6. Conclusions and Outlook
6.1 Main outcome of the study

The principal aim of this study was to increase knowledge on the occurrence and fate of the sulfonamides p-TSA, o-TSA and BSA in an urban water cycle. The general conclusions are summarised in the following. In addition, some suggestions will be given for the focus of future projects.

- A specific analytical method was developed based on solid-phase extraction coupled to reversed-phase liquid chromatography and tandem mass spectrometry (HPLC-MS/MS). The HPLC-MS/MS detection is the first method that enables the sensitive, simultaneous routine analysis of p-TSA, o-TSA and BSA in water.

- The use of a deuterated sulfonamide as an internal standard (p-TSA-d₃) provides an optimal quantification with a limit of quantification of 0.05 µg/L of the analytes p-TSA, o-TSA and BSA in aqueous matrixes.

- This method is suitable for a comprehensive investigation of the occurrence, behaviour and fate of the three compounds in wastewater influents and effluents, surface water, bank filtrate, ambient groundwater and drinking water.

- This investigation provides an example of an environmental study of three sulfonamides which are mainly used as industrial chemicals and pharmaceuticals. Measurements in the urban semi-closed water cycle of Berlin showed that the sulfonamides p-TSA, o-TSA and BSA are ubiquitous.

- The observed ranges of concentration vary for each compound and each aqueous matrix. Highest 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 wastewater treatment plants (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). In surface water and
drinking water samples the substances were found in lower concentration ranges.

- The crucial importance of the investigated sulfonamides entering and leaving the wastewater treatment plants in high concentrations was shown. Wastewater resulted in a significant reduction of p-TSA, ambiguous behaviour of o-TSA and a significant formation of BSA. Around 90 % of p-TSA is eliminated during wastewater treatment. Depending on the WWTP, o-TSA concentrations may increase, decrease or remain stable during treatment. The concentrations of BSA increase during the wastewater treatment process. It can only be speculated about the specific process that is responsible for the formation of BSA: presumably biodegradation or bioconversion of sulfonamides with a higher molecular weight.

- Because of the high concentrations of these three sulfonamides in wastewater, they can help to identify the influence of wastewater and treated wastewater in environmental water samples. Likewise, p-TSA, o-TSA and BSA can help to identify bank filtrate processes, if the surface water contains proportions of treated wastewater (unless a former irrigation farm is in the vicinity).

- Because of the omnipresence of p-TSA in the aquatic environment it should generally be monitored in drinking water.

- This is the first study to examine the behaviour of p-TSA, o-TSA and BSA during drinking water treatment of contaminated groundwater. The behaviour observed strongly depends on the investigated compound. P-TSA is mainly eliminated (~90 % reduction), whereas o-TSA and BSA are not removed during drinking water treatment.

- Incubation experiments revealed that microorganisms play a primary role in the elimination of p-TSA during drinking water treatment. Microbial degradation of p-TSA only occurs in filters of drinking water treatment plants abstracting polluted groundwater, showing that the microbiology has to be adapted to be able to eliminate the substances.
- The microorganisms specialised in p-TSA degradation are unable to degrade o-TSA and BSA. They are not adapted to eliminate o-TSA and BSA. These substances are persistent during drinking water treatment under the conditions in Berlin, presumably because concentrations are too low to attract a specialised microbiology.

- Irrespective of the filtration velocities (2 m/h to 6 m/h), p-TSA was efficiently removed (~93 %) in an experimental filter unit simulating drinking water treatment. O-TSA and BSA were not removed under any of the different filtration velocities applied.

- Backwash intervals of the experimental filter unit did not have any effect on the elimination of p-TSA, o-TSA and BSA.

- Higher initial concentrations of p-TSA appear to result in a slightly higher degradation potential. The constant degradation rate in the experimental filter was around 0.0063 1/s.

- The groundwater downstream of a former sewage farm which operated for almost 70 years until the 1980s is highly contaminated with anthropogenic substances. In particular, high concentrations of sulfonamides are characteristic for the groundwater downstream of the former sewage farm at Münchehofe.

- Residual concentrations of p-TSA, o-TSA and BSA in the aquifer strongly influence the production well galleries of the nearby drinking water treatment plant at Friedrichshagen. The contamination plume is large (25 m * 2000 m * 3000 m). Although the sewage farming ended in the 1980s, its effects will continue to influence the quality of the abstracted raw water over decades. Studies of the behaviour of sulfonamides during drinking water treatment suggest that higher concentrations probably do not constitute a high risk for the drinking water quality, but are nevertheless undesirable.

- The elevated concentrations of the sulfonamides in the contaminated groundwater show that they persist over decades under anoxic conditions in an aquifer environment.
- The removal of p-TSA depends on the availability of oxygen, which is the limiting factor. The redox conditions (anoxic or oxic), as well as microbiological status (sterile or non-sterile) are important factors affecting the removal of the sulfonamides p-TSA and o-TSA.

- Adding oxygen to the groundwater would be a suitable bioremediation method to eliminate p-TSA and o-TSA.

- The persistence of the sulfonamides in combination with their widespread applications suggests that they have a wide distribution in groundwater under the influence of sewage farming or wastewater in general. Therefore, the substances should generally be monitored in water samples that are affected by wastewater or treated wastewater.

- Maintaining in-situ conditions with regard to oxygen concentration and microbiology is essential to ensure that concentrations of the sulfonamides in groundwater remain unchanged after sampling.
6.2 Suggestions for future investigations

The study has shown a considerable relevance of three sulfonamides for wastewater treatment plants. An assessment of the following important characteristics of wastewater treatment plants is needed to identify the specific degradation and formation processes of sulfonamides during different forms of treatment and different source areas:

1. The individual sources of the sulfonamides in wastewater of industry and/or households should be studied to estimate their importance in different wastewater treatment plants.

2. The variability of the sulfonamides in wastewater treatment plants with different catchment areas, sizes, different proportions and types of industrial wastewater as well as different levels of organic loads should be investigated.

3. Additionally, for a comprehensive understanding of their behaviour and fate during wastewater treatment, it will be necessary to study different wastewater treatment technologies such as ozonation, membranous technologies, as well as secondary and tertiary treatment steps and operational conditions (e.g. sludge retention time).

4. The identification of specific microorganisms in the wastewater treatment plants which are in charge of the main degradation and formation processes of organic compounds, especially sulfonamides during treatment is necessary.

5. The parent compound of BSA should be identified in a study on the pathways of the metabolism.

6. The reason for the different behaviour of o-TSA between individual wastewater treatment plants should be traced.
Conclusions and Outlook

On the basis of the obtained data, the relevance of the sulfonamides in surface water, bank filtrate and groundwater was shown. Following the investigations presented here, further studies would be of interest:

1. Studies on their temporal (long time monitoring) and spatial variability in the surface water of Berlin, as well as their impact in other locations are needed to assess the relevance of the sulfonamides in different, partly closed water cycles and under different conditions.

2. To obtain a better overview of the temporal variations of the sulfonamides in bank filtrate and to identify the role of different redox conditions during infiltration, an extensive study including hydraulic and hydrochemical investigations is recommended. This would also enable removal rates to be calculated under different redox regimes in the field.

3. Because of the applied in-situ decontamination concept (BIOXWAND, bioremediation) of the BWB in Friedrichshagen, continuous field measurements at the site are essential. The behaviour of the sulfonamides under oxygen addition to the groundwater should be monitored.

4. The results of the incubation experiment look very promising. Therefore, the dependence of degradation of sulfonamides on hydrochemical and microbiological parameters should be investigated in subsequent laboratory experiments (e.g. column studies). In particular, these should include the simulation of variable redox conditions (nitrate reducing, anoxic, sulfidic, methanogenic).

5. Because the behaviour of o-TSA during different experiments varied largely, further studies would be of interest.

6. Measurements below other former sewage farms could improve knowledge about the relevance and fate of these sulfonamides in groundwater and potentially drinking water in general.

7. More information on the ecotoxicological and human-toxicological relevance of p-TSA, o-TSA and BSA is needed.
Intensive studies on the microbiological processes in **drinking water** treatment should be initiated.

1. The specified adapted microbiology should be identified. Which microorganisms actually cause p-TSA degradation?

2. More information on the bioavailability of these compounds with regard to different concentration ranges is essential. Also, details about the density of the microorganism population on the filter medium used for drinking water treatment are needed.

3. In addition, the influence of the filter flow velocities and different concentration ranges of the sulfonamides on the elimination rates during drinking water treatment should be investigated further.