Spatiotemporal resolved sampling for the interpretation of micropollutant removal during riverbank filtration

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HIGHLIGHTS

- OMP fate was studied along an RBF system under normal and elevated conditions
- Benzotriazole was almost fully removed during RBF under oxic conditions
- Carbamazepine and sulfamethoxazole showed a relatively persistent behavior
- Increase in load of several OMPs in the river observed during flood events
- OMP concentrations in the groundwater were far below drinking water guideline values

GRAPHICAL ABSTRACT
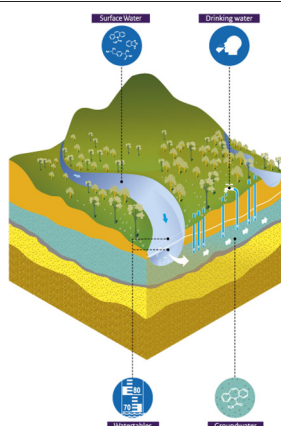
ARTICLE INFO

ABSTRACT

Riverbank filtration (RBF) systems along rivers are widely used as public water supplies. In these systems, many organic micropollutants (OMPs) are attenuated, but some compounds have shown to be rather persistent. Their fate and transport has been studied in RBF sites along lakes and small rivers, but not extensively along large and dynamic rivers. Therefore, the influence of flood events on OMP behavior in these large and dynamic RBF sites was investigated. Monthly samples were taken from surface- and groundwater up to a distance of 900 m from the riverbank of the Danube from March 2014 till May 2016. Two flood events were sampled more extensively nearby the river. Results showed that changes in flow conditions in the river not only caused changes in OMP concentrations, but also in their load. It was seen that the load of benzotriazole, carbamazepine and

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sulfamethoxazole in the river increased with increasing river discharges. After a relatively long, oxic groundwater passage, several OMPs were reduced. In contrast to previous work, we found that benzotriazole was almost fully removed under oxic conditions. When entering the aquifer, benzotriazole concentrations were significantly reduced and at a distance of 550 m from the river, >97% was degraded. Carbamazepine and sulfamethoxazole showed relatively persistent behavior in the aquifer. The concentrations measured during flood events were in the same range as seasonal sampling. Furthermore concentrations in the groundwater were higher during these events than in the Danube and can reach further into the aquifer. During flood events some highly degradable compounds (i.e. diclofenac) were found up to a distance of 24 m from the river. These results implied that drinking water utilities with RBF wells in oxic, alluvial aquifers located close to highly dynamic rivers need to consider a potential reduction in groundwater quality during and directly after flood events.

1. Introduction

Along large rivers such as the Danube, millions of people use drinking water from riverbank filtration (RBF). RBF systems are used in many countries (Heberer et al., 2001; Hiscock and Grischek, 2002; Ray et al., 2002; Tufenkji et al., 2002) due to the availability of large quantities of potential drinking water. They are however under much more anthropogenic stress than other, pristine groundwater sources. Due to the infiltration of low quality river water, the pristine groundwater can get contaminated with chemical and microbial substances. Substances that have been receiving increased attention are the organic micropollutants (OMPs) (Schwarzenbach et al., 2006). These pollutants comprise many different substances, such as industrial chemicals, pharmaceuticals and personal care products, but also pesticides or herbicides. Most of the pharmaceuticals and personal care products enter the environment through wastewater treatment plants (WWTPs) where they – depending on their persistence – are removed or remain in the effluent to a certain extent (Joss et al., 2005; Radjenović et al., 2009). Due to their persistence during treatment and their widespread presence in wastewater as main pathway to the aquatic environment, certain compounds have been suggested as indicators for impacts from waste water (Jekel et al., 2015), such as the corrosion inhibitor benzotriazole (BTri), the antiepileptic drug carbamazepine (CBZ) and the antibiotic sulfamethoxazole (SMZ).

Several studies have examined the behavior of these and other OMPs during RBF or similar systems (Heberer et al., 2008; Kahle et al., 2009; Rauch-Williams et al., 2010; Reemtsma et al., 2010; Regnery et al., 2015; Scheurer et al., 2011). Many of these studies however were conducted in RBF systems connected to small rivers or lakes. The range of water level fluctuations in these systems was much lower than along dynamic rivers such as the Danube (with water level fluctuations of up to 8 m).

Several factors such as groundwater residence times, redox conditions and mixing with pristine groundwater have shown their importance for the attenuation of OMPs (Burke et al., 2014b; Epting et al., 2018; Massmann et al., 2008, 2006; Storck et al., 2012; Wiese et al., 2011). Changing redox conditions and groundwater residence times for example can have an effect on removal rates of OMPs in the groundwater (Bertelkamp et al., 2016b) due to their effect on the biodegradation processes taking place in the aquifer. Not only the seasonal dynamics can influence the transport of the OMPs in the groundwater, flood events can also have an effect on their behavior. During a flood event, groundwater residence times can be shortened due to increased flow velocities (Derx et al., 2013; Sprenger et al., 2011). Furthermore, the composition of the infiltrating surface water can change the redox conditions in the aquifer and simultaneously have an influence on the micropollutant removal. Electron acceptors or donors can react abiotically with OMPs in the environment. The feasibility of these reactions is dependent on the prevailing environmental (redox) conditions (Schwarzenbach et al., 2017). Under oxic conditions for example, aerobic respiration can take place and OMPs can be oxidized. Especially oxic

RBF systems are highly vulnerable to flood events due to a possible shift in redox conditions (Sprenger et al., 2011). Unfortunately, little is known so far on this removal in large and dynamic RBF systems. Therefore it is of paramount importance to gain more insight in the behavior of OMPs in these RBF systems. The aim of this paper was therefore to investigate the influence of flood events on the behavior of OMPs along a large and dynamic river. This was done by addressing the following questions: (i) What is the behavior of OMPs in an alluvial porous aquifer during RBF along a large and highly dynamic river? and (ii) Do flood events change the presence and behavior of OMPs in surface- and groundwater along this large and dynamic river? For this purpose, river and groundwater samples were taken from two surface water locations, six groundwater monitoring wells and a drinking water abstraction well in an alluvial porous aquifer (PGA). Seasonal samples were taken monthly between March 2014 and May 2016 and were analyzed for a mixture of 7 OMPs and standard chemical parameters. To account for changes during extreme river level fluctuations, two flood events with water level fluctuations of up to 5 m (with a recurrence of 1 year) were sampled at a higher temporal resolution.

2. Materials and methods

2.1. Study area and instrumentation

The study was conducted at an RBF system on the left bank of the Danube, downstream of the Austrian capital of Vienna, as previously described by van Driezum et al. (2018) (Fig. 1). The water quality in the studied section of the Danube is impacted by upstream wastewater treatment plant discharges (Frick et al., 2017). The total amount of wastewater discharges is based on 13 million inhabitants and a corresponding PE of 20 million inhabitants (Zessner and Lindtner, 2005). It thus contributes to 2.5% of the discharge of the Danube under mean flow conditions. Discharges of the Danube in Vienna can range from 700 m^3/s during low flow conditions up to 11,000 m^3/s, such as during the 2013 flood (Blöschl et al., 2013). The discharge regime of the river at this point was classified as alpine influenced (Wimmer et al., 2012). The RBF system is part of an alluvial backwater and floodplain area containing five groundwater abstraction wells used for drinking water. The daily extraction capacity of all five wells is 109,000 m^3. A transect containing several monitoring wells and a groundwater abstraction well was chosen which was continuously fed by the infiltrating Danube, resulting in predominantly oxic conditions (Mayr et al., 2014). The main layers of the unconfined aquifer consist of gravel and sand and have a thickness varying from 3 to 15 m. Hydraulic conductivities in the transect ranged from 5×10^{-4} m/s to 5×10^{-2} m/s, determined by pumping tests conducted in the area and a 3D groundwater flow and transport model (for calibration details refer to Farnleitner et al. (2014)). Local groundwater flow is directed from the southwest to the northeast. Underneath the aquifer are alternating sand and clay/silt layers with hydraulic conductivities of at least 2 orders of magnitude lower.
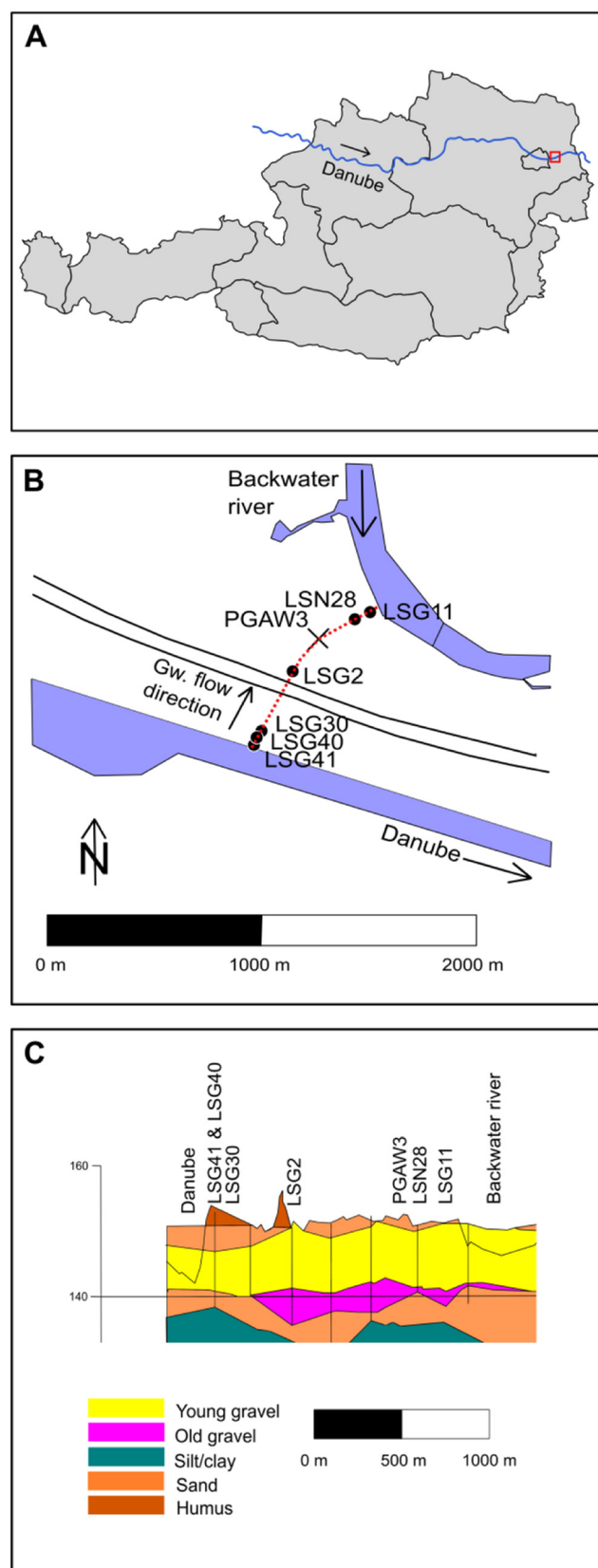
Fig. 1. a) Situation of the Natura 2000 protected area (red square) in Austria, b) the sampled transect including monitoring wells LSG41, LSG40, LSG30, LSG2, LSN28 and LSG11. The groundwater abstraction well is depicted as PGAW3 and c) Schematic cross section (dotted red line in b) of the transect with the hydrogeological layers and the groundwater monitoring wells (shown as black vertical lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The transect with the sampled wells extends from the Danube towards the backwater river. It consists of 2 surface water locations, 6 groundwater monitoring wells and one groundwater abstraction well with a maximum extraction capacity of 0.28 m^3/s (PGAW3, Fig. 1). Three wells (LSG41, LSG40 and LSG30) are located close to the river and are subjected to high variability in river and groundwater levels. One well (LSG2) is located between these three wells and PGAW3. Wells LSN28 and LSG11 are located between PGAW3 and the backwater river. All wells are screened over the full length of the saturated aquifer. Travel times from the Danube towards PGAW3 based on the hydraulic gradient can be found in van Driezum et al. (2018) and range between 11.5 days to 47.4 days. Travel times towards the three nearest monitoring wells (LSG41, LSG40 and LSG30) ranged from 1 h to LSG41 (10 m away from the Danube) to 5.4 days to LSG30 (24 m away from the Danube) during the monitoring period from March 2014 to May 2016.

The backwater river is a sequence of connected ponds which is connected to the Danube when water levels in the river exceed 150.5 m a.A. (meter above the Adriatic Sea) at the river gauge station *Fischamend* (river kilometer 1908, occurring just below a flood event with a recurrence of 1 year).

Hourly hydraulic pressures and water temperatures were recorded continuously during the monitoring period in all groundwater monitoring wells. Hourly Danube water level and discharge values were measured at the station *Fischamend*.

2.2. Sampling strategy

Monthly samples were taken at all sampling locations from March 2014 to May 2016 ($n = 22$, Supplementary Fig. S1). During this period, discharges in the Danube ranged from 693 m^3/s to 6197 m^3/s. In addition to the monthly samples, two flood events with a one-year return period (HQ2015 and HQ2016) were sampled with an increased sampling frequency ($n = 25$) in the Danube and in wells LGS41 and LSG30.

Groundwater samples for micropollutants and standard chemical parameters were taken after pumping 3 well volumes at an abstraction rate of 0.77×10^{-3} m^3/s (van Driezum et al., 2017). A portable Sension + MM150 sensor system (Hach-Lange, Austria) and a portable Profiline multi 3320 sensor system (WTW, Germany) were used in the field to measure temperature, pH, electrical conductivity and dissolved oxygen.

2.3. Chemical analysis

2.3.1. Inorganic and organic parameter analysis

A volume of 250 mL of ground- and surface water was taken in clean plastic bottles which were cooled at 4 °C and immediately transported to the lab. Anion and cation analyses were performed using ion chromatography. Absorption photometry was used to measure ammonium and nitrite (Supplementary Table S1).

2.3.2. OMP analysis and quantification

For this study, seven OMPs were selected based on their potential to serve as indicator substances for wastewater sources (Jekel et al., 2015). One-liter samples were filled in cleaned, clear glass bottles and transported to the lab in cooling boxes at 4 °C immediately. All samples were stored at 4 °C until analysis. Analysis of OMPs by solid phase extraction (SPE) followed by high performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) was performed using the method described in van Driezum et al. (2017). The LC-MS/MS system consisted of a Primaide HPLC with 1210 Autosampler (Hitachi High Technologies, USA) coupled to a hybrid triple quadrupole linear trap ion trap tandem mass spectrometer Q Trap 3200 (Applied Biosystems, Foster City, CA, USA) equipped with electrospray ionization (ESI) source operated in negative- and positive-ion mode. Details on analyte data and precursor-product ion can be found in Supplementary Table S2. The compounds were identified by retention time match and their specific HPLC-MS/MS transitions. The recoveries and LOQs of the

different compounds can be found in the supporting information (Supplementary Table S3).

2.4. Mixing ratios of Danube and backwater river in PGAW3

In order to give an indication of the behavior of the OMPs, mixing ratios of the Danube and backwater river in PGAW3 were calculated based on daily 2-D groundwater flow simulations during the study period. As stated previously, river water enters the backwater when water levels exceed a certain threshold value. When water levels in the backwater rise, groundwater flow paths towards PGAW3 might change and water of a different composition can be extracted in PGAW3. The 2-D variable saturated groundwater flow model was previously developed for the studied transect (Naus, 2015). The mean deviation between measured and simulated groundwater levels was 0.2 m at maximum after calibration. For calculating the daily mixing ratios the simulated inflow rates were summed along river beds of the Danube and the backwater, respectively, over the full simulation time. With the results from the mixing ratio procedure, OMP concentrations were calculated in PGAW3. Calculations were made for 6 mixing scenarios. Two scenarios with solely Danube water and solely backwater river water were taken as extremes, whereas the scenarios with a mixture of both sources were more likely to occur (Supplementary Table S4, van Driezum et al., 2018). For CBZ, no degradation is assumed (Clara et al., 2004). SMZ removal under oxic conditions is slow and only partial (Table 4). For simplification, no degradation was assumed. Danube and backwater river concentrations were taken for the calculation of CBZ and SMZ. Calculated BTri concentrations were based on concentrations measured in LSG2 and in the backwater river.

2.5. Flow intervals and load calculation

The dataset was divided in classes depending on flow intervals for comparison of OMP loads in the Danube during the studied period. The flows were categorized according to the percentage of exceedance, as follows (US Environmental Protection Agency, 2007): *flood events* (0–2.5%), *high flows* (2.5–5%), *moist conditions* (5–10%), *mid-range flows* (10–40%), *dry conditions* (40–70%) and *low flows* (70–100%). The calculation of the cumulative frequency was based on hourly mean discharges measured at the gauging station *Fischamend* from March 2014 till May 2016. The discharges corresponding to these intervals are shown in Table 1.

The hourly loads *L* were calculated based on the method using flow intervals, as described by Zoboli et al. (2015).

2.6. Data analysis and statistics

Correlation analyses of micropollutants with hydrological, physical and chemical variables were performed using the Pearson product correlation and the Spearman rank order correlation. A *P*-value of 0.05 was set as a significance threshold for all parameters. One-way analysis of variance (ANOVA) tests and the associated *post-hoc* Tukey's range test were used (function aov and TukeyHSD) to determine if any significant difference existed between the OMP concentrations in the surface water samples and in the groundwater samples. All statistical analyses were performed using R 3.1.1., partly using the *Hmisc* package (v. 4.1.1). All graphs were prepared using Grapher 10.5 (Golden Software, Colorado, USA).

3. Results

3.1. Hydrological and chemical characterization of surface water and groundwater

The Danube showed strong fluctuations during the studied period with changes in water levels as high as 6 m (Supplementary Fig. S2). Continuously low flow periods were observed early 2014 and from July 2015 till January 2016. Discharges in these periods were mostly below 1500 m^3/s. Higher discharges were observed during spring and summer 2014 and in spring 2015 and 2016. The discharges on the days when seasonal sampling took place ranged from 862 m^3/s to 2960 m^3/s. Water level fluctuations during HQ2015 were 2.6 m and discharges ranged from 2500 m^3/s to 5200 m^3/s. Water level fluctuations during HQ2016 (4.8 m) were almost twice as high and discharges ranged from 1000 m^3/s to 5200 m^3/s.

The backwater river was only connected to the Danube during flood events. During these events, water levels increased up to 3 m, much less than in both the Danube and the groundwater (Supplementary Fig. S2).

Water level fluctuations in all groundwater monitoring wells were nearly 4 m over the entire study period. During both flood events, groundwater levels close to the river fluctuated >1 m during HQ2015 and >2 m during HQ2016. Long-term oxygen concentrations of PGAW3 (minimum of 1.9 mg/L, maximum of 4.6 mg/L, data not shown) and the measured oxygen concentrations during sampling showed conditions in the aquifer were oxic. Average nitrate concentrations (Supplementary Table S5) in the wells between the Danube and PGAW3 were well above 5 mg/L, further confirming oxic conditions. Manganese and iron concentrations taken in the PGA were predominantly below 0.1 mg/L (Mayr et al., 2014).

The portion of groundwater at well PGAW3 coming from the backwater river showed large variations from January 2014 till May 2016 (Supplementary Fig. S3). By the end of June and beginning of July 2014, the water flowing into the aquifer was almost solely coming from the backwater river. From March to July 2015 on the contrary, most of the groundwater originated from the Danube except during HQ2015 when the proportion of backwater river increased shortly to 20% (Supplementary Fig. S3).

3.2. OMP occurrence in surface waters

3.2.1. Seasonal sampling

All seven OMPs were found in both the Danube and the backwater river (Table 2) with substantial higher detection frequencies for all compounds in the Danube. Highest concentrations in the Danube were found for BTri, ranging from 58 ng/L up to 402 ng/L. The concentrations of CBZ and SMZ were 1 order of magnitude lower, ranging from 7.48 ng/L to 42.0 ng/L and from 1.86 ng/L to 15.1 ng/L respectively. Although the detection frequencies of BTri and CBZ in the backwater river were high, the concentrations were substantially lower than in the Danube (Fig. 2). Although a negative correlation with water levels was present for these compounds in the Danube ($r = -0.58$, $P = 0.005$ for BTri and $r = -0.62$, $P < 0.005$ for CBZ), the backwater showed a positive correlation between water levels and the compounds ($r = 0.87$, $P < 0.005$ for BTri and $r = 0.87$, $P < 0.005$ for CBZ, Pearson correlation). SMZ had a much lower detection frequency in the backwater river than BTri and CBZ. No clear seasonal patterns could be seen for BTri, CBZ and SMZ (Fig. 2).

Bezafibrate and diclofenac were frequently measured in the Danube, but had much lower detection frequencies in the backwater river.

Table 1
Range in discharge at Fischamend for the flow intervals. *n* is the amount of water quality samples per flow interval.

	Low flows (Q$_L$)	Dry conditions (Q$_d$)	Mid-range flows (Q$_m$)	Moist conditions (Q$_{mo}$)	High flows (Q$_h$)	Flood events (Q$_{FL}$)
Discharge (m^3/s)	<1250	1250–1700	1700–2500	2500–3000	3000–3500	>3500
N	10	6	6	7	10	8

Table 2
Min-max concentration values and min-max values of the ratios between the OMPs in the surface- and groundwater samples during the seasonal sampling. The values in brackets for the concentrations represent the detection frequencies; the italic values in brackets for the ratios represent the average values. Ratios were only given between values above LOQ and when >30% of the concentrations could be determined. A statistically significant correlation (P < 0.05, based on the Pearson correlation) between the compounds was indicated by an asterisk. Values in meters are the distances to the Danube.

Seasonal sampling	Danube 0 m	LSG41 10 m	LSG40 13 m	LSG30 24 m	LSG2 283 m	PGAW3 551 m	LSN28 704 m	LSG11 782 m	Backwater 882 m
Concentration in ng/L									
Benzotriazole	58.0–402 (22/22)	31.6–201 (22/22)	22.0–171 (22/22)	19.4–150 (22/22)	n.d.-4.65 (10/22)	<LOQ-12.9 (22/22)	LOD-10.9 (19/22)	<LOQ-31.3 (22/22)	LOD-83.4 (21/22)
Carbamazepine	7.48–42.0 (22/22)	8.05–27.9 (22/22)	7.66–26.1 (22/22)	9.58–26.1 (22/22)	7.79–19.8 (22/22)	5.70–13.7 (22/22)	2.38–6.05 (22/22)	1.82–14.4 (22/22)	<LOQ-10.8 (22/22)
Sulfamethoxazole	1.86–15.1 (22/22)	2.30–11.0 (22/22)	1.76–11.9 (22/22)	2.23–13.3 (22/22)	1.21–6.51 (22/22)	<LOQ-3.58 (22/22)	n.d.-1.42 (17/22)	n.d.-2.79 (7/22)	n.d.-3.31 (4/22)
Bezafibrate	LOD-10.1 (21/22)	n.d.-<LOQ (3/22)	n.d.-<LOQ (1/22)	n.d.-<LOQ (2/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d.-3.94 (3/22)
Bisphenol A	n.d.-155 (4/22)	n.d. (0/22)	n.d.-32.2 (1/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d.-<LOQ (1/22)
Diclofenac	<LOQ-88.2 (22/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d.-LOD (1/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d.-22.6 (3/22)
Ibuprofen	n.d.-7.29 (7/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d. (0/22)	n.d.-LOD (1/22)
OMP ratios (−)									
Benzotriazole/carbamazepine	3.49–15.7 (10.5) *(r=0.85)	3.21–9.31 (6.42)	2.43–9.98 (6.28) *(r=0.78)	1.97–8.93 (5.89) *(r=0.75)	N/A	0.07–1.35 (0.79)	0.33–2.21 (1.21)	0.18–6.00 (1.71) *(r=0.57)	2.28–7.74 (4.88) *(r=0.96)
Benzotriazole/sulfamethoxazole	20.7–75.6 (36.7) *(r=0.80)	9.49–33.9 (18.9) *(r=0.65)	9.84–34.2 (18.5) *(r=0.68)	7.84–32.6 (15.6) *(r=0.50)	N/A	0.75–12.4 (4.59)	N/A	N/A	N/A
Carbamazepine/sulfamethoxazole	2.47–6.00 (3.54) *(r=0.93)	1.75–4.28 (3.00)	1.74–5.17 (3.06) *(r=0.69)	1.30–4.51 (2.74) *(r=0.66)	1.84–7.21 (3.60) *(r=0.56)	2.39–9.63 (4.28)	N/A	N/A	N/A

Similarly to BTri, CBZ and SMZ, no seasonal patterns were observed. Peak concentrations were encountered at the same time as the previously mentioned compounds. Bisphenol A and ibuprofen were only sporadically measured in both surface waters.

3.2.2. Flood event sampling

The same detection frequencies of BTri, CMZ and SMZ in the Danube were observed during both flood events as during seasonal sampling. Concentrations in the Danube were slightly lower during HQ2015 than during seasonal sampling (Fig. 2). The concentrations of BTri, CBZ and SMZ in the Danube measured during HQ2016 were in a similar range as the seasonal samples (Table 3).

Bezafibrate, bisphenol A, diclofenac and ibuprofen were sporadically detected in the Danube during HQ2015. During HQ2016, detection frequencies of these compounds were similar as during the seasonal sampling campaign, although their concentrations were clearly lower during the flood events than during seasonal sampling.

3.2.3. Load calculations

The load of these compounds was calculated in order to gain more understanding of OMP dynamics under different discharges in the Danube. A pearson correlation performed using log-transformed loads of BTri, CBZ and SMZ indeed showed all loads significantly correlated with discharges ($r = 0.58, 0.77$ and 0.66 for BTri, CBZ and SMZ, respectively, with $P < 0.005$) and during HQ2015, they even doubled (Fig. 3).

3.3. OMP attenuation during RBF

3.3.1. Seasonal sampling

BTri, CBZ and SMZ had similar detection frequencies in the groundwater as in the surface water (Table 2). Bezafibrate was only sporadically detected in the groundwater close to the river, with values around the LOQ. Bisphenol A, diclofenac and ibuprofen were not detected in any of the groundwater samples during the seasonal sampling campaigns.

Fig. 4 shows the results of the seasonal sampling for BTri, CBZ and SMZ. As can be seen, the highest OMP concentrations were found for BTri. During the first 24 m of aquifer passage (wells LSG41 (10 m), LSG40 (13 m) and LSG30 (24 m)), BTri concentrations decreased from an average value of 183 ng/L in the Danube to 103 ng/L in LSG30,

which was an average removal of 44%. After another 260 m of aquifer passage (LSG2), BTri dropped to an average concentration of 1.42 ng/L and was only detected 10 out of 22 times. In PGAW3, after another 268 m of aquifer passage, BTri remained at a similarly low level and detection frequencies increased simultaneously. The removal in PGAW3 was up to 97%. Concentrations in LSN28 and LSG11 were slightly higher than in PGAW3 and seemed to be influenced by the backwater river. The temporal variations in BTri concentrations seen after 260 m of aquifer passage (LSG2) were substantially lower than in the first 24 m. Fig. 4 shows that the removal of BTri is not constant throughout the year. During an extended period of higher discharges (for example from April 2015 till the end of June 2015), the groundwater in the first meters of aquifer passage had a higher BTri concentration than the Danube.

CBZ was found in all groundwater samples and reached a maximum concentration of 27.9 ng/L in well LSG41, which was closest to the river. Concentrations were stable during the first 24 m of aquifer passage, but a decrease of up to 48% was observed towards PGAW3 (Fig. 2). The results of an ANOVA test further indicated that CBZ was not fully persistent in the PGA. According to these results, LSG41, LSG40 and LSG30 group together ($P = 0.98$), just as LSG2 and PGAW3 ($P = 0.28$). The concentrations and temporal variation in LSG2 and PGAW3 were higher than in wells LSN28 and LSG11.

A similar pattern can be seen for SMZ. The concentrations in the first 24 m of the aquifer passage stayed stable (1.76 ng/L–15.1 ng/L) and decreased towards PGAW3 (up to 56% attenuation). The temporal variability in SMZ concentrations simultaneously decreased with longer groundwater residence times. In LSN28 and LSG11, SMZ was only sporadically above the LOQ.

3.3.2. Flood event sampling

Samples were taken with a higher frequency during two flood events (HQ2015 and HQ2016) and analyzed for the studied OMPs (Table 3). It can be seen that the detection frequencies of BTri, CBZ and SMZ in the groundwater were similar during both events and comparable with the seasonal sampling campaign. No statistically significant difference between the seasonal and flood sampling events (ANOVA, $P > 0.05$) was observed for all three compounds (Fig. 2). Concentrations of the three compounds at LSG41 (10 m from the riverbank) and LSG30 (24 m from the riverbank) were even higher than in the
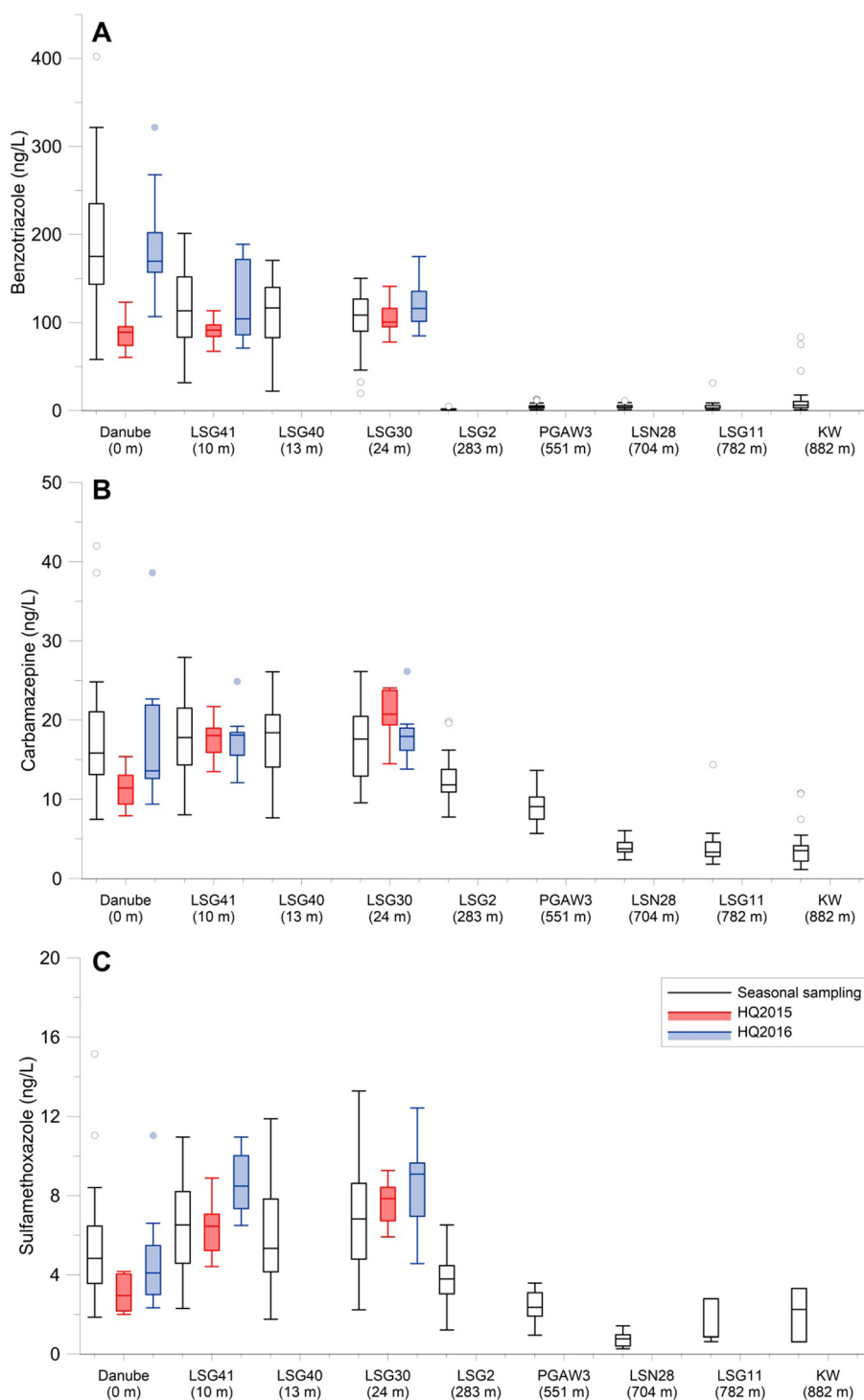
Fig. 2. Boxplots of A) benzotriazole, B) carbamazepine and C) sulfamethoxazole. White boxes represent the seasonal samples, red boxes the HQ2015 samples and blue boxes the HQ2016 samples. The boxes cover the 25th to 75th percentile, the line within the boxes the median and whiskers the 10th to 90th percentile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Danube during both events. This was especially seen for the more conservative compounds CBZ and SMZ and was most evident during HQ2015. A much lower attenuation of BTri was observed during HQ2015 (30%) and HQ2016 (0%) than during seasonal sampling (44%) after 24 m of groundwater passage. In contrast to the seasonal sampling and HQ2016, where BTri significantly correlated with CBZ and SMZ in both the Danube and the groundwater, this was only the case in the Danube during HQ2015. CBZ and SMZ significantly correlated with each other during all events in both surface- and groundwater.

Of the other measured OMPs, only bezafibrate and diclofenac were detected in the groundwater up to a distance of 24 m (LSG30) during HQ2016.

3.4. OMP ratios

In order to assess the fate of biodegradable compounds, their ratios can be calculated (Scheurer et al., 2011). The ratios between BTri, CBZ and SMZ concentrations were calculated for all samples taken in the

Table 3
Min-max values of the water table difference and gradient and of the OMPs in the surface- and groundwater samples during HQ2015 and HQ2016. The values in brackets represent the detection frequency. Values in meters are the distances to the Danube.

	Danube		LSG41		LSG30	
	0 m		10 m		24 m	
	HQ2015	HQ2016	HQ2015	HQ2016	HQ2015	HQ2016
Water table difference (m a.A.)	150.10–152.74	147.95–152.78	149.63–150.70	147.80–149.74	149.62–150.71	147.80–149.71
Gradient (%)	n.a.	n.a.	5.77–20.4	1.50–31.0	−0.08-0.10	0.01–0.19
Benzotriazole (ng/L)	60.4–123 (15/15)	107–268 (9/9)	67.3–118 (15/15)	70.9–189 (9/9)	77.8–141 (15/15)	85.1–175 (9/9)
Carbamazepine (ng/L)	7.93–15.4 (15/15)	9.40–22.7 (9/9)	13.5–21.7 (15/15)	12.1–19.2 (9/9)	14.5–30.6 (15/15)	13.8–19.5 (9/9)
Sulfamethoxazole (ng/L)	2.00–4.16 (15/15)	2.33–6.60 (9/9)	4.41–8.88 (15/15)	6.49–10.3 (9/9)	5.91–9.26 (15/15)	4.56–9.95 (9/9)
Bezafibrate (ng/L)	n.d.-0.58 (5/15)	3.58–5.92 (9/9)	n.d.	n.d.-<LOQ (2/9)	n.d.	n.d.-<LOQ (3/9)
Bisphenol A (ng/L)	n.d.-93.2 (1/15)	n.d.	n.d.	n.d.	n.d.	n.d.
Diclofenac (ng/L)	6.90–21.6 (15/15)	31.0–50.2 (9/9)	n.d.	n.d.-LOQ (4/9)	n.d.	n.d.-8.60 (5/9)
Ibuprofen (ng/L)	n.d.	LOD-<LOQ (9/9)	n.d.	n.d.	n.d.	n.d.

river and the groundwater wells for both the seasonal sampling (Table 2) and the two flood events (not shown). For BTri, it can be seen that the ratios of this compound with either CBZ or SMZ decrease from the river towards the groundwater. During the first 24 m of aquifer passage, the ratios between BTri and CBZ or SMZ stayed stable and the compounds correlated significantly with each other. When moving towards PGAW3, the ratios decrease and a relatively higher amount of CBZ and SMZ is found. In contrast, the ratios between CBZ and SMZ stayed stable from the river towards PGAW3, which was confirmed by ANOVA. The compounds also correlate significantly with each other in both the groundwater and the surface water samples.

The ratios calculated for the flood events were not consistently different than during seasonal sampling. OMP concentrations and the corresponding ratios in the Danube during HQ2015 were substantially different from HQ2016 and the seasonal sampling while the difference in concentrations of the compounds was not similar. During groundwater infiltration, the OMP ratios only differed significantly ($P < 0.05$, ANOVA) between HQ2015 and HQ2016, with higher ratios during HQ2016.

4. Discussion

4.1. The behavior of OMPs during RBF along a large dynamic river

Concentrations of BTri, SMZ, bezafibrate, diclofenac, bisphenol A and ibuprofen found in the Danube samples were consistent with previous measurements in the Danube (Loos et al., 2017, 2010b) and other large European rivers (Ruff et al., 2015; Sjerps et al., 2017; Wolschke et al., 2011). The median concentration of CBZ was also consistent with previous measurements in the Danube (Loos et al., 2010b) but slightly lower than in the Rhine (Ruff et al., 2015) and much lower than in the river Thames (Nakada et al., 2017). OMP concentrations and detection frequencies were generally much lower in the backwater river than in the Danube. Since the backwater river can be seen as a series of connected ponds fed by groundwater and precipitation rather than as a river, an increase in OMP concentrations was only detected during irregular inflows of Danube water.

Bezafibrate, bisphenol A, diclofenac and ibuprofen were not found in the oxic groundwater. These compounds have been known to be fully removed during RBF under oxic conditions (Burke et al., 2014b;
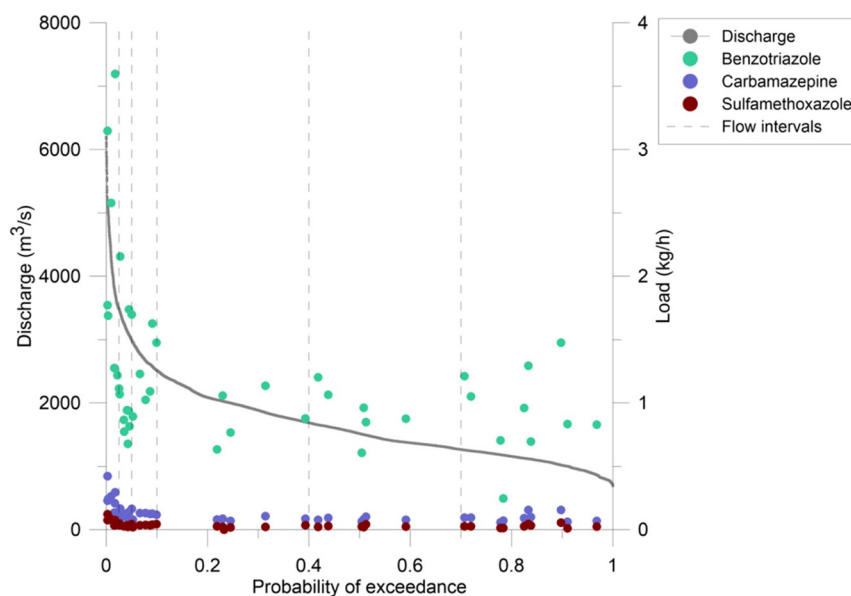

Fig. 3. Flow duration curve showing the flow intervals and the corresponding loads during these days. BTri is shown in green, CBZ in blue and SMZ in dark red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
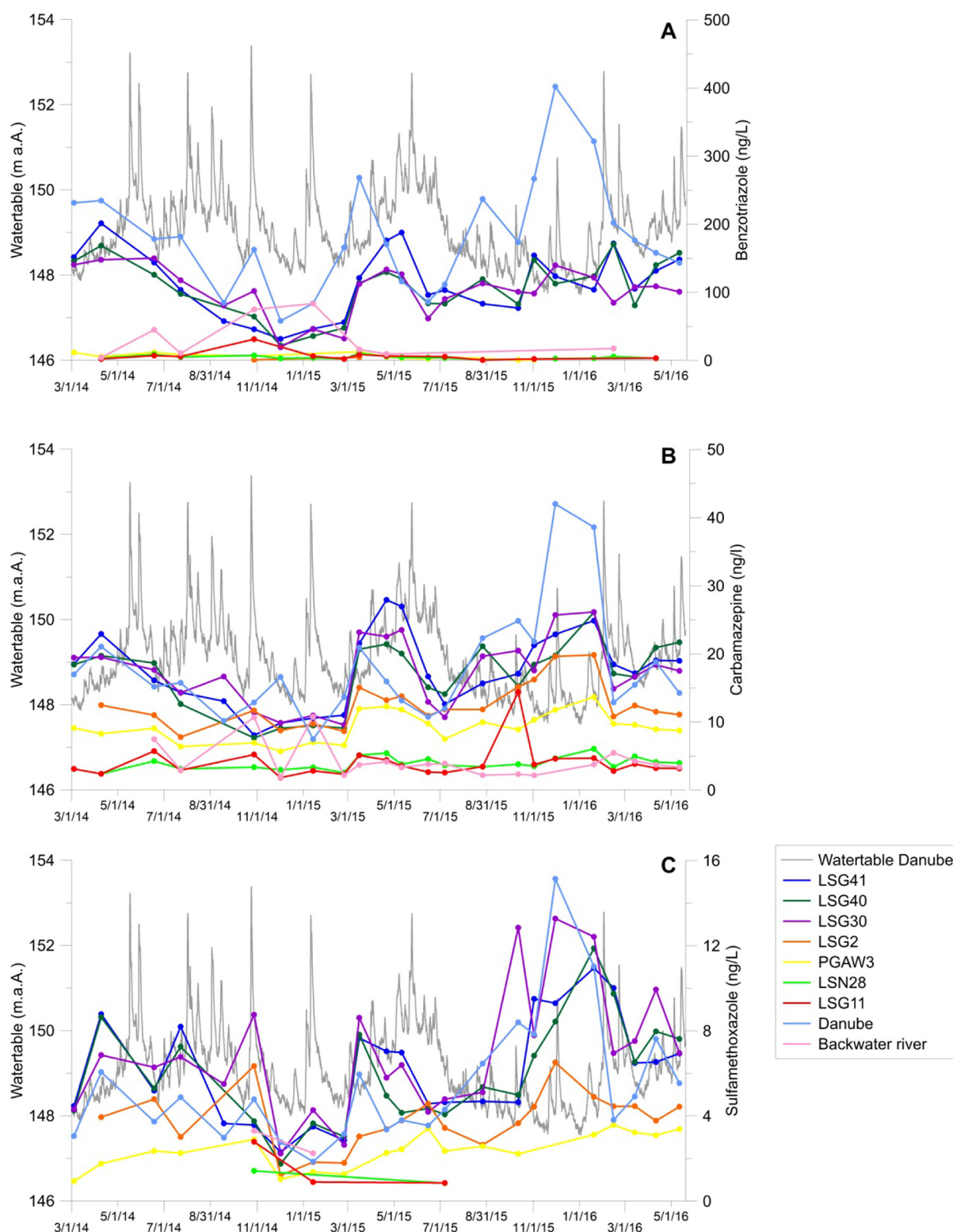
Fig. 4. Seasonal sampling results for **A)** BTri, **B)** CBZ and **C)** SMZ. Concentrations were given for both surface waters and all monitoring wells.

Heberer et al., 2004; Rauch-Williams et al., 2010; Wiese et al., 2011). Concentrations of BTri, CBZ and SMZ in the groundwater were in a similar range as in other studies (Huntscha et al., 2013; Loos et al., 2010a; Scheurer et al., 2011), but they were attenuated differently. Previously, they were known to be either fully or mostly persistent under different hydrogeological conditions (Table 4). Concentrations of these compounds in the drinking water abstraction well were far below

(provisional) drinking water guideline values derived in several EU countries (Baken et al., 2018).

As for BTri, most of the degradation was found to take place in the first few meters of the aquifer. In contrast to our results, BTri was previously found to be never fully removed except for the study of Reemtsma et al. (2010), which had unstable redox conditions in the aquifer. We found an average removal of 44% after 24 m of aquifer passage. A similar

Table 4

Literature values for attenuation of BTri, CBZ and SMZ.

Compound	Removal	Aquifer properties		Travel time	Hydrological characteristics	Comments
		Hydrogeology	Redox conditions			
Benzotriazole	No removal [b), d), h)]	Unconsolidated sandy gravels [b)], predominantly sand [h)], undisturbed sandy core [d)],	Oxic [b), h)], fluctuation between oxic and anoxic [d)]	67–113 h [b)], 1–3 months [h)]	Q_{max} 160 m³/s [b)], undisturbed core [d)], river Ijssel [h)]	Redox dependent removal, probably only full removal under anoxic conditions
	Partial removal [a), e), f), g), i)]	Unconsolidated sandy gravels [a)], microcosms with aquifer sediment [f)], alluvial aquifer [i)]	Oxic [a)], fluctuation between oxic and anoxic [e)]	7 h–3d 4 h transect A; 0–35 h transect B [a)],	Q_{max} 160 m³/s [a)], microcosm [f)], river Rhine [g)], Q_{max} 100 m³/s [i)]	
	90% [c)]	Predominantly sand [c)]	Fluctuation between oxic and anoxic [c)]	4–5 months [c)]	Lake [c)]	
Carbamazepine	Persistent [a), b), e), g), h), k), i), m), n), o), p)]	Unconsolidated sandy gravels [a), b)], predominantly sand [h)], sand and gravel [n), o)]	Oxic [a), b), h), n), o)], fluctuation between oxic and anoxic [e), m), o), p)], anoxic [k), o)]	7 h–3d 4 h transect A; 0–35 h transect B [a)], 67–113 h [b)], 1–3 months [h)], 1.65–3.65 years [k)], 7–30 days [n)], 25 days [o)]	Q_{max} 160 m3/s [a), b)], lake [m)], river Rhine [g)], river Ijssel [h)], Q_{max} 100 m³/s [i)], river Lek [k)], Q_{max} 120 m³/s [o)], $Q_{average}$ 3300 m³/s [o)], $Q_{average}$ 106 m³/s [o)], infiltration ponds [p)]	Overall low removal, probably due to retardation; no removal at high discharges
	Slight attenuation [d), i), l), m)]	Predominantly sand [l), m)], undisturbed sandy core [d)], alluvial aquifer [i)]	Fluctuation between oxic and anoxic [d), l)]	4–5 months [l), m)]	Lake [l), m)], undisturbed core [d)], Q_{max} 100 m³/s [i)],	
	Degradation [j)]	Predominantly sand [j)]	Fluctuation between oxic and anoxic [j)]	4–5 months [j)]	Lake [j)]	
Sulfamethoxazole	Rather persistent [a), b), n)]	Unconsolidated sandy gravels [a), b)], sand and gravel [n)]	Oxic [a), b), n)],	7 h–3d 4 h transect A; 0–35 h transect B [a)], 67–113 h [b)], 7–30 days [n)]	Q_{max} 160 m3/s [a), b)],	Redox dependent removal; slow and only partial under oxic conditions, up to full removal under anoxic conditions
	Partial removal [h), j), l), q), r)]	Predominantly sand [h), j), l), q), r)]	Oxic [h)], fluctuation between oxic and anoxic [j), l), q), r)]	4–5 months [j), l), q), r)], 1–3 months [h)]	Lake [j), l), q), r)], river Ijssel [h)],	
	Full removal [j), k), q), r)]	Predominantly sand [j), k), q), r)]	Fluctuation between oxic and anoxic [j), q), r)], anoxic [k)]	1.65–3.65 years [k)], 4–5 months [j), q), r)],	Lake [j), q), r)], river Lek [k)]	

a) (Huntscha et al., 2013), b) (Huntscha et al., 2012), c) (Reemtsma et al., 2010), d) (Burke et al., 2014a), e) (Kahle et al., 2009), f) (Liu et al., 2013), g) (Scheurer et al., 2011), h) (Bertelkamp et al., 2016a), i) (Epting et al., 2018), j) (Henzler et al., 2014), k) (Hamann et al., 2016), l) (Wiese et al., 2011), m) (Heberer et al., 2004), n) (Storck et al., 2012), o) (Hoppe-Jones et al., 2010), p) (Massmann et al., 2006), q) (Heberer et al., 2008), r) (Grünheid et al., 2005).

removal was found under similar hydrogeological characteristics as at our site at the Thur river (Huntscha et al., 2013). In contrast to Huntscha et al. (2013), BTri was almost fully removed at the drinking water abstraction well at our site. This difference can be explained because we sampled at wider distances (and higher residence times) from the river and therefore observed significantly more BTri removal. Other studies showed no significant removal under oxic conditions (Table 4), e.g., as shown by Bertelkamp et al. (2016a) in a low conductive aquifer, even after up to 4 months of groundwater travel times. This suggests that travel time combined with oxic conditions alone does not explain BTri removal. Reported literature found no or very little removal of BTri in the environment. Under conditions with a highly active microbial community, like a WWTP, partial removal was shown (e.g. Mazioti et al., 2015). Sorption was found to be negligible (Yu et al., 2009). In our study, a high degree of river-groundwater interaction was apparent due to the high conductivity of the aquifer. Furthermore, the microbial activity was found to be relatively high (van Driezum et al., 2018). Based on previous studies, we therefore conclude that biodegradation was the main mechanism responsible for the high BTri removal. Highly conductive RBF systems, such as the PGA and along the river Thur (Huntscha et al., 2013), are more favorable to biodegradation of compounds like BTri.

CBZ has generally been classified as persistent (Table 4). Some attenuation was sporadically found, e.g. studies from lake Tegel and lake Wannsee in Berlin showed that some degradation of CBZ can occur during aquifer passage (Burke et al., 2014a; Henzler et al., 2014; Wiese et al., 2011). Bertelkamp et al. (2016a) did not find attenuation of CBZ directly in the field, but column tests indicated some removal of the compound. Our study showed that CBZ concentrations are stable during the first 24 m of aquifer passage but then slightly decreased during an extra 527 m of aquifer passage towards PGAW3. A possible explanation for this decrease in CBZ could have been mixing of the Danube and backwater river at PGAW3. This was only partially confirmed by the mixing ratio calculations (Supplementary Table S4). The proportion of backwater river must be between 30 and 60% assuming a conservative behavior of CBZ, but this is not very likely for our system (Supplementary Fig. S3).

Also SMZ was only partially removed under oxic conditions. A similar behavior was shown along the river Rhine (Storck et al., 2012), although concentrations were slightly lower in the PGA. A full removal of SMZ during RBF was previously found only under anoxic conditions (Table 4). Mixing with backwater river water could again only account for part of the decrease in concentration of SMZ as shown for CBZ.

Based on the marker ratios during seasonal sampling, the difference in attenuation between BTri on one hand and CBZ and SMZ on the other hand was clearly visible, with the latter two being similar. Several studies have shown differences in biodegradation and retardation of CBZ and SMZ (Bertelkamp et al., 2016b; Hamann et al., 2016; Henzler et al., 2014; Nham et al., 2015). Since no distinction was made between retardation and biodegradation in this study only an indication of a similar rate of attenuation between CBZ and SMZ can be given.

4.2. Do flood events change the presence and behavior of OMPs in surface and groundwater?

As was seen in Van Driezum et al. (2018), the flood events had an influence on the microbial activity and increased cell counts in the Danube. It was expected, that OMP concentrations in the Danube, on the contrary, were lower during the flood events than during seasonal sampling due to dilution. CBZ for example, is not removed during wastewater treatment (Joss et al., 2005; Radjenović et al., 2009; Zhang et al., 2008), so its load into the river is expected to be stable even when processes like combined sewer overflow (CSO) occur. BTri and SMZ are partly removed during wastewater treatment (Huntscha et al., 2014; Radjenović et al., 2009) and their loads might therefore slightly increase during flood events due to CSOs. A stable load, especially of CBZ, was however not seen in our study. Since CSOs could not be primarily

responsible for the increase in OMP loads, another explanation was proposed.

During flood events, total suspended solids (TSS) can be mobilized. The TSS concentration, and also in stream phosphorus (P) concentrations can therefore increase significantly, as was seen previously in the Danube (Zessner et al., 2005; Zoboli et al., 2015). A significant trend was shown between discharge of the Danube and the TSS concentration (Nachtnebel et al., 1998). Some OMPs are partly sorbed to TSS and can desorb under conditions like flooding (da Silva et al., 2011). Consequently, the amount that can desorb is higher during flood events and can lead to an increase in OMP loads (Rivetti et al., 2015). The positive relationship of CBZ concentration (but also other pharmaceuticals) to phosphorus dynamics and TSS was also shown by Acuna et al. (2015). An increased and extended influence of the Danube on the microbial compartment of the groundwater was observed during HQ2016 as compared to HQ2015 (van Driezum et al., 2018), due to the higher increase in river water levels during the event. Because of the influence of flood events on the microbial compartment, we expect that OMP concentrations could be similarly influenced by the infiltrating surface water. It was shown that groundwater concentrations of BTri, CBZ and SMZ during the flood events slightly increased and were even higher than in the surface water. A similar increase in OMP concentrations in groundwater was also observed by Huntscha et al. (2013) along the river Thur after flood events. We observed higher OMP concentrations in the Danube and the groundwater prior to HQ2016 and to a lesser extent prior to HQ2015 relative to periods without flood events. During these events, more surface water can enter the aquifer, i.e. during HQ2015 and HQ2016 over 3 and 24 times more "fresh" water respectively can enter the aquifer during the flood peak than during the days prior to the peak as can be calculated following the procedure of Ubell (1987). This "fresh" surface water with lower concentrations mixes with older groundwater with higher OMP concentrations. Mixing occurs at a slower pace than the flow velocities during these events. This can explain why OMP concentrations reached further into the aquifer and were higher in groundwater than in the Danube during the flood events, even more so during HQ2016 than during HQ2015.

Similar to bacterial abundance (van Driezum et al., 2018), an increase of several OMPs was found in the groundwater up to 24 m away from the river during HQ2016. Bezafibrate and diclofenac were observed in the groundwater, although no correlation was found with groundwater flow velocity. Although no measurements were taken in the drinking water abstraction well during the flood events, we expect a negligible impact of the river on the groundwater quality in the abstraction well at 550 m from the river. This was supported by the lack of substantial variations in OMP concentrations in the drinking water abstraction well throughout the entire study period. The observation wells closer to the river however did show an extended impact of the river on groundwater quality. Drinking water abstraction wells that would be located closer to the river in highly conductive RBF systems can therefore be under direct stress during flood events. In these cases, more intensive monitoring of OMPs is proposed during flood events.

5. Conclusion

The results show that drinking water abstraction wells in particular close to the river and under oxic conditions can be vulnerable to an extended contamination during flood events, even from highly degradable compounds.

In contrast to previous studies, this study showed that BTri is almost fully removed by the time it reaches the drinking water abstraction well. CBZ and SMZ are attenuated to a certain extent, since mixing of groundwater with low-concentrated backwater river could only partly explain the decrease of these compounds. A similar rate of attenuation could be presumed for CBZ and SMZ. Several marker OMPs (e.g. bezafibrate,

diclofenac and ibuprofen) were not detected in the aquifer under oxic conditions.

Unexpectedly, the results during the flood events showed that most of the OMP concentrations in the Danube were similar as during the seasonal sampling period.

The load of BTri, CBZ and SMZ in the Danube was higher, possibly due to an increase in TSS in the river or to the inflow of the Donaukanal in this section of the Danube. Groundwater concentrations of BTri, CBZ and SMZ during the flood events were higher than in the Danube and reached further into the aquifer, in comparison with seasonal sampling. During the flood in 2016, highly degradable compounds such as diclofenac and bezafibrate could enter the aquifer up to a distance of 24 m from the river and BTri was significantly less attenuated than during the seasonal sampling period.

Conflict of interest

None.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2018.08.300.

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