Synergistic Treatment of BTEX Compounds Using Oxidation and Free Radical Chemistries

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ABSTRACT: In an unusual delivery process, prompted by the historical in-situ delivery via permanent points, the unconventional introduction of a remedial solution to the groundwater using numerous pits effectively overcame site specific obstacles. A two phase program effectively at the site in Saint Augustine, Florida, introduced the remedial chemicals sodium persulfate, hydrogen peroxide and zero-valent iron (ZVI) directly into the soil and groundwater using constructed reaction pits, in which the remedial materials were first loaded than dispersed through the effected soil interface by backfilling the pit with clean fill or screened soil. The first element of the degradation program produced hydroxyl and sulfate free radicals, the second utilized the decomposition products of the phase one reactions to effect facultative biological activity. A modified Fenton's chemistry and persulfate chemistry was integrated at the site, utilizing zero-valent iron as a catalyst for both reactions. The result of the remediation was an overall reduction in BTEX concentrations of over 70% in eight months.

INTRODUCTION: The former gasoline service station located in St. Augustine, Florida had two 3,000 gallon (5,610 L) underground storage tanks (UST) removed in July 1990 and a 6,000 gallon (11,220 L) UST removed in 2003. In 2002, during a Phase II ESA, it was determined that the presence of soil and groundwater impact by petroleum hydrocarbons as a part of a Phase II ESA. Oxygen Releasing Compound (ORC®) was applied to the bottom of the 2003 UST excavation. Levels of dissolved hydrocarbon in the groundwater were reduced but remained above the Natural Attenuation Default Concentrations (NADC) standard in the area of the UST.

Previous remedial actions included the injection of MicroblazeOut® into the surficial aquifer at the site. MicroblazeOut® was injected into thirty deep wells approximately 8 feet (2.4 m) below ground surface (bgs) and eighty-five shallow wells approximately 4.5 feet (1.4 m) bgs. MicroblazeOut® is a mixture of non-pathogenic bacteria, nutrients and surfactants that is used in the oxidation of hydrocarbons. In 2007, soil and groundwater samples were found to be above the Florida Department of Environmental Protection's (FDEP) cleanup target levels for petroleum products. In November 2007, all of the existing structures on-site were demolished and a new retail structure has since been built in the area of concern.

Hydrogeology. The surficial aquifer system is comprised of undifferentiated clastic material including sands, clayey sands, marine shell beds and permeable limestone. These deposits range in age from Upper Miocene to Recent. The thickness of these deposits varies across the County, and is estimated to be 90 feet (27.4 m) thick in Central

Saint John's County (the location of the project site). Groundwater within the surficial aquifer is under unconfined conditions. The lithology of the site consists of silty fine sands to coarse sands from land surface to a depth of 33 feet (10 m) with sandy clay lenses intermittently encountered at depths from 8 to 12 feet (2.4 m to 3.7 m). Groundwater occurs at depths ranging 3 to 5 feet (1-1.5 m) below ground surface, and groundwater flow at the site is north-northwest at a hydraulic gradient of approximately 0.01 ft/ft (3 mm/mm).

MATERIALS AND METHODS: The site in St. Augustine, Florida was treated using two oxidizing materials and a catalyst. The oxidants used were hydrogen peroxide and sodium persulfate and the catalyst was zero-valent iron powder (2-5 micron). The remedial materials were emplaced using two methods, an in-situ injection (United States Patent # 7,044,152) and creating reaction pits with a backhoe. The remedial materials were injected into the saturated zone on the site using a high-pressure injection process. Due to previous remedial activities at the site, one inch permanent wells were present on the site. These permanent injection points allowed for preferential pathways to form, causing surfacing of the remedial materials. Twenty-two reaction pits were excavated using a backhoe to ensure distribution of reagents in the subsurface. These reaction pits were approximately five feet wide and were twelve feet deep. The remedial materials were pumped into the pits which were than filled with clean fill or pre-screened excavated material after the material had been emplaced. The remedial materials were a 3.5 M suspension of zero-valent iron that was injected or pumped the subsurface, followed by a 0.25 M solution of sodium persulfate in a 15% by weight solution of hydrogen peroxide. The location of the remedial activities is shown below in Figure 1.

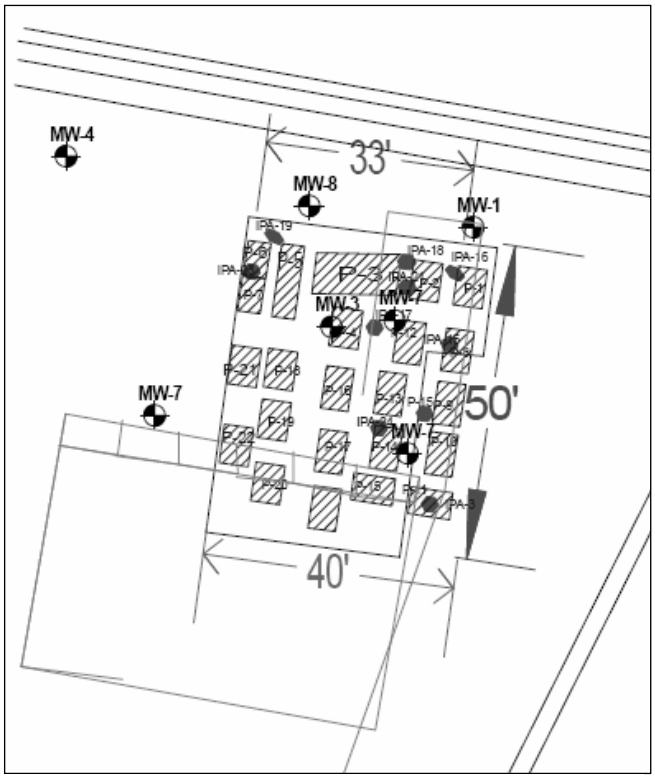

Figure 1: Map of Remedial Activities

The first phase, oxidation, oxidizes the majority of dissolved and sorbed targeted compounds. The second phase, biological attenuation, polishes and maintains the achieved treatment goals. The oxidation reactions utilize an activation process, which includes Fenton's Reagent (hydrogen peroxide and iron) and activated persulfate. The advantage of activated processes is the evolution of free radicals, which offer higher oxidation capabilities and a broader spectrum of applicable targeted compounds. The disadvantage of the evolution of free radicals is that the half-life for these species is relatively fast. The remedial approach taken at the site in Florida

utilizes free radical chemistry, oxidation chemistry and facultative biological activity in such a way as to extend the oxidant and free radical residuals while enhancing the in-situ environment such that it is suitable for biologically based attenuation. When these oxidants react with BTEX compounds, they form carbon dioxide and water as the final end products. The reactions that occur in the chemical oxidation are:

$$H_2O_2 + Fe^0 \rightarrow Fe^{+3} + OH^- + OH^{\cdot} \quad (1)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ HO_2^{\cdot} \quad (2)$$

$$S_2O_8^- + Fe^0 \rightarrow Fe^{+3} + SO^{4-} + SO_4^{-2\cdot} \quad (3)$$

Direct oxidation of NaS_2O_8 and H_2O_2

The biological processes of the remediation of BTEX compounds occur after the dissolved oxygen has been depleted in the treatment area and the subsurface becomes reductive, i.e. anaerobic. The two by-products of the oxidation reactions, sulfate and ferric iron, may be used as electron acceptors for anaerobic biodegradation. The use of sulfate as an electron acceptor is termed sulfanogenesis and results in the production of sulfide. Sulfate can play an important role in bioremediation of petroleum products, acting as an electron acceptor in co-metabolic processes as well. An example of benzene mineralization under sulfate reduction is as follows:

$$C_6H_6 + 3.754\ SO_4^{2-} + 3\ H_2O \rightarrow 2.25\ H^+ + 6HCO^{3-} + 3.75HS^- \quad (4)$$

Ferric iron is also used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons in conjunction with sulfate, or after sulfate concentrations have been depleted. During this process, ferric iron is reduced to ferrous iron, which is soluble in water. Ferrous iron may then be used as an indicator of anaerobic activity.

RESULTS AND DISCUSSION: Eight months after the treatment, BTEX concentrations decreased over 70% in source area monitoring wells (MW-1, MW-2, and MW-3) affected by the remedial activities. An initial rebound in BTEX concentration was observed in monitoring wells MW-1 and MW-3 due to the desorbtion of BTEX compounds from soil during oxidation. A significant decrease in BTEX concentrations was evident after the initial rebound, partially due to the landfall of Hurricane Fay. Due to the large amount of rainfall (approximately 10 in) that occurred in the area, BTEX concentrations may have been diluted in source area monitoring wells.

The effect of the remedial event is seen in Figures 2, 3, and 4 of BTEX compounds from the monitoring wells in and around the source area.

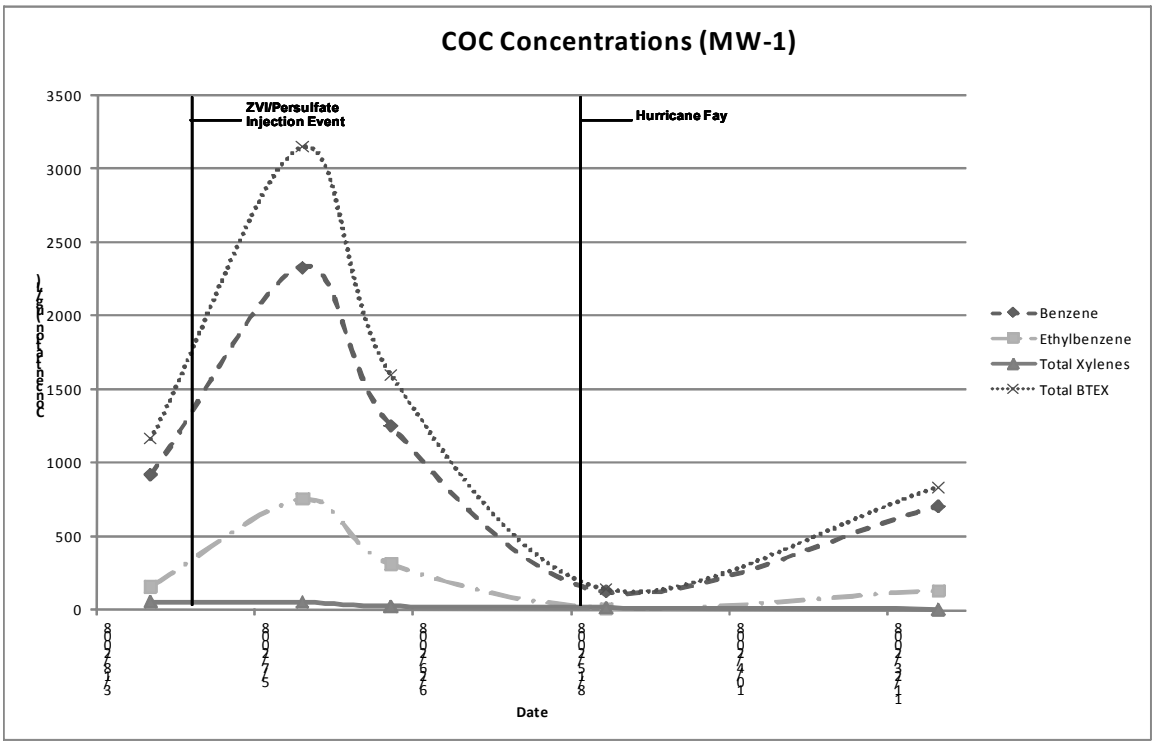

Figure 2: MW-1 BTEX Concentrations

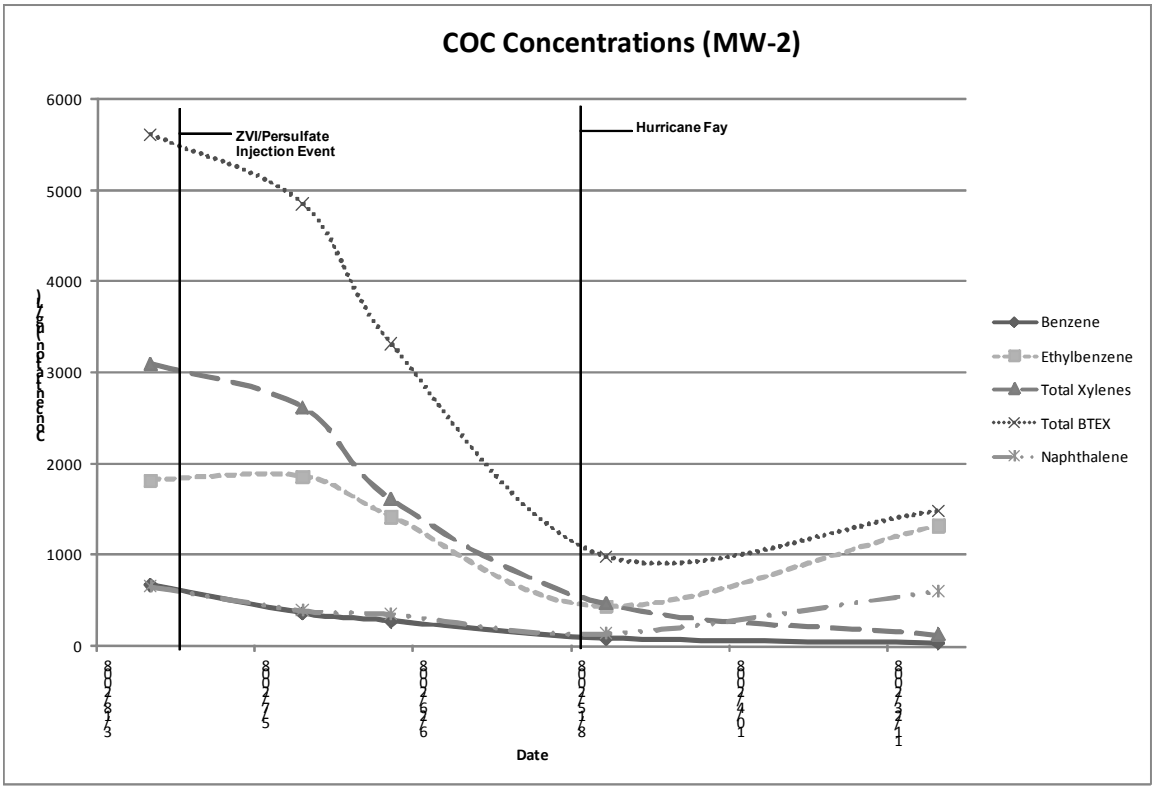

FIGURE 3: MW-2 BTEX Concentrations

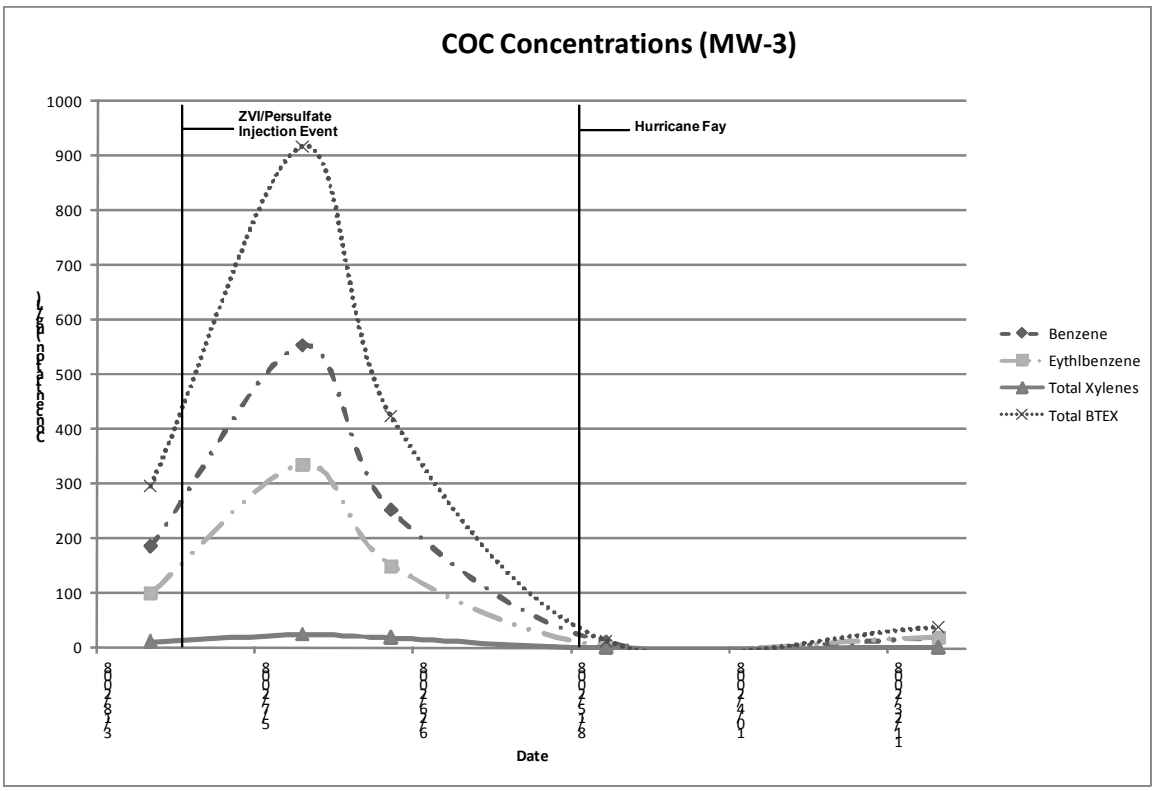

FIGURE 4: MW-3 BTEX Concentrations

The redox potential measured in source area monitoring wells shows that the areas impacted by the remedial event remained under reducing conditions after the initial oxidation (Table 1). The measured redox potentials indicate that the site was very oxidative directly following the oxidation event and remained oxidative for between 2 and 4 weeks. Groundwater at the site then reverted to the reductive condition present at the site before oxidation. Anaerobic biological activity then progressed with the microbes utilizing the ferrous iron and sulfate present after the chemical oxidation.

Table 1: Redox Potentials for Source Area Wells

	ORP (mV)						
Well Number	**4/4/2008**	**4/8/2008**	**5/1/2008**	**5/7/2008**	**5/22/2008**	**8/26/2008**	**12/9/2008**
MW-1	-88	733	-124	158	-510	-246	-260
MW-2	-10	545	409	156	-395	-247	-153
MW-3	-162	540	-128	-173	-96	-92	-187

Comparison of BTEX concentrations detected in MW-1 shows a 74% reduction in total BTEX compound concentrations has occurred since the initial rebound in May 2008. The highest BTEX concentrations (5,612 ug/l) detected at the site prior to injection of oxidants occurred at MW-2, which experienced the largest decrease in BTEX concentrations since the baseline sampling event in April 2008. BTEX concentrations detected at MW-2 decreased by 74 percent during the post-injection monitoring period. BTEX concentrations measured at MW-3 showed the largest percentage reduction (96%) since the initial increase observed in May 2008. MW-3 has also not seen the same

increase in BTEX concentrations during the December 2008 sampling event as the other source area monitoring wells in the remediation area.

CONCLUSIONS: The site in St. Augustine, Florida has seen dramatic reductions in the concentrations of BTEX due to both the chemical oxidation and anaerobic degradation of the contaminants of concern. The redox potential at the site has gone from reducing conditions prior to the remedial events to extremely oxidative after injection of chemical reagents. Approximately one month after introduction of the reagents into the subsurface, the groundwater chemistry reverted back to a reducing environment, allow for the anaerobic degradation of BTEX compounds through the utilization of residual chemical byproducts remaining in the subsurface at the St. Augustine, Florida site. The reductions observed at the site indicate that oxidation processes can be combined with biological processes to significantly reduce BTEX concentrations in source areas impacted by gasoline releases.