



Innovative Environmental Technologies, Inc.

November 2016

**Use of ZVI Catalyzed Hydroxyl & Sulfate
Free Radicals to Address BTEX
Contamination via In-Situ Chemical
Oxidation Followed by Intrinsic
Facultative, Biologically Mediated Processes**

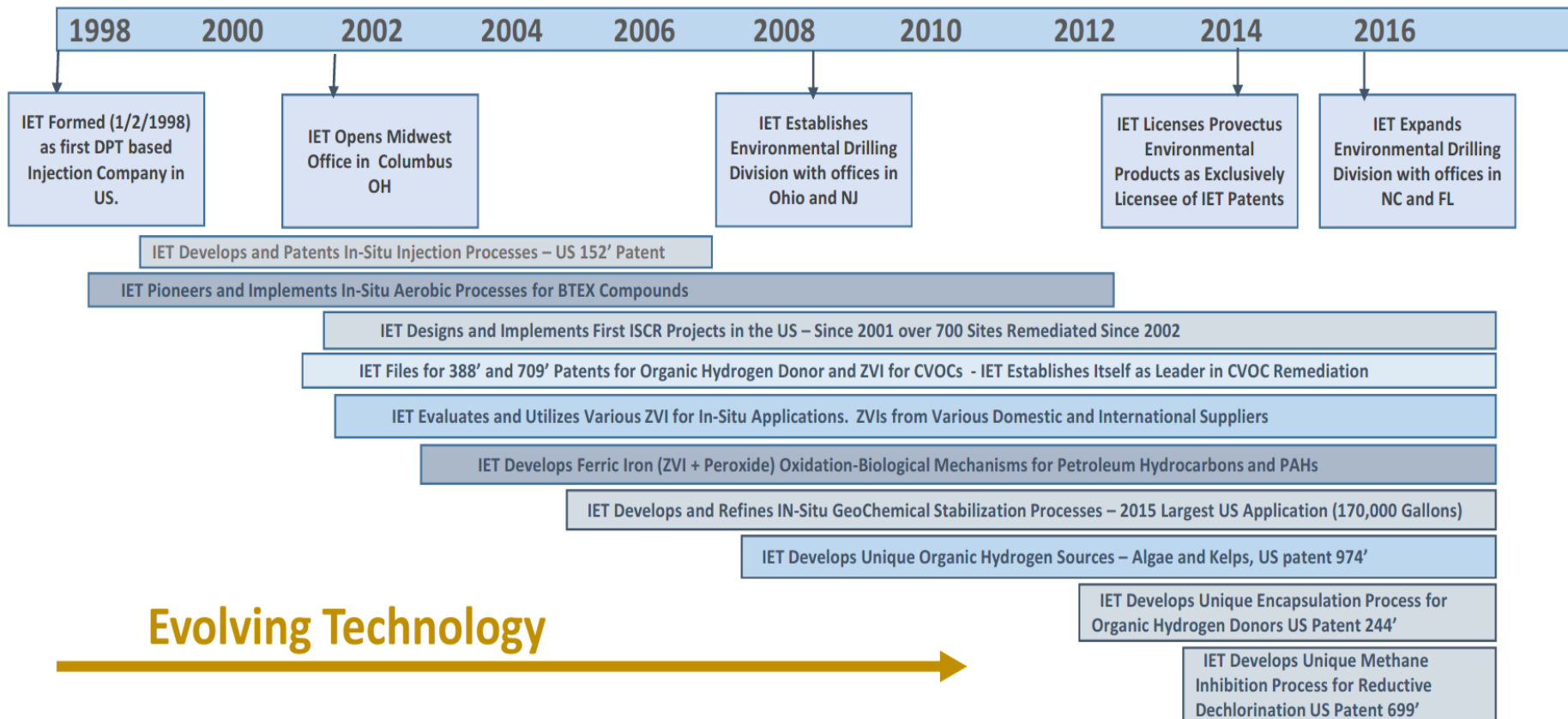
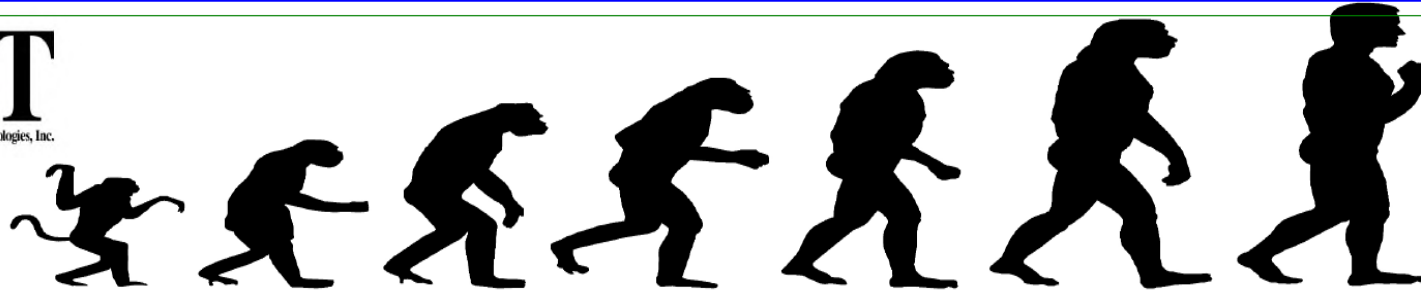


Outline – Topics/Focus

- Introduction
- ISCO/Bio System
- Clinton, NY
- St. Augustine, FL
- Summary
- Questions



IET Evolution



Evolving Technology



In-Situ Delivery Methods Direct Push - Apparatus



AMS 9600 Series



GeoProbe – 66 Series



AMS 9600- P Series



AMS 9700 VTR



Geoprobe 7720DT



In-Situ Delivery Methods

Direct Push - Tooling



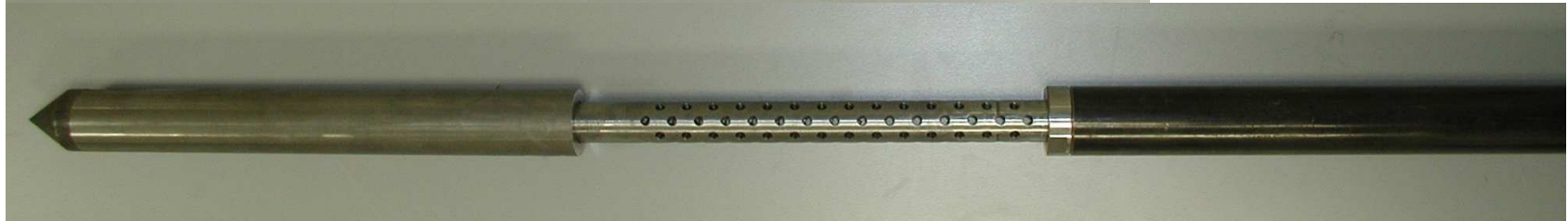
- Expendable Points
- Permanent and Semi Permanent Points
- Retractable Points
- Sealed Points (open under pressure)

In-Situ Delivery Methods Injection Rod Options



Retractable Injection Zone

Exchangeable Injection Zone



Replaceable points

No Flow Velocity loss to
Injection Zone





In-Situ Delivery Methods

Injection Rod Options

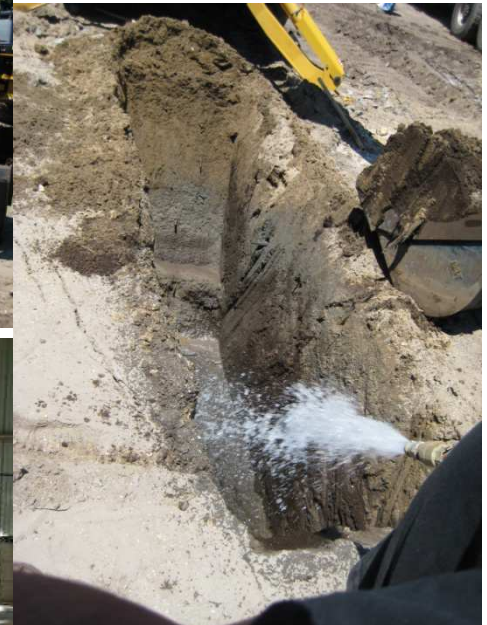


Pressure Activated Injection Probe





Excavation and Back-Fill



Potential Reactive Species in an Activated Persulfate System		
Species		Potential (V)
Persulfate anion	$S_2O_8^{-2}$	+2.1
Sulfate radical	$SO_4^{\cdot-}$	+2.6
Hydrogen peroxide	H_2O_2	+1.8
Hydroxyl radical	OH^{\cdot}	+2.8
Monopersulfate	HSO_5^-	+1.4
Hydroperoxide	HOO^{\cdot}	
Superoxide	$O_2^{\cdot-}$	-0.2



Limitations of Traditional Persulfate Activation Techniques



- **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

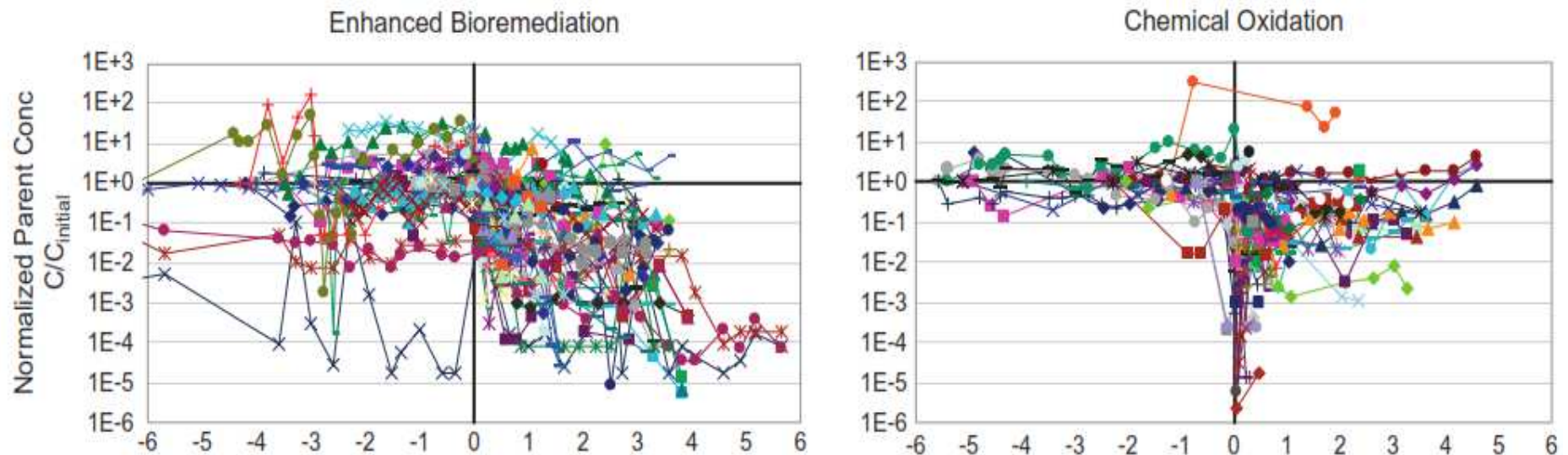
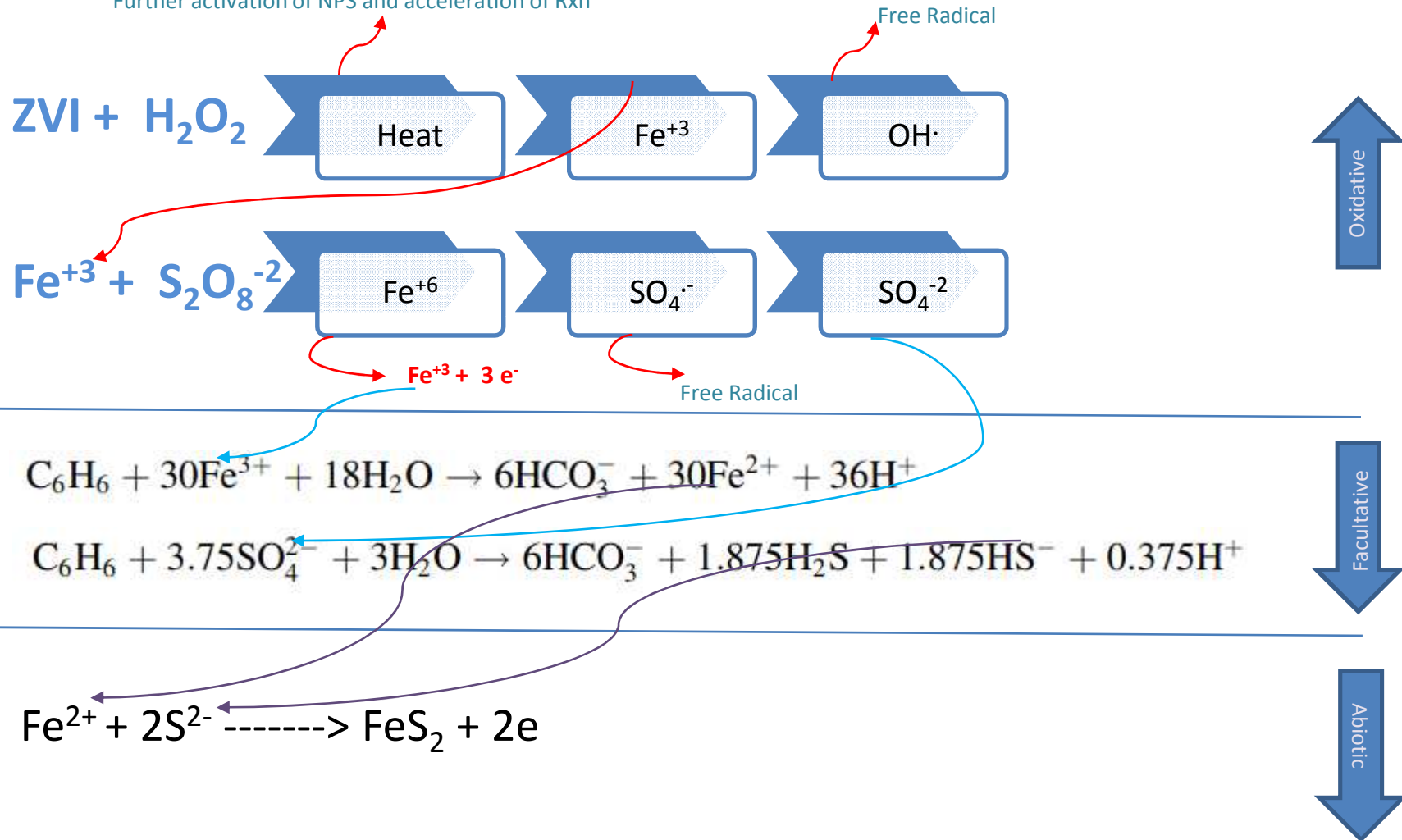


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

Further activation of NPS and acceleration of Rxn



- Peroxide is activated by ZVI – generating hydroxyl free radicals and heat
- 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) 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
- The generated sulfate ion from the decomposition of the persulfate acts as a terminal electron acceptor for sulfate reducers

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:



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)

Pyrite Formation

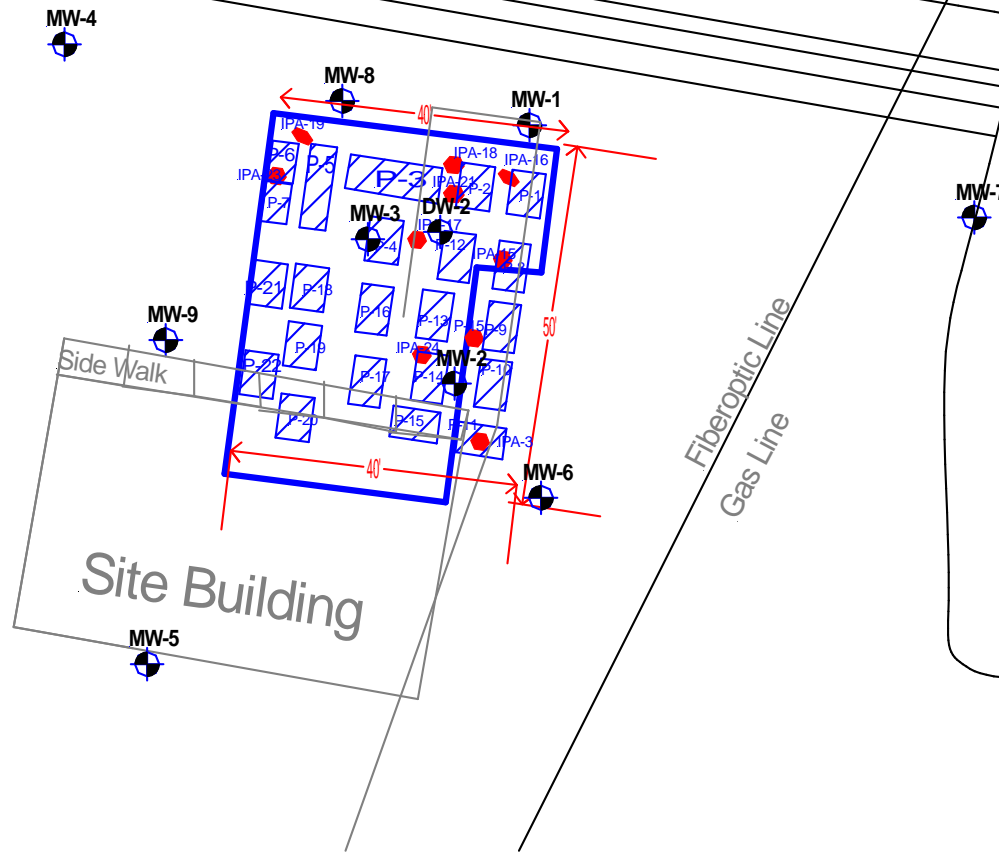
- Sulfate residual is utilized as terminal electron acceptor by facultative organisms thereby generating sulfide
- The ferrous iron and the sulfide promote the formation of pyrite as a remedial byproduct
- This reaction combats the toxic effects of sulfide and hydrogen sulfide accumulation on the facultative 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



- Safely catalyzed process without the Hazards of Extreme Activators Caustics
- ZVI particles remain in place if subsequent injection events are necessary
- Safely distributed in the field
- Biotic and Abiotic processes are easily traced with field monitoring of Fe^{+2} , Fe^{+3} , SO_4^{-2} , SO_3^{-2} , S^{-2} , ORP and pH
- Conserves Oxidant – Unlike other Persulfate Activators
- Multiple ISCO processes via formation of reactive ferrate species = better ISCO
- Enhances bio attenuation utilizing both iron and sulfate reduction
- Encourages the formation of pyrite / Prevents H_2S formation
- Long-lived reactions – sustained treatment manages rebound
- Cost-effective – reduces need for multiple injection events

Case Study #1 – St. Augustine, Florida

State RT 16



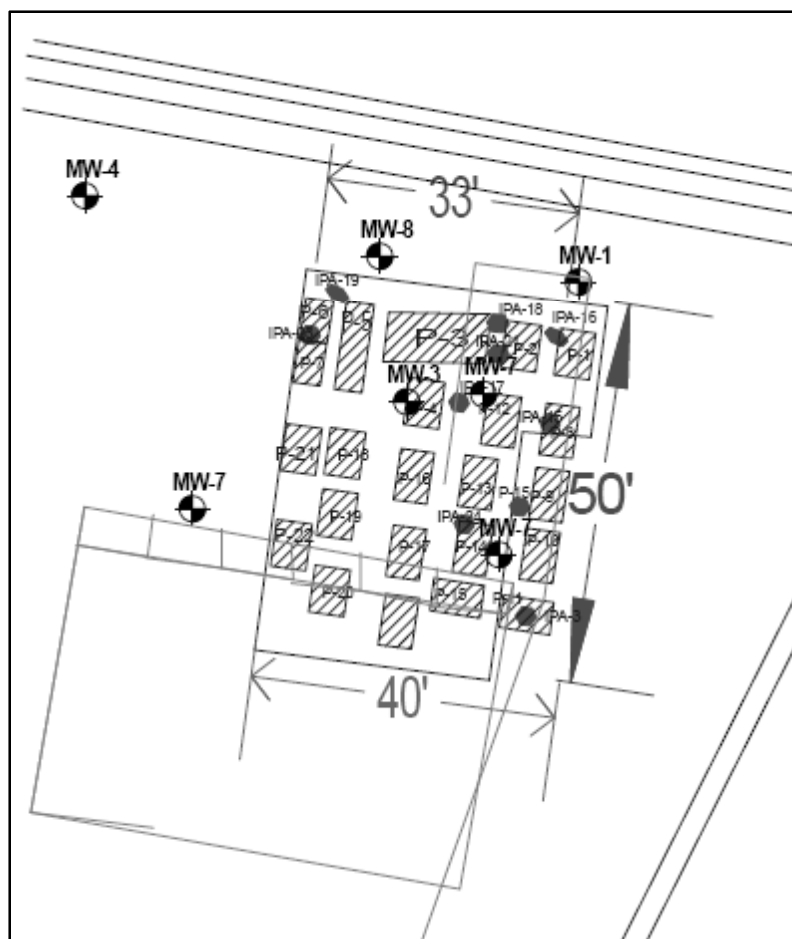
Case Study #1 – St. Augustine, Florida



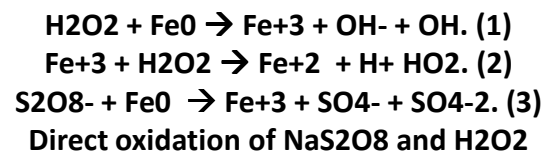
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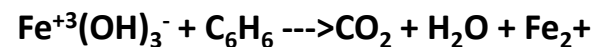
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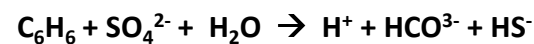
Phase #1 - Oxidation



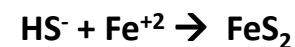
Phase #2 – Iron Reduction



Phase #3 – Sulfate Reduction



Phase #4 – Ferrous Sulfide Formation

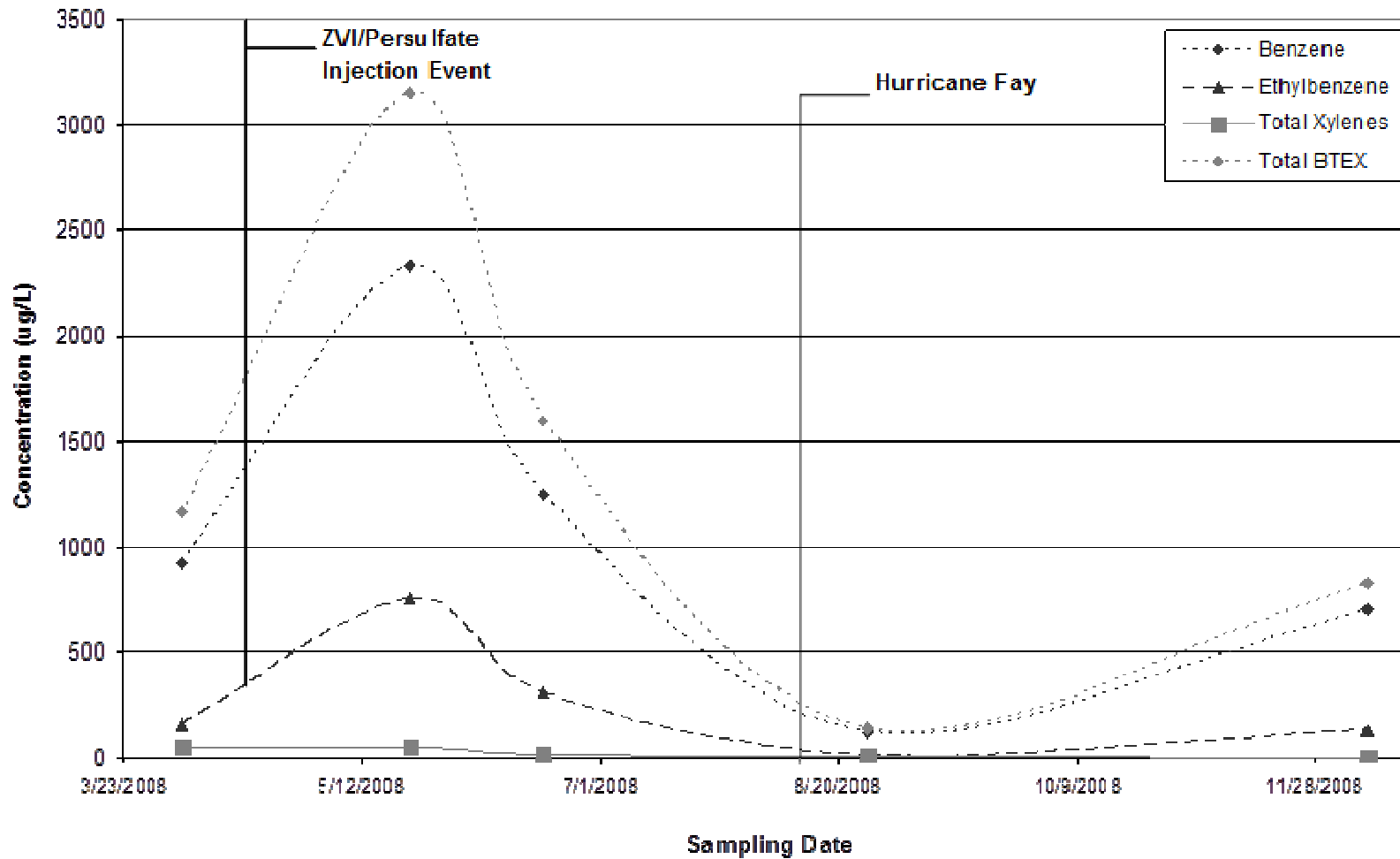


Case Study #1 – St. Augustine, Florida



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COC Concentrations (MW-1)

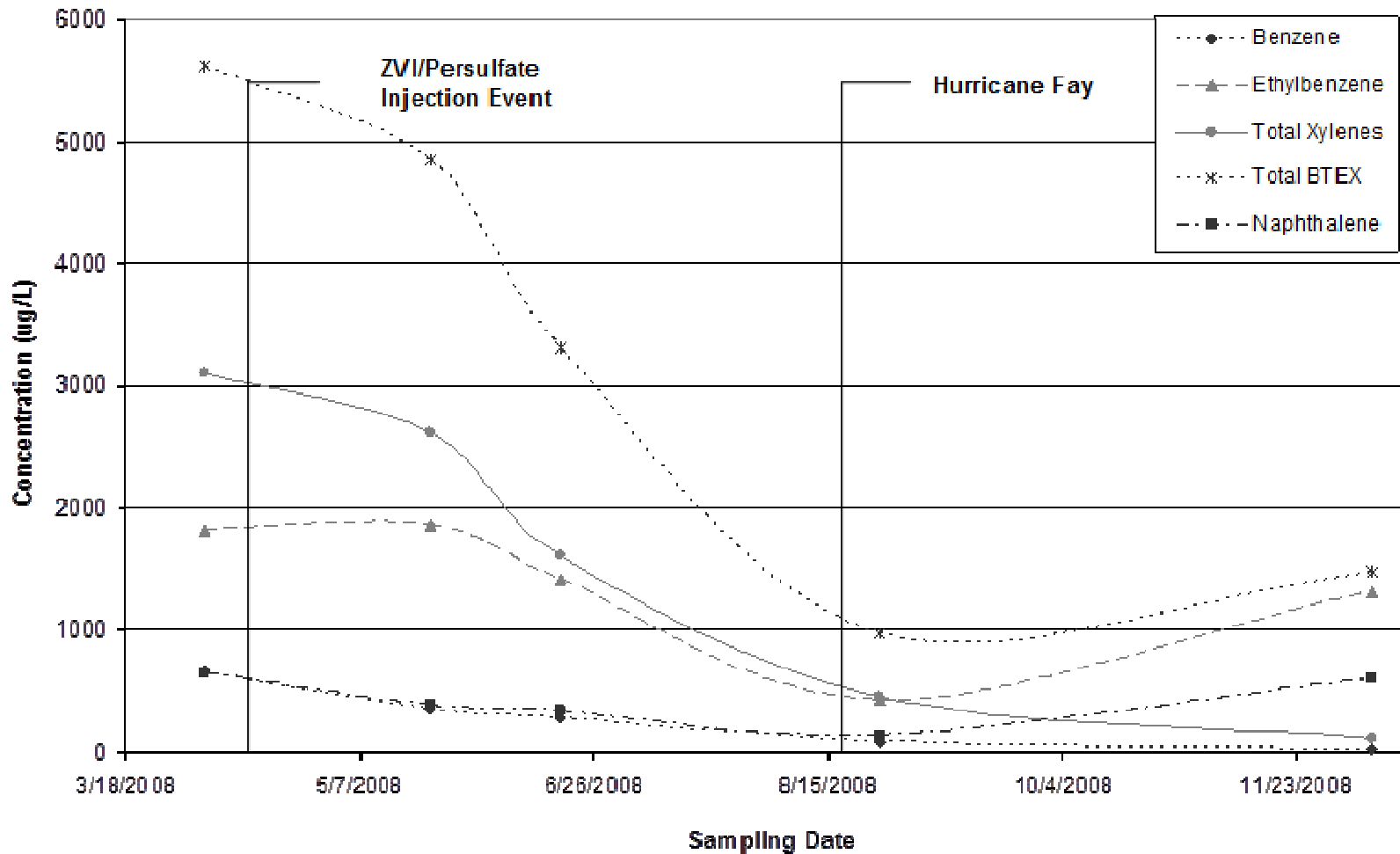


Case Study #1 – St. Augustine, Florida



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COC Concentrations (MW-2)

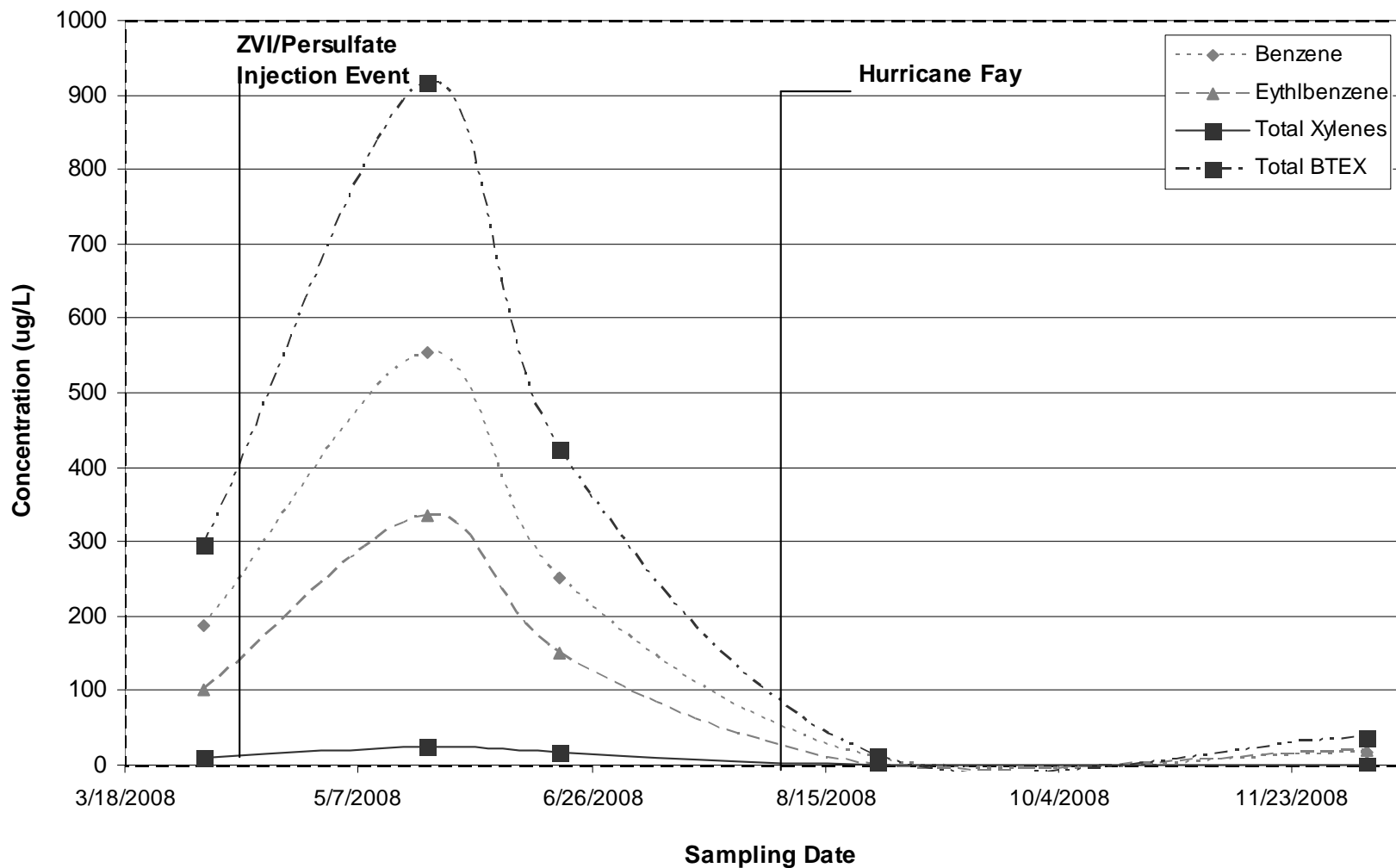


Case Study #1 – St. Augustine, Florida



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COC Concentrations (MW-3)

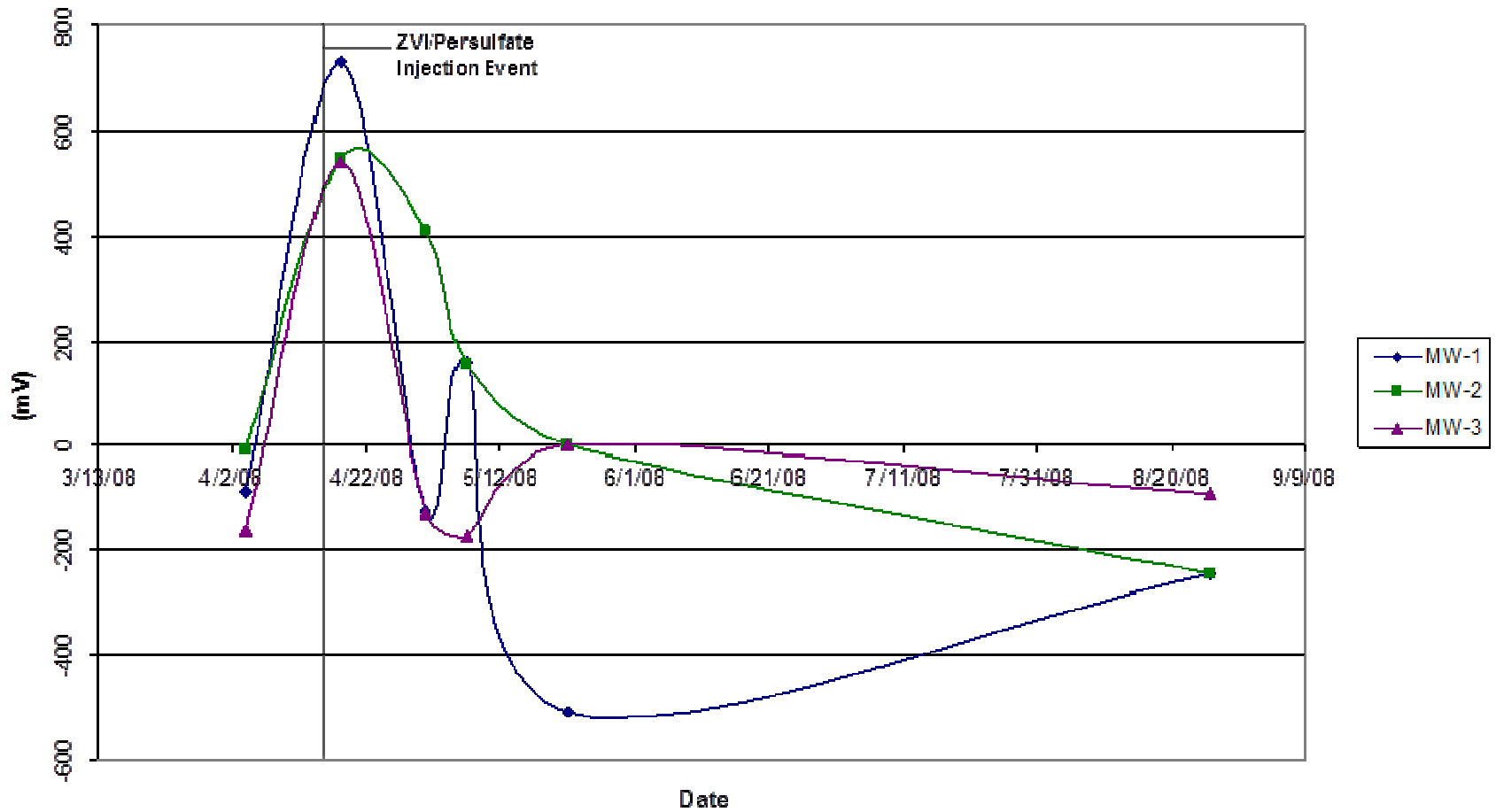


Case Study #1 – St. Augustine, Florida



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

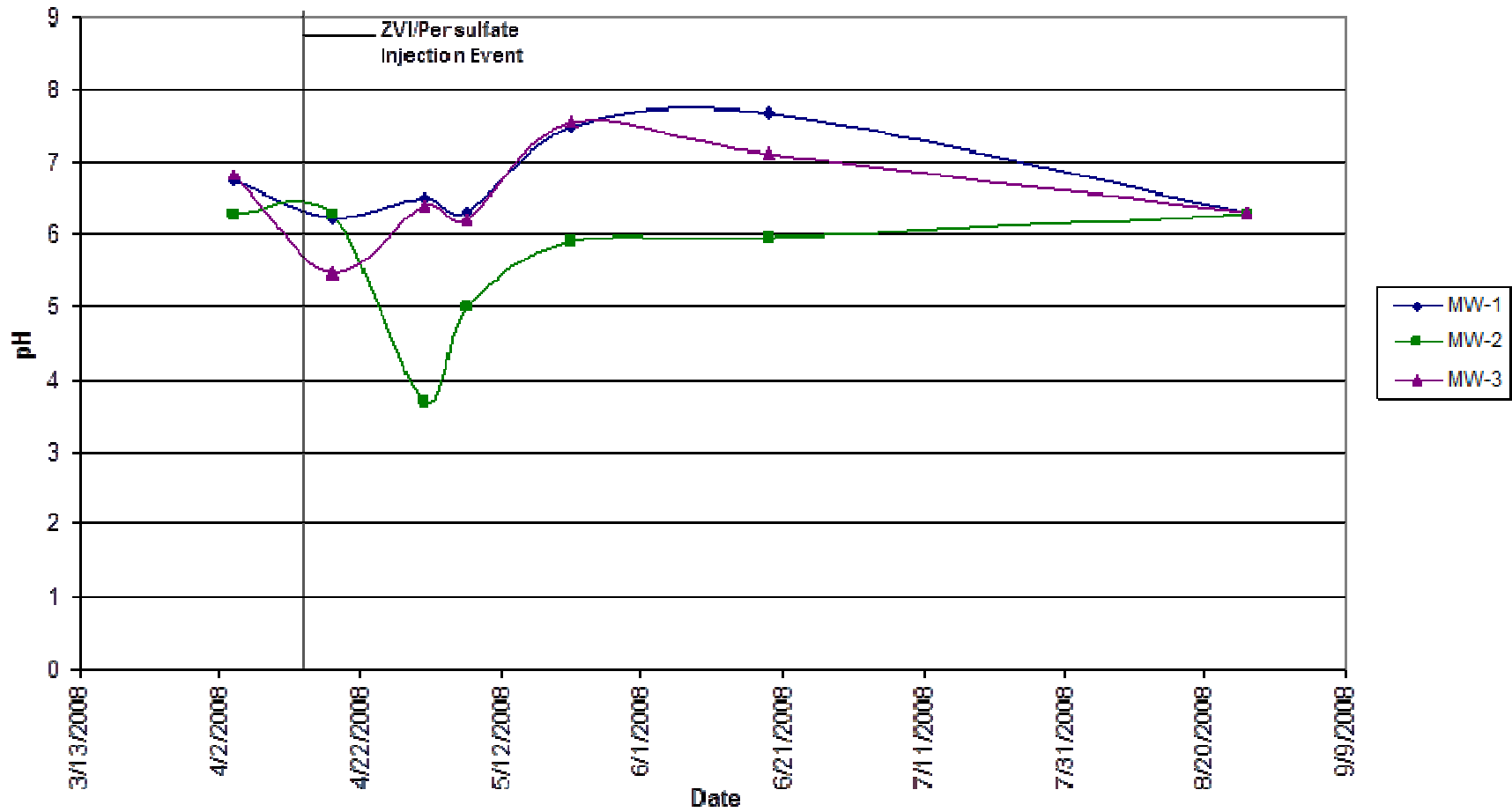


Case Study #1 – St. Augustine, Florida



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pH for Monitoring Wells 1,2, and 3



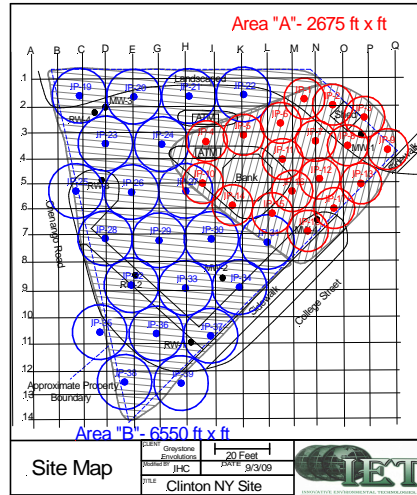
ABSTRACT: The use of in situ oxidation was applied at a site in Clinton, New York in order to reduce concentrations of volatile organic compounds (VOCs).

These compounds included BTEX and trimethylbenzene which were required to be measured below action levels, concentrations ranging from 1-10 ug/L. The oxidation technology implemented utilizes both abiotic and biotic processes that involve the use of free radical chemistry, oxidation chemistry and facultative biological oxidation. The combination of these processes extends oxidant and free radical residuals while enhancing the in-situ environment for biologically based attenuation of the constituents of interest (COI). The abiotic portion of the remedial program uses a unique blend of hydroxyl, peroxy and sulfate free radicals to oxidize the COI's. This process uses a combination of Fenton's and persulfate chemistry where zero valent iron acts as a catalyst for both reactions. The decomposition products of the oxidation process are then utilized in the subsurface to stimulate facultative biological attenuation of the targeted compounds.





October 27th, 28th and 29th, 2009



Time Zero Data

	MW-1	MW-2	MW-3	MW-4	RW-1	RW-2	RW-3
Benzene	1200	1400	31	4500	200	44	31
Ethylbenzene	920	59	2.1	1500	46	67	2.1
Toluene	110	25	1.8	520	8.6	1	1.8
Xylenes, Total	1100	1100	3.2	4100	540	83	3.2
Isopropyl Benzene	180	65	52	170	42	13	52
n-Propylbenzene	220	120	19	220	84	15	19
Naphthalene	230	19	8.7	460	2.4	4.4	8.7
p-Cymene	NS	NS	NS	NS	NS	NS	NS
1,2,4-Trimethylbenzene	1000	40	18	2300	250	53	18
1,3,5-Trimethylbenzene	18	ND	ND	120	ND	12	ND
n-Butylbenzene	ND	ND	ND	ND	6.6	0.69	ND
sec-Butylbenzene	42	19	7.6	52	5.8	1.9	7.6
tert-Butylbenzene	ND	ND	ND	ND	ND	ND	ND
MTBE	42	370	42	150	42	ND	42
Total VOCs	5020	2847	143.4	13942	1185.4	294.99	143.4

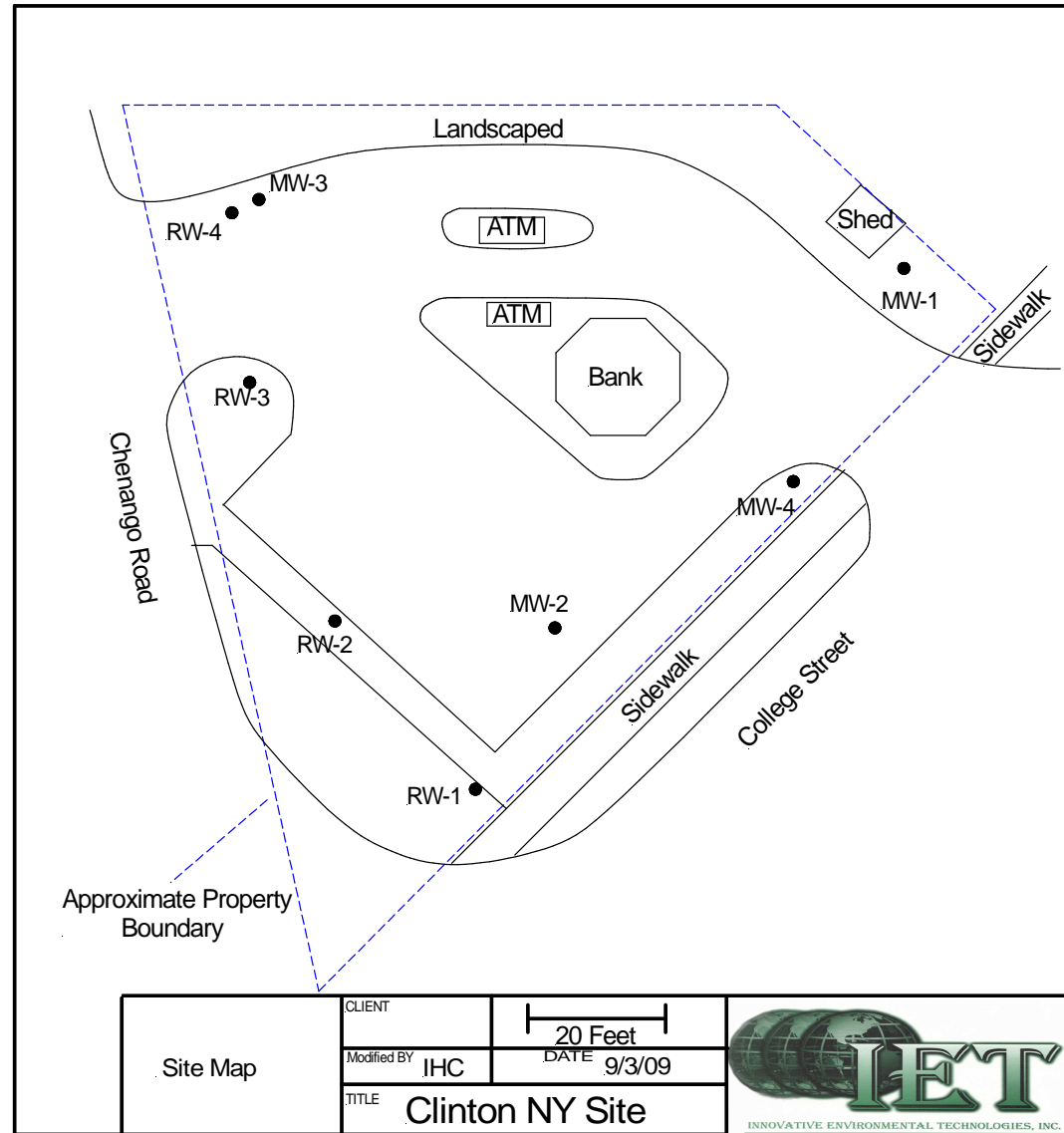
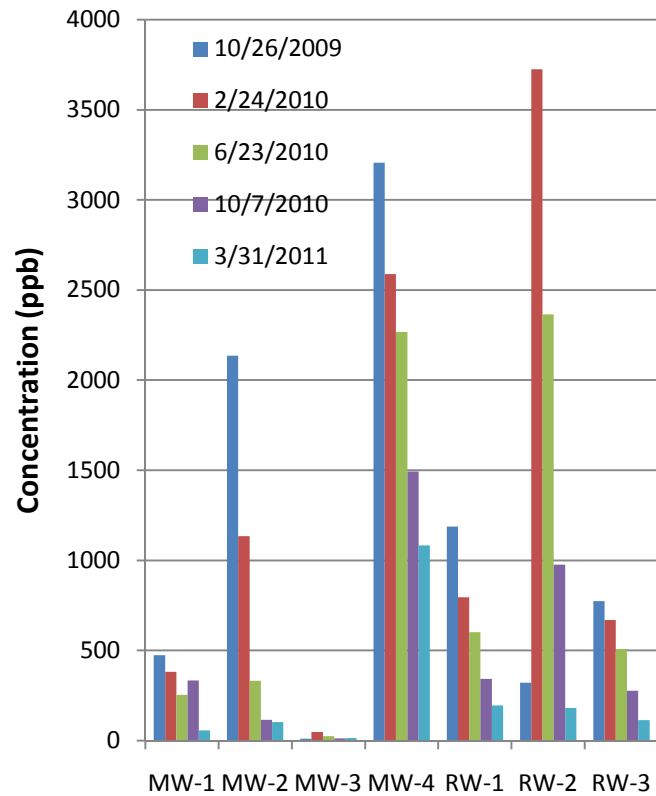


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Figure 5: Total STARS VOC Concentrations

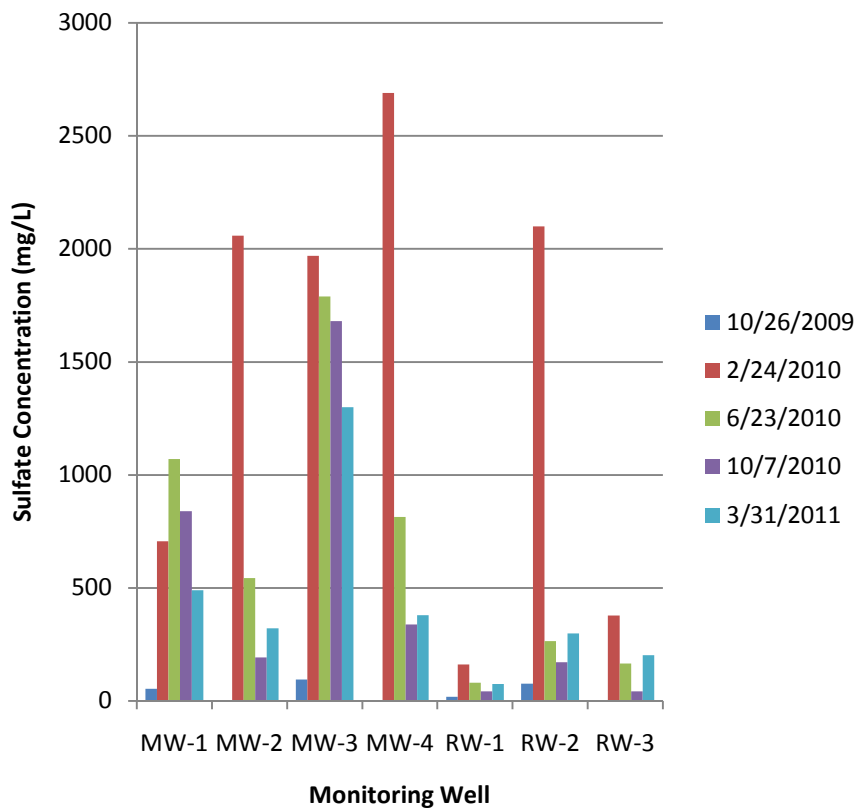




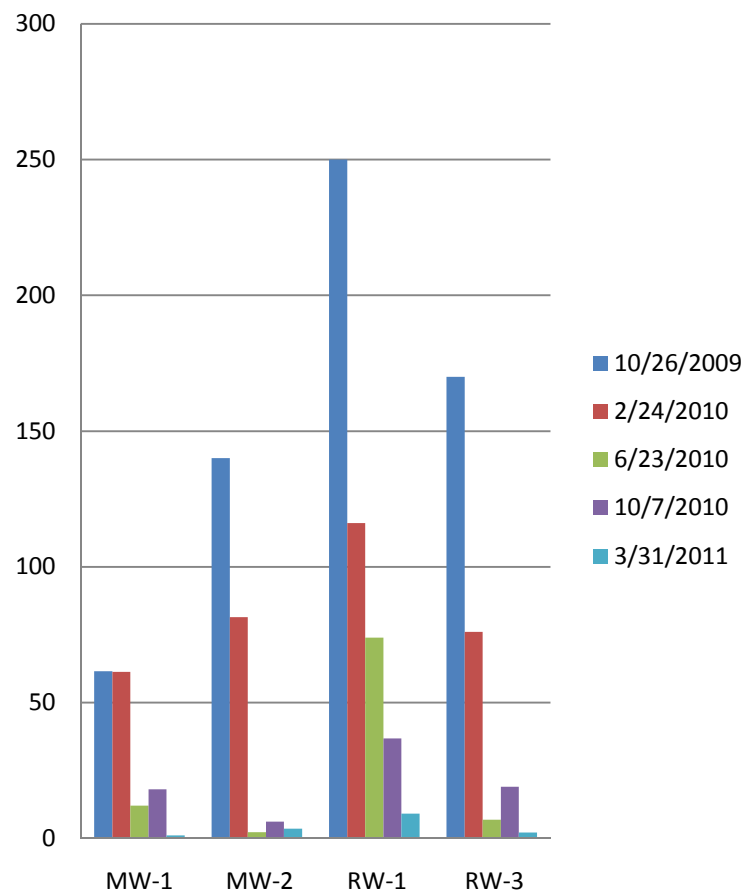
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Sulfate Concentrations in Groundwater



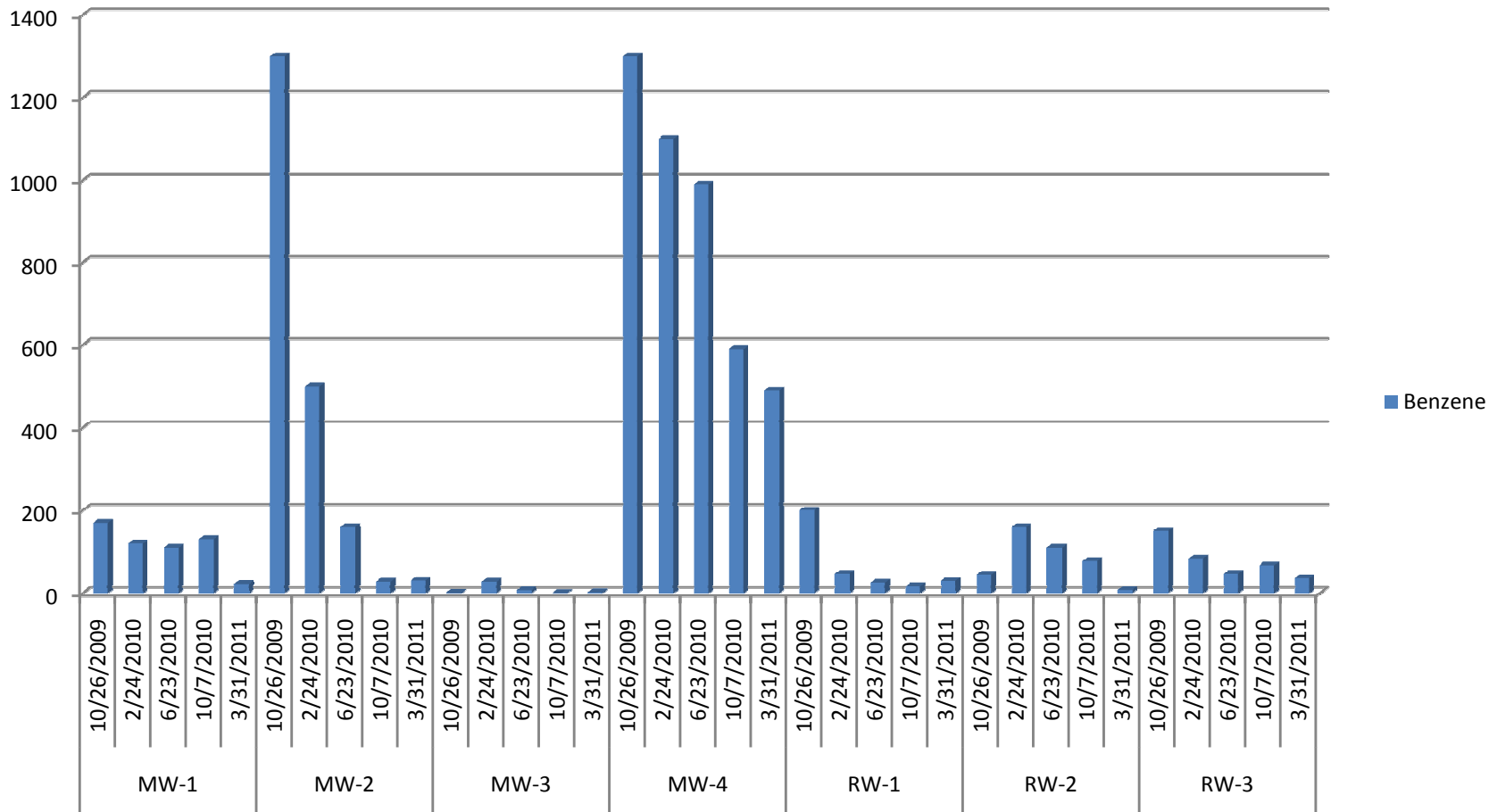
Total Trimethylbenzenes (ug/L)





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Benzene





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Injection Systems







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Questions

