Chemical Oxidation - Aerobic/Anaerobic Biodegradation Effective Despite Aggressive Geochemical Alterations Results of Field Application with Advanced Diagnostics

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ADVANCED DIAGNOSTICS MONITOR SUCCESSFUL CHEM/BIO TREATMENT: A Case Study

Background/Objectives.

In relation to *in situ* chemical oxidation remediation technologies, there is concern by some regulators and consultants that non-destructive processes such as dilution are more important than destructive processes in reducing contaminant concentrations. Furthermore, concern has been expressed by some over the viability of pursuing coupled-sequential chemical oxidation and enhanced aerobic and/or anaerobic biodegradation treatment strategies that depend in part on aggressive alteration of subsurface geochemical conditions. High quality field and laboratory data are presented to directly address these concerns.

Approach/Activities.

Klozur® CR (sodium persulfate and enhanced calcium peroxide) was applied at full-scale to a site in New York USA exhibiting unacceptable benzene contaminated groundwater. Klozur® CR provides three different but coupled chemistries to attenuate petroleum-affected groundwater in a single application. In addition to being a strong chemical oxidant, Klozur® CR has aerobic and anaerobic biostimulant properties.

Application of 24,030 lbs. of Klozur® CR using direct push slurry injection methods resulted in a strong downward trend in benzene concentrations (13,000 to less than 500 ug/L) over two years of monitoring. This was followed by a rebound in benzene concentrations after the depletion of the biostimulants provided by the Klozur® CR application.

Prior to treatment, benzene concentrations fluctuated from 13,000 to 600 ug/L, potentially due to seasonal effects. Site closure conditions were achieved but a review of the benzene concentration data alone does not provide strong evidence that the treatment achieved the desired outcome.

Fortunately, the project planning team foresaw the desirability of attempting to demonstrate that destructive processes were largely responsible for concentration reductions observed. Advanced site diagnostics (ASDs), based on microbial phospholipid fatty acid, nucleotide and contaminant stable isotope analysis, were included in the project scope and applied to directly demonstrate contaminant degradation and identify the mechanisms of destruction.

Results/Lessons Learned. ASDs definitively attributed decreased post-application concentrations to destructive degradation. Specifically, the CSIA data showed fractionation (Delta^{13}C value of -23.03 ‰) outside the typical non-degraded benzene range (-23.5 ‰ to -31.5 ‰) thereby definitively proving destructive degradation. CSIA data also attributed the benzene concentration rebound to influx from an upgradient source.

The ASDs also identified a diverse community structure including up to 75 percent Proteobacteria and a class of naphthalene dioxygenase-producing microbes that adapted over a series of weeks to significant geochemical changes caused by the Klozur® CR oxidation reactions including groundwater pH elevated above 12 s.u. Messenger ribonucleic acid (mRNA) qPCR data documented microbes actively producing large quantities (1.73E+10 gene copies/Bio-Sep® bead) of naphthalene dioxygenase. As the monitoring program continued, a change in enzyme expression from naphthalene dioxygenase to toluene monooxygenase was observed.

Klozur® CR Treatment

Klozur® CR consists of sodium persulfate and enhanced calcium peroxide that provides three chemistries to attenuate petroleum-impacted groundwater in a single application:

- Klozur® CR generates radicals including the persulfate radical and the hydroxyl radical both of which are strong oxidizing species.

  $S_2O_8^{2-}$ + activator → SO_4

- Calcium peroxide elutes oxygen stimulating aerobic microbes that metabolize petroleum compounds.
- Sulfate formed during decomposition of the persulfate ion can stimulate native anaerobic petroleum-oxidizing microbes.

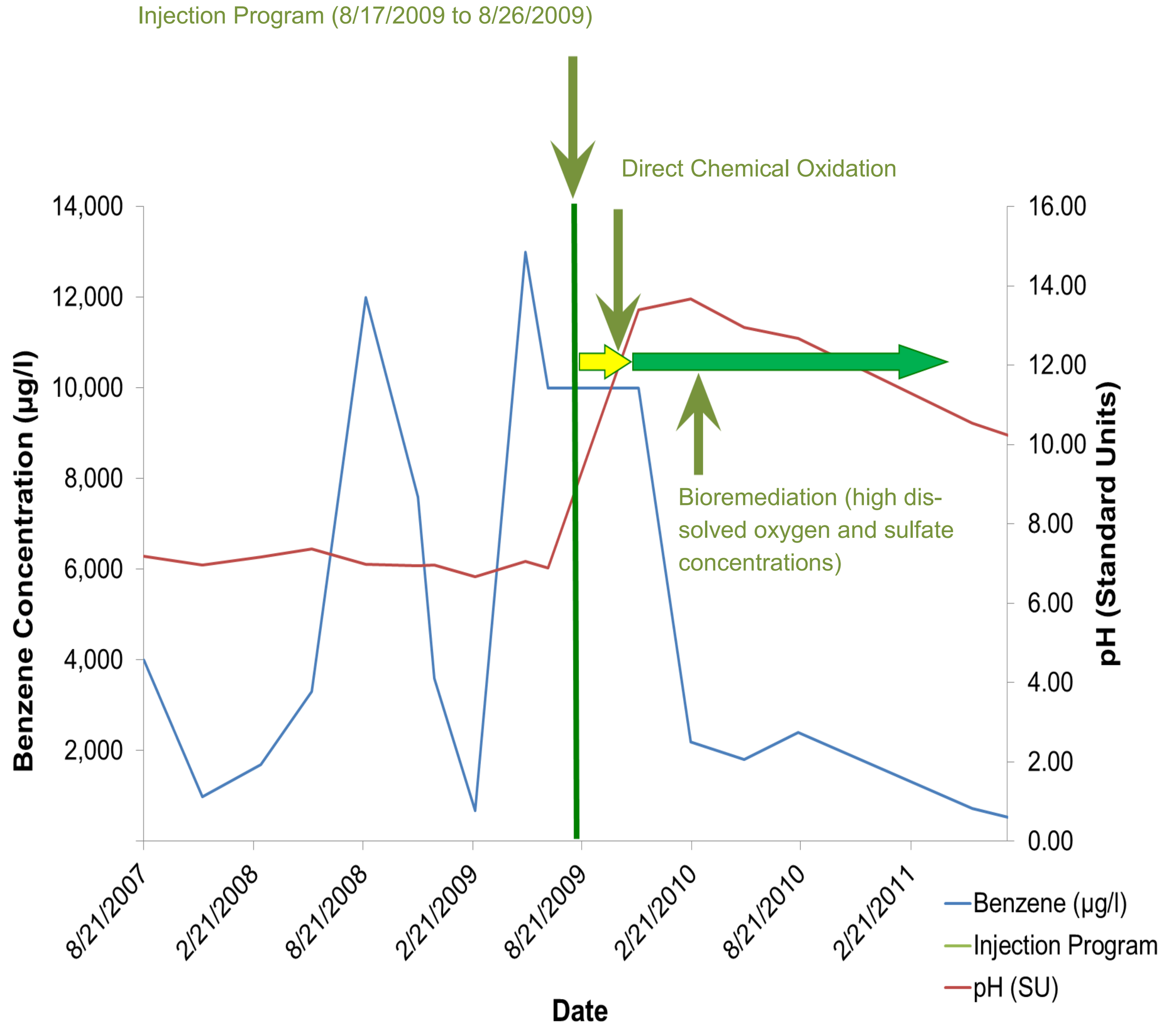
The Application

- 3,600 square foot area; 10 foot saturated thickness
- Silty sand saturated matrix
- 36 points on a 10 foot grid
- 24,030 lbs. of Klozur® CR applied using direct push techniques

Three Lines of Evidence Confirm Contaminant Degradation and Identify Novel Microbial Response

1. Concentration Data

Decrease in benzene concentration following Klozur® CR injections.



Site heterogeneities surrounding MW-9 caused calcium peroxide to accumulate and locally increase pH. pH in the MW-9 area became more neutral as calcium peroxide elutes oxygen and is depleted. However in the winter of 2011 the well was replaced by MW-9R located directly adjacent to MW-9. pH in MW-9R was neutral.

2. Compound Specific Isotope Analysis Confirms Contaminant Destruction

Microseeps, Inc.'s CSIA data for naturally occurring stable carbon isotopes is reported as a concentration ratio of ^{13}C to ^{12}C and normalized to an international standard. In carbon bond-breaking reactions, molecules containing ^{13}C react slower than molecules containing ^{12}C and accumulate (i.e. the concentration ratio becomes less negative). Enrichment of ^{13}C definitively proves isotopic effects of contaminant destruction.

	06/26/09	02/18/10	05/19/10	08/17/10	6/3/2011
Benzene CSIA, δ^{13}C (‰)	-21.13	-24.06	-25.41	-23.03	-24.54
Benzene (µg/l)	14,700	1,500	2,400	730	420

Baseline data rejected because another compound co-eluted with benzene in the sample.

Fractionation value beyond the published, non-degraded benzene range (-23.5 to -31.5) indicates that degradation has occurred.

3. Molecular/Biological Data Identifies the Biological Mechanism of Destruction

	MW-9				
	Baseline	Performance Monitoring			
	6/26/2009 (DNA)	2/18/2010 (mRNA)	5/19/2010 (mRNA)	8/17/2010 (mRNA)	6/6/2011 (mRNA)
CENSUS (qPCR)					
Functional Genes (cells/bead)					
Benzyl Succinate Synthase (bssA)	<1.00E+00	<5.00E+01	<5.00E+01	<5.00E+01	<5.00E+01
Naphthalene Dioxygenase (NAH)	1.37E+08	<5.00E+01	<5.00E+01	1.73E+10	<5.00E+01
Phenol Hydroxylase (PHE)	4.06E+04	4.47E+01 J	<5.00E+01	<5.00E+01	<5.00E+01
Toluene Monooxygenase (RMO)	<1.00E+00	-	<5.00E+01	<5.00E+01	1.78E+03
Toluene Dioxygenase (TOD)	1.01E+06	3.50E+01 J	<5.00E+01	<5.00E+01	<5.00E+01
Biphenyl Dioxygenase (PPH4)	2.34E+04	<5.00E+01	<5.00E+01	<5.00E+01	<5.00E+01
Xylene Monooxygenase (TOL)	2.00E-01 J	3.14E+01 J	<5.00E+01	<5.00E+01	<5.00E+01

Oxygenase genes which produce the enzymes required to digest petroleum constituents are common.

Microbial Insights BioTrap® qPCR data quantifies the expression of genes for protein synthesis and identifies two classes of microbes able to adapt to elevated pH levels. High naphthalene dioxygenase production in August 2010 and moderate toluene monooxygenase production in June 2011 show that microbes producing petroleum attenuating enzymes are active. Enzyme production in samples collected before August 2010 was below detection limits and is likely attributable to the time required to adapt to the elevated pH (10.5 to 13 S.U.) since Klozur® CR application.

Upgradient Saturated Soil Cleanup Criteria

Equilibrium Partitioning Calculation with 1 mg/kg Benzene in Soil Below the Water Table

$$C_t = C_w[K_{oc}F_{oc} + (\theta_w + \theta_a H')/\rho_b]$$

Symbol	Parameter	Typical Value	Low Value (a)	High Value (a)	RSL Calc	Units
C_t	Total concentration in soil	1	1	1	0.0026	mg/kg
K_{oc}	Organic carbon partition coefficient	59	59	59	59	l/kg
H'	Henry's Law constant	0.23	0.23	0.23	0.23	dimensionless
F_{oc}	Fraction organic carbon	0.002	0.01	0.001	0.002	dimensionless
ρ_b	Dry bulk density	1.5	1.3	1.8	1.5	g/cm^3
θ_w	Water-filled porosity	0.43	0.43	0.15	0.3	dimensionless
θ_a	Air-filled porosity	0	0	0.28	0.13	dimensionless
C_w	Concentration in groundwater	2.5	1.1	5.6	0.008	mg/l

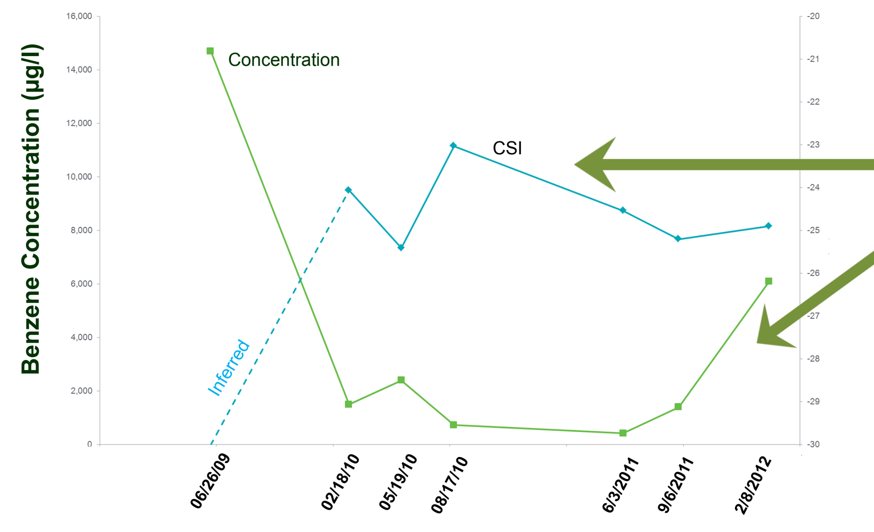
a/ "Low" and "High" parameter values refer to values that result in a lower or higher calculated C_w.

With 1 mg/kg total benzene in soil, would expect 1.1 mg/l to 5.6 mg/l in groundwater (best estimate 2.5 mg/l).

Note for comparison: EPA Regional Screening Level for benzene in soil to protect groundwater to the MCL (0.005 mg/l) is 0.0026 mg/kg.

Concentration and Isotopic Effect of Upgradient Cleanup Criteria

Concentration and isotopic rebound seen in the data.



Isotopic depletion shows influx of lesser degraded benzene which mirrors the benzene concentration increase

Klozur® CR Treatment Results: Mass Removal

Calculations that compare baseline (10 mg/l) and treated (0.42 mg/l) benzene concentrations in groundwater at equilibrium with saturated soil show a Klozur® CR treatment efficiency of 96% or destruction of 10 kg of benzene.

Saturated soil benzene concentrations in equilibrium with measured groundwater concentrations

Symbol	Parameter	Baseline Value (a)	Treated Value (a)	Units
C_t	Total concentration in soil	1	1	mg/kg
C_w	Concentration in groundwater	10	0.42	mg/l
K_{oc}	Organic carbon partition coefficient	59	59	l/kg
H'	Henry's Law constant	0.23	0.23	dimensionless
F_{oc}	Fraction organic carbon	0.002	0.002	dimensionless
ρ_b	Dry bulk density	1.5	1.5	g/cm^3
θ_w	Water-filled porosity	0.43	0.43	dimensionless
θ_a	Air-filled porosity	0	0	dimensionless
C_t	Total concentration in soil	4.0	0.17	mg/kg

Mass destroyed in each matrix and treatment efficiency

C_t Destroyed:	baseline - treated: 4 mg/kg - 0.17 mg/kg:	3.9	mg/kg
C_w Destroyed:	baseline - treated: 10 mg/l - 0.42 mg/l:	9.6	mg/l
% Destroyed:	(baseline - treated) / baseline: (10 mg/l - 0.42 mg/l) / 10 mg/l:	96	%

Total benzene mass removed

Soil:			
	Treatment area	3,600	ft^2
	Treated saturated thickness	10	ft
	Soil mass (ρ_b: 1.5 g/cm^3)	1,500,000	kg
	Mass of benzene destroyed in soil	6	kg
Groundwater:			
	Groundwater Volume (θ_w: 0.43)	440,000	l
	mass of benzene destroyed in groundwater	4	kg
total:			
	soil + groundwater	10	kg