



Innovative Environmental Technologies, Inc.

**“Comparative Study for ZVI/Peroxide vs Ferric Iron Oxide Persulfate
Activation Followed by Intrinsic Facultative, Biologically Mediated Processes”**

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Overview of ISCO Technologies

- Introduction
- Oxidizing agents
- General chemistries of reactions

Use of Persulfate for ISCO Treatment

- Traditional Persulfate Activation Methods
- Limitations of convectional activation technologies

ISCO/Enhanced Bioremediation

- ZVI/Peroxide Persulfate Activation
- Ferric Iron Oxide Persulfate Activation
- Biological Attenuation Process

Cases Studies

➤ ISCO involves:

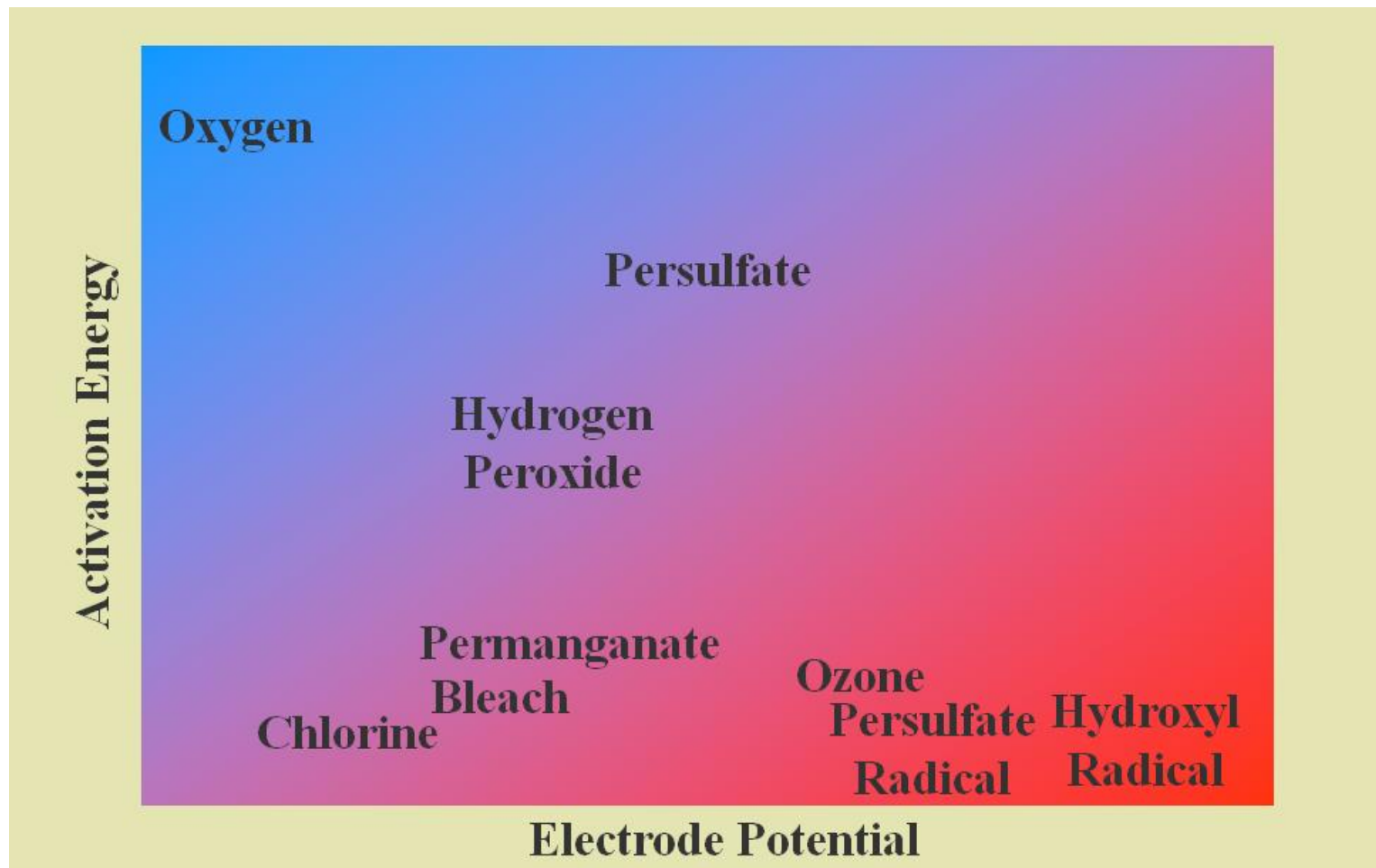
- ❖ Injection of an oxidizing agent into the subsurface to destroy organic compounds
- ❖ The by-products for complete mineralization include carbon dioxide (CO₂), water (H₂O) and oxygen (O₂)

➤ Goal is to mineralize or transform contaminants of concern (COCs)

Common Oxidizing Agents

Oxidant	Potential (V)	Form
Fenton's Reagent (OH^\cdot)	2.80	Liquid
Activated Persulfate ($\text{SO}_4^{\cdot-}$)	2.60	Salt/Liquid
Ferrate (Fe^{6+})	2.20	
Ozone (O_3)	2.07	Gas
Persulfate ($\text{S}_2\text{O}_8^{2-}$)	2.01	Salt/Liquid
Hydrogen Peroxide (H_2O_2)	1.78	Liquid
Permanganate (MnO_4^-)	1.68	Salt (KMnO_4) Liquid (NaMnO_4)

Reactivity of Oxidizing Agents



Basic Oxidizing Agent Reactions

Ozone (No Activator)

- $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ $E_o = 2.07 \text{ V}$
- Hydroxyl Radical
 - $O_3 + H_2O \rightarrow O_2 + 2OH\cdot$
 - $2O_3 + 3H_2O_2 \rightarrow 4O_2 + 2OH\cdot + 2H_2O$
 - $2OH\cdot + 2H^+ + 2e^- \rightarrow 2H_2O$ $E_o = 2.76 \text{ V}$

Persulfate (Requires Activation)

- $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ $E_o = 2.01 \text{ V}$
- $S_2O_8^{2-} \rightarrow 2(SO_4^{\cdot-})$ $E_o = 2.50 \text{ V}$

Hydrogen Peroxide (Requires Activation)

- $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E_o = 1.77 \text{ V}$
- $H_2O_2 \rightarrow 2OH\cdot$; $2OH\cdot + 2H^+ + 2e^- \rightarrow 2H_2O$ $E_o = 2.76 \text{ V}$

Permanganate (No Activator)

- $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ $E_o = 1.70 \text{ V}$
 - K^+, Na^+

Accepted Oxidizing Techniques for Specific COCs

Oxidant	Amenable VOC's	Reluctant VOCs	Recalcitrant VOCs	Limitations
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂	TCA, CT, CHCl ₃	Stability (25-95% decomp/hr), low pH
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂ , TCA, CT, CHCl ₃		Stability (10-50% decomp/hr)
Potassium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl ₃ , DCA, CB, CH ₂ Cl ₂	Soil oxidant demand
Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl ₃ , DCA, CB, CH ₂ Cl ₂	Soil oxidant demand
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH ₂ Cl ₂ , CHCl ₃	TCA, CT	Stability (10-25% decomp/wk), low pH
Sodium Persulfate, Base	All VOCs			Stability (10-25% decomp/wk), NaOH costs
Sodium Persulfate, Heat	All VOCs			Stability (10-50% decomp/day), low pH, heating costs
Ozone	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA		DCA, CH ₂ Cl ₂ , CHCl ₃ , TCA, CT	Mass Delivery, Volatilization

➤ **Divalent Metal Activation**

- ❖ Oxidant consumption during conversion of ferrous iron to ferric iron
- ❖ Inhibition of biological utilization of the generated ferric species (EDTA)
- ❖ High oxidant consumption due to overdosing of the ferrous chelated iron

➤ **Caustic Activation**

- ❖ Significant health and safety issues
- ❖ Unsuitably high (extreme) pH environment for biological attenuation
- ❖ Self-limiting biological attenuation process due to hydrogen sulfide generation

➤ **Heat Activation**

- ❖ Difficult Implementation
- ❖ High Cost
- ❖ Elevated hydrogen sulfide production

➤ **Hydrogen Peroxide Activation**

- ❖ Limited efficacy on many targeted compounds
- ❖ Elevated hydrogen sulfide production
- ❖ Produces heat and (excessive) gassing which can lead to surfacing issues

The ISCO reactions are short lived

- ❖ Ozone (minutes to hours) Fenton's (hours to days) Persulfate (days to weeks) Permanganate (months).
- ❖ The ISCO process can enhance COC desorption
- ❖ Lack of secondary treatment mechanism mandates subsequent treatments

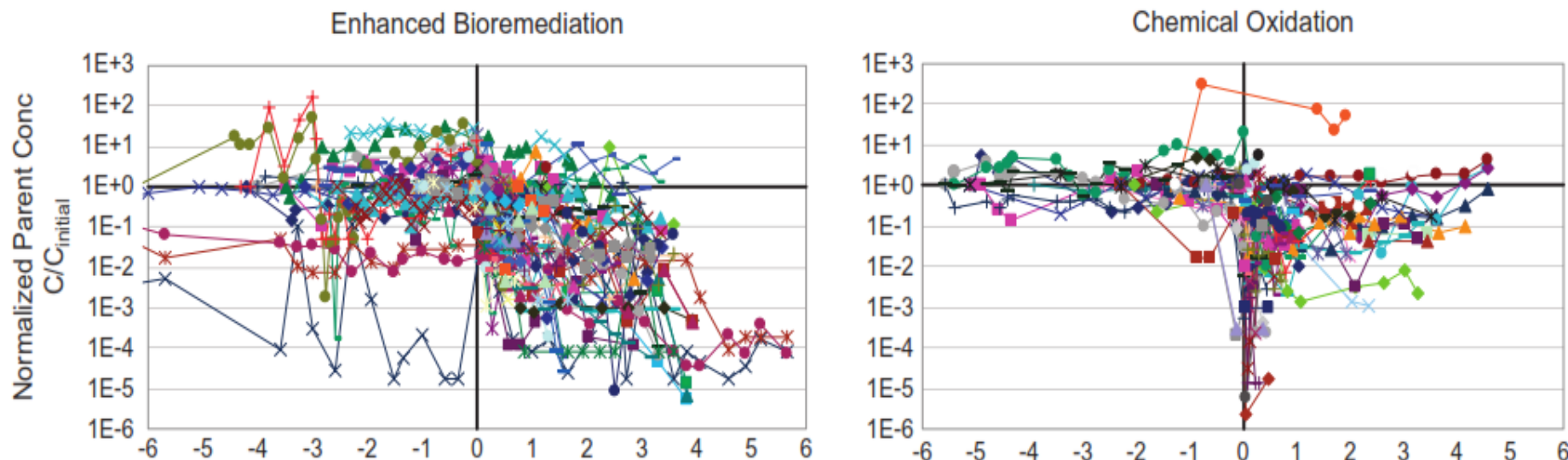


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

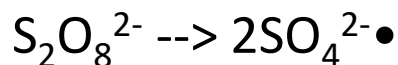
- Iron catalyzed peroxide oxidation (Fenton reactions) utilize iron to catalyze the decomposition of hydrogen peroxide, producing OH radicals



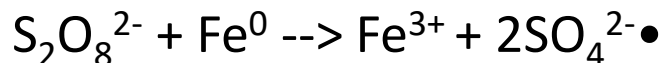
- Advantage of the evolution of free radicals
 - ❖ Offer higher oxidation capabilities
 - ❖ Broader spectrum of applicable targeted compounds
- In addition to the reactions occurring between the oxidant and the organics present, radical-propagating reactions also occur involving the excess H_2O_2
- More radicals are available to react with the contaminants

ZVI/Peroxide Persulfate Activation

- The persulfate anion ($S_2O_8^{2-}$) has a high redox potential and can be chemically activated to form the sulfate radical ($SO_4^{2-\bullet}$)



- Persulfate oxidation commonly uses sodium persulfate, to produce sulfate radicals that attack most petroleum hydrocarbons

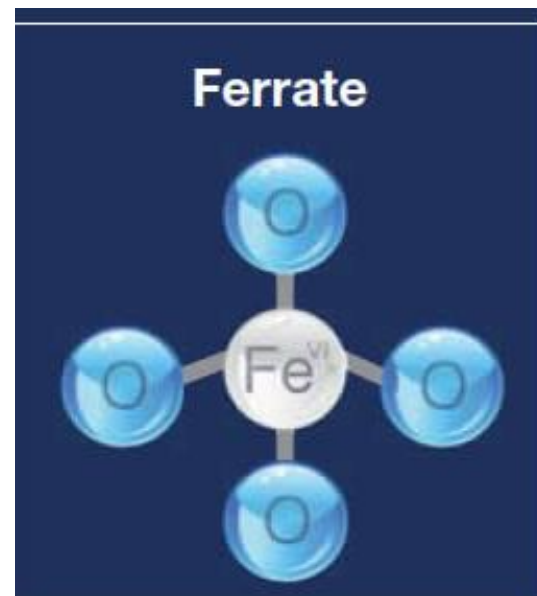
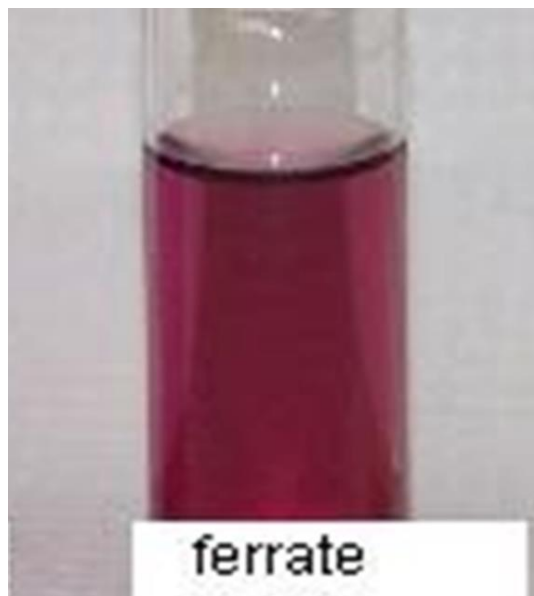
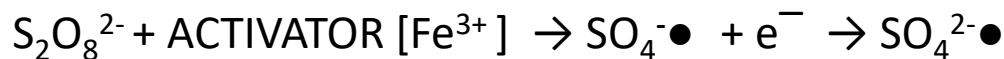
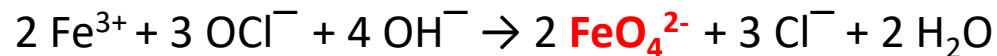


- Persulfate activation with iron requires a lower activation energy than thermal activation, making iron activated persulfate a more efficient and rapid way of degrading contaminants
- The generated sulfate ion from the decomposition of the persulfate acts as a terminal electron acceptor for sulfate reducers

- Persulfate is activated by Fe(III) requiring lower activation energy than alternative mechanisms
- No consumption of persulfate oxidant
- Elevation of iron oxidation state to a supercharged iron ion, ferrate species (Fe^{6+}) which can itself acts as an oxidant
- The supercharged iron cation consumption results into ferric species that act as a terminal electron acceptor for biological attenuation

Sodium Persulfate + Ferric Oxide (Fe_2O_3)

- Chemical Oxidation via Sulfate (SO_4^\bullet) Radical
- Chemical Oxidation via Ferrate ($\text{Fe}^{6+\bullet}$) Radical



Ferric Iron Reactions

- Ferric iron used as electron acceptor during anaerobic biodegradation of contaminants
- Stoichiometrically, the degradation of 1.0 mg/L of BTEX results in the average consumption of approximately 22 mg/L of ferric iron



- Ferric iron is reduced to Ferrous iron, which is soluble in water
- Ferrous iron is oxidized to Ferric iron and the iron cycling provides sustained secondary bioremediation via one electron transfer reactions (Weber *et al*, 2006)

Sulfate Reduction

- After dissolved oxygen depletion sulfate is used as an electron acceptor for anaerobic biodegradation by indigenous microbes (sulfidogenesis)
- Stoichiometrically, 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX compounds
- Sulfate acts as an electron acceptor in co-metabolic processes during bioremediation of petroleum products
- Basic reactions for the mineralization of benzene and toluene under sulfate reducing conditions:



Pyrite Formation

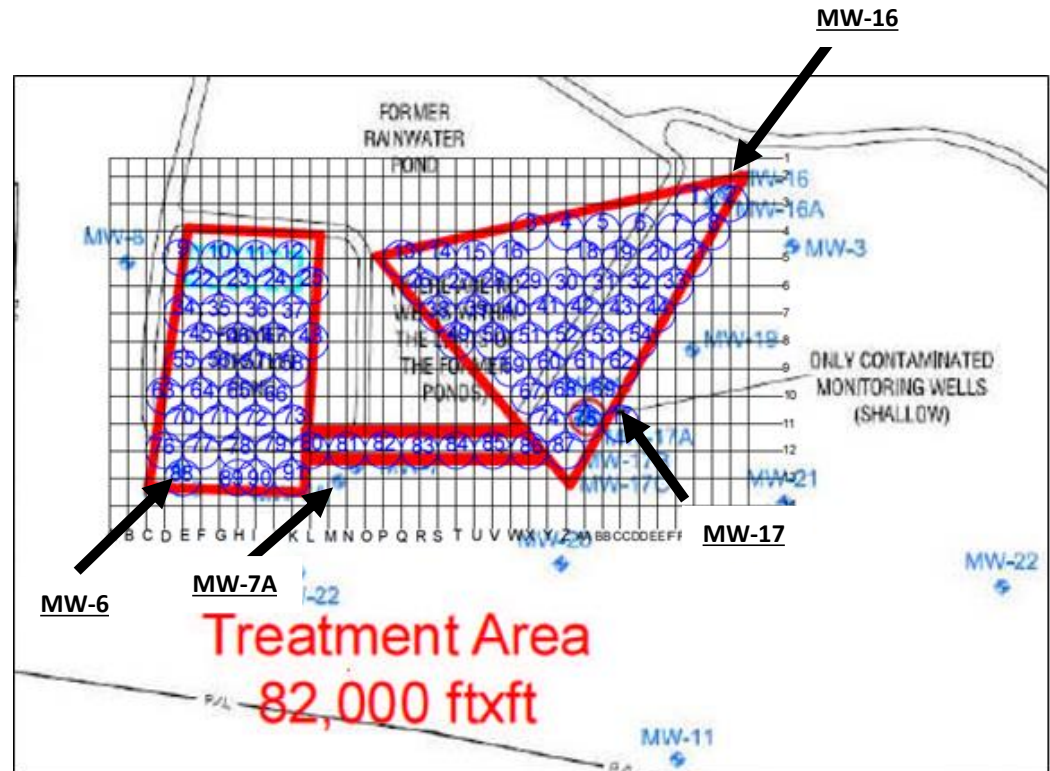
- Sulfate residual is utilized as terminal electron acceptor by facultative organisms thereby generating sulfide
- The ferrous iron and the sulfide promote the formation of pyrite as a remedial byproduct
- This reaction combats the toxic effects of sulfide and hydrogen sulfide accumulation on the facultative bacteria
- Provides a means of removing targeted organic and inorganic COIs via precipitation reactions
- Pyrite possesses a high number of reactive sites that are directly proportional to both its reductive capacity and the rate of decay for the target organics



Ferric Iron Oxide Persulfate Activation - Case Study 1

- Single injection event at a wood treating facility in Midwestern United States in July 2013 to remediate soils and groundwater impacted by the historical release of heavy ended petroleum compounds.
- Total treatment area of approximately 82,000 square feet, treating between 13 and 22 feet below ground surface.

- 91 injection points
- Spaced 34 ft apart
- 22,022 lbs of Ferric Iron and Persulfate Mixture



Injection Equipment

IET INJECTION SYSTEM
UNITED STATES PATENT 7,044,152



Injection Trailers Include: Multiple Liquid Feed Systems, Stainless Steel Piping, Isolated Compressed Gas Containment, Safety Shower, Eyewash Station, Onboard Generator, Chemical Resistant Construction, Mobile Office Space



Table 1. VOC Data for MW-6 (µg/L).

MW-6				
Sampling Date	07/2013	10/2013	01/2014	04/2014
Benzo(a)pyrene	17,000	ND	ND	ND

ND: Not Detected

Table 2. VOC Data for MW-7A (µg/L).

MW-7A				
Sampling Date	07/2013	10/2013	01/2014	04/2014
Benzo(a)pyrene	18,000	ND	ND	ND

ND: Not Detected

Table 3. VOC Data for MW-16 (µg/L).

MW-16				
Sampling Date	07/2013	10/2013	01/2014	04/2014
Benzo(a)pyrene	20,000	ND	ND	ND

ND: Not Detected

Table 4. VOC Data for MW-17 (µg/L).

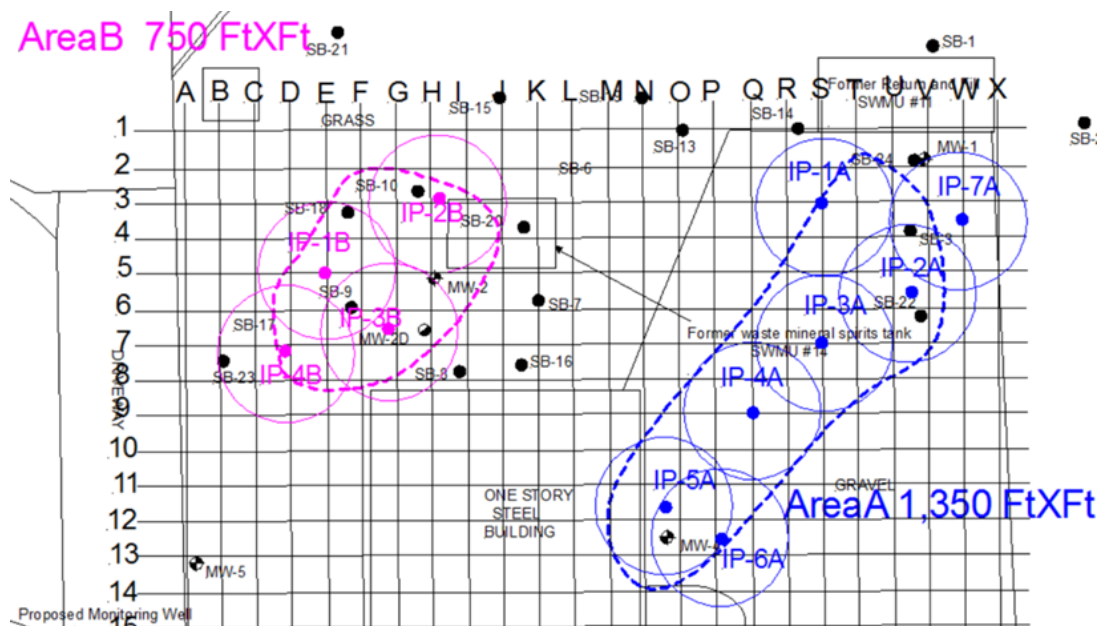
MW-17				
Sampling Date	07/2013	10/2013	01/2014	04/2014
Benzo(a)pyrene	19,000	ND	ND	ND

ND: Not Detected

Ferric Iron Oxide Persulfate Activation - Case Study 2

- Single injection event implemented at a former gas station in Raleigh, North Carolina in September 2012 to remediate soils and groundwater impacted by the historical release of BTEX compounds.
- Total treatment area of approximately 2,100 square feet, treating between 12 and 27 feet below ground surface.

- 11 injection points
- Spaced 15-20 ft apart
- 3,750 lbs of Ferric Iron and Persulfate Mixture



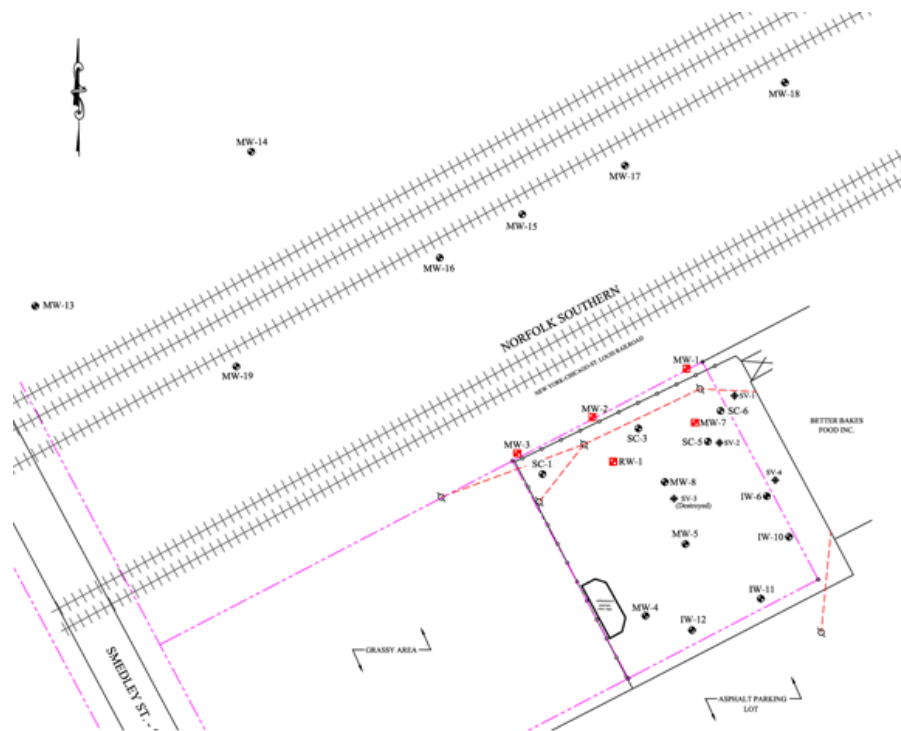
Ferric Iron Oxide Persulfate Activation - Case Study 2

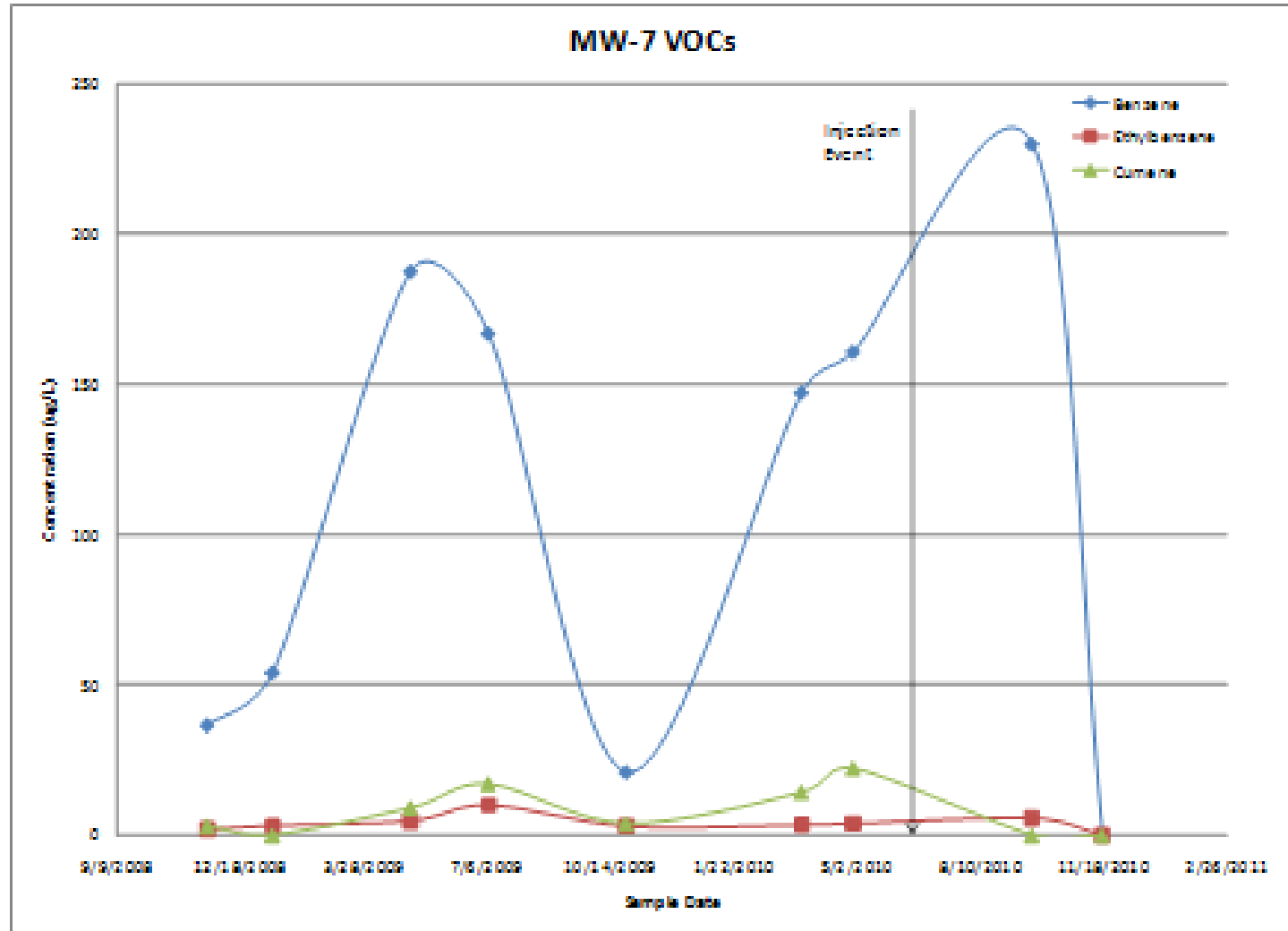
MW-1			
Sampling Date	09/12/2012	03/20/2013	10/02/2013
Benzene	0.3J	ND	ND
Chlorobenzene	1.0	ND	ND
1,2-Dichlorobenzene	18	2.0	ND
1,3-Dichlorobenzene	2.7	1.0	ND
1,4-Dichlorobenzene	9.9	5.4	3.2
Ethylbenzene	2.5	ND	ND
Isopropylbenzene	12	ND	ND
Naphthalene	6.6	ND	ND
Toluene	0.8J	ND	ND
Xylene (Total)	82	3.8	0.9

MW-4			
Sampling Date	09/12/2012	03/20/2013	10/02/2013
Benzene	13	ND	ND
Chlorobenzene	13	ND	ND
1,2-Dichlorobenzene	18	ND	ND
1,3-Dichlorobenzene	0.8J	ND	ND
1,4-Dichlorobenzene	3.6	ND	ND
Ethylbenzene	ND	ND	ND
Isopropylbenzene	4.2J	ND	ND
Naphthalene	8.4	ND	ND
Toluene	ND	ND	ND
Xylene (Total)	16	ND	ND

- Single injection event implemented at a former gas station in Northwestern, Pennsylvania in June 2010 to remediate soils and groundwater impacted by the historical release of BTEX compounds.
- Total treatment area of approximately 10,775 square feet, treating between 8 and 17 feet below ground surface.

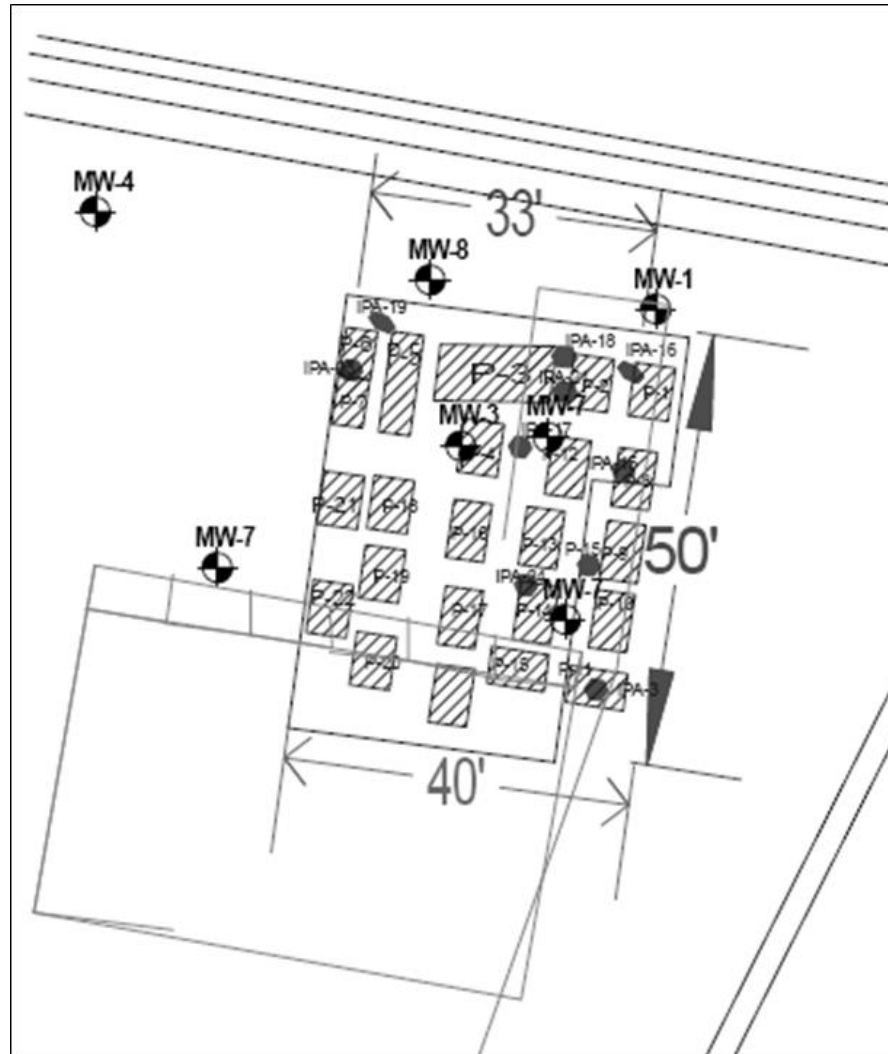
- 70 injection points
- Spaced 15-20 ft apart
- 15,500 lbs of Ferric Iron and Persulfate Mixture





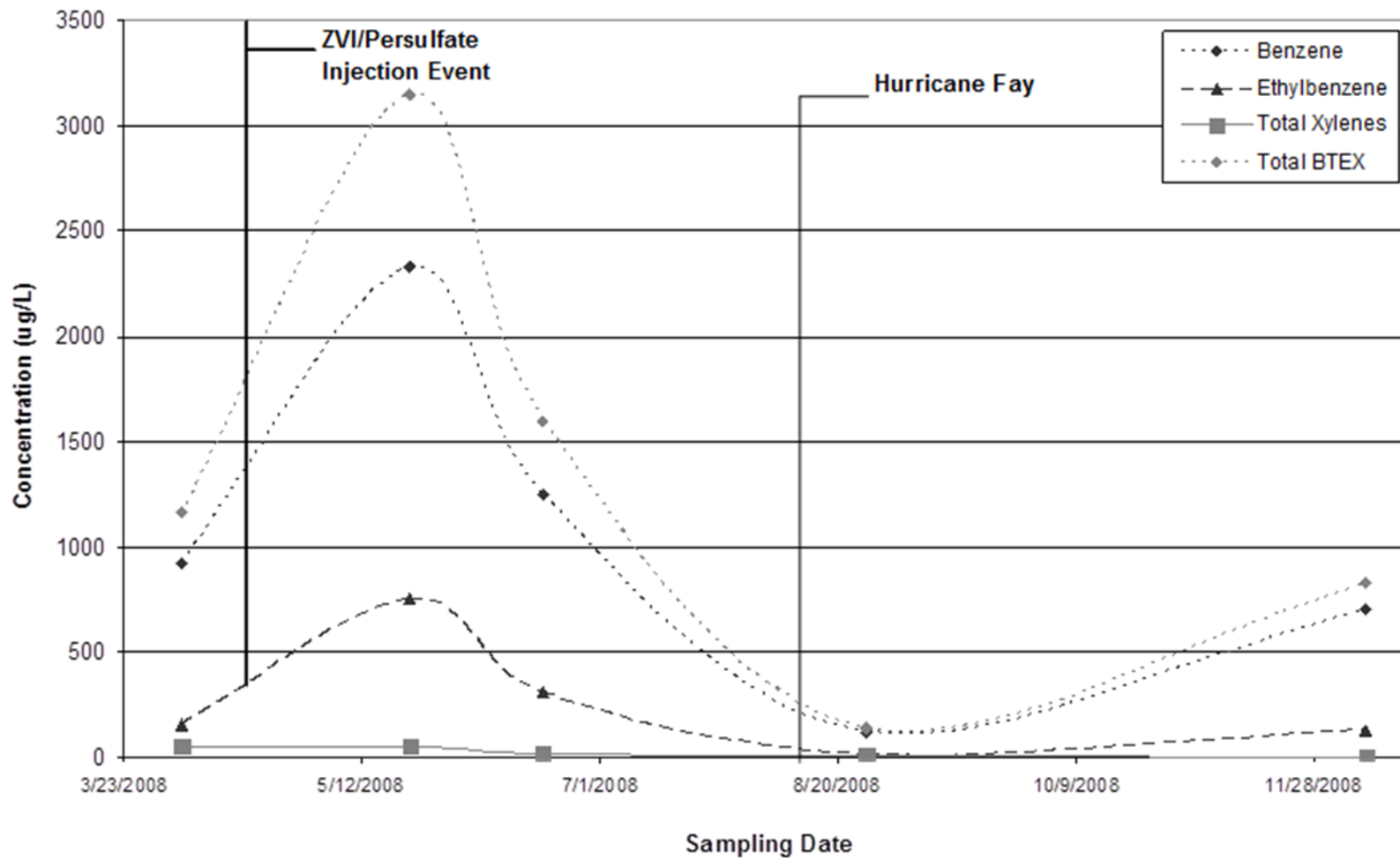
ZVI/Peroxide Persulfate Activation - Case Study 1

- Single injection event at a wood treating facility in site in St. Augustine, Florida



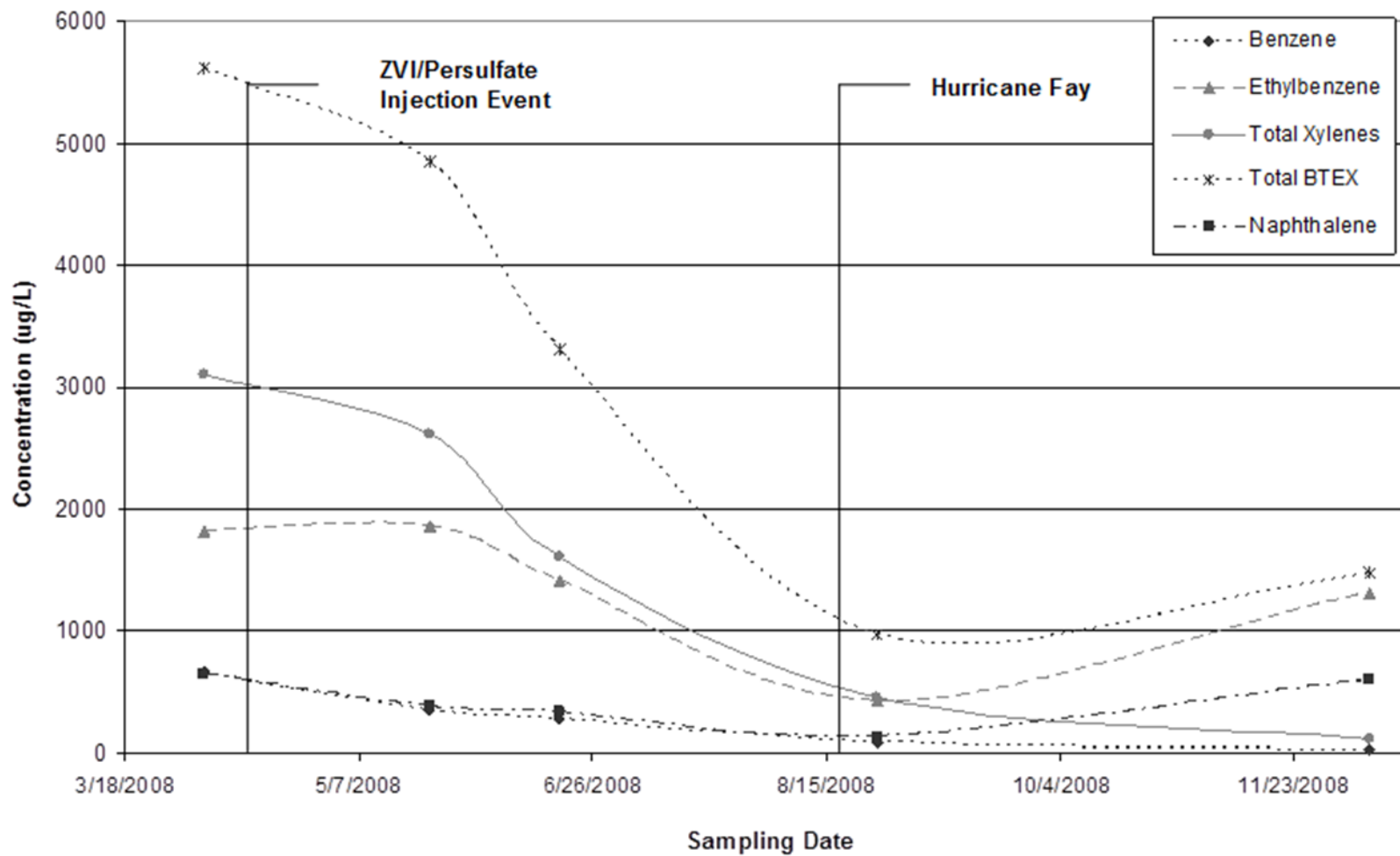
ZVI/Peroxide Persulfate Activation - Case Study 1

COC Concentrations (MW-1)



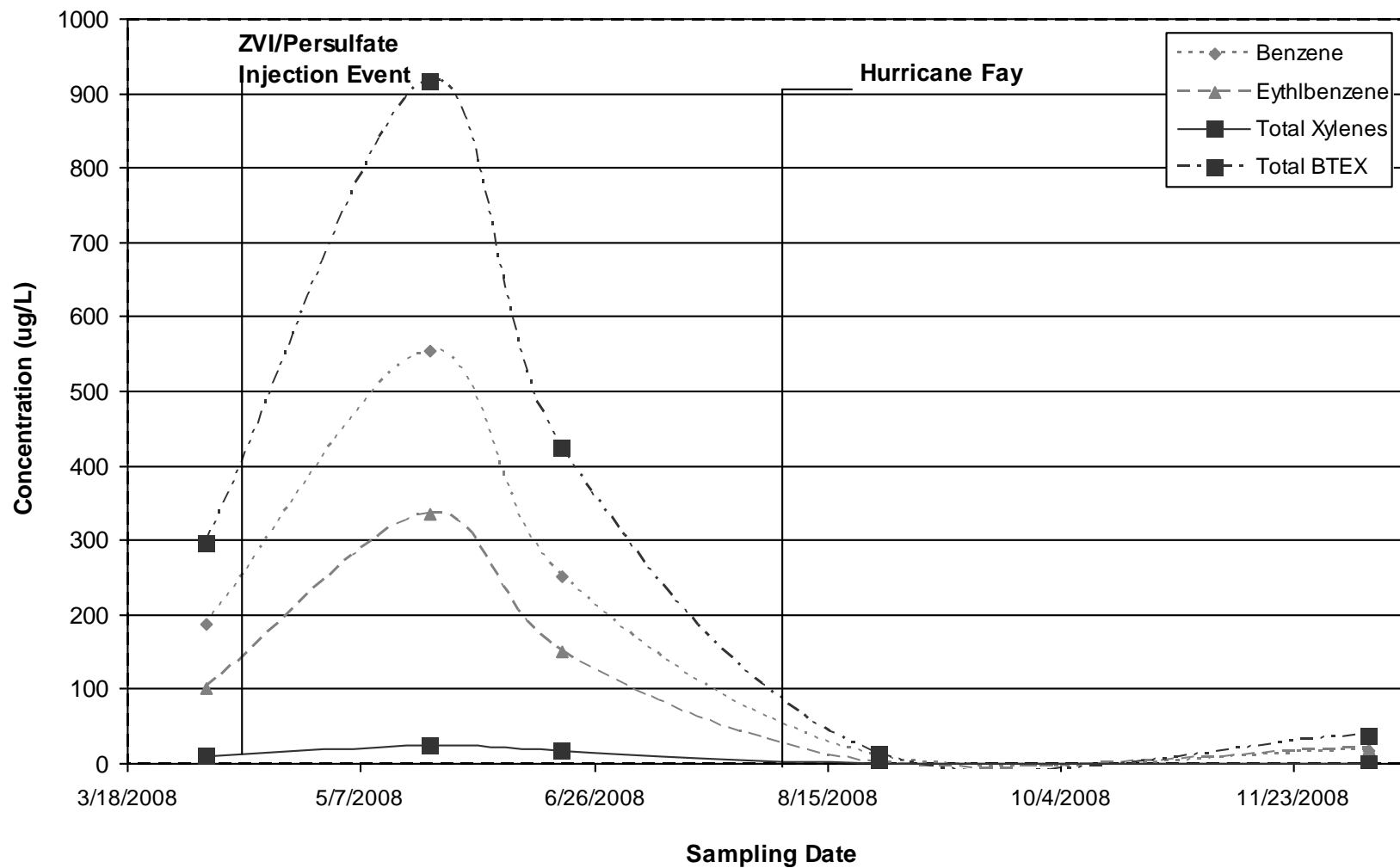
ZVI/Peroxide Persulfate Activation - Case Study 1

COC Concentrations (MW-2)



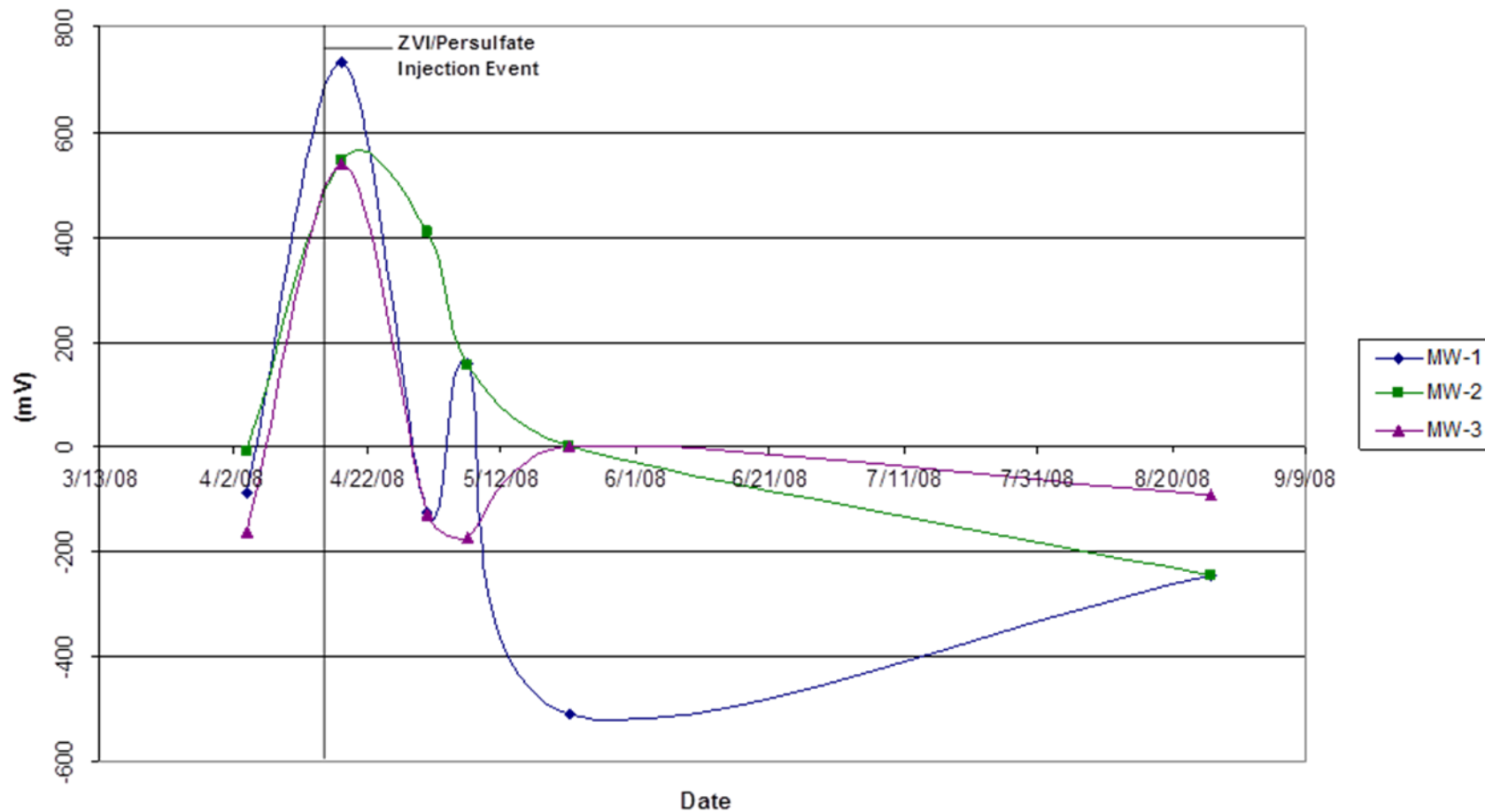
ZVI/Peroxide Persulfate Activation - Case Study 1

COC Concentrations (MW-3)



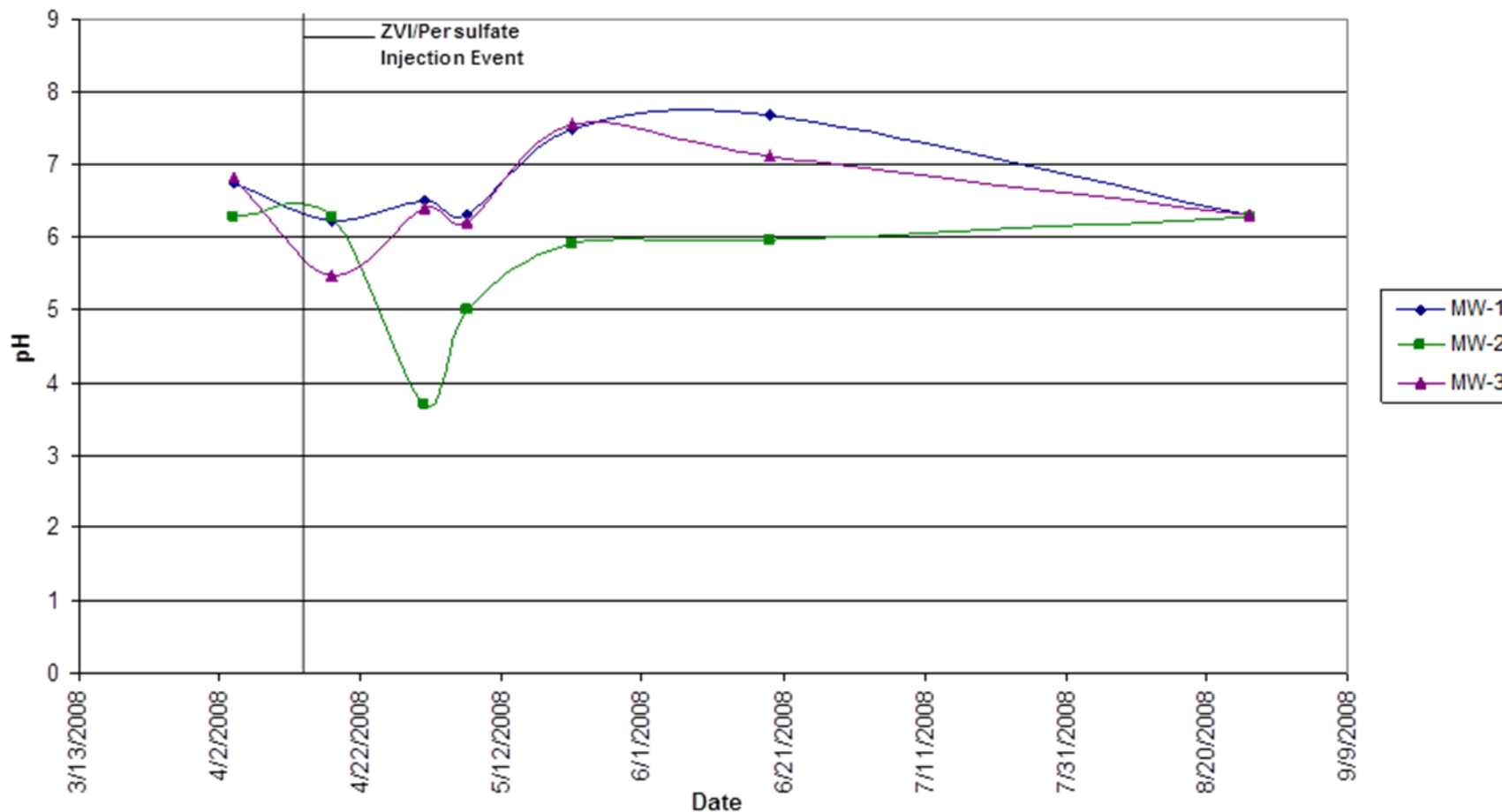
ZVI/Peroxide Persulfate Activation - Case Study 1

Oxidation Reduction Potential (ORP) for Monitoring Wells 1,2 and 3

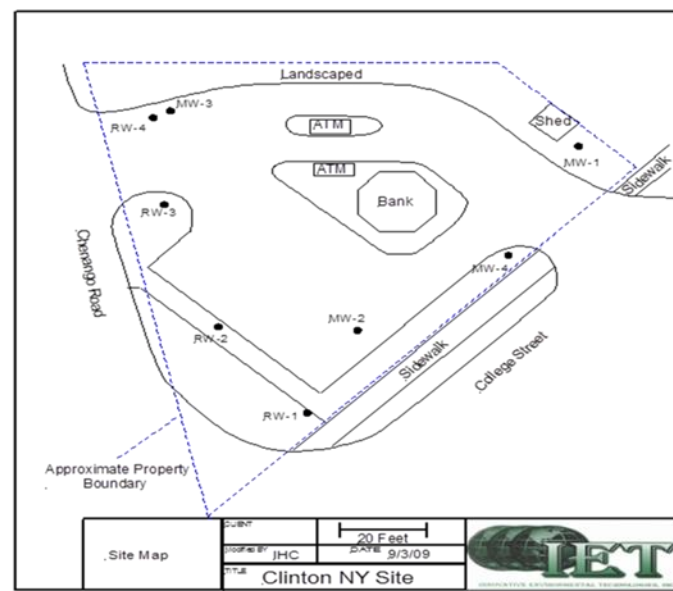
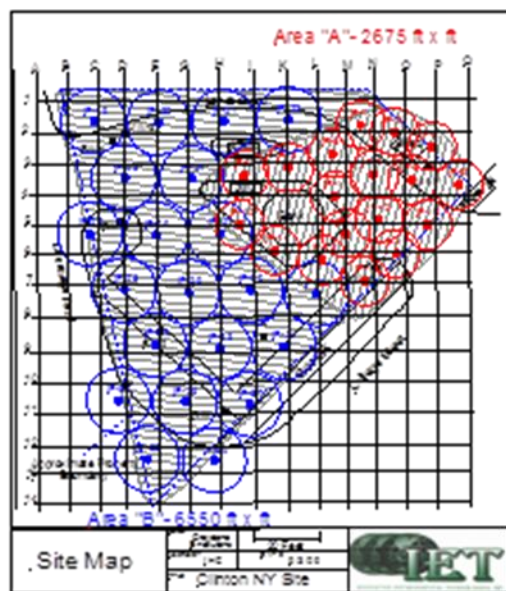


ZVI/Peroxide Persulfate Activation - Case Study 1

pH for Monitoring Wells 1,2, and 3



- In situ chemical oxidation remedial event at a former gas station in Clinton, NY, from October 27 to October 29, 2009
- Targeted BTEX compounds while promoting biological mineralization.
- Total treatment area of 9,225 square foot area, treating between 9 and 15 feet below ground surface.



ZVI/Peroxide Persulfate Activation - Case Study 2

MW-1						
Field Parameter	10/26/2009	12/28/2009	02/24/2010	06/23/2010	10/07/2010	03/31/2011
pH	6.70	5.28	7.57	6.92	6.81	6.86
ORP (mV)	-67	+339	-142	-151	-100	-88
DO (mg/L)	0	0.24	0	0	0	0

MW-2						
Field Parameter	10/26/2009	12/28/2009	02/24/2010	06/23/2010	10/07/2010	03/31/2011
pH	6.92	5.44	7.58	6.75	6.62	6.77
ORP (mV)	-140	+286	-127	-153	-91	-81
DO (mg/L)	0	0.12	0	0	0	0

MW-4						
Field Parameter	10/26/2009	12/28/2009	02/24/2010	06/23/2010	10/07/2010	03/31/2011
pH	7.05	5.56	7.54	6.85	6.67	6.94
ORP (mV)	-143	+277	-122	-145	-106	-102
DO (mg/L)	1.54	3.36	1.79	1.84	0.11	0

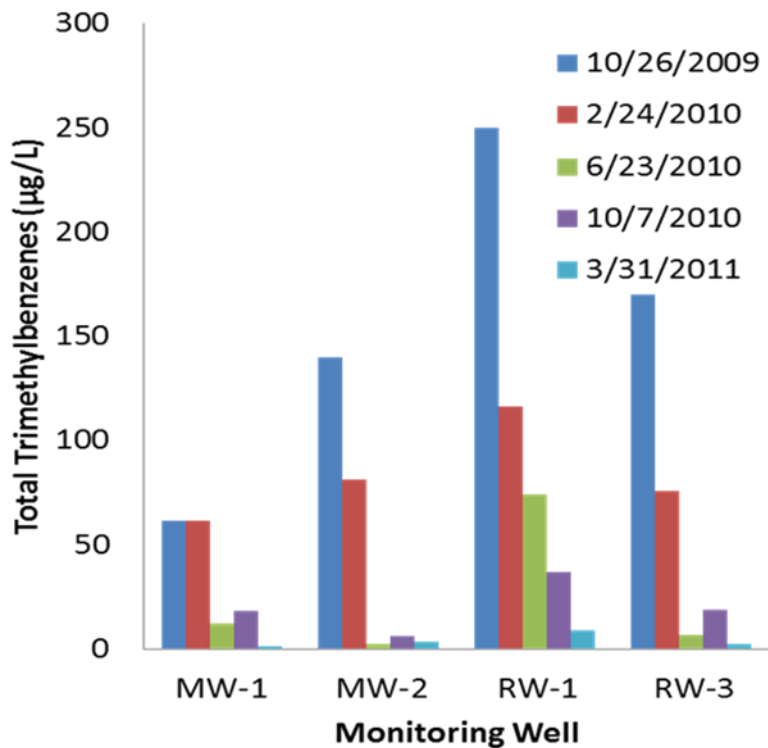
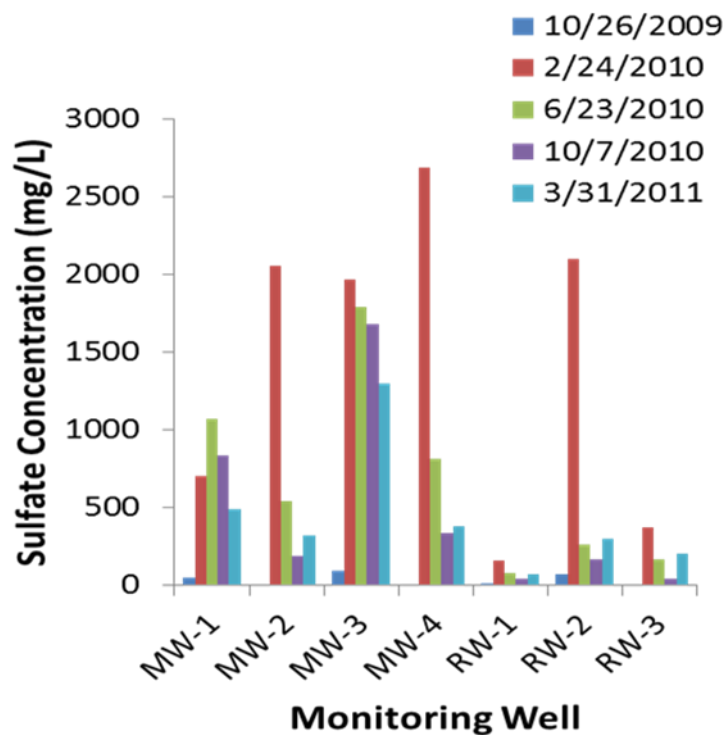
RW-1						
Field Parameter	10/26/2009	12/28/2009	02/24/2010	06/23/2010	10/07/2010	03/31/2011
pH	7.13	5.69	7.75	6.96	6.81	7.01
ORP (mV)	-160	+253	-139	-147	-104	-92
DO (mg/L)	0	0.09	0	0	0	0

➤ Four monitoring wells are located in the vicinity of the injection area:

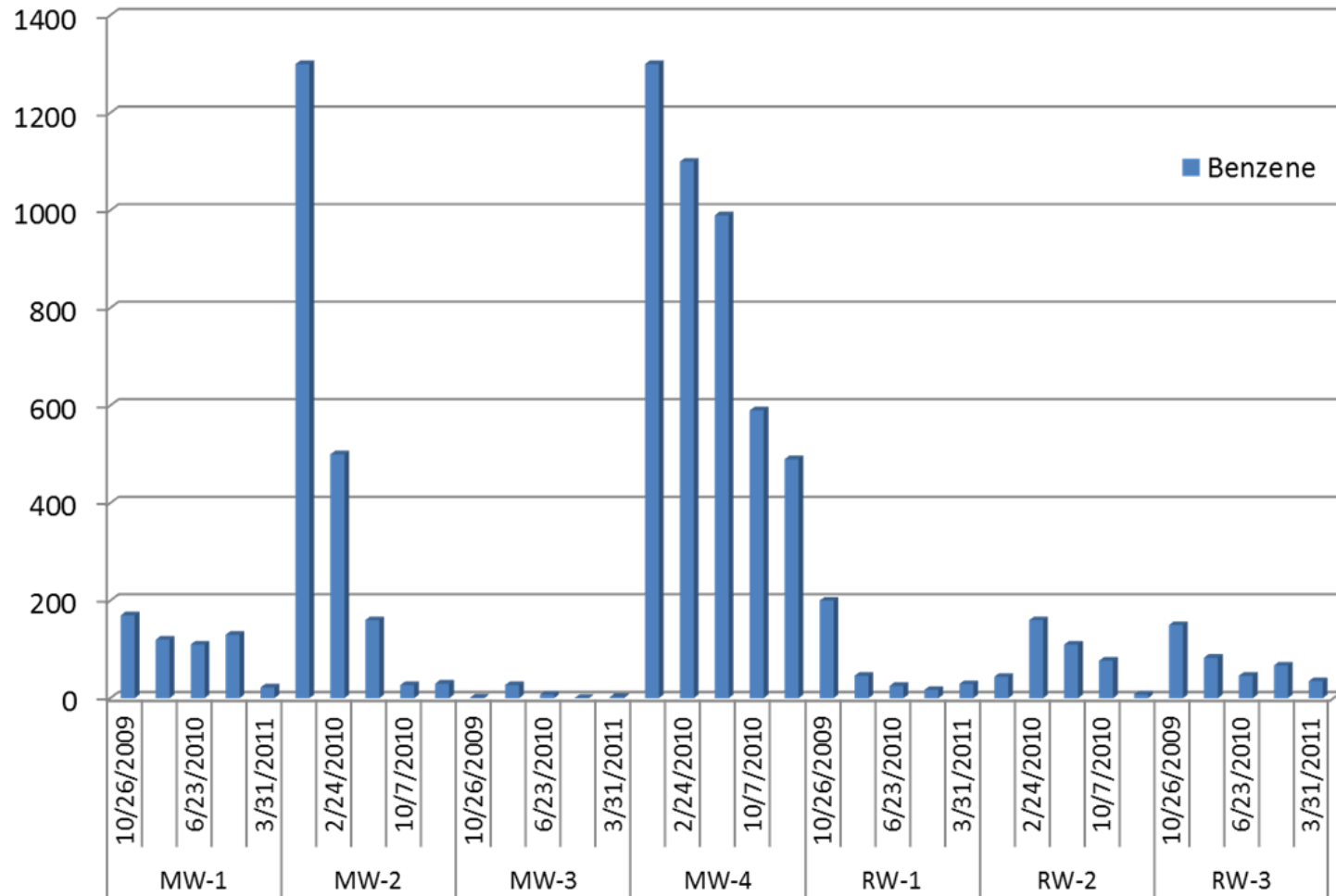
❖ **MW-1 & MW-2 & MW-4 & PW-1**

- ✓ Geochemical parameters ideal for biological attenuation
- ✓ Iron present in the ferrous state
- ✓ Sulfate concentrations elevated
- ✓ pH remains neutral
- ✓ Redox Potential is negative

ZVI/Peroxide Persulfate Activation - Case Study 2



ZVI/Peroxide Persulfate Activation - Case Study 2



ZVI/Peroxide Persulfate Activation - Case Study 3

- Single injection event implemented at a former gas station in Herkimer, New York in April 2017 to remediate soils and groundwater impacted by the historical release of BTEX compounds.
- Total treatment area of approximately 19,515 square feet, treating between 10 and 18 feet below ground surface.
- 56 injection points
- Spaced 20 ft apart



ZVI/Peroxide Persulfate Activation - Case Study 3

MW2017-2				
Sampling Date	06/29/2017	08/30/2017	11/09/2017	04/24/2018
Water Level (ft)	9.66	16.89	9.39	8.70
pH	6.62	6.02	7.22	6.81
ORP (mV)	-28.7	-68.0	-35.7	-32.7
D.O. (mg/L)	0.26	7.54	4.16	4.76
Conductivity (mS/cm)	4.574	3.330	2.260	1.098
Turbidity (NTU)	799	NA	370	53.4
Temperature (oC)	15.92	20.97	16.50	9.96
Total Iron (µg/L)	NA	84,600	51,400	57,700
Dissolved Iron (µg/L)	NA	2,500	347 J	200
Sulfate (µg/L)	NA	1,600,000	740,000	270,000

MW2017-2				
Sampling Date	06/29/2017	08/30/2017	11/09/2017	04/24/2018
Benzene	10 J	8.0 J	ND	0.32 J
Toluene	20 J	ND	ND	ND
Ethylbenzene	440	350	100	9.2
Total Xylenes	22 J	ND	ND	ND
Isopropylbenzene	180	200	67.0	11.0
n-Propylbenzene	530	660	220	40.0
1,2,4-Trimethylbenzene	3,000	3,800	1,200	120
Acetone	86 J	ND	ND	ND

**“Safer, More Effective ISCO Remedial Actions Using Non-Extreme Persulfate Activation
to Yield Sustained Secondary Treatment”**



Questions

