

Christine Baus<sup>a</sup>,  
HsuWen Hung<sup>a,b</sup>,  
Frank Sacher<sup>a</sup>,  
Michael Fleig<sup>a</sup>,  
Heinz-Jürgen Brauch<sup>a</sup>

<sup>a</sup> DVGW-Technologiezentrum  
Wasser, Karlsruher Str. 84,  
76139 Karlsruhe, Germany

<sup>b</sup> Department of Environmental  
Engineering, National Cheng  
Kung University, Tainan City,  
Taiwan

## MTBE in Drinking Water Production – Occurrence and Efficiency of Treatment Technologies\*

In Germany, the gasoline additive methyl *tert*-butyl ether (MTBE) is almost constantly detected in measurable concentrations in surface waters and is not significantly removed during riverbank filtration. The removal of MTBE from water has been the focus of many studies that mostly were performed at high concentration levels and centred in understanding the mechanisms of elimination. In order to assess the performance of conventional and advanced water treatment technologies for MTBE removal in the low concentration range further studies were undertaken. Laboratory experiments included aeration, granulated activated carbon (GAC) adsorption, ozonation and advanced oxidation processes (AOP). The results show that the removal of MTBE by conventional technologies is not easily achieved. MTBE is only removed by aeration at high expense. Ozonation at neutral pH values did not prove to be effective in eliminating MTBE at all. The use of ozone/H<sub>2</sub>O<sub>2</sub> (AOP) may lead to a partly elimination of MTBE. However, the ozone/H<sub>2</sub>O<sub>2</sub> concentrations required for a complete removal of MTBE from natural waters is much higher than the ozone levels applied nowadays in waterworks. MTBE is only poorly adsorbed on activated carbon, thus GAC filtration is not efficient in eliminating MTBE. A comparison with real-life data from German waterworks reveals that if MTBE is detected in the raw water it is most often found in the corresponding drinking water as well due to the poor removal efficiency of conventional treatment steps.

### MTBE in der Trinkwassergewinnung – Vorkommen und Entfernung während der Aufbereitung

Der Benzinzusatzstoff Methyl-*tert*-butylether (MTBE) wird nahezu ständig in deutschen Oberflächengewässern nachgewiesen. Darüber hinaus wird er während der Uferfiltration kaum eliminiert und ist somit im Rohwasser von Wasserwerken zu finden. In der Literatur wurden bereits Studien über die Entfernung von MTBE durchgeführt, wobei diese meist bei hohen Konzentrationen erfolgten und das Verständnis der grundlegenden Mechanismen der Elimination im Vordergrund stand. Im Rahmen der vorliegenden Studie wurden herkömmliche und erweiterte Verfahren in der Trinkwasseraufbereitung auf ihr Eliminationspotential bezüglich MTBE in niedrigen Konzentrationen untersucht. Es wurden Laborexperimente zur Belüftung, Aktivkohlefiltration, Ozonung und Kombination Ozon/H<sub>2</sub>O<sub>2</sub> durchgeführt. Im Vergleich zu Benzol lässt sich MTBE durch Belüftung nur mit erhöhtem Aufwand eliminieren; Ozonung zeigt bei neutralen pH-Werten keine Wirkung auf die MTBE-Konzentration. Bei der Kombination von Ozonung mit H<sub>2</sub>O<sub>2</sub>-Zugabe wird die MTBE-Konzentration deutlich erniedrigt; für eine vollständige Elimination jedoch wird eine wesentlich höhere Ozondosis benötigt als heutzutage in Wasserwerken üblich. MTBE wird darüber hinaus nur schlecht an Aktivkohle adsorbiert, so dass die Aktivkohlefiltration kein geeignetes Verfahren darstellt, um MTBE zuverlässig zu entfernen. Ein Vergleich mit Daten aus deutschen Wasserwerken zeigt deutlich, dass aufgrund der schlechten Eliminierungsleistung herkömmlicher Technologien im Falle eines Auftretens von MTBE im Rohwasser ein Durchtritt ins Trinkwasser zu erwarten ist.

**Keywords:** Aeration, GAC Adsorption, Ozonation, AOP, Riverbank Filtration

**Schlagwörter:** Belüftung, Aktivkohlefiltration, Ozonung, AOP, Uferfiltration

\* Paper presented in part as a poster at the annual meeting of the Water Chemical Society – a Division of the German Chemical Society (Wasserchemische Gesellschaft – Fachgruppe in der Gesellschaft Deutscher Chemiker), Stade, May 2003.

**Correspondence:** C. Baus, E-mail: baus@tzw.de

## 1 Introduction

Methyl *tert*-butyl ether (MTBE) is used as a fuel additive since the late 1970's. Because of its high octane number and high solubility in gasoline MTBE is predestined for replacing toxic aromatic substances such as benzene that are added as a substitute for the organic lead compounds. Furthermore, by the addition of MTBE the oxygen content of the gasoline is increased thus leading to a more complete combustion and reducing exhaust emissions [1, 2].

In the U.S. these arguments in favour of MTBE led to an extensive use in gasoline. This was enforced by the government releasing the "Clean Air Act" in 1990 in which a minimum content of 2.7% w/w oxygen is compulsory in cities where smog is a problem. In 1995 the "Reformulated Gasoline (RFG) Program" was passed which aims at lowering the air pollution by ozone generating compounds. Since then the use of MTBE has increased dramatically and nearly 30% of all sold gasoline in the U.S. contain MTBE in volume fractions of about 11% [3, 4]. In Europe the EU started its program against air pollution in 1992 with the Council Directive 98/69/EC "Measures to be taken against air pollution by emissions from motor vehicles". However, in the Council Directive 98/70/EC "The quality of petrol and diesel fuels" a maximum level for oxygen of 2.7% is set and for certain ethers (among them MTBE) the limit is 15% v/v. Thus less MTBE is added to gasoline in Europe, the average content of MTBE in gasoline amounting to 2%. The use in the European member states, however, is varying, the average concentrations ranging from 0.1% (Great Britain) to 9% (Finland). In Germany, the MTBE levels vary from 0.4% v/v in "Normalbenzin" up to 11.9% v/v in "Super-Optimax". A recently launched new gasoline type uses 15% v/v MTBE. Overall, the concentration of MTBE in gasoline in Europe averages 1.6% v/v [1, 2, 5].

A comprehensive overview of the use and production numbers of MTBE, its physical and chemical characteristics and toxicity data are given in literature [6–12]. The taste and odour threshold of MTBE in drinking water ranges between 15 µg/L and 50 µg/L depending on the experience of the consumers [8].

The acute toxicity level given by  $LD_{50}$  amounts to 3.8 to 3.9 g/kg for rodents. Lethal air concentrations for inhalation ( $LC_{50}$ ) on rats are reported at 65 to 126 g/m<sup>3</sup>. This justifies the characterisation of MTBE as a substance with low acute toxicity. In long-term exposure studies with rats the occurrence of a rat specific cancer was noticed. No effects were noticed on short-term exposure of humans to air containing MTBE in concentrations of 180 mg/m<sup>3</sup>. Carcinogenic effects on humans exposed to MTBE could not be proved [10].

MTBE has received much attention in the last few years. It is not only very well soluble in gasoline but also partitions

readily into the water phase almost without adhesion onto soil. This means that once released in the aquatic environment it travels with the same velocity as the aquifer in contrast to other gasoline ingredients such as BTEX. Because of its extensive use in the U.S. it occurred nationwide in drinking water wells. In Southern California, the MTBE concentrations in some drinking water sources reached up to 600 µg/L leading to a closure of these wells. These incidents have led to a debate which culminated in banning the use of MTBE as a fuel oxygenate in California [3, 4, 13, 14].

This study focuses on the environmental situation in Germany and the implications of MTBE appearing in the raw water of drinking water treatment plants.

## 2 Materials and methods

### 2.1 Materials

MTBE was used as purchased from Sigma Aldrich, Taufkirchen, Germany, analytical grade.

For adsorption experiments a bituminous activated carbon, F300, was applied after pulverisation in an agate-ball mill and subsequent washing in a Soxhlet device. Other charcoal types might show better capacities for MTBE, e.g. coconut carbons [15, 16], however, the F300 is typically used in German waterworks and has therefore been investigated in this study.

Ozonation and AOP experiments were carried out using demineralised water, drinking water from the city of Karlsruhe, groundwater from a sampling site near the city of Karlsruhe and riverbank filtrated water from the lower river Rhine. Each of the natural waters were either used immediately after sampling or stored at 4 °C under exclusion of light for a week at maximum before conducting the experiments.

The chemical characteristics of these waters are given in Table 1. The groundwater exhibits a rather high level of NOM and correlating a high  $SAC_{254nm}$ . Other parameters such as pH, conductivity, ammonia, nitrate and iron are in the same range in all three waters. Manganese and MTBE are detected in measurable concentrations in the bank filtrate only. Concerning alkalinity the bank filtrate shows lower values than the other two water types.

Ozone was generated by an ozone generator provided by Anseros, Tübingen, Germany, from pure oxygen, purchased from Messer Griesheim, Griesheim, Germany, medical

**Table 1:** Characteristic parameters for different types of natural waters used in oxidation experiments.

Charakteristische Parameter natürlicher Wässer (Oxidationsversuche).

Parameter	Drinking water	Groundwater	Riverbank filtrate
DOC in mg/L	0.83	3.0	1.0
SAC <sub>254nm</sub> in 1/m	1.0	7.2	2.0
Conductivity in mS/m	70.9	73.2	79.6
pH	7.4	7.1	7.2
K <sub>S 4.3</sub> in mmol/L	5.41	5.85	3.89
K <sub>B 8.2</sub> in mmol/L	0.70	1.15	0.59
Fe in mg/L	< 0.01	0.01	< 0.01
Mn in mg/L	< 0.005	< 0.005	0.044
MTBE in µg/L	< 0.05	< 0.05	0.08

grade. H<sub>2</sub>O<sub>2</sub> was used as purchased from Sigma Aldrich, Taufkirchen, Germany, analytical grade.

## 2.2 Methods

### 2.2.1 Analytical methods

MTBE was analysed according to the method 524.2 of the U.S. Environmental Protection Agency. The method was adapted using a Tekmar 3000 purge & trap concentrator with an autosampler Precept II and a VARIAN 3400 gas chromatograph equipped with an ion-trap mass spectrometer ITS 40. Technical details of the analytical method are described elsewhere [17, 18]. The method detection limit is 0.02 µg/L, the limit of determination is calculated to 0.05 µg/L [17].

Ozone was measured using the Indigo method in congruence with DIN 38 408 part 3 [19].

Water samples were taken from various rivers, lakes and groundwater wells in Germany. During sampling 100 mL glass bottles were filled completely with a gentle stream of water. The samples were stored at 4 °C throughout the transportation and until the analysis was performed.

### 2.2.2 Laboratory-scale experiments

Laboratory-scale experiments provide a fast and inexpensive way to basically assess the removal efficiency. The purpose of these tests is gaining a fast and reliable prediction

of the behaviour of single organic compounds with small experimental and financial expenses and under concentrations close to the range found in the environment. These tests are not meant to provide information for process dimensioning or optimisation of an industrial plant; neither are they apt for the exact determination of physico-chemical parameters.

Laboratory-scale set-ups were used for the following treatment steps: adsorption on activated carbon, stripping and ozonation (plus advanced oxidation processes such as the combination of ozone and H<sub>2</sub>O<sub>2</sub>).

These treatment technologies have already been investigated in literature ([20] and literature cited therein). However, these studies mainly focused on treatment options for contaminated groundwater sites with MTBE concentrations exceeding by far the concentrations usually found in the aquatic environment. In the study presented here the evaluation of treatment technologies as used in German waterworks with MTBE concentrations as found in German raw water sources was of main interest. The experiments filled in knowledge gaps relevant for German waterworks.

The efficiency of subsoil passage was studied by taking samples from river water and corresponding riverbank filtrate.

**Stripping experiments.** In order to predict the behaviour of MTBE during aeration, stripping experiments were carried out in a laboratory-scale reactor using demineralised water at 20 °C. A bubble column reactor was filled with 7 L demineralised water spiked with MTBE at 10 and 1.5 µg/L. Nitrogen was added at the bottom at 830 mL/min. A frit made of glass is ensuring the formation of small bubbles and a good distribution of the nitrogen gas in the liquid phase. Optical measurements showed an average bubble diameter of around 3.6 mm and an average ascending time of the bubbles of 1.5 s. Thus the gas/liquid interphase was estimated to be 0.035 m<sup>2</sup>. According to Henry's law the upstreaming gas bubbles saturate with MTBE and water. Samples were taken in regular time intervals and analysed for MTBE.

**Ozonation and AOP experiments.** In order to avoid MTBE loss by air stripping, ozonation experiments were carried out in batch mode. In a reaction vessel made of glass, 4.5 L of demineralised or natural water – depending on the experimental conditions – were spiked at 10 µg/L MTBE. During the experiments with demineralised water the pH was adjusted by addition of buffer solution (phosphate buffer for pH 5 to 7 and borate buffer for pH 9). In the experiments with natural water the pH was not modified.

Ozone concentration was adjusted adding different amounts of ozone stock solution. Latter was produced in a bubble

column where gaseous ozone was directed through demineralised water at 5 °C. After some time a dynamic equilibrium is achieved between gas and liquid phase. The ozone concentration in the liquid phase is dependent only on the temperature and was adjusted as high as possible in order to minimise the dilution effects in the reaction mixture.

When conducting AOP experiments, H<sub>2</sub>O<sub>2</sub> is added prior to the addition of ozone stock solution. Time was started when admixing the ozone stock solution. At time intervals samples were taken and concentrations of MTBE and ozone were determined.

**Adsorption isotherm determination.** For the determination of adsorption isotherms bottle-point technology was implemented. For these experiments 200 mL of deionised water were used as matrix and spiked with MTBE at 400 µg/L. To this mixture different amounts of charcoal were added. The addition of charcoal was dimensioned in such a manner that the reduction of MTBE concentration in the reaction solution enfolded at least two orders of magnitude. The mixture was then shaken for 24 h, filtrated over 0.2 µm polycarbonate filter and analysed for the residual concentration of MTBE. Preliminary experiments showed that 24 h were sufficient for reaching equilibrium conditions.

Since MTBE is quite volatile, bottles with limited headspace were chosen. A blind sample without charcoal was treated as the samples and measured concurrently in order to assess the volatilisation effect. No significant loss of MTBE was observed during the experiments.

The data was summed up in a diagram in double logarithmic scale according to Freundlich [21] and the parameters *n* and *K* were determined. In previous studies [22] a parameter *m/L* was determined from *n* and *K* (Eq. (1)) describing the amount of activated carbon necessary to reduce the concentration *c* of an organic substance from 100 µg/L to 10 µg/L.

$$\frac{m}{L} = \frac{1}{K} \frac{c_0 - c}{c^n} \quad (1)$$

This parameter is an indicator for the relevance of the substance to drinking water production. An *m/L* value above 50 mg/L means that the substance is not easily removed by filtration on activated carbon and thus may be found in the drinking water if no other measures are taken. The limit value for very poor adsorbable to not adsorbable is set at 200 mg/L.

Experience showed, however, that the adsorption capacity of charcoals worsens if they are used for a longer operating period. Therefore additional adsorption isotherms were determined with charcoal already used in waterworks. For this

“preloaded” charcoal the test system was slightly modified [21]. The reaction bottles were shaken for 72 h instead of 24 h and the added amount of activated carbon was higher. The water flow in the waterworks over the activated carbon used in this study totalled 35 m<sup>3</sup>/kg.

### 3 Occurrence of MTBE in the aquatic environment

MTBE can be released into the aquatic environment by punctual sources (i.e. LUST – leaking underground storage tanks), accidental spills by road accidents or during tank filling) or via diffusive entries (i.e. elution of air by precipitation (rain and snow), contaminated water from road run-offs etc.) [11, 23–25]. In Germany, a measurement program was undertaken in 1999/2000 that showed the relevance of

**Table 2:** MTBE in German rivers. Concentrations in µg/L.

MTBE in deutschen Flüssen. Konzentrationsangaben in µg/L.

River Rhine	Rhine km			
	434	588	740	
<b>Median value 1999</b>	<b>0.13</b>	<b>0.20</b>	<b>n.m.*)</b>	
90 percentile	0.56	0.35	n.m.*)	
Max. value	0.99	0.43	n.m.*)	
<b>Median value 2000</b>	<b>0.20</b>	<b>0.38</b>	<b>0.26</b>	
90 percentile	0.31	0.74	0.35	
Max. value	0.39	9.8	0.48	
River Neckar	km from estuary into river Rhine			
	2	104	165	200
<b>Median value 1999</b>	<b>0.08</b>	<b>0.08</b>	<b>0.10</b>	<b>0.06</b>
90 percentile	0.19	0.86	0.15	0.07
Max. value	0.24	1.2	0.16	0.08
River Main	1999		2000	
<b>Median value</b>	<b>0.16</b>		<b>0.17</b>	
90 percentile	0.28		0.41	
Max. value	0.49		0.93	
River Elbe	Oct. 2002		June 2003	
<b>Spot samples</b>	<b>0.12</b>		<b>0.43</b>	

\*) n.m.: not measured

MTBE for drinking water production. In groundwaters an average concentration of MTBE of 0.2 µg/L was found whereby in most cases the positive findings could be attributed to the vicinity of highly frequented roads. As expected, MTBE was detected in the groundwater of urban areas more often (at approx. 50% of 80 sampling locations) than in rural areas (10% of 90 sampling locations). The highest measured concentration of MTBE in groundwater was 730 µg/L near a gasoline station [15, 16, 26].

Surface waters were analysed for MTBE as well. In Table 2 median, 90 percentile and maximum values for MTBE concentrations in the river Rhine during the sampling period 1999/2000 are given for different locations along the river

Rhine. MTBE was detected in all samples. A significant rise in concentration was observed at km 588 after the tributary Main reaches the river Rhine and after passing the cities of Mainz and Wiesbaden. From 2000 the concentrations in the river Rhine were measured monthly for a period of two years at km 740 (Fig. 1). In 2000 the median concentration was 0.26 µg/L – an indication that in the course of the river Rhine the concentration of MTBE is not rising significantly but that input from tributaries or industrial wastewater and dilution as well as evaporation of MTBE are balanced.

Occasional maximum peaks might be due to ship accidents, spills of fuel or unwanted inlet from industries or sewage plants. Measurements in a municipal sewage treatment

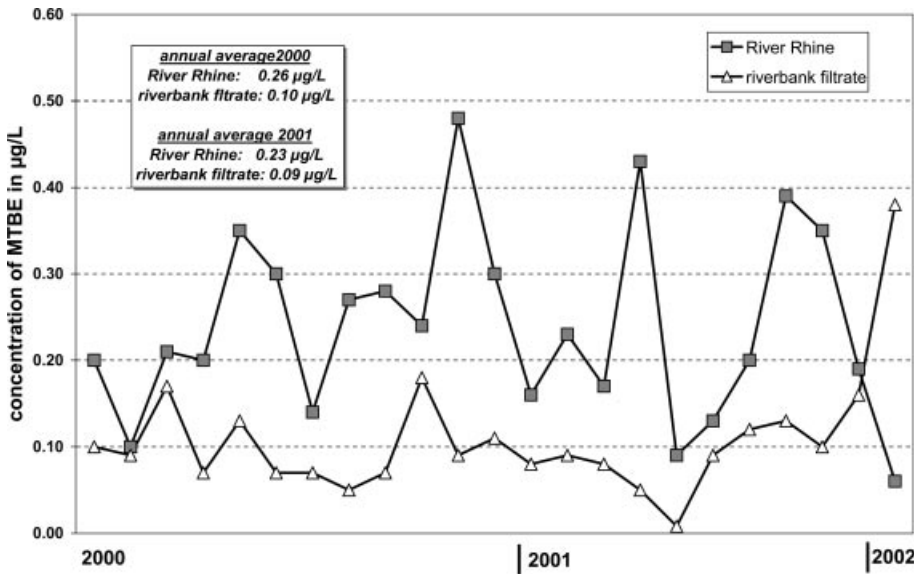


Fig. 1: Long-term monitoring of the river Rhine (approx. km 740) and the corresponding riverbank filtrate (2000–2001).

Langzeitüberwachung des Rheins bei km 740 und des korrespondierenden Uferfiltrates (2000–2001).

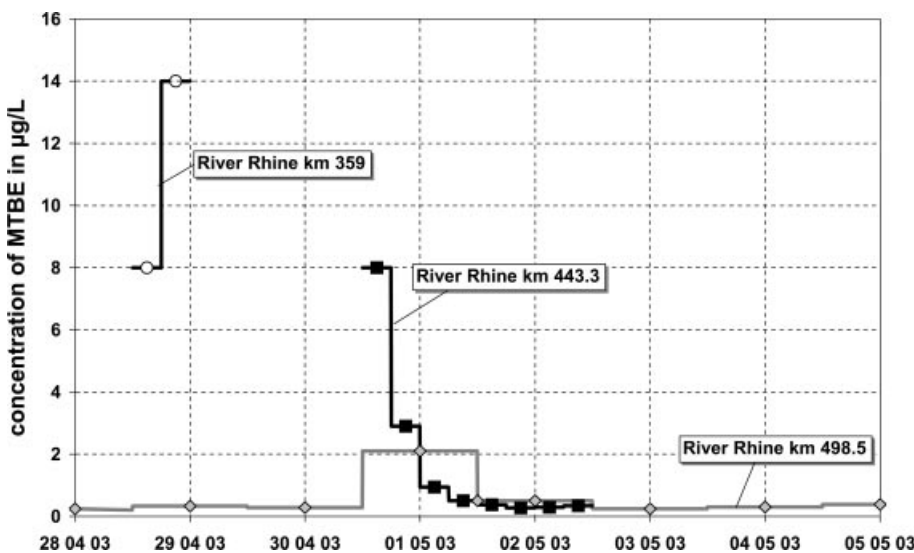


Fig. 2: MTBE concentration in the river Rhine (km 443.3) – decline after major spill of MTBE during ship accident (for details see text).

MTBE-Konzentration im Rhein (km 443.3) – Abnahme nach MTBE-Schadensfall durch Schiffshavarie.

plant (MSTP) in April 2002 showed that the latter are not able to reduce MTBE concentrations significantly. Concurrently taken samples showed a concentration of MTBE of 0.35 µg/L at the inlet of the MSTP. The same amount was found after the first biological treatment (0.36 µg/L). At the outlet the concentration was still at 0.30 µg/L.

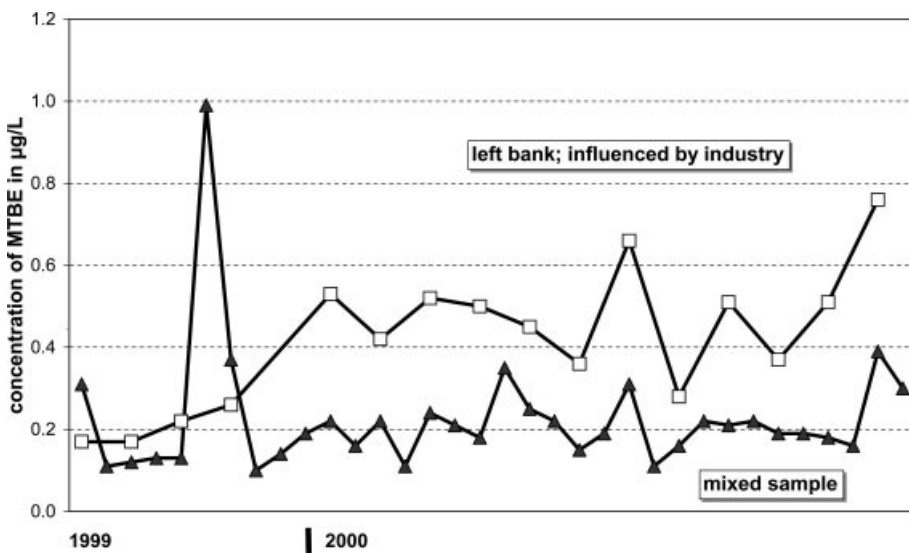
In Figure 2 monitoring results are shown from the river Rhine where a MTBE peak was detected by chance. At km 359 an elevated MTBE level of 8 µg/L was measured in a 6 hours mixed sample on April 29th, 2003. In the following 6 hour mixed sample the concentration increased to 14 µg/L. Afterwards no more samples were taken at this sampling location, but two days later at km 443.3 MTBE was analysed in eight 6 hours mixed samples. The concentration declined quite rapidly from a value of 8 µg/L to levels in the range of the normally detected background concentration. The maximum peak concentration was probably not detected; it is more likely that only the declining part was measured. 24-hour samples taken at Rhine km 498.5 (another 50 km downstream) showed an increase in concentration during the same day as at km 443.3. The average concentration on May 1st, at km 443.3 amounts to 3.1 µg/L (measured in a 6 hours mixed sample) which is still higher than the value of 2.1 µg/L measured at km 498.5. This indicates the influence of dilution and eventual evaporation of MTBE. However, these data show clearly that shock loads from industrial inlets or accidental spills travel fast and are detectable for more than 150 km from the releasing source. Similar findings were reported from the lower river Rhine at Kleve/Bimmen (km 865) where occasional “waves” of MTBE were reported. The source of these concentration profiles might be attributed to illegal tank ship releases during tank washings etc. [27].

The impact of industrial discharges of MTBE is very important for the absolute concentration value. As can be seen in Figure 3, samples taken from the left bank of the river Rhine, which is influenced by industrial discharges, show almost constantly higher concentrations than the sample representative for the cross section of the river.

Similar results were found when studying the inlet plume of MTBE from a company that releases MTBE into the river. MTBE was measured directly at the discharge point and around 20 km downstream from that site. In Figure 4 the average concentrations and 10 and 90 percentile values of the river cross section are on display. As can be seen, the distribution across the river is not uniform but an MTBE plume is spreading near the right riverbank – the industrial inlet being located on the right side as well. In congruence with the concentrations measured in the effluent (up to 1300 µg/L) the highest values were found on the right side – up to 2 µg/L.

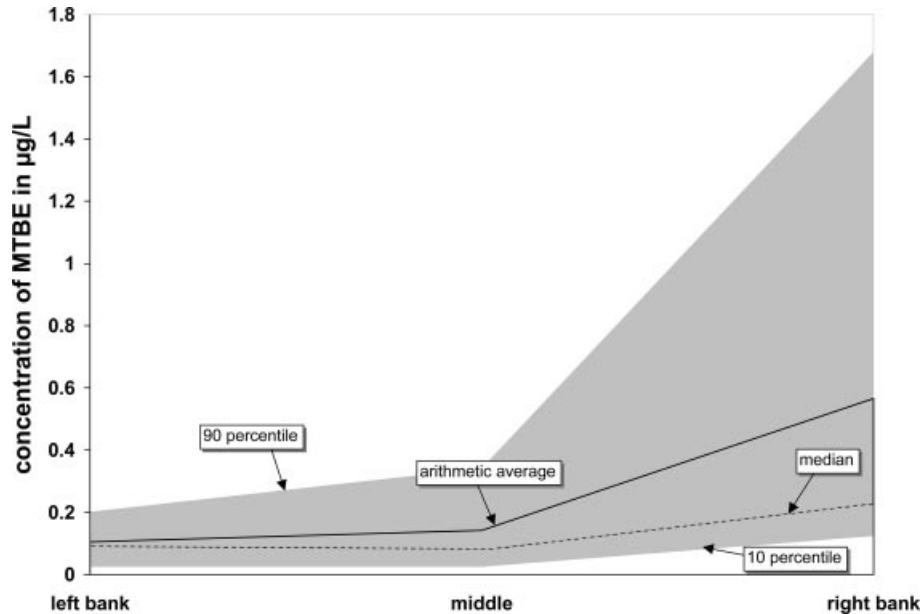
In Table 2 the results for measurements in the river Neckar are given as well. MTBE is detected in measurable concentrations at all times. Median values lie around 0.08 µg/L. Each sampling location was sampled four times from September to December 1999. Near the estuary into river Rhine 90 percentile values rise significantly and the highest measured concentrations (up to 1.2 µg/L) exceeded the median values by far.

The river Main was monitored constantly during 1999 and 2000 (cf. Table 2). Measured concentrations are in the same range as in the river Rhine with maximum levels up to 1 µg/L. For river Elbe, more recent sampling programs showed that spot samples exhibited 0.12 µg/L and 0.43 µg/L in October 2002 and June 2003, respectively (Table 2).



**Fig. 3:** MTBE in the river Rhine at km 434 – influence of the industry.

MTBE im Rhein (km 434) – Einfluss der Industrie.



**Fig. 4:** MTBE in the river Rhine in summer 2002 (cross section 20 km downstream from industrial inlet – inlet concentrations ranging from 30 to 1300 µg/L).

MTBE im Rhein im Sommer 2002 (Querschnitt 20 km flussabwärts von industrieller Einleitung – Einleitungskonzentrationen zwischen 30 µg/L und 1300 µg/L).

In 1999 the Danube River was sampled three times, but MTBE was not detected.

These findings alerted waterworks in Germany since the occurrence of MTBE in groundwater and surface water is directly affecting the raw water source of many waterworks and the replenishing of such water sources may be influenced by river water passing through the subsoil [28, 29]. Furthermore, some waterworks use riverbank filtrate as a raw water source, the quality of which is in turn directly dependent on the quality of the river water. Additional monitoring programs from waterworks showed that MTBE occurs in the raw water of waterworks and thus a study was commissioned to show how waterworks can cope with rising MTBE concentrations.

#### 4 Elimination of MTBE during subsoil passage

Riverbank filtration is one possible source of raw water for waterworks. Since river water is charged with MTBE the possibility of MTBE appearing in the corresponding bank filtrated water has to be investigated. No laboratory-scale experiments were carried out concerning the elimination of MTBE during riverbank filtration but monitoring programs allowed a concurrent measurement of river water and bank filtrate.

When looking at Figure 1 it becomes clear that MTBE is detected in the river Rhine at all times during a more than two years period. The concentration fluctuates strongly rang-

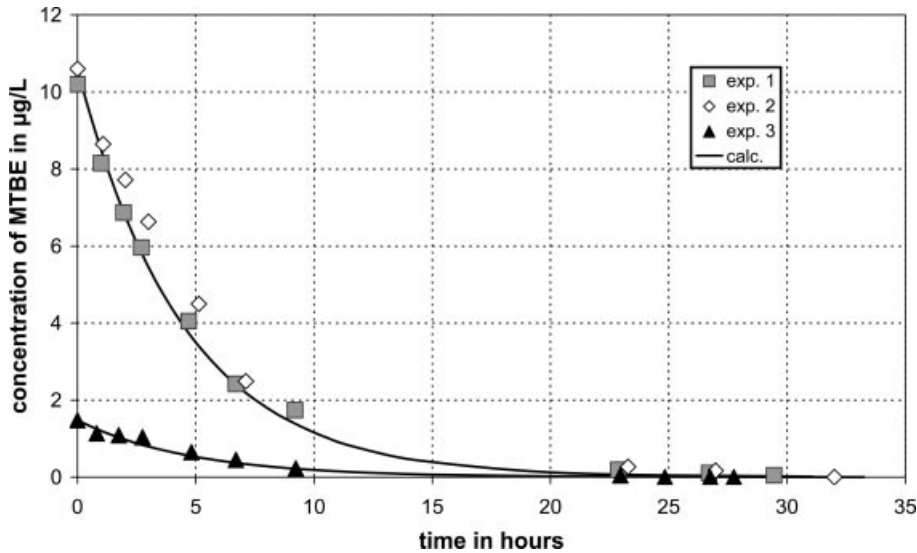
ing between 0.1 µg/L and 0.5 µg/L. At the same time samples were taken in the riverbank filtrate. The concentrations are decisively lower than in the river Rhine and the fluctuations are less pronounced. This is a special characteristic of riverbank filtration – peak concentrations (or organic shock loads) are smoothed out [30].

However, the diagram shows clearly, that MTBE is not totally removed by riverbank filtration. Although the concentrations in the bank filtrate and in the river water cannot be directly compared to each other, a comparison of the annual average concentrations reveals that at least 40% of the MTBE is passing through the subsoil unchanged.

#### 5 Elimination of MTBE during aeration

Stripping experiments were carried out in a lab scale bubble column reactor in order to assess the stripping efficiency for MTBE at low concentrations. In Figure 5 the results of the experiments are shown. At an initial concentration of 10 µg/L, 80% of the MTBE are stripped after a period of 7 to 8 hours. Similar results are achieved at lower concentrations, the time span elongating slightly.

Generally spoken, the removal of MTBE by stripping is possible. However, the question whether it is economically feasible in terms of operating conditions in waterworks can only be answered after a theoretical consideration of mass transfer and a comparison with substances, which are usually removed from drinking water by aeration.



**Fig. 5:** Concentration decline of MTBE during stripping in a lab-scale bubble column (for experimental details see text).

Konzentrationsabnahme von MTBE durch Belüftung im Laborreaktor (experimentelle Details im Text).

**Table 3:** Physical constants of MTBE and water used for the calculation of the stripping process.

Physikalische Konstanten von MTBE und Wasser für die Berechnung des Strippprozesses.

	MTBE	Water
Diffusion coefficient in aqueous solution $\delta_l$ in $\text{m}^2/\text{s}$	$8.1 \cdot 10^{-10}$ [33]	–
Diffusion coefficient in the gas phase $\delta_g$ in $\text{m}^2/\text{s}$	$7.7 \cdot 10^{-6}$ [33]	$2.64 \cdot 10^{-5}$ [31]
Henry's law coefficient $H_{px}$ in $\text{bar}^*$	51.8 [9]	–

<sup>\*)</sup> 1 bar = 100 kPa

In Figure 5 the results of calculations with mass transfer equations according to Schlünder [31] are depicted as well. These calculations include only physical constants such as Henry's law coefficient and diffusion coefficient as described in Table 3 and are not fitted to the experimental data. A detailed description of the mathematical model is given in literature [31, 32].

As one can see a good congruence is achieved although the calculated efficiency is a bit higher than measured in the experiment. This might be due to the estimated value of the

**Table 4:** Calculation of a technical aeration column – column diameter 2  $\text{m}^2$ , countercurrent flow, air-to-water ratio 18.4.

Berechnung einer technischen Belüftungskolonie – Kolonnendurchmesser 2  $\text{m}^2$ , Gegenstrombetrieb, Luft/Wasser-Verhältnis 18.4.

	CO <sub>2</sub>	PCE	MTBE
Henry's law constant in $\text{bar}^*$	1666 [34]	637 [35]	51.8 [9]
Efficiency with a column height of 2 m	87.5%	74%	57%
Column height at an efficiency of 87.5%	2 m	3.3 m	13 m ( $\eta_{\text{max}} = 75\%$ )

<sup>\*)</sup> 1 bar = 100 kPa

interphase or temperature fluctuations during the experiment, which are not accounted for in the model.

However, on the basis of these mass transfer equations a technical stripping or aeration process can be dimensioned using the HTU/NTU concept [31]. A comparison with substances normally removed by aeration in waterworks yields the results depicted in Table 4. One major application of aeration is for decarbonisation, i.e. the removal of CO<sub>2</sub>, or for the removal of volatile halogenated hydrocarbons (e.g. tetra-



chloroethene (PCE)). A countercurrent packed column designed for an 87.5% removal of  $\text{CO}_2$  yields at the same operating conditions a 75% reduction of PCE concentration. However, when looking at MTBE the removal efficiency is breaking down – only 57% of the MTBE are evaporated. One method to improve removal efficiency is to enlarge the column. For an 87.5% removal of PCE, e.g., a column height of 3.3 m would be necessary. For MTBE at the given operating conditions a maximal removal efficiency of 75% could be achieved with a column height of 13 m. To obtain higher elimination rates the air-to-water ratio would have to be raised and thus would increase the operating costs.

It can be concluded that the removal of MTBE from water by aeration is principally possible but considerably less feasible than for PCE or  $\text{CO}_2$ . Stripping columns have to be much larger and the operating conditions have to be changed. This raises not only the investment costs but also operating costs.

## 6 Elimination of MTBE by chemical oxidation: the ozonation and combined ozone/ $\text{H}_2\text{O}_2$ process

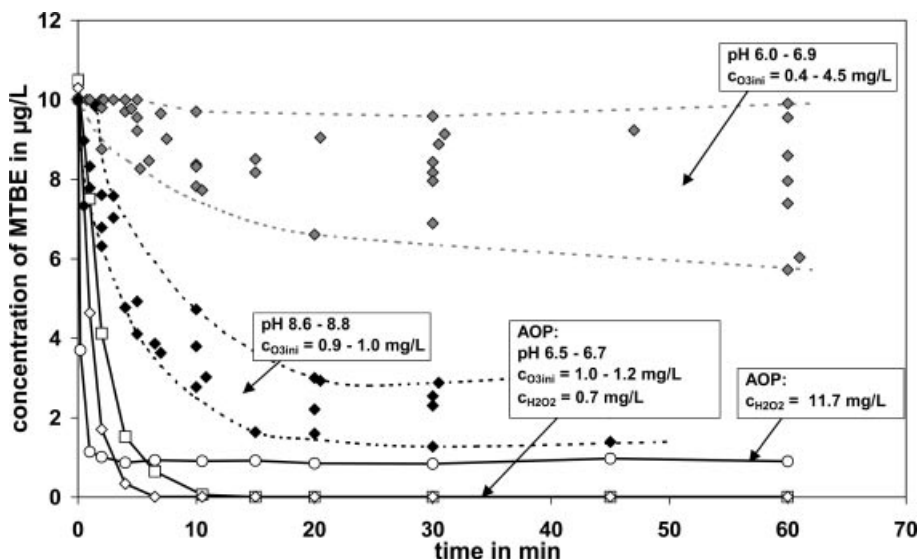
The impact of ozone on MTBE has already been studied in literature [18, 36–40]. For the reaction of ozone with MTBE two major reaction mechanisms have to be considered: firstly the direct reaction of ozone with MTBE and secondly the elimination via the so-called AOP (advanced oxidation processes), where the reaction is induced by OH radicals as oxidants. The mechanism is strongly dependent on the pH. At low pH values the direct reaction with ozone prevails, especially if functional groups with high electron density are present (e.g. olefinic double bounds). As the milieu is getting

more alkaline, radical mechanisms gain importance since ozone is decomposing into OH radicals in the presence of hydroxyl ions. Above pH 11 only radical reactions are taking place [41].

However, in the studies mentioned above the concentrations of MTBE chosen were considerably higher than those occurring in the aquatic environment. They focused mainly on determining reaction pathways or understanding kinetic behaviour. For waterworks the elimination of MTBE in concentrations more closely to environmental conditions is of interest, thus experiments were carried out illuminating the behaviour during ozonation and AOP under circumstances relevant in waterworks.

### 6.1 Ozonation and ozone/ $\text{H}_2\text{O}_2$ in demineralised water

Pure ozonation of demineralised water spiked with  $10 \mu\text{g/L}$  MTBE yields almost no decline in MTBE concentrations. In Figure 6 the results for experiments at low pH values (pH 6.0 to 6.9) and different ozone concentrations are displayed as the area between the grey dotted lines. A maximum elimination of about 40% is achieved with an ozone concentration of 4.5 mg/L. At higher pH values (pH 8.6 to 8.8, data points between black dotted lines) and medium ozone concentrations (around 1 mg/L), a considerable decrease in MTBE concentrations can be noted. This indicates that the reaction pathway for elimination of MTBE via ozone is dominated by OH radical formation. Molecular ozone is not able to destruct MTBE, only via formation of highly reactive OH radicals a conversion of MTBE is achieved.



**Fig. 6:** Elimination of MTBE during ozonation – experiments in demineralised water at different pH values and ozone concentrations.

Elimination von MTBE durch Ozonung – Experimente in demineralisiertem Wasser bei verschiedenen pH-Werten und Ozonkonzentrationen.

The yield of OH radical formation can be enhanced by artificially inducing the decomposition of ozone. Via addition of  $H_2O_2$  a rapid destruction of ozone is initiated that leads to the formation of OH radicals. In Figure 6 the results of experiments with the combination of ozone and  $H_2O_2$  are additionally shown in order to be compared to pure ozonation experiments. The destruction of MTBE is more rapid and more efficient if  $H_2O_2$  is added. Moreover, a good elimination is achieved at pH values where pure ozonation does not show any effect at all. Compared to ozonation experiments at high pH values, the MTBE elimination achieved with combined ozone/ $H_2O_2$  is much more efficient.

The amount of added  $H_2O_2$  plays an important role. If  $H_2O_2$  is added far in excess, ozone is converted to OH radicals very quickly and accordingly the concentration of MTBE is declining very fast. However, after the first few seconds all ozone is consumed and the OH radicals are spent, their lifetime being very short due to their high reactivity, and thus the residual concentration of MTBE reaches a finite level.

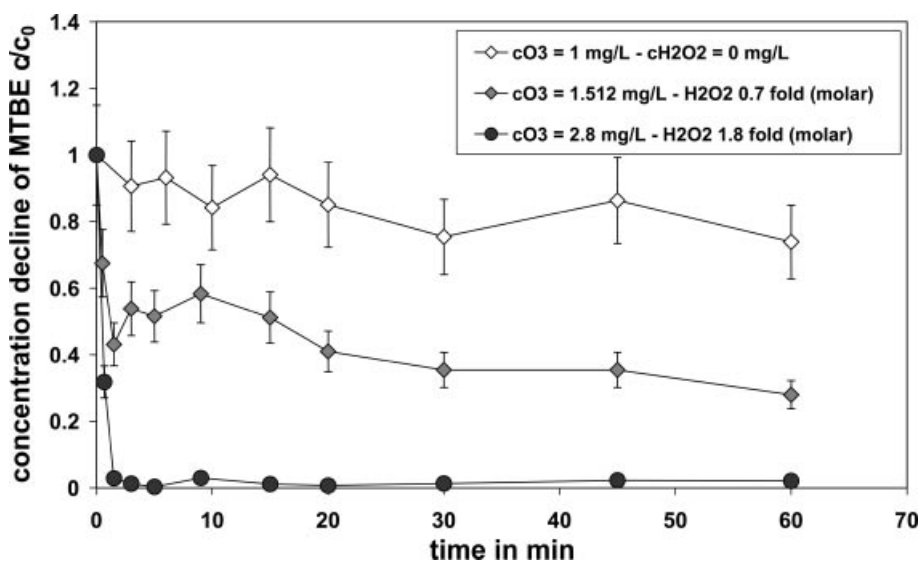
It can be concluded that the application of ozonation for removing MTBE from water is only efficient if applied at high pH values or associated with the additional use of  $H_2O_2$ .

However, even in the experiments where MTBE is fully eliminated, no total mineralisation is achieved. Screening measurements (results described in [42]) showed that more stable intermediates such as *tert*-butyl alcohol and *tert*-butyl formate are formed as expected from studies described in literature [1, 24, 25]. Detailed theoretical considerations of the ozonation process are published elsewhere [42].

## 6.2 Ozonation and ozone/ $H_2O_2$ in natural waters

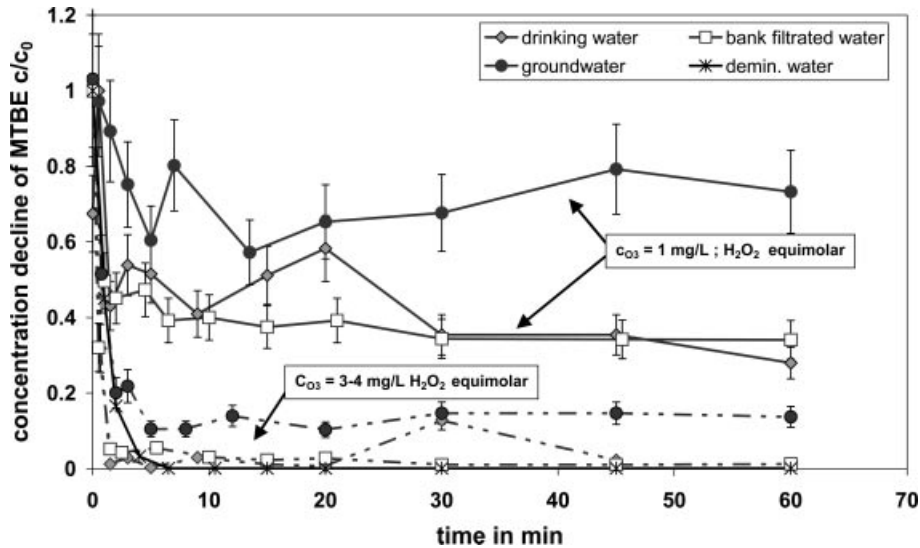
In Figure 7 the results for drinking water are exemplified. It can clearly be seen that pure ozonation does not have any significant effect on the MTBE concentration. That could be anticipated since the pH value of the drinking water under investigation amounts to 7.4 and thus no significant OH radical formation could be expected. When adding  $H_2O_2$  in almost equimolar concentrations to an initial ozone concentration of 1.5 mg/L a 60% elimination of MTBE is achieved. Increasing the amount of initial ozone to 2.8 mg/L with constant ozone/ $H_2O_2$  ratio leads to a 98% reduction. However, even with this high initial ozone concentration no complete elimination can be achieved. The residual MTBE concentration is achieved within the first ten minutes of the experiment. Since the ozone concentration is reduced to nil in the same time range, the assumption can be made that the formation of OH radicals is limited to the first minutes of the experiment and that the highly reactive OH radicals do not only react with MTBE but also with other water ingredients. These so-called scavenger species include  $HCO_3^-$  or NOM. This process leads to a fast consumption of OH radicals.

Similar results were achieved for the other water types under investigation. Figure 8 shows a comparison between the different natural waters. Only high initial concentrations of ozone and  $H_2O_2$  yield a noticeable reduction of MTBE concentration. A decisive difference between groundwater and bank filtrate/ drinking water has to be noted. For both initial ozone concentration (1 mg/L and 4 mg/L, respectively) the residual concentration of MTBE in groundwater is significantly higher than in drinking water and bank filtrate – only 30% elimination at 1 mg/L initial ozone concentration com-



**Fig. 7:** Elimination of MTBE during ozonation/AOP treatment of natural waters – drinking water at different ozone/ $H_2O_2$  concentrations.  $c_{0,MTBE} = 10 \mu\text{g/L}$ .

Elimination von MTBE aus natürlichen Wässern durch Ozon und AOP – Leitungswasser bei verschiedenen Ozon/ $H_2O_2$ -Konzentrationen.  $c_{0,MTBE} = 10 \mu\text{g/L}$ .



**Fig. 8:** Elimination of MTBE during ozonation/AOP treatment of natural waters – comparison of experiments carried out in different natural waters.  $c_{0,MTBE} = 10 \mu\text{g/L}$ .

Elimination von MTBE aus natürlichen Wässern durch Ozon und AOP – Vergleich verschiedener natürlicher Wässer.  $c_{0,MTBE} = 10 \mu\text{g/L}$ .

pared to 60 to 70% in drinking water and bank filtrate. At higher initial ozone concentrations the difference is also clearly visible: 85% instead of 98%. These differences are due to the higher NOM content of the groundwater. Here the influence of OH radical scavenging species is clearly shown. More compounds compete with MTBE for the OH radicals and thus less MTBE can be converted. This indicates again that MTBE is not the first choice of the OH radicals as a reaction partner.

Conclusively can be said that the elimination of MTBE from natural waters is possible with the application of AOP, i.e. the combination of ozone with  $\text{H}_2\text{O}_2$ . However, high initial doses of ozone and  $\text{H}_2\text{O}_2$  are needed to yield a good elimination. These concentrations are much higher than the concentrations nowadays applied in waterworks. Moreover, pure ozonation at natural pH values is not effective in removing MTBE.

Another drawback for ozonation with high initial ozone doses is the formation of bromate in bromide containing waters [42–44].

## 7 Elimination of MTBE during activated carbon filtration

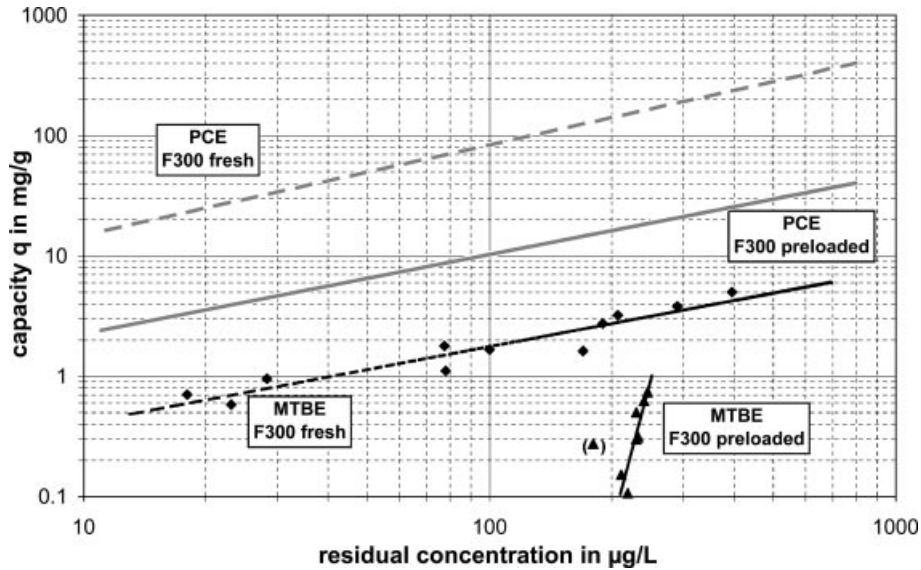
For a first assessment of the elimination potential of activated carbon filtration towards an organic substance, adsorption isotherms can be used. These comprise equilibrium data of the distribution between the liquid and solid phase. Possible kinetic hindrances during the filtration process are not taken into account.

In Figure 9 the adsorption isotherm of MTBE on fresh charcoal is shown. Additionally the isotherm for tetrachloroethene (PCE) is displayed. This substance is regarded as efficiently removable by activated carbon filtration. The isotherm of MTBE lies considerably lower than that of PCE, that means a higher amount of charcoal is needed to remove the same quantity of MTBE as PCE.

If preloaded charcoal is used the adsorption capacity for both substances is lower indicating a decline in removal efficiency during operation in a waterworks. Furthermore, the adsorption isotherm of MTBE runs steeper than that of PCE. This means that the achievable capacities for MTBE are very low even for large amounts of charcoal. Similar performance (low slope on fresh carbon, high slope on preloaded carbon) was observed e.g. for the complexing agents NTA and EDTA, both of them being known not to be sufficiently removed in activated carbon filtration steps as commonly applied in waterworks [22].

The adsorption of PCE on both fresh and preloaded F300 has to be assessed as very good according to the  $m/L$  ratio (cf. Table 5). However, a comparison of the value for MTBE yields a classification of MTBE to be only poorly adsorbable on fresh activated carbon. With charcoal that has been used for some time the elimination of MTBE by adsorption on activated carbon becomes almost impossible. As the Freundlich parameters determined by adsorption isotherm experiments are much higher, the ratio  $m/L$  cannot be determined reasonably.

When extrapolating these data to lower concentrations of MTBE—as found in the aquatic environment—one has to



**Fig. 9:** Adsorption isotherms for MTBE and tetrachloroethylene (PCE) on F300 (fresh and preloaded with 35 m<sup>3</sup>/kg).

Adsorptionsisothermen von MTBE und Tetrachlorethen (PCE) an F300 (Frischkohle und mit 35 m<sup>3</sup>/kg vorbeladene Kohle).

consider that the adsorption behaviour may change. Experience shows that adsorption isotherm slopes tend to run more steeply at lower concentrations. Thus, the adsorption capacity is even worse for low concentrations because of the competing influence of the still present DOC becoming stronger. Therefore it can be assumed that the adsorption of MTBE in low concentrations will be even worse than at higher concentration.

In addition, experience shows that the presence of NOM in higher concentrations (as found in natural water) leads to a decline in adsorption capacity for the substance under investigation.

It can thus be concluded that an elimination of MTBE from raw water sources for drinking water production by activated carbon filtration can only be achieved with high amounts of charcoal and short filter regeneration cycles. However, this is considered as economically not feasible.

These findings are confirmed by experiences made with an industrial scale groundwater treatment plant for the elimination of MTBE and trichloroethene [45]. While trichloroethene is removed reliably by adsorption on activated carbon the break-through of the ether occurred quite rapidly.

## 8 Comparison with data from waterworks

For studying the fate of MTBE during drinking water treatment under real-life conditions samples were taken at different waterworks. Most of the samples were spot checks in order to determine the waterworks' need for action concerning MTBE. However, these measurements allow a first comparison with the information gained from the laboratory-scale experiments.

In Table 6 data is given from a waterworks (WW I) that uses aeration as a treatment step. As can clearly be seen, at all

**Table 5:** Freundlich parameters and value  $m/L$  for PCE and MTBE on fresh and preloaded activated carbon.

Freundlich-Parameter und  $m/L$ -Werte von PCE und MTBE an frischer und vorbeladener Aktivkohle.

	PCE on fresh activated carbon	MTBE on fresh activated carbon	PCE on preloaded activated carbon	MTBE on preloaded activated carbon
$n$	0.75	0.64	0.66	12.7
$K$	477	7.6	39.8	> 1 000 000
$m/L$ in mg/L	6.1	220	39.8	n.c. <sup>*)</sup>

<sup>\*)</sup> n.c.: not calculated since not reasonably evaluable

**Table 6:** Data from a waterworks WW I with aeration as a treatment step for decarbonisation.

Elimination von MTBE im Wasserwerk WW I (Belüftungsschritt zur Entsäuerung).

Concentration of MTBE in µg/L	Raw water	After aeration
15.12.1999	0.08	0.08
07.11.2000	—*)	0.39
14.12.2000	0.39	0.28

\*) no samples taken

three sampling dates MTBE is not decisively removed during aeration, though a small reduction of concentration is achieved if higher influent concentrations appear. Unfortunately no samples were taken from the influent on November 7th, so it is not clear whether a reduction occurred in this case or not.

In Figure 10 continuous monitoring results are shown from a waterworks (WW II) that uses riverbank filtrate as a raw water source. Treatment steps applied in this waterworks include ozonation with ozone concentrations of about 0.5 mg/L and subsequent activated carbon filtration.

MTBE is almost constantly present in the raw water of WW II, concentrations ranging from 0.05 to 0.2 µg/L. It becomes clear that MTBE cannot be totally removed with the treatment steps used in this waterworks. The MTBE concen-

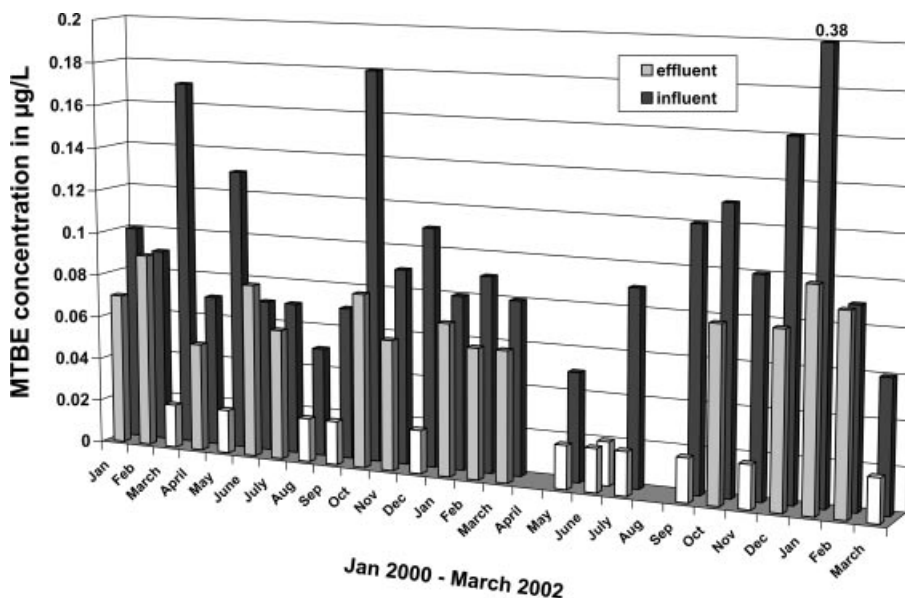
tration is occasionally reduced, in a few cases actually below limit of determination.

Another waterworks (WW III) was sampled once for MTBE showing the inefficiency of both ozonation and activated carbon filtration. In WW III the following concentrations were measured: the raw water contains 0.32 µg/L MTBE, after ozonation the concentration is lowered to 0.19 µg/L and at the waterworks' outlet – i.e. after a.c. filtration – 0.11 µg/L MTBE are detected in the drinking water. Though a reduction of MTBE concentration occurred the treatment steps were not able to fully eliminate MTBE.

These examples show that MTBE will most certainly break through waterworks using conventional treatment technologies as predicted by the laboratory-scale experiments.

## 9 Conclusions

The data presented in this study and other data from literature show a ubiquitous occurrence of MTBE in the aquatic environment. MTBE is not significantly retarded by subsoil passage and can thus be found in the raw water of waterworks. Especially waterworks that use bank filtrated water as raw water source are affected. Laboratory-scale experiments show that though MTBE might be reduced by aeration this treatment step is not efficient and feasible especially in the low concentration range. Other technologies commonly used for drinking water treatment such as ozonation and activated carbon filtration prove similarly inefficient in reliably reducing the MTBE concentration. More advanced technologies – e.g. the combination of ozone with H<sub>2</sub>O<sub>2</sub> – carry



**Fig. 10:** MTBE concentration in a waterworks' (WW II) in- and effluent – treatment steps: ozonation and activated carbon filtration.

MTBE-Konzentrationen im Wasserwerksein- und -austritt (WW II) – Aufbereitungsschritte: Ozonung und Aktivkohlefiltration.

potential of eliminating MTBE; however, high doses of ozone/H<sub>2</sub>O<sub>2</sub> are needed to yield a significant reduction.

These results indicate that MTBE is not easily removed during conventional drinking water treatment. Comparison with data from waterworks confirms this conclusion.

However, the concentrations detected in the aquatic environment nowadays are still below any taste and odour threshold and far below any toxicological effect level [7, 10]. Therefore the need for action in waterworks is to be questioned at the momentary state, but this study implies the problems waterworks will have to face if the concentrations of MTBE rise. Since the use of MTBE is expected to increase in the future, the possibility that waterworks are affected by MTBE in higher concentrations will rise. It is therefore necessary to strive towards a precautionary policy and reduce the usage of MTBE. One way to realise that is to substitute MTBE by better biodegradable substances. Moreover, the occurrence of MTBE should be more thoroughly monitored and a new assessment of MTBE should be made considering the potential risk to water sources.

## Acknowledgements

The authors thank the DVGW–Deutsche Vereinigung des Gas- und Wasserfaches e.V. for funding this project. Further thanks are given to Biejan Ardabili, Sabine Gabriel and Corinna Stieler whose support in the laboratory ensured a successful outcome of the project.

## References

- [1] Hansen, B. G., Munn, S. J., Pakalin, S., Musset, C., Luotamo, M., de Bruijn, J., Berthault, F., Vegro, S., Pellegrini, G., Allanou, R., Scheer, S. (Eds.): EUR 20417 EN–European Risk Assessment Report *tert*-Butyl Methyl Ether. Environment and Quality of Life, 19. Office for Official Publications of the European Communities, Luxembourg, 2002.
- [2] Schmidt, T. C., Morgenroth, E., Schirmer, M., Effenberger, M., Haderlein, S. B.: Use and occurrence of fuel oxygenates in Europe. In: Diaz, A. F., Drogos, D. L. (Eds.): Oxygenates in Gasoline – Environmental Aspects. American Chemical Society, Washington D.C., 2001, pp. 58–79.
- [3] Johnson, R., Pankow, J. F., Bender, D., Price, C., Zogorski, J. S.: MTBE – To what extent will past releases contaminate community water supply wells? *Environ. Sci. Technol.* **34**, 210A–217A (2000).
- [4] Schirmer, M.: Das Verhalten des Benzininhaltsstoffes Methyltertiärbutylether (MTBE) in Grundwasser. *Grundwasser* **3**, 95–102 (1999).
- [5] Pahlke, G., Leanhard, H., Tappe, M.: Mögliche Umweltbelastungen durch die Nutzung von MTBE als Kraftstoffzusatz in Deutschland und Westeuropa. *Erdöl Erdgas Kohle* **116** (10), 498–504 (2000).
- [6] Howard, P. H., Sage, G. W., Jarvis, W. F., Gray, D. A.: Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Volume 2. Lewis, Chelsea (Mich.), 1991.
- [7] Lyman, W. J., Reehl, W. F., Rosenblatt, D. H.: Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Chemicals. American Chemical Society, Washington DC, 1990.
- [8] Stocking, A. J., Suffet, I. H., McGuire, M. J., Kavanaugh, M. C.: Implications of an MTBE odor study for setting drinking water standards. *J. Am. Water Works Assoc.* **93** (3), 95–105 (2001).
- [9] Robbins, G. A., Wang, S., Stuart, J. D.: Using the static headspace method to determine Henry's Law constants. *Anal. Chem.* **65**, 3113–3118 (1993).
- [10] Tesseraux, I., Koss, G.: Toxikologie von Methyl-tertiärer-Butylether (MTBE) als Bestandteil des Otto-Motoren-Kraftstoffs. *Bundesgesundheitsblatt* **4**, 332–343 (1999).
- [11] Squillace, P. J., Pankow, J. F., Kortess, N. E., Zogorski, J. S.: Environmental Behavior and Fate of Methyl *tert*-Butyl Ether (MTBE). US Department of the Interior – US Geological Survey – National Water Quality Assessment Program (NAWQA), USGS Series Fact Sheet, USGS Library Call Number (200)F327 No. 96–203, 1996.
- [12] Williams, P. R. D., Benton, L., Warmerdam, J., Sheehan, P. J.: Comparative risk analysis of six volatile organic compounds in California water. *Environ. Sci. Technol.* **36**, 4721–4728 (2002).
- [13] Effenberger, M., Weiß, H., Popp, P., Schirmer, M.: Untersuchungen zum Benzininhaltsstoff Methyl-tertiär-butylether (MTBE) in Grund- und Oberflächenwasser in Deutschland. *Grundwasser* **2**, 51–60 (2001).
- [14] Small, M. C., Martinson, M., Kuhn, J.: Opening Pandoras box: overview of states' responses to the methyl *tert*-butyl ether enigma. In: Diaz, A. F., Drogos, D. L. (Eds.): Oxygenates in Gasoline – Environmental Aspects. American Chemical Society, Washington D.C., 2001, pp. 42–57.
- [15] Wilhelm, M. J., Adams, D., Curtis, J. G., Middlebrooks, E. J.: Carbon adsorption and air-stripping removal of MTBE from river water. *J. Environ. Eng.* **128**, 813–823 (2002).
- [16] Sutherland, J., Adams, C., Kekobad, J.: Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters. *Water Res.* **38**, 193–205 (2004)
- [17] Klinger, J., Stieler, C., Sacher, F., Brauch, H.-J.: MTBE (methyl tertiary-butyl ether) in groundwaters: monitoring results from Germany. *J. Environ. Monit.* **4**, 276–279 (2002).
- [18] Klinger, J., Sacher, F., Brauch, H.-J., Stieler, C.: Untersuchungen zur Bedeutung von Methyl-tertiär-butylether (MTBE) für die Trinkwasserversorgung aus Grundwasser. Final Report to DVGW Project W 08/99, Deutsche Vereinigung des Gas- und Wasserfaches (DVGW), Bonn, 2000.

- [19] Bader, H., Hoigné, J.: Determination of ozone in water by the indigo method. *Water Res.* **15**, 449–456 (1981).
- [20] Melin, G. (Ed.): Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water. NWRI-99-06, National Water Research Institute, Fountain Valley, CA, USA, 2000.
- [21] Freundlich, H.: Über die Adsorption in Lösungen. *Z. Phys. Chem.* **57**, 385–470 (1906).
- [22] Sacher, F., Karrenbrock, F., Knepper, T. P., Lindner, K.: Untersuchung der Adsorbierbarkeit von organischen Einzelstoffen als ein Kriterium ihrer Trinkwasserrelevanz. *Vom Wasser* **96**, 173–192 (2001).
- [23] Achten, C., Püttmann, W.: Methyl *tert*-butyl ether (MTBE) in urban and rural precipitation in Germany. *Atmos. Environ.* **35**, 6337–6345 (2001).
- [24] Schmidt, T. C., Duong, H.-A., Berg, M., Haderlein, S. B.: Analysis of fuel oxygenates in the environment. *Analyst* **126**, 405–413 (2001).
- [25] Schmidt, T. C., Bittens, M., Arp, H. P., Haderlein, S. B.: Transfer pathways of MTBE into groundwater: the role of diffuse vs. point sources. In: Proceedings of First European Conference on MTBE, Dresden, September 8–9, 2003. First European Conference on MTBE, September 8–9. In: Billetewski, B., Werner, P. (Eds.): Beiträge zu Abfallwirtschaft/Altlasten, Band 31, pp. 8–15.
- [26] Klinger, J., Sacher, F., Brauch, H.-J.: MTBE (Methyl-tertiär-Butylether) – Ein Problemstoff für die Wasserversorgung? *GWF Gas Wasserfach: Wasser-Abwasser* **143** (3), 166–171 (2002).
- [27] Gerke, T.: MTBE waves in the lower Rhine. In: Proceedings of First European Conference on MTBE, Dresden, September 8–9, 2003. First European Conference on MTBE, September 8–9. In: Billetewski, B., Werner, P. (Eds.): Beiträge zu Abfallwirtschaft/Altlasten, Band 31, 128–136.
- [28] Arbeitsgemeinschaft Rhein-Wasserwerke – ARW: 58. Bericht der Arbeitsgemeinschaft Rhein-Wasserwerk e. V. 2001. ISSN 0343–0391.
- [29] Arbeitsgemeinschaft Wasserwerke Bodensee-Rhein – AWBR. 33. Bericht. 2001. ISSN 0179–7867.
- [30] Kühn, W., Müller, U.: Riverbank filtration – an overview. *J. Am. Water Works Assoc.* **92** (12), 60–69 (2000).
- [31] Schlünder, E. U.: Einführung in die Stoffübertragung. 2. Auflage. Vieweg, Braunschweig, 1996.
- [32] Baus, Ch., Sacher, F., Brauch, H.-J.: Untersuchungen zur Entfernung von MTBE bei der Trinkwasseraufbereitung. Final Report to DVGW Project W11/00, Deutsche Vereinigung des Gas- und Wasserfaches (DVGW), Bonn, 2000.
- [33] Pankow, J. F., Thomson, N. R., Johnson, R. L., Baehr, R. L., Zogorski, J. S.: The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds (VOC's) to shallow groundwater. *Environ. Sci. Technol.* **31**, 2821–2828 (1997).
- [34] Atkins, P. W.: Physical Chemistry. 4th Edition. Oxford University Press, Oxford, 1990.
- [35] Bächle, A., Baldauf, G., Brummel, F., Nahrstedt, A., Schredelseker, F.: Entfernung von flüchtigen Schadstoffen aus Wasser durch Strippverfahren. DVGW-Schriftenreihe Wasser Band 87, Bonn, 1995.
- [36] Acero, J. L., Haderlein, S. B., Schmidt, T. C., Suter, M. J.-F., von Gunten, U.: MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: efficiency of the process and bromate formation. *Environ. Sci. Technol.* **35**, 4252–4259 (2001).
- [37] Karpel del Leitner, N., Papailhou, A.-L., Croué, J.-P., Peyrot, J., Doré, M.: Oxidation of methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether by ozone and combined ozone/hydrogen peroxide. *Ozone Sci. Eng.* **16**, 41–54 (1994).
- [38] Liang, S., Yates, R. S., Davis, D. V., Pastor, S. J., Palenciy, L. S., Bruno, J.-M.: Treatability of MTBE-contaminated groundwater by ozone and peroxone. *J. Am. Water Works Assoc.* **93** (6), 110–120 (2001).
- [39] Mitani, M. M., Keller, A. A., Bunton, C. A., Rinker, R. G., Sandall, O. C.: Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water. *J. Hazard. Mater.* **B89**, 197–212 (2002).
- [40] Safarzadeh-Amiri, A.: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment of methyl *tert*-butyl ether (MTBE) in contaminated waters. *Water Res.* **35**, 3706–3714 (2001).
- [41] Sotelo, J. L., Beltrán, F. J., Benitez, F. J., Beltrán-Heredia, J.: Ozone decomposition in water: kinetic study. *Ind. Eng. Chem. Res.* **26**, 39–43 (1987).
- [42] Baus, Ch., Sacher, F., Brauch, H.-J.: Efficiency of ozonation and AOP for MTBE removal in waterworks. *Ozone Sci. Eng.* **27** (1), 27–35 (2005).
- [43] von Gunten, U., Hoigné, J.: Bromate formation during ozonation of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. *Environ. Sci. Technol.* **28**, 1234–1242 (1994).
- [44] Sacher, F., Schmidt, W., Böhme, U., Brauch, H.-J.: Bromat – Ein Problem für die Trinkwasserversorgung in Deutschland? *GWF Gas Wasserfach: Wasser-Abwasser* **138** (4), 199–207 (1997).
- [45] McKinnon, R. J., Dyksen, J. E.: Removing organics from groundwater through aeration plus GAC. *J. Am. Water Works Assoc.* **76** (5), 42–46 (1984).

[Received: 23 December 2003; accepted: 30 November 2004]