

Implementation and Evaluation of an Innovative Treatment of Xylenes and Naphthalene Using Oxidation and Biological Mechanisms

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ABSTRACT: Subsequent to initial source area excavation and backfill, residual xylenes and naphthalene were treated via a biotic and abiotic approach. The remedial technology utilized free radical chemistry, oxidation chemistry and facultative biological oxidation. These processes extended the oxidant and free radical residuals while enhancing the in-situ environment for biologically based attenuation. The three remedial approaches were combined to achieve synergistic chemical and biological removal of dissolved and sorbed compounds at the site. The chemical oxidation process causes a large and fairly complete removal of targeted compounds, while biological processes refine the site and allow for the further reduction of concentrations of targeted compounds. The remedial program resulting from the data collected incorporated hydroxyl and sulfate radicals and a zero valent iron catalyst to remediate the site. Ferric iron and sulfate species were relied on to promote facultative anaerobic mineralization of the residual targeted compounds. A second oxidation event followed the primary event in which only the oxidants were applied allowing for a conversion of the ferrous species back to ferric iron while achieving additional oxidation of entrained xylenes and naphthalene. Through this combination of remedial techniques, compounds of interest in the source area have decreased by as much as 98%.

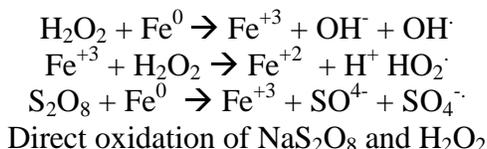
INTRODUCTION: A site in northern New Jersey was contaminated with petroleum based distillates. Bedrock was identified as being between 18-26 feet (5.5-8 m) below ground surface (bgs) throughout the site and sandy soils were predominant. The residual area contaminated was found to be approximately 1-2 (0.3-0.6 m) feet above the bedrock. A biologically based remedial program was designed to target the soils and groundwater impacted by petroleum hydrocarbons.

In December of 2006, the initial injections of oxygen release compound (ORC) and calcium oxide were introduced using thirty-nine injection points, followed by the injection of liquid petroleum degrader (LPD) and a bio-slurry using direct push technology via sixty-nine injection points. In August 2007 and February 2008, two oxidation events were implemented to address the remaining petroleum compounds in the soil and groundwater.

Two 3,150 ft² (960 m) areas, MW-21S and MW-6S, were delineated and treated based on the chemical demand and the longevity of the oxidant. Xylene and Naphthalene were identified as being the compounds of concern (COC) with concentrations in groundwater higher than the NJ Ground Water Quality Standard of 300 µg/L and 1,000 µg/L, respectively. The in-situ remediation program was designed to utilize both facultative biological processes and advanced oxidation technologies including a mix of

hydroxyl, peroxy and sulfate free radicals allowing for Fenton reactions and long term oxidation. A direct push injection technique was used to introduce the remedial materials to the targeted soil horizon. A combination of Fenton's and Persulfate Chemistry where Zero Valent Iron (ZVI) acts as a catalyst for both reactions was implemented within these areas.

The remediation technology chosen for the site in northern New Jersey was an advanced, activated oxidation process. 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 disadvantages of activation processes and the evolution of free radicals typically focus on the limited half-lives of these species. The remedial approach taken at the northern New Jersey site utilizes free radical chemistry, oxidation chemistry, and facultative biological oxidation 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. The oxidation reactions that occurred at the site are:



The biologically based attenuation occurs due to the reaction products formed from the oxidation of the zero valent iron and the sodium persulfate. After dissolved oxygen has been depleted in the treatment area, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulfanogenesis and results in the production of sulfide. Sulfate concentrations may be used as an indicator of anaerobic degradation of fuel compounds. Stoichiometrically, each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX. 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:



Ferric iron is also used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons either after sulfate has been depleted from the groundwater or occasionally in conjuncture with sulfanogenesis. 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. Stoichiometrically, the degradation of 1 mg/L of BTEX results in the production of approximately 21.8 mg/L of ferrous iron.

MATERIALS AND METHODS: IET applied three remedial materials to the subsurface via a patented injection process and apparatus (United States Patent # 7,044,152) such that the activation processes occur in a controlled manner in-situ. In a unique application of zero-valent iron metal (BASF, 2-4 microns in size), IET activated both the persulfate and the peroxide species in-situ, effecting the oxidation and biological remedial processes in a single injection process. 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.

Two injection events were implemented to address source area concentrations, as well as those down-gradient of the source area soils and groundwater. During the injections 1,100 lbs (500 kg) of ZVI was used as well as 6,700 lbs (3,045.5 kg) of sodium persulfate and 550 gallons (1,028.5 L) of 35% H₂O₂ was distributed throughout the seventeen injection points.

These injections were completed using direct push technology which uses high pressure air injections, approximately 175 psi (12,303 g/cm²) in order to open voids in the soil interface capable of transporting the remedial materials to be injected. The slurry injections were then performed via perforated rods with 18-24in. (0.45-0.61 m) injection zones and backflow protection. The rods were employed by the use of a skid loader equipped with AMS 9600 probe. A second oxidation event took place in February 2008 to further treat areas identified by the MIP investigations. Seventeen injections centered around the area of MW-6S were conducted. The areas treated at the manufacturing facility are shown below in Figure 1.

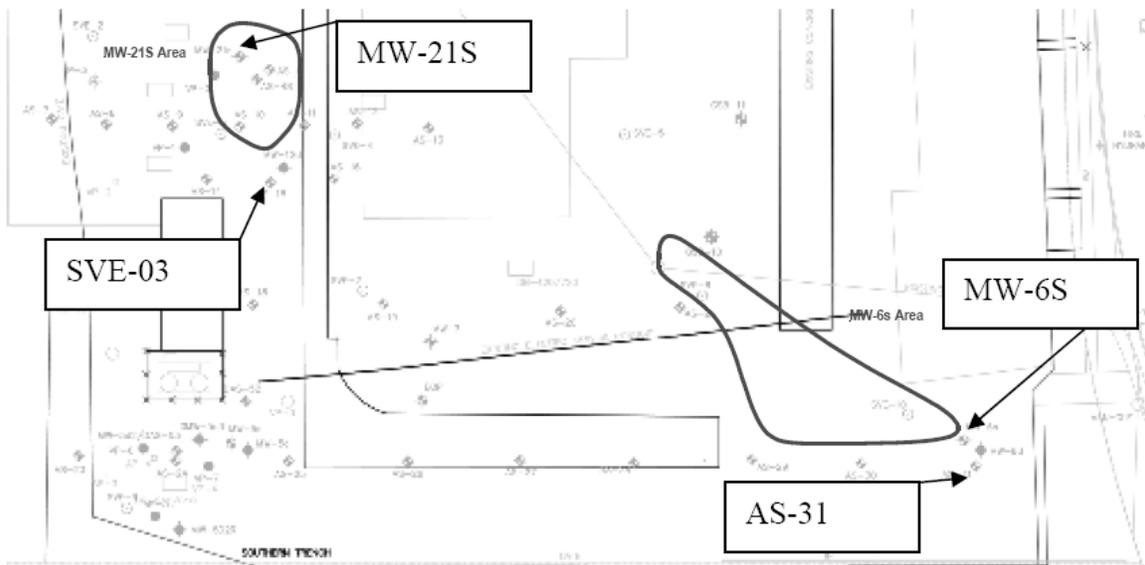


FIGURE 1: Map of the Remediation

RESULTS AND DISCUSSION: The two targeted areas are represented in the map located in Figure 1 above. Each area has two sampling points, one centrally targeted and a second down gradient of the injection area. The primary sample point for the 21-S area is MW-21S with the down gradient sample location being SVE-03; the primary sample location for the 6S area is MW-6S with the down gradient sample location being AS-31.

MW-21S. MW-21S is located in the treatment area for both oxidation events. The area around MW-21S is the source area of the contamination, with the contaminants of concern being primarily the isomers of Xylene. The first sets of injections were focused around MW-21S. Table 1 shows the concentrations of the contaminants of concern before the injections and after the August 2007 and February 2008 oxidation events. There was an initial rebound in COC concentrations two months following the first

injection event, with concentrations reaching upwards of 7.5 mg/L meta- and para-Xylene. These concentrations were further reduced after the February 2008 oxidation event again rebounding two months after the oxidation to 0.4 mg/L. The concentrations at the site as of January 2009 have reached all time lows with ortho-Xylene concentrations below laboratory detection limits and meta- and para-Xylene concentrations at 0.085 mg/L. Naphthalene and Ethylbenzene concentrations have also decreased significantly since the baseline sampling events in July 2007. The xylene trends are seen in Figure 2.

TABLE 1: COC Concentrations for MW-21-S

Parameter	7/26/2007	9/26/2007	10/24/2007	1/14/2008	3/12/2008	4/14/2008	7/15/2008	10/16/2008	1/20/2009
Ethyl Benzene (ug/l)	650	320	1,000	140	0.6	120	420	480	170
m+p Xylene (ug/l)	6,600	2,900	7,500	530	<10	400	850	110	85
o-Xylene (ug/l)	3,100	1,800	2,100	40	<5	50	47	<25	<25
Napthalene (ug/l)	120	120	170	73	9.3	24	96	140	64

MW-21S: Xylenes

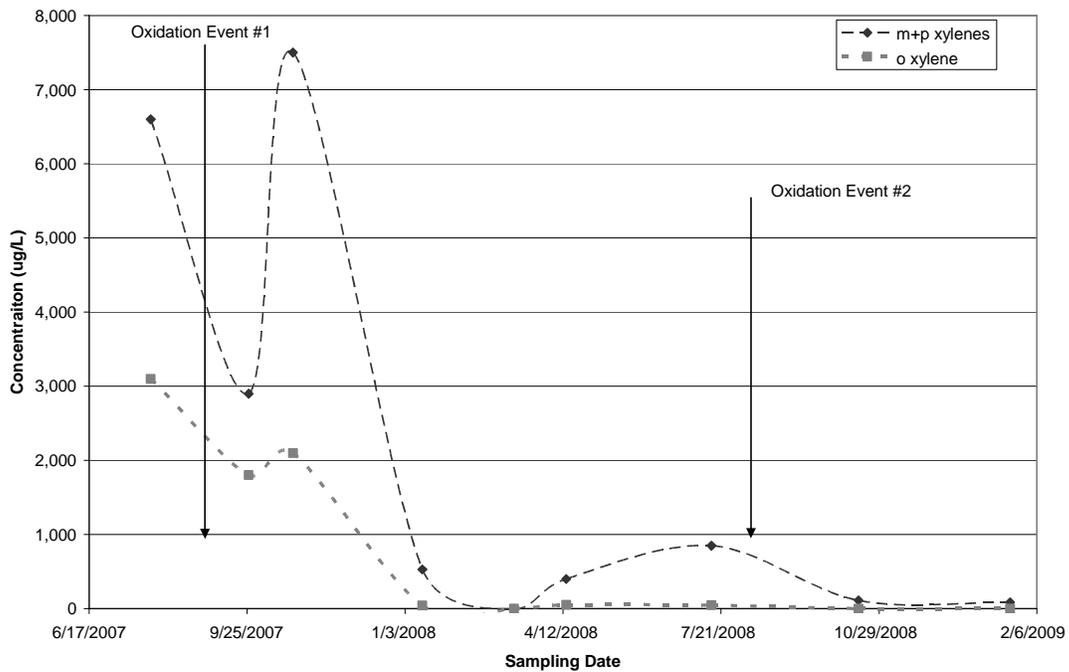


FIGURE 2: MW-21S Xylene Isomer Concentrations

SVE-03. SVE-03 is located in immediately down-gradient of the treatment area for both oxidation events. The area up-gradient of SVE-03 is the source area of the contamination, with the contaminants of concern being primarily the isomers of Xylene. Table 2 shows the concentrations of the contaminants of concern before the injections and after the August 2007 and February 2008 oxidation events. There was an initial rebound in COC concentrations two months following the first injection event like MW-21S. The increase in concentrations is due to releasing sorbed mass present on the soil, as well as from the displacement and release of contaminations up-gradient of SVE-03. These concentrations were reduced shortly after as noted in the January 2008 data. The concentrations of all of the contaminants of concern are still elevated from the increase noted in October 2008 and have since decreased appreciably. The data suggests that the

oxidation events successfully mitigated the contamination in the source area, MW-21S, as well the down-gradient well, SVE-03.

TABLE 2: COC Concentrations for SVE-03

Parameter	7/26/2007	9/26/2007	10/24/2007	1/14/2008	3/12/2008	4/14/2008	7/15/2008	10/16/2008	1/20/2009
Ethyl Benzene (ug/l)	3.7	13	290	140	0.7	1.3	53	190	110
m+p Xylene (ug/l)	32	24	3,000	660	3.4	5.2	180	1,300	560
o-Xylene (ug/l)	13	47	1,700	340	1.8	3.5	52	300	84
Napthalene (ug/l)	36	1.2	120	6.8	0.2	4.2	1.4	19	4.1

MW-6S. MW-6S is located in the treatment area surrounding a secondary source area. The source area in the area of MW-6S has a different ratio of Xylene isomers and Naphthalene than the source area located at MW-21S. The contaminant of concern in the area of MW-6S is primarily Naphthalene, with lower concentrations of Xylenes and Ethylbenzene. Table 3 shows the concentrations of the contaminants of concern before the injections and after the August 2007 and February 2008 oxidation events.

TABLE 3: COC Concentrations for MW-6S

Parameter	7/26/2007	9/26/2007	10/24/2007	1/14/2008	3/12/2008	4/14/2008	7/16/2008	10/17/2008	1/20/2009
Ethyl Benzene (ug/l)	98	160	100	73	34	47	88	85	86
m+p Xylene (ug/l)	410	680	430	360	150	170	230	200	290
o-Xylene (ug/l)	52	69	36	36	16	13	20	<250	23
Napthalene (ug/l)	1500	1500	1800	1300	520	470	720	680	640

Based on the post injection sampling results from the August 2007 oxidation event, it was estimated that the initial injections at MW-21s were successful. The results for MW-6S, however, were not within an acceptable range. A Membrane Interface Probe (MIP) investigation was implemented in both areas to better delineate the horizontal and vertical extent of COCs. These results were used to target supplemental injections locations and depths. Golder Associates contracted S2C2, of Raritan NJ, to provide direct push sampling using a membrane interface probe (MIP) to provide continuous stratigraphic and semi-quantitative concentrations of volatile organic compounds. A MIP investigation was completed in February 2008 to delineate the COCs in the MW-21s and MW-6s areas in order to develop the supplemental injection plan which occurred during the February 2008 oxidation event.

There did not appear to be a rebound in COC concentrations in MW-6S, as was seen in MW-21S. The concentrations at the site as of January 2009 have experienced a 57% reduction in Naphthalene, a 55% reduction in ortho-Xylene, a 29% reduction in meta- and para-Xylenes, and a 9% reduction in Ethylbenzene. The Naphthalene trends are seen in Figure 3.

MW-6S: Naphthalene

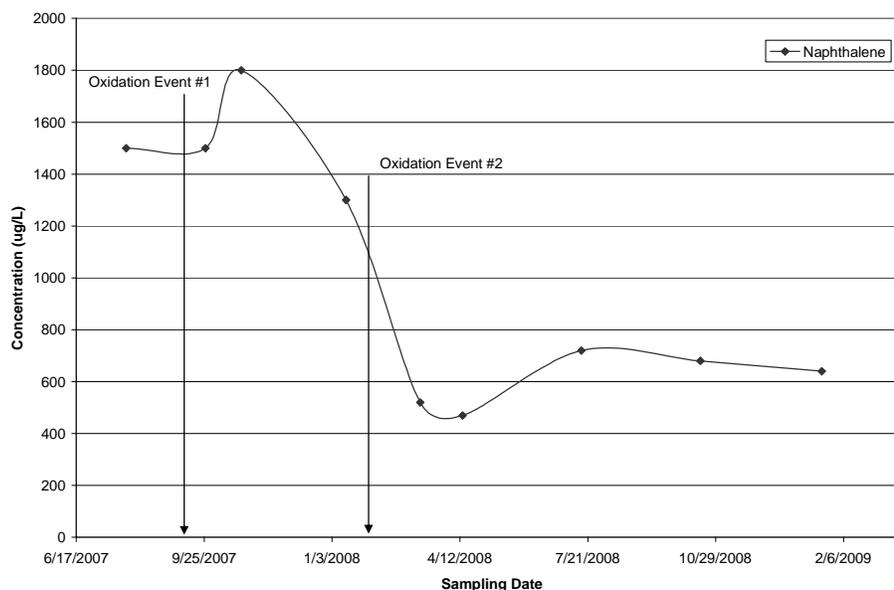


FIGURE 3: MW-6S Naphthalene Concentrations

AS-31. AS-31 is located in immediately down-gradient of the MW-6S treatment area. The contaminant of concern for AS-31 is Naphthalene. Table 4 shows the concentrations of the contaminants of concern before the injections and after the August 2007 and February 2008 oxidation events. There was no rebound in COC concentrations following the first injection event; however, a rebound was seen after the February 2008 oxidation event. The increase in the Naphthalene concentration is due to proximity of the injections to AS-31 which caused the release of sorbed mass present on the soil, as well as an increase in concentration due to the displacement of groundwater around MW-6S. These concentrations were reduced shortly after as noted in the October 2008 and January 2009 data. The data suggests that the oxidation events successfully mitigated the contamination in the down-gradient well, AS-31.

TABLE 4: COC Concentrations for AS-31

Parameter	7/26/2007	9/26/2007	10/24/2007	1/14/2008	3/12/2008	4/14/2008	7/16/2008	10/17/2008	1/20/2009
Ethyl Benzene (ug/l)	52	27	38	58	46	50	45	43	37
m+p Xylene (ug/l)	ND	4.5	4.9	0.6	200	130	47	<50	20
o-Xylene (ug/l)	2.9	3.6	1.2	0.4	17	16	2.5	<25	10
Napthalene (ug/l)	180	93	74	9.6	320	320	190	18	16

Iron Conversion. The use of a zero valent iron surface was critical in the activation process of the persulfate. The use of the hydrogen peroxide during each of the two oxidation events provided ferric species both at the surface of the particles and within the bulk groundwater. However, unlike traditional iron activation mechanisms, the use of the zero valent iron particle allowed for the reuse of the iron without additional iron introduction during the February 2008 oxidation event. The value of the zero valent iron as an activator cannot be over emphasized both because of its ability to be recycled

between the ferrous and ferric species via the oxidants but also because of its value as a ferric source. The short comings of alternative activation processes and their inability to facilitate sustained facultative conversions is a consequence of the residual sulfate produced by the persulfate oxidation process. As a site returns to reducing conditions, the use of sulfate as a terminal electron acceptor most often results in sulfites and sulfides, the latter proving toxic to many facultative process. This conversion results in an unsustainable biological attenuation. The recycling of the iron particle through multiple oxidation events provides continued ferric species which serve as a terminal electron acceptor in the attenuation phases after the environment returns to reducing conditions.

The resulting ferrous species further provides for a mechanism for sustained, biological mediated sulfate reduction by-way of sulfide precipitation as ferrous sulfide. Ferrous sulfide is insoluble in water and is an effective mechanism for the remove of the evolved toxic sulfides. Figure 4 illustrates the ferric-ferrous conversions across the two oxidation events at the four monitoring points. These conversions are most pronounced at the MW-6S and AS-31 area, where surface water infiltration is less pronounced. The former excavation immediately up gradient of 21S and SVE-03 prevents the return to reducing conditions and maintains elevated dissolved oxygen levels. In contrast there is no influence of surface infiltration in the 6s and AS-31 area.

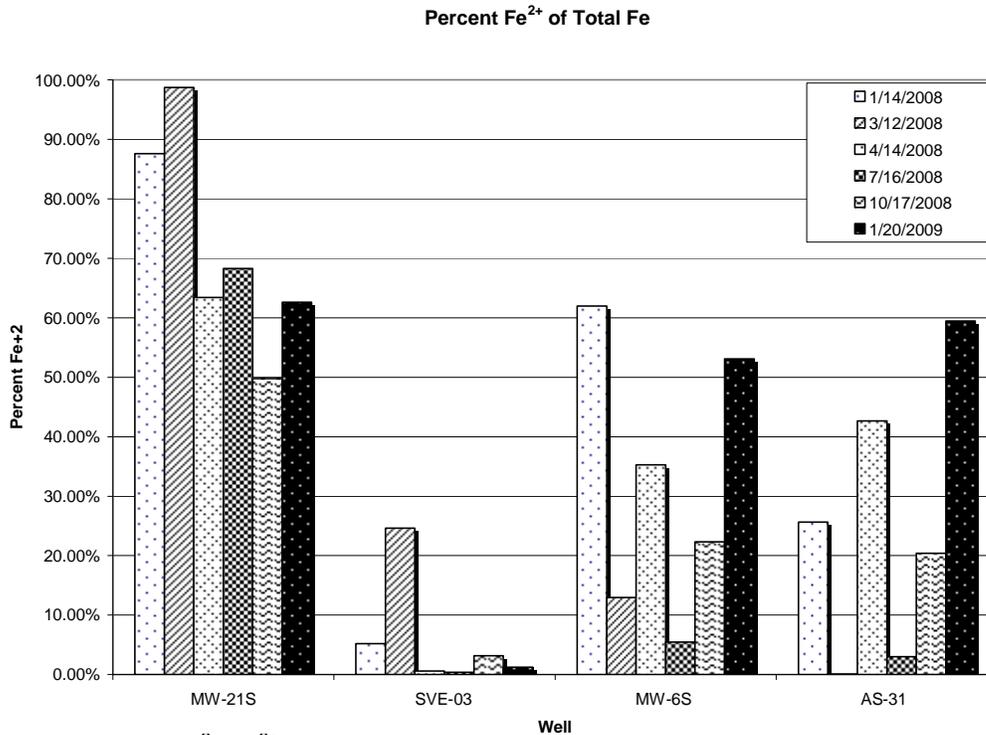


FIGURE 4: Fe²⁺/Fe³⁺ Conversion Ratio as a Consequence of Oxidation Event and Biological Conversion

The efficacy of the sulfide precipitation mechanism is substantiated by the maintained sulfide concentrations of less than 2 ppm across the site. These levels of sulfides have been maintained in environments undergoing sulfate and iron reduction where sulfate concentrations exceed 500 ppm.

CONCLUSIONS: The two oxidation events at the site in northern New Jersey were successful in the reduction of COC concentrations in both source areas and down-gradient of the remediation. Xylene isomer concentrations were reduced by greater than 98% in the source area well MW-21S. These removal rates have been in the presence of up gradient sources, have occurred biotically and abiotically with sustained biologically mediated mineralization nearly one year after the last oxidation event.