

2. Analytical method

An analytical method was developed to detect the three sulfonamides para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) in environmental water samples at concentrations down to 0.02 µg/L using liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS). Wastewater, surface water, groundwater and drinking water samples from Berlin (Germany) were analysed for all three compounds which appear to be ubiquitously present in the aquatic environment. P-TSA was found in high concentrations in the wastewater (< 0.02 to 50.8 µg/L) and in groundwater below a former sewage farm (< 0.02 µg/L to 41 µg/L), and in lower concentrations in the surface water (< 0.02 to 1.15 µg/L) and drinking water (< 0.02 to 0.27 µg/L). O-TSA and BSA were detected in considerably lower concentrations. The study makes clear that p-TSA should be monitored because of its comparatively high concentration in Berlin's drinking water.

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Quantitative determination of three sulfonamides in environmental water samples using liquid chromatography coupled to electrospray tandem mass spectrometry.

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2.1 Introduction

The increasing content of organic pollutants in environmental water samples is a matter of great public concern. REEMTSMA ET AL. (2006) state that poorly biodegradable polar compounds which are not effectively removed during wastewater treatment can be problematic in partly closed water cycles, since they may travel along the water path from wastewater to raw water. KNEPPER ET AL. (1999) note that knowledge about the behaviour of polar organic contaminants during surface water infiltration and drinking water production is of crucial importance to ensure a safe drinking water supply. In Berlin, the receiving waters into which treated wastewater is released are used for drinking water production via bank filtration. Until 1985, untreated wastewater was also irrigated directly onto the soils of several sewage farms (SENSTADT, 2007). In 2003, the Berliner Wasserbetriebe carried out a screening via gas chromatography-mass spectrometry (GC-MS) for organic pollutants in groundwater below one of the former sewage farms. The screening revealed elevated concentrations (high microgram per litre level) of three sulfonamides, identified as paratoluenesulfonamide (p-TSA, GC-MS screening in Figure 2.1), orthotoluenesulfonamide (o-TSA) and benzenesulfonamide (BSA), necessitating the development of a qualitative and quantitative method to enable the sensitive analysis of these substances and to track their fate in the water cycle.

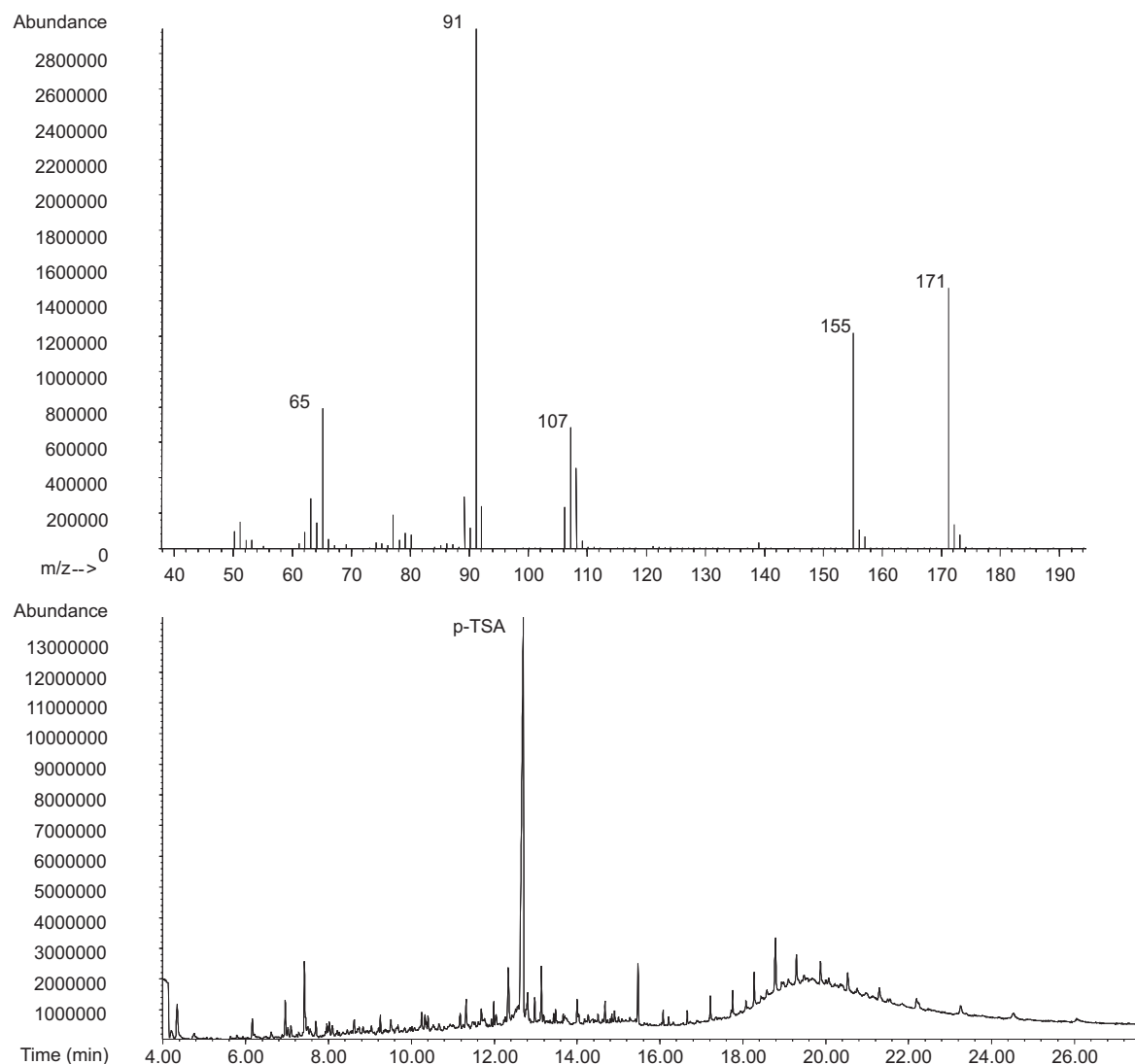


Figure 2. 1 GC-MS Screening of a groundwater sample (MID chromatogram and mass spectra of p-TSA).

The compounds (structure formulas given in Figure 2.2) have various sources in wastewater. Chloramine-T (N-sodium-N-chloro-p-toluenesulfonamide) is commonly used as an anti-microbial agent. It has widespread applications 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 a variety of fish species (BELJAARS ET AL., 1994; GAIKOWSKI ET AL., 2004; HANEKE, 2002; HARRIS ET AL., 2004; MEINERTZ ET AL., 1999; SMAIL ET AL., 2004) as well as a drug for treating different diseases of swine and poultry (HANEKE, 2002). P-TSA is the primary degradation product and a marker residue for this disinfectant and has been

described in a number of studies (BELJAARS ET AL., 1993; BELJAARS ET AL., 1994; DUIN AND NUIJENS, 1981; GAIKOWSKI ET AL., 2004; MEINERTZ ET AL., 1999; MEINERTZ ET AL., 2001). P-TSA itself is also used as a plasticizer, an intermediate for pesticides and drugs, and as a fungicide in paints and coatings (HSDB, 2003; HSDB, 2004; LEWIS, 1997). Mixtures of p-TSA and o-TSA are used as reactive plasticizers in hot-melt adhesives (HSDB, 2003). Both p-TSA and o-TSA are basic contaminants of the saccharin production process (HSDB, 2003; HSDB, 2004; LEWIS, 1997). Fingernail polishes and enamels consist of up to 10 % of toluenesulfonamide/formaldehyde resin (LIEBERT, 1986). BSA is applied as an intermediate for synthesis dyes, photo chemicals and disinfectants. HANEKE (2002) reported aggregated production volumes of 50-230 tons for chloramine-T and 500-5000 tons for p-TSA in the United States in 1998.

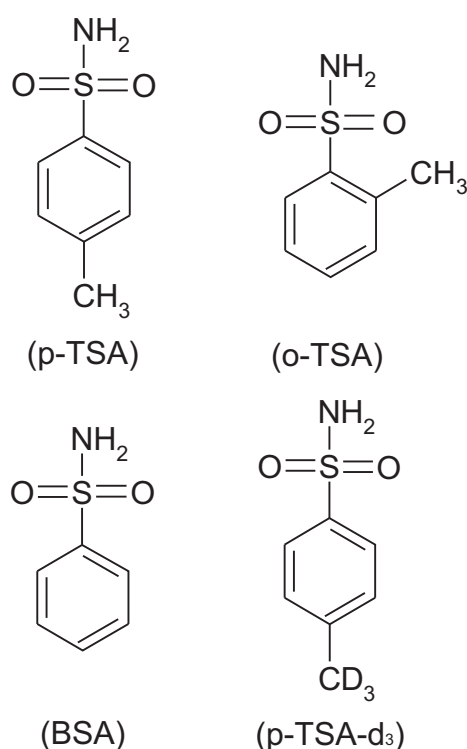


Figure 2. 2 Structures of the studied compounds and the internal standard (p-TSA-d₃).

At present, methods exist for the detection of p-TSA in groceries, e.g. in ice cream, whipped cream, baby food, minced meat, and fish, and for the detection of both p-TSA and o-TSA in artificial sweeteners (BELJAARS ET AL., 1993; BELJAARS ET AL., 1994; DUIN AND NUIJENS, 1981; GAIKOWSKI ET AL., 2004; HARRIS ET AL., 2004;

MEINERTZ ET AL., 1999; MEINERTZ ET AL., 2001; MOOSER, 1984; SMAIL ET AL., 2004; STAVRIC AND KLASSEN, 1975). A variety of qualitative and quantitative analytical methods were reported for detecting chloramine-T via the hydrolysis product p-TSA, including gas chromatography (GC) or liquid chromatography (LC) in combination with detection by mass spectrometry or by fluorescence detection (BELJAARS ET AL., 1993; BELJAARS ET AL., 1994; DUIN AND NUIJENS, 1981; HARTIG AND JEKEL, 2001; MEINERTZ ET AL., 2001; MOOSER, 1984; STAVRIC AND KLASSEN, 1975). To our knowledge, no routine method exists for the combined quantitative analysis of p-TSA, o-TSA and BSA in water samples. Only HARTIG AND JEKEL (2001) and HENDRIKS ET AL. (1994) detected p-TSA and o-TSA in screenings of wastewater in Berlin (HARTIG AND JEKEL, 2001) and surface water in the Netherlands (HENDRIKS ET AL., 1994). HARTIG AND JEKEL (2001) developed a method for the simultaneous quantitative analysis of a large set of wastewater sulfonamides residues (antibiotics, herbicides and plasticizer) but later discarded p-TSA and o-TSA because of interference with other wastewater and surface water components. HARTIG AND JEKEL (2001) did not publish any actual values of p-TSA and o-TSA in environmental water samples. HENDRIKS ET AL. (1994) presented one p-TSA value from the Rhein river but did not develop a quantitative method for the simultaneous routine analysis of p-TSA, o-TSA and BSA.

This paper presents a new analytical method which enables the simultaneous detection and quantification of p-TSA, o-TSA and BSA in wastewater, surface water, groundwater and drinking water samples, which, to our knowledge, has not been reported elsewhere. The method is based on enrichment of the analytes by automated solid-phase extraction (SPE), high performance liquid chromatography (HPLC), followed by tandem mass spectrometry (MS/MS). The analytical method was developed in order to quantify the concentrations of p-TSA, o-TSA and BSA in the Berlin water cycle. It forms the basis for the subsequent study on degradation pathways in the aquatic environment which are currently in progress. It will help to achieve a reliable basis for environment risk assessment in the future. This paper also compiles first results of p-TSA, o-TSA and BSA detected in a range of environmental water samples from Berlin.

2.2 Experimental

2.2.1 Materials

HPLC-grade methanol, acetonitrile, water and SDB 1 extraction cartridges were purchased from J.T. Baker (Deventer, Holland). Reference substances (BSA, o-TSA) were purchased from Sigma-Aldrich (Taufkirchen, Germany). P-TSA was obtained from Acros (Geel, Belgium). A deuterated sulfonamide standard (p-TSA-d₃, Figure 2.2) was synthesized by Witega Laboratories Berlin-Adlershof GmbH (Berlin, Germany). Standard solutions in methanol/water (1:1 vol%) were stored at 4 °C.

2.2.2 Sample types and collection

Surface water samples were taken in September 2006 throughout Berlin from the rivers Spree, Dahme, Upper Havel, Lower Havel and from the Teltowkanal, a canal heavily loaded with treated sewage. Altogether, 34 samples were taken at a single sampling campaign from the middle of the watercourses at a depth of 1 m. Groundwater samples were retrieved in accordance to the official DVWK GUIDELINES (1992) from below a former sewage farm. Grab samples of the influents and effluents of four wastewater treatment plants (WWTPs) in Berlin were collected weekly to monthly depending on the WWTP between May 2005 and December 2005. The number of WWTP influent and effluent samples lay between 5 and 39. In detail, the effective numbers of WWTP influents sampled was 39 (WWTP 1), 6 (WWTP 2), 7 (WWTP 3), 5 (WWTP 4). The number of WWTP effluents samples was 25 (WWTP 1), 7 (WWTP 2), 8 (WWTP 3) and 6 (WWTP 4). In addition, composite influent and effluent samples over 24 hours (2 hours) were taken on 04.09.2006 to 05.09.2006 to test whether or not concentrations vary over the day. Drinking water samples were collected from taps in the waterworks after treatment. Both groundwater and drinking water samples were collected in different sample intervals from May 2005 to December 2005.

2.2.3 Sample preparation and solid-phase extraction (SPE)

The water samples were filled into glass bottles (1 L) and, as far as possible, extracted immediately or kept at 4 °C for less than 2 days. The influent water

samples of the WWTPs were filtrated as soon as possible through 0.45 µm filters (Machery Nagel, Germany) and extracted directly. The extraction was carried out within a few days to avoid potential analyte losses by microbial degradation.

The sample volume was 250 mL for groundwater, surface water, drinking water, wastewater effluents and blanks. The sample volume for matrix-containing samples (filtered wastewater influents) was 100 mL filled up to 250 mL with deionised water. The dilution was done in order to suppress matrix effects which would have otherwise interfered with the analysis. For external standard calibration a mixture of all analytical compounds (multicomponent standard solutions) in individual concentrations of 0.04, 0.1, 0.4, 1, 5 µg/L was added to purified water. For quantification, an internal standard solution (250 ng p-TSA- d₃ in methanol/water) was added to all samples.

SPE was performed on 6-mL SDB 1 sorbent cartridges (200 mg), using an automated extraction system (AutoTrace SPE Workstation) from Zymark (Hopkinton, MA, USA). The sorbent material used is a copolymer (styrene divinyl benzene). The cartridges were preconditioned twice with 5 mL of methanol and twice with 5 mL of deionised water. The samples were percolated through the cartridges at a flow rate of 12 mL/min. The cartridges were washed with 10 mL of water, which was then discarded. Subsequently, the cartridges were dried completely for 50 min in a nitrogen flow. The analytes were eluted twice with 2 mL of methanol.

The eluates were reduced to 500 µL by a nitrogen flow at 25 °C (Zymark TurboVap II Concentration Workstation, Hopkinton, MA, USA). The sample volume was filled up to 1 mL with water. Finally, higher concentrated samples (> 5 µg/L) were diluted (1:10) in methanol/water. Because large numbers of samples could not always be analysed immediately, the extracts were stored in vials at 4°C for up to 2 weeks prior to analysis.

2.2.4 Analysis by high-performance liquid chromatography (HPLC) - tandem mass spectrometry (MS/MS)

HPLC analyses were performed using an Alliance 2690 LC instrument (Waters, Milford, MA, USA). Sample aliquots of 10 µL were injected. Liquid

chromatographic separation was carried out at room temperature using a Sunfire C18 column (3.5 μm ; 2.1 x 150 mm; Waters, Milford, MA, USA) and a RP1 guard column (2 x 10 mm UltraSep ES; Sepserv, Berlin, Germany). For the separation of the isomeric analytes (p-TSA and o-TSA) isocratic liquid chromatography was applied with a total time per analysis of 40 min. The flow rate of the mobile phase was 0.20 mL/min. The composition of the mobile phase was 10 % acetonitrile and 90 % water. Reliable results were obtained in a linear concentration range of 0.02 $\mu\text{g/L}$ to 5 $\mu\text{g/L}$.

The addition of buffers to the mobile phase caused an intensive decrease of the response of the analytes due to the lower ionization ratios and was therefore omitted. The retention times of the individual analytes for the isomeric separation method are given in Table 2.1. Figure 2.3 shows an exemplary chromatogram of an analysed surface water sample to illustrate the separation of the analytes.

Table 2. 1 Retention times, precursor ions, product ions, cone voltage, collision energy and MRM conditions used for LC-MS/MS measurements

compound	Retention time (min)	Precursor ion (m/z)	Cone voltage (V)	Collision energy (V)	Product ions	
					m/z	formula
p-TSA	36.38	170.1	30	16	106.0	$\text{C}_7\text{H}_8\text{N}^-$
				25	78.9	HNO_2S^-
o-TSA	34.61	170.1	30	16	106.0	$\text{C}_7\text{H}_8\text{N}^-$
				25	78.9	HNO_2S^-
BSA	15.05	156.0	28	17	92.0	$\text{C}_5\text{H}_4\text{N}^-$
				20	78.9	HNO_2S^-
p-TSA-d ₃	35.59	173.0	30	16	109.0	$\text{C}_7\text{H}_5\text{D}_3$
				25	78.8	HNO_2S^-

A tandem mass spectrometer, Quattro Micro (Micromass/Waters, Milford, MA, USA), equipped with electrospray ionization (ESI) was used for detection. The ESI source operated in the negative ionization mode at 120 °C, and desolvation was performed at 350 °C with a desolvation gas flow of 800 L/h and a cone gas flow of 100 L/h. For desolvation and nebulization high-purity nitrogen was used, and argon (99.998 %) served as the collision gas. MS/MS parameters were optimized

in the continuous flow mode injecting 1 ng/ μ L of the standard solution (acetonitrile/water (1:1)) of each analyte. The precursor ions were used for selecting the corresponding deprotonated molecular ion ($[M-H]^-$). Detection was performed in the multiple reaction monitoring (MRM) mode using the two most intense and specific fragment ions. Table 2.1 lists the monitored transition and energy for the analysis. The detection of the compounds was divided into retention time windows with dwell times for single reaction monitoring (SRM), which were set to 0.05 and 0.20 s (per SRM), depending on the intensity of the product ions for the transition.

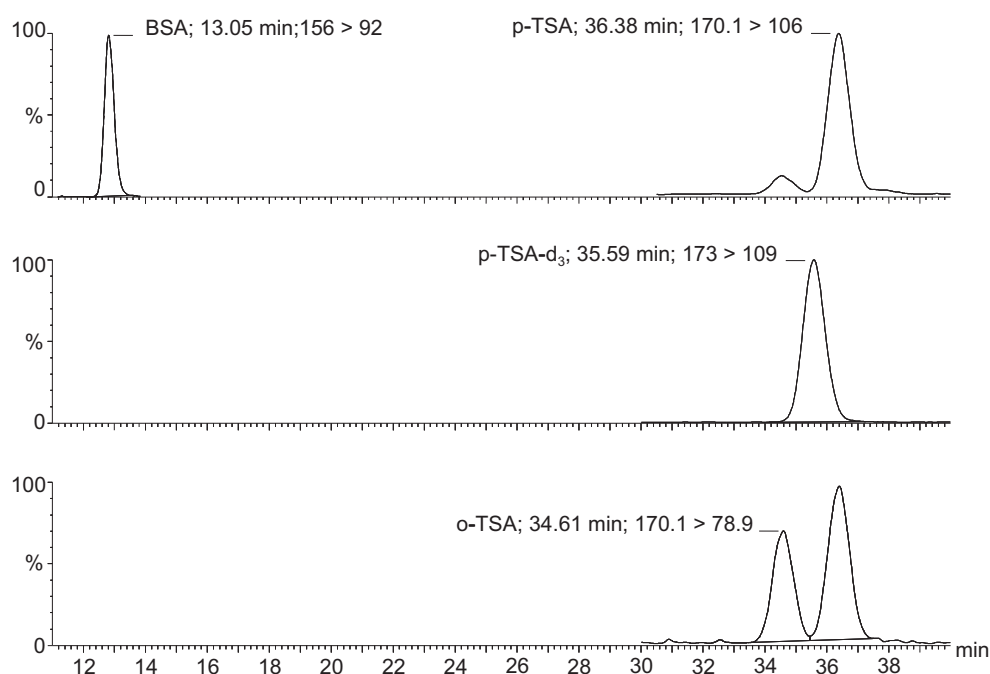


Figure 2. 3 LC-MS/MS SRM chromatograms for all analytes (p-TSA=0.44 μ g/L; o-TSA=0.21 μ g/L; BSA=0.31 μ g/L) and the surrogate of a surface water sample; only the strongest trace is shown.

2.3 Results and discussion

2.3.1 Quantification and limits of quantification (LOQs)

Five concentration points (external standard calibration) of 0.04, 0.1, 0.4, 1, 5 μ g/L were used for the quantification of each substance, covering a concentration range

of two orders of magnitude. The calibration curve was linear for all substances, with correlation coefficients (r^2) of 0.9987 (p-TSA), 0.9992 (o-TSA) and 0.9993 (BSA). All concentrations were weighted equally. Quantification was performed using the ratio of the peak areas of the analytical compounds and corrected with the internal standard compound p-TSA- d_3 . The internal standard quantification was necessary since matrix-containing samples caused peak suppression or enhancement and slight deviations in sample extract volumes. The surrogate compound compensated this deviation.

Together with the retention times, two transitions of the precursor ion were monitored to ensure correct peak identification. P-TSA and o-TSA have the same precursor ion (m/z 170.1). Details on the selection are summarised in Table 2.1. Because p-TSA and o-TSA have the same transitions, their chromatographic separation is based on an isocratic method with high water contents, separating the position isomerism. The quantification was done using the most intense product ion respectively (106.0 for p-TSA and 78.9 for o-TSA).

For each substance, the limit of quantification (LOQ) was defined as 10 times the signal to noise (S/N) ratio of the analyte peak. This procedure was performed for each type of aqueous matrix to be analysed. To determine the LOQs, non-contaminated water samples were spiked at concentrations in the range of 0.01-0.1 $\mu\text{g/L}$ of the standard compounds. The blank value of p-TSA was set to 0.01 $\mu\text{g/L}$ because of the added internal standard (250 ng), which contains 1 % of p-TSA. This restricts the lowest possible LOQ to 0.01 $\mu\text{g/L}$. During routine analysis, the limit of quantification was set to 0.05 $\mu\text{g/L}$. LOQs in surface water and in influent and effluent samples of the WWTPs could not be determined for all substances because of their ubiquitous occurrence in these matrixes. LOQs could only be calculated in purified water and drinking water, which were assumed to be valid for all matrixes (LOQ: p-TSA 0.01 $\mu\text{g/L}$; o-TSA and BSA 0.02 $\mu\text{g/L}$).

2.3.2 Method recoveries and accuracy

Analyte recoveries were determined by adding standards of all substances at environmental concentrations to previously analysed samples. All sample types were spiked with 1 $\mu\text{g/L}$ of a multi-compound standard mixture. Recoveries were calculated by subtracting the concentrations of the non-spiked sample from the

spiked sample (standard addition method). The recovery for each type of aqueous matrix (n=4-12) was 94-120 % for all analytes (Table 2.2). Relative standard deviations (RSDs) lay between 4-18 % of the analyte recoveries in this spiking experiment. Recoveries and RSDs for all three substances are acceptable for all sample matrixes.

Table 2. 2 Analyte recoveries (without IS correction; %) / analyte recoveries (with IS correction; %) and relative standard deviations (RSDs; %) of all analytes added to four different types of aqueous matrixes

compound	drinking water	surface water	WWTP (RSD)	
	(RSD)	(RSD)	Influent; 4 / 6	Effluent; 2 / 4
n	5 / 5	1 / 12	Influent; 4 / 6	Effluent; 2 / 4
p-TSA	76 (7) / 101 (4)	98 / 100 (11)	94 (16) / 104 (10)	77 (10) / 107 (4)
o-TSA	84 (3) / 96 (10)	92 / 94 (8)	115 (17) / 102 (12)	75 (7) / 103 (9)
BSA	74 (5) / 96 (6)	88 / 102 (14)	70 (21) / 120 (18)	64 (3) / 120 (5)

To prove that the addition of an internal standard is a suitable procedure for all three analytes, the analyte recoveries without IS correction are also shown in Table 2.2. By comparison, acceptable recoveries for BSA were observed in the spiking experiment with surrogate correction. Analyte recoveries without IS correction lay between 64 % in WWTP effluent and 88 % in surface water of BSA. Much better recoveries (96-120 %) were observed for all sample types for BSA with IS correction. Thus, the surrogate compensated the matrix effects for p-TSA, o-TSA and also for BSA, despite the 22 minute difference in retention time. The recovery for BSA in the samples will not lead to any problems in quantification.

2.3.3 Screening of environmental water samples

Analysis of p-TSA, o-TSA and BSA in surface water, groundwater, drinking water and wastewater revealed the suitability of the analytical method described above and preliminary results are given in the following. Since wastewater was believed to be the source of the contamination, wastewater influents and effluents were studied in greater detail. To our knowledge, no attempt has ever been made to quantify these three sulfonamides in aquatic water samples. As mentioned above,

HENDRIKS ET AL. (1994) measured a single value of p-TSA in a semi-quantitative GC-MS screening of a large set of organic compounds in river Rhine water (Germany) in 1989 (0.063 µg/L p-TSA; HENDRIKS ET AL., 1994). He did, however, not analyse for o-TSA or BSA. HARTIG AND JEKEL (2001) analysed water samples for sulfonamides, but did not present any actual values for p-TSA and o-TSA, as explained above.

P-TSA, o-TSA and BSA were detected in surface water samples throughout Berlin at concentrations up to 1.15, 0.80 and 0.52 µg/L, respectively. The corresponding concentrations in groundwater samples from observation wells directly below a former sewage farm in eastern Berlin were up to 40.8, 6.32 and 1.22 µg/L respectively. In drinking water samples of the waterworks of Berlin, concentrations up to 0.27 µg/L for p-TSA, 0.09 µg/L for o-TSA and < 0.05 µg/L for BSA were analysed.

Wastewater samples were taken from four urban WWTPs in Berlin, Germany. In all cases, mechanically treated wastewater passes through a biological treatment stage, followed by anoxic zones for the biological removal of phosphate and nitrate. All three compounds were detected in influents and effluents of the WWTPs. In- and effluent data from each WWTP is presented as box plots in Figure 2.4. Since the samples are grab samples and not 24-hour composite samples, the results can merely show whether or not the compounds occur. Furthermore, the data indicates the order of magnitude of the concentrations and gives hints on the potential removal or formation of these compounds during treatment. However, the results will need to be verified with 24-hour composite sampling, which is currently undertaken.

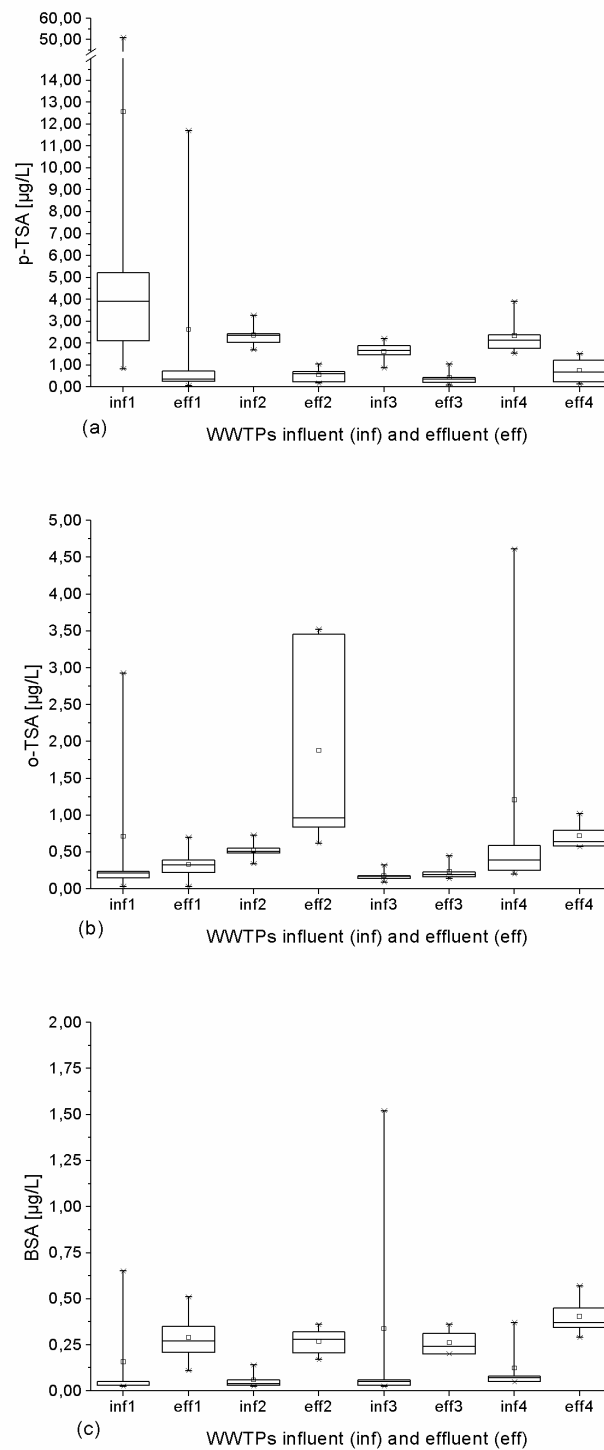


Figure 2. 4 Results (grab samples) for influents and effluents of 4 WWTPs of Berlin (box plots). Concentrations of (a) p-TSA (b) o-TSA (c) BSA are displayed (n=5-39), median value (horizontal centre line), the 25 %- and 75 %-quartiles (box) and the minimum and maximum values (vertical line) in the respective WWTP are shown. The number of samples taken was 39 for the WWTP 1 influent, 25 for the WWTP 1 effluent and 5-8 for the remaining WWTPs (2-4).

P-TSA is typically present in high concentrations in the influents of the WWTPs ($\geq 1 \mu\text{g/L}$) and in smaller amounts in their effluents. Highest influent concentrations were encountered at WWTP 1. Occasionally, concentrations above $20 \mu\text{g/L}$ were found (maximum $50.8 \mu\text{g/L}$). The origin of these high concentrations is unknown and currently under investigation. The reduced effluent concentrations indicate that the compound is partly eliminated during treatment. Depending on the WWTP, $\sim 90\%$ (median) of p-TSA is removed (Figure 2.4). O-TSA was detected in lower amounts than p-TSA (median concentrations $< 0.5 \mu\text{g/L}$). Influent and effluent concentrations lie within the same order of magnitude. The effluent concentrations of WWTPs 1 and 2 exceeded the influent concentrations. I suspect that a site-specific process might be responsible for the formation of o-TSA during wastewater treatment. BSA can be found in small amounts ($\sim 0.05 \mu\text{g/L}$) in the influent, but higher concentrations above $0.35 \mu\text{g/L}$ appear in the effluent. Because the effluent concentrations are always 5 to 8 times higher than the influent concentrations, the increase of BSA is significant and BSA appears to form during treatment in all WWTPs. This process is presumably caused by biodegradation or bioconversion. KNEPPER ET AL. (1999) described metabolism studies of phenylsulfonamides. The results of these degradation studies show that N-butyl-N-phenylsulfonyl may undergo an ω -oxidation with a subsequent β -oxidation to form glycine-N-(phenylsulfonyl) (KNEPPER ET AL., 1999). Therefore I assume that BSA is a metabolite of sulfonamide with a higher molecular weight.

In summary, the wastewater treatment increases the concentrations of o-TSA and the concentration of BSA in all WWTPs. In order to check, whether or not grab samples are reliable, composite influent and effluent samples were taken over 24 hours from the WWTP 1 (Figure 2.5). Influent p-TSA concentrations lie between 5 to $8 \mu\text{g/L}$ while 0.5 to $1 \mu\text{g/L}$ were detected in the effluent, with removal rates remaining around 90% . As described before, both o-TSA and BSA increase significantly 2 to 4 times during wastewater treatment in the WWTP 1. Clearly, the concentrations of p-TSA, o-TSA and BSA do not show significant variations during the course of the day. However, the wastewater influents samples from different days (long time monitoring) show fluctuant concentrations over longer time periods in the WWTPs.

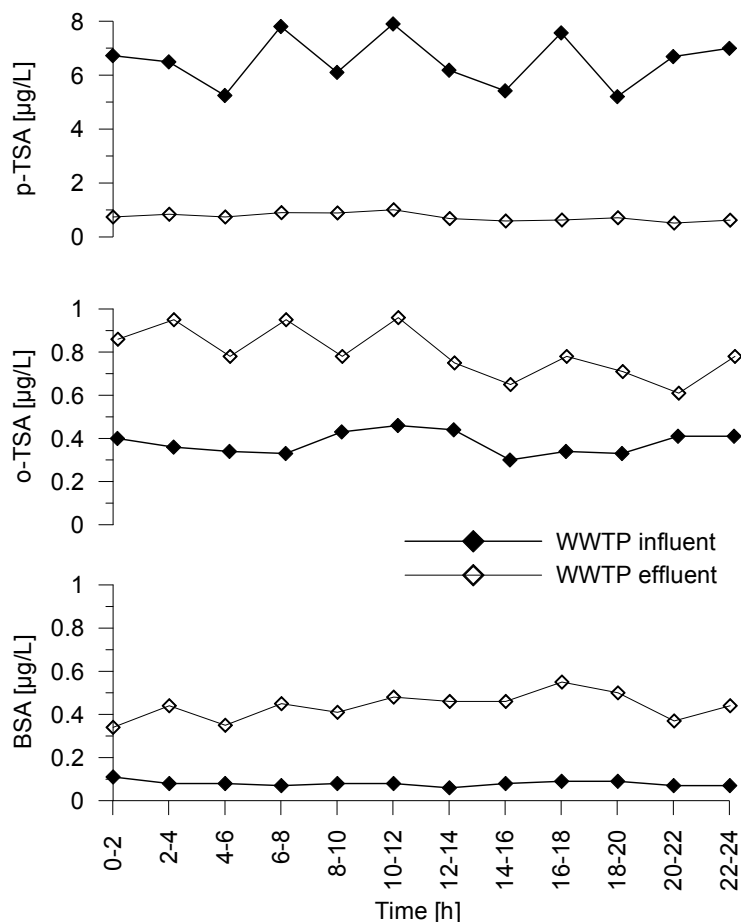


Figure 2. 5 The analytical results of p-TSA, o-TSA and BSA of composite influent and corresponding effluent samples (2 hours) over 24 hours (04.09.2006 to 05.09.2006) of the WWTP 1.

The results demonstrate that all three compounds are present in significant concentrations in the environmental water samples from Berlin. The German Federal Environmental Protection Agency (UBA) recommends maximum concentrations of 0.1 µg/L for unknown substances in drinking water, if toxicological and environmental information on the substance is insufficient. An initial assessment report of p-TSA by the Organisation for Economic Cooperation and Development (OECD), with screening information and toxicological tests showed moderate toxicity and recommended additional tests if large amounts of p-TSA are used in consumer products in the future. Investigations by the 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). The drinking water

concentrations of p-TSA analysed in Berlin were below this recommended concentration level. However, the fact that p-TSA is ubiquitously present in concentrations above this limit in surface water, groundwater and wastewater and close to this limit in the drinking water raises concerns. It is therefore essential to carry out further investigations on the processes controlling the presence, behaviour and degradation of p-TSA in the environment and during wastewater and drinking water treatment. The same is true for the lower, but still significant concentrations of o-TSA in the water cycle (some concentrations above the limit of 0.1 µg/L for unknown substances). For o-TSA and BSA, the toxicological relevance is yet unknown.

2.4 Conclusions

A method was developed for the sensitive and simultaneous detection of the sulfonamides p-TSA, o-TSA and BSA in various aqueous matrixes. It is based on solid-phase extraction coupled with reversed-phase chromatography and tandem mass spectrometry. The use of a surrogate provides an optimal quantification of the analytes in all types of environmental samples tested. It is the first method that enables the simultaneous routine analysis of p-TSA, o-TSA and BSA in water. In comparison to previous methods in the food industry, the limits of detection are much lower. High concentrations of the substances were found in influent and effluent samples of four WWTPs and in groundwater below a former sewage farm. Lower concentrations were also detectable in surface water and drinking water samples from Berlin. Results show a significant decrease of p-TSA during wastewater treatment. P-TSA concentrations in the drinking water are below the tolerable concentration level of 0.3 µg/L, but I recommend that p-TSA should generally be included in the group of compounds monitored in drinking water analysis because of its omnipresence in the aquatic environment. The fate of these compounds through the various steps of municipal wastewater treatment can be accurately investigated with this method in future studies which are currently undertaken. The resulting information may be used for optimizing the municipal WWTPs with the aim of minimizing the input of sulfonamides into the surface water, thus reducing the environmental risk.