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Chapter 14

FULL SCALE IMPLEMENTATION OF SULFATE ENHANCED BIODEGRADATION TO REMEDIATE PETROLEUM IMPACTED GROUNDWATER

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ABSTRACT

Anaerobic degradation is the dominant driving force in natural attenuation of petroleum contamination in the subsurface. The contribution to natural attenuation by electron acceptors other than oxygen, such as nitrate, iron III, manganese IV, sulfate, and even carbon dioxide, has been the subject of considerable research in recent years. The addition of these alternative electron acceptors has been shown to have many potential advantages over the traditional approach of attempting to add dissolved oxygen to the plume. Kolhatkar et al. (2000), Wiedemeier et al. (1999), and Wilson et al. (2002) have shown that of these natural anaerobic processes, sulfate reduction accounts for most of the degradation. Cuthbertson et al. (2006) presented case studies that demonstrated the benefits of using Magnesium Sulfate solution to stimulate the biodegradation of petroleum contaminants in groundwater under field conditions at various sites.

Following a successful on site treatability study in 2006, full scale groundwater remediation using Delta's Patented Sulfate Enhanced Biodegradation (SEB) process was initiated in 2006 at a large former service station and bulk storage facility in Upstate New York. Applications of a concentrated solution of magnesium sulfate (Epsom Salt) in water were made in 2006 and 2007. The applications were highly successful for remediation of MTBE, as well as, other petroleum constituents. The results obtained from this site represent the first field scale demonstration of MTBE remediation utilizing this technique.

Keywords: BTEX, MTBE, sulfate, hydrocarbon, petroleum, contamination, groundwater

1. INTRODUCTION

Over the last decade, numerous publications have demonstrated that natural attenuation of hydrocarbons in the subsurface is dominated by anaerobic processes (Kolhatkar, et al., 2000;

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Wiedemeier et al., 1999; Wilson et al., 2002). Biological degradation involves the creation of biochemical energy through microbial respiratory metabolism, which couples the oxidation of an organic compound (petroleum hydrocarbons in this case) with the terminal reduction of an inorganic compound (electron acceptor). Aerobic respiration utilizes oxygen as the terminal electron acceptor, while anaerobic respiration utilizes nitrate, sulfate, ferric iron, manganese oxide, and/or carbonate as the terminal electron acceptor.

The distribution and availability of electron acceptors control the rate of in-situ biodegradation. Other factors (microbial population, pH, temperature, nutrients, etc.) rarely limit the amount and rate of biodegradation. In the presence of organic contaminants, such as petroleum hydrocarbons, terminal electron acceptors are depleted at a rate significantly higher than can be naturally replenished, thus inhibiting biological degradation. The introduction of additional electron acceptors to the subsurface can accelerate the rate of biological degradation.

There are many benefits of providing sulfate as the terminal electron acceptor to the subsurface environment. As anaerobic conditions naturally prevail under petroleum-impacted sites, there is less acclimation time necessary for microbial populations, thus sulfate injection stimulates processes that are already occurring. The high solubility and stability of sulfate solutions relative to traditional electron acceptors allows for improved subsurface delivery and coverage, and higher concentrations of sulfate can be added to groundwater due to its high solubility (as compared to oxygen). One mole of sulfate also has twice the oxidizing or electron-accepting capacity of oxygen. The lower energy reactions of sulfate reduction require less nutrient supplementation and produces less biomass and secondary precipitates, which can plug an aquifer. There is less non-target demand on sulfate when compared to oxygen, which provides better utilization efficiencies.

This paper describes the implementation and results of a full scale implementation of anaerobic biodegradation at a site in Ogdensburg, New York, USA. In addition, this paper demonstrates that SEB is a viable technique for remediation of MTBE.

2. MATERIALS AND METHODS

The subject site consists of approximately 7.0 acres of commercial property occupied by three vacant buildings which include an office, a former restaurant, and another outbuilding. Prior to 2006, the site had also been occupied by a retail fueling facility (including a service kiosk, underground fuel lines, pump islands and a canopy) that had been located on the eastern side of the site, and also a petroleum bulk storage plant (including a loading rack, pump island, aboveground storage tanks, and containment structure) that had been located on the western side of the site. Spill incident numbers were assigned to the former retail facility area in 2004 and to the bulk storage area in 2006.

2.1 Soil Impact

Site assessment activities identified three areas of soil impact described as follows:

- **AREA -1:** Soil impacts were defined in the eastern area of the site in the area surrounding the former retail fueling facility. Investigation findings indicated that petroleum-impacted soils were located in areas around the former pump islands and along the numerous product lines that were encountered in the area. The vertical extent of impacts in this area generally appeared to extend from between 0.5 feet and 8 feet below grade. Soils in isolated areas were impacted to greater depths; however, those areas appeared to be limited in extent. Petroleum impacts were also present in saturated soils beyond the immediate area of the fueling facility, with impacts appearing to be related to migration of petroleum products via the groundwater pathway.
- **AREA-2:** Soil impacts were defined in the central area of the site in an area located between the office building and former restaurant, where product lines and the remnants of a suspected fuel island were encountered during line removal activities. The horizontal extent of the impacts appeared to be limited to an area that was located along the former supply lines and the area of the suspected pump island. Vertical impacts were observed to extend to depths of 3 feet to 5 feet in the area along the former supply lines. In the area surrounding the suspected pump island, impacts extended to between 5 feet and 6 feet in depth.
- **AREA-3:** Soil impacts were encountered in the western area of the site in the area located beneath the former bulk storage plant. The horizontal extent of impacts appeared to be limited to the area located beneath the footprint of the former bulk plant, with the greatest impacts in the area of the former fuel rack and beneath the older sections of the former containment area. The vertical extent of impacts was variable across the area and extended from near grade to depths of up to approximately 5 feet below grade.

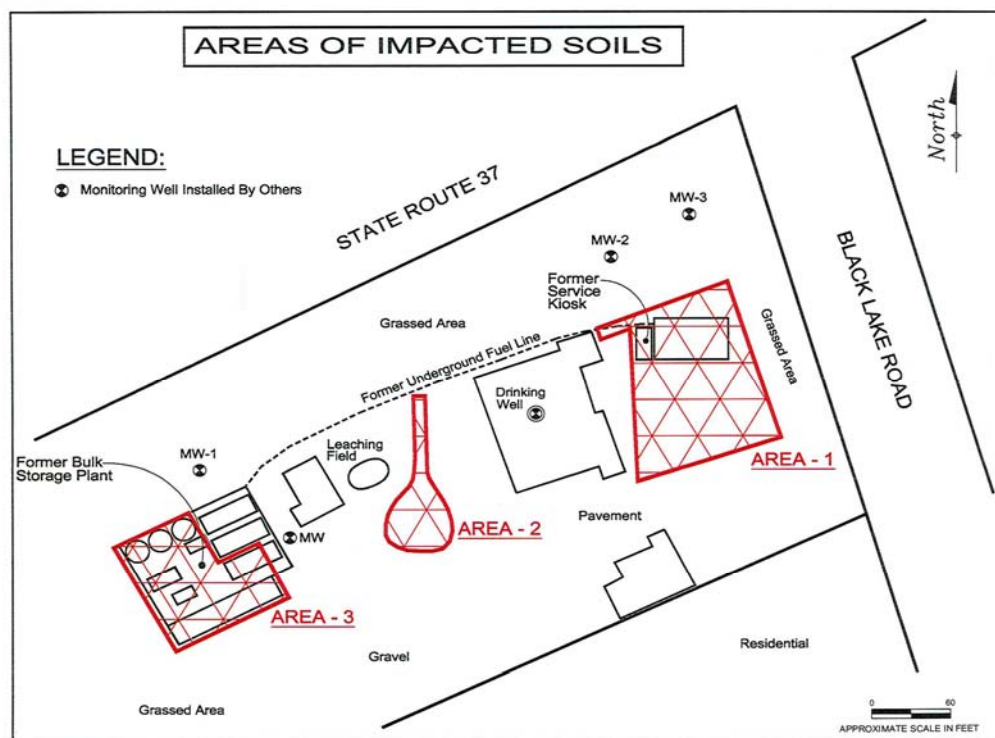


Figure 1. Estimated Areas of Impacted Soils Prior to Excavation

The remedial approach selected for the soils at the site consisted of excavation of shallow unsaturated soils. Soil excavation from the three previously described soil impact areas was conducted between 30 October and 28 November 2006 with subsequent offsite disposal of petroleum-impacted soils. During excavation activities, subsurface soil samples were collected from the excavations at varying depths and locations and screened for the presence of volatile organic compounds (VOCs) using a photoionization detector (PID). PID readings and field observations (i.e., staining, odor, etc.) were used to evaluate whether or not soil was considered as clean or impacted. Generally, when PID readings were either at or below 10 ppm the area was considered to be clean. Following completion of excavation activities, confirmation soil samples were collected from the limits of the excavated areas to verify the adequate removal of petroleum-impacted soils. Overall, 4,682.49 tons of petroleum-impacted soil was removed from the site during excavation activities.

2.2 Groundwater Impact

Assessment of the extent of dissolved phase groundwater impact identified two distinct areas of concern described as follows:

- The first area (East Area) is located in the eastern portion of the site in the area surrounding the former retail fueling facility. The extent of impacts in groundwater generally mirrored those encountered in soils and was limited to the area between the entrance driveways and the former restaurant building.
- The second area (West Area) is located in the western portion of the site and centered on monitoring well MW, which is located to the immediate east of the former bulk storage plant. Groundwater impacts in this area of the site were limited to MTBE in groundwater.

Historic groundwater elevation measurements indicate that groundwater flow is generally to the east to northeast across the site. Analytical data indicate that the limits of affected groundwater onsite are generally defined. Based on the available data, it does not appear that petroleum-impacted groundwater has migrated offsite.

2.3 Remedial Design

Between May and August 2006, a pilot test consisting of a limited application of a 20% by weight magnesium sulfate solution was conducted in an impacted area of the eastern site (near the former retail facility pump islands) to assess the effectiveness of the SEB remedial alternative. Following the collection of baseline groundwater samples on May 18, 2006, the pilot test was initiated by applying approximately 100 gallons of magnesium sulfate solution. Following application of the magnesium sulfate, aquifer conditions in the pilot test area were monitored during three monthly monitoring events (20 June, 17 July and 10 August 2006) to assess the effectiveness of the remedial technology. Monitoring included sampling of groundwater and analysis for VOCs and MTBE (EPA Method 8021), ferrous iron, nitrate, sulfate

and magnesium. Samples were also analyzed in the field for dissolved oxygen, pH and ORP. Water levels and groundwater flow direction were also evaluated during the monitoring events.

Following a review of the pilot test data, it was determined that the magnesium sulfate application was effective in reducing VOC concentrations and increasing sulfate concentrations in test wells at least 20 feet away from the application well over the three month study period. Based on the reductions in VOC's observed during the three month post application monitoring period, it was determined that the magnesium sulfate technology would be an effective remedial alternative for treating petroleum-impacted groundwater at the site.

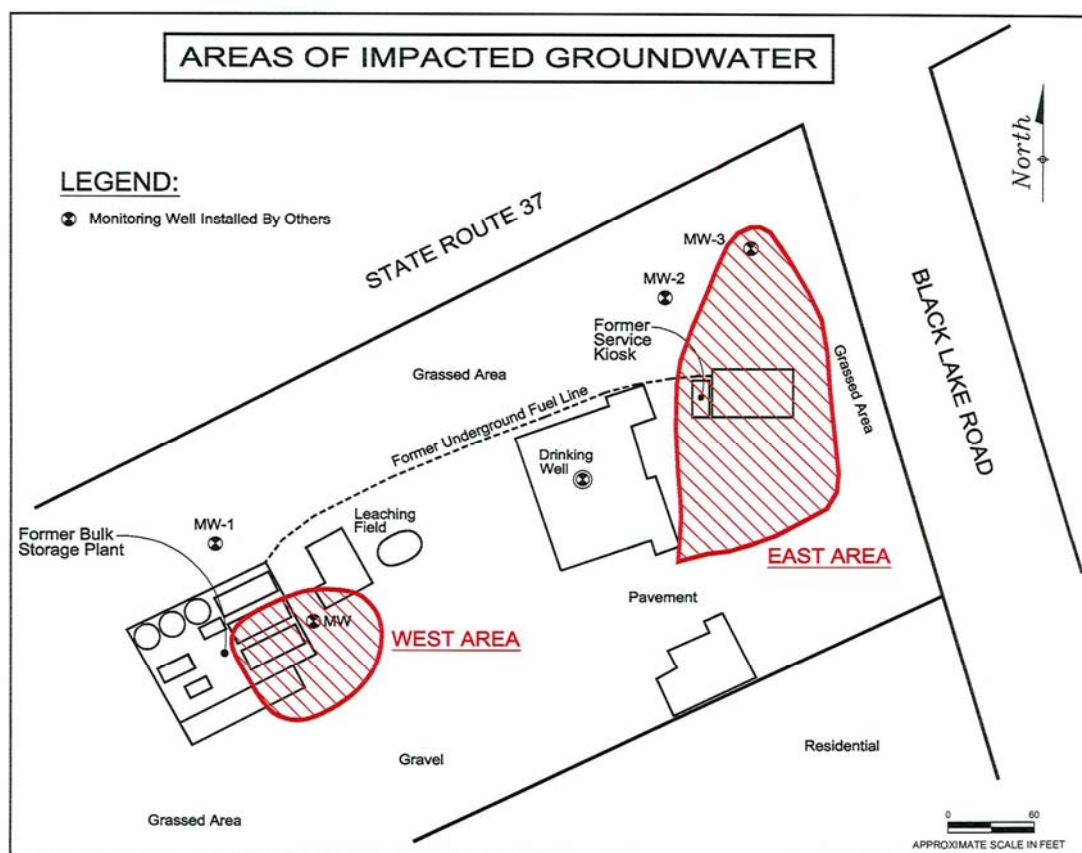


Figure 2. Estimated Areas of Impacted Groundwater

The remedial approach selected to remediate groundwater and petroleum impacted soils below the groundwater at the site after the completion of soil excavation was SEB.

Based on the 2006 pilot test data, a final remedial design was developed for application of SEB in the eastern and western areas of groundwater impacts at the site. The remedial design provided estimated application quantities, system infrastructure requirements, and monitoring

frequency. A series of vertical two-inch-diameter wells were installed by hollow stem auger drilling techniques to depths that screened the saturated treatment zone in each area of concern (15 feet in depth). Wells were installed on approximately 30-foot centers in a distribution pattern that allowed for coverage of the area of impacted groundwater in both affected portions of the site. Twenty seven wells were installed in the eastern area of concern and eight wells were installed in the western area of concern (Figure 3). Following installation, each was developed by purging a minimum of ten well volumes and until waters were visibly sediment free.

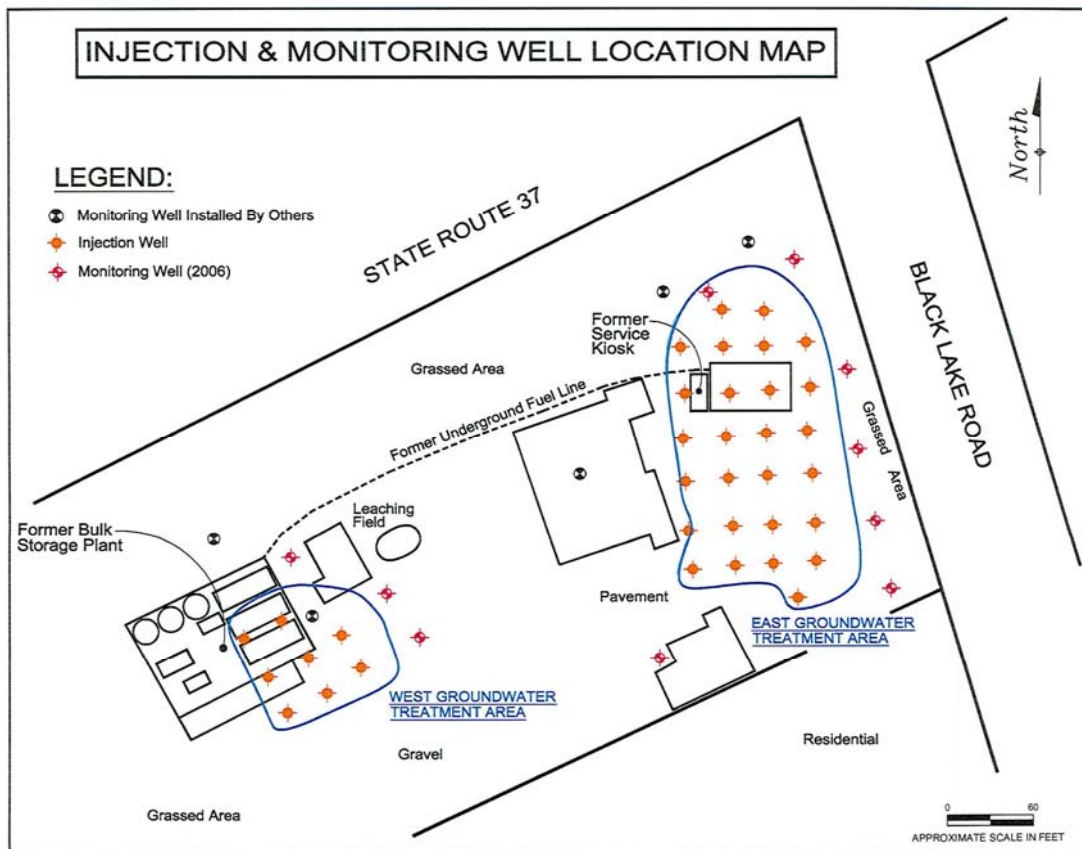


Figure 3. Injection & Monitoring Well Location Map

3. SEB IMPLEMENTATION

The initial application was performed on December 5 and 6, 2006. Approximately 3,800 gallons of 20% by weight magnesium sulfate solution supplied by Livingston Fluid Service of Howell, Michigan was equally distributed across 35 wells, located in the eastern and western areas of concern, with approximately 108 gallons of solution being gravity fed to each well.

Based on evaluation of post application monitoring results, a subsequent application was made on August 13, 2007. Approximately, 1,165 gallons of 20% by weight magnesium sulfate

solution supplied by PQ Corporation of Utica, Illinois was applied to the site. A total of approximately 180 gallons of solution was applied to nine wells in the eastern area of concern and a total of approximately 985 gallons was applied to 32 wells located in the western area of concern.

On November 28, 2007, approximately 850 gallons of 20% by weight magnesium sulfate solution supplied by PQ Corporation of Utica, Illinois was applied across 32 wells located within the eastern area of concern. No application was made to the western area of concern because remedial objectives had been achieved.

4. RESULTS AND DISCUSSION

Subsequent to the soil excavation activities and the initial application of SEB solution ten of the sixteen performance monitoring points were demonstrated to have been remediated to below target remedial goals prior to the first or second sampling event. There were five wells (IJ-12, IJ-16, IJ-18, IJ-24, and MW-E4) located in the eastern area of concern and one well (IJ-30) located in the western area of concern that had residual impacts that were sampled four to seven times over an approximately 22 month period (Figure 4). In these six wells, Ethylbenzene, Xylene, and MTBE were the compounds with the highest residual concentrations. The highest concentrations of these three compounds after vadose zone soil excavation and prior to implementation of SEB were Ethylbenzene of 1,900 microgram per liter (ug/l) at IJ-16, Xylene of 750 ug/l at IJ-12, and MTBE of 140 ug/l at IJ-18.

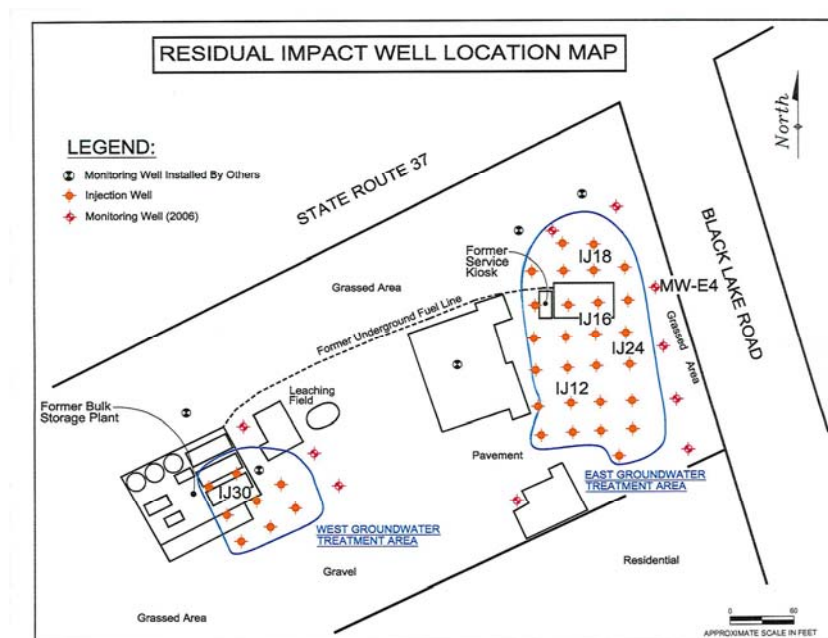


Figure 4. Residual Impact Well Location Map

Graphs depicting the Ethylbenzene, Xylene and MTBE concentrations in these six wells are presented below. In addition, Total VOC concentrations reported are presented on the graphs.

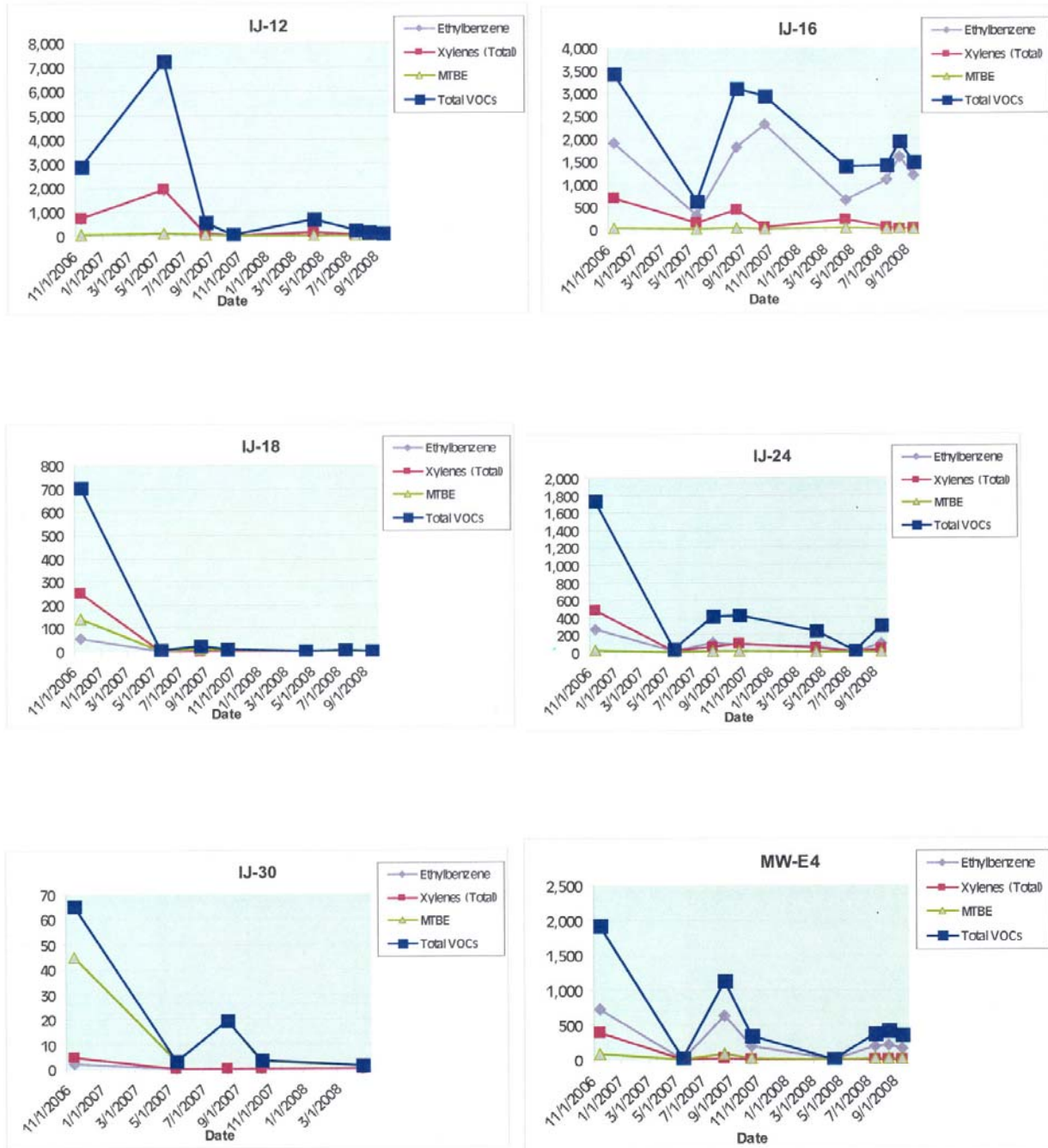


Figure 5. Six Graphs Depicting Concentrations of Selected Contaminants over Time

The following table presents the percentage reductions in Ethylbenzene, Xylene, MTBE and Total VOC concentrations after implementation of SEB for groundwater remediation.

Table 1. Contaminant Reduction Percentages

Well	Ethylbenzene	Xylenes	MTBE	Total VOCs
IJ-12	92.8	>99	98	96.3
IJ-16	36.8	96.6	79.3	57.1
IJ-18	>99	>99	>99	>99
IJ-24	61.9	92.1	>99	82.9
IJ-30	>99	>99	97.1	98
MW-E4	78.1	98.4	79.2	81.4

Overall, the groundwater contaminant concentrations have been significantly reduced due to the remedial efforts and the majority of performance monitoring locations met remedial objectives within two years of implementation. Ethylbenzene was surprisingly recalcitrant in wells MW-E4, IJ-24 and especially IJ-16, but an average reduction of 77.9% was observed in these six wells. Xylenes and MTBE were observed to have average concentration reductions of 97.3% and 91.9%, respectively.

Potential causes for the recalcitrance of Ethylbenzene are currently being evaluated along with other remedial alternatives for the remaining residual impact.

4. CONCLUSION

SEB was demonstrated to be an effective technique for the remediation of petroleum impacted groundwater including MTBE. However, Ethylbenzene was somewhat recalcitrant in three of the sixteen performance monitoring wells.

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