

Review of the Environmental Behavior and Fate of Methyl *tert*-Butyl Ether

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Abstract—A review of pertinent equations and current research indicates when gasoline that has been oxygenated with methyl tert-butyl ether (MTBE) comes in contact with water, large amounts of MTBE can dissolve. At 25°C the water solubility of MTBE is about 5,000 mg/L for a gasoline that is 10% MTBE by weight, whereas for a nonoxygenated gasoline, the total hydrocarbon solubility in water is typically about 120 mg/L. MTBE sorbs only weakly to subsurface solids; therefore, sorption does not substantially retard the transport of MTBE by ground water. In addition, MTBE generally resists biodegradation in ground water. The half-life of MTBE in the atmosphere can be as short as 3 days in a regional airshed. MTBE in the air tends to partition into atmospheric water, including precipitation. However, washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gas-phase concentration of the compound in the air. The partitioning of MTBE to precipitation can nevertheless result in concentrations as high as 3 µg/L or more in precipitation and can contribute to the presence of MTBE in surface and ground water.

Keywords—MTBE, Fuel oxygenate, Behavior, Fate, Water quality

INTRODUCTION

Fuel oxygenates are voluntarily added to gasoline to enhance the octane of gasoline in many areas of the United States, and fuel oxygenates have been used since 1988 to improve air quality [1] in some metropolitan areas. However, since November 1, 1992, the 1990 Clean Air Act Amendments require areas that exceed the national ambient air-quality standard for carbon monoxide (carbon monoxide nonattainment areas) to use oxygenated gasoline during the winter when the concentrations of carbon monoxide are highest. Furthermore, since January 1995, the 1990 Clean Air Act Amendments also require nine metropolitan areas that have the most severe ozone pollution to use year-round reformulated gasoline that contains fuel oxygenates. Numerous additional metropolitan areas have chosen to participate in the reformulated gasoline and oxygenated gasoline programs.

Currently, oxygenates are added to more than 30% of the gasoline used in the United States [2] and the percentage may increase in the future. Indeed, it has been projected that by the year 2000 fuel oxygenates will be added to 70% of the gasoline used in the United States [3]. Because of its low cost, ease of production, and favorable transfer and blending characteristics, methyl *tert*-butyl ether (MTBE) is the most commonly used fuel oxygenate [3, 4]. It can be produced at the refinery, it blends easily without separating from gasoline, and the MTBE gasoline blend can be transferred through existing pipelines. In the United States, almost all MTBE is used in gasoline. The second most-used fuel oxygenate is ethanol. Other oxygenates in limited commercial use, or that have been used in the past, include methanol, *tert*-butyl alcohol, ethyl *tert*-butyl ether, *tert*-amyl methyl ether, and diisopropyl ether [5].

The U.S. Environmental Protection Agency (USEPA) has tentatively classified MTBE as a possible human carcinogen, and no drinking-water regulation has been established for MTBE [6]. The USEPA has classified MTBE as a possible human carcinogen on the basis of studies that show that MTBE is a carcinogen in animals [7-9]. The USEPA has issued a draft lifetime health advisory of 20-200 $\mu\text{g}/\text{L}$; the health advisory is the maximum concentration in drinking water that is not expected to cause any adverse noncarcinogenic effects over a lifetime of exposure with a specified margin of safety. MTBE is not expected to bioaccumulate in surface water aquatic organisms [10].

MTBE has been detected in ground water [11] and stormwater [12]. Of the 60 volatile organic chemicals (VOCs) analyzed in samples of shallow ambient ground water that were collected from eight urban areas during 1993-94 as part of the U.S. Geological Survey's National Water-Quality Assessment Program, MTBE was the second most frequently detected chemical (after chloroform) [11]. The ground-water samples were collected from 5 drinking-water wells, 12 springs and 193 monitoring wells. At a reporting level of 0.2 µg/L, MTBE was detected in water from 27% of the 210 wells and springs sampled, but no MTBE was detected in water from the drinking-water wells. Measurable concentrations of MTBE were also found in some of 592 stormwater samples collected by the U.S. Geological Survey in 16 cities and metropolitan areas required to obtain National Pollutant Discharge Elimination System permits [12]. MTBE was the seventh most frequently detected VOC, occurring in 6.9% of the stormwater samples. The reporting level for MTBE was 1.0 µg/L for most of the stormwater samples, and it is likely that this higher reporting level resulted in fewer detections when compared to some of the other VOCs that had a reporting level of 0.2 µg/L for all of the samples. When MTBE was detected, concentrations ranged from 0.2 to 8.7 µg/L. Eighty-three percent of all stormwater samples that had detectable concentrations of MTBE were collected between October 1 and March 31. This period of time is approximately when oxygenated gasoline is used in carbon monoxide nonattainment areas.

At the request of the USEPA, the Office of Science and Technology Policy, Executive Office of the President, has initiated an interagency assessment of the scientific basis and efficacy of the winter oxygenated gasoline program. This paper summarizes part of the water-quality section [5] of this interagency assessment report. Where appropriate, this paper contrasts the properties of MTBE with those of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds. BTEX compounds are present in all gasoline and are the most soluble and toxic compounds associated with nonoxygenated gasoline.

The purpose of this paper is to provide a review of the environmental behavior and fate of MTBE by reviewing pertinent equations and current research. The importance of this review is driven by MTBE's ubiquitous use, potential health effects, and frequent detection in shallow urban ground water and urban stormwater runoff.

ENVIRONMENTAL BEHAVIOR OF MTBE

The manner in which MTBE behaves in the environment is largely determined by how it partitions between water, subsurface solids, and air. The behavior of MTBE in water is affected by its partitioning between: (1) water and gasoline; (2) water and air, as occurs in the atmosphere with precipitation and also in the subsurface above the water table; and (3) water and subsurface solids.

Partitioning between water and gasoline

The partitioning of MTBE between water and gasoline is affected in part by the solubility of MTBE in water. At a given temperature, the solubility of a pure organic liquid (for example, benzene or MTBE) in water is a constant, represented as c_s^o (mg/L). However, the solubility is reduced below c_s^o when other organic compounds are present in a separate liquid phase (for example, gasoline); at a given temperature, the solubility of a compound from the organic mixture will be reduced from c_s^o by the factor X_m , which is the mole fraction of the compound in the mixture. An additional coefficient γ is needed when the chemical properties of the compound differ greatly from the properties of the mixture as a whole [13]. The result is that the equilibrium water solubility of the compound from the mixture will be:

$$c_s \text{ (mg/L)} = \gamma X_m c_s^o \text{ (all compounds).} \quad (1)$$

For a compound that has a molecular weight that is similar to the mean molecular weight of gasoline (~100 g/mol), X_m is closely approximated as the fraction of the compound on either a weight or a volume basis. For example, for a gasoline that is 10% by weight MTBE, X_m for MTBE will be ~0.10. For the dissolution of low-polarity compounds (like the BTEX group) from gasoline, γ will be close to 1, and equation 1 then can be approximated as:

$$c_s \text{ (mg/L)} = X_m c_s^o \text{ (low-polarity compounds).} \quad (2)$$

For equation 2 it is assumed that dissolution is occurring into a water phase in which there are no large amounts of alcohols or other possible cosolvents that could increase the value of c_s^o . The value of c_s will decrease with lower temperatures because the value of c_s^o decreases with temperature. Equilibrium solubility data obtained by Barker et al. [14] indicated that equation 2 is valid for MTBE; their data indicated that $\gamma = 1.1$. Additional information on the dissolution of gasoline, and other organic mixtures, into water is discussed by Shiu et al. [15], Cline et al. [16] and Mackay et al. [17].

The high solubility of MTBE in water combined with its high concentrations in an oxygenated gasoline can result in high concentrations of MTBE in surface water and ground water contaminated by point sources of oxygenated gasoline. For a gasoline that is 10% by weight MTBE, assuming no depletion of the MTBE concentration in the gasoline due to dissolution into the water and a water solubility of 50,000 mg/L (Table 1), the water solubility of the MTBE from oxygenated gasoline would be about 5,000 mg/L at room temperature. By comparison, the total hydrocarbon water solubility for a nonoxygenated gasoline is generally about 120 mg/L [18].

High concentrations of MTBE in ground water near gasoline-release sites are consistent with experimental water-solubility data. Garrett et al. [19] and Davidson [20] have reported MTBE concentrations as high as 200 mg/L in water. These values are not as high (for example, thousands of mg/L) as might be expected for water equilibrated with gasoline containing a large percentage of MTBE; however, relatively uncontaminated water will dilute organic compounds to concentrations less than what would be calculated using equation 2 [21].

As the ratio of water to gasoline increases, the concentrations of MTBE in the water will decrease and the MTBE in the gasoline will become depleted (Fig. 1). The distribution of MTBE between gasoline and water can be calculated for various water/gasoline ratios. At equilibrium, C_w is the concentration of MTBE in water and C_g is the concentration of MTBE in gasoline. K_w is the dimensionless water/gasoline partitioning coefficient where

$$K_w = \frac{C_w}{C_g} \quad (3)$$

Assuming that the density of gasoline is about 750 g/L (table 1) and that γ for MTBE is close to 1, then we can use the solubility of MTBE in water (50 g/L) from pure MTBE (750 g/L, table 1) to estimate that $K_w = 0.067$. This value is very similar to an average value (0.065) for 31 gasoline samples reported by Cline [16]. The total mass of MTBE in the mixture (M) is equal to the sum of the mass of MTBE in the water and the mass in the gasoline. If V_g is the volume of gasoline, the concentration of MTBE in the water can be calculated where:

$$C_w = \frac{M}{V_w + \left(\frac{V_g}{K_w}\right)} \quad (4)$$

Figure 1 was constructed for a gasoline that is initially 10% by weight MTBE so that $M = 0.1 V_g$.

The high concentrations of MTBE that can occur in ground water at gasoline release sites have raised the question as to whether MTBE could enhance the subsurface transport velocities of the BTEX group through a cosolvency effect. In fact, research has indicated that cosolvency effects generally arise only when the cosolvent is present in water at 1% (10,000 mg/L) or more by volume [22,23]. These concentrations are generally much higher than those in water that is in equilibrium with gasoline containing MTBE. Gasoline that contains 15% MTBE by volume, when equilibrated with water, results in no more than 7,500 mg/L (~0.75% by volume) of MTBE in the water [14]. These conclusions regarding the potential for cosolvent effects are supported by laboratory research that used a gasoline-to-water ratio of 1:10 volume/volume (v/v). Under these conditions, no cosolvency effect was noted for gasoline containing 15% MTBE [14, 18].

Partitioning between water and air

Air/water partitioning for a compound is described by its Henry's Law constant (H), which gives the ratio of the partial pressure of the compound in the gas phase to the concentration in the water that is at equilibrium with that partial pressure [13]. Typical units for H are atmospheres cubic meters per mole ($\text{atm}\cdot\text{m}^3/\text{mol}$).

When H is divided by the product of the gas constant R ($8.2 \times 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}\cdot^\circ\text{K}$) and the temperature T ($^\circ\text{K}$), the resulting H/RT value is referred to as the dimensionless Henry's Law constant. H/RT gives the ratio of the air-to-water volume based concentrations at equilibrium; that is,

$$H/RT = \frac{\text{concentration in air}}{\text{concentration in water}} \quad (5)$$

A compound with an H/RT value of 0.05 or larger is very volatile from water. A compound with a low value of H/RT tends to remain in the water phase or tends to partition strongly from the gas phase into the water phase if contaminated air contacts the clean water.

At 25°C, H/RT for MTBE was measured by Robbins et al. [24] at 0.0216 (Table 1). Other alkyl ether oxygenates have H/RT values that are similar to the values for MTBE (Table 1). These low values are the reason why the fuel oxygenates partition substantially into water (for example, into precipitation falling through the atmosphere). These values also explain why MTBE is somewhat difficult to remove from water by aeration. In contrast, benzene has an H/RT value of 0.22 at 25°C (Table 1), making it rather volatile from water as compared to MTBE.

Partitioning between water and subsurface solids

Organic compounds like MTBE and the BTEX compounds, even though they are water soluble compared to other organic compounds in gasoline, will sorb to some extent on subsurface solids. Subsurface solids include soils, deeper materials in the unsaturated zone, and aquifer materials. Concentrations of anthropogenic organic compounds sorbed to subsurface solids, unlike aqueous concentrations, are expressed as a ratio of the mass of contaminant to the mass of subsurface solid (for example, $\mu\text{g/g}$ or $\mu\text{g/kg}$). The extent to which an organic contaminant is sorbed to a given subsurface solid at equilibrium is quantified by its distribution (sorption) coefficient, K_d , which is defined as:

$$K_d = \frac{C_s}{C_e}, \quad (6)$$

where C_s is the concentration of a contaminant sorbed to a specific weight of subsurface solid and C_e is the concentration of the same contaminant dissolved in an equal weight of water [13]. However, sorption of hydrophobic nonpolar-organic compounds generally increases as the organic compounds in the subsurface solid increases. Therefore, for nonionic compounds, K_d values are often estimated using the equation:

$$K_d = f_{oc} K_{oc}, \quad (7)$$

where f_{oc} is the weight fraction of the subsurface solid that is organic carbon, and K_{oc} is the organic-carbon-based partition coefficient.

Assuming an organic carbon content of 0.1% in a sand aquifer [25] and a concentration of $3.0 \mu\text{g/L}$ in the water [11], it is estimated that about 8% of the total MTBE present in the aquifer would be sorbed to the aquifer material, whereas about 40% of the total benzene would be sorbed to the aquifer material. A K_d of 0.011 is calculated for MTBE using equation (7), assuming a calculated K_{oc} of 11 for MTBE (Table 1, based on water solubility) and an estimated f_{oc} of 0.001 (0.1% organic carbon by weight), which is fairly typical for a sand aquifer. Using this calculated K_d and assuming a C_e of $3.0 \mu\text{g/L}$, C_s is calculated to be $0.033 \mu\text{g/kg}$ using equation (6). In 1 L of aquifer there is about 2.0 kg of sand and 0.25 kg of water. Multiplying the concentrations of MTBE by the quantity of water and subsurface solid, there is $0.066 \mu\text{g}$ on the subsurface solid (about 8% of the total MTBE) and $0.75 \mu\text{g}$ of MTBE in the water (about 92% of the total MTBE). Similar calculations can be done for benzene; assuming a K_{oc} of 80, a f_{oc} of 0.001, and C_e of $3.0 \mu\text{g/L}$, there is $0.48 \mu\text{g}$ of benzene on the subsurface solid (about 40% of the total benzene) and $0.75 \mu\text{g}$ in the water (about 60% of the total).

When a nonionic organic compound is dissolved in ground water and that ground water is moving in a porous subsurface medium, a primary factor determining the velocity of the compound compared to the ground-water velocity is the partition coefficient, K_d . The ratio of the water velocity to the velocity at which the compound is being transported is frequently referred to as the retardation factor, R [26]. A compound that is not retarded at all will move with the same velocity as the water and has an R value of 1. A compound that moves at one-half the velocity of the ground water has an R value of 2. In porous media, R values can be calculated using the equation:

$$R = 1 + \frac{\rho_b K_d}{n} \quad (8)$$

where ρ_b is the bulk density of the subsurface solid and n is the porosity.

Although the K_{oc} values of the BTEX compounds are not large enough to cause highly retarded transport (K_{oc} ~80 for benzene and ~160 for m-xylene), the K_{oc} value for MTBE is even lower (K_{oc} of 11). Thus, under most circumstances, MTBE would move at velocities that are similar to the velocities of the local ground water (that is, with R values fairly close to 1). In an injection study in the Borden aquifer, Ontario Canada [27], the movement of benzene, ethylbenzene, and xylenes was slightly retarded ($R = 1.1$, 1.5, and 1.5, respectively), whereas the movement of MTBE was not retarded ($R = 1.0$). These results are in reasonable agreement with what would have been predicted on the basis of the organic carbon content of the Borden aquifer ($f_{oc}=0.0002$), namely $R=1.1$, 1.8 and 1.2 for benzene, ethylbenzene, and the xylenes, respectively, and $R=1.01$ for MTBE. Data from actual spills also have demonstrated that MTBE migrates more rapidly than the BTEX compounds [20, 28].

Given the greater mobilities of MTBE compared to the BTEX compounds, the leading edge of a plume from an MTBE-oxygenated gasoline spill could contain substantial levels of MTBE with very little or no BTEX contamination. This effect would be further amplified by the greater biodegradabilities of the BTEX compounds compared to MTBE; BTEX compounds would be removed from water because of biodegradation whereas MTBE would persist longer in ground water. The half lives of BTEX compounds in ground water can vary considerably from as short as 1 week to as long as 2 years [29] while MTBE generally resists biodegradation in ground water (discussed later in this paper).

FATE OF MTBE IN THE HYDROLOGIC CYCLE

In air

The production, transport, and use of MTBE and other VOCs in gasoline inevitably results in their release to the atmosphere; releases to the atmosphere occur during vehicle refueling and from evaporative emissions and incomplete combustion. Once in the atmosphere, the compounds can be removed by chemical degradation and, to a much lesser extent, by precipitation.

A limited amount of work has been conducted investigating the atmospheric half-lives of selected fuel oxygenates. Wallington et al. [30] reported that reaction with hydroxyl radical (OH) is the main determining factor affecting the atmospheric fate of these compounds; Wallington et al. [30] reported that photolysis [31], reaction with the ozone [32], and reaction with NO₃ radicals [33, 34] are all negligibly slow for MTBE.

Estimates of the atmospheric half-life of MTBE at 25°C can be as short as 3 days in a regional airshed [5, 30, 35]. This estimated half-life assumes a OH concentration of 10⁶ radicals/cm³ in the regional airshed. However, concentrations of OH could be lower in air near metropolitan areas, and therefore, MTBE could resist degradation until advection carries MTBE outside the metropolitan area. The major degradation product of MTBE in the atmosphere is *tert*-butyl formate. Other degradation products include methyl acetate (acetic acid), acetone, *tert*-butyl alcohol, and formaldehyde [36].

As with other VOCs in the atmosphere, MTBE tends to partition into atmospheric water, including precipitation. The pertinent equilibrium constant for this partitioning is the Henry's Law constant H , or alternatively the dimensionless Henry's Law constant H/RT . The H and H/RT values for MTBE are listed in Table 1. For the organic compounds of interest here, partitioning equilibrium can be expected between precipitation arriving at the land surface and the concurrent atmospheric concentrations, at the ground surface [37]. A fall distance of a few tens of meters is required to achieve partitioning equilibrium, which means that the assumption of a gas-phase concentration at the land surface can be used to predict the corresponding concentration in the precipitation arriving at the land surface [37]. As a result, when concentrations immediately surrounding local sources are high when averaged over timeframes of months to years, concentrations in rainfall passing through these areas could be similarly elevated. Conversely, a measured precipitation concentration can be used to calculate a corresponding atmospheric gas-phase concentration. For such calculations, the temperature dependence of H and H/RT for all compounds needs to be considered.

For MTBE, falling precipitation removes (washes out) only a negligible amount of the gas-phase compound. Assuming equilibrium, the air/water mass ratio is obtained by multiplying H/RT by the air/water volume ratio:

$$\frac{\text{mass in air}}{\text{mass in water}} = H/RT \times \frac{\text{volume of air}}{\text{volume of water}} \quad (9)$$

For a 1-m² area at ground surface and a tropospheric mixing height of 1,000 m, the air volume is 1,000 m³. For precipitation of 0.025 m, the water volume is 0.025 m³. At 20°C, H/RT for MTBE is 0.018 (Table 1). Thus, the air/water mass ratio for the single storm would be $0.018 \times (1,000/0.025) = 720$. Only one part in 720 (0.14%) would be removed by precipitation. Therefore, storms would not provide an important loss conduit for MTBE from the atmosphere. However, even when little net loss occurs from the atmosphere, the loss, nevertheless, may be an important source of MTBE to natural waters. The concentrations of MTBE in airsheds and around local sources then become the most important factor in determining the strength of the atmosphere as a source of these compounds to surface water and ground water.

In Surface Water and Storm Runoff

MTBE can enter streams in association with urban stormwater runoff or ground-water discharge. Direct spills of gasoline to streams are also possible. Many variables affect the presence and concentrations of fuel oxygenates in stormwater and in streams and rivers. These variables include fuel-use patterns, weather, unpredicted spills, and so forth. Comments, nevertheless, can be made concerning the length of time that would be needed for MTBE or BTEX compounds to be lost by volatilization from flowing surface water, such as a stream, river, or stormwater channel.

Volatilization from flowing water is affected by the rate of mass transport from the bulk water to the air/water interface and by the mass transport from the air/water interface into the bulk air [38]. Three factors primarily affect the water transport process: (1) water velocity, (2) depth, and (3) temperature. Two factors affect air transport: (1) wind speed, and (2) air temperature. The inherent volatility of the compound from water as measured by the dimensionless Henry's Law constant H/RT also has an effect. For those compounds that are considered highly volatile on the basis of their H/RT values, the transport from deep, slow-moving surface water to air is limited by the transport of the compound within the water phase to the air/water interface. This condition results in a transport-rate-determining concentration gradient in the water phase; volatilization rates are much less dependent on the value of H/RT . For example, MTBE and benzene can volatilize to the atmosphere during certain flow conditions at essentially the same rate even though they have different H/RT values.

Using methods outlined in Schwarzenbach et al. [13], calculations can be done that yield the half-life ($t_{1/2}$) values for MTBE and benzene in flowing surface water [39], where losses are a result of volatilization to a clean atmosphere as a function of water velocity and water depth. Biodegradation of the compounds is not included in the analysis. Results for MTBE at a winter air and water temperature of 5°C under calm air conditions are listed in Table 2. For very deep, slow-moving rivers or lakes, the half-lives can be important (for example, $t_{1/2} = 52$ days or 450 km of travel distance for a depth of 10 m and a velocity of 0.1 m/s). MTBE entering a river under such conditions would remain in the water for months. Corresponding calculations for a summer air and water temperature of 25°C are listed in Table 3. Increasing the summer temperature to 25°C reduces the half-life by a factor of generally 2 to 3. Somewhat greater reductions are predicted for very short half-life conditions such as occur in fast-moving, shallow streams and urban-runoff channels. Calculations for windy conditions yield results that are similar to the results for calm conditions, which are due to the predominance of water-side mass transport for all but the shallowest, fastest moving streams.

Predicted half-lives for benzene are very similar to those for MTBE, with the higher volatility of benzene from water causing the benzene $t_{1/2}$ values to be a little smaller than those for MTBE. The differences in $t_{1/2}$ values for these two compounds increase in shallow streams with higher velocities.

In ground water

There are two sources for the entry of fuel oxygenates into the subsurface—point sources and nonpoint sources. For the latter, the movement of MTBE from the atmosphere through the unsaturated zone and into the saturated zone by infiltration and diffusion is discussed.

A numerical one-dimensional transport model was used to calculate the movement of MTBE and several other VOCs from the atmosphere downward through the unsaturated zone and into shallow ground water [40]. Results show that percolation of water (infiltration) is primarily responsible for the transport of MTBE to shallow ground water, whereas the effects of gas-phase diffusion are minor. Furthermore, assuming a sand, depth to water table of 5 m, and tens of cm of infiltration at the land surface, simulations showed that less than 5 years will be required for the shallow ground water to attain MTBE concentrations that correspond to saturation with respect to the atmospheric gaseous concentrations.

Median concentrations of MTBE in urban air seem to be on the order of a ppb-v or less [5]. For a mean winter temperature of 5°C, H for MTBE is 1×10^{-4} atm-m³/mol [24]. Therefore, for an atmospheric concentration of 1 ppb-v, the equilibrium concentration of MTBE would be about 1 µg/L [11]. Similarly, if a specific city had a high MTBE median concentration, such as 3 ppb-v, then the equilibrium concentration in water would be about 3 µg/L. If the atmospheric concentrations are systematically much higher around certain source areas such as parking garages, gas stations, or roadways, precipitation falling near those areas would have higher MTBE concentrations, which could result in higher concentrations of MTBE in ground water near these sources. For example, if the ambient concentration in air near a parking garage remained consistent at 30 ppb-v of MTBE, then 30 µg/L could occur in ground water (and stormwater) immediately around the parking garage.

In general, most studies to date have indicated that MTBE is difficult to biodegrade and some have classified MTBE as recalcitrant [27, 41-43], which means that no degradation occurred under the conditions used for their examination [44]. In contrast, BTEX compounds are readily biodegraded. The difficulty with which MTBE degrades may be due to the resistance to microbial attack of the tertiary or quaternary carbon atoms [41] and the very stable and chemically unreactive ether linkage [45, 46]. Research has shown that MTBE biodegradation does not occur with anaerobic microcosms including denitrifying conditions, sulfate-reducing conditions, methanogenic-reducing conditions, and anaerobic conditions in landfill aquifer material, soils, and sludges [41, 42, 47-50]. Yeh and Novak [43] also reported that there was no degradation of MTBE in aerobic microcosms after more than 100 days of incubation. Hubbard et al. [27] reported that MTBE was recalcitrant in an aquifer, exhibiting no mass loss over a 16-month period.

In contrast to results described in the preceding paragraph, degradation of MTBE has been recorded on occasion. In a recent study of a fuel spill, MTBE appeared to be degrading (decay rate of 0.18% per day), but only near the source area [28]. In addition, laboratory studies performed as part of that study showed aerobic degradation in microcosms prepared from soil collected at the source of the spill. *Tert*-butyl alcohol (TBA) was produced in the microcosms, but degradation ceased when the concentration of MTBE reached 1 mg/L. Degradation also has been reported in oxygen-limited microcosms after 4 weeks of incubation [51] and in one of three microcosms similarly prepared using Ohio River sediment [42]. In the latter experiment, the degradation product was TBA, which was persistent. Other laboratory studies have indicated degradation under conditions described as anaerobic or methanogenic, but only near pH 5.5 and only when more easily degraded organic matter was not present [49].

Concern has been expressed that MTBE would have an inhibitory effect on the degradation of fuel hydrocarbons such as BTEX. Consequently, several studies have evaluated this possibility. In a study by Hubbard et al. [27], the presence of MTBE had no measurable effect on the degradation of BTEX in an aquifer. Similarly, no effect on the BTEX respiration rate of sludge was observed for a hydrocarbon mixture that contained MTBE [47]. In contrast, 200 mg/L of MTBE reportedly caused a weak inhibitory effect on the biodegradation of BTEX [48], and 740 mg/L inhibited the mineralization of the fuel component hexadecane [52].

REMEDICATION AT POINT-SOURCE RELEASE SITES

Remedial action often is needed to remove gasoline that enters water from point sources or to prevent the gasoline from reaching the water. Currently, the primary remedial technology for ground water contaminated with gasoline is removal by pumping followed by above-ground treatment. Another commonly used method, soil vapor extraction (SVE), often used with pumping, relies on the high vapor pressure and biodegradability of gasoline. With SVE, a vacuum is used to remove the volatile hydrocarbons. The increased air flow resulting from the induced vacuum provides additional oxygen to enhance naturally occurring biodegradation of gasoline. Because of MTBE's high water solubility and resistance to biodegradation, it complicates these remedial activities.

There have been several evaluations of remedial technologies for MTBE, but these generally have indicated low efficiency and high costs. For example, Garrett et al. [19] concluded that filtration of MTBE-contaminated ground water through activated carbon was not cost-effective; a 0.06-m³ bed of activated carbon lasts only a month or less on a household treatment system that has an influent concentration of MTBE of only a few milligrams per liter. In other studies, MTBE-contaminated water was remediated, and air stripping with or without carbon adsorption had the lowest treatment costs [53, 54]. A recent survey of 15 air-stripping installations indicated that 56 to 99.9% of the MTBE was removed; the median removal rate was 91% [55]. Because of the relatively low efficiency of air stripping for MTBE, increasing the Henry's Law constant by heating the process water may be a cost-effective approach [56]. Regarding the removal of MTBE from water, heating the air-stripper influent stream to 27°C over a 9-m column packed with activated carbon was equivalent to using 10°C water and a 18-m column packed with activated carbon. To eliminate air emissions, use of oxidation with ultraviolet light/peroxide/ozone also is a feasible water-treatment alternative. This approach, however, has high capital and operating costs relative to other treatments [5].

Hydrogen peroxide, provided initially as a source of oxygen to support microbial degradation, has been found to hydrolyze MTBE with the immediate formation of *tert*-butyl alcohol and some acetone [43]. The reaction occurred only when iron was added to act as a catalyst for the release of hydroxyl radicals from the hydrogen peroxide. This reaction, however, does not have wide applicability because it is inefficient in aerobic or in near-neutral (pH greater than 6.5) to alkaline environments.

An increasingly common approach for managing gasoline spills is intrinsic bioremediation, also termed passive remediation. For this approach, protocols are being developed that indicate if the activity of the indigenous microbial population is containing the contamination. When containment is indicated, active remediation is not performed, and the site is monitored to ensure that containment and natural removal continues. The presence of MTBE will complicate use of this approach because it can resist degradation and can inhibit degradation of other fuel components [49, 52]. Although degradation can occur, laboratory studies indicate that slightly acidic conditions and very low levels of organic matter are required for the process [49]. Such conditions are common in aquifers, but the aquifers generally lack the nutrients needed to sustain biodegradation.

Despite the resistance of MTBE to biodegradation by indigenous bacteria, biotreatment methods might still be developed. Recent research has demonstrated that bacterial populations and certain pure bacterial strains, when isolated from biotreated sludges and other sources, have the ability to use MTBE as a sole carbon source [46, 57].

CONCLUSIONS AND RESEARCH NEEDS

When gasoline containing MTBE comes in contact with water, large amounts of MTBE can dissolve. In fact, the concentrations of MTBE in ground water near gasoline-release sites can exceed the combined concentrations of BTEX compounds. Although concentrations of MTBE can be high in ground water, they are typically not high enough to increase either the water solubilities or the transport rates of the BTEX compounds in ground water. MTBE sorbs only weakly to subsurface solids. Therefore, sorption does not retard the transport of MTBE by ground water. MTBE generally resists biodegradation by indigenous bacteria in ground water. Additional research is needed to determine the long term fate of MTBE in ground water and the half life of MTBE in ground water under aerobic and anaerobic conditions in various aquifers. Certain pure bacterial strains, when isolated from biotreated sludges and other sources, have the ability to use MTBE as a sole carbon source. Additional research is needed to identify and characterize these bacterial strains and if possible develop a technology to use these bacteria for cleanup at gasoline-release sites.

The half-life of MTBE in the atmosphere can be as short as 3 days in a regional airshed. A major degradation product is believed to be *tert*-butyl formate, but little is known about the long term transport and fate of this compound in the environment. Some of the MTBE in the air tends to partition into atmospheric water, including precipitation. Washout of gas-phase MTBE by precipitation would not, by itself, greatly reduce the gas-phase concentration of the compound in the air; however, the partitioning of MTBE to precipitation can nevertheless result in concentrations as high as 3 $\mu\text{g/L}$ or more in precipitation and can contribute to the presence of MTBE in surface and ground water. More research is need to understand the transport of MTBE from land surface to storm water and to shallow ground water, and its transport from shallow ground water to deeper aquifers. While MTBE will volatilize from surface water, in large rivers and some streams this compound will not be lost quickly (e.g. half life > 1 day) by volatilization, especially at low temperatures. Additional research and data are needed to verify the volatilization rates of MTBE from surface water.

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Table 1: Reported chemical and physical properties of gasoline, MTBE, and BTEX compounds.

Property	Gasoline	MTBE	Benzene	Toluene	Ethylbenzene	m-xylene	o-xylene	p-xylene
Molecular weight (g/mole)	~100 ⁷ 100-105 ^{5,6}	88.15	78.11	92.13	106.16	106.16	106.16	106.17
Specific gravity	0.72-0.78 ^{6,7} 0.74 ⁵	0.744 ^{2,7} 0.7404-0.7578 ³	0.88 ² 0.8765 ³	0.8669 ³	0.867 ³	0.8842 ³	0.8802 ³	0.8611 ³
Boiling temperature, °C	27-225 ^{6,7}	53.6-55.2 ³	80.1 ¹	110.6 ¹	136.25 ³	139.3 ¹	144.4 ¹	137-138 ¹
Water solubility, [c ₂], mg/L	100-200 ⁷	43,000-54,300 ³	1,780 ³ 1,791 ¹	534.8 ¹	181 ³	146 ¹	175 ¹	156 ¹
Vapor pressure @ 25°C, mm Hg		245-251 ³	95.19 ¹	28.4 ¹	9.53 ³	8.3 ¹	6.6 ¹	8.7 ¹
Log K _{ow}		1.20 ² 0.94-1.30 ³	2.13 ¹ 1.56-2.15 ³	2.73 ¹ 2.11-2.80 ³	3.15 ³ 2.68-3.26 ³	3.20 ¹ 3.09-3.37 ³	3.12 ¹ 2.77-3.12 ³	3.15 ¹ 3.08-3.29 ³
Henry's Law constant, (H), (atm-m ³ /y (g-mole)		5.87E-4 ³ 1.4E-3 ³ 3E-3 ³ 5.28E-4 ⁴	5.43E-3 ¹	5.94E-3 ¹	8.44E-3 ³ 6.60E-3- 8.75E-3 ³	7.68E-3 ¹	5.1E-3 ¹	7.68E-3 ¹
Dimensionless Henry's Law constant (H/RT)		2.399E-2 ³ 5.722E-2 ³ 1.226E-1 ³ 2.16E-2 ⁴ 1.8E-2 (@ 20°C) ⁴	2.219E-1 ¹	2.428E-1 ¹	3.45E-1 ³ 2.89E-1- 3.83E-1 ³	3.139E-1 ¹	2.084E-1 ¹	3.139E-1 ¹
Log K _{oc}		1.05 ² K _{oc} ≅ 11	1.1-2.5 median value=1.9 ¹ K _{oc} ≅ 80	1.56-2.25 ³	1.98-3.04 ³	2.04-3.15 ³ K _{oc} ≅ 160	1.68-1.83 ³	2.05-3.08 ³
CAS no.		1634-04-4	71-43-2	108-88-3	100-41-4	108-38-3	95-47-6	106-42-3

Values are at 25°C unless otherwise stated. The ranges are from one reference and multiple listings are from multiple sources. Dimensionless Henry's Law constants were generally calculated from the documented reference. MTBE, methyl *tert*-butyl ether; TBF, *tert*-butyl formate. Sources: ¹Howard et al. [58]; ²calculated value using Lyman et al. [59]; ³Mackay et al. [60, 61]; ⁴Robbins et al. [24]; ⁵Cline et al. [62]; ⁶API [63]; ⁷Conrad [64]; ⁸Howard et al. [65].

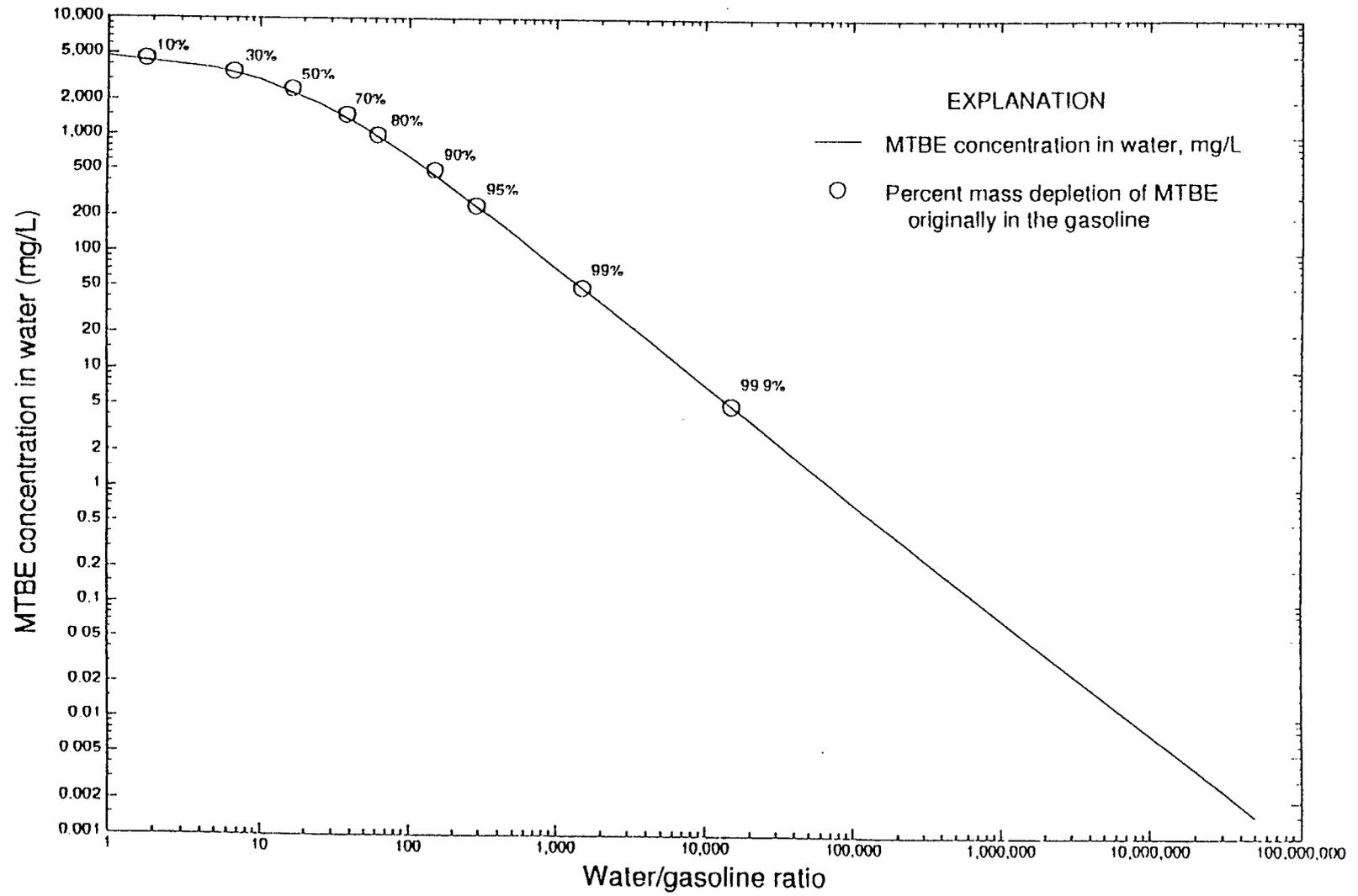
Table 2: *Estimated half-life of MTBE in a stream or river under calm air conditions at 5°C.*

Water depth (meters)	Half-life (days) for the following water velocities (meters per second)				
	0.032	0.1	0.32	1.0	3.2
0.1	0.17	0.14	0.12	0.11	0.10
.32	.72	.54	.43	.37	.34
1.0	3.3	2.3	1.7	1.4	1.2
3.2	16	11	7.2	5.4	4.3
10	85	52	35	23	17

Table 3: *Estimated half-life of MTBE in a stream or river under calm air conditions at 25°C.*

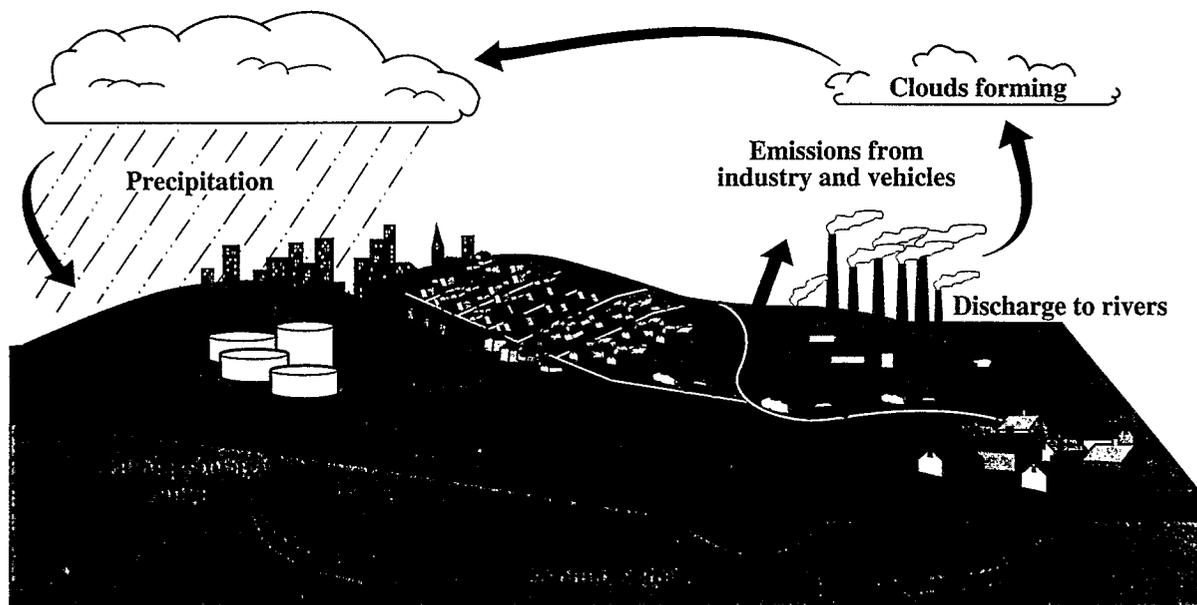
Water depth (meters)	Half-life (days) for the following water velocities (meters per second)				
	0.032	0.1	0.32	1.0	3.2
0.1	0.063	0.042	0.031	0.024	0.021
.32	.32	.20	.13	.10	.077
1.0	1.7	1.0	.63	.42	.31
3.2	8.9	5.2	3.2	2.0	1.3
10	49	28	16	10	6.3

Fig. 1. Equilibrium concentrations of MTBE in water in contact with gasoline versus the water/gasoline ratio, and the percent mass depletion of MTBE originally in the gasoline.



Information on MTBE (and other VOCs) on the Web

<http://www.sd.cr.usgs.gov/nawqa/vocns>



This site includes:

- Publications and abstracts (of national scope)
(including an MTBE bibliography--now on the internet)
- VOC Team

Also see:

- NAWQA page: <http://www.rvares.er.usgs.gov/nawqa>
- USGS Water page: <http://water.usgs.gov>
- OSTP page: (for fuel oxygenate report) <http://www.epa.gov/OMSWWW/fuels.htm>

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