Environmental Molecular Diagnostics Demonstrate Chem-Bio Treatment Train Effectiveness for Benzene

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Setting

- Massive remediation project of a former Manufactured Gas Plant in downtown Buffalo, New York
- The project was stalled for nearly a decade
- Looking for a single remedy to address complex soil, waste and groundwater problems
- State and City wanted a remedy that allowed the site to be put back into productive use.
- Real answer was moving to correct regulatory program, implementing multiple complementary remedial actions and a business solution

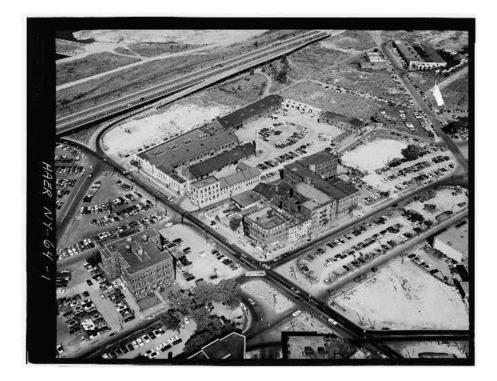




MGP Site History

- Manufactured Gas Plant

 Operated from the mid-1800's and closed circa 1948
- Serviced by the Erie Canal – Wilkeson Slip
- Storage and Distribution from 1948 to 2004
- Idle from 2004 to 2005





Site Conditions

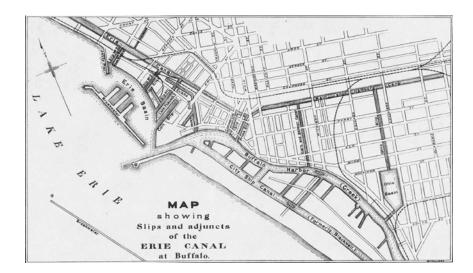
- MGP Buildings removed in 2000
- Former Wilkeson Slip backfilled in 1940s/1950s
- Waterfront School built over portion of site and slip in 1970s
- Site Investigation Identified the presence of NAPL at depth
- Affected soil and groundwater conditions representative of decades of MGP production byproducts
- Primary Compounds
 - BTEX
 - PAHs
 - Cyanide





Surrounding Properties

- US Postal Service
- Television Studio
- Parking
- Subsidized Housing





The Project - 2004

- MGP property owned by utility (environmental liability through acquisition of MGP operator)
- Former Order on Consent
- Site Investigations had been ongoing for years
- WSP enters the project at Remedy Selection Stage
- No remedial actions other that structure demolition
- Historic Façade designated a local landmark





The Business Solution

- Developer and major tenant identified
- Site location was perfect, but needed shovel ready site in less than 12 months
- The liability cost shared by utility and buyer
- Developer willing to share in liability cost as a function of purchase
- Liability transferred to a sole purpose entity
- Insured program Pollution Legal Liability Insurance





The Regulatory Solution

- Met with the State, City and parties to define time line
- Consent Order entered for adjacent school/Wilkeson Slip component
- BCP applications accepted for other areas sold to developer by the City of Buffalo
- Agreed to revised submittals:
 - Work Plan/FFS
 - Aggressive Schedule with full time onsite presence for state
 - Aerial monitoring of daily progress





School Property/Wilkeson Slip





- Protect the school structure
- Remove impacted fill and saturated soil
- Soil cleanup level of 1mg/kg
- Install sub-slab vapor mitigation system
- Coordinated remediation and new construction to meet the schedule for development



One Hundred Sixty Thousand Tons





On Time Completion Allowed Redevelopment

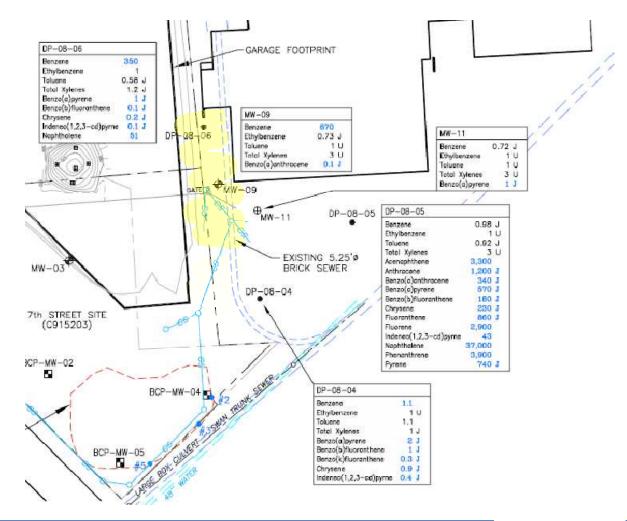








Elevated Benzene in Groundwater





Supplemental In Situ Remedy



- Complete delivery testing
- Assess the genetic capacity of native microbes to attenuate petroleum compounds

	Baseline 6/26/2009
	(DNA)
<u>CENSUS (qPCR)</u>	
Functional Genes (cells/bead)	
Benzyl Succinate Synthase (bssA)	<1.00E+00
Naphthalene Dioxygenase (NAH)	1.37E+08
Phenol Hydroxylase (PHE)	4.06E+04
Toluene Monooxygenase (RMO)	<1.00E+00
Toluene Dioxygenase (TOD)	1.01E+06
Biphenyl Dioxygenase (PPH4)	2.34E+04
Xylene Monooxygenase (TOL)	2.00E-01 J

 Applied of 24,030 lbs. of Klozur® CR using direct push slurry injection methods



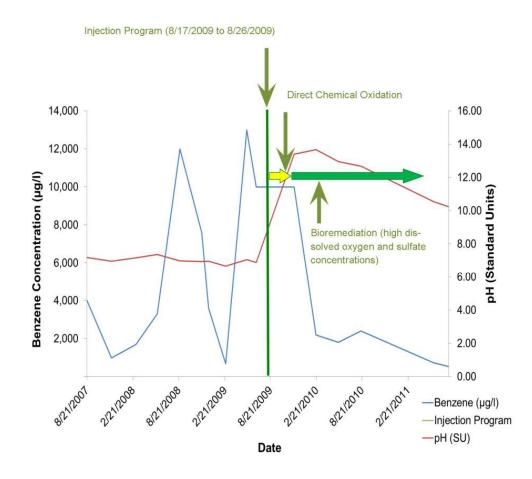
Klozur CR



- Consists of sodium persulfate and calcium peroxide
- Three different but coupled chemistries to attenuate petroleum-affected groundwater in a single application.
 - strong chemical oxidant (base activated persulfate)
 - aerobic biostimulant (calcium peroxide is an oxygen releasing comound)
 - anaerobic biostimulant properties (persulfate decomposes to the electron acceptor sulfate)
- Groundwater monitoring limited to one well but included monitoring included EMDs



Concentration Data

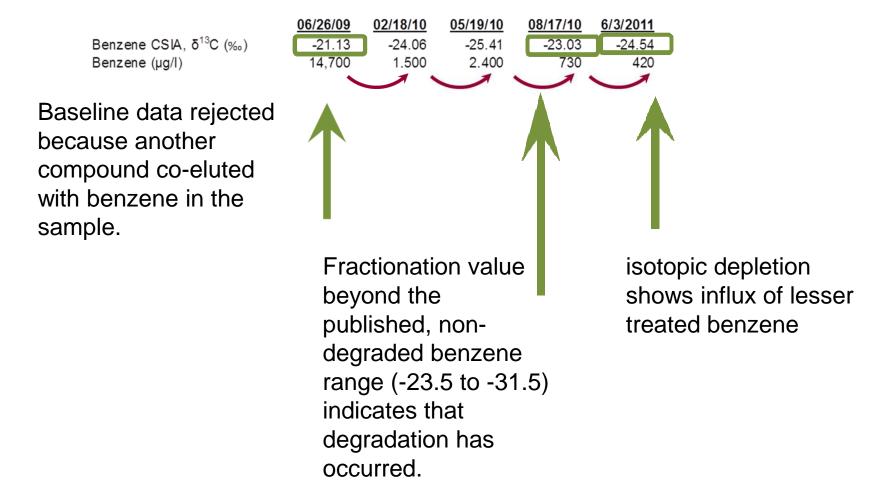


- Decrease in benzene concentration following Klozur® CR injections
- pH elevated throughout due to calcium peroxide accumulation in well screen pack

(in the winter of 2011 the well was replaced by MW-9R located directly adjacent to MW-9. pH in MW-9R was neutral)



Compound Specific Isotope Analysis Confirms Contaminant Destruction



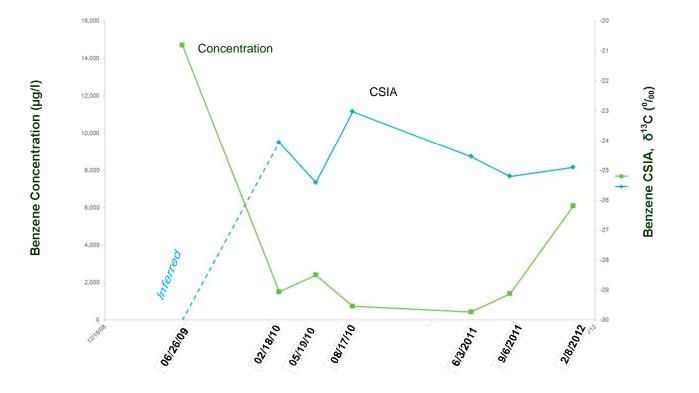


Molecular/Biological Data Identifies the Biological Mechanism of Destruction

	MW-9				
	Baseline Performance Monitoring				
	6/26/2009	2/18/2010	5/19/2010	8/17/2010	6/6/2011
	(DNA)	(mRNA)	(mRNA)	(mRNA)	(mRNA)
<u>CENSUS (qPCR)</u>					
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					
					•
degrade petroleum constituents BioTrap® qPCR data quantifies the					antifies the
are common.					
		expression of genes for protein synthesis ar			
	identifies two classes of microbes able				microbes able to
	adapt to elevated pH levels.				els



Additional Round of Concentration and Isotopic Data Definitively Shows Benzene Mass Influx





Explanation: Upgradient Saturated Soil Cleanup Criteria 1 mg/kg

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

 $Ct = Cw[KocFoc + (\theta w + \theta aH')/\rho b]$

		Typical	Low	High	RSL	
Symbol	<u>Param eter</u>	Value	Value (a)	Value (a)	Calc	<u>Units</u>
Ct	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	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
θa	Air-filled porosity	0	0	0.28	0.13	dimensionless
	• • • • • • • • •					
Cw	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 $C_{\scriptscriptstyle W}$.

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.



Groundwater Treatment Results/Lessons Learned

- Advanced Site Diagnostics was able to definitively attribute decreased postapplication concentrations to destructive degradation.
 - the CSIA data showed fractionation (Delta13C value of -23.03 ‰) outside the typical non-degraded benzene range (-23.5 ‰ to -31.5 ‰) thereby definitively proving destructive degradation.
 - the expression of oxygenase enzyme activity as measured by RNA gene copies identifies the degradation mechanism for at least some of the benzene
- CSIA data also attributed the benzene concentration rebound to influx from an upgradient source.
- Achieved goals to lower benzene concentrations but influx of upgradient benzene limited complete attenuation.



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