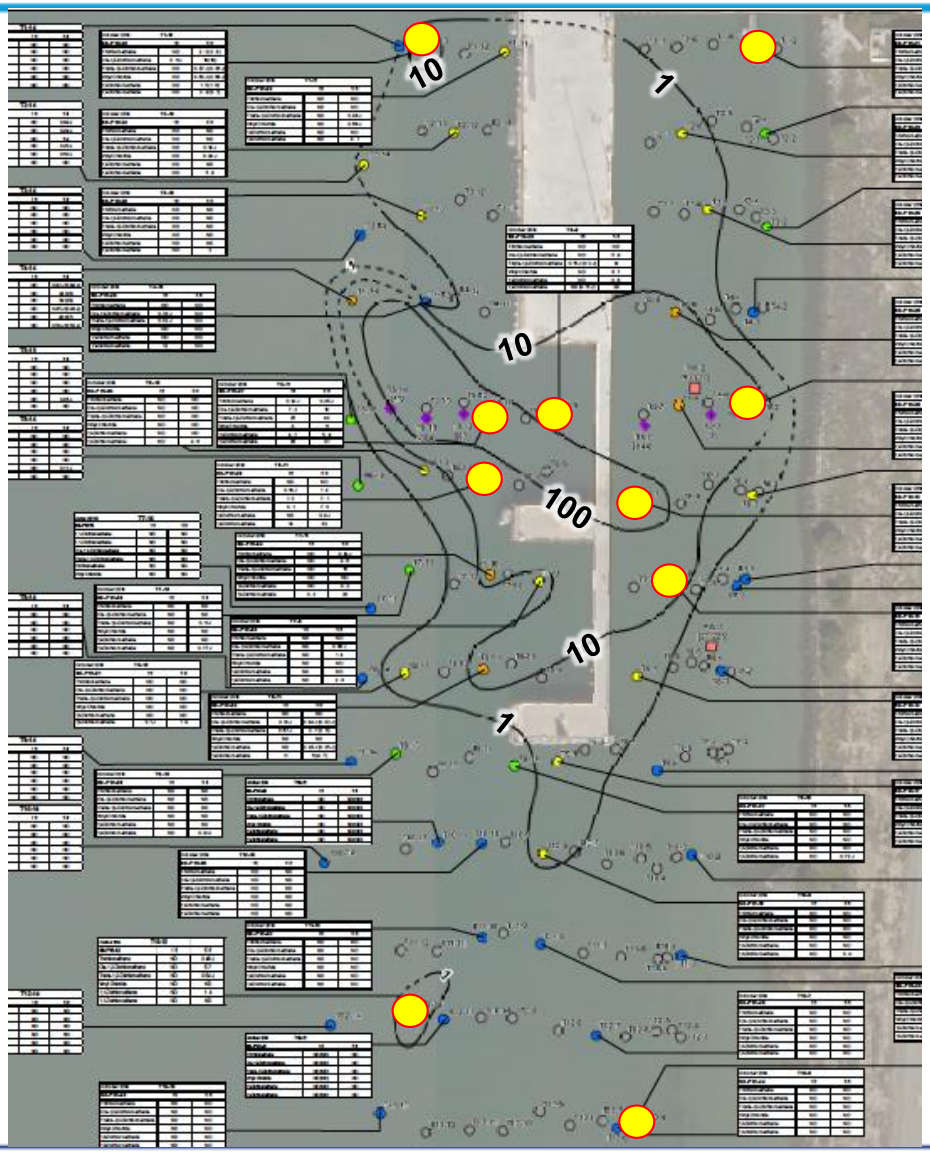
Offshore Sampling Locations – IR Site 9



Analyses

Method	Purpose
vcrA & Next Generation Sequencing	• Identify bacterial species and relative proportions. • Determine whether dechlorinating bacteria other than *Dehalococcoides* are present; • assess growth of sulfate reducers
Magnetic Susceptibility	Detect magnetite
Acid Volatile Sulfides (AVS)	Detect FeS
Sulfur	Supplement AVS
Total Organic Carbon	Measure presence of naturally-occurring electron donor
Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometry (EDS) And X-Ray Diffraction (XRD)	Quantify concentrations of minerals in sediments that can act as abiotic reductants

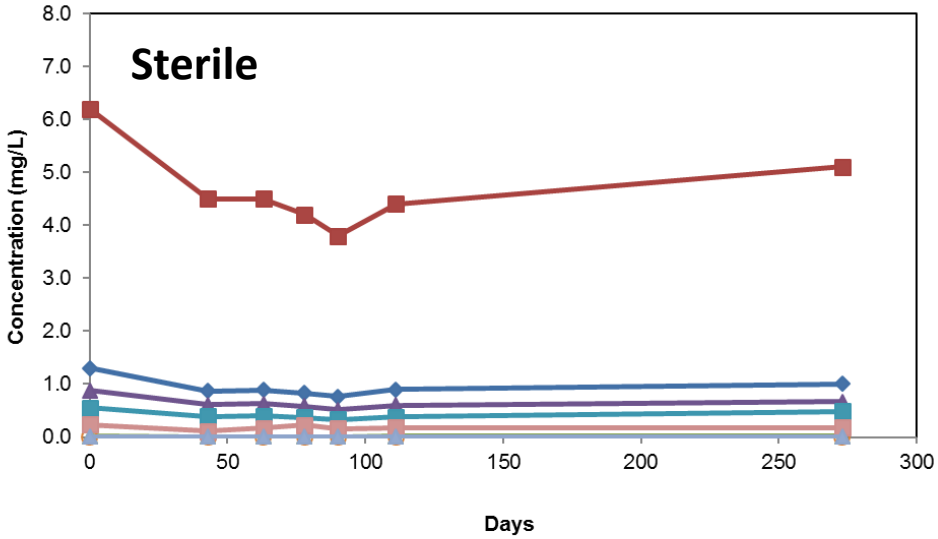
Porewater Sample Locations for CSIA

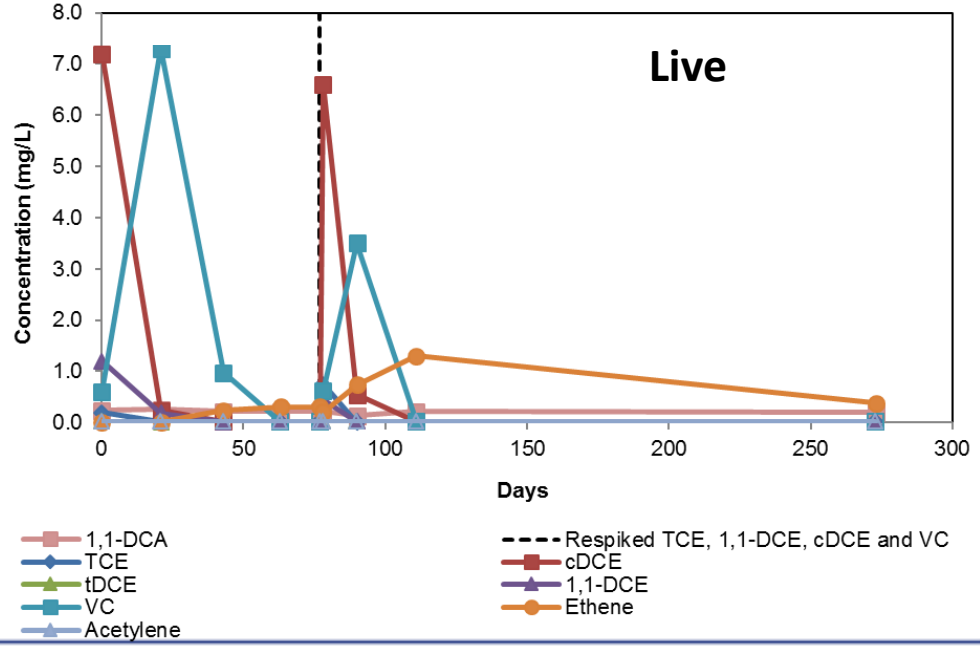


- 10 piezometer locations
- three depths at each location (1-ft, 5-ft, 8-ft)
- measure $\delta^{13}C$ enrichment factors for TCE, cDCE, VC, 1,1-DCE, and 1,1-DCA

Results

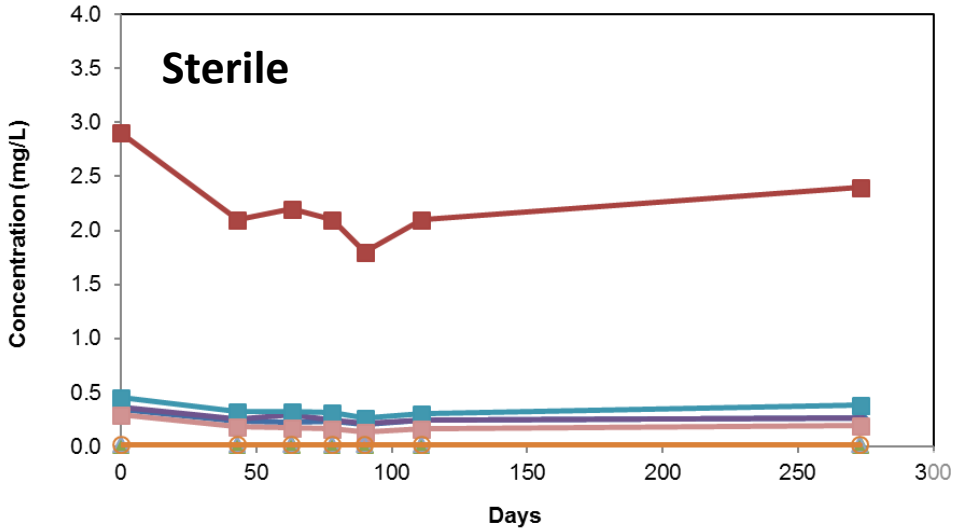
Anaerobic Microcosms CVOC Trends T5-11-1 (1-ft depth)



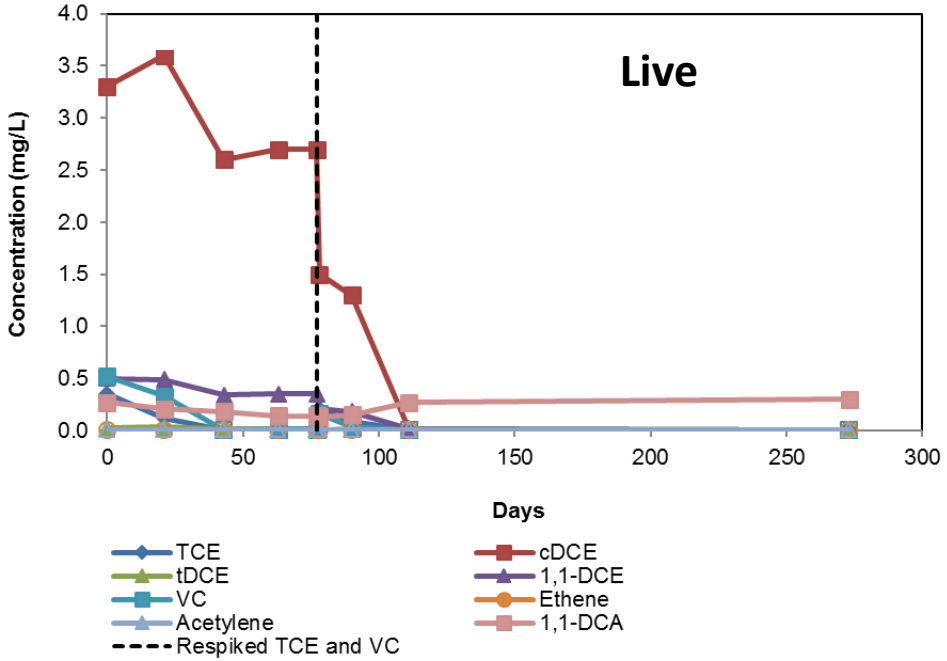


COC	Initial Conc. C_0 (mg/L)	Final Conc. C (mg/L)	% Removed	Half-Life (days)
TCE	0.19	< 0.01	99%	4
cDCE	7.2	< 0.01	> 99%	4
1,1-DCE	1.2	< 0.01	> 99%	5
VC	0.6	< 0.01	99%	9*

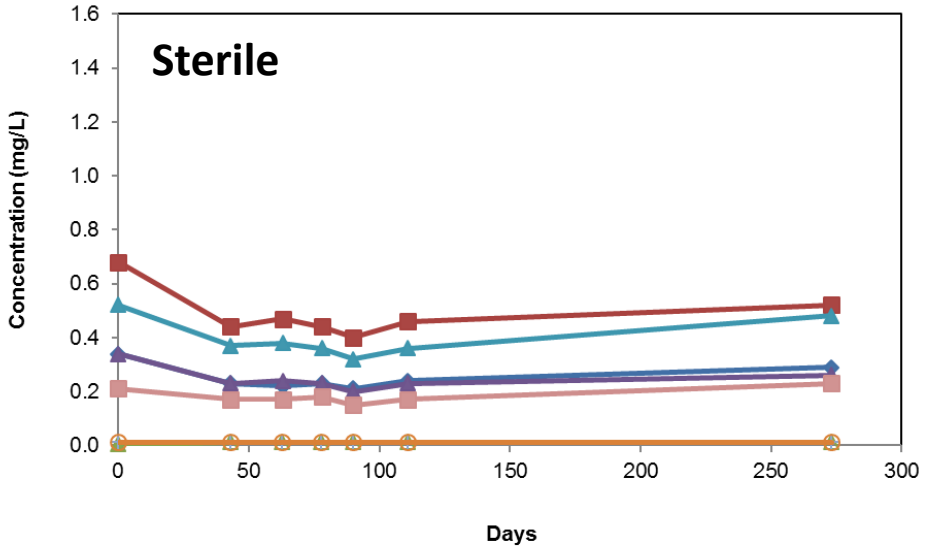
Anaerobic Microcosms CVOC Trends T5-11-5 (5-ft depth)

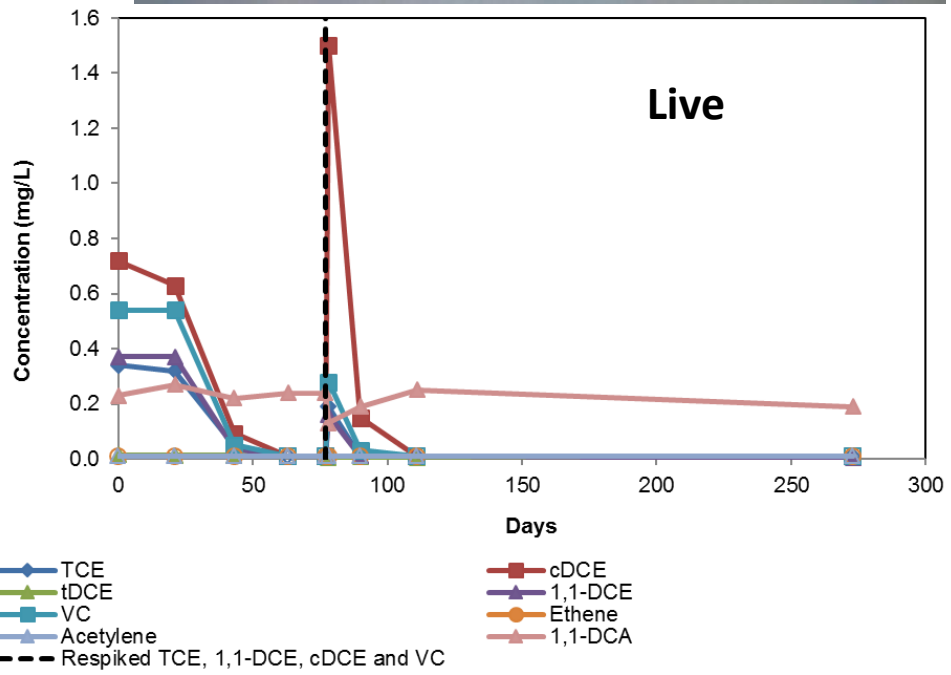


COC	Initial Conc. C_0 (mg/L)	Final Conc. C (mg/L)	% Removed	Half-Life (days)
TCE	0.35	< 0.01	99%	10
cDCE	0.33	< 0.01	> 99%	12
1,1-DCE	0.5	< 0.01	99%	41
VC	0.52	< 0.01	99%	17



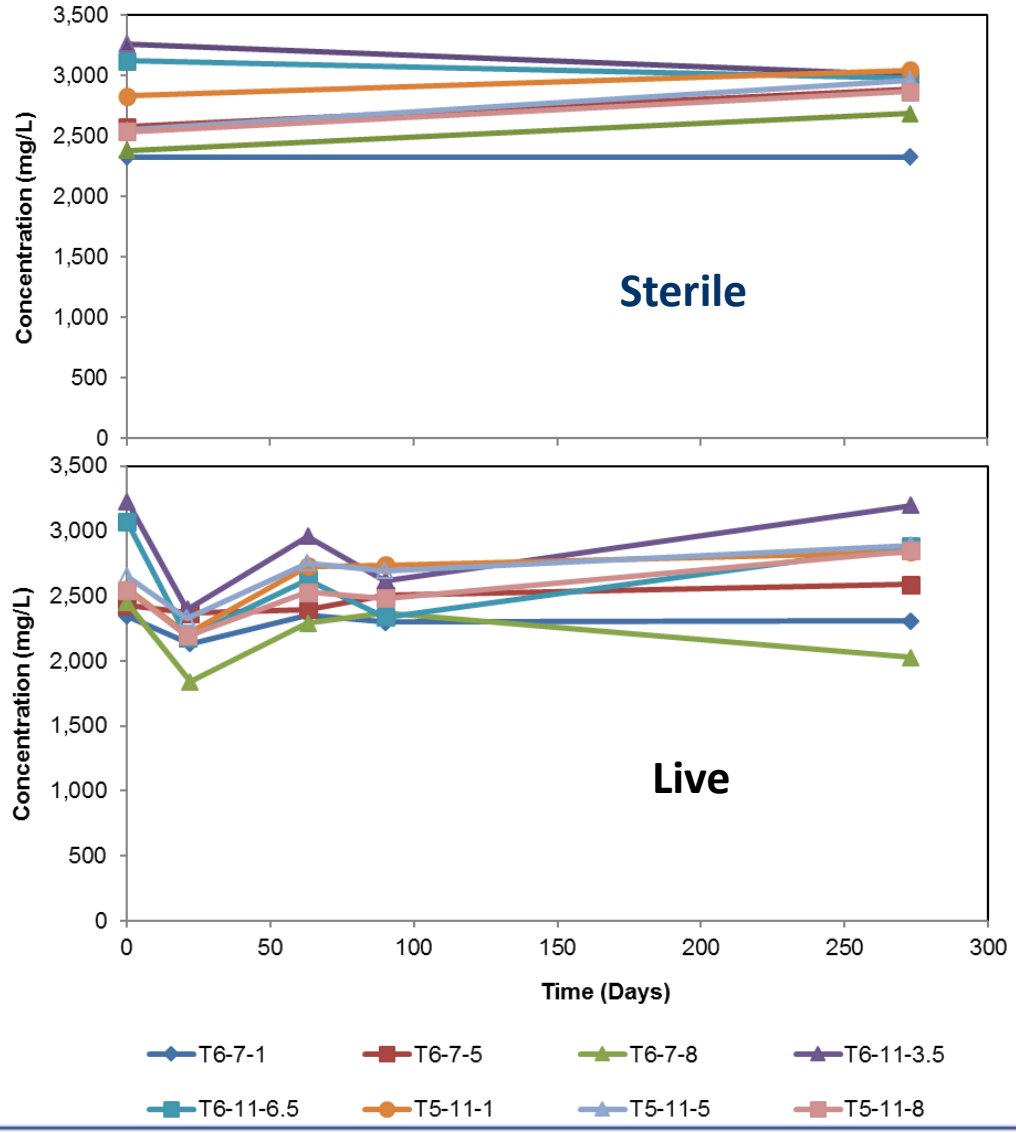
Anaerobic Microcosms CVOC Trends T5-11-8 (8-ft depth)





COC	Initial Conc. C_0 (mg/L)	Final Conc. C (mg/L)	% Removed	Half-Life (days)
TCE	0.34	< 0.01	99%	10
cDCE	0.72	< 0.01	> 99%	9
1,1-DCE	0.37	0.0037	99%	10
VC	0.54	< 0.01	99%	9

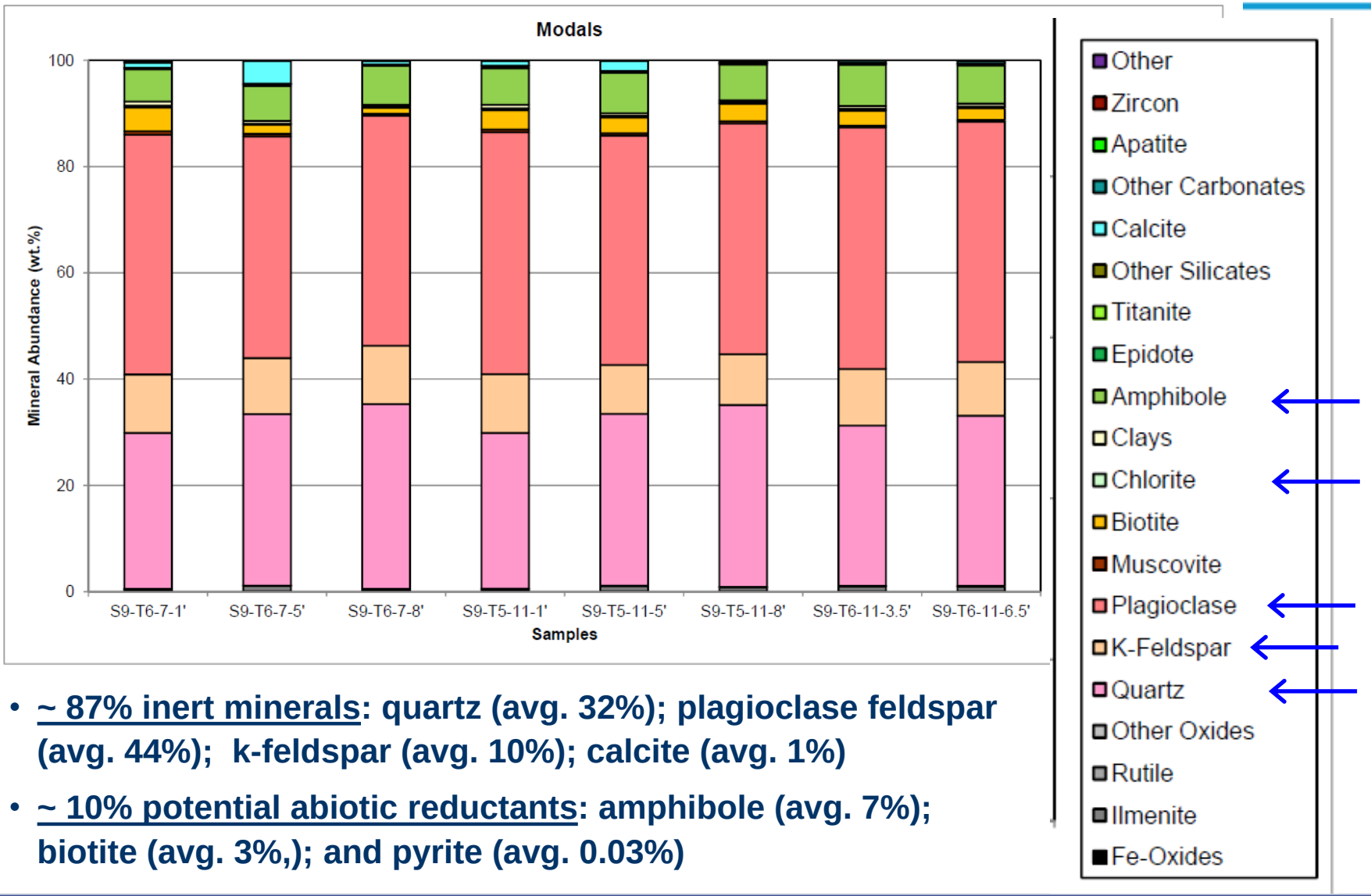
Anaerobic Microcosms Sulfate Trends All Locations



- *Sulfate concentrations remained above 2 g/L in all but one location*
- *Reductive dechlorination occurring under high (sea water) sulfate conditions*

Minerals in the Sediments

(Live Controls)

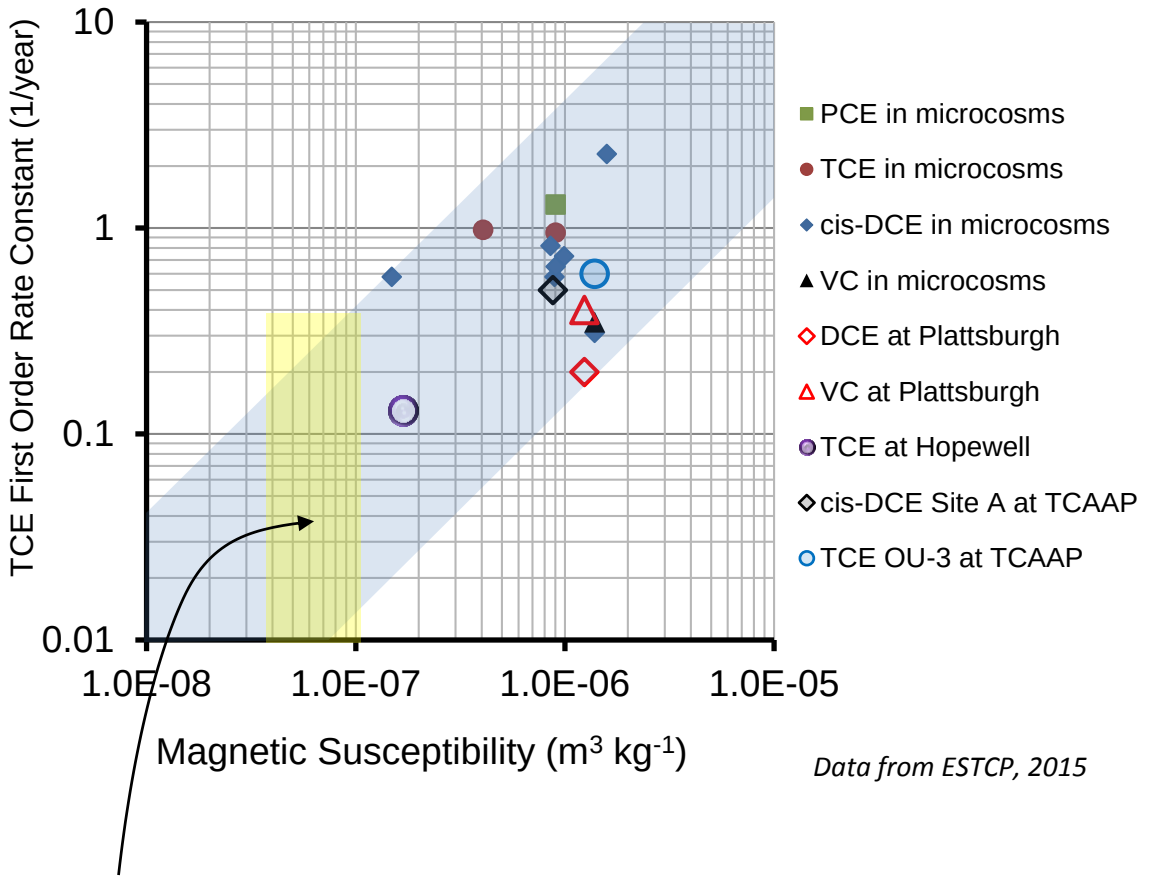


- **<u>~ 87% inert minerals</u>: quartz (avg. 32%); plagioclase feldspar (avg. 44%); k-feldspar (avg. 10%); calcite (avg. 1%)**
- **<u>~ 10% potential abiotic reductants</u>: amphibole (avg. 7%); biotite (avg. 3%,); and pyrite (avg. 0.03%)**

Magnetic Susceptibility in Sediments
(live controls)

Sample ID	MS (m^3/kg)
S9-T6-7-1'	1.7E-07
S9-T6-7-5'	5.5E-08
S9-T6-7-8'	7.0E-08
S9-T5-11-1'	1.3E-07
S9-T5-11-5'	1.7E-07
S9-T5-11-8'	2.0E-07
S9-T6-11-3.5'	1.9E-07
S9-T6-11-6.5'	2.2E-07

- *MS is 10 – 100 X lower than values for aquifers where magnetite has been shown to catalyze abiotic dechlorination (e.g.,Ferrey et al., 2004)*

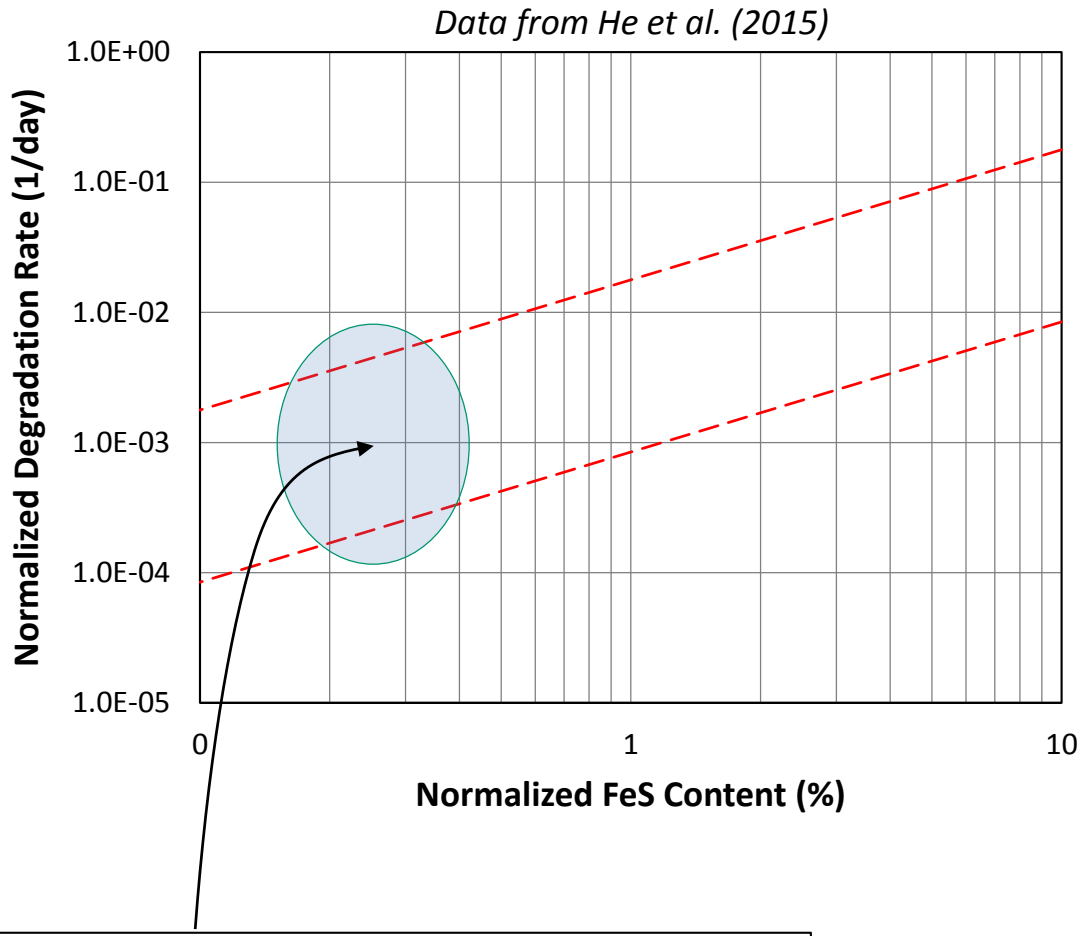


Data from ESTCP, 2015

Predicted Half-lives of several months vs. 10-20 day observed in the microcosm test

Iron and Sulfur in Sediments
(live controls)

Sample ID	FeS (AVS) (%)	FeS +FeS2 (Total S) (%)
S9-T6-7-1'	0.038	0.22
S9-T6-7-5'	0.002	0.16
S9-T6-7-8'	0.000	0.11
S9-T5-11-1'	0.011	0.17
S9-T5-11-5'	0.003	0.14
S9-T5-11-8'	0.001	0.18
S9-T6-11-3.5'	0.002	0.10
S9-T6-11-6.5'	0.003	0.11



Half-lives of 200 – 400 days vs. 10-20 days observed in the microcosm test

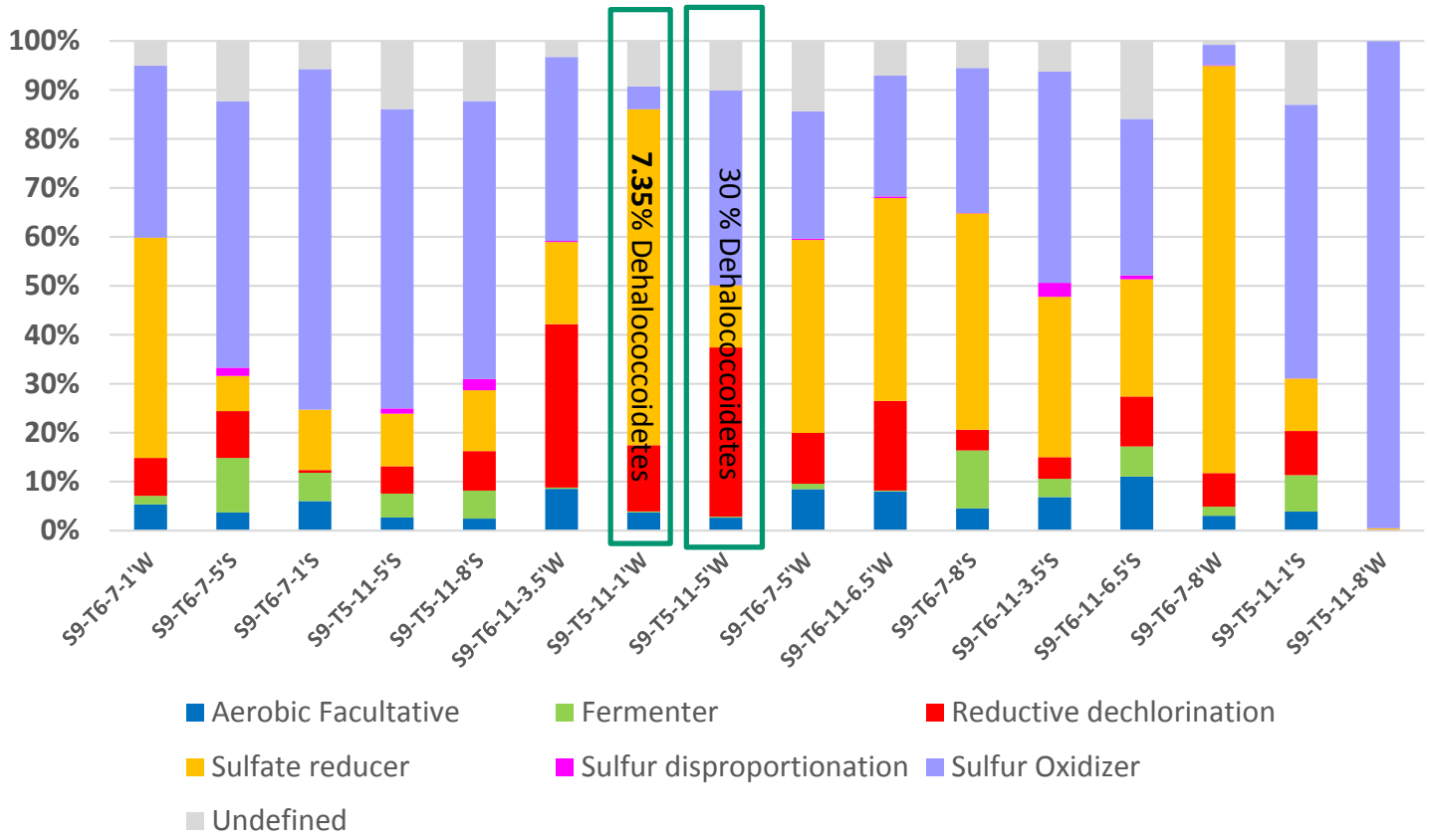
Total Organic Carbon in the Sediments

(Live Controls)

Sample ID	Total Organic Carbon (% or g/Kg)
T6-7-1	0.19
T6-7-5	0.25
T6-7-8	0.09
T5-11-1	0.09
T5-11-5	0.06
T5-11-8	0.08
T6-11-3.5	< 0.05
T6-11-6.5	< 0.05

- TOC within the range (0.02 – 0.12%) reported by Rectanus et al. (2007) and range (0.013% - 5.5%) reported Butler et al. (2009) for aquifer sediments that supported dechlorination
- Slowest degradation of CEs was observed in sediments where TOC concentrations were non-detect (T6-11-3.5 and T6-11-6.5)
- Results indicate that organic matter in sediment can serve as an electron donor and carbon source to support microbial activity and biodegradation of CEs

Functional Analysis on Gene-Trac NGS Data

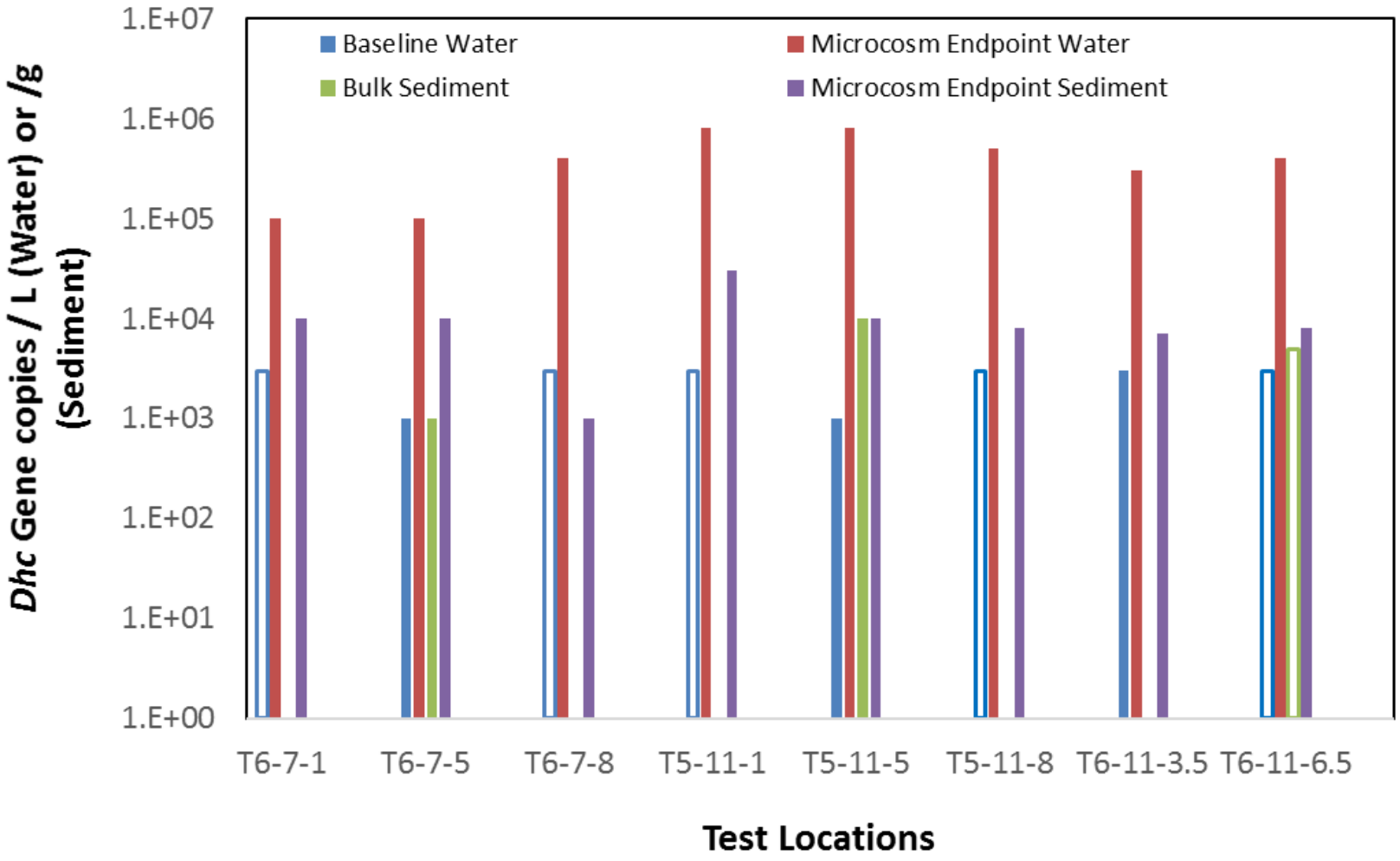


T5-11-5 despite being Dhc ND has significant dechlorinating population, likely *a Dehalogenimonas*

T5-11-1 has a significant Dhc population

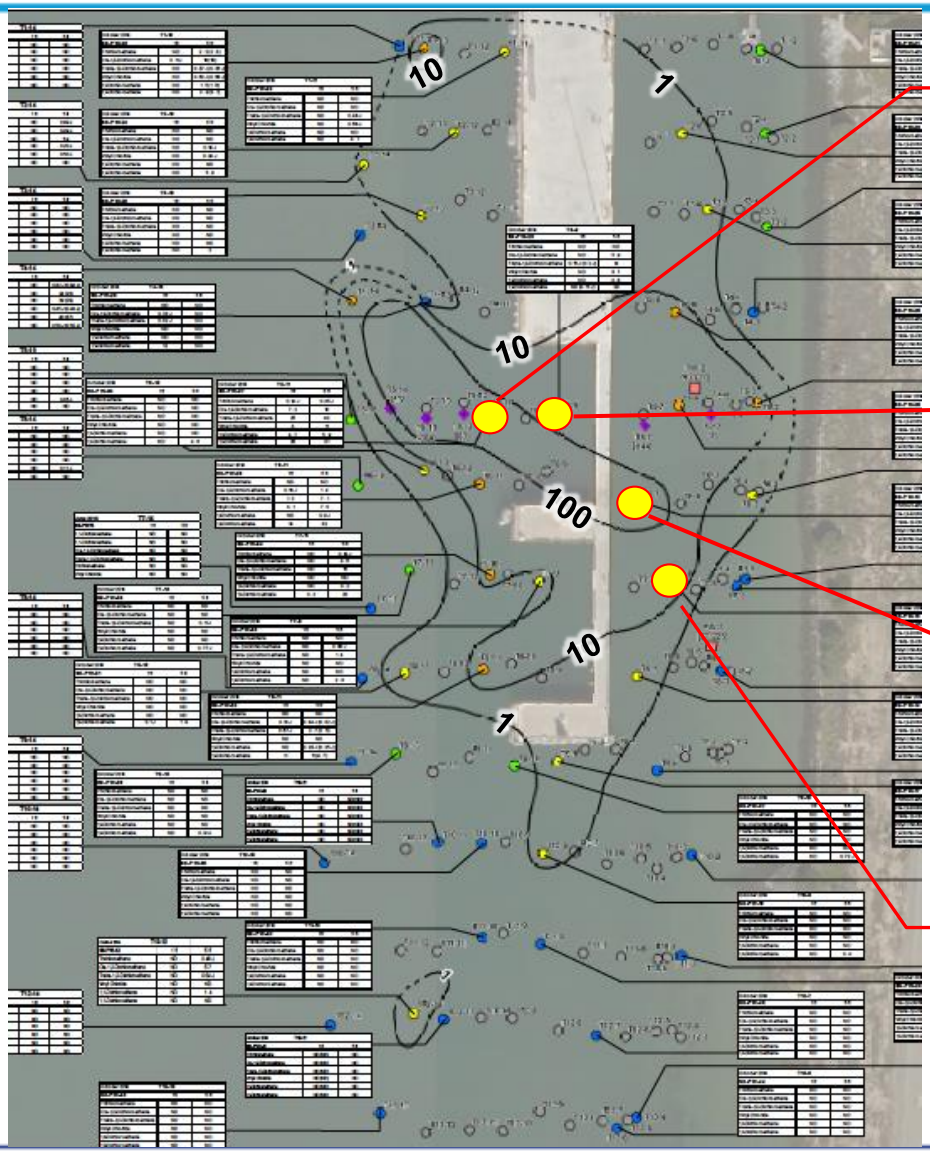
- Microbial community was dominated by sulfur metabolism
- Reductive dechlorinators (putative *Dehalogenimonas*) was detected in most samples at up to 30% of the total microbial community population

Gene-Trac® Results – *Dehalococcoides*



- *At all locations, Dhc gene copy (concentrations) increased over course of 39 week incubation*

Porewater $\delta^{13}C$ Enrichment Factor Results (‰)



T5-11

Depth	$\delta^{13}C$ TCE	$\delta^{13}C$ cDCE	$\delta^{13}C$ VC
1	-16.51	-11.85	-19.05
5	-19.12	-23.62	-29.21
8	-20.60	-26.63	ND

T5-9

Depth	$\delta^{13}C$ TCE	$\delta^{13}C$ cDCE	$\delta^{13}C$ VC
1	ND	ND	ND
5	ND	58.22	28.58

T6-7

Depth	$\delta^{13}C$ TCE	$\delta^{13}C$ cDCE	$\delta^{13}C$ VC
1	ND	ND	7.81
8	ND	14.82	8.99

T7-6

Depth	$\delta^{13}C$ TCE	$\delta^{13}C$ cDCE	$\delta^{13}C$ VC
1	ND	ND	ND
5	ND	59.03	ND
8	ND	99.07	51.25

Conclusions

Conclusions

- Microcosm studies confirm that natural biodegradation of CVOCs is occurring the San Diego Bay Sediments, limiting discharge to the Bay
- CEs degraded completely (≥ 99%) in presence of > 2000 mg/L sulfate
- Anaerobic degradation rates are rapid in a several locations, with half-lives on the order of 4 to 10 days
- Microbial processes were most likely responsible for observed degradation. No degradation was observed in sterile controls
- ^{13}C-cDCE and ^{13}C-VC highly enriched in sediment porewater, indicating biological dechlorination
- Natural organic carbon is present in sediments at concentrations that can support biological dechlorination
- Increases in *Dehalococcoides* were observed in all locations over of 39 week incubation, indicating presence of naturally-occurring *Dhc. Dehalogenimonas* also was detected

Conclusions, continued

- Classic sequential reductive dechlorination was observed only at T5-11 at 1 foot interval.
- Other locations: No accumulation of daughter products, ethene or acetylene, suggesting involvement of microbial and abiotic processes other than *Dehalococcoides*
- Highest *vcrA* counts detected in microcosms showing fastest dechlorination (T5-11-1). *vcrA* nondetect in microcosms showing slowest dechlorination (T6-11-3.5, and – 6.5)
- Hypothesis: The lack of observed ethene in some microcosms may indicate ethene losses that could be mediated by ethene oxidizing sulfate reducing microbes
- FeS and magnetite are present with potential to degrade chlorinated ethenes abiotically, but not at concentrations high enough to achieve the rapid degradation rates observed

Questions?