MTBE in Florida Groundwater Resources
May 14, 2007

MTBE (methyl tertiary-butyl ether) is a fuel additive that is manufactured by the chemical reaction of methanol and isobutylene. Methanol used in this process is produced from natural gas. MTBE 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) as an octane enhancement. At the time, use of 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 the EPA as non-attainment areas for air pollution such that they are subject to either the Oxyfuel or RFG programs. For this reason it has been assumed that the majority of gasoline fuels sold in Florida have had maximum 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 has sometimes been sold in Florida. It is not practical 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 fuel with MTBE in higher concentrations is not necessary. This phenomenon has been 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 problem is not significant in Florida due to our remoteness relative to other RFG and Oxyfuel areas but this cannot be readily verified.

Manufacturers of motor fuels are not required to use MTBE in gasoline to fulfill requirements of the RFG and Oxyfuel programs. MTBE is in a class of chemicals known as oxygenates. This name comes from the fact that addition of these chemicals to gasoline increases the oxygen content of the fuel mixture, which affects the combustion process and results in less air emissions from motor vehicles. Oxygenates other than

MTBE could fulfill the RFG and Oxyfuel program requirements but MTBE had historically been preferred because of economic considerations and blending characteristics. In recent years several states have banned MTBE in gasoline and other states are considering similar legislation. As a result of bans and other lawsuits and general public perception, petroleum companies have been reducing the use of MTBE in petroleum fuels in recent years and increasing the use of other oxygenates. The most common replacement oxygenate for MTBE is ethanol but other oxygenates may also be used including tert butyl alcohol (TBA) and tert-amyl methyl ether (TAME).

MTBE reaches groundwater due to the discharge of the petroleum products (gasoline) in which it is found. At last count, Florida had 24,463 known sites that have had reported discharges of petroleum fuels. Approximately 9,331 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 a large number of individual chemicals such as benzene, toluene, ethylbenzene, and xylenes. 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 for identifying the existence of contamination and gauging cleanup progress 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 required monitoring of 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 (CTL) for MTBE in Florida was established at that time as 50 ug/L (micrograms per liter, = parts per billion, or ppb), and the CTL 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 CTL concentration for MTBE to 35 ppb based on information concerning the human health effects from long term chronic exposure. However, the reliability of the Department's toxicological information was subsequently reconsidered and it was determined that there was no substantial information to support the 35 ppb CTL, and in August 1999 the CTL was changed back to the 50 ppb organoleptic standard. The CTL was lowered to 20 ppb in April 2005 based on revised information of the detectable level in water for organoleptic (taste and odor) considerations. The Department is monitoring ongoing research into the toxicological effects of MTBE. 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 CTL for that chemical is 1 ppb.

MTBE has distinctive physical/chemical properties that result in different behavior in the environment than the other chemicals found in gasoline fuel. One important measure of behavior based on chemical properties is solubility. MTBE has a much higher solubility than other chemicals found in gasoline. One important result from this chemical property is that it is much more mobile in the environment than other chemicals found in petroleum products. 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 as 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 at petroleum contaminated sites has not been 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 that has been sold here is likely to be lower than in some other areas of the country, 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 is directly related to 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 had 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 many 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 the other petroleum chemicals 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 may 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 MTBE to advance more rapidly and further than the other chemicals due to its solubility. A greater 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. When the MTBE

CTL was 50 ppb, it was estimated by Department staff that the MTBE plume, on average, was on the order of 10% to 30% further advanced 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 much greater. There are reported incidents of MTBE migration in some other states many times the distance of the migration of the other petroleum chemicals. As a result, there are a 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. The relative difference in average plume size between benzene and MTBE plumes since the CTL for MTBE was changed to 20 ppb has not been evaluated sufficiently by Department staff to quantify the effect at this time.

An additional area of controversy is whether or not MTBE has a significant effect on the cost to clean up petroleum contaminated sites. The significance in Florida is related to the relative CTL 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 an estimated 3% to 8% of MTBE in fuel mixtures that have historically been sold in Florida. MTBE has therefore been present in gasoline fuels sold in Florida in concentrations 2 to 5 times higher than benzene. However, because the CTL for benzene is lower (20 times less), and because the extent of dissolved contamination of MTBE in groundwater does not typically advance significantly beyond the other petroleum chemicals in Florida (as compared to what some other states have experienced), 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. The change in the MTBE groundwater CTL from 50 ppb to 20 ppb will increase the frequency of circumstances in which MTBE will drive the cost of site cleanup rather than benzene. However, the available information on the effects of this change is currently considered anecdotal and has not been evaluated sufficiently by Department staff to quantify the effect at this time.

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 difference 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 for treating public water supply systems that have been contaminated with volatile organic chemicals.

This summary is not to suggest that there are no problems with MTBE contamination in Florida. There are some instances of incidents where drinking water wells have been contaminated with only MTBE and no other petroleum chemicals, 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, and also instances in which only MTBE contamination is present in groundwater at a petroleum product

discharge site; however, these are a minority of the sites and less frequent and severe than the problems that many other states are experiencing and which has brought national attention to this issue.

The other oxygenates being used in place of MTBE are not currently listed as Petroleum Products' Contaminants of Concern in the Petroleum Contamination Site Cleanup Criteria Rule, and therefore analysis for those chemicals in groundwater samples from petroleum contaminated sites is not currently being conducted. The percent of total petroleum discharge incident sites yet to be cleaned up for which the discharge occurred in the last few years, and therefore likely had other oxygenates than MTBE present in the petroleum fuel, is relatively small compared to the total discharge sites yet to be cleaned up (estimated at less than 20% of the total sites yet to be cleaned up). The Department is currently giving consideration to whether other oxygenates are likely to be present in concentrations of concern at petroleum product discharge sites and whether consideration should be given to revising the Petroleum Contamination Site Cleanup Criteria Rule to add other oxygenates to the Petroleum Products' Contaminants of Concern list for which analysis will be required in groundwater samples and for which CTLs would have to be achieved in groundwater to qualify the site for site rehabilitation completion.

* These statistics on number of contaminated sites and number of cleanups completed is accurate as of March, 2007. The most current information can be found at http://www.floridadep.gov/waste/petroleum-restoration/content/petroleum-cleanup-programs and clicking on the most recent monthly summary report.