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Spatial variations in MTBE-biodegradation activity near a biobarrier in Port Hueneme, California

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Abstract MTBE has been found to be resistant to natural attenuation processes at many sites creating very large plumes. In Port Hueneme, California, a long MTBE plume has been extensively characterized. In this plume, MTBE-degrading cultures were injected more than four years ago and this biobarrier has been effective in degrading MTBE. The objective of this study was to determine the current spatial distribution of the microbial activity along the biobarrier, and to determine which portions of the aquifer are actively degrading MTBE. The approach used was to collect discrete soil aquifer samples and groundwater near the biobarrier. Microcosms were prepared and MTBE was periodically monitored for any degrading activity. The main result from this study was the recognition of heterogeneous MTBE-degrading activity zones throughout the biobarrier. Of special interest is that well oxygenated zones, where no MTBE is presently being biodegraded, showed a high MTBE-degrading activity.

Key words MTBE; Port Hueneme, California; biobarrier; biodegradation; microcosms

INTRODUCTION

In recent years, the gasoline additive MTBE (methyl tert-butyl ether) has been regarded as a high pollution threat to groundwater resources (Squillance *et al.*, 1996). MTBE has been found to be resistant to natural attenuation processes at many sites creating very large plumes (Einarson *et al.*, 1999; Salanitro *et al.*, 2000; US EPA, 2000). When natural attenuation processes are considered too 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 (King *et al.*, 1997). When the required microbial population is not present, or is present at very low concentrations and is not easily biostimulated, bioaugmentation may be a suitable alternative (Alexander, 1999). Bioaugmentation is performed by 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.

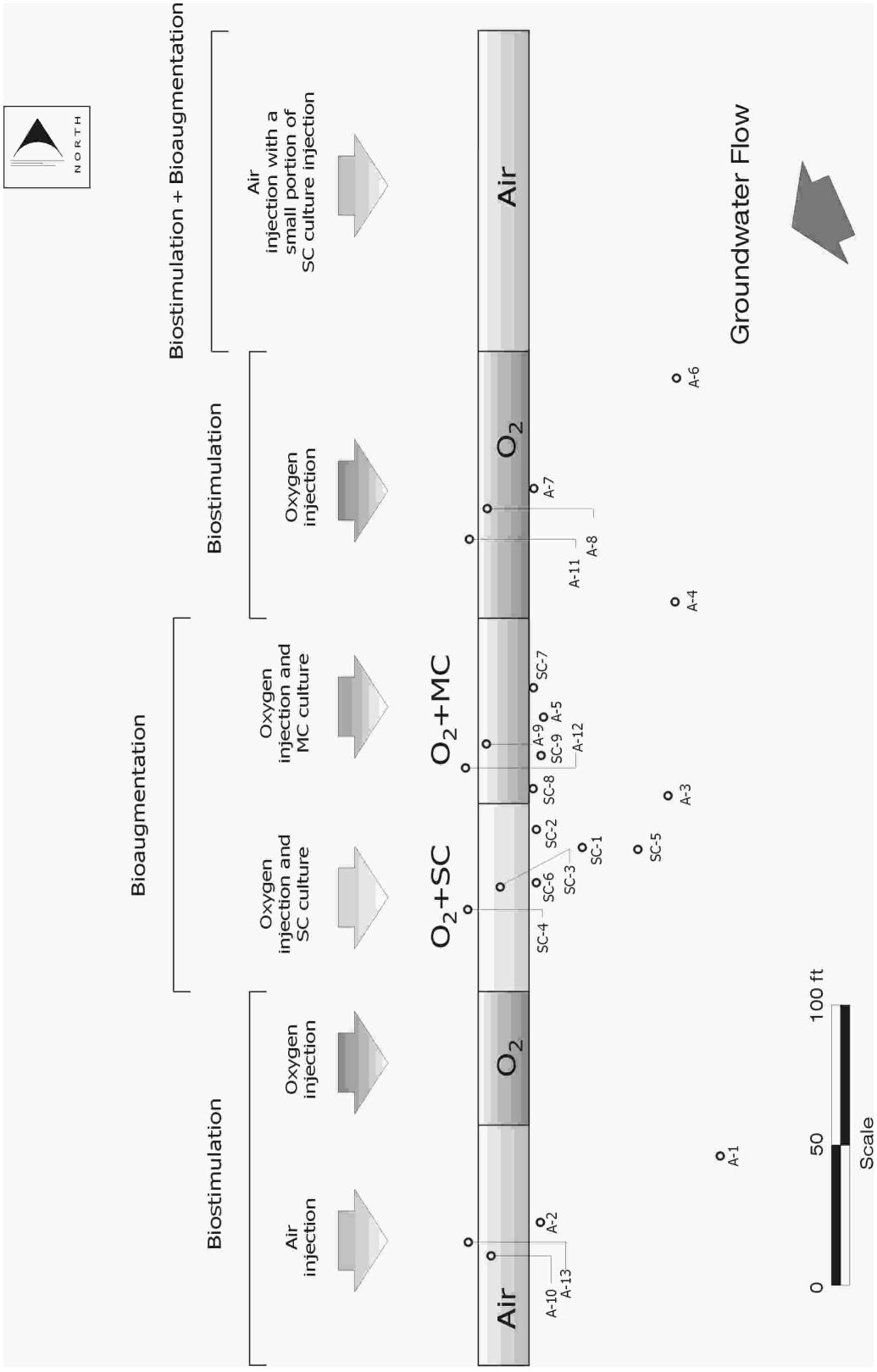

Fig. 1 The different zones of the biobarrier, and the location of the microcosms.

We have been involved in the development of MTBE biobarrier technology at Port Hueneme, California, USA, where an MTBE plume larger than 1500 m has developed. Pilot scale studies were initiated five years ago (Salanitro *et al.*, 2000) and full-scale demonstration started three years ago (Bruce *et al.*, 2002), involving a combination of both biostimulation and bioaugmentation (Fig. 1). The biobarriers have been effective in degrading MTBE (Fig. 2). However, it is unknown if the biobarrier system degrades MTBE homogeneously, or if there are portions of the aquifer where it preferentially degrades. The objective of this study was 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 two years of biobarrier performance.

METHODS

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 (Fig. 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 at around 8 ft deep (1 ft ≈ 0.3 m), 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 groundwater was collected at two different depths: a "shallow" sample near the water table (8 to 10 ft b.g.s.) and a "deep" sample at the deepest point cored (18 to 20 ft b.g.s.).

MICROCOSMS

Each soil core was divided into 2-ft long mixed and homogenized sections (six soil sections per location). The microcosms were performed using 125-ml vials (20-mm neck) with crimp-seal caps. From each 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 six microcosms.

A groundwater sample corresponding to each location was filtered using a 0.7 μm filter (GF/F Whatman filters) to avoid inoculating the microcosms with micro-organisms that might be present in the groundwater. The filtered groundwater was sparged with pure oxygen until the dissolved oxygen reached saturation at about 40 mg l^{-1} (1–2 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 briefly purged with oxygen gas. The vials were then crimp sealed with a Teflon septa and an aluminium cap. Each microcosm was spiked with MTBE to a concentration of approximately 1 mg l^{-1}. The microcosms were kept in a constant temperature room (23°C) on a shaker table.

The microcosms were periodically analysed for MTBE using headspace gas chromatography (GC) analyses. The GC (SRI Model 8610C) was equipped with a

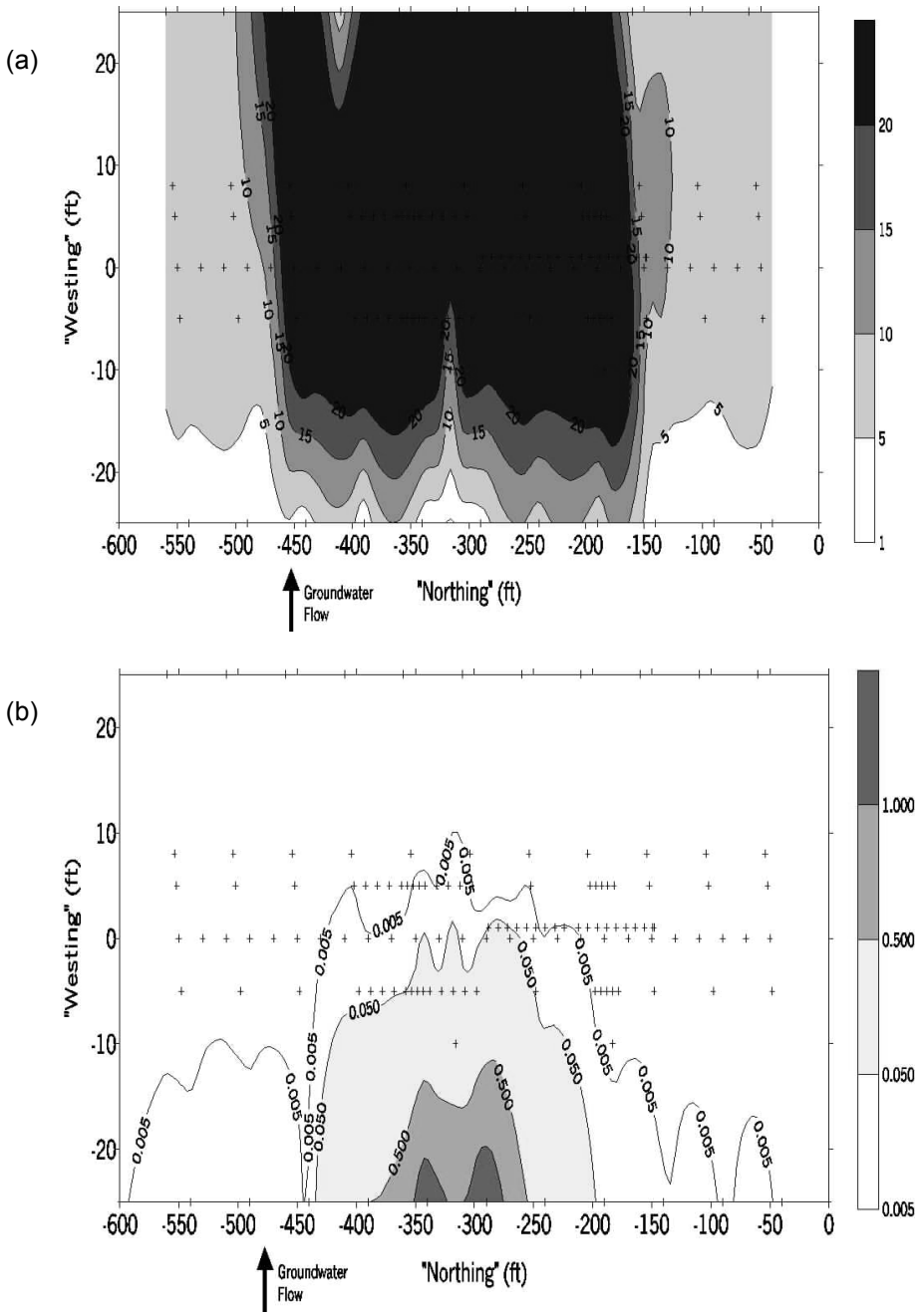

Fig. 2 Dissolved oxygen (a), and MTBE (b) concentrations in the biobarrier as of October 2002 (after two years of performance of the biobarrier), at a depth of 15ft b.g.s. Contours are in mg l^{-1}.

0.53 mm ID × 60 m MXT-Vol glass capillary column with a 2.0 μm d.f. A flame ionization detector (FID) was used for most samples, and a photo ionization detector (PID) was used to analyse low MTBE concentrations. The analyses were performed by injecting 0.5 ml of headspace gas into the GC set isothermally at 70°C for 4 min. When other BTEX compounds were present in the sample, the GC conditions were as follows: 70°C for 4 min, heating at 15°C $min\ l^{-1}$ to a final temperature of 180°C, hold final temperature for 10 min. For every 10 samples, a standard was run.

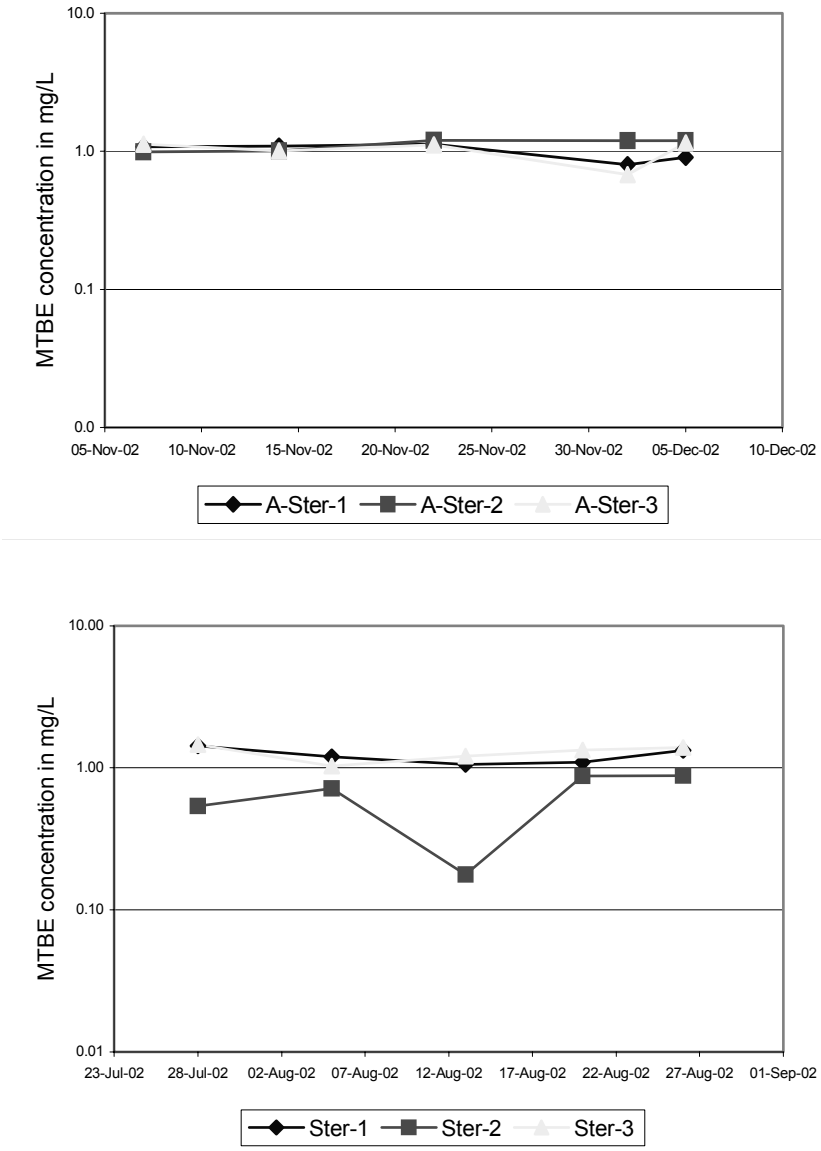

Fig. 3 Respiratory inhibited microcosms controls.

RESULTS

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

1. *High activity*: if MTBE concentrations dropped below 0.1 mg l^{-1} in one month (at least one order of magnitude drop in concentration).
2. *Low activity*: if MTBE concentrations seemed to decline, but failed to drop to less than 0.1 mg l^{-1} in one month, and
3. *Inactive*: no MTBE concentration drop could be observed in one month.

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

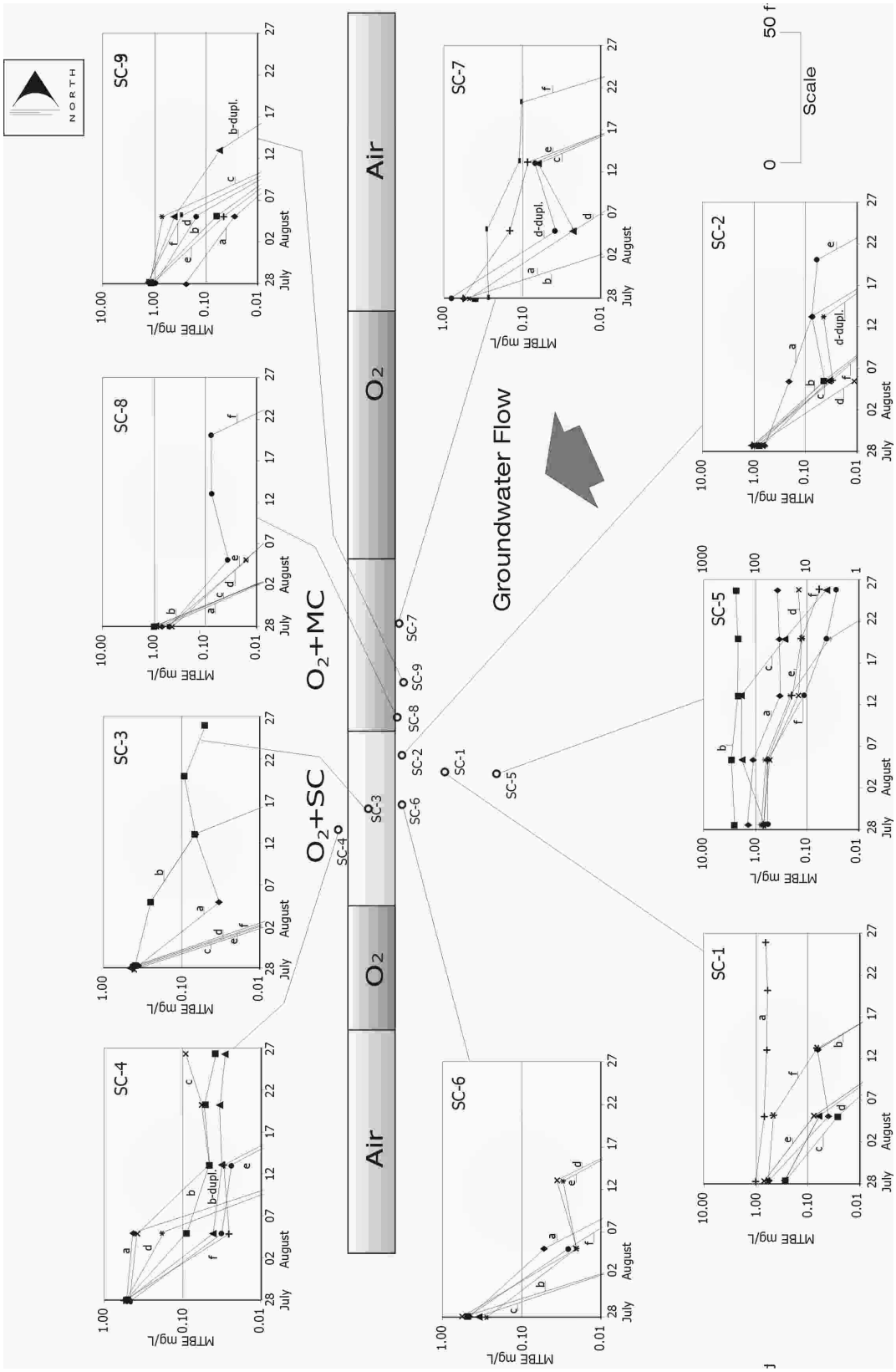

Fig. 4 Results for the "A" degrading microcosms. The subscripts *a* and *f* denote microcosms from the shallower and deeper zone, respectively. Samples collected from 8 to 20 feet b.g.s.

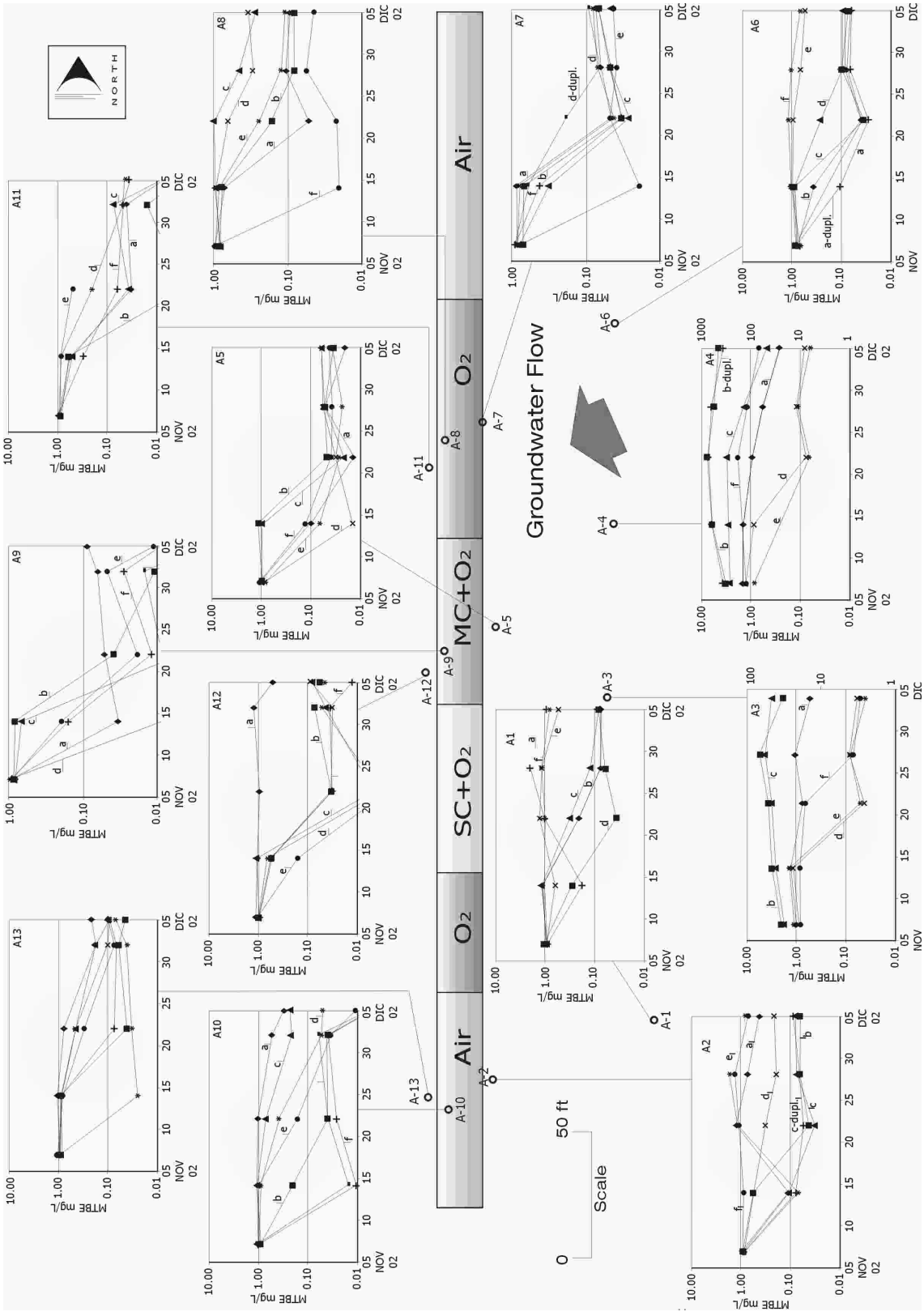

Fig. 5 Results for the "SC" degrading microcosms. The subscripts *a* and *f* denote microcosms from the shallower and deeper zone, respectively. Samples collected from 8 to 20 feet b.g.s.

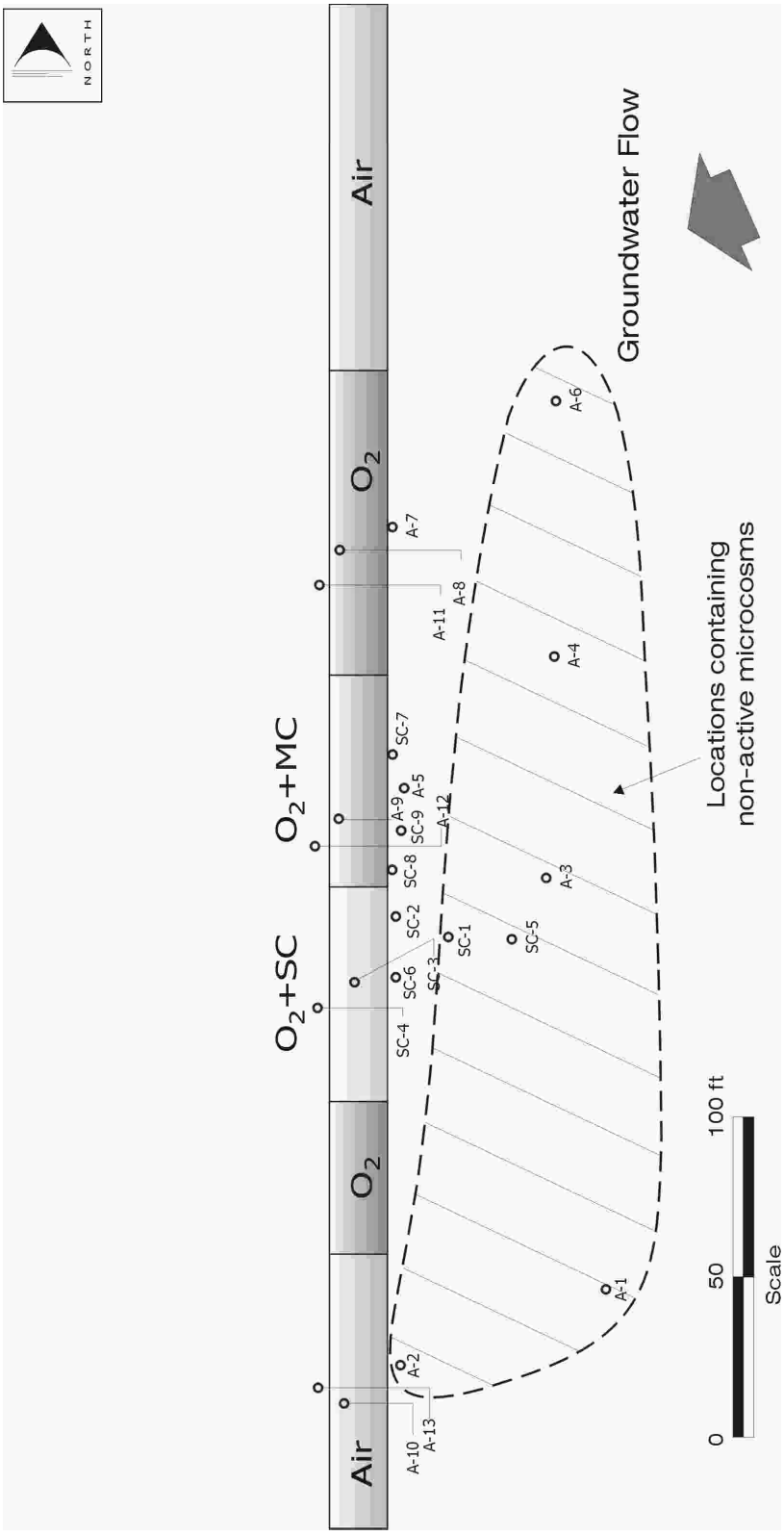

Fig. 6 Location of non-active microcosms.

that there is a high MTBE-degrading activity in well oxygenated zones, where MTBE is not present because it was degraded upgradient. Also, all the locations containing inactive microcosms were located in zones which are upgradient of the biobarrier and are not well oxygenated (Fig. 6).

REFERENCES:

Alexander, M. (1999) *Biodegradation and Bioremediation*, second edn. Academic Press, Ithica, New York, USA.

Amerson, I. & Johnson, R. L. (2003) Natural gradient tracer test to evaluate natural attenuation of MTBE under anaerobic conditions. *Ground Water Monitor. Remed.* **23**(1), 54–61.

Bruce, C. L., Miller, K. D. & Johnson, P. C. (2002) Full scale bio-barrier demonstration for treatment of a mixed MTBE/TBE/BTEX plume at Port Hueneme. *Contaminated Soil Sediment and Water July/August* 2002, 80–84.

Einarson M. D., Schirmer, M., Pezeshkpour, P., Mackay, D. M. & Wilson, R. (1999) Comparison of eight innovative site characterization tools used to investigate an MTBE plume at site 60, Vandenberg Air Force Base, California. In: *Proc. 2000 Petroleum Hydrocarbons and Organic Chemicals in Groundwater; Prevention, Detection and Remediation* (November 1999, Houston, Texas, USA), 145–157.

King, R. B., Long, G. M. & Sheldon, J. K. (1997) *Practical Environmental Bioremediation, The Field Guide.* Lewis Publishers, Boca Raton, Florida, USA.

Salanitro, J. P., Johnson, P. C., Spinnler, G. E., Maner, P. M., Wisniewski, H. L. & Bruce, C. (2000) Field-scale demonstration of enhanced MTBE bioremediation through aquifer bioaugmentation and oxygenation. *Environ. Sci. Technol.* **34**(19), 4152–4162.

Squillance, P J., Pankow, J. F., Korte, N. E. & Zogorski, J. S. (1996) Environmental behavior and fate of Methyl tert-Butyl Ether (MTBE). *US Geological Survey, Fact Sheet FS-203-96* (revised 1998).

US EPA (2000) Methyl tertiary butyl ether (MTBE); advance notice of intent to initiate rulemaking under the toxic substances control act to eliminate or limit the use of MTBE as a fuel additive in gasoline. 40 CFG Part 755. *Federal Register* **65**(58), 16094–16109.