

Occurrence of Methyl *tert*-Butyl Ether (MTBE) in Riverbank Filtered Water and Drinking Water Produced by Riverbank Filtration. 2

CHRISTINE ACHTEN,* AXEL KOLB, AND WILHELM PÜTTMANN

J.W. Goethe-Universität Frankfurt am Main, FB Geowissenschaften, Institut für Mineralogie -Umweltanalytik-, Georg-Voigt-Strasse 14, 60054 Frankfurt am Main, Germany

Bank filtration of river or lake water represents an efficient and natural purification process used for the drinking water production in many countries and at an amount of about 15–16% in Germany. From experiences over decades particularly at the river Rhine and Elbe, it is known that the occurrence of persistent pollutants in river water can represent a problem for the quality of drinking water produced by bank filtration. The common detection of the gasoline additive methyl *tert*-butyl ether (MTBE) in drinking water and the announced phase-out of the oxygenate in the U.S. show that MTBE can contaminate large water amounts due to its physicochemical properties. The MTBE situation in the U.S. differs from Europe, and significantly lower concentrations in the German environment can be expected. Average MTBE concentrations of 200–250 ng/L in the Lower Main and Lower Rhine river in 2000/2001 were reported. At two sites at the Lower Rhine and Lower Main rivers MTBE concentrations in bank filtered water ($n = 22$), recovering well water, raw water, and drinking water produced by the water utility at the Lower Rhine site ($n = 30$) and tap water at Frankfurt/M City ($n = 13$) were analyzed from 1999 to 2001. Sample analysis is performed by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC/MS) with a detection limit of 10 ng/L and a relative standard deviation of 11%. At the Lower Rhine site up to 80 m from the river an average MTBE concentration of 88 ng/L in riverbank filtered water, recovering well water, and raw water ($n = 7$) and of 43–110 ng/L in drinking water ($n = 3$) result. At the Lower Main site up to 400 m from the river MTBE concentrations from 52 to 250 ng/L ($n = 7$) were measured. Tap water samples at Frankfurt/M (mean of 35 ng/L, maximum of 71 ng/L) were in the same range as MTBE amounts in drinking water at the Lower Rhine site. Measured MTBE amounts eliminated by bank filtration at the Lower Rhine site are comparable to other contaminants. The results of this study show that concentrations measured in river water and drinking water are approximately 2–3 orders of magnitude lower than the U.S. drinking water standard of 20–40 $\mu\text{g/L}$, represent trace-level concentrations, and are not of major concern nowadays. However, the unfavorable combination of the occurrence of nonpoint MTBE emissions

and the persistent behavior of the ether in water even at low concentrations should not be neglected in future discussion. The reported MTBE concentrations are relevant for precautionary aspects. MTBE concentrations in German river water show a tendency toward increasing concentrations since 1999, and in the future possible higher concentrations could represent a risk for the quality of drinking water that is being produced by water utility using bank filtered river water.

Introduction

In many countries of the world river water represents an important source of drinking water, and, simultaneously, the same rivers are used for sewage disposal. This multifunctional use of rivers can lead to serious concern about the drinking water quality. In favorable hydrogeological formations a low-cost process for significantly improving the quality of surface source waters is provided by bank filtration. Surface water is infiltrated into the bank or bottom sediments of a river or lake and is filtered comparable to a slow sand-filter from shallow wells at tens to hundreds of meters distance from the bank by pumping groundwater activity of groundwater. Naturally occurring physicochemical and biological transformations in the bank filtered water during the underground passage are used as a basic step in the purification process that is necessary to meet drinking water quality.

In Europe for more than 100 years (1) bank filtration of surface water has been used for the drinking water production at the river Rhine (1–5) and Elbe (4, 6–8) and more recently elsewhere (4, 9–12). About 15–16% of the drinking water used is produced by bank filtration and artificial infiltration in Germany (4, 5, 13), and most of this part is produced by water utility at the Rhine and Elbe. The dramatic increase in pollution of river water at the river Rhine in the 1970s resulted in various studies about the removal of anthropogenic organic and inorganic compounds (14) like adsorbable organic halogens (AOX), polycyclic aromatic hydrocarbons (PAHs), pesticides, surfactants, aromatic sulfonates, aliphatic and aromatic amines, complexing agents, benzene, toluene, ethylbenzene, xylenes (BTEX), phenols, adsorbable organic sulfur (AOS), pharmaceutical residues, endocrine disrupting chemicals, organic iodine compounds, byproducts of the vitamin C production, particles, bacteria, viruses, parasites, micropollutants, ammonia, heavy metals, and others (3, 4, 6–9, 15–26). It has been proven that microorganisms and aquifer sediments from the riverbank naturally purify the infiltrating river water of suspended solids, parasites, bacteria, viruses, and easily degradable pollutants (1, 3). Additionally, the underground passage acts as a barrier particularly against shock loads resulting from emergency situations as chemical spills or defects in industrial wastewater plants (1). However, some compounds (e.g. ethylenedinitrilotetraacetic acid, EDTA, some aromatic sulfonates, the pharmaceutical carbamazepine) are persistent during bank filtration and, hence regularly occur in raw water of the water utility (4, 26). During the past decades water quality has been improved by the reduction of the amount of chemicals released into river water (5, 27) and by substitution of toxic and persistent by less toxic and biodegradable substances.

The recent occurrence of the oxygenate methyl *tert*-butyl ether (MTBE) in aquatic environments (28–32) has caused concern in the U.S. and in Germany about the possible national extent of contamination (33, 34). Since 1985, MTBE

* Corresponding author phone: ++49/(0)/69-798x28791; fax: ++49/(0)/69-798x28702; e-mail: achten@kristall.uni-frankfurt.de.

has been added to German gasoline as an octane enhancer and to reduce emissions. The use of MTBE, however, has increased, and in Germany by 1999 it had reached an amount of about 500 000 tons (t) (34). The mean average MTBE content in German gasoline is about 1.2–1.7% (volume/volume) (v/v) (34–37). The consumption of MTBE in Europe has increased remarkably by 23% between the years 1995–1999 (37). In 2005 a new guideline will be introduced by the European Union limiting the amount of aromatic compounds in gasoline to 35% (v/v), and it is not yet clear how the required octane values will be reached from 2005 on. With increasing frequency of detection the occurrence of MTBE is observed in the atmospheric and aquatic environment not only on the American continent (28, 29, 38–40) but also in Europe (30–32, 34, 41–50). In 1999, the U.S. Environmental Protection Agency (EPA) adopted a drinking water advisory of 20–40 $\mu\text{g/L}$ for MTBE (51). Undoubtedly, most amounts of MTBE from oxygenated gasoline reach water by leakage from underground storage tanks [LUSTs] into groundwater. However, another possible pathway for the occurrence of lower MTBE concentrations in drinking water is represented by nonpoint MTBE input into river water used for the drinking water production by riverbank filtration. The fuel additive is detected in river water in the range of ng/L to $\mu\text{g/L}$ (28–30, 32, 45, 50). In Germany average MTBE concentrations of about 250 nanograms/liter (ng/L) in river Rhine water and about 200 ng/L in Main water in 1999/2001 (32, 45) might lead to detectable concentrations of MTBE in water from streambed wells. The oxygenate occurred in river water mostly in agglomerated areas due to urban runoff, MTBE containing precipitation (in wintertime only), and industrial effluents (45). It is notable that nonpoint source emissions (e.g. vehicle emissions) are not limited to specific sites and hence cannot easily be remediated within a short time. Additionally, river water quality in Germany has significantly increased due to legislation that focuses on “reduction at the source principle” and “polluter pays principle” (4). The former principle fails for diffuse source contaminants as it has been demonstrated for nutrients and pesticides; therefore, the “precautionary principle” is of outstanding importance for the drinking water supply with respect to dangerous substances which may come from diffuse sources (4).

Although the persistent behavior of MTBE in water has often been reported (37), it has recently been shown to be degradable in surface-water sediments (52, 53), particularly under oxic, denitrifying, or iron reducing conditions even at sites that had never been contaminated by MTBE before and were artificially contaminated in the laboratory (54, 55). It is still unclear, however, whether MTBE is attenuated or not during a bank passage. In groundwater from the Lower Susquehanna River Basin, MTBE was detected in 16 of 118 well water samples at a concentration range of 110–510 ng/L (14), and in the Connecticut, Housatonic, and Thames River Basins a maximum concentration of 5.8 micrograms/liter ($\mu\text{g/L}$) MTBE in water from urban streambed wells was reported (56). Unfortunately, it is not clear if LUSTs were at least partially responsible for the described detected amounts of the ether. In Germany MTBE was detected in raw water samples produced from bank filtration at the Lower Rhine in the range of 50–180 ng/L in 1999/2000 (32, 57). Recently, MTBE has been detected in tap water (80–400 ng/L) from different groundwater sources in Italy (50).

In the future the recalcitrance of the widely used additive in river water could represent a problem for water utilities that produce drinking water from riverbank filtration if river water concentrations will increase. The aim of this study was to investigate the relevance of this pathway at two study sites.

Site Locations

Water Utility at the Lower River Rhine. The drinking water supply for many cities in the Lower Rhine embayment/Germany is provided by water utility situated at the river Rhine. At the investigated site a gallery of recovering wells for the drinking water production is situated at a distance of about 50 m, parallel to the Rhine. The aquifer consists of Pleistocene gravel and sand of the Rhine lower and middle terraces that show a thickness of about 20 m. It is characterized by a field velocity of 5–10 m/day (m/d), a coefficient of permeability of about 1.6×10^3 meters/second (m/s), and a porosity of 20%. Three multilevel groundwater wells, at distances of about 20 m (well A), 40 m (well B), and 80 m (well C) from the Rhine bank, have been used for several bank filtration quality investigations (Figure 1). The same wells (A, B, and C at three different depths) were sampled in this study to compare data obtained with existing data. Generally, the water in wells A and B originates from bank filtration. Water from well C mostly groundwater inflow from land is found although at high Rhine water levels bank filtration water infiltrates into well C, leading to a mixture of the two different water types. Due to a colmated and plastered bottom of the Rhine near the bank, river water infiltration mainly occurs at a distance of about 80–250 m from the bank by filtration into the river bottom. A residence time of about 15–70 days (d) is needed by water infiltrating from the Rhine bottom to reach the monitoring and recovering wells. At the water utility about 75% of bank filtration water is mixed with approximately 25% groundwater from natural groundwater recharge. The hydrochemical situation of the aquifer is aerobic and characterized by oxygen reducing conditions. Significant biological activity is observed in the bank sediments, and it has been proven that transformation of pollutants by microorganisms is most effective in the first decimeters of the river sediment (6). Contamination of the investigated bank filtered water by LUSTs could be excluded.

Drinking Water Purification Processing at the Water Utility 1. Pumped water from the recovering wells is treated at the water utility 1 (Figure 2) in order to meet drinking water quality requirements. In the first step raw water provided by the wells is treated by ozone which evokes flocking of mainly ferrous and manganese compounds, while also improving odor and taste of the water. The carbonic acid concentration is reduced by aeration in the tank to a soluted calcite concentration less than 5 milligrams/liter (mg/L). In a third step the water is pumped through two different layers of activated carbon filters. Finally, phosphate and silicate (1 mg/L) and chloride dioxide (0.06 mg/L) are added to the water to prevent corrosion of pipes and biological contamination. During the entire water purification process the temperature of the water remains roughly constant at 13–14 °C. Water from the water utilities 2 and 3 was also investigated.

Eddersheim at the Lower River Main in the Vicinity of Frankfurt/M/Germany. Bank filtration water of the river Main is used for the drinking water production at several sites in the vicinity of Frankfurt/M. The study location at Eddersheim has been used for several water quality investigations (19, 25). Water from four monitoring wells at distances of 60 m (well 1123), 400 m (well 1184), 1050 m (well 1128), and 1150 m (well 1132) from the Main was investigated in this study. The gallery of recovering wells for the nearby water utility Hattersheim is mostly situated approximately 1300 m parallel to the Main, with a few recovering wells situated as close as about 200 m from the Main. Groundwater in wells 1123 and 1184, situated near the Main, mostly originates from bank filtration, although to a small amount inflow of groundwater from the land occurs at 400 m (25). It is noted that all four

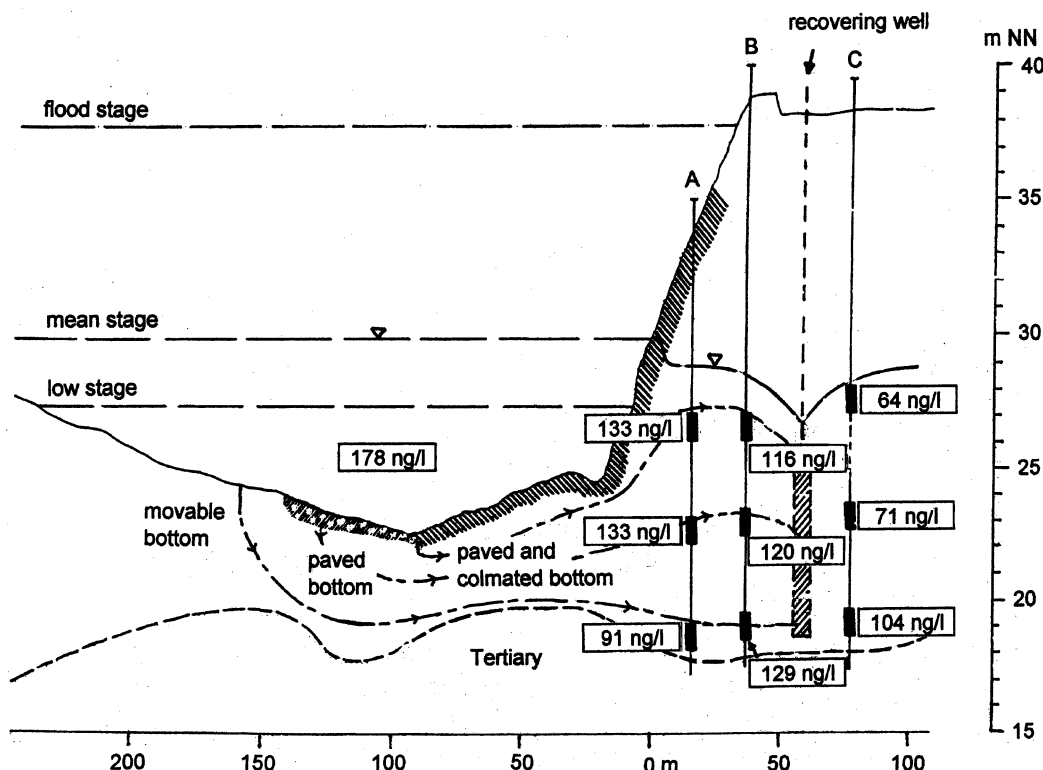


FIGURE 1. Hydrogeological cross section through the river Rhine and bank at the Lower Rhine site (water utility 1). Bank filtration water pathways and flow direction are indicated by dotted lines with arrows. Methyl *tert*-butyl ether (MTBE) concentrations (ng/L) in water of three monitoring wells up to about 80 m from the bank at three different depths (black) are shown. Samples were collected on the 02/13/01. The MTBE concentration of Rhine water at the site represents a mean value ($n = 3$). The location of a recovering well near the monitoring wells is shown (ruled).

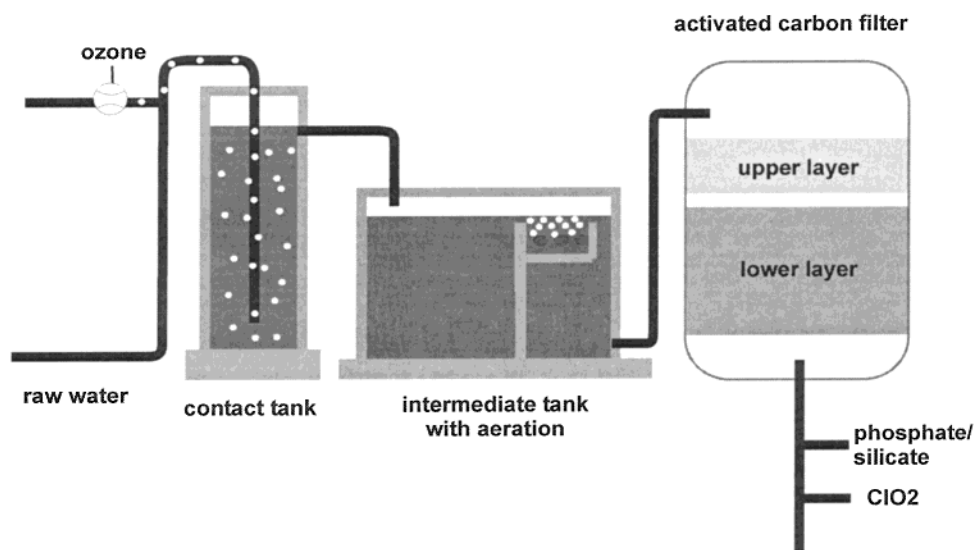


FIGURE 2. Drinking water purification processing at the water utility 1.

investigated wells are not situated in a line within the same flow direction near the river as is the case at Lower Rhine site. Nowadays, groundwater in wells at distances of more than 1000 m from the Main originates from land only. In the past however, water from bank filtration was transported into the aquifer from the river toward the water utility Hattersheim due to significantly higher pumpages. The aquifer consists of about 10–15 m Pleistocene and about 65–70 m Pliocene gravel and sand (containing some confined clay lenses), with characteristic coefficients of permeability of about 2×10^{-4} – 2×10^{-3} m/s and 3 – 5×10^{-4} m/s, respectively. Groundwater between the Main and the

well 1184 at 400 m distance is characterized by a field velocity of 0.7–1.3 m/d with resulting residence times of 45–85 d for well 1123 and 310–570 d for well 1184. The hydrochemical situation in the aquifer, up to well 1184, is characterized by iron- (up to 3.6 mg/L) and manganese- (up to 5.2 mg/L) reduction. Median Main water concentrations from 1995 to 1999 show that the oxygen- (11 mg/L) and nitrate concentrations (23 mg/L) in the Main water are reduced during the passage from the Main to well 1123 (1.3 mg/L oxygen and <0.5 mg/L nitrate at –90 mV redox potential) and do not change significantly until well 1184 (2.4 mg/L oxygen and <0.5 mg/L nitrate at –25 mV redox potential). Therefore,

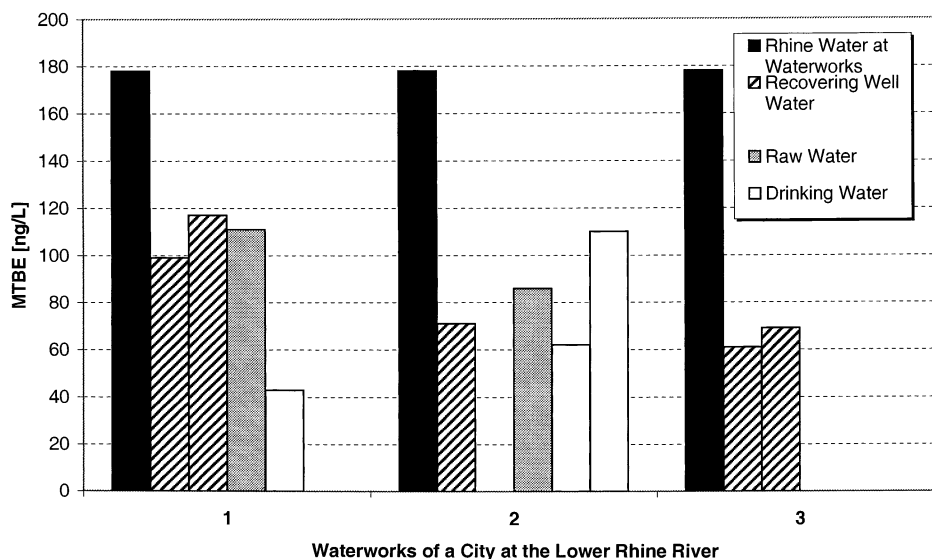


FIGURE 3. Methyl *tert*-butyl ether concentrations in recovering well water, raw water, drinking water, and Rhine water (mean) at three water utility in the Lower Rhine embayment.

biological activity under oxygen-, nitrate-, iron-, and manganese-reducing conditions during the riverbank passage can be expected. At a distance of more than 1000 m from the riverbank, oxygen concentrations (about 10 mg/L) and nitrate concentrations (about 60 mg/L), fall within the normal range for agriculturally used land. Contamination of the investigated bank filtered water by LUSTs or leakage from sewage pipes cannot be excluded because the wells are situated in a housing and industrialized area.

Experimental Section

Collection of all samples was performed by single point sampling. Three Lower Rhine water samples near the site were collected on the 02/06/01, 02/08/01, 02/10/01, with the mean value of the measured MTBE concentrations subsequently calculated. Samples at the monitoring wells A, B, and C, at three different depths, were taken on the 02/13/01. Water from the recovering wells, raw water, and drinking water at three water utilities were collected on 02/07/01, 02/08/01, and 02/12/01, respectively. The results obtained did not correspond to the monitoring well samples data. Additionally, samples from a water storage tower (02/08/01) and other groundwater from a cross link (02/07/01) were taken. Samples from the four monitoring wells at Eddersheim were collected on 11/18/99, 04/06/00, 01/31/01, and 05/09/01. Potable water samples ($n = 13$) were collected from taps at the University of Frankfurt/M, situated in the center, from the 11/16/00 until 03/01/01.

The sampling and the description of the analytical method by a combination of headspace-solid-phase microextraction (HS-SPME) and gas chromatography-mass spectrometry (GC/MS) is published elsewhere (58).

Results

MTBE in Bank Filtration Water and in Water from Water Utility at the Lower River Rhine. Rhine water samples showed MTBE concentrations of 310 ng/L, 125 ng/L, and 99 ng/L on 02/06/01, 02/08/01, and 02/10/01, respectively, with a mean concentration of 178 ng/L resulting. After a distance of about 20 m (well A) from the river bank the MTBE concentration was reduced by about 35% compared to the mean Rhine water concentration. (Figure 1). The deepest monitoring well only receives water infiltrating through the movable and paved bottom of the Rhine with the residence time about twice as high as compared to the upper and middle

wells. This results in a measurable reduced MTBE concentration of about 50% compared to the mean Rhine water concentration and represents 25% less than the concentrations in the middle and upper wells. At a distance of about 80 m (well C) from the Rhine riverbank MTBE is detected at concentrations of about 60–100 ng/L (about 35–55% of the mean Rhine water concentration) which represents a diluted concentration by groundwater from the land (MTBE was not analyzed in groundwater from the land only). Lower concentrations occur in the upper wells. The conditions in the aquifer during the sampling were period oxidic (5–9 mg/L oxygen, except lowest monitoring well C with 0.3 mg/L).

About a week before sampled water at the water utility 1 from two recovering wells and raw water showed MTBE concentrations in the range of 100–120 ng/L (Figure 3). The mean concentration of 101 ng/L in the monitoring wells near a recovering well (middle and deep monitoring wells B and C) a week later was in a comparable range. In recovering well water and raw water at water utility 2 and 3 the MTBE contents were slightly lower with values of 60–90 ng/L. Also a lower MTBE concentration of 43 ng/L was detected in drinking water at water utility 1 due to the purification processing. At water utility 2 the concentrations of 62 ng/L and 110 ng/L were in the range of recovering well and raw water data. The persistent behavior of MTBE is further documented by measurable concentrations in water of a watertower (42 ng/L). MTBE was not detected in the sample of other groundwater transported to the water utility by a cross link.

MTBE in Bank Filtration Water at the River Main. Median and mean Main water concentrations for the three bank filtration sampling dates on the 11/18/99, 04/06/00, and 01/31/01 were calculated from analyzed Main water samples at Frankfurt/M (45). Due to the small sample amount ($n = 15$) and the constantly low concentrations (maximum of 116 ng/L) in the period from 01/14/99 to 04/06/00 the median (mean) MTBE concentration of 29 ng/L (39 ng/L) in Main water was used for comparison to both bank filtration samplings on 11/18/99 and 04/06/00. For the third bank filtration sampling on the 01/31/01 measured MTBE concentrations in Main water during 10/24/00–01/28/01 were used, and a median (mean) MTBE concentration of 71 ng/L (100 ng/L) was calculated. For the sampling on 05/09/01 a median (mean) concentration of 211 ng/L (580 ng/L) in the time from 02/05/01 to 05/09/01 resulted according to the residence times needed for river water being transported to

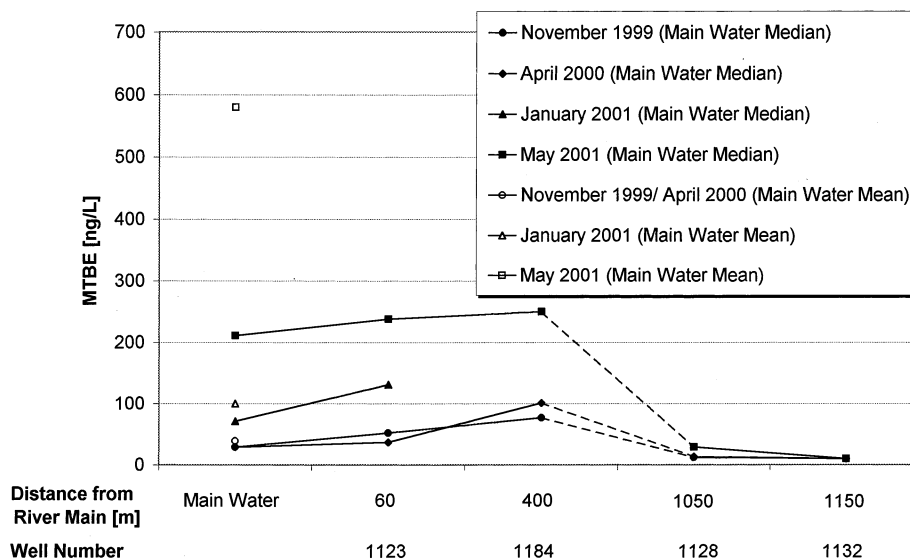


FIGURE 4. Methyl *tert*-butyl ether concentrations in Main water (mean/median) and during bank filtration at the Hattersheim site in the vicinity of Frankfurt/M from 1999 to 2001.

well 1123 and 1184. The results of the different samplings are shown in Figure 4. At the sampling dates in the years 1999 and 2000 low MTBE concentrations of about 50 ng/L are observed in Main water and in the well 1123 at a distance of 60 m from the Main. In January 2001 the MTBE concentration slightly increased in Main water (71 ng/L) and in the well 1184 at 60 m distance (131 ng/L). At all sampling dates the MTBE concentrations in water from well 1184 did not vary significantly from the data of well 1123 except that they generally are even slightly higher and not lower as it would be expected with increasing distance from the river due to attenuation processes. In May 2001 MTBE concentrations in Main water (02/05/01–05/09/01) increased to a median (mean) concentration of 211 ng/L (580 ng/L) and also concentrations in bank filtration water were higher (238 ng/L in 1123, 250 ng/L in 1184). In groundwater from the landside at a distance of 1050 m from the Main only traces of MTBE were detectable and at a distance of 1150 m from the river MTBE was below the detection limit of 10 ng/L in all samples of well water.

In the winter months of 2000/2001 MTBE was also present in drinking water samples ($n = 13$) from the tap at the Institut für Mineralogie -Umweltanalytik of the University Frankfurt/M with a median (mean) concentration of 32 ng/L (35 ng/L) and a maximum of 71 ng/L.

Discussion

All analyzed MTBE concentrations were far below the EPA drinking water advisory of 20–40 $\mu\text{g/L}$ and represented trace level concentrations. The calculated mean MTBE concentration of 178 ng/L in Rhine water at the sites of the water utility is slightly lower but in the range of reported data of 210 ng/L (32), 234 ng/L and 216 ng/L (45) in 1999–2001. This is confirmed by observed mean values in Rhine water between Mainz and Duisburg of 255 ng/L ($n = 50$) (45) and 235 ng/L ($n = 29$) (32) in 1999–2001. MTBE concentrations, obtained from water in the monitoring wells and raw water, show that the reported MTBE data in the monitoring wells represent the MTBE situation at the water utility 1 during the sampling periods. MTBE of roughly 200 ng/L in the river water was reduced during the riverbank passage to roughly 100 ng/L and was not eliminated to a great extent. This observation is supported by MTBE concentrations in the range of 70–110 ng/L obtained at water utility 2 and 3 during the same period.

The data allow for conclusion that the behavior of MTBE, during the riverbank passage at the described Lower Rhine site, is even approximately 100–400 times lower compared with river water concentrations of other persistent compounds present in the Rhine water like EDTA (4), adsorbable organic halogenated hydrocarbons (AOX), or AOS (Figure 5).

It is important to note that the AOX concentrations have decreased significantly since 1988 (4). In this study however, the AOX concentration profiles measured in 1988 are only used to compare the behavior of the different compounds. In future discussion of the water utility/Lower Rhine data only wells situated closest to the river bank (up to 20 m) are considered, as microbial activity is highest in the first centimeters of the bank and with increasing distance from the river the influence of other diluting groundwater also increases. During the first 20 m of bank filtration at water utility 1 EDTA, AOX, AOS, and MTBE were eliminated by approximately 20–30%, 35–55%, 20–55% (1), and 25–50%, respectively, due to natural attenuation processes under aerobic conditions. Lower concentrations in the lowest well A were often observed, presumably resulting from degradation and minor adsorption processes, as the residence time was higher than that of the upper and middle wells, volatilization processes can be excluded and a 100% origin of river filtration water a few meters below the river bottom can be assumed. As MTBE is poorly adsorbed, the degradation of the ether under oxygen reducing conditions (55) is likely. During several sampling times, EDTA, which has been widely reported as being poorly degradable (4, 59), was persistent even in the lowest well A (1), whereas AOX and AOS were present in lower concentrations which is indicative of some degradation/adsorption abilities that were reported in previous studies (22, 26). During further transport through the underground network at water utility 1 low MTBE elimination is observed, occurring mainly in the upper wells, probably due to volatilization or dilution by other groundwater. Eighty meters from the bank 104 ng/L of MTBE were still detectable in the deepest monitoring well C (Figure 1), and it remains unclear if it originates from river water or from groundwater from the land.

Much effort has been spent to understand the behavior of pollutants during the riverbank passage up to hundreds of meters from the river (1, 9, 16, 20). Extensive investigations at different locations revealed that simple dilution with other groundwater that does not originate from bank filtration and

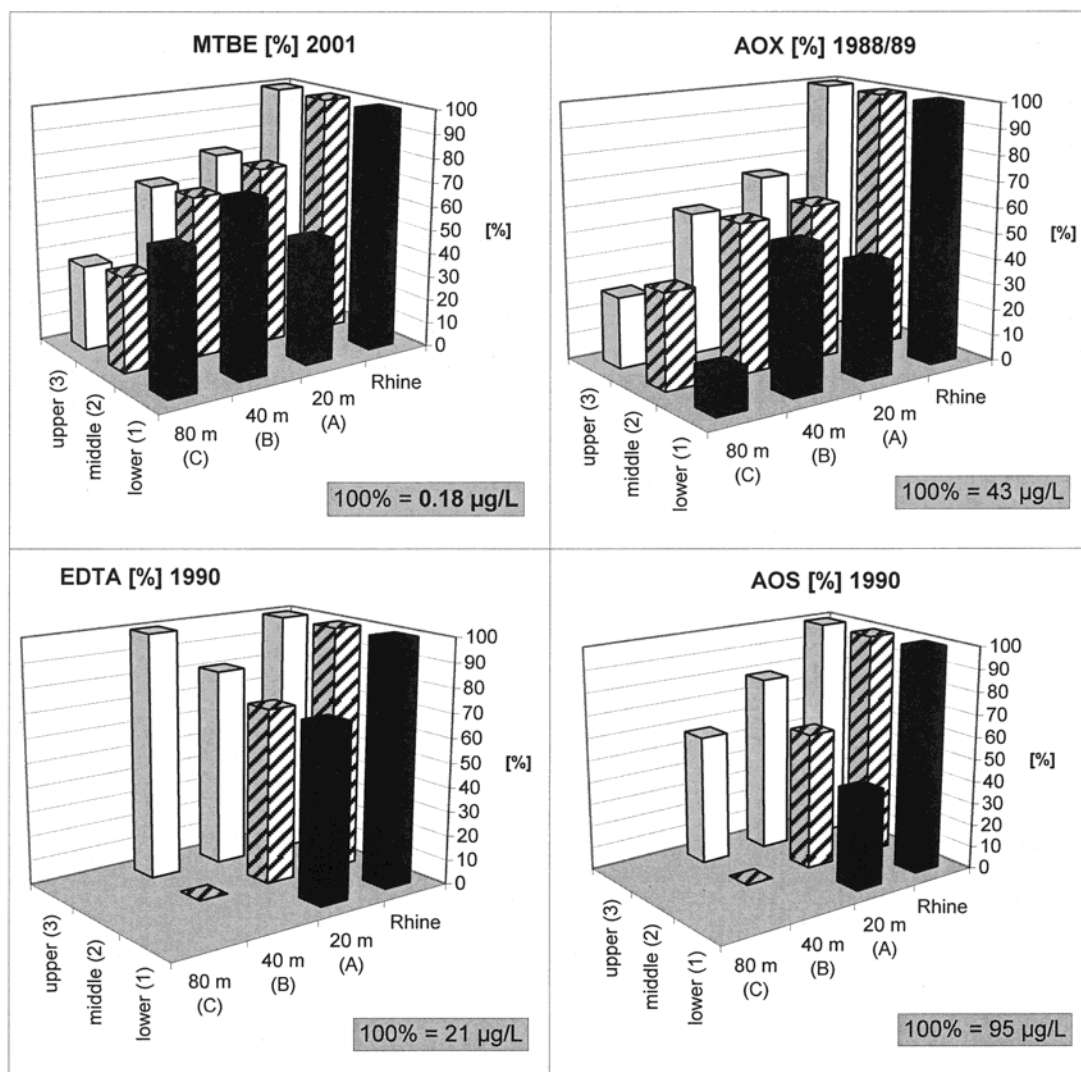


FIGURE 5. Methyl *tert*-butyl ether concentrations during the riverbank passage at water utility 1 in the Lower Rhine embayment in relative comparison (%) to concentrations of adsorbable organic halogenated hydrocarbons (AOX), ethylenedinitrilotetraacetic acid (EDTA), and adsorbable organic sulfur (AOS) (7). Note that MTBE concentrations in Rhine water are at least 2 orders of magnitude lower than other pollutant concentrations.

different hydrogeological/hydrochemical settings (e.g. aquifer material, field velocity, residence times, chemical conditions) were the most important factors which made comparison of different study locations difficult. Since 1995, the behavior of pollutants during the riverbank passage at the study location "Böckinger Wiesen" near Heilbronn at the river Neckar has been thoroughly investigated (9, 20, 24). Concentration profiles of some selected compounds at the "Böckinger Wiesen" site up to 50 m from the river are presented in Figure 6. At a distance of 50 m, under suboxic conditions, AOS, the complexing agent EDTA and AOX were less degraded compared to toluene, anionic surfactants, atrazine, and fragrance compounds. Generally, sufficient degradability of the latter compounds (atrazine is well degradable under anoxic conditions only) and rather persistent behavior of the former group is also frequently noted in the literature (16, 59). Different water utility at the river Rhine investigated the elimination of persistent and common pollutants such as EDTA, AOX, and AOS in raw water of the water utility compared to corresponding river water concentrations (1, 26).

Different studies conducted at the Rhine (Wittlaer, Cologne, and Mündelheim) and the Neckar ("Böckinger Wiesen"/Heilbronn) which investigated the behavior of organic pollutants during bank filtration with similar hy-

drogeological settings to the situation at water utility 1 were chosen for comparison and are summarized in Table 1. For comparison also only the first 20 m from the bank at the different sites were considered to minimize misinterpretation due to dilution by other groundwater. At the study locations Mündelheim, Cologne, and Wittlaer approximately 20%, 20–50%, and 50% EDTA were eliminated, respectively. The corresponding amounts of AOS eliminated were approximately 30%, 50%, and 40%, respectively. AOX concentrations were reduced by 30% at Mündelheim (1, 26). At the "Böckinger Wiesen" site at a distance of 20 m EDTA, AOX, and AOS concentrations were reduced by approximately 15%, 40%, and 20%, respectively (Figure 6). By summarizing all presented data it is shown that EDTA, AOS, and AOX were eliminated at the investigated locations within the first 20 m from the bank by approximately 15–50%, 20–55%, and 30–55% of the river water concentrations, respectively. From the limited sample set of this study it can be concluded that MTBE (roughly 25–50% elimination of river water concentrations after 20 m) is eliminated to higher amounts than EDTA and in a comparable range or to lower amounts than the AOX and AOS compounds.

The MTBE concentrations in recovering well water and raw water at water utility 1 (60–120 ng/L) are comparable to published data of 50–100 ng/L (32). An elimination rate

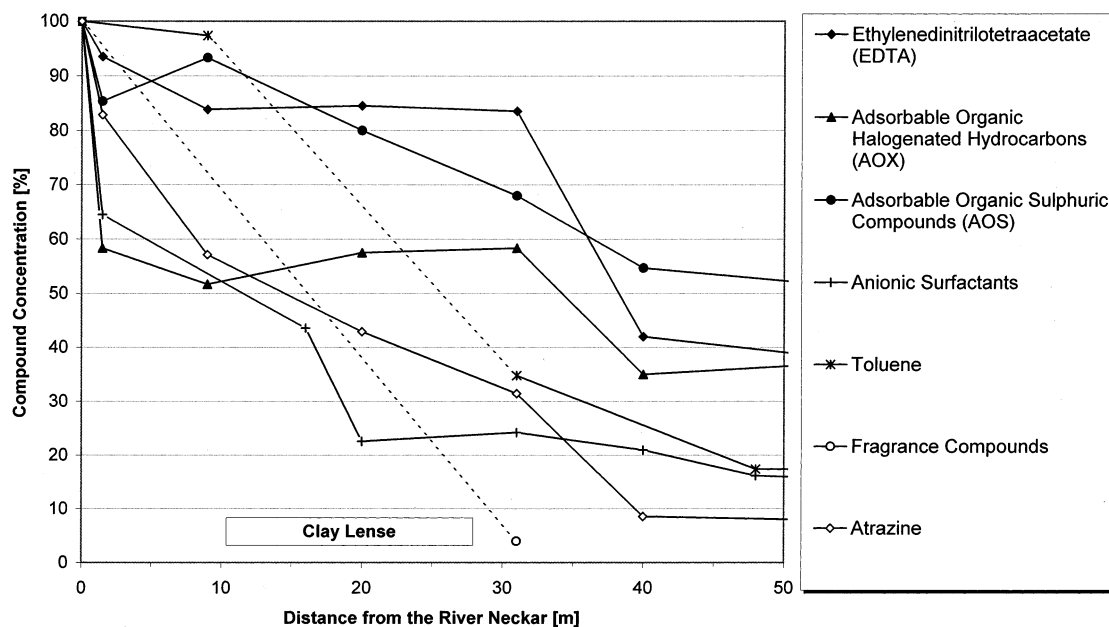


FIGURE 6. Pollutant concentrations (%) in river Neckar water and during the river bank passage of 50 m from the river at the "Bückinger Wiesen" site near Heilbronn (20).

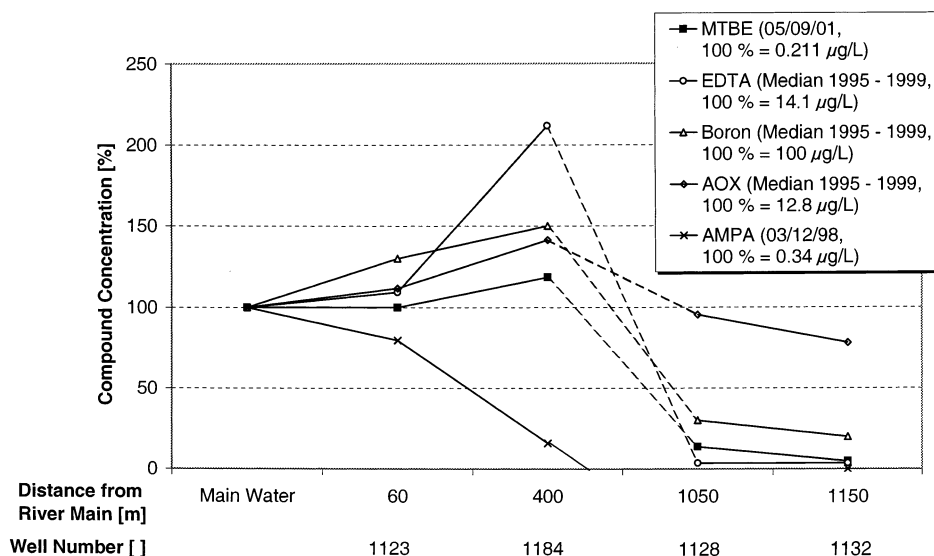


FIGURE 7. Methyl *tert*-butyl ether concentrations during the riverbank passage at the Lower Main (Hattersheim) in relative comparison (%) to concentrations of ethylenedinitrilotetraacetic acid (EDTA), boron, adsorbable organic halogenated hydrocarbons (AOX), and aminomethylphosphonic acid (AMPA) (25). AMPA concentrations were not analyzed in water from well number 1184 but from an adjacent recovering well (ASB1). Dotted lines indicate that to date, bank filtration at Hattersheim only occurs up to about 400 m from the river Main.

for MTBE in raw water cannot be calculated as a result of low sample numbers, low concentrations, and the fact that the sampling time of the river water and raw water did not correspond. The amounts of EDTA, AOX, and AOS eliminated by bank filtration during transport from Rhine water toward raw water at water utility 1 are 40%, were 60–80% in 1988, and are 50–80%, respectively (26). From the reported data a decrease in EDTA, AOX, and AOS concentrations of roughly 20% during transport from well A toward raw water due to dilution by groundwater from the land, volatilization, or aerobic degradation may be assumed. An eliminated MTBE amount in the range of 45–70% during transport from Rhine water toward raw water of water utility 1 would result if this loss of roughly 20% during transport from well A toward raw water at the water utility 1 was also assumed for MTBE and added to the amount of about 35% MTBE loss measured during transport from Rhine water toward well A.

In bank filtration water at the river Main MTBE concentrations were also detected in the trace level range. No conclusions about MTBE attenuation during the riverbank passage can be made as the concentrations were not decreasing but even slightly increasing. Higher MTBE concentrations were measured with increasing distance from the river. Also slightly increasing concentrations of other contaminants were measured. Concentrations of EDTA, boron, and AOX were analyzed in water from the same wells (Figure 7). The well-known persistent behavior of EDTA and AOX were confirmed at the Hattersheim site. Boron, originating from sewage, is also poorly degradable (59, 60). Aminomethylphosphonic acid (AMPA) concentrations were not analyzed in water from well number 1184 but from an adjacent recovering well (ASB1). Significant AMPA reduction was observed up to about 400 m from the Main bank (25). From the analyzed pollutant concentrations at Hattersheim it can

TABLE 1. Hydrogeological and Hydrogeochemical Data of the Groundwater at Waterworks 1 and Comparable Study Locations at Duisburg-Mündelheim, Düsseldorf-Wittlaer, Cologne-Rheinkassel, and at the Study Location Böckinger Wiesen/Heilbronn

river	location	geology	coeff of permeability [m/s]	field velocity [m/d]	distance of recovering wells from the bank [m]	residence time [m]	amt of bank filtration water in raw water [%]	oxygen [%]	conditions	reference
Lower Rhine	Waterworks 1	20 m Lower and Middle Rhine terrace	1.6×10^{-3}	5–10	60	15–70	75 (60–80)	<9	oxic, O ₂ , and NO ₃ reduction, no Fe and Mn reduction oxic?	this study
Lower Rhine	Waterworks Duisburg-Mündelheim	7 m Lower and Middle Rhine terrace	1×10^{-3} – 5×10^{-2}		30		50			(1)
Lower Rhine	Waterworks Düsseldorf-Wittlaer	15 m Lower and Middle Rhine terrace	2×10^{-3} – 1×10^{-2}	2–10	170	15–90	60 (50–60)	4–10	oxic, O ₂ , and NO ₃ reduction, no Fe and Mn reduction oxic?	(1, 26, 59)
Lower Rhine	Waterworks Cologne-Rheinkassel	20–25 m Lower Rhine terrace			160		50 (30–50) (30% young, 20% old)			(1)
Neckar	Böckinger Wiesen/Heilbronn	3–5 m Valley gravel, at 10–30 m from the bank: clay lense	8×10^{-3} – 1×10^{-2}	2–3	study distance: 150	40–80	0–40 m: 80 40–150 m: 30–80	<3	0–70 m: suboxic, Fe- and Mn reduction, 70–150 m: oxic, O ₂ , and NO ₃ reduction	(9, 20, 24)

be concluded that MTBE is as persistent as other poorly attenuable compounds present in the Main water. The slightly increasing concentrations cannot be the result of decreasing pollutant concentrations in Main water, adsorption effects to aquifer materials, fluctuating Main water levels, additional input of contaminants into the groundwater or different sampling techniques and remain unclear. The significantly differing median (211 ng/L) and mean (580 ng/L) MTBE concentrations in Main water in May 2001 are the result of some exceptional high MTBE concentrations from industrial effluents. The mean concentration should not be used for comparison because it is not representative of MTBE concentrations in river water. Anyhow, shock concentrations can be neglected if bank filtration water is considered as described above.

Traces of MTBE were detected in the drinking water supply at the Lower Rhine site and at Frankfurt/M in similar concentrations roughly in the range of 50 ng/L. In these regions bank filtration of river water is used for the drinking water production that shows MTBE concentrations roughly in the range of 200–250 ng/L (45). The research conducted revealed that traces of the oxygenate were still detectable in riverbank filtered water although MTBE concentrations in water from the rivers Rhine and Main were already in the ng/L range. Neither riverbank filtration nor drinking water processing was able to eliminate MTBE concentrations to a greater extent. The unfavorable combination of occurrence of nonpoint MTBE emissions and the persistent behavior of the ether in water even at low concentrations should not be neglected in future discussion. Recently, MTBE has been evaluated as “a compound of relevance for water utility” (32). Nowadays the presence of MTBE in river water are not of major concern in Germany. The results of this study show that concentrations measured in river water and drinking water are approximately 2–3 orders of magnitude lower than the U.S. drinking water advisory of 20–40 µg/L or the odor/taste threshold of 20 µg/L. However, the MTBE concentrations in river water show a tendency toward increasing concentrations since 1999 (45) and measured MTBE concentrations are relevant for precautionary aspects. If the rate of increase in European MTBE consumption of 23% from 1995 to 1999 continued in the future, MTBE concentrations in German gasoline would nearly have doubled by 2010 and lower Rhine/Main concentrations would be 300–500 ng/L. In the future, possible higher concentrations could represent a risk for the quality of drinking water that is being produced by water utility using bank filtered river water.

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