Activated Persulfate Chemical Oxidation and Biostimulation Using Klozur® CR and PermeOx® Plus to Achieve Significant Plume Reduction:

A CASE STUDY

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To achieve rapid site closure as compared to more traditional approaches (e.g., groundwater extraction and treatment or air sparging/soil vapor extraction), a coupled chemical oxidation and biostimulation or "chem-bio" treatment was applied by WSP Environment & Energy 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 cm maximum) of LNAPL was present in a 56-square-meter area. Klozur® CR (5384 kg) was applied to the source area (450 m2) 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 m below ground surface.

These products are manufactured by FMC Corporation with technical support by ChemRem.

Significant treatment was achieved.

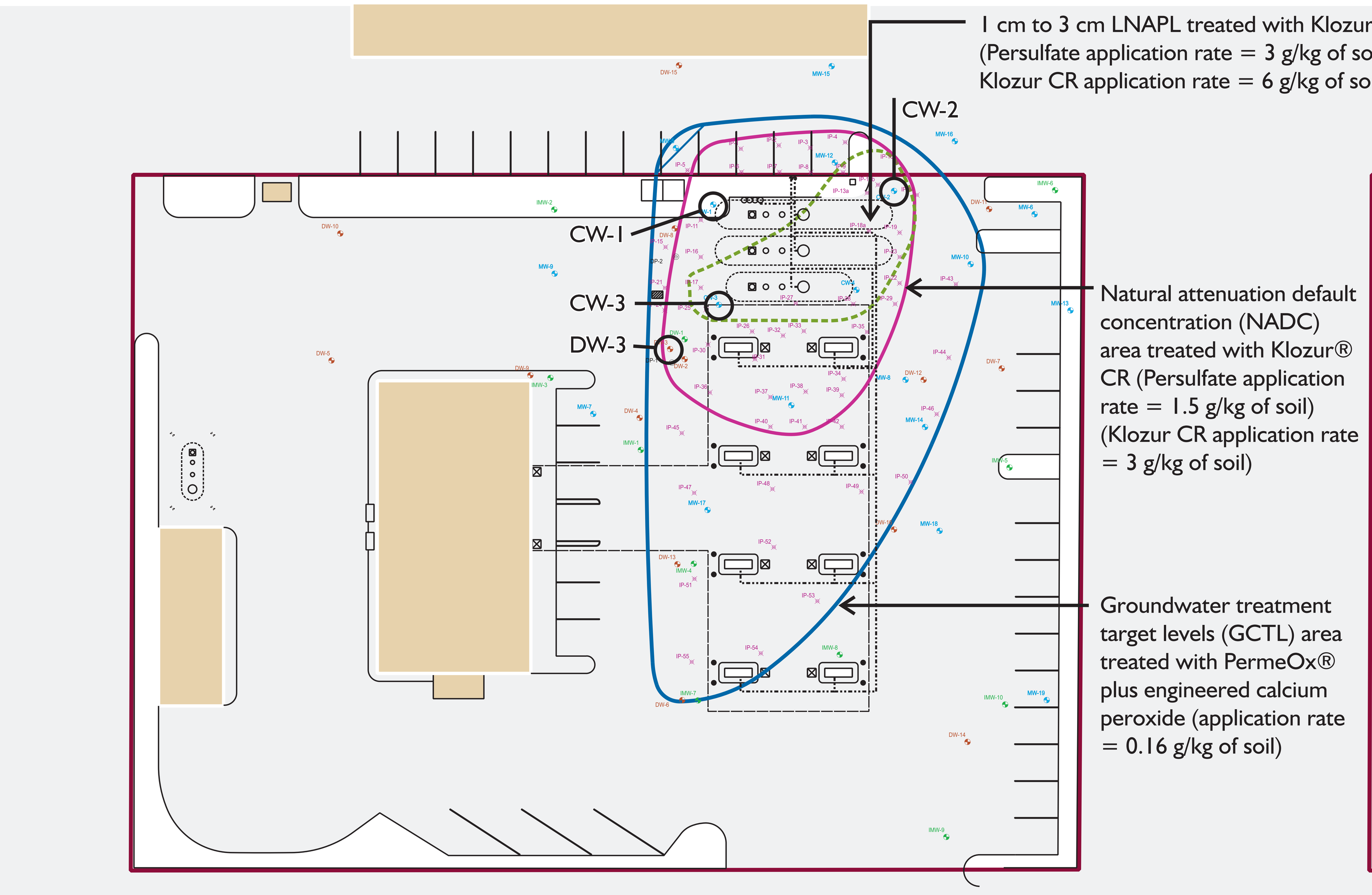
Three month post-amendment application the size of the plume area was reduced by 70 percent and the Florida Groundwater Target Cleanup Levels (similar to potable water standards) were achieved within the PermeOx® Plus application area.

Three-month post application data in the Klozur® CR application area showed 90-plus percent treatment efficiency for benzene and increases in the aqueous concentrations of less soluble hydrocarbons which is likely attributable to high-pH induced desorption from soils or dissolution from the NAPL.

Six month post treatment data shows treatment of less soluble hydrocarbons, likely by biodegradation, but continued desorption/dissolution mask total mass removal rates and remedial progress.

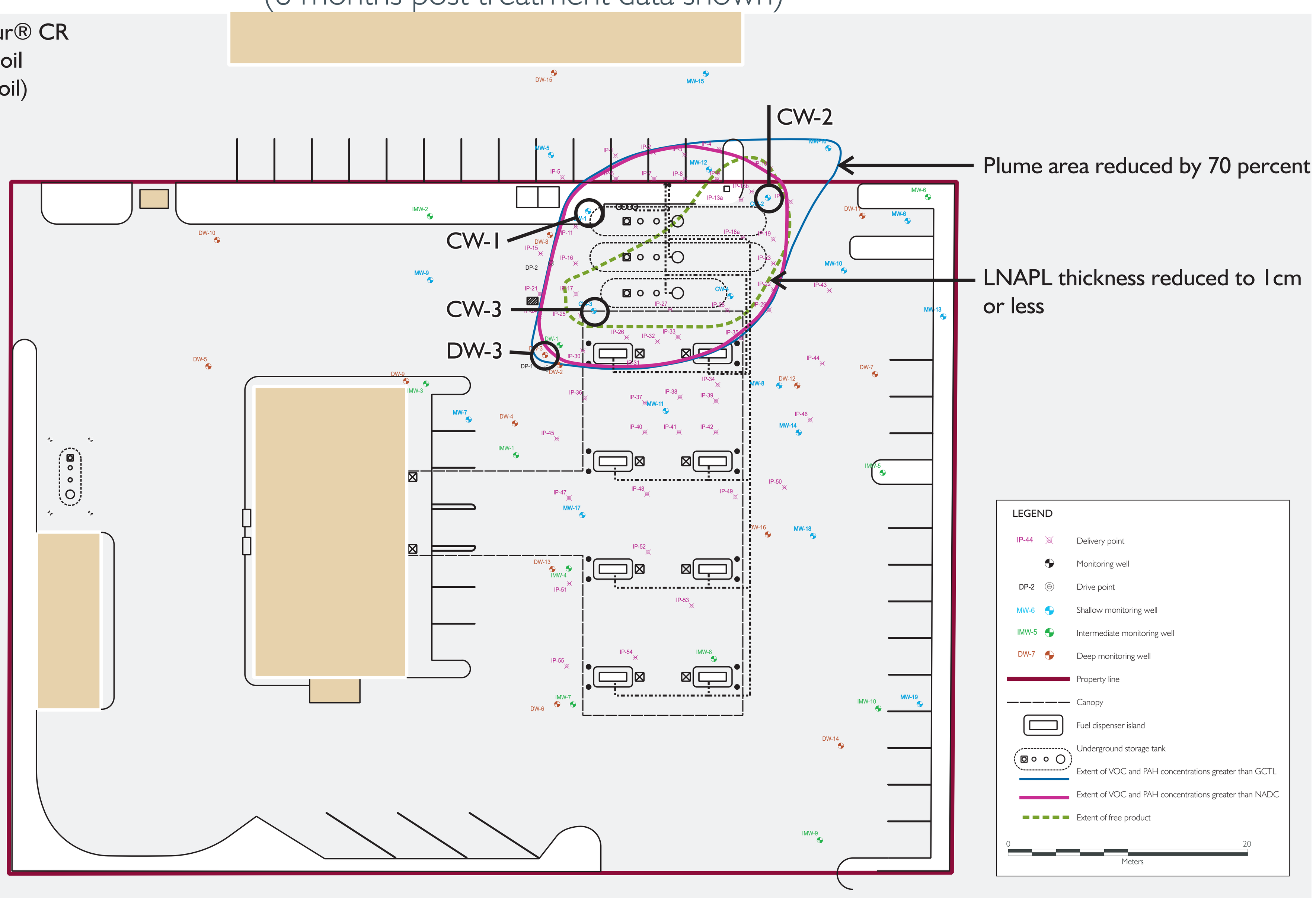
Additional treatments may be necessary to address the NAPL. Advanced diagnostic tools were used to monitor contaminant destruction and to identify biologically-mediated mechanisms responsible for contaminant destruction.

Plume Extent Before Treatment



Plume Extent After Single Treatment

(6 months post treatment data shown)



Description of the Subject

Chemical oxidation and to a lesser extent biostimulation are emerging technologies. Each of the technologies has applicability limitations that may limit 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 is a recently-introduced formulated product consisting 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 radicals are also generated.

$$S_2O_8^{-2} + activator \rightarrow SO_4\bullet$$

- The persulfate anion is a strong oxidant with an oxidation potential of 2.1 volts (V) and activated persulfate produces an even stronger oxidant, the sulfate radical, with an oxidation potential of 2.6 V. Below is a list of common oxidants and their oxidation potentials:

  - 2.7 V Hydroxyl Radical (•OH)
  - **2.6 V Sulfate Radical ($SO_4\bullet$)**
  - 2.2 V Ozone (O_3)
  - **2.1 V Persulfate anion ($S_2O_8^{-2}$)**
  - 1.8 V Hydrogen Peroxide (H_2O_2)
  - 1.7 V Permanganate Anion (MnO_4^-)
  - 1.4 V Peroxymonosulfate Anion (HSO_5^-)

- Klozur® CR is formulated with engineered calcium peroxide for radical activation which also elutes oxygen which can stimulate native 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.

Representative Source Area Data

Chem-Bio Amendment Application 12/08

Parameters	Florida Groundwater Cleanup Target Levels: GCTL	NADC	CW-1 Baseline	CW-1 04/08/09	CW-1 07/08/09	CW-2 Baseline	CW-2 04/09/09	CW-2 07/07/09	CW-3 Baseline	CW-3 04/09/09	CW-3 07/07/09
VOCs (µg/l)											
Benzene	1	100	**16,000**	**3,340**	**525**	**7,700**	76.4	**8,510**	**13,000**	84.4	**913**
Ethylbenzene	30	300	**550**	**2,380**	231	200	234	**1,900**	**910**	16.1	110
Methyl tert butyl ether (MTBE)	20	200	**130**	**107**	3.53	15	100	47.7	**150**	**61.3**	**59.7**
Toluene	40	400	**420**	**9,330**	**1,540**	**140**	**493**	**6,900**	**210**	**71.9**	**458**
O+M+P-Xylene	20	200	**1,200**	**15,420**	**8,330**	**930**	**6,910**	**12,461**	**268**	**495**	**3,610**
1,2,4-Trimethylbenzene	10	100	**160**	**8,350**	**2,160**	**160**	**6,560**	**2,830**	60	**102**	**1,830**
Isopropylbenzene	0.8	8	**83**	**40**	**57.9**	**83**	**53.2**	**72.7**	**88**	2.9	**25**
1,3,5-Trimethylbenzene	10	100	79	**2,540**	**670**	79	**2,040**	**880**	23	49.3	**773**
PAHs (µg/l)											
Naphthalene	14	140	**740**	0.2	**142**	**650**	**166**	**191**	**850**	4.01	134
2-Methylnaphthalene	28	280	180	0.2	53.5	160	7.17	53.3	230	2.23	52.9

Apparent Initial Treatment Efficiency Better for Lighter more soluble Hydrocarbons

Apparent treatment of heavier hydrocarbons likely affected by high-pH induced desorption from soils or dissolution from the NAPL

Carbon Isotopic signature shows probable "Rebound" attributable to desorption from aquifer sediments or dissolution from LNAPL

	CW-3 11/27/2007	CW-3 7/7/2009
Benzene: CSIA, δ ^{13}C (‰)	-24.61	-26.39
MTBE: CSIA, δ ^{13}C (‰)	-24.63	-26.28

CSIA data for naturally occurring 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 with chem-bio treatment (i.e., the concentration ratio becomes less negative). Depletion of the ^{13}C isotope within the pool of carbon as shown here indicates an influx of untreated benzene and MTBE molecules likely from high-pH induced soil desorption and NAPL dissolution.

Advanced Site Diagnostics

Microbial Insights BioTrap® PCR data shows that oxygenase genes, which code for enzymes that are functional in aerobic conditions, are common.

Client Sample ID:		CW-3	DW-3
Sample Date:		07/07/2009	07/07/2009
Units:		cells/bead	cells/bead
Analyst:		ab	ab
Functional Genes			
Benzyl Succinate Synthase	bssA	<5.00E+01	<5.00E+01
Napthalene Dioxygenase	NAH	1.08E+09	7.28E+08
Phenol Hydroxylase	PHE	2.71E+04	1.12E+05
Toluene Monooxygenase	RMO	2.31E+03	<5.00E+01
Toluene Dioxygenase	TOD	3.20E+08	2.18E+08
Biphenyl Dioxygenase	BPH4	2.87E+02	6.34E+02
Xylene Monooxygenase	TOL	5.29E+01	4.32E+01 (J)

Conclusions and Future Activities

The combined treatment train of sequential chemical oxidation and biostimulation broadens the applicability of these technologies. New products such as Klozur® CR are being developed to 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. Six months after a single chem-bio treatment using these amendments, areas outside of the LNAPL source area achieved site cleanup goals.

Compound specific isotope analysis (CSIA) data showed that the less than complete treatment of groundwater in the LNAPL area is likely attributable to phase transfer from LNAPL or soil sorbed petroleum to groundwater.

Removal of LNAPL by targeted Klozur® CR application or other technology is needed before groundwater cleanup will be achieved.

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. Future microbial evaluation will examine ribose nucleic acid (RNA) production as a measurement of active oxygenase synthesis.