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compounds through the use of respirometry. *Proc. 66th Annual Cont: Wat Env. Federation,* 1:361-3727 1993.

IN-SITU BIODEGRADATION OF MTBE USING BIOSPARGING

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The potential for accidental release of gasoline containing high percentages of MTBE (e.g., 11-15 wt%) has raised concerns about the cost and efficiency of soil and groundwater remediation impacted by this tertiary ether. MTBE is perceived to be a mobile and relatively persistent compound in the environment due to its high water solubility and relatively slow biodegradability. At present, an ex-situ pump-and-treat system, is the only proven option to remediate groundwater with high MTBE concentrations, which includes the use of air steppers and possibly, off-gas thermal or catalytic treatment options for air emission control. The high cost and low efficiency of pump-and-treat are well documented.

The objective of this study was to investigate the possibility of in-situ biodegradation of MTBE in an actual field site. Since 1992, Amoco has been successful in biodegrading MTBE in the laboratory using soil and groundwater from several locations and under a variety of conditions. The field study was designed to duplicate some of the lab conditions that have been important in acclimating the indigenous bacteria to biodegrade MTBE.

The field investigation was conducted at an Amoco site in Michigan. The MTBE concentration in groundwater was between 5-10 ppm. The geology of the site consisted of uniform medium sand with depth to water of approximately 5 feet. The pilot study was conducted for three months and four low flow air injection (biosparging) wells were used to oxygenate the groundwater in the study area. MTBE and dissolved oxygen (DO) concentrations were measured at different depths below the groundwater surface. Weekly or biweekly samples were collected during operation and monthly samples were analyzed after shut-down.

MTBE concentrations in groundwater decreased to non-detect during operation in the oxygenated areas of the plume whereas there was no significant change in non oxygenated (low DO level) areas. DO concentrations were increased from 0. 5 ppm to approximately 9 ppm during biosparging in oxygenated areas whereas the DO levels remained below 1 ppm in non-oxygenated areas.

Laboratory microcosm studies were conducted to verify that biosparging stimulated indigenous bacteria to biodegrade MTBE in the field. Three sets of sacrificial microcosms were set-up in the laboratory and sampled for a period of six months. The first set of microcosms contained soil and groundwater samples from the study area prior to biosparging. The second set of microcosms contained soil and groundwater samples from both oxygenated areas and non-oxygenated areas after 45 days of biosparging operation. The third set was similar to the second set except the samples were collected after three months of biosparging and prior to shut-down. Control (abiotic) microcosms were run simultaneously with live microcosms to account for non biological losses. All the microcosms were spiked with MTBE at 10 ppm starting concentration.

The results of the microcosm studies showed no noticeable MTBE biodegradation prior to biosparging during the six month analysis period. However, microcosms containing soil and groundwater samples from aerated portion of the plume showed significant biodegradation of MTBE with half-life of approximately 30 to 45 days whereas the ones from non-aerated portion of the plume exhibited no change in MTBE concentration during six month analysis period.

The results of the field and laboratory studies strongly indicate that it is possible to stimulate indigenous bacteria in the field to biodegrade MTBE at significant rates.

EFFECT OF ETHANOL ON ANAEROBIC TOLUENE DEGRADATION IN AQUIFER MICROCOSMS

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Introduction

Bioremediation holds great promise as an approach to manage aquifer contamination by benzene, toluene, ethylbenzene, and xylenes (BTEX) from leaking underground fuel storage tanks. While many factors in bioremediaiion have been studied, limited attention has been placed on the effect that ethanol can have on in situ BTEX degradation. Ethanol is widely used in several states of the USA and in Brazil as a fuel oxygenate at high concentrations (10 to 22%) to increase the octane of gasoline and to minimize air pollution from fuel combustion. Ethanol also used as an alternate fuel to beuer manage hydrocarbon resources. Therefore, the presence of ethanol may become common in hydrocarbon plumes.

The number of sites that require management and remediation increases, while the resources available for performing the cleanups do not increase proportionally. This has stimulated the use of passive bioremediation as a management strategy to alleviate the resource allocation problem. In passive bioremediation, the contamination is monitored, but no enhancement of

natural remediation processes is performed as long as the pollutants do not present a serious environmental or health risk (e.g., when biodegradation rates exceed migration rates). Due to the lack of oxygen addition in a passive system, it is thought that anaerobic processes are an important part of the containment and removal of the BTEX contamination [Rifai et al., 1995]. Therefore a better understanding of the effect of ethanol on BTEX degradation in anaerobic systems is warranted for proper application of passive bioremediation of ethanol-hydrocarbon plumes.

Many terminal electron acceptors are possibly available for passive bioremediation of hydrocarbon-contaminated groundwater systems, including nitrate, ferric iron, manganate, sulfate, and carbonate. This study used aquifer microcosms to investigate the effect of ethanol on anaerobic benzene and toluene degradation using sulfate and carbonate as electron acceptors.

Methods

Microcosms were prepared in 250 rnL bottles capped with Mini-nert valves. Each contained 200 mL minimal medium and 20 g of sediments. The sediments were obtained from a pond near Iowa City, IA. The medium for sulfate reducing conditions was per the recipe of Ferry [Aceti and Ferry, 19883. The methanogenic medium was per the recipe of Novak [Novak, 19941. The methanogenic reactors were also seeded with an existing methanogenic mixed culture growing on acetate Benzene and toluene were added concurrently to each microcosm at concentrations between 0.4 to 0.7 ppm. Ethanol, which is completely soluble in water and may be present at higher concentrations than BTEX in gasoline, was also added at 100 ppm. No-treatment controls were prepared without ethanol to discern its effect on monoaromatic hydrocarbon biodegradation. Sterile controls (autoclaved and poisoned with 500 mglL $HgCl_2$) were also prepared to discern biodegradation from volatilization losses. Each set was run in triplicate. The microcosms were kept in an anaerobic glove box to preclude oxygen intrusion. The incubation temperature was 25°C. Benzene, toluene, ethanol and methane concentrations were measured over time by gas chromatography using in series PID and FID detectors. Sulfate was analyzed by ion chromatography.

Results

No significant loss of benzene, toluene, or ethanol occurred in the sterile controls within 99 days. Toluene degradation was observed in some of the microcosms, while benzene was not degraded in any of the microcosms within this period. Under both sulfidogenic and methanogenic conditions, ethanol was completely degraded before any measurable toluene degradation occurred. In the sulfate reducing microcosms amended with ethanol, all the ethanol was degraded within 23 days, and all the toluene was removed within 52 days. Toluene persisted for a longer time in sulfate reducing microcosms not amended with ethanol, and greater than 50% of the added toluene remained after 99 days (Figure 1).

Ethanol was degraded faster in the methanogenic microcosms, and all the ethanol was removed within 10 days. Unlike the sulfidogenic microcosms, methanogeruc microcosms amended with ethanol showed no significant toluene degradation within 99 days, while ethanol-free methanogenic microcosms degraded toluene by more than 80% within the same time period (Figure 2).

Discussion

The removal of toluene from viable anaerobic microcosms but not from sterile controls indicates that toluene was biodegraded under both sulfidogenic and methanogenic conditions. The presence of ethanol affected the extent of toluene degradation within the 99 day incubation period. Under both sulfidogenic and methanogenic conditions, ethanol was preferentially degraded over toluene5 and benzene was recalcitrant. The preferential utilization of ethanol suggests that its presence in dissolved hydrocarbon plumes might hinder anaerobic BTEX biodegradation, as was the case with the methanogenic microcosms (Figure 2), even when ethanol is present at sub-toxic levels (commonly less than 10,000 mg/L [Ingram and Buttke, 1984]). Indeed, the presence of ethanol has been shown to hinder aerobic benzene and toluene degradation in aquifer microcosms by exerting diauxy [Corseuil et al., 1996].

Interestingly, this work shows that there may be some exceptions to the detrimental effect of ethanol on BTEX degradation, as observed in triplicate sulfidogenic microcosms (Figure 1). In these microcosms, the presence of ethanol enhanced toluene degradation, even though ethanol was preferentially degraded. The reason for this enhancement is unclear; it may, however. be related to the role of ethanol in overcoming the common limitation to natural degradative processes that is associated with the insufficient presence of appropriate catabolic capacities. For example, the lag time commonly observed before the onset of BTEX biodegradation frequently reflects the time required to establish a critical concentration of active degraders capable of exerting measurable degradation rates [Alvarez et al., 1994; Corseuil and Weber, 1994]. In theory, ethanol could enhance BTEX degradation by serving as a growth substrate for microbes that are coincidentally capable of degrading BTEX. A simple mathematical model that considers sequential substrate utilization and diauxic growth suggests that the poteniial for ethanol to have a beneficial effect on BTEX degradation increases when the initial concentraiion of BTEX degraders is relatively low. Note that this hypothesis does not imply that ethanol is selecting for BTEX degraders, which is highly unlikely. Albeit, an enrichment of BTEX degraders does not need to be preferential for ethanol to enhance BTEX degradation. A higher total concentration of BTEX degraders would be conducive to enhanced BTEX degradation rates even if their relative abundance in the microbial consortium decreases following growth on ethanol.

In summary, this work implies that the diversity of microbial consortia in the environment precludes generalizations about the ability of ethanol to enhance or hinder anaerobic BTEX degradation by mixed cultures. Further research on substrate interactions and population shifts under different electron acceptor conditions is needed to develop unifying principles that facilitate the management aquifers contaminated with ethanol-gasoline mixtures.

Acknowledgments

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Figure 1: Toluene degradation in sulfidogenic aquifer microcosms. The results are the average of three reactors, and the error bars represent one standard deviation.
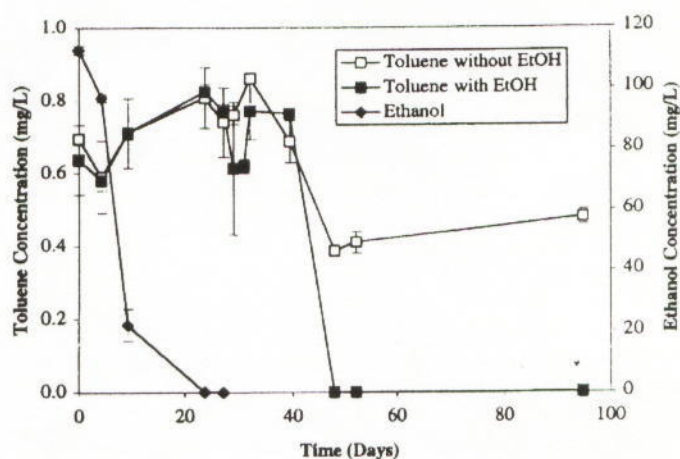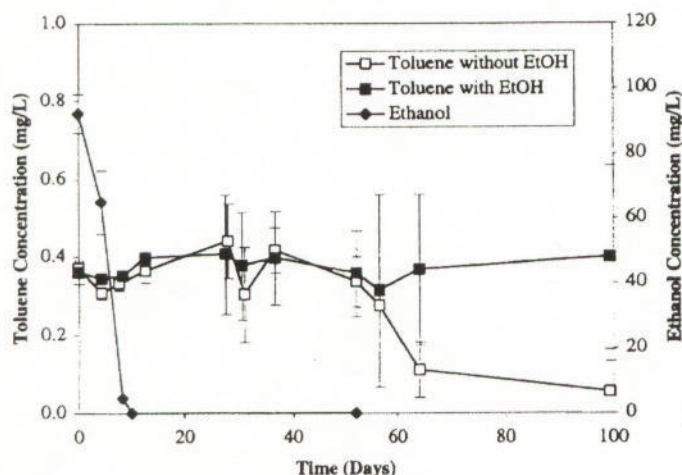
Figure 2: Toluene degradation in methanogenic aquifer microcosms The results are the average of three reactors, and the error bars represent one standard deviation.

INTRINSIC BIOREMEDIATION OF MTBE AND BTEX: FIELD AND LABORATORY RESULTS

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An extensive field and laboratory study was conducted at an UST release in Sampson County, NC, to improve our understanding of those factors limiting intrinsic bioremediation of dissolved gasoline components in groundwater. Field-scale first-order decay rates for MTBE and BTEX were estimated using a mass flux approach that does not require fitting a solute transport model to concentrations at individual wells. Near the source, first-order decay rates were highest for toluene and ethylbenzene and lowest for o-xylene, benzene, and MTBE. Downgradient, the mass decay rates for all compounds declined. The decline in the toluene and ethylbenzene decay rates is at least partially due to the complete removal of these

ENVIRONMENTAL FATE AND EFFECTS OF GASOLINE OXYGENATES

Organized by

P.G. Tratnyek, B.J. Bauman and J.S. Zogorski

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EPA FUEL PROGRAMS

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This paper contains a description of two of EPA's fuel programs as well as a recent assessment by the White House Office of Science and Technology Policy of the oxygenated fuels program (the assessment findings are quoted from a draft report, the final report will be published in early 1997).

The concept of reformulated gasoline is not a new one. Gasoline has undergone reformulation along with the evolution of the automobile and the passage of new environmental regulations to control air pollution. Gasoline has been reformulated to reduce evaporative and tailpipe emissions and to meet the ever changing requirements of new engine technologies. One example of the way gasoline has undergone reformulation is through the addition of chemical additives. Methyl tertiary butyl ether (MTBE) is an example of a chemical additive that has been used as an octane enhancer since the 1970s. Typically the oxygenate content was lower than that required under EPA's current fuel programs. For example, MTBE was typically used at 5-7 volume % for octane boost. To achieve 2.0% oxygen content (by weight) under the reformulated gasoline program (RFG), about 11 volume % MTBE would be required. To achieve 2.7% oxygen content (by weight) under the oxygenated fuels program, about 15 volume % MTBE would be required. The other principle oxygenate used today is ethanol.

In the late 1980's ARCO Petroleum began successfully marketing reformulated gasoline in California to help reduce emissions from motor vehicles. Other petroleum refiners also began marketing their own gasoline reformulations. When the 1990 Clean Air Act Amendments (CAAA) required EPA to initiate Federal and state reformulated fuel programs to reduce harmful levels of certain air pollutants, oxygenates such as MTBE were used to meet certain requirements of these mandates. States with carbon monoxide (CO) non-attainment areas were required to implement oxygenated gasoline programs. Areas with the worst ozone pollution in the country were required to implement Federal RFG programs. Several other ozone non-attainment areas elected to "opt" into the RFG program as well. Prior to developing the required guidances and regulations, EPA entered into regulatory negotiations (REGNEG) with the petroleum industry, oxygenate industry, state and local organizations, environmental groups, auto manufacturers, organizations representing the public, and other government agencies to lay the framework for these programs and the subsequent guidance and rulemakings.

To combat CO air quality problems, the Act required all states containing CO non-attainment areas with design values of 9.5 parts per million (ppm) or more to implement the winter oxygenated gasoline programs which requires a minimum oxygen content of 2.7% by weight. The oxygenated gasoline program is pnmarily a winter time program which began in November of 1992 and included 39 areas throughout the country which had levels of CO that exceeded the National Ambient Air Quality Standards (NAAQS). Analyses of ambient CO measurements in some cities with winter oxygenated gasoline programs find a reduction in ambient CO concentrations of about 10%. To date, there are approximately 25 areas that continue to implement the program. Once these areas reach CO attainment and are officially redesignated they are no longer required to implement the program as long as they can demonstrate continued maintenance of the air quality standard without it. However, states often choose to maintain the program to help them continue to meet the CO standard.

Another major gasoline program required by the CAAA is the RFG program. The program, designed to reduce automotive emissions of ozone-forming pollutants and toxic chemicals, is a year round program. The first phase of the program began in January of 1995 and is required to reduce both volatile organic compounds (VOCs) and toxic emissions by more than 15%; the second phase (2000 and beyond), is required to achieve even greater reductions. Compared to conventional gasoline, RFG has lower levels of certain compounds that contribute to air pollution and a minimum oxygen content of 2.0% by weight, and a maximum benzene content of 1% by volume. Although the CAAA only required the RFG program in areas that are designated as severe non-attainment, states may voluntarily "opt-in" to the program for other non-attainment areas, as needed.

Subsequent to the implementation of the winter oxygenated gasoline and/or RFG programs there were complaints from the public of health effects including headaches, dizziness, nausea, and flu-like symptoms in a few ofthe areas that sold these fuels. Most of these complaints were associated with gasoline containing MTBE. There were also some concerns expressed with regard to vehicle performance and fuel economy. EPA investigated these concerns and was not able to