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Comparative Environmental Performance of Two Diesel-Fuel Oxygenates: Dibutyl Maleate (DBM) and Triproplyene Glycol Monomethyl Ether (TGME)

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ABSTRACT

Many studies have shown that the addition of oxygen-bearing compounds to diesel fuel can significantly reduce particulate emissions. To assist in the evaluation of the environmental performance of diesel-fuel oxygenates, we have implemented a suite of diagnostic models for simulating the transport of compounds released to air, water, and soils/groundwater as well as regional landscapes. As a means of studying the comparative performance of DBM and TGME, we conducted a series of simulations for selected environmental media. Benzene and methyl tertiary butyl ether (MTBE) were also addressed because they represent benchmark fuel-related compounds that have been the subject of extensive environmental measurements and modeling. The simulations showed that DBM and TGME are less mobile in soil because of reduced vapor-phase transport and increased retention on soil particles. The key distinction between these two oxygenates is that DBM is predicted to have a greater potential than TGME for aerobic biodegradation, based on chemical structure.

INTRODUCTION

Increasingly stringent regulations governing particulate emissions from diesel engines have prompted research directed toward methods for reducing the in-cylinder formation of soot and soot precursors by modifying fuels or controlling particles by after-treatment technologies (e.g., regenerative particulate traps). Many studies have shown that the addition of oxygen to a base diesel fuel will result in a reduction of particulate emissions (see Stoner and Litzinger [1] for a review). The primary parameter influencing the formation of particles appears to be the amount of oxygen in the fuel, and secondarily, the chemical structure of the oxygenate providing the oxygen. For example, the work of Miyamoto et al. [2] demonstrated that it was the oxygen content of the fuel additive that had the primary influence on soot reduction—not its chemical form. Curran et al. [3] *completed chemical* kinetic modeling of selected oxygenates in N-heptane as a base diesel fuel and demonstrated that the generation of soot precursors decreased with the increasing oxygen content of the fuel mixture. There were differences in the production of soot precursors among the compounds, suggesting a chemical-specific factor in soot production, but these differences were less important than the weight fraction of oxygen in the fuel. Nevertheless, the chemical structure of a fuel compound will have significant implications on the composition and quantity of air toxics formed during combustion [3] as well as on its fate in environmental media.

Although there are potentially many different kinds of oxygenates that could be used beneficially to reduce particulate emissions from diesel engines, the ultimate determination of which of them are the best to use will be based on their costs, compatibility with engines and fuels, and importantly, the potential health and environmental risks associated with their overall life cycle. From an environmental standpoint, this means that analyses should also be carried out on the fate of such compounds when released to environmental media during their production, distribution, storage, and use. A case in point is the compound methyl tertiary butyl ether (MTBE), a gasoline oxygenate. Under the Clean Air Act (CAA) amendments of 1990, gasoline sold in selected areas of the country is required to contain specified levels of oxygen in order to limit automotive emissions degrading air quality. The oxygenate of choice for most refiners was MTBE, due in part to previous experience with this compound as a high octane, antiknock additive used during the phase out of tetraethyl lead. Unfortunately, this compound became a source of groundwater contamination as a result of leaks from underground fuel storage tanks and its mobility in soil/groundwater systems.

In retrospect, MTBE may have performed well as an additive that decreased emissions from older vehicles without advanced emissions control systems, however, in newer vehicles its air-quality benefits are limited [4]. As Franklin et al. [5] note in their analysis of the use of scientific information in the development of reformulated fuels, the multimedia environmental impacts of MTBE were never fully appreciated and the existing regulatory framework was unable to deal with this type of fuel compound.

Given this background, an important technical challenge regarding the evaluation of potential oxygenates for diesel fuel is to provide relevant information on their expected performance in the environment in order to identify compounds that could pose a threat to specific resources (e.g., degrade ground- or surface-water quality) or human health. Accordingly, we have implemented a series of contaminant transport and fate models that can be used to (1) provide diagnostic information on the behavior of a fuel oxygenate or additive in different environmental media, (2) identify data gaps and topics for experimental studies, and (3) determine the relative importance of various exposure pathways to support subsequent risk assessments regarding human health. The models have modest input requirements and are particularly well suited for conducting assessments at the pre-commercial stage of product development. Results from the simulations can guide subsequent decisions regarding additional studies (e.g., toxicity testing, determination of odor and test thresholds, etc.) that would be required before expanded use as commercial fuel additives.

METHODOLOGY

The introduction of an oxygenate into the Nation's diesel fuel supply would inevitably result in various kinds of releases to the environment during its production, distribution, storage, and use. Such releases will often occur within a specific environmental medium (e.g., subsurface leak to soil from an underground fuel storage tank), but the released substance can also disperse to other media (e.g., transport within soil to ground water as well as surface air). As a means of assessing different kinds of fuel-oxygenate releases, we have implemented a suite of models that address various environmental media, cross-media transfers, and also the multimedia distribution and fate within a regional landscape. These models require two sets of input parameters--one set that consists of chemical-specific physicochemical parameters and the other, properties that define the environmental media (e.g., organic carbon content of soil, porosity, wind velocity, rainfall, infiltration, etc.).

The primary oxygenates considered in this assessment are DBM and TGME. The selection of these compounds was based on a comprehensive screening process on 71 potential oxygenates that was funded jointly by the US Department of Energy and industry. Southwest Research Institute conducted a number of tests including flash point, solubility in a low-aromatic, low-sulfur diesel fuel, lubricity, and corrosion potential. The preliminary screening eliminated 51 out of the 71 original oxygenates on the basis of low flash points or limited solubility in the base diesel fuel. Eventually six oxygenates (i.e., 2-ethoxy ethyl acetate, diethyl adipate, 2-ethoxy ethyl ether, tributyrin, DBM, and TGME) were selected for engine-emissions tests. Based on the results of subsequent engine tests that included measurement of NOx and particulate emissions as well as consideration of other factors, DBM and TGME were identified as the most promising oxygenates for further study. To supplement our analysis of these particular compounds, we will also examine the benchmark fuel compounds benzene and MTBE.

PHYSICOCHEMICAL PROPERTIES

The chemical structures of the two oxygenates are depicted in Figure 1. Compounds like DBM and TGME are not widely used in commerce, and consequently, experimental data are not always available on their physicochemical properties (summarized in Table 1), or if they are available, may not have been obtained at the same reference temperature. In the absence of experimental data, we have utilized property estimation techniques to develop default property values.

DBM

TGME

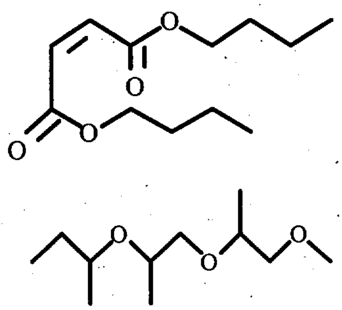

Figure 1. Chemical structures of DBM and TGME.

Specifically, we have used a series of property-estimation algorithms contained in the EPI Suite^{TM} v3.10, which is a software package available from the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency [6]. Most of the algorithms are based on structure-activity relationships (e.g., property predictions that are a function of the chemical structure of a compound, including contributions of substituent groups). We estimated the diffusivities of the compounds using Eqs. 17-12 and 17-24 in Lyman et al. [7]. Significant trends among the compounds include decreasing vapor pressure and increasing boiling point as the molecular weight increases. Structurally dependent properties include octanol-water partition coefficient and solubility in water. These two properties are also inversely related.

TRANSFORMATION PROCESSES

The degradation of fuel compounds by biotic and/or abiotic processes determines to a large extent whether they will persist in environmental media. For surface water and groundwaters, biotransformation under both oxidizing and reducing conditions can be the main degradation process. For some compounds, notably esters such as DBM, hydrolysis can represent a major degradation pathway. In the atmosphere, oxidation by hydroxyl radicals is mostly responsible for the destruction of organic molecules.

The biodegradation of a chemical compound is a complex process affected by many variables: pH, temperature, substrate composition, oxygen availability, microorganism population, and others; therefore, it is difficult to make accurate quantitative predictions of biodegradation rates. However, qualitative predictions can be made that generally classify compounds as readily biodegradable or not, based on structural and functional similarities to other compounds whose behavior is known. The program BIOWIN [6] estimates the probability of a compound to biodegrade under aerobic conditions based on regression models using critically reviewed data. The regression variables are relevant molecular fragments and molecular weight. The BIOWIN models predict that benzene and DBM are readily biodegradable while MTBE and TGME are not.

There are no experimental data on the biodegradation of DBM or TGME. In general, organic compounds that have a natural product function (e.g., alcohol, ester, acid) are readily biodegradable. As an ester, DBM is expected to biodegrade rapidly. On the other hand, TGME contains aliphatic ether groups (C–O–C) known to be recalcitrant (e.g., MTBE). There is also some experimental data whose trend supports TGME as a potentially recalcitrant compound [8, 9].

DBM and TGME have very low vapor pressures compared to benzene or MTBE. The half-life of these compounds in the atmosphere can be calculated based on the reaction with hydroxyl radicals. Using the program AOPWIN v1.90 [6], we estimated half-lives of 7.5 and 2.0 hours for DBM and TGME, respectively. In the case of MTBE and benzene, this calculation yields 56.8 and 65.8 hours. The calculation assumes a 12-hour day and a hydroxyl concentration of 1.5×10^6 molecules/cm^3. The hydrolysis of DBM can also be estimated using the program HYDROWIN v1.67 [6]. At neutral pH, the half-life is estimated at 122 days.

MEDIA-SPECIFIC MODELS

Fuel-related compounds such as MTBE and benzene have contaminated environmental media as a result of spills, leaks, emissions, etc. associated with different components of their life cycles. Using MTBE and benzene releases as analogues for DBM and TGME, we have implemented models for simulating the fate of these oxygenates under the following cases: (1) transport in soils to reflect subsurface leaks from tanks, (2) transport in a river after an accidental discharge, (3) cross-media transport from air to ground water, and (4) the multimedia transport in a regional landscape.

Table 1. Physicochemical properties of oxygenates and reference fuel compounds at 25 °C. Experimental or estimated values are from EPI Suite™ v3.10 [6].

		Compound			
Property	Units	DBM	TGME	MTBE	Benzene
MW	g/mol	228	206	88.2	78.1
Wt% O	%	28	31	18.2	0
BP[a]	°C	281	261	55.2	80
Log K_{ow}[b]	unitless	4.16	-0.2	0.94	2.13
K_{oc}[c]	mL/g	126	10	5.26	165
VP[d]	kPa	8.3×10^{-5}	2.0×10^{-4}	33.3	12.6
S[e]	mg/L	500	1.9×10^5	5.1×10^4	1.8×10^3
H[f]	Pa-m^3/mol	0.0379	4.6×10^{-8}	59.5	562
D_{air}[g]	cm^2/sec	0.051	0.053	0.081	0.092
D_{water}[h]	cm^2/sec	5.3×10^{-6}	5.5×10^{-6}	8.7×10^{-6}	1.0×10^{-5}

[a] Boiling point. [b] Octanol-water partition coefficient. [c] Organic carbon absorption coefficient. [d] Vapor pressure. [e] Solubility in water. [f] Henry's law constant. [g] Diffusivity in air. [h] Diffusivity in water.

Soils and groundwater are particularly vulnerable to leaks from underground fuel storage tanks. MTBE and benzene dissolved in gasoline have contaminated these media at thousands of subsurface tanks across the U.S.—even after tank upgrades. Since DBM and TGME would also be stored in subsurface tanks prior to distribution to diesel-powered vehicles, it is important to compare their behavior in the subsurface environment with the benchmark fuel compounds.

SOIL

Transport in unsaturated soil was simulated using an analytical advection-diffusion model developed by Jury et al. [10]. The model simulates transport of an organic compound uniformly incorporated to a fixed depth in soil at or below the surface. Transport processes include volatilization to air, downward migration via infiltrating water, and tortuosity-adjusted diffusion in soil air and water. Degradation is represented as a first-order decay process. Table 2 presents the properties of sandy and clayey soils, which are meant to reflect the extremes of soil conditions influencing transport in the vadose zone (i.e., the unsaturated soils above an aquifer). Important differences between the two soil types include the weight

Table 2. Properties of sandy and clayey soils used in transport calculations. From Jury et al. [10] and Wiedemeier et al. [11].

		Soil type	
Property	Units	Sandy soil	Clayey soil
Bulk density	g/mL	1.59	1.32
OC content	g OC/g soil	0.0075	0.025
Soil porosity	L voids/L soil	0.4	0.5
Water content	L water/L soil	0.18	0.375
Air content	L air/L soil	0.22	0.125
Infiltration rate[a]	m/yr	0.18	0.018

[a] Based on an annual rainfall rate of 100 cm/yr.

fraction organic carbon (OC), the air and water contents of soil voids, and the infiltration rate of rainfall into soil. As the organic carbon content of soil increases, sorption of an organic compound to soil matter increases, which reduces the amount of a compound available for advection/diffusion in soil gas and water. In addition, compounds with high organic carbon partition coefficients (K_{oc}) will preferentially partition to soil particles. The clayey soil has a higher OC content than the sandy soil, nevertheless, as shown in Figure 2, both DBM and benzene partition primarily to soil particles. This is due to their elevated K_{oc} values and the mass of OC available for sorption. Similarly, the larger distributions of TGME and MTBE to soil water are due in part to their lower K_{oc} values (which results in reduced partitioning to soil particles).

The partitioning of the compounds between soil water and air is controlled by their Henry's law constant and the air/water contents of the two soils. The partitioning of a compound to soil water increases as its H value decreases, and conversely, as a compound's H value increases, more of the compound will be present in soil air. Thus MTBE and benzene have higher partitioning to soil air than DBM and TGME, which are almost solely in the soil water and particle phases. Although the amounts of the MTBE and benzene in soil air are not as large for soil water and solids, the diffusivities of the compounds in air are orders of magnitude higher than diffusion in water, as shown in Table 1. Consequently, the vapor phase transport for these compounds can be significant.

For purposes of the comparative simulations, the initial contamination sources were assumed to be uniformly distributed between 1.00 and 1.30 m beneath the surface of reference sandy and clayey soils. The total initial concentration is 1 mg/L. We have also fixed the degradation half-lives for each of the compounds to 10 years in order to focus our evaluation on the effects of chemical and soil properties on contaminant transport. Figure 3 shows the concentration profiles after one year for DBM, TGME, benzene, and MTBE. For the clayey soil with limited water infiltration, diffusion of benzene and MTBE in the gas phase redistributes them through the soil column, while DBM and TGME are essentially immobile because of their association with soil particles and water. In the sandy soil, TGME moves with infiltrating water, but DBM has barely moved due to its affinity for the solid phase.

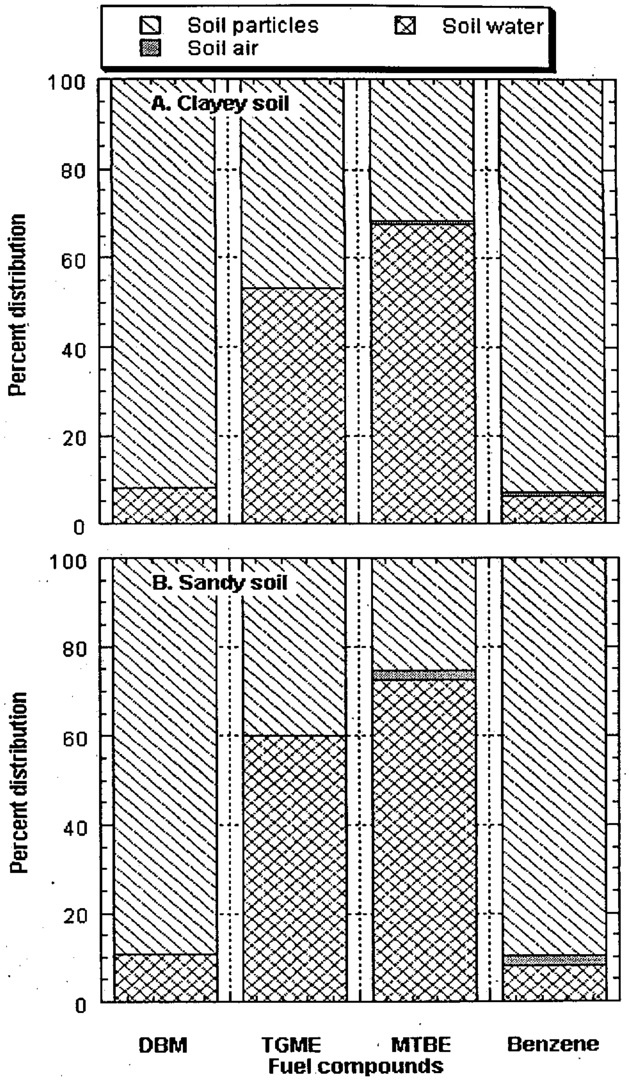

Figure 2. Distributions of oxygenates and reference fuel compounds among soil components consisting of particles, air, and water: (a) clayey soil and (b) sandy soil.

Robinson [12] presented solutions to the transport model of Jury et al. [10] that provide estimates of the cumulative masses lost from the initial mass in the uniform contamination layer as a result of volatilization flux, advection and diffusion, and degradation. In the sandy soil after one year, about 30% of the initial mass was volatilized to the atmosphere, while for MTBE, 13% was

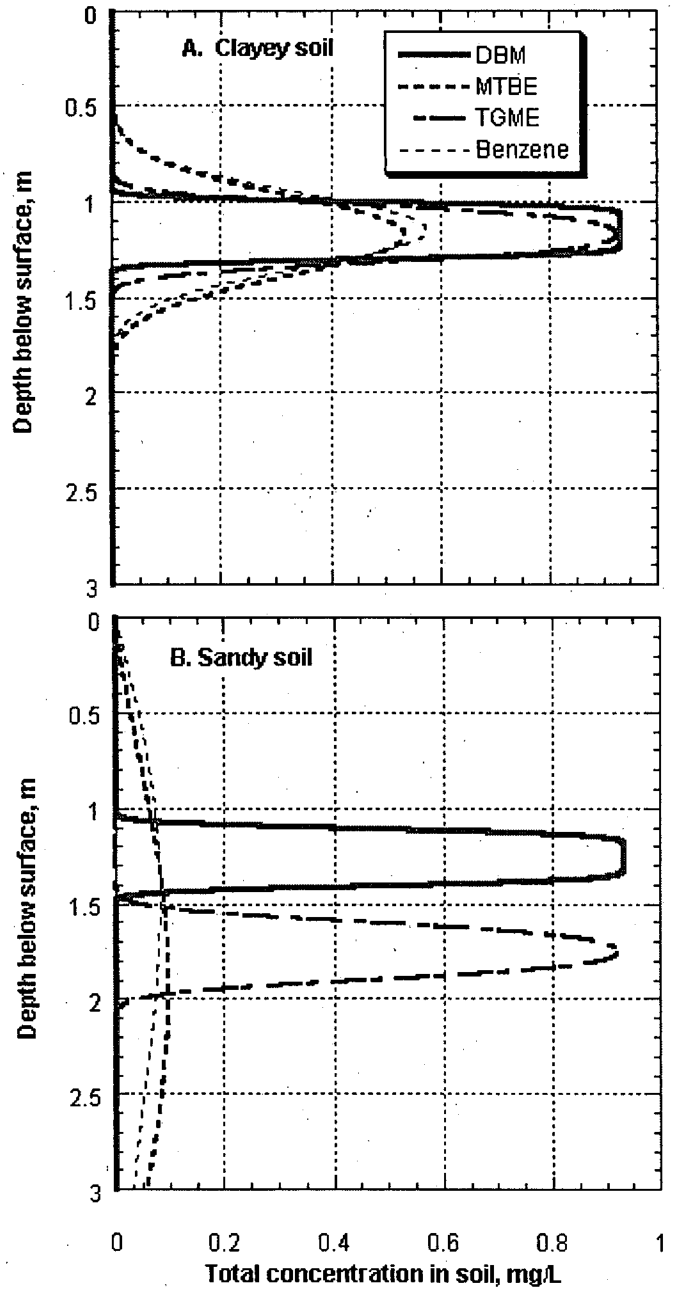

Figure 3. Transport of DBM, TGME, MTBE, and benzene in (a) clayey and (b) sandy soils after one year from a uniform source located at depth of 1 to 1.3 m below the surface with an initial concentration of 1 mg/L.

volatilized. However, volatilization losses for DBM and TGME in the sandy soil are predicted to be minimal. With the clayey soil, volatilization losses were negligible for all compounds. In terms of potential threats to ground water, DBM and TGME are less mobile than MTBE and benzene. DBM, though, not only exhibits limited mobility because of its strong sorption to soil, but it also has a greater potential for transformation by biodegradation as well as hydrolysis. Moreover, because its movement is retarded due to soil sorption, the travel time to an aquifer will be longer than for the other compounds, thereby allowing more time for the dual transformation processes to reduce the DBM concentrations in soil to insignificant levels before reaching the water table.

SURFACE WATER

Fuel-related compounds can enter lakes and rivers via spills or discharges from watercraft. For example, Reuter et al. [13] demonstrated that MTBE concentrations in a lake were directly related to recreational boating activities that discharged gasoline to water during their operation. The concentrations of a fuel compound in a surface water are a function of the nature and magnitude of the release, the transport-related properties of the compound, and the characteristics of the receiving water. As a means of comparing the environmental fate of the two oxygenates in surface water, we simulated their transport in a river after a pulse release produces a concentration of 1 mg/L at the source location.

The riverine transport of a pulse release of a water-soluble compound produces a plume that spreads longitudinally in the direction of river flow, creating a gaussian-shaped concentration profile as the plume passes by a fixed location downstream from the release. The longitudinal dispersion increases as the travel time of the plume increases, which reduces the peak concentration of the dispersing plume. The dispersion is influenced by the river's channel properties, flow rate, etc. In addition, the compound's concentration can decrease as a result of volatilization losses to the atmosphere and degradation processes. Therefore, to simulate the plume's transport, we implemented a model developed by Jobson [14] that incorporates both a dispersion term reflecting the influence of river properties on transport as well as a term to represent losses via mass transfer and degradation.

The Jobson model uses an empirical relationship that describes the dispersion-induced reduction of the peak plume concentration as a function of travel time. In our simulations travel time was calculated from an estimate of the maximum probable river velocity (calculated using an empirical relationship between watershed area, average annual discharge rate of the river, discharge rate at the time of the release, and the slope of the watershed). Volatilization was modeled using a two-layer mass-transfer model that predicts the mass transfer velocity of a compound across stagnant films of air and water at the air-water exchange boundary [15, 16, 17].

We simulated the riverine transport of a spill occurring in a watershed in northern California with a drainage area of 1100 km^2, a slope of 0.015 m/m, an annual average flow rate of 32 m^3/s, and a depth of 1 m. A flow rate of 5.7 m^3/s was chosen to represent the actual velocity during the hypothetical release (based on a flow rate that occurred during a previous spill on the river) along with a wind speed of 2 m/s [18]. In order to examine the influence of volatilization-driven losses on the predicted peak concentrations as a function of downstream distance, we arbitrarily assigned a degradation half-life of 10 years for each compound. Figure 4 depicts the resulting decreases in peak concentrations for fuel compounds with distance from a spill site with an initial concentration of 1 mg/L.

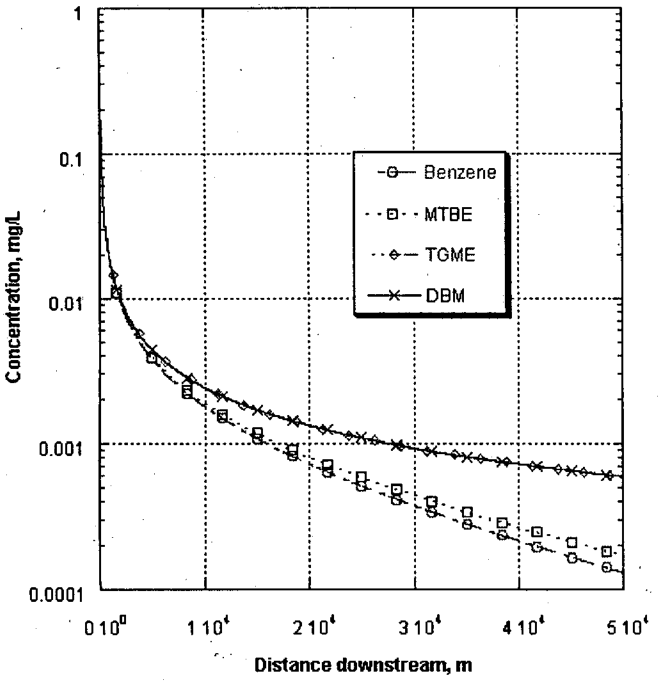

Figure 4. Peak concentrations of DBM, TGME, MTBE, and benzene down-river from pulse releases that produce 1 mg/L concentrations of the compounds at the source area. Concentrations reflect volatilization losses and longitudinal dispersion of the plume as it moves at the predicted maximum probable river velocity.

The volatilization half-lives of benzene and MTBE are estimated to be 11 and 13 h, respectively, under the transport case considered, while DBM and TGME have a *negligible amount* of volatilization due to their low Henry's law constants. Consequently, DBM and TGME have higher down-river concentrations than the other fuel compounds. DBM, though, is more likely to undergo biotransformation and hydrolysis than TGME, and so its ultimate fate in surface water will depend on the rates at which those processes operate. The other significant factor affecting the fate of these compounds in surface water is solubility. DBM is sparingly soluble in water (i.e., 500 mg/L), while TGME and MTBE have elevated solubilities in water, which means that spills or other releases could produce significantly higher dissolved levels of these particular compounds.

AIR-TO-GROUNDWATER TRANSPORT

Fuel compounds emitted to the atmosphere as a result of incomplete combustion or evaporative losses from fuel systems can be a source of ground-water contamination. Air-to-ground water transport pathways include rainout of airborne substances onto the land surface followed by infiltration into soil as well as diffusion from air to soil. The magnitude of the atmospheric source term for a given organic compound depends on its concentration in air, its Henry's law constant (which controls the compound's partitioning between rainwater and air), and the amount of rainfall. Once in the soil matrix, the degree of natural attenuation is controlled largely by sorption and degradation processes.

To evaluate the air-to-ground water transfer potentials of DBM, TGME, and the other reference fuel compounds, we determined their attenuation (defined as the ratio of the compound's concentration in rainwater to the concentration in soil water at the top of the water table) for the two soil types. Attenuation factors presented in Figure 5 were calculated using a formula (i.e., Eq. 11) given in Baehr et al. [19], input parameters derived from Tables 1 and 2, and effective diffusivity defined in Jury et al. [10]. Under steady-state conditions (i.e., the source concentration in air is constant with time) the greatest amount of attenuation occurs in the clayey soil due to increased sorption onto soil particles and low infiltration of rainfall. DBM has the greatest attenuation, followed by TGME, benzene, and MTBE. With the reduced amount of organic carbon in sand (0.0075 wt.% compared to 0.025 wt.% for clay) and increased infiltration (18 cm/y compared to 1.8 cm/y for clay) the compounds with the least amount of attenuation become MTBE and TGME—with TGME showing the greatest increase in mobility due to reduced soil sorption. Benzene's transport is retarded because of its affinity for soil OC and its limited distribution to infiltrating soil water. However, it is more mobile than DBM because of its enhanced vapor-phase transport.

Although it appears that DBM would not represent a threat to ground water, TGME, however, may be too mobile in some landscapes, especially if it does not degrade rapidly enough. Baehr et al. [19] completed a

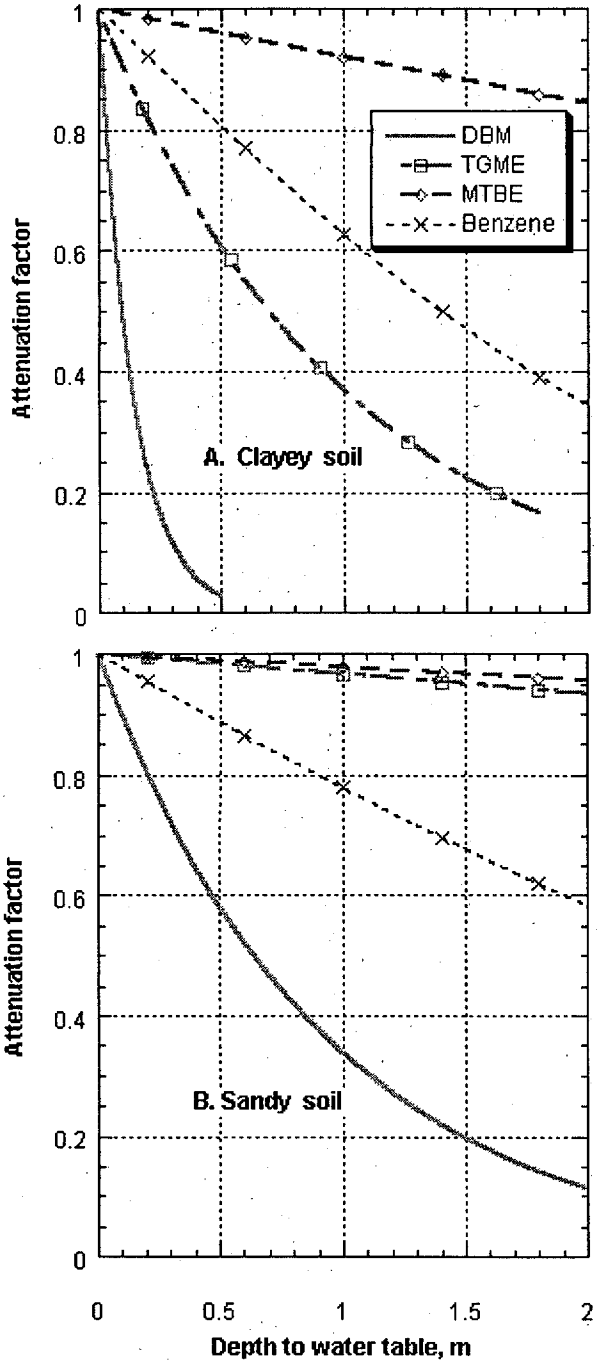

Figure 5. Attenuation of DBM, TGME, MTBE, and benzene in clayey and sandy soils under the steady-state transport from the atmosphere. The attenuation factor is defined as the ratio of the compound's concentration in soil water at the top of the water table to its concentration in rainwater.

study dealing with the role that the atmosphere played as a source of volatile organic compounds (VOCs) in shallow aquifers in New Jersey. Based on measured concentrations of VOCs in air and ground water as well as transport modeling, they concluded that the *atmosphere* could indeed be the source of MTBE in ground water. TGME attenuation, though, would likely be more sensitive to variations in soil properties, recharge rates, and depths to groundwater—given the attenuation profiles for clayey and sandy soils given in Figure 5.

TRANSPORT AND FATE IN A REGIONAL LANDSCAPE

Fuel-related compounds can be released into regional landscapes via direct emissions to air, discharges to surface water, spills onto soils, etc. These media-specific releases can be redistributed to other environmental media by intermedia transfers controlled both by advection (e.g., rainout of contaminants) and mass-transfer processes (e.g., mass-transfers based on concentration gradients between media). The redistribution among the landscape media will be governed by the nature of the releases, properties of the released chemicals as well as the receiving environment. Figure 6 portrays the key transfer and loss processes associated with an idealized landscape consisting of an air compartment, surficial soil, surface water and associated sediments. Mass-transfer processes act to move contaminants between water and air, sediment and water, and soil and air. Advective processes include surface water runoff, infiltration of rainfall into soil, airborne transport, water flow, etc.

These complex multimedia interactions have been simulated by Mackay et al. [20] using a fugacity-based approach to determine the behavior of chemicals released to soils, air, water, and sediments. We have implemented a four compartment Level III fugacity model representing a regional landscape of 100,000 km^2 (with surface water representing 10% of the surface area). The parameters defining the compartmental properties are from Mackay et al. [20] except that we chose an annual average wind speed of 4.8 m/s to reflect typical conditions in the Midwest along with ground water recharge and runoff values estimated to be 20% of annual average rainfall. The discharge scenario for each of the four fuel compounds consisted of 1000 kg/h to air, 50 kg/h to water, and 50 kg/h to soil [20].

To represent variable degradation rates of organic compounds in the different environmental media, Mackay et al. [20] defined a series of degradation rate bins that reflect potential half-lives ranging from hours to years. Based on the more rapid degradation rates in the atmosphere for DBM and TGME, we assigned them a Class 1 half-life, which is 5 h. Benzene and MTBE were assigned a Class 3 half-life value of 55 h for degradation in the air compartment. The degradation half-lives for the other compartments were assigned a Class 7 value of 5500 h to reflect slow rates of transformation for comparative purposes.

The resulting distributions of compounds under steady-state conditions are depicted in Figure 7. The most notable difference between the compounds is the depleted levels of DBM and TGME in the atmospheric

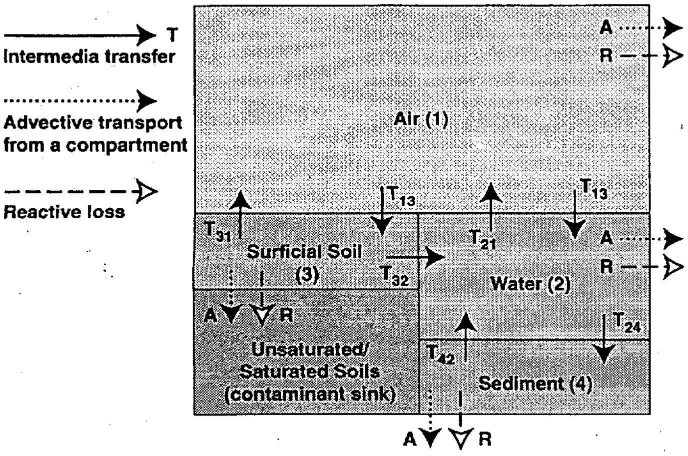

Figure 6. Conceptual diagram of the intermedia transfer processes that control the movement of contaminants released in the environmental media of a regional landscape.

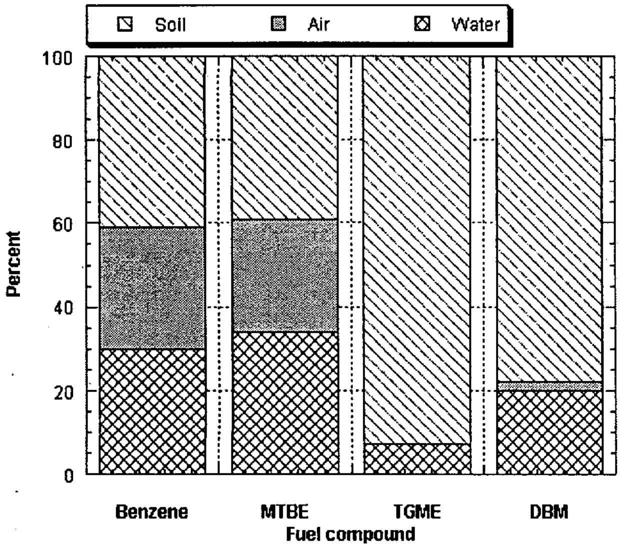

Figure 7. Steady distribution of DBM, TGME, MTBE, and benzene among the air, soil, and surface water of a reference regional landscape. Releases occur to air, soil, and water. The sediment compartment retains very little of the fuel compounds and is therefore not shown.

compartment. This is due to their abbreviated residence time in the atmosphere caused by enhanced OH-mediated oxidation as well as the increased level of rainout (due to low Henry's law values) that depletes their ambient levels in the atmosphere. The primary reservoir for the two oxygenates is soil, due primarily to wet deposition onto the land surface.

For benzene and MTBE, the principal intermedia transfer processes are mass transfer from water-to-air and soil-to-air. Once in the atmosphere, the principal loss mechanisms are wind-driven advection from the compartment and reaction with OH radicals. The ultimate distribution of these compounds will depend in part on the in-situ degradation rates that occur and the interplay between degradation and advective losses.

Results from a multimedia model can subsequently be used to evaluate the significance of various exposure pathways that link the fuel compounds in different environmental media to human contacts via ingestion, inhalation, and dermal contact. While it is beyond the scope of this paper to predict such exposures for the fuel compounds of interest, we note that Hertwich et al. [21] found that chemical-related parameters (i.e., physicochemical properties and especially degradation half-lives) contributed the most to uncertainties in the human exposures predicted by a multimedia model for a broad range of chemicals. Therefore, experimental studies of degradation processes controlling the fate of the oxygenates would also help reduce uncertainties in exposure predictions used in health-risk assessments completed prior to commercialization of the compounds.

CONCLUSION

The oxygen contents of DBM and TGME are nearly the same, and consequently, their effectiveness as diesel-fuel blending agents to reduce soot emissions should be comparable. However, their chemical structures and associated physicochemical properties are distinctly different. DBM is sparingly soluble in water and has a high affinity for organic matter in environmental media. TGME, in contrast, is quite soluble in water and does not adsorb strongly to organic matter. Moreover, based on structure-activity relationships, DBM is expected to undergo both aerobic biodegradation and hydrolysis in soil/groundwaters and surface waters. TGME, though, is likely to be recalcitrant in those media because of its ether groups, which are know to inhibit biotransformation. Nevertheless, TGME would be less mobile than MTBE in soil systems due to increased sorption and reduced vapor phase transport.

In summary, we have demonstrated the application of a suite of contaminant transport and fate models that provide diagnostic information on the relative environmental performance of fuel-related compounds. The use of such models at the pre-commercial stage of product development can help avoid the introduction of compounds that may have beneficial engine/emission properties, but whose environmental performance produces undesirable impacts, such as groundwater contamination that is costly to remediate. In addition, the early application of these diagnostic models can help guide experimental studies to provide data on key parameters. For example, the simulations presented here indicate that the biodegradation potentials of DBM and TGME need to be examined in more detail to determine whether they are likely to persist in the environment.

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