Ecological Risk of MTBE in Surface Waters

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INTRODUCTION

MTBE is rapidly becoming one of the most ubiquitous synthetic chemicals in our environment. Introduced as a gasoline additive to promote more complete combustion of hydrocarbons, it can be a major constituent of gasoline in locations that do not meet U.S. EPA ozone emission standards. Contamination of groundwater and surface waters by MTBE is well documented, resulting in potential exposure of humans and ecological systems. As yet, there is little understanding of the potential adverse effects of MTBE, particularly in ecological systems.

The ecological systems that potentially are at greatest risk are lake ecosystems subject to recreational activities. Two cycle engines commonly used on recreational watercraft are particularly inefficient in their use of fuel. Estimates are that as much as 25% of the fuel is passed through the engine and out the exhaust into the water. MTBE comprises 11-15% of gasoline by volume, and consequently, on heavily used lakes a significant amount of MTBE is passed into the water column.

Recent monitoring of lakes in California indicate that during the boating season, MTBE is found in the water column at concentrations that range from 2-3 ppb to 20-30 ppb, depending on the relative amount of boat traffic within the previous few days. These monitoring studies indicate that most of the MTBE is found within the epilimnion, concentrating the MTBE in the area where most aquatic life is found.

As a result of these findings, we report the results of a screening-level ecological risk assessment for aquatic ecosystems. Adverse effects in any ecological system can occur as a result of either direct effects or indirect effects. Direct effects are the result of acute toxicity and the death of organisms. Indirect effects are changes in the population dynamics of nontarget species as a result of either acute or chronic effects on a target species. For example, the death of the prey base due to acute toxicity will undoubtedly affect the abundance of predators. In this paper, we concentrate on the potential for direct effects of MTBE on aquatic organisms. The analyses presented here provide a foundation for assessing the potential ecological risk of MTBE to aquatic organisms. We also present an assessment of the research needs to better assess the effects of MTBE in aquatic ecosystems.

ECOLOGICAL RISK ASSESSMENT FRAMEWORK

This analysis was conducted using the state of California's framework for ecological risk assessment (Polisini et al. 1998). The framework provides a logical methodology for assessing the potential ecological risks accruing from chemical or physical stressors. For the assessment of the potential ecological impacts of exposure to MTBE, we perform the Scoping assessment and Phase I predictive assessment stages. While these assessments are usually performed to evaluate site-specific problems, we use the processes outlined in these assessments to evaluate the potential adverse effects of MTBE in aquatic systems on a statewide basis.

Scoping Assessment

The scoping assessment is meant to determine if the potential exists for adverse ecological effects at a particular site. It utilizes a habitat approach rather than an endpoint-specific approach in that it identifies habitats in which exposure would be possible. For aquatic ecosystems, this includes both the pelagic and sediment components. Once the critical habitats are identified, potential ecological receptors within those habitats are identified. Typically, these receptors will include all California species of special concern, and species that are state or federally listed or recommended for listing as rare, threatened, or endangered. Additional species that are expected to be - exposed are also identified. In site-specific scoping assessments, identification of potential contaminants of concern is performed and the potential for the contact between the chemicals and the endpoints is established. In our assessment, the contaminant of concern is MTBE, and the concern is the presence of potential exposure pathway(s) for the aquatic biota. A preliminary scoping assessment was performed for MTBE in two water bodies that indicated that completed exposure pathways did exist for the ecological receptors. Hence, the bulk of the analysis consisted of the next stage of analysis, the Phase I predictive assessment.

Phase I Predictive Assessment

The goal of the Phase I predictive assessment is to estimate the magnitude of the potential ecological risk to the receptors. The assessment is concentrated on locations that are expected to be maximally contaminated (Polisini et al. 1998). Toxicity information is obtained and a reference dose is determined for the endpoints using appropriate uncertainty factors. The appropriate toxicological endpoint is the No Observed Adverse Effects Level (NOAEL) in the representative species. A NOAEL can be generated from other toxicological endpoints such as a LC_{50} or a Lowest Observed Adverse Effects Level (LOAEL) concentration by dividing these endpoints by an appropriate uncertainty factor. The NOAEL is then divided by one or more additional uncertainty factors to account for the extrapolation of the NOAEL from one species to another, deficiencies in the original toxicity study, or significant differences in body mass between species. The reference dose is the quotient of the NOAEL and the uncertainty factors. This reference dose is compared against the expected exposure of the ecological endpoints and a hazard quotient is calculated. The hazard quotient is the ratio of the reference dose to the expected exposure. If the hazard quotient is greater than 1.0, the potential exists for adverse ecological effects.

Toxicity data for species that exist at a site can be difficult to obtain. Often, data may not exist for the chemical of concern, or the species present may not have undergone toxicological testing. For freshwater pelagic systems in which there is an absence of site-specific representative species, several species are recommended for use including the green algae *Selanastrum capricornutum*, a microcrustacean *Ceriodaphnia dubia*, and the rainbow trout *Oncorhynchus mykiss*. These species represent three trophic levels in aquatic systems, and substantial data exist for them for a wide range of chemicals including MTBE.

The Phase I assessment is meant to be followed by a Phase II validation study that attempts to reduce the uncertainty in the analyses. The Phase II study often involves toxicity testing and addresses the issue of bioaccumulation. We could not perform a complete Phase II assessment as part of this analysis, but we document the data gaps that exist and provide recommendations as to how these might be addressed during a Phase II assessment.

CHARACTERIZATION OF ECOLOGICAL RISK

We are interested in the ecological effects of MTBE in the large number of lakes and reservoirs in California that support recreational activities. However, an evaluation of the effects of MTBE at this scale is beyond the scope of this analysis. Therefore, we selected two water bodies as representative of systems in California, Donner Lake and Lake Perris. Donner Lake is a high altitude lake located in the Sierra Nevada mountain range, and Lake Perris is a low elevation coastal range reservoir. Both water bodies support multiple uses including recreation and drinking water supply. Both also support a diverse aquatic ecosystem. Donner Lake maintains a sport fishery with trout as the primary fish species. Lake Perris is stocked with salmonid and centrarchid species to provide a diverse sport fishery. Recreational boating and the use of personal watercraft are common on both lakes.

The two primary habitats potentially exposed to MTBE are the pelagic zone of the lake above the epilimnion, and the nearshore sediments. Monitoring data indicate that MTBE remains in the water column above the epilimnion for a short period of time before it volatilizes. Maintaining concentrations of MTBE in the water column depends on continual input of the chemical to the system.

Nearshore sediments

Nearshore benthic communities typically consist of rooted aquatic vegetation and a diverse invertebrate community that lives on the vegetation, on the surface of the sediment, and burrowing within the sediment. Even simple communities can support dozens of species of invertebrates, some with numerous larval instar stages. Food habits of these species range from detritus, to algae, and other invertebrates. These invertebrates serve as a food source for some of the vertebrate predators including fish and some amphibians.

MTBE does not sorb to sediment or soils to any significant degree. Often, compounds that do sorb to sediment and organic material are not bioavailable to benthic organisms i.e., organisms may not exposed to chemicals that sorb to sediment. The chemical properties of MTBE suggest that all MTBE would be dissolved in the interstitial water in the sediment and would be bioavailable to benthic organisms. Benthic organisms also would be exposed to MTBE at the sediment-water interface.

Two types of information are necessary to fully establish the ecological effects of MTBE to the benthic community (1) concentration of MTBE in the interstitial water in the sediment, and (2) toxicity of MTBE to benthic organisms. No information was found on the amount of MTBE found in interstitial water or any relationship for the partitioning of MTBE between surface water and interstitial water. Also, no information was found to establish the toxicity of MTBE or other fuel oxygenates to benthic organisms. It is assumed that the general toxicity of MTBE to benthic invertebrates is similar to the toxicity of MTBE to microcrustaceans. Consequently, while we are unable to fully develop the assessment of adverse impacts to organisms in the benthic community, we will assume that they are similar to the risk experienced by organisms in the pelagic community.

Potential Ecological Receptors/Endpoints

Because of the broad range of plankton and fish species present in the two lakes, we use representative species as the ecological endpoints for this analysis. These species, *Selanastrum capricornutum* (an algae), *Ceriodaphnia dubia* (a microcrustacean), and *Onchorrynchus mykiss* (rainbow trout), represent the range of trophic levels in the pelagic zone. Data on toxicity of MTBE to rainbow trout (*Oncorhynchus mykiss*) are available allowing an analysis of the potential ecological risk. Additionally, toxicity data exist for other species that can be extrapolated to trout.

Trout

Based on its chemical properties (log K_{ow} = 1.2), it is generally assumed that MTBE does not bioaccumulate to a substantial degree in biota. Both modeling and experimental studies indicate that when MTBE is brought into the body of fish, it is rapidly excreted across the surface of the gills and through urine. The chronic No Adverse Effects Level (NOAEL) concentration for reproduction of fathead minnows is 288 ppm (288,000 ppb), and the LC_{50} (concentration at which half of the test organisms die) for rainbow trout is between 880-1240 ppm. A Maximum Allowable Toxic Concentration (MATC) level of 66 ppm is proposed as the benchmark concentration for fathead minnows (Mancini and Stubblefield 1997).

To characterize the ecological risk to trout, several simplifying assumptions are made including (1) fish spent all of their time in the epilimnion where they are continually exposed to MTBE at the concentration found in the water; (2) fish are exposed through ingestion, inhalation, and dermal contact; (3) fish are omnivorous consuming insects, crustaceans, and small fish; and (4) trout exposure, bioaccumulation, and excretion of MTBE is fundamentally the same as in other species of fish for which data currently exist.

Three additional assumptions are made that could underestimate the effects of MTBE. First, the analyses were performed as if MTBE is the only contaminant to which fish are exposed. It is clear that gasoline from personal watercraft enters the water column as does storm water from the surrounding watershed. Both inputs contain numerous contaminants, and aquatic biota are exposed to these in combination. It is not clear how the exposure to chemical mixtures containing MTBE affects the analyses. Also, the concentration of MTBE varies throughout the period of exposure. This variation is included in the deterministic analysis by selecting an average concentration (arithmetic mean) for calculating the hazard quotients. In the probabilistic analysis, the distribution of concentrations in the water over the period of exposure is used as the distribution of concentrations for the exposure. This analysis assumes that each individual is exposed to a single concentration over the period of exposure, with that concentration drawn at random from the distribution of daily concentrations. It is assumed that this is sufficient to represent the range of potential exposure concentrations, but it is unknown how variability in MTBE concentration over the period of exposure affects an individual fish. This assumption can be evaluated by additional modeling, although the modeling will require experimental analyses to provide the parameter values necessary run the model. The final assumption is that the only significant effects are direct toxicity and that these effects are manifested only at the trophic level experiencing the toxicity. This assumption eliminates the potential for indirect ecological effects. Indirect effects are changes in the abundance of one species due to interactions with another species in the ecosystem. Elucidating indirect effects requires an understanding of site-specific ecological interactions, and is beyond the scope of this analysis.

Ecological risk can be quantified as a hazard quotient, which is the ratio of the expected exposure of the ecological receptor to the Toxicity Reference Value (TRV). The TRV is the lowest concentration of a contaminant at which chronic toxicity might be expected to occur. Hazard quotients larger than 1.0 indicates that the organism is exposed to concentrations of the contaminant that are known to result in adverse effects in laboratory toxicity tests. The assumption is that this exposure will result in adverse ecological effects as well.

Two values for the TRV were developed using the available toxicity data and the uncertainty factors provided in Polisini et al. (1998). One TRV was calculated using the lowest LC_{50} value available for rainbow trout, 880 ppm. It was then adjusted for the extrapolation from an LC_{50} to a chronic NOAEL by dividing the LC_{50} (880 ppm) by 125, the product of three uncertainty factors (one each for the extrapolation of LC_{50} to acute LOAEL, acute LOAEL to chronic LOAEL, chronic LOAEL to chronic NOAEL). The TRV of 7 ppm, or 7,000 ppb was used in the calculation of the hazard quotient.

The second TRV was calculated from the MATC data for the fathead minnow of 66,000 ppb, the lowest chronic value found. This value was adjusted for the interspecies extrapolation by dividing by two to account for the different families within the same taxonomic order. A TRV of 33,000 was used in the calculations of the hazard quotient. The TRV of 33,000 ppb was much higher than the TRV of 7,000 ppb based on the rainbow trout toxicity data, so the hazard quotient was calculated based on the smaller value.

Eight-week exposure studies were conducted by Fujiwara et al. (1984). In these studies, Japanese carp were continually exposed to water containing MTBE. Carp accumulated MTBE in their tissues at 1.5 X the concentration of MTBE in their water. After the

MTBE was removed from the test water, the concentration of MTBE in the body tissues dropped rapidly to zero.

Hazard quotients are calculated using an expected exposure that is 1.5 X the concentration of MTBE in lakewater. Concentration of MTBE in the water column is obtained from modeling scenarios for the two lakes. A one dimensional lake mixing model is used along with information on boating traffic to generate the concentration of MTBE in the both lakes. The expected exposure is calculated as 1.5 X the maximum concentration of MTBE in the upper water column.

In all scenarios, the expected exposure is several orders of magnitude lower than the TRV of 7,000 ppb giving Hazard Quotients ranging from 1×10^{-3} to 6×10^{-3} with a mean value of 4×10^{-3}. These HQs are far smaller than 1.0, indicating that there is little risk of adverse impacts to trout from exposure to MTBE. Assuming that there is a linear relationship between concentration and toxicity, adverse ecological impacts on trout are not expected to occur until concentrations of MTBE in the water column reach 4,600 ppb to 4,700 ppb.

Selanastrum capricornutum and *Ceriodaphnia dubia*

Toxicity of MTBE to aquatic organisms is very low. Acute toxicity tests indicate that green algae have the lowest tolerance to MTBE with an LC_{50} of 184 ppm (Mancini and Stubblefield 1997). LC_{50}s for zooplankton range from 340-680 ppm, and the chronic NOAEL for zooplankton is 200 ppm (Mancini and Stubblefield 1997). However, all of these values are quite large compared to the expected exposure indicating that hazard quotients would be small. Again, these results indicate that there is low potential for adverse ecological effects from levels of MTBE currently in surface waters.

Toxicity tests performed at UC Davis Aquatic Toxicology Laboratory showed no adverse developmental effects or decreases in egg hatchability or fry viability for Japanese medaka exposed to MTBE. These results indicate little potential adverse impact of MTBE on aquatic organisms.

Potential ecological impacts of other fuel oxygenates

Comparisons of the toxic effects of some other fuel oxygenates can be made based on the limited toxicity data available and Quantitative Structure Activity Relationship information. There is a statistically significant relationship between the solubility of the chemical and its toxicity such that higher solubility results in lower toxicity. Tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), diisopropyl ether (DIPE), and tertiary-amyl ethyl ether (TAEE) all have somewhat lower solubility in water and are expected to have somewhat greater toxicity to aquatic organisms. All are expected to produce between 2-6 times higher hazard quotients than MTBE (as great as 3.6×10^{-2}). However, none of the hazard quotients are expected to exceed 1.0. Tertiary-butyl alcohol (TBA), methanol, and ethanol are expected to produce 3-15 times lower hazard quotients than MTBE.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- MTBE is present in California's surface waters and aquatic organisms are exposed.
- There is little toxicity of MTBE to aquatic organisms, with the most sensitive taxonomic group tested being green algae.
- One experimental study indicates that fish accumulate MTBE to about 1.5 times the concentration of MTBE in the water column.
- The most conservative toxicity reference value calculated for rainbow trout is 7,000 ppb.
- The most conservative hazard quotients for rainbow trout exposed to MTBE in two selected surface waters range from 1×10^{-3} to 6×10^{-3}, well below the level that indicates potential adverse ecological effects.
- Adverse effects on rainbow trout are not expected until concentrations of MTBE in the water column reach 4,600 ppb to 4,700 ppb. These levels are much greater than the human health standards for MTBE in drinking water supplies.

Recommendations

The following recommendations are made given the assumption that MTBE will continue to be discharged into surface water in California. Although available information indicates that there is low potential for adverse ecological impacts, several gaps in the available information do exist. These recommendations are made to fill those gaps.

- Evaluate the potential ecological risk to benthic invertebrate communities from MTBE.
- The complete risk assessment relies on a single study conducted in 1984 that characterizes the concentration of MTBE in fish tissue after exposure to contaminated water. The study should be repeated with additional species including species common in California surface waters.
- A majority of the toxicity studies on MTBE and fish are short-term investigations. A chronic toxicity study should be undertaken with a full evaluation of histopathological effects.
- Evaluate the joint toxicity to aquatic organisms from MTBE and other common constituents of gasoline and constituents of stormwater runoff.
- No information is available for the presence of MTBE in estuarine environments. Large volumes of MTBE are shipped by tanker into estuaries such as San Francisco

Bay. An assessment of the probability of an MTBE spill into an estuary such as San Francisco Bay should be undertaken as well as an assessment of the ecological risk associated with such a spill.

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