

3. Occurrence in the water cycle of Berlin

Because of the nature of the water cycle in Berlin, a number of persistent wastewater residues are present in the surface water and may potentially reach the groundwater via bank filtration and artificial recharge. The occurrence and behaviour of the wastewater residues para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) through wastewater treatment, surface water, bank filtration and drinking water treatment was studied. In addition, groundwater below a former sewage farm was investigated. All three compounds are ubiquitous in the aquatic environment of Berlin. P-TSA concentrations are much higher than those of o-TSA and BSA. P-TSA was found in high concentrations in the wastewater influent (2 to 15 µg/L), in the wastewater effluent (< 0.15 to 2.34 µg/L) and in sewage farm groundwater (< 0.05 µg/L to 20 µg/L) and in lower concentrations in the surface water (< 0.05 to 1.15 µg/L), bank filtrate (< 0.05 µg/L to 0.30 µg/L) and drinking water (< 0.05 to 0.54 µg/L). P-TSA is considerably depleted during waste- and drinking water treatment (~90 % reduction each). The concentration ranges for o-TSA and BSA in wastewater influents were 0.11 to 8 µg/L and < 0.05 to 0.64 µg/L respectively, while the values for wastewater effluents were 0.14 to 4 µg/L for o-TSA and 0.25 to 0.49 µg/L for BSA. Wastewater treatment and drinking water treatment do not reduce the concentrations of o-TSA and BSA. The behaviour of o-TSA during wastewater

treatment varies largely between different wastewater treatment plants where concentrations increase, remain constant or decrease. BSA forms during treatment. The concentrations measured in surface water, sewage farm groundwater, bank filtrate and drinking water were < 0.05 to 1.74 µg/L for o-TSA and < 0.05 to 0.53 µg/L for BSA.

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Identification and significance of sulfonamides (p-TSA, o-TSA, BSA) in an urban water cycle (Berlin, Germany).

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3.1 Introduction

The increasing mass load of organic pollutants in environmental water samples is a matter of great public and scientific concern. In a recent review paper SCHWARZENBACH ET AL. (2006) conclude that the worldwide contamination of freshwater systems with chemical pollutants is one of the key environmental problems facing humanity. REEMTSMA ET AL. (2006) note that poorly degradable compounds in wastewater treatment plants (WWTPs) can be problematic in partly closed water cycles if drinking water is produced via bank filtration. According to KNEPPER (2000) and KNEPPER ET AL. (1999) persistent polar organic contaminants can be critical for the quality of the drinking water. Various studies showed that pharmaceutical residues from human and animal use are not fully eliminated during wastewater treatment. Despite dilution, degradation and desorption they are found in increasingly rising concentrations in rivers, lakes and also in groundwater (e.g. in bank filtrate; HEBERER, 2002A; LOFFLER ET AL., 2005; ZUEHLKE ET AL., 2007).

In Berlin, treated wastewater is released into the surface water which is used indirectly for drinking water production via bank filtration. Until the 1980s, untreated wastewater was also irrigated directly onto the soils of several sewage farms (SENSTADT, 2007). During a gas chromatography-mass spectrometry screening (GC-MS) the three sulfonamides para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) were identified in groundwater within a catchment area of one drinking water treatment plant (DWTP), downstream of a former sewage farm. This raised concerns and led to the development of an analytical method to enable the sensitive analysis of these substances in wastewater, surface water, groundwater and drinking water (RICHTER ET AL., 2007).

Sulfonamides have a widespread application as pharmaceuticals and as industrial chemicals. Therefore, these compounds have various sources in wastewater. P-TSA is the primary degradation product and a marker residue for the disinfectant N-sodium-N-chloro-p-toluenesulfonamide (chloramine-T) in water (BELJAARS ET AL., 1993, 1994; DUIN AND NUIJENS, 1981; MEINERTZ ET AL., 1999, 2001).

Chloramine-T is used as an anti-microbial agent in the food industry (farming, slaughterhouses, canteen kitchens) to disinfect surfaces, instruments and machinery (BELJAARS ET AL., 1994; HANEKE, 2002). Chloramine-T is also a therapeutic drug for bacterial gill diseases of fish species, swine and poultry (GAIKOWSKI ET AL., 2004; HANEKE, 2002; HARRIS ET AL., 2004; MEINERTZ ET AL., 1999; SMAIL ET AL., 2004). P-TSA is used as a plasticizer, an intermediate for pesticides and drugs, and as a fungicide in paints and coatings (e.g. fingernail polishes; HSDB, 2003; HSDB, 2004; LEWIS, 1997; LIEBERT, 1986). O-TSA is used for production process of the artificial sweetener saccharin (MOOSER, 1984; STAVRIC AND KLASSEN, 1975). BSA is applied as an intermediate for synthesis dyes, photo chemicals and disinfectants.

Investigations by the German Federal Environment Agency (UBA) were carried out to prove the toxicological relevance of p-TSA. The report recommends a maximum concentration of 0.3 µg/L in drinking water as being tolerable for lifetime consumption (GRUMMT AND DIETER, 2006). Recommended maximum concentrations in drinking water for o-TSA and BSA do not exist. The German Federal Environmental Protection Agency recommends maximum concentrations of 0.1 µg/L for unknown substances in drinking water, if toxicological and environmental information of the substance insufficient.

The purpose of this investigation was to (i) analyse environmental water samples from different sites in Berlin for the organic components p-TSA, o-TSA and BSA. (ii) study the elimination of these substances during waste- and drinking water treatment and (iii) investigate their behaviour in the groundwater (during bank filtration and in contaminated sewage farm groundwater). So far to our knowledge, there has been no comprehensive previous study about the occurrence and fate of the sulfonamides p-TSA, o-TSA and BSA in the aquatic environment. An overview of studies investigating other sulfonamides is included below.

3.1.1 Literature review

Many recent studies have revealed the occurrence of sulfonamides in environmental water samples (GRUENHEID ET AL., 2005; HARTIG, 2000; HARTIG AND JEKEL, 2001; HEBERER AND STAN, 1994, 1997; KNEPPER, 2000; KNEPPER ET AL., 1999, 1995; KRAUSE ET AL., 1998, 2000). Sulfonamides have a widespread

application as pharmaceuticals and as industrial chemicals (benzene- and toluenesulfonamides, BTS). Therefore, these compounds have various sources in wastewater.

HARTIG (2000) reported about the relevance of four BTSs and three antibiotic sulfonamides in WWTPs effluents and their presence in surface water and bank filtrate in Berlin. The concentrations found were up to 2 µg/L in WWTP effluents and up to 0.25 µg/L in surface water and bank filtrate. HARTIG (2000) assumed that the redox conditions within the groundwater characteristics of the aquifer sediments are also important for the sulfonamide removal. Studies by GRUENHEID ET AL. (2005) showed that 50 % to 80 % of the antibiotic drug sulfamethoxazole is degraded during bank filtration and artificial recharge in Berlin at travel times of \geq 50 days under aerobic and anaerobic conditions. Furthermore, GRUENHEID ET AL. (2005) reported that three naphthalenesulfonic acids are not efficiently (from 0 % to 60 %) degraded at the bank filtration sites.

Several studies that investigated phenylsulfonamides are reported in the literature. KNEPPER ET AL. (1995) measured sarkosine-N-(phenylsulfonyl) in river Rhine and Main river water (Germany), and HEBERER AND STAN (1994) detected this compound in sewage farm groundwater (near Berlin, Germany). These studies demonstrated the occurrence in environmental water samples and the relevance of the phenylsulfonamides in the drinking water treatment processes (HEBERER AND STAN, 1994, 1997; KNEPPER, 2000; KNEPPER ET AL., 1999, 1995). Sarkosine-N-(phenylsulfonyl) is a metabolite of a corrosion-inhibiting agent relevant to drinking water treatment (HEBERER AND STAN, 1994, 1997; KNEPPER, 2000; KNEPPER ET AL., 1999; KNEPPER ET AL., 1995). KRAUSE ET AL. (2000, 1998) measured the sulfonamides N-(phenylsulfonyl)-glycine, -aneline and sarkosine in WWTP effluents and in the Rhine and Neckar rivers (Germany). They assumed that N-(phenylsulfonyl)-glycine and N-(phenylsulfonyl)-sarkosine are formed during WWTP treatment (KRAUSE ET AL., 2000, 1998).

To our knowledge, no attempt has ever been made to analyse (or quantify analyses of) the sulfonamides p-TSA, o-TSA and BSA in aquatic water samples. Only HENDRIKS ET AL. (1994) measured p-TSA in a semi-quantitative screening of a large set of organic compounds in Rhine water (Germany) in 1989. P-TSA

concentrations found were up to 0.063 µg/L. BETOWSKI ET AL. (1996) characterized the groundwater at two Superfund sites (USA) and identified several unknown polar organic components, including p-TSA.

3.1.2 The water cycle of Berlin

Berlin's WWTPs (location Figure 3.1) discharge their effluents into the surface water system. In all WWTPs, mechanically treated wastewater passes through a biological treatment stage, followed by anoxic zones for the biological removal of phosphate and nitrate (BWB, 2007). In 2005, 227 million m³ (= 7.20 m³/s) wastewater were treated and released in the Berlin surface water system (WWTPs discharge points Figure 3.1; BWB, 2007). The relationships within the water cycle are illustrated in Figure 3.2 of Berlin.

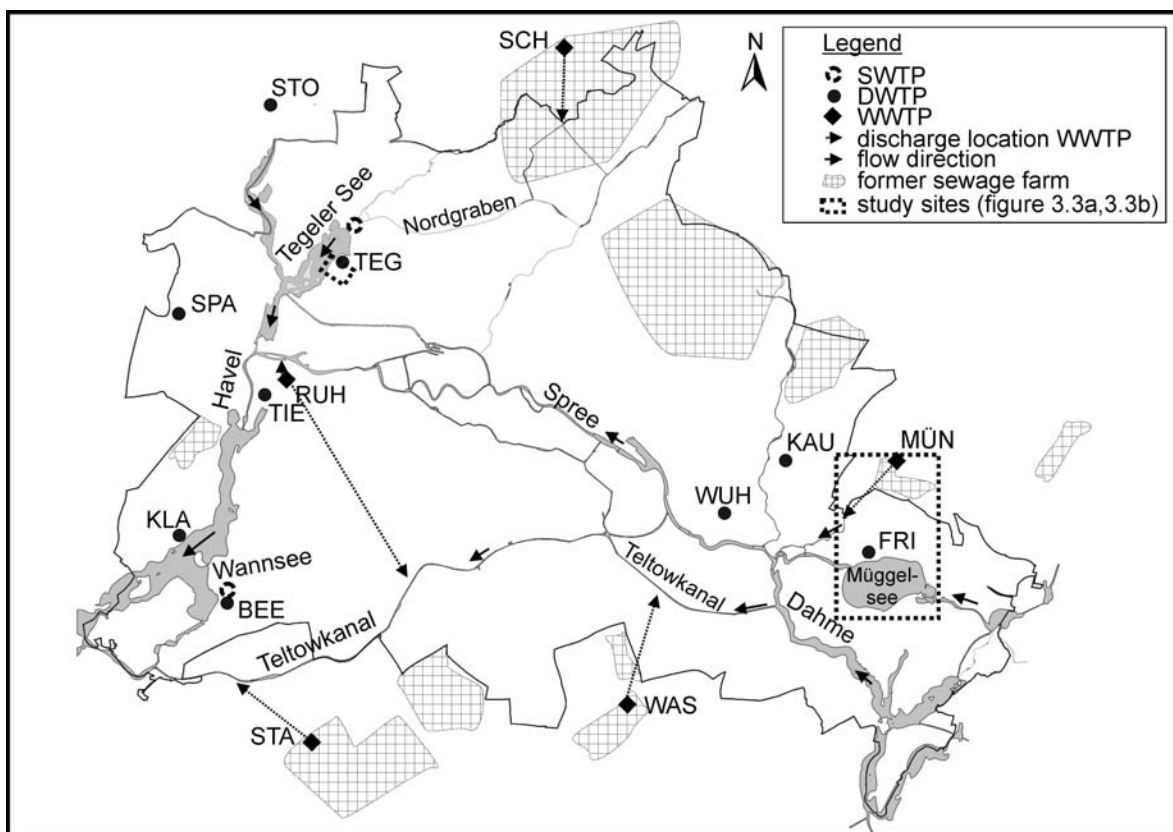


Figure 3. 1 Overview of Berlin with the surface water system (grey shading) and location of wastewater treatment plants (WWTPs), surface water treatment plants (SWTPs), drinking water treatment plants (DWTPs) and former sewage farms. Squares mark groundwater-sampling field sites (study sites Figure 3.3a, 3.3b). Surface water flow is from south-east and north towards the south-west (arrows).

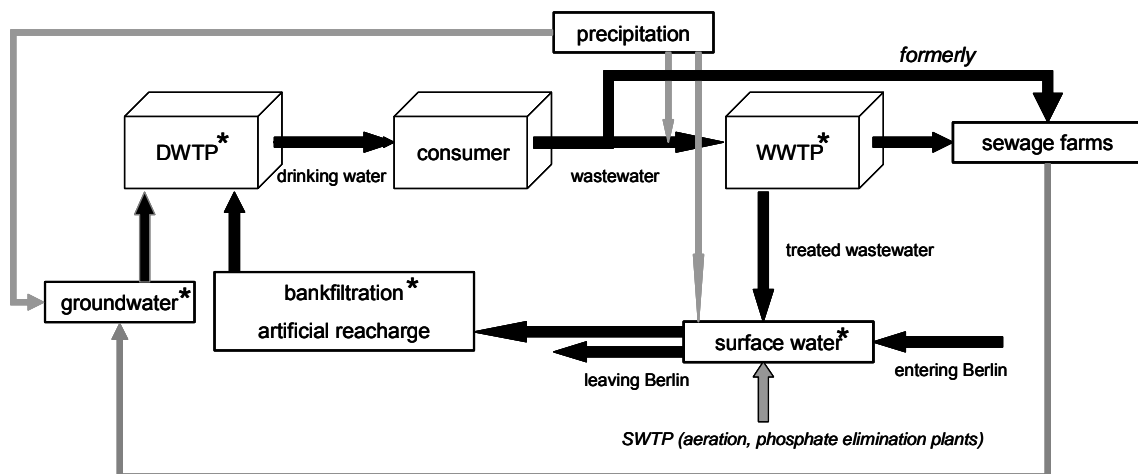


Figure 3. 2 Scheme of the Berlin water cycle with (signature*) sample locations shown. The interaction of the WWTPs, SWTPs and DTWPs with the groundwater (ambient and bank filtrate) are displayed (semi-closed water cycle) [modified after ZIEGLER, 2001].

The surface water system is formed by the Spree, Dahme and Havel Rivers with a hydraulic gradient far below 0.1 ‰ (JAHN, 1998). The rivers are shallow, slow-flowing lowland rivers with a low natural discharge (average 36 m³/s; January to December 2006; SENSTADT, 2007). The proportion of treated wastewater in the surface water varies largely, depending on space (distance from the discharge points) and time (natural discharge, water-level changes, input from WWTPs and loss from waterworks; MASSMANN ET AL., 2004). According to MASSMANN ET AL. (2004), the surface water contains between 15 % to 53 % treated wastewater.

The drinking water supply is provided via induced surface water infiltration (bank filtration and artificial recharge) into the groundwater body, where the infiltrate admixes with ambient groundwater. In 2005, 206 million m³ (= 6.53 m³/s) of drinking water were produced in DWTPs (location Figure 3.1) of the Berliner Wasserbetriebe (BWB, 2007). All DWTPs require only a minimal, quasi-natural treatment (aeration, rapid sand filtration; BWB, 2007).

Today, the WWTPs discharge their effluents into the surface water, but in former times (1874-1976 and partly by 1985), the untreated wastewater was irrigated directly onto sewage farms. Sewage farms were located within the city boundaries or just outside of Berlin (Figure 3.1). Relicts of this practice remain a potential risk for the surface water and groundwater (semi-closed water cycle). The principal

method of sewage farming is sedimentation of the sludge (gravity treated), followed by irrigation or field flooding of the wastewater (SENSTADT, 2007). In 1928, 20 sewage farm districts (10 000 ha) were in operation. The sewage farms were heavily loaded with roughly 185 million m³ of wastewater per year (= 5.87 m³/s; SENSTADT, 2007).

Figure 3.1 shows a map of Berlin rivers, lakes, WWTPs, surface water treatment plants (SWTPs), former sewage farms, DWTPs and the investigated field sites in or near Berlin (Figure 3.3a, 3.3b).

3.2 Materials and methods

3.2.1 Sample collection

Composite samples (over 24 h) of WWTP influents and effluents were collected fortnightly using an automatic sampler between May 2006 and December 2006 (n=11-14). WWTP influents and effluents were taken with a time offset of 24 hours to account for the treatment time.

Nineteen surface water samples were taken from the middle of the waters throughout Berlin at a water depth of 1 m (Table 3.1, Figure 3.5). Surface water sampling was done in September 2006 at the rivers Spree, Dahme, Upper Havel, Lower Havel and at the Teltowkanal, a canal heavily loaded with treated wastewater.

Groundwater samples were pumped from observation wells at a bank filtration site. The wells are orientated in flow direction between Lake Tegel and a production well (well 13) of the DWTP Tegel (TEG, Figure 3.3a). In addition, groundwater was collected from a production well gallery of the DWTP Friedrichshagen (FRI) downstream of a former sewage farm (gallery B, Figure 3.3b). The well gallery runs parallel to Lake Müggelsee shore. Groundwater production and observation wells were sampled in accordance with the official DVWK GUIDELINES (1992).

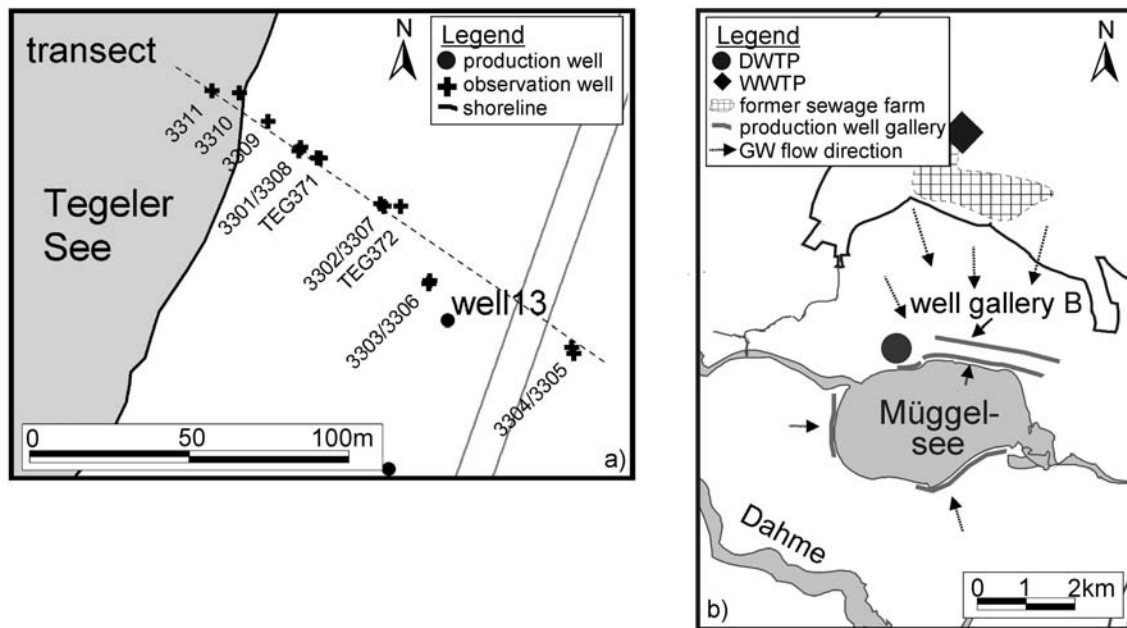


Figure 3. 3 Map of groundwater study sites (a) Transect Tegeler See, an example of bank filtration (b) Müggelsee, example of contaminated sewage farm groundwater (GW).

Drinking water samples were collected from taps in the DWTPs before and after treatment. Both groundwater and drinking water samples were collected in different sample intervals from May 2005 to December 2006. All samples were filled into glass bottles (0.5 L) and extracted immediately or kept at 4 °C for less than 2 days. The wastewater influents were filtered through 0.45 µm filters (Machery Nagel, Germany) and extracted directly. The extraction was carried out within a few days to avoid analyte losses by microbial degradation.

3.2.2 Analytical method

Water samples were analyzed in the laboratory of the Berliner Wasserbetriebe (BWB). The procedure for the analysis of p-TSA, o-TSA and BSA is described in detail in RICHTER ET AL. (2007) The analytical method is based on sample preparation by automated solid-phase extraction, followed by reversed-phase liquid chromatography (HPLC) coupled to tandem mass spectrometry detection (MS/MS), using negative electrospray ionisation. The analytes were detected in wastewater (treated and untreated), surface, ground and drinking water at concentrations down to 0.02 µg/L (limit of detection; limit of quantification [LOQ] =

0.05 µg/L). The analyte recoveries were in the range of 94 % to 120 % for all sample types.

3.3 Results and discussion

3.3.1 Sulfonamides in wastewater influents and effluents

All three compounds were detected in influents and effluents of the WWTPs in Berlin. Influent and effluent data from the WWTPs Münchehofe (MÜN), Ruhleben (RUH), Schönerlinde (SCH) and Wassmannsdorf (WAS) are presented as box plots in Figure 3.4.

P-TSA is typically present in high concentrations in the influents of the WWTPs (median 3.15-8.20 µg/L) and in smaller amounts in the effluents (median 0.39-0.57 µg/L). Highest individual influent concentrations were encountered at the WWTP Münchehofe with maximum concentrations of 15 µg/L. The reduced effluent concentrations show that the compound is largely eliminated during treatment. Depending on the WWTP, 88 % to 94 % (median) of the p-TSA is removed.

O-TSA was detected in lower amounts than p-TSA (median 0.22-1.51 µg/L) in the WWTP influents. The behaviour of o-TSA during wastewater treatment varies largely between individual WWTPs, and the specific process responsible for the variation remains unclear at this stage. Influent and effluent concentrations of the WWTPs Schönerlinde and Wassmannsdorf lie within the same order of magnitude, indicating that o-TSA is not eliminated during treatment. On the contrary, the increased effluent concentrations of the WWTP Münchehofe suggest that o-TSA may even be formed during treatment while the WWTP Ruhleben shows a slight depletion of o-TSA during treatment.

BSA can only be found in small amounts (< 0.05-0.39 µg/L) in the WWTP influents, but higher concentrations above 0.25 µg/L appear in the effluents of all WWTPs. Because the effluent concentrations are 4 to 6 times higher than the influent concentrations, the increase of BSA is significant and BSA clearly forms during treatment in all WWTPs. At this stage, I can only speculate about the specific process forming BSA, which is presumably caused by biodegradation or bioconversion. KNEPPER (2000) and KNEPPER ET AL. (1999) carried out metabolism

studies of phenylsulfonamides. They postulated that N-butyl-N-phenylsulfonyl might undergo ω -oxidation with subsequent β -oxidation to form glycine-N-(phenylsulfonyl), a sulfonamide with a similar structure to BSA, during wastewater treatment (KNEPPER, 2000; KNEPPER ET AL., 1999). Therefore I believe that BSA may be a metabolite formed by bioconversion or degradation of sulfonamides with a higher molecular weight. Further studies investigating these processes are in progress.

In summary, the wastewater treatment increases the concentrations of o-TSA in one WWTP (Münchehofe) and the concentration of BSA in all WWTPs. Composite influent and effluent samples were taken over 24 hours from the WWTP Münchehofe (RICHTER ET AL., 2007), revealing that daily fluctuations are negligible. However, the wastewater influent samples from different days (long-term monitoring) show fluctuating concentrations over longer time periods in the WWTPs.

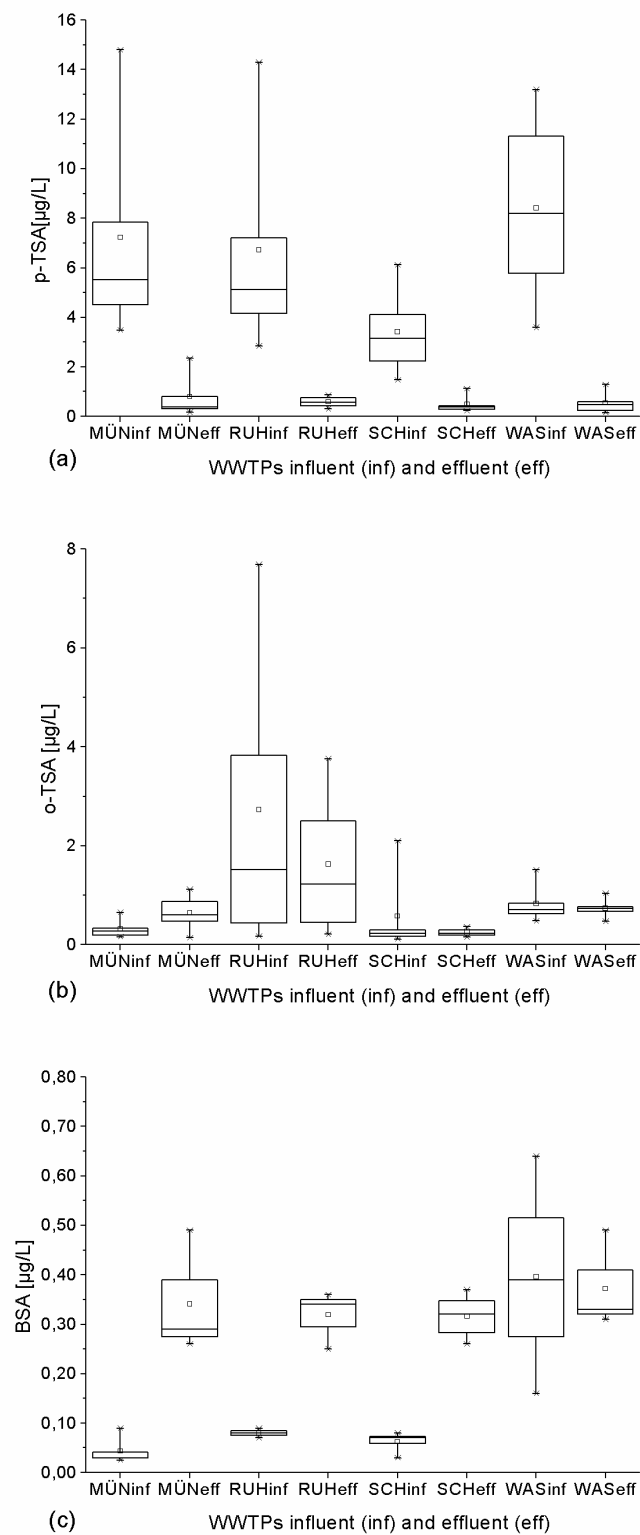


Figure 3. 4 Concentrations (box plots) of (a) p-TSA, (b) o-TSA and (c) BSA influents and effluents of 4 WWTPs (n=11-14), median value (horizontal centre line), the 25 %- and 75 %- quartiles (box) and the minimum and maximum values (vertical line) in the respective WWTPs from May 2006 to December 2006 are shown.

3.3.2 Sulfonamides in the surface water

Concentrations of p-TSA in the surface water of the western part of Berlin (River Havel) are illustrated in Figure 3.5 (n=1); corresponding o-TSA and BSA concentrations are given in Table 3.1. The direct correlation between the discharge from the municipal WWTPs and the sulfonamide concentration in Berlin's surface water can be seen very clearly in the river Havel. The Havel enters the city from the north where it has the lowest concentrations of p-TSA (< 0.1 µg/L, no. 905), representing the background concentrations of the river Havel. The strongest wastewater influence in the north can be seen in the north-east of Tegeler See (no. 800). The surface water in this area contains treated wastewater from the WWTP Schönerlinde, brought in via the Nordgraben ditch. The influence of the Schönerlinde WWTP can be traced further into Tegeler See. The proportion of treated wastewater is much lower in the Havel downstream of Tegeler See (MASSMANN ET AL., 2004). The decrease of the sulfonamides concentrations can be explained by dilution caused by the tailback of the Havel into Tegeler See. The impact of the Upper Havel on the Lower Havel is small because of the fact that the discharge of the Spree is higher than the discharge of the Upper Havel (discharge in September 2006 given in Figure 3.5). The highest influence of wastewater in the south-west of Berlin can be seen in the Teltowkanal (no. 420, 425, 430). The Teltowkanal receives wastewater effluents of three WWTPs (WAS, RUH (April to September) and Stahnsdorf (STA)). The concentrations of two sampling points in the south-west and in the south (small lakes) of the Lower Havel (no. 340 and 355) are very high > 0.50 µg/L of p-TSA. Both the discharge of treated wastewater and/or the use of disinfectants for boat cleaning or boat paints used in harbours in the area could be responsible for these high concentrations. In a study by MASSMANN ET AL. (2004) the wastewater influence in the surface water and bank filtrate was traced with chloride, boron (washing powder additive) and anthropogenic gadolinium (contrast agent). Like these wastewater residues, p-TSA is also a sensitive wastewater indicator and can be measured with high precision. MASSMANN ET AL. (2004) showed that the concentrations of the wastewater indicators in the surface water varied greatly over the year, depending to a large extent on dilution with seasonal natural discharge. I therefore assume that concentrations of the sulfonamides will likewise show seasonal variabilities.

Due to the fact that samples were only taken once, the results can only give a first impression on the spatial variability, while the extent of the temporal variability is so far unknown.

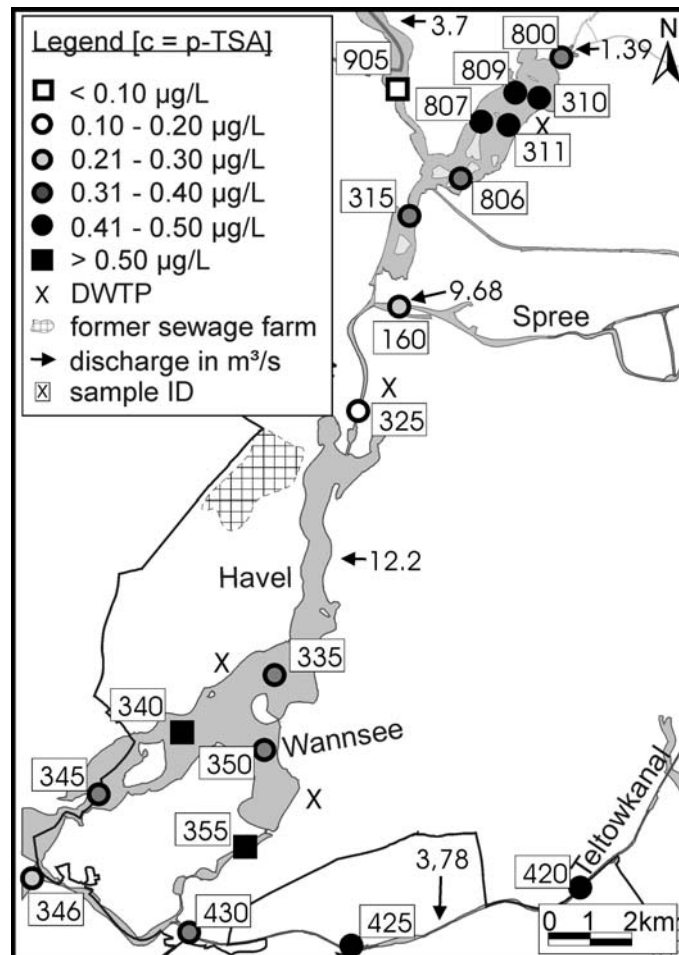


Figure 3. 5 P-TSA surface water concentrations and the corresponding sample ID of the western part of the city of Berlin, River Havel (n=1; September 2006) are shown. Flow direction of the surface water system is shown in Figure 3.1. The discharge in September 2006 is given. O-TSA and BSA data is listed in Table 3.1.

O-TSA and BSA were not detectable in the water of the river Havel entering the city of Berlin (no. 905). Increased treated wastewater loads in flow direction cause the concentrations to rise, reaching a concentration range of 0.1 to 0.3 µg/L (Table 3.1).

Remeasuring samples after storage under light at room temperatures for 2 weeks showed that no microbial and photochemical reduction of p-TSA, o-TSA and BSA occurs in the surface water (no changes in concentrations were observed).

Table 3. 1 Sample type (surface water (SW) and groundwater (GW)), X and Y coordinates (Gauß-Krüger) and filter-screen depths [m below ground] of the production wells (pw) observation wells (ow) and concentrations of p-TSA, o-TSA and BSA [$\mu\text{g/L}$] with number of samples (n)

sample ID	sample type	well	Coordinates		filter screen depth		n	p-TSA	o-TSA	BSA
Havel			X	Y	from	to		single value		
160	SW Spree	-	4582594	5823292	-	-	1	0.27	0.07	0.08
310	SW Tegeler See	-	4585753	5828346	-	-	1	0.43	0.16	0.23
311	SW Tegeler See	-	4585244	5827091	-	-	1	0.46	0.18	0.24
315	SW Upper Havel	-	4582768	5825026	-	-	1	0.31	0.11	0.15
325	SW Lower Havel	-	4581640	5819990	-	-	1	0.18	0.08	0.09
335	SW Lower Havel	-	4580414	5814067	-	-	1	0.39	0.13	0.13
340	SW Lower Havel	-	4577899	5812985	-	-	1	1.15	0.22	0.16
345	SW Lower Havel	-	4575174	5810707	-	-	1	0.40	0.36	0.23
346	SW Lower Havel	-	4573927	5808886	-	-	1	0.27	0.21	0.16
350	SW Wannsee	-	4579863	5812339	-	-	1	0.33	0.21	0.15
355	SW Lower Havel	-	4579322	5809996	-	-	1	0.90	0.59	0.37
420	SW Teltowkanal	-	4589378	5811700	-	-	1	0.41	0.36	0.37
425	SW Teltowkanal	-	4582059	5807650	-	-	1	0.43	0.49	0.36
430	SW Teltowkanal	-	4577837	5808050	-	-	1	0.36	0.32	0.42
800	SW Tegeler See	-	4586735	5829495	-	-	1	0.37	0.21	0.35
806	SW Tegeler See	-	4584579	5826433	-	-	1	0.37	0.14	0.19
807	SW Tegeler See	-	4584181	5827010	-	-	1	0.42	0.14	0.20
809	SW Tegeler See	-	4584904	5827940	-	-	1	0.43	0.17	0.24
905	SW Upper Havel	-	4582730	5827915	-	-	1	0.09	< 0.05	< 0.05
Gallery B, FRI								median value		
well 1	contaminated GW	pw	5408128	5814480	24	39	16	10.05	1.74	0.53
well 2	contaminated GW	pw	5408387	5814440	22	41	19	12.10	1.71	0.49
well 3	contaminated GW	pw	5408481	5814429	26	42	19	12.80	1.57	0.46
well 4	contaminated GW	pw	5408572	5814414	27	34	19	14.10	1.56	0.49
well 5	contaminated GW	pw	5408685	5814396	19	38	16	13.00	1.55	0.52
well 6	contaminated GW	pw	5408780	5814378	19	38	17	12.50	1.43	0.51
well 7	contaminated GW	pw	5408879	5814367	25	38	9	11.70	1.24	0.47
well 8	contaminated GW	pw	5408940	5814356	25	39	11	11.10	1.17	0.39
well 9	contaminated GW	pw	5408956	5814317	26	39	10	7.25	0.70	0.26
well 10	contaminated GW	pw	5409089	5814330	26	40	10	4.50	0.44	0.15
well 11	contaminated GW	pw	5409152	5814315	25	30	5	5.31	0.56	0.15
well 12	contaminated GW	pw	5409249	5814305	20	40	12	8.00	0.77	0.23
well 13	contaminated GW	pw	5409348	5814283	28	41	10	10.40	0.88	0.29
well 14	contaminated GW	pw	5409482	5814265	26	39	10	8.40	0.75	0.17
well 15	contaminated GW	pw	5409541	5814254	25	40	7	3.20	0.28	0.06
well 16	contaminated GW	pw	5409536	5814208	20	39	8	0.31	< 0.05	< 0.05
well 17	contaminated GW	pw	5409755	5814225	27	38	8	< 0.05	< 0.05	< 0.05
well 18	contaminated GW	pw	5409825	5814214	28	38	10	< 0.05	< 0.05	< 0.05
Transect Tegel								single value		
well 13	GW (bank filtrat)	pw	-	-	20	30	1	0.13	0.05	0.06
GWM 3301	GW (bank filtrat)	ow	-	-	21	24	1	0.21	0.07	0.06
GWM 3302	GW (bank filtrat)	ow	-	-	22	25	1	0.23	0.16	0.24
GWM 3303	GW (bank filtrat)	ow	-	-	19	22	1	0.24	0.15	0.18
GWM 3304	GW (bank filtrat)	ow	-	-	19	22	1	0.05	< 0.05	< 0.05
TEG371OP	GW (bank filtrat)	ow	-	-	10.3	12.3	1	0.15	0.10	0.15
TEG371UP	GW (bank filtrat)	ow	-	-	16.2	18.2	1	0.17	-	0.05
TEG372	GW (bank filtrat)	ow	-	-	9.7	11.7	1	0.18	0.13	0.24
TEG374	GW (bank filtrat)	ow	-	-	37	39	1	0.11	0.05	0.05
Tegeler See	SW Tegeler See	-	-	-	-	-	1	0.25	0.10	0.21

3.3.3 Sulfonamides in the groundwater of a bank filtration site (Transect Tegeler See)

In order to study whether the sulfonamides persist during underground passage, samples were taken at a bank filtration site. The site consists of a transect of several observation wells screened in different depths and oriented in flow direction between the lake (Tegeler See) and a production well (MASSMANN ET AL., 2007). Two observation wells are located inland of the abstraction well in order to sample the ambient groundwater (MASSMANN ET AL., 2007).

This cross section (Figure 3.6) shows the simplified hydrogeology of the research transect. The sediments of the uppermost aquifer containing bank filtrate are Pleistocene, porous, glaciofluvial and fluvial sands of the Saale and Weichsel glaciation (HANNAPPEL AND ASBRAND, 2002). The local aquitard is a till of the Saale glaciation.

MASSMANN ET AL. (2007) used multiple environmental tracers to estimate travel times from the surface water to individual observation and production wells at the Tegel site (Figure 3.6). The study revealed a strong vertical age stratification throughout the upper aquifer with travel times varying from a few months to several decades in greater depth (TEG374, Figure 3.6).

P-TSA was detected in all observation wells between the lake and the production well and in the production well itself in concentrations between 0.11 and 0.25 µg/L, hence all of these wells contain bank filtrate. The concentrations of p-TSA in the surface water and in the bank filtrate are within the same order of magnitude. The travel times to these wells vary from months (shallow to intermediate observation wells) to 25 years in TEG374 (travel time estimated with $^3\text{H}/^3\text{He}$ age dating; MASSMANN ET AL., 2007). Hence, p-TSA can probably persist in an aquifer environment for years or even decades.

The inland groundwater (3304) displayed no p-TSA signal (< 0.05 µg/L). This was expected, since the ambient groundwater is only recharged by natural precipitation. The production well abstracts a mixture of bank filtrate and ambient groundwater and shows a concentration of 0.13 µg/L p-TSA. The relatively high concentration of p-TSA in this production wells indicates a high proportion of bank filtrate.

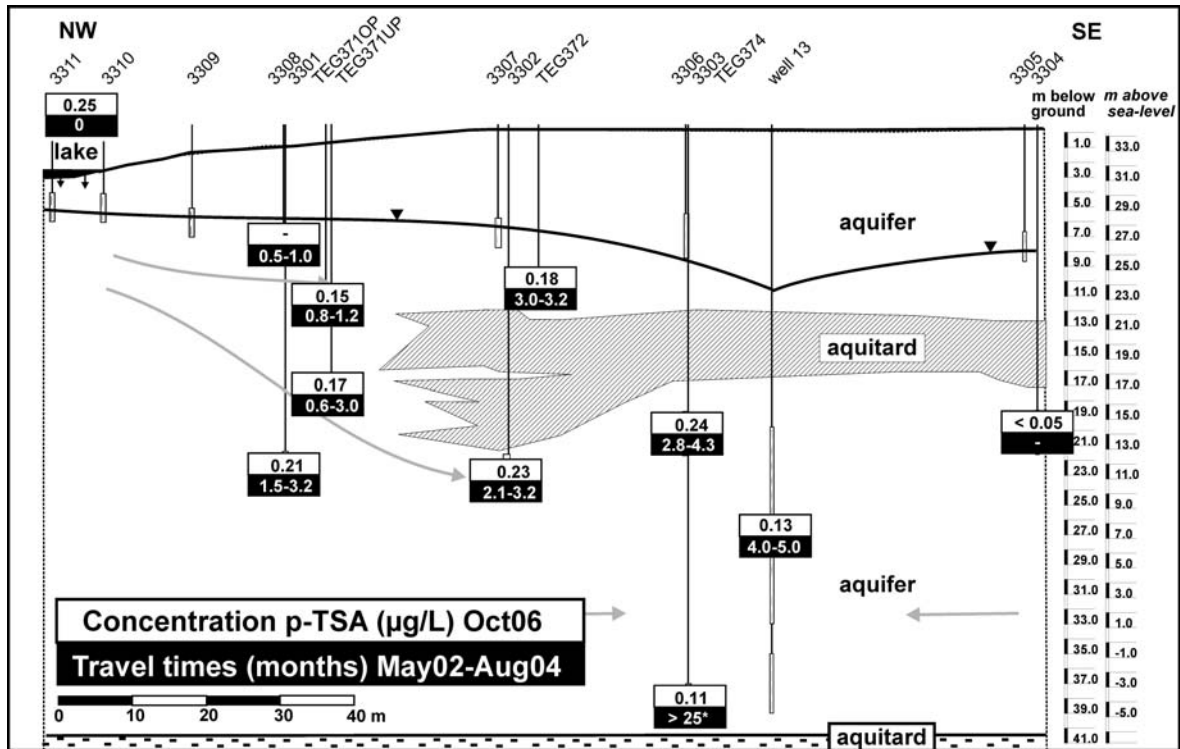


Figure 3. 6 Schematic hydrological cross section of the Tegel field site. The black numbers on white background represent concentrations of p-TSA [$\mu\text{g/L}$; $n=1$] in October 2006. The white letters on black background give the approximate spectrum of travel times [months], estimated from time-variant tracer data (May 2002 to August 2004). An exception is the value (signature*), giving the effective $^3\text{H}/^3\text{He}$ age in years (sampling date 16.03.2004). Travel times are plotted at the depth of the respective filter screen [modified after MASSMANN ET AL., 2007].

Because the site was only sampled once, the variation of the p-TSA concentration over time in the surface water and the observation wells is unknown. The concentrations of the wastewater indicators vary seasonally in the lake (MASSMANN ET AL., 2004, 2007) and a similar variation in the p-TSA concentration can be expected. Because the magnitude of the variation is unknown, removal rates during bank filtration cannot be calculated. Also, the local redox conditions (anoxic/anaerobic, aerobic) may influence the degradation rates, as described for other trace compounds (e.g. GRUENHEID ET AL., 2005). To obtain a better overview of the temporal variations and to calculate removal rates, more data would be necessary.

3.3.4 Sulfonamides in production wells downstream of a former sewage farm

The investigated DWTP in the eastern part of Berlin (Figure 3.1 and 3.3b) purifies about 230 000 m³ of raw groundwater per day (BWB, 2007). The water is abstracted by vertical wells screened at depths of 20 to 40 m below ground (BWB, 2007). The sediments of the aquifer are porous, glaciofluvial and fluvial, mainly fine to medium-sized sand of the Saale and Weichsel glaciation (BWB, 2007). The aquifer is generally not divided by aquitards, since the glacial tills often encountered in Berlin are almost completely missing in the north of the Müggelsee. The DWTP is located downstream of a former sewage farm. The investigated groundwater production wells are part of gallery B, located along the shores of lake Müggelsee (Figure 3.3b). The gallery abstracts mainly ambient groundwater. One part of gallery B (well nos. 1 to 16) abstracts mainly ambient groundwater which contains a number of anthropogenic compounds including p-TSA, o-TSA and BSA in high concentrations due to the influence of the former sewage farm.

Figure 3.7 shows p-TSA box plots of the production wells nos. 1-59 of gallery B, the concentrations of p-TSA, o-TSA and BSA of wells nos. 1-18 are given in Table 3.1. The concentrations of the sulfonamides are very high in the western wells (nos. 1-16), exceeding concentrations measured in today's WWTP influents. The values from gallery B are in the range from < 0.05 to 21.4 µg/L for p-TSA, from < 0.05 to 2.78 µg/L for o-TSA, and from < 0.05 to 0.89 µg/L for BSA. The highest concentrations of p-TSA were found in abstraction well no. 4 with a median concentration of 14 µg/L. The concentrations decrease in an eastward direction and fall below the LOQ east of well no. 16. The production wells in the west (up to production well no. 16) reveal the strongest influence of earlier wastewater irrigation, since they are directly downstream of the main contaminated plume. The lower concentrations in well no. 9-11 deviate from the generally falling concentration trend towards the east and are caused by mixing with deeper unpolluted groundwater (leakage in the deeper aquitard (glacial tills); saline deeper groundwater). The well galleries with high proportions of bank filtrate further south (Figure 3.3b, data not shown) show concentrations < 0.2 µg/L.

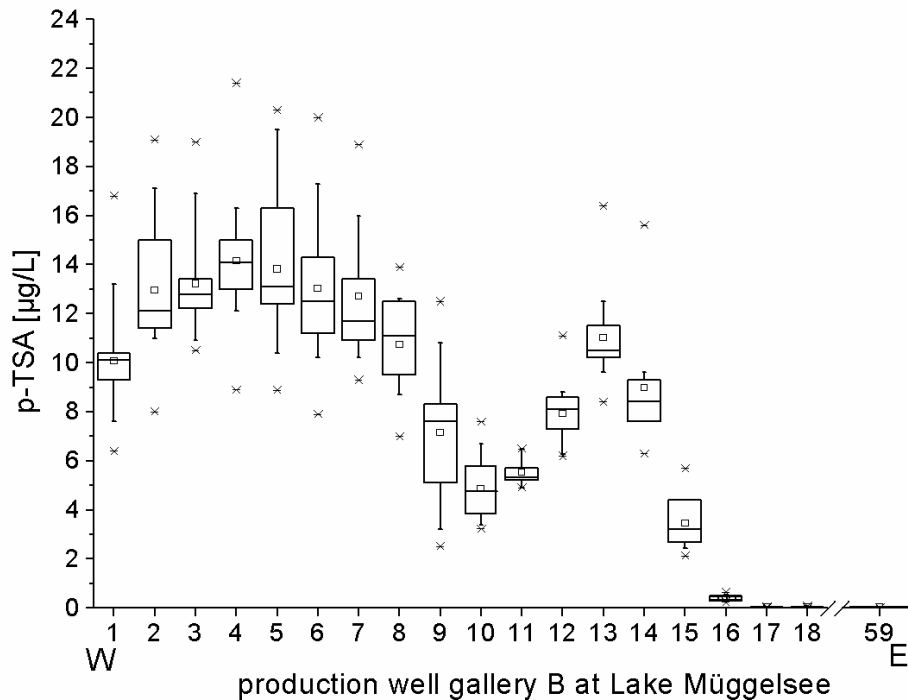


Figure 3. 7 Box plots of p-TSA in the production well gallery B (n=5-19 (detailed number is shown in Table 3.1); May 2005 to December 2006) adjacent to the Müggelsee (location Figure 3.3b).

3.3.5 Sulfonamides in raw and drinking water

The raw water entering the DWTP and the filtered final drinking water were sampled and analysed. Because the samples are not composite samples, the raw water and the filtered water cannot be directly correlated. However, the high number of samples provides a high statistical certainty. In detail, the effective number of DWTP influents sampled was 120 in FRI and from 3 to 14 in all DWTPs except FRI. The number of DWTPs effluents sampled was 62 in FRI and 7 to 9 in all DWTPs except FRI.

The raw water (aerated groundwater) and the drinking water from all DWTPs except FRI do not contain concentrations above 0.1 µg/L (median) of all three compounds (Figure 3.8). The highest raw water concentrations (95th percentile) of p-TSA found in all DWTP except FRI are 0.31 µg/L and in drinking water 0.15 µg/L (Figure 3.8). The drinking water concentrations are below the recommended maximum concentration of 0.30 µg/L in drinking water (GRUMMT AND DIETER, 2006).

Raw water concentrations from DWTP FRI are always below 0.2 µg/L for o-TSA and BSA. P-TSA concentrations are up to 1.68 µg/L (95th percentile). In the final drinking water, p-TSA is present in concentrations up to 0.24 µg/L (95th percentile), o-TSA in concentrations up to 0.16 µg/L (95th percentile) and BSA in concentrations up to 0.06 µg/L (95th percentile). P-TSA is significantly reduced during drinking water treatment (~90 % reduction) in FRI, where the highest concentrations in raw water are 2.92 µg/L and in filtered water up to 0.54 µg/L p-TSA (Figure 3.8). Since 2007, these high concentrations are not reached anymore, because of changes in the production process of the DWTP FRI.

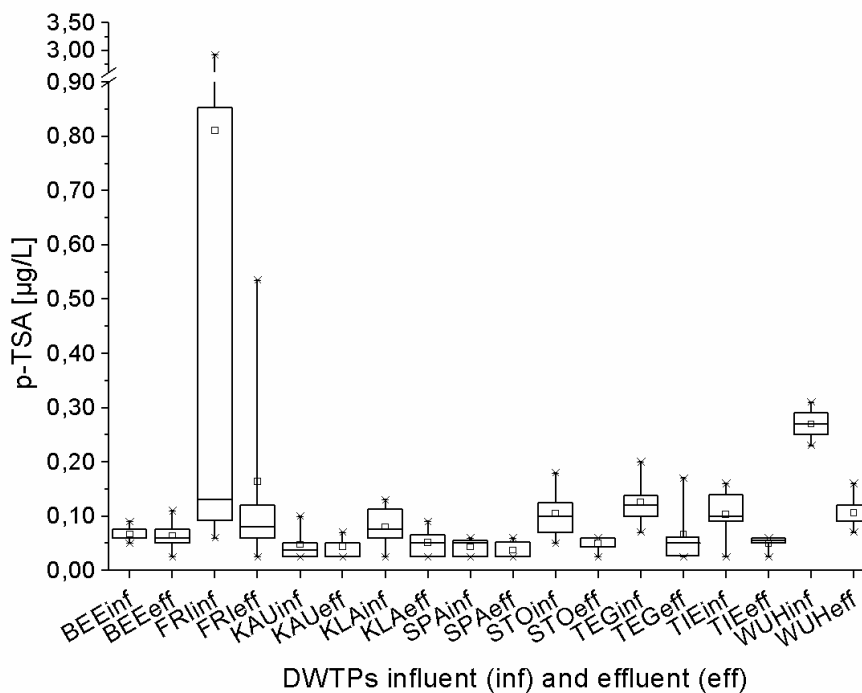


Figure 3. 8 Box plots of p-TSA in the DWTPs (n=3-120; May 2005 to December 2006).

The filter medium used during treatment is composed of sand and is biologically active. The reduction of the concentration of p-TSA is presumably caused by adsorption to particles and/or by microbiological degradation. Drinking water treatment does not reduce the concentration of o-TSA and BSA (data not shown in detail). I suspect that o-TSA and BSA are either not utilisable and/or the concentrations are too low to attract a specialised microbiology. Detailed investigations on the elimination of the sulfonamides during drinking water treatment using a test filter in a DWTP in the eastern part of Berlin are in progress.

3.4 Conclusions

The sulfonamides p-TSA, o-TSA and BSA were found to be ubiquitous in environmental water samples from an urban semi-closed water cycle (Berlin). High concentrations of the substances were found in influent (p-TSA: 2 to 15 µg/L; o-TSA 0.11 to 8 µg/L; BSA: < 0.05 to 0.64 µg/L) and effluent (p-TSA: 0.15 to 2.34 µg/L; o-TSA: 0.14 to 4 µg/L; BSA: 0.25 to 0.49 µg/L) samples of four WWTPs and in groundwater below a former sewage farm (p-TSA: < 0.05 to 20 µg/L; o-TSA: < 0.05 to 1.74 µg/L; BSA: < 0.05 to 0.53 µg/L). Lower concentrations were also detectable in surface water (p-TSA: 0.09 to 1.15 µg/L; o-TSA: < 0.05 to 0.59 µg/L; BSA: < 0.05 to 0.42 µg/L) and drinking water (p-TSA: < 0.05 to 0.54 µg/L; o-TSA: < 0.05 to 0.24 µg/L; BSA: < 0.05 to 0.08 µg/L) samples. The three substances behave differently during wastewater treatment: P-TSA is considerably depleted during wastewater treatment (~90 % reduction). Depending on the WWTP, o-TSA concentration may increase, decrease or remain stable during treatment. BSA effluent concentrations are 4 to 6 times higher than the influent concentrations; hence BSA clearly forms during treatment. The three sulfonamides can help to identify the influence of wastewater or treated wastewater in environmental water samples. If surface water contains proportions of treated wastewater, p-TSA can help to identify bank filtrate (unless in the vicinity of former irrigation farm). P-TSA is largely eliminated during drinking water treatment (~90 % reduction). Because of the omnipresence of p-TSA in the aquatic environment I recommend that it should generally be monitored in drinking water.