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Remediation and Characterization Products and Support

Magnesium Sulfate (Nutrisulfate®) for Anaerobic Bioremediation:

- 1. John Sankey, True Blue Technologies
- 2. Magnesium sulfate
- 3. MSDS & Technical Data Sheet Attached
- 4. Number of Field-scale Applications to Date: 20+sites.
- 5. Case Studies Attached
- 6. Technical Summary:

Sulfate reduction and methanogenesis is the dominate natural degradation processes at most sites; and therefore, adding oxygen to the anaerobic portion of the plume may be disadvantageous.

Magnesium Sulfate (Nutrisulfate®) stimulates biodegradation by providing a soluble, readily available electron acceptor solution. In the presence of elevated sulfate, anaerobic groundwater bacteria use BTEX, MTBE and other petroleum hydrocarbons for carbon and energy while mineralizing the hydrocarbons to carbon dioxide and water. Sulfate addition enhances natural conditions and reduces the carbon footprint when compared to conventional remediation.

Sulfate Enhanced Bioremediation

Petroleum Hydrocarbon + Magnesium Sulfate (Nutrisulfate®) + Dissolved Iron \rightarrow Iron Sulfide + H2O + MgCO3 + CO2 Please call if you have any questions.

Regards, John Sankey, True Blue Technologies **Material Safety Data Sheet**



Nutrisulfate™ Bioremediation Nutrient

Section 1: Chemical Product and Company Identification

Product Name: Sulfate Enhanced Yeast Fermentation Product Catalog Codes: Nutrisulfate™ CAS#: TSCA: NA HMIS Code: NA Trade Name and Synonyms: Nutrisulfate™, Nutrimens-SEB™, Nutrimens™ Hydrocarbons – Liquid

Chemical Family: Yeast & Magnesium sulfate (magnesium sulphate) Contact Information: Tersus Environmental, LLC 109 E. 17th Street, Suite #3880 Cheyenne, WY 82001 Ph: 307.638.2822 • info@tersusenv.com www.tersusenv.com For emergency assistance, call: 919.638.7892

Section 2: Composition and Information on Ingredients

| COMPONANT | % | CAS # | OSHA TWA | OSHA STEL | ACGIH TWA | ACGIH STEL |
|--|---------|---------------|-------------|--------------|--------------|---------------|
| Yeast Fermentation Product | 9 to 10 | | | | | |
| Magnesium Sulfate Solution (MgO₄S; magnesium sulfate) | Balance | 7487 – 88 – 9 | | | | |

HAZARDOUS INGREDIENTS: NONE AS DEFINED UNDER THE U.S. OSHA HAZARD COMMUNICATION STANDARD (29 CFR 1910.1200) OR THE CANADIAN HAZARDOUS PRODUCTS. ACT S.C. 1987, C.30 (PART 1).

SARA HAZARD: NONE NOTED (SECTION 311/312) TITLE III SECTION 313 - NOT LISTED All components of this product are listed on the TSCA registry.

Section 3: Physical/Chemical Characteristics

| Boiling Point | 212 degrees F |
|---------------------------------|---------------------------------------|
| Vapor Pressure (mmg Hg) | N/A |
| Vapor Density (AIR = 1) | N/A |
| Solubility in Water | . dispersible |
| Appearance and Odor | brown liquid, yeast aroma |
| Specific Gravity ($H_2O = 1$) | varies by concentration & temperature |
| Melting Point | N/A |
| Evaporation Rate | N/A |
| (Butyl Acetate = 1) | |



Section 4: Fire and Explosion Data

| FLASH POINT (METHOD USED) | N/A |
|----------------------------------|------|
| FLAMMABLE LIMITS | N/A |
| LEL | N/A |
| UEL | N/A |
| EXTINGUISHING MEDIA | none |
| SPECIAL FIRE FIGHTING PROCEDURES | none |
| UNUSUAL FIRE FIGHTING HAZARDS | none |

Section 5: Reactivity Data

STABILITY: Generally stable. HAZARDOUS POLYMERIZATION: Will not occur.

Section 6: Health Hazard Data

Based on specific concentration as sold

ROUTE(S) OF ENTRY: Inhalation

HEALTH HAZARDS (ACUTE AND CHRONIC)...... Respiring yeast generates carbon dioxide. Over exposure to carbon dioxide gas may cause asphyxiation.

CARCINOGENICITY: No

NPT..... No

OSHA REGULATED..... No

SIGNS AND SYMPTIONS OF EXPOSURE Over exposure to carbon dioxide include: stupor, dizziness, unconsciousness, death.

EMERGENCY AND FIRST AID PROCEDURES If exposed to carbon dioxide, move to fresh air. Give respiratory support if needed. Seek medical attention.

Eye contact: Causes mild irritation to the eyes.

Skin contact: No known adverse effects.

Inhalation: Causes nausea, vomiting, abdominal cramps, and diarrhea.

Ingestion: Causes nausea, vomiting, abdominal cramps, and diarrhea.

Chronic hazards: No known chronic hazards. Not listed by NTP, IARC or OSHA as a carcinogen.

Physical hazards: Spilled material can be slippery



Section 7: Precautions for Safe Handling and Use

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED: Conventional cleanup

WASTE DISPOSAL METHOD: In accordance with Federal, State and Local regulations

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING: Store in a cool area.

OTHER PRECAUTIONS: None

Section 8: Control Measures

RESPIRATORY PROTECTION (SPECIFY TYPE): Confined spaces that held yeast fermentation product could potentially contain carbon dioxide gas. Use NIOSH/MSHA approved self-contained breathing apparatus or supplied respirator if oxygen content below 19%. Use in accordance with 29 CFR 1901.134

IS RESPIRATORY PROTECTION NECESSARY: UNNECESSARY IF VENTILATION IDENTIFIED BELOW IS USED

VENTILATION LOCAL EXHAUST: Use adequate mechanical ventilation.

PROTECTIVE GLOVES: Work Type

EYE PROTECTION: Safety glasses a good practice

OTHER PROTECTIVE CLOTHING OR EQUIPMENT: None

HYGENIC PRACTICES: Good manufacturing practices

PROTECTIVE CLOTHING UNNECESSARY IF OTHER CONTROL MEASURES ARE USED

Section 9: Disclaimer and/or Comments

We suggest that containers be either professionally reconditioned for re-use by certified firms or properly disposed of by certified firms to help reduce the possibility of an accident. Disposal of containers should be in accordance with applicable federal, state and local laws and regulations. "Empty" drums should not be given to individuals.

The conditions of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of the product.

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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;

[§] Corresponding Author: Jim Cuthbertson, P.E., Delta Consultants, 39810 Grand River, Suite C-100, Novi, MI 48375, Tel: 248-699-0259, Email: jcuthbertson@deltaenv.com 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:

183

- **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

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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

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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 Sulfate Enhnaced Biodegradation to Remediate Petroleum Impacted Groundwater

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.

5. **REFERENCES**

- Bruce, L, Cuthbertson, J, Kolhatkar, A, Ziegler, S and Graves, B 2007, 'Anaerobic Degradation of Benzene was Enhanced through Sulfate Addition Substantially Increasing the HC Degradation Rate at a Central Indiana Site' paper presented to the NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, Houston, 5-6 November
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Comparison of BTEX Attenuation Rates Under Anaerobic Conditions

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COMPARISON OF BTEX ATTENUATION RATES UNDER ANAEROBIC CONDITIONS

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ABSTRACT

Over the last decade data have been published that demonstrate that natural attenuation of hydrocarbons in the subsurface is dominated by anaerobic processes. Some data have indicated that benzene is recalcitrant; some have shown it degrades but at a slower rate than alkyl benzenes (primarily TEX) under anaerobic conditions. Many natural attenuation studies have pointed to the sequential order of attenuation. This paper evaluated data from four sites in the Midwestern U.S. (Illinois, Indiana, Michigan, and Missouri) that explain and contrast existing impressions. Although the actual attenuation rates varied from site to site, primarily dependent upon the relative availability of electron acceptors, data from these sites indicated that attenuation of BTEX compounds under anaerobic conditions is concurrent. The benzene attenuation rate appeared to be a function of the relative abundance of TEX. The ratios of attenuation rates between the compounds, however, appear to be relatively constant within certain brackets. For example, of the BTEX compounds, at the four sites in this study, toluene attenuated at the highest rate followed by benzene which attenuated at average rates between 70 and 80% of toluene, xylenes which attenuated at average rates between 60 and 70% of toluene (which may be dependent upon which xylenes are most abundant), and lastly ethylbenzene which attenuated at average rates 50 to 60% as high as toluene. These were observed at both natural and sulfate-enhanced attenuation sites.

Keywords: attenuation rate, BTEX, 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 and Wilson 2000; Wiedemeier et al 1999; Wilson and Kolhatkar 2002). Some, however have indicated that benzene is either recalcitrant or that it attenuates at a slower rate than toluene, ethylbenzene, and xylenes (TEX) (Cunningham et al 2001; Suarez and Rifai 1999). In this paper we compare the ratio of attenuation rates of each of the BTEX compounds to the rate for toluene in multiple wells at four field sites. Because toluene

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usually had the highest attenuation rate, it was used as a basis for comparison for the other compounds at each monitoring point.

This paper describes and compares the attenuation rate, not specifically the biodegradation rate. The attenuation rate also includes physical parameters such as dispersion, dilution, sorption, and retardation that will affect concentrations of individual compounds at different magnitudes downgradient of a contaminant source.

2. MATERIALS AND METHODS

This study evaluated the relative rates of attenuation of BTEX components under anaerobic conditions at four sites. Actual first order attenuation rates at any given site vary according to the geologic conditions and the availability of electron acceptors. The goal of this study was to determine if B, T, E, and X compounds degraded concurrently in field anaerobic conditions, and if so, if there was a general ratio or order of fastest to slowest. Because the sites studied are actual field sites and not controlled laboratory tests or pilots, we cannot say that any one process such as iron reduction, nitrate reduction, sulfate reduction or methanogenesis is exclusive at any site. However, based on the consumption of available electron acceptors in the plume, geochemical data indicated that sulfate reduction is a prominent process at each site.

The four sites in the Midwestern United States chosen for this study were Antioch, Illinois, Clio, Michigan, Indianapolis, Indiana, and St Clair, Missouri. All four sites had reported leaking underground storage tank incidents. The sites had all undergone routine assessment under state and federal regulations. Three of the sites had had some form of remediation such as UST excavation or pump and treat followed by enhanced monitored natural attenuation (MNA) through the addition of an electron acceptor (sulfate). The fourth site had only undergone natural attenuation. On sites where electron acceptors had been added, attenuation rates before and after the applications were reviewed.

The following criteria were used for site selection and subsequent monitor point screening:

- 1. Each site had a stable or decreasing plume.
- 2. Each site was in a stage of monitored natural attenuation or enhanced monitored natural attenuation with the addition of an electron acceptor as the only enhancement.
- 3. Geochemical profiles from background across the plume indicated the dominance of anaerobic processes in the zone of attenuation.
- 4. Attenuation rate calculations were based on at least 2 years of decreasing concentrations over time for B, T, E, and X
- 5. Regression analysis for each compound at a monitoring point had a statistically significant slope within at least a 90% confidence limit with a p value <0.05.

2.1 Site Data

2.1.1 Antioch, Illinois

The Antioch, Illinois, site (Figure 1) had a reported LUST incident in 1991. The source at the time included a long linear LNAPL plume that extended from near the current eastern dispensers south off the property line. The course of remediation included pulling the old USTs, over excavating, and installing LNAPL recovery trenches. By 2004, there was no longer any measurable LNAPL. BTEX concentrations, however, were stable but not declining. The geology was permeable sand and the groundwater gradient was to the south. Through both geochemical and biological analyses (plate counts and PLFA), the plume was determined to be anaerobic with a strong component of sulfate reduction. In late 2005 a series of sulfate injections were begun to provide electron acceptors to the sulfate reducing bacteria. Subsequently BTEX concentrations in most wells began to decline with statistically significant slopes in concentration vs. time plots.



Figure 1. Site map of Antioch, Illinois with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

2.1.2 Clio, Michigan

The Clio, Michigan site (Figure 2) had a reported LUST incident in 1980. The source at the time included a LNAPL plume that extended from near the UST cavity and the former western dispensers and northerly towards the property line. Remediation included pulling the old USTs and implementation of Mobile Multi-Phase Extraction events. Measurable LNAPL thicknesses were periodically encountered at OW-9R and OW-23. The geology in the aquifer is predominately silty sand and the groundwater gradient is to the northeast. Through geochemical analyses, the plume was determined to be anaerobic predominantly under sulfate reduction.



Figure 2. Site map of Clio, Michigan with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

2.1.3 Indianapolis, Indiana

This site was a candidate for enhanced attenuation via addition of sulfate and was the focus of a prior paper (Bruce et al 2007a). At this Central Indiana site (Figure 3), dissolved BTEX levels were relatively high fifteen years after the service station closed. The geology was a sandy zone overlain by silty clay. The groundwater gradient was toward the west-northwest. Although the UST source area had been over excavated and

a pump and treat system had operated for a period of time after the facility closed, concentrations were still too high to qualify for remediation by MNA under state guidelines. The remaining source zone lies on the west side of the former UST pit. In 2004, dissolved benzene levels near the source area hovered near 1,000 ppb. The dissolved plume was neither growing nor shrinking. If the source area could be addressed, the plume should shrink. Excavating again was not an option because the site had already been redeveloped. Inorganic analyses showed that dissolved sulfate was present naturally in the aquifer outside the hydrocarbon plume with a mean concentration of 78 mg/l. In the dissolved phase BTEX plume area, however, sulfate concentrations were substantially reduced to concentrations less than 10 mg/l. Additionally, a shadow of reduced sulfate concentration plume had gone anaerobic and was under sulfate reducing conditions. In 2004, high concentration sulfate solutions were added to the source area through an infiltration trench three times over a five month period.



Figure 3. Site map of Indianapolis, Indiana with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

2.1.4 St. Clair, Missouri

This location was described in a paper by Bruce et al 2007b. This site in central Missouri (Figure 4) is underlain by fractured bedrock. Groundwater flow in the area is affected both by northwest-southeast and northeast-southwest fracture orientations and by a north-south trending groundwater divide that caused dissolved phase to move both east and west of the source area. The primary aquifer is the Jefferson City Dolomite with a water table at about 60 feet below ground surface. However, relatively persistent shallow perched zones exist. Two adjacent service stations (one former) appear to have commingled plumes. A pump and treat system was implemented and then shut down on the southern property. The northern property had been undergoing monitored natural attenuation since contamination was discovered in 1990. The data used here was from the northern property only.



Figure 4. Site map of St. Clair, Missouri with benzene concentration contours. The outer contour is 5 ppb. The contours increased in value inward

2.2 Geochemical Profiles

Field measurements and laboratory analyses of groundwater are relatively easy to perform and inexpensive. Observing simple groundwater geochemical parameters, such as the change in concentration of electron acceptors across a plume, can provide definitive evidence of microbial degradation of contaminants, and provide quantitative data regarding rates of degradation and the contribution of different processes (Chapelle, 2001). Bruce et al (2007a) also provides a detailed guidance on use of geochemistry to define the terminal electron-accepting zones (aerobic, or iron-reducing, nitrate-reducing, sulfate-reducing, or methanogenesis) in which attenuation is occurring. A brief list of parameters that help define the anaerobic zone is given below.

- 1. Decrease in dissolved oxygen (field measure) from several mg/l background to less than 1 mg/l in the plume. Caution: Many DO measurements have historically been inaccurate and have given false positives. Use of appropriate and calibrated instruments to ensure correct DO measurements is highly recommended.
- 2. Change in redox potential in millivolts (field measure) from positive outside the plume to negative in the plume, preferably with -100 millivolts or lower in the plume.
- 3. Decrease in nitrate concentration, if present outside the plume, should decrease significantly in the plume.
- 4. Increase in dissolved iron concentration (Fe II only from filtered samples) from very low or near non-detect in the background to several mg/l in the plume.
- 5. Decrease in sulfate concentration in the plume as compared to natural background concentration.
- 6. Optional: increase in dissolved CO2, dissolved methane, and/or dissolved hydrogen in the plume as compared to background.

These parameters should be viewed as a profile from background across the plume. However, not every parameter is required. Only some of these parameters had been measured historically at each site. Therefore if at least three of these criteria were met, with no significant conflicting data, the attenuation areas were deemed anaerobic.

2.3 BTEX Attenuation Rates

2.3.1 Graphical Estimation

This paper estimated attenuation rates for each BTEX compound in groundwater at monitoring points in or downgradient of a source. The first order attenuation rates were calculated by linear regression analysis of time profiles of the natural logarithm of the concentration of contaminant of concern [i.e. ln(CoC) vs time]. Methods of calculating attenuation rates and first order rate constants are discussed by Newell, et al. 2002. Figures 5, 7, 8 show the concentration profile of BTEX in each chosen well at 3 of the sites (Antioch, Indianapolis, St. Clair). The lines in these graphs display least squares exponential fits of the data to show the trends that correspond to the measured concentrations. Ln(CoC) vs time was used in the linear regression and statistical

calculations. Figure 6 (Clio) provides an example graph of ln(CoC) vs time illustrating the graphs used for estimations of the attenuation rates and for statistical analyses.

The slope of the graph of natural log of concentration of contaminant of concern (CoC) versus time (t) was estimated graphically by applying the "least squares" best fit method over the time of interest. This slope is the attenuation rate (k day-1) of each component and is illustrated in equation 2.

 $(CoC)_{t} = e^{-kt}(CoC)_{o} \qquad ------(1)$ $ln(CoC)_{t} = -k t * ln(CoC)_{o} \qquad ------(2)$ where $(CoC)_{t} = concentration of contaminant of concern at some time t after time zero (CoC)_{o} = concentration of contaminant of concern at time zero k= attenuation rate (day-1) = slope of ln(CoC)_{t} vs time, t$ t = time in days after time zero

half-life (days) = $\ln(2) / k$ (day-1) ------(3)

Equation 3 can be used to calculate the half-life of a CoC. For example, a "k" equal to -0.001 day^{-1} is equal to a half life of approximately 693 days or about 1.9 years.

2.3.2 Statistical Analyses:

Excel®'s regression data analysis tool was used to calculate the confidence level at which the slope of B, T, E, or X attenuation was statistically significant. Wells with slopes (of ln(CoC) vs time) that were statistically significant at less than 90% confidence level were not selected for this paper. Another statistical parameter, which we used as the 2nd selection sieve, was the p-value. A threshold of 0.05 was used for the p value (p<0.05) to demonstrate that for a given compound in the selected well there was less than 5% chance that ln(CoC) was unrelated to the independent variable, time (t).

Hence, wells that had statistically significant slopes at $\geq 90\%$ confidence levels and had p-values <0.05 for slope of ln(CoC) vs time for each contaminant, were chosen for this study. Two wells with < 90% confidence limits for ethylbenzene were exceptions. At the Indianapolis site, the slope for ethylbenzene in wells OW-3R and OW-23 fell below the 90% confidence limit because of scatter in the data for that compound. However the slopes for the other compounds in those wells were statistically significant at 95% confidence limits and we chose to include these wells in the study.

2.3.3 Correlation of CoC Concentration with Groundwater Elevation

A similar statistical analysis was carried out to evaluate the relationship between CoC concentration and groundwater elevation. This is illustrated in the lower left graph of Figure 5. No statistically significant correlation was observed between the concentration of CoCs and groundwater elevation in any well at any site. This proved that the attenuation of BTEX compounds at these sites was not due to fluctuations in groundwater levels.

3. **RESULTS AND DISCUSSION**

Attenuation rates for B, T, E, X were calculated by plotting the concentration profiles of each of these compounds for each well at the four sites (Figures 5, 6, 7, 8). The choice of wells was based on the criteria discussed in Section 2. Attenuation rate calculation was based on at least 2 years of decreasing concentrations over time for B, T, E, and X. Regression analysis for each compound at a monitoring point was performed and wells that had a statistically significant slope of at least 90% confidence limit with a p value <0.05 were used for estimation of attenuation rate k(day-1). The ratio of attenuation rate of benzene, ethylbenzene, and xylenes to the attenuation rate of toluene (kCoC/kT) was also calculated. These are shown in tables 1 through 4. This ratio qualitatively serves as an indicator for the hierarchy of attenuation. Toluene had the highest rate of attenuation in about 80% of the wells in this 4-site data set and was chosen as a basis for comparison.

Table 1. Site : Antioch, Illinois: Rates of attenuation (k, day^{-1}) of each of the CoCs calculated and compared to that of toluene (k_{CoC}/k_T) . At this site, attenuation was enhanced through addition of sulfate as an electron acceptor. Before enhancement, concentrations were stable but not declining. The top rows show benzene and TEX concentrations at the beginning of the time of interest. The initial benzene/ TEX ratio is also shown.

| ANTIOCH | MW-2 | | MW-7 | | MW-17 | | |
|----------------------|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|----------------------------------|--|
| B ppm (initial) | 0.25 | | 0.45 | | 5 | | |
| TEX ppm (initial) | 0.4 | | 2.94 | | 5.42 | | |
| B/TEX | 0 | .6 | 0.15 | | 0.92 | | |
| | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T | |
| В | 0.0009 | 0.4 | 0.0008 | 0.6 | 0.0024 | 0.7 | |
| Т | 0.0021 | 1.0 | 0.0012 | 1.0 | 0.0036 | 1.0 | |
| Е | 0.0009 | 0.4 | 0.0021 | 1.7 | 0.0032 | 0.9 | |
| Х | 0.0011 | 0.5 | 0.0021 | 1.7 | 0.0034 | 0.9 | |

In addition to concentration profiles of B, T, E, X, Figure 5 also displayed a graph in the lower left showing the relationship between benzene concentration and groundwater elevation for all three wells at Antioch. Regression and statistical analyses were also performed on this data. As seen from the graph, there was no significant correlation between the benzene concentration and groundwater elevation. Similar graphs were plotted and analyses performed for each of the other 3 sites and no correlation was observed between contaminant concentration and the groundwater elevation (data not shown). This demonstrated that the decrease in concentration of contaminant was not due to groundwater fluctuation.



Figure 5. Site: Antioch, Illinois: Profiles of CoCs in wells 2, 7, 17 used to calculate attenuation rate (-k day⁻¹); The graph in the lower left, benzene vs groundwater in the 3 wells, showed that there was no correlation between CoC concentration and groundwater fluctuation.

Table 2. Site : Clio, Michigan: Rates of attenuation $(k \text{ day}^{-1})$ of each of the CoCs calculated and compared to that of toluene $(k_{\text{CoC}}/k_{\text{T}})$. The top rows show benzene and TEX concentrations at the beginning of the time of interest. The initial benzene/ TEX ratio is also shown.

| CLIO | OW-19 | | OW-21 | | OW-22 | |
|----------------------|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|----------------------------------|
| B ppm (initial) | 1.8 | | 0.6 | | 0.9 | |
| TEX ppm (initial) | 46.6 | | 31.4 | | 1.9 | |
| B/TEX | 0. | 04 | 0.02 | | 1.9 | |
| | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T |
| В | 0.0012 | 1.3 | 0.0010 | 0.9 | 0.0024 | 0.7 |
| Т | 0.0009 | 1.0 | 0.0011 | 1.0 | 0.0036 | 1.0 |
| Е | 0.0005 | 0.6 | 0.0002 | 0.2 | 0.0018 | 0.5 |
| Х | 0.0003 | 0.3 | 0.0002 | 0.2 | 0.0023 | 0.6 |



Figure 6. Site: Clio, Michigan: The left hand column of graphs are profiles of CoCs in wells 19, 21, and 22. The right hand column of graphs are ln(CoC) vs time. The natural log data were used to calculate regression statistics and attenuation rate (-k day⁻¹). Rate constants obtained for this site are in Table 2.

Table 3. Site : Indianapolis, Indiana: Rates of attenuation (k day⁻¹) of each of the CoCs calculated and compared to that of toluene (k_{CoC}/k_T). Attenuation was enhanced through addition of sulfate as an electron acceptor. Before enhancement, concentrations were stable but not declining. The top rows show benzene and TEX concentrations at the beginning of the time of interest. The initial benzene/ TEX ratio is also shown. *Note the attenuation rate for toluene from OW-3R was used at OW-17R because at the beginning of the time of interest toluene was practically depleted in OW-17R.

| INDIANAPOLIS | OW-3R | | OW-10R | | OW-17R | | OW-23 | |
|-------------------|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|---------------|------------------------|---------------|
| B ppm (initial) | 0.3 | | 0.73 | | 0.12 | | 0.33 | |
| TEX ppm (initial) | 11.9 | | 16.5 | | 1.02 | | 17.4 | |
| B/TEX | 0.0 |)3 | 0.04 | | 0.12 | | 0.02 | |
| | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k_{CoC}/k_T | k (day ⁻¹) | k_{CoC}/k_T |
| В | 0.00446 | 0.78 | 0.00106 | 0.34 | 0.00413 | 0.73 | 0.00150 | 0.54 |
| Т | 0.00569 | 1.00 | 0.00313 | 1.00 | 0.00569* | 1.00 | 0.00280 | 1.00 |
| Е | 0.00066 | 0.12 | 0.00133 | 0.42 | 0.00471 | 0.83 | 0.00100 | 0.36 |
| Х | 0.00234 | 0.41 | 0.00280 | 0.89 | 0.00277 | 0.49 | 0.00160 | 0.57 |



Figure 7. Site: Indianapolis, Indiana: Profiles of CoCs in wells 3R, 10R, 17R, and 23 used to calculate attenuation rate (-k day⁻¹). Rate constants obtained for this site are in Table 3.

Table 4. Site : St. Clair, Missouri: Rates of attenuation (k day⁻¹) of each of the CoCs calculated and compared to that of toluene (k_{CoC}/k_T). The top rows show benzene and TEX concentrations at the beginning of the time of interest. The initial benzene/ TEX ratio is also shown.

| ST. CLAIR | MW-2 | | MW-3 | | MW-6 | |
|----------------------|------------------------|----------------------------------|------------------------|----------------------------------|------------------------|----------------------------------|
| B ppm (initial) | 0.8 | | 1.25 | | 1.10 | |
| TEX ppm (initial) | 8.78 | | 8.47 | | 11.70 | |
| B/TEX | 0. | 09 | 0.15 | | 0.09 | |
| | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T | k (day ⁻¹) | k _{CoC} /k _T |
| В | 0.0002 | 0.67 | 0.0004 | 0.50 | 0.0007 | 0.64 |
| Т | 0.0003 | 1.00 | 0.0008 | 1.00 | 0.0011 | 1.00 |
| Е | 0.0001 | 0.33 | 0.0004 | 0.50 | 0.0006 | 0.55 |
| Х | 0.0004 | 1.33 | 0.0008 | 1.00 | 0.0009 | 0.82 |





Figure 8. Site: St. Clair, Missouri: Profiles of CoCs in wells 2, 3, and 6 used to calculate attenuation rate (- k day⁻¹).); Rate constants obtained for this site are in Table 4.

Although some individual wells had some wide ranges, on average the ratios of attenuation rates between the compounds were relatively constant within certain brackets from site to site. In this study involving four sites, toluene attenuated at the highest rate followed by benzene which attenuated at rates roughly between 50 and 80% of toluene (average of 70 - 80%), xylenes attenuated at rates roughly between 50 and 95% (average of 60 - 70%) of toluene (which may be dependent upon which xylenes are most abundant), and lastly ethylbenzene attenuated at rates roughly between approximately 45 and 90% (average 50 - 60%) of toluene. These ratios were observed at both natural and sulfate-enhanced attenuation sites and tended to be relatively consistent on a site wide average basis whether natural attenuation was occurring rapidly or slowly. Table 5 shows the average attenuation rates for each compound at each site and the corresponding ratios of attenuation rates. Table 6 illustrates the difference between natural and enhanced and shows the average attenuation rates and ratio of rates (kCoC/kT) from wells under similar conditions.

The rate of attenuation of each compound under enhanced attenuation conditions (by providing electron acceptors like sulfate) is greater than the rates observed under natural conditions. This has been observed in past studies and has been a focus of many publications (Bruce et al 2007a and Kolhatkar et al 2008). However, regardless of the conditions, the ratio of attenuation rate of B, E, or X to that of T does not differ significantly from site to site. The consistent nature of these ratios indicate that attenuation of B, T, E, and X is taking place concurrently at all of these anaerobic sites. The attenuation rate of benzene in the range of 50 to 80% of that of toluene clearly indicates that it is attenuating simultaneously.

This paper also looked at the relationship of benzene attenuation rate with the concentration of B with respect to TEX. Under both natural and sulfate-reducing conditions, qualitatively there was an inverse relationship between benzene attenuation rate and the ratio of the concentration of benzene to that of TEX. However, statistical calculations of this data set did not fall within our defined range for significance. Therefore further research is required to determine if this relationship is valid.

| | Average Attenuation Rates at Each Site | | | | | | | | |
|---|--|----------------------------------|----------------------------|----------------------------------|----------------------|----------------------------------|-----------------------|----------------------------------|--|
| | Antioch (enhanced) | | Indianapolis (enhanced) | | Clio (natural) | | St Clair (natural) | | |
| | -k day ⁻¹ | k _{CoC} /k _T | -k day ⁻¹ | k _{CoC} /k _T | -k day ⁻¹ | k _{CoC} /k _T | -k day ⁻¹ | k _{CoC} /k _T | |
| В | 0.00135 | 0.59 | 0.00279 | 0.72 | 0.00153 | 0.82 | 0.00043 | 0.59 | |
| Т | 0.00229 | 1.00 | 0.00387 | 1.00 | 0.00187 | 1.00 | 0.00073 | 1.00 | |
| Е | 0.00202 | 0.88 | 0.00193 | 0.50 | 0.00083 | 0.45 | 0.00037 | 0.50 | |
| X | 0.00218 | 0.95 | 0.00238 | 0.61 | 0.00093 | 0.50 | 0.00070 | 0.95 | |

Table 5. Site wide average attenuation rates and their ratios compared to toluene

| | average k (day ⁻¹) enhanced | average k (day ⁻¹) natural | k _{CoC} /k _T enhanced | k _{C₀C} /k _T natural |
|---|---|--|--|---|
| В | 0.0021 | 0.0010 | 0.7 | 0.8 |
| Т | 0.0031 | 0.0013 | 1.0 | 1.0 |
| Е | 0.0020 | 0.0006 | 0.6 | 0.5 |
| X | 0.0023 | 0.0008 | 0.7 | 0.6 |

Table 6. Average attenuation rate for 6 wells under natural attenuation and 7 wells under enhanced attenuation conditions. $\mathbf{k}_{CoC}/\mathbf{k}_{T}$ gives the ratio of attenuation rate of B, E, or X to that of toluene

4. CONCLUSION

This study demonstrated that under anaerobic conditions there is a hierarchy of attenuation rates for B, T, E, and X independent of whether a site is degrading rapidly or slowly or whether attenuation is natural or enhanced via a supply of electron acceptors. At the four Midwestern sites in this study, toluene attenuated at the highest rate followed by benzene which attenuated at average rates of 70 - 80% of toluene, xylenes which attenuated at average rates of 60 - 70% of toluene (which may be dependent upon which xylenes are most abundant), and lastly ethylbenzene which attenuated at average rates of 50 - 60% as high as toluene. The consistent nature of these ratios demonstrated that attenuation of B, T, E, and X took place concurrently at all of these anaerobic sites, and that benzene was not recalcitrant. The addition of electron acceptors, such as sulfate, increased the overall attenuation rates, but did not affect the order or ratios in the hierarchy.

Qualitatively there was an inverse correlation between the benzene attenuation rate and the ratio of benzene concentration to the combined concentration of toluene, ethylbenzene, xylenes (B/TEX). But this correlation was not statistically significant in this data set and will be the focus of a future study.

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Anaerobic Degradation of Benzene was Enhanced through Sulfate Addition Substantially Increasing the HC Degradation Rate at a Central Indiana Site. Lyle Bruce, Jim Cuthbertson, Arati Kolhatkar, J. Scott Ziegler, and Brent Graves

At this Central Indiana site, dissolved BTEX levels were relatively high fifteen years after the service station closed. Despite the facts that the UST source area had been over excavated at the time the facility closed and a pump and treat system had operated for a period of time, concentrations were still too high to qualify for MNA. In 2004, dissolved benzene levels near the source area hovered at 1000 ppb. The dissolved plume was neither growing nor shrinking. If the source area could be addressed, the plume should shrink. Excavation was not an option because the site had already been redeveloped. Inorganic analyses showed that dissolved sulfate was present naturally in the aquifer outside the hydrocarbon plume with a mean concentration of 78 mg/l. In the dissolved phase BTEX plume area, however, sulfate concentrations were substantially reduced to concentrations less than 10 mg/l. Additionally, a shadow of reduced sulfate concentration extended downgradient of the plume area. This was a very strong indicator that the hydrocarbon plume had gone anaerobic and was undergoing sulfate reducing conditions. In 2004, high concentration sulfate solutions were added to the source area through an infiltration trench three times over a five month period. Within 841 days from the last application, dissolved benzene concentrations had decreased an order of magnitude and the site met criteria for MNA. Wells in the source area progressed from stable benzene concentrations (no apparent trend) to attenuation rates between -0.0022 to -0.0064 per day (half lives between 315 and 108 days). This site demonstrates that if a plume is already undergoing natural sulfate reduction, the addition of concentrated sulfate solution to the source area will increase the attenuation rate. Ethylbenzene did not decrease in concentration in some wells that had substantial benzene declines. This is evidence of selective degradation by the microorganisms and that dilution was not a factor in the attenuation rates.

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INTRODUCTION

Petroleum contamination was discovered at this site on the south side of Indianapolis, Indiana, one year before it closed in 1990. It had been a service station for 26 years. The response to the contamination was to take out the underground storage tanks and overexcavate the tank basin to remove contaminated soil.

Dissolved phase contamination persisted. Therefore, a pump and treat system with air strippers was installed in 1996. It was deactivated a year later because poor groundwater recharge caused the system to run inefficiently. The system had treated approximately 124,000 gallons of groundwater, or about one pore volume from the contaminated area.

It was thought that the contamination would attenuate naturally. But 15 years after discovery (as of 2004), the plume was stable but not shrinking, and hydrocarbon concentrations were more or less constant. Concentrations were too high for closure using monitored natural attenuation (MNA).

The limiting factor for site closure was the benzene concentration which hovered near 1000 ppb in the heart of the plume just downgradient of the former tank basin. Based on the location of highest dissolved phase hydrocarbon contamination, a backward "L" shaped smear zone source area appeared to extend roughly north-south and east west from the west side of the former tank basin.

The stable plume indicated that attenuation was occurring, but that a source was adding contamination at about the same rate as it was degrading. The remediation team decided to try to increase the rate of hydrocarbon degradation and thereby lower concentrations and shrink the plume. This could be done by adding oxygen releasing compounds (ORC) to the plume and source area. However, recent experience indicated that adding ORC would be costly and would probably require adding much more oxygen than simple calculations specified.

Additionally, there were geochemical indications that the plume was degrading anaerobically. For oxygen to work it would require changing the natural system that had developed, which would take time and probably require even more ORC treatment material.

Based on recent experience, and a solid body of published research (Anderson and Lovely, 2000; Chapelle, 2001; Cunningham, et al., 2001; Kolhatkar, et al., 2000; Wiedemeir, et al., 1999; and Wilson, et al., 2002) the team decided to try to enhance the natural processes already at work on the site. The chosen solution was to add concentrated Epsom salt solution (hydrated magnesium sulfate) to the source area and plume. This method utilized a nontoxic household chemical to provide a needed electron acceptor for preexisting sulfate-reducing-bacteria (SRB) to flourish and increase their rate of hydrocarbon degradation.

GEOLOGY AND HYDROGEOLOGY

The location is in the Central Lowlands physiographic province. The geology beneath the site consists of unconsolidated glacial drift deposits. The primary water bearing formation is sand and clayey sand with an average hydraulic conductivity of about one foot per day. The excavation at the former UST basin was backfilled with gravel which has a much higher hydraulic conductivity than the sand. Only the base of the gravel intersects the water table. The sandy zone is overlain by silt and silty clay to the surface. The contact between sand and silty clay plunges toward the north-northwest and intersects the water table in the northwest quarter of the site. Figure 1 is a base map of the site. Figures 2 and 3 are geologic cross sections from west to east and north to south respectively.



Figure 1: Base map.



Figure 2: Cross section X-X' vertical exaggeration 7.5X



Figure 3: Cross Section Y-Y' vertical exaggeration 7.5X

Figure 4 is a water table map as of January, 2007. Gradient is predominantly toward the northwest at 0.035 ft/ft. Groundwater seepage velocity is approximately 37 feet per year.



Figure 4: Water table map as of January 25, 2007. CI 1 ft. Artificial datum with a surface point set at 100.

Figure 5 shows contours of the benzene concentrations in May, 2004 before any sulfate addition. The contaminant source zone was projected to lie beneath the area of highest dissolved benzene concentration. It coincides with the downgradient side of the former tank basin and where product lines ran from the USTs to dispensers (aka "the gas pumps").



Figure 5: Benzene concentration map at the Indianapolis site as of May, 2004, and a graph showing a benzene concentration over time on the upgradient side of the source zone. The source area is projected to be a backward "L" shaped smear zone located on the west side of the former tank basin.

EVIDENCE OF ANAEROBIC DEGRADATION

Lateral changes in the concentration of some inorganic ions in groundwater across a hydrocarbon plume may provide indicators that microbial degradation is occurring and whether it is aerobic or anaerobic (Chapelle, 2001).

For example, if oxygen is abundant in background-groundwater and it is essentially depleted in the dissolved phase plume area, then we can assume that aerobic degradation has occurred. Similarly, if sulfate is present in the background and depleted in the plume area, we can assume that sulfate reduction has occurred, which is anaerobic. Both

systems may be active, but in different zones or areas of the plume. In most cases where groundwater is contaminated with petroleum hydrocarbons, oxygen is consumed on the upgradient side of the contaminant source area. The plume then undergoes anaerobic degradation in a hierarchy of successive zones depending on the availability of electron acceptors. Table 1 shows this hierarchy.

| TEAP Zone Processes and Parameters | | | | | | | | |
|---|-----------|----------------|-------------|-----------------|--|--|--|--|
| Electron | Reaction | Metabolic | Utilization | Thermodynamic | | | | |
| Acceptor | | Byproduct | Factor for | Reaction | | | | |
| | | | BTEX | Preference | | | | |
| Oxygen | Aerobic | CO_2 | 314 | Most Preferred | | | | |
| Nitrate | Anaerobic | N_2 , CO_2 | 4.9 | ↓ | | | | |
| Fe III (solid) | Anaerobic | Fe II* | 21.8* | ↓ | | | | |
| Sulfate | Anaerobic | H_2S | 4.7 | ↓ | | | | |
| CO ₂ | Anaerobic | Methane* | .78* | Least Preferred | | | | |

Table 1: Hierarchy of terminal electron acceptor process (TEAP) zones and their associated processes and parameters. Utilization factors indicate how many grams of an electron acceptor are required to degrade one gram of BTEX (those with an asterisk use the metabolite rather than the electron acceptor). They are from Wiedemeier, et al., 1999.

The typical distribution of these TEAP zones in a petroleum contaminated aquifer is shown in Figure 6. The relative size or area of a given process is usually dependent on the availability of a given terminal electron acceptor. Oxygen is usually only available in near surface groundwater in concentrations up to 7 or 8 mg/l. Nitrate is seldom available in quantity, and iron III (ferric iron) is nearly insoluble in water and is taken up by iron reducing bacteria from bio-available iron in soil minerals. In the iron reduction process, iron III is reduced to soluble iron II (ferrous iron) which is the primary cause for increased dissolved iron in the contaminated zone. This iron stays in solution until it either mineralizes with available sulfide from the sulfate reducing zone, or precipitates when redox conditions change in the aquifer downgradient of the plume.



Figure 6: Typical profile of TEAP zones at a petroleum contaminated aquifer with a contaminant source area.

Sulfate is a very common and abundant natural groundwater ion. Sulfate concentrations average 25 to 100 mg/l in many areas of the United States, and it is not uncommon to have concentrations in the several hundred mg/l range. Because of this natural abundance, sulfate reduction is a major process in natural attenuation of hydrocarbon contamination.

At the Indianapolis site, in addition to BTEX compounds, nitrate and sulfate were analyzed in groundwater from background and plume observation wells. There was little or no nitrate in the background or the plume, and therefore no contrast to compare.

Background sulfate concentrations, however, were as high as 155 mg/l and averaged 78 mg/l. Sulfate depleted rapidly to less than 10 mg/l as groundwater migrated through the contaminant source area. There is also a shadow of low sulfate concentration immediately downgradient of the plume. Figure 7 shows the distribution of sulfate in groundwater in the area of interest before any treatments were applied.

The inverse relationship between the presence of BTEX contamination and the depletion of natural sulfate in the plume area is direct evidence that hydrocarbon degradation through sulfate reduction is occurring at the site. Figure 8 is a graph of sulfate versus benzene concentration across the plume before any sulfate treatment.



Figure 7: Sulfate distribution at the Indianapolis site prior to any treatment to enhance degradation.



Figure 8: Benzene versus sulfate concentration across the plume prior to any sulfate addition.

TREATMENT STRATEGY

The remediation team decided to enhance the preexisting sulfate reduction process by providing sulfate as an electron acceptor to the part of the plume where it was most needed – the smear zone source area. Sulfate requirements were estimated based on the stoichiometric mass of sulfate required to biodegrade the mass in the source zone.

We determined the most effective means to address the source area at this site was with an "L" shaped trench through the most contaminated region. The trench was about 160 feet north-south by 80 feet east-west (Figure 1) with eight sump-access-points evenly spaced along the length. Depth to groundwater was about eight feet, so the trench was installed to a depth of 10 feet and backfilled with coarse gravel.

Concentration, Mass, and Volume

Note that because the plume is stable, we have already demonstrated that the amount of dissolved phase contamination being contributed by the source is being degraded by and in balance with the available natural electron acceptors. Because the contaminant concentrations in the plume were still too high, we needed to reduce the source. To estimate the mass of sulfate required, we estimated the mass of contaminants in the source area to be addressed.

There is considerable uncertainty involved in estimating the mass of dissolvable contaminants in the source zone. Nevertheless, in order to estimate treatment volumes an estimate of the source must be made. Fortunately, there was no free phase contamination to deal with.

Gallagher (1995) proposed that the source area be divided into three zones: 1) the vadose zone, 2) the smear zone which is the residual in the area of groundwater fluctuation and 3) the dissolved phase in the phreatic zone. We considered the vadose zone to be already

in balance. The phreatic zone source was addressed by over excavation when the USTs were removed. Therefore we focused on the smear zone.

In most cases, detailed soil analyses are not available to calculate contaminant mass accurately. Gallagher suggested that the contaminant mass in the smear zone can be estimated using a map of dissolved phase concentration, the average contaminant concentration in the soil of the smear zone, and the smear zone thickness. He used the following equations:

M = p * V

Where: $p = soil density in kg/ft^3$ (approximately 65 kg/ft³) And V = calculated volume as given below

 $\mathbf{V} = (\mathbf{T}\mathbf{x} * \mathbf{C}\mathbf{x} * \mathbf{A}\mathbf{x})$

Where:

Tx = thickness of smear zone in feet
Cx = Average contaminant concentration in smear zone soil (mg/kg)
Ax = Area of smear zone (using the area within a designated contaminant contour)*

*Ax may be estimated by contouring the dissolved phase contamination and measuring the area inside a selected contour. Gallagher suggested using the 3000 ppb total BTEX contour.

| Tx | 10 | ft | Input |
|------|-------------|--------------------|------------|
| Cx | 200 | mg/kg | Input |
| Ax | 4,000 | ft^2 | Input |
| V | 8,000,000 | mg/kg-ft3 | calculated |
| р | 65 | kg/ft ³ | given |
| Mass | 520,000,000 | mg | calculated |

The following table shows the estimate for the Indianapolis site.

Table 2: Estimated mass of BTEX contamination in the source zone

The calculated mass of the source was about 520 kilograms, or almost 1150 pounds (equivalent to about 175 gallons of gasoline). Based on a utilization factor of 4.7 grams of sulfate to one gram of benzene, it was estimated that 2,444 kilograms (5,388 pounds) of sulfate would be needed. Based on experience, demand is usually somewhat higher because of the presence of other organic chemicals or contaminants. Therefore a safety factor is frequently applied which ranges approximately between 2 and 4 times the estimated amount. At this site we used 1.75 to minimize initial sulfate mass.

In addition to being a household chemical, Epsom salts solution is also sprayed on fields as an agricultural soil amendment. The standard agricultural concentration is 3 pounds

per gallon which yields a sulfate solution of approximately 140,000 mg/l. Because this is readily available, we decided to base the volume of solution to be applied using this concentration.

TREATMENTS

Sulfate solution was applied to the trench through the application sumps according to the schedule shown in Figure 9. There were three major applications on June 3, July 27 and October 26, 2004 and one minor application December 15, 2005. Total volume applied from all treatments was 6,781 gallons (30,800 liters), which provided 4,312 kilograms (9,500 pounds) of sulfate which was a safety factor of 1.75 over the calculated volume.



Figure 9: Schedule of sulfate applications

<u>RESULTS</u>

Within 841 days from the last application, dissolved benzene concentrations had decreased an order of magnitude and the site met criteria for MNA. Wells downgradient of the application trench progressed from stable benzene concentrations (no apparent downward trend) to attenuation rates between -0.0022 to -0.0064 per day (half lives between 315 and 108 days). The plume visibly shrank (Figures 10 and 11). A contaminated control well upgradient of the trench showed no decreasing trend in benzene concentration.



Figure 10: Benzene concentrations pre-application and during applications.



Figure 11: Benzene concentrations 532 days and 841 days after October 4 application.



Figure 12: Water table maps before, and one day after the first application

Decreased concentrations were not due to dilution. The applied volumes were insignificant (maximum 2500 gallons in an application) compared to the plume pore volume of approximately 124,000 gallons. Figure 12 shows groundwater contour maps from before, and one day after the initial treatment. There is no appreciable change.

Based on groundwater flow calculations, the applied volume of sulfate resulted in a dilution of less than 4 to 8% per month and less than 2% per year during the application period. This was within the analytical variability.

Additionally, benzene and toluene concentrations declined at a substantially greater rate than xylenes or ethylbenzene. In fact ethylbenzene hardly declined at all, indicating a preferred sequence of degradation. If dilution were significant the concentrations would have decreased proportionately.

Figures 13 and 14 are example BTEX graphs. Well OW-10R is seven feet from the trench and within the sulfate treatment zone. Benzene and toluene degraded before ethylbenzene and xylenes.

Well OW-22 is 28 feet upgradient of the trench and was used as a control well. This well did have one 21 gallon sulfate treatment, but overall it was not in the treatment zone, and did not show decreases in concentrations of benzene, ethylbenzene or xylenes.



Figure 13: BTEX graphs from well OW-10R from March 2004 to January 2007. The well is seven feet from the application trench. Arrows indicate dates of sulfate application to the trench. Concentrations are in ppb. Note decreases in benzene and toluene.



Figure 14: BTEX graphs from well OW-22. This well is a control well 28 feet upgradient of the trench. It had one 21 gallon treatment (arrow) on 10/26/04.

Regulators asked if a significant volume of dissolved oxygen, inadvertently added with the treatment fluid, would have affected degradation. The answer is no. Assuming the treatment water carried dissolved oxygen at a concentration of approximately 8 mg/l, and there were no sinks other than BTEX, with the utilization factor for oxygen equal to 3.14 grams of oxygen per gram of BTEX, the amount of introduced oxygen would have degraded less than 80 grams of BTEX versus an estimated 520,000 grams degraded by sulfate addition.

Another concern was the concentration of sulfate at the compliance point which should meet the secondary MCL of 250 mg/l sulfate. Figure 15 is a contour map of sulfate concentration 841 days after the last application. It appears that nearly the entire amount of added sulfate was consumed. The calculated rate of sulfate consumption was -0.01 per day yielding a half life for sulfate in the plume of approximately 69 days.



Figure 15: Sulfate concentration 841 days after sulfate applications – there was still reduced sulfate concentration in the plume area with no appreciable increase downgradient.

CONCLUSION

The addition of sulfate enhanced the natural anaerobic process, increasing the rate of sulfate reduction and hydrocarbon degradation. Within 841 days of the last sulfate treatment, the plume had shrunk and benzene concentrations were within regulatory levels to apply for MNA closure.

This site demonstrates that if a plume has already entered the sulfate reduction phase, the addition of sulfate to the source area will stimulate the existing processes and increase the hydrocarbon biodegradation rate.

Sampling results also suggest that, through proper planning, the sulfate concentrations in the aquifer can be controlled during the application process in order to prevent sulfate concentrations above the secondary drinking water standard from leaving the site location if receptors downgradient are a concern. Finally, sulfate enhanced biodegradation appears to be a viable alternative remediation approach for developed properties that are sensitive to disruptions associated with more invasive remedial actions such as excavation or large pump and treat systems.

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Enhanced Anaerobic Biodegradation of Petroleum Hydrocarbons in Groundwater

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Abstract

At many sites, sulfate reducing bacteria have been demonstrated to be a dominant factor in the natural anaerobic biodegradation of petroleum hydrocarbons dissolved in groundwater. There are many benefits of providing sulfate as a 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 enhancement 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 (as compared to oxygen) can be added to groundwater due to its high solubility. 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. Case studies that demonstrate the benefits of enhancing the sulfate concentrations in groundwater to stimulate the biodegradation of petroleum contaminants under field conditions are presented.

1.0 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; Wiedemeier et al., 1999). 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 full scale implementation of anaerobic biodegradation at sites in Michigan, Washington, D.C. and Maryland.

2.0 PROCESS OVERVIEW

The process of providing supplemental sulfate in order to enhance the rate of biodegradation of hydrocarbons dissolved in the groundwater can be accomplished utilizing a variety of techniques. The process utilized in the case studies presented here involves the use of a nearly saturated, aqueous solution of sulfate. There are several advantages associated with using this application material including the bioavailabilty of the applied sulfates, ease of application to the subsurface and relative low cost per unit of electon acceptor mass. Since the sulfate is already dissolved in water, it is immediately available for utilization by the existing bacteria present in the formation. The aqueous solution can be applied by gravity flow via specifically designed and installed application wells/trenches; previous remediation system structures which may be suitable depending on specific site conditions (i.e., soil vapor extraction wells, air sparge points, recovery trenches, etc.); or under certain circumstances sprayed on the ground surface and allowed to infiltrate to the groundwater.

3.0 GENERAL SITE SELECTION CRITERIA

In general, the following criteria are evaluated to consider the feasibility of implementing sulfate enhanced biodegradation:

- 1. Decrease in dissolved oxygen (field measure) from several mg/l background to less than 1 mg/l in the plume. However, due to equipment limitations DO measurements have frequently been found to be inaccurate. Use of appropriate, calibrated instruments and well trained technicians to ensure correct DO measurements is highly recommended.
- 2. pH should be near neutral to 8. Care should be taken under acidic conditions due to the increased potential for generation of hydrogen sulfide.
- 3. Change in redox potential in millivolts (field measure) from positive outside the plume to negative within the plume, preferably with -100 millivolts or lower in the plume.
- 4. Decrease in nitrate concentration, if present outside the plume, should decrease significantly within the plume.
- 5. Increase in dissolved iron concentration (Fe II only from filtered samples) from very low or near non-detect in the background to several mg/l in the plume.
- 6. Decrease in sulfate concentration in the plume as compared to natural background concentration.
- 7. Phospolipid Fatty Acid (PLFA) analysis to confirm the presence of a population of sulfate reducing bacteria.

These parameters should be viewed as a profile from background across the plume. However, not every parameter is required.

4.0 CASE STUDIES

4.1 Potterville, Michigan – Benzene, Toluene, Ethylbenzene and Xylenes

A former gasoline service station located in Potterville, Michigan had confirmed releases of gasoline reported to the state regulatory agency in 1992 and 2001 (Cuthbertson, et al., 2006). The general site lithology is predominately silty clay with sand fill associated with the former underground storage tank (UST) system installation. The first groundwater encountered is perched and is located approximately one to two feet beet below ground surface (bgs). Measurable thicknesses of liquid phase hydrocarbons were present through March of 2003. The majority of the site pavement was removed during site decommissioning work. Prior to implementing sulfate enhanced biodegradation, several other remedial technologies including high vacuum multiphase extraction, monitored natural attenuation, bioaugmentation and oxygen infusion were attempted and deemed to be ineffective.

An evaluation of existing geochemical conditions indicated that the contaminant plume was highly anaerobic with depleted (in comparison to non-impacted background samples) dissolved oxygen, nitrate and sulfate along with elevated dissolved iron concentrations. Since the groundwater was quite shallow, the sulfate solution was applied by spreading across the ground surface and allowing it to infiltrate through the overburden soils. Seven applications of sulfate solution were made between September of 2003 and January of 2005. A total of approximately 2,500 pounds of sulfate were applied to the site.



Figure 1. Total benzene, toluene, ethylbenzene and xylene (BTEX) and sulfate concentrations over time at monitoring well OW-18.

Figure 1 shows that when the sulfate concentrations were enhanced, the BTEX concentrations declined by more than 75% in OW-18 which was located within the former UST pit. Over time, the BTEX concentrations remained below target remedial objectives for that location and sulfate concentrations dropped below drinking water criteria.



Figure 2. BTEX and sulfate concentrations over time at monitoring well OW-4.

OW-4 was located downgradiant of the former UST pit, but was within the area treated with sulfate solution applications. Figure 2 shows that when the sulfate concentrations were enhanced the BTEX concentrations declined by more than 95%. Over time the BTEX concentrations remained below target remedial objectives for that location and sulfate concentrations dropped below drinking water criteria.



Figure 3. BTEX and sulfate concentrations over time at monitoring well OW-24.

In Figure 3, BTEX and sulfate concentrations over time are presented for OW-24 which was located further downgradiant of the former UST pit and OW-4, but was more than 25 feet outside the area treated with sulfate solution applications. At OW-24, when the sulfate concentrations were enhanced, the BTEX concentrations declined by more than 70%. However, since this monitoring point was outside of the area of direct application of sulfate the reductions in BTEX concentrations were less rapid due to the time needed for residual sulfates to migrate downgradient.

4.2 Washington, D.C. – Methyl Tert Butyl Ether

Four active petroleum service stations with releases of unleaded gasoline located in Washington, D.C. were selected to evaluate the effectiveness of sulfate enhanced biodegradation for the remediation of methyl tert butyl ether (MTBE) (Hansen, et al., 2009). General lithology consisted of tight clays and silts with interbedded saturated sand seams from one to three feet in thickness. An aqueous solution of sulfate was applied by gravity flow to four to seven application wells installed within the source area(s) at each site. Depending on the size of the contaminant plume and the overall MTBE concentrations, approximately 300 to 1,000 pounds of sulfate were applied at each site.



Figure 4. MTBE concentations pre and post application at four wells at a site in Washington, D.C.

Post application performance data was collected four times during a 180 day period and the results in comparison to the average MTBE concentrations from the 12 month interval prior to application at one of the sites are summarized on the Figure 4. The results presented in Figure 4 are typical for all four of these sites with a 57% overall reduction in MTBE concentrations observed across the four sites during the 180 day post application monitoring period. Radiuses of influence from 10 to 45 feet were observed.

4.3 Silver Springs, Maryland – Tertiary Butyl Alcohol

The site is an active petroleum service station located in Silver Spring, Maryland with a historical release of unleaded gasoline (Hansen, et al., 2010). The site was selected for the evaluation of sulfate enhanced biodegradation due to the presence of well documented tertiary butyl alcohol (TBA) impact. The lithology at the site consists of saturated coarse sand seams interbedded with saprolite. The target area for remediation was an area of approximately 10,000 square feet (100 feet by 100 feet). Approximately 1,250 pounds of sulfates were applied in an aqeous solution distributed by gravity through seven application wells installed throughout the target remediation area. Post application monitoring was performed five times during a 14 month period.



Figure 5. TBA concentations pre and post application in four wells at the Silver Spring, Maryland site.

Figure 5 shows that post-application TBA concentrations have declined an average of 80% across the test wells during the 14 month monitoring period. Observed radius of influence was between 20 and 80 feet. Similar reductions of post-application BTEX and MTBE concentrations in conjunction with declining sulfate concentrations were also noted in these wells.

5.0 CONCLUSIONS

Sulfate enhanced biodegradation has been demonstrated to be an effective technique for expediting the remediation of groundwater impacted with petroleum hydrocarbons by releases from leaking USTs. Case studies demonstrate successful implementation for a variety of contaminants including BTEX, MTBE and TBA. No adverse impacts associated with the implementation of sulfate enhanced biodegradation were noted at any of the case study sites. Sulfate enhanced biodegradation is not only a highly effective remediation technology, but is also very cost effective in comparison to other more conventiontial remedial technologies.

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