NATIONAL PETROCHEMICAL & REFINERS ASSOCIATION
1899 L STREET, NW, SUITE 1000
WASHINGTON, DC 20036

ENV-02-188

Treatment of MTBE Impacted Sites Using Biostimulation

By

William R. Morse
William J. Brochu

Sunoco, Inc.
Philadelphia, PA

Sean R. Carter
Julie A. Gibbs

Matrix Environmental Technologies Inc.
Orchard Park, NY

Presented at the

NPRA
2002 Environmental Conference
September 9-10, 2002
Sheraton New Orleans Hotel
New Orleans, Louisiana

NPRA
FOUNDED 1902
www.npradc.org

Part A. Oxygen Injection

A Sunoco retail gasoline station with MTBE impacted groundwater near Albany, NY was successfully treated to New York State groundwater standards using an oxygen injection process (U.S. Patent No. 5,874,001) to stimulate biodegradation (Carter, July 1998, *Soil & Groundwater Cleanup*, p.22). The system was installed in 1995 and operated less than two years for closure. This site was the first known full-scale demonstration of groundwater bioremediation for MTBE. Since the completion of this successful project, Sunoco has implemented oxygen injection at numerous retail locations and major oil storage facilities in the Northeast and Midwest for the treatment of groundwater and soil impacted with MTBE and petroleum hydrocarbons.

The oxygen injection system consists of a pressure-swing adsorption oxygen generator, rotary screw compressor and automated oxygen delivery manifold. Oxygen gas is produced at 90% purity and pulse injected using a timer-automated system to small diameter injection points that are placed in the plume using direct push or rotary drilling methods. Due to the high solubility of oxygen gas, groundwater dissolved oxygen (DO) increases up to 40 mg/L and transports in the plume by dispersion and advective groundwater flow. The intermittent injection of oxygen at low rates results in a very high oxygen transfer efficiency and prevents contaminant volatilization. Naturally occurring bacteria use the available oxygen to degrade MTBE and hydrocarbons. Microbial data indicates that MTBE degrading bacteria are widespread in subsurface soils but an oxygen-enriched environment is required for efficient degradation to occur.

Design Considerations

Biostimulation with the injection of oxygen is applied to sites with hydrogeologic conditions that are conducive to DO transport. Generally, subsurface soils with an effective porosity of 30% or greater and fractured bedrock are acceptable sites, although less ideal conditions may be treated effectively depending on the remediation goals. Injection points are installed in rows perpendicular to groundwater flow at a distance of 15 to 20 feet. Rows are generally spaced further apart depending on the rate of groundwater flow. Underground utilities, storage tanks and surface features often influence the location of the injection points. The points are constructed of ¾-inch diameter PVC piping with a slotted diffuser at the bottom. The diffuser is installed at a depth consistent with the limits of contamination or at the top of a confining layer. Polyethylene tubing is installed in shallow trenches to connect the injection points to the oxygen delivery system. For retail gasoline stations, oxygen injection systems are trailer-mounted for mobility.

Oxygen injection is used as a stand-alone remedial technology or in conjunction with source removal, soil vapor extraction and/or product recovery. Although most frequently used to stimulate indigenous contaminant degraders, bioaugmentation in highly impacted source areas or in barriers to prevent plume migration are also applied.

Groundwater impacted with petroleum hydrocarbons and MTBE is usually oxygen deficient with DO less than 1 mg/L and oxidation-reduction potential (ORP) in the range of a strongly reducing environment. Anaerobic bacteria using sulfate or iron as an electron acceptor typically dominate the microbial community. The injection of oxygen results in relatively rapid changes in these conditions. Groundwater DO will increase sharply resulting in the competitive growth of aerobic and facultative anaerobic bacteria. Obligate anaerobic bacteria are inhibited by the high concentrations of DO. This provides a secondary benefit by reducing or ceasing the biological production of ferrous iron.

As changes in the microbial community occur, groundwater DO will actually decline even though the supply of oxygen has not changed. During this period of exponential growth and the high availability of soluble organics, oxygen utilization is at its highest level. Groundwater DO will cycle throughout the remediation process, primarily due to higher oxygen solubility and slower utilization during seasons with lower groundwater temperatures, as shown in Figure 1.

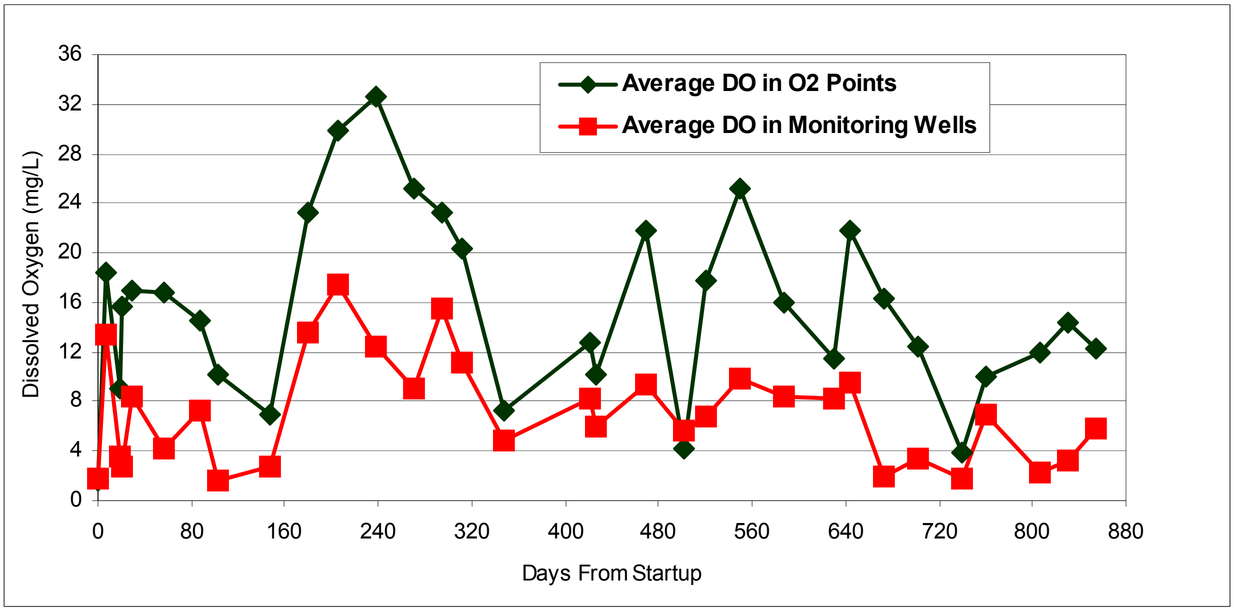

Figure 1. Groundwater dissolved oxygen concentrations with peaks during cold seasons and declines during warm seasons.

As the groundwater plume is oxygenated, ORP will shift from reducing to oxidizing conditions (Figure 2). This change occurs gradually and is less likely to fluctuate unless a source area, such as highly impacted soils above the water table, release contaminants to groundwater during a seasonal high water table or periods of high precipitation. Although ORP data is considered less quantitative compared to DO and groundwater contaminant levels, tracking ORP trends is useful in evaluating the effectiveness of the remediation process. Often, increasing DO and ORP is an indicator of declining contaminant concentrations. When these conditions occur, the contaminant becomes the biologically limiting factor and sufficient DO is available to attain maximum site-specific degradation rates.

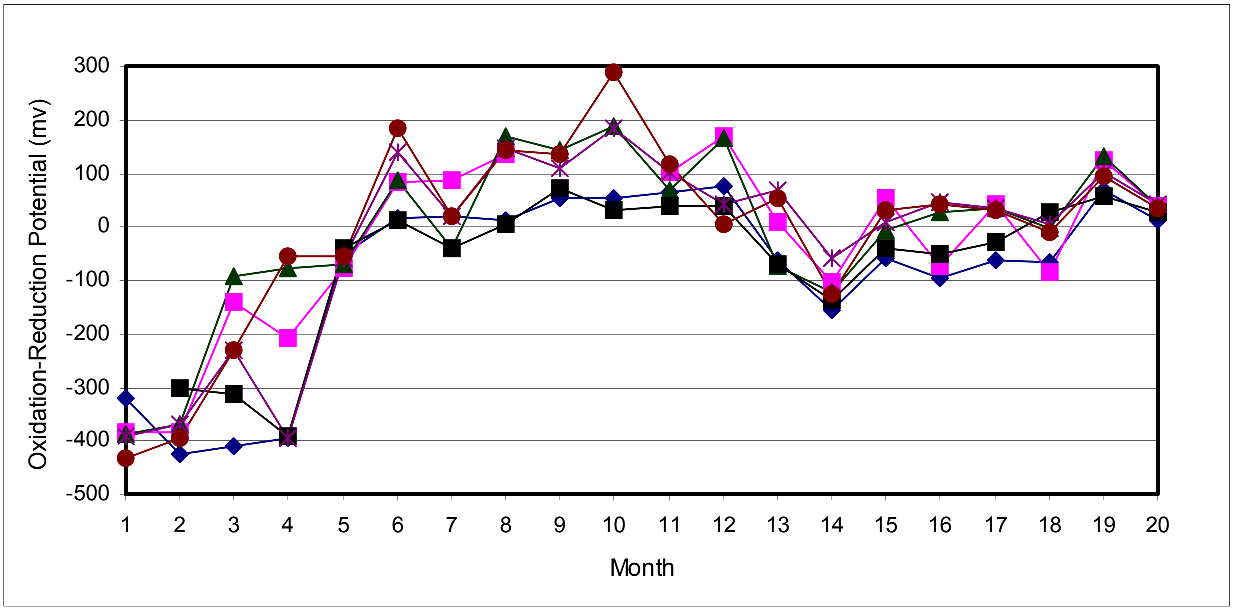

Figure 2. Groundwater ORP as measured from monitoring wells showing change from reducing to oxidizing conditions.

MTBE Field Results

Based on successful cleanups at retail gasoline stations, a major oil storage facility with groundwater highly impacted with MTBE was selected for a larger scale application of the technology in 1997. The site conditions presented a number of design and operational challenges listed below.

- The upper 15 to 20 feet of soil consists of low permeability silty clay with high concentrations of volatile aromatic compounds (BTEX at 17 mg/kg). Due to the geologic conditions, volume of impacted soil and location within the AST area of an active terminal, removal or *in situ* remediation of these soils is not practical.
- Beneath the silty clay, soils consist of high permeability sands and gravels. This zone provides a conduit for contaminant transport.
- In the source area, the water table extends into the silty clay soils, providing an on-going source of groundwater BTEX contamination.
- The water table is tidally influenced with fluctuations of 3 to 4 feet and a gradient of 3%.
- Prior to remediation, the MTBE groundwater concentration in the source area was 870 mg/L and over 100 mg/L at a downgradient distance of 80 feet.
- The downgradient receptor is a major river that is strongly regulated and the focus of heightened community awareness.
- The MTBE plume was migrating towards the river in the sands and gravels.

Based on the complexity of the site conditions, potential magnitude of the cleanup and the limited MTBE remediation options in 1997, the initial effort was focused in the source area to reduce the MTBE groundwater concentrations and prevent migration. Six oxygen injection points were installed in the sand and gravel near a source area monitoring well with the highest

MTBE concentration. Oxygen was pulse injected at a flow rate of 30 standard cubic feet per hour (SCFH) to each injection point. DO and ORP was monitored monthly and groundwater contaminant levels quarterly from the monitoring wells. After one year of operation, MTBE concentrations dropped to 100 mg/L in the source area well and 49 mg/L in the well located 80 feet downgradient. Groundwater BTEX concentrations dropped from 76 to 58 mg/L in the source area and from 43 to 31 mg/L downgradient. The decline in BTEX does not appear as significant due to the on-going contribution from the silty clay soils. Groundwater contaminant levels did not increase in the downgradient wells located between the plume edge and the river. Based on these very promising results, operation of the system was continued with regulatory approval.

Following 3 years of operation, groundwater MTBE concentrations decreased by over 90% and the plume was shrinking in size. BTEX concentrations had declined by approximately 50% in the source area and up to 75% downgradient. The initial goal of containing the plume in the source area was achieved and the total reduction in contaminant mass was substantially greater than anticipated. In August of 2000, the remediation system was expanded to 18 oxygen injection points. Additional points were added to the source area and downgradient to a distance of approximately 100 feet. Prior to adding the additional injection points, DO averaged 2 to 6 mg/L with peak concentrations of 12 to 17 mg/L. After operating on all 18 points, DO increased substantially with peaks exceeding 20 mg/L and averages up to 11 mg/L.

The oxygen injection system has now been operating for 5 years. MTBE in groundwater has been reduced by 98% to 99% and the furthest downgradient well that was impacted in 1997 has been in compliance with drinking standards since February of 2000. The change in MTBE concentrations over the 5-year period is shown in Figure 3 for the most highly impacted wells. Figure 4 illustrates the two order of magnitude decrease in MTBE with distance from the source area.

Following the expansion of the system in 2000, groundwater BTEX concentrations declined more rapidly downgradient of the source area due to the dispersion of oxygen over a much larger area of the plume. BTEX continues to decline in the source area, but at a slower rate. However, this does not imply that biodegradation is slower. The silty clay soils in the source contain high concentrations of BTEX that continue to impact groundwater with the fluctuations in groundwater elevation. But similar to MTBE, the BTEX plume is contained and shrinking as shown in Figure 5.

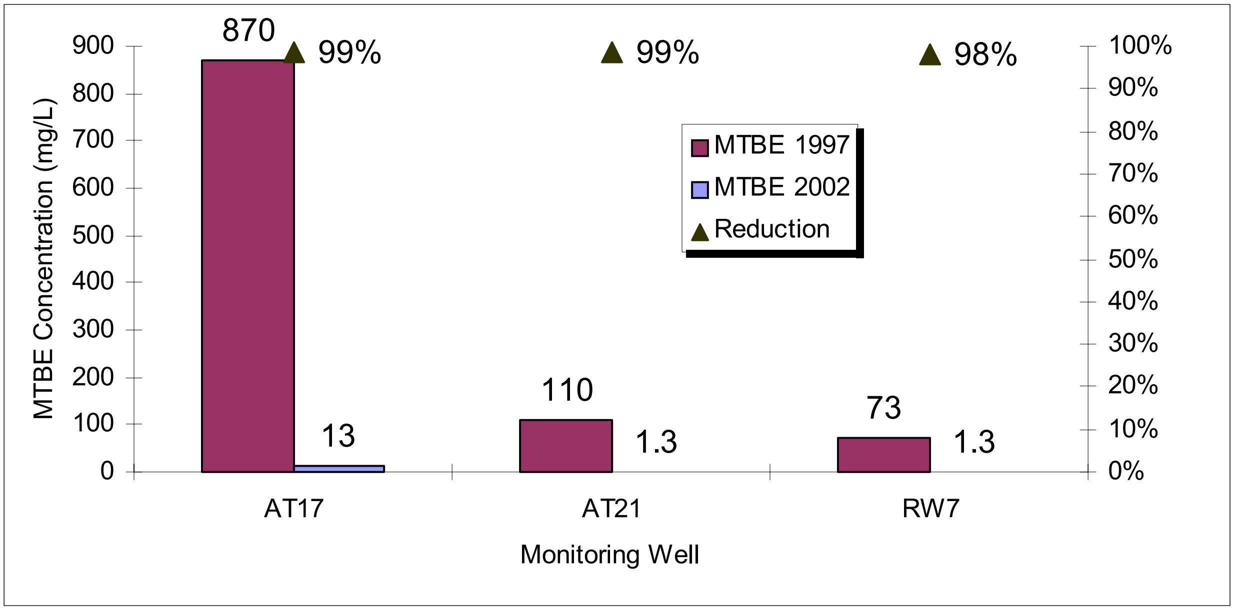

Figure 3. MTBE reduction in highly impacted wells. AT17 is in the source area. AT21 and RW7 are located 80 and 140 feet downgradient, respectively.

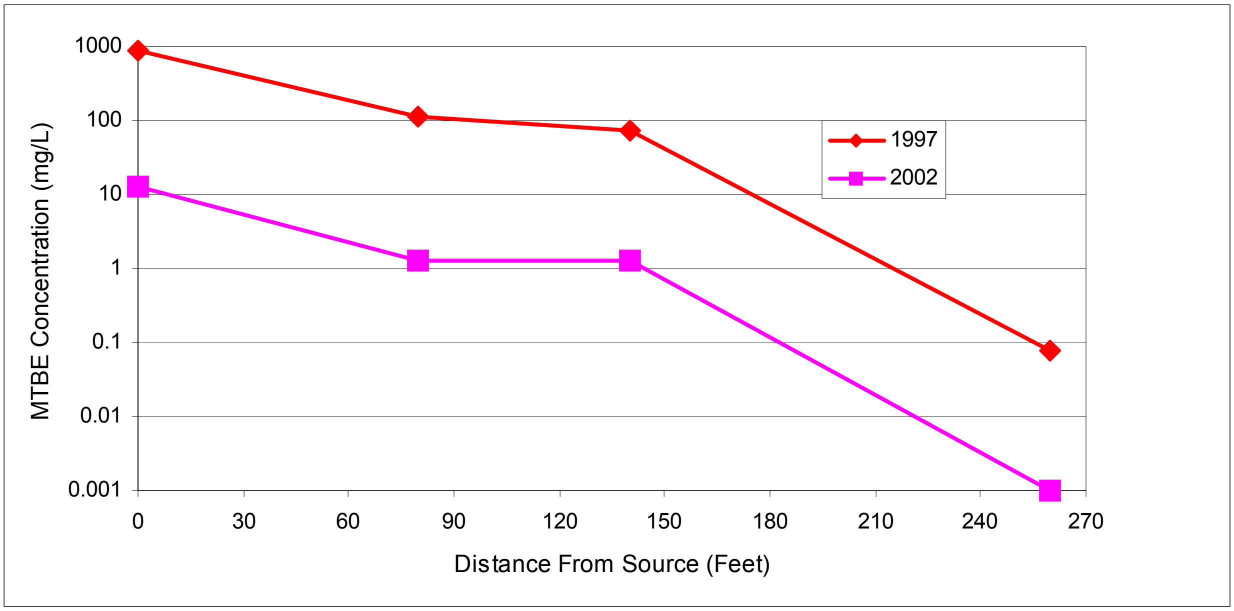

Figure 4. Two order of magnitude decrease in MTBE concentrations. MTBE measured from the furthest downgradient well was non detectable in 2002.

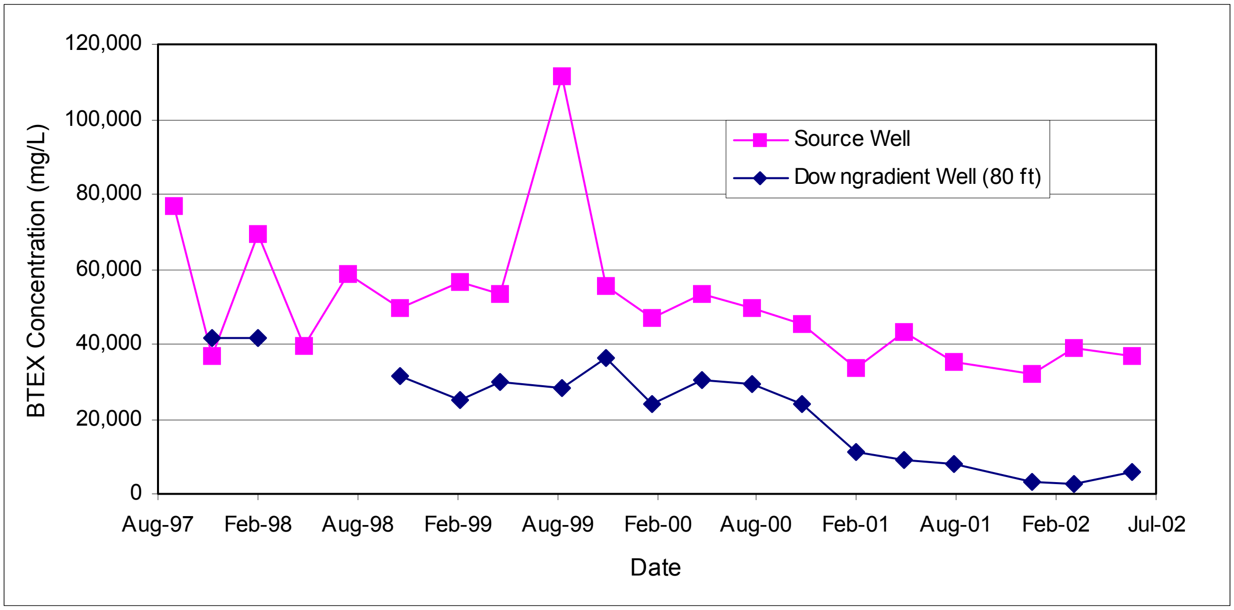

Figure 5. Groundwater BTEX concentrations in AT17 and AT21 over 5 year remediation period.

Tertiary-butyl alcohol (TBA) is an intermediate product of MTBE biodegradation. It is also found in gasoline that contains MTBE. Groundwater samples at the site were first analyzed for TBA in 2001, due to the concern that TBA degrades at a slower rate than MTBE and may migrate downgradient. Based on the results of the initial samples, TBA was included in the analytical parameters for quarterly sampling. Interpretation of the TBA results is complicated by the small data set, lack of baseline data and the fact that TBA is both a component of gasoline and a biological MTBE intermediate. Also, the oxygen injection system was expanded one year prior to the collection of TBA data. The system expansion resulted in the sharp decline in BTEX over a larger area of the plume. The effect this had on TBA is unknown.

However, the available data shows a trend of TBA increasing in the wells located within the network of oxygen injection points and decreasing downgradient with the exception of a slight increase in one well. The furthest downgradient well, located between the MTBE plume edge and river, has remained non detectable for TBA. The change in TBA concentration with distance from the source area over the one year sampling period is shown in Figure 6.

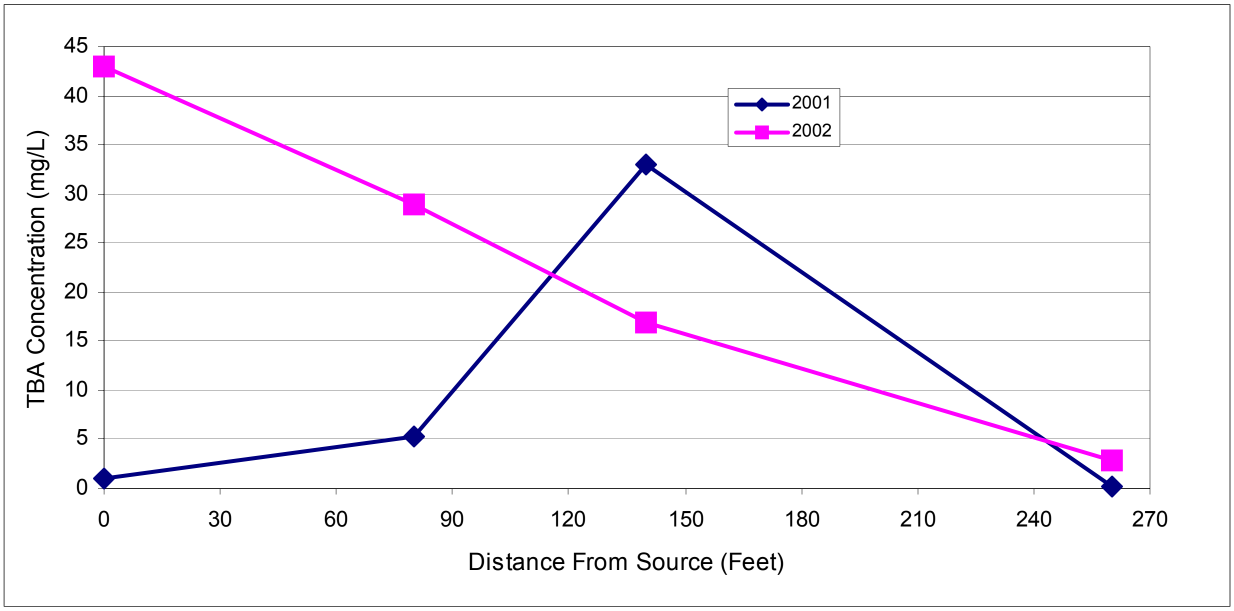

Figure 6. TBA concentrations with distance from MTBE source area. TBA has increased substantially in source area and decreased downgradient.

Microbial Study Results

Soil samples were collected during the expansion of the oxygen injection system in 2000 for microbial analyses to confirm the biodegradation of MTBE and identify the dominant bacterial species. Samples were collected from the saturated zone in three locations: the source area where oxygen was being injected, an area of the plume unaffected by the remediation system and an area of the terminal that was not impacted by contaminants (control sample). The microbial communities from the samples were characterized by phospholipid fatty acid content (PLFA analysis), profiling a conserved region of the 16S rDNA gene by denaturing gradient gel electrophoresis (DGGE), and enrichment cultures for MTBE utilizing bacteria. As summarized below, the results of the analyses suggest that the conditions in the plume are favorable for biodegradation and that oxygen injection is enhancing the process.

- PLFA analysis showed that biomass content was 4 times higher in the plume sample receiving oxygen than in the plume sample not receiving oxygen (Figure 7).
- Comparison of the PLFA profiles showed that both plume samples shifted to more of a contaminant utilizing community structure based on the increased proportions of Gram negative bacteria (typically involved in remediation of petroleum products due to their ability to utilize a wide range of carbon sources, adapt quickly to a variety of environments, and have relatively fast growth rates).
- Biomarkers found in anaerobic metal reducers were significantly higher in the control sample (Control; 24.0% > Plume non-oxygenated; 3.0% > Plume oxygenated; 1.2%).
- Gram negative communities in the plume samples had faster turnover rates and were showing more evidence of adapting to their environment (decreased membrane permeability).
- DNA profiles showed distinct patterns for each of the three samples.

- The DNA profile for the control sample showed a very diverse bacterial population with no member comprising more than 1-2% of the population.
- Although different, the DNA profiles for both plume samples showed shifts in the bacterial populations suggesting a shift to a more contaminant utilizing community.
- Sequence analysis of individual bands from the plume samples revealed that the majority of the organisms were closely affiliated with the genus *Acidovorax*.
- *Acidovorax* are aerobic chemolithoautotrophic (obtain energy from oxidation of inorganic compounds and able to use CO_2 as sole carbon source) hydrogen-oxidizing bacteria.
- Enrichment cultures showed that all three samples contained bacteria capable of utilizing MTBE.
- The abundance of MTBE degraders was one order of magnitude higher in the sample receiving oxygen.

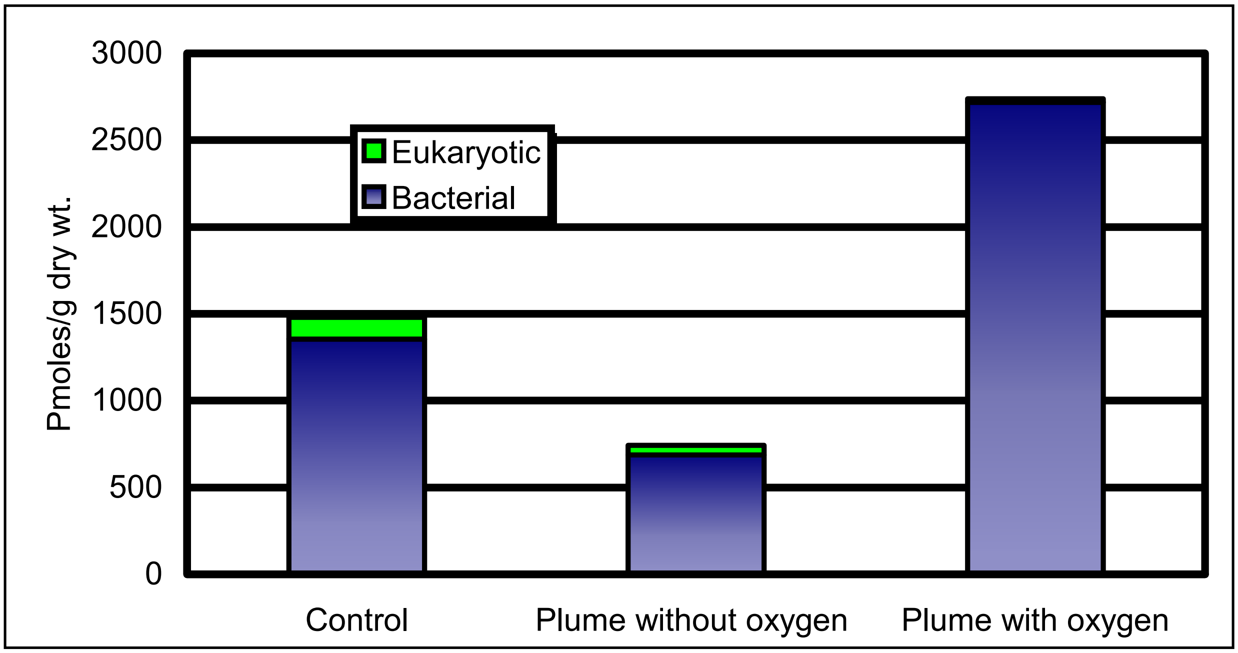

Figure 7. Biomass content by PLFA.

Soil samples were again collected in July 2002 for a detailed microbial study. MTBE degrading bacteria will be identified and isolated from the soil samples. Enrichment cultures, chemical/microbiological assays and a radiorespirometry study are being conducted to measure MTBE degradation rates, determine the degradation pathway and intermediates and to assess the structure and metabolic activity of the microbial community. Information from the study will be used to determine if TBA is being degraded at rates sufficient to prevent migration, to evaluate the overall status and long range potential of the remediation process and to advance our understanding of MTBE biodegradation for application at other remediation sites.

Conclusions

Oxygen injection has been used at numerous remediation sites for the biostimulation of groundwater impacted by MTBE and hydrocarbons. Many successful projects have been completed to regulatory closure. Groundwater cleanup goals have included drinking water standards, risk based levels and protection of potential sensitive receptors. The technology is very cost competitive and operating costs are 1 to 2 times lower than extraction and treatment technologies. Establishing site-specific goals, understanding the subsurface processes and operating the system based on the results of the monitoring data are the key elements to successful projects. Every site is biologically diverse but the fundamentals of biodegradation are universal.

Our understanding of MTBE biodegradation is advancing and the ability to contain and cleanup plumes has been proven. The regulatory community is recognizing the effectiveness of bioremediation, responsible parties are benefiting from cost-effective cleanups and reduced liabilities and our natural resources are being protected by enhancing a naturally occurring process.