

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*

Vorkommen und Verteilung organischer Kontaminanten im aquatischen System in Berlin. Teil I: Arzneimittelrückstände und weitere polare Kontaminanten im Berliner Oberflächen- und Grundwasser

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Keywords: Pharmaceuticals, *N*-(phenylsulfonyl)-sarcosine, Sewage Works Effluents, Groundwater Contamination, Capillary Gas Chromatography-Mass Spectrometry, GC-MS, GC-MS/MS

Summary: Several polar contaminants were found in screening analyses of 30 representative surface water samples collected from rivers, lakes, and canals in Berlin. Residues of pharmaceuticals and *N*-(phenylsulfonyl)-sarcosine originating from various sewage treatment plants effluents were found at concentrations up to the µg/L-level in the surface water, whereas the concentrations of polar pesticides such as dichlorprop and mecoprop were always below 0.1 µg/L. The pharmaceuticals most frequently detected in the surface water samples include clofibric acid, diclofenac, ibuprofen, propiphenazone, and two other drug metabolites. Additional investigations of groundwater wells of a drinking water plant have shown that polar contaminants such as drug residues or *N*-(phenylsulfonyl)-sarcosine easily leach through the subsoil into the groundwater aquifers when contaminated surface water is used for groundwater recharge in drinking water production.

Schlagwörter: Pharmazeutika, *N*-(Phenylsulfonyl)-sarcosin, Klärwerkseinleitungen, Grundwasserkontamination, Kapillargaschromatographie-Massenspektrometrie, GC-MS, GC-MS/MS

Zusammenfassung: Im Rahmen eines Screenings von 30 repräsentativen Oberflächenwasserproben aus Flüssen, Seen und Kanälen Berlins wurden eine Reihe polarer organischer Kontaminanten detektiert. Rückstände von Arzneimitteln und von *N*-(Phenylsulfonyl)-sarcosin, die über die verschiedenen Klärwerke in die Oberflächengewässer eingetragen werden, wurden in Konzentrationen bis in den µg/L-Bereich in den Proben gefunden. Zu den am häufigsten gefundenen Pharmazeutika gehörten Clofibrinsäure, Diclofenac, Ibuprofen und Propiphenazon sowie zwei weitere Metabolite von Arzneimitteln. Die Konzentrationen der ebenfalls gefundenen polaren Pestizide Dichlorprop und Mecoprop lagen hingegen immer unterhalb von 0.1 µg/L. Zusätzliche Untersuchungen von Wasserproben, die den Grundwasserbrunnen bzw. den Grundwasserbeobachtungsrohren eines Wasserwerkes entnommen wurden, zeigten, daß polare Kontaminanten wie Arzneimittelrückstände oder *N*-(Phenylsulfonyl)-sarcosin aus kontaminierten Oberflächengewässern in die Grundwasseraquifere eingetragen werden können, wenn die Uferfiltration oder die künstliche Grundwasseranreicherung zur Trinkwassergewinnung eingesetzt wird.

1 Introduction

The occurrence of drug residues in the aquatic environment has become a matter of public concern since clofibric acid was found in some Berlin groundwater samples in 1992 [1]. Clofibric acid is the active metabolite of clofibrate-ethyl, etofibrate, and etofyllin clofibrate which are used as blood lipid regulators in human medical care. Applying a new, more sensitive, analytical method [2–5], clofibric acid was also detected in Berlin tap water samples at concentrations up to 165 ng/L [6]. Further investigations have shown that the concentrations of clofibric acid found in tap water samples of the individual Berlin water works correlate well with the proportions of artificial ground

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level replenishment and bank filtration used by the particular water works in drinking water production [7]. The geographical situation of the water works and the relative contamination of the neighboring watercourses used as a source for groundwater enrichment are the factors determining the concentration level of clofibric acid [7].

Clofibric acid has since been found in many places in Germany during a number of investigations of sewage effluents, surface and ground waters [5, 6, 8–11]. The occurrence of clofibric acid in environmental water samples has been proven to be neither a local nor a national phenomenon because it has also been found in surface water samples in Italy [12]. Recent investigations show that several other drugs and drug metabolites also occur in the aquatic environment [9–11, 13–19].

In Berlin, municipal wastewater contaminations are of great relevance because of the high contributions of sewage works effluents to the surface waters resulting from low surface water flows and large amounts of raw sewage produced by its population of around 3.5 million. In regard to the high proportion of bank filtrate and artificial groundwater enrichment of approximately 75% used in drinking water production in Berlin, monitoring of known organic contaminants and tracking down new contaminants in the surface water is a matter of high priority. It helps in recognition of groundwater contamination sources as early as possible.

30 surface water samples representative of the Berlin area were analyzed in a first screening analysis for various chemical groups known to be environmental pollutants, namely phenols [20], synthetic musks [21], some polar pesticides, pharmaceutical residues, and other polar organic compounds. In this paper, the results of the investigations concerning drug residues, polar pesticides, and other polar contaminants are presented.

2 Experimental

2.1 Sample Collection and Analytical Program

For the screening of the Berlin surface waters, 30 representative sampling locations were selected as shown in Figure 1.

Samples were taken from sewage works effluents and along the different canals, rivers, or lakes upstream and downstream of sewer works outlets into the surface water. Whenever possible, the samples were collected from the middle of the waters at a depth of 2 meters. All samples were analyzed for residues of pharmaceuticals, polar pesticides, and other target compounds immediately after sample collection. The results obtained with phenols and synthetic musks are to be reported elsewhere [20, 21]. Physico-chemical parameters (pH, temperature, conductivity, redox potential) and some indicative chemical parameters such as DOC, COD, nitrate, nitrite, ammonia, phosphate, phenolic index, and boron were additionally determined.

2.2 Materials

All solvents were highly purified products from Merck, Darmstadt, Germany. Pentafluorobenzyl bromide and *N*-(*tert*-butyldimethylsilyl)-*N*-methyl-trifluoroacetamide (MTBSTFA) were obtained from Aldrich, Steinheim, Germany; triethylamine was from Merck, Darmstadt, Germany. Sample vials, screw caps, and septa were purchased from Zinsser, Frankfurt, Germany, 200- μ L inserts for the sample vials from CS-Chromatographie Service, Langerwehe, Germany. Pharmaceuticals and pesticides were of analytical purity, purchased from Promochem, Wesel, Germany, from Riedel de Haen, Seelze, Germany, from Aldrich or from Sigma, Deisenhofen, Germany. *N*-(phenylsulfonyl)-sarcosine and 2-(4-chlorophenoxy)-butyric acid were synthesized according to procedures described elsewhere [1, 5]. Stock solutions of all compounds were prepared in methanol. Solid-phase extraction (SPE) was carried out with a vacuum manifold (spe 12G) using cartridges of polypropylene with a volume of 6 mL and BAKERBOND Polar Plus RP-C18 material all from Mallinckrodt Baker, Griesheim, Germany. Nitrate, nitrite, ammonia, phosphate, DOC, COD, and boron were analyzed using test kits and the LASA 10 photometer from Dr. Lange, Berlin, Germany. Adjustable transferpetteors (1...10 μ L and 10...100 μ L) were from Brand, Wertheim, Germany.

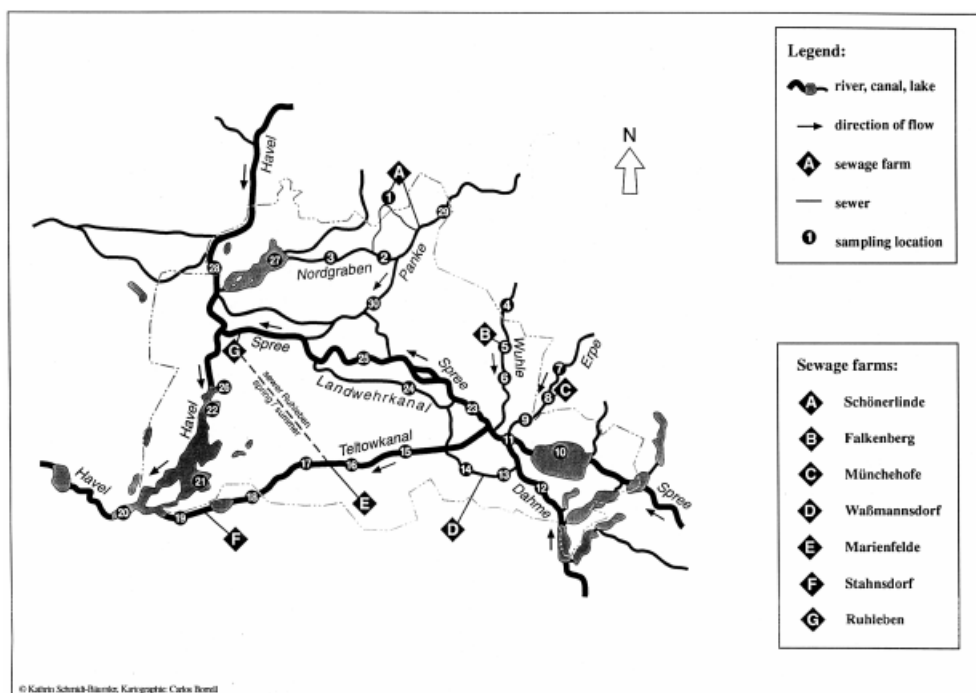


Fig. 1: Map showing the 30 sampling locations of the surface water monitoring in Berlin in September 1996.

Übersichtskarte der 30 Probenahmeorte des Oberflächenwassermonitorings vom September 1996 in Berlin.

2.3 Sample Preparation

A water sample of 0.5 L was mixed with 100 μ L of a solution of 2-(4-chlorophenoxy)-butyric acid in methanol (1 mg/L) as surrogate standard to give a concentration of 200 ng/L. The sample was prepared at two different pH values (pH 8.5 and pH <2) to analyze the samples for neutral and acidic pollutants. Each SPE-cartridge was filled with 1 g of RP-C18 adsorbent. Conditioning was performed successively with 10 mL acetone, 10 mL methanol, and finally 10 mL of distilled, deionized water. The solvents were drawn through the cartridges by means of a gentle vacuum and the cartridge was not permitted to run dry during the whole conditioning procedure. The water sample was then percolated through the cartridge at a maximum flow rate of approximately 8 mL/min by applying a low vacuum.

After drying the cartridge for 2 to 3 hours by flushing with nitrogen, the analytes were eluted with 2.5 mL of methanol and the eluate was dried under a gentle stream of nitrogen. The residue from the neutral sample preparation was dissolved in 100 μ L of toluene and injected directly into the gas chromatograph. The residue from the acidic sample preparation was derivatized to make the analytes amenable to gas chromatography.

2.4 Derivatization

The residues obtained from the acidic sample preparation were derivatized using pentafluorobenzyl bromide and MTBSTFA, respectively. Derivatization with pentafluorobenzyl bromide was performed at 110°C for one hour using 100 μ L of pentafluorobenzyl bromide (2% in toluene) and 2 μ L of triethylamine as catalyst as previously described [2, 3, 5]. The derivatized sample was then dried under nitrogen and finally dissolved in 100 μ L of toluene. Derivatization with MTBSTFA was performed at 80°C for one hour using 50 μ L of MTBSTFA and 50 μ L of acetonitrile as previously described for the analysis of phenols [5, 22]. The solution containing the derivatives was injected directly into the gas chromatograph.

2.5 GC-MS Parameters

Mass spectrometric measurements were performed using an Hewlett-Packard HP 5970 MSD combined with an HP 5890 gas chromatograph fitted with a 25 m \times 0.2 mm i.d. \times 0.33 μ m HP-5 capillary column and a 1.5 m \times 0.32 mm i.d. \times 0.33 μ m HP-5 pre-column. Additionally, mass spectrometric measurements were performed with a Finnigan GCQ quadrupole ion-trap GC-MS/MS system fitted with a 30 m \times 0.25 mm i.d. \times 0.25 μ m J&W DB5MS capillary column. In both cases, carrier gas was helium (purity: 99.999%) set to a flow of 28 cm/s at the initial temperature. The oven temperature was held at 100°C for 1 min following injection, then programmed at 30°C/min to 150°C, which was held for 1 min, then at 3°C/min to 205°C followed by 10°C/min to 260°C and finally held for 23 min. Injection port and transfer line temperatures were 230°C and 250°C (GCQ: 275°C), respectively. 2- μ L quantities of sample were injected using hot splitless injection with the split closed for 0.9 min. Using Selected Ion Monitoring (SIM), three characteristic ions were selected for each compound and scanned in time windows corresponding to their expected retention times with dwell times of 150 to 300 ms per ion. Using the GCQ in the MS-MS mode, suitable parent ions were selected for each analyte which were fragmented again. The resulting daughter ion mass spectra were scanned in corresponding time windows. The tuning of both mass spectrometers was performed weekly using the auto-tuning macro. Pre-column and/or insert liner were exchanged after 50 injections at the latest.

3 Results and Discussion

3.1 Results from the Surface Water Screening for Pharmaceutical Residues and other Polar Contaminants

The screening analyses of surface water samples provided us with an overall picture of the degree of contamination of Berlin waters by drug residues and other organic contaminants. Table 1 gives an overview on all organic compound classes that have been investigated and found in this surface water monitoring. The results obtained for the phenols, the synthetic musks, and for bis(chlorophenyl)acetic acid (DDA) will be reported in detail elsewhere [20, 21, 24].

Pharmaceuticals and pharmaceutical metabolites have been found at all sampling sites located downstream from the municipal sewage treatment plants (see Fig. 1). Figure 2 shows the GC-MS/MS chromatogram of a surface water sample which has been derivatized with pentafluorobenzyl bromide. In this sample, clofibric acid, the analgesic propiphenazone, the antirheumatic diclofenac, and some other polar contaminants could be unequivocally identified by their characteristic daughter ion spectra, as will be shown in detail elsewhere [25].

In Table 2 the concentrations of clofibric acid, diclofenac, ibuprofen, and propiphenazone are compiled which were most frequently found at concentrations up to the μ g/L-level in the surface water samples. A derivative of clofibric acid and *N*-methylphenacetin have also been found in some of the water samples. Since for both compounds no pure standards were commercially available, they could only be identified but not quantified. In a few water samples, phenazone has been detected but only at low concentration levels.

The prominent acidic herbicides mecoprop and dichloroprop have also been found in some surface water samples but always at concentration levels clearly below 0.1 μ g/L. Significant amounts of the DDT metabolites *o,p'*- and *p,p'*-DDA were only detected in surface water samples collected from the Teltowkanal. As shown in detail elsewhere [23, 24], these residues result from a point source by mobilization of DDT residues bound in the sediment of a canal in the vicinity of a former DDT production site of the former GDR.

Considerable amounts of *N*-(phenylsulfonyl)-sarcosine up to the μ g/L-level were detected in the surface water samples as can be drawn from Table 2. *N*-(phenylsulfonyl)-sarcosine was found for the first time as environmental pollutant in investigations of aquifers below sewage farm areas south of Berlin [26]. It infiltrated the subsoil together with other contaminants after application of municipal wastewater to the surface [5]. This persistent environmental contaminant has meanwhile been found in surface water samples both within Germany [5, 7, 12, 27–29] and recently also outside of Germany [12]. Due to its high mobility in the subsoil, *N*-(phenylsulfonyl)-sarcosine was found to leach easily into the groundwater [5, 7, 12, 28, 29], and it has also been detected together with clofibric acid in Berlin drinking water [7]. Recently, Knepper and Haberer [29] postulated *N*-(phenylsulfonyl)-sarcosine to be a metabolite of the corrosion inhibitor *N*-(phenylsulfonyl)-capronic acid.

3.2 Impact of Sewage Effluents on the Water Quality of the Teltowkanal

The surface water quality of the Teltowkanal in the south of Berlin (see Fig. 1) is of great importance because the surface

Table 1: Organic compounds investigated and found in the Berlin surface water screening of samples collected from 30 representative sampling locations.

Organische Verbindungen, die bei der Screeninguntersuchung von 30 repräsentativen Oberflächenwasserproben untersucht und gefunden wurden.

parameter (compound class)	individual contaminants detected	maximum concentration levels*
pharmaceutical residues	clofibric acid, diclofenac, ibuprofen, propiphenazone, phenazone, <i>N</i> -methylphenacetin, clofibric acid derivative	up to 1.9 µg/L
polar pesticides	mecoprop, dichlorprop, bis(chlorophenyl)acetic acid [24]**	always below 0.1 µg/L
other polar contaminants	<i>N</i> -(phenylsulfonyl)-sarcosine	up to 0.3 µg/L
phenols [20]**	phenol, <i>m</i> -, <i>o</i> -, <i>p</i> -cresol, 2-ethylphenol, 2-chlorophenol, 4-chloro-3-methylphenol, <i>o</i> -nitrophenol, <i>p</i> -nitrophenol, pentachlorophenol	up to 2.25 µg/L up to 7.8 µg/L
nitro musks [21]**	musk ketone, musk xylene, musk moskene	up to 0.39 µg/L
polycyclic musks [21]**	ADBI, HHCb, AHTN	up to 12.5 µg/L

*: maximum concentrations found for the individual compound; **: reported in detail elsewhere

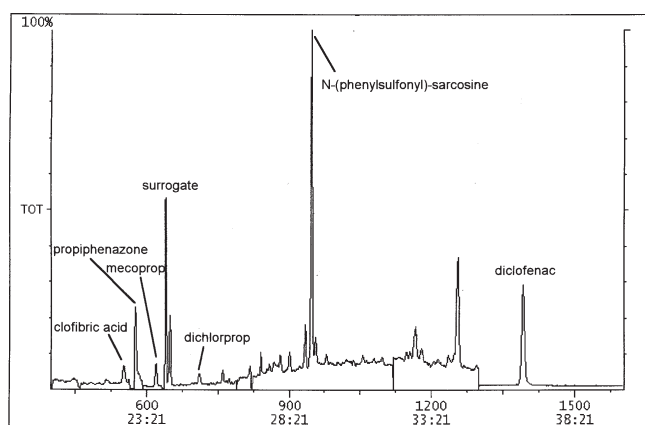


Fig. 2: GC-MS/MS chromatogram of the pentafluorobenzylated sample extract of a surface water sample collected from the Teltowkanal.

GC-MS/MS-Chromatogramm des pentafluorbenzylierten Extraktes einer Oberflächenwasserprobe des Teltowkanals.

water is used for bank filtration in drinking water production. The water in the Teltowkanal is characterized by high proportions of treated municipal sewage. During the sampling period in September 1996, three sewage treatment plants deposited their effluents into the canal. In summer time, the canal is fed by additional effluents from Berlin's largest sewage treatment plant in Ruhleben.

The impact of the municipal sewage treatment plants on the surface water quality of the Teltowkanal is demonstrated by the values of the chemical parameters compiled in Table 3. When the effluents from the sewage treatment plant of Waßmannsdorf are disposed of into the Teltowkanal significant increases of the concentration levels were observed for many of the common chemical parameters, but especially for nitrate, total nitrogen, phosphate, and boron. However, a direct correlation between the values of the common chemical parameters and the inputs of all three sewage treatment plants was to a certain degree only observed for the chemical oxygen demand (COD).

As presented in Figure 3 for the pharmaceutical contaminants clofibric acid and diclofenac, the impact of sewage works

effluents on the surface water quality is much more significant than observed for any of the common chemical parameters. Both compounds occur in the surface water samples at maximum concentration levels of 0.5 and 1 µg/L, respectively. With both compounds, peak concentrations were observed in the canal where sewage effluents were deposited by the three purification plants. The concentration levels of the antirheumatic ibuprofen which has also been detected in the Teltowkanal have been found to be much lower and the concentration profile to be different from those of clofibric acid and diclofenac. This might be explained by different forms of therapy in the eastern and western districts of Berlin, because ibuprofen is detected at higher concentration levels in the effluents of the sewage treatment plants clarifying wastewater from the western parts of Berlin.

As presented in Figure 4, the distribution pattern found for *N*-(phenylsulfonyl)-sarcosine in the Teltowkanal matches those of clofibric acid and diclofenac. Only at the last sampling site, where the canal has already merged with the river Havel, the concentration of *N*-(phenylsulfonyl)-sarcosine is found to be significantly higher. Obviously, the major contamination originates from sources upstream from the river Havel confluence that are not municipal wastewater effluents.

Moreover, an overall evaluation of all parameters investigated in this surface water monitoring shows that the concentration levels of drug residues also correlate well with those of synthetic musks [21] which are also characteristic contaminants of municipal wastewater.

3.3 Impacts on the Groundwater Resources

The polar contaminants which were found in the surface water may also cause problems to drinking water supplies wherever contaminated surface water is used for groundwater recharge in drinking water production. This has already been demonstrated in investigations of tap water samples collected from 14 waterworks in Berlin [7]. Clofibric acid and *N*-(phenylsulfonyl)-sarcosine, which were investigated in this study, were found at maximum concentrations of 270 ng/L and 105 ng/L, respectively [7].

In another study, several pharmaceuticals and other organic pollutants were found at maximum concentrations up to the

Table 2: Results of the Berlin surface water monitoring for some pharmaceutical contaminants and *N*-(phenylsulfonyl)-sarcosine. Ergebnisse des Berliner Oberflächenwassermonitorings auf pharmazeutische Kontaminanten und *N*-(Phenylsulfonyl)-sarcosin.

no.	sampling location	waters	date	clofibric acid in ng/L	diclofenac in ng/L	ibuprofen in ng/L	propiphenazone in ng/L	<i>N</i> -(phenylsulfonyl)-sarcosine in ng/L
1	Schönerlinde	sewer	16. Sep 96	450	760	n.d.	1 900	290
2	Brombeerweg	Nordgraben	16. Sep 96	135	60	n.d.	120	n.d.
3	Am Nordgraben	Nordgraben	16. Sep 96	320	160	5	210	130
4	An der Wuhle	Wuhle	16. Sep 96	n.d.	5	2	n.d.	n.d.
5	Köthener Straße	Wuhle	16. Sep 96	660	165	35	350	90
6	Eisenacher Str.	Wuhle	16. Sep 96			– not evaluable –		
7	Neuenhagen	Erpe	19. Sep 96	n.d.	n.d.	n.d.	20	n.d.
8	Münchehofe	sewer	19. Sep 96	680	135	10	360	85
9	Friedrichshagen	Erpe	19. Sep 96	875	580	15	200	215
10	Müggelsee	Müggelsee	19. Sep 96	15	15	5	5	75
11	Alt-Köpenick	Spree	19. Sep 96	230	60	40	100	315
12	Grünau	Dahme	19. Sep 96	n.d.	n.d.	n.d.	n.d.	15
13	Treptow	Teltowkanal	24. Sep 96	65	25	5	210	85
14	Rudow	Teltowkanal	24. Sep 96	460	960	3	135	1 650
15	Tempelhof	Teltowkanal	24. Sep 96	125	200	n.d.	150	1 000
16	Lankwitz	Teltowkanal	24. Sep 96	190	320	45	45	860
17	Lichterfelde	Teltowkanal	24. Sep 96	190	350	50	40	1 050
18	Kleinmachnow	Teltowkanal	24. Sep 96	30	10	5	10	400
19	Dreilinden	Teltowkanal	24. Sep 96	260	410	75	35	1 450
20	Potsdam	Havel	24. Sep 96	100	110	10	35	2 250
21	Wannsee	Wannsee/Havel	24. Sep 96	145	120	40	135	190
22	Stößensee	Havel	24. Sep 96	100	35	10	40	70
23	Treptow	Spree	26. Sep 96	180	25	30	20	90
24	Kreuzberg	Landwehrkanal	26. Sep 96	n.d.	35	280	40	165
25	Tiergarten	Spree	26. Sep 96	110	30	10	25	105
26	Spandau	Havel	26. Sep 96	150	200	10	70	135
27	Tegeler See	Tegeler See/Havel	26. Sep 96	190	40	25	50	420
28	Tegelort	Havel	26. Sep 96	80	20	10	40	170
29	Buch	Panke	26. Sep 96	n.d.	20	15	5	n.d.
30	Wedding	Panke	26. Sep 96	n.d.	20	45	n.d.	n.d.

n.d.: not detected.

Table 3: Results for common chemical parameters, some pharmaceuticals, and *N*-(phenylsulfonyl)-sarcosine in the Teltowkanal. Ergebnisse für allgemeine chemische Parameter, für Pharmazeutika und für *N*-(Phenylsulfonyl)-sarcosin im Teltowkanal.

sampling location	ammonia mg/L	nitrate mg/L	nitrite mg/L	total nitrogen mg/L	penolic index mg/L	phosphate mg/L	total organic carbon (TOC) mg/L	chemical oxygen demand (COD) mg/L	boron mg/L	cyanide mg/L	clofibric acid ng/L	diclofenac ng/L	ibuprofen ng/L	propiphenazone ng/L	<i>N</i> -(phenylsulfonyl)- sarcosine ng/L
Dahme. Grünau	0.03	<1.00	<0.05	2.02	0.25	0.42	9.6	30.5	<0.05	<0.01	n.d.	n.d.	n.d.	n.d.	15
Teltowkanal. Treptow	0.08	1.33	0.05	3.55	0.21	0.58	13.2	32.4	<0.05	<0.01	65	25	5	210	85
Teltowkanal. Rudow	0.12	38.5	0.14	15.80	0.34	3.24	13.5	33.6	0.56	<0.01	460	960	3	135	1 650
Teltowkanal. Tempelhof	0.26	7.65	0.08	6.28	0.23	0.56	11.5	30.0	0.23	<0.01	125	200	n.d.	150	1 000
Teltowkanal. Lankwitz	1.49	10.20	0.18	8.10	0.31	0.46	–	30.4	0.31	<0.01	190	320	45	45	860
Teltowkanal. Lichterfelde	1.69	10.50	0.19	10.90	0.31	0.94	12.3	34.2	0.27	<0.01	190	350	50	40	1 050
Teltowkanal. Kleinmachnow	1.67	13.80	0.50	13.80	0.31	0.53	15.1	31.0	0.30	<0.01	30	10	5	10	400
Teltowkanal. Dreilinden	1.29	15.10	0.75	9.82	0.25	0.54	13.7	37.2	0.32	<0.01	260	410	75	35	1 450
Havel. Potsdam	0.53	8.86	0.43	6.92	0.21	0.84	–	29.2	0.26	<0.01	100	110	10	35	2 250

n.d.: not detected.

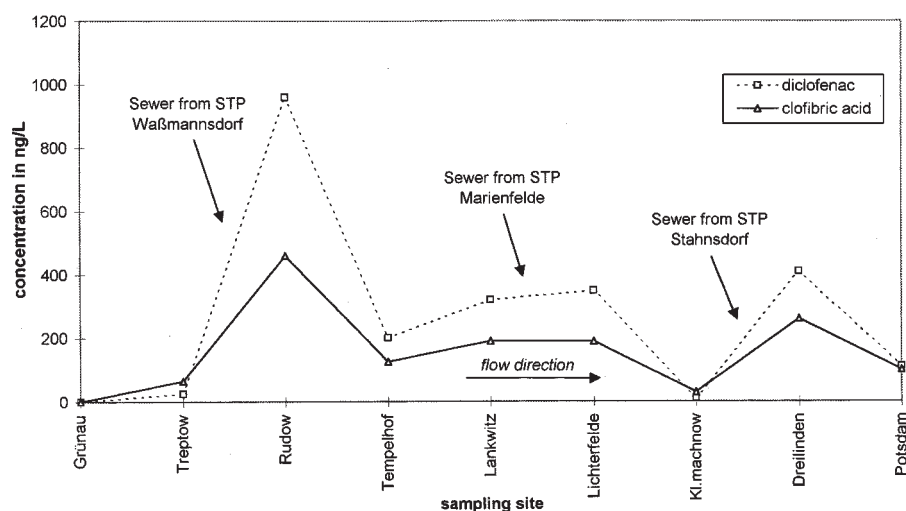


Fig. 3: Distribution of clofibric acid and diclofenac in the Teltowkanal. Precise concentrations are given in Table 3. STP: sewage treatment plant.

Verteilung von Clofibrinsäure und Diclofenac im Teltowkanal. Die präzisen Konzentrationen sind in Tabelle 3 angegeben. STP: Klärwerk.

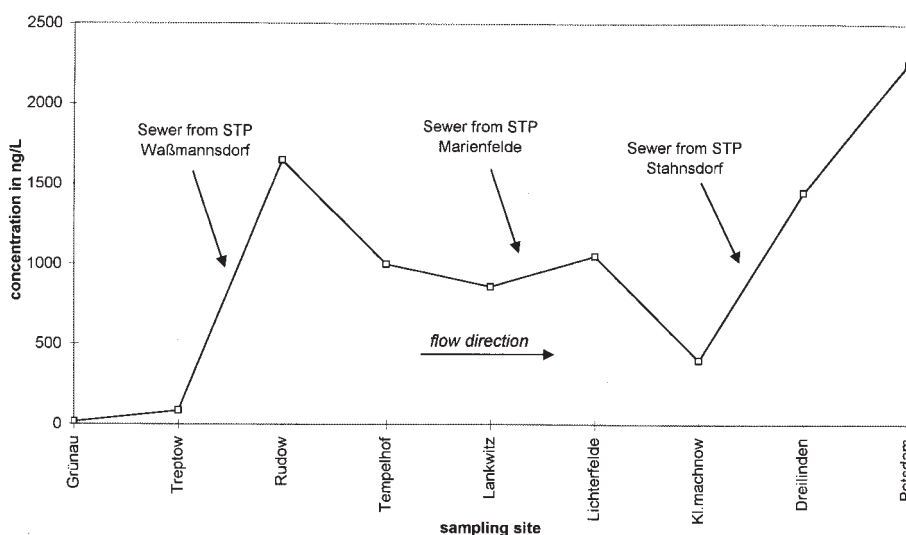


Fig. 4: Distribution of *N*-(phenylsulfonyl)-sarcosine in the Teltowkanal. Precise concentrations are given in Table 3. STP: sewage treatment plant.

Verteilung des *N*-(Phenylsulfonyl)-sarcosins im Teltowkanal. Die präzisen Konzentrationen sind in Tabelle 3 angegeben. STP: Klärwerk.

µg/L-level in groundwater wells of a drinking water plant located at a canal downstream of two sewage treatment plants and a disused pharmaceutical production plant. This particular drinking water plant uses a high proportion of bank filtrate in drinking water production. A compilation of the results of these investigations is given in Table 4.

17 water samples were collected from groundwater wells in the catchment area of the drinking water plant. Large variations in the concentrations of the contaminants were observed between the different groundwater wells. For diclofenac and ibuprofen the highest concentration levels were detected in those groundwater wells located close to the neighboring watercourse. This demonstrates the direct influence of the treated sewage effluents which are disposed of into the neighboring canal upstream of the drinking water plant.

However, the distributions of clofibric acid and the derivative of clofibric acid were different from those of the other pharmaceuticals and indicated that there was an additional point source of clofibric acid most probably a disused chemical production plant also located upstream of the canal. Independent of the contamination source, the results show that the pol-

Table 4: Concentrations of drug residues and of *N*-(phenylsulfonyl)-sarcosine found in 17 groundwater wells of a drinking water plant (Heberer et al. [19]).

Konzentrationen von Arzneimittlrückständen und von *N*-(Phenylsulfonyl)-sarcosin, die in insgesamt 17 Grundwasserbrunnen bzw. Grundwasserbeobachtungsrohren eines Wasserwerkes gefunden wurden (Heberer et al. [19]).

contaminant	concentration range in ng/L
clofibric acid	70...7 300
diclofenac	n.d. ... 380
fenofibrate	n.d. ... 45
ibuprofen	n.d. ... 200
phenazone	<10 ... 1 250
propiphenazone	n.d. ... 1 465
clofibric acid derivative	(50 ... 2 900)*
<i>N</i> -methylphenacetin	(<5 ... 470)*
<i>N</i> -(phenylsulfonyl)sarcosine	165 ... 1 440

n.d.: not detected;

*: concentration range only estimated, because no pure standard was available.

lutants detected are also not eliminated on their way through the subsoil and leach easily into the groundwater aquifers of the drinking water plant.

4 Conclusions

Drug residues and *N*-(phenylsulfonyl)-sarcosine are disposed of into the Berlin surface waters by treated municipal sewage effluents. They are found at concentrations up to the µg/L-level in surface water samples collected from canals and rivers in Berlin. Using groundwater recharge in drinking water production these contaminants can leach easily from the contaminated watercourses into the groundwater aquifers.

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