



## Odour and flavour thresholds of gasoline additives (MTBE, ETBE and TAME) and their occurrence in Dutch drinking water collection areas

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### ABSTRACT

The use of ETBE (ethyl-*tert*-butylether) as gasoline additive has recently grown rapidly. Contamination of aquatic systems is well documented for MTBE (methyl-*tert*-butylether), but less for other gasoline additives. Due to their mobility they may easily reach drinking water collection areas. Odour and flavour thresholds of MTBE are known to be low, but for ETBE and TAME (methyl-*tert*-amylether) hardly information is available. The objective here is to determine these thresholds for MTBE, ETBE and TAME, and relate these to concentrations monitored in thousands of samples from Dutch drinking water collection areas.

For ETBE odour and flavour thresholds are low with 1–2  $\mu\text{g L}^{-1}$ , for MTBE and TAME they range from 7 to 16  $\mu\text{g L}^{-1}$ .

In most groundwater collection areas MTBE concentrations are below 0.1  $\mu\text{g L}^{-1}$ . In phreatic groundwaters in sandy soils not covered by a protective soil layer, occasionally MTBE occurs at higher concentrations. For surface water collection areas a minority of the locations is free of MTBE. For river bank and dune infiltrates, at a few locations the odour and flavour threshold is exceeded. For ETBE fewer monitoring data are available. ETBE was found in 2 out of 37 groundwater collection areas, in concentrations below 1  $\mu\text{g L}^{-1}$ . In the surface water collection areas monitored ETBE was found in concentrations near to the odour and flavour thresholds.

The low odour and flavour thresholds combined with the high mobility and persistence of these compounds, their high production volumes and their increased use may yield problems with future production of drinking water.

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### 1. Introduction

Methyl-*tert*-butylether (MTBE), methyl-*tert*-amylether (TAME) and ethyl-*tert*-butylether (ETBE) are fuel oxygenates which are in use as gasoline additives. The use of ETBE as gasoline additive recently increases rapidly in Europe, as a result of the highly debated European Biofuels Directive (2003/30/EG) which sets a minimum market share for biofuels of 5.75% in 2010. Bio-ETBE can be etherised from bioethanol and is considered a biofuel for 47 vol%, and similarly bio-MTBE from biomethanol is considered a biofuel for 36 vol% (2002/30/EG). Addition of bio-MTBE and especially bio-ETBE to gasoline can thus help to fulfil the obligation set by the Biofuel Directive.

The commercial production of MTBE started in the seventies (DeWitt & Company Inc., 2000) and MTBE was introduced into pet-

rol in the late 1970s to mid-1980s (Kraayer von Krauss and Harremoës, 2001). With a worldwide annual production of about 21.4 Mt in 1999 (3.4 Mt in the EU) MTBE is a very high production-volume chemical.

Production volumes of TAME and ETBE are lower, with, respectively, 287 and 568 kt in 2002 (EC, 2005; ECB, 2006). However, the production of ETBE is increasing (Vierhout, 2005). In 2006, a third of the European production capacity of MTBE was adapted to produce ETBE. The production capacity in The Netherlands is high compared to most other EU member states, but emissions of these compounds are not registered routinely (pers. comm. C. Peek, Netherlands Environmental Assessment Agency).

Due to their high solubility and volatility the gasoline additives disperse rapidly in the environment, and due to their low biodegradability they are persistent. Contamination of the aquatic environment is well documented for MTBE, but less for TAME and ETBE. In the 1990s MTBE was reported in groundwater and surface waters with increasing frequency, initially in the USA (Squillace et al., 1996; Happel et al., 1998; Johnson et al., 2000) and thereafter also in Europe (Achten et al., 2002; Klinger et al., 2002; Morgenstern

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et al., 2003; Rosell et al., 2003, 2006; Arambarri et al., 2004; Kolb and Puttmann, 2006a,b). Tap water from various regions (USA, Germany and The Netherlands) was found to contain generally low ( $\text{ng L}^{-1}$ ) levels of MTBE (Deeb et al., 2003; Morgenstern et al., 2003; Kolb and Puttmann, 2006b; Cardinali et al., 2008).

A study in the Los Angeles area concluded that although alternative ether oxygenates (such as TAME and ETBE) are detected in groundwater beneath leaking underground fuel tanks less frequent and at lower concentrations than MTBE, these alternative ether oxygenates pose groundwater contamination threats similar to MTBE if their scale of use is expanded (Shih et al., 2004).

MTBE and other oxygenates dissolved in water, exhibit a potent and unpleasant odour for which the human olfactory system is highly sensitive. Odour and flavour thresholds of MTBE are low compared to other chemicals, ranging from 2.5 to  $190 \mu\text{g L}^{-1}$  and from 2.5 to  $680 \mu\text{g L}^{-1}$ , respectively, (Shen et al., 1997; Davis and Farland, 2001; ECB, 2002; WHO, 2005). For ETBE and TAME, hardly any information is available on odour and flavour thresholds in the open literature.

Toxicological effects of the oxygenates occur at much higher concentrations than the odour and flavour threshold (ECB, 2002, 2006). Therefore problems related to human health are not expected at the level of these thresholds. The EPA (1997) set a non-statutory drinking water advice for MTBE of  $20\text{--}40 \mu\text{g L}^{-1}$ . WHO considered setting a drinking water health-based guideline value unnecessary (Fawell, 2007). In The Netherlands, for MTBE a guideline for remediation of contaminated groundwater was advised of  $15 \mu\text{g L}^{-1}$  based on the odour threshold, whereas for ETBE no such indicative guideline could be advised thus far because reliable information on odour and flavour thresholds is lacking (TCB, 2007, 2008).

Consumers' perception of the presence of gasoline additives in drinking water sources might be negative. Because of their physical-chemical properties, removal of the fuel oxygenates is incomplete in routine drinking water treatment. A high concentration of gasoline additives in sources of drinking water will thus lead to problems for perception of drinking water quality by consumers.

The objective of this study was to determine odour and flavour thresholds of MTBE, ETBE and TAME, in order to complete the lacking information for ETBE and TAME, and to compare these thresholds to concentrations of MTBE and ETBE determined in thousands of samples collected from Dutch water collection areas for drinking water production, taking into account the geohydrological conditions of the collection areas. We hypothesize that an increased use of these gasoline additives will be reflected in increased concentrations in surface- and groundwaters. Comparing the concentrations observed in the drinking water sources with the odour and flavour thresholds gives an indication of the relevance for emission reduction measures for these gasoline additives.

## 2. Materials and methods

### 2.1. Panel test for odour and flavour thresholds of MTBE, ETBE and TAME

Odour and flavour thresholds of MTBE, ETBE and TAME were determined according to the European standard method EN 1622-1, a forced-choice paired test (CEN, 2006). In short, at least 8 panelists tested seven concentrations of MTBE, ETBE and TAME ranging between 0 and  $32 \mu\text{g L}^{-1}$ , prepared in odour and flavour free drinking water at a temperature of  $23^\circ\text{C}$ . The threshold is defined as the odorant/flavorant concentration which has a probability of 0.5 of being detected under the conditions of the test. Panelists were preliminary trained and experienced with the procedure.

### 2.2. Occurrence of MTBE and ETBE in Dutch water collection areas

Monitoring data of MTBE and ETBE in samples from water collection areas for drinking water production in the period 2002–2007 were collected from Dutch water companies and evaluated. MTBE and ETBE were analyzed by several laboratories using analytical purge and trap GC–MS based on ISO 15680. Water samples were conserved at  $1 \leq \text{pH} \leq 2$  with sulfuric acid.

The analyses included 11,680 and 1206 individual data for MTBE and ETBE, respectively, and included groundwater as well as surface water samples of in total 196 Dutch water collection areas for the production of drinking water. The water samples were not beforehand suspected of contamination related to historical soil contamination. Collection areas were classified depending on their geohydrological properties (see Table 1). The concentration of MTBE or ETBE in the collection area was classified as follows:  $<0.1$ ,  $0.1\text{--}1$ ,  $1\text{--}5$ ,  $5\text{--}15$ ,  $15\text{--}26$ ,  $26\text{--}260$ ,  $260\text{--}9400$  or  $>9400 \mu\text{g L}^{-1}$ . This classification was based on proposed guidelines for MTBE for environmental and health protection in The Netherlands (Swartjes et al., 2004). The highest concentration measured in each water collection area was used in the data evaluation.

Based on the Dutch contaminated soil database (Kernteam Landsdekkend Beeld, 2005; Van Wezel et al., 2008), 785 potentially contaminated sites were selected with (former) gas stations and fillings. The number of potentially contaminated sites per vulnerable water collection areas was determined by geographic information system analysis. To assess potential risks to raw water quality, traveling times of these sites to the water collection areas were calculated by interpolation of isochrones.

## 3. Results

Table 2 presents the odour and flavour thresholds derived in this study for MTBE, ETBE and TAME. Especially for ETBE, odour and flavour thresholds are low, at a level of  $1\text{--}2 \mu\text{g L}^{-1}$ . For MTBE and TAME the odour and flavour threshold are similar to each other, ranging from 7 to  $16 \mu\text{g L}^{-1}$ .

Table 3 presents data on the occurrence of MTBE in various types of water collection areas in The Netherlands. In general, water collection areas related to groundwaters are clean. However, at 20 freatic groundwater locations from sandy soils not covered by a protective top soil layer of clay, and in 16 groundwaters from sandy soil or limestone MTBE was found. In one groundwater collection area the observed concentration of MTBE exceeded the odour and flavour thresholds. In water from collection areas related to surface water MTBE was almost invariably detected. At a few locations for river bank and dune infiltrates, the concentration of MTBE exceeds the odour and flavour threshold (Table 3). MTBE concentrations measured repeatedly over time at a single location may vary from 4- to 15-fold (data not shown); however, the number of data available per location over time is too scarce to draw conclusions on temporal trends.

For ETBE, in use as a gasoline additive relatively short compared to MTBE, fewer monitoring data are available. Out of a total of 37 groundwater collection areas monitored, in two areas ETBE was detected in concentrations between  $0.1$  and  $1 \mu\text{g L}^{-1}$ . In all three water collection areas related to surface water that were monitored, ETBE was found in concentrations between  $0.1$  and  $1 \mu\text{g L}^{-1}$ . These ETBE concentrations are near to the odour and flavour thresholds determined in this study.

The number of potentially contaminated sites – which can act as a source of MTBE – per water collection area varies from one to up to 40 sites per vulnerable water collection area in urbanized regions (Fig. 1). All water collection areas mentioned in Table 1 are vulnerable for leakage from a source site, except for GW and SW. Travelling



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