5. Distribution and persistence in polluted groundwater

The drinking water production of a drinking water treatment plant in Berlin is affected by ambient contaminated groundwater. The groundwater pollution is a result of former sewage farm irrigation in the area, operating for almost 70 years until the 1980s. The three organic compounds para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) were identified in the catchment area of the respective drinking water treatment plant. The distribution of the sulfonamides in the anoxic groundwater was investigated, and a large number of observation and production wells were sampled for this purpose. The contaminant plume is 25 m * 3000 m * 2000 m in size. The high concentrations of p-TSA, o-TSA and BSA in the groundwater show that the sulfonamides persist over decades in an anoxic aquifer environment. Groundwater quality assessment revealed that elevated concentrations of the analytes can be expected in the abstraction well galleries in the future. Therefore, sulfonamides should periodically be monitored in the drinking water. Because of the widespread application and the persistence of the sulfonamides under anoxic conditions, our local investigations suggest that the substances may generally be present in groundwater under the influence of wastewater irrigation. Incubation experiments

were conducted under formation pressures (in-situ pressure) to study the behaviour of these trace organic compounds under different redox conditions (oxic and anoxic). Sterile groundwater sampling was performed to distinguish between microbiological processes occurring in the aquifer and those representing sampling and storage artefacts (non-sterile incubation experiments). Results showed that the addition of oxygen to the anoxic groundwater facilitates p-TSA and o-TSA degradation. Hence, while the substances are persistent under anoxic conditions, they are more degradable in the presence of oxygen. Results also illustrate that maintaining anoxic conditions and in-situ pressures is necessary to ensure accurate analysis.

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The influence of sewage farming and redox conditions on the distribution and persistence of sulfonamides in groundwater.

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5.1 Introduction

Xenobiotics (anthropogenic organic compounds) have gained widespread attention as contaminants of aquatic and terrestrial ecosystems. Worldwide, the occurrence, bioaccumulation, persistency and toxicity of xenobiotics in the environment are major points of concern (REEMTSMA AND JEKEL, 1996).

In many parts of the world, wastewater disposal on to agricultural land and/or wastewater treatment farms was common practice in the past 150 years (ABOULROOS ET AL., 1989; BLUME ET AL., 1980; BOUWER, 2000; HOFFMANN ET AL., 1999; SIEBE AND FISCHER, 1996). Many recent studies have revealed the occurrence of anthropogenic organic compounds in environmental water samples due to sewage farm irrigation (HEBERER, 1995; HEBERER AND STAN, 1997; SCHENK, 1995; TRÖGER AND ASBRAND, 1995).

In Berlin, more than one century of wastewater irrigation resulted in the accumulation of soil organic matter, salts, nutrients (e.g. N and P) and heavy metals (e.g. Pb, Zn, Cu) in the soils and the subsequent percolation into the groundwater below the sewage farms (SAVRIC, 2001). In addition, groundwater below former sewage farms was found to be heavily contaminated with different organic compounds such as pesticides, AOX (adsorbable organic halogen compounds) and phenols (BAUER AND POHL, 1998; HEBERER, 1995; HOFFMANN ET AL., 2000; SCHENK, 1995; SCHEYTT ET AL., 2000; TRÖGER AND ASBRAND, 1995). Different projects have studied the contaminant loads of soils and groundwater of several former sewage farms in and near Berlin, Germany (e.g. BLUME ET AL., 1980; HEBERER, 1995; HEBERER AND STAN, 1994; HOFFMANN AND RENGER, 1998; MARSCHNER ET AL., 1995; REEMTSMA AND JEKEL, 1996; SAVRIC, 2001; SCHEYTT ET AL., 2000; WESSOLEK AND FAHRENHORST, 1994). Because of their general presence and partial persistence in groundwater, anthropogenic organic compounds are considered to be highly relevant for the aquatic environment, in particular, if they are present in the close vicinity of a drinking water treatment plant.

HEBERER AND STAN (1994) investigated a former sewage farm south of Berlin. Two organic contaminants, N-(phenylsulfonyl)-sarcosine (metabolite of a corrosion-

inhibiting agent) and the drug metabolite clofibric acid (lipid lowering drug) were identified. N-(phenylsulfonyl)-sarcosine and clofibric acid were detected in sewage farm groundwater samples at concentrations up to 150 µg/L and 4 µg/L, respectively (HEBERER AND STAN, 1997). The analytical results of HEBERER AND STAN (1997) showed that these two compounds are relevant for drinking water purification. Recently a study by BOUWER (2000) demonstrated the human and environmental risk that arises when wastewater effluent is used for irrigation. It was assumed that the groundwater below sewage-irrigated areas will become unfit for drinking water supply in the long term.

Para-toluenesulfonamide (p-TSA), ortho-toluenesulfonamide (o-TSA) and benzenesulfonamide (BSA) were identified during a gas chromatography–mass spectrometry (GC-MS) screening of groundwater within a catchment area of a drinking water treatment plant downstream of a former sewage farm in Berlin (Germany). P-TSA is a hydrolysis product of the antimicrobial agent chloramine-T in water and is used to treat swine, poultry and fish diseases or in the food industry (BELJAARS ET AL., 1994; HANEKE, 2002; HARRIS ET AL., 2004; MEINERTZ ET AL., 2004). The main application for o-TSA is its use in the production process of the artificial sweetener saccharin. BSA is used for synthesis dyes, photo chemicals and disinfectants (HANEKE, 2002; MOOSER, 1984; STAVRIC AND KLASSEN, 1975).

The presence of these three sulfonamides within the catchment area of a drinking water treatment plant gave rise to subsequent studies (RICHTER ET AL., 2007, 2008A, 2008B). First, a sensitive analytical method was developed to enable the analysis of these three substances in aquatic samples (RICHTER ET AL., 2007). Information on the occurrence and behaviour of p-TSA, o-TSA and BSA in the water cycle of Berlin was presented in RICHTER ET AL. (2008B), where wastewater, surface water, bank filtrate and drinking water were analysed. The results showed that p-TSA is ubiquitous in these environmental water samples. Furthermore, RICHTER ET AL. (2008B) showed that this group of compounds can generally help to identify the influence of treated wastewater in surface water and bank filtrate. The results also revealed that p-TSA is considerably depleted during waste- and drinking water treatment (~90 % reduction respectively). Furthermore, different experiments provided evidence that p-TSA removal during drinking water

treatment is conducted by an adapted microbiology that only occurs in polluted groundwater (RICHTER ET AL., 2008A). RICHTER ET AL. (2007, 2008A, 2008B) also showed that o-TSA and BSA are not removed during waste- and drinking water treatment. O-TSA concentrations increased, decreased or remained stable during treatment, depending on the wastewater treatment plant. The BSA concentrations increased around 4 to 6 times during wastewater treatment. It was assumed that BSA is formed by bioconversion or degradation of sulfonamides with a higher molecular weight. The specific processes responsible for the o-TSA and BSA behaviour remained unclear.

Even though sewage farming was abandoned 30 years ago in the area, the compounds p-TSA, o-TSA and BSA have been detected in high concentrations in preliminary groundwater samples below a former sewage farm (RICHTER ET AL., 2008B). At least for p-TSA, these results were surprising, because p-TSA is quickly degraded during both wastewater and drinking water treatment (90 % elimination within less than a day in each case). The fact that the sampled groundwater was anoxic, whereas the wastewater and drinking water treatment involves oxic treatment steps, leads to the hypothesis that the prevailing redox conditions are decisive for the degradation of p-TSA, and possibly also of o-TSA and BSA. Therefore, detailed field investigations on the presence and distribution of sulfonamides in groundwater and lab experiments on their redox sensitivity were required.

The aim of this study was (i) to characterise the groundwater downstream of a former sewage farm in order to (ii) carry out a risk assessment of the area to ensure the drinking water quality and (iii) to clarify the redox sensitivity of these three sulfonamides with incubation experiments.

5.2 Study site characteristics

5.2.1 Location, instrumentation and technical information on the treatment plants

The research sampling site is located in the north of Lake Müggelsee, in the eastern part of Berlin, Germany (Figure 5.1). The investigated site, namely

Machnow/KrummendammerHeide, lies downstream of the former sewage farm in Münchehofe and upstream of production well galleries of the Friedrichshagen drinking water treatment plant (Figure 5.1).
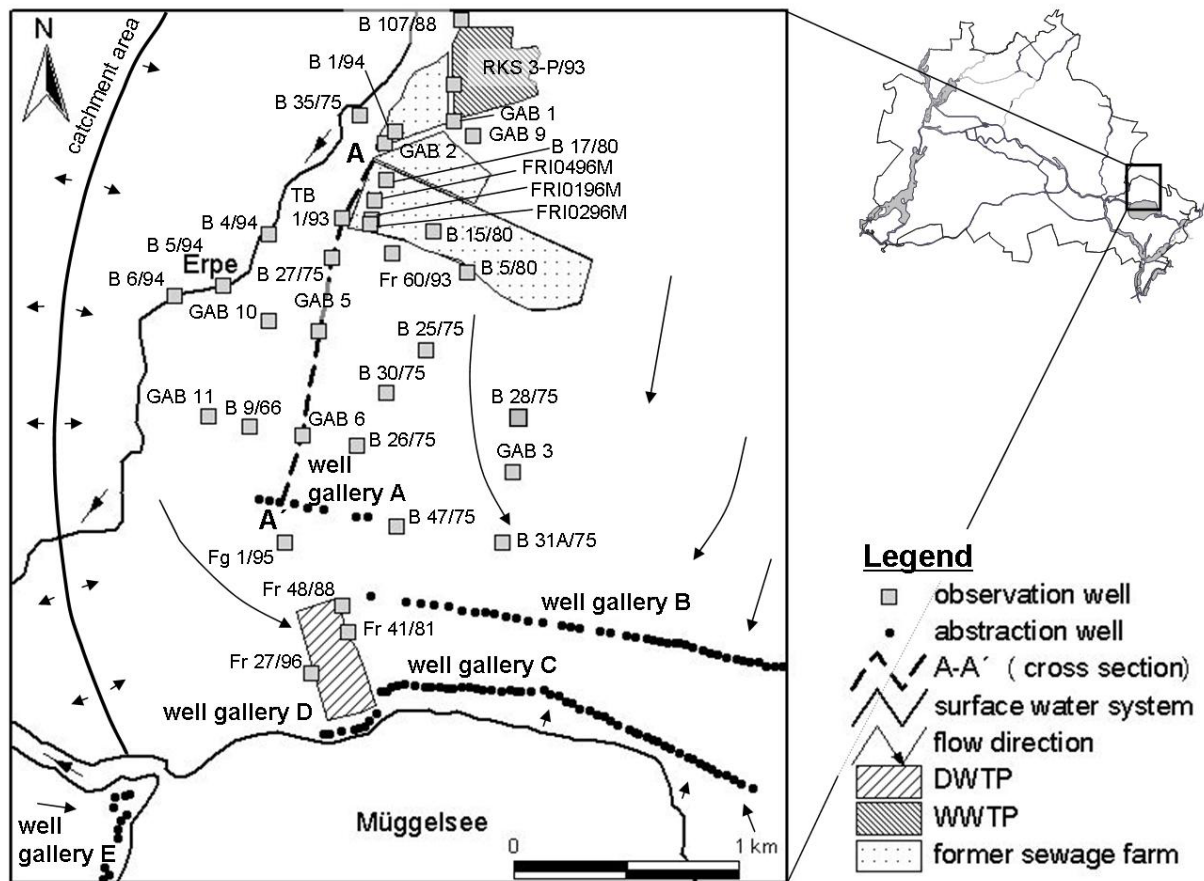

Figure 5. 1 Map of the study site Machnow/KrummendammerHeide with location of wastewater treatment plant (WWTP), drinking water treatment plant (DWTP) and former sewage farm district. Map of the groundwater-sampling field site (observation and abstraction wells) and the position of the cross section (cross section see Figure 5.6). Arrows show main groundwater flow direction of the study site with the catchment area of the Friedrichshagen drinking water treatment plant.

The study site consists of sixty-nine observation wells screened at various depths below ground (from 3.5 m to 87.3 m below ground; Table 5.1). The abstraction wells (~170 vertical wells) of the Friedrichshagen drinking water treatment plant are screened at depths of 20 to 40 m below ground (BWB, 2007). The investigated abstraction well galleries (gallery A, B, C and D) are located along the shores and to the north of lake Müggelsee (Figure 5.1). The well galleries abstract ambient groundwater and infiltrated surface water (bank filtrate) from lake Müggelsee.

Gallery A was placed inland of the production well galleries B, C and D. Gallery A (8 wells, Figure 5.1) is meant to avert the anthropogenic contamination originating from the former sewage farm. The abstracted contaminated groundwater of gallery A is pumped directly to the wastewater treatment plant at Münchehofe (hydraulic protective action). Gallery B abstracts mainly ambient groundwater, whereas the galleries C and D generally extract mainly bank filtrate.

In 2005, 2500 m³ per day were produced from gallery A. On average, the north galleries B, C and D abstracted around 73 000 m³ per day, which is equivalent to 55 % of the total groundwater volume produced at the Friedrichshagen drinking water treatment plant in 2005 (BWB, 2007). The abstracted groundwater 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 with velocities of 3 or 4 m/h, to remove iron and manganese.

5.2.2 Hydrogeology

The porous sediments in the study area are of Quaternary age. The aquifer consists of porous, glaciofluvial and fluvial, mainly fine to medium-sized sand of the Saale and Weichsel glaciation (ENGELMANN ET AL., 1992). The aquifer is generally not divided by aquitards. The glacial tills often encountered in Berlin are almost completely missing to the north of the Müggelsee. A simplified cross section will later be shown in combination with p-TSA, ammonium (NH_4^+) and boron (B) concentrations of the study site (Figure 5.6). The aquifer has a medium hydraulic conductivity with a k_f value of around 10^{-4} m/s (BWB, 2007). A map of the groundwater flow direction, including the catchment area of the Friedrichshagen drinking water treatment plant in the investigation area is shown in Figure 5.1 (BWB, 2007).

5.2.3 Sewage farming

The first sewage farm of the city of Berlin started operation in 1876. Until 1928, 20 sewage farms with a total area of about 10 000 ha were in operation. The principal method of sewage farming is sedimentation of the sludge (gravity treated) in a sedimentation basin, followed by irrigation or field flooding of the wastewater without the sludge on to the soils (SENSTADT, 2007).

In Münchehofe, the method of sewage farm treatment was application on to soils in horizontal terraces. The terraces were flooded by surrounding distribution ditches. Wastewater passed through the soils, and about 40% of the filtered water flowed through the drainage system back into the discharge system, while the rest (around 60%) of the filtered wastewater percolated into the groundwater (BJARSCH, 1997; SENSTADT, 2007). Figure 5.2 shows the schematic set-up of the horizontal terrace treatment. Berlin´s sewage farms were heavily loaded with roughly 185 million m³ of wastewater per year (SENSTADT, 2007). The wastewater amount per year of the Münchehofe sewage farm (Figure 5.1, eastern part of Berlin, ~12 ha) is displayed in Figure 5.3. In the 1970s, wastewater treatment plants were constructed on former sewage farm sites as a result of strongly increased wastewater amounts (e.g. Figure 5.3). The sewage farms were gradually closed. The sewage farm at Münchehofe was closed in the 1980s.
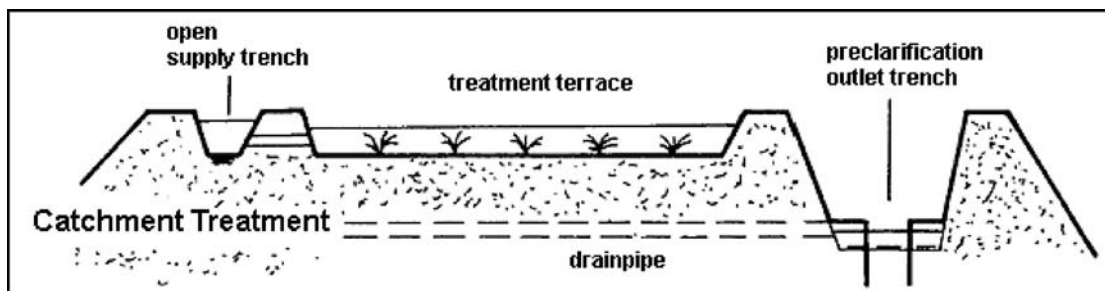

Figure 5. 2 Schematic set-up of horizontal terrace wastewater treatment applied at the Münchehofe sewage farm (SENSTADT, 2007).
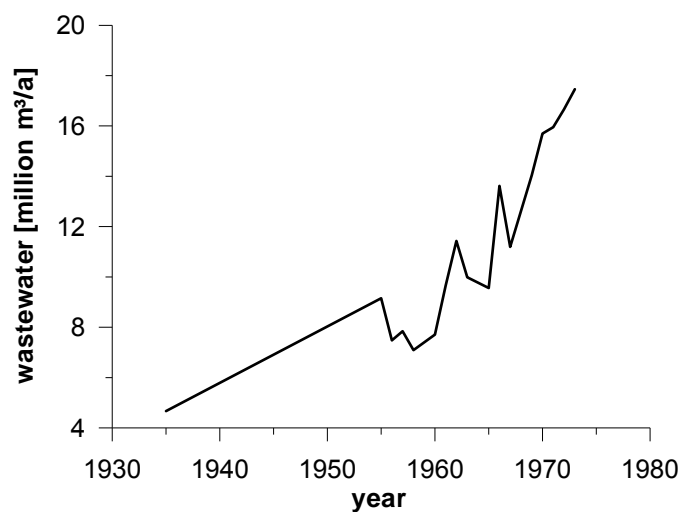

Figure 5. 3 Time series (1935 to 1973; BAUER, 1964) of wastewater applied to the sewage farm at Münchehofe (eastern part of Berlin, ~12 ha).

5.3 Experimental section

5.3.1 Sampling and sample preparation

Regular groundwater sampling was conducted every six months between April 2005 and April 2007 (n=4-5). Groundwater samples were collected in accordance with the official DVWK GUIDELINES (1992). Samples were filled into glass bottles, stored at 4 °C, and full water analysis was carried out one or two days after sampling. Redox potential, pH, oxygen (O_2), temperature and electric conductivity (EC) were measured in the field in a flow cell.

The groundwater for the incubation experiment was sampled on 30.11.2005 from the observation well GAB 5 UP (filter screen depth: 41.5 m to 47.5 m below ground). Fifteen litres of groundwater were collected under pressure and filled into an aluminium tank to prevent degassing of the groundwater (see below, incubation experiment design). The aluminium tanks were stored at 15 °C.

5.3.2 Analytical methods and techniques

The DOC measurements were carried out according to the DIN EN 1484 method with a DOC analyser. Cations in the water were determined with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) according to the DIN EN 11885 method. Anions in water were measured by ion chromatography (DIN EN ISO 10304-1/2). A photometric method was used to detect NH_4^+-N in water (DIN 38406 -E05-1).

The analytical method for p-TSA, o-TSA and BSA, based on solid-phase extraction (SPE) and reversed-phase liquid chromatography (HPLC) coupled to tandem mass spectrometry detection (MS/MS) after electrospray ionisation, is described in RICHTER ET AL. (2007).

5.3.3 Incubation experiment design

Aluminium tanks (height 40 cm, diameter 22 cm, volume ~20 L, maximum pressure 7 bar) were applied for the incubation experiment (Figure 5.4). Altogether, eight tanks were used to simulate four different incubation conditions. Four tanks were completely aerated for the oxic conditions. For the anoxic

conditions, the remaining four tanks were flooded with argon gas. Whereas two aliquots each of the oxic and anoxic tanks were sterilised by autoclavation for 15 minutes at 1bar and 120 °C, the other tanks were not. In the sterilised tanks, conditions present in the groundwater were preserved, ensuring that only the microbiology brought in with the groundwater was present. In the non-sterile cases, bacteria (microbiology) from outside the groundwater may have been present. This was done in order to test if and how long samples can be stored without removal of the organic compounds. Figure 5.5 contains an overview of the conditions of the tanks.
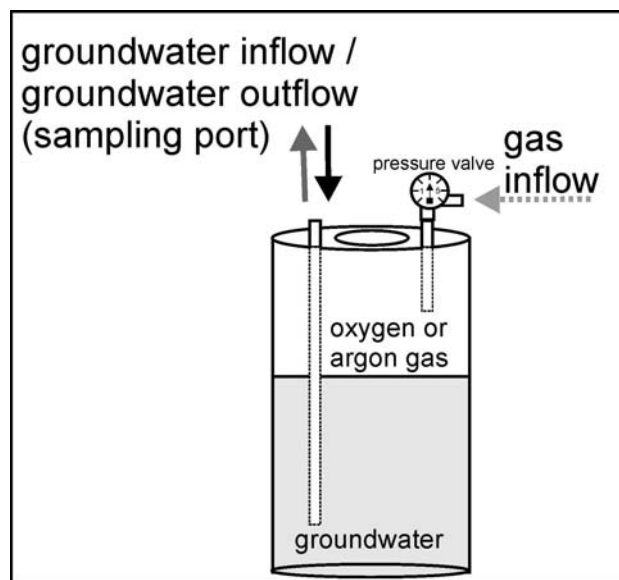

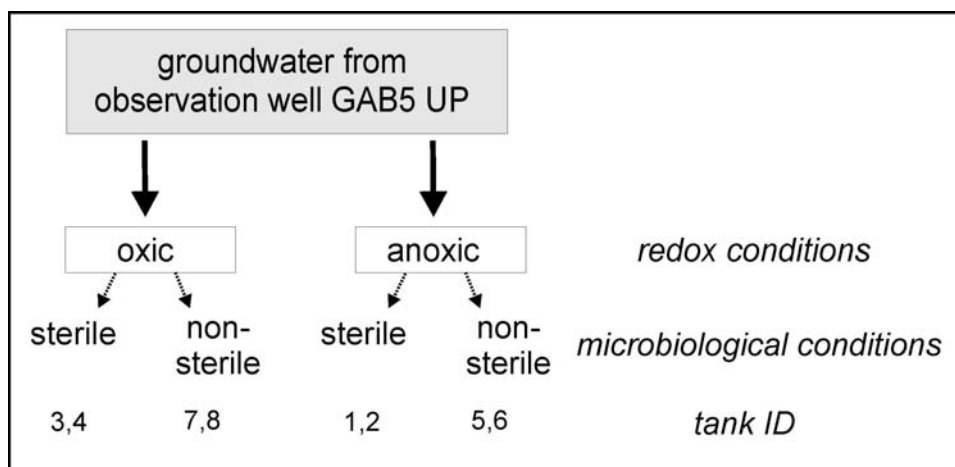**Figure 5. 4 Sketch of the incubation tanks.**

Figure 5. 5 Diagram of the experimental conditions during the incubation experiments in the aluminium tanks.

Nearly 15 L of groundwater were transferred from observation well GAB 5 UP into each aluminium tank via tank damp valves. The entire sampling equipment was sterilised via autoclavation (tubes and stainless steel valves) and with sodium hypochloride (pump).

All pressurised experiment tanks were kept under formation pressure (~2 bar) to prevent any hydrochemical changes caused by degassing. The polluted groundwater was subsequently sampled with tank damp valves. Again, the sampling ports as well as sampling tubes were sterilised before sampling to avoid microbiological contamination. A maximum of 1 L of sample was collected from the tanks. Sampling was done after 1, 5, 9, 12, 15, 34, 42 and 61 days in each case. Oxygen (O_2) concentrations were determined with an O_2 sensor after sampling (measured after 9, 12, 15, 34 and 42 days). The gas pressure was kept constant in the tanks over the whole time of the experiment (pressure ~2 bar) by adding argon. Experiments were performed in duplicates.

5.4 Results and discussion

5.4.1 Distribution of the sulfonamides in the study area

A detailed summary of the relevant parameters in groundwater of each observation well is given in Table 5.1. To simplify, one cross section of the study area in flow direction between the former sewage farm and the abstraction well A19 of the drinking water treatment plant at Friedrichshagen is discussed in detail in the following. The simplified hydrogeological cross section (Figure 5.6) shows median p-TSA concentrations plotted on to the filter screens of the different multi–level wells. P-TSA was detected in high concentrations in both the shallow and the deeper groundwater (B 1/94; GAB 2; TB 1/93; B 27/75; GAB 5; GAB 6). Clearly, all groundwater wells of the cross section (from 5 m to 50 m below ground) display a significant anthropogenic influence. The median concentrations in the groundwater along the cross section are in the range of 2.40 to 38.00 µg/L for p-TSA (Figure 5.6, Table 5.1), from 0.26 to 3.60 µg/L for o-TSA (Table 5.1), and from 0.09 to 0.52 µg/L for BSA (Table 5.1). In the north of the study area, the multi-level observation wells B 1/94 and GAB 2 show a strongly dampened p-TSA signal (median < 10

µg/L) in comparison to the other observation wells along the cross section in all depth levels with the exception of GAB 2 OP (median 15 µg/L). The concentrations increase in the southward flow direction. The groundwater

Table 5. 1 X- and y- coordinates (Gauß-Krüger), filter screen depths of the observation wells and median concentrations of EC, B, Fe, Mn, DOC, SO_4^{2-}, NH_4^+-N, p-TSA, o-TSA and BSA from April 2005 to April 2007 (n=4-5)

GWM-ID		Coordinates		filter screen depth [m below ground]		EC [µS/cm]	B [µg/L]	Fe [mg/L]	Mn [mg/L]	DOC [mg/L]	SO_4^{2-} [mg/L]	NH_4^+-N [mg/L]	p-TSA [µg/L]	o-TSA [µg/L]	BSA [µg/L]
		X	Y	from	to										
B 47/75	OP	5408317	5814962	8.0	12.0	1160	315	5.35	0.89	5.15	249.0	6.45	15.00	1.02	0.43
	MP1	5408317	5814962	26.1	30.1	1170	330	5.10	0.48	5.50	199.0	11.00	15.50	1.40	0.41
	UP	5408317	5814962	83.3	87.3	5260	655	1.65	0.17	2.30	25.5	1.10	< 0.05	< 0.05	< 0.05
B 31A/75	MP1	5409062	5814854	19.0	21.0	855	260	2.20	0.24	1.70	12.5	0.58	0.42	< 0.05	< 0.05
	UP	5409062	5814854	43.0	45.0	1385	195	2.25	0.24	1.95	6.5	1.10	1.10	0.16	< 0.05
GAB 3	OP	5409139	5815355	8.3	10.3	1030	340	4.05	0.38	4.25	251.0	14.00	21.00	0.79	0.61
	MP1	5409139	5815355	16.7	18.7	820	235	3.10	0.36	2.65	180.0	5.80	12.00	0.72	0.29
	UP	5409139	5815355	34.1	36.1	760	70	1.70	0.88	2.05	153.0	1.60	5.70	0.39	0.05
B 28/75	OP	5409646	5841965	5.3	7.3	630	175	1.80	2.40	3.45	150.5	0.07	0.83	0.10	0.05
	MP	5409206	5815649	10.8	12.8	920	210	5.35	1.40	4.10	196.0	1.90	6.80	0.36	0.14
	UP	5409206	5815649	20.7	22.7	905	175	2.60	0.49	3.20	201.0	5.30	10.25	0.55	0.31
B 25/75	OP	5408527	5816207	10.5	12.5	980	490	2.95	1.20	6.55	192.0	5.50	5.70	0.44	0.52
	MP2	5408527	5816207	39.0	41.0	930	160	4.30	0.31	4.60	122.0	20.00	11.00	1.10	0.45
	UP	5408527	5816207	43.5	45.5	910	155	3.50	0.47	3.85	128.0	18.00	11.00	1.00	0.35
B 9/66	OP	5407283	5815675	25.0	27.0	1000	155	6.20	0.76	4.25	176.0	4.20	3.40	0.90	0.28
GAB 6	OP	5407652	5815605	4.5	10.5	870	170	1.25	2.20	4.05	215.0	12.00	15.00	1.60	0.20
	UP	5407652	5815605	30.5	40.5	1320	240	3.30	0.28	6.40	198.5	42.50	26.00	3.60	0.52
B 26/75	OP	5408034	5815536	10.3	12.3	1120	300	5.00	1.05	5.35	259.0	12.00	17.50	1.30	0.64
	MP1	5408034	5815536	17.9	19.9	1160	325	5.50	0.50	5.50	251.0	13.50	19.00	1.80	0.77
	UP	5408034	5815536	40.8	42.8	1425	93	5.40	0.34	5.60	123.5	3.00	2.65	1.00	0.47
GAB 5	OP	5407766	5816345	3.5	11.5	1060	270	2.40	1.60	5.40	217.5	25.00	23.00	1.40	0.32
	UP	5407766	5816345	41.5	47.5	1225	250	2.85	0.38	5.70	171.0	48.50	38.00	3.20	0.38
B 27/75	OP	5407863	5816859	5.9	7.9	1020	280	2.90	1.00	6.60	218.0	19.00	17.00	0.94	0.28
	MP	5407863	5816859	12.8	14.8	970	210	2.80	0.94	5.10	182.0	28.00	24.00	1.50	0.32
	UP	5407863	5816859	23.6	24.6	955	220	10.60	0.79	4.95	179.5	27.00	26.50	1.65	0.32
GAB 2	OP	5408231	5817674	7.3	9.3	1500	320	3.00	0.50	11.00	276.5	89.00	15.00	0.58	0.86
	MP1	5408231	5817674	14.8	16.8	865	130	16.00	0.60	4.40	170.5	26.00	7.40	0.37	0.18
	UP	5408231	5817674	32.2	34.2	775	67	12.00	0.80	3.30	150.5	8.90	5.00	0.26	0.09
GAB 1	OP	5408718	5817823	8.4	10.4	1450	200	0.05	0.89	8.10	198.0	< 0.04	0.08	0.06	< 0.05
	MP1	5408718	5817823	19.7	21.7	960	63	1.30	1.60	2.80	218.0	0.20	9.20	1.10	0.19
	UP	5408718	5817823	38.2	40.2	610	< 50	0.40	0.71	1.50	69.0	0.16	0.21	< 0.05	< 0.05
B 30/75	OP	5408247	5815908	7.4	8.4	1130	300	1.10	2.00	5.60	247.0	3.80	8.10	0.50	0.36
	MP	5408247	5815908	11.2	12.2	1160	350	7.75	0.76	5.15	239.0	5.90	15.00	1.35	0.58
	UP	5408247	5815908	23.5	24.5	1150	350	4.70	0.64	5.30	239.0	6.90	16.00	1.40	0.58
B 35/75	MP1	5408060	5817873	18.6	20.6	550	64	2.30	0.61	2.00	22.0	3.50	3.10	0.21	< 0.05
	MP2	5408060	5817873	31.8	33.8	540	59	1.90	0.56	1.90	21.0	2.80	3.60	0.68	< 0.05
	UP	5408060	5817873	43.2	45.2	940	58	4.90	0.26	3.60	84.0	5.90	1.60	0.50	0.44
B 15/80	OP	5408577	5817051	5.5	7.5	720	200	0.16	0.08	14.00	155.0	0.16	0.11	< 0.05	< 0.05
	MP1	5408577	5817051	15.4	17.4	900	180	11.00	1.20	5.10	161.0	16.00	19.00	1.25	0.20

Table 5. 1 X- and y- coordinates (Gauß-Krüger), filter screen depths of the observation wells and median concentrations of EC, B, Fe, Mn, DOC, SO_4^{2-}, NH_4^+-N, p-TSA, o-TSA and BSA from April 2005 to April 2007 (n=4-5)

GWM-ID		Coordinates		filter screen depth [m below ground]		EC [µS/cm]	B [µg/L]	Fe [mg/L]	Mn [mg/L]	DOC [mg/L]	SO_4^{2-} [mg/L]	NH_4^+-N [mg/L]	p-TSA [µg/L]	o-TSA [µg/L]	BSA [µg/L]
		X	Y	from	to										
	UP	5408577	5817051	24.5	26.5	810	150	2.10	0.32	3.60	145.0	4.00	22.50	3.00	0.30
B 5/80	OP	5408820	5816762	5.0	7.0	500	170	< 0.03	0.14	21.00	47.0	< 0.04	0.09	< 0.05	0.05
	MP1	5408820	5816762	15.3	17.3	840	110	2.70	1.00	3.20	152.0	7.10	10.00	0.78	0.22
	UP	5408820	5816762	35.0	37.0	560	< 50	1.20	0.29	1.70	65.0	0.46	0.09	< 0.05	< 0.05
GAB 9		5408852	5817722	25.0	29.0	820	< 50	0.60	0.58	1.55	184.0	< 0.04	< 0.05	< 0.05	0.37
B 17/80	OP	5408246	5817411	4.3	6.3	320	110	0.73	0.11	7.60	55.0	< 0.04	0.06	< 0.05	< 0.05
	MP1	5408246	5817411	14.0	16.0	1110	150	22.00	1.70	5.80	188.0	25.00	22.00	1.50	0.33
	MP2	5408246	5817411	29.0	31.0	590	< 50	8.80	1.40	2.40	118.0	3.00	3.30	0.21	< 0.05
	UP	5408246	5817411	42.2	44.2	570	96	2.70	0.59	2.40	84.0	3.20	6.90	1.20	0.08
TB 1/93		5407937	5817139	34.0	37.0	830	120	3.50	1.40	3.70	140.0	25.00	16.00	1.50	0.18
RKS 3-P/93		5408717	5818086	8.0	10.0	990	120	17.00	1.70	4.70	81.0	4.30	1.10	0.16	< 0.05
B 4/94		5407412	5817026	3.7	5.7	710	110	0.24	0.44	3.10	134.0	0.73	2.30	0.35	0.09
B 5/94		5407094	5816671	3.7	5.7	1230	130	7.60	0.32	8.00	292.0	2.30	0.62	0.09	0.16
B 6/94		5406754	5816598	3.7	5.7	1100	80	6.00	0.32	4.60	262.0	1.60	0.74	0.16	0.05
GAB 10	OP	5407412	5816415	5.6	7.6	950	240	2.50	0.20	4.30	175.5	3.00	2.40	0.51	0.16
	UP	5407413	5816416	26.6	29.6	1190	150	3.80	0.49	5.20	118.0	23.00	27.00	5.60	0.66
GAB 11	OP	5406987	5815741	5.6	7.6	780	85	0.62	0.10	2.80	121.0	0.23	0.44	0.08	< 0.05
	UP	5406987	5815739	28.6	32.6	825	< 50	3.40	0.24	2.40	139.5	0.30	0.46	0.10	< 0.05
Fg 1/95		5407527	5814857	15.6	17.6	1040	110	2.90	0.42	3.50	219.0	1.30	0.94	0.13	0.05
Fr 27/96		5407721	5813926	29.8	31.8	860	70	3.30	0.28	3.50	139.0	0.62	< 0.05	< 0.05	< 0.05
Fr 60/93		5408290	5816894	21.5	23.5	900	170	3.10	0.36	3.50	161.0	14.00	24.00	2.40	0.17
B 107/88	OP	5408778	5818544	37.0	39.0	680	< 50	2.30	0.21	1.90	110.0	0.31	0.09	< 0.05	< 0.05
FRI 0196M		5408138	5817131	23.7	25.7	610	62	5.20	1.10	2.30	63.0	4.30	6.00	0.77	0.05
FRI 0296M		5408135	5817103	28.2	30.2	1290	120	15.00	2.90	5.70	258.0	20.00	13.00	0.96	0.29
FRI 0496M		5408167	5817268	26.1	28.1	1260	140	18.00	3.30	5.90	254.0	19.00	14.00	0.90	0.29
B 1/94	OP	5408308	5817752	15.0	17.0	1280	370	17.00	0.80	11.00	263.0	43.00	7.20	0.42	0.33
	MP	5408308	5817752	26.0	28.0	720	< 50	11.00	0.74	2.40	144.0	2.00	2.40	0.18	< 0.05
	UP	5408308	5817752	37.0	39.0	650	79	4.50	0.81	2.10	91.0	3.70	8.90	0.70	< 0.05
Fr 48/88		5407929	5814412	35.3	39.3	1540	190	4.90	0.41	6.80	173.0	13.00	7.80	1.65	0.28
Fr 41/81		5407971	5814224	26.0	28.0	920	69	1.20	0.72	3.70	170.0	0.35	< 0.05	< 0.05	< 0.05

observation wells in the middle of the cross section (B 27/75; GAB 5; GAB 6) display the highest p-TSA signals with median concentrations of 23.0 to 38.0 µg/L. The deepest observation well GAB 5 UP reveals the strongest influence of anthropogenic substances and the highest p-TSA median concentration of 38 µg/L. In abstraction well 19 (gallery A), the southernmost well of this cross section, median concentrations of around 11.7 µg/L of p-TSA were measured, but this being an abstraction well, it produces a mixture of contaminated and uncontaminated groundwater. It becomes evident that since irrigation stopped, the plume moved in the southern direction towards the drinking water abstraction well galleries of the Friedrichshagen drinking water treatment plant.

The sewage indicators o-TSA and BSA show similar plume patterns, only with lower concentrations (data shown in Table 5.1).

Because the groundwater body is polluted with anthropogenic compounds originating from wastewater, a number of other anthropogenic marker compounds such as NH_4^+ and B were detectable besides the sulfonamides. In wastewater, NH_4^+ is mainly a primary degradation product of organic matter (proteins, e.g. FREEZE AND CHERRY, 1979). Boron is used as a washing powder additive and also a wastewater indicator (VENGOSH ET AL., 1994). Boron was used as a wastewater indicator in surface water and bank filtrate to estimate the influence of treated wastewater in Berlin (MASSMANN ET AL., 2004). The p-TSA results in the cross section were compared to NH_4^+ and B concentrations (Figure 5.6). In general, the concentrations of NH_4^+ and B show similar results to p-TSA, with higher concentrations in the middle of the cross section and lower concentrations in the north (deeper observation wells) and south (abstraction well 19) of the cross section. Clearly, the deeper groundwater in the north is largely unaffected by anthropogenic input (B 107/88, Table 5.1). In contrast to p-TSA, the concentrations in the shallow groundwater wells in the north (B 1/94 and GAB 2) displayed very high concentrations of NH_4^+ (43 to 89 mg/L) and B (320 to 370 µg/L). The highest concentrations of NH_4^+ and B were found directly below the former sewage farm (B 1/94 OP and GAB 2 OP). Like p-TSA, NH_4^+ was detected with high a median concentration of 48.5 mg/L in the deepest observation well GAB 5 UP.

a) Concentrations p-TSA [µg/L] Apr05-Apr07

b) Concentrations NH₄⁺- N [mg/L] Apr05-Apr07
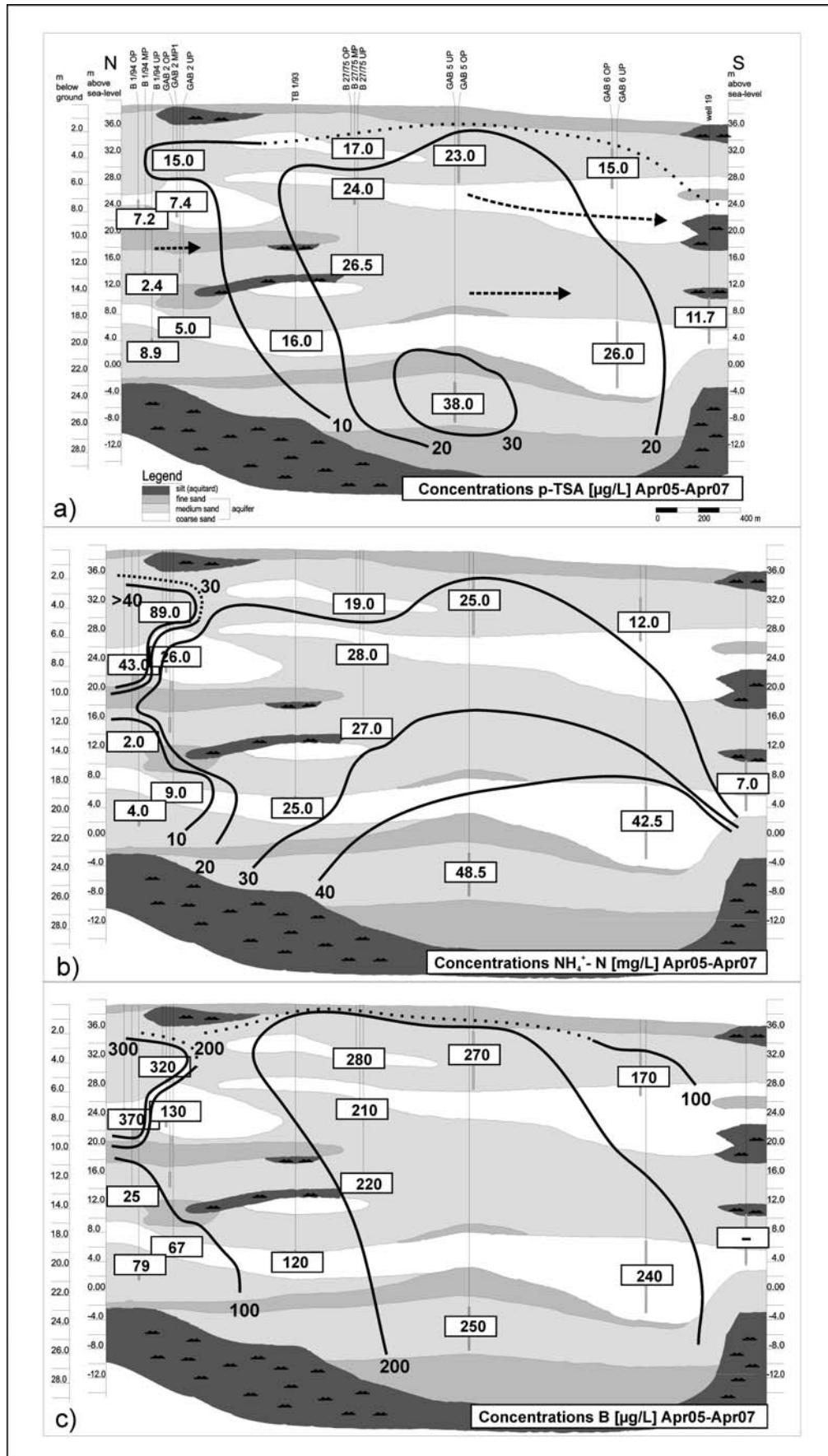
c) Concentrations B [µg/L] Apr05-Apr07

Figure 5. 6 Schematic hydrological cross section of the field site Machnow/Krummen-dammerHeide (location see Figure 5.1). The concentrations are plotted against the filter screen depth (middle of the screen). The black numbers on white background represent median concentrations of (a) p-TSA [µg/L] (b) NH$_4^+$-N [mg/L] and (c) B [µg/L] from April 2005 to April 2007 (n=4-5). Isolines of different concentration levels are shown for p-TSA, NH$_4^+$-N and B (lines drawn by hand). Groundwater flow direction shown as arrows.

The retardation factors of NH$_4^+$ reported in the literature vary between 1.3 and 1.7 (EHBRECHT AND LUCKNER, 2000; EHBRECHT AND LUCKNER, 2004) and between 1.3 and 2.1 for B (DESIMONE ET AL., 1997). The similar general shape of the plume of B and p-TSA may indicate that their retardation factors are within the same range. I can only speculate about the different plume shapes of NH$_4^+$ and B in comparison to the sulfonamides directly below the sewage farm. I assume that the very high concentrations of NH$_4^+$ and B compared to the lower concentration of p-TSA under the former sewage farm indicate that the infiltration times of the peak loads of the respective substances were different. I suspect that the NH$_4^+$ and B concentrations in the wastewater were relatively constant, whereas the concentrations of sulfonamides in the wastewater may have varied greatly over time. Figure 5.6 shows that the contaminant plume has a maximum thickness of ~25 m.

The horizontal shape of the contamination plume below ground is illustrated in Figure 5.7. The length and width of the contamination plume are around 3 000 m and 2 000 m, respectively. Figure 5.7 shows that the lowest p-TSA concentrations of the contamination plume are found along the plume margin. The same applies to o-TSA and BSA (Table 5.1, data not shown). The ambient groundwater north of the former sewage farm (B 107/88, Figure 5.1, Table 5.1) does not contain elevated concentrations of anthropogenic substances (p-TSA, o-TSA, BSA, NH$_4^+$ and B; Table 5.1). The concentrations measured represent a typical geogenic background level. Clearly, the highest concentrations of sulfonamides were found in the middle of the plume, extending from the sewage farm area to the galleries A and B (length around 2 km, along the cross section). The shape of the plume was strongly affected by the abstraction well galleries A (protection wells) and B (production wells) of the drinking water treatment plant at Friedrichshagen. The abstraction well gallery A is meant to divert and focus the plume. However, the high production volume of the eastern part of the abstraction well gallery B

(compare groundwater flow direction, Figure 5.1) leads to an eastward diversion of the contaminant plume. Because of the large size of the contamination plume, it can be assumed that the raw water production of the Friedrichshagen drinking water treatment plant will be affected by the remains of wastewater irrigation over decades.

The elevated concentrations of the sulfonamides throughout the study area 30 years after closure of the sewage farm show that the substances persist over decades in an anoxic aquifer environment. In view of the drinking water production the sulfonamides, once brought into the environment, may potentially influence the raw water quality under similar conditions over a long period of time. However, results from RICHTER ET AL. (2008A) revealed that p-TSA is largely removed during drinking water treatment and, therefore, the presence of p-TSA in the groundwater does not necessarily constitute an acute risk. If the aquifer is contaminated with sulfonamides, they can be applied as a qualitative indicator of wastewater in abstracted groundwater and in drinking water.
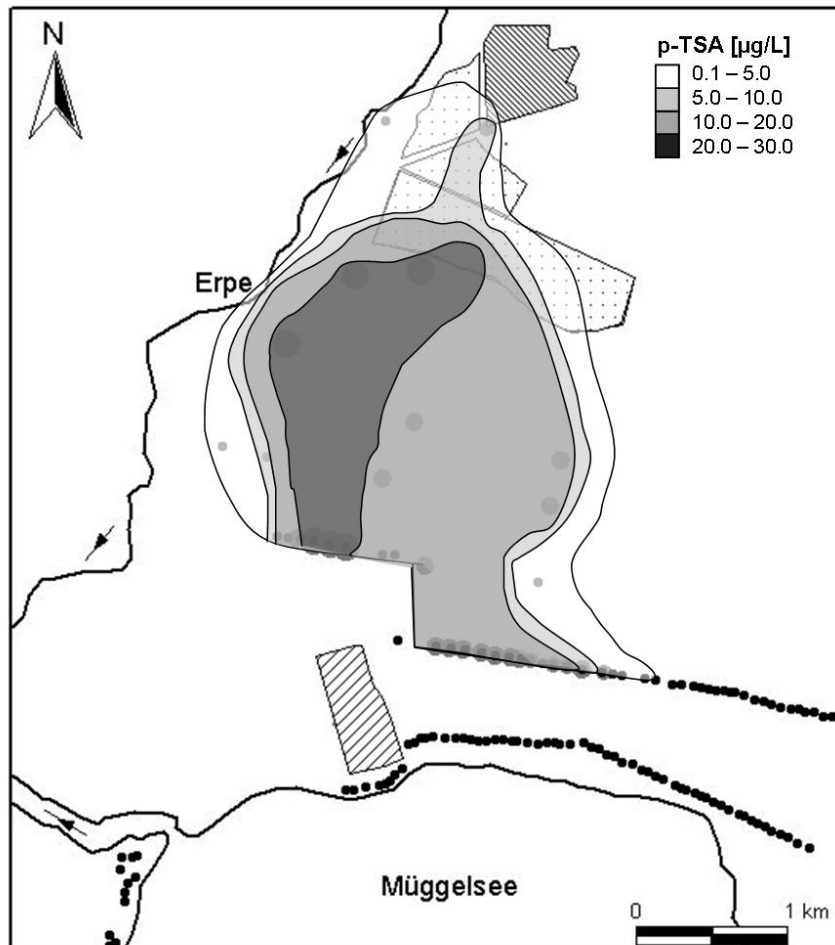
Figure 5. 7 Concentrations of p-TSA [µg/L] at a depth of 17 to 33 m below ground from the respective observation wells (n=4-5; April 2005 to April 2007) and abstraction wells (gallery A n=10-12 and gallery B n=5-19; April 2005 to December 2006) at the field site. Flow direction of the groundwater is shown in Figure 5.1.

5.4.2 Redox sensitivity of the sulfonamides

Oxygen concentrations under different conditions throughout the experiment are illustrated in Figure 5.8. Measurements of O_2 were carried out immediately after sampling with an O_2 sensor. Short contact with atmospheric O_2 during sampling was unavoidable. Therefore, the O_2 concentrations in all tanks were probably even lower. The tank water under oxic conditions was saturated with O_2 (~10 mg/L) at the beginning of the experiment (Figure 5.8). The concentrations decreased over the whole time of the experiment to ~1 mg/L. This decrease is due to the fact that the gas pressure was kept constant in the tanks by adding argon, thereby diluting the O_2 concentration over time. The O_2 concentrations under oxic/non-sterile and oxic/sterile conditions were mostly similar, but a large difference was observed on

day 34. A clear difference between the O_2 of the oxic and anoxic tanks can be seen as expected (Figure 5.8). Because of the sampling technique, I assume that the anoxic incubation tanks were completely O_2 free.
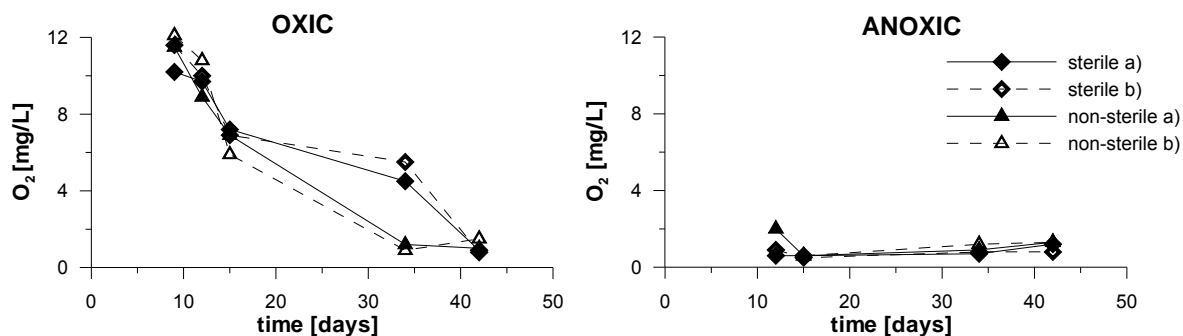

Figure 5. 8 O_2 concentrations [mg/L] plotted versus time of storage under oxic (left) and anoxic (right) conditions.

Figure 5.9 shows the p-TSA, o-TSA and BSA concentrations during the incubation experiment (duplicates). The different conditions in the tanks were anoxic/sterile (tank ID: 1, 2) and anoxic/non-sterile (tank ID: 5, 6) or oxic/sterile (tank ID: 3, 4) and oxic/non-sterile (tank ID: 7, 8).

Under oxic conditions (oxic/sterile and oxic/non-sterile) and under anoxic/non-sterile conditions p-TSA concentrations decreased from the beginning of the experiment up to the last sampling campaign after 42 days. In these cases, the detected final concentrations of p-TSA were < 0.05 µg/L (Limit of Quantification; LOQ) at the end of the experiment. No concentration changes of p-TSA were observed in the combination of anoxic/sterile conditions. P-TSA concentrations at the end of the experiment were unchanged (~35 µg/L). The duplicates yielded similar results. Under oxic conditions, p-TSA concentrations in the stored groundwater were fully removed (~100 % reduction) after 15 days. At the time of removal, the O_2 concentrations were near saturation (~10 mg/L). Under anoxic/non-sterile conditions, p-TSA was fully removed after 9 and 34 days. The reason for the different behaviour in the duplicates is unclear.
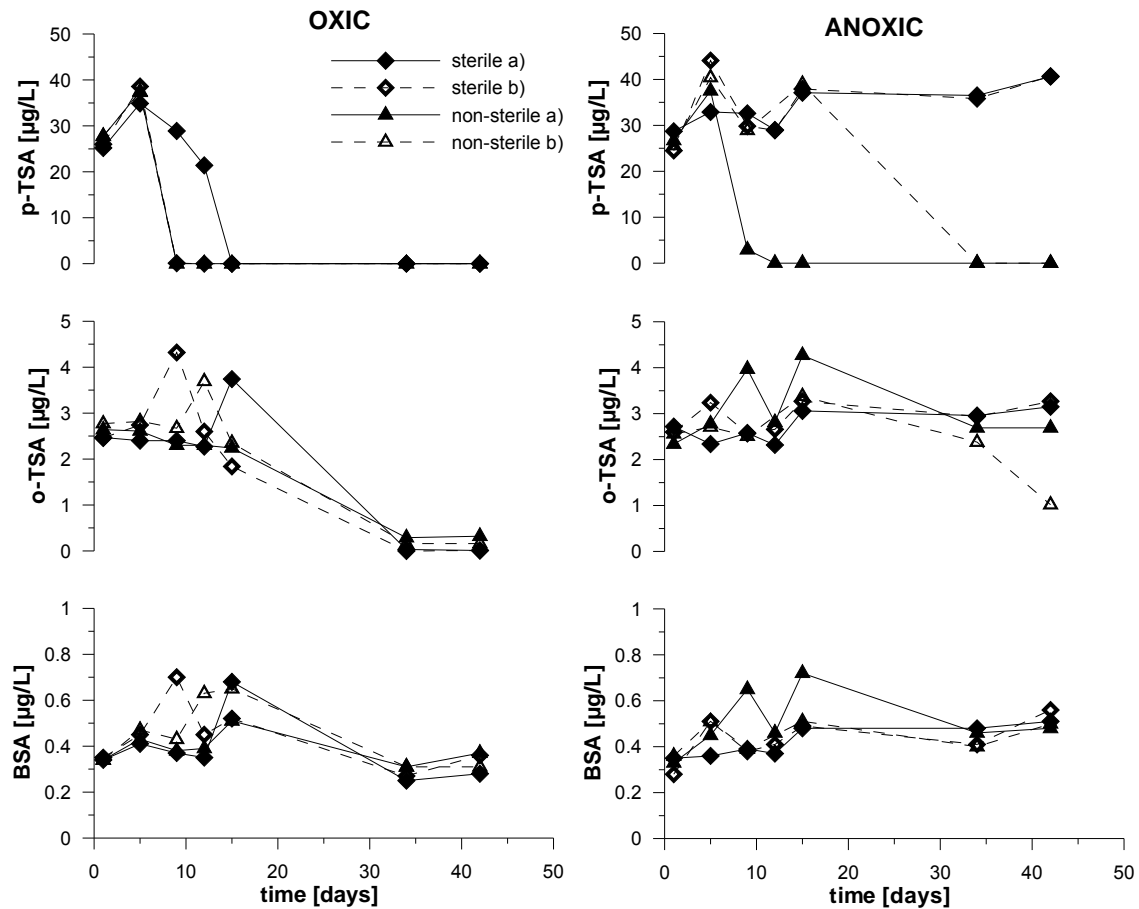
Figure 5. 9 P-TSA, o-TSA and BSA concentrations [µg/L] plotted versus time under oxic (left) and anoxic (right) conditions.

Under oxic conditions (oxic/sterile and oxic/non-sterile) o-TSA showed a significant decrease from ~2.5 µg/L to < 0.2 µg/L. O-TSA reduction commenced after 15 experimental days and ended after 34 days. O-TSA concentrations were near initial concentrations in the anoxic/sterile tanks over the entire duration of the incubation experiment. The behaviour of o-TSA under anoxic/non-sterile conditions varied greatly between the duplicates. In one case, o-TSA was almost fully depleted, and in the other case o-TSA was not depleted.

BSA was measured under all conditions in the same order of magnitude (around 0.35 µg/L). In the anoxic tanks a slight increase of BSA was observed (> 0.4 µg/L) over the whole duration of the experiment. The final concentration of BSA lay between 0.14 and 0.18 µg/L above the initial concentrations. However, these changes are probably not significant. I assume that BSA may be formed under these conditions by substances with a higher molecular weight.

The assumption that anoxic conditions are disadvantageous for p-TSA degradation resulting from the field investigations was confirmed. P-TSA was fully degraded under oxic conditions, as well o-TSA. Degradation of p-TSA and possibly o-TSA also occurred under anoxic and non-sterile conditions. Hence, the microbiology brought in from outside the aquifer during sample preparation was able to eliminate these organic compounds. Only under anoxic and sterile sampling conditions did p-TSA concentrations remain unchanged. The microorganisms which are present in the groundwater itself are not able to degrade p-TSA and o-TSA under anoxic conditions and require O_2 for the process. Oxygen was a significantly remove in the oxic tanks over the whole duration of the experiment. The O_2 consumption was higher under non-sterile conditions (Figure 5.8), probably due to larger turnover rates caused by the additional microbiology from outside the groundwater.

Under oxic conditions an elimination of p-TSA and o-TSA is possible in an aquifer environment. Addition of O_2 into an anoxic, contaminated aquifer such as the studied one would facilitate p-TSA and o-TSA degradation.

The incubation results also showed that maintaining the in-situ conditions with regard to microbiology, O_2 concentration and possibly pressure is essential to prevent changes in p-TSA, o-TSA and BSA concentrations during storage and ensure proper analysis. Groundwater samples should always be kept under anoxic and sterile conditions.

To obtain a better overview and for comparison with other hydrochemical redox parameters, further experiments would be needed.

5.5 Conclusions

The groundwater downstream of a former sewage farm which operated for almost 70 years until the 1980s is highly contaminated with sulfonamides. The contamination plume is 25 m * 2000 m * 3000 m in size, and its shape is strongly influenced by the production well galleries of a nearby drinking water treatment plant. The elevated concentrations show that the sulfonamides persist over decades under anoxic conditions in an aquifer environment. Because of the size of

the plume, the remains of wastewater irrigation will influence the quality of the abstracted raw water over decades. On the basis of the results of RICHTER ET AL. (2008A), higher concentrations probably do not constitute a high risk for the drinking water quality but are nevertheless undesirable. If the aquifer is contaminated with sulfonamides, they can be applied as a qualitative indicator of wastewater in ground- and drinking water. The presence of O_2 aids the degradation of p-TSA. If the redox conditions are anoxic and sterile, p-TSA is not degraded. Degradation of p-TSA only occurs under anoxic and non-sterile or oxic (sterile and non-sterile) conditions, showing that under anoxic/non-sterile conditions the microbiology from outside the groundwater is able to carry out the degradation. O-TSA degradation requires the presence of O_2. BSA was not eliminated in any experiments. Under anoxic conditions a slight increase was seen. Addition of O_2 to the anoxic groundwater would enhance the bioremediation of p-TSA and o-TSA. Maintaining in-situ conditions with regard to oxygen concentration, microbiology and possibly pressure is essential to ensure that the groundwater concentrations of the sulfonamides remain unchanged after sampling. The persistence of the sulfonamides in combination with their widespread applications suggests that they are common constituents in groundwater under the influence of sewage farming or wastewater in general. Therefore, the substances should be monitored in water samples that are affected by wastewater or treated wastewater.