

THE OCCURRENCE OF MTBE IN GROUND WATER IN EUROPE

Alette Langenhoff¹, Tom van Teunenbroek¹, Mathias Effenberger², Mario Schirmer³

¹TNO Environment, Energy and process Innovation
P.O. Box 342, 7300 AH Apeldoorn, The Netherlands

²University of Stuttgart, Environmental Engineering Study Program, Institute of Sanitary Engineering, Water Quality and Solid Waste Management Technology
Bandtäle 2, D-70569 Stuttgart, Germany

³UFZ Centre for Environmental Research Leipzig-Halle
Interdisciplinary Department of Industrial and Mining Landscapes
Permoserstr. 15, D-04318 Leipzig, Germany

1 Introduction

Methyl tertiary-butyl ether (MTBE) is one of several fuel oxygenates added to petrol to both increase octane and provide oxygen concentration. Fuel oxygenation results in improved fuel combustion and reduces the resulting concentrations of carbon monoxide and unburned hydrocarbons, a quality highly approved by oil companies, governments and even several environmental organisations. MTBE is relatively inexpensive, easy to produce, and blends well with gasoline without phase separation. It is therefore by far the most commonly used oxygenate. Other fuel oxygenates include ethanol (ranks second), methanol, ethyl tertiary-butyl ether (ETBE), tertiary-butyl alcohol (TBA), *tert*-amyl methyl ether (TAME), and di-isopropyl ether (DIPE). The "California Air Resources Board" has predicted a decrease in ozone precursors of 15%, benzene emission of 50 %, and CO emission of 11% with the addition of oxygenates, equal to the exhaust of 15 million cars (Davis 1998).

Since the 1970s, MTBE has been used in the United States. Its oxygenating effects have resulted in more extensive usage in recent years as a result of legislation on air quality, e.g. 1990 Clean Air Act Amendments in the US. According to these amendments, oxygenates have to be added at least during fall and winter (when CO concentrations in the air are at their highest) to achieve an oxygen content in petrol of 2.7 % (by mass), which corresponds to a MTBE content of 15 % (by volume). In 2000, it is expected that MTBE is added to approximately 70 % of American petrol (Squillace et al. 1997). In the Netherlands, the used concentrations of MTBE are maximum 1.5%, which is much lower than in the US.

However, the enthusiasm about the use of MTBE is declining. MTBE is highly soluble, and extremely mobile in groundwater, making it an important groundwater pollutant. A leaking petrol station in the vicinity of a drinking water well will cause drinking water of unacceptable quality in terms of taste and odour in no time. Concentrations as low as 20–50 $\mu\text{g/l}$ can already cause this effect. As of 1994, MTBE was the second most persistent contaminant in urban aquifers in the US (Squillace et al. 1996). Diffusion from the gas phase is less important. The USEPA (US Environmental Protection Agency) has classified MTBE as a possible human carcinogen and issued a provisional drinking water advisory of 20 to 40 $\mu\text{g/l}$, based on a life time intake and non-human carcinogenicity. Keeping concentrations in this range will likely avert unpleasant taste and smell (USEPA 1997). In Canada, MTBE is not on the list of toxic compounds.

In Europe, the International Agency for Research on Cancer (IARC) in Lyon is performing an inventory of the available data and studies on MTBE toxicity. Toxicity studies with animals have shown that MTBE can be classified as carcinogenic for animals (Belpoggi 1995, 1998). Due to the discussions about the possible health risks associated with MTBE, some states in the US (California and Maine) are about to ignore the 1990 Clean Air Act Amendments and refuse to add MTBE to their petrol (Renner 1999). A study to evaluate the effect of the better combustion of petrol versus the effect of ground- and drinking water will be started soon. Most recently, the USEPA and the Clinton-Gore Administration released a legislative framework that encourages Congressional action to immediately reduce or eliminate the use of MTBE in the United States (USEPA 2000).

The presence of MTBE in Europe and related ground water problems are to our knowledge underestimated, and in some countries even unknown. One of the given reasons for the lack of attention is that the added MTBE concentration in European petrol can not be compared to the concentrations that are used in the US. Furthermore, the facilities at petrol stations in Europe vary from the American facilities. In Europe, double wall containers are used to store the petrol, and these containers are less likely to cause underground leakage. However, the accident in 1998 when an MTBE tank exploded during cleaning and MTBE was released into the environment, shows that emphasising the facilities at petrol stations only will not prevent MTBE leakage (Aarden 1999). Besides, MTBE is used widespread, making it very difficult to prevent world wide MTBE leakage.

Up to date it is uncertain whether MTBE will give similar problems in Europe. It can be expected that MTBE can cause health problems in Europe and will affect the taste and odour of drinking water already at low concentrations. To our knowledge, MTBE is not a part of routine analyses.

2 MTBE in Europe

The Dutch government and the German "Umweltbundesamt" (Federal Environmental Agency) came to the conclusion that the use of MTBE in gasoline does not pose an acute risk to the environment in these countries. This was explained mainly by the facts that, compared to the situation in the United States, MTBE contents of most of the gasoline used in the Netherlands and Germany are considerably lower and leakage of pipelines and filling stations is significantly less probable due to high technical standards (Anonymous 2000). The configurations of the petrol tanks, with double walls, will cause less underground leakage (Aarden 1999). However, this conclusion was drawn without collecting any actual environmental data.

As MTBE is a hot topic in the US, it is difficult to believe that MTBE will be harmless in Europe. It is very likely that MTBE will affect European surface- and groundwater in one way or the other. MTBE is not part of a routine analyses data set, which could be helpful to generate information about the occurrence of MTBE in European surface- and ground water.

3 MTBE in the Netherlands

At present, there are insufficient data to make an accurate assessment of the current risk posed by MTBE to Dutch groundwater resources. A recent accident in 1998 when a MTBE tank exploded during cleaning and the soil was contaminated with MTBE, demonstrates that care should be taken with such statements (Shell 1998).

Groundwater from a few petrol stations has been analysed for MTBE, and MTBE was found in various wells in concentrations up to 120 µg/l.

4 MTBE in Germany

The total MTBE demand in Germany was an estimated 400.000 tonnes in 1998, and the average MTBE content of all gasoline sold in this year approximated to 1.3 per cent (by mass) (Miller 2000). In Germany, MTBE is contained mainly in 95 RON ("Super") and 98 RON ("Super Plus") gasoline. As of January 2000, "Super" and "Super Plus" fuels accounted for 63 and 5 per cent of all gasoline sold in Germany, respectively (Blasius 2000).

In groundwater samples taken from a former petroleum storage facility, MTBE was found at concentrations of 0.73 µg/L to 2,120 µg/L, with a median value of 782 µg/L (n = 6). This site is currently being remediated by pump and treat, yet

without consideration of MTBE contamination. Benzene concentrations in these samples were between 0.19 and 5,759 $\mu\text{g/L}$.

In the case of a leaking petroleum station that had been remediated with respect to BTEX and petroleum hydrocarbons, MTBE was measured at concentrations of 141 $\mu\text{g/L}$ and 17,603 $\mu\text{g/L}$ in groundwater from two monitoring wells.

At another petroleum station spill site, groundwater samples were obtained along a transection through the source of contamination which had been partially removed within remediation efforts. In this case, the concentrations of MTBE exhibited a pattern clearly distinctive of that of the BTEX compounds. While the concentrations of the latter ones were highest at the location of the spill (up to tens of mg/L) and clearly decreased in the downstream direction, the level of contamination with MTBE was highest in a sample taken 50 m downstream of the source, with a value of 1,868 $\mu\text{g/L}$. The concentrations of MTBE in samples taken at and near the source were 29 $\mu\text{g/L}$ and 45 $\mu\text{g/L}$, respectively. These values indicate that MTBE has been effectively leached out of the source zone and that a significant mass of the oxygenate has been transported downstream with groundwater (Effenberger 2000).

This data base is, of course, not sufficient to finally assess the threat of MTBE to European water resources. However, it clearly shows that considerable contamination of ground water with this fuel oxygenate has already occurred in Europe and cannot be treated easily.

5 Workshop

The MTBE workshop focuses on the key questions of the MTBE debate:

MTBE a blessing for the air, a menace for groundwater?

5.1 Procedure

The workshop will be open to a limited number of participants (50 max.). After a short introduction on the state of affairs concerning MTBE in Europe, a discussion will start. Your seating will decide whether you are pro or contra, much like the British Parliament. The issues open for debate focus on the question whether MTBE poses a threat to European Environment and whether and what actions have to be taken.

Workshop results are foreseen to serve as a guiding principle for an EU concerted action on MTBE. Discussion will be guided by several statements that will be put to a vote. Statements are provocative in order to jump-start the discussion. Factsheets regarding the statements will be presented at the start of the

workshop. Opinions and the facts that they are based on is what we are after. Participants will be present from the MTBE industry as well as the regulating community.

- Statement 1: MTBE; a menace to groundwater and drinking water?
- Statement 2: MTBE; a health threat?
- Statement 3: MTBE; can polluted sites be remediated?
- Statement 4: MTBE; should use be regulated stringently?

References

- Aarden, M. (1999) Amerikaanse benzine bederft grondwater. *Volkskrant*.
- Achten, C., Püttmann, W. (26-2-2000) Determination of Methyl tert-Butyl Ether in Surface Water by Use of Solid-Phase Microextraction. *Environmental Science & Technology* 34(7): 1359-1364. Published on Web 02/26/2000
- Anonymous (2000) World Oxygenates Monthly, December 1999: MTBE - A World-wide Outlook. Electronic Citation. Accessed 26/01/2000.
<http://www.ofa.net/doc/intl/doc/worldox/Ofadecember.htm>
- Belpoggi, F., Soffriit, M., Maltoni, C. (1995) MTBE - a gasoline additive - causes testicular and lymphohaematopoietic cancer in rats. *Toxicology and Industrial Health*. 11:119-149
- Belpoggi, F., Soffriit, M., Maltoni, C. (1998) Pathological characterization of testicular tumours and lymphomas-leukaemias, and of their precursors observed in Sprague-Dawley rats exposed to MTBE. *European Journal of Oncology*. 3:201-206
- Blasius, H.-P. (2000) Marktanteile Kraftstoffsorten. Internet Communication. 01/03/2000
- Davis, U. (1998) What is MTBE. Internet.
- Effenberger, M. (2000) The Potential Impact of the Gasoline Additive Methyl tert-Butyl Ether (MTBE) on Groundwater. M.Sc. Thesis at the University of Stuttgart, Department of Civil Engineering and Surveying (in preparation)
- Miller, K.D. Jr. (2000) World Oxygenates Monthly, February 2000: After California, a Breath of Fresh Air from Germany. Electronic Citation. Accessed 31/03/2000.
<http://www.ofa.net/doc/intl/doc/worldox/OfaFebruary2000.html>
- Renner, R. (1999) Maine seeks to drop MTBE from its clean fuel program. *Environmental Science and Technology*. 33(1):A9-A10
- Shell (1998) Dodelijk ongeval door explosie bij Shell Pernis, Internet.
- Squillace, P.J., Pankow, J.F., Korte, N.E., Zogorski, J.S. (1997) Review of the environmental behavior and fate of methyl tert-butyl ether. *Environmental Toxicology & Chemistry*. 16(9):1836-1844
- Squillace, P.J., Zogorski, J.S., Wilber, W.G., Price, C.V. (1996) Preliminary assessment of the occurrence and possible sources of methyl tert-butyl ether in groundwater in the United States. *Environmental Science & Technology*. 30:1721-1730
- USEPA (2000) USEPA Headquarters Press Release (March 20th, 2000): Clinton-Gore Administration Acts to Eliminate MTBE, Boost Ethanol. Electronic Citation.
<http://yosemite.epa.gov/opa/admpress.nsf/b1ab9f485b098972852562e7004dc686/2054b28bf155afaa852568a80066c805?OpenDocument>

Additional remarks:

We have also sampled a number of surface water bodies in the Leipzig area and other parts of Saxony, between March 13th and 21st, 2000. Concentrations of MTBE in water of the Elbe, Saale, and Mulde rivers as well as smaller rivers in Leipzig ranged between 18 ng/L and 199 ng/L, with a median value of 45 ng/L (n = 10). Two water samples taken from small ponds in downtown Leipzig and a suburb had MTBE concentrations of 25 ng/L and 70 ng/L, respectively (Effenberger 2000).

The authors know of one earlier study of the occurrence of MTBE in German rivers. In samples that had been taken from the Rhine, Elbe, Main, and Oder rivers in winter and early spring of 1998/99, MTBE was measured at concentrations of 7-160 ng/L, with a median concentration of 67 ng/L (n = 7) (Achten and Püttmann 2000).