

Appendix 7B

Methyl Tertiary-Butyl Ether (MTBE)

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1.0 Background

MTBE was introduced in the United States in 1979 as a replacement octane booster for alkyl lead compounds, which were being phased out because of lead toxicity concerns and its incompatibility with catalytic converters. By the 1980s, MTBE was in widespread use throughout the U.S. in the gasoline mix at concentrations up to 8 percent, especially in the premium grades of gasoline. A few years later, MTBE was found to be useful as an oxygenate, i.e., an oxygen-containing compound that improves the combustion of gasoline, and thus reduces air pollution. Oxygenates were mandated by Congress in the Reformulated Gasoline (RFG) and Winter Oxygenated Fuels (Oxyfuels) program as a result of the 1990 Clean Air Act Amendments. Oxyfuels require an oxygen content of 2.7 percent by weight in gasoline to reduce carbon monoxide emissions during the cold months in certain non-attainment areas of the U.S., including El Paso, Texas and Tucson, Arizona, two markets targeted by the Longhorn pipeline. Since MTBE contains approximately 18 percent oxygen by weight, the Winter Oxy requirement translates into 15 percent MTBE by volume in gasoline. The RFG program mandates 2 percent oxygen by weight (11 percent MTBE by volume) year-round to reduce ozone and smog in selected metropolitan areas, including El Paso; Arizona participates voluntarily in the RFG program (EPA, 1998). RFG areas predominantly use MTBE. Currently, the Winter Oxy program primarily uses ethanol, with Los Angeles being the only area that uses MTBE. Refiners have chosen MTBE as the main oxygenate in RFG in cities outside of the Midwest primarily for economic reasons and for its blending characteristics.

In some areas of high MTBE use, such as Midwestern cities in winter, people particularly exposed to MTBE, such as gas station attendants, have complained during the start-up of RFG of symptoms such as nausea and dizziness that were linked to the inhalation of MTBE. Subsequent studies of these health effects in the U.S. and Finland were inconclusive (Moolenaar et al., 1994, Hakkola et al., 1996). Additionally, OSTP's 1997 report states that, "with regard to exposures to lower concentrations as experienced by the general population and motorists, the limited epidemiological studies to date do not support the contention that MTBE, as used in winter oxygenated fuels programs, is causing significant increases over background in acute symptoms or illnesses" (OSTP 1997). However, the report does note that attention should focus on workers exposed to high levels of MTBE and anecdotal reports of acute health symptoms among some individuals cannot yet be explained or dismissed.

Later, trace amounts of MTBE were detected in surface and ground water, particularly in California, which uses approximately 40 percent of the U.S. MTBE production, and 6 percent of the world's output, because of its many air pollution concerns. The detections of MTBE in water were often caused by leaking underground gasoline storage tanks and from older marine engines. Eventually, some water supplies were affected; the City of Santa Monica shut down the majority of the city's drinking water wells in 1996 due to MTBE contamination (EPA, 2000, Ghirelli et al., 1997). EPA issued a Drinking Water Advisory in December 1997, recommending that

MTBE concentrations in the range of 20 to 40 μ g/L will provide control levels for taste and odor acceptability that will also protect against adverse health effects. The advisory also notes that these concentrations are 20,000 to 100,000 times lower than at the range of exposure levels in which cancer or non-cancer effects were observed in laboratory animals (EPA, 1997).

As a result of the growing concern, a number of actions are currently underway to address MTBE. In March 1999, Governor Gray Davis issued an executive order to ban MTBE in California by the end of 2002. It was subsequently relaxed by California Senate Bill 989 to “as soon as possible” (Chang, 1999). Similar changes are afoot in several other states. For example, Rep. Bob Franks (R-NJ) introduced H.R. 1367 in April 1999 to repeal the oxygenate mandate of the Clean Air Act and ban MTBE within 3 years (Anon. 2000). In January 1999, EPA convened a Blue Ribbon panel on MTBE, with experts representing the various stakeholders in the controversy. The panel presented its final report in September 1999, which recommended that existing clean air regulations be modified to minimize or eliminate MTBE use (Blue Ribbon Panel, 1999). On March 20, 2000, the EPA Administrator outlined a two-pronged strategy to reduce or eliminate MTBE use: (a) to begin regulatory action under the Toxic Substances Control Act (TSCA) to significantly reduce or eliminate use of MTBE in gasoline while preserving clean air benefits and (b) to ask Congress to amend a section of the 1990 Clean Air Act that mandates a fuel oxygen content of 2 percent in non-attainment areas (Brasher, 2000).

2.0 Local Occurrence

In the area crossed by the proposed Longhorn pipeline, the Lower Colorado River Authority (LCRA) performed a biased sampling (i.e., looking for areas of maximum MTBE concentration) in the Highland Lakes area during the 1999 summer holidays. They sampled surface water around docks and marinas. LCRA found levels as high as 45 μ g MTBE/L on Lake LBJ, though that level dropped to 7 μ g/L within a week. Levels in the 10s and 20s of μ g/L in Lake Travis. The only Texas lake with higher MTBE levels was Lake Houston. Texas Parks and Wildlife recorded MTBE levels between 5.5 and 7.0 in Lake Austin during the summer of 1999. These MTBE detections are clearly linked to recreational boating, which is allowed on these lakes. MTBE was detected in the drinking water supply of the City of Austin, which draws its water from local lakes: 4.1 μ g/L at the Davis drinking water treatment facility, 3.9 μ g/L at the Ullrich facility, and 2.8 μ g/L at the Green facility. These facilities are not equipped to remove MTBE from drinking water, but the levels are well below the lower limit (20 μ g/L) of EPA’s Drinking Water Advisory. Finally, some MTBE detections are also reported in the Edwards Aquifer (Buchholz, 2000). Note that the spill modeling exercises conducted for this EA and the Responsiveness Summary are set up for an MTBE concentration of 20 μ g/L at Mansfield Dam. Longhorn’s commitments have been adjusted to fully prevent spills that could result in concentrations exceeding this level.

3.0 The Concerns about MTBE

While a number of studies have been conducted on the inhalation of MTBE, there have been no human or animal health effects studies concerning the ingestion of MTBE in drinking water. MTBE toxicological studies have been performed on laboratory animals; these studies suggest that it is not a particularly toxic or carcinogenic compound; in fact, it is less carcinogenic to laboratory animals than some other constituents of gasoline (OSTP, 1997). Although EPA has not formally reviewed and classified the weight of evidence on the carcinogenicity of MTBE, it has concurred with the conclusion stated in the Interagency Assessment of Oxygenated Fuels (OSTP, 1997) that MTBE is an animal carcinogen and may be regarded as “having a carcinogenic hazard potential for humans.” The evidence on the potential of MTBE for human carcinogenicity has been subject to multiple interpretations, however, and some other review groups have not yet judged the evidence sufficient to classify MTBE as a likely human carcinogen (e.g., the national Toxicology program [NTP], the State of California Proposition 65 Advisory Panel, and the International Agency for Research on Cancer [IARC]).

MTBE has a very low taste and odor threshold, meaning that it can be detected by the human nose or palate at low concentrations (NSTC, 1997; Young et al., 1996; API 1993; Prah et al., 1994; Dale et al., 1997). Humans vary widely in the concentrations they are able to detect. Additionally, the presence or absence of other natural or water treatment chemicals can mask or reveal the taste or odor effects. Due to its low taste and odor threshold, MTBE has the potential to render drinking water unpalatable at very low concentrations. Concentrations in the range of EPA’s Drinking Water Advisory (20-40 µg/L) are 20,000 to 100,000 times lower than the range of exposure levels in which cancer or non-cancer effects were observed in rodent tests.

4.0 Chemical and Physical Nature of MTBE

MTBE is soluble in water, does not adsorb well to soil particles, and is relatively slow to biodegrade. In surface water, MTBE often volatilizes quickly at the air-water interface. In ground water, MTBE can have half-lives in the range of 1.6 and 1.9 years (Thomson, 2000; EPA 2000). When a gasoline spill reaches the ground water, MTBE tends to dissolve rapidly into the water and may separate ahead of the gasoline plume. This problem can persist over the long-term because of MTBE’s slow rate of natural attenuation. However, recent fieldwork suggests that there is often no significant difference between benzene and MTBE plume lengths (Thomson, 2000).

Additionally, treatment of MTBE-contaminated water supplies can be difficult and expensive compared to the treatment of other gasoline components. The conventional treatment techniques include air stripping and granular activated carbon (GAC) adsorption in the liquid phase. Air stripping requires high air-to-water ratios because MTBE does not readily separate from water into the vapor phase and GAC needs to be frequently replaced due to MTBE’s poor sorption. This often drives up treatment costs.

5.0 Status as of March 2000

In this section, the MTBE controversy as of March/April 2000 is summarized, reflecting current views on the issue in an attempt to ascertain the future of MTBE as it could affect the Longhorn pipeline. The main parties involved appear to have the following at stake:

- **The gasoline producers.** They have installed billions of dollars worth of MTBE production capacity in response to earlier government mandates. This group has diverse opinions on the subject, but seems to have generally accepted the fact that MTBE may be on its way out. Some refiners have developed reformulated gasolines that meet antiknock specifications and air emissions standards without oxygenates.
- **The methanol producers.** MTBE is made from methanol and isobutylene, and MTBE represents approximately 30 percent of the methanol demand. One major methanol manufacturer (Methanex Corp., Vancouver, BC) filed notice with the U.S. Government in December 1999 of its intent to seek compensation under NAFTA for losses suffered due to the California ban on MTBE (Parkinson, 2000).
- **The ethanol producers.** Ethanol is an alternative oxygenate and can replace MTBE. It is produced from renewable sources, which is ecologically beneficial. The US Department of Agriculture has concluded that ethanol can fully meet all oxygenate requirements of the U.S. within four years (Glickman, 2000). On the other hand, ethanol's renewability is debated, since it is estimated that it takes 81 Btu of fossil fuel to produce 100 Btu of ethanol (Shapouri et al., 1995). Ethanol cannot be blended into gasoline at the refinery because it tends to separate from the gasoline when shipped through pipelines and exposed to water. Consequently, it must be trucked to the distribution points for blending. The resulting large-scale truck traffic has societal and environmental impacts ranging from accidents to air emissions (Hanson, 1999). There is concern about its potential for increasing emissions of volatile organic compounds under certain conditions (Bleu Ribbon Panel, 1999; Chang 1999). Ethanol increases the Reid Vapor Pressure (RVP, a measure of fuel volatility), requiring the use of more costly low RVP blendstock. There are also concerns about ethanol's ability to inhibit BTEX degradation, since the microbes preferentially degrade ethanol over BTEX (EPA, 2000). Finally, ethanol is suspected of increasing the mobility of benzene in the subsurface (Thomson, 2000).
- **The air quality community.** Some note that the use of MTBE, whatever its other environmental costs, has led to a very significant improvement in air quality in the areas where it is used. This continues to have beneficial health effects for millions of people in those areas. They also observe that there is no "drop-in" replacement for MTBE, which has the best combination of low-vapor pressure and low ozone generation potential of any additive being considered (Chang, 1999). In other words, it is more difficult to meet the summer RVP requirements with ethanol, but it is possible. The National Research Council (NRC) concluded that MTBE has had only a slight impact on reducing ozone production. It claims that much more air pollution was prevented by gasolines with lower vapor pressure and lower sulfur content. Use

of MTBE may actually increase automobile emissions of some toxic chemicals, such as formaldehyde (Hanson, 1999). However, the EPA's Blue Ribbon Panel states that NRC overemphasized ozone reduction and that it failed to highlight significant air toxics reductions achieved. For example, from 1990 to 1998, VOCs were reduced in Dallas and Houston by 40 percent, and toxics by 34 percent (Blue Ribbon panel, 1999).

- **The water quality community.** They are alarmed by the increasing number of detections of MTBE in ground water and surface water nationwide. As discussed in Section 2.0 (Local Occurrence) of this Appendix, it has also been detected in the Texas Highland Lakes. Most of these detections are well below the taste/odor threshold, and there is little likelihood these levels will cause adverse health effects. However, a number of drinking water supplies, including the City of Santa Monica in California, have been contaminated by MTBE, forcing condemnation and reliance on other supplies, or expensive treatment (EPA, 2000; Ghirelli, 1997).

Other points have been raised concerning the controversy:

- Stationary sources (that do not use automotive fuel) are now the biggest air pollution sources, so the focus should shift to them in order to improve air quality. Automobile air emissions continue to decline as older, "dirtier" cars are retired (Frank, 1999). At a minimum, this supports the position that fuel composition regulations should be more flexible and should include the option of removing the oxygen-content requirement.
- Any replacement compound could have negative impacts that are presently unsuspected, so further study of these replacements should be carried out before using them (Frank, 1999).
- Only about one percent of MTBE-contaminated water supplies tested have concentrations exceeding the minimum EPA drinking water advisory level of 20 µg/L (Chang, 1999). A recent assessment of household exposures to MTBE in California drinking water concluded that the lifetime cancer risk from five years of exposure at the highest reported taste and odor threshold (748 µg/L) is 5 per million. At average drinking water detections in the 0.14 to 4.3 µg/L range, the lifetime cancer risk is 9 per 100 million based on current exposure, and 1 in 10 million based on current and anticipated exposure (Williams et al., 2000).
- The MTBE Blue Ribbon panel used pre-1997 data on ground water contamination to reach its conclusions. In 1997, only 44 percent of underground storage tanks (UST) complied with UST regulations. The PEA Office of Underground Storage Tanks states that based on reports at the end of September 1999, approximately 85 percent of the RCRA-regulated universe of USTs met the EPA upgrade requirements. By the end of 2000, EPA expects 90 percent of USTs will be in compliance, leaving 70,000 substandard USTs (EPA, 2000).

6.0 Prospects

The ban on MTBE in California has a considerable impact on the future of MTBE in the U.S., since California uses one third of the U.S. MTBE production. Other states (Maine, New Hampshire, Connecticut, and New York) have similar proposals on their legislative agendas. The EPA's Blue Ribbon panel came out in favor of reduction or elimination of MTBE. The EPA Administrator has also advocated a nationwide elimination or significant reduction of MTBE and outlined a strategy to achieve this.

7.0 Constraints on the Longhorn Pipeline

The intended markets for Longhorn pipeline products, El Paso, and Arizona, are under various Oxyfuel and RFG mandates, so they may continue to require an oxygenate for the time being. There is no local MTBE-producing capacity in El Paso, Arizona, or New Mexico. The nearest MTBE production plant is in Sunray, Texas, 600-road miles northeast of El Paso. Most of the nation's ethanol production capacity is located in the Midwest. Currently, no MTBE is used in El Paso (Washington Valdez, 2000).

Longhorn has added a commitment that will not carry petroleum products containing any MTBE (initially, the option of carrying up to 100 percent MTBE had been considered).

8.0 Conclusions

- The Longhorn Pipeline will not carry MTBE; and
- Most MTBE contamination of water will not cause adverse health effects in humans, but it could cause substantial economic damage by rendering a drinking water supply unusable.

9.0 References

Allen et al., 1985, In EPA 1997.

Anon, 1998, Risk Policy Report, December 18, 1998, p. 31, In Anon, 2000.

Anon, 2000, *While Seeking Administrative Ban to Fuel Additive, Second Franks MTBE Bill Calls for further Testing*, Research, Risk Policy Report - February 21, 2000, pp. 32-33.

API 1993, In EPA 1997.

Blue Ribbon Panel, 1999, *Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*, September 15, 1999, EPA-420-R-99-021.

Brasher, P., *Feds to Phase Out MTBE Gas Additive*, Associated Press, March 20, 2000.

Buchholz, B., 2000, "Water Examined for Fuel Additive," *Austin American-Statesman*, Friday, February 25, 2000, pp. A1 and A7.

Chang, T., 1999, "Controversy over MTBE in Gasoline Rages on," *Oil & Gas Journal*, December 20, 1999, pp. 34-35.

Dale et al., 1997, In EPA 1997.

EPA, 1997, *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*, EPA-822-F-97-009.

EPA, 1998, MTBE Fact Sheet #1 - Overview, EPA 510-F-97-014, Available at www.epa.gov/OUST/.

EPA, 2000, 40 CFR Par 755, Advance Notice of Intent to Initiate Rulemaking Under the Toxic Substances Control Act to Eliminate or Limit the Use of MTBE as a Fuel Additive in Gasoline; Advance Notice of Proposed Rulemaking. Dated March 20, 2000, Federal Register; March 24, 2000 (Vol. 65, No. 58); Proposed Rules, pp. 16093-16109. (Available at <http://www.epa.gov/oppt/docket/mtbe/anprm.txt>).

Frank, J.L., 1999, "New Mandates Present Fuel Challenges for US Refiners," *Oil & Gas Journal*, December 13, 1999, pp. 118-121.

Ghirelli, R.P., H. Amini, B.D. Kerger, A. Hillman, and R.O. Richter, 1997, "MTBE Water Contamination: Key Considerations for Remediation, Risk Assessment, and Risk Management," Paper presented at: Pacific Conference on Chemistry and Spectroscopy - ACS, October 21-25, 1997, Irvine, California.

Glickman, D. Letter from Agriculture Secretary Dan Glickman to Senator Tom Harkin, dated November 15, 1999, Attached Analysis entitled "Economic Analysis of Replacing MTBE with Ethanol in the United States," In EPA 2000.

Hakkola et al., 1996, In EPA 1997.

Hanson, 1999, "MTBE: Villain or Victim?" *Chemical & Engineering News*, October 18, 1999, p. 49.

Juliani et al., 1985, In EPA 1997.

Klass, D., Highlights of Bioenergy '96/ASAE Joint Conference, SERBEP Update, Southeastern Regional Biomass Energy Program - TVA, November 1996.

Moolenaar et al., 1994, In EPA 1997.

NSTC, 1997, In EPA 1997.

OSTP, The Interagency Assessment of Oxygenated Fuels, Office of Science and Technology Policy National Science and Technology Council, June 1977.

Parkinson, G., 2000, "Gasoline Minus MTBE," *Chemical Engineering*, 107 (1), January 2000, pp. 45-46.

Prah et al., 1994, In EPA 1997.

Shapouri, H., J.A. Duffield, and M.S. Graboski, *Estimating the Net Energy Balance of Corn Ethanol*, USDA, *Economic Research Service, Office of Energy*, Agricultural Economic Report No. AER-721.

Thomson, J., "Prospects for Natural Attenuation of MTBE," *Soil, Sediment & Groundwater*, MTBE Special Issue, March 2000, pp. 41-42.

Washington Valdez, D., "Juarez Use of Gas Additive Concerns U.S.," *El Paso Times*, March 23, 2000.

Wigglesworth, 1999, In Chang, 1999.

Williams, P.R.D., Scott, P.K., Hays, S.M., and Paustenbach, D.J., "A Screening Level Assessment of Household Exposures to MTBE in California Drinking Water," *Soil, Sediment & Groundwater*, MTBE Special Issue, March 2000, pp. 63-69.

Wyngaarden, 1986, In EPA 1997.

Young et al., 1996, In EPA 1997.