

Innovative Treatment of BTEX and Trimethylbenzene using Zero Valent Iron Catalyzed Hydroxyl & Sulfate Free Radical In-Situ Chemical Oxidation

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ABSTRACT: In situ chemical oxidation via zero valent iron activated sodium persulfate and hydrogen peroxide was used at a former gas station located in Clinton, NY in order to reduce the concentration of volatile organic compounds (VOCs) such as BTEX and trimethylbenzene in soil and groundwater. The implementation of the oxidation technology presents the advantage of utilizing both the biotic and abiotic processes that include the use of free radical chemistry, oxidation chemistry and facultative biological oxidation. The potential 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.

The remedial design was implemented by Innovative Environmental Technologies, Inc. on October 28th and 29th, 2009. The concentrations of VOCs across the site showed a significant decrease, with total VOC concentrations decreasing by 78.5% across the site, 17 months after the baseline sampling event, successfully receiving site closure. Compounds that are more readily biodegraded, such as xylene, readily disappeared and compounds that are more recalcitrant, such as benzene, were degraded at high rates and eventually disappeared. Trimethylbenzene compounds were targeted in the remedial design and were successfully reduced to standard within 12 months of the remedial event.

INTRODUCTION

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are widely distributed contaminants in soil, groundwater, and sediments due to their relatively high aqueous solubility. The United States Environmental Protection Agency (U.S. EPA) estimates that 35% of the gasoline and diesel fuel underground storage tanks (USTs) located in the U.S. are leaking and approximately 40% of these leaking USTs have most likely resulted in soil and groundwater BTEX contamination. BTEX are volatile and water-soluble constituents that comprise 50% of the water-soluble fraction of gasoline. The presence of BTEX in groundwater can create a hazard to public health and the environment.

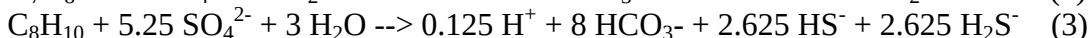
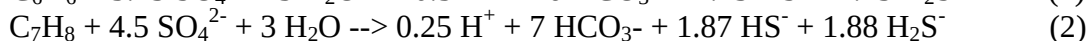
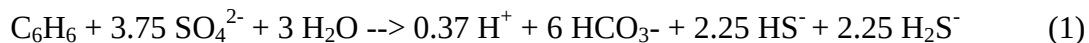
BTEX are readily degradable in aerobic surface water and soil systems; however, in the subsurface environment, contamination by organic compounds often results in the complete consumption of available oxygen by indigenous microorganisms and the development of anaerobic conditions. In the absence of oxygen, degradation of BTEX can take place only with the use of alternative electron acceptors, such as nitrate, sulfate, or ferric iron, or fermentatively in combination with methanogenesis.

In Situ Chemical Oxidation (ISCO) remedial process utilizes the injection of an oxidizing agent, such as hydrogen peroxide (H_2O_2), activated sodium persulfate ($Na_2S_2O_8$), or other, into the subsurface, to destroy organic compounds. The by-products for complete mineralization of

carbon-based compounds by most chemical oxidizers include carbon dioxide (CO₂), water (H₂O), and oxygen (O₂) as well as minor concentrations of nontoxic ions, salts, and acids.

Both hydrogen peroxide and sodium persulfate are strong oxidants that can be injected into a contaminated zone to destroy petroleum contaminants. When injected into groundwater, they are unstable, and react with organic contaminants and subsurface materials. They decompose to oxygen and water, generating heat, free radicals and electron acceptors in the process. Free radicals are molecular fragments that have an unpaired electron, causing them to be highly reactive and short-lived. Because they were first discovered by H. J. H. Fenton, the reaction of iron catalyzed peroxide oxidation is called a “Fenton’s reaction,” and the iron/peroxide mixture is known as “Fenton’s reagent”. Fenton reactions utilize ferrous iron (Fe²⁺) to catalyze the decomposition of hydrogen peroxide, producing a much more powerful oxidizer in the form of OH radicals. Hydrogen peroxide in the presence of Fe²⁺ reacts to form hydroxyl radicals (OH•), ferric iron (Fe³⁺), and hydroxyl ions (OH⁻). The hydroxyl ions are very powerful oxidizers, and react particularly well with organic compounds. The hydroxyl radicals break the petroleum hydrocarbon bonds of common petroleum constituents such as BTEX, as well as petroleum aromatic hydrocarbons (PAHs) and methyl tertiary butyl ether (MTBE), a common gasoline additive.

The basic reactions of the mineralization of benzene, toluene and xylenes under sulfate reduction are presented in equations 1, 2, and 3 respectively:



Site Description and Treatment Areas. A chemical oxidation remedial event was implemented at a former gas station located in Clinton, NY and targeted the oxidization of BTEX compounds while promoting biological mineralization. The site was identified as having soils and groundwater impacted by the historic release of petroleum hydrocarbons and the remedial event took place from October 27 to October 29, 2009.

There were two treatment areas targeted in order to address the source area and the residual contamination on the site. The first treatment area, Area “A” targeted a 2,675 square foot area and required eighteen injection points, treating between 9 and 15 feet below ground surface. The second treatment area, Area “B” targeted a 6,550 square foot area and required twenty-one injection points, treating between 9 and 15 feet below ground surface.

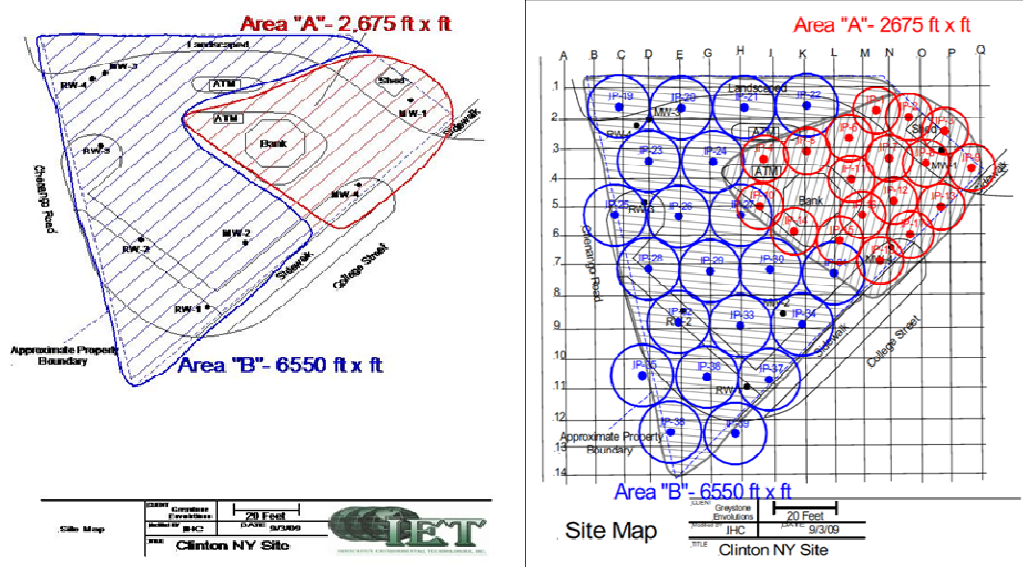


Figure 1. Site map and injection points in Clinton, NY

MATERIALS AND METHODS

A two phase program was implemented to introduce the remedial chemicals sodium persulfate, hydrogen peroxide and zero-valent iron (ZVI) directly into the soil and groundwater using direct push technologies, and retractable injection points through which the remedial materials were pumped into the targeted zones. The first phase of the degradation program targeted BTEX compounds via hydroxyl and sulfate free radicals; the second phase 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 mechanisms employed in the injection process utilized compressed air followed by the remedial liquid introduction. The liquid injection was accomplished via a double diaphragm pump. As a result of the injection process, the pre-existing pore volume was displaced both laterally and vertically. The overall effect was an in-situ mixing and homogenization of the subsurface conditions.

RESULTS AND DISCUSSION

Four monitoring wells are located in the vicinity of the injection area and were all significantly affected by the remedial event. The changes in the field parameters and their respective CVOC concentrations are presented below.

MW-1. In MW-1, total xylenes and 1,2,4-trimethylbenzene decreased 12 months after the injection event to values below the NYSDEC groundwater standard. Benzene decreased 87% compared to the baseline sampling event, while ethylbenzene decreased by 61%. Overall, total VOCs decreased by 88% in MW-1 in the seventeen month period following the injection event (Table 1).

The geochemical parameters are ideal for biological attenuation. Iron is still present, existing mostly in the ferrous oxidation state (Fe^{2+}), indicating that a reducing environment is present. Total and dissolved iron concentrations are at 20.4 mg/L and 19.7 mg/L, respectively. Sulfate concentrations remain elevated with a concentration of 490 mg/L. The pH remains neutral at 6.86 and the redox potential is negative with a recorded value of -88 mV in March 2011. Sulfate concentrations remain elevated above the pre-injection baseline sampling event concentration of 54.3 mg/L. Sulfate concentrations appear to be sufficient for sustained biological mineralization at MW-1 (Table 2).

MW-2. In MW-2, isopropylbenzene, total xylenes and 1,2,4-trimethylbenzene decreased 12 months after the injection event to values below the NYSDEC groundwater standards. The total concentration of all VOCs decreased by 95% compared to the pre-injection sampling event of October 2009. Benzene decreased by 97.6%, while the concentration of n-propylbenzene decreased by 96.8% (Table 1).

The geochemical parameters indicate that conditions are ideal for biological attenuation. Iron is still present, existing primarily in the ferrous oxidation state, indicating that a reducing environment is present. Total and dissolved iron concentrations are at 25.1 mg/L and 25 mg/L, respectively. Sulfate concentrations remain elevated at 321 mg/L. The pH remains neutral at 6.77 and the redox potential is negative with a recorded value of -81 mV in March 2011. Sulfate concentrations remain elevated above the pre-injection baseline sampling event concentration of 2.73 mg/L. While the concentration of sulfate is lower than the post-injection concentration of 2,059 mg/L, it remains elevated enough to sustain sulfate reducing bacteria (Table 2).

Table 1. Total VOC concentrations in MW-1 and MW-2.

MW-1	10 26 2009	2 24 2010	6 23 2010	10 7 2010	3 31 2011
Benzene	170	120	110	130	22
Ethylbenzene	59	99	80	120	23
Methyl tert-Butyl Ether	ND	ND	ND	2.2	ND
Naphthalene	17	14	9.7	3.4	ND
n-Propylbenzene	17	20	14	21	5.2
sec-Butylbenzene	ND	ND	0.88 J	1.5	ND
tert-Butylbenzene	ND	ND	ND	ND	ND
Toluene	10	ND	ND	0.51 J	ND
Xylenes, total	120	48	9.4	16	ND
1,2,4-Trimethylbenzene	59	54	12	18	1.1
1,3,5-Trimethylbenzene	2.5	7.3	0.97 J	ND	ND
MW-2	10 26 2009	2 24 2010	6 23 2010	10 7 2010	3 31 2011
Benzene	1300	500	160	27	30
Ethylbenzene	21	200	14	4.8	ND
Methyl tert-Butyl Ether	23	12	ND	4.8	5.5
Naphthalene	2.2	7.9	ND	ND	ND
n-Propylbenzene	200	120	93	37	6.5
sec-Butylbenzene	9.8	8.2	7	4.8	1.1
tert-Butylbenzene	0.47 J	ND	ND	ND	ND
Toluene	30	ND	ND	ND	ND
Xylenes, total	340	140	5.4	9.4	4.1
1,2,4-Trimethylbenzene	140	76	2.2	6.1	3.5
1,3,5-Trimethylbenzene	ND	5.5	ND	ND	ND

Table 2. Field Parameters in MW-4 and RW-1.

Field Parameters: BBI-Clinton - MW-1								
Time	pH	Specific Conductivity (mS/cm)	ORP (mv)	DO (mg/l)	Turbidity (NTU)	Temperature (°C)	Volume Purged (gal)	DTW (feet below TOC)
October 26, 2009								
15:00	6.7	3.62	-67	0	5.6	15.86	6	13.85
February 24, 2010								
11:12	7.57	3.82	-142	0	340	10.49	4	11.53
June 23, 2010								
11:47	6.92	4.32	-151	0	147	12.52	3.75	12.6
October 7, 2010								
10:37	6.81	8.09	-100	0.35	209	16.95	5.5	11.11
March 31, 2011								
11:45	6.86	3.5	-88	0	3.5	10.64	4	11.48
Field Parameters: BBI-Clinton - MW-2								
Time	pH	Specific Conductivity (mS/cm)	ORP (mv)	DO (mg/l)	Turbidity (NTU)	Temperature (°C)	Volume Purged (gal)	DTW (feet below TOC)
October 26, 2009								
14:05	6.92	5.23	-140	0	3.8	16.89	5.5	10.38
February 24, 2010								
14:18	7.58	6.76	-127	0	21.7	11.73	3.5	11.06
June 23, 2010								
14:07	6.75	4.68	-153	2.11	41.9	13.9	3.5	12.33
October 7, 2010								
12:00	6.62	5.55	-91	5.69	4.8	17.54	4	10.74
March 31, 2011								
10:02	6.77	4.79	-81	0	0	12.3	3.5	10.95

MW-4. In MW-4, the concentration of total VOCs decreased by 66% compared to the baseline sampling event. Benzene concentrations decreased by 62% and total xylenes decreased by 86% indicating that the biological activity was successfully implemented (Table 3).

The geochemical parameters sampled indicate that conditions are acceptable for biological attenuation. Iron is still present in MW-4, existing primarily in the ferrous oxidation state, indicating that a reducing environment is present. Total and dissolved iron concentrations are at 17.5 mg/L and 17.4 mg/L, respectively. Sulfate concentrations remain elevated at 380 mg/L. The pH remains neutral at 6.94 and the redox potential is negative with a recorded value of -102 mV in March 2011. Sulfate concentrations remain elevated above the pre-injection baseline sampling event concentration of 1.57 mg/L (Table 4).

RW-1. In RW-1, total VOC concentrations decreased by 84% following the injection event. Benzene concentrations decreased by 89%, while the concentrations of total xylenes and 1,2,4-trimethylbenzene decreased significantly through biological attenuation, by 89% and 96%, respectively (Table 3).

The pH and redox potential remain ideal for attenuation with a pH of 7.01 and a redox potential of -92 mV. Biodegradation continues at RW-1, based on the continuing reduction of the more readily biodegradable compounds such as xylenes and ethylbenzene (Table 4).

Table 3. Total VOC concentrations in MW-4 and RW-1.

MW-4	10/26/2009	2/24/2010	6/23/2010	10/7/2010	3/31/2011
Benzene	1300	1100	990	590	490
Ethylbenzene	240	370	350	250	220
Methyl tert-Butyl Ether	14	18	ND	6.6	ND
Naphthalene	36	61	43	31	16
n-Propylbenzene	77	62	73	71	55
sec-Butylbenzene	ND	3.6	ND	4.9	ND
tert-Butylbenzene	ND	ND	ND	ND	ND
Toluene	43	17	13 J	8.9	3.5
Xylenes, total	860	510	410	250	120
1,2,4-Trimethylbenzene	580	390	320	230	140
1,3,5-Trimethylbenzene	14	20	15 J	9.9	6.7
RW-1	10/26/2009	2/24/2010	6/23/2010	10/7/2010	3/31/2011
Benzene	200	46	25	17	29
Ethylbenzene	46	220	190	110	73
Methyl tert-Butyl Ether	ND	ND	ND	ND	3.3
Naphthalene	2.4	13	9.2	6.9	1.6
n-Propylbenzene	84	52	49	23	8.1
sec-Butylbenzene	5.8	3.5 J	3.1	1.4	ND
tert-Butylbenzene	ND	ND	ND	ND	ND
Toluene	8.6	3.4 J	2.2	2.2	2.2
Xylenes, total	540	310	210	130	60
1,2,4-Trimethylbenzene	250	110	69	34	9.1
1,3,5-Trimethylbenzene	ND	6.1	4.9	2.8	ND

Table 4. Field Parameters in MW-4 and RW-1.

Field Parameters: BBI-Clinton - MW-4								
Time	pH	Specific Conductivity (mS/cm)	ORP (mv)	DO (mg/l)	Turbidity (NTU)	Temperature (°C)	Volume Purged (gal)	DTW (feet below TOC)
October 26, 2009								
16:10	7.05	3.43	-143	1.54	13.3	16.77	11	14.25
February 24, 2010								
15:30	7.54	6.93	-122	1.79	>1000	11.45	11	17.15
June 23, 2010								
15:08	6.85	4.45	-145	1.84	613	14.51	11	15.87
October 7, 2010								
12:40	6.67	6.81	-106	0.11	48.6	18.22	12	13.34
March 31, 2011								
13:45	6.94	3.39	-102	0	13.7	11.67	12	13.65
Field Parameters: BBI-Clinton - RW-1								
Time	pH	Specific Conductivity (mS/cm)	ORP (mv)	DO (mg/l)	Turbidity (NTU)	Temperature (°C)	Volume Purged (gal)	DTW (feet below TOC)
October 26, 2009								
13:25	7.13	2.64	-160	0	194	16.14	16	13.71
February 24, 2010								
13:37	7.75	4.57	-139	0	38.1	11.55	17	12.6
June 23, 2010								
13:23	6.96	4.35	-147	0	55.6	12.82	17	13.08
October 7, 2010								
11:35	6.81	6.67	-104	0	5.9	17.06	20	11.83
March 31, 2011								
12:50	7.01	3.05	-92	0	13	11.62	18	11.68

CONCLUSIONS

The site in Clinton, New York has seen dramatic decreases in the concentrations of BTEX due to both the chemical oxidation and anaerobic degradation of the contaminants of concern. The concentrations of VOCs across the site showed a significant decrease in concentration, with total VOC concentrations decreasing by 78.5% across the site since the baseline sampling event. Biological attenuation appeared to be occurring at a fast rate in many of the monitoring wells. Compounds that are more readily biodegraded, such as xylene, disappeared. Additionally, compounds that are more recalcitrant such as benzene started to degrade at higher rates. Trimethylbenzene compounds were targeted in the remedial design and were successfully

reduced below the standard values within 12 months of the remedial event. Following one round of injections, the subject site was closed and awarded a No “Further Action” letter.

Overall, the advantages of this approach are:

- 1) Management and containment of the activating iron species within the treatment area,
- 2) Evolution of multiple free radicals,
- 3) Extended residual of persulfate and the sulfate radical in-situ,
- 4) Attenuation following the exhaustion of the persulfate via $\text{Fe}^{2+}/\text{Fe}^{3+}$ interactions,
- 5) In-situ management of sulfate via in-situ precipitation of sulfate iron salts as the in-situ conditions revert back to a less oxidizing environment.
- 6) Attenuation via SO_4^{2-} and Fe^{3+} following the exhaustion of the persulfate as the conditions reverts back to a less oxidizing state.
- 7) Single Injection Event