

# OCCURRENCE AND FATE OF PHARMACEUTICALS DURING BANK FILTRATION – PRELIMINARY RESULTS FROM INVESTIGATIONS IN GERMANY AND THE UNITED STATES

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## ABSTRACT

The growing need for clean drinking water worldwide has increased the interest in natural surface-water treatment techniques such as bank filtration. Bank filtration has been used for more than a century in drinking water production. Historically, it was recognized as an efficient natural attenuation process ensuring sustainability of drinking-water supply. If bank-filtration facilities are designed and constructed properly, the ground water used for drinking-water supply can be protected efficiently from contamination with microbial organisms and inorganic or organic pollutants. Recently, however, several new types of organic contaminants, such as pharmaceuticals, have been found in the aquatic environment. Some of the polar pharmaceuticals also have been detected in ground water and drinking-water samples, especially when water from induced recharge is used for drinking-water production. In 2001, two projects were initiated at bank-filtration sites in Berlin, Germany, and in Nebraska, U.S.A., to investigate the natural attenuation of pharmaceutical residues and several other environmentally relevant contaminants systematically under natural conditions. Preliminary results of the studies in Germany and the United States revealed that several polar organic compounds, especially several pharmaceutically active compounds (PHACs), are

relevant to drinking-water production at bank-filtration sites.

## INTRODUCTION

At the end of the 19<sup>th</sup> century, water pollution issues were becoming more and more evident in growing metropolitan centers. The presence of anthropogenic substances, including pharmaceuticals, that potentially can affect the endocrine systems of aquatic organisms and human health through drinking water or aquatic recreational activities, is creating a high level of concern among scientists and policymakers throughout the world (Ghijsen & Hoogenboezem, 2000). Treatment technologies for drinking-water supplies such as bank filtration, slow-sand filtration, ozonation, chlorination, granular activated carbon, or membrane filtration were developed to reduce or remove undesirable chemicals in drinking water and to provide sufficient amounts of quality drinking water for public-water supply.

More than 100 years ago, bank filtration was recognized as an efficient natural attenuation process ensuring sustainability of drinking-water supplies (Stuyfzand, 1989; Kruhm-Pimpl, 1993; Mathys, 1994; Grischek et al., 1997; Verstraeten et al., 1999; Brauch et al., 2000; Verstraeten et al., in press A and B). These researchers found that quality of bank-filtered water depends not

only upon the contaminant itself, but also upon the hydraulic and chemical characteristics of the bottom sediment and the aquifer, the local recharge-discharge conditions, and biochemical processes. They also established that fate and transport of organic chemicals are complex and can include microbial degradation, adsorption/desorption, photolysis, oxidation, and transport from one medium in the hydrologic system, e.g. surface-water bodies and river banks, to another medium. Organic contaminants that are not readily biodegradable may occur in bank-filtered water, often in lower concentrations than those in the river (Verstraeten et al., 1999).

#### Importance of Bank Filtration for Drinking-Water Production in Berlin, Germany

In the metropolitan area of Berlin, Germany, 100 percent of public-water supply originates from ground water with approximately 70 percent from bank filtration and artificial recharge (Verstraeten et al., in press B). At Lake Müggelsee in Berlin, bank filtration was used as a method of drinking-water treatment about 100 years ago. Currently (2001), it is used at several locations in Berlin. Supply wells generally are drilled within short distances (as little as 600 m) from rivers, canals, and lakes (Pekdeger, 2001). The sewage treatment plants (STPs) often discharge their purified sewage water into the surface-water system upstream from well fields and their corresponding bank filtration or ground water recharge facilities. Especially during low-flow conditions (primarily summer), the proportion of purified sewage in several waterways may be equal to or even greater than the natural surface-water discharge (SenSUT, 1999). Due to the progress in environmental analytical chemistry, increasing numbers of persistent organic compounds are being found in Berlin's surface water often released by municipal STPs (Heberer et al., 1998, 1999). Thus, monitoring of the quality of surface and bank-filtered water and understanding of local biochemical and hydraulic processes are needed to achieve and control a sustainable drinking-water supply.

#### Importance of Bank Filtration for Drinking-Water Production in the United States

In the United States, the growing need for quality drinking water has led to an increasing interest in the use of bank filtration as an inexpensive means of water-supply pretreatment. The interest of utilities in using bank filtration as part of their drinking-water treatment techniques recently has increased substantially. Utilities can request credit from their state environmental or regulatory agencies for removal of microorganisms through use of natural bank filtration as part of their

drinking-water treatment process. Drinking-water systems using bank filtration may be classified as either ground water, ground water under the direct influence of surface water, or surface water (U. S. Environmental Protection Agency, 1989). To date, only two drinking-water utilities have received credit for virus and Giardia inactivation and/or removal by bank filtration from their respective State agencies. These utilities are Kearney, Nebraska, and Sonoma County, California (Schijven et al., in press).

In the United States, the number of utilities receiving bank-filtered water for drinking water is steadily increasing. For example, most cities in Nebraska historically have developed along the Platte River or its tributaries; as the population increases the dependence on this river is steadily increasing. Utilities have used bank-filtered water in states such as Iowa, Kansas, Kentucky, Nebraska, New Jersey, New York, Ohio, Texas, and Wyoming. In fact, bank-filtration sites probably exist along most major and some smaller rivers in the United States. Thus far, the use of bank-filtered water has not been quantified in the United States. In many cases, utilities do not recognize that their water substantially is derived from surface water, or, if they do, have yet to quantify how much of the water pumped from a well originated as surface water.

#### Relevance of Pharmaceuticals in Bank Filtration

Pharmaceuticals are used in large quantities in human and animal health care as well as in the fruit production industry. Drugs used in human and animal health care may enter the environment by discharges of municipal sewage or hospital effluents, sewage sludges, landfill leachates (waste disposal), domestic septic tanks, production residues, feedlot runoff, contaminated liquid manure, or direct introduction via aquacultures.

In human health care, the sales of drugs reached \$210.7 billion worldwide from March 1999 through February 2000 (U.S. Environmental Protection Agency, 2001). The main therapeutic markets were cardiovascular, alimentary, antidepressants, anti-infectives, and respiratory. In 1997, the United States' per capita expenditure on drugs was one of the highest in the world (\$319) after Belgium, Japan, and France (\$321-351). About 1 to 2 percent of the sales in the United States were used for veterinary purposes. In the United States, although pharmaceutical sales amount to hundreds of kg (kilograms) per year, production of personal care products is an order of magnitude larger (U.S. Environmental Protection Agency, 2001).

Several pharmaceutical compounds, such as carbamazepine, diclofenac, and ibuprofen, are

prescribed in quantities as large as 100 t/yr (tons/year) in Germany (Stan & Heberer, 1997). Over-the-counter pharmaceutical sales and hospital use of compounds such as aspirin are as much as 1,000 t/yr in Germany, which implies that the annual use of pharmaceuticals is similar to pesticide use (Verstraeten et al., in press B). Therefore, pharmaceutical residues could be present in surface water at concentrations similar to, or even greater than, those of the pesticide residues. Large concentrations of pharmaceutical residues may be found especially near urban areas, because they enter the surface water by discharges from municipal STPs, which are point sources for these compounds. In contrast, pesticides applied extensively on agricultural land tend to enter the streams as nonpoint sources. Nevertheless, pharmaceuticals also can enter the environment as nonpoint sources when manure containing traces of pharmaceuticals is applied to the fields, as is the practice in the United States (Meyer et al., 2000).

Data on the occurrence of pharmaceutical residues in the environment often have been only a random by-product from other investigations, such as studies of the occurrence of pesticide residues. To date, a substantial amount of data exists on the presence of antibiotics in the environment (Daughton & Ternes, 1999). The first detection of antibiotics in wastewater was reported in the 1970s in the United States (Daughton & Ternes, 1999), but these findings were largely ignored. In Europe, information on the presence of antibiotics in water has been gathered since the 1980s. Data on pharmaceuticals have been collected because of their potential effects on native biota and development of resistance in potential human pathogens.

Important factors affecting the occurrence of pharmaceutical residues in the environment include the amounts prescribed and the fate of the individual compounds both in the STPs and the aquatic environment. Some pharmaceuticals are not eliminated or degraded in the human body. They are excreted by the human body unchanged or only slightly transformed, mostly conjugated to polar molecules, such as the glucuronides. These conjugates are cleaved easily in the raw sewage or during sewage treatment. Thus, some pharmaceutically active compounds (PhACs) are discharged almost unchanged from municipal STPs into the receiving water (Stan & Heberer, 1997; Halling-Sørensen et al., 1998; Heberer & Stan, 1998; Ternes, 1998; Daughton & Ternes, 1999; Möhle et al., 1999; Wilken et al., 2000; Heberer, in press; Heberer et al., in press).

In 1990, after the reunification of East and West Germany, the Senate of Berlin commissioned

monitoring of water collected from wells near the former Berlin wall. The purpose of this monitoring was to identify and quantify pesticide residues caused by the intensive use of these compounds along the Wall. As a result of these investigations, 2-(4-chlorophenoxy)-2-methylpropionic acid (clofibric acid) was first detected in Berlin ground water samples in 1991 (Stan & Linkerhägner, 1992). Clofibric acid is the pharmacologically active metabolite of the drugs clofibrate, etofyllin clofibrate, and etofibrate, used as blood-lipid regulators in human health care. It was detected in an analytical method for the analysis of phenoxyacid herbicides. In fact, clofibric acid is a structural isomer of the herbicide mecoprop, frequently used as a preemergent herbicide in agriculture; and initially, its occurrence in ground water samples was not linked with its medical application. However, between 1992 and 1995, clofibric acid also was detected at concentrations at the  $\mu\text{g/L}$ -level in ground water samples collected from former sewage irrigation fields near Berlin and in Berlin tap-water samples (Heberer & Stan, 1996; 1997). It became evident that these residues were caused by the infiltration of sewage effluents into the soil and that clofibric acid is a very mobile compound that is not substantially adsorbed in the subsoil and is leached easily into the aquifer. Clofibric acid was found even in samples collected from an aquifer at depths of more than 70 m (meters). In Germany, the first detections of clofibric acid in ground water put focus on the presence of drug residues in the aquatic system as a new emerging issue (Umweltbundesamt, 1996) and researchers began to investigate the occurrence and fate of pharmaceutical residues in the aquatic environment, during drinking-water purification, and in drinking-water samples.

In 1994, by analyzing drinking-water samples collected from 14 utilities in Berlin (Heberer & Stan, 1996 and 1997), a relation was found between bank filtration, artificial ground water recharge, and the level of drinking-water contamination by the drug clofibric acid. Several other polar PhACs also were identified as contaminants relevant to bank-filtration processes. Diclofenac, ibuprofen, propyphenazone, gemfibrozil, or primidone, also have been detected in ground water wells from different bank-filtration sites in Berlin (Heberer et al., 1997; Heberer, in press). In a recent bank-filtration study by Brauch et al. (2000), the behavior of several selected polar organic contaminants, including diclofenac and carbamazepine, was studied in water from two utilities near the lower Rhine River. The transport of diclofenac, clofibric acid, and propyphenazone during bank filtration also has been studied at Lake Tegel in Berlin (Schyett et al., 2001). These studies indicate that PhACs are attenuated partially by bank filtration and that several of these

compounds can be transported through the subsoil without any substantial attenuation.

### STUDY OF THE OCCURRENCE AND FATE OF DRUG RESIDUES ALONG TRANSECTS IN BERLIN, GERMANY

The first detections of PhACs in ground water samples from bank-filtration sites in Germany encouraged more intensive study of their behavior during bank filtration. The fate of organic residues, including PhACs, seven polar pesticides, two flame retardants, and a metabolite of an anticorrosive substance, currently is being investigated at two bank-filtration sites in Berlin, Germany. The bank-filtration research is carried out cooperatively by the Senate of Berlin (Senate Department of Urban Development, Environmental Protection and Technology) and the Hydrogeology Research Team of the Free University Berlin. Two transects (“Lieber Bucht” and “Lake Wannsee”) are along the Havel River (Figure 1), a river heavily impacted by municipal sewage effluent. Residues of PhACs have been detected in the water of the Havel River at individual concentrations of as much as 600 ng/L (nanograms per liter) (Heberer et al., 1998). The objective of the current study is to evaluate bank-

filtration processes and the transport and attenuation of contaminants such as PhACs under natural conditions. Beginning in April 2001, water samples collected monthly from the river and wells are analyzed for more than 40 polar organic contaminants to obtain representative data and to identify the effect of temporal (seasonal) variations, changes in environmental conditions, and hydraulic effects. The PhAC data will be put in context with the hydrogeologic framework being characterized with physico-chemical parameters and major-ion concentrations. The preliminary results obtained for samples collected in April 2001 from the Lake Wannsee transect are presented in a later section.

#### Description of Lake Wannsee Transect

The transect at the east bank of Lake Wannsee (Großer Wannsee) is at a bank-filtration area of an active utility (Beelitzhof) of the Berliner Wasserbetriebe, which is using infiltrated water from the lake. The utilities in Beelitzhof use about 66 percent of bank filtrate in drinking-water production (Heberer, in press). Ground water samples from seven monitoring wells and one water-supply well (WWK 4) drilled at various distances from Lake Wannsee (Figure 2) along a line of about 150 m were analyzed for a variety of compounds.

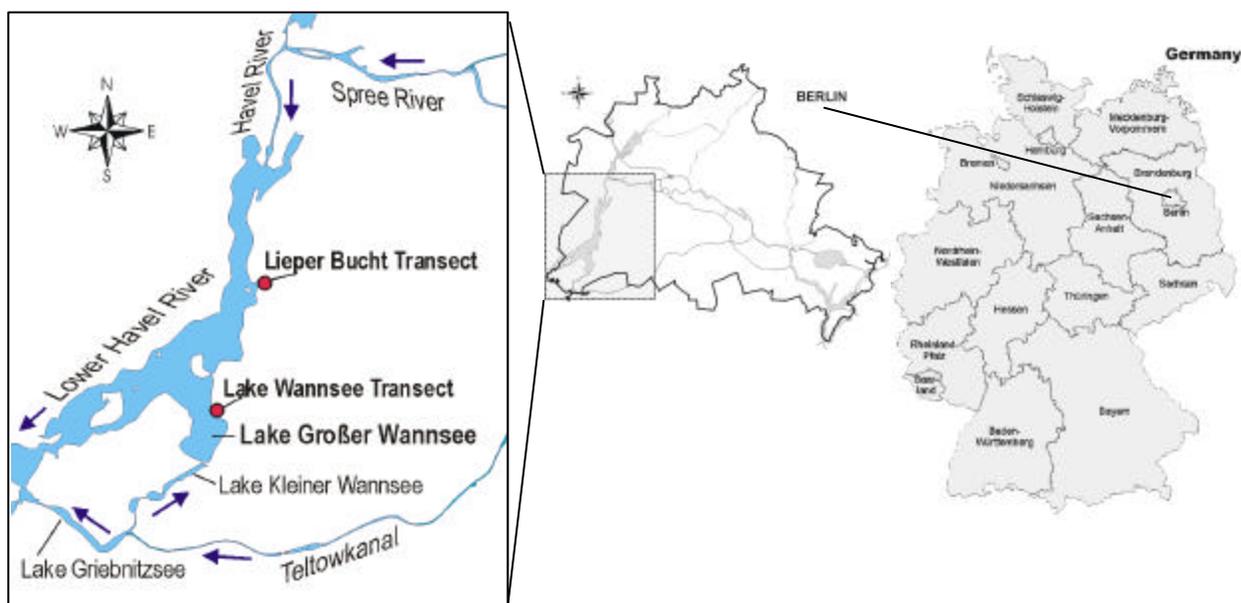


Figure 1: Maps showing the locations of both transects along the Lower Havel River (left), Berlin (middle), Germany (right).

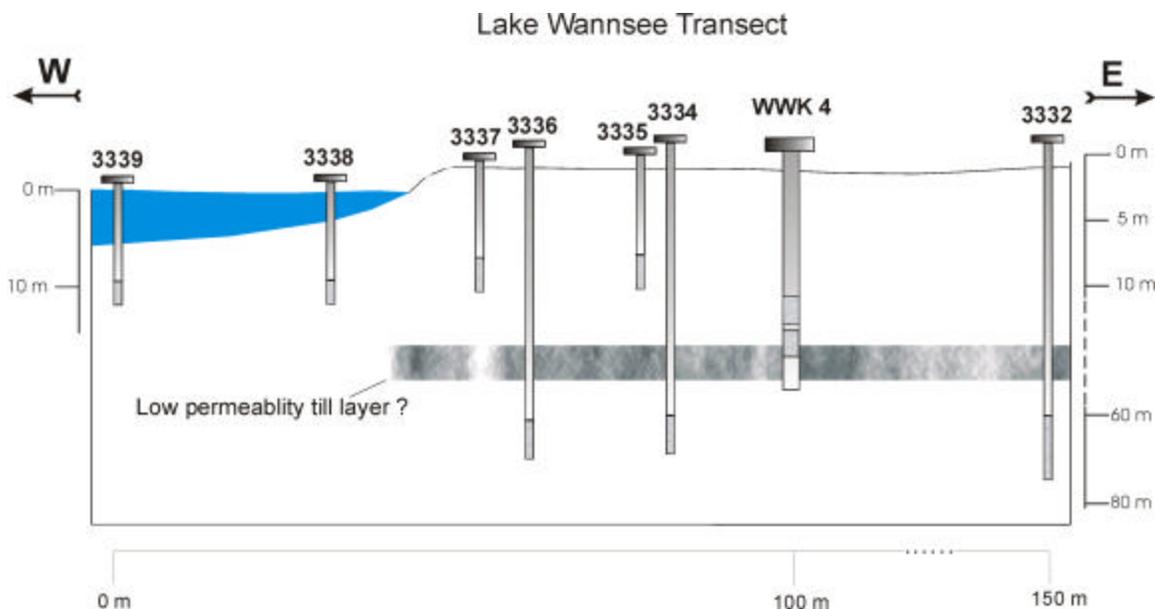


Figure 2: Preliminary schematic hydrogeologic section of the Lake Wannsee transect, location of monitoring wells (shallow and deep) and a water-supply well (WWK4) (Adopted and modified from Pekdeger, Workgroup of Hydrogeology at the FU Berlin, written communication, 2001). The darker areas on the bottom of the wells are the individual screens.

The shallow wells are screened in a shallow aquifer at an average depth between 10 and 15 meters. The deep wells are screened in a deep aquifer underneath a till layer at an average depth of about 70 meters. The small permeability of this layer and the discontinuity of this layer, commonly observed in the Berlin area, are a subject of these investigations. The water works wells, including water works well 4 (WWK 4) in Figure 2, are usually screened at two depths (between 15 and 40 meters) in the intermediate aquifer. The second ground water aquifer commonly is connected with the shallow (first) aquifer, and may be influenced by contaminants that are mobile in the subsol.

Lake Wannsee receives its water mainly from the Lower Havel River but also from the Teltowkanal, a canal in the south side of Berlin (Figure 1). About half of the surface water from the Teltowkanal flows through Lake Griebnitzsee (Figure 1) into the Lower Havel River. The remainder of the surface water flows through Lake Kleiner Wannsee into Lake Wannsee. The Teltowkanal carries substantial loads of treated sewage discharges (Heberer, in press). Sewage effluents are discharged into the canal by three STPs along the canal including the two largest STPs of Berlin (Stahnsdorf and Ruhleben). In autumn and winter, the effluents from the STPs in Ruhleben are discharged into the Spree River, which converges with the Upper Havel River. Thus, the Lower Havel River always carries loads of treated

sewage from three STPs, and during autumn and winter, also from STPs in Ruhleben, located in the north-western districts of Berlin.

#### Preliminary Results of Analysis of Pharmaceutical Residues and Related Organic Compounds

Water samples are being analyzed for 43 environmentally relevant organic contaminants. Of the samples collected in April 2001, 15 (13 of them are listed in Table 1) of the 43 compounds were detected in surface-water and ground water samples (Table 1). Seven of these compounds, namely compound X (not identified because of potential legal ramifications), bezafibrate, carbamazepine, clofibrac acid, diclofenac, primidone, and propyphenazone were PhACs. They were detected only in the shallow wells, and the water-supply well but not in the deep monitoring wells. A significant decrease in concentrations along the transect away from the lake was observed for bezafibrate, a compound used as a blood-lipid regulator in human health care. About 10 percent of the bezafibrate concentration detected in surface water was found in water from shallow well 3339. It was not detected in water from shallow wells 3337 and 3335. Other PhACs, such as carbamazepine and primidone, both anti-epileptic drugs, were detected in all of the shallow wells. They also were found further away from the lake in water from well 3335 at concentrations similar to or

even larger than those found in the surface water. The results for carbamazepine confirm soil-column experiments indicating that carbamazepine was not substantially adsorbed into the sediments (TU Berlin, written communication, 2001). Diclofenac appeared to be attenuated during transport through the sediments (Table 1). This observation also confirms the results obtained by laboratory column experiments of Mersmann et al. (TU Berlin, written communication, 2001). In contrast to bezafibrate, diclofenac reached well 3337 and its concentrations decreased less from the surface water to well 3339 (only about 30 percent of the surface-water concentration) than those of bezafibrate.

Five of the PhACs also were detected in the samples from the water-supply well (Table 1). Two of the PhACs were found at larger concentrations than those measured in the surface water or the shallow wells. This might be explained by seasonal differences and will be evaluated further using results of additional sampling. This phenomenon may also be explained by the history of this type of contamination. The use of the precursor compounds of clofibric acid in Germany has decreased during the last ten years and clofibric acid is being substituted for other pharmaceuticals. The larger

concentrations in the water-supply well may be because of larger concentrations of these compounds in sewage in the past. The concentrations of clofibric acid measured in the Berlin sewage effluents decreased during the last five years from about 1 to 0.5 µg/L. This phenomenon will be evaluated further when the contributing areas to wells and tracer velocities are determined as a result of the hydrogeologic studies that are being conducted at the study site.

In addition to the detections of PhACs in water samples, several pesticides were detected. Again, the results indicate that recent and past contamination of surface water is contributing to the concentrations of compounds found in ground water. The pesticides bentazone and MCPP are used frequently as herbicides in agriculture, but also in gardens, on sporting grounds, and on sealed surfaces. The largest concentrations of herbicides in Berlin's surface waters were detected during spring and early summer (Heberer & Reddersen, in press). Nevertheless, during all seasons, the concentrations of the pesticides measured remained substantially lower than the concentrations of PhACs (Heberer et al., 1998; Heberer & Reddersen, in press).

Table 1. Concentrations of selected organic compounds detected in water samples from Lake Wannsee transect, Berlin, Germany, April 18, 2001.

[ND: not detected; detection level, 1 to 10 nanograms per liter; data are reported in nanograms per liter]

Compound	Surface water		Shallow wells				Deep wells			Water-supply well 4*
		3339	3338	3337	3335	3336	3334	3332		
Pharmaceutically active compounds										
Compound X**	200	155	350	185	135	ND	ND	ND	100	
Bezafibrate	170	20	10	ND	ND	ND	ND	ND	ND	
Carbamazepine	235	160	235	360	325	ND	ND	ND	20	
Clofibric acid	50	20	60	20	ND	ND	ND	ND	70	
Diclofenac	50	35	40	15	ND	ND	ND	ND	ND	
Primidone	105	195	210	215	535	ND	ND	ND	15	
Propyphenazone	280	170	145	10	70	ND	ND	ND	50	
Pesticides										
Bentazone	<10	10	30	<10	<10	ND	ND	ND	ND	
MCPP	20	10	15	<10	ND	ND	ND	ND	ND	
o,p'-DDA	<10	<10	10	ND	ND	ND	ND	ND	15	
p,p'-DDA	15	25	35	ND	ND	<10	15	ND	20	
Other organic compounds										
TCEP	250	100	260	70	10	ND	ND	ND	105	
TCIPP	510	440	1025	580	390	ND	ND	ND	180	

\* Water-supply well number 4 (WWK4) was out of use during the sampling series of April 2001; the given value was obtained in May 2001  
 \*\* Compound X 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. (TU Berlin, written communication, 2001)). This compound is not identified because of potential legal ramifications (Reddersen et al. (TU Berlin, written communication, 2001)).

As reported by Meitzler et al. (1996), bentazone is very mobile in the subsoil. In the transect study, it was detected at trace-level concentrations from <10 to 30 ng/L in all samples from the shallow wells (Table 1). Neither bentazone nor MCPP was found in the deep well. Based on the results in Table 2, MCPP appears to be attenuated along the transect. It was not detected in water from well 3335 nor from the water-supply well. The compounds *o,p'*- and *p,p'*-DDA are the polar metabolites of the insecticide DDT. DDT was produced until 1986 by a former chemical production plant in the eastern part of Berlin. The release of DDT residues into the environment resulted in a DDT Superfund site at the eastern part of the Teltowkanal (Heberer & Dünnbier, 1999). DDA residues continue to be found in the surface water of the Teltowkanal down to the Lower Havel River (Heberer, TU Berlin, written communication, 2001). As described previously, the Teltowkanal provides water to Lake Wannsee. The DDT metabolites in the water-supply well also may have originated from former applications of DDT, considering that they are very persistent in ground water (Heberer & Dünnbier, 1999). The detections of *p,p'*-DDA in two of the deep wells supports this hypothesis.

The flame retardants tris-(chloroethyl)-phosphate (TCEP) and tris-(chloroisopropyl)-phosphate (TCIPP) frequently are detected in municipal sewage effluents and surface-water samples in Berlin. In surface water, the concentrations of TCIPP generally are about twice as high as those of TCEP (Heberer & Reddersen, in press). Both compounds were found in high concentrations and in similar proportions in water from the shallow wells (Table 1). In the deep wells, neither compound was detected; however, TCIPP (180 ng/L) and TCEP (105 ng/L) were detected in the water-supply well.

#### Preliminary Conclusions

The preliminary results of the Lake Wannsee bank-filtration project indicate that several polar organic compounds, especially several PhACs, probably are relevant to bank-filtration pretreatment near urban areas. Several compounds, such as bezafibrate, diclofenac, or MCPP seem to be removed effectively during bank filtration. But several other compounds, namely carbamazepine, clofibric acid, primidone, propyphenazone, compound X, bentazone, DDA, TCIPP, and TCEP were present at concentrations between 15 and 180 ng/L in the water-supply well. Further study may clarify some unresolved questions about the origin of several compounds and their behavior (temporal and spatial) during the bank-filtration process. Investigators also will obtain information on the presence and fate of compounds

other than the 41 compounds for which samples were analyzed already.

## **INVESTIGATIONS ON THE OCCURRENCE AND FATE OF DRUG RESIDUES AT BANK-FILTRATION SITES, NEBRASKA, UNITED STATES**

### Background

In the United States, the use and eventual fate of antibiotics by humans and in livestock production are a concern. About 90 percent of the approximately 2.5 million kg of antibiotics sold in the United States are given as growth-promoting and prophylactic agents in sub-therapeutic doses instead of being used to treat active infections, thereby lowering the cost of animal care (Kolpin et al., 2000). Researchers report that antibiotics have been detected in the United States at trace levels (0.05-2.1 µg/L (micrograms per liter)) in surface water and ground water (Thurman, written communication, 2001; Meyer et al., 2000) and that tetracycline and sulfonamide antibiotics have been detected in samples collected from ground water and wastewater of (confined) animal feeding operations (AFOs/CAFOs) (Thurman & Hostetler, 2000; Lindsey & Thurman, 2000). Tetracycline and sulfonamide antibiotics are believed to occur at levels on the order of 100 µg/L in wastewater from CAFOs (Meyer et al., 2000; Lindsey & Thurman, 2000). Meyer et al. (2000) reported that in the United States tetracyclines were the most frequently detected class of antibiotics, followed by sulfonamides, macrolides, and beta-lactams, in liquid waste from hog wastewater lagoons, with concentrations of as much as 700 µg/L. Therefore, a concern exists in the United States that these contaminants can be transported at trace levels from lagoon discharges or after application of manure and compost onto the land, into a riverine environment, and ultimately into drinking water. Siler (1999) reported that caffeine and pharmaceuticals in water from wells could be used to trace wastewater.

Little is known about the presence of pharmaceuticals in the aquatic environment in the United States. A national study has been conducted to evaluate the presence of antibiotics and other organic compounds in surface water (Kolpin et al., in press). These investigators report that pharmaceuticals, hormones, or other emerging contaminants were found in the surface water in the United States. At this time, almost no information is available on the presence of pharmaceuticals in bank-filtered water and drinking water produced from bank-filtered water. A preliminary data collection effort was conducted by the U.S. Geological Survey (USGS) at the City of Lincoln bank-filtration site (Verstraeten et al., in press B) near

Ashland, Nebraska. Water samples were collected from surface water, a water-supply well (bank-filtered water), raw water (before chemical and physical treatment), and treated drinking water (finished water) at this site on September 9, 1999. Samples were analyzed for 24 antibiotics. Sulfamethoxazole and trimethoprim were detected at concentrations of less than 1 µg/L in bank-filtered and raw water. Both compounds are components of the Bactrim antibiotic. No traces of pharmaceuticals were detected in the treated drinking-water sample. Previous studies indicated that herbicide concentrations such as atrazine decreased from 10 to 60 percent by bank filtration depending on how the well field is managed (Verstraeten et al., in press A).

Recently (2001), the USGS initiated a study in cooperation with U.S. Environmental Protection Agency (USEPA) and the City of Lincoln to evaluate the transport of pharmaceuticals and other endocrine disrupting compounds, including hormones and herbicides, from the Platte River, through an alluvial aquifer into a municipal water supply in Nebraska. This study will collect and interpret data in support of the development of drinking-water treatment guidance pertaining to bank-filtration efficiency. Data will be compared to similar studies conducted in the United States and other nations, including Germany.

In this paper, preliminary results of another study are presented. Samples were collected from surface water, bank-filtered water, combined untreated water from all active water-supply wells of a municipal well field, and

drinking water at three bank-filtration sites (the sites are not identified on Figure 3 at the request of the utilities) along the Platte River in Nebraska, United States (Figure 3). At the bank-filtration sites, drinking water is produced for cities and towns with population from about 30,000 to almost 500,000 people.

#### Description of Sites Along the Platte River

Three unidentified bank-filtration sites are along the Platte River, in Nebraska, United States (Figure 3). At its mouth, the Platte River has a drainage area of about 218,000 km<sup>2</sup> (square kilometers). The mean annual discharge of the Platte River is about 200 m<sup>3</sup>/s (cubic meters per second) near its confluence with the Missouri River.

During low discharges in the summer months, the Platte River becomes braided into multiple channels with exposed sandbars. At times and at places, its flow consists almost entirely of wastewater from STPs (Patrick O'Brian, Nebraska Department of Environmental Quality, written communication, 2001). The Platte River and its tributaries receive municipal waste from most cities along their courses, except the City of Omaha, which releases its wastewater into the Missouri River near and above its confluence with the Platte River. Along the Platte River and its tributaries, there are an estimated 200 STPs that release treated or untreated wastewater at rates from about 0.4 ML/d (million liters per day) to about 200 ML/d (Ronald Ash,

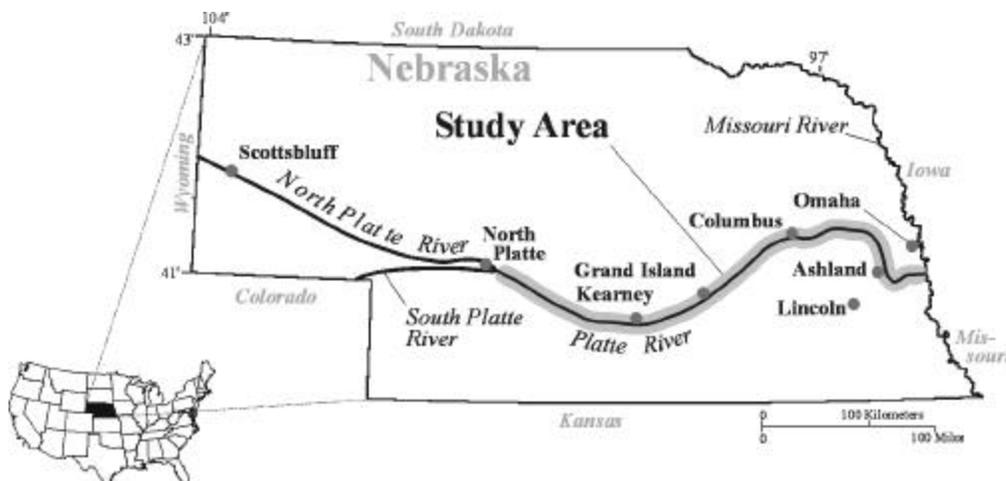


Figure 3: Generalized location of study area and unidentified bank-filtration sites along the Platte River, Nebraska, United States.

Nebraska Department of Environmental Quality, oral communication, 2001). In addition, an estimated 7,000 or more AFOs, including about 1,000 CAFOs, exist in Nebraska (Dennis Heitmann, Nebraska Department of Environmental Quality, oral communication, 2001). They vary in size from more than 1 to almost 100,000 cattle and pigs. During runoff events or chronic wet periods (several rainfalls within 1 month leaving the soils very saturated and standing water in collection pits high), discharges occur from these AFOs into nearby streams.

Nebraska was ranked second in 1997 in the production of cattle and calves in the United States with more than 14 million, or about 6.8 percent of the national production (U.S. Department of Agriculture, tbl36.pdf, accessed June 28, 2001). Moreover, Nebraska was ranked seventh in 1997 and sixth in 2000 in the production of pigs in the United States with about 3.5 million, or 5.7 percent of the national production (U.S. Department of Agriculture, 2001a; U.S. Department of Agriculture, 2001b).

The alluvial sediments deposited by the Platte River, consisting mainly of sand and gravel and some silt and clay, are increasingly developed for drinking-water supply by large and small cities along the river. Water supplies along the river generally are affected by the quality of water from the local streams and the main channel (e.g. Verstraeten et al., 1999; Steele & Verstraeten, 1999). Drinking-water utilities developed along the Platte River have wells completed in these alluvial sediments, generally at depths of less than 40 m. All but one well sampled during the project were vertical water-supply wells completed at depths of less than 30 m and varying in distance from tens to hundreds of meters from the river. The vertical water-supply wells typically produce as much as 5 ML/d. The other well is a horizontal collector well on an island in the Platte River less than 30 m from the banks of the river. The collector well consists of a main vertical caisson and seven horizontal laterals, totaling more than 400 m in length. It is completed at a depth of less than 30 m. The collector well is equipped with three large pumps and has a capacity of 45 ML/d.

#### Preliminary Results for Pharmaceutical Residues

Representative water samples were collected from the Platte River (representative integrated samples), from water-supply wells, and at the drinking-water treatment plants including raw (a combination of bank-filtered water from as many as 50 water-supply wells) and treated water following USGS sampling protocols to prevent cross contamination. The physical and chemical treatments used at the three bank-filtration sites include

filtration, chlorination, or ozonation but do not include the use of ultra-violet and granular-activated-carbon treatment. The samples were collected June 4-6, 2001, from the three sites when the Platte River had a moderate discharge (28 to 240 m<sup>3</sup>/s). The samples were analyzed at the site for physical parameters and in the laboratory for (1) endocrine disrupting compounds and wastewater indicators, including 63 compounds and 4 nonionic detergent metabolites, with 23 compounds having known or suspected endocrine-disrupting potential (Zaugg et al., in press); (2) 24 pharmaceuticals derived from cattle and other animals (Kolpin & others, in press; Meyer, U.S. Geological Survey, written commun, 2001); and (3) 22 over-the-counter and prescription pharmaceuticals used by humans, and their metabolites (Kolpin & others, in press). The analyte concentrations reported for the wastewater indicators are for filtered water and may greatly underrepresent the total amount of some analytes present in whole surface-water samples for low-solubility analytes that strongly sorb to suspended material. This effect is suspected to be smaller for ground water and treated drinking water.

In general, dissolved-oxygen concentrations in water from water-supply wells were as much as 4.0 mg/L (milligrams per liter) and were less than 1 mg/L in water from two of four water-supply wells, suggesting potential reducing conditions may exist at some sampling sites. The pH of the river exceeded 8.0. Based on previous studies in Nebraska (Steele & Verstraeten, 1999; Verstraeten et al., 1999; Verstraeten et al., in press A), and based on water temperature and pH of water in the water-supply wells measured during this investigation, there is sufficient evidence that these wells receive bank-filtered water, except water-supply well W3 (Table 2). Previous studies established that, at times, water in the collector well sampled consisted of more than 50 percent surface water under similar conditions to those used during this investigation (Steele & Verstraeten, 1999).

Preliminary results of the analyses of water samples from the bank-filtration sites for selected endocrine-disrupting compounds and wastewater products (Table 2) suggest that endocrine disrupting compounds, including herbicides, can occur in river water, well water, and drinking water, further suggesting that transport of these compounds can occur through bank filtration. Transport of contaminants would depend upon the proximity of contaminant sources, the concentrations of compounds occurring in the river, the efficiency of bank filtration, the characteristics of the compounds (hydrophobic versus hydrophilic, vulnerability to microbial degradation, etc.), and local drinking-water treatment methods. Twelve of the 63 compounds for which the samples were analyzed were

Table 2. Selected results from the analysis of water samples at three bank-filtration sites, Nebraska, United States, June 4-6, 2001.

[BF, bank filtration; \*, where shown, the level reported is not the method reporting level but the method detection level; RV, water from the Platte River; W, water from water-supply well; UW, untreated water combined from all active wells in the drinking-water treatment plant; DW, treated drinking water; ° C, degrees Celsius; mg/L, milligrams per liter; H, herbicide; ND, not detected; NA, not analyzed; E, estimated because concentrations are below the method reporting level; ng/L, nanograms per liter]

Parameter	Reporting units	Method reporting * level	BF Site A				BF site B				BF site C			
			RV1	W1	DW1	RV2	W2	W3	UW	DW2	RV3	W4	UW2	DW3
Physical parameters														
Temperature water	° C	0.5	18.5	16.5	16.5	18.0	14.0	4.5	17.5	16.0	17.0	17.5	18.0	17.0
PH	Units	0.1	8.2	7.8	7.8	8.2	7.8	7.8	7.5	7.6	8.9	7.6	7.2	8.3
Dissolved oxygen	mg/L	0.01	6.10	1.75	2.84	6.54	0.88	3.82	1.30	5.14	7.13	0.41	1.29	3.11
Selected endocrine-disrupting compounds including pharmaceuticals and other wastewater indicators*.														
Caffeine	ng/L	500	ND	ND	ND	ND	ND	ND	ND	E 43	ND	ND	E 43	ND
Phenol (Disinfectant)	ng/L	500	ND	E 330	ND	ND	E 27	ND	E 490	ND	ND	ND	ND	ND
Prometon (H)	ng/L	500	E 29	E 21	ND	ND	ND	ND	ND	E 50	ND	ND	ND	ND
Bromacil (H)	ng/L	500	E 54	ND	ND	ND	ND	ND	ND	ND	E 140	E 73	E 47	ND
Metolachlor (H)	ng/L	500	E 79	E 10	E 22	E 48	E 160	ND	E 130	E260	E 340	E 220	E 270	E 280
Bisphenol A	ng/L	1 000	ND	ND	ND	ND	ND	ND	ND	ND	ND	E 88	ND	ND
Triphenyl phosphate	ng/L	500	ND	ND	ND	ND	ND	ND	ND	ND	ND	E 120	ND	ND
3-β-coprostanol (Fecal indicator)	ng/L	2 000	ND	E 200	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cholesterol (Fecal indicator)	ng/L	2 000	E 680	E 1 700	ND	ND	ND	ND	ND	ND	E 510	ND	ND	ND
β-sitosterol (Plant sterol)	ng/L	2 000	E 710	E 2 100	ND	ND	ND	ND	ND	ND	E 1 100	ND	ND	ND
1,7 Dimethylxantine (derivative of caffeine)	ng/L	19*	ND	ND	ND	E 5.8	ND	ND	ND	ND	ND	ND	ND	ND
Sulfamethoxazole (antibiotic, Bactrim compound)	ng/L	23*	E 7	E 2	ND	ND	ND	ND	E 9	E 6	ND	ND	E 9	ND

Note: Data on endocrine disrupters other than pharmaceuticals and wastewater indicators are presented but not discussed in detail in the text.

detected in the water samples. They were more often detected in river water (six compounds) and water from the water-supply wells (10 compounds), than in drinking water (two compounds, one a drinking-water treatment by-product and the other, a herbicide). Two of the 12 compounds detected were fecal indicators. Two plant sterols were found at one of the three bank-filtration sites in the river and well water. Caffeine was detected in one raw-water sample at one bank-filtration site (43 ng/L).

The concentration of a compound was not always less in the water from the water-supply well than in the river, as one would expect because of attenuation by processes such as adsorption-desorption, photodegradation, or microbial degradation. The sampling scheme did not take into account the travel time of water from the river into the well or area of contribution to this well. All samples at a bank-filtration site were collected within 4 hours of each other. Therefore, the same aliquot of water from the river was not collected from the water-supply wells and the potential for removal of a

compound cannot be determined from the data collected during this study.

One of 27 pharmaceutical compounds used by humans (sulfamethoxazole) was detected. Sulfamethoxazole was detected in river, well, and treated drinking water. Because the same aliquot of water was not collected at a bank-filtration site, no attempt to interpret the degree of attenuation during bank filtration was made for this compound. However, smaller concentrations of this antibiotic were detected in well and drinking water than in river water, except at bank-filtration site C.

Samples were not analyzed for ethylenediaminetetraacetate (EDTA), which is thought to be a very good indicator of wastewater contamination that occurs in large concentrations throughout the year. As mentioned previously, a larger study evaluating these temporal variations and actual transport mechanisms of these compounds recently has been initiated by the USGS in the United States. This study and other studies in the United States, Germany, and other nations will provide more answers to some of the questions raised herein.

### Preliminary Conclusions

The data collected during this reconnaissance indicate that transport of wastewater and endocrine-disrupting compounds from a river through ground water into drinking water may occur. However, the data collected during this reconnaissance do not identify the potential temporal variations in detections and concentrations of the compounds analyzed. When lower discharges occur and surface water is dominated by wastewater effluent, or during and immediately after a rain event, when STPs cannot treat all of their water, one might detect more compounds in river water, water from water-supply wells, and treated drinking water. At these times, more compounds could be detected in water at concentrations that can be an order of magnitude different (smaller or larger) than those found during this study.

### **CONCLUSIONS**

The investigations in Germany and the United States revealed that several polar organic compounds, especially several PhACs, are relevant to drinking-water production at bank-filtration sites. In Germany, several compounds, such as bezafibrate, diclofenac or MCPP, seem to be removed effectively during bank filtration, but other compounds, such as carbamazepine, clofibrac acid, primidone, propyphenazone, compound X, bentazone, DDA, TCIPP, and TCEP, are not. The latter were detected at concentrations between 15 and 180 ng/L in the water-supply well of the Lake Wannsee transect in Berlin, Germany. Endocrine disrupting compounds including herbicides and one pharmaceutical were detected in surface water, water-supply wells, or drinking water at three bank-filtration sites in Nebraska, United States. Further investigations are needed to answer questions about the origin of several compounds and their behavior during the bank-filtration process.

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