

Stimulation of Biodegradation of Carbon Tetrachloride using Emulsified Vegetable Oil

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Background

- Former herbicide and pesticide distribution facility in Sacramento, CA
- Area undergoing redevelopment for commercial and residential use
- Pesticide-impacted soil already removed
- CTET in GW ~ 1,400 $\mu\text{g/L}$

Background—cont'd

- Stimulation of anaerobic biodegradation proposed GW remediation option
 - CTET more easily reduced than oxidized
 - Biodegradation requires little to no on-site activity after initial injection
 - EOS™ emulsified oil preferred substrate
- Bench-scale tests conducted to assess biodegradation
- Field pilot test conducted based on lab results

- LEGEND:**
- MW01 1.0 SHALLOW GROUNDWATER MONITORING WELL WITH CTCL CONCENTRATION (ug/L)
 - MW04 1.0 DEEP GROUNDWATER MONITORING WELL WITH CTCL CONCENTRATION (ug/L)
 - MW01 ND DEEPER GROUNDWATER MONITORING WELL WITH CTCL CONCENTRATION (ug/L)
 - CTCL CARBON TETRACHLORIDE ISOCOCONCENTRATION CONTOUR FOR DEEP GROUNDWATER (DASHED WHERE INFERRED)
 - CTCL CARBON TETRACHLORIDE
 - ND NOT DETECTED ABOVE METHOD DETECTION LEVEL

ALL WELL SAMPLES COLLECTED OCTOBER 29-31, 2007

**CTET contours,
deep wells**

1,000 $\mu\text{g/L}$ →

100 $\mu\text{g/L}$ →

1 $\mu\text{g/L}$ →

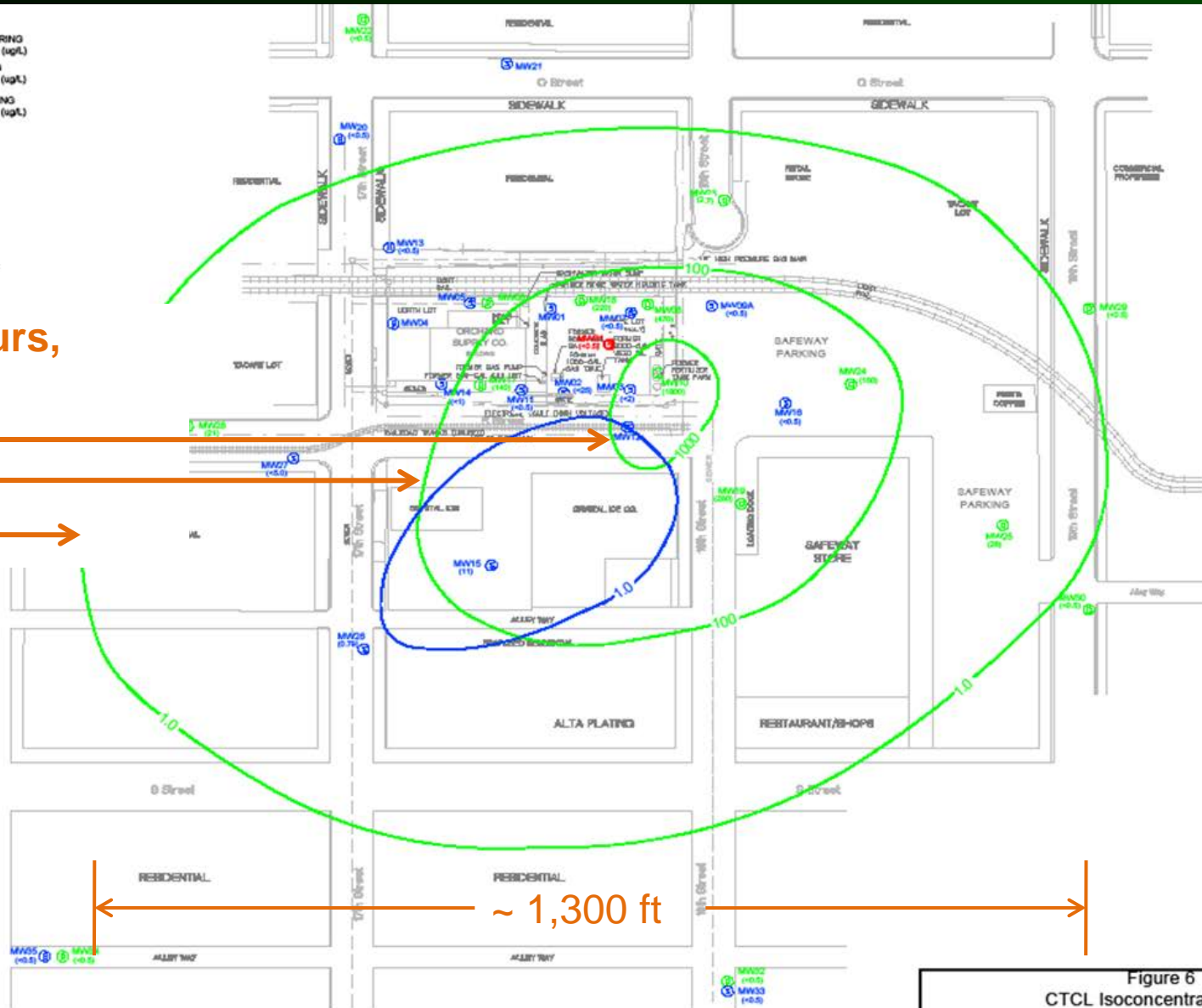


Figure 6
CTCL Isoconcentration Map

Sacramento, CA

CTET Background

Property	Value
Chemical formula	CCl_4
Carbon oxidation state	+4
Aqueous solubility	790 mg/L
Density	1.59 g/cm ³
Henry's constant, H_c	1.25
Partition coefficient, $\log(K_{ow})$	2.64
Uses (former):	Pesticide, dry cleaning solvent, fire extinguishers
Hazards:	Toxic; suspected carcinogen

EOS™ Background

EOS™ Emulsified Oil

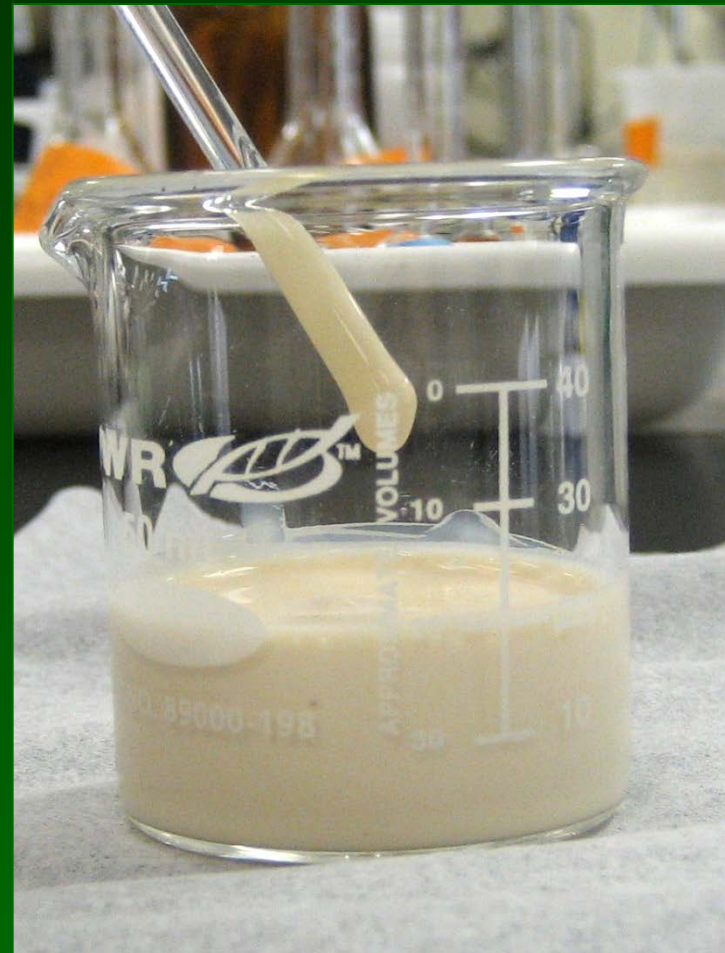
Cream-colored liquid

~ 60% Soybean oil

~ 74% TOC

Density ~ 1 g/cm³

Viscosity: thicker than water; normally diluted up to 19:1 for injection



Bench-test Objectives

- Determine whether CTET can be anaerobically biodegraded by EOS™
- Estimate dose of EOS™ required
- Identify potential intermediates/by-products (e.g. CF, DCM)
- Identify potential adverse effects (e.g. mobilization of arsenic)

Soil & GW Characterization

- Untreated soil:
 - sand, some clay
 - Composited prior to testing
- Untreated groundwater
 - received in multiple containers
 - Composited prior to testing

Parameter	Soil	GW
CTET, ppb	< 20	1,800
CF, ppb	< 20	44
DCM, ppb	< 40	< 120
Alk., ppm	--	380
DO, ppm	--	6.9
Nitrate, ppm	--	27
Sulfate, ppm	--	140
ORP, mV	--	253
pH	--	7.36

Test Design

- 13 Reactors
 - 1 Time 0 – non-sterile
 - 4 Controls (A-D)—non-sterile
 - 4 EOS-Low Dose (A-D)
 - 4 EOS High Dose (A-D)
- Combined soil, GW
 - Glass reactors with screw-cap
 - 360 g soil
 - 1,800 mL GW
 - About 290 mL headspace
- Added EOS™ and vitamin B-12 as appropriate



Test Design – cont'd

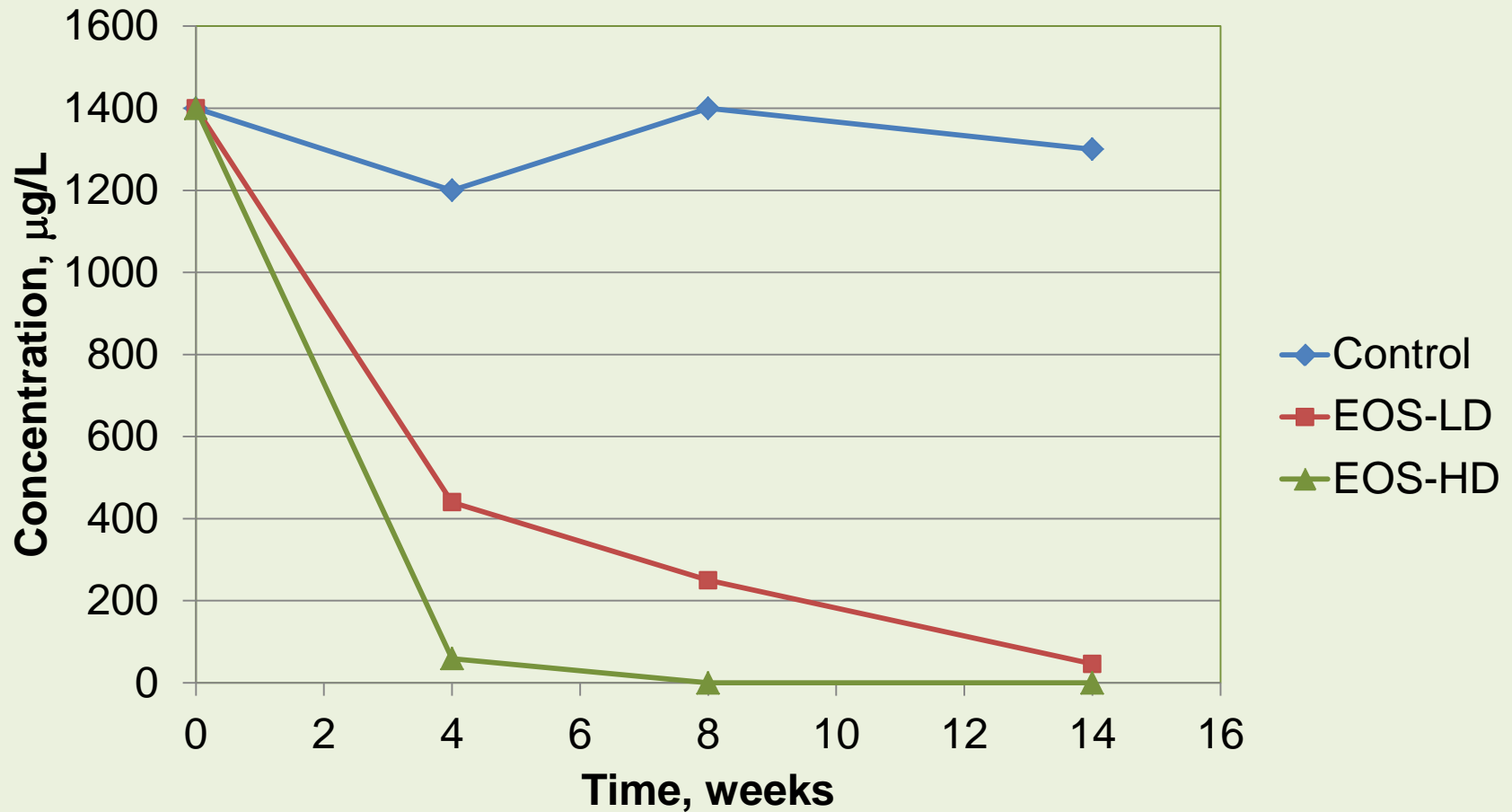
- Stored upside down in dark
- Inverted ~ 1/wk to mix
- Periodically, destructively sampled 1 replicate per test condition
 - analyzed water for VOCs and other parameters
 - did NOT analyze soil
 - collected samples at 0, 2, 4, 8, 14 wks

Initial Conditions

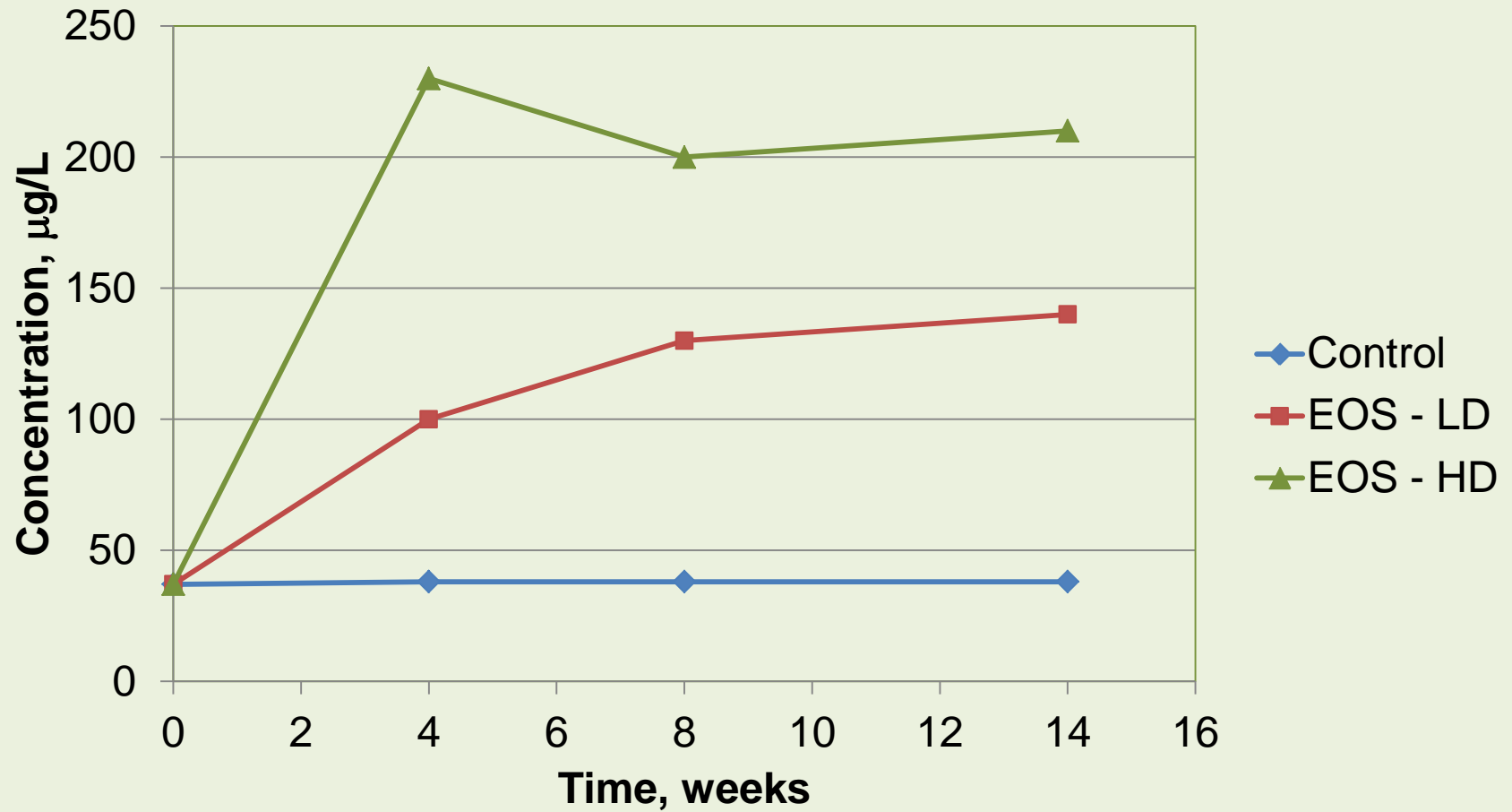
Test	EOS™ (mL/L GW)	B-12 (μL/L GW)
Time 0	0	0
Controls	0	0
EOS-LD	2	4.4
EOS-HD	4	8.8

Results

CTET Remaining



Chloroform



Methylene Chloride

Time (weeks)	Control	EOS – LD	EOS - HD
0	< 80	< 80	< 80
4	< 40	< 20	< 8
8	< 80	< 8	< 8
14	< 80	< 8	26

Mass Balance (14 weeks)

Analyte	micromoles		
	Control	EOS – LD	EOS - HD
CTET	18	0.65	< 0.03
Chloroform	0.69	2.5	3.8
Methylene Chloride	< 2	< 0.2	0.66
Total	19	3.2	4.5

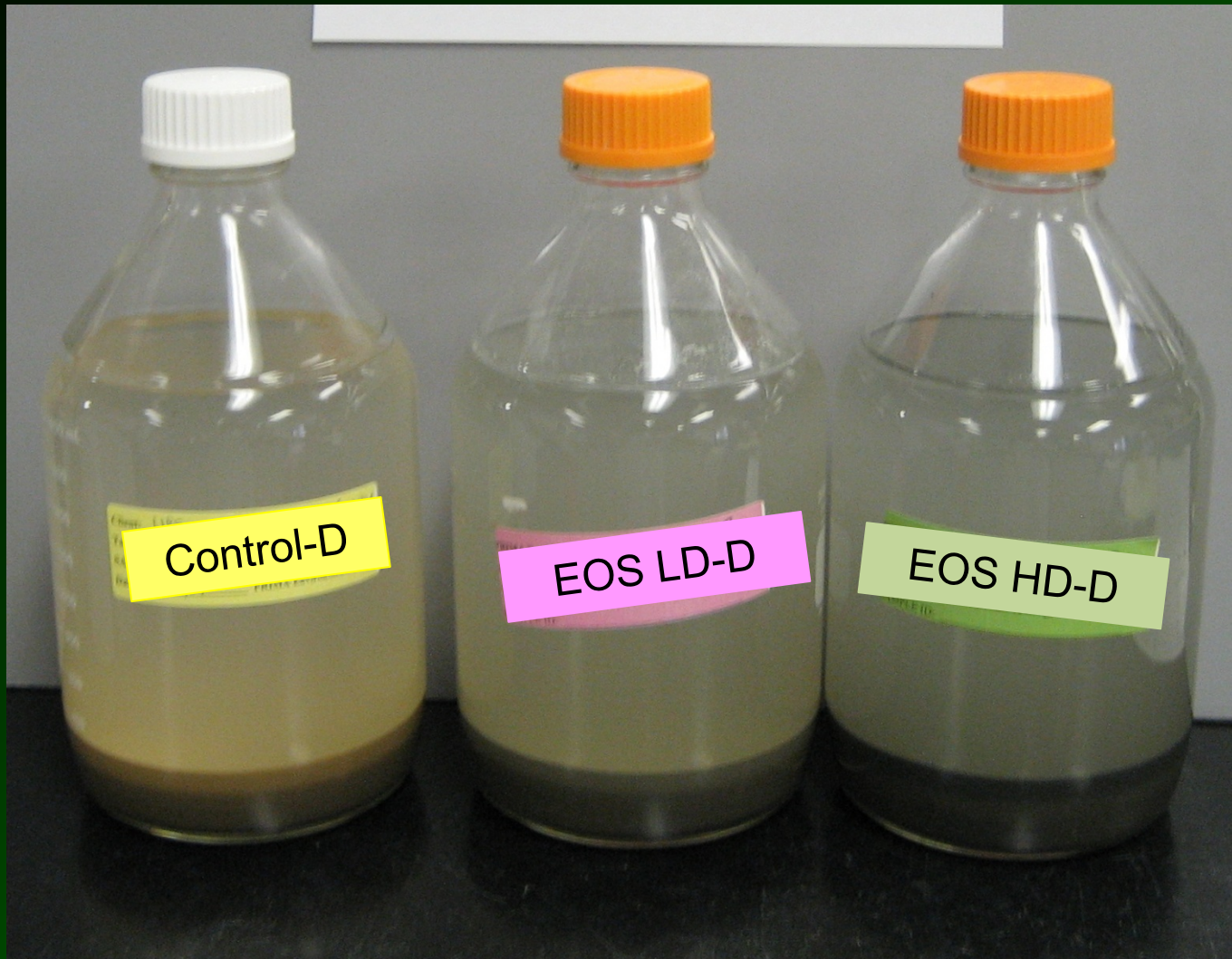
Notes:

- Values include amount in aqueous phase and in headspace, where headspace amounts were calculated from measured aqueous phase concentrations and Henry's constants.
- Mass balance assumes amount in soil is negligible.

Evidence of Biological Activity (Week 14)

Parameter	Control	EOS – LD	EOS - HD
Color	Tan	Gray	Dark gray
Diss. oxygen (mg/L)	6.9	2.3	0.7
Nitrate (mg/L)	27	< 0.25	0.34
ORP (mV)	381	-3	-18
pH	7.08	6.41	6.25
Anaerobic heterotrophs (cfu/mL)	1 x10 ²	3 x 10 ⁵	2 x 10 ⁵
Sulfate	140	83	1.8
Total Organic Carbon (mg/L)	1.1	44	120

Note: Nitrite, methane not detected in any sample.



Set "D" Reactors before 14 week sampling.

Other Secondary Parameters (Week 14)

Parameter	Control	EOS – LD	EOS - HD
Dissolved Metals (mg/L)			
arsenic	0.0072	0.024	0.028
chromium	0.015	< 0.005	< 0.005
iron	< 0.3	1.9	6.2
manganese	0.0059	6.5	6.7
sodium	81	85	83
vanadium	0.032	< 0.003	0.0075

Pilot Test

- Field pilot test in progress
 - begun June 2008
 - 25 gallons EOS™ mixed with 250 gallons well water was injected
- Initial results indicate enhanced biodegradation in some areas
 - CTET decreased
 - CF, nitrite, sulfide and methane increased
- Variable groundwater flow and low gradient may have limited contact between CTET and EOS™

Conclusions

- Addition of EOS™ enhanced biodegradation of CTET in bench tests
 - higher dose of EOS™ resulted in faster CTET removal
 - Chloroform and methylene chloride were generated, confirming destruction
- Secondary effects were minor
 - dissolved arsenic increased from 0.0079 mg/L to up to 0.024 mg/L
 - no change in sodium
- Multiple lines of evidence indicate increased biological activity
 - DO, nitrate, sulfate, pH, ORP, dissolved chromium decreased
 - Dissolved iron, manganese, plate counts increased
- Based on lab results, a field pilot test conducted.

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