USING VEGETATION TO TREAT METHYL-TERT-BUTYL ETHER CONTAMINATED GROUNDWATER

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ABSTRACT

Methyl-tert-butyl ether (MTBE) is a commonly used gasoline additive. Leaking underground storage tank systems, spills, and pipeline failures are the causes of reported groundwater contamination with MTBE. The impact of vegetation on MTBE plume transport in groundwater and volatilization was experimentally examined. The experimental system consists of six channels, five of which are planted with alfalfa plants and one of which is unplanted to allow an investigation of the impact of vegetation. Water with 100 µl/ L (0.844 mM) MTBE was continuously fed into each channel at 1 L/day for 72 days, then the feeding was switched back to distilled water. The channel groundwater effluent MTBE concentrations and the soil gas MTBE fluxes were monitored. The experimental results from planted channels and the unplanted channel are compared.

Key words: *MTBE, groundwater, vegetation*

INTRODUCTION

The 1990 Clean Air Act Amendments (CAAA) require that oxygenates be added to reformulated gasoline to improve combustion and to reduce harmful carbon monoxide emissions. The two most commonly used compounds for this purpose are ethanol and methyl-tert-butyl ether (also called MTBE). MTBE has become widely used in the petroleum industry by companies that add the chemical to gasoline. Companies also use small amounts of MTBE to make high-purity isobutylene.

In recent years, the persistence of MTBE in groundwater has been observed (Angel, 1991; Garrett et al., 1986; McKinnon and Dyksen, 1984; Newman, 1995; Oil & Gas Journal, 1995; Squillace et al, 1996; Taylor and O'Brien, 1993; and Worthington and Perez, 1993). The environmental properties, behavior, and fate of MTBE have been described by Squillace et al. (1997). MTBE is a colorless, flammable liquid with a strong odor. It has water solubility of 43,000-54,300 mg/L. Its organic carbon-based partition coefficient (K_{oc}) is 11 cm^3/g, which results in minimal sorption and retardation in natural aquifers. Robbins et al. (1993) measured the dimensionless Henry's Law constant for MTBE to be 0.0216 at 25^0C. Its vapor pressure at 25^0C is 245 mmHg (Budavari et al., 1989). Because MTBE does not bind well to soil and is highly soluble in water, it can migrate with groundwater rapidly (EPA, 1998). In an Army Aberdeen Proving Ground (APG) field site study, the baseline contour maps indicated that MTBE migrated approximately 1.5 times the distance the BTEX constituents migrated (Damera et al., 1997). Accidental spills of gasoline containing MTBE or leaks from storage tanks can pose a hazard to groundwater supplies.

Although MTBE is generally believed to be resistant to biodegradation, recent studies show that *in situ* biodegradation may be an effective remediation alternative (Borden et al., 1997; Daniel,

1995; Daniel and Borden, 1997; Dvorak, 1993; Horan and Brown, 1995; and Park and Cowan, 1997). At least two MTBE-degrading cultures have been identified (Salanitro et al., 1994; Mormile et al., 1994). Biodegradation of MTBE by pure or mixed bacterial cultures has been reported in several laboratory studies. An aerobic mixed culture has been developed which is capable of degrading MTBE as sole carbon and energy source, and mixtures of MTBE, benzene, and toluene showed enhanced MTBE degradation due to growth of the culture on benzene and toluene (Park and Cowan, 1997). Laboratory microcosm studies conducted under aerobic and denitrifying conditions and field-scale reports have shown similar patterns of biodegradation of BTEX and MTBE. That is, biodegradation rates were higher near the contaminant source and lower further downgradient (Daniel and Borden, 1997).

Plants have been found to be able to pump water from saturated zone to vadose zone of an aquifer, to uptake and transform some contaminants in plant tissues, to increase the rate of biodegradation of many organic compounds, and to enhance immobilization (Narayanan et al., 1995; Davis et al., 1993; Newman et al., 1997; Schnoor et al., 1995; Strand et al., 1995). Phytoremediation is the use of plants to clean up contaminated soil and groundwater (Cunningham et al., 1995; Schnoor et al., 1995). Our previous studies (Zhang et al., 1996; Zhang et al., 1997a) have shown that alfalfa plants can grow well in the presence of trichloroethylene (TCE), and that vegetation can enhance TCE transport and volatilization within the planted channels. However, little was reported about phytoremediation of MTBE-contaminated soil or groundwater. In this study, we present the effects of growing alfalfa plants on MTBE transport within an experimental channel system.

MATERIALS AND METHODS

The experimental system consists of six channels with identical geometric size of 110 cm x 60 cm x 10 cm. Each channel is packed to a depth of 60 cm with sandy silt soil with less than 10% silt. Five of the six channels (channels 1, 2, 3, 5, and 6) were planted with a row of alfalfa plants with 10 cm between plants. Channel 4 is unplanted. Water tables of channels are controlled at 35 cm from the channel bottoms. The whole system is illuminated continually with 12 cool white fluorescent lights 50 cm above the soil surface.

The schematic diagram of one representative planted channel is shown in Figure 1. Distilled water is supplied through inlet water jugs to every channel at 1L/day. Groundwater effluent amount was measured daily using collecting bottles. MTBE solution of 100 µl/ L (0.844 mM) was fed to channels 1, 2, 4, 5, and 6 at 1 L/day for 72 days, and then the inlet feeding was switched back to distilled water. Immediately after the switching, we started to take samples at the groundwater effluent sampling ports. The head space method, which has been described in detail and employed to measure TCE concentration in groundwater by us (Zhang et al., 1996), was used to analyze for

MTBE in groundwater. MTBE concentration was monitored with respect to time until no MTBE could be detected by gas chromatography. The whole experiment lasted four months.

In order to measure the gas phase flux of MTBE into the atmosphere, we placed six identical one-end-opened gas-collecting containers (with volume of 400 ml, and cross sectional area of 38.4 cm^2) along the top of each channel. Gas samples were collected with 1 ml gas syringes through septa in the tops of the containers 20 minutes after placement. Gas phase concentrations of MTBE were measured by using gas chromatography. MTBE flux rates from each collecting point and the distance-weighted flux rates for each whole channel were derived by using the same assumptions and calculations as explained in one of our previous studies (Zhang et al., 1997b).

RESULTS AND DISCUSSION

During the MTBE feeding, we monitored aqueous MTBE concentration and found that the inlet and outlet concentrations reached essentially the same level several days after the MTBE introduction. Thus we can assume that after 72 days of feeding MTBE, water within the channels had reached a steady state, such that water in the saturated zone and the capillary fringe area contained MTBE of the inlet concentration. Before the switch back to water, soil waters in the unsaturated zones were sampled at different depths from the soil surface. It was found that the unsaturated zone water has an approximately linear concentration distribution over the depth from zero at the surface to the inlet concentration at the capillary fringe, which is about 5 cm above the water table. The unsaturated zone is about 20 cm deep from soil surface. Based on these assumptions, we can estimate the amount of MTBE retained within each channel at the time we switched back to pure water feeding. That is,

$$M = \theta_{v,sat}\left(V_{sat} + V_{capi}\right)C_{in} + \frac{1}{2}\theta_{v,unsat}C_{in}V_{unsat}$$

where M is the amount (mmoles) of MTBE retained within each channel; the volumetric water content (cm^3/cm^3) for both saturated zone and capillary fringe area is $\theta_{v,sat}$, for the unsaturated zone it is $\theta_{v,unsat}$; C_{in} is the inlet MTBE concentration (mM) in water, which is 0.844 mM; and V_{sat}, V_{capi} and V_{unsat} are the volumes (L) of the saturated zone, the capillary fringe area and the unsaturated zone, respectively.

Assuming the porosity of the soil channels is 0.30 and 80% of the void in the unsaturated zone is occupied by water, then $\theta_{v,sat} = 0.30$ and $\theta_{v,unsat} = 0.3*80\% = 0.24$. The estimated value for M is 13.3 mmoles.

Figures 2, 3, and 4 show the MTBE concentrations in channel groundwater effluents with respect to water volume collected at the channel outlets. While Figure 3 is for the unplanted channel 4, Figures 2 and 4 are for two planted channels (channels 2 and 5), which appear to have lower

groundwater effluent concentration of MTBE than the unplanted one at the same water volume washed out. Due to evapotranspiration associated with the presence of plants, the horizontal flow of MTBE in the saturated groundwater was slower in the planted channels.

The distance-weighted MTBE gas phase fluxes from the same channels are shown in Figures 5, 6, and 7, in which time zero corresponds to the day of step change. The first flux measurement was performed one week after switching the feeding from MTBE in water solution to pure water. At this time, higher flux rates were obtained from the two planted channels than from the unplanted one. This may be partly attributed to the larger upward water movement resulting from evapotranspiration in planted channels.

The average fractions of water collected in groundwater effluents for all six channels are listed in Table 1. The average fraction of water consumed by each channel through transpiration and/or evaporation is simply the difference between unity and that fraction collected in groundwater effluent. Accordingly, the fractions of upward water consumption (evapotranspiration) turned out to be 0.61 and 0.55 for channel 2 and channel 5, and 0.27 for the unplanted channel 4. After about 80 days, when there was little MTBE detected from the gas phase of the planted channels, there was still detectable MTBE from the unplanted channel 4, as shown in Figures 5, 6, and 7. This indicates that MTBE is dissipated more quickly in planted channels than in the unplanted channel.

The integration of groundwater effluent MTBE concentration over water volume washed out, and the integration of distance-weighted MTBE gas phase flux over time give the amount (mmoles) of MTBE collected in groundwater effluent and in gas phase. After 45 and 48 days of MTBE feeding, we did two measurements of fluxes. The results are reported in the figure captions of Figures 5, 6, and 7. While the channel groundwater effluent MTBE concentrations reached steady values five days after the start of MTBE feeding, the flux to the atmosphere was not in steady state in terms of MTBE concentration after 45 days of MTBE feeding. The flux values reported in the figure captions are all less than the first fluxes measured after MTBE feeding was terminated. The values at 45 days are all lower than the values at 48 days; this suggests that MTBE fluxes to the atmosphere are increasing during this period of time. In Figures 5, 6, and 7, the MTBE flux at the soil surface is present at measurable levels for the first 72 days in all of the channels. In channel 4 (Figure 6), which is unplanted, the time required for MTBE to disappear is considerably longer.

The first flux rates of those measured after termination of MTBE feeding were used to estimate the amount of MTBE lost in atmosphere during the first week after the step change. The results of all five testing channels are presented in Table 1 together with the average fraction of water collected in the effluent groundwater. More MTBE was recovered from the unplanted channel than from the planted ones.

The mean residence time of water and MTBE which leaves through the soil surface appears to be considerably longer than that which leaves as groundwater. If we assume a porosity of 0.3,

water saturation in the lower 40 cm, and 80% of saturation in the top 20 cm, there is about 18 liters of water in each channel. With 1 liter fed per day, the mean residence time is about 18 days. The data for MTBE show that the water which leaves as groundwater has mean residence times of 3.87, 7.44, and 4.23 days for channel 2, channel 4, and channel 5. These values are considerably less than 18 days, while the measured surface fluxes show that the mean residence time of water evapotranspired is more than 18 days. For channel 4, if one assumes 27% of the water (0.27 L/day) leaves at the soil surface and a water volume of 18 liters of each channel, the mean residence time is 67 days. For planted channels, the corresponding estimation for mean residence time is about 35 days. The mean residence times for the evapotranspired water obtained from the experimental data measured using the gas collecting containers are 35.2, 48.6, and 34.1 days for channel 2, channel 4, and channel 5, respectively.

The results presented in Figures 2-7 show that the washout of MTBE is in reasonable agreement with expectations based on the estimated mean residence times. There is no evidence of retardation due to MTBE adsorption to soil.

In this work, no attempt was made to measure the rate of biodegradation of MTBE. There was also no attempt to determine the amount of MTBE lost due to plant uptake and transpiration. The results in Table 1 show that the recovered amount of MTBE is significantly less than the amount estimated to be present at the start of the washout experiment.

CONCLUSION

Vegetation increases MTBE gas phase flux to the atmosphere and reduces the groundwater effluent flow rate. The presence of plants enhanced the rate of evapotranspiration and reduced the time required to remove MTBE from the system. Alfalfa plants grew well during both MTBE feeding and washout periods. Most of the MTBE was removed from the system during the 120-day period following the termination of MTBE feeding.

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Figure 1. Schematic diagram of the experimental system.

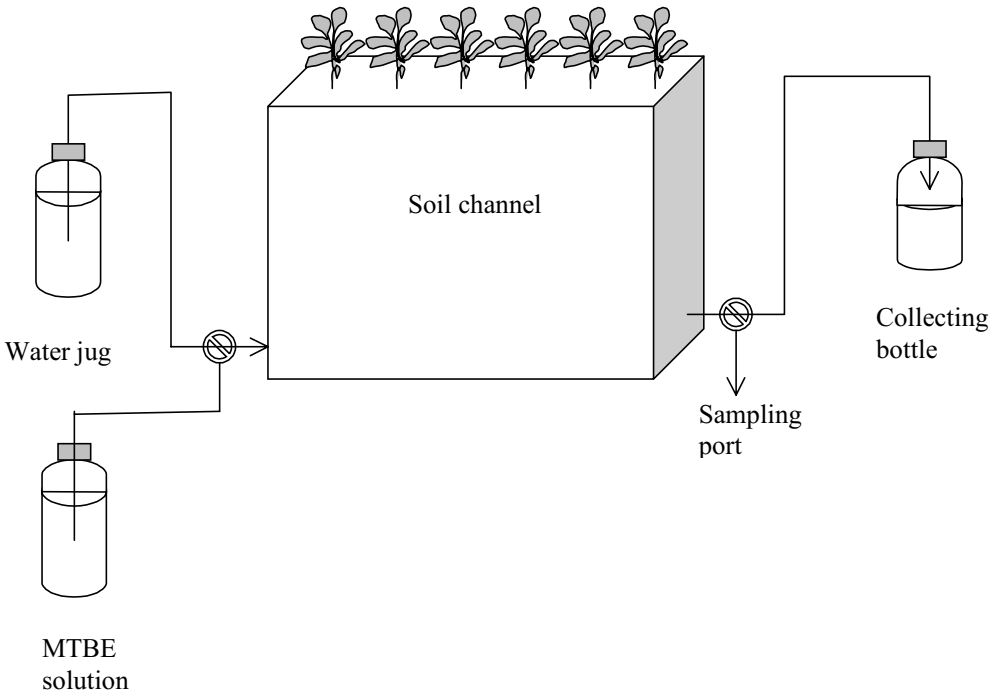

Figure 2. Groundwater effluent MTBE concentration versus water volume collected from channel 2 (planted); the washout lasted 4 months and the mean residence time of MTBE is 3.87 days.

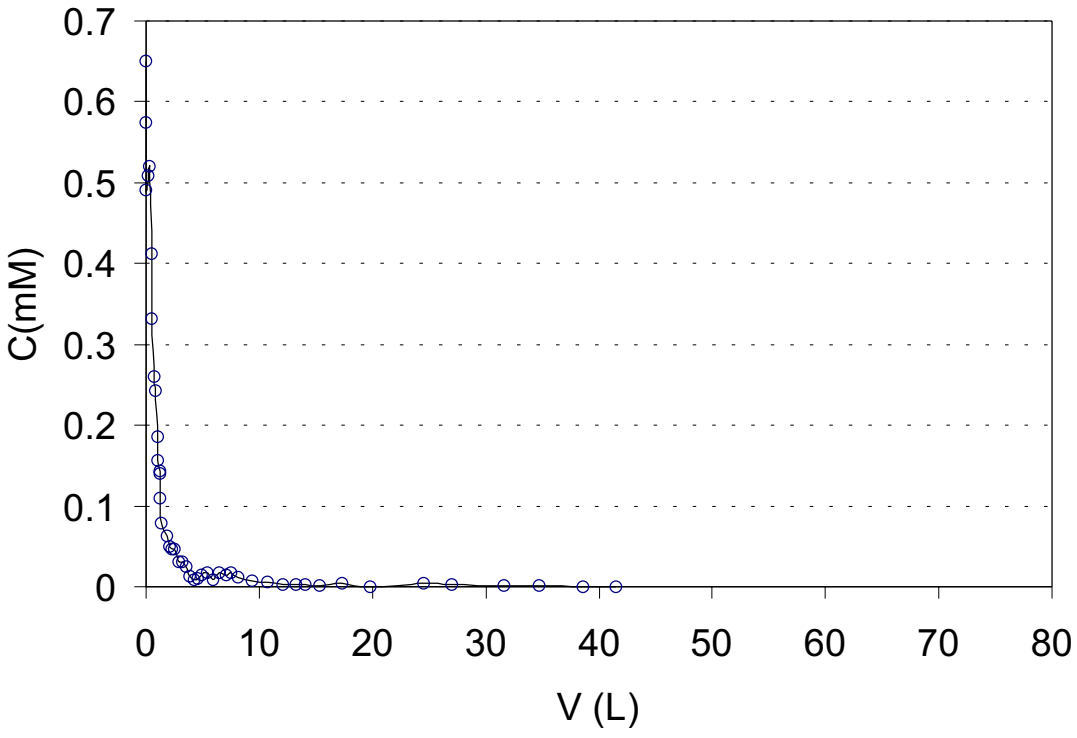

Figure 3. Groundwater effluent MTBE conc. vs water volume collected from channel 4 (unplanted); the washout lasted 4 months and the mean residence time of MTBE is 7.44 days.

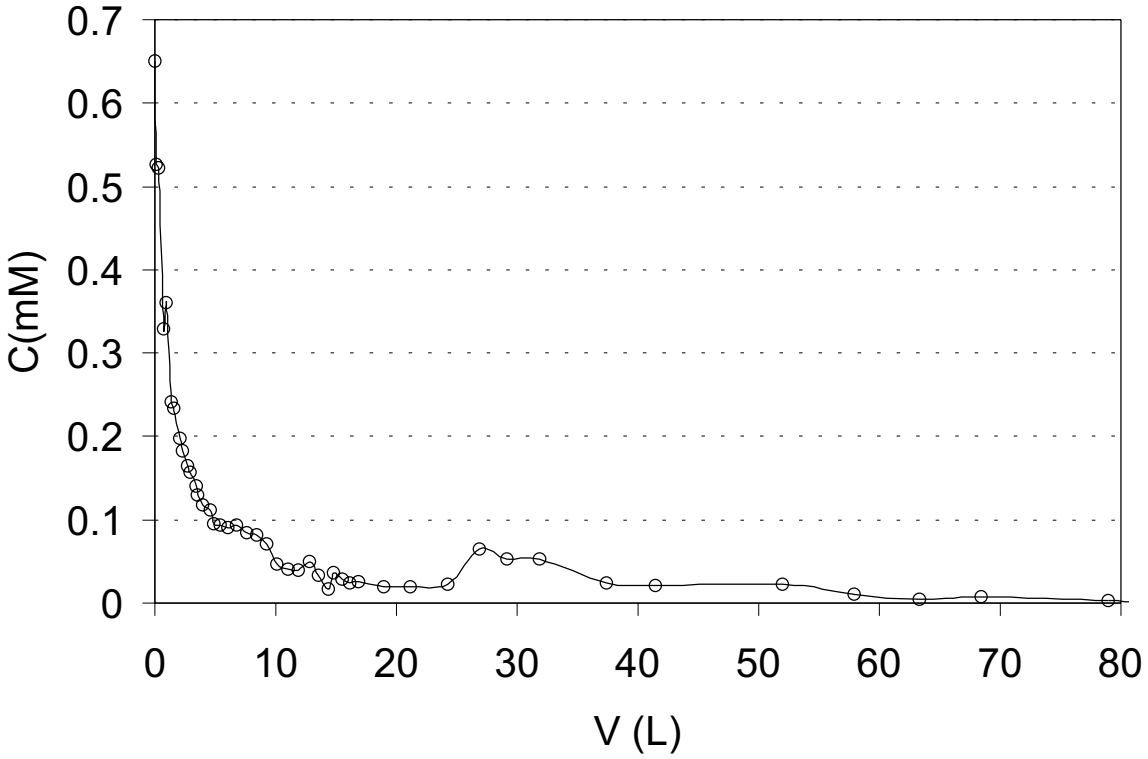

Figure 4. Groundwater effluent MTBE conc. vs water volume collected from channel 5 (planted); the washout lasted 4 months and the mean residence time of MTBE is 4.23 days.

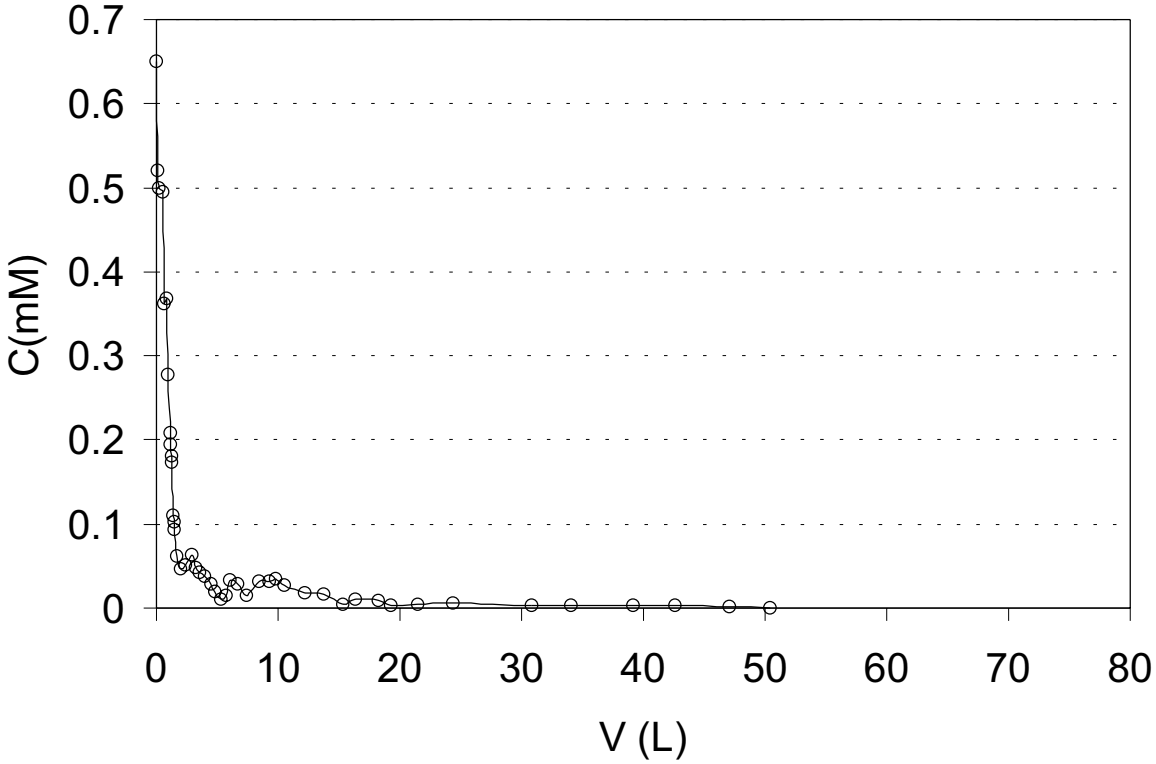

Figure 5. Distance-weighted MTBE gas phase flux from channel 2 (planted); the fluxes measured on the 45th and 48th day of MTBE feeding were 0.094 and 0.109 mmoles per channel per day.

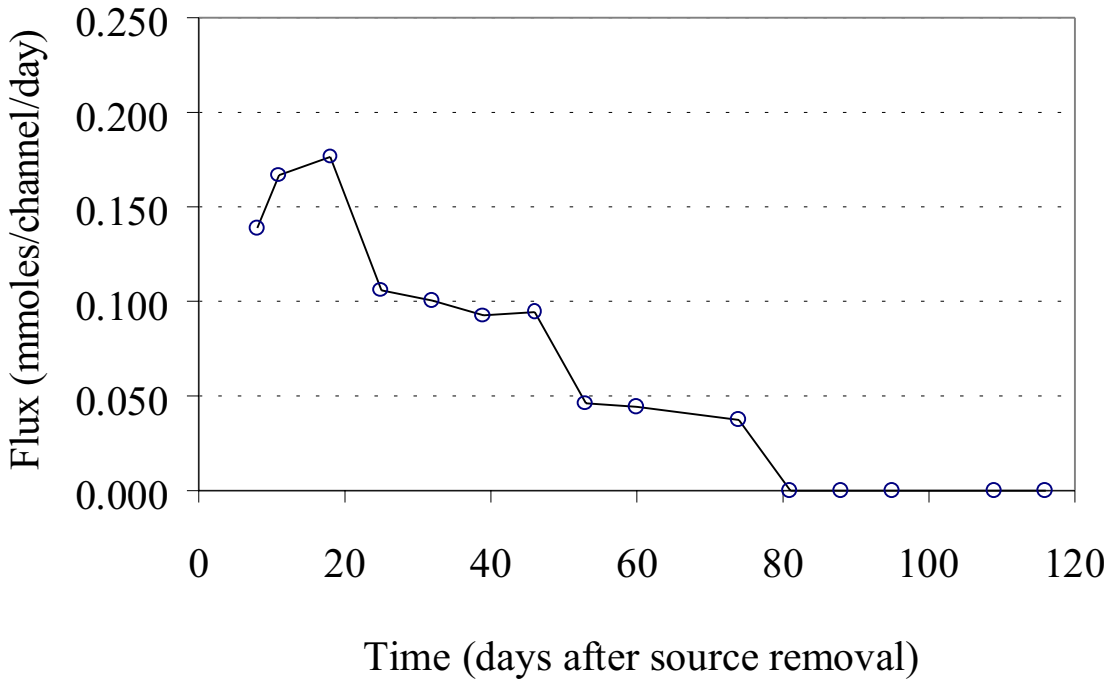

Figure 6. Distance-weighted MTBE gas phase flux from channel 4 (unplanted); the fluxes measured on the 45th and 48th day of MTBE were 0.026 and 0.053 mmoles per channel per day.

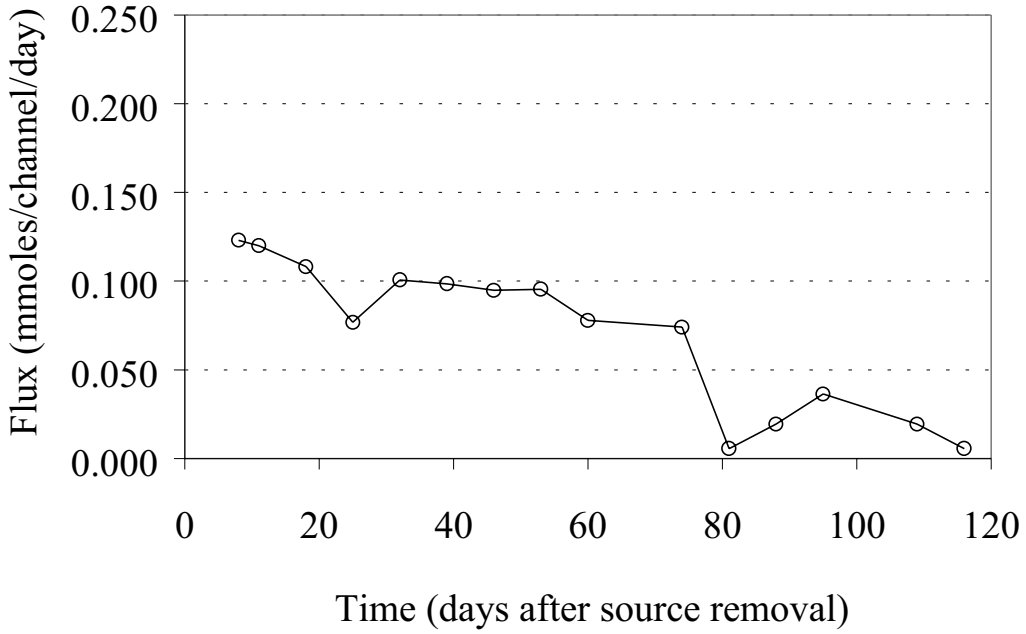

Figure 7. Distance-weighted MTBE gas phase flux from channel 5 (planted); the fluxes measured on the 45th and 48th day of MTBE feeding were 0.085 and 0.115 mmoles per channel per day.

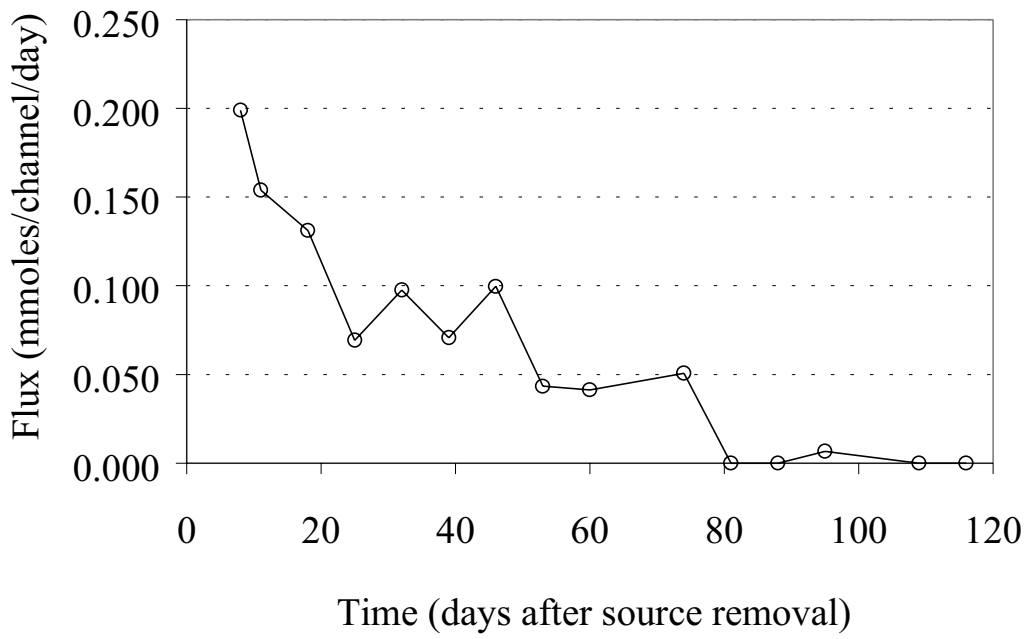

Table 1. Recovery of water and MTBE; amount of MTBE present within each channel at the start of the washout is estimated to be 13.3 mmoles.

channel #	1	2	3	4	5	6
average fraction of water collected in groundwater effluent	0.51	0.39	0.43	0.73	0.45	0.36
amount of MTBE collected in groundwater effluent (mmoles)	3.89	0.68	---	3.06	1.03	0.73
amount of MTBE collected in gas phase (mmoles)	6.69	7.32	---	8.16	7.27	7.18