

MTBE in Florida Groundwater Resources

MTBE (methyl tertiary-butyl ether) is a fuel additive made from natural gas. It has been used in the United States since 1979 as an octane enhancer in gasoline fuels, usually in concentrations of 3 to 8 percent by volume of the gasoline mixture. Use of MTBE began at that time as a replacement for lead (tetraethyl lead). At the time lead had known serious health and environmental consequences and as a result the US Environmental Protection Agency (EPA) mandated the phase-out of its use in the 1970s.

More recently MTBE has come into use as an oxygenate in automotive fuel at higher concentrations of between 11 and 15 percent for the purpose of reducing carbon monoxide and ozone concentrations in the areas of the country with more serious air pollution problems. The use of MTBE as a mechanism for air pollution control was initiated by the EPA in 1992 by the creation of the oxygenated fuel (Oxyfuel) program and enhanced in 1995 by the creation of the reformulated gas (RFG) program. The Oxyfuel program requires 2.7% oxygen (by weight) in gasoline during the winter months to reduce carbon monoxide emissions. The RFG program requires 2.0% oxygen (by weight) in the most polluted metropolitan areas to reduce ozone and smog. When MTBE is used to meet the Oxyfuel requirements it is added at a concentration of about 15% of gasoline. When MTBE is used to meet the RFG requirements, its volume concentration is about 11% of gasoline.

No areas of Florida are currently designated by EPA as non-attainment areas for air pollution such that they are subject to either the Oxyfuel or RFG programs. For this reason it is believed that the majority of gasoline fuel sold in Florida has MTBE concentrations of between 3 and 8 percent of the fuel mixture. Based on the regional fuel distribution networks of petroleum companies, however, it is possible that gasoline with higher concentrations is sometimes sold in Florida. It is not easy for petroleum product distribution companies that are involved in multistate commerce in large volumes of fuel to segregate fuels with higher concentrations of MTBE that may be mandated in one area from being distributed to other areas for which MTBE in higher concentrations is not necessary. This distribution of gasoline fuel with higher concentrations of MTBE to areas where it is not required for air emissions control is sometimes known as "spillover." This is a common problem in the northeastern United States where there are a number of RFG and Oxyfuel areas in close proximity to other areas where use of higher concentrations of MTBE in fuels is not required. It is believed that this spillover problem is not significant in Florida due to our remoteness relative to other RFG and Oxyfuel areas but this cannot be readily verified because the companies that do reformulation and distribution of fuels are not required to report this type of information to the government.

MTBE reaches groundwater due to the discharge of the petroleum products (gasoline) in which it is found. At last count, Florida has 18,404 known sites that have had reported discharges of petroleum fuels. Approximately 4,652 of the sites with reported discharges have been cleaned up. Many of the contaminated sites were not identified or reported until some time after the discharge occurred so there are no good statistics on the number of those discharges that occurred after 1979 and therefore likely had MTBE in the

gasoline that was discharged. Gasoline is a mixture of over a hundred individual chemicals such as benzene, toluene, xylenes, and ethylbenzene. The relative proportion of each chemical is related to the source of the crude oil used for the petroleum products and also the refining process. Some chemicals are found in gasoline at relatively higher proportions than others. Not all of the chemicals found in gasoline are monitored at petroleum contaminated sites. Indicator chemicals have been selected from among all the chemicals in gasoline because they appear in relatively greater abundance or have greater risk to the human population due to exposure to the chemicals.

Florida has monitored the concentration of MTBE at petroleum contaminated sites since February, 1990 when the Petroleum Contamination Site Cleanup Criteria Rule, Chapter 62-770, F.A.C., was revised and MTBE was added to the list of chemicals for which to monitor by laboratory analysis of groundwater samples. The cleanup target level for MTBE in Florida was established at that time as 50 ug/L (parts per billion, or ppb). The cleanup target level was based on organoleptic considerations. This means that water with a concentration of 50 ppb or higher would have a taste or odor that would make it unpalatable to drink. There is some evidence that MTBE is a carcinogen. In September 1997, the Department modified the cleanup target level concentration for MTBE to 35 ppb based on information concerning the human health effects from long term chronic exposure. However, the Department's toxicological information was subsequently reconsidered and it was determined that there was not substantial information to support the 35 ppb cleanup target level and in August 1999 it was changed back to the 50 ppb organoleptic standard. EPA currently has an ongoing toxicological study of MTBE that the Department is closely monitoring. Toxicological and epidemiological studies take time to perform and validate, however. EPA has estimated that they will not have a recommendation for a health-based cleanup target level for MTBE prior to the year 2005. Currently the chemical found in gasoline that is of most concern to human health and the environment is benzene. Benzene is a known carcinogen and the current cleanup target level for that chemical is 1 ppb.

MTBE has distinctive physical properties that result in different behavior in the environment than the other chemicals found in gasoline fuel. One important measure of physical properties of the chemicals in gasoline is solubility. MTBE has a much higher solubility than other chemicals found in gasoline. One important result from this is that it is much more mobile in the environment. Other chemicals in petroleum fuel have a tendency to adsorb to soil particles above the groundwater or after reaching the groundwater, and as a result the migration of the chemicals is retarded to varying degrees. Because MTBE is much more soluble its migration is not significantly retarded. For this reason it typically may migrate further from a site of a petroleum release than other chemicals. Additionally, due to its molecular structure, MTBE is not readily biodegraded in the environment and as a result has a tendency to persist longer at sites than other chemicals in gasoline.

MTBE is not as controversial of an issue in Florida as in some other parts of the country due to several factors. One reason is that because Florida is not an Oxyfuel state or RFG state, the concentration of MTBE in fuel sold here is less, and as a result, the MTBE

problems at sites that have a gasoline discharge are less severe compared to some other areas of the country that do use Oxyfuel or RFG fuel mixtures. The other primary reason has to do with the different geological and hydrogeological conditions somewhat unique to Florida. Florida is a relatively flat state and two distinctive characteristics typical of Florida hydrogeology are a relatively shallow groundwater table and relatively low groundwater gradients. The gradient is the slope of the groundwater table and directly affects the rate (velocity) of groundwater movement. Because of the shallow groundwater conditions and highly permeable soils in the majority of the populated areas of the state, most sites that have a discharge of petroleum products result in groundwater contamination by the fuel mixture, meaning the sites are contaminated with both MTBE and other petroleum chemicals. In other areas of the country, groundwater may be predominantly deeper in most of the populated areas. As a result, on many sites in those other states the migration of other petroleum chemicals is retarded or attenuated in the unsaturated zone above the groundwater table and they never reach the groundwater in concentrations detectable in monitoring wells. Because MTBE is much more soluble and more mobile, many of these sites with no detectable levels of other petroleum chemicals have MTBE detected in monitoring wells. As a result other states have a greater proportion of sites that would not have groundwater contamination at all were it not for the presence of MTBE in the fuel.

The groundwater gradient and rate of groundwater movement has a direct bearing on the relative difference in the MTBE problem relative to the extent of the problem caused by other petroleum chemicals. As described earlier, once both MTBE and other petroleum chemicals reach the groundwater, there is a tendency for the MTBE to advance more rapidly and further than the other chemicals due to its solubility. The groundwater gradient and velocity has a tendency to accentuate the difference in advance of the different chemicals. In Florida, the dissolved plume of MTBE in groundwater usually advances further than the other chemicals, but not usually significantly further, estimated to be on the order of 10% to 30% further than the other important petroleum chemicals that are monitored (primarily benzene). In other states with higher groundwater gradients and more rapid groundwater movement, the differential in migration of MTBE relative to other petroleum chemicals may be greatly enhanced. There are reported incidents of MTBE migration in some other states many times the distance of the migration of the petroleum chemicals. As a result, there are a much higher proportion of incidents in other states for which a receptor (e.g., drinking water well) has been impacted by only MTBE and not the other chemicals found in gasoline.

An additional area of controversy is whether or not MTBE has a dramatic effect on the cost to clean up petroleum contaminated sites. The significance in Florida is related to the relative cleanup target levels for the chemicals of concern as well as the MTBE content of the fuel and mobility issues discussed above. Benzene is one of the more abundant chemicals in gasoline and occurs in a range of between less than 1% by weight up to 3.5% by weight. This compares to 3% to 8% of MTBE in fuel mixtures sold in Florida. MTBE is therefore found in gasoline fuels in concentrations 2 to 5 times higher than benzene in Florida. However, because the cleanup target level for benzene is much lower (50 times less), and because the extent of dissolved contamination of MTBE in

groundwater does not typically advance much beyond the other petroleum chemicals in Florida, benzene typically controls the time to clean up a site and also has the most effect on the overall cost to achieve cleanup objectives at a gasoline contaminated site. One notable consideration is that once a private or public drinking water well has been impacted by MTBE, the cost to provide a treatment system on the water supply well to remove the MTBE could be greater than what would be necessary for other petroleum chemicals. This is because the physical properties of MTBE make it difficult and costly to remove with the conventional processes of air stripping or activated carbon filtration that have been traditionally used.

This summary is not to suggest that there are no problems with MTBE contamination in Florida. There are some instances of incidents where a drinking water well has been contaminated with only MTBE and no other petroleum chemicals and other instances in which the cost to clean up a petroleum contaminated site was driven by the MTBE contamination rather than benzene or other petroleum chemicals; however, these are a small minority of the sites and much less than the problems that many other states are experiencing and which has brought national attention to this issue.