PS Source Area MIP Investigation and Pilot-Scale Groundwater Remediation Using Activated Persulfate*

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Search and Discovery Article #80246 (2012)**
Posted August 20, 2012

*Adapted from poster presentation at AAPG Annual Convention and Exhibition, Long Beach, California, April 22-25, 2012
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Abstract

Background/Objectives. AECOM performed a pilot test at a site in Southern California to assess the applicability and effectiveness of in situ chemical oxidation (ISCO) using activated persulfate for treating residual gasoline free product and high concentrations of dissolved-phase petroleum hydrocarbons as gasoline, BTEX, and MTBE. A former leaking UST, which was removed in 1995, was the apparent source of soil and groundwater impacts at the site. Several site investigations were performed in the late 1990s and interim remedial actions were performed at the source area in the early 2000s.

Approach/Procedures. The pilot test was performed in 2010, starting with a membrane interface probe (MIP) investigation to characterize the lithology and total VOCs in the source area in high-resolution. The MIP results were then used to design the ISCO injection grid. Soil and groundwater samples were collected for a bench-scale study to evaluate the total oxidant demand (TOD) of three persulfate activation methods (iron, alkaline, and peroxide). The TOD results were then used to choose the most cost-effective activator and calculate reagent mass and volume.

6,600 lbs of sodium persulfate were mixed with 660 pounds of iron EDTA and water before being injected across the top 10 feet of the saturated zone using direct-push methods. Five groundwater monitoring events were performed: baseline and 1, 2, 3, and 6 months following the injection, to track changes in geochemical conditions, assess the distribution of injected reagent, and evaluate changes in VOC and metal concentrations.

Results/Conclusions. The MIP results indicated that the source in the unsaturated zone is beneath the former UST and sorbed onto tight silty soils. There is also a significant mass in the saturated zone set in more permeable/sandy soils. The bench-scale study indicated high TODs for alkaline and peroxide activation methods (approximately 20 grams of oxidant per kilogram of saturated soil [g/kg]) and a lower TOD for iron activation (4.8 g/kg).

Persulfate distribution and oxidation were achieved within the injection zone and as far as 20 feet cross-gradient and 35 feet downgradient of the

injection zone. Iron-activated persulfate was effective in reducing concentrations of dissolved-phase VOCs and enhancing free-phase desorption and dissolution. Concentration rebound was observed indicating that repeated injections would be required to achieve a sustained cleanup of the source area saturated zone.

Source Area MIP Investigation and Pilot-Scale Groundwater Remediation Using Activated Persulfate

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AAPG 2012 Annual Convention & Exhibition (ACE)

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Problem Statement

Impacts to soil and groundwater from a subsurface hydrocarbon release at an active emergency response facility.

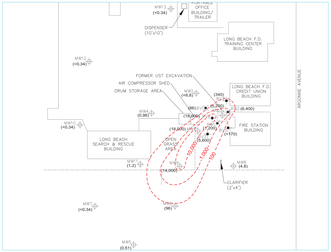
Source:
A former 550-gallon gasoline underground storage tank.

Risk:
Three active potable water supply wells are located within ½ mile of the site.

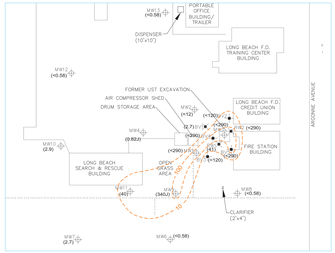
Risk Drivers:
- Gasoline–range hydrocarbons.
- Volatile Organic Compounds (BTEX).
- Fuel Oxygenates (MTBE).

Remediation Program Goal

Remediate the impacts to soil and groundwater to acceptable risk-based levels.



Benzene Isoconcentration Map (µg/L)



MTBE Isoconcentration Map (µg/L)

Technical Objectives

Delineate the source area in saturated and unsaturated media
Low resolution site investigations were performed from 1995 to 1999. Data gaps – updated lateral and vertical delineation.

Delineate impact to groundwater
Ongoing groundwater monitoring since 2003.

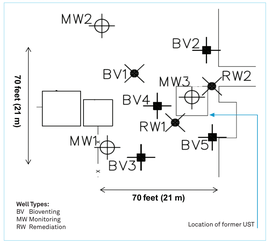
Evaluate remedial alternatives
In Situ Chemical Oxidation (ISCO) using activated persulfate was proposed and approved in 2007.

Test the selected remedial alternative
ISCO Pilot Test Work Plan was approved in February 2010.

Pilot test Objectives
- Demonstrate the applicability of ISCO
- Evaluate the effectiveness of ISCO at reducing contaminant mass and concentration
- Develop parameters for full-scale implementation

Design and implement full-scale remediation

Pilot Test Area



Pilot Test Technical Approach

Membrane interface probe (MIP) investigation
High resolution source delineation in saturated and unsaturated media.

Bench-scale total oxidant demand (TOD) study
Determine a cost effective activation method for sodium persulfate.

One injection event of activated persulfate
- Target the source area
- Injection grid and vertical intervals guided by MIP results
- Direct-push injection points

Monitor and sample groundwater at the source area using existing wells to assess
- Geochemistry changes and oxidant distribution
- Contaminant concentration reductions
- Potential mobilization of metals

Membrane Interface Probe (MIP) Investigation

Source Area Delineation in the Vadose Zone

Extent and magnitude
- ~30' by 15' (~10 m by 5 m) beneath the former UST
- Vertical interval: 12' – 17' (3.5 – 5 m) bgs
- Sorbed to tight silty soils

Maximum soil concentrations
- TPHg = 9,000 mg/kg
- Total BTEX = 1,400 mg/kg

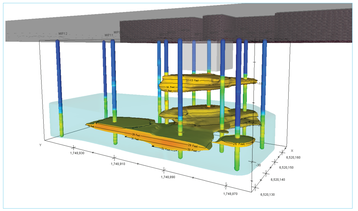
Source Area Delineation in the Saturated Zone

Extent and magnitude
- Vertical interval: 23' – 33' (7 – 10 m) bgs
- Sorbed to silts and sandy soils

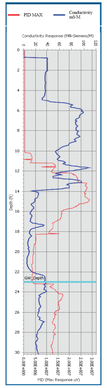
Maximum soil concentrations
- TPHg = 15,000 mg/kg
- Total BTEX = 2,300 mg/kg

Maximum groundwater concentrations
- TPHg = 4,600 mg/L
- Total BTEX = 1,510 mg/L

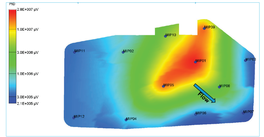
Total VOCs - West View



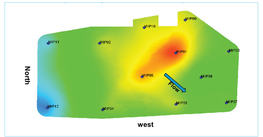
MIP01 PID Response Curve



Total VOCs - 15' bgs (center of vadose zone source)



Total VOCs - 25' bgs (2' below groundwater surface)



Bench-Scale Study

Parameter	Reagent	Vadose Zone	Saturated Zone
Buffering Capacity (L NaOH / kg soil)	Sodium hydroxide (NaOH)	0.10	0.11
Soil Bulk Density (g/cc)	—	2.032	2.53
Soil Moisture (%)	—	24.43	15.32
Total Oxidant Demand (TOD) (grams persulfate / kilogram soil)			
Control	Sodium persulfate ($Na_2S_2O_8$)	0.52	1.31
Chelated Metal Activation	$Na_2S_2O_8$ + iron EDTA	1.57	4.83
Alkaline Activation	$Na_2S_2O_8$ + NaOH	20.81	21.69
Hydrogen Peroxide Activation	$Na_2S_2O_8$ + H_2O_2	11.67	19.90

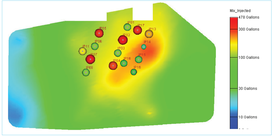
- *The high TOD values for alkaline and peroxide activation are most likely due to greater oxidant decomposition during the study period (5 days).*
- *Other factors affecting the TOD are: mass of contaminants, natural organic matter (NOM), persulfate dose, and reduced minerals.*

Performed in the AECOM Treatability Laboratory (Orlando, FL)

Iron-Activated Persulfate Injection

Injection System Setup

Persulfate "Artwork" on a Direct-push Rod



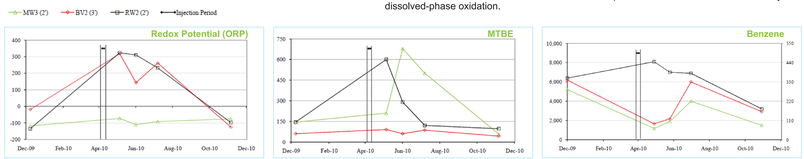
Injection Grid in Groundwater Source Area (25' bgs)

Injection Summary

Parameter	Quantity
Reagent	
Klozur™ sodium persulfate	6,600 lbs (3,000 kg)
Dissolvine iron EDTA	660 lbs (300 kg)
Total solution volume	5,030 gallons (19,000 liters)
Solution concentrations	11% – 20% by weight
Injection Operations	
Injection interval	20' – 30' (6 – 9 m) bgs
Pressure / Flow rate	10 – 90 psi / 2.5 gpm (9.5 lpm)

Groundwater Results – Source Area

- ORP substantially increased following the injection indicating the presence of persulfate. ORP then gradually decreased thereafter indicating the gradual depletion of persulfate.
- Concentrations of benzene (and other gasoline-range compounds) significantly decreased compared to baseline (50%-79%).
- The initial effects of oxidation were exhibited as free-phase dissolution of MTBE followed by dissolved-phase oxidation.



Pilot Test Conclusions

- Soil and groundwater analytical results, and a continuous soil core collected in the source area, indicate the presence of LNAPL in the vadose zone and saturated zone.
- The apparent residual mass of LNAPL may render ISCO cost-prohibitive as a sole technical approach for source remediation.
- Iron EDTA appears to be a more cost effective persulfate activator than NaOH and H_2O_2.
- Iron-activated sodium persulfate was effective in reducing concentrations of dissolved-phase COCs and enhancing free-phase desorption and dissolution in the source area.
- Persulfate distribution and oxidation was achieved within the injection zone and as far as 20' cross-gradient (Well BV1) and 35' downgradient (Well MW1) of the injection zone.

Overview of ISCO

In Situ Chemical Oxidation

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Chemical oxidation is a remediation technology that introduces oxidants to the contaminated subsurface by injection or mechanical mixing. Physical placement of the chemicals into the subsurface is referred to as *in situ* chemical oxidation (ISCO).

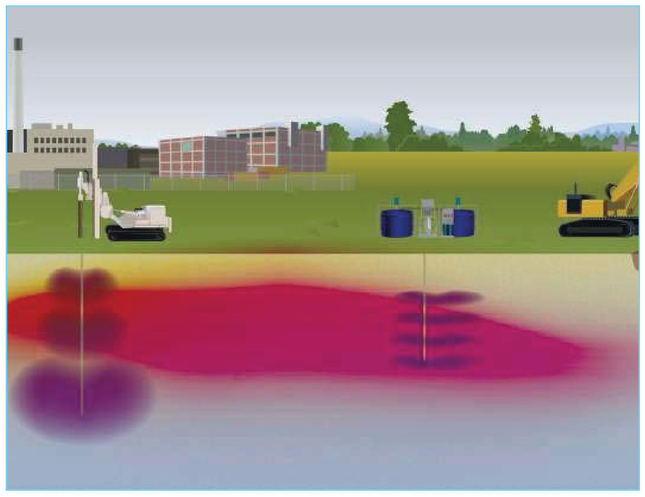
Effective chemical oxidation may be achieved using a strong oxidant only, or in combination with other chemicals that function as catalysts. The oxidants chemically react with contaminants, and convert them to non-toxic end products such as carbon dioxide and water.

In situ chemical oxidation is an attractive option at many hazardous waste sites, because:

- Complete contaminant destruction is possible
- Rapid treatment times are achievable
- It is a green and sustainable remedial option
- It is an innovative remedy, compatible with mechanical and biological cleanup approaches

Chemical oxidation effectiveness, especially ISCO, is dependent on achieving contact between the contaminant and delivered oxidant. Challenges to successful implementation are presented by subsurface heterogeneities, preferential flow paths, the presence of non-target consumptive demand by naturally occurring organic compounds, dissolved metals (such as ferrous iron), and the potential for formation of undesirable reaction byproducts (such as sulfate or manganese dioxide).

Although a chemical oxidation reaction is relatively simple, not all oxidants react effectively with any given contaminant; therefore, selection of the appropriate oxidant is critical to successfully achieving the remediation endpoint.



Conceptual implementation of ISCO

Oxidant	Reactive Species	Form	Persistence [1]
Permanganate	MnO_4^-	powder/liquid	>3 months
Hydrogen Peroxide	H_2O_2, ·OH, $\cdot O_2^-$, $\cdot HO_2$, HO_2^-	liquid	minutes - hours
Ozone	O_3, ·OH	gas	minutes - hours
Persulfate	SO_4^{2-}, $\cdot SO_4^-$	powder/liquid	hours - weeks

Oxidant and Reactions	Electrode Potential (E_h) [2]
Permanganate	
$MnO_4^- + 4 H^+ + 3 e^- \longrightarrow MnO_2 + 2 H_2O$	1.7 V (permanganate ion)
Fenton's (H_2O_2 Derived Reactants)	
$H_2O_2 + 2 H^+ + 2 e^- \longrightarrow 2 H_2O$	1.8 V (hydrogen peroxide)
$2 \cdot OH + 2 H^+ + 2 e^- \longrightarrow 2 H_2O$	2.8 V (hydroxyl radical)
$\cdot HO_2 + 2 H^+ + 2 e^- \longrightarrow 2 H_2O$	1.7 V (perhydroxyl radical)
$\cdot O_2^- + 4 H^+ + 3 e^- \longrightarrow 2 H_2O$	-2.4 V (superoxide radical)
$HO_2^- + H_2O + 2 e^- \longrightarrow 3 OH^-$	-0.88 V (hydroperoxide anion)
Ozone	
$O_3 + 2 H^+ + 2 e^- \longrightarrow O_2 + H_2O$	2.1 V (ozone)
$2 O_3 + 3 H_2O_2 \longrightarrow 4 O_2 + 2 \cdot OH + 2 H_2O$	2.8 V (hydroxyl radical)
Persulfate	
$S_2O_8^{2-} + 2 e^- \longrightarrow SO_4^{-2}$	2.1 V (persulfate)
$S_2O_8^{-2} + Fe^{+2} \longrightarrow \cdot SO_4^- + SO_4^{-2} + Fe^{+3}$	2.6 V (sulfate radical)

1 Persistence of the oxidant varies depending on site-specific conditions. Durations specified here are based on general observations.
2 Reactive species in parentheses; reduction potential is negative.

Hydrogen Peroxide Injection field

Indoor temporary injection system

Hydrogen Peroxide tank

Ozone sparging system

Sodium Persulfate crystals

Permanganate Soil Mixing

Contaminant	Oxidant: Permanganate (MnO_4^-)	Catalyzed Hydrogen Peroxide (H_2O_2/Fe)	Persulfate ($S_2O_8^{2-}$)	$\cdot SO_4^-$ (Activated Persulfate)	Ozone (O_3)	Ozone/Peroxide (Perozone)
Petroleum hydrocarbons	G	E	G/E	E	E	E
BTEX	E	E	E	E	G/E	E
Benzene	P/G	E	G	G/E	G/E	E
Phenols	G/E	E	P/G	G/E	E	E
PAH	G/E	G/E	G	G/E	G/E	G/E
MTBE	G	G/E	P/G	E	G/E	E
tert-butyl alcohol	P/G	G/E	P/G	E	E	G/E
Chlorinated ethenes	E	E	G	E	E	E
Carbon tetrachloride	P	P/G	P	P/G	P/G	P/G
Chloroform	P	P	P/G	G/E	P/G	P
Methylene chloride	P	P/G	P/G	G/E	G	P/G
Chlorinated ethanes	P	P/G	P	G/E	P/G	P
Trichloroethane	P	P/G	P	P/G	P/G	P/G
Dichloroethane	P	P/G	P	G/E	G	P/G
Chlorobenzene	P	E	P/G	E	E	E
PCBs	P	P/G	P	P/G	P/G	G/E
Energetics (RDX, HMX)	E	E	G	E	E	E
Explosives	E	G/E	G	G/E	E	E
Pesticides	G	P/G	P/G	G/E	P/G	P/G
1,4-dioxane	P	E	P/G	E	E	E

P = poor, G = good, E = excellent

Activated Persulfate Pilot Test

Additional Groundwater Results

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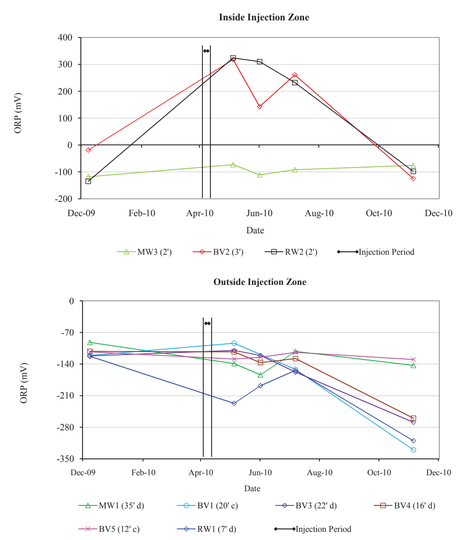
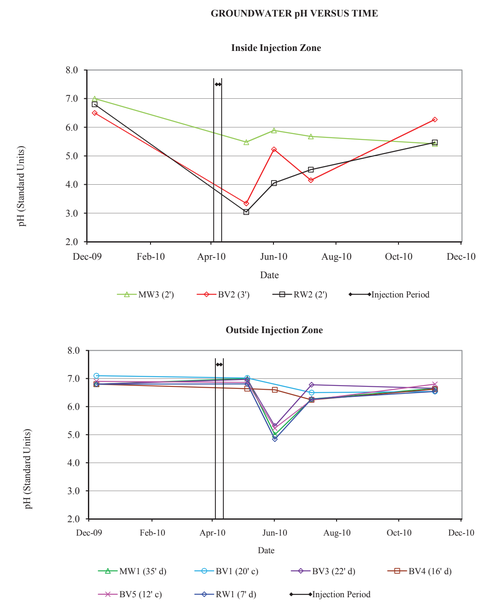
Geochemical Parameters



Notes:
Numbers in parentheses are distance to the nearest injeciton point
c cross-gradient
d downgradient
mV millivolts
ORP oxidation-reduction potential



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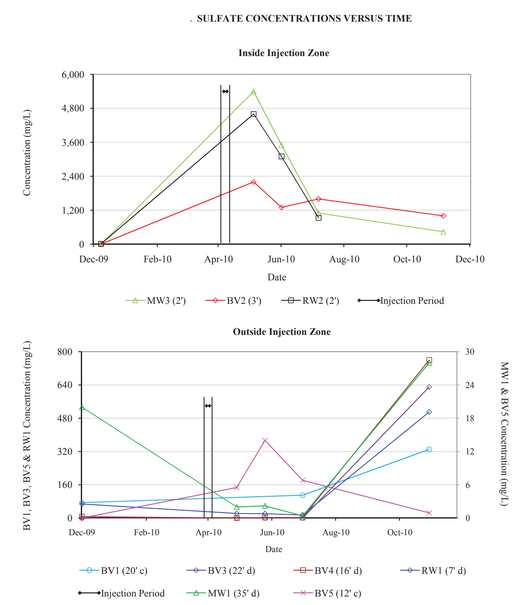
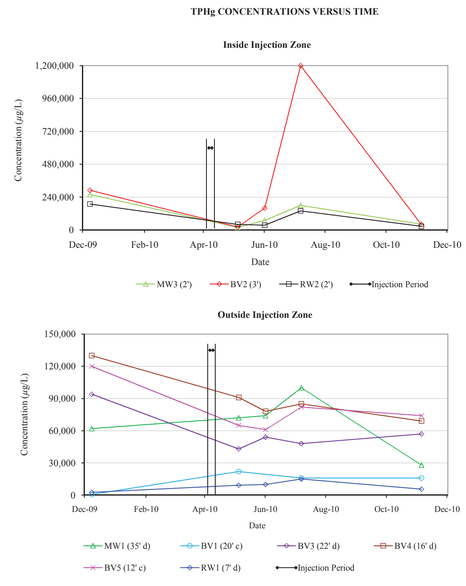
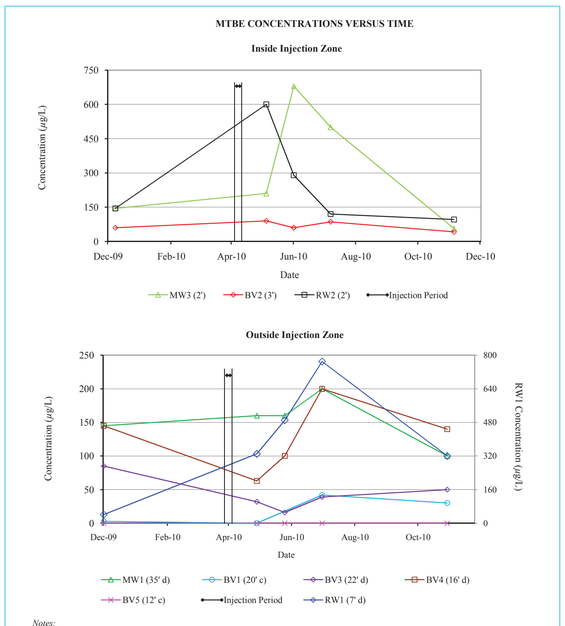


Notes:
Numbers in parentheses are distance to the nearest injeciton point
c cross-gradient
d downgradient
mg/L micrograms per liter

Contaminants of Concern

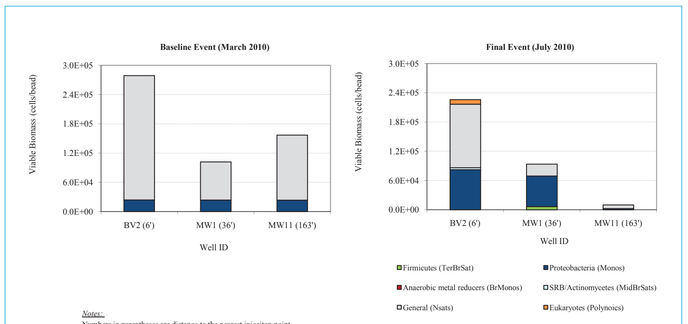


Notes:
Numbers in parentheses are distance to the nearest injeciton point
µ g/L micrograms per liter
c cross-gradient
d downgradient
TPHg total petroleum hydrocarbons as gasoline



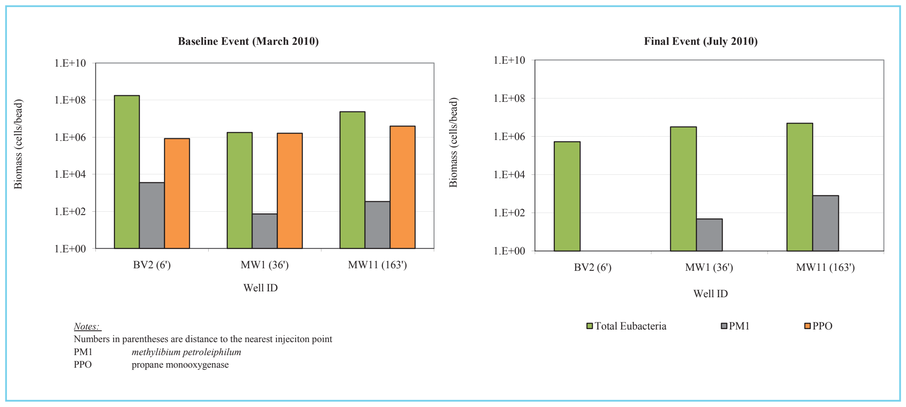
Notes:
Baseline concentrations for Wells MW1, MW3, BV2, BV3, BV4, and BV5 are shown here as equal to half the method detection limit.
Numbers in parentheses are distance to the nearest injeciton point
µ g/L. micrograms per liter
c cross-gradient
d downgradient
MTBE methyl tert-butyl ether

Microbial Study



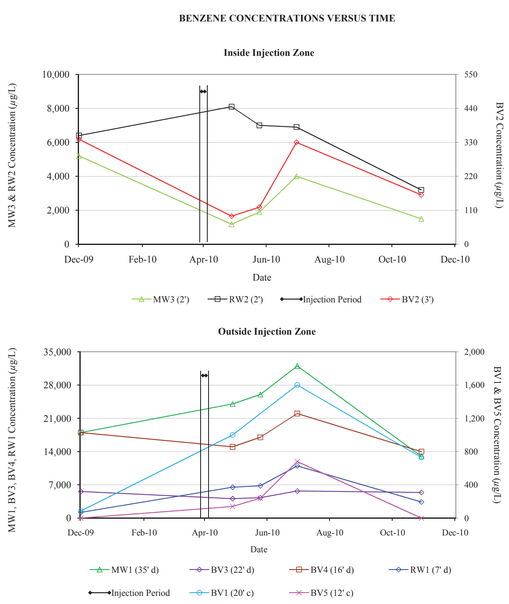
Notes:
Numbers in parentheses are distance to the nearest injeciton point
BrMonos branched monounsaturated
ID identification
MidBrSats mid-chain branched saturated
Monos monounsaturated
Nsats normal saturated bacteria
PLFA phospholipid fatty acids
SRB sulfate reducing bacteria
TerBrSat terminally Branched Saturated

PLFA Total Biomass and Community Structure



Notes:
Numbers in parentheses are distance to the nearest injeciton point
PM1 *methylibium petroleiphilum*
PPO propane monooxygenase

DNA Total Biomass and MTBE-degrading Bacteria



Notes:
Numbers in parentheses are distance to the nearest injeciton point
µ g/L micrograms per liter
c cross-gradient
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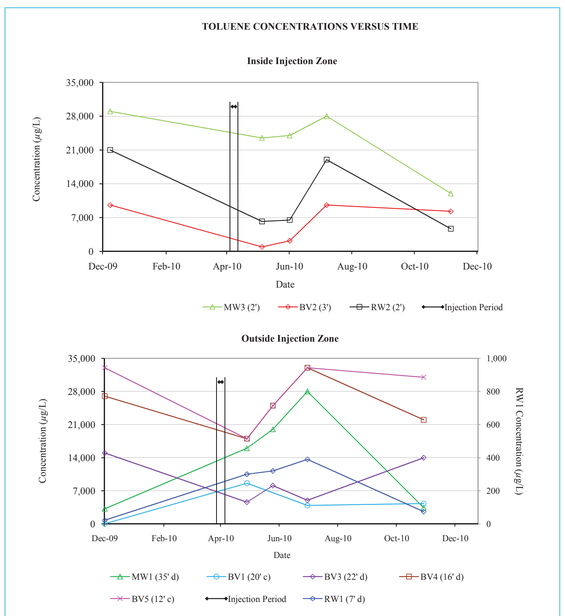

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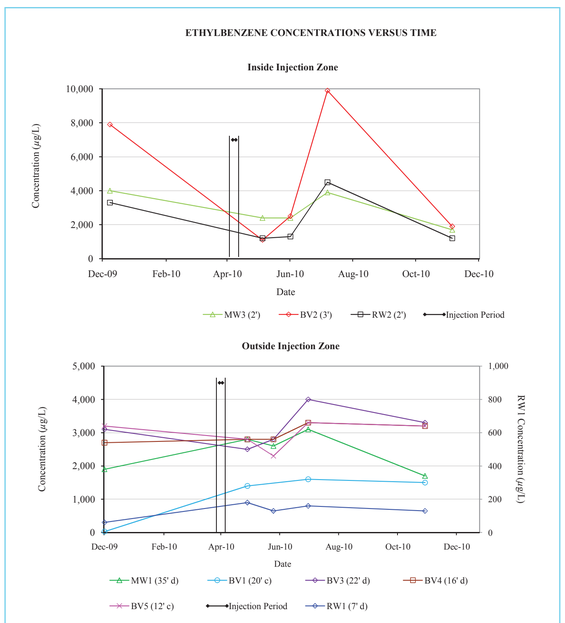

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µ g/L. micrograms per liter
c cross-gradient
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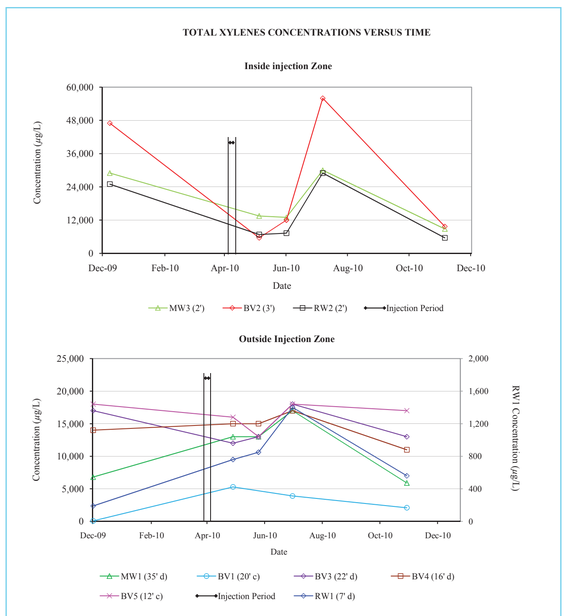

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