"OCCURRENCE AND BEHAVIOUR OF TRACE SUBSTANCES IN THE PARTLY CLOSED WATER CYCLES OF BERLIN AND ITS RELEVANCE TO DRINKING WATER"

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ABSTRACT

The daily use of pharmaceutically active compounds and industrial chemicals results in significant effects of trace substances on the environmental media water and soil. Despite effective treatment in the wastewater treatment plants, the load of trace substances on the environmental media is approximately half of the former load in raw sewage. Therefore, trace substances are present in the partly closed water cycles of Berlin.

Berlin has sensitive water bodies with different aspects, e.g. low flow rates, high portions of advanced treated wastewater in the partly closed water cycles and a shallow fresh water aquifer. The water supply system is based on bank filtration and artificial groundwater recharge, and thus a water treatment process close to nature without chemicals can be maintained. Further, no disinfection is necessary.

Several trace substances are removed effectively during bank filtration. Due to higher sludge concentrations and sludge ages, membrane bioreactors show a slightly better performance for the removal of these compounds. Sorption, membrane filtration or oxidation processes can be introduced as a further treatment step at the wastewater treatment plants. For further removal, conventional and new treatment processes have to be applied.

Pharmaceuticals, hormone-disrupting chemicals and cosmetics are not considered to be relevant for drinking water supply due to the low risk level. But there is the need for research activities in terms of the effects of trace substances and the mixture of several compounds on aquatic life or soil organisms.

Measures for minimising the emissions of trace substances in the environment can only be achieved by the implementation of certain targeted minimising strategies in consideration of the application areas. In particular the understanding of the population of the environmental dangers from the use of trace substances is of highest importance. Despite all efforts to protect our environment, a substantial amount of trace substances will also continue to pollute the environment in the future.

Considering the challenge of water management in Berlin, the large research program NASRI "Natural and Artificial Systems of Recharge and Infiltration", which is oriented towards the specific requirements in Berlin, has already been launched. This concerted research action was developed to study in detail all relevant processes in bank filtration and artificial groundwater recharge concerning the hydro-geological conditions and chemical and microbiological quality. The outcome will be a sound basis for optimized operation of existing sites and for the integrated design of new field sites all over the world.

KEYWORDS

Trace substances, partly closed water cycle, drinking water, risk assessment,

TRACE SUBSTANCES AND PATHWAYS INTO THE WATER BODIES

The development of our industrial society has brought about inestimable improvements in human living conditions. But this was accompanied by the development of countless substances and products made for limited-period use, e.g. pharmaceuticals and industrial chemicals. After expiry of the useful life of the products, these substances get into the environment, possibly in modified form. Due to their qualities and their effects, which are partly long term (persistent), the term "problematic substances" was created for them. Since they are occur only in small quantities they are designated trace substances. Regarding the environmental media, water is of highest importance in connection with micro-pollutants because of its function as dissolving agent and means of transport as well as food.
The following emission pathway into the water cycle has to be particularly mentioned:

- Urine and faecal matter in unchanged or metabolised form, improper disposal of substances into toilets and after wastewater collection, leaking sewerage systems, combined sewer overflows, municipal wastewater treatment plants (WWTPs), industrial WWTPs and infiltration plants for rainwater and treated sewage (small WWTPs).
- Recent statistical data on wastewater disposal in Germany shows that 83.4 % of the domestic wastewater are discharged into surface waters via central sewerage systems and WWTPs, while 9.7 % get into the water bodies without being treated, and 6.9 % are infiltrated into soil via decentralized wastewater disposal plants. The share of wastewater infiltrating into the soil through leaking sewers might not be more than 1 % [Dohmann, 2003].

The emissions pathway of pharmaceuticals, which can appear also as hormone disrupting chemicals are shown in Figure 1.

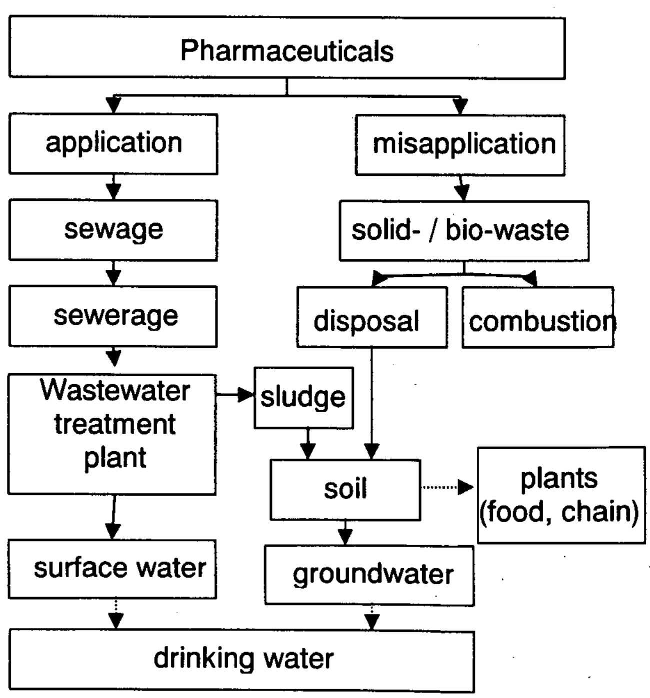

Figure 1 Pathways of pharmaceuticals into the water bodies

BERLIN'S WATER SITUATION AND WATER SUPPLY SYSTEM WITH PARTLY CLOSED WATER CYCLES

Water situation

Approximately 6% of the area of Berlin consists of freshwater (see Figure 2): lakes (e.g. Schlachtensee), river lakes (e.g. Tegeler See, Müggelsee, Wannsee), rivers (e.g. Panke, Wuhle, Erpe), regulated rivers (e.g. Spree, Havel and Dahme) and canals (e.g. Landwehrkanal,

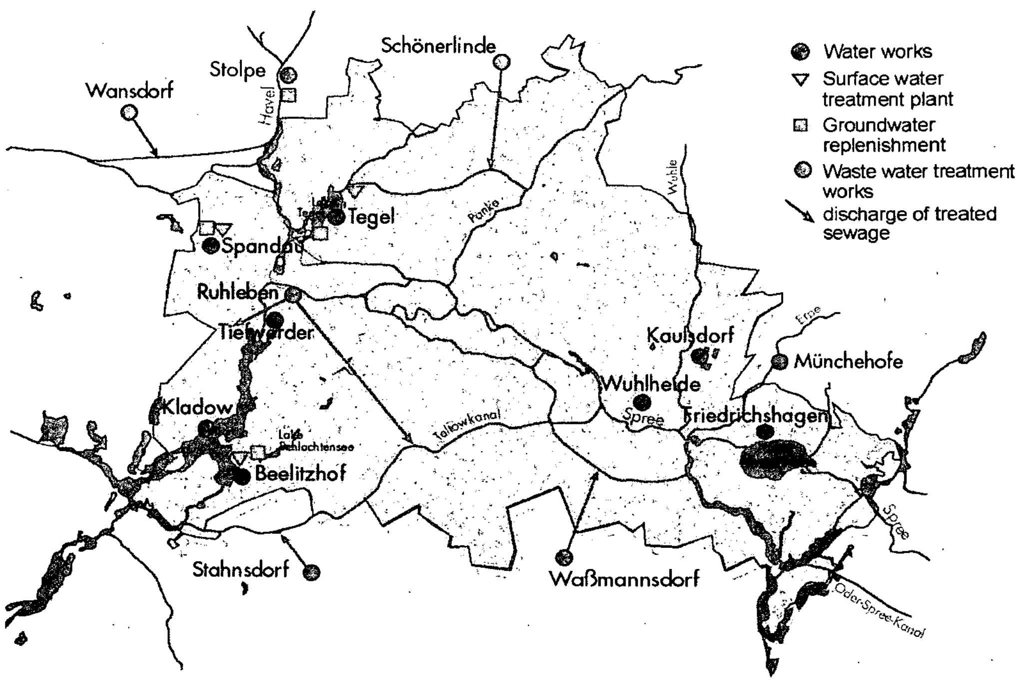

Figure 2 Map of water bodies, water works and treatment plants in the Berlin region

Teltowkanal). The flow rates through Berlin are low (approximately 50 m^3/s) and unsteady and for the river Spree decreasing, because of the closure of open lignite mines from which approximately 1 billion m^3 per year of water was pumped into this river. That means: higher portion of treated wastewater in the receiving waters and longer retention time of the surface water of our regulated rivers and increasing problems with the water quality, particularly in summer when the flow rates of the rivers is very low. The water bodies are therefore very sensitive.

The water bodies are intensively used for different purposes. For the population of the region the water bodies have a high value for recreation but on the other hand they are used economically such as inland fishery and waterways and are important also for water supply. In addition to that, the water bodies are recipients for treated sewage and stormwater from separate system and overflow of the combined sewer system.

Approximately 680 000 m^3 per day of treated municipal wastewater were discharged into the water bodies of the Berlin region in 2002. As a result of the discharge of treated wastewater the water bodies are loaded with nutrients - phosphorus and nitrogen -, ammonia, the bacteriological load, residual organic compounds, particular non-biodegradable compounds and sulphates and chlorides. Investigations have shown that the concentration and the load of several constituents of urban stormwater from the separate sewer are very high. Zinc, lead, copper, aluminium, iron, organic compounds, phosphorus, filterable solids, suspended substances with adsorbed anthropogenic pollutants - heavy metals and organic micropollutants (e.g. PAH and PCB) - and the bacteriological load, which varies depending upon location, in the storm drainage are an important pollution factor [Heinzmann, 1994]. The quantity of annual stormwater discharge into the water bodies of Berlin is estimated to be at about 60 million m^3 for a mean annual quantity of precipitation of approximately 600 mm.

The quantity of combined sewer overflow at pumping stations is approximately 1 million m^3 per year and of stormwater tanks approximately 3 million m^3 per year. The total quantity of combined sewer overflow is estimated at approximately 7 million m^3 per year. In general, organic substances, ammonia, aluminium, some heavy metals (in decreasing concentrations: zinc, iron, copper, lead, manganese and chromium), and phosphorus and the bacteriological load (in-house investigations) in the overflow of the combined sewer system are an important pollution factor for the water bodies.

Water supply

The glacial sediments found in Berlin and in the surrounding represent excellent aquifers and the vulnerability of the groundwater is obviously high. As a consequence the City of Berlin has been able to sustain its own water supply for several decades based on these following principles:

- The inhabitants of Berlin, just about 3.4 million, are supplied with drinking water by its own groundwater resources exclusively.
- 100% of public water supply in the Berlin metropolitan region comes from groundwater with a contribution of approximately 70% from bank filtration and artificial recharge. The use of bank-filtered water for drinking water supply is very important due to the limited available quantity of natural groundwater. The fresh water aquifer in Berlin is very shallow and beneath an impermeable till layer a huge salty groundwater reservoir follows. At several parts of the city the aquitard between the fresh water aquifer and the salt-water aquifer has holes were salt water is upcoming. The water works has to balance very carefully their pumping regime in order to avoid salt-water intrusion into the fresh water aquifer. No surface water is used in a direct way.
- Regular monitoring investigations for groundwater as well as for surface water are carried out intensively.
- For drinking water treatment only simple techniques (water intake - aeration - manganese and iron removal through filtration) are used. No disinfection is needed. A water treatment process close-to-nature without chemicals can be maintained.

Partly closed water cycles

The Berlin Water works are located nearby the surface water system. Their discharging wells are drilled mostly at a short distance (1 - 600 meter) around the rivers and lakes near the bank to extract bank-filtered surface water. Depending on the location of the water works and the discharge points of for treated sewage and stormwater from separate system and overflow of the combined sewer system, the intensive use of the water bodies for different purposes results in a partly closed water cycle (see Figure 4), which follows a succession of utilisation: water intake - drinking water supply - sewage and stormwater treatment - dilution and self purification in the remaining waters - bank filtration and groundwater replenishment - water intake. Treated wastewater has an influence on the composition of the groundwater and bank-filtered water, particularly in summer, when the flow rate of the Spree River is very low. There is a strong influence of the water works Beelitzhof because a part of the water usually flows from the Teltow canal into the Wannsee (see Figure 2). The drinking water generated at the water works in Tegel is influenced by treated wastewater of the WWTP Schönerlinde throughout the year (see Figure 2). Highest portion of about 17 - 35 % (mean values, 1993-1998) of advanced treated wastewater are determined in the lake. In addition; one of the largest water works of Berlin (water works Tegel) extracts lake water (80 %) via bank filtration and artificial groundwater recharge. Thus, in Tegel's drinking water it was found that advanced treated wastewater portions were calculated to be 14 – 28 % (mean values, 1993-1998) [Ziegler; 2001]. Because 100 % of the advanced treated wastewater is not recycled at any of these water catchments areas, we do not have a closed water cycle in Berlin. There is no water cycle for the water works Friedrichshagen.

For this reason we have to take sure that these partly closed water cycles are hygienically acceptable and doesn't harm the receiving waters in this densely populated area with approximately 4.3 million people. If we have partly closed water cycles we can not avoid the existence of trace substances at the moment. Berlin's water system with indirect wastewater reuse is limited in its (self-)purification capacity, especially when looking at these persistent, polar organic compounds.

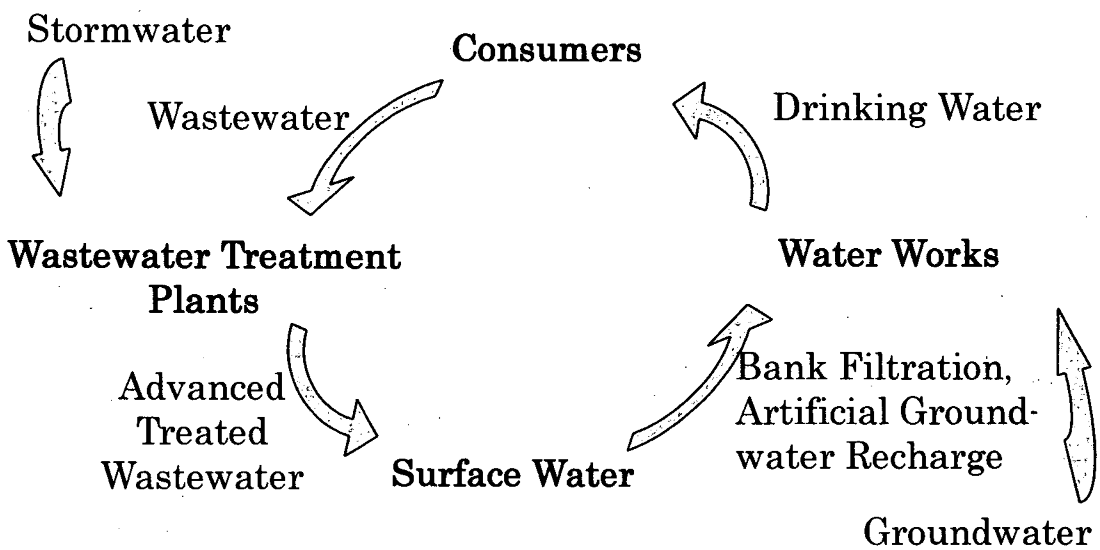

Figure 3 Partly closed water cycle

OCCURRENCE AND BEHAVIOUR OF TRACE SUBSTANCES PARICULARLY PHARMACEUTICALLY ACTIVE COMPOUNDS (PHACS) IN THE AQUATIC SYSTEM OF BERLIN

PhACs in municipal sewage effluents

Several PhACs were observed in repeated investigations of 24h composite samples from different WWTPs in Berlin [Heberer, 2002]. More than 30 PhACs and several similar compounds detected in several investigations of WWTPs 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 WWTPs in Berlin. However, synthetic estrogens such as 17a-ethinylestradiol and mestranol were only detected at trace-level concentrations in the sewage effluents of the Berlin WWTPs because of their low total amounts in annual prescription. Otherwise, the "phytoestrogen" ß-sitosterol was found at average concentrations of 1.9 μg/L in the effluents from Berlins WWTPs. The estrogenic potential of this compound is, however, very low compared with the above mentioned compounds.

Table 1. Concentrations and removal rates for three drug residues and for caffeine detected in composite samples (24h) of influents (n=10...20) and effluents (n=20...27) from different WWTPs in Berlin* [Heberer, 2002].

Analyte	Average influent concentration in μg/l	Average effluent concentration in μg/l	Removal rate in %
Carbamazepine	1.78	1.63	8
Clofibric acid	0.46	0.48	- **
Diclofenac	3.02	2.51	17
Caffeine	230	0.18	> 99.9

* WWTPs in Berlin: Ruhleben, Schönerlinde, Waßmannsdorf (mixed samples: 24 hours, sampling series in May-December 1999). ** - : no removal was observed.

As exemplarily shown in 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 Berlins WWTPs. 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 WWTPs and in the aquatic environment [Heberer et al., 2002].

PhACs in Berlins water ways (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 the discharged points of advanced treated sewage. 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 behaviour of these residues in the aquatic system. In 1999, further studies on the occurrence of PhACs [Heberer, 2002] 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. Some positive findings of PhACs obtained from the first 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 Berlins 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. 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 has been clarified by calculating the PhAC loads. But some other interesting aspects can already be drawn from the PhAC concentrations. At the sampling location in the Dahme river PhACs were only detected at very low concentrations or not at all, whereas high concentrations of PhACs were detected in the Teltowkanal caused by discharges of sewage effluents into the canal. Peak concentrations were observed where purified municipal sewage was discharged by the WWTPs. 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].

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.

Compound	Concentrations in ng/l	Compound	Concentrations in ng/l
Amdoph*	n.d. – 830	Mefenamic acid	n.d. – 20
Carbamazepine	25 – 1075	Naproxen	n.d. – 95
Clofibric acid	n.d. – 450	Oxazepam	n.d. – 70
Caffeine	80 – 265	Pentoxifylline	n.d. – 30
Diclofenac	n.d. – 1030	Primidone	n.d. – 635
Gemfibrozil	n.d. – 35	Propiphenazone	n.d. – 1970
Ibuprofen	n.d. – 55	Tolfenamic acid	n.d. – 20
Ketoprofen	n.d. – 65		

* This compound has been identified as a metabolite of a pharmaceutical substance originating from a source at the Upper Havel River outside of Berlin [Reddersen et al., 2002].

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 WWTP 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 pressure pipe-line by additional effluents from the WWTP in Ruhleben. The switching of the force main can be seen very clearly looking at the concentrations of the PhACs [Heberer, 2002]. The concentration profiles of the different PhACs are very similar. Nevertheless, the total amounts of diclofenac detected in December are much higher than those detected in June or September. This is mainly caused by an enhanced photodegradation of diclofenac as also described by Buser et al. (1998).

Behaviour 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, 2002]. 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., 2001]. 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. Some preliminary results obtained for samples collected in April 2001 from the "Wannsee" transect are presented by Heberer et al. (2001). A small compilation of results is also shown in Table 3. Higher concentration found for amdoph in groundwater are due to former infiltration of amdoph from a pharmaceutical plant upstream from the bank filtration site. The average concentration for carbamazepine and primidone are equal or higher in surface water compared to groundwater.

Seven PhACs, namely amdoph (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, 2001]. But carbamazepine, clofibric acid, primidone, propyphenazone, and amdoph were also present at concentrations of as much as 100 ng/L in the water-supply wells.

Table 3. Concentrations/concentration ranges of some PhACs detected in the surface water of lake Wannsee and in the shallow wells and deep wells from the bank filtration site "transect Wannsee" [Heberer et al., 2001], Berlin, Germany, April, 2001.
[n.d.: not detected; detection level, 1 to 10 nanograms per liter; data are reported in nanograms per liter]

Analyte	Surface water	Shallow wells	Deep wells	Water supply well
Amdoph*	200	135 – 350	n.d.	100
Bezafibrate	170	n.d. - 20	n.d.	n.d.
Carbamazepine	235	160 - 360	n.d.	20
Clofibric acid	50	n.d. – 60	n.d.	70
Diclofenac	50	n.d. – 40	n.d.	n.d.
Primidone	105	195 – 535	n.d.	15
Propyphenazone	280	10 – 170	n.d.	50

* This compound has been identified as a metabolite of a pharmaceutical substance originating from a source at the Upper Havel River outside of Berlin [Reddersen et al., 2002].

OCCURRENCE AND BEHAVIOUR OF IODINATED X-RAY CONTRAST MEDIA IN THE AQUATIC SYSTEM OF BERLIN

Triiodinated benzene derivatives are widely used as X-ray contrast media by intravenous injection. The triiodinated compounds enhance the contrast between organs and the surrounding tissues and enable visualization of organs which otherwise could not be investigated. The compounds are very stable and hydrophilic and are excreted unchanged after some hours of application. The required properties for the application to humans are a disadvantage form the environmental point of view. WWTPs are not able to remove the compounds and thus they are recharged into the receiving surface waters. The concentration of organic iodine compounds, measured as adsorbable organic iodine (AOI), in the effluent of Berlins largest WWTP varies between 50 and 140 μg/L (24 h mixed samples) [Oleksy-Frenzel et al., 2000] and thus, high concentrations of iodinated X-ray contrast media are expected to occur in the receiving waters. Within a partly closed water cycle the AOI decreases, e.g. from 33 μg /L in the initial receiving channel down to 12 μg /L in a receiving lake. A further AOI decrease is recognized during anoxic bank filtration down to 2 to 3 μg/L AOI. Under oxic bank filtration condition the AOI stays nearly constant. Besides monitoring of the sum parameter AOI the concentration of selected iodianed X-ray contrast media were quantified [Putschew et al., 2000, 2001a,b; Putschew and Jekel, 2003; Schittko et al., 2004]. All selected contrast media (Iopromide, Iopamidol, Diatrizoat, Iohexol) are detectable in the influenced partly closed water cycle. The concentration of the compounds in the receiving lake is in the upper ng/L range (e.g. Iopromide 860 ng/L, Diatrizoate 960 ng/L, mean values n=10). During anoxic bank filtration the concentrations are decreased and, in the raw drinking water concentrations in the lower ng/L range are determined (e.g. Iopromide 17 ng/L, Diatrizoate 140 ng/L). Even in the finished drinking water low concentrations of contrast media were detectable.

Comparison of AOI with the single compound concentrations indicates, that the iodinated compounds are transformed during anoxic bank filtration, whereby the transformation products are still iodinated. By LC-ICP-MS analysis, conducted to trace unknown iodinated compounds, some unknown compounds could be detected. Beside the fact, that the ecotoxicological relevance of the transformations product are unknown the emission of the iodinated compounds should be reduced as far as possible e.g. by collection hospital wastewater or separated urine.

REMOVAL OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) OUT OF WWTP EFFLUENTS

Wastewaters from houses and hospitals are usually discharged into the sewers and reach the municipal WWTP. Consequently, persistent organic compounds originating from personal care products and pharmaceuticals are being treated in the plant. Depending on their specific properties, they are biodegraded, adsorbed on activated sludge and removed with the excess sludge, stripped out during aeration or leave the plant and appear in the WWTP effluent. Especially extremely polar substances like iodinated X-ray contrast media and neutral compounds like the pharmaceuticals carbamezapine and diclofenac will pass a conventional activated sludge treatment with only minor reduction. If the adjacent water bodies are a further source of water supply, measures have to be taken to remove these compounds out of the WWTP effluent. The situation is as follows:

- The investigated organic compounds usually have a low molecular weight with a maximum of 500 g/M.
- The compounds have a neutral to polar character.
- The compounds appear in a matrix with an organic spectrum of natural organic matter.
- Concentrations of salts can be somewhat elevated.

As a first step, it can be tried to avoid the discharge of these compounds into the water. This can include a separated treatment of hospital effluents as well as a decentralized wastewater treatment with urine separation. However, this is not always feasible and consequently conventional and new treatment processes have to be applied. Due to higher sludge concentrations and sludge ages, membrane bioreactors (MBR) show a slightly better performance for the removal of these compounds. Nevertheless, their application can not avoid the release of these compounds into the aquatic environment. Sorption, membrane filtration or oxidation processes can be introduced as a further treatment step at the WWTP effluent.

Sorption processes:
It is possible to remove organic compounds by sorption on activated carbon or metal oxides. Usually, non-polar substances have a better affinity to the sorption material. Most polar and therefore persistent substances will remain in the water phase. Moreover, high molecular humic substances will cover the sorption places and avoid the transfer of the adsorbent agents into the pores of the activated carbon. Regarding the amount of WWTP effluent to be treated, a treatment by sorption is not feasible in large scale plants.

Membrane filtration:
The aim is to separate polar and small molecular weight compounds. Consequently, a filtration with a low molecular weight cut off like reversed osmosis or nanofiltration processes have to be applied. These techniques will also reject salts and therefore not only fouling (clogging the membrane by organic and inorganic compounds), but also scaling (exceeding the solubility product and precipitation of salts in the concentrate) will occur. The permeate has a low content of salts and quite corrosive. Moreover, even in a multi stage system, 10 % of the influent will reappear in the concentrate stream and has to undergo further treatment. These filtration processes can only be run economically, if the concentrate stream does not need to be treated and if a low salt content is a special requirement e.g. like during groundwater recharge to avoid salt water intrusion into drinking water aquifers.

Oxidation processes
Treatment by sorption and filtration does remove the compounds out of the water phase, whereas an oxidation step aims at a transformation of persistent compounds. The oxidation will be optimised that the oxidation products do not show their former bioactivity any more and are mostly biodegradable. The oxidation processes generally include ozone, ozone/hydrogen peroxide, UV/hydrogen peroxide, and UV/ozone. Out of these, ozone and ozone/hydrogen

peroxide are the most efficient in terms of removal efficiency, energy requirement and cost effectiveness.

At the Technical University Berlin a research project has recently been launched dealing with an ozonation of WWTP effluent with the aim of groundwater recharge. Figure 4 shows the direct oxidation of DOC and the formation of biodegradable DOC with increasing ozone consumption for a WWTP effluent [Schumacher et. al, 2003].

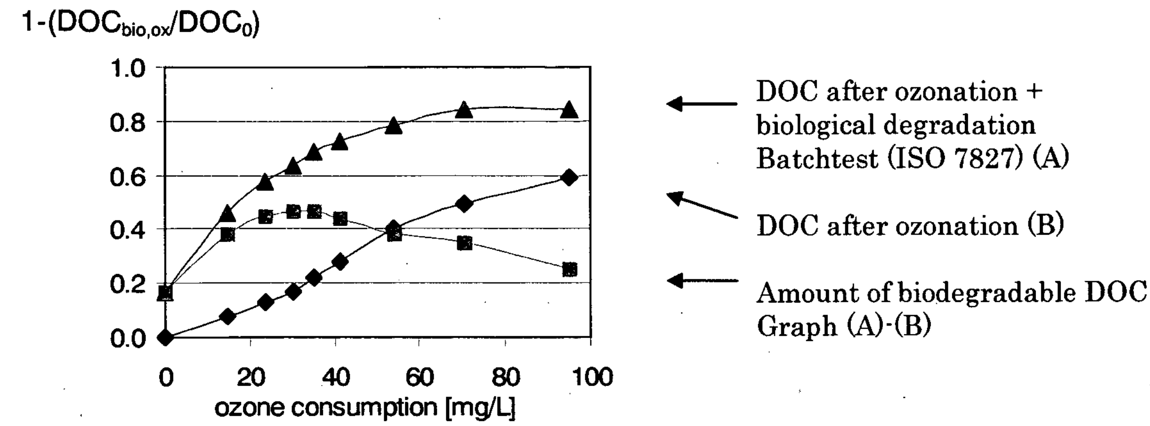

Figure 4: DOC removal during ozonation and enhancement of biodegradability, DOC_0 = 11.5 mg/L.

In this WWTP effluent, 18 % of DOC is biodegraded after a treatment with batch tests for 28 days. By using ozone, DOC can be removed immediately, but very high amounts of ozone have to be applied. For example 60 % of DOC are removed while applying 95 mg ozone/L. A combination of ozonation and biodegradation is much more efficient. Here, the same amount of DOC is reduced by using just 25 mg/L of ozone and a subsequent biodegradation step. A slow sand filtration or a soil passage with a wide range of redox conditions from aerobic to anaerobic will further enhance the removal of organic compounds.

In order to investigate the behaviour of extremely persistent compounds, WWTP effluent was spiked with iopromide, an X-ray contrast compound. It contains an aromatic ring system with three iodine groups, making it polar and poorly degradable. During ozonation, iopromide concentration was quickly decreased. However, the analysis of adsorbable organic iodine (AOI) proved that most of the iopromide was transformed, but only 20 % are removed while applying 25 mg ozone/L.

In a combination of ozonation with 25 mg ozone/L and a subsequent treatment in soil columns with a retention time of 14 days, the results are as follows: DOC, UVA(254), colour and molecular size distribution can be adapted to natural groundwater characteristics. AOI can be decreased by around 35 %, but remains much higher (92 μg/L) than groundwater levels (2.2 μg/L). Anoxic and anaerobic redox conditions will further improve the performance. Moreover, the treatment can be improved by an efficient combination of ozone and hydrogen peroxide. As prices for ozone have decreased tremendously in recent years, overall costs of less than 0.05 Euro per m^3 are realistic.

RELEVANCE OF TRACE SUBSTANCES TO DRINKING WATER QUALITY

The pharmaceuticals, hormone-disrupting chemicals and cosmetics, are not considered to be relevant for drinking water supply due to the low risk level. In order to safeguard against any risk as well as for ecological reasons, water pollution due to persistent synthetic trace substances should, however, be minimised by suitable water protection measures.

Besides the oral taking of drugs, the exposure to endocrine substances basically occurs via ingestion. According to recent findings, water pollution as a result of endocrine substances also at trace-level is to be avoided by means of water protection measures, natural filtration processes and physical-chemical treatment methods, which are to be applied during the drinking-water treatment process .

Owing to their substance properties, cosmetics are to kept out of the drinking water in the course of the natural and physical-chemical treatment processes. For humans, possible exposure to hormone-disruptors via drinking water can be disregarded in comparison to other exposure risks.

According to recent scientific and technical findings, no health risks can be identified as a result of exposure to pharmaceuticals, including veterinarian pharmaceuticals and animal feed additives, as well as to hormone-disrupting chemicals and cosmetics absorbed via the drinking water cycle. On the quantification of the above-mentioned trace substances, their possible furnish and further behaviour in both surface and groundwater should be taken into account. In terms of pharmaceuticals and animal feed additives in particular, the possibility cannot be ruled out that they may get into the wastewater cycle, respectively into liquid manure, subsequently into the surface waters and directly or via bank filtration also into the groundwater.

MINIMISING OF THE EMISSIONS OF TRACE SUBSTANCES IN THE ENVIRONMENT

A decrease in the emissions of pharmaceuticals, hormone-disrupting chemicals and cosmetics can only be achieved by the implementation of certain targeted minimising strategies in consideration of the application areas. The following measures, comprising also additional consumer information, would be suitable:

- Safe disposal of pharmaceutical residues as waste (via pharmacies) and no improper disposal also of cosmetic residues via toilet flush, resp. in case of veterinarian pharmaceuticals via the sewer system,
- Restricted use of cosmetics bearing any health risks and having a high accumulation potential in aquatic animals,
- Critical handling of pharmaceuticals.

The reorganisation of the current application practices and habits should be accompanied by generic suitable measures such as:

- availability of all data relating to consumption quantities and to the ecological impact potential of the marketed substances,
- uniform risk assessment of the environmental behaviour of pharmaceuticals for humans and animals as well as of animal feed additives within the scope of specific admission procedures,
- securing the non-polluting disposal of pharmaceuticals,
- substitution of environmentally relevant cosmetics and industrial chemical by substances having a lower risk potential,
- stopping the use of particularly risky substances which are dispensable for health protection, if necessary restricting or even prohibiting their use as it is already practised with some pesticides and industrial chemicals.

To provide for any risks that would jeopardise future water protection, the main objective of all measures cited above is to safeguard the aquatic ecosystems and existing drinking water resources against avoidable emissions produced by pharmaceuticals, hormone-disrupting chemicals and cosmetics.

CONCLUSIONS

PhACs are found as very persistent residues at the µg/L-level in the effluents of Berlin's municipal WWTPs. 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. In particular, several of the polar PhACs were identified as excellent markers for sewage contamination in surface and groundwater 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.

The removal of trace substances from raw water has a long tradition (e.g. pesticides) in the drinking water treatment process. In accordance with current knowledge ozonation and sorption by activated carbon can in some cases successfully remove trace substances. The additional pollution in raw water for drinking water supply is lower than in sewage, making a more effective treatment possible. As already mentioned, the water passage through the ground significantly removes several trace substances.

Pharmaceuticals, hormone-disrupting chemicals and cosmetics are not considered to be relevant for drinking water supply due to the low risk level.

OUTLOOK

A sustainable water management in Berlin is based on protection of the quality of surface water as well as groundwater. Berlin has to handle with different aspects e.g. low flow rates, high portions of advanced treated wastewater in the water cycle and a shallow fresh water aquifer. Considering the challenge of water management in Berlin the special R&D project "Natural and Artificial Systems of Recharge and Infiltration" oriented towards the specific requirements in Berlin has been already launched [Fritz et. al, 2003]. The initiated interdisciplinary co-operation project of the Berlin Centre of Competence for Water will continue until May 2005. The project is funded by Veolia Water and the Berlin Water Company (Berliner Wasserbetriebe). The main objective is to develop expertise in the overall management of water resources in terms of bank filtration, artificial groundwater recharge and reuse of sewage and stormwater in a partly closed water cycle [Jekel and Heinzmann, 2003].

In recent years, polar and poorly degradable organic pollutants are gaining increasing attention as a factor of water quality. Industrial chemicals as well as household products, certain pesticides and their polar metabolites and pharmaceutically active compounds are among these polar pollutants. These compounds are not necessarily removed in wastewater treatment and in drinking water preparation processes. Thus, the mechanisms of the removal of impurities and of the chemical reactions of the water components have not been understood sufficiently. As far as some hydrological trends and development of anthropogenic pollutants may threat the future of the groundwater resource in Berlin, it is important to measure the capacity of ground filtration to answer to such developments, and to secure the use of bank filtration and water recharge systems through the development of the most appropriate practices and the related technologies.

REFERENCES

Buser H.-R., Poiger Th. and Müller M. D. (1998) Occurrence and Fate of the Pharmaceutical Drug Diclofenac in Surface Waters: Rapid Photodegradation in a Lake, Environ. Sci. Technol. 32, 3449-3456.

Dohmann M. (2003) Spurenstoffe in der Umwelt – Ein Spannungsfeld zwischen umweltpolitischen Anforderungen und Strategien zur Entfernung. In: Spurenstoffe in

Gewässern (Pharmazeutische Reststoffe und endokrin wirksame Substanzen) von T. Track und G. Kreysa (Herausgeber); Wiley-VCH GmbH & Co; S. 1 - 20.

Fritz, B.; Heinzmann, B.; Jekel M. and Luck F. (2003): The R&D project "Natural and Artificial Systems of Recharge and Infiltration" oriented towards the specific requirements in Berlin. Proceedings of the second Conference on Efficient Use and Management of Water in Urban Areas. Tenerife.

Heberer Th. (2002) Tracking down persistent pharmaceutical residues from municipal sewage to drinking water. In: *Attenuation of Groundwater Pollution by Bank Filtration,* Th. Grischek and K. Hiscock (eds.), J. Hydrol. 266, 175-189.

Heberer Th., Schmidt-Bäumler K. and Stan H. J. (1998) Occurrence and Distribution of Organic Contaminants in the Aquatic System in Berlin. Part I: Drug Residues and Other Polar Contaminants in Berlin Surface and Groundwater. Acta Hydrochim. Hydrobiol. 26:272-278.

Heberer Th., Verstraeten I. M., Meyer M. T., Mechlinski A. and Reddersen K. (2001) Occurrence and Fate of Pharmaceuticals during Bank Filtration – Preliminary Results from Investigations in Germany and the United States. Water Research Update, 120, 4-17.

Heinzmann, B. (1994) Beschaffenheit und Bedeutung städtischer Regenabflüsse im Trennsystem. gwf-Wasser/Abwasser 135, Nr. 7, S. 381 - 390.

Jekel, M. and Heinzmann, B. (2003): The R&D project NASRI - Orientation towards the specific Water Management Requirements in Berlin and its International Reference. Proceedings of the Conference "Wasser Berlin 2003".

Reddersen K., Heberer Th. and Dünnbier U. (2002) Identification of new drug metabolites in groundwater samples from a drinking water treatment plant. Chemosphere 49: 539-545.
J. B. Rose and C. P. Gerba (1991) Use of Risk Assessment for Development of Microbial Standards, Wat. Sci. Tech., **24** (2), 29-34

Oleksy-Frenzel, J., Wischnack, S., Jekel, M., 2000. Application of ion-chromatography for the determination of the organic-group parameters AOCl, AOBr and AOI in water. Fresenius J. Anal. Chem. 366, 89-94.

Putschew A., Wischnack S. and Jekel M. (2000) Occurrence of triiodinated X-ray contrast agents in the environment. *The Science of the Total Environment*, 255, 129-134.

Putschew A., Schittko S. und Jekel M. (2001a) Quantification of triiodinated benzene derivatives and X-ray contrast media in water samples by liquid chromatography-electrospray tandem mass spectrometry. *Journal of Chromatography* A, 930, 127-134.

Putschew A. und Jekel M. (2001b) Iodierte Röntgenkontrastmittel im anthropogen beeinflussten Wasserkreislauf. *Vom Wasser*, Band 97, 103-114.

Putschew A. and Jekel M. (2003) Induced in-source-fragmentation for the selective detection of organic bound iodine by liquid chromatography electrospray mass spectrometry. *Rapid Communications in Mass Spectrometry*, 17(20), 2279.2282.

Schittko S., Putschew A., Jekel M. (2003) Bank Filtration: a suitable process for the removal of iodinated X-ray contrast media?. *Water Science and Technology*, submitted.

Schumacher J., Yunzheng P. and Jekel M. (2004) Ozonation of Persistent DOC in municipal Wastewater Treatment Plant Effluent for Groundwater Recharge. Water Science and

Technology, accepted.

Ziegler, D. (2001) Untersuchungen zur nachhaltigen Wirkung der Uferfiltration im Wasserkreislauf Berlins) Ph.D. thesis at the Technical University of Berlin.