# 1. Introduction

## 1.1 Xenobiotics in the environment

A xenobiotic is a chemical found in the aquatic environment that is not naturally produced or expected to be present in it. Xenobiotics have gained importance world-wide since the 1990s (STAN AND LINKENHÄGER, 1992).

Worldwide, a large number of contaminants were identified in the water resources by many environmental research studies that were carried out to protect the aquatic environment. The contaminants are chemicals applied in agriculture, industry and households. Especially, human and veterinary pharmaceuticals and personal care products (PPCPs) play an important role in recent investigations.

Around 3000 pharmaceutical ingredients are used in the EU today and comprise a broad spectrum of substances, for example therapeutic drugs and diagnostic agents (e.g. antibiotics, antidepressants, lipid regulators, contraceptives and tranquilizers; TERNES, 2004). In many recently published papers attention has been drawn to the occurrence, behaviour and fate of pharmaceuticals and industrial chemicals in the environment (e.g. DAUGHTON AND TERNES, 1999; HALLING-SORENSEN ET AL., 1998; HEBERER, 2002A; KNEPPER ET AL., 1999; KUMMERER, 2001; REEMTSMA AND JEKEL, 1996; REEMTSMA ET AL., 2006; STAN AND LINKENHÄGER, 1992; TERNES, 1998). Meantime, scientific research has developed a broad variety of analytical methods allowing a sensitive quantification of a large number of organic compounds in different water matrixes (PESCHKA ET AL., 2006). Poorly degradable substances in wastewater treatment plants can be problematic in partly closed water cycles if drinking water is produced via bank filtration (REEMTSMA ET AL., 2006). Hence, it is necessary to understand the occurrence, fate, bioaccumulation, persistency and toxicity of the industrial chemicals, unchanged pharmaceuticals and their metabolites in the aquatic ecosystem after their application (GÖBEL, 2004; REEMTSMA AND JEKEL, 1996).

The study of the behaviour of mostly high-polar and hydrophilic substances in the aquatic environment was fostered by the availability of liquid chromatographic-mass spectrometry, allowing a sensitive determination of these trace compounds in water (REEMTSMA ET AL., 2006). Many classes of such polar organic contaminants have been studied intensively in wastewater, surface water, bank filtrate, ambient groundwater and drinking water.

The treatment processes employed in different wastewater treatment plants have been investigated under different aspects (BRUN ET AL., 2006; GOBEL ET AL., 2005; KNEPPER ET AL., 1999, 1998; KUMMERER, 2001; REEMTSMA ET AL., 2006; TERNES, 1998, 2004). Nevertheless, the behaviour and fate of many organic chemicals during wastewater treatment is still largely unknown. Their frequent detection in wastewater influents, effluents and wastewater sludge suggests complex elimination processes for complete and incomplete removal of many chemicals (TERNES, 1998, 2004). So far, the main focus of various studies has been the occurrence and concentration ranges of xenobiotics in surface water systems subject to groundwater/aquifer interaction, for example in GRUENHEID ET AL. (2005), HEBERER (2002A, 2002B), HEBERER ET AL. (2004), MASSMANN ET AL. (2004, 2007), PESCHKA ET AL. (2006), REEMTSMA ET AL. (2006). TERNES (1998) performed the first comprehensive monitoring study of clofibric acid in groundwater. Furthermore, clofibric acid (lipid lowering drug), diclofenac (analgesic), phenazone (analgesic), carbamazepine (antiepileptic), as well as persistent contrast agents (adsorbable organic halogens, AOX) and other several persistent organic pollutants have been detected in surface water and groundwater (GRUENHEID ET AL., 2005; HEBERER, 2002B; HEBERER ET AL., 2004; REDDERSEN ET AL., 2002). In Berlin (Germany) and many other parts of the world, wastewater disposal on to agricultural land and/or wastewater treatment farms was common practice in the past 150 years. Therefore, many recent studies have revealed the occurrence of anthropogenic organic compounds in groundwater samples due to sewage farm irrigation (HEBERER, 1995; HEBERER AND STAN, 1997; SCHENK, 1995; TRÖGER AND ASBRAND, 1995). Some organic contaminants were also detected in drinking water and studied intensively, for example by EICHHORN ET AL. (2002), HEBERER ET AL. (2002), TERNES (2004), ZUEHLKE ET AL. (2007).

It is of great importance to understand the occurrence, behaviour and fate of xenobiotics in the environment to protect the limited resources of freshwater for drinking water production. Therefore, risk assessments are needed for several organic compounds of wastewater origin.

## 1.2 Previous research in the catchment area of the Friedrichshagen drinking water treatment plant

In Berlin untreated wastewater was directly irrigated on several sewage farms for more than one century. This was a common practice of wastewater treatment from 1876 to the 1980s. It resulted in a significant anthropogenic contamination of the environment. The groundwater below the former sewage farm is heavily loaded with different anthropogenic compounds (HEBERER, 1995; HEBERER AND STAN, 1997; SCHENK, 1995; TRÖGER AND ASBRAND, 1995).

The Friedrichshagen drinking water treatment plant is located downstream of the earlier sewage farm at Münchehofe in the eastern part of Berlin (Figure 1.1). Since 1992, periodic sampling was done to evaluate the extent of the contamination area to ensure the drinking water quality of the Friedrichshagen drinking water treatment plant (chapter 5).

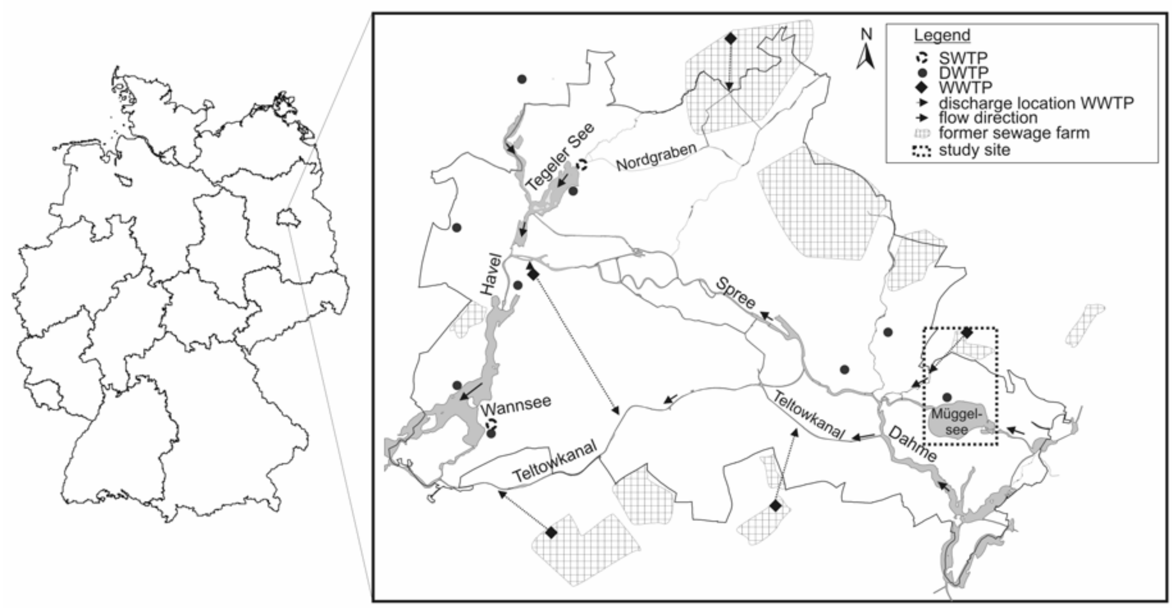


**Figure 1. 1 Overview of the study area Berlin (Germany) with the surface water system (grey shading) and location of the wastewater treatment plants (WWTPs), surface water treatment plants (SWTPs), drinking water treatment plants (DWTPs) and former sewage farms. Square mark groundwater-sampling field site Friedrichshagen (study site). Surface water flow is from south-east and north towards the south-west (arrows).**

Hydraulic and groundwater quality investigations in the area were, for example, performed by FUGRO CONSULT GmbH, HGN and BWB. The hydraulic studies (e.g. ROSCHER AND DOOGS, 2005) were mainly conducted to understand the groundwater flow system to maintain the water supply without anthropogenic contamination caused by the former sewage farm at Münchehofe. Since then, the typical parameters of anthropogenic origin (e.g. ammonium, boron, dissolved organic carbon and sulphate) have been observed. An appraisal of the study area was summarised in ENGELMANN ET AL. (1992). Since 1992 periodical reports on the hydraulic and hydrochemical situation of the groundwater in the northern catchment area of the Friedrichshagen drinking water treatment plant have been published by the BWB (ENGELMANN, 1994, 1995; ENGELMANN ET AL., 1998; SCHMOLKE, 2003, 2007; SCHMOLKE AND PADET, 2000) for the periods from 1992 to 1997 and from 1998 until today.

Because of the overload of the groundwater with anthropogenic compounds, especially ammonium, in the catchment area of the Friedrichshagen drinking water treatment plant it was necessary to develop an efficient decontamination concept for the abstracted groundwater.

The Berliner Wasserbetriebe searched for an efficient and quick reclamation concept to ensure a high drinking water quality in Friedrichshagen. The reclamation concept “pump and treat” is currently in progress. Part of the abstracted contaminated groundwater is pumped to the wastewater treatment plant (chapter 5, hydraulic protective action). Because of the high cost of decontaminating the groundwater in the wastewater treatment plant at Münchehofe, the BWB looked for a more efficient decontamination concept. Different studies have dealt with the decontamination of the anthropogenic polluted aquifer in Friedrichshagen. Financial support was provided by the Federal Ministry of Education and Research (BMBF) and the BWB. The research projects – NIDESI (*„Entwicklung eines gekoppelten Nitrifikations-/Denitrifikations-Verfahrens zur in situ Reinigung stark stickstoffbelasteter Grundwasserleiter“;* EHBRECHT AND LUCKNER, 2000) and BIOXWAND (*„Entwicklung und Erprobung einer Bio-Oxidationswand im Abstrom eines hoch mit Ammonium kontaminierten Grundwasserleiters*“; EHBRECHT AND LUCKNER, 2004) aimed to develop an aerobic in-situ nitrification and de-nitrification technology to decontaminate the anthropogenically polluted aquifer. Another alternative decontamination concept was investigated by JEKEL ET AL. (2006). The main goal of this project was to remove ammonium from the polluted groundwater above ground via physico-chemical processes (ion exchange on to zeolites).

Since autumn 2006, the decontamination concept of the BIOXWAND project has been applied (EHBRECHT AND LUCKNER, 2004). An oxygen barrier/wall was induced into the contaminated aquifer. Decontamination is caused by nitrification of the groundwater during passage through the oxygen wall, thereby converting ammonium to nitrate under induced oxic conditions (bioremediation).

The decontamination process of the study area is accompanied by an intensive monitoring programme of groundwater constituents and by hydraulic modelling (HORNER AND NÜTZMANN, 2005A , 2005B).

## 1.3 Objectives

The purpose of this study was to gain detailed knowledge of the behaviour of the three sulfonamides p-TSA, o-TSA and BSA in the Berlin water cycle. Subsequently, the pathways of these substances were traced from the wastewater treatment plant influents and effluents, over the surface water system, bank filtrate, ambient groundwater, and finally the drinking water. The aim of the study regarding the occurrence, behaviour and fate of these substances in the environment was to address the following questions and tasks:

1. The development of a sensitive, simultaneous and routine analytical method necessary to measure p-TSA, o-TSA and BSA in wastewater, surface water, groundwater and drinking water samples.

2. How relevant are these substances in the aquatic environment, i.e. the urban water cycle of Berlin? What are the concentration ranges in different water samples types?

3. Are these substances eliminated during waste- and drinking water treatment?

4. How do these substances behave in the groundwater during bank filtration?

5. What are the major processes dominating the removal of these trace organic compounds during waste- and drinking water treatment and in natural sediments?
6. What are the degradation mechanisms of the sulfonamides during drinking water treatment? Are microbiological processes involved in the elimination of the sulfonamides?
7. Do filtration velocities, the raw water quality (abstracted groundwater) and backwash intervals have any influence on the elimination rates in sand filters used for the drinking water treatment?
8. What is the distribution of the sulfonamides in the aquifer downstream of a former sewage farm? Are there major differences between deeper and shallow aquifer parts and what is the size of the contaminant plume?
9. Does this contamination constitute a risk with regard to the drinking water quality? Do the concentrations of the sulfonamides in drinking water have a toxicological relevance for humans?
10. Do redox conditions have a significant influence on the degradation of sulfonamides in groundwater?