APPENDIX 4
Kingler et al Wasserkonzentrationen

MTBE (methyl tertiary-butyl ether) in groundwaters: Monitoring results from Germany

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Received 17th December 2001, Accepted 14th February 2002
First published as an Advance Article on the web 7th March 2002

In Germany information on the occurrence of MTBE in groundwaters is scarce. In order to assess the German situation, in 1999 a monitoring programme on MTBE in groundwater was set up. Within this survey 170 wells were examined, which are used as groundwater monitoring points or which are foreseen for drinking water extraction in emergency cases or for irrigation purposes. In rural areas MTBE was found only in 9% of all samples in concentrations above the limit of determination (LOD) of 0.05 μg L^{-1}. In urban areas MTBE was detected in 49% of all wells under investigation and the median concentration was calculated to 0.17 μg L^{-1}. In one case a maximum MTBE concentration of almost 700 μg L^{-1} was detected. As a first result of this survey one can conclude, that MTBE is regularly present in German groundwaters under urban areas. Although investigations about the occurrence of MTBE in German groundwaters have to be extended in future, this first snapshot can lead to the assumption, that MTBE concentrations due to diffuse sources are lower than the ones found in the USA. Nevertheless, *e.g.* accidental spills can lead to elevated MTBE concentrations.

Introduction

Fuel oxygenates have been used since the mid eighties as gasoline additives. Because of its low cost, ease of production and favourable transfer and blending characteristics, methyl tertiary-butyl ether (MTBE) is worldwide the most commonly used additive. Originally, MTBE was added in order to replace lead in gasoline as an "anti-knock agent" but at present it is predominantly used for the reduction of both the fuel vapour pressure and the exhaust emissions, particularly carbon monoxide, un-burned hydrocarbons and polycyclic aromatics.[1,2] Nevertheless, there is an ongoing debate on the effect of MTBE addition to gasoline on exhaust emissions.[3] A comprehensive overview of the use of MTBE, its production numbers, chemical properties and toxicity data is already given in the literature.[4] In recent years the debate about the environmental risks and benefits of greater use of MTBE has increased, particularly in the USA. Reasons were the possible human toxicity and the results of extensive monitoring programmes carried out in the USA, which have demonstrated that MTBE occurs in groundwaters and even in wells used for drinking water extraction in concentrations up to several hundred micrograms per litre.[5–7] Especially in California there is much concern regarding the use of MTBE since in 1996 seven wells supplying 50% of the water for the city of Santa Monica were removed from service because of tremendous MTBE concentrations.[8] As a consequence, in March 1999 Governor Davis decided to phase out MTBE in gasoline until the end of 2002 in California.[9] In order to ensure drinking water consumers' acceptance using parameters such as odour, taste and appearance as measures of acceptability, for MTBE the secondary maximum contaminant level is given as 5.0 μg L^{-1} by the California state department. This value ensures that consumers are not exposed to drinking water with objectionable taste and odour related to MTBE contamination[10] and will also ensure that MTBE levels are below current health based advisory levels, *e.g.* the US Environmental Protection Agency advisory level of 20 to 40 μg L^{-1}.[11]

In parallel to the 1990 Clean Air Act in the USA the European Union started in 1992 its programme against air pollution by emissions from motor vehicles, which is specified in the recently amended Council Directive 98/69/EC "Measures to be taken against air pollution by emissions from motor vehicles". Additionally, Council Directive 98/70/EC about "The quality of petrol and diesel fuels" gives regulations for the properties of fuels. In the EU for oxygen a maximum level of 2.7% and for certain ethers a maximum level of 15% in gasoline is set. Regarding the oxygen content in California for reformulated gasoline a minimum of 1.8%, which holds only during wintertime, and a maximum of 2.7% is given.[12] Although the figures are quite similar, the actual MTBE contents in gasoline in many European countries are much lower than in California. There, the average MTBE contents are about 10 vol.% whereas in Europe values range from 0.1 vol.% in Great Britain up to a maximum content of 9 vol.% in Finland. In Germany the average MTBE content is 1.3 vol.%.[13] Whereas in the USA the increasing frequency of MTBE detection in groundwaters is receiving more and more attention from the media, scientists and environmental agencies, in Europe and especially in Germany information on the occurrence of MTBE in groundwaters is rather scarce.[14,15] In order to fill the knowledge gap concerning the occurrence of MTBE in German groundwaters a monitoring programme was performed, of which results will be presented and discussed.

Experimental section

Sampling

Water samples were taken using a mobile pumping station. The possible impact on the water samples caused by emissions of the pumping station was recognised but test runs demonstrated that there was no detectable impact. Samples were taken in 100 mL glass bottles, which were completely filled with a gentle stream of water in order to avoid MTBE losses by vaporisation. All samples were stored at 4 °C during sample transportation and until the analysis was performed.

DOI: 10.1039/b111488n