INTRODUCTION

In recent years, the gasoline additive MTBE (Methyl tert-butyl ether) has been regarded as a high pollution threat to groundwater resources. MTBE has been found to be resistant to natural attenuation processes at many sites creating very large plumes. When natural attenuation processes are considered slow or inefficient to pursue the desired remediation goals, biostimulation may be a desirable remediation technique. Biostimulation is the practice of adding nutrients like nitrogen or phosphorus, and/or electron acceptors such as oxygen or nitrates, to the subsurface to stimulate or enhance the activity of indigenous microbes. For this technique to be feasible, the specific microbial population capable of degrading the desired contaminants must be present at the site sediments. When the required microbial population is not present in the site, or is present at very low concentrations and is not easily biostimulated, bioaugmentation may be a suitable alternative. It is carried out through the injection of a specific microbial culture into the aquifer, and if necessary, the accompanying nutrients, to target a specific contaminant.

When natural attenuation, biostimulation or bioaugmentation are chosen as remediation techniques, their performance is often conceptualized as being homogeneous throughout the aquifer. It is accepted however, that the inherent heterogeneous nature of the subsurface generates heterogeneous microbial distributions and remediation patterns.

ASU has been involved in the development of MTBE biobarrier technology at Port Hueneme, CA. Pilot scale studies were initiated 5 years ago and full-scale demonstration started 2 years ago, involving a combination of both biostimulation and bioaugmentation (Figure 1).

The biobarriers have been effective in degrading MTBE (Figure 2). However, it is unknown if the biobarrier system degrades MTBE homogeneously, or if there are portions of the aquifer that preferentially degrade it.

OBJECTIVE

The objective of this study is to assess the spatial distribution of MTBE-degrading activity in the vicinity of the full-scale biobarrier, and to determine which portions of the aquifer are actively degrading MTBE after 2 years of biobarrier performance.

METHOD

This study involved collecting discrete aquifer material and groundwater in the vicinity of the biobarrier. Microcosms were prepared from the soil and groundwater samples and these were monitored for MTBE-degrading activity (Figure 1).

In the field, samples were collected using a Geoprobe® (direct push coring device). Taking into account that the water table throughout the Port Hueneme site is on average located around 8 ft deep, and a clay aquitard was expected at 20 ft, all locations were cored from 8 to 20 ft in 4 ft intervals.

Within the shallow aquifer in Port Hueneme, groundwater quality has been found to vary with depth. Therefore at each location ground water was collected at 2 different depths: a "shallow" sample near the water table (8 to 10 ft BGS) and a "deep" sample at the deepest point cored (18 to 20 ft BGS).





Figure 1. The different zones of the Biobarrier, and the location of microcosms through the Biobarrier



Figure 2. Dissolved Oxygen (a) and MTBE (b) concentrations in the biobarrier as of October 2002 (after 2 years of performance of the biobarrier), at depth of 15 ft BGS. Contours are in mg/L.

MICROCOSMS

Each soil core was divided into 2-ft sections, that were mixed and homogenized in Ziplock® bags (6 soil sections per location). The microcosms were performed using 125 ml vials (20 mm neck) with crimp-seal caps. From each stomached section, 80 g of soil were deposited into a vial. Duplicate microcosms were performed randomly on 10% of the microcosms. Respiratory inhibited controls were prepared by adding 2 g of solid sodium azide to 6 microcosms.

The groundwater sample corresponding to each location was filtered with a 0.7 µm filters (GF/F Whatman filters). This was done to avoid inoculating the microcosms with microorganisms that might be present in the groundwater. Then, the groundwater was sparged with pure oxygen until the dissolved oxygen reached saturation at about 40 mg/L of oxygen (1 to 2 min). In a plastic syringe, 60 ml of groundwater were measured and deposited in each vial, leaving approximately 40 ml of headspace. The headspace was then briefly purged with oxygen gas. The vials were then crimp sealed with a Teflon septa and an aluminum cap. Then, the microcosms were spiked with MTBE to a concentration of approximately 1 mg/L. The microcosms were kept in a constant temperature room (23°C) on a shaker table, set at a speed speed as rapid as possible for continuous use.

The microcosms were periodically analyzed for MTBE using headspace gas chromatography (GC) analyses. The GC (SRI Model 8610C) was equipped with a 0.53mm ID x 60m MXT-Vol glass capillary column with a 2.0 µm df. A flame ionization detector (FID) was used for most samples, a photo ionization detector (PID) was used to analyze low MTBE concentrations. The analyses were performed by injecting 0.5 ml of headspace, and the GC was set isothermally at 70°C for 4 min. When other BTEX compounds were found in the sample, the GC conditions were as follows: 70°C for 4 min, heating at 15°C/min to final temperature of 180°C, hold final temperature for 10 min. For every 10 samples, a standard was run.

RESULTS

A total of 151 microcosms were prepared, including 13 duplicates and 6 respiratory inhibited controls (Figure 3). The activity results were arbitrary classified into 3 different categories (Figures 4 and 5):

High activity: if MTBE concentrations dropped below 0.1 mg/L in one month (at least one order of magnitude drop in concentration).

Low activity: if MTBE concentrations seemed to decline, but failed to drop to less than 0.1 2) mg/L in 1 month.

Inactive: No MTBE concentration drop could be observed in 1 month. 3)

• Using these guidelines, 103 microcosms had high activity, 10 low activity and 18 were inactive (excluding controls, duplicates and a broken microcosm).

• It was found that there is a high MTBE-degrading activity in well oxygenated zones, where MTBE is not present because is degraded upgradient.

• Also, all the locations containing inactive microcosms were located in zones which are upgradient of the biobarrier and are not well oxygenated (Figure 6).











Figure 4. Results of the A degrading microcosms. Microcosms with the subscript *a* are the shallower samples, with subscripts *f* are the deepest samples. Samples collected from 8' to 20' BGS.

Figure 5. Results of the SC degrading microcosms. Microcosms with the subscript *a* are the shallower samples, with subscripts f are the deepest samples. Samples collected from 8' to 20' BGS.