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## Cover Page Footnote

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# AN EXPERIMENTAL STUDY OF PHYTOREMEDIATION OF METHYL-TERT-BUTYL ETHER (MTBE) IN GROUNDWATER

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## ABSTRACT

The feasibility of phytoremediation of groundwater contamination with methyl-tert-butyl ether (MTBE) was examined experimentally using a six-channel soil system with or without plants. Two bacterial strains capable of degrading MTBE were each added to two out of six channels. A solution of 0.84 mM MTBE was continuously fed into each channel at 1 L/day until a stable MTBE concentration level in the groundwater was established; then the feeding was switched back to distilled water. The channel groundwater effluent MTBE concentration and the soil gas MTBE fluxes were monitored from the beginning of the MTBE solution feeding until no MTBE was detected. Integration of the gas flux data indicated that the four vegetated channels with introduced bacteria had less MTBE at the soil surface than channel 3 which was vegetated but without any introduced bacteria. The total mass balance for MTBE showed that the fractions of MTBE that were not recovered in the planted channels were significantly higher than in the unplanted channel. Analysis of the experimental data indicates that, due to the presence of the plants, MTBE might have been undergoing enhanced rhizosphere biodegradation.

***Key words:*** *phytoremediation, MTBE, biodegradation, mass balance*

## INTRODUCTION

Methyl-tert-butyl ether (MTBE), other ethers such as ethyl-tertiary-butyl ether, tertiary-amyl-methyl ether, tertiary-amyl-ethyl ether, dimethyl ether, diisopropyl ether, tertiary-butyl alcohol, and ethanol and methanol have been used as fuel oxygenates since 1988 to improve air quality. Most refiners have chosen to use MTBE because it can be produced at the refinery (ease of production and lower cost); it blends easily without separating from gasoline; and the MTBE-gasoline blend can be transferred through existing pipelines. MTBE was first added to gasoline in the late 1970's to replace lead as an anti-knocking agent (NSTC, 1997). In the United States, almost all MTBE is used in gasoline. As a principal fuel additive, MTBE is added to gasoline in high concentrations (approximately 15% on a volumetric basis) to increase octane levels and to enhance combustion of gasoline.

Gasoline spills and leaks from pipelines, underground and aboveground storage tanks, and other transport modes are major sources of MTBE contamination. In addition, uncombusted gasoline is also spilled from boats and recreational equipment directly to surface waters, which may be water supply reservoirs (MTBE Fact Sheet, 1998). Several events have raised concern over the safety of MTBE. In 1996, the city of Santa Monica closed some of its major drinking water wells after discovering MTBE contamination.

As part of the U. S. Geological Survey's (USGS) National Water Quality Assessment program, samples of shallow groundwater were taken from eight urban areas during 1993 to 1994

(Squillace et al., 1996). The results show that, of the 60 volatile organic compounds (VOCs) analyzed, MTBE was the second most frequently detected compound. Having been found in 6.9% of the storm water samples collected by the USGS in 16 cities and metropolitan areas, MTBE was the seventh most frequently detected VOC (Squillace et al., 1997, 1998).

Vapor pressure reflects the volatilization potential of a chemical. The vapor pressure for MTBE at 25$^oC$ is 245 mmHg (about one-third of the atmosphere), which is 2.5 times higher than that for benzene.

Water solubility is an indication of the extent to which the compound can dissolve into the water phase. MTBE is very water soluble compared to the BTEX compounds (benzene, toluene, ethyl benzene, and xylene) and other compounds in gasoline. The solubility of MTBE in water is about 50g/L, whereas the next most soluble component of gasoline is benzene, which has a solubility of 1.8g/L. Most gasoline constituents have solubilities of less than 1 g/L, and some dissolve to only a few mg/L. This is the key characteristic that causes so much of the mass of an MTBE release to dissolve in groundwater. The higher solubility is associated with the greater polarity of the compound.

The Henry's Law constant is an indicator of the equilibrium distribution of a compound between water and air. When compared to benzene, MTBE tends to partition strongly into the water phase. If the same units are selected for the air and water concentrations, then Henry's Law constant is dimensionless. The value of the dimensionless Henry's Law constant for MTBE is 0.0216 at 25$^oC$ (Robbins et al., 1993). In contrast, the dimensionless Henry's Law constant for benzene is 0.22 at 25$^oC$, which indicates that it transfers easily from water and can be removed by aeration. Compared to benzene, MTBE tends to stay in the water phase, which explains why MTBE is somewhat difficult to remove from water by aeration.

The organic carbon water partition coefficient ($K_{oc}$) is a reflection of the compound's tendency to sorb to the organic carbon matrix within soil systems. The organic carbon sorption will retard the migration of the compound. With a value of $K_{oc}$ equal to 11 and an octanol water partition coefficient ($K_{ow}$) of 17.4 (Zhang et al., 1998a; Squillace et al., 1997), MTBE is less retarded than other gasoline constituents.

Compared to other gasoline constituents, the physicochemical properties of MTBE and many other oxygenates present significant issues when considering treatment options and the fate and transport of these pollutants in the environment. Given the high water solubility, MTBE is quite mobile in the environment. It partitions weakly to the organic fraction in soils, sediments, and suspended particles, preferentially remaining in the aqueous phase. It is expected to move essentially at the same rate as groundwater flow, with practically no retardation due to sorption.

Ethers are a class of compounds that are characteristically unreactive over a wide range of industrial and laboratory conditions, so it is unlikely that MTBE will be degraded rapidly in the aquatic environment (Church et al., 1997). MTBE is a persistent molecule in the environment for several reasons: (1) the ether bond is stable and requires acidic conditions to cleave it; (2) the bulky tert-butyl group does not allow easy access to the ether linkage; (3) MTBE is not a naturally occurring hydrocarbon unlike most oil and gasoline constituents; and (4) it has only been in the environment for a relatively short time, so there has been little selection for indigenous microbes to transform MTBE. The biodegradability of MTBE is generally presumed to be significantly less than the degradability of other gasoline constituents. Initial studies indicate that biodegradation of MTBE in the environment is slow (Borden et al., 1997; Mormile et al., 1994; Suflita and Mormile, 1993). A field study by LeBrun (1993) utilized a contaminant mass flux approach to estimate rates of intrinsic bioremediation for MTBE and BTEX at a gasoline-contaminated shallow aquifer in Sampson County, N.C. His results suggested that MTBE degradation was occurring near the source area at a rate of 0.13%/day. Since the contaminant plumes appear to have been degrading under a mixture of aerobic and denitrifying conditions, it is unclear which mechanism would have contributed to MTBE decay.

However, a substantial record of MTBE biodegradation in both laboratory and full-scale treatment operations has now been accumulated. At least a few bacterial species are able to use MTBE as a growth substrate and mineralize the compound (Park and Cowan, 1997; Mo et al., 1997; Steffan et al., 1997). Biodegradation of MTBE has been observed to occur in a full-scale biofilter operating at a gasoline soil vapor extraction site in Richmond, Calif. (Romstad et al., 1998), and in a pilot-scale biofilter operating at the Los Angeles County Sanitation Districts Joint Water Pollution Control Plant in Carson, Calif. (Eweis et al., 1997). A review of recent studies of biodegradation and remediation of MTBE indicated that *in situ* biodegradation may be an effective remediation alternative for soil and groundwater contaminated with MTBE (Zhang et al., 1998a). Liquid-phase biological treatment in which MTBE was mineralized has been demonstrated at laboratory scale at University of California, Davis (Reuter, 1998).

Phytoremediation has been described as a natural process carried out by plants and trees in the cleaning up and stabilization of contaminated soils and groundwater. A huge number of studies have demonstrated that plants have a role in the degradation of persistent organic contaminants such as trichloroethylene (TCE), tetrachloroethylene (PCE), and polynuclear aromatic hydrocarbons (Erickson et al., 1994; Davis et al., 1993; Newman et al., 1997; Zhang et al., 1997a; Zhang et al., 1997b; Zhang et al., 1998c; Makepeace et al., 1996; Walton and Anderson, 1990; Ferro et al., 1994; Narayanan et al., 1995; Schnoor et al., 1995).

Because the recognition of MTBE as an environmental problem is a relatively new area, studying the feasibility of phytoremediation of MTBE has only recently been reported by a couple of research groups (Zhang et al., 1998b; Newman et al., 1999). Using a six-channel experimental system, Zhang et al. (1998b) investigated the fate of MTBE by monitoring MTBE concentration in the groundwater flow and MTBE flux from the soil surface into the atmosphere. The comparison between the results from the planted channels and the unplanted one indicated that vegetation increases MTBE flux to the atmosphere and reduces the groundwater effluent flow rate, and that MTBE is dissipated more quickly in planted channels than in the unplanted channel. In the study of Newman et al. (1999), whole plants (hybrid poplars and eucalyptus) in mass balance chambers were used to determine their ability to take up $C^{14}$–labeled MTBE from the soil. Hybrid poplars were found to be able to incorporate 0.37% of the dosed MTBE into their tissues while transpiring 5.1%. Eucalyptus incorporated 0.4% of the dosed MTBE and transpired 16.52%.

In this study, with the same experimental system as used by Zhang et al. (1998b), we examined the effect of additional bacterial strains, which were capable of degrading MTBE in laboratory cultures, on the fate of MTBE in soil channels under vegetation conditions.

## MATERIALS AND METHODS

The experimental six-channel system has been schematically described in detail by Zhang et al. (1998b and 1998c). Each channel is 110 cm long, 65 cm deep and 10 cm wide, packed with sandy soil, and has influent and effluent ports on each end of the channel. Five of the six channels (channels 1, 2, 3, 5, and 6) were planted with ten alfalfa plants (*Medicago sativa*) with 10 cm between plants and channel 4 was unplanted. Channels 1 and 6 were air sparged through gas distributors installed at the channel bottoms (Zhang et al., 1998c). Distilled water was supplied through inlet water jugs to every channel at 1L/day to maintain a water table of 35 cm from channel bottom up. Water exiting from each channel was collected and recorded daily using collecting bottles. After entering the system, the water contained in the saturated zone (i.e., below the water table) was examined as groundwater in this study.

Two bacterial strains capable of degrading MTBE were introduced into four of the six channels before the MTBE feeding. We obtained the strains from Dr. Kulpa's group at the University of Nortre Dame. The strains were identified as *Rhodococcus* (#33) and *Arthrobacter* (#41) (Mo et al., 1996 and 1997). Each of the two bacterial strains was mixed into four liters of distilled water to make a 1.5 g cells/L suspension. Two liters of the strain #33 suspension were added into channel 1 such that one liter was uniformly spread on the top and the other was injected through the inlet port of the channel. The other two liters were added into channel 2 similarly. The same method was used to inoculate the suspension with strain #41 into channels 5 and 6.

Ten days after the strain inoculation, a solution of 0.84 mM MTBE was continuously fed into each channel at 1 L/day until a stable MTBE concentration level in the groundwater was established; then the feeding was switched back to distilled water. MTBE solution (0.84 mM) was fed for 83 days before the influent was switched back to distilled water for 96 days. The experimental conditions and treatments in each channel are summarized in Table 1.

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Groundwater effluent concentrations and soil gas fluxes were monitored from the beginning of MTBE feeding until no MTBE was detected from either the effluent groundwater streams or the gas-collecting containers placed at the channel soil surface. The methods for sampling and analyzing MTBE were described in Zhang et al. (1997b, 1998b, and 1998c). By estimating the amount of MTBE added into each soil channel and the amount of MTBE recovered from the groundwater effluent and the soil surface, we employed the mass balance approach to investigate the fate of MTBE during the entire testing period. The alfalfa plants were harvested monthly by cutting the whole plants from approximately 6 cm above soil surface. The biomass production was recorded as the dry weight of the harvested part.

To look into the MTBE concentration in plant water, the growing plants were cut and the parts in between the harvesting point and 8-10 cm above were sealed into bottles so as to measure the headspace concentrations for MTBE. The amount of water in fresh plants was obtained by the difference between the weight of fresh plants and that of plants oven dried ($80^0$C) for 24 hours. We converted the headspace concentration into plant water concentration by assuming equilibrium between the gas phase and the plant water and neglecting MTBE adsorption to plant biomass in making the mass balance on MTBE that is required for accurate headspace analysis (Zhang et al., 1998c). All ten plants in each channel were sampled under steady state conditions and distributed into six bottles.

## RESULTS AND DISCUSSION

The groundwater effluent concentrations of MTBE are plotted versus the channel effluent water volume in Figures 1, 2, and 3. Figures 1 and 2 each show the results for two vegetated channels, which had the same bacterial strain added except that one was aerated and the other was not. Figure 3 presents the results of the two channels without any bacteria added; however, channel 3 was vegetated while channel 4 was not. All of the five planted channels demonstrated similar profiles for the effluent MTBE concentration as a function of effluent water volume, whereas the unplanted channel had a different tendency.

After around three weeks, the groundwater effluent concentrations reached a relatively stable level. We assume that the system was under steady state from this point on through the day of feed switching (i.e., day 83 since the MTBE feeding). To analyze the standard deviations of these concentration measurements, the concentration data from day 39 through day 83 were chosen. The standard deviations for measurements of the channels ranged from 0.14 mM to 0.27 mM and are given in the captions of Figures 1-3. The relative measurement error for groundwater effluent concentration was within 18~34% of the respective mean values.

The concentration data were used to estimate the amounts of MTBE recovered from the groundwater effluents of channels through integrating the groundwater effluent concentration over the effluent water volume. The subsequent results are listed in Table 2 as *from groundwater* in terms of millimoles recovered. With the same influent feeding rate, more water went through the unplanted channel as groundwater flow due to the lack of plant transpiration. Consequently, more MTBE was recovered from the groundwater flow of channel 4 (unvegetated) than those of the vegetated channels.

The soil gas fluxes of MTBE are presented in Figures 4, 5, and 6 as a function of days from the beginning of MTBE feeding. Gas fluxes for the four inoculated and planted channels are shown in Figures 4 and 5, while gas fluxes for the non-inoculated channel 3 (planted) and channel 4 (unplanted) are in Figure 6. From Figures 4 and 5, we observe that the soil surface gas fluxes reached steady state on around day 60, which is one month later than the groundwater effluent concentrations. Therefore, the flux data of day 67 through day 114 were chosen for standard deviation analysis and the results are indicted in the captions of Figures 4-6. The relative measurement error for gas fluxes was within 27~38% of the respective mean values. The air sparged channels 1 and 6 had slightly lower gas flux than channels 2 and 5, which were not air-sparged. Among all the six channels, channel 3 had the highest fluxes and channel 4 had the lowest fluxes most of the time.

By integrating over time the MTBE flux data in Figures 4-6, we can have the amounts of MTBE recovered from the channel soil surfaces. Figure 7 shows the accumulated amount recovered as a function of time from the beginning of MTBE feeding. Channel 3, vegetated but non-inoculated, had the highest loss of MTBE, whereas the non-vegetated channel 4 had the lowest loss of MTBE into the atmosphere. The four vegetated channels with introduced bacteria had less MTBE loss from the soil surface than channel 3, which was vegetated but without any introduced bacteria. The total integrated amount of MTBE from soil surface for the entire testing period was put into Table 2 as *from gas* in terms of millimoles recovered.

The mass balance results for MTBE are summarized in Table 2, in which the *Added* amount of MTBE was obtained by summing the volume of the MTBE solution added every day and then multiplying by the influent concentration (i.e., 0.84 mM). The values for *from groundwater* and *from gas* are the amounts recovered from the groundwater effluent and the surface soil gas, respectively. More MTBE was recovered in the groundwater for the unplanted channel 4, while its soil gas recovery was lower than for the planted channels. For the four channels with additional bacteria, the two aerated channels had lower soil gas recovery than the two without aeration. Air sparging appeared to reduce the amount of MTBE released into the atmosphere from the soil. This may be because the aeration improved the aerobic biodegradation of MTBE in the vadose zone by supplying oxygen, or it may be due to the method of measuring the gas flux. The convective flow of gas caused by air sparging may go around the containers because of pressure difference.

The total recoveries from the groundwater effluent and from the soil surface are presented as *Recovered/Added* in Table 2. The value greater than 1.0 for channel 4 reflects experimental errors

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that may be caused by several factors. First of all, due to the high temperature sensitivity of MTBE solubility, the use of Henry's Law constant at 25°C to obtain the groundwater concentration from the headspace measurement may give higher or lower values depending on whether the actual temperature is higher or lower than 25°C. This is why in Figures 1, 2, and 3 we can see MTBE groundwater concentrations greater than the influent concentration, 0.84 mM. According to Robbins et al. (1993), the relationship of the Henry's Law constant for MTBE can be expressed as follows:

$$H = \exp\left(18.4 - \frac{7666}{T}\right)$$

where H has the unit of atm $m^3$/mole and T is absolute temperature (°K). From this correlation, one degree higher or lower than 25°C will cause the Henry's Law constant to increase or decrease by 8-9%. The second factor might be the instrument error. By making triplicate measurements for 10 samples under the same temperature, we found both positive and negative errors ranging from -14.5% to 7.5%. This is of the same magnitude as the effect a one-degree change in temperature has on the Henry's Law constant. Other possible systematic errors include water volume measurement errors, errors in adding water to the influent bottle, volatilization loss of water from the effluent collecting bottles, and errors involved in the integrating process.

Since all the measurements were made for all channels by using the same methods and under the same conditions, we can make corrections for the total recoveries of all the six channels by the same factor. In order to obtain a recovery of 1.0 for channel 4, we need to divide the measured value by 1.08; dividing the recoveries for all other channels by 1.08 gives rise to the values in the last row of Table 2. Consequently, we may estimate that up to 31% of MTBE was lost in the vegetated channels due to the presence of the plants and added microorganisms.

The soil gas fluxes were obtained by measuring MTBE coming out from the soil surface, not including that portion transpired by the plants. Table 3 contains, for each channel and for all channels sampled, the highest, lowest, and average values of MTBE concentrations in plant water in terms of fraction of the influent concentration (0.84 mM). As a result, the concentration level in plant water ranges from 2.7% to 18% of the influent concentration. The concentration of MTBE in plant water was much lower than that in the groundwater. It has been observed that plant tissues may transform MTBE, or MTBE might diffuse out into the unsaturated soil from the plant roots in the process of being taken up by plants (Hu et al., 1998). A study using pure cell cultures of hybrid poplar to determine if plant cells were capable of metabolizing MTBE has demonstrated that the poplar cells were able to oxidize 0.03% of the dosed $C^{14}$-labeled MTBE to CO2, while 0.05% was fixed in cell tissue over a three-day testing period (Newman et al., 1999).

We obtained the monthly soil gas flux of MTBE for each channel by arithmetically averaging all the values measured within each month, as shown in Figure 8 with standard deviations of multiple data points of that month. Each month all channels had an equal number of samples, although the number varied from month to month. Among the six months, October had the largest monthly gas flux for all five planted channels. Table 4 lists the ratios of monthly flux to the largest monthly flux and the standard deviations for each channel. The standard deviations are significant, especially for the months which included transient periods associated with changes in MTBE feeding. During the transient periods, MTBE concentration in the system quickly rose (after starting MTBE feeding) or dropped (when MTBE feeding was terminated). The fluxes from the soil surface exhibit transient responses with larger time constants. As a result, the standard deviations involved in averaging fluxes for each month were relatively large. To examine the loss of MTBE through the plants, we assume that MTBE concentration in the plant-transpired water is proportional to the gas flux. When we had the highest gas flux in the channel, the system was assumed to be in steady state. Accordingly, the plant water also reached its highest MTBE concentration level at the same time. When the gas flux is lower, the concentration of MTBE in plant water is assumed to decrease proportionally based on the ratio of the monthly gas flux relative to the highest monthly flux of each channel. Because of possible errors introduced in estimating monthly averaged fluxes, the results of MTBE transpired through plants are just rough estimates.

The total water added into each channel during the whole testing period is listed in Table 5, together with the evapotranspired water amounts. The latter were obtained by subtracting the total water volume collected from the channel groundwater effluent from the total water added into each channel.

We estimated the quantity of MTBE lost through plant transpiration and/or plant transformation by making use of the monthly flux data, the measured MTBE concentration in the plant water of each channel, and the amount of water transpired by the plants. The fractional amount shown in Table 5 was found by multiplying the transpired water amount (L) by the MTBE concentration in plant water (mmoles/L) for each month, adding the results of all six months for each channel, and then dividing the sum by the total amount of MTBE added. When the overall average fraction (i.e., 0.078) is used from Table 3 for MTBE concentration in plant water, the results are presented as *Estimated average plant uptake of MTBE.* Using the overall highest fraction among the four channels sampled (0.18) gives the *Estimated greatest plant uptake of MTBE* in Table 5. Adding the *Estimated average plant uptake of MTBE* to the *Corrected recovery* from Table 2 gives the *Recovery with plant uptake* for MTBE for each channel, as shown in the last row of Table 5.

We have total recoveries of less than 1.0 for all the vegetated channels, even if we add the *Estimated greatest plant uptake of MTBE* to the *Corrected recovery*. The fractions of MTBE, which were not recovered in the vegetated channels, might have been lost due to enhanced rhizosphere biodegradation in the soil and/or transformation within the plants. To verify this hypothesis, microcosm experiments with soils from the channels system were conducted, and a disappearance

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rate for MTBE of up to 5 mg per kilogram soil per day was observed (unpublished data). The disappearance in the vegetated channels was of the order of 0.2 mg per kg soil per day; however, aerobic conditions conducive to biodegradation were only present in a portion of each channel.

## CONCLUSIONS

The presence of alfalfa plants accelerated the upward movement of water and MTBE from the groundwater to the soil surface. The soil gas recovery at the soil surface was larger with plants than without plants. More mass loss was observed for MTBE in planted cases than the unplanted one. Plants may have a key role in removing MTBE from groundwater. Introduced bacteria in the presence of plants appeared to increase biodegradation of MTBE in the soil. In the aerated channels, less MTBE was lost into the atmosphere, and more oxygen was provided to support aerobic degradation in the unsaturated zone. The mass balances suggest that approximately 20% of the MTBE might have been undergoing biodegradation in the channel soils and/or transformation within the plants. More detailed work is needed to get a mass balance closure where biodegradation and plant transformation are included.

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**Table 1.** Experimental conditions and treatments in each channel of the six-channel system*.

| Channel | Planted with 10 alfalfa plants | Air sparged at 0.24 L/channel/day | Additional bacteria (two liters of suspension added on June 20, 1998) |
|---|---|---|---|
| Channel 1 | yes | yes | #33 (*Rhodococcus*) |
| Channel 2 | yes | no | #33 (*Rhodococcus*) |
| Channel 3 | yes | no | no |
| Channel 4 | no | no | no |
| Channel 5 | yes | no | #41 (*Arthrobacter*) |
| Channel 6 | yes | yes | #41 (*Arthrobacter*) |

* For all channels, dimensions are 110 cm long, 65 cm deep, and 10 cm wide; soil is alluvial silty sand soil (with <10% silt) collected near a landfill in Riley County, Kansas; the system was illuminated with 12 cool white fluorescent lights (40W) at a height of 50 cm above the soil; light intensity is approximately 160 $\mu E/m^2/s$; each channel was fed with MTBE water solution of 0.84 mM at 1 L/day from June 30, 1998 to Sept. 20, 1998 (the duration was 83 days); distilled water was fed from Sept. 21, 1998 to Dec. 25, 1998 (the duration was 96 days).

**Table 2.** Mass balance of MTBE during the test period.

| **Channel #, description** | **1*, planted and aerated** | **2*, planted but not aerated** | **3, planted but not aerated** | **4, not planted and not aerated** | **5 **, planted but not aerated** | **6**, planted and aerated** |
|---|---|---|---|---|---|---|
| **Added (mmoles)** | **68.1** | **69.1** | **68.5** | **69.1** | **68.8** | **71.7** |
| from groundwater (mmoles)[a] | 42.4 | 34.5 | 37.6 | 63.0 | 44.7 | 41.2 |
| from gas (mmoles)[b] | 15.3 | 17.0 | 21.8 | 12.0 | 19.1 | 14.0 |
| **Recovered (mmoles)** | **57.7** | **51.5** | **59.4** | **75.0** | **63.8** | **55.2** |
| groundwater recovery (fraction) | 0.62 | 0.50 | 0.55 | 0.91 | 0.65 | 0.57 |
| Soil gas recovery (fraction) | 0.22 | 0.25 | 0.32 | 0.17 | 0.28 | 0.20 |
| **Recovered/Added** | **0.85** | **0.75** | **0.87** | **1.08** | **0.93** | **0.77** |
| **Corrected recovery** | **0.78** | **0.69** | **0.8** | **1.0** | **0.85** | **0.71** |

* Strain #33 (*Rhodococcus*) was added.

** Strain #41 (*Arthrobacter*) was added.

[a] "from groundwater" is the MTBE mass recovered from the groundwater effluent.

[b] "from gas" is the MTBE mass recovered from the soil surface based on gas fluxes.

**Table 3.** The highest, lowest, and average values, and standard deviations of MTBE concentration in plant water in terms of the fraction of the influent concentration. Six samples were measured for each channel when the system was in steady state.

| **Channels** | **Highest value measured** | **Lowest value measured** | **Average** | **Standard deviation** |
|---|---|---|---|---|
| Channel 1 | 0.102 | 0.028 | 0.068 | 0.022 |
| Channel 2 | 0.110 | 0.037 | 0.066 | 0.026 |
| Channel 5 | 0.180 | 0.045 | 0.118 | 0.042 |
| Channel 6 | 0.091 | 0.036 | 0.063 | 0.023 |
| Overall | 0.121 | 0.028 | 0.079 | 0.031 |

These values were collected under steady state conditions on July 1, 1999, during a second experiment that started on February 7, 1999. Inlet MTBE concentration was 0.84 mM.

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**Table 4.** Monthly gas fluxes of five planted channels relative to the corresponnding highest flux value among six months (i.e., the flux in October). The standard deviations of flux data within each month are also presented. These ratios were used to estimate the MTBE concentration level in plant water during each month.

| **Time** | **Monthy flux relative to the corresponding highest values** | | | | |
|---|---|---|---|---|---|
| | **Channel 1** | **Channel 2** | **Channel 3** | **Channel 5** | **Channel 6** |
| July '98 | 0.09±0.08 | 0.16±0.16 | 0.12±0.12 | 0.12±0.13 | 0.22±0.24 |
| Aug. '98 | 0.29±0.19 | 0.54±0.33 | 0.32±0.22 | 0.44±0.21 | 0.65±0.23 |
| Sept. '98 | 0.55±0.11 | 0.64±0.16 | 0.53±0.02 | 0.64±0.15 | 0.96±0.20 |
| Oct. '98 | 1.00±0.30 | 1.00±0.14 | 1.00±0.29 | 1.00±0.28 | 1.00±0.31 |
| Nov. '98 | 0.24±0.12 | 0.21±0.05 | 0.31±0.11 | 0.32±0.14 | 0.40±0.04 |
| Dec. '98 | 0.03±0.03 | 0.04±0.05 | 0.04±0.04 | 0.05±0.06 | 0.11±0.15 |

**Table 5.** Mass balance of water and estimated fraction of MTBE transpired by plants during the test period.

| **Channel #, description** | **1*, planted and aerated** | **2*, planted but not aerated** | **3, planted but not aerated** | **4, unplanted and not aerated** | **5**, planted but not arerated** | **6**, planted and aerated** |
|---|---|---|---|---|---|---|
| Total water addded (L) | 186 | 192 | 191 | 185 | 199 | 197 |
| Evapotranspired water (ET) (L) | 81 | 116 | 109 | 37[a] | 106 | 108 |
| **Estimated average plant uptake of MTBE (fraction)** | **0.015** | **0.029** | **0.024** | **0.0**[b] | **0.032** | **0.035** |
| **Estimated greatest plant uptake of MTBE (fraction)** | **0.035** | **0.068** | **0.056** | **0.0**[b] | **0.075** | **0.080** |
| Corrected recovery (fraction) | 0.78 | 0.69 | 0.80 | 1.0 | 0.85 | 0.71 |
| **Recovery with average plant uptake (fraction)** | **0.80** | **0.72** | **0.82** | **1.0** | **0.88** | **0.75** |

* Strain #33 (*Rhodococcus*) was added.

** Strain #41 (*Arthrobacter*) was added.

[a] There was only evaporation of water in this unplanted channel.

[b] No plant uptake for this channel.

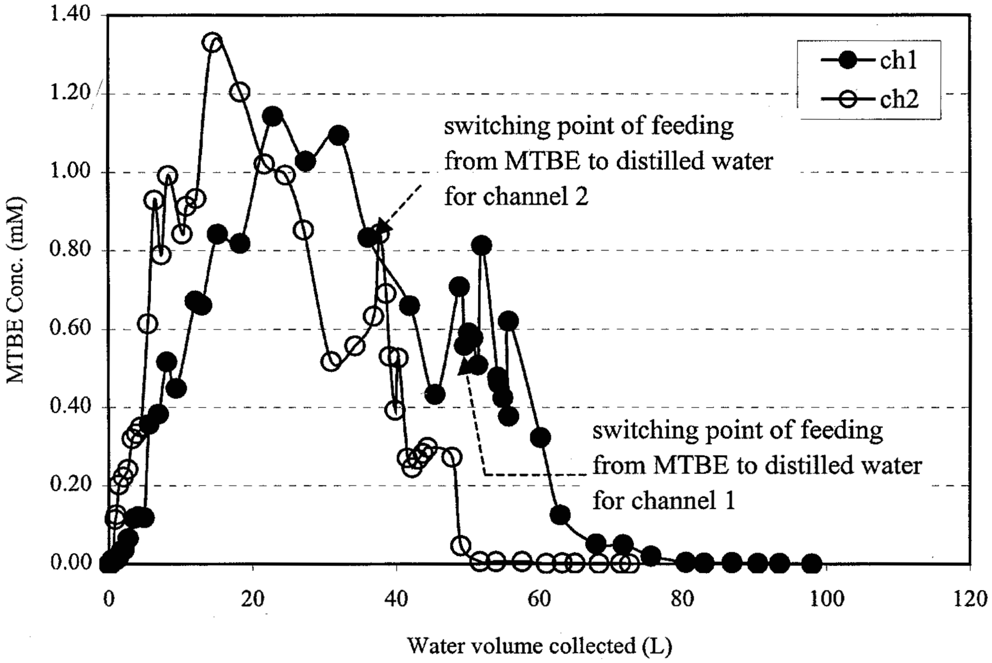

**Figure 1.** Comparison of the groundwater effluent concentrations from channels 1 and 2 as a function of effluent water volume. Both channels were planted with alfalfa plants and were inoculated with strain #33 (*Rhodococcus*), but ch1 was aerated while ch2 was not. The standard deviation for channel 1 during steady state is 0.26 mM; for channel 2 , it is 0.24 mM.

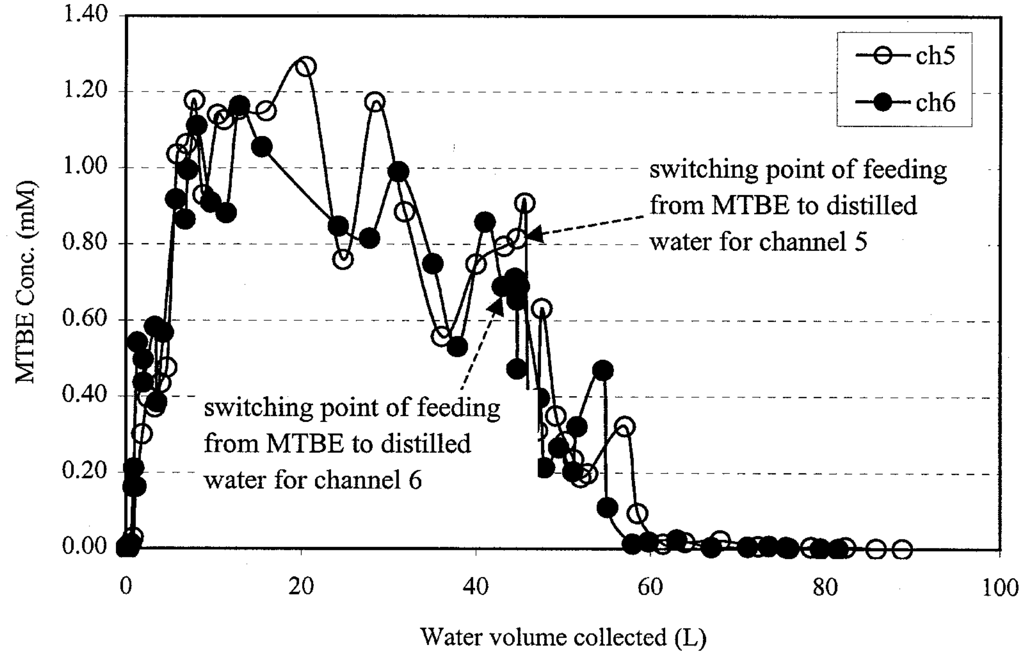

**Figure 2.** Comparison of the groundwater effluent concentrations from channels 5 and 6 as a function of effluent water volume. Both channels were planted with alfalfa plants and were inoculated with strain #41 (*Arthrobacter*), but ch6 was aerated while ch5 was not. The standard deviation for channel 5 during steady state is 0.23 mM; for channel 2, it is 0.14 mM.

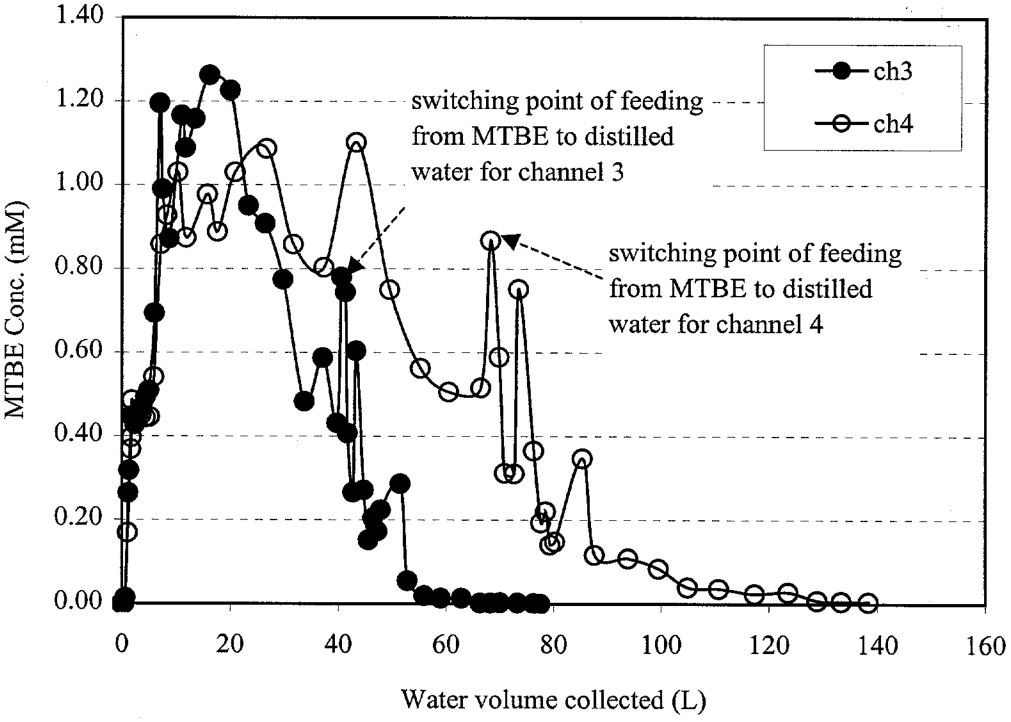

**Figure 3.** Comparison of the groundwater effluent concentrations from channels 3 and 4 as a function of effluent water volume. Neither channel was inoculated with any additional strain. Channel 3 was planted while channel 4 was not. The standard deviation for channel 3 during steady state is 0.27 mM; for channel 4 , it is 0.21 mM.

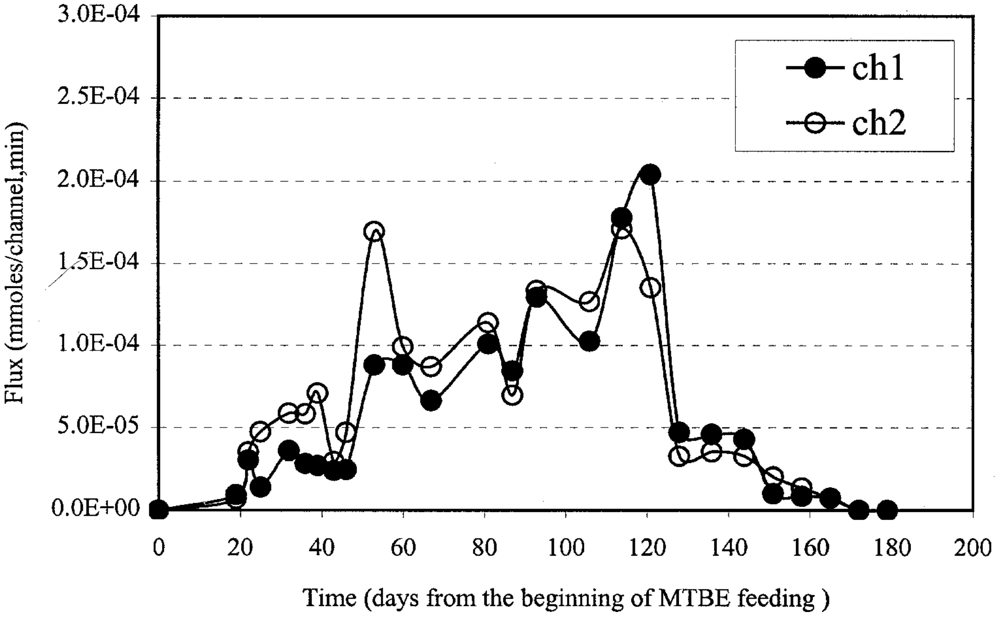

**Figure 4.** Gas fluxes from channels 1 and 2 as a function of days from the beginning of MTBE feeding. Both channels were planted and inoculated with strain #33, but channel 1 was air sparged while channel 2 was not. The feeding was switched from MTBE to distilled water on the 83rd day. The standard deviation for channel 1 during steady state is 3.9 x $10^{-5}$ mmoles/channel/min; for channel 2, it is 3.6 x $10^{-5}$ mmoles/channel/min.

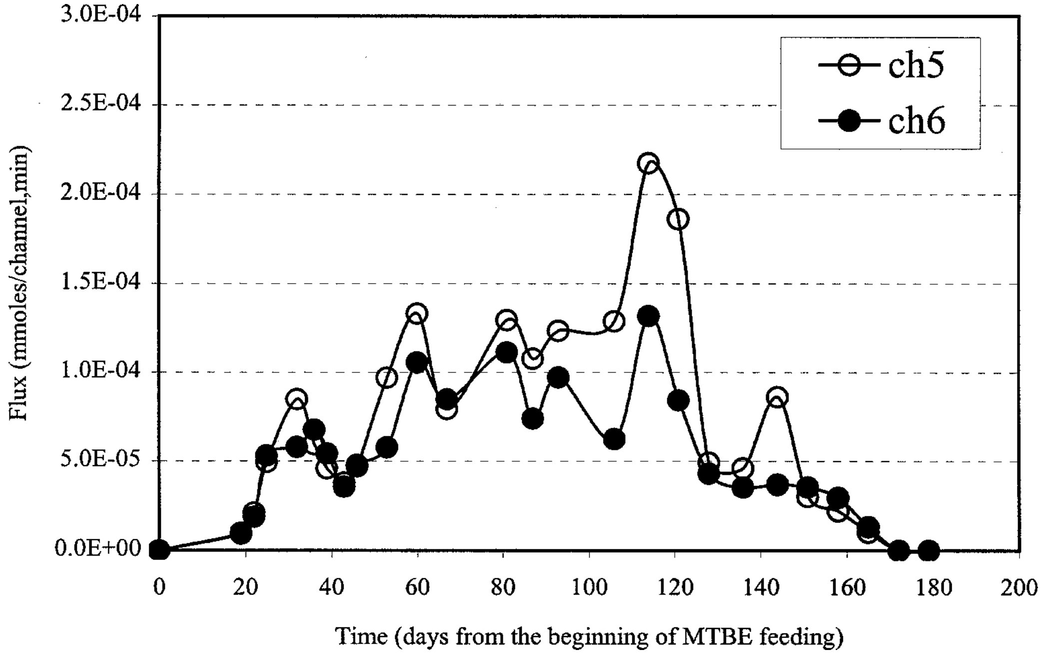

**Figure 5.** Gas fluxes from channels 5 and 6 as a function of days from the beginning of MTBE feeding. Both channels were planted and inoculated with strain #41, but channel 6 was air sparged while channel 5 was not. The feeding was switched from MTBE to distilled water on the 83rd day. The standard deviation for channel 5 during steady state is 4.6 x $10^{-5}$ mmoles/channel/min; for channel 6, it is 2.5 x $10^{-5}$ mmoles/channel/min.

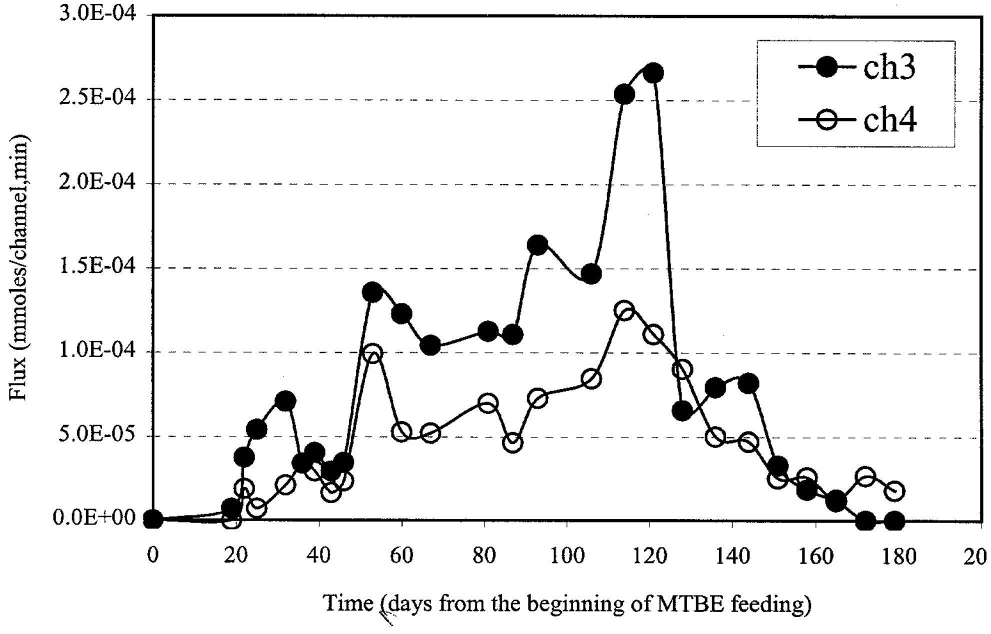

**Figure 6.** Gas fluxes from channels 3 and 4 as a function of days from the beginning of MTBE feeding. Neither channel was inoculated with any additional strain. Channel 3 was planted while channel 4 was not. The feeding was switched from MTBE to distilled water on the 83rd day. The standard deviation for channel 3 during steady state is 5.7 x $10^{-5}$ mmoles/channel/min; for channel 4, it is 2.8 x $10^{-5}$ mmoles/channel/min.

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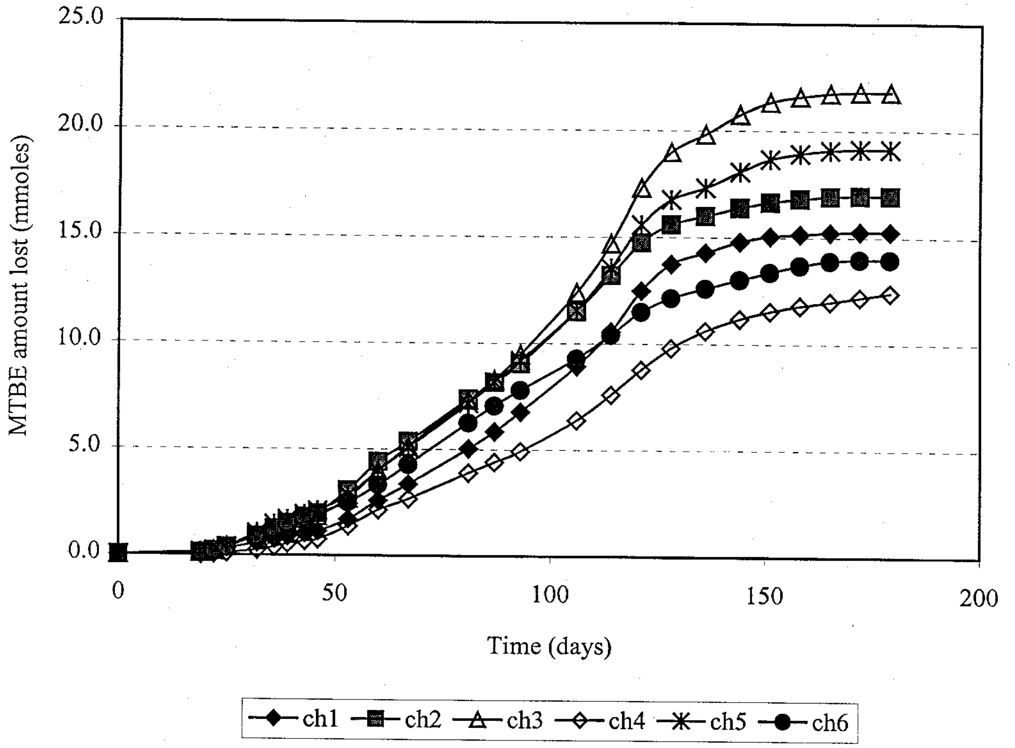

**Figure 7.** Integrated amount of MTBE lost to the atmosphere over time from the soil surface of six channels.

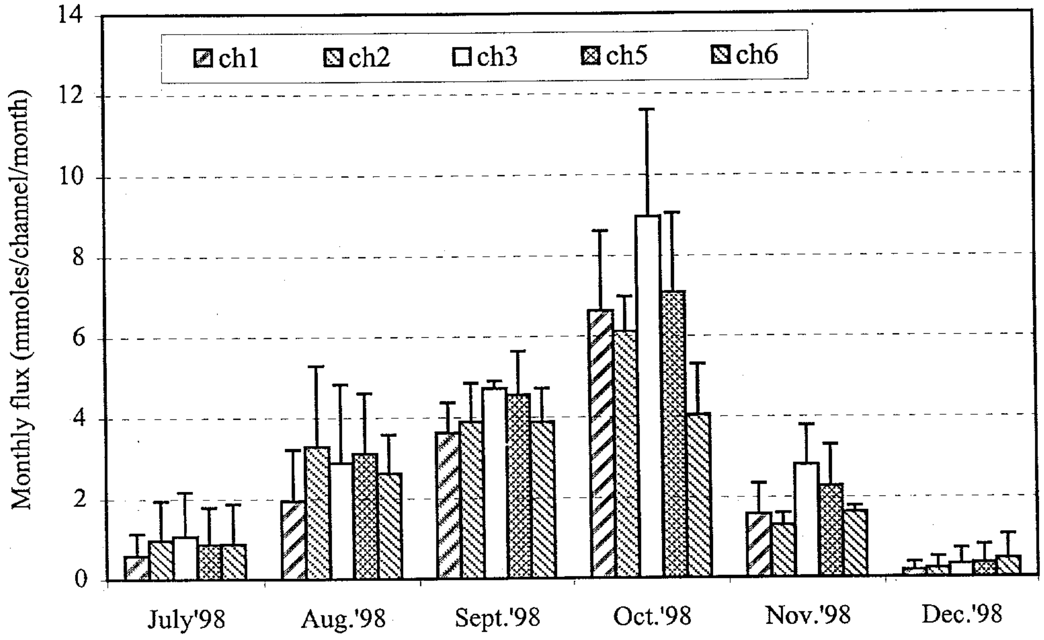

**Figure 8.** Channel soil gas flux of MTBE for each month for the planted channels. Bars represent the standard deviations. Sample numbers for all channels in each month are 4, 7, 3, 4, 4, 4, from July '98 to Dec. '98, respectively.