ENVIRONMENTAL BEHAVIOR OF METHYL TERT-BUTYL ETHER: A STUDY OF HENRY'S LAW CONSTANT AND THE DISPERSION OF MTBE THROUGH RIVER BOTTOM SAND AND SOIL

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ABSTRACT

The Henry's Law constant was determined for methyl *tert*-butyl ether (MTBE) at four temperatures through a new, accurate, and experimentally simple method, based on the work of Gossett (Environ. Sci. Technol. 21:202-208, 1987). The constant was calculated to be 0.032 at 25 °C, suggesting that MTBE is more volatile than previously reported. Analysis of unpublished data collected earlier, using the method of Gossett, is consistent with the most recent estimate, giving median estimates of 0.046 and 0.032 in two series. The value of H was also determined by consecutive additions of water to a single bottle containing a solution of MTBE. Duplicate bottles gave median values of 0.030 and 0.036 at 25 °C. The only published measures of H are 0.022 at 25 °C and 0.048 at 30 °C, but neither value lies very close to the regression line determined for the range 25 to 50 °C [each value deviates from the line by the equivalent of ~2 °C] (Robbins et al.; Anal. Chem. 65:3113-3118, 1993). The dispersion of MTBE through course and fine river bottom sands and silty sand was also analyzed. A simulated MTBE spill on the three materials was studied for a seven-day period by sampling of the headspace gas of effluent collected daily after application of measured amounts of water to simulate precipitation. Core samples at precise depths were taken at the fifth, sixth, and seventh days for replicate columns. It was determined that for the more porous material, MTBE traveled through the material rapidly and with lower recovery in the effluent water. No MTBE remained in the coarse, freely draining sand after five days; while in the silty sand, a significant portion remained in the soil even after seven days. The loss of MTBE mass is presumably due to volatilization, and this work indicated that rapidity of loss of MTBE to the atmosphere will vary greatly with soil properties.

Key words: MTBE, Henry's constant, volatilization, dispersion, soil contamination

INTRODUCTION

Methyl *tert*-butyl ether (MTBE) is a colorless, flammable liquid with a strong distinctive odor. MTBE has been the number one oxygenate to lower emission levels since the Clean Air Act Amendment (CAAA) was established in 1990. MTBE makes up about 85% of the oxygenates used nationally. Gasoline in the U.S. is composed of levels between 5% and 15% MTBE. Most refiners have chosen MTBE because it can be produced at the refinery (ease of production and lower cost), and it blends easily with gasoline. The introduction of MTBE to gasoline may pose significant wastewater treatment and groundwater remediation problems because of accidental release of gasoline into the environment (Johnson et al., 2000). Possible sources of MTBE in groundwater include point sources such as leaking tanks and nonpoint sources such as recharge of soil water by precipitation carrying MTBE in storm water runoff. MTBE is volatile and would typically be expected to volatilize rapidly from soil surfaces or water, but because MTBE is soluble in water and highly mobile in soils, it poses a particular environmental threat (Squillace et al., 1997). The EPA has

issued a drinking water advisory which indicates that the hazards of MTBE are relatively low, but it produces highly undesirable taste and odor in water at quite low concentrations, on the order of 25-50 μg/L (USEPA, 1997).

We redetermined the Henry's constant value over a range of temperatures in order to make use of headspace gas analysis to monitor movement of MTBE through contaminated soil. We then analyzed simulated spills of MTBE-contaminated water on columns representing different kinds of soils including coarse fill sand, fine sand, and a sandy loam. Although there are a number of reports of field observations on spills and leaks, it is usually unknown exactly how much material was spilled and under what environmental conditions, such as varied temperature and precipitation. For highly volatile and water-soluble compounds such as MTBE, both temperature and frequency and duration of precipitation will affect the likelihood that it is leached to groundwater. It does not sorb to soils, so it is readily mobilized by water. Squillace et al. (1997) have reviewed in more detail the environmental properties of MTBE, including its mobility in various soil types. We anticipated that a larger fraction of input MTBE would be lost from a coarser soil by volatilization, but that it would also migrate more rapidly downward through a coarse soil under the influence of precipitation.

METHODS

Determining Henry's Law constant

Experiment 1: The dimensionless Henry's Law constant (H) was determined by analyzing the concentration of MTBE in known volumes of headspace gas of closed systems (~125 mL, calibrated and matched for volume beforehand), each containing a known mass of MTBE solution and a volume of water from 0.5 to 4.0 mL. To improve precision, each bottle plus its stopper was weighed empty, then with an appropriate volume of water added: 0, 0.5, 1.5, or 3.5 mL. The bottles were then sealed. Next a half mL of stock solution of MTBE was added and the bottles were reweighed. The balance used has a vernier precision of hundredths of a mg, so that the amounts of water or solution added were determined to be better than 1 μL per 500 μL. After equilibration to 15 °C, a fine syringe needle was inserted to each bottle to allow influx of air to equilibrate the pressure. Gas samples of 500 μL were withdrawn with a Hamilton syringe and immediately injected to the gas chromatograph. The 3 ft x 1/8 in-column was packed with Porapak R and maintained at 200 °C. Peak heights were measured on a recorder at constant attenuation and allowed to return to baseline between samples.

From the concentration (peak height) of MTBE in the headspace gas of the four known volumes of MTBE solutions, the Henry's Law constant was calculated using Gossett's version of the EPICS formula:

$$H_c = [V_{W2} - (C_{g1}/C_{g2})V_{W1}]/[(C_{g1}/C_{g2})V_{g1} - V_{g2}]$$

where H_c=Henry's Law constant; V_w=volume of liquid in sample; C_g=concentration of MTBE in the gas phase; and V_g=volume of headspace gas in sample.

The Henry's Law constant was determined at 15, 20, 25, and 30 °C, taking 0.5 mL gas samples from the same set of four bottles at all

four temperatures. Corrections were applied for sampling volume and the change of bottle pressure with temperature. The increase in gas volume as temperature was increased is about 1.6% for each 5 °C, about three times the size of the gas sample taken for analysis. Three independent series of measurements were run and compared using this method. In each series, each temperature yielded six pairwise comparisons from four bottles. Because these are not truly independent comparisons, the median value is used for graphical analysis.

Experiment 2: Two series of four bottles each were run in duplicate at 25 °C with either five or 10 µL of liquid MTBE added per bottle and water levels of 2.5 mL, 5 mL, 10 mL, or 20 mL in four different bottles. Water was added first, then the bottle was equilibrated to temperature; pressure was released, then the MTBE was added. Sampling and analysis was done as above, taking 1-mL gas samples in duplicate from each bottle.

Experiment 3: The value of H was also determined by consecutive additions of water to a single bottle containing a solution of MTBE at 25 °C. In this case, the 0.5-mL headspace gas samples were the same size as the water additions up to 3 mL, so that pressure remained constant. Duplicates of the entire series were run and the value of H was determined using the modified EPICS formula as above.

Dispersion examination

The dispersion of MTBE through washed, coarse (C), and fine (F) river bottom sands from a sand production plant and silty sand (D) from a field near the Kaw River was analyzed using carefully packed soil columns. A simulated MTBE spill on three columns of each of the three materials was studied by sampling the headspace gas of effluent collected daily after application of measured amounts of water to simulate precipitation. Core samples at precise depths were taken at the fifth, sixth, and seventh days for three columns, one of each soil. Total recovery of each column was calculated based on the amounts found in core sample and drainage collections.

Columns were constructed of nominal 1.5-inch PVC pipe (actual inside diameter 4.0 cm), cut to 30-cm lengths. Two sets of holes were bored 90 ° from each other with the first set at 3, 9, 15, 21, and 27 cm and the other at 6, 12, 18, and 24 cm from one end. Holes were 15/32 inch (~11.7 mm) in diameter so that serum bottle stoppers could be tightly placed in them. The outlet was closed by use of a # 9 one-hole rubber stopper on which two layers of plastic window screen was placed. A portion of 1-mL disposable syringe was installed in the stopper so that the luer tip was projected on the outside, while the cut-off syringe was flush with the inner surface of the stopper. Actual volume available after adding the stopper was 365 mL.

A layer of 40-g coarse sand (1-3 mm) was added to each column, bringing it up to 3.5 cm from the bottom, just covering one sampling port. The sand was packed into place, then covered with the desired fill material which was added in 3-cm increments and packed. All columns were packed dry, using 495 g of fine sand, 550 g of coarse sand, or 403 g of silty sand soil to fill them. The fine sand and silty

sand had been sieved to pass a #18 sieve (1 mm). Table 1 provides a distribution of particle sizes indicating the silty nature of the field soil, and the relatively uniform sizing of the commercially produced washed sand.

The porosity and water-holding capacity of each soil type was determined by filling the columns from the bottom with water until the column was just filled to the surface of the matrix. The water added was determined by weight difference. Then the columns were allowed to drain freely overnight and reweighed to determine the water retention. The available air porosity was the difference between the saturated and drained masses. This provided a column at nominal field capacity, so that any added solution containing contaminant ought to displace water from the column. The coarse sand held about 42 mL water and had 46 mL air space. The fractional drained water content by weight was 0.07. Total porosity was near 0.3 with a bit over half that porosity being air-filled. The packed-bulk density was near 1.85. The fine sand held 85 mL water and had 21 mL air space. The fractional drained water content was thus 0.145. The calculated porosity was 0.33 with only 1/5 of that air-filled. Bulk density was near 1.7. The silty sand held 125 mL water and had only 4-mL air space. Based on later experiments, the 4-mL loss may represent

mainly evaporation from the surface rather than open pore space in the column. The weight fractional water content was 0.24, giving a porosity of 0.33, while the packed bulk density was only 1.4. The above values are reasonable for the materials used, with the fine sand having the same packed density and porosity as for our more extensive studies of planted systems (Davis et al., 2001).

To simulate a spill of contaminated water, 10 mL of distilled water containing MTBE were applied uniformly to the top of the column (~8 mm deep). A collection bottle, vented with a fine (# 26 ga) needle was attached directly to the column outlet by a needle (# 21 ga). As solution was added to the top of the column, liquid was displaced into the collection bottle. The potential loss of MTBE from the vented bottle was determined and found to be only a few percent per day. Appropriate correction was made in calculating the recovery.

Each day, 15 mL of water were applied to the top of the column with a fresh collection bottle in place. The mass of MTBE recovered in each bottle was determined by headspace gas analysis. The H value of 0.03 was used in calculations. Based on liquid inputs and recoveries, it is evident that about 3 mL/d of water were lost by evaporation from the columns. This corresponds to ~2.5 mm/d for a column of the

Table 1. Fraction of each soil type passing sieves of indicated sizes.

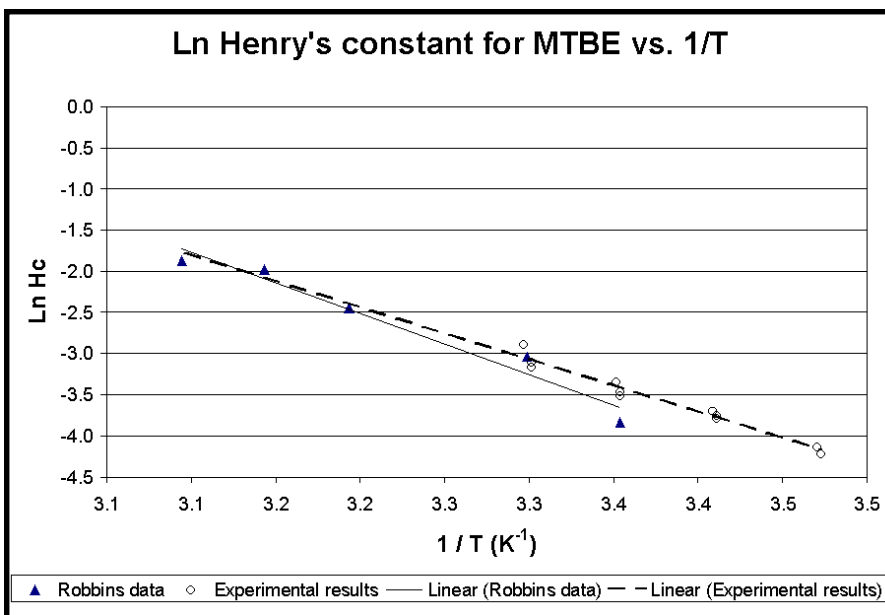| soil type	0.7-1.0 mm (#25 sieve)	0.25-0.7 mm (#60 sieve)	0.18-0.25 mm (#80 sieve)	<0.18 mm (< #80)
fine sand	0.25	0.30	0.32	0.14
silty sand	0.09	0.46	0.09	0.36

Figure 1. Ln of Henry's Law constant as a function of inverse absolute temperature. Data are shown comparing our results at 15-30 °C with Robbins et al. from 25-45 °C. A best-fit regression line is indicated for the combined data set (triplicate) for this work and as given by Robbins et al. for their data.

indicated cross section (4 cm diameter or 12.4 mL/cm height). The extent of downward displacement of MTBE depends on the water-holding capacity of the soil, which is different in each treatment. In the absence of preferential flow, elution of MTBE from the silty sand would be predicted to take about 10 days, while for the coarse sand it would take only three days.

On day five, one column of each treatment was sampled at eight ports. A cork borer was inserted into one of the holes bored in the column, withdrawn, and placed into a serum bottle. The core was displaced into the bottle using a close-fitting plunger and then the bottle was quickly stoppered. The recovery of MTBE was determined by headspace gas analysis. By weighing the sample wet, and again after drying, it was possible to estimate the MTBE in each 3-cm segment of the column based on the fraction of the total weight sampled in each core. The

dry weight provided an estimate of the packing density of the column, and the wet weight indicated the relative saturation of the section. Because these are freely draining columns, not all sections have the same relative water content. The soil is a bit less wet at the top of the column. This effect varies with soil type.

RESULTS AND DISCUSSION

Henry's Law constant

The dimensionless Henry's Law constant (H) was determined by analyzing the concentration of MTBE in known volumes of headspace gas of closed systems (~125 mL), each containing a known mass of MTBE solution and volume of water from 0.5 to 4.0 mL. From the concentration of MTBE in the headspace gas of the four known volumes of MTBE solutions, the Henry's Law constant was calculated using Gossett's version of the EPICS formula. The

Henry's Law constant was determined at 15, 20, 25, and 30 °C, taking 0.5-mL samples from the same set of four bottles at all four temperatures. Corrections were applied for sampling volume and the change of pressure with temperature. This approach reduced both the labor required and variability associated with having multiple bottles to analyze. Three independent series of measurements were done. In experiment one, Henry's Law constant was calculated to be 0.032 at 25 °C. See Figure 1 for a comparison at different temperatures and the previously published results of Robbins et al. (1993). The present results and those of Robbins et al. were obtained over different temperature intervals with a few degrees of overlap. Thus we cannot reliably determine whether the results of Robbins differ significantly from ours or whether the main effect is a possible non-linearity in the Henry's Law constant as a function of temperature.

In experiment two, the median value of H was found to be 0.044 for 5 μL MTBE and 0.032 for 10 μL MTBE at 25 °C. As discussed by Gossett, this approach of adding liquid MTBE to varied amounts of water is limited by the accuracy of dispensing small volumes of volatile solvent.

In the third experiment, the median value of H was calculated to be 0.030 and 0.036 at 25 °C for two series of water additions to a single bottle. While simple for MTBE where small increments of water addition have a large impact on gas-phase concentration of the volatile, this approach would be unsuitable for compounds where a large volume of water had to be added to change the gas-phase concentration significantly.

Results of these three somewhat different experimental approaches suggest that MTBE is more volatile than previously reported. The only published experimental determinations of H are 0.022 at 25 °C and 0.048 at 30 °C, but neither value lies very close to the regression line determined for the range 25 to 50 °C [each value deviates from the line by the equivalent of ~2 °C (Robbins et al., 1993)]. See Figure 1 where this is apparent. For many purposes such a discrepancy might be of little significance, but having a reliable value of H is critical for quantitative studies of MTBE behavior when headspace gas analysis is used. The slope of a van t'Hoff plot for our results is lower than reported by Robbins et al. (1993), but the reason for this is uncertain. They filled the bottles completely with the stock solution and then carefully withdrew a portion of it after equilibration to temperature. In contrast to this approach, we added a fixed amount of solution with MTBE into varied amounts of water, which minimizes the possiblity of volatilization transfer of MTBE from liquid to gas phase. Possibly the gas phase of our bottles was not sufficiently chilled for long enough to assure transfer equilibrium to the liquid. The studies should be repeated with a longer equilibration time and at lower temperatures to resolve this question, which is important for prediction of MTBE volatilization losses from cold soils during winter.

The value of H calculated by Robbins et al. (1993) doubles between 20 and 30 °C, which results in quite appreciable errors in mass
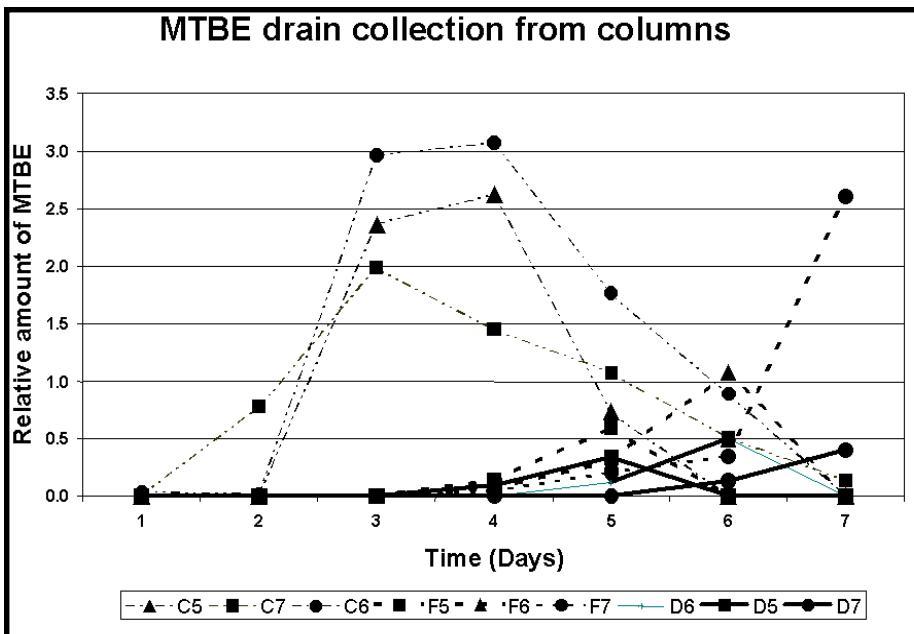
Figure 2. Daily recovery of MTBE in eluant from soil columns of different porosity.

balances determined using estimated H values extrapolated from a temperature different from that of actual measurement. Even with the somewhat lesser temperature dependence that we observed, the error is still large. Each change of one degree leads to about a 10 % different fraction of MTBE in the gas phase at around 25 °C. Values given in Table 2 show this effect.

Dispersion examination

For the more porous material, MTBE traveled through the material rapidly and with lower recovery, all appearing in the effluent water (Figure 2). As predicted from the water-holding capacity of the columns, no MTBE remained in the coarse, freely draining sand after five days, while in the silty sand a significant

Table 2. Dimensionless Henry's constants at different temperatures.

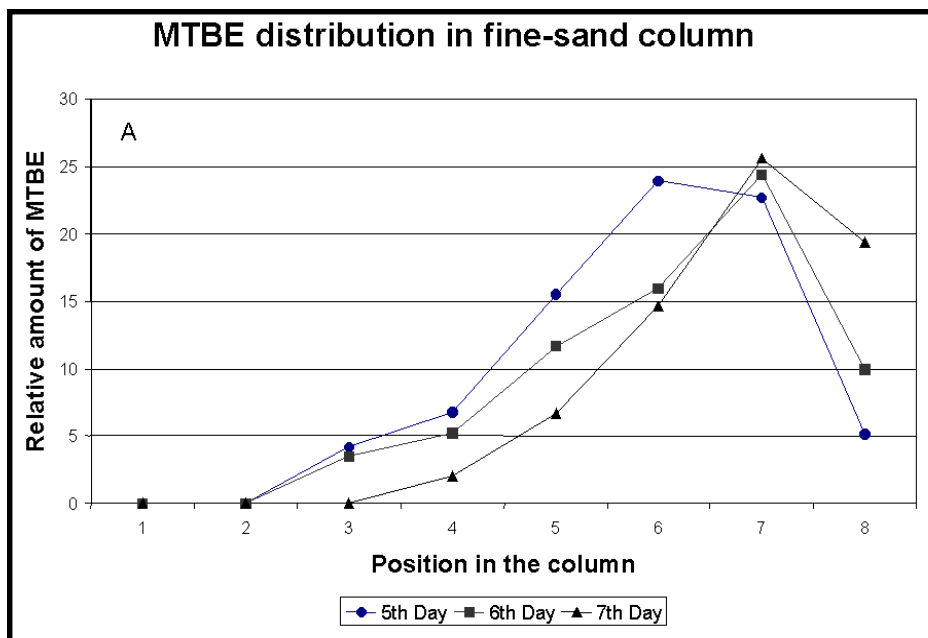| Temperature		Experimental results			Literature values
(°C)	(K)	Series 1	Series 2	Series 3	
14.8	287.95	0.015			
15.0	288.15		0.016	0.016	
20.0	293.15	0.023		0.023	
20.2	293.35		0.025		
25.0	298.15		0.031	0.030	0.022
25.2	298.35	0.036			
29.8	302.95		0.042	0.045	
30.0	303.15				0.048
30.2	303.35	0.056			
40.0	313.15				0.086
45.0	318.15				0.139
50.0	323.15				0.154

Figure 3a. Distribution of MTBE in fine-sand column after three different times of elution with water.

portion remained in the soil even after seven days (Figures 3a and 3b). The weight fraction of water in the coarse sand core samples was about 0.06, while that in the fine sand was 0.14-0.15, and in the silty sand > 0.2. This is consistent with the relative travel time of MTBE through each soil and with the fractional water content estimated at the beginnning of the experiment.

The loss of MTBE mass is presumably due to volatilization, and this work indicated that rate of loss of MTBE to the atmosphere will vary greatly with soil properties. Evaporative loss of water was about 2.5 mm/d (3 mL per column), so it is not surprising that at least 30 % of the 10-mL, applied MTBE would be lost evaporatively from a fully saturated soil. With a porosity of ~0.35, the applied volume of 10 mL would penetrate less than 2.4 cm into the loam soil. For the loam, little further loss was expected to occur once the first 15-mL water was applied to displace the MTBE solution into the column. During 24 hr, a significant fraction of the applied

MTBE would be lost by liquid-phase diffusion, even if the soil had no air-filled pore space. The analysis by Rose for diffusion from slabs indicates that half of the material in a half-cm-deep slab would be lost in 24 h when $D = 10^{-5}$. Given a tortuosity factor of ~2 for the soil, losses would be somewhat less than half at a depth of 0.5 cm. Overall we can estimate that up to 20% of the total applied MTBE might be lost by aqueous-phase diffusion in the first day. When the soil has some air-filled porosity, diffusive losses would be much greater.

The fine sand had a porosity of ~0.33, giving a slightly deeper penetration of the contaminated water. The air-filled pore space would be expected to allow continued loss of MTBE even after application of water to the soil surface each day. The modeling work of Davis et al. (2001) indicates that for MTBE, the extent of such loss is a sensitive product of air-filled porosity, H value, and vertical water velocity.
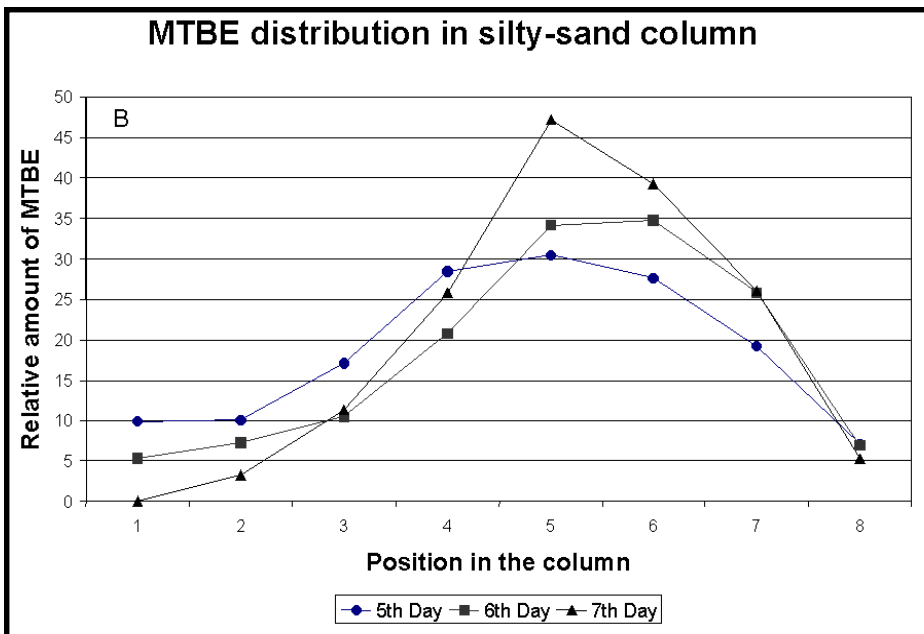
Figure 3b. Distribution of MTBE in silty- sand column after three different times of elution with water.

The coarse sand, which had a heterogenous grain size, packed down to give a lower total porosity than either of the above two soils. The bulk density was 10 % higher than for the fine sand and 25 % higher than for the silty sand. The retained water and air-filled pore space were about equal, with the air space twice that of the fine sand and at least ten times that of the silty sand. With such a high air-filled porosity, it was expected that more MTBE would be lost from these columns.

The overall recoveries confirm expectations (Figure 4). For the coarse sand (C), total recovered MTBE varied from 14-22 % (mean 16.7 %); for fine sand (F) it varied from 21-25 % (mean 22.4 %); for loam (D) it varied from 38-41% (mean 38.9 %). These results were obtained at a room temperature of ~24 °C. Because the H value is very temperature dependent, losses from soil will vary greatly depending on season and climatic regime.

Overall, these results indicate that a large but unpredictable fraction of MTBE from a spill might be lost to the atmosphere immediately following a spill, unless it was eluted into the soil by application of water, whether by rainfall or efforts to wash it away from the spill site. Once in the soil, loss by diffusion would depend on the net water velocity and air-filled porosity of the soil. The paper of Davis et al. (2001) shows the theoretical response of MTBE and other contaminants when the net vertical water velocity is in the upward direction. Further modeling is needed to predict the effect of a net downward velocity on contaminant losses.

ACKNOWLEDGEMENTS
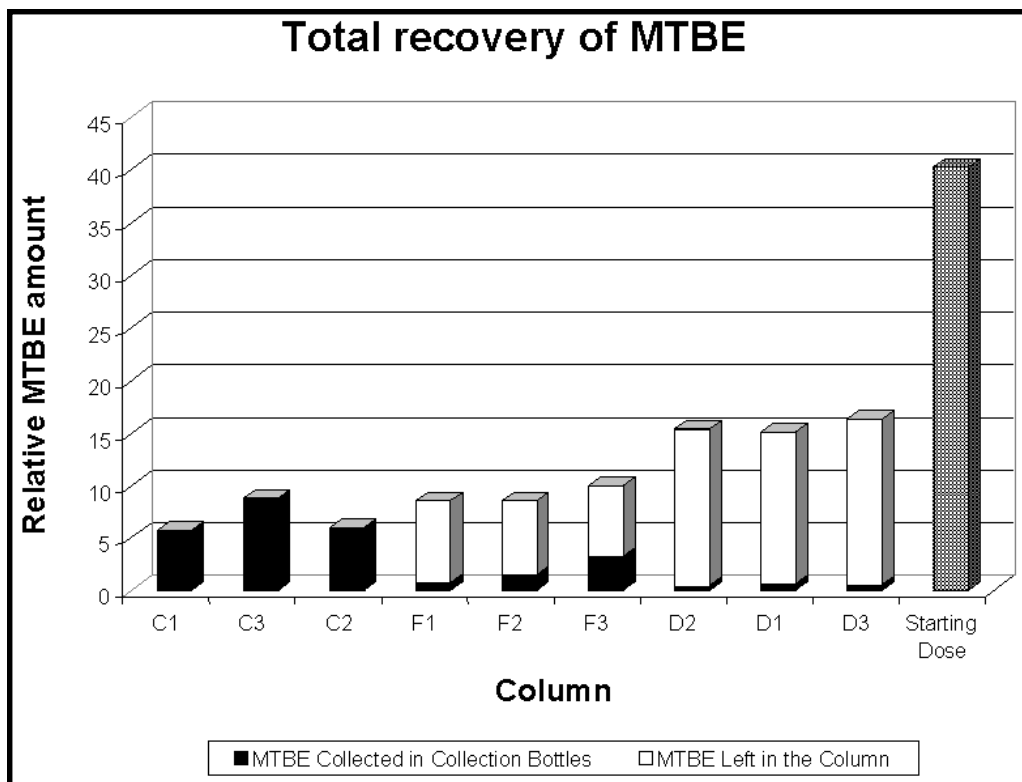
Total recovery of MTBE

Figure 4. Total recovery for each column, compared to input concentration, showing relative fraction recovered in eluant and remaining within the column.

819563, R-825549, and R-825550 through the Great Plains/Rocky Mountain Hazardous Substance Research Center for regions 7 and 8 under project 98-3. It has not been subjected to the EPA for peer and administrative review and, therefore, may not necessarily reflect views of the agency and no official endorsement should be inferred.

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