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Innovative Coupled Chem-Bio Treatability Study Leading to Large Scale Pilot Test at a Wood Treating Facility

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Presentation Outline

- Project Objectives - Active Wood Treating Facility
- Project Background
- “Assisted” Natural Attenuation Remedy
- Coupled Chemical Oxidation and Aerobic Biodegradation
- Treatability Study Design
- Study Analytical Results
- Pilot Test Design, Implementation, and Preliminary Results
- Conclusions

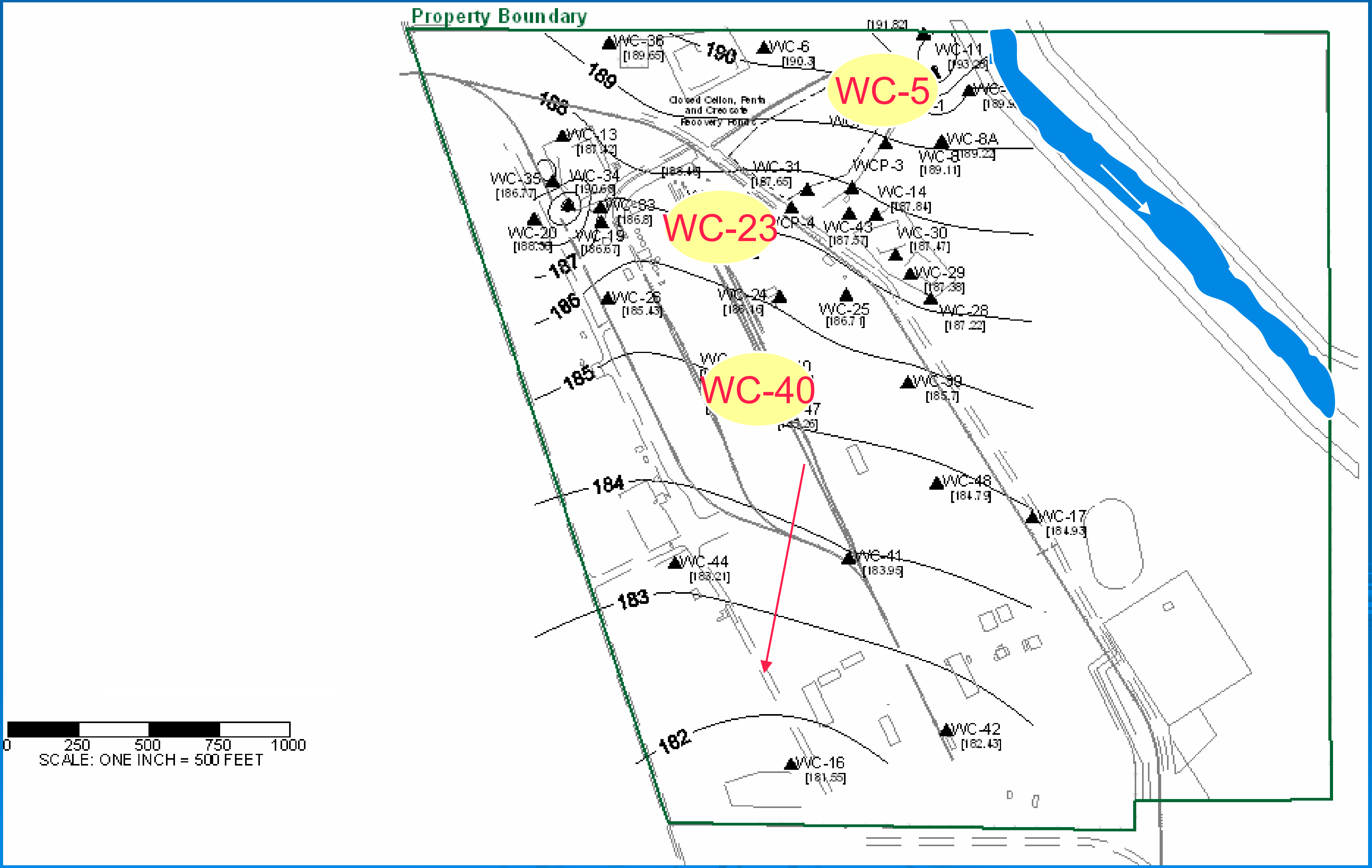
Project Objectives

- Achieve regulatory “go-head” for initiating a Monitored Natural Attenuation (MNA) remedy leading to closure.
- Address the regulatory concern that focused “hot spots” along the plume centerline represent threats to MNA success.
- Bench and field pilot test a PCP/naphthalene plume attenuation strategy involving tactical integration of in-situ chemical oxidation (Chem) and enhanced aerobic biodegradation (Bio) technologies.
- Satisfy “hot spot” concern via pilot test, or if necessary, limited additional treatment based on pilot test results.

Project Location

Central Mississippi

Site Plan with Potentiometric Surface

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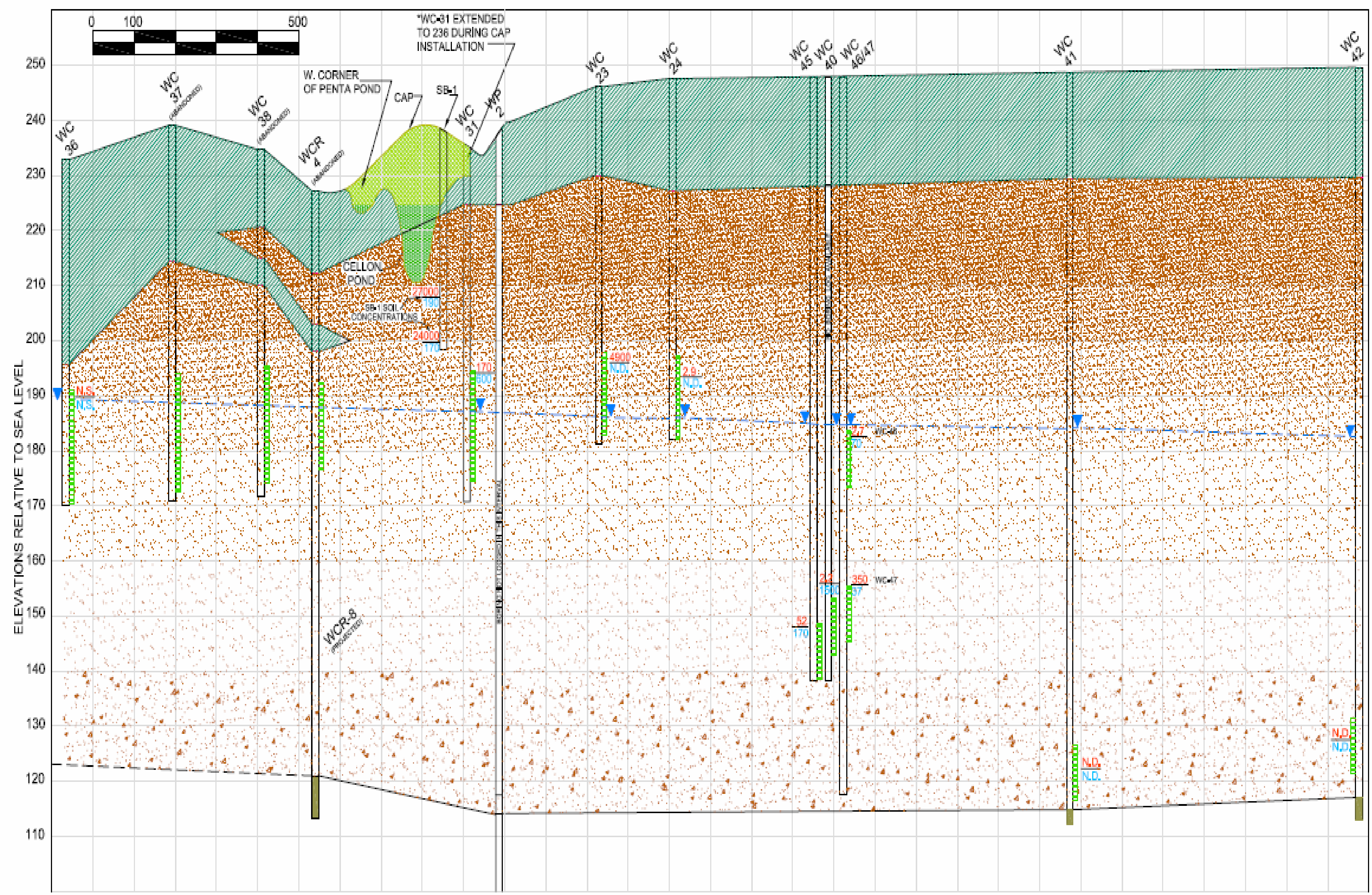
North-South Hydrogeologic Profile



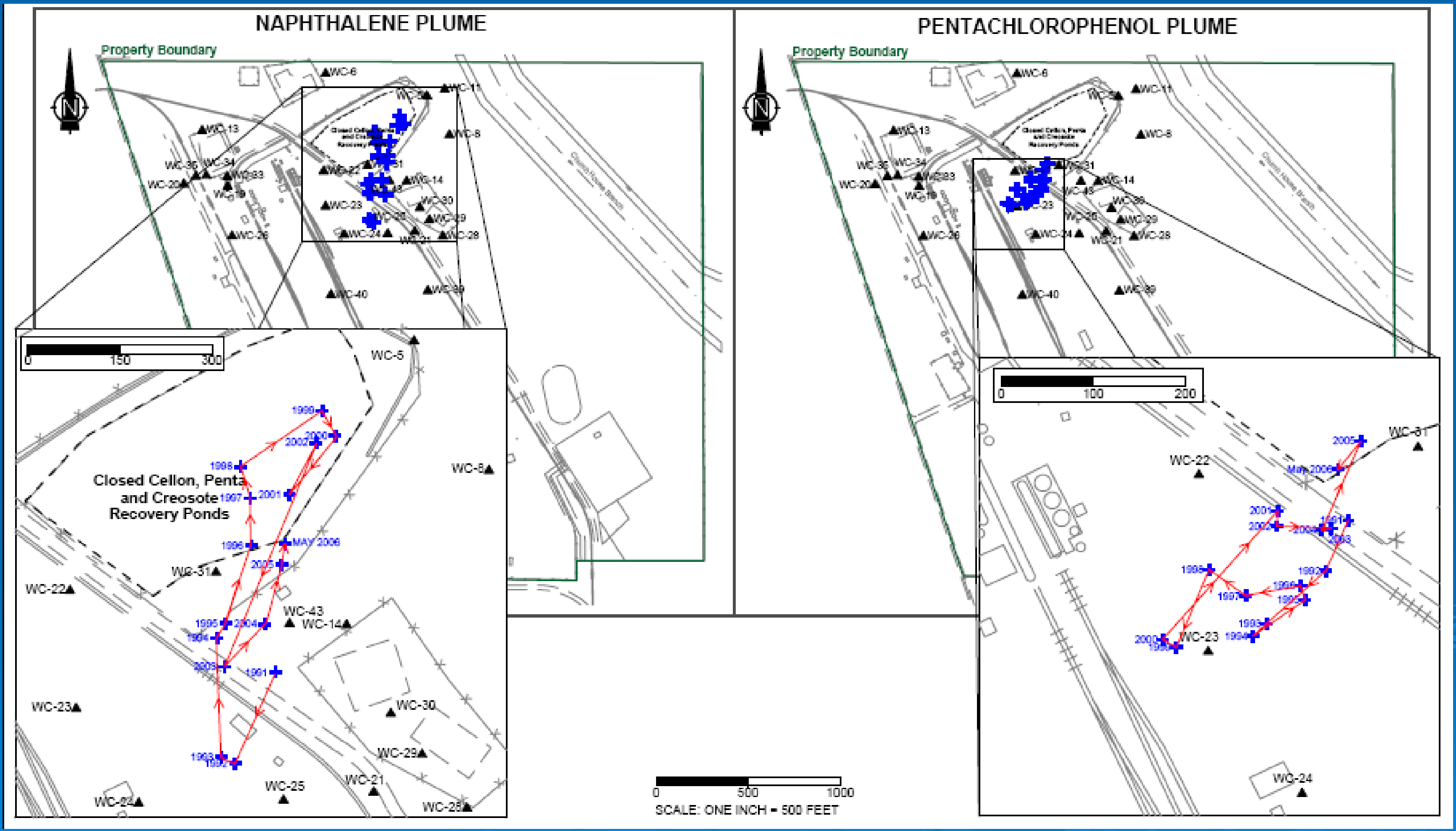
Groundwater Characterization

- Persistent PCP and naphthalene concentrations (mg/l) in WC-5, WC-23, and WC-40 areas. Product droplets observed in WC-5 area.
- Acidic pH in range of 4.0 – 5.0.
- Low dissolved oxygen with utilization of various electron acceptors across the site.
- Active biological population.

“Assisted MNA” Concept

- Regulators approve of MNA remedy with exception
- Concerned about three hot spots
- Requested that limited effort go into mass reduction at these three areas
- In situ approach involving aggressive treatment and compatibility with MNA remedy desirable

NA Demonstration - Plume Centroid Position



Coupled ISCO-BIO Concept

• In-situ approach involving chemical oxidation technology capable of degrading PCP and Naphthalene and other detected organic contaminants.

• The chem-ox technology is compatible with planned MNA. Microbial community should not be severely impacted. No by-products toxic to desirable micro-organisms. Even better if chem-ox technology supports enhanced aerobic biodegradation.

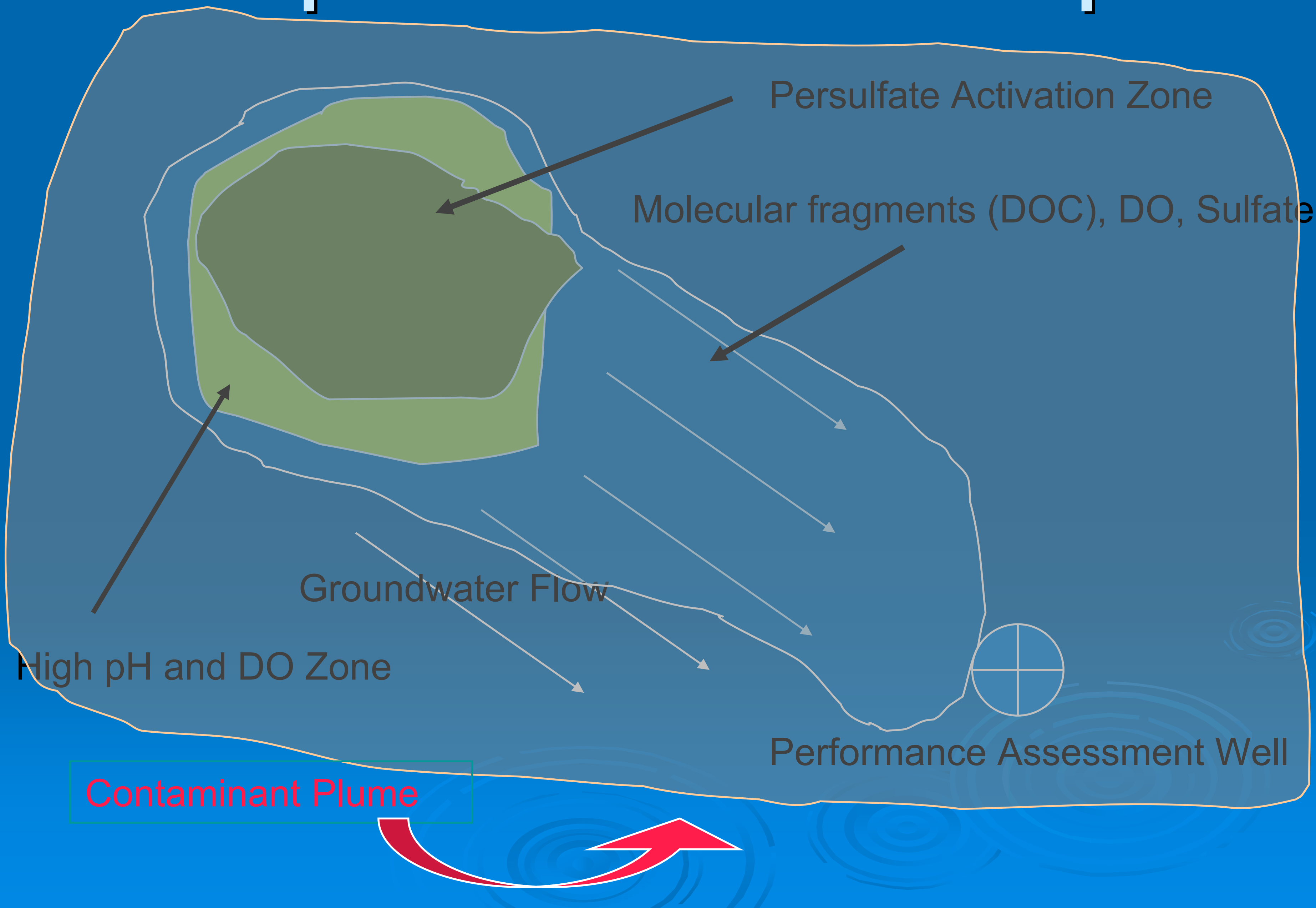
• Oxygen and sulfate addition as result of the chem-ox action desirable. Increase in dissolved organic carbon and nutrients as result of chem-ox action desirable.

• Provide a consistent amount of additional oxygen (and other AEA) over an extended period of time to support microbial rebound from chem-ox action and to support growth cycle and ultimately a high level of contaminant degradation.

• Klozur ® OBC chosen for chem-ox; PermeOx® Plus chosen to assist in persulfate activation and to provide the stable long-term oxygen source.

• Conduct treatability study to show efficacy and efficiency and as appropriate pilot test to demonstrate at field scale.

Coupled ISCO-BIO Concept



PermeOx® Plus

- Timed Oxygen Release Product consisting of Engineered Calcium Peroxide manufactured by FMC Corporation.
- Selected from several alternative products.
- $CaO_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2O_2$
- $2H_2O_2 \longrightarrow O_2 + 2H_2O$

Klozur® OBC

- First combined chemical oxidation and enhanced aerobic biodegradation product manufactured by FMC Corporation.
- Based on alkaline activation of Klozur ® sodium persulfate using PermeOx Plus ®, which imparts alkalinity.
- Oxygen from PermeOx ® Plus activator component of the product is available as electron acceptor for aerobic metabolism

Klozur® OBC

- Klozur activation by iron, hydrogen peroxide, heat and other alkaline agents were options. Use of PermeOx Plus offers the longest oxygen release profile along with alkaline activation.

- $S_2O_8^{-2} + 2H^+ + 2e^- \longrightarrow 2HSO_4^-$
- $S_2O_8^{-2}$ + activator $\longrightarrow SO_4^{\bullet -} + (SO_4^{\bullet -}$ or $SO_4^{-2})$

Treatability Study Design

- Initial soil & water sample characterization
- Soil oxidant demand using Klozur ® OBC
- Determine chemical oxidant efficiency
- Evaluate aerobic biodegradation
  - Straight soil and groundwater
  - 10x diluted soil and groundwater to simulate less contaminated area or aerobic bioremediation polishing after ISCO

Initial Characterization

Soil	Units	Results	Groundwater	
TOC	mg/kg	3400		
COD	mg/kg	448	mg/L	46
pH	20 g soil 100 mL DI	3.8		4.3
ORP	mV	-38	mv	24
Acidity	mL 1 N NaOH/20 g soil	1.45		
NaOH Demand	g NaOH/kg soil	2.9		
Conductivity	uS/cm			219

Initial Characterization

Soil	Units	Results	Qual.	Groundwater		Qual.
2,4-Dimethylphenol	ug/kg	360	J	ug/L	<500	U
2,4,6-Trichlorophenol	ug/kg	<11000	U	ug/L	60	J
Pentachlorophenol	ug/kg	1500	J	ug/L	4900	
Naphthalene	ug/kg	120000		ug/L	<500	U
Acenaphthylene	ug/kg	1000	J	ug/L	<500	U
Acenaphthene	ug/kg	62000		ug/L	<500	U
Fluorene	ug/kg	46000		ug/L	<500	U
Phenanthrene	ug/kg	130000		ug/L	<500	U
Anthracene	ug/kg	13000		ug/L	<500	U
Fluoranthene	ug/kg	60000		ug/L	<500	U
Pyrene	ug/kg	37000		ug/L	<500	U
Benzo(a)anthracene	ug/kg	8600		ug/L	<50	U
Chrysene	ug/kg	7500	J	ug/L	<500	U
Benzo(b)fluoranthene	ug/kg	2100		ug/L	<50	U
Benzo(k)fluoranthene	ug/kg	2400		ug/L	<50	U
Benzo(a)pyrene	ug/kg	2100		ug/L	<50	U
Benzo(g,h,i)perylene	ug/kg	430	J	ug/L	<500	U

Klozur® OBC Study Results

Soil					% Rem.		
Day	Units	0	29	64	Days 0-64		
Total SVOCs	ug/kg	598290	458970	378400	36.8		
Groundwater							% Rem.
	Units	0	1	8	29	64	Days 0-64
Total SVOCs	ug/L	14011	19003	8348	9756	9317	33.5
OBC by Titration	mg/L	7985	4649	3257	3257	1865	76.6
pH		11.0	10.4	8.5	7.3	8.8*	
ORP	mV	257	70	163	182	124	
DO	mg/L	8.6	8.3	9.5	9.4	7.4	
	*added 192 mg NaOH on Day 50						

Bioremediation Results with PermeOx ® Plus

Bio Straight Soil and Groundwater							% Rem.
Solids	Day	0	29	56	84	93	Days 0-93
Sum BNA	µg/kg	854640		722990		251520	70.6
Groundwater							
Sum BNA	µg/L	13515		7173		3865	71.4
% App. Active Oxygen	%		0.483	0.424	0.4698	0.3435	
%Active Oxygen	%		0.652	0.589	0.665	0.476	
%PermeOx Plus	%		2.94	2.68	2.99	2.15	
pH			11.2	12.3	11.2	11.6	
ORP	mV		-91	-80	-104	-14	
Dis. Oxygen	mg/L		9.6	9.3	8.4	11.4	

Bioremediation Results with PermeOx ® Plus

Diluted Soil and Groundwater							% Rem.
Solids	Day	0	29	56	84	93	Days 0-93
Sum BNA	µg/kg	130120		68872		28406	78.2
Diluted Groundwater							
Sum BNA	µg/L	8372		4786		1429	82.9
% App. Active Oxygen	%		0.019	0.012	0.0080	0.0068	
%Active Oxygen	%		0.023	0.014	0.0090	0.0081	
%PermeOx Plus	%		0.10	0.064	0.043	0.036	
pH			10.2	10.6	9.0	9.8	
ORP	mV		-60	-78	-30	46	
Dis. Oxygen	mg/L		9.3	9.0	6.4	7.0	

Advanced Molecular Biological Analyses

- Phospholipid Fatty Acids (PLFA) are essentially the "skin" of the microbe and provide an effective tool for monitoring microbial responses to their environment. PLFA analysis provides a broad understanding of the entire microbial community with information obtained in the following key areas:

Viable Biomass
Community Structure
Metabolic Activity

PLFA Analysis Results – Straight Soil and Groundwater

Day	Biomass	Firmi-cutes	Proteo-bacteria	Anaerobic Metal Reducers	SRB/Actino-mycetes	General	Eukar-oytes	Slowed Growth	Decreased Permeability
	cells/g	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA
0	2.08E+07	26.16	47.96	7.42	4.62	10.22	3.62	0.88	0
56	2.19E+06	0	14.9	0	0	85.1	0	0	0
93	6.65E+06	0	63.11	0	0	36.89	0	0	0

PLFA Analysis Results – Diluted Soil and Groundwater

Day	Bio-mass	Firmi-cutes	Proteo-bacteria	Anaerobic Metal Reducers	SRB Actino-mycetes	General	Eukar-oytes	Slowed Growth	Decreased Permeability
	cells/g	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA	% Total PFLA
0	1.85E+07	33.98	39.36	8.94	4.4	10.44	2.9	0.48	0
56	3.63E+06	9.17	21.64	0	0	65.74	0	1.94	0
93	2.98E+07	0	90.85	0	0	9.15	1	0	0

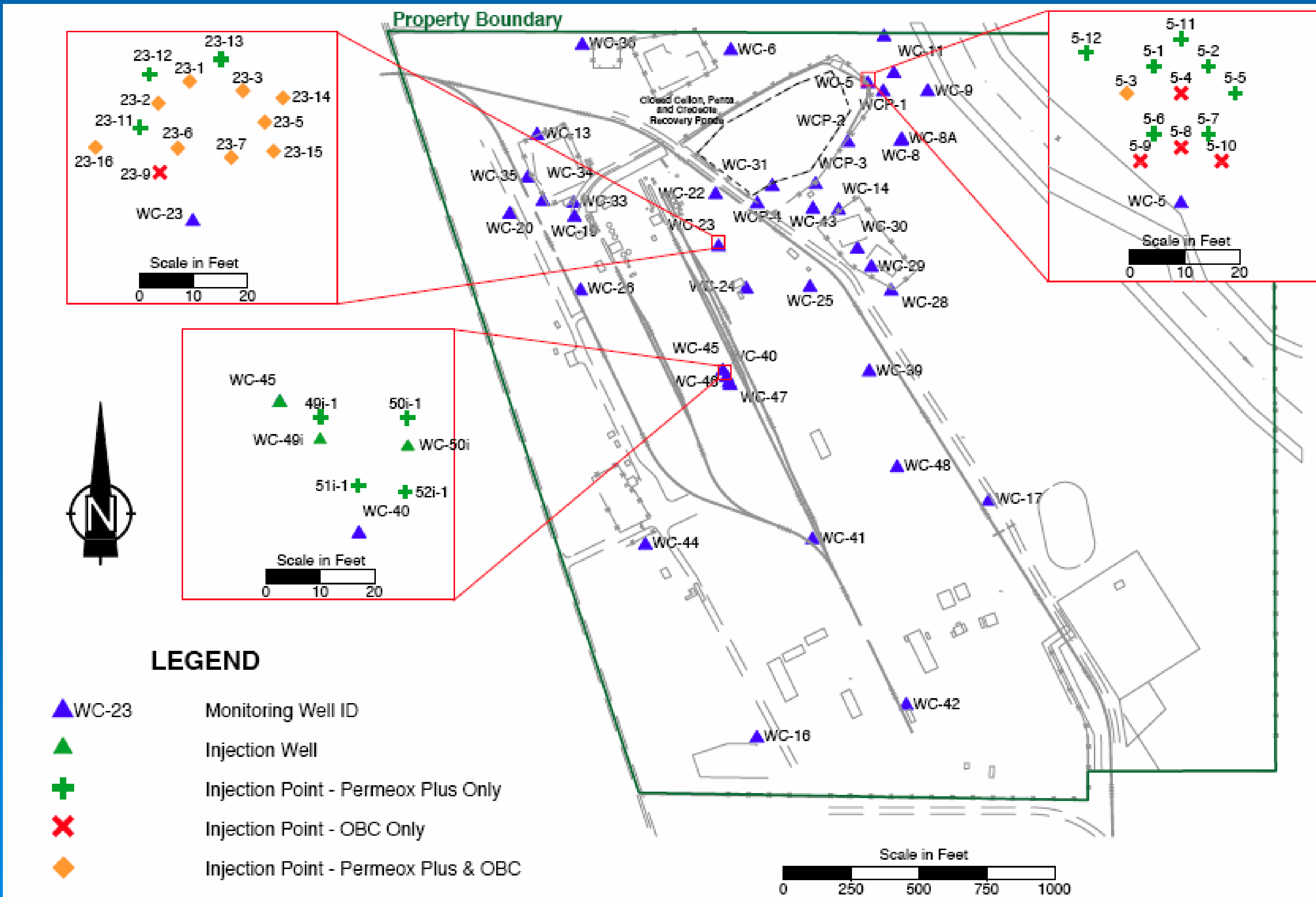
Study Conclusions
Klozur ® OBC

- Total Oxidant Demand for Klozur® OBC is about 41 pounds per cubic yard
- Additional sodium hydroxide (or equivalent) needed
- Klozur® OBC persisted for > two months
- Over 37% of SVOCs in soil and 34% in groundwater removed in 64 days

Study Conclusions PermeOx ® Plus

- PermeOx ® Plus promoted biodegradation of 70% SVOCs in highly contaminated soil and 71% in groundwater over 3 months
- PermeOx ® Plus demand estimated to be 37 pounds per cubic yard
- With diluted soil and groundwater, PermeOx Plus removed 76% SVOCs in soil and 83% in groundwater over 3 months – suggests potential for treatment of highly contaminated soil with Klozur ®OBC followed by aerobic bio polishing

Injection Pattern: WC-5, WC-23, and WC-40 Areas



Injection Process

- Target: 6900 PoxP/8400 OBC
- Actual in WC-5: 5200 PoxP/1786 OBC

- Target: 6900 PoxP/8400 OBC
- Actual in WC-23: 5032 PoxP/8400 OBC

- Target: 1300 PoxP
- Actual in WC-40: 1522 PoxP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BOTTOM
TOP
HOMER
PAINT
BUCKET

Preliminary Observations

- Connection with injectate noted in WC-5 and WC-23. Products could be direct pushed into subsurface. Difficult to inject into wells.
- Concentrations of PCP and naphthalene rise due to desorption in WC-5 and WC-23 areas, then decline. Little change in WC-40 area.
- pH increased to >11 and remains in WC-5. Similar increase in WC-23, but beginning to fall. Slight increase in pH for WC-40 area.
- Droplets in WC-5 have disappeared.

Next Steps

- Add remaining Klozur ® OBC and PermeOx ® Plus based on new injection scheme.
- Continue monitoring program.
- Define endpoint for the pilot test.
- Determine if additional injection is warranted.