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Bench- and Pilot-Scale Treatability Testing of ISCO and Surfactant Enhanced Biodegradation of Long Chain Petroleum Hydrocarbons

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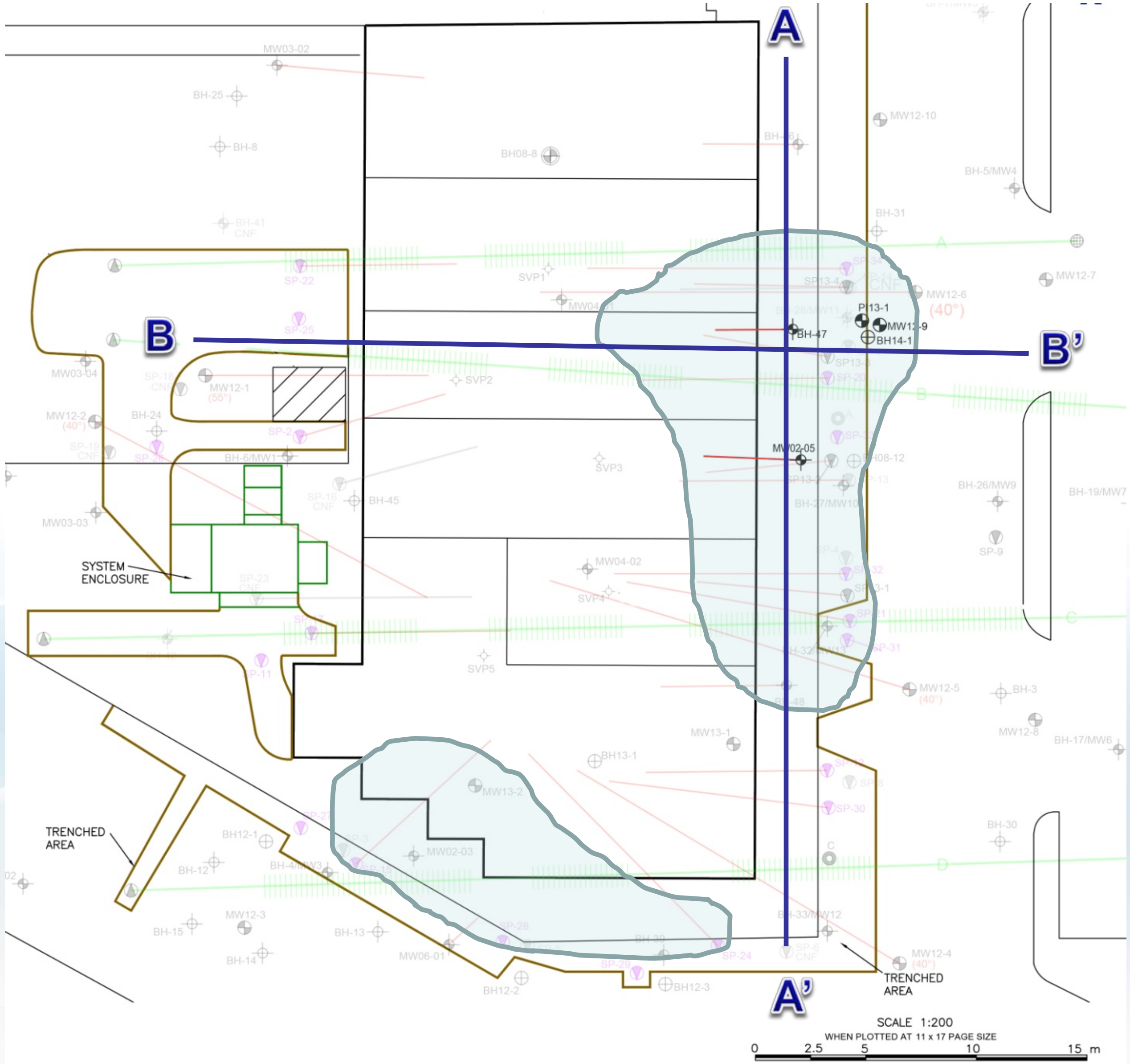
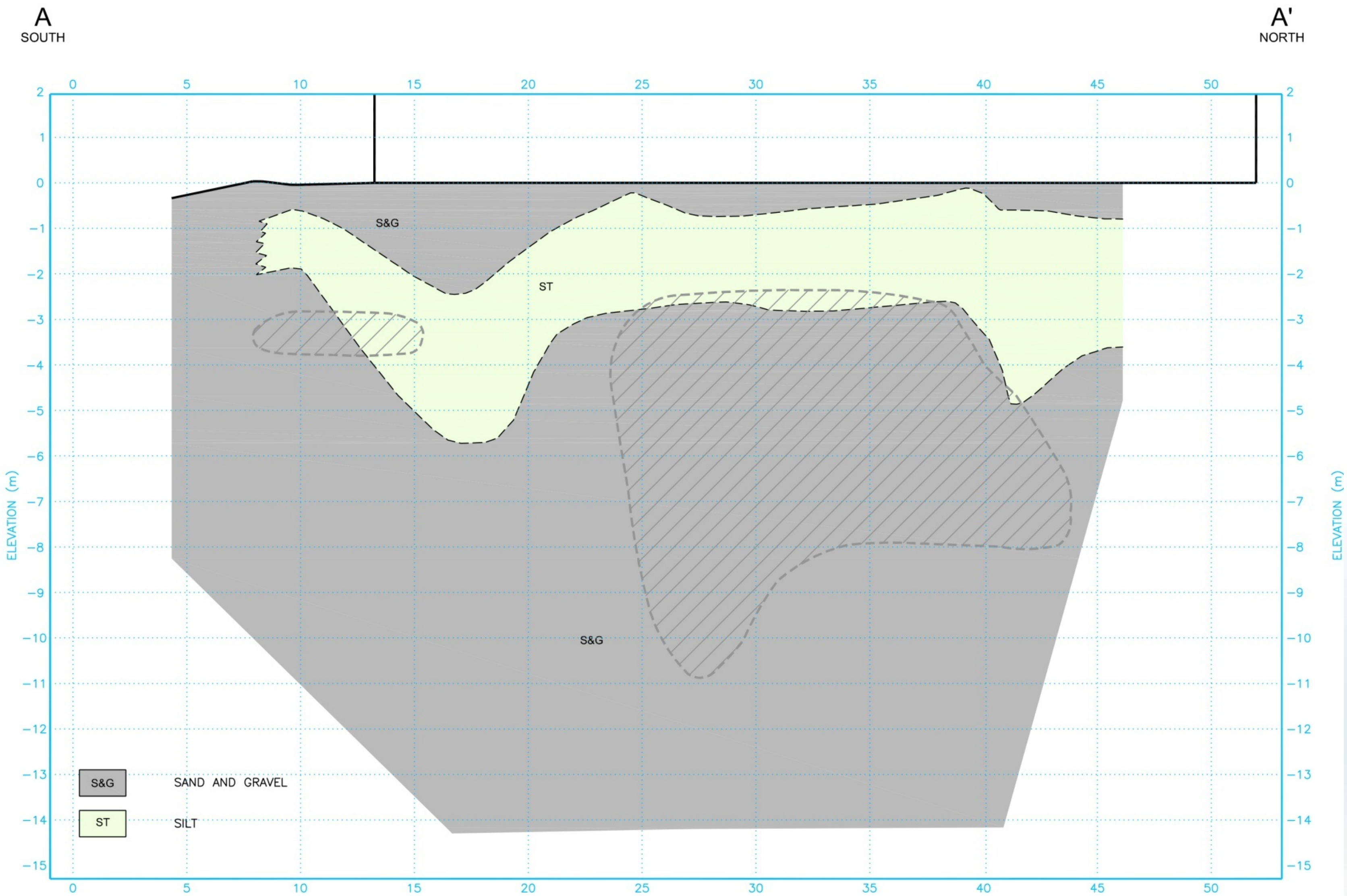
Our Site

- Current site use is as a strip mall
- Historical operations from the early 1900s had boilers that used fuel oil / bunker fuel
- Geology consists of silts to approximately 4 meters below ground underlain by a silty sand and gravel
- Groundwater is observed at approximately 3.5 meters below ground, i.e. in the silty sand and gravel
- Historical releases of fuel oil / bunker oil
- Much of the oil has “sunk”, some to as deep as 11 m below ground


A
A’
B
B’
SYSTEM ENCLOSURE
TRENCHED AREA
TRENCHED AREA
MW03-02
BH-25
BH-8
BH08-8
MW12-10
BH-5/MW4
BH-31
SVP1
MW12-7
MW12-6
(40°)
P13-1
MW12-9
BH-47
BH14-1
MW03-04
MW12-1
(55°)
SVP2
MW12-2
(40°)
BH-24
BH-6/MW1
MW02-05
BH08-12
SVP3
BH-26/MW9
BH-19/MW7
BH-45
MW03-03
BH-27/MW10
MW04-02
SP-9
SVP4
SVP5
MW12-5
(40°)
BH-3
MW12-8
BH-17/MW6
MW13-1
BH13-1
MW13-2
SP-30
BH-30
BH12-1
MW02-03
BH-12
BH-4/MW3
BH-33/MW12
MW12-3
BH-15
BH-13
MW06-01
MW12-4
(40°)
BH-14
BH12-2
BH12-3
SCALE 1:200
WHEN PLOTTED AT 11 x 17 PAGE SIZE
0
2.5
5
10
15 m



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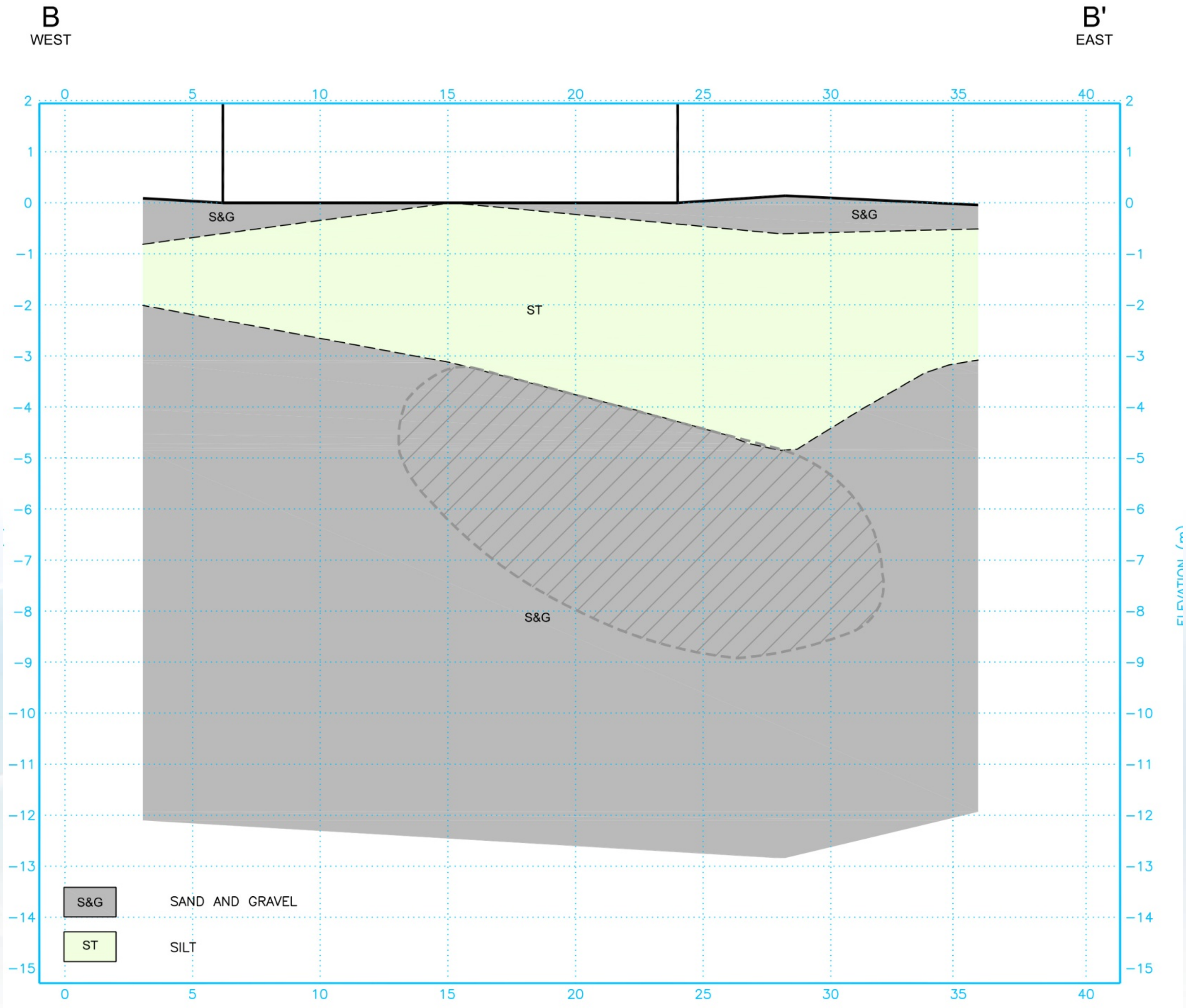

B
WEST
B'
EAST
S&G
S&G
ST
S&G
S&G
SAND AND GRAVEL
ST
SILT

Unusual Drivers

- The site may be a candidate for a risk-based closure, particularly with the relatively low mobility of the longer chain hydrocarbons
- Due to business drivers, the client would strongly prefer active remediation to reduce soil and groundwater concentrations to below cleanup levels
- Groundwater concentrations are looking good
- The remaining hydrocarbons at the site are most likely present in small droplets of separate phase hydrocarbons (SPH), adsorbed onto soil particles and/or trapped and non-mobile in the soil matrix

Previous Remedial Actions

- Site has been under investigation for many years
- Past remedial actions include
- Excavation to remove impacted soils away from site structures
- Soil vapour extraction (SVE) and air sparging to promote biodegradation (bioventing and biosparging)
- Due to the high water table intruding into the near ground surface silt layer, horizontal SVE wells were installed, but they can only operate seasonally
- Air sparging operates year round
- Due to low levels of volatiles on site, no vapour intrusion has been observed
- Soil and groudwater is aerobic, and groundwater is nearly clean, but residual fuel oil impacts remain in soil

The Current Project

- The goal of the current project is to remediate the residual fuel oil in soil.
- Cleanup level is 2,000 mg/kg in soil for diesel range hydrocarbons
- Excavation is only an option if the mall buildings are removed
- Air sparging and SVE, under current conditions, have reached the point of diminishing returns
- SLR was asked to evaluate the feasibility and cost of a more aggressive in-situ approach
- We conducted bench- and pilot-scale testing of six in-situ chemical oxidation (ISCO) and bioremediation approaches

Bench Test Program

- The bench scale test evaluated six treatment approaches, which included four ISCO approaches and two biodegradation approaches.

- Treatability tests were conducted in December 2013 and January 2014 using soil and water samples collected from the site. Bench-scale treatability testing was conducted on the following treatment chemistries:

  1. No treatment (control)
  2. ISCO using base-catalyzed sodium persulfate
  3. ISCO using hydrogen peroxide-catalyzed sodium persulfate
  4. ISCO using Fenton's oxidation
  5. ISCO using RegenOx® (sodium percarbonate)
  6. Biostimulation with hydrogen peroxide (active control)
  7. Biostimulation / Bioaugmentation with dilute hydrogen peroxide, surfactant, nutrients, and a hydrocarbon-degrading bacterial consortium

Bench Test – Baseline Screening

Parameter	Contaminated		Clean	
	Groundwater	Soil	Groundwater	Soil
pH	7.7	7.6	7.6	7.5
ORP (mV)	+125	NA	+108	NA
Benzene (mg/L or mg/kg)	<0.001	<0.028	<0.001	<0.0058
Toluene (mg/L or mg/kg)	<0.005	<0.14	<0.005	<0.029
Ethylbenzene (mg/L or mg/kg)	<0.001	<0.028	<0.001	<0.0058
Xylenes (mg/L or mg/kg)	<0.003	<0.083	<0.003	<0.017
VPH (mg/L or mg/kg)	<0.1	200	<0.1	<0.58
LEPH (mg/L or mg/kg)	7.8	1,800	<0.1	<4.6
HEPH (mg/L or mg/kg)	1.5	<550	<0.25	<12
Soil buffering capacity (mg/kg)	--	9,800	--	11,200
FOC (%)	--	0.56	--	0.39
Oxidant demand: H_2O_2 (g/kg)	--	156	--	106
Oxidant demand: persulfate (g/kg)	--	127	--	9.4
Total Cr (mg/kg)	--	7.7	--	5.1

Bench Test Results

Batch	Percent Removal for Soil Plus Groundwater			
	VPH	LEPH	HEPH	Total PH
Control	0%	0%	0%	0%
Peroxide Activated Persulfate	70%	30%	40%	40%
Base Activated Persulfate	0%	30%	40%	30%
Fenton's Oxidation	50%	-10%	-20%	-10%
RegenOx	0%	-10%	-20%	-10%

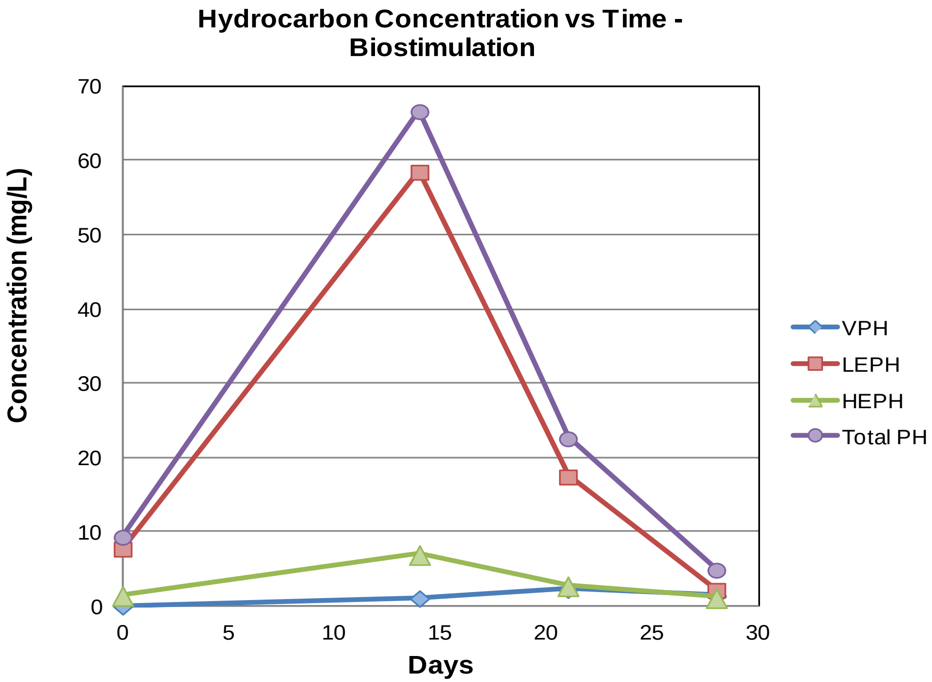
- Concentrations in the Fenton's Oxidation and RegenOx treated samples were greater than in the control. There were relatively significant heterogeneities in even the composited soil samples.

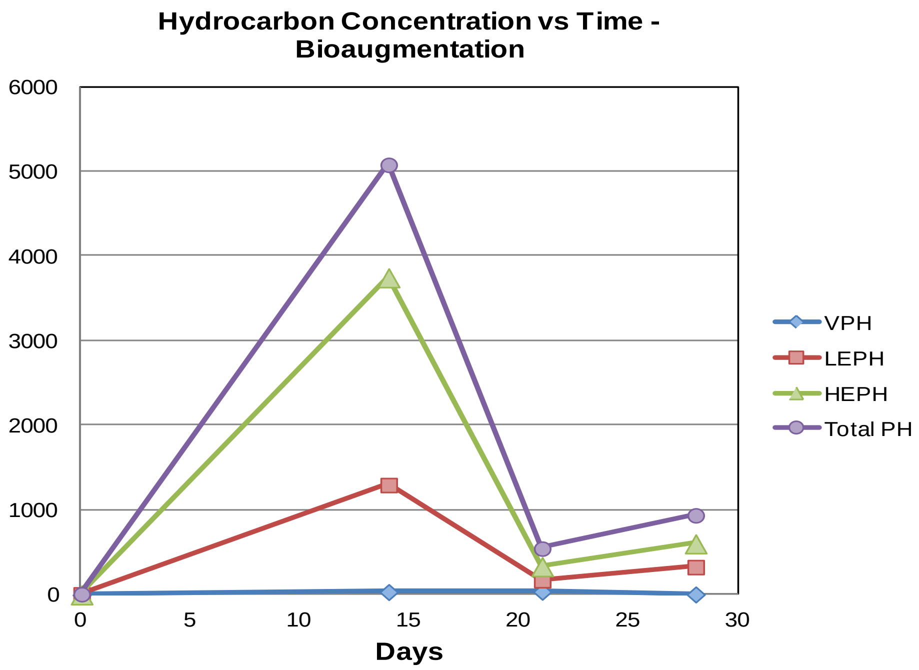
Batch	Percent Removal in Soil			
	VPH	LEPH	HEPH	Total PH
Control	90%	11%	27%	21%
Biostimulated	75%	53%	56%	56%
Bioaugmented	86%	77%	78%	78%

- The greatest reductions were seen in the bioaugmented sample. Contaminant reductions are most likely the result of both biodegradation and soil flushing, i.e. the release of hydrocarbons from the soil into the SPH.

Bench Test Results, Continued

- Increases in the concentrations of VPH, LEPH, and HEPH were observed for biostimulation and bioaugmentation. The concentrations declined relatively rapidly, indicating that biodegradation appeared to be occurring.





Bench Test Conclusions

- The bench test data resulted in the following general conclusions:
  - All treatment technologies tested resulted in the release of SPH from the soil into the groundwater
  - SPH recovery, if possible, should be attempted
  - The biodegradation approaches appear to have produced higher removal efficiencies than the ISCO approaches; however…
    - The bench test contractor didn't notify us of the release of the SPH and didn't quantify the quantity of SPH released; therefore, quantitative conclusions as to the mass destruction for the various technologies was not possible, and
    - Obvious heterogeneities in the soil, despite aggressive compositing, clearly affected the results.

Pilot Test Planning

- Results for the bench testing were positive for biodegradation approaches
- Biodegradation amendments are less expensive than typical ISCO chemicals
- SLR proposed a pilot test to evaluate the effectiveness of the bioaugmentation approach
- The plan was to conduct the pilot test as a “push-pull” test on one new injection well installed in the area of expected highest residual soil hydrocarbon concentrations
  - Inject hydrogen peroxide to provide oxygen and potential release of SPH
  - Pump the well to recover SPH
  - Inject surfactant to provide release of SPH
  - Pump the well to recover SPH
  - Inject nutrients to promote biodegradation
  - Monitor

Keys to Successful Bioremediation

- CONTACT: Must deliver nutrients & electron acceptors throughout plume zone
- MASS BALANCE FOR ELECTRON ACCEPTORS: DO, Nitrate, Sulfate must be added in ratio to existing fuel mass.
- MASS BALANCE FOR NUTRIENTS: N, P, K and micronutrients needed for amino acids, cellular growth.
- pH: GW pH between 5 and 8.
- SURFACTANT: Use surfactant to mobilize sorbed, weathered petroleum.

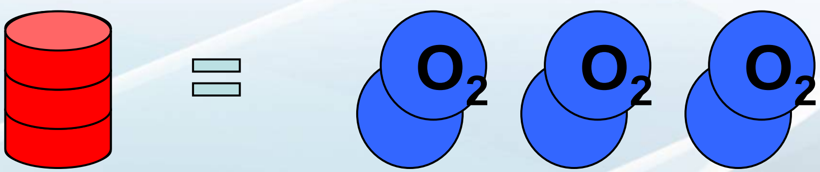
Mass Relationships

- NUTRIENTS:

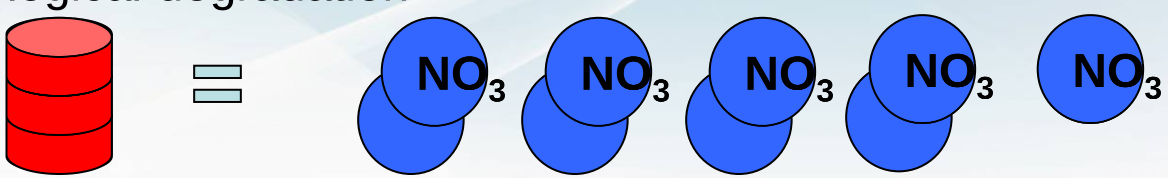
C:N:P Ratio = 100:20:5

Based on chemical makeup of a bacterial cell ($C_5H_7O_2N$)

- OXYGEN AS ELECTRON ACCEPTOR: 1 part of TPH requires 2 to 3 parts of dissolved oxygen for biological degradation



- NITRATE AS ELECTRON ACCEPTOR: 1 part of TPH requires 4½ parts of nitrate for biological degradation



Graphic courtesy of Etec LLC

Pilot Test Description

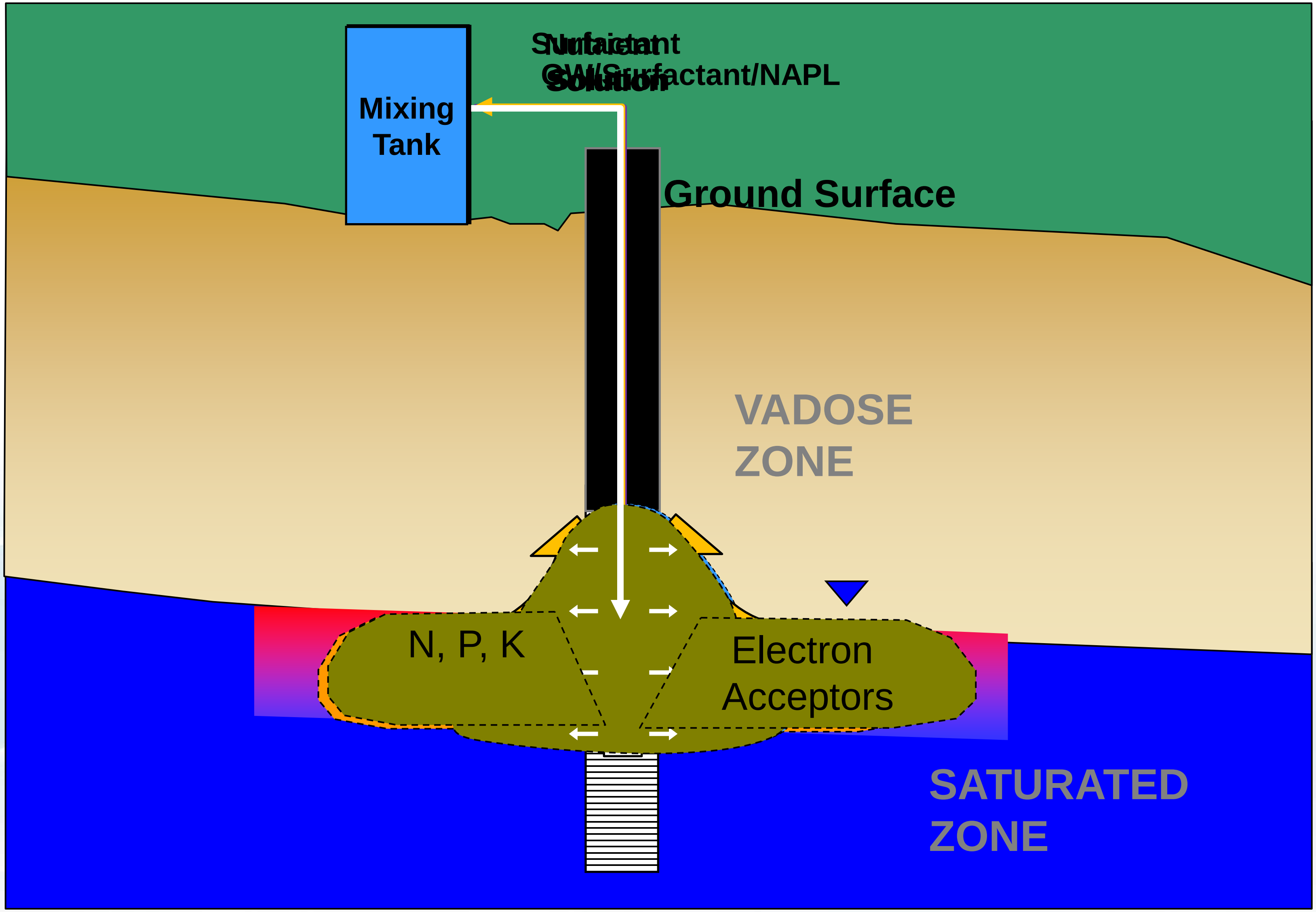
- Baseline groundwater samples were collected from the pilot test well and two nearby monitoring wells.
- Baseline sample from the pilot test well was analyzed for BTEX, LEPH, HEPH, nitrate, sulfate, ammonia, dissolved metals, speciated alkalinity, and hydrocarbon-degrading bacteria.
- Interim groundwater samples were collected from the pilot test well several times during the 4-day injection program.
- Interim samples were analyzed for BTEX, LEPH, and HEPH
- After the injections, groundwater samples were collected at 1 week, 2 weeks, 3 weeks, 4 weeks, 8 weeks, 12 weeks, and 16 weeks.

Pilot Test Description, Continued

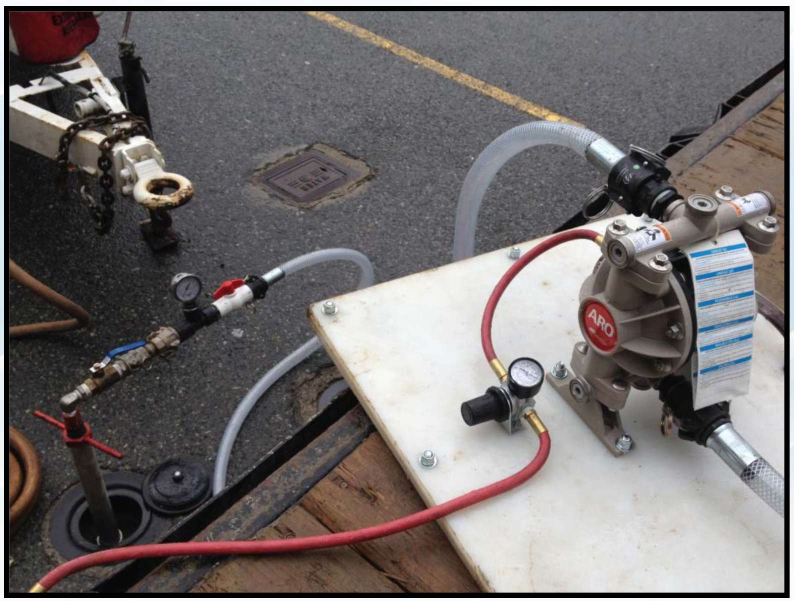
- Day 1
  - Measure field parameters and collect baseline groundwater samples
  - Inject 1,900 L of 4% hydrogen peroxide
  - Injection flow rate approximately 25 L/min
- Day 2
  - Measure field parameters and collect groundwater sample
  - Extract 3,800 L of groundwater
  - Measure field parameters and collect groundwater sample midway through extraction and after extraction
  - Inject 1,900 L of surfactant
  - Injection flow rate approximately 27 L/min

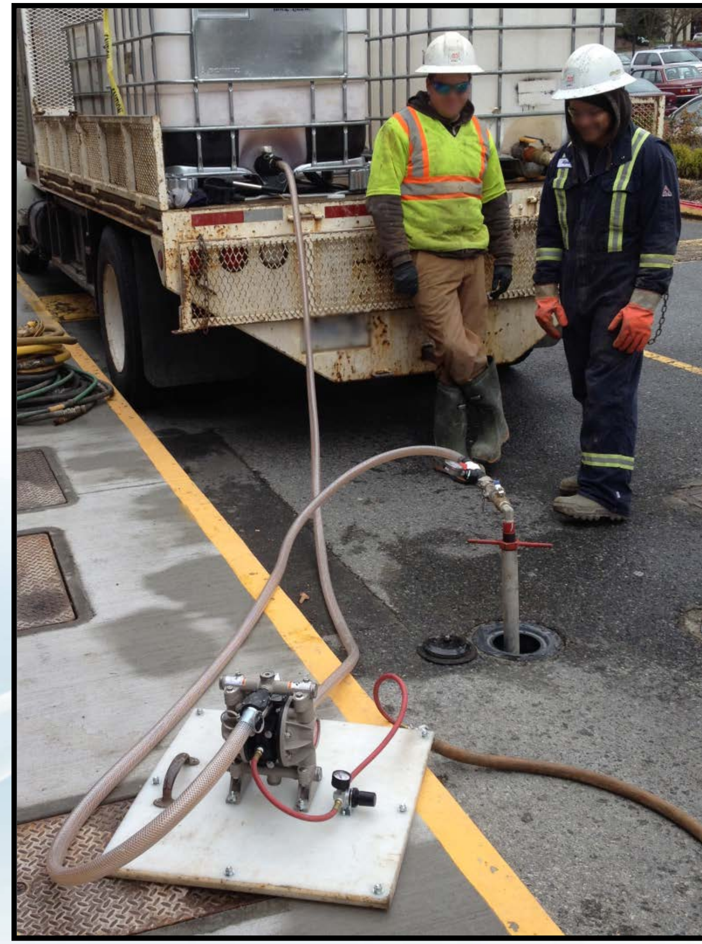
Pilot Test Description, Continued

- Day 3
  - Measure field parameters and collect groundwater sample
  - 2 mm layer of SPH observed
  - Extract 5,700 L of groundwater
  - Measure field parameters and collect groundwater sample midway through extraction and after extraction
  - Inject 1,000 L of 3% hydrogen peroxide
  - Inject 3,800 L of nutrient solution containing 91 kg of ammonium nitrate
    - Approximately 18,500 mg/L of nitrate
    - Could degrade up to 15 kg of hydrocarbon
    - Translates to approximately 500 mg/kg of soil in the injection area using estimate effective porosity of 20%

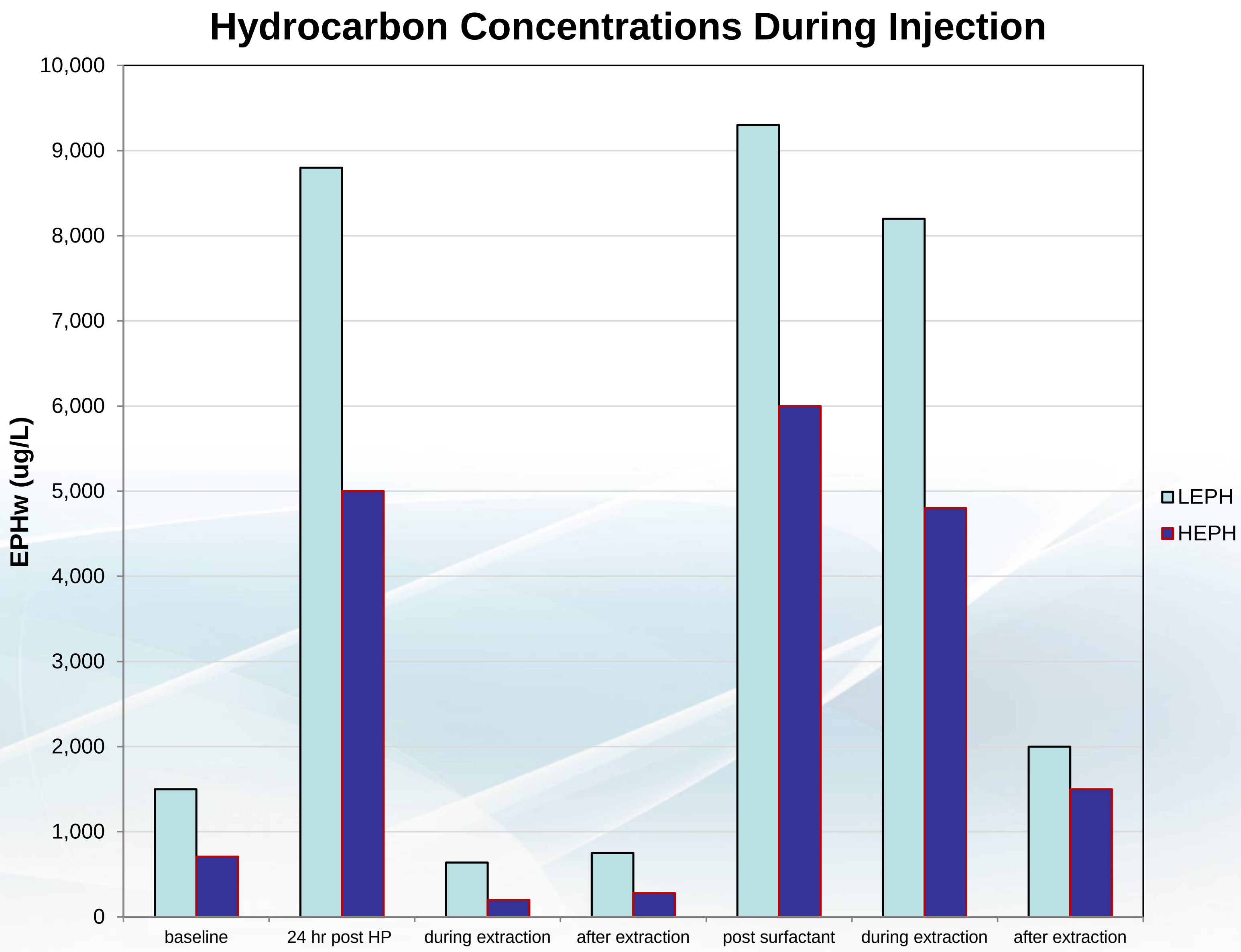


Graphic courtesy of Etec LLC

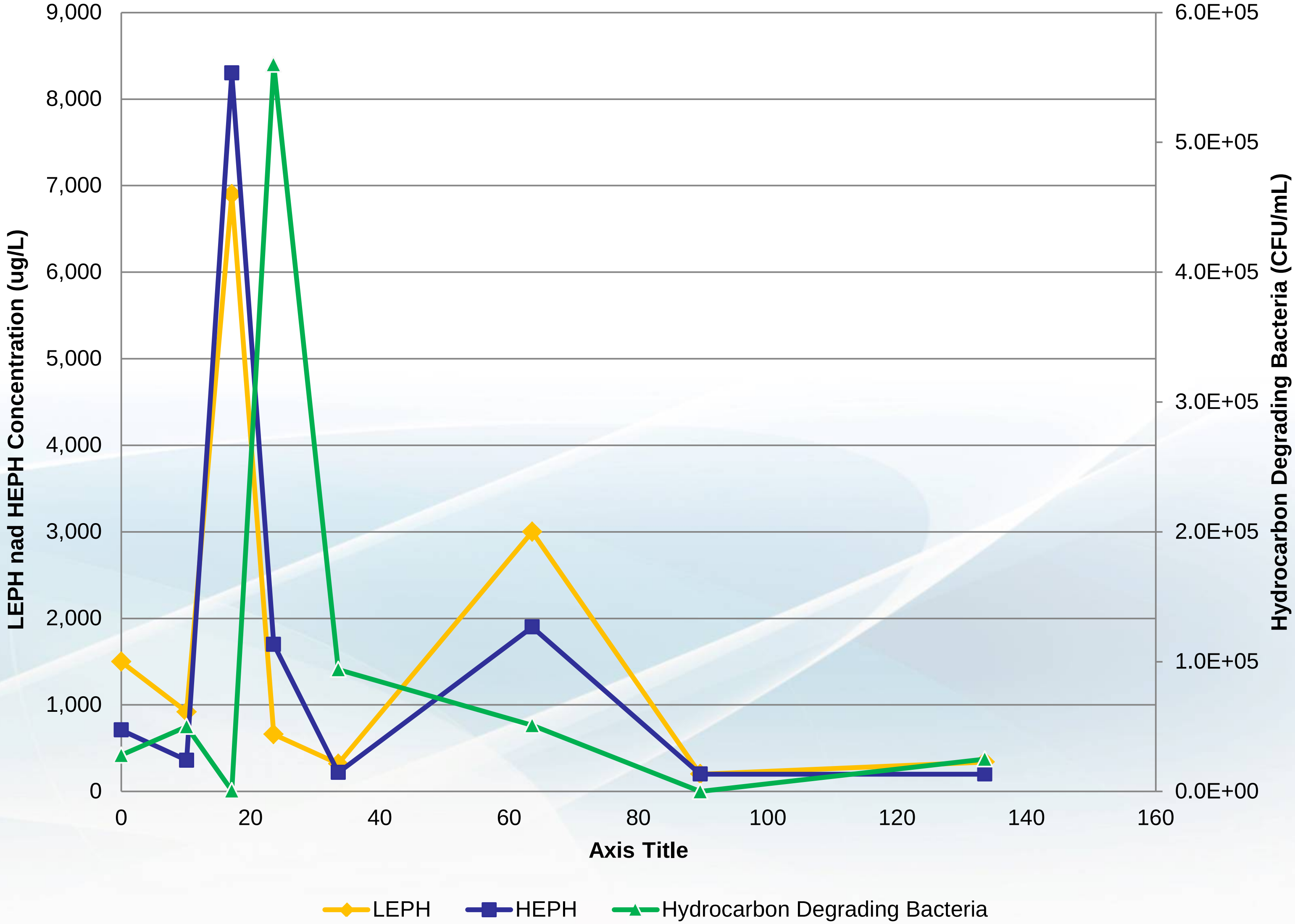

ARO



So, what happened?


Hydrocarbon Concentrations During Injection
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
EPHw (ug/L)
baseline
24 hr post HP
during extraction
after extraction
post surfactant
during extraction
after extraction
LEPH
HEPH

Hydrocarbon Concentrations and Microbial Population vs. Time



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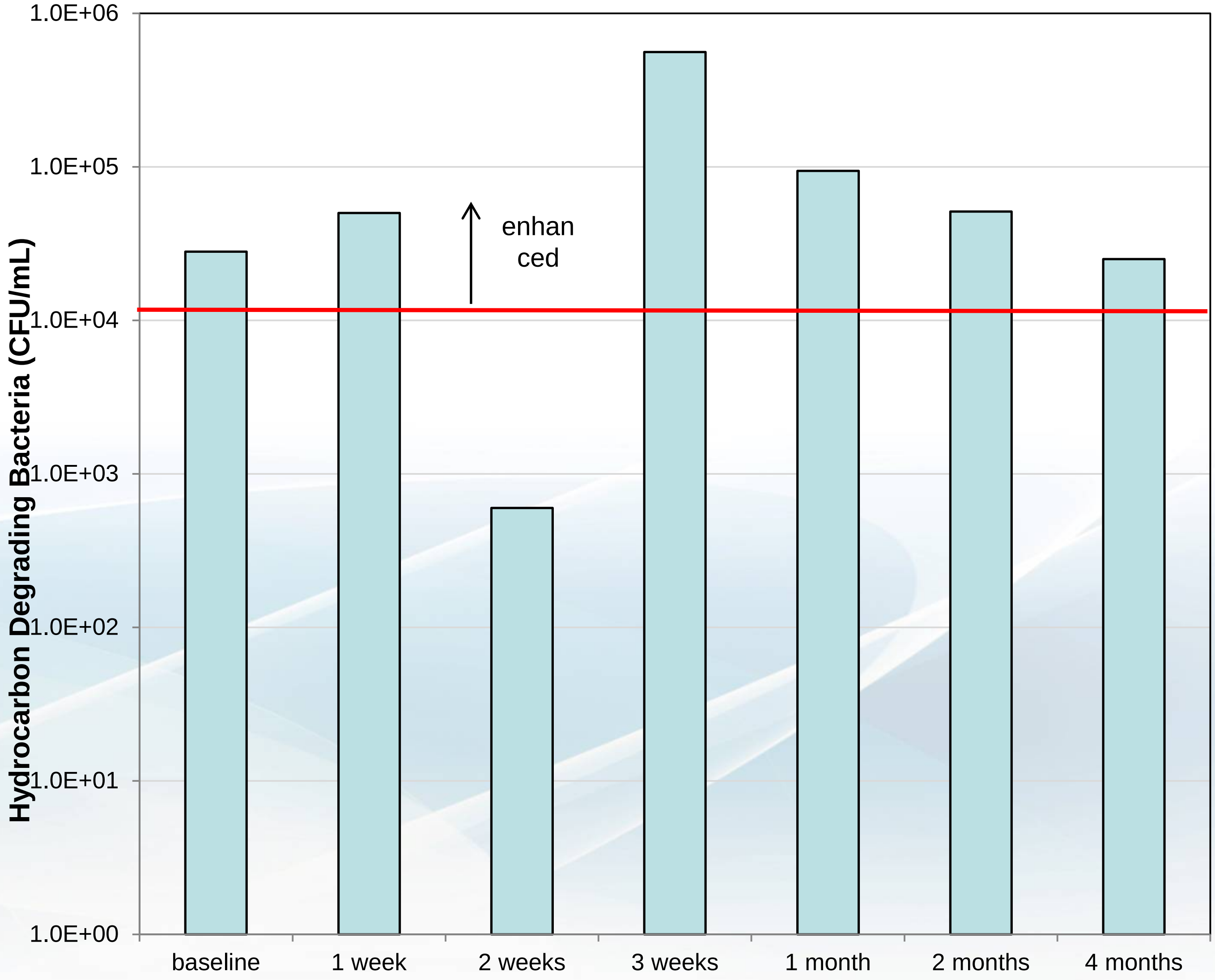
Graph 3. PI13-1 Hydrocarbon Degrading Bacteria



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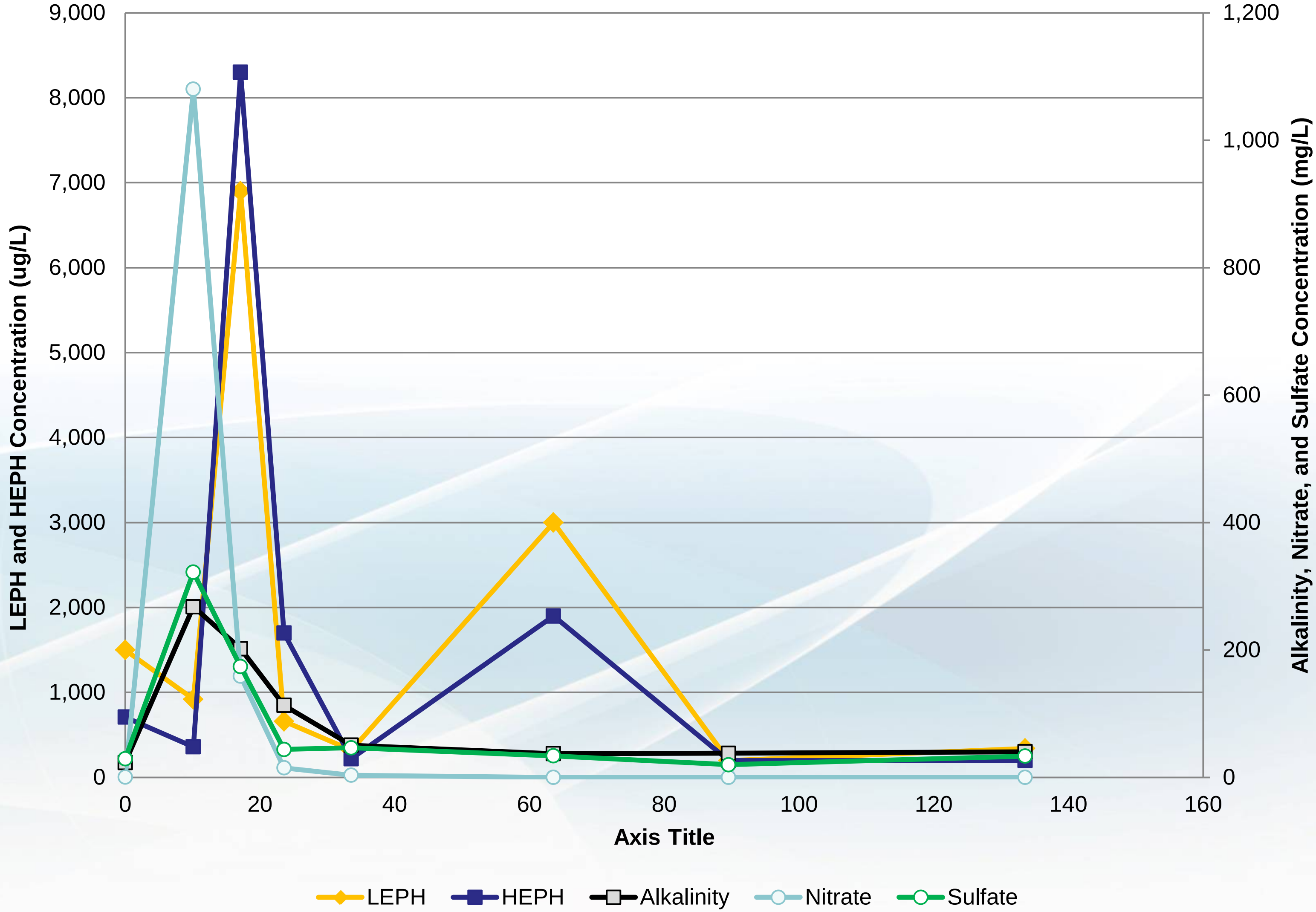
Hydrocarbon Concentrations and Nutrient Concentrations vs. Time



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				LEPHs			HEPHs		
				Before	After		Before	After	
Depth	Screen	PI13-1	BH14-1	PI13-1	BH14-1	% Change	PI13-1	BH14-1	% Change
(mbgs)				(mg/kg)	(mg/kg)		(mg/kg)	(mg/kg)	
3.7				1,410	<100	-93%	781	<100	-87%
3.8				1,410	<100	-93%	781	<100	-87%
3.9			Silt	1,410	<100	-93%	781	<100	-87%
4.0				1,410	<100	-93%	781	<100	-87%
4.1									
4.2									
4.3					2,540	NA		1,170	NA
4.4					2,540	NA		1,170	NA
4.5					2,540	NA		1,170	NA
4.6		Gravelly			2,540	NA		1,170	NA
4.7		Sand							
4.8									
4.9				2,040		NA	791		NA
5.0			Gravelly	2,040		NA	791		NA
5.1			Sand	2,040		NA	791		NA
5.2				2,040	2,720	33%	791	1,140	44%
5.3					2,720	NA		1,140	NA
5.4					2,720	NA		1,140	NA
5.5					2,720	NA		1,140	NA
5.6									
5.7									
5.8				2,560	1,140	-55%	1,170	527	-55%
5.9				2,560	1,140	-55%	1,170	527	-55%

5.8				2,560	1,140	-55%	1,170	527	-55%
5.9				2,560	1,140	-55%	1,170	527	-55%
6.0				2,560	1,140	-55%	1,170	527	-55%
6.1				2,560	1,140	-55%	1,170	527	-55%
6.2									
6.3					124	NA		<100	NA
6.4		**Gravel**			124	NA		<100	NA
6.5					124	NA		<100	NA
6.6					124	NA		<100	NA
6.7				435		NA	235		NA
6.8				435		NA	235		NA
6.9				435		NA	235		NA
7.0				435	159	-63%	235	<100	-57%
7.1					159	NA		<100	NA
7.2					159	NA		<100	NA
7.3		**Silt**			159	NA		<100	NA
7.4				**1,611**	**1,337**	**-17%**	**744**	**946**	**27%**
7.5									
7.6									
7.7			**Gravel**						
7.8									
7.9					235			123	
8.0					235			123	
8.1					235			123	
8.2					235			123	
8.3									

Conclusions - Groundwater

- Hydrogen peroxide and surfactant injections resulted in mobilization, albeit limited, of hydrocarbons within the radius of influence of the injection well.
- Nitrate injections resulted in biodegradation of hydrocarbons in groundwater.
- We injected 200 lbs of nutrients, resulting in a concentration of approximately 18,500 mg/L nitrate in the injection water
- Nitrate concentrations declined rapidly, falling below the detection limit during the pilot test time frame.

Success

Conclusions - Soil

- Soil results are encouraging, but inconclusive, due to:
  - The heterogeneity of soils
  - The limited amount of nitrate that could be injected during one injection event
  - The nature of contaminants at the site, i.e. long chain hydrocarbons
  - Results did show that the lighter hydrocarbons were degraded suggesting that the heavier hydrocarbons may also be degraded by additional injections.

Promising