4. Behaviour during drinking water treatment

Three sulfonamides – para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) – have recently been detected in groundwater within a catchment area of one drinking water treatment plant (DWTP), which is located downstream of a former sewage farm. The degradation pathways of p-TSA, o-TSA and BSA were investigated during drinking water treatment with incubation experiments and an experimental filter. Incubation experiments showed that p-TSA is removed during the treatment by microbiological processes. Removal of p-TSA is performed by adapted microorganisms only present in polluted groundwater. The elimination in an experimental filter of 1.6 m length applying filtration velocities from 2 m/h to 6 m/h was ~93 % of p-TSA. The microbial degradation rates in the incubation experiment were ~0.029 µg/L/h (zero order reaction). In the experimental filter, the reaction rate constants were around 0.0063 1/s for all filtration velocities (1st order reaction). Drinking water treatment does not reduce the concentration of o-TSA and BSA under conditions encountered in Berlin. P-TSA, o-TSA and BSA were only measured in the low µg/L concentrations range in the purified water.

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Behaviour and biodegradation of sulfonamides (p-TSA, o-TSA, BSA) during drinking water treatment.

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4.1 Introduction

Information on the transport and degradation behaviour of wastewater residues in the aquatic environment (organic micropollutants such as pharmaceutical and personal care products, PPCPs) is discussed in different studies (DAUGHTON AND TERNES, 1999; HEBERER, 2002A, 2002B; PESCHKA ET AL., 2006; YU ET AL., 2006; KIM ET AL., 2007; LOOS ET AL., 2007). The presence and persistence of these organic micropollutants is considered to be a key environmental issue in the future (SCHWARZENBACH ET AL., 2006). Since several organic micropollutants are not fully removed during conventional wastewater treatment, they may reach the receiving surface water system (HEBERER, 2002A, 2002B; DERKSEN ET AL., 2004; REEMTSMA ET AL., 2006; YU ET AL., 2006). If wastewater residues are found in surface water and groundwater, they may be relevant for the drinking water purification of bank filtrate (if the surface water contains treated wastewater) or of contaminated groundwater.

Various authors have studied the behaviour, elimination and metabolism of organic micropollutants during drinking water treatment. For example, KNEPPER ET AL. (1999, 2000) investigated some phenylsulfonamides during drinking water treatment. The specific elimination of sarkosin-N-(phenylsulfonyl) and metabolites was between 0 % and almost 100 % when activated carbon and chlorine dioxide were applied. A study by ZUEHLKE ET AL. (2007) presented removals of phenazone-type pharmaceutical residues (analgesics and antipyretics) during rapid sand filtration. The elimination lay between 46 % and 94 % depending on the substance (ZUEHLKE ET AL., 2007). They found that removal rates can be enhanced by decreasing filtration velocities resulting in longer contact times. Results by EICHHORN ET AL. (2002) showed the differential elimination during the sand filtration processes of sulfophenyl carboxylates (SPC) in two European drinking water treatment plants (DWTPs). During the sand filtration step 0 % and 85 % of SPC were removed in the DWTPs in Spain and in Germany respectively. EICHHORN ET AL. (2002) assumed that rapid sand filtration has no effect on the removal of SPC due to the prechlorination of the raw water (no or little microbiological action) in the DWTP in Spain. LOOS ET AL. (2007) presented an insufficient removal of a large

range of organic pollutants during sand filtration and chlorination used in a DWTP at Lake Maggiore (Italy). The drinking water produced from the surface water contains almost the same concentrations (5-60 ng/L) of organic pollutants compared to the raw water.

Benzene- and toluenesulfonamides (BTS), especially p-TSA, o-TSA and BSA have a broad application as industrial chemicals. P-TSA is used as a plasticizer, an intermediate for pesticides and drugs, and is the primary degradation product of the disinfectant chloramine-T (N-sodium-N-chloro-p-toluenesulfonamides) in water. Chloramin-T is used as an antimicrobial agent in the food industry to disinfect surfaces, instruments and machinery and also a therapeutic drug for bacterial gill diseases of fish species, and for bacterial diseases of swine and poultry. The main application for o-TSA is its use for the production process of the artificial sweetener saccharin. BSA is used for synthesis dyes, photo chemicals and disinfectants (e.g. RICHTER ET AL. 2007).

The removal of these trace compounds during conventional wastewater treatment has recently been investigated (RICHTER ET AL., 2007, 2008B). While p-TSA was largely removed (~90 % removal), no removal was observed for o-TSA. BSA concentrations increased significantly during wastewater treatment. It was suspected that BSA forms of sulfonamides with a higher molecular weight during treatment (RICHTER ET AL., 2007). The compounds have recently been detected in polluted groundwater samples below a former sewage farm in Berlin, Germany (RICHTER ET AL., 2007, 2008B). Preliminary results showed a significant decrease of p-TSA concentrations during rapid sand filtration in the DWTPs (RICHTER ET AL., 2008B). The drinking water concentrations of p-TSA were less than 10 % compared to those analysed in the raw water. The elimination processes have not yet been identified and the role of sorption and microbial degradation remains unclear. Therefore, detailed investigations on the elimination of these sulfonamides (p-TSA, o-TSA, BSA) during drinking water treatment were needed. It was suspected that the behaviour of the sulfonamides is strongly influenced by microbiological processes.

So far, few laboratory studies on the elimination of BTS have been conducted. The biodegradation of BTS as aquifer contaminants was studied by KUHN AND SUFLITA

(1989). They examined the degradation of p-TSA and BSA in aquifer slurries from a sulphate reducing (anoxic) and a methanogenic site (anoxic). In the methanogenic aquifer slurries, about 20 % of p-TSA was degraded, while a reduction of BSA was only measured in one of eight cases. In the sulphate reducing aquifer slurries no removal of p-TSA and BSA was observed. WELLENS (1990) studied the elimination of p-TSA, o-TSA and BSA in water dosed with activated sludge under aerobic conditions (OECD 302B Zahn-Wellens). The results showed 93 % p-TSA elimination in 12 days and no o-TSA and BSA removal in 25 days (dissolved organic carbon (DOC) 50-400 mg/L).

The objectives of this study were to investigate the degradation mechanisms of the sulfonamides p-TSA, o-TSA and BSA during drinking water treatment. For this purpose, various incubation experiments and a filter experiment were conducted. In order to (i) identify the impact of the microbiology on elimination, incubation experiments with sterile drinking water and with a non-sterile mixture of backwash water from a rapid sand filter and drinking water were compared. It was suspected that the microbiology was adapted at the specific DWTP treating groundwater polluted with sulfonamides. Therefore, to study (ii) the role of the adapted microbiology, the substances were added to a suspension of drinking water with backwash water from rapid sand filters originating from two different DWTPs (unpolluted and polluted catchment areas with regard to the substances in question). Additionally, the influences of (iii) filtration velocities, raw water quality and backwash intervals on the degradation rates were evaluated using an experimental filter unit at the specific DWTP treating polluted groundwater in Berlin.

Investigations by the Federal Environmental Protection Agency recommend p-TSA concentrations below 0.3 µg/L in drinking water (GRUMMT AND DIETER, 2006). So far, the concentrations of p-TSA in drinking water samples in Berlin were below 0.3 µg/L (RICHTER ET AL., 2007). The fact that p-TSA, o-TSA and BSA are ubiquitous in environmental water samples from Berlin does, however, confirm the need to study their behaviour during drinking water treatment.

4.2 Experimental section

4.2.1 Site description

Part of the abstracted groundwater treated at the investigated DWTP Friedrichshagen (FRI) has high concentrations of anthropogenic pollutants (e.g. ammonium and boron). The catchment area of the DWTP is located at Lake Müggelsee, in the eastern part of Berlin, Germany. Part of the DWTP catchment area is located downstream of a former sewage farm where untreated wastewater had been irrigated directly onto the soils for decades. The p-TSA concentrations measured in the polluted groundwater (observation well field measurements from 96 wells) lay between < 0.05 to 41 µg/L (median value 5.70 µg/L).

The investigated DWTP FRI purifies about 230 000 m³ of raw groundwater per day (BWB, 2007). The water is abstracted by vertical wells (~170 wells) screened at depths of 20 to 40 m below ground (BWB, 2007). The well galleries run parallel to the shore of Lake Müggelsee. The treated raw water is a mixture of infiltrated surface water (bank filtrate from the river Spree and Dahme) and ambient groundwater. Generally, the raw water requires only minimal treatment to ensure a high drinking water quality. The quasi-natural treatment consists of aeration and rapid sand filtration through open bed filters (sand thickness ~1.6 m, particle size 0.5 to 2.5 mm) with velocities of 3 or 4 m/h, to remove iron and manganese. The filter medium is composed of sand and is biologically active.

Additionally, for comparison, the DWTP Spandau (SPA) was sampled. It is located in the western part of Berlin. Here, the concentrations of p-TSA in the raw water are very low (< 0.1 µg/L; RICHTER ET AL., 2008B). The DWTP SPA purifies ~160 000 m³ of raw groundwater per day using a similar natural treatment technology (~44 wells at depth from 35 to 52 m below ground). The abstracted groundwater is bank filtrate from the river Havel mixed with ambient groundwater.

4.2.2 Analytical method

The analytical method is based on sample preparation by solid-phase extraction (SPE), followed by reversed-phase liquid chromatography (HPLC) coupled to tandem mass spectrometry detection (MS/MS). The limit of detection for all

analytes is 0.02 µg/L. For routine analysis, the limit of quantification (LOQ) was set to 0.05 µg/L. The analyte recoveries (%) were 98/101 for p-TSA, 98/96 for o-TSA and 90/96 for BSA for groundwater and drinking water, respectively. The analytical method is described in detail in RICHTER ET AL., 2007.

4.2.3 Experimental design

Incubation experiment

250 mL-samples of sterile distilled water (A), sterile drinking water (B) and drinking water from the two different DWTPs (C: DWTP FRI with polluted groundwater, D: DWTP SPA with unpolluted groundwater; additionally spiked with 1 mL backwash water each) were spiked with 2.5 µg of p-TSA, o-TSA and BSA each (see scheme in Figure 4.1).

In the first set of experiments, the elimination in sterile drinking water (B) was compared to the elimination in non-sterile drinking water spiked with 1 mL backwash water (biologically active material) collected from an operating filter unit in FRI (C). This was done to identify the role of the microbiology in the elimination process.

In the second set of experiments, drinking water samples were fortified with 1 mL of backwash water (biologically active material) collected from two different operating filter units of DWTPs to study the role of the adapted microbiology (C and D). The backwash water originated from the DWTP FRI (polluted water) and the DWTP SPA (unpolluted water).

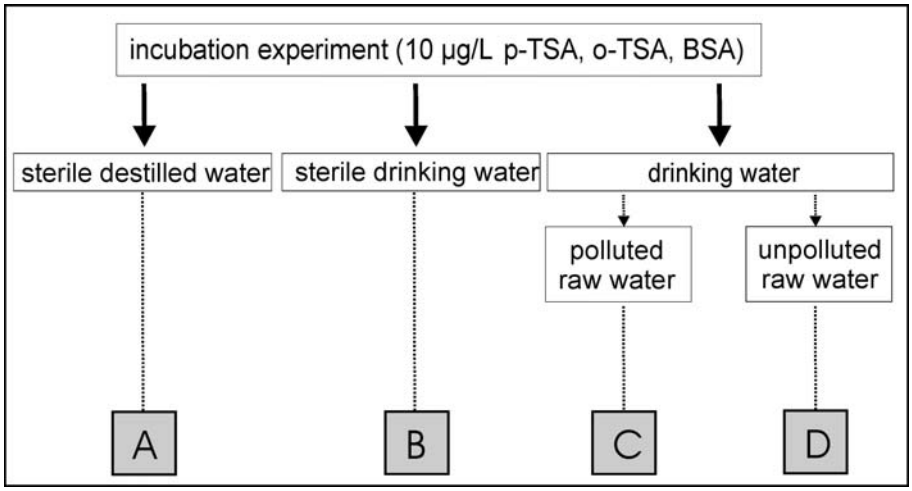

Figure 4. 1 Scheme of the experimental design of the incubation experiment.

The initial concentrations were measured at the beginning of the experiments (~10 µg/L). All experiments were conducted in the dark at room temperatures (~20 °C). The glass flasks were always sampled with sterilised material (sample volume of 50 mL each) to avoid contamination. The samples taken (50 mL) were filled up to 250 mL with deionised water before the extraction was carried out. Oxygen concentrations were determined during each experiment. Sampling was done after 0, 4, 6 and 11 days. Experiments were always performed in duplicates. Spiked sterile distilled water served as a blank (A).

As an additional experiment to exclude the possibility of sorption as the responsible removal process during drinking water treatment, routine filter sludge samples were extracted. For this purpose, samples were freeze dried and extracted with 20 mL of methanol in an ultrasonic bath. The eluate was reduced to a final volume of 500 µL under a gentle stream of nitrogen. The reduced eluate was added to 250 mL of deionised water and the extraction was carried out.

Experimental filter

The experimental filter was installed in the filter hall of the DWTP FRI. The aim was to evaluate the potential to further reduce p-TSA, o-TSA and BSA during drinking water treatment. With regard to the treatment technology, process parameters which could potentially be optimised were (1) filtration velocity, (2) water quality and (3) backwash intervals. Therefore, their effect on the sulfonamide elimination was studied.

Construction of the experimental filter was similar to the rapid sand filters at the DWTP. It was built as an open filter (cylindrical tube, length 4.0 m, diameter 0.15 m), packed with the same filter medium (~25 years of operation) as in the original sand filters (1.6 m silica sand). Sample ports were placed in different depths of the experimental filter. The distance between the sample ports was 0.25 m. The filter was loaded with the same raw water that is used in the routine treatment at the DWTP FRI. The velocity was regulated via the effluent flow and lay between 2 m/h and 6 m/h. After a short regulation phase of about two weeks at 2 m/h, the filtration velocity was raised in steps from 3, 4, 5 to 6 m/h. The backwashing (only with drinking water, lasting ten minutes at a velocity of 40 m/h) of the experimental filter was performed every three to four days, similar to the real filters.

Samples were collected from the experimental sand filter in- and outflow, as well as from taps in different depths of the filter (Figure 4.2). Between November 11, 2005 and April 26, 2006, the in- and outflow was sampled and analysed 66 times. The high number of samples provides a high statistical certainty. The taps were sampled once for each filter velocity. Figure 4.2 shows the schematic design of the experimental filter.

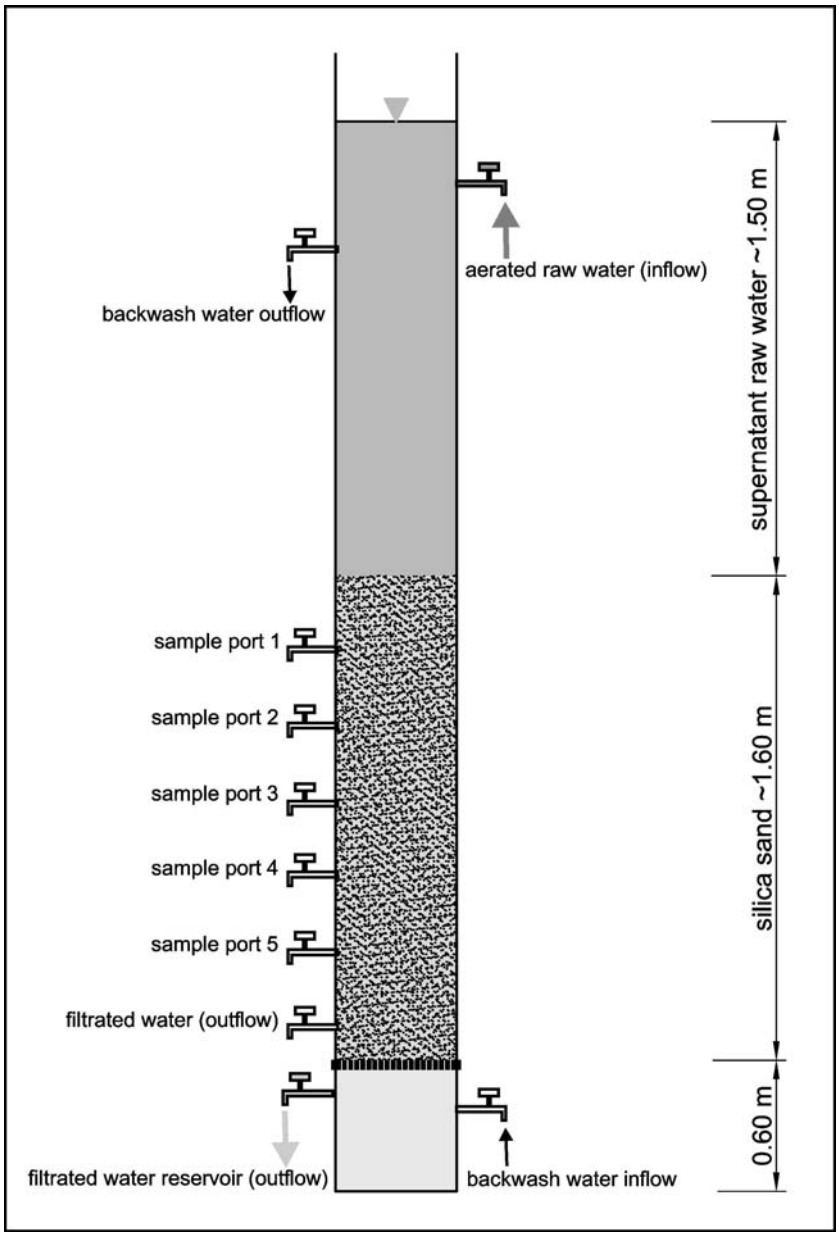

Figure 4. 2 Schematic design of the experimental filter in the DWTP FRI (Berlin, Germany). Inflow of the tube is at the top (aerated raw water; influent), and the outflow (effluent) of drinking water is at the base. The water sample ports are located in different depths along the column with a distance of 0.25 m between the ports.

4.3 Results and discussion

4.3.1 Influence of the microbiology on the elimination of p-TSA, o-TSA and BSA during drinking water treatment

Prior to the incubation experiments, storage experiments revealed that polluted groundwater stored for several days showed a decrease in p-TSA concentration. The measured concentrations of p-TSA of three samples directly after sampling and after seven days were (1) 10.90/< 0.05 µg/L, (2) 9.50/< 0.05 µg/L and (3) 17.10/6.40 µg/L, respectively. Since the groundwater samples were free of solid material, sorption of p-TSA could be excluded. O-TSA and BSA were not considerably reduced during the storage experiment (data not shown).

Comparing the results of the incubation experiments with sterilised (B) and non-sterilised (C) drinking water (see scheme in Figure 4.1) revealed that degradation of p-TSA only occurred under non-sterile conditions over the whole duration (11 days) of the experiment (Figure 4.3). Because degradation was not observed under sterilised conditions I assume that microorganisms are responsible for the degradation of p-TSA. Figure 4.3 shows that o-TSA and BSA concentrations were almost constant over the entire duration of the experiment. Hence, o-TSA and BSA were not reduced during the experiments under both sterile and non-sterile conditions. The monitored oxygen concentrations during the whole incubation experiment were around 8 mg/L assuring aerobic conditions.

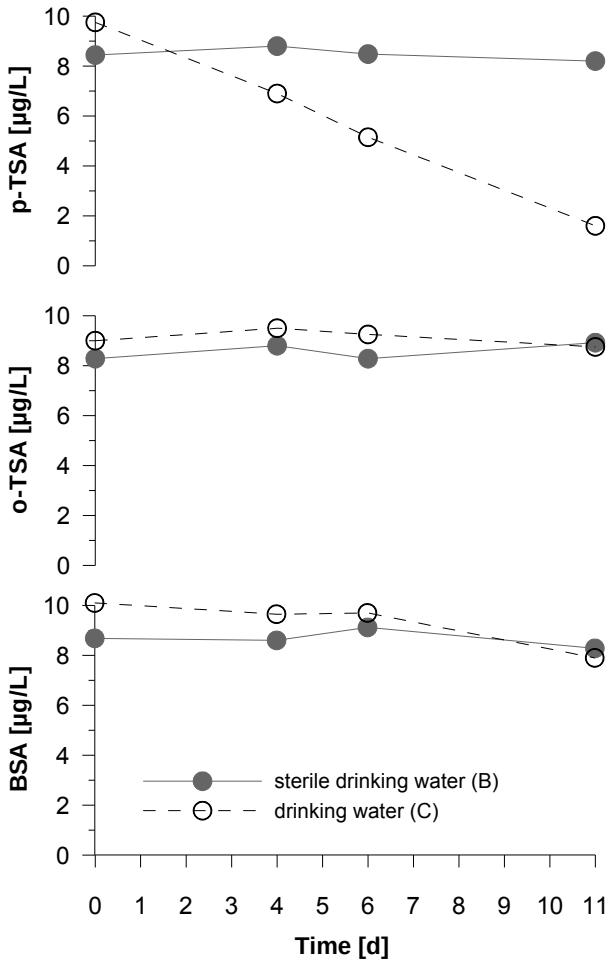

Figure 4. 3 Degradation curve of p-TSA, o-TSA and BSA for sterile (B) and non-sterile (C) cases of the incubation experiment.

4.3.2 Influence of the adaption of the microbiology on the elimination of p-TSA, o-TSA and BSA during drinking water treatment

The measured concentrations of p-TSA, o-TSA and BSA over time in the incubation experiments from the two different DWTPs are given in Figure 4.4 (duplicates). P-TSA concentrations decreased from the beginning (~10 µg/L) of the experiment up to the last sampling campaign after 11 days in the polluted groundwater/backwash water suspension from the DWTP FRI. The detected final concentrations of p-TSA were ~2 µg/L at the end of the experiments (C1, C2: polluted groundwater), resulting in a final p-TSA reduction of 75 % in 11 days. The duplicates yielded similar results (Figure 4.4). The concentration decreased linearly over time indicating a zero order reaction according to rate laws (APELLO AND POSTMA, 1996), irrespective of the reactant concentration. This is probably due

to the fact that the reactants were added in very high concentrations to the samples. The degradation rate (equivalent to the slope in Figure 4.4) was ~0.029 µg/L/h. Hence, 8 % to 10 % of p-TSA was removed per day at the given initial concentration and the amount of backwash water added. Figure 4.4 shows that the compound p-TSA was not eliminated during incubation experiments with biologically active material from the DWTP SPA (D1, D2: unpolluted groundwater). The reason must be that microorganisms have to be adapted. Adapted microorganisms specialised for the degradation of p-TSA only occur in groundwater from polluted areas. The time-frame of the experiments was obviously not long enough for the microorganisms to adapt.

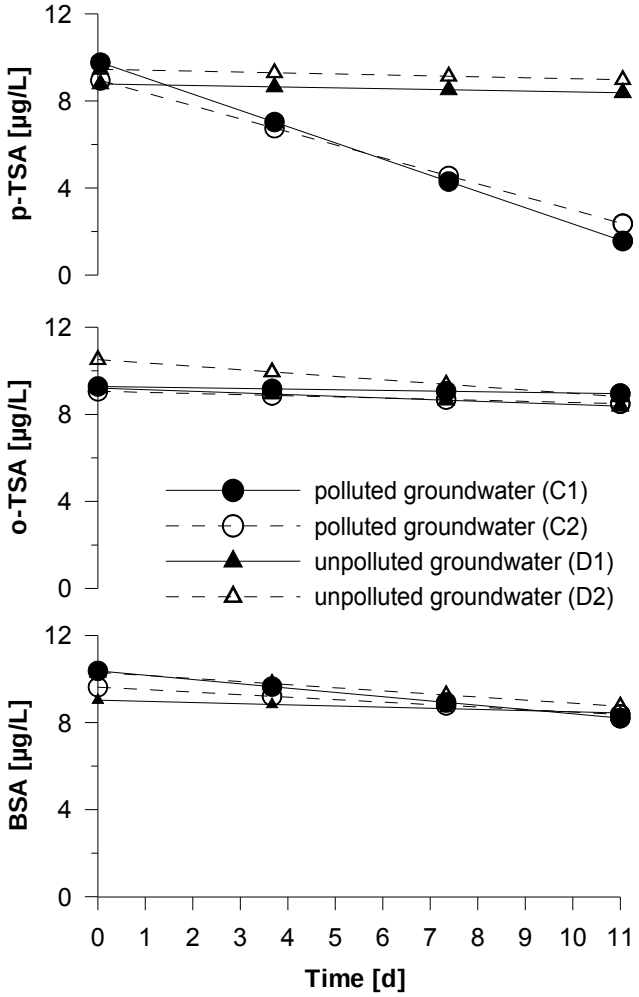

Figure 4. 4 Degradation curve (linear fits) of p-TSA, o-TSA and BSA in drinking water dosed with backwash water from the DWTP treating polluted (C) and unpolluted (D) groundwater during the incubation experiment.

Again, the experiments revealed the persistence of o-TSA and BSA (Figure 4.4). Hence, the microorganisms specialised for the p-TSA degradation are unable to degrade o-TSA and BSA. I suspect that o-TSA and BSA are either not utilisable and/or the concentrations were too low to attract a specialised microbiology under the conditions encountered during drinking water treatment in Berlin. Note that o-TSA and BSA concentrations in the inflow of the DWTP FRI are considerably lower than p-TSA concentrations (< 0.2 µg/L).

In the sludge extracts from the backwash water of a DWTP FRI filter p-TSA, o-TSA and BSA could not be detected. This also confirms that reduction is not caused by adsorption to particles.

4.3.3 Influence of filter velocities, raw water quality and backwash intervals on the elimination of p-TSA, o-TSA and BSA during drinking water treatment

Detailed investigations of the filter velocities during the drinking water treatment process were conducted in the experimental filter operated with the same aerated groundwater used for the routine drinking water treatment by the DWTP FRI, which treats the polluted groundwater. Influent (raw water/aerated groundwater) and effluent (filtered water/drinking water) concentrations of the experimental filter of p-TSA and o-TSA are shown as box plots in Figure 4.5 (n=66, various filter velocities).

At first, after a short regulation phase of two weeks, the efficient operating mode of the experimental filter was tested with measurements of ammonium, iron and manganese. The analyte concentrations (n=1, mg/L) were 1/< 0.04 for ammonium, 1.6/0.03 for iron and 0.35/< 0.01 for manganese for inflow and outflow of the experimental filter, respectively. This data shows an efficient removal of ammonium, iron and manganese. Hence, the optimal operation of the experimental filter was ensured.

The median influent concentration of p-TSA was 1.30 µg/L (maximum 2.4 µg/L; Figure 4.5a). P-TSA was present in smaller amounts in the effluent (median 0.09 µg/L). By contrast, the influent (median 0.14 µg/L, maximum 0.24 µg/L) and effluent (median 0.13 µg/L, maximum 0.26 µg/L) concentrations of o-TSA lay

within the same order of magnitude (Figure 4.5b). Median BSA concentrations measured in the influent and effluent were very low (0.05 µg/L; data not shown). The total median reduction of p-TSA between raw water and the filtered water was 93 %. Sand filtration as a water treatment step does not lead to the reduction of o-TSA and BSA.

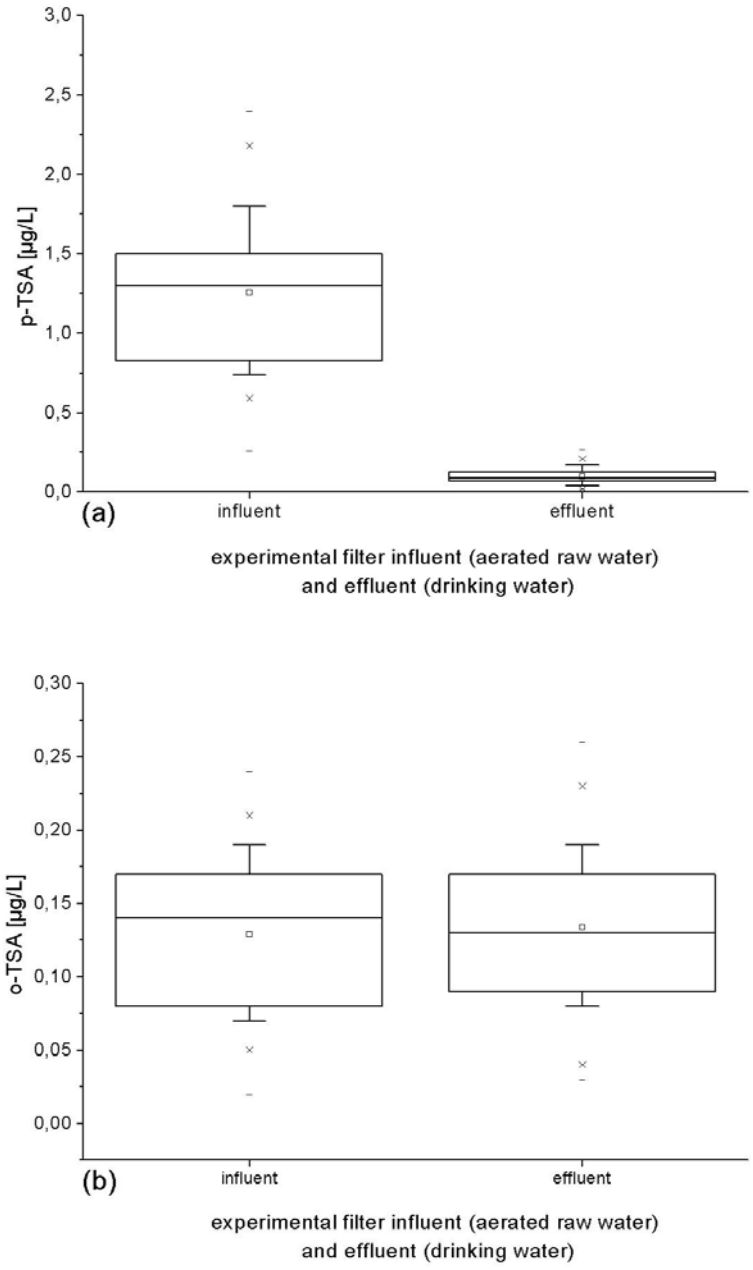

Figure 4. 5 Box plots of (a) p-TSA and (b) o-TSA in influents (n=66) and effluents (n=67) of the experimental filter (sampling November 2005 to April 2006). During the time of sampling, different sand filtration rates were tested (filtration velocity from 2 to 6 m/h).

Figure 4.6 shows the relative concentration depth profiles (c/c_o) of the experimental filter for p-TSA and o-TSA for different filtration velocities (3 to 6 m/h). The initial concentrations varied in the experiments with different filter velocities due to the variability of the raw water over time. For p-TSA, the initial concentrations at the time of sampling the depth profile were 0.72 µg/L (4 m/h), 0.82 µg/L (6 m/h), 1.40 µg/L (5 m/h) and 1.76 µg/L (3 m/h). The effluent concentrations of p-TSA were smaller than 0.1 µg/L for 3, 4 and 6 m/h and 0.15 µg/L for 5 m/h. The depth profile for 5 m/h shows no removal between the influent and port 1 and 2 and these results may be questionable. The total elimination was best at 3 m/h (96 %), followed by 4 m/h (92 %), then 6 m/h (91 %) and lowest at 5 m/h (89 %). Figure 4.6 shows that the total elimination is rather similar for all velocities. The main degradation of p-TSA occurs within the uppermost 0.50 m (Figure 4.6) of the filter or rather in the first ~250 seconds (Figure 4.7).

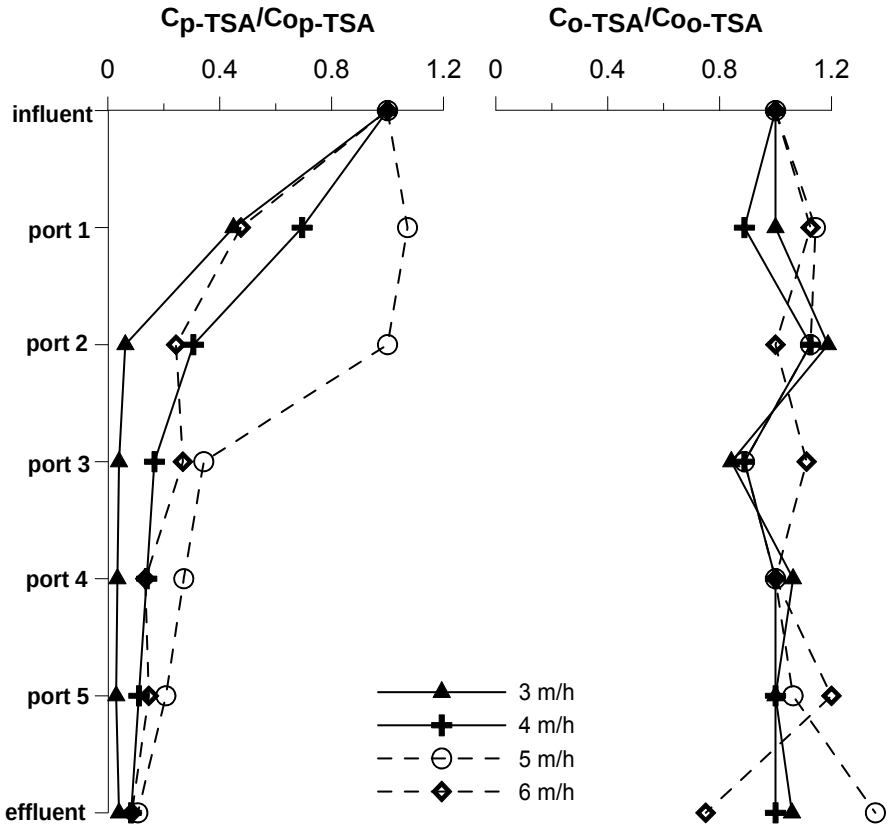

Figure 4. 6 Depth profiles of p-TSA and o-TSA from the experimental filter for filtration velocities from 3 to 6 m/h. C/C_o of p-TSA and o-TSA are plotted against the respective port depth.

Figure 4.7 shows p-TSA concentrations as a function of time for the different filtration velocities (3 m/h to 6 m/h). The times were calculated from the filtration velocities which were converted to flow velocities, assuming an effective porosity of 30 %, a typical value for loosely packed medium sized sands. The elimination appears to be a function of the influent concentration, rather than the filtration velocity, since the degradation rate constants appear to decrease with decreasing initial concentrations and not with increasing filter velocities (Figure 4.7). The concentration decreased exponentially over time (Figure 4.7), indicating a 1st order reaction dependent on the reactant concentrations (APELLO AND POSTMA, 1996). The degradation rate constants were 0.0061 1/s (3 m/h), 0.0063 1/s (4 m/h), 0.0062 1/s (6 m/h) and 0.0075 1/s (5 m/h) (Figure 4.7). In comparison, the concentration versus time graphs in the incubation experiment were (nearly) linear (Figure 4.4), whereas in the experimental filter they were exponential (Figure 4.7). I suspect that the difference in the reaction order is a result of the higher initial concentrations in the incubation experiments (order of magnitude higher than in the experimental filter). A similar effect was also observed by ARVIN ET AL. (1991). ARVIN ET AL. (1991) showed that the aerobic biodegradation of phenols was a 1st order reaction at concentrations below 20 µg/L and a zero order reaction at concentrations above 200 µg/L. Hence, the concentrations of phenols when zero order degradation processes were observed was ten times higher than when a 1st order reaction took place, which is similar to the relation in our experiments.

Overall, the excess of substrate in the experimental filter in comparison to the incubation experiment causes the degradation to proceed much faster (almost complete degradation within hours compared to days). More precisely, only ~75 % of p-TSA were eliminated after 11 days in the incubation experiments whereas ~90 % of p-TSA were eliminated in the experimental filter in less than five minutes only. In both experiments the responsible elimination process is microbial degradation.

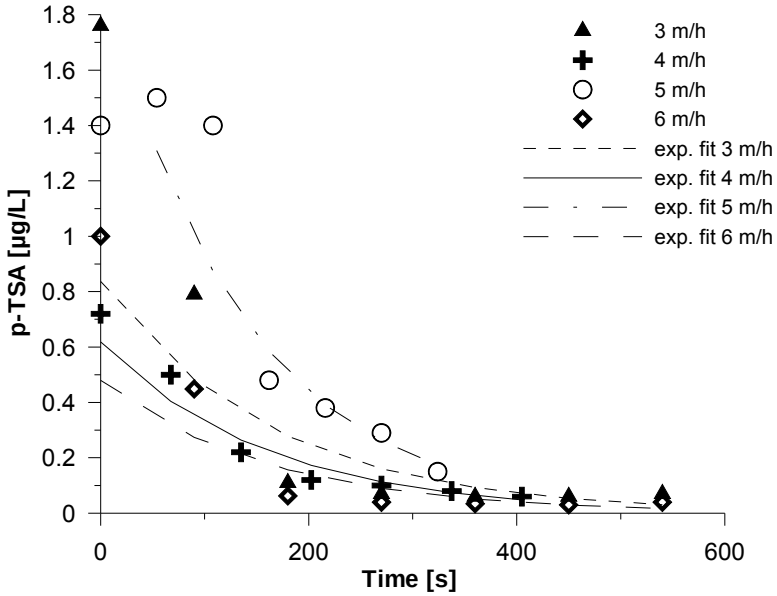

Figure 4. 7 P-TSA concentrations as a function of time for the different filtration velocities (3 m/h to 6 m/h). The times were calculated from the filtration velocities which were converted to flow velocities, assuming an effective porosity of 30 % (exponential fit) from the experimental filter.

Our experiments were conducted under aerobic conditions and with an adapted microorganism population. KUHN AND SUFLITA (1989) examined the degradation of p-TSA and BSA in aquifer slurries from a sulphate reducing (anoxic) and a methanogenic site (anoxic) and observed no removal of p-TSA under sulphate reducing conditions and minor removal under methanogenic conditions. Hence, the redox environment appears to play an important role. Experiments on the redox sensitivity of p-TSA are currently being undertaken.

O-TSA was detected at constant levels during the experiments with different filtration speeds and at different depths (Figure 4.6). Thus, o-TSA was not degraded in the filter.

Backwash intervals did not have an effect on the elimination of p-TSA, o-TSA and BSA (data not shown).

4.4 Conclusions

This study is the first to examine the behaviour of p-TSA, o-TSA and BSA during drinking water treatment of contaminated groundwater. The drinking water relevant

substances behaved differently during all experiments. O-TSA and BSA were stable in all cases and proved to be persistent. The storage and the incubation experiments showed that p-TSA is removed during drinking water treatment by microbiological processes. Microbial degradation of p-TSA only occurs in filters of DWTPs abstracting polluted groundwater, showing that the microbiology has to be adapted to the substances. Concentration versus time plots revealed a zero order reaction in the incubation experiments and a 1st order reaction in the experimental filter, the former probably being the result of the higher initial concentrations. The degradation rate for p-TSA in the incubation experiments was 0.029 µg/L/h (nearly constant). P-TSA was significantly removed (~93 % reduction in 1.6 m) when filtration velocities from 2 m/h to 6 m/h were applied in the experimental filter. The best total elimination of p-TSA was obtained at the lowest filtration rate (3 m/h), though all filtration rates yielded a similarly good removal. Given that it is a first order degradation, differences in the removal efficiency were originally expected (better removal during longer residence times in the filter). I suspect that the differences in the filter velocities are probably too small to show significant differences in the degradation rates. The degradation rate constants in the experimental filter were around 0.0063 1/s.