From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas

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Abstract
Recently, the occurrence and fate of pharmaceutically active compounds (PhACs) in the aquatic environment was recognized as one of the emerging issues in environmental chemistry and as a matter of public concern. Residues of PhACs have been found as contaminants in sewage, surface, and ground- and drinking water samples.

Since June 2000, a new long-term monitoring program of sewage, surface, ground- and drinking water has been carried out in Berlin, Germany. Samples, collected periodically from selected sites in the Berlin area, are investigated for residues of PhACs and related contaminants. The purpose of this monitoring is to investigate these compounds over a long time period to get more reliable data on their occurrence and fate in the different aquatic compartments. Moreover, the surface water investigations allow the calculation of season-dependent contaminant loads in the Berlin waters. In the course of the monitoring program, PhACs and some other polar compounds were detected at concentrations up to the µg/L-level in all compartments of the Berlin water cycle. The monitoring is accompanied and supported by several other investigations such as laboratory column experiments and studies on bank filtration and drinking water treatment using conventional or membrane filtration techniques.

Keywords
Contamination; drinking water; groundwater; pharmaceutically active compounds (PhACs); sewage effluents; surface water

Introduction
Ten years ago, clofibric acid, the pharmacologically active metabolite of blood lipid regulating drugs used in human medical care, was detected in ground- and drinking water samples in Berlin (Stan and Linkerhängner, 1992; Stan et al., 1994; Heberer and Stan, 1996, 1997). Meanwhile, the occurrence of the so-called pharmaceutically active compounds (PhACs) in sewage, surface and groundwater has been investigated and confirmed in several investigations (Stan and Heberer, 1997; Halling-Sørensen et al., 1998; Heberer and Stan, 1998; Daughton and Ternes, 1999). More than 50 PhACs from various prescription classes such as analgesics, antibiotics, anti-epileptics, anti-rheumatics, beta blockers, chemotherapeutics, steroid hormones, and X-ray contrast media have been detected in the aquatic environment (Stan and Heberer, 1997; Ternes, 1998; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Möhle et al., 1999; Heberer, in press). The studies show that some PhACs originating from human therapy are not eliminated completely in the municipal sewage treatment works and are, thus, discharged as contaminants into the receiving waters. Especially in urban areas such as Berlin (Germany), with high municipal sewage water outputs and low surface water flows, there is a potential risk of drinking water contamination by some polar PhACs when groundwater recharge is used in drinking water production (Heberer and Stan, 1997; Heberer et al., 1997; Heberer, in press).

In terms of two monitoring studies carried out in 1996 and 1999, several PhACs such as clofibric acid, diclofenac, ibuprofen, propyphenazone, primidone and carbamazepine were detected at individual concentrations up to the µg/L-level in the Berlin surface waters.
(Heberer et al., 1998; Heberer, in press). Other investigations have also shown a relation between the municipal sewage discharges and the contamination of Berlin surface and groundwater samples by persistent drug residues (Heberer and Stan, 1997; Heberer, in press). Thus, several compounds were also found at individual concentrations up to 7.3 µg/L in groundwater aquifers near to contaminated water courses (Heberer et al., 1997), whenever bank filtration and/or artificial ground water enrichment are used in drinking water production. A few of these compounds also occur at the low ng/L-level in Berlin tap water samples (Heberer and Stan, 1997; Heberer, in press). The results obtained from these and many other occurrence studies on PhACs provided some important information on the origin, the distribution, and the fate of these contaminants in the aquatic environment. A continuous investigation of the occurrence and fate of these compounds in all compartments of a water cycle has, however, never been carried out. Often only random samples were analyzed and sampling was not repeated.

Therefore, a new long-term monitoring program of sewage, surface, and drinking water is currently carried out in Berlin, Germany. As described in the following section, the city of Berlin represents an excellent location to study the occurrence and fate of PhACs in the water cycle of an urban environment. In the course of the monitoring program, samples collected periodically from selected sites in the Berlin area are investigated for residues of PhACs and some other polar contaminants. The purpose of this monitoring, carried out in co-operation with the Senate of Berlin and the Berlin water works (BWB), is to investigate these compounds over a long time period to get more reliable data on their occurrence and fate in the different aquatic compartments. Moreover, the surface water investigations allow the calculation of season-dependent contaminant loads in the Berlin waters. The monitoring is accompanied and supported by several other investigations such as laboratory column experiments (Scheytt et al., 2001), studies on bank filtration (Heberer et al., 2001b) and investigations of drinking water treatment using conventional or membrane filtration techniques (Heberer et al., 2001a, submitted; Drewes et al., 2001). This paper presents first results from the monitoring program for PhACs in the Berlin water cycle which started in June 2000 and some preliminary results from the bank filtration study at lake Wannsee.

**Description of the Berlin (Germany) water cycle**

The contamination of the surface waters by municipal wastewater discharges is of great relevance in the Berlin area. High concentrations of sewage contaminants are found in the receiving waters due to the high proportions of municipal sewage effluents in the surface waters. These result from low surface water flows and from the large amounts of raw sewage produced by its population of around four million people. On the other hand, Berlins most important waterways the Havel and the Spree river have average flow rates of only 35 and 13 m³/s, respectively. Due to the high proportions of bank filtrate and artificial ground water enrichment of approximately 75% used in drinking water production in Berlin (SenSUT, 1997) polar organic compounds such as residues from pharmaceutically active compounds (PhACs) and pesticides may under unfavorable conditions leach into the ground water aquifers (Heberer et al., 1998). Thus, polar organic contaminants have been detected at concentrations up to the low µg/L-level in ground water wells near to the contaminated surface waters (Heberer and Stan, 1997; Heberer, in press).

Figure 1 shows a map of Berlin and its important lakes, rivers and canals. This map also shows the locations and drainages of the sewage treatment plants (STPs), the sampling locations of the surface water monitoring carried out since June 2000, and the two newly constructed transects at the Havel river (Heberer et al., 2001b). In total, the municipal area of Berlin includes an area of 889 km²: 59 km² are used for agriculture, 155 km² are forests
and a total water area of 57 km² consists of several rivers, approximately 60 lakes (>1 ha) and about 500 natural ponds (SenSUT, 1997, 1999). Berlin’s most important rivers, the Spree and the Havel, are typical shallow and slow flowing lowland rivers with a mean water depth of 7 m (max. depth: 16 m). The Spree river enters Berlin from the south-east, passes through the whole city and discharges into the Havel river in the north-western districts of Berlin. The Havel river enters Berlin from the north-west and leaves the city in a south-west direction.

The municipal sewage produced in the Berlin area is purified by six (formerly seven) STPs. With regard to their capacities, Berlins most important STPs are located south of Berlin in Waßmannsdorf and in the north-west of Berlin in Ruhleben. During autumn and winter time, the sewage effluents from the STP in Ruhleben are discharged into the Spree river which merges with the Upper Havel river. From April to September (bathing season), the Teltowkanal, a canal in the south of Berlin (shown in Figure 1), is fed via a force main by additional effluents from Berlin’s largest STPs in Ruhleben. In several small brooks located in inner city districts, downstream of STPs, the mean proportions of sewage in the surface waters are very high (SenSUT, 1999).

The Teltowkanal carries the highest loads of sewage effluents being discharged into the canal by Berlin’s two largest STPs (Waßmannsdorf and during spring and summertime Ruhleben) and by the STPs in Stahnsdorf. Until September 1999, the STPs in Marienfelde also discharged their effluents into this canal. At several locations in the canal, municipal sewage effluents account for up to 40% of the average surface water flow (SenSUT, 1999). Under extreme conditions (dry periods with low surface water flows), the proportions of municipal sewage may reach up to 84% (SenSUT, 1999). With regard to contaminations from municipal sewage discharges, the canal represents a scenario that may be called a “worst-case situation”. This is also the reason why many of the sampling sites selected for the surface water monitoring studies are located in the Teltowkanal (Figure 1). The other sampling sites are located in the Havel river to consider the loads of PhACs entering Berlin.

**Figure 1** Map of Berlin, Germany, showing the waterways, the medium flow rates (in m³/s), the sewage treatment plants (STPs) and their sewers, the proportions of sewage in the waterways (for average discharge in dry water), the sampling sites of the new surface water monitoring program, and the locations of the two newly constructed transects at the Havel river (on the left).
(locations 225 and 305) and the loads discharged into the Spree River and the Upper Havel river (locations 325 and 330).

Results from the investigation of PhACs in the aquatic system of Berlin

PhACs in municipal sewage effluents

Several PhACs were observed in repeated investigations of 24 h composite samples from different STPs in Berlin (Heberer, in press). More than 20 PhACs and several similar compounds detected in several investigations of STPs in Berlin. Residues of pharmaceuticals from various prescription classes such as blood lipid regulators, analgesics, bacteriostatics, and anticonvulsants were detected up to the µg/L-level in the effluents of the sewage treatment plants in Berlin (Heberer, in press). However, synthetic estrogens such as 17α-ethinylestradiol and mestranol were only detected at trace-level concentrations in the sewage effluents of the Berlin STPs because of their low total amounts in annual prescription. Otherwise, the “phytoestrogen” β-sitosterol was found at average concentrations of 1.9 µg/L in the effluents from Berlin's STPs (Heberer, in press). The estrogenic potential of this compound is, however, very low compared with the above mentioned compounds.

As shown in Table 1, PhACs such as clofibric acid, the anti-epileptic drug carbamazepine and the analgesic drug diclofenac were not (or only to a very small extent) removed during sewage purification. On the other hand, caffeine, also originating from PhACs but to a larger extent from beverages and often used as indicator compound for the presence of municipal sewage in the aquatic system, was found to be readily biodegradable and removed by more than 99.9% in Berlin's STPs. Some PhACs were found in the sewage effluents at concentrations similar or even larger than those of compounds often described as markers for municipal sewage in surface waters, e.g. caffeine or coprostanol (metabolite of cholesterol). The studies of the PhACs showed that some of them are much better suited as marker compounds for municipal sewage than the classical organics because of their persistence in the STPs and in the aquatic environment (Heberer, in press).

PhACs in Berlin's waterways (new results from the surface water monitoring)

Residues of PhACs were identified as important pollutants in a monitoring study carried out in Berlin, Germany, in 1996 (Heberer et al., 1998). Samples were collected from 30 sampling locations upstream and downstream from municipal sewers. The impact and the extend of contamination by the sewage discharges showed the need for further investigations to get more reliable data on the occurrence and fate of these residues in the aquatic system. In 1999, further studies on the occurrence of PhACs (Heberer, in press) were carried out. Additionally, a new long-term monitoring program of sewage, surface, and drinking water for PhACs and several other emerging organic contaminants was initiated in June 2000. In terms of this monitoring program, samples are collected periodically from selected sites in the Berlin area (Figure 1). Some positive findings of PhACs obtained from the first

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Average influent concentration in µg/l</th>
<th>Average effluent concentration in µg/l</th>
<th>Removal rate in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamazepine</td>
<td>1.78</td>
<td>1.63</td>
<td>8</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>0.46</td>
<td>0.48</td>
<td>–**</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>3.02</td>
<td>2.51</td>
<td>17</td>
</tr>
<tr>
<td>Caffeine</td>
<td>230</td>
<td>0.18</td>
<td>&lt; 99.9</td>
</tr>
</tbody>
</table>

* STPs in Berlin: Ruhleben, Schönerlinde, Waßmannsdorf (mixed samples: 24 hours, sampling series in May–December 1999). ** – : no removal was observed
three sampling series in June, September, and December 2000 are compiled in Table 2. Several PhACs have been detected at individual concentrations up to 2 µg/L in Berlin’s waterways.

More interesting than the total figures are the concentration profiles of the individual compounds measured at the different sampling locations in the Teltowkanal, the Havel river, and the connecting waterways. Therefore, the concentration profile for carbamazepine is shown in Figure 2. As expected from the preliminary studies in 1996 and 1999, the highest concentrations for the PhACs were found in the Teltowkanal. Nevertheless, the total loads in the Havel river may be similar or even higher due to the higher flow rates. This question will be clarified when the loads are calculated. But some other interesting aspects can already be drawn from these figures. At sampling location no. 225 in the Dahme river (Figure 1) PhACs were only detected at very low concentrations or not at all. This confirms that the high concentrations of PhACs detected in the Teltowkanal are almost totally caused

Table 2  Concentrations of PhACs and caffeine detected in terms of the surface water monitoring in Berlin, Germany. Results from the sampling series carried out in June, September, and December 2000. n.d.: not detected

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentrations in ng/l</th>
<th>Compound</th>
<th>Concentrations in ng/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anonymous*</td>
<td>n.d. – 830</td>
<td>Mefenamic acid</td>
<td>n.d. – 20</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>25 – 1075</td>
<td>Naproxen</td>
<td>n.d. – 95</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>n.d. – 450</td>
<td>Oxazepam</td>
<td>n.d. – 70</td>
</tr>
<tr>
<td>Caffeine</td>
<td>80 – 265</td>
<td>Pentoxifylline</td>
<td>n.d. – 30</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>n.d. – 1030</td>
<td>Primidone</td>
<td>n.d. – 635</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>n.d. – 55</td>
<td>Tolfenamic acid</td>
<td>n.d. – 20</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>n.d. – 65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* This compound cannot be identified because of potential legal ramifications but a publication is planned (Reddersen et al., in prep.)

Figure 2  Concentration profile of carbamazepine in the Teltowkanal and the Havel river determined at three different sampling series in June, September, and December 2000 (06, 09, 12, 2000). The arrows labeled with Teltowkanal and Havel rivers show the flow direction of the waterways. Sampling location 355 (Figure 1) is in lake “Kleiner Wannsee” which connects the Teltowkanal with lake “Großer Wannsee” (Havel river)
by discharges of sewage effluents into the canal. Peak concentrations were observed where purified municipal sewage was discharged by the STPs. Generally, the impact of sewage effluents on the surface water quality was found to be much more significant for the PhACs than for any of the common chemical parameters (Heberer et al., 1998).

Another very interesting question is the fate of the drain from the Teltowkanal. For many years, it was assumed that the main flow direction of the Teltowkanal is into the lake Griebnitzsee and finally into the Lower Havel River (Figure 1). Today, it is clear that the main flow direction is into lake “Kleiner Wannsee” which connects the Teltowkanal with lake “Großer Wannsee” (Havel river). As shown in Figure 2, the concentrations of the anti-epileptic drug carbamazepine in lake “Kleiner Wannsee” (no. 355) are almost as high as those detected at the end of the Teltowkanal (location no. 425) and much higher than those detected in the Havel river. Thus, the surface water from lake “Kleiner Wannsee” mainly consists of water from the Teltowkanal which is then discharged into the lake “Großer Wannsee”. This effect is very important as it shows that the surface water quality of lake “Großer Wannsee” is not only affected by the Havel river but also to a high extent by the Teltowkanal. The surface water quality of lake “Großer Wannsee” is important for public drinking water supply because the waterworks in Beelitzhof, located near this lake, produce more than 60% of their drinking water from bank filtrate (Heberer et al., 2001b). Additionally, the lake is used for recreational activities (e.g. open air bath, water sports).

The concentration profiles of the PhACs also show some seasonal differences, especially, between the sampling series in June and December 2000. During autumn and winter, the sewage effluents from the STP in Ruhleben are discharged into the Spree river which merges with the Upper Havel river. From April to September (bathing season), the Teltowkanal is fed via a force main by additional effluents from the STPs in Ruhleben. The switching of the force main can be seen very clearly looking at the concentrations of the PhACs at locations no. 415 and 420 in Figure 2. The increase of the concentrations observed in the sampling series in June 2000 was missing in December whereas the concentrations of the PhACs detected in the Havel river are increasing.

The concentration profiles of the PhACs are very similar. Nevertheless, the total amounts of diclofenac detected in December are much higher than those detected in June or September. This may be caused by an enhanced photodegradation of diclofenac as also described by Buser et al. (1998). This may, however, more likely be due to a higher consumption of the analgesic and anti-rheumatic drug diclofenac during winter! This assumption is also supported by the results of several other analgesics showing a similar distribution pattern and also higher winter loads. This and several other questions will be answered in the following sampling series.

Fate and transport of PhACs during bank filtration

Several PhACs have also been detected up to µg/L concentrations in wells from different bank-filtration sites in Berlin (Heberer in press). In 2001, a new scientific project has been initiated to investigate the natural attenuation of pharmaceutical residues and several other environmentally relevant contaminants systematically under natural conditions at different bank-filtration sites in Berlin (Heberer et al., 2001b). This research is carried out in cooperation with the Senate of Berlin (Department of Urban Development, Environmental Protection and Technology) and the Hydrogeology Research Team of the Free University Berlin. Both transects (“Lieper Bucht” and “Wannsee”) were built along the Havel River (Figure 1). Some preliminary results obtained for samples collected in April 2001 from the “Wannsee” transect are presented by Heberer at al. (2001b). A small compilation of results is also shown in Table 3.
Seven PhACs, namely anonymous (cannot be identified because of potential legal ramifications), bezafibrate, carbamazepine, clofibric acid, diclofenac, primidone, and propyphenazone, were only detected in the shallow wells but not in the deep wells. Several compounds, such as bezafibrate and diclofenac seem to be removed effectively during bank filtration (Heberer et al., 2001b). But carbamazepine, clofibric acid, primidone, propyphenazone, and anonymous were also present at concentrations of as much as 100 ng/L in the water-supply wells.

**Conclusions**

PhACs are found as very persistent residues at the µg/L level in the effluents of Berlin’s municipal STPs. These residues are discharged into the surface waters where they are also detected at concentrations up to the µg/L level in samples collected from several canals, lakes, and rivers. Especially, several of the polar PhACs were identified as excellent markers for sewage contamination in surface and ground waters because of their persistence in the aquatic environment. Whenever bank filtration or other methods for groundwater recharge are used in drinking water production, these compounds can leach from the contaminated watercourses into the groundwater aquifers and may also appear at trace-level concentrations in drinking water.

**Outlook**

The monitoring study of Berlin’s surface water already revealed some important information on the occurrence, seasonal distribution, and fate of sewage contaminants such as PhACs in the aquatic environment. Depending on further funding, the study will be continued until the end of 2003 to obtain some long-term results, to recognize certain trends, and to get much more reliable data on the loads of the PhACs in the water cycle. Additionally, the study will be combined with and supported by several other investigations such as laboratory column experiments (Scheytt et al., 2001), studies on bank filtration (Heberer et al., 2001b), and investigations of drinking water treatment using conventional or membrane filtration techniques (Heberer et al., 2001a; Drewes et al., 2001).

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