Abstract—In a gasoline-contaminated site in Düsseldorf, Germany a two-year monitoring program was carried out to determine the presence, behavior, and fate of 12 gasoline additives in a total of 96 samples from 14 groundwater wells. The origin of contamination was suspected to be a gasoline spill at a gas station. Target compounds were methyl-tert-butyl ether (MTBE), its main degradation products, tert-butyl alcohol (TBA) and tert-butyl formate (TBF); other gasoline additives, oxygenate dialkyl ethers: Ethyl-tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and diisopropyl ether (DIPE); aromatics: Benzene, toluene, ethylbenzene and xylenes (BTEX), and other compounds causing odor problems: Dicyclopentadiene and trichloroethylene. Purge and trap coupled with gas chromatography-mass spectrometry permitted detection of ng/L concentrations. Ninety of the 96 samples analyzed contained MTBE at levels varying between 0.01 to 645 μg/L. Five contaminated hot spots were identified with levels up to U.S. Environmental Protection Agency (U.S. EPA) drinking water advisory values (20–40 μg/L) and one of them doubling Danish suggested toxicity level of 350 μg/L at a depth of 11 m. No significant natural attenuation was found in MTBE degradation, although samples with high levels of MTBE contained 0.1 to 440 μg/L of TBA. These levels were attributed to its presence in the contamination source more than MTBE degradation. tert-Butyl alcohol was found to be recalcitrant in groundwater. In all cases, BTEX were at low concentrations or not detected, showing less persistence than MTBE. The monitoring of the contamination plume showed that the distribution of the MTBE and TBA in the aquifer formed a similar vertical concentration profile that was influenced by the groundwater flow direction.

Keywords—Methyl-tert-butyl ether Degradation products Aromatic hydrocarbons Purge/trap Groundwater

INTRODUCTION

Contamination of groundwater by motor vehicle fuels and fuel additives is not a new problem, given the history and pervasive use of fuels in the last centuries. Against this background of experience, recent events have focused attention on fuels containing chemicals known as oxygenates [1]. Many case studies of groundwater contamination have been completed in the United States [2–5], and many others have been carried out in Europe in the last five years [6–10].

Fuel oxygenates are added to gasoline to increase combustion efficiency and to reduce air pollution. Since the ban of tetraalkyl lead compounds, methyl tert-butyl ether (MTBE) is the most commonly used octane enhancer and one of organic chemical with the highest production volume worldwide [11]. In Europe, large amounts (several million tons) of MTBE are manufactured and used each year, which puts it into the category of high production volume chemicals [12]. Several other ethers and alcohols also serve as oxygenates and could become prevalent, depending on various factors such as cost, ease of production and transfer, and blending characteristics. These additives include methanol, ethyl-tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), diisopropyl ether (DIPE), and tert-butyl alcohol (TBA), but except for ethanol its use is, in general, secondary.

In European gasoline the average MTBE content is approximately 2% volume although the percentage varies considerably between countries and commercial types of gasoline [13]. In Germany, where this average was calculated at 1.35%, MTBE is used at different concentrations in regular (0.4%), eurosuper (0.4–4.2%), super premium unleaded (9.8%), and Optimax (11.9%) gasoline [14]. Beginning in 1985, MTBE was added to gasoline in Germany. Since then, the use of MTBE in this country has increased significantly and reached approximately 450,000 to 500,000 tons in 1997 [15,16]. Inevitably, some of this MTBE is released to the environment during the manipulation or storage of petrol fuel and becomes a groundwater pollutant due to its high solubility, high mobility, and slow degradation [17]. However, in Germany, contamination sources are being minimized by improved technology, such as the use of doubled-sided tanks at gasoline stations [18].

Information on the specific contents of other oxygenates in gasoline and their impact on the environment are very scarce. In Europe, ETBE and TAME also are used in substantial amounts [13] and in France, Italy, and Spain, the consumption of ETBE probably will increase even more rapidly than the use of MTBE due to tax incentives for the application of ethanol which is used to produce this compound [13]. Also, approximately 0.1 million tons annually of TAME are used as a fuel oxygenate in Finland [16].

Maximum permissible levels of MTBE in groundwater have not yet been established in Europe. Instead of health effects concerns (low acute and probably also chronic toxicity), there is much interest in the esthetic implications of MTBE in water resources used for the production of drinking water. Taste and odor thresholds for this compound in water have been reported at very low concentrations, approximately 25 to 60 μg/L for
concerns of 20 to 40

Although the rates generally are slow, the major products of

MTBE-contaminated sites were available due to the dif®culty

in determining the MTBE situation in the country and decided not to implement a drinking water and surface water standard because MTBE concentrations in Germany are believed generally to be low [18] (www.umweltbundesamt.de/verkehr/kraftubst/additiva/mtbe.htm). Nevertheless the German Environment Agency (UBA) recommended a maximum permissible concentration of 0.1 µg/L to reduce the occurrence of anthropogenic compounds with unknown toxicity or un-

specific regulation in the environment [21].

Furthermore, whether the resulting contamination will be-
come an important environmental issue depends, in part, on

the degradation rates and transformation products of MTBE.

To achieve such objectives, the sampling protocol included

conventional and multilevel wells to have a deeper insight into

the contamination plume, which in most occasions are reported

as thin and highly strati®ed [26]. Conventional monitoring

wells, with screened intervals of 3 m or more, blend the

groundwater over the entire length of the screen. This can mask

the true concentrations and distribution of contaminants. Mul-

tilevel wells with short-screened intervals overcome this prob-

lem and offer more precise identi®cation with a better under-

standing of the three-dimensional groundwater ®ow and dis-

tribution of contaminants. Compared to multiple individual

wells, these are low cost and easy use [27].

This study also ®lls the gap indicated in a recent overview

paper [28], which pointed out that no data on TBA levels at

MTBE-contaminated sites were available due to the dif®culty

of TBA analysis at trace concentrations. In addition, no pre-

vious studies include data on potential MTBE degradation

products, importance of the depth-oriented sampling, and fate

within the aquifer.
Determination of the presence, degradation and fate of MTBE

Environ. Toxicol. Chem. 24, 2005 2787

Fig. 2. Map of methyl-tert-butyl ether–contaminated site in Düsseldorf, Germany. The monitoring wells are marked with dark gray points and the suspected source of contamination with a star. The lines of equal groundwater level measured in August 2003 are given with the height in meters above mean sea level.

with filters installed at different depths. A map of the study site with the location of the monitoring wells, distribution of the groundwater level according to measurements performed in August 2003, and the derived isohypses is given in Fig. 2. The sampling periodicity of these wells depended on the significance of the levels found in previous campaigns (see Table 1). Physicochemical properties of the groundwater were elucidated in June 2003 (Table 2) to assess the potential biological or chemical degradation of the pollutants.

Sampling and sample preparation

The U.S. EPA water sampling techniques for volatile organic compounds were used [29], except that samples were

Table 1. List of monitored wells (from east to west), sampling dates, and the total concentration of all target oxygenates (including tert-butyl alcohol) expressed in μg/L. Blank cells indicate that no sample was taken. In the multilevel (ML) wells, the maximum concentrations of the profile are reported.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>00090</td>
<td>0.59</td>
<td>1.84</td>
<td></td>
<td></td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10156</td>
<td></td>
<td>4.24</td>
<td>5.56</td>
<td></td>
<td>20.14</td>
<td>7.55</td>
<td>10.53</td>
<td>9.57</td>
<td>4.43</td>
</tr>
<tr>
<td>17/02</td>
<td>232</td>
<td>48.73</td>
<td>30.87</td>
<td>23.84</td>
<td>1,088</td>
<td>385</td>
<td>78.56</td>
<td>74.51</td>
<td>73.52</td>
</tr>
<tr>
<td>10988</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>608</td>
<td>765</td>
<td>924</td>
<td>187</td>
<td>529</td>
</tr>
<tr>
<td>ML1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.34</td>
<td>28.54</td>
<td>74.31</td>
<td>271</td>
<td>214</td>
</tr>
<tr>
<td>ML2</td>
<td>1.45</td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>15197</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.34</td>
<td>28.54</td>
<td>74.31</td>
<td>271</td>
<td>214</td>
</tr>
<tr>
<td>12452</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.44</td>
<td></td>
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<tr>
<td>10968</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.31</td>
<td>1.43</td>
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<td>10979</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.34</td>
<td>1.19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
approximately 1.0 m$^3$/h was used to recover groundwater, except in emergency well 17/02, which has its own pump at 10 m$^3$/h. Ethylbenzene, Toluene, TCE, and DCPD were added to the sample at a concentration of 0.5 mg/L during 4 min and transported directly to the GC/MS system (Trace GC coupled to a Voyager MS by ThermoQuest Finnigan, Austin, TX, USA).

Extracts were transferred onto a 75-× 0.53-mm i.d. DB-624 (J&W Scientific, Folsom, CA, USA) fused silica capillary column with a 3-μm film thickness where they were separated as described in a preceding study [24]. Detection and quantitation of target compounds were performed as depicted in previous studies [24,31], although TCE and DCPD were added to the acquisition program and another internal standard (1,2-dichlorobenzene-d$_4$) was used, as reported in Table 3.

**Quality assurance/quality control**

Fully automated purge and trap GC/MS permitted to resolve 12 target compounds in groundwater at trace levels.

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**Table 2. Physico-chemical properties of the groundwater in multilevel wells and ML1 and ML2 on the sampling of June 2003**

<table>
<thead>
<tr>
<th>Well</th>
<th>Depth (m)</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>O$_2$ (mg/L)</th>
<th>Conductivity (μS/cm)</th>
<th>Chloride (mg/L)</th>
<th>Nitrate (mg/L)</th>
<th>Nitrite (mg/L)</th>
<th>Ammonia (mg/L)</th>
<th>Sulfate (mg/L)</th>
<th>Sulfide (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML1</td>
<td>7</td>
<td>6.88</td>
<td>16.4</td>
<td>1.0</td>
<td>871</td>
<td>31</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>5.4</td>
<td>103</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>7.01</td>
<td>17.6</td>
<td>1.1</td>
<td>877</td>
<td>33</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>7.8</td>
<td>113</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>7.03</td>
<td>17.2</td>
<td>1.1</td>
<td>866</td>
<td>34</td>
<td>&lt;0.25</td>
<td>0.05</td>
<td>7.8</td>
<td>110</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>7.12</td>
<td>16.9</td>
<td>0.7</td>
<td>788</td>
<td>30</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>5.1</td>
<td>72</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7.11</td>
<td>18.3</td>
<td>0.9</td>
<td>769</td>
<td>32</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>1.1</td>
<td>85</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>ML2</td>
<td>8</td>
<td>6.76</td>
<td>14.2</td>
<td>0.8</td>
<td>856</td>
<td>36</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>6.1</td>
<td>84</td>
<td>&lt;5</td>
</tr>
<tr>
<td>10</td>
<td>6.95</td>
<td>14.7</td>
<td>0.7</td>
<td>994</td>
<td>48</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>11.3</td>
<td>102</td>
<td>&lt;5</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6.90</td>
<td>15.8</td>
<td>0.7</td>
<td>1,107</td>
<td>46</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>14.5</td>
<td>119</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6.94</td>
<td>15.8</td>
<td>0.8</td>
<td>1,070</td>
<td>47</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>17.2</td>
<td>113</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>6.93</td>
<td>14.8</td>
<td>0.9</td>
<td>1,135</td>
<td>53</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>19.4</td>
<td>121</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>6.99</td>
<td>17.6</td>
<td>0.8</td>
<td>1,086</td>
<td>54</td>
<td>&lt;0.25</td>
<td>&lt;0.02</td>
<td>9.5</td>
<td>117</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

---

**Table 3. Gas chromatography–mass spectrometry (GC–MS) in time-scheduled selected ion monitoring (SIM) acquisition program in three retention time windows: CAS number, retention time (Rt), molecular weight (MW), quantitation, and confirming ions**

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS no.</th>
<th>Rt (min.)</th>
<th>MW (m/z)</th>
<th>Quantitation</th>
<th>Selected ions (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-Butyl alcohol</td>
<td>75-65-0</td>
<td>13.11</td>
<td>74</td>
<td>59</td>
<td>Secondary: 57, 43</td>
</tr>
<tr>
<td>Methyl-tert-butyl ether-d$_4$*</td>
<td>29366-08-3</td>
<td>13.43</td>
<td>91</td>
<td>76</td>
<td>Tertiary: 77, 52</td>
</tr>
<tr>
<td>Methyl-tert-butyl ether</td>
<td>1634-04-4</td>
<td>13.51</td>
<td>88</td>
<td>73</td>
<td>Secondary: 57, 43</td>
</tr>
<tr>
<td>Diisopropyl ether</td>
<td>108-20-3</td>
<td>15.11</td>
<td>102</td>
<td>45</td>
<td>Secondary: 87, 59</td>
</tr>
<tr>
<td>Ethyl-tert-butyl ether</td>
<td>637-92-3</td>
<td>16.30</td>
<td>102</td>
<td>59</td>
<td>Secondary: 87, 57</td>
</tr>
<tr>
<td>tert-Butyl formate</td>
<td>762-75-4</td>
<td>18.10</td>
<td>102</td>
<td>59</td>
<td>Secondary: 56, 57</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
<td>20.02</td>
<td>78</td>
<td>78</td>
<td>77, 52</td>
</tr>
<tr>
<td>tert-Amyl methyl ether</td>
<td>994-05-8</td>
<td>20.52</td>
<td>102</td>
<td>73</td>
<td>55, 87</td>
</tr>
<tr>
<td>Fluorobenzene*</td>
<td>462-06-6</td>
<td>21.25</td>
<td>96</td>
<td>96</td>
<td>70, 50</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>79-01-6</td>
<td>22.88</td>
<td>130</td>
<td>130</td>
<td>132, 95</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
<td>27.97</td>
<td>92</td>
<td>91</td>
<td>92, 65</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>100-41-4</td>
<td>32.96</td>
<td>106</td>
<td>91</td>
<td>106, 77</td>
</tr>
<tr>
<td>m+p-Xylene</td>
<td>108-38-3</td>
<td>33.32</td>
<td>106</td>
<td>91</td>
<td>106, 77</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>106-42-3</td>
<td>34.51</td>
<td>106</td>
<td>91</td>
<td>106, 77</td>
</tr>
<tr>
<td>Dicyclopentadiene</td>
<td>77-73-6</td>
<td>39.43</td>
<td>132</td>
<td>66</td>
<td>132, 39</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene-d$_4$*</td>
<td>2199-69-1</td>
<td>40.35</td>
<td>150</td>
<td>150</td>
<td>152, 115</td>
</tr>
</tbody>
</table>

* International standards.
Fig. 3. Total ion chromatogram (TIC) in selected ion monitoring (SIM) mode for a 1-μg/L spiked groundwater. Compound identification number: 1 = tert-butyl alcohol (m/z = 59), 2 = methyl-tert-butyl ether-d3 (IS1: m/z = 76) + methyl-tert-butyl ether (2': m/z = 73), 3 = diisopropyl ether, 4 = ethyl-tert-butyl ether, 5 = tert-butyl formate (m/z = 59), 6 = benzene, 7 = tert-amyl methyl ether, IS2 = fluorobenzene, 8 = trichloroethylene, 9 = toluene, 10 = ethylbenzene, 11 = m+p-xylene, 11' = o-xylene, 12 = dicyclopentadiene, and IS3 = 1,2-dichlorobenzene-d4.

(Fig. 3). Limits of detection were calculated by a signal-to-noise ratio of three, and they are given in Table 4. Special consideration was given to the determination of polar MTBE degradation products, TBA and TBF, because not much data on method performance and environmental levels had been reported on these compounds in groundwater.

Simultaneous to GC/MS acquisition, the trap was programmed at 230°C during 10 min to remove adsorbed compounds (bake conditions). Using these conditions, system blanks were attained. Additionally, each analytical sequence included quality control standards and procedural blanks to check noise and background levels and possible carryover effects and to cover little retention time variations. In all cases, blank concentrations were below limits of quantitation.

The calibration equations were obtained by analyzing blank groundwater samples spiked with target compounds in a range of 0.01 to 10 μg/L and internal standards at a constant concentration of 0.5 μg/L. Linear regression of base peak area versus concentration (calculated relative to the nearest internal standard using m/z 76 for MTBE-d3, m/z 96 for fluorobenzene, and m/z 150 for 1,2-dichlorobenzene-d4) gave a good fit (typically, r² > 0.990) for all compounds. Exceeding the upper concentration range, the system suffered from memory effects and poor linearity. Therefore, in case the samples were suspected of being highly polluted, an automated dilution was analyzed to avoid system contamination. The limits of quantitation were set at the most diluted calibration standard for each compound.

For all groundwater samples, two replicates were analyzed. Different dilution factors were chosen for each sample, taking into consideration MTBE last campaign concentrations. Some of these factors were changed for the second replicate to fit the signal into linear range. Normally the average value between these two replicates is reported in the tables or figures. In all cases, the relative standard deviation was less than 20%.

RESULTS AND DISCUSSION

General remarks

The affected area originated from a leakage in the tanks of a petrol station. Foul-smelling groundwater was detected in the neighborhood and was attributed to the migration of MTBE
from oil into the aqueous phase. Added to this problem, and taking into account previous knowledge about the site and the aquifer, the groundwater under study was considered to be of poor quality, influenced by former pesticide spills and the runoff off from a former rubbish dump. Sulfate-reducing conditions are likely (see Table 2). So, the concentrations of the pollutants should be related to the activity of anaerobic microorganisms.

It is obvious that MTBE poses a problem of groundwater contamination, and detailed monitoring data are needed to determine the magnitude of this contamination to prepare remediation actions. In this study, the results were clear: MTBE was detected in 91 of 96 groundwater samples analyzed at concentrations that varied between 0.01 and 188 μg/L (measured in the conventional monitoring wells as is given in Fig. 4) and a maximum detected level of 645 μg/L at the depth of 11 m (in a multilevel well, ML1, as shown in Tables 4 and 5). Samples with high levels of MTBE contained TBA and expected because they are added to gasoline at lower levels (although the specific contents is not available in the literature), and they have a lower solubility in water (between 3 and 4 times less soluble than MTBE [11]). These values were comparable to the concentrations found in a leakage from corroded,

Table 4. Minimum, maximum, average, and median of detected levels found in Düsseldorf, Germany, contaminated groundwater samples (Nov. 01–Nov. 03, n = 96). The limits of detection (LODs) were calculated by a signal-to-noise ratio of three and the limits of quantitation (LOQs) were set at the most diluted calibration standard for each compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>LODs (μg/L)</th>
<th>No. of samples</th>
<th>≥LOQs (n = 96)</th>
<th>Min. (μg/L)</th>
<th>Max. (μg/L)</th>
<th>Average (μg/L)</th>
<th>Median (μg/L)</th>
</tr>
</thead>
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<tr>
<td>Oxygenate additives</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl-tert-butyl ether</td>
<td>0.001</td>
<td>91</td>
<td>—</td>
<td>0.01</td>
<td>645</td>
<td>67.6</td>
<td>8.70</td>
</tr>
<tr>
<td>Ethyl-tert-butyl ether</td>
<td>0.009</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>tert- Amyl methyl ether</td>
<td>0.013</td>
<td>27</td>
<td>—</td>
<td>0.02</td>
<td>0.15</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Diisopropyl ether</td>
<td>0.008</td>
<td>37</td>
<td>0.01</td>
<td>0.29</td>
<td>0.07</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Degradation products</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-Butyl alcohol</td>
<td>0.110</td>
<td>93</td>
<td>0.18</td>
<td>443</td>
<td>35.1</td>
<td>3.38</td>
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</tr>
<tr>
<td>tert-Butyl formate</td>
<td>0.034</td>
<td>7</td>
<td>0.08</td>
<td>5.42</td>
<td>1.59</td>
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* BTEX = Benzene, toluene, ethylbenzene and xylenes.
underground storage tanks in two large oil refinery factories in Tarragona (Catalonia, Spain), where concentrations ranged from 0.13 to 0.68 μg/L and from 0.20 to 1.53 μg/L of ETBE and DIPE respectively, but TAME was not detected [24]. The TBF was found in a total of seven samples during the whole monitoring study. In November 2003, it was detected at 5.42 μg/L in well ML2 at 10 m depth. However, it is not usual to detect this compound in aquatic environment. Church et al. [22] indicated that TBF was formed as an MTBE degradation product by atmospheric photooxidation due to the attack of hydroxyl radicals. Although this reaction is also possible in aqueous phase, TBF accumulation was not found in water because it was hydrolyzed readily to TBA [22]. In other studies, TBF was observed as an intermediate and it was suggested that tert-butoxy methanol (compound proposed as a first intermediate in the oxidation of MTBE but not yet observed directly) preferentially might be oxidized rapidly to yield TBF and formic acid, thus excluding the formation of formaldehyde [28].

Generally, BTEX compounds were detected at concentrations <1 μg/L. Their lower solubility and higher degradation rates could explain their low levels in groundwater. For this reason, a single spill event was considered as the main source of MTBE contamination. However, in the last sampling campaign, it was observed that some of these compounds had not been detected previously due to the application of necessary high dilution factors to avoid the MTBE contamination of the analytical system. Total BTEX was up to 9.24 μg/L in some samples from multilevel wells. In all cases, the most abundant compound detected was toluene, with a maximum concentration of 5.52 μg/L, followed by xylenes (m + p-xylene > o-xylene), ethylbenzene, and benzene. This pattern essentially fit with the conventional gasoline contents (% in volume) and their individual solubilities in water from this gasoline at 20°C: 5% toluene (25 mg/L), 10% xylenes (20 mg/L), 1.5% ethylbenzene (3 mg/L), and 1% benzene (18 mg/L) [11].

Once more, MTBE was found to be more suitable than the historically used BTEX as a tracer or indicator of long-term gasoline contamination [24]. As an example, in 2000, Davidson and Creek [35] demonstrated how MTBE played a critical role in the forensic investigation by helping establish the spill source and spill timing.

Traces of the other two volatile organic compound substances were detected at maximum concentrations of 0.06 and 1.04 μg/L for TCE and DCPD, respectively.

Most TCE in air comes from metal degreasing activities associated with tool and automobile production. At the low concentrations detected in the relatively shallow aquifer, the presence of TCE concentrations was explained by diffuse emission via soil air in the vadose zone [36]. It also could enter groundwater from industrial discharges or from improper disposal of industrial wastes at landfills. These low TCE levels did not represent an important contamination problem according to the U.S. EPA drinking water standard set at 5 μg/L (http://www.epa.gov/safewater/dwh/c-voc/trichlor.html).

Dicyclopentadiene is produced by heating crude oil products and it is used as intermediate in the manufacture of a large variety of products such as pesticides, rubbers, flame-retardant resins, etc. Dicyclopentadiene is also a minority compound in gasoline formulations, added at 0.005% v/v in the new unleaded gasoline from CEPSA, one of the first Spanish petrol companies [37]. Although, to our knowledge, DCPD

<table>
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<th>188 Jun. 03</th>
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MTBE and from 0.21 to 1.82 m downstream of the petrol station. Data from well 15197 was very useful to observe the movement of the plume, during year 2003, the contamination plume movement basically followed by means of five monitoring wells, three of them installed in November 2002 to find the center of the plume at approximately 200 m westerly from the petrol station. Data from well 15197 was very useful to observe the behavior of the pollutants. Until August 2003, MTBE concentration increased up to 166 µg/L in this point and decreased to 123 µg/L in November 2003, as shown in Figure 4. This fact indicated the movement of the MTBE plume center and proved a high persistence of this compound in the groundwater. After two years of monitoring, the MTBE concentration was practically the same as what had been detected at approximately a 100-m distance (188 µg/L in well 10688 in November 2001). Therefore, plume migration rate of the MTBE plume was calculated to be around 55 m/year. This value is not so extraordinarily high if it is compared with flow velocities, between 300 and 400 m/year, measured in a nearby BTEX-contaminated site [38,39]. In addition, this estimation depends on whether or not the center of the plume really was located.

No MTBE mass loss was observed in groundwater. According to its physicochemical properties, MTBE’s relatively low partitioning coefficient to organic carbon (K_{OC} = 41 vs. K_{OC} = 191 for benzene [40]) indicates that it will remain preferentially in the water phase instead of partitioning into soil organic matter [35]. For example, in a sand aquifer with moderate organic carbon content (0.1%), only 8% of the total mass of MTBE was sorbed to the organic matter, whereas 92% remained in solution. By contrast, 39% of the total mass of benzene and 72% of ethylbenzene was sorbed to the organic matter [41].

In addition, in anaerobic groundwater conditions (see Table 2), MTBE is more resistant to degradation than other fuel constituents [42]. Recently, the degradation of MTBE and TBA in laboratory microcosms was described [28]. Although, MTBE and TBA degradation has been reported in the presence of all environmentally relevant terminal acceptors (nitrate, sulphate, Fe(III), Mn(IV), methanogenesis, etc.), except for oxic conditions, results are controversial in literature or very limited studies have been performed so far [43,44].

When the MTBE concentration found in groundwater is between 0.2 and 3 µg/L, the source of contamination can be punctual (such as at the leading edge of the contamination plume), but it normally is considered diffuse due to atmospheric deposition or rain runoff close to urban areas or motorways [13]. This observation is confirmed by a study of the German Technical and Scientific Association for Gas and Water, which considers MTBE concentrations between 0.1 and 0.5 µg/L in groundwater as normal for areas with high motor traffic [8,45]. In fact, these intakes have been calculated recently in urban precipitation of Germany [14]. About 20% of the MTBE detected in urban runoff already is transported in the atmosphere before precipitation, whereas about 80% can be attributed to direct uptake of vehicles emissions and gasoline on road. Therefore, the MTBE concentrations detected from 0.02 to 0.38 µg/L in the most external monitoring wells (00090 and 10156 just upstream of the petrol station in the east; 10968, 10983, and 10982 downstream in the north; and 12452 and 12451 downstream in the south), which are not located in the center of the plume, can be regarded as background levels and not as significant MTBE pollution.

In contrast, the TBA plume origin cannot be clarified easily. This compound showed a similar profile as its hypothetical parental, except that its concentration seemed to be higher after two years. The highest concentration, 105 µg/L found in August 2003, was twice as much as the maximum level detected in November 2001 (44 µg/L). Methyl MTBE degradation was not the main source of TBA. For this reason, its possible presence in the contamination source and its complete solubility in water [13] could explain its occurrence in groundwater similarly to MTBE. Probably, the maximum peak of TBA concentration was not identified at the beginning of the monitoring.

In the literature, TBA is considered to be the key intermediate in the degradation of several dialkyl ethers used as fuel oxygenates, not only MTBE, but also ETBE (as indicated in a biodegradation study in France, where ETBE has been used for several years [46]). However, other authors do report that partitioning of TBA present in gasoline also may contribute to elevated concentrations in groundwater at contaminated sites. These authors concluded that TBA was added intentionally to the fuel because TBA impurities in MTBE should be below 2% [47]; however, in other cases, the low concentrations of TBA in gasoline presumably were due to impurities of fuel-grade MTBE [48]. In both studies, aqueous-phase concentrations of TBA in batch equilibrium experiments reached the high mg/L to low g/L range [28]. For Germany, the use of TBA in mixtures with methanol as fuel oxygenate has been reported at more than 30,000 tons/year in the past [13]. On the other hand and in contrast to MTBE, which almost exclusively is used as a fuel oxygenate, TBA also is a widely used solvent and intermediate in industrial processes [49], so a part of TBA found in the aquifer could have other sources. Once TBA is in groundwater, removal time under anaerobic conditions is relatively long [44,50].

Under anoxic field conditions, MTBE degradation has been shown only a few times. Most of these studies evidenced TBA accumulation in the absence of molecular oxygen [51,52]. Until today, TBA degradation has not been shown under methanogenic conditions, and it currently is accepted widely that TBA is a recalcitrant dead-end product of MTBE under these conditions [28]. Under sulfidogenic conditions, this has not yet been shown unambiguously, although Soimak et al. [53] found a stoichiometric accumulation of TBA that suggested TBA degradation to be rate-limiting in overall removal of MTBE.

In spite of these uncertainties, it can be concluded that similar behavior of MTBE and TBA was observed in the present study. Specifically, from the beginning of the survey of well 10688, both compounds decreased 70 to 80% in the first 78 d. This drop represents the movement of the pollutants through the aquifer. This means that it takes between 30 and 40 d to sweep away 50% of the initial concentrations. At a
second stage, this estimated movement slowed down from February 2002 until the end of the study.

**Multilevel wells**

The two multilevel wells (ML1 and ML2) installed at the contaminated site permitted the study of the vertical profile and evolution of MTBE and TBA plumes (see Table 5). In addition to confirm how narrow the contamination plume was, two trends have been observed since their installation in November 2002. The center of the plume (the highest detected values) had been moving from the north to the south well and also up toward the surface (from 11 m to 7 and 10 m, respectively). In August 2003, the main part of the contamination had passed through ML1 and ML2 because MTBE concentration decreased 80% (from 645 μg/L in ML1 in November 2002 to 129 μg/L in ML2 in August 2003). In November 2003, higher values were detected again in ML2 (365 μg/L), confirming the movement of the plume to the southwest.

These variations in the distribution of the contamination plume probably were displaced by slight changes in the groundwater flow direction. In August 2003, this fact was attributed to a dryer period in summer time. The Düsseldorf precipitation data from June to August in 2002 (217 mm) and 2003 (139 mm) declined in addition to higher maximum temperatures registered with differences up to 3°C (www.weatheronline.co.uk/Europe.htm).

The same profile was observed for TBA with a maximum detected concentration of 443 μg/L at 11 m for ML1 in November 2002 and a final highest level of 163 μg/L at 10 m for ML2 one year later.

Similar behavior of both compounds can be observed by studying the drop of concentrations in the multilevel well ML1 within one year (342 d). It takes between 44 and 60 d to sweep away 50% of MTBE through the aquifer and 49 to 70 d in the case of TBA.

Differences between MTBE and TBA concentrations in conventional and multilevel wells were evaluated in November 2003. A comparison among the levels obtained in mixed samples (a mixture of water from the different depths), the calculated averages (among concentrations detected in the different depths), and the nearest conventional well (15197) values was done in the last campaign. In three of the four cases, the value of the mixed sample was higher than the calculated average with differences from 25 to 40%; this might be attributed to the fact that the contamination plume is concentrated in the first filters of the well in which the water is extracted more easily than from the deeper ones. On the other hand, the values of ML2 mixed samples fitted better with the concentrations found in the conventional well 15197 (differences of 5 and 13% were calculated for MTBE and TBA, respectively) than with the calculated averages (22 and 47%, respectively). Figure 5 serves as an example.

The knowledge of the setup of the contaminated area, the hydrogeological conditions, the chemical and physical properties of the pollutant, and their spatial distribution is essential to predict the fate of MTBE, degradation products, and other gasoline oxygenates in affected groundwater tables. Selection of appropriate monitoring wells to screen both the horizontal and vertical profiles is necessary to track the contamination plume and to assess the processes (transformation, degradation, and dilution) that determine their final fate. Although MTBE may be detected at values below the odor threshold, more knowledge is needed to assess the stability of their degradation products in groundwater and to explore all contamination sources. Such information is needed for better risk assessment and decision-making.

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**REFERENCES**


