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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.

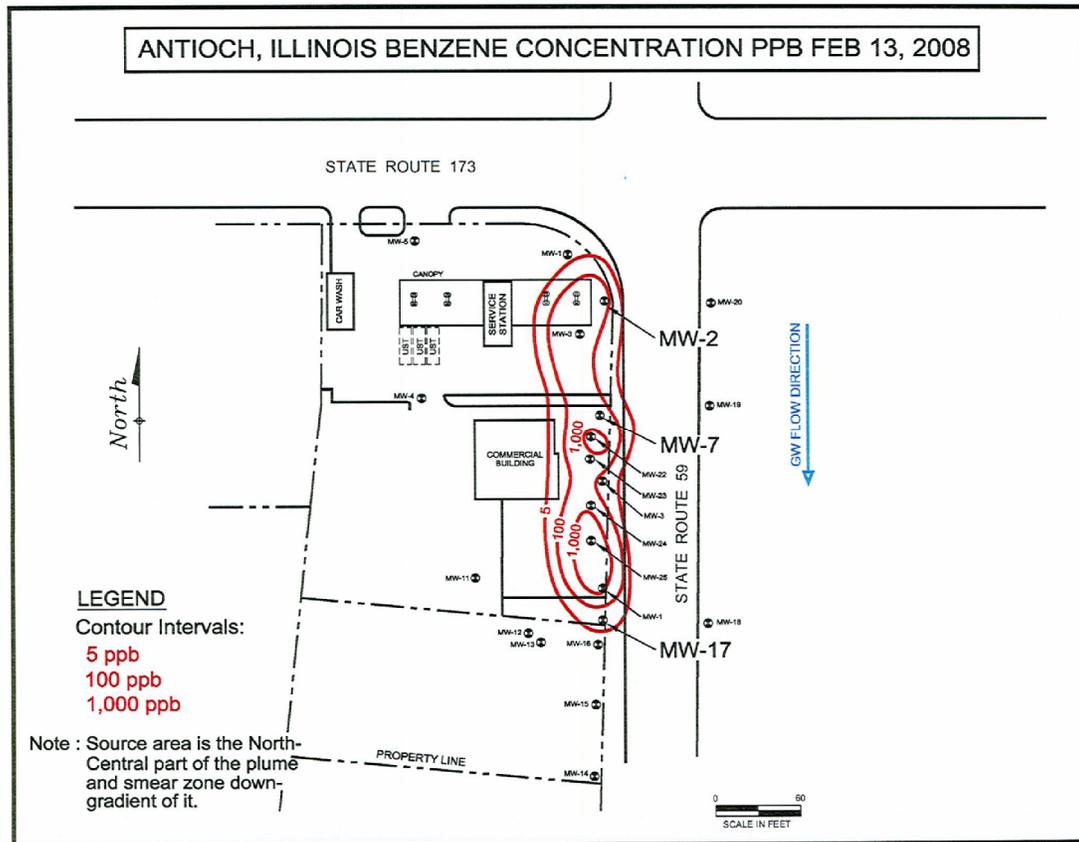


Figure 1. Site map of Antioch, Illinois with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

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.

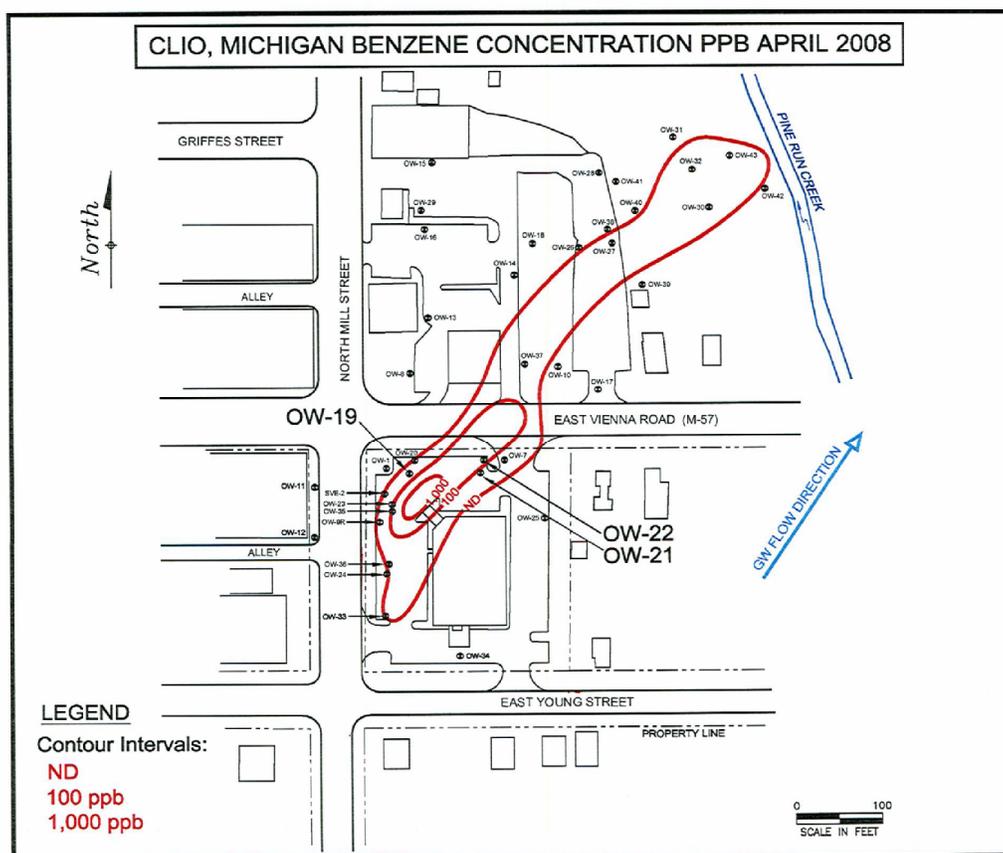


Figure 2. Site map of Clio, Michigan with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

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 extended downgradient of the plume area. This was a very strong indicator that the hydrocarbon 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.

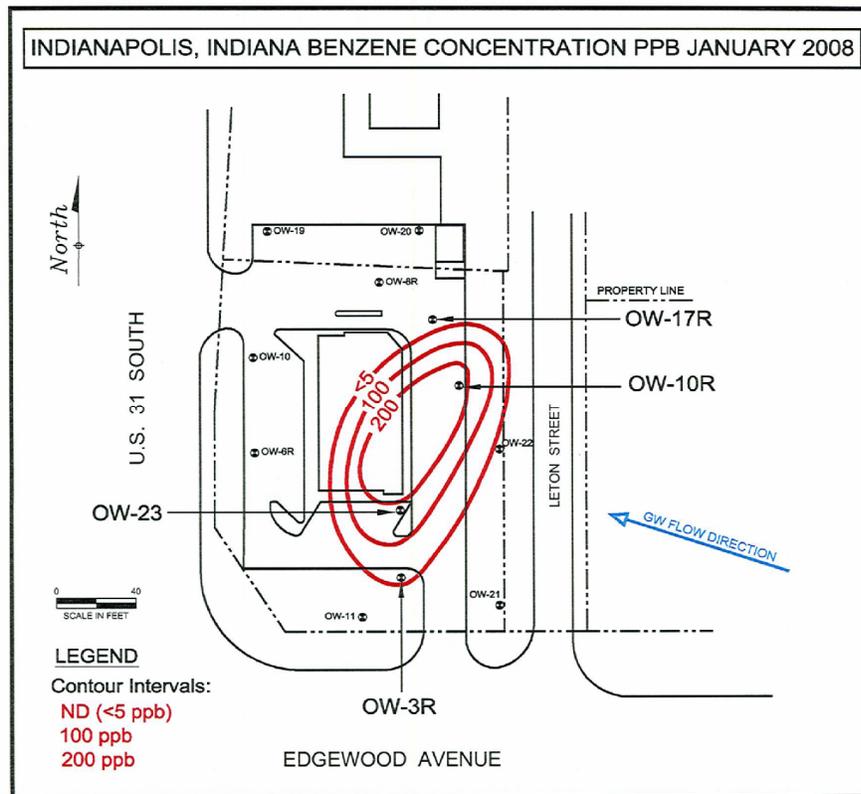


Figure 3. Site map of Indianapolis, Indiana with benzene concentration contours. The outer contour is 5 ppb. The contours increase in value inward.

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.

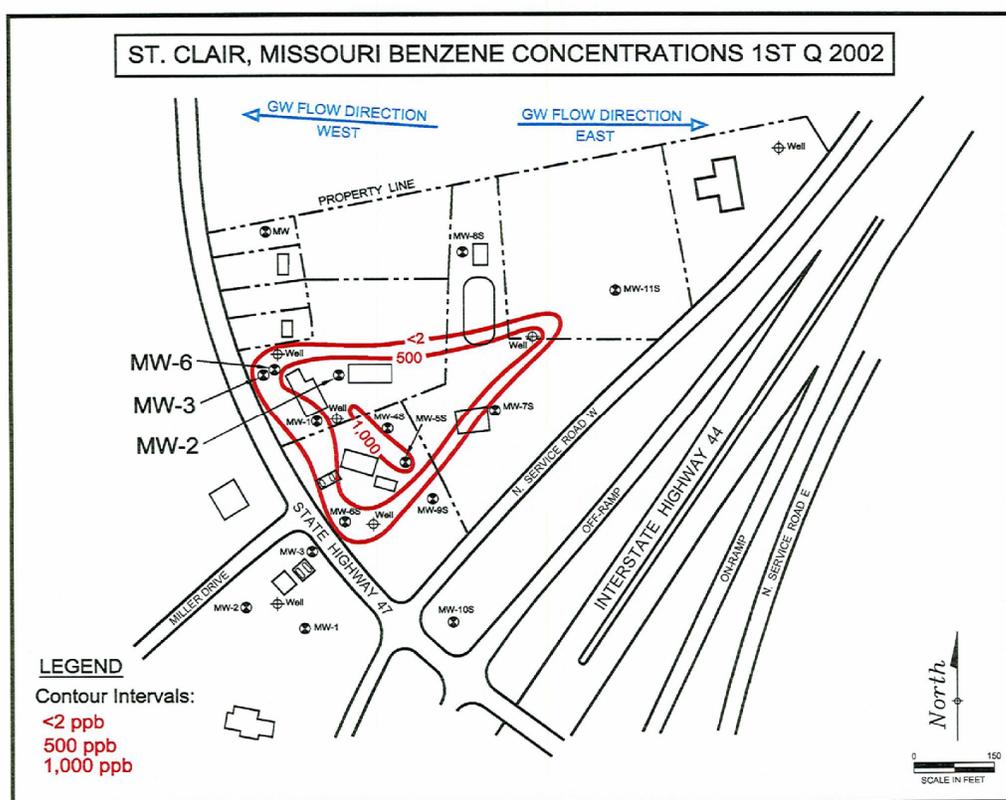


Figure 4. Site map of St. Clair, Missouri with benzene concentration contours. The outer contour is 5 ppb. The contours increased in value inward

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. $\ln(\text{CoC})$ 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. $\ln(\text{CoC})$ 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.

$$(CoC)_t = e^{-kt}(CoC)_o \quad \text{-----(1)}$$

$$\ln(CoC)_t = -k t * \ln(CoC)_o \quad \text{-----(2)}$$

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

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

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 ≥ 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 $k(\text{day}^{-1})$. The ratio of attenuation rate of benzene, ethylbenzene, and xylenes to the attenuation rate of toluene ($k_{\text{CoC}}/k_{\text{T}}$) 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 ($k_{\text{CoC}}/k_{\text{T}}$). 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 | |
| | $k (\text{day}^{-1})$ | $k_{\text{CoC}}/k_{\text{T}}$ | $k (\text{day}^{-1})$ | $k_{\text{CoC}}/k_{\text{T}}$ | $k (\text{day}^{-1})$ | $k_{\text{CoC}}/k_{\text{T}}$ |
| B | 0.0009 | 0.4 | 0.0008 | 0.6 | 0.0024 | 0.7 |
| T | 0.0021 | 1.0 | 0.0012 | 1.0 | 0.0036 | 1.0 |
| E | 0.0009 | 0.4 | 0.0021 | 1.7 | 0.0032 | 0.9 |
| X | 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.

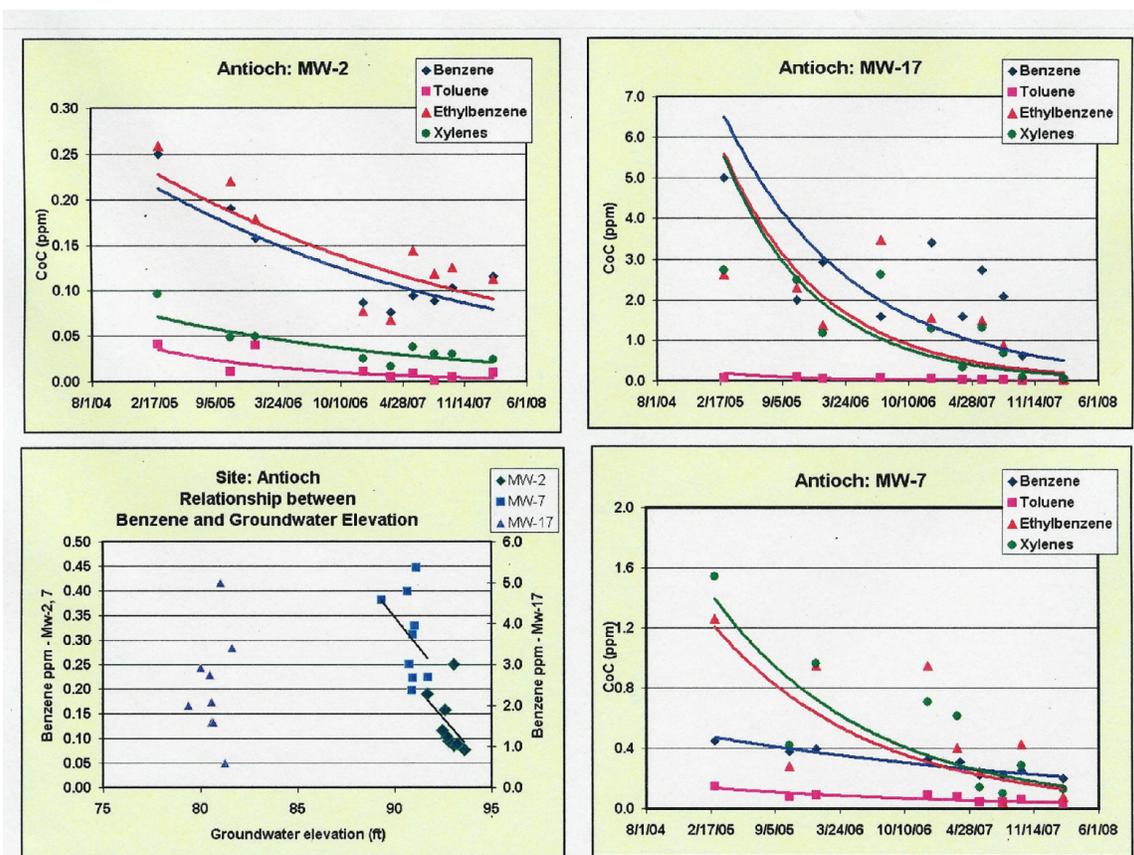


Figure 5. Site: Antioch, Illinois: Profiles of CoCs in wells 2, 7, 17 used to calculate attenuation rate ($-k \text{ day}^{-1}$); The graph in the lower left, benzene vs groundwater in the 3 wells, showed that there was no correlation between CoC concentration and groundwater fluctuation.

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_{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.

| 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 | |
| | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T |
| B | 0.0012 | 1.3 | 0.0010 | 0.9 | 0.0024 | 0.7 |
| T | 0.0009 | 1.0 | 0.0011 | 1.0 | 0.0036 | 1.0 |
| E | 0.0005 | 0.6 | 0.0002 | 0.2 | 0.0018 | 0.5 |
| X | 0.0003 | 0.3 | 0.0002 | 0.2 | 0.0023 | 0.6 |

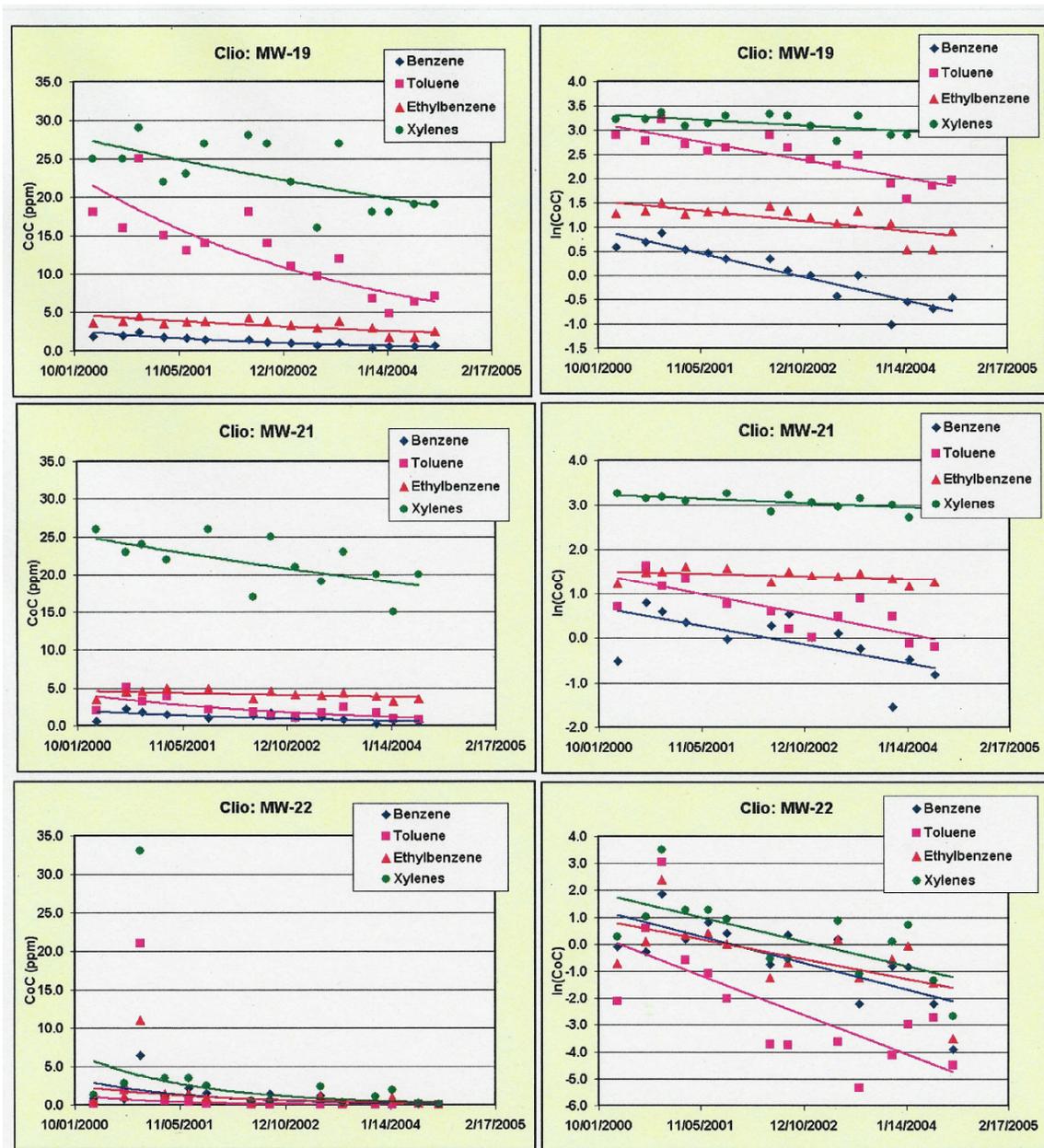


Figure 6. Site: Clio, Michigan: The left hand column of graphs are profiles of CoCs in wells 19, 21, and 22. The right hand column of graphs are ln(CoC) vs. time. The natural log data were used to calculate regression statistics and attenuation rate ($-k \text{ day}^{-1}$). Rate constants obtained for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

Table 3. Site : Indianapolis, Indiana: Rates of attenuation ($k \text{ day}^{-1}$) 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 | 0.03 | | 0.04 | | 0.12 | | 0.02 | |
| | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T |
| B | 0.00446 | 0.78 | 0.00106 | 0.34 | 0.00413 | 0.73 | 0.00150 | 0.54 |
| T | 0.00569 | 1.00 | 0.00313 | 1.00 | 0.00569* | 1.00 | 0.00280 | 1.00 |
| E | 0.00066 | 0.12 | 0.00133 | 0.42 | 0.00471 | 0.83 | 0.00100 | 0.36 |
| X | 0.00234 | 0.41 | 0.00280 | 0.89 | 0.00277 | 0.49 | 0.00160 | 0.57 |

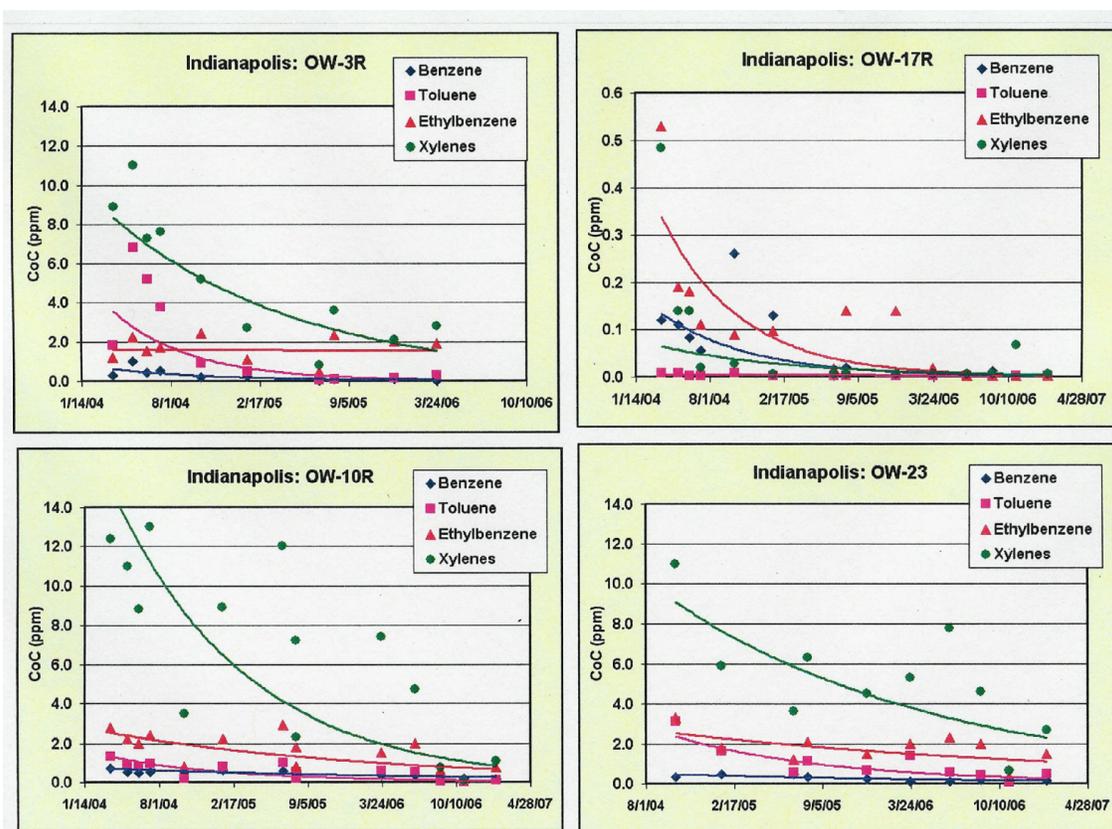


Figure 7. Site: Indianapolis, Indiana: Profiles of CoCs in wells 3R, 10R, 17R, and 23 used to calculate attenuation rate ($-k \text{ day}^{-1}$). Rate constants obtained for this site are in Table 3.

Table 4. Site : St. Clair, Missouri: Rates of attenuation ($k \text{ day}^{-1}$) 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 | |
| | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T | $k \text{ (day}^{-1}\text{)}$ | k_{CoC}/k_T |
| B | 0.0002 | 0.67 | 0.0004 | 0.50 | 0.0007 | 0.64 |
| T | 0.0003 | 1.00 | 0.0008 | 1.00 | 0.0011 | 1.00 |
| E | 0.0001 | 0.33 | 0.0004 | 0.50 | 0.0006 | 0.55 |
| X | 0.0004 | 1.33 | 0.0008 | 1.00 | 0.0009 | 0.82 |

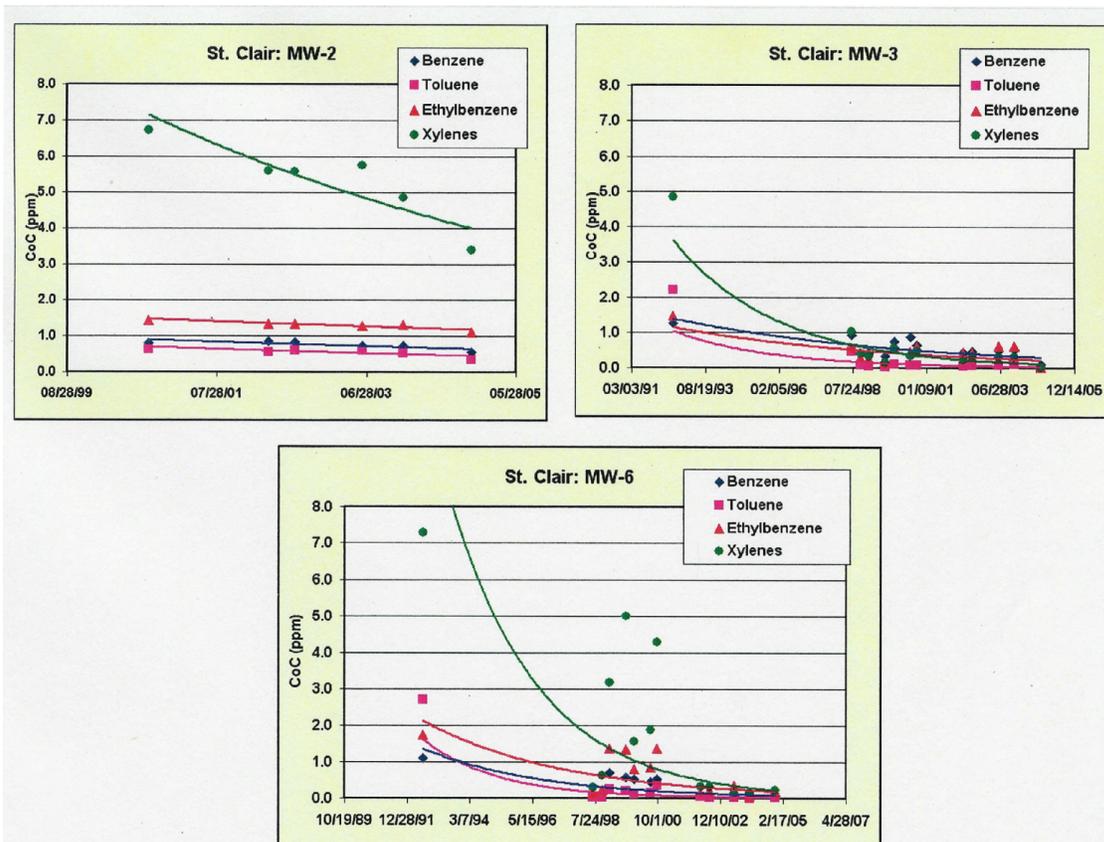


Figure 8. Site: St. Clair, Missouri: Profiles of CoCs in wells 2, 3, and 6 used to calculate attenuation rate ($-k \text{ day}^{-1}$); Rate constants obtained for this site are in Table 4.

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 (k_{CoC}/k_T) 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.

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

| | Average Attenuation Rates at Each Site | | | | | | | |
|---|--|---------------|-------------------------|---------------|-----------------------|---------------|-----------------------|---------------|
| | Antioch (enhanced) | | Indianapolis (enhanced) | | Clio (natural) | | St Clair (natural) | |
| | $-k \text{ day}^{-1}$ | k_{CoC}/k_T | $-k \text{ day}^{-1}$ | k_{CoC}/k_T | $-k \text{ day}^{-1}$ | k_{CoC}/k_T | $-k \text{ day}^{-1}$ | k_{CoC}/k_T |
| B | 0.00135 | 0.59 | 0.00279 | 0.72 | 0.00153 | 0.82 | 0.00043 | 0.59 |
| T | 0.00229 | 1.00 | 0.00387 | 1.00 | 0.00187 | 1.00 | 0.00073 | 1.00 |
| E | 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 6. Average attenuation rate for 6 wells under natural attenuation and 7 wells under enhanced attenuation conditions. k_{C_0C}/k_T gives the ratio of attenuation rate of B, E, or X to that of toluene

| | average k (day ⁻¹) enhanced | average k (day ⁻¹) natural | k_{C_0C}/k_T enhanced | k_{C_0C}/k_T natural |
|---|---|--|----------------------------|---------------------------|
| B | 0.0021 | 0.0010 | 0.7 | 0.8 |
| T | 0.0031 | 0.0013 | 1.0 | 1.0 |
| E | 0.0020 | 0.0006 | 0.6 | 0.5 |
| X | 0.0023 | 0.0008 | 0.7 | 0.6 |

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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