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ASSESSING AND MANAGING THE RISKS OF FUEL COMPOUNDS: ETHANOL CASE STUDY

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ABSTRACT

We have implemented a suite of chemical transport and fate models that provide diagnostic information about the behavior of ethanol (denoted EtOH) and other fuel-related chemicals released to the environment. Our principal focus is on the impacts to water resources, as this has been one of the key issues facing the introduction of new fuels and additives. We present analyses comparing the transport and fate of EtOH, methyl tertiary butyl ether (MTBE), and 2,2,4 trimethyl pentane (TMP) for the following cases (1) discharges to stratified lakes, (2) subsurface release in a surficial soil, (3) cross-media transfer from air to ground water, and (4) fate in a regional landscape. These compounds have significantly different properties that directly influence their behavior in the environment. EtOH, for example, has a low Henry's law constant, which means that it preferentially partitions to the water phase instead of air. An advantageous characteristic of EtOH is its rapid biodegradation rate in water; unlike MTBE or TMP, which degrade slowly. As a consequence, EtOH does not pose a significant risk to water resources. Preliminary health-protective limits for EtOH in drinking water suggest that routine releases to the environment will not result in levels that threaten human health.

KEYWORDS

Renewable energy, ethanol, fuel compounds, transport and fate, groundwater, surface water

INTRODUCTION

Gasolines that are sold in areas of the U.S. that have not attained compliance with the national air quality standard for ozone are required to contain up to 2.7 wt% oxygen. Although there are potentially several oxygen-bearing compounds that could be added to gasoline to meet this requirement, MTBE ended up being the oxygenate of choice for many refiners. Unfortunately, MTBE became a source of groundwater contamination at many leaking underground tank sites due to its mobility and persistence in soil/groundwater systems. Because of the threat that MTBE poses to water resources, several states have decided to ban it from gasoline. EtOH, a renewable fuel that is already in widespread use as a fuel/additive in gasoline, is the most viable

replacement. Another regulatory alternative, though, would be to obtain an exemption from the oxygenate provisions of the U.S. Clean Air Act. In this case, a nonoxygenated gasoline would be required that does not generate any more air pollution than does the oxygenated blend. The most likely solution would then be to add alkylates (branched alkanes such as TMP that have high octane ratings) to a base, low-vapor pressure gasoline.

The challenges associated with the introduction of gasoline formulations that not only meet air pollution and fuel regulations, but also do not degrade other environmental media, suggest that a more systematic approach needs to be adopted to assess and manage the risks of such compounds. Ideally, the assessment approach would address the principal components of the compound's life cycle, namely, its production, distribution, storage, and use. Each component of the life cycle can produce releases to environmental media that need to be assessed. However, the regulations governing gasoline composition are controlled almost entirely by air quality and engine performance considerations that are associated only with the use component of a fuel's life cycle.

METHODOLOGY

There are two risk-based approaches that can be used to evaluate fuel compounds. The first approach involves an analysis of the relative risks of a given compound based on comparisons with other reference or benchmark fuel compounds. The second approach is to assess the likelihood that the use of a target compound will result in environmental levels that exceed "safe" levels for humans or ecosystems. For the relative risk analysis, we compare the environmental performance of EtOH with MTBE and TMP in terms of its transport characteristics in surface and groundwaters. A "high" risk substance from an environmental standpoint is one that is mobile and persistent, whereas a "low" risk compound has limited transport potential and degrades rapidly. As a means of evaluating the possibility that EtOH would exceed levels in water that are harmful to humans, we compare predicted concentrations in water to a health protective concentration of 1,100 mg/L (OEHHA, 1999).

ENVIRONMENTAL PERFORMANCE

Surface water releases

Releases of fuel compounds to surface waters can occur from accidental spills as well as chronic releases. Once in the water column, the transport and fate of an organic fuel compound is controlled by loss mechanisms (e.g., volatilization from water to air and degradation) and dilution via advection and dispersion. As means of assessing the behavior of the fuel compounds in surface water, we have simulated a release scenario in which recreational watercraft powered by two-cycle engines discharge fuel into a thermally stratified lake. Using the methodology given in Layton and Daniels (1999), the concentrations of the fuel compounds discharged to the epilimnion of a reference lake are a function of the lake volume, mass discharge rate, and losses from volatilization and degradation. Volatilization losses are estimated using a dual film mass-transfer model in which the transport parameters are determined for the air- and water-side layers. The basic inputs are wind velocity and the Henry's law constant of the compounds (i.e., 0.51, 60, and 3.1×10^5 Pa-m³/mol at 25°C for EtOH, MTBE, and TMP, respectively, from EPI Suite 3.1; U.S. EPA, 2001).

The reference scenario for each compound consists of a constant discharge of 50 kg/day for a period of 7 days, a 10 m surface layer, and an average wind speed of 3 m/s. The predicted half-lives due to volatilization are 15, 18, and 100 days, respectively, for MTBE, TMP, and EtOH. Nevertheless, the loss of EtOH due to aerobic biodegradation will be more rapid, with a half-life of about a day. MTBE and TMP, in contrast, are recalcitrant to aerobic biodegradation. Using a conservative biodegradation half-life of 24 hr for EtOH, the predicted concentrations in the epilimnion are depicted in Figure 1. From the results it is clear that EtOH will diminish much

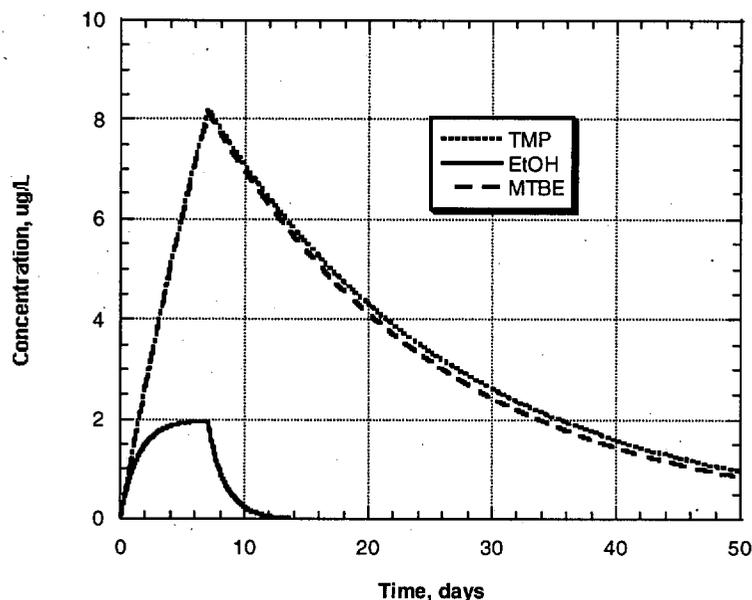


Figure 1. Concentrations of fuel compounds in a reference lake after a continuous discharge of 50 kg/day for 7 days.

more rapidly than the other fuel compounds—even using a slow biodegradation rate. Moreover, the EtOH levels are far below concentrations that would constitute a threat to human health.

Subsurface releases

From an environmental standpoint, the storage component of fuel compound's life cycle requires special evaluation because leaking underground tanks can result in the contamination of soils and groundwaters. We used a contaminant transport model developed by Jury et al. (1990) to study the behavior of the fuel compounds in a sandy soil in which the fuel compounds are uniformly mixed in a 30 cm zone 1 m below the surface. The reference sandy soil addressed in the simulations has a total porosity of 0.4, a volumetric water content of 0.18, an organic carbon content of 0.0075, and a recharge rate of 18 cm/yr. The organic carbon partition coefficients of EtOH, MTBE, and TMP are 1.0, 5.3, and 276 (from EPI Suite 3.1). The diffusivities in water are 1.6×10^{-5} , 1.0×10^{-5} , and 8.1×10^{-6} cm²/s, and in air are 0.12, 0.081, and 0.067 cm²/s, respectively (estimated from Lyman et al., 1982). Although the biodegradation rate of EtOH in soil is expected to be fairly rapid, no controlled studies are available to define in-situ degradation rates. We have therefore conducted the simulation with a biodegradation half-life of 36 days (~0.1 yr) to define an upper-bound concentration. We adopted a 640 day half-life for MTBE in soil, based on the mean of two values for groundwater summarized by Stocking et al. (2000). Marchetti et al. (1999) estimated a half-life of TMP of about 100 days, based on an analysis of a biodegradation experiment. Figure 2 shows the total concentrations of the compounds in soil as

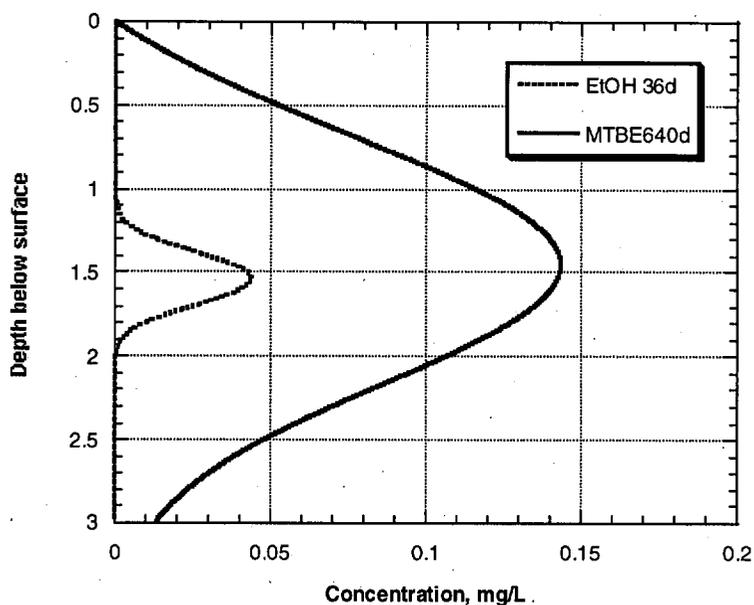


Figure 2. Concentrations of fuel compounds in soil produced after 150 days of dispersion from a uniform source consisting of a 30 cm layer that is 1 m below the soil surface. Initial concentration of each compound in the source region is 1 mg/L.

a function of depth after a 150 day simulation time. By the end of the simulation period, volatilization of TMP to the atmosphere has essentially depleted it from soil, however, MTBE is still present as well as EtOH. Because EtOH resides almost entirely in soil water, its transport is dominated by the downward movement of infiltrating water, whereas MTBE also disperses via diffusion in soil air. If a half-life of 1 day was assigned to EtOH, only trace levels would be present in soil at the end of the simulation period.

Air-to-groundwater transfer

Urban atmospheres will also become contaminated with low levels of the fuel compounds due to releases caused by incomplete combustion from engines as well as evaporative losses from fuel systems. The atmosphere can also serve as a source of contaminants in shallow groundwater as a result of rainout onto the land surface. Baehr et al. (1999), for example, showed that low levels of MTBE in shallow aquifers in New Jersey could be predicted by contaminant transport parameters and aquifer characteristics. They used an analytical advection-dispersion model to evaluate the pollution potential of airborne VOCs that we have adapted to study the relative impacts to groundwater of EtOH, MTBE, and TMP present in the atmosphere. The reference case consists of a shallow sandy soil (with the same properties as described above) and an aquifer that is 5 m below the surface.

To demonstrate the importance of a compound's degradation rate on the potential for groundwater contamination caused by rainout, Fig. 3 presents the results as a function of degradation rate and ratio of the compound's concentration in groundwater to its concentration in air. EtOH is predicted to have the highest ground-water pollution potential for biodegradation half-lives greater than 0.1 years. However, with half-lives on the order of days or weeks, EtOH does not constitute a threat to shallow groundwaters. In contrast, the slow rates of MTBE degradation mean that it is a greater threat to groundwater, but TMP's high Henry's law constant reduces greatly its transport to groundwater via rainout.

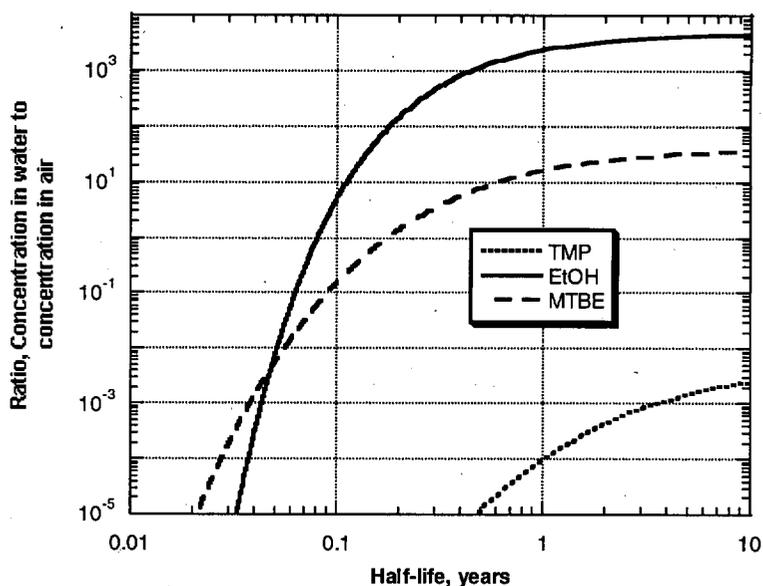


Figure 3. Comparison of the relative impacts on groundwater quality resulting from steady-state concentrations of fuel compounds in the atmosphere over a soil/groundwater system.

Multimedia fate in a regional landscape

The environmental fate of a fuel compound released into a regional landscape can be simulated using a compartmental modeling approach in which the landscape is composed of air, soil, surface water, and sediment compartments. Intercompartmental transfers of contaminants are a function of chemical and compartment properties. We used a level III fugacity model developed by Mackay et al. (1992) to evaluate the distribution of the fuel compounds in a regional Midwestern landscape covering 100,000 km², 10% of which is surface water. Steady-state discharge rates simulated for each compound are 1000 kg/hr to air, 50 kg/hr to water, and 50 kg/hr to soil. In addition to the chemical properties defined above, the log octanol-water partition coefficients of the fuel compounds from EPI Suite 3.1 are -0.14, 0.72, and 4.1, for EtOH, MTBE, and TMP, respectively. In addition, the atmospheric half-lives predicted for the three compounds are 36, 57, and 28 hr, respectively, for OH-mediated oxidation. To represent the rapid degradation of EtOH in water, sediments, and soil, we chose a degradation half-life of 24 hr (from Layton and Daniels, 1999). MTBE and TMP are more resistant to biodegradation and consequently, they have longer half-lives in environmental media. We chose a half-life of 66 days to represent the biodegradation of MTBE in water and sediments (derived from Bradley et al., 2001). We used a half-life of 640 days for MTBE in soil and a 100 day half-life for TMP in soils, water, and sediment (see above).

The steady-state releases of EtOH into the different environmental compartments and associated intermedia transfer processes distribute the EtOH so that most of it resides in the atmospheric compartment (73% of the mass in all of the compartments), followed by 16% in surface water, and 11% in soil. In contrast, the primary compartments for MTBE and TMP are soil (42%) and water (54%), respectively. Very little of any of the compounds end up in sediment. Moreover, under steady-state conditions, the compartmental landscapes containing MTBE and TMP have 3.3 and 1.7 times more mass than the EtOH landscape due to differences in degradation and

transfer processes. Finally, the concentration of EtOH in the water compartment is about a factor of 6 lower than the other fuel compounds.

RELATIVE RISKS AND MANAGEMENT IMPLICATIONS

The results of these diagnostic evaluations of the environmental behavior of EtOH indicate that it does not pose a significant risk to surface or groundwater quality due to its rapid biodegradation. Furthermore, in soil systems EtOH is not very mobile, compared to MTBE and TMP, because its movement is controlled by the downward movement of infiltrating rainwater, which is a slower transport mechanism than diffusive transport in soil air. It is unlikely that levels of EtOH would exceed health-protective limits in water supplies, except in cases of accidental spills. Consequently, an important consideration from a risk-management perspective is the need to identify and implement controls to minimize the occurrence of such releases.

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