Chemical Oxidation and Biostimulation Achieves Significant Plume Reduction with Single Amendment Application

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A CASE STUDY

To achieve rapid site closure as compared to more traditional approaches (e.g., groundwater extraction and treatment or air sparging/soil vapor extraction), WSP implemented a coupled chemical oxidation and biostimulation or "chem-bio" *in situ* treatment to an active petroleum service station site in the coastal plain of Florida, USA.

A historical release of gasoline affected a 1,550-square-meter area and a volume of 9,600 cubic meters of a sandy aquifer. A layer (3 centimeter maximum) of LNAPL was present in a 56-square-meter area. Klozur® CR (5384 kg) was applied to the source area (450 square meters) and PermeOx® Plus (2455 kg) was applied to the balance of the plume as aqueous slurries using temporary direct push points to a maximum depth of 17 meters below ground surface. These products are manufactured by FMC Corporation with Technical Support by ChemRem.

Significant treatment was achieved.
Three months post-amendment application, the size of the plume area was reduced by 70 percent and Florida Groundwater Target Cleanup Goals (similar to MCLs) were achieved within the PermeOx® Plus application area and have been maintained through four consecutive quarterly monitoring events. Initial results in the Klozur® CR application area showed near complete treatment of lighter hydrocarbons, and higher concentrations of heavier hydrocarbons which is likely attributable to high-pH induced desorption from soils or dissolution from the NAPL. One year post treatment data shows the horizontal and vertical extent of affected groundwater to be limited to the LNAPL area, continued remedial progress via biodegradation, and abatement of temporally elevated concentrations of dissolved inorganic chemicals related to application of these amendments. Additional treatments may be necessary to address the NAPL.

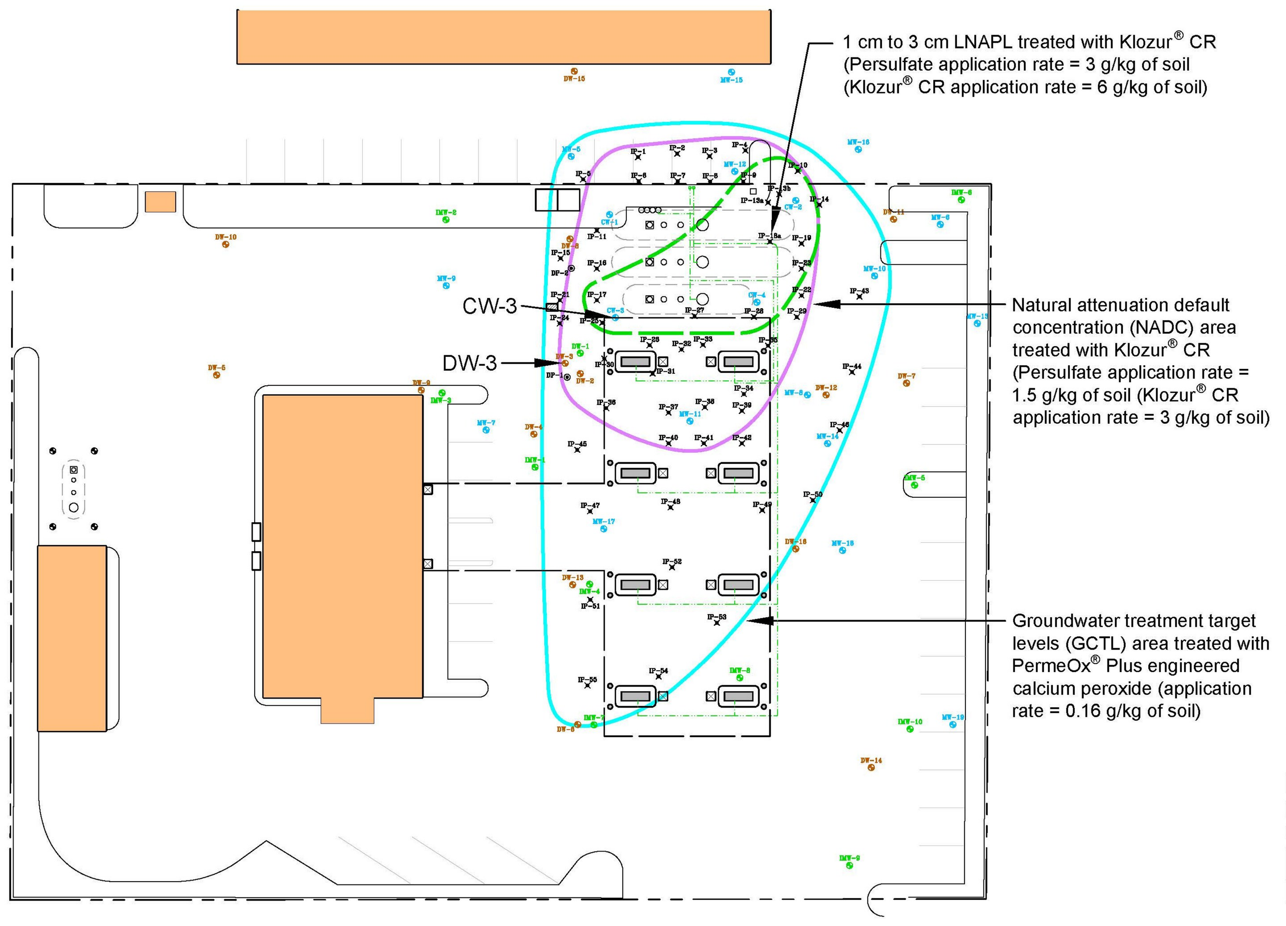
Advanced diagnostic tools were used to monitor contaminant destruction and to identify biologically-mediated mechanisms responsible for contaminant destruction. Stable carbon isotope data showed effects of desorption/dissolution "rebound" and confirm destructive bioattenuation of key petroleum constituents. Microbiological data, including DNA and mRNA qPCR evaluation, show an abundant population of native microbes capable of synthesizing key oxygenase genes, and track decreased mRNA expression of oxygenase synthesis as dominant terminal electron accepting processes transitioned from aerobic respiration to sulfate reduction.

Description of the Subject

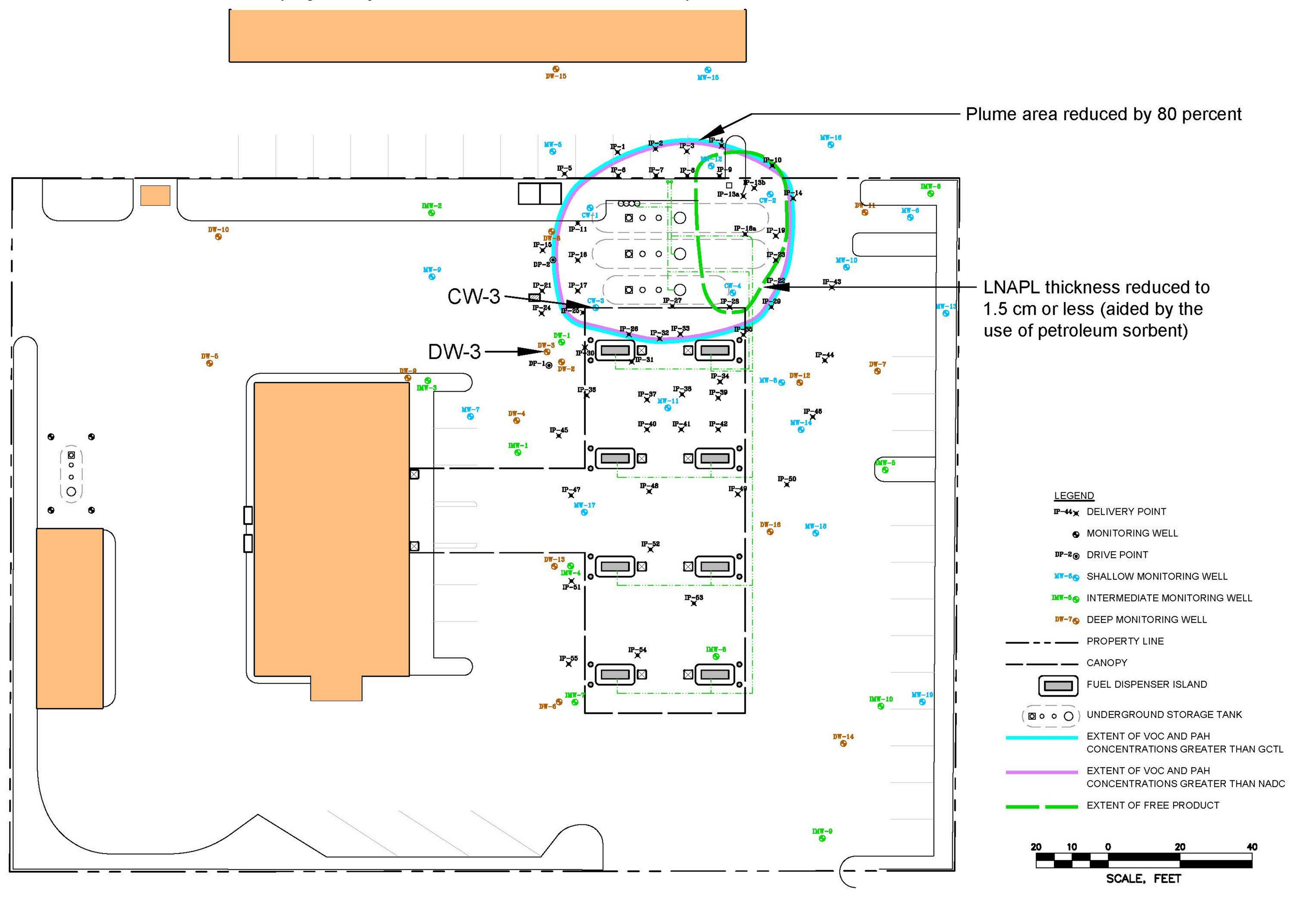
Chemical oxidation and biostimulation are late stage emerging technologies. Each of the technologies has applicability limitations that may limit their discrete use. These limitations are for the most part not common to both technologies. Sequential application of the technologies in a "chem-bio" treatment train broadens the applicability of the combined technology.

- Klozur® CR consists of sodium persulfate and engineered calcium peroxide.
- Klozur® CR provides three separate chemistries to attenuate petroleum-affected groundwater in a single application:
- Klozur® CR generates the sulfate radical, one of the strongest oxidizing species available. Hydroxyl and other radicals are also generated.
- $S_2O_8^{-2}$ + *activator* $SO_4\bullet$
- Klozur® CR is formulated with engineered calcium peroxide for radical activation which also elutes oxygen which can stimulate native or introduced aerobic microbes to metabolize amenable contaminants including many petroleum compounds and mono/di-halogenated ethenes and ethanes, among others.
- Sulfate is formed during the decomposition of the persulfate anion. At many sites sulfate has been shown to stimulate native anaerobic petroleum-oxidizing microbes.

Plume Extent Before Treatment



Plume Extent After Single Treatment
(1 year post treatment data shown)



Representative Temporal Data

Chem-Bio Amendment Application 12/08

Sample ID:			DW-3					CW-3				
Remediation Amendment:			(PermeOx® Plus Applied)					(Klozur® CR Applied)				
Sample Date: Florida Groundwater Cleanup Target Levels			Baseline	04/08/09	07/08/09	10/12/09	01/05/10	Baseline	04/09/09	07/07/09	10/13/09	01/06/10
Parameters	GCTL	NADC										
VOCs (µg/l)												
Benzene	1	100	**140**	0.5 U	0.58	0.39 I	0.5 U	**13,000**	84.4	**913**	**386**	**129**
Ethylbenzene	30	300	1.9 U	0.5 U	0.5 U	0.5 U	0.5 U	**910**	16.1	110	**364**	138
Methyl tert butyl ether (MTBE)	20	200	20	21	121	36.6	1 U	**150**	**61.3**	**59.7**	16.1	12.3
Toluene	40	400	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	**210**	**71.9**	**458**	54.1	5.61
O+M+P-Xylene	20	200	12 U	1.5 U	1.5 U	1.5 U	1.5 U	**268**	**495**	**3,610**	**915**	**1414**
1,2,4-Trimethylbenzene	10	100	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	60	**102**	**1,830**	**287**	**1790**
Isopropylbenzene	0.8	8	2.9	0.58 I	1.09	0.5 U	0.5 U	**88**	2.9	**25**	4.21	**15.9**
1,3,5-Trimethylbenzene	10	100	1 U	1 U	1 U	1 U	1 U	23	49.3	**773**	**184**	**513**
PAHs (µg/l)												
Naphthalene	14	140	40 U	0.2 U	0.529	0.2 U	0.2 U	**850**	4.01	134	61.8	62.1
2-Methylnaphthalene	28	280	5.7 U	0.2 U	0.2 U	0.2 U	0.2 U	230	2.23	52.9	14.8	15.2
Electron Acceptors (mg/l)												
Dissolved Oxygen			0.16	0.3	4.4	1.6		0.27	2.6	0.71	3.7	0.89
Sulfate			2 U	29.2	49.7	454	219	4 J	182	189	27	2 U

Apparent initial treatment efficiency is better for lighter more soluble hydrocarbons

Bold value indicate concentration greater than NADC and GCTL
Boxed value indicate concenration greater than GCTL but less than NADC
U = Not detected at concentrations greater than laboratory reporting limit.
J = Estimated concentration

DW-3: Aerobic Respiration → Sulfate Reduction
CW-3: Chemical Oxidation → Aerobic Respiration → Sulfate Reduction

Terminal Electron Accepting Processes

Molecular Biological Tools

Microbial Insights BioTrap® qPCR data shows that oxygenase genes, which code for enzymes that are functional in aerobic conditions, are common. mRNA data quantifies the expression of these genes for protein synthesis and shows reduced production of oxygenase enzymes with decreased oxygen tension.

CENSUS (qPCR) Functional Genes (cells/bead)	CW-3 7/7/09 (DNA)	DW-3 7/7/09 (DNA)	DW-3 10/12/09 (mRNA)	DW-3 1/5/10 (mRNA)
Benzyl Succinate Synthase	< 5.00E+01	< 5.00E+01	< 1.00E+03	< 5.00E+01
Napthalene Dioxygenase	1.08E+09	7.28E+08	< 8.33E+00	< 5.00E+01
Phenol Hydroxylase	2.71E+04	1.12E+05	1.17E+03	< 5.00E+01
Toluene Monooxygenase	2.31E+03	< 5.00E+01	-	-
Toluene Dioxygenase	3.20E+08	2.18E+08	7.50E+03	< 5.00E+01
Biphenyl Dioxygenase	2.87E+02	6.34E+02	-	-
Xylene Monooxygenase	5.29E+01	4.32E+01	-	-

The absence of the Benzyl Succinate Synthase gene, which is responsible for anaerobic oxidation of petroleum constituents in some microbes, is not indicative of successful anaerobic oxidation at this site

Oxygenase genes are common

mRNA data shows decreased expression of oxygenase synthesis as dissolved oxygen is depleted

Aerobic Respiration → Sulfate Reduction

Terminal Electron Accepting Processes

Compound Specific Isotope Analysis

CW-3	4/8/09	7/10/09	10/13/09	1/6/10
Benzene: CSIA, $\delta^{13}C$ (‰)	-24.61	-26.39	-25.50	-25.77
Benzene: Concentration (µg/l)	84	913	386	129
MTBE: CSIA $\delta^{13}C$ (‰)	-24.63	-26.28	-25.57	-23.91
MTBE: Concentration (µg/l)	61.3	59.7	16.1	12.3

Concentrations decreased slightly but CSIA data shows that the decrease is not attributable to destructive means (no enrichment of ^{13}C within the pool of carbon that comprises the MTBE). Instead, CSIA data shows a net efflux of treated MTBE and an influx of untreated MTBE.

CSIA data (analysis provided by Microseeps, Inc.) 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 (natural abundance approximately 1%) react slower than molecules containing ^{12}C and accumulate (i.e., the concentration ratio becomes less negative). Isotopic effects of naturally occurring physical processes are less pronounced and not significant. Depletion and enrichment of the ^{13}C here show isotopic effects of rebound and attenuation:

- After Klozur® CR application there is an enrichment of ^{13}C within the pool of carbon comprising MTBE and benzene as compared to average isotopic signatures of these compounds in "fresh" gasoline.
- After the persulfate concentrations decrease there is a depletion of ^{13}C as untreated gasoline desorbes and dissolutes
- During the last 2 monitoring periods the rate of biodegradation exceeds the rate of desorption/dissolution and the ^{13}C within the carbon pool is enriched

Conclusion

The combined treatment train of sequential chemical oxidation and biostimulation broadens the applicability of these technologies. Products such as Klozur® CR provide the chem-bio treatment train via a single amendment application.

Klozur® CR and PermeOx® Plus were applied to a site in Florida's coastal plain to address a gasoline release. One year after a single chem-bio treatment using these amendments, areas outside the LNAPL source area achieved site cleanup goals. Compound specific isotope analysis (CSIA) data showed that contaminant concentration "rebound" which occurred in the LNAPL area is likely attributable to phase transfer from LNAPL or soil sorbed petroleum to groundwater. CSIA data also confirm bioattenuation of key petroleum constituents as opposed to non destructive attenuation mechanisms (e.g., dilution and displacement).

Microbial ecology data showed a large population of microbes containing genes that code for oxygenase synthesis. Stimulation of these microbes by increased dissolved oxygen afforded by the PermeOx® Plus application is the likely mechanism of the observed cleanup outside of the LNAPL area. mRNA data which show active expression or synthesis of the oxygenase genes were tracked and showed decreased expression as dominant terminal electron accepting processes transitioned from aerobic respiration to sulfate reduction (afforded by the decomposition of the persulfate anion). Data also show the bioattenuation via sulfate reduction is ongoing but removal of LNAPL by targeted Klozur® CR application or other technology will likely be needed before groundwater cleanup will be completed.

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