In situ removal of four organic micropollutants in a small river determined by monitoring and modelling★

Andrea F. Brunsch [a, c, *], Alette A.M. Langenhoff [c], Huub H.M. Rijnaarts [c], Alexander Ahring [a], Thomas L. ter Laak [b]

[a] *Erftverband, Department of River Basin Management, Am Erftverband 6, 50126, Bergheim, Germany*
[b] *KWR Watercycle Research Institute, P.O. Box 1072, 3430 BB, Nieuwegein, the Netherlands*
[c] *Wageningen University and Research, Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, the Netherlands*

A B S T R A C T

Organic micropollutants (OMPs) are widely detected in surface waters. So far, the removal processes of these compounds *in situ* in river systems are not yet totally revealed. In this study, a combined monitoring and modelling approach was applied to determine the behaviour of 1-H benzotriazole, carbamazepine, diclofenac and galaxolide in a small river system. Sewage treatment plant effluents and the receiving waters of the river Swist were monitored in 9 dry weather sampling campaigns (precipitation < 1 mm on the sampling day itself and <5 mm total precipitation two days before the sampling) during different seasons over a period of 3 years. With the results gained through monitoring, mass balances have been calculated to assess fate in the river. With the DWA Water Quality Model, OMP concentrations in the river were successfully simulated with OMP characteristics gained through literature studies. No removal was determined for 1-H benzotriazole and carbamazepine, whereas diclofenac showed removal that coincided with light intensity. Moreover, modelling based on light sensitivity of diclofenac also suggested relevant degradation at natural light conditions. These two approaches suggest removal by photodegradation. The highest removal in the river was detected for galaxolide, presumably due to volatilisation, sorption and biodegradation. Furthermore, short-term concentration variability in the river was determined, showing that daily concentration patterns are influenced by dynamics of sewage treatment plant effluent volumes and removal processes in the river.

1. Introduction

Organic micropollutants (OMPs) stemming from domestic or industrial wastewater are only partially removed in conventional sewage treatment plants (STPs) and are emitted into surface waters (Daughton and Ternes, 1999; Ternes, 2007) where they are widely detected (Luo et al., 2014). An extensive exposure assessment of OMPs in rivers is therefore necessary. This implies not only monitoring emission and input pathways, but also behaviour and fate of OMPs in surface waters. Compound specific physico-chemical properties influence the behaviour of OMPs in the water cycle and have to be taken into account together with the characteristics of the studied environment.

Behaviour of OMPs is often investigated in laboratory studies and/or water treatment processes (Luo et al., 2014; Onesios et al., 2009; Zhang et al., 2008). There are only limited studies testing and evaluating environmental behaviour *in situ*, since sampling, controlling and accounting for varying conditions is difficult or not feasible. A mass balance approach according to the Lagrangian sampling scheme (correct timing of sampling suited to fully encompass a mass of water along its way downstream) to determine OMP behaviour in rivers was introduced by Schwientek et al. (2016). They calculated net removal of OMPs with samples taken over 24 h on two representative river locations. A reactive tracer test along a small river in Sweden revealed the *in situ* removal of ibuprofen and clofibric acid (Kunkel and Radke, 2011). Moreover, removal of pharmaceutical compounds (ibuprofen, ketoprofen, naproxen, diclofenac), musk fragrances (tonalide, galaxolide) and caffeine concentration along a river have already been determined

(Bendz et al., 2005; Musolff et al., 2009; Osorio et al., 2012; Poiger et al., 2003), but the various removal mechanisms potentially responsible for this are not easy to reveal.

Both emission data and environmental monitoring data do not give an exhaustive picture of the OMP situation in the river as there are data-gaps on temporal and spatial scales. Models can be applied to fill these data-gaps. By combining modelling with dedicated sampling and monitoring strategies under specified conditions and with a high temporal resolution enables to unravel *in situ* fate and behaviour of OMPs in surface waters, thereby giving the highest confidence in exposure assessment to enable better risk assessment (Johnson et al., 2008).

A number of Geographic Referenced Point Source Water Quality Models (e.g. PhATE, GREAT-ER, and LF2000-WQX) predict concentrations of "down the drain chemicals" in catchments, starting from the moment they enter the sewage pipe until they reach the tidal limit, or the end of the catchment, as defined by the model (Johnson et al., 2008). LF2000-WQX and GREAT-ER predict effluent concentrations according to public consumption data. Removal in STPs or rivers is predicted by removal constants and/or first order removal kinetics, which can be applied to the resulting chemical concentrations. OMP concentrations (μg/L) or loads (g/d) for e. g. propranolol and diclofenac with LF2000-WQX and various beta blockers as well as sulfamethoxazole with GREAT-ER could be well described (Alder et al., 2010; Archundia et al., 2018; Johnson et al., 2007).

The DWA Water Quality Model is specialised in predicting concentrations in rivers by distinguishing various removal processes. In contrast to GREAT-ER or LF2000-WQX, STP effluent concentrations are not predicted but given as input information by the user from e. g. monitoring results. Behaviour of OMPs is predicted in consideration of interaction processes with various conditions such as global radiation, shadowing, temperature or concentrations of suspended solids, each influencing removal processes. Under incorporation of these processes, it is possible to predict the evolution of concentration for OMPs over defined time windows. Simulation time steps can be chosen individually by the user. For example, the DWA Water Quality Model has been used to successfully simulate short term behaviour of bentazone and diclofenac in the river Main in Germany (Bach et al., 2010; Letzel et al., 2009). However, larger rivers exhibit a complex set of tributaries, with various point sources and diffuse sources that complicate quantitative *in situ* assessment of OMP behaviour. Hence, smaller rivers, with defined system monitoring transects and a limited set of (point) sources offer a better model for such *in situ* assessments. Therefore, we selected the river Swist, with a 44 km transect and 4 discharging STPs, in this study. Its mouth ends in the river Erft, a tributary of the river Rhine in western part of Germany.

The aim of this study is to determine concentration variability of four OMPs (1-H benzotriazole, galaxolide, carbamazepine and diclofenac) in a small river catchment with a high temporal resolution and to identify the processes responsible for their persistence or *in situ* removal in the river. We used two approaches: first, a monitoring study was performed, covering OMP input sources such as STP effluent discharge points and the monitoring of OMP concentrations in the river itself. Second, a water quality model was used with a removal part that distinguishes between the different potential processes. By a mass balance analysis approach, we aim to quantify *in situ* persistence and removal and relate these to relevant environmental conditions (such as solar radiation and temperature) controlling these processes. This unique detailed monitoring and modelling effort in a real river system enables better understanding of mechanisms for selected substances as well as model evaluation.

2. Materials and methods

2.1. Sampling

Samples were taken at the STP effluent and the water quality station at the river Swist close to the mouth (Fig. 1). The four STPs are described in Brunsch et al. (2018b). All samples were taken by autosamplers that produced composite samples for the individual sampling duration. 1-h or 2-h composite samples over one whole day (b, c) were taken for daily concentration variability assessment. With the aim to calculate daily mass balances for a broad variety of dry weather scenarios, 24-h composite samples were taken (a and c) in addition to the composite samples of shorter time windows (b and c). In more detail, the following samplings were performed:

a) seven samplings were performed in 2016/2017, three in winter and four in summer with 24-h composite samples, taken time proportionally at the STPs and the river (5 min time intervals between each sub-sample). Sampling start was 12 a.m. for both the STP effluent and the river.
b) one sampling was performed on March 20/21, 2015 with 2-h composite samples, taken time proportionally over a period of 24-h at the STPs (6 min time intervals between each sub-sample) and correspondingly 1-h composite samples taken at the river (12 min time intervals between each sub-sample). Sampling at STPs started at 10 a.m. and at the river at 2 p.m.
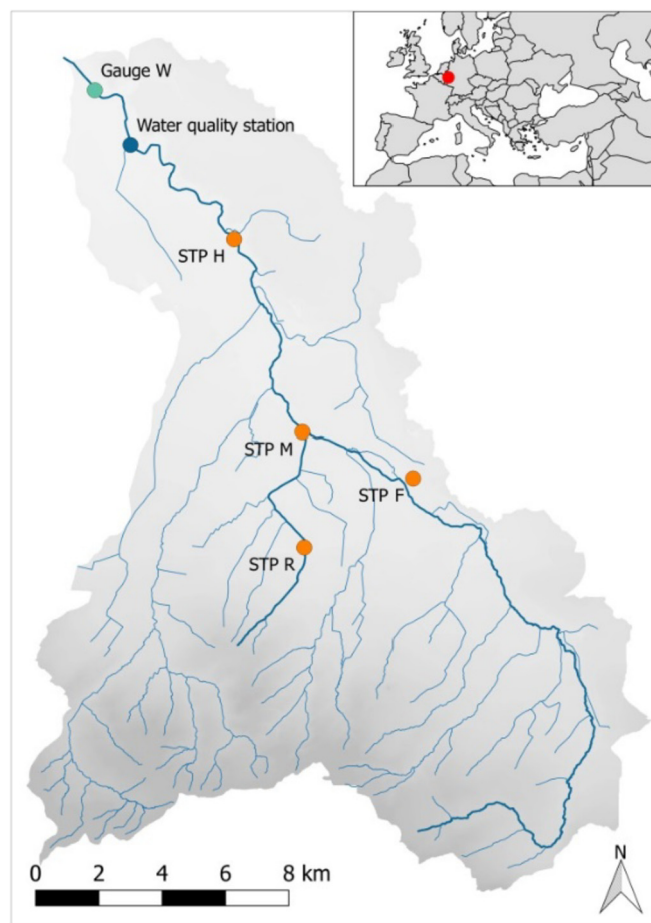
Fig. 1. Swist catchment area with the gauge for water level measurement (gauge W), sewage treatment plants (STP H, STP M, STP F, STP R) and the water quality station. Flow direction from south to north.

to cover the average hydraulic retention at dry weather time between the sampling points.

c) one additional sampling was performed on August 07/08, 2018 with 24-h composite samples, taken time proportionally at the STPs (5 min time intervals between each sub-sample) and 2-h composite samples taken correspondingly at the river (5 min time intervals between each sub-sample). Here, sampling at the STPs started at 2 p.m. and at the river at 4 p.m.

Samples were stored in the autosampler in glass vessels and refilled in brown glass bottles before transport and stored at 4 °C until analysis (within seven days).

Sampling was accomplished during dry weather conditions with precipitation <1 mm on the sampling day itself and <5 mm total precipitation two days before the sampling. Hence, no direct influence of storm water e.g. through combined sewer overflows, storm water basin effluent or surface runoff is expected in the river.

The more detailed sampling on March 20/21, 2015 represents a typical dry weather scenario, with <1 mm precipitation on 16 days before sampling and maximum air temperatures of 20 °C. The campaign on August 07/08, 2018 represents an exceptional dry weather scenario with maximum air temperatures of 38 °C and a dry river bed upstream STP F due to the high temperatures and the lack of precipitation during the summer of 2018 (sum of precipitation in June and July 2018 was 32 mm which is 4.4 times lower than the average of the last 12 years for this period). The conditions found during that sampling session, are similar to situations found in arid regions such as southern Europe. However, in the sampling night on August 8, there was an approximately 2-h rain event with around 5 mm of precipitation, which did result in increasing STP inflow and outflow and consequently an increasing water volume in the river.

The daily average water flow, measured at gauge W (Fig. 1), was 0.29–0.43 m^3/s for the 2016/2017 samplings and 0.58 and 0.27 m^3/s respectively for the sampling in 2015 and 2018. The sampling events in 2015 and 2018 represent two different dry weather scenarios; with around 32% (2015) and 71% (2018) of the water volume in the river at the mouth stemming from STP discharges.

2.2. Analyses

Four OMPs have been analysed, the corrosion inhibitor 1-H benzotriazole (1HB), the musk fragrance galaxolide (HHCB), the anti-epileptic drug carbamazepine (CBZ) and the anti-inflammatory drug diclofenac (DCF). Different behaviour in the river is expected for these four OMPs, e. g. CBZ is known to be persistent (Clara et al., 2004), 1HB and DCF are possibly transformed by photodegradation (Andreozzi et al., 1998; Moore et al., 1990) and HHCB is expected to have higher tendency to sorb to the organic fractions by hydrophobic interactions related to its hydrophobicity expressed by its high K_{OW} (see Table 2).

The chemical analysis was performed according to Brunsch et al. (2018a). In short: a HPLC (1260, Agilent, USA) with a triple quad mass spectrometer (6460, Agilent, USA) was used to determine the concentrations of 1HB and CBZ. The limit of quantification was 0.05 μg/L for 1HB and 0.10 μg/L for CBZ. A GC (Trace GC, Thermo, USA) with a triple quad mass spectrometer (TSQ 8000, Thermo, USA) was used to determine concentrations of DCF and HHCB. Limit of quantification was 0.05 μg/L for HHCB and 0.02 μg/L for DCF.

Non-detectable values were set to the limit of quantification. 123 samples were analysed in total. Thereof 72 in 2015 (12 × 4 at the STPs and 24 in the river), 35 in 2016/2017 (7 × 4 at the STPs and 7 at the river) and 16 in 2018 (1 × 4 at the STPs and 12 in the river). The number of non-detectable OMPs were 12 (HHCB) and 1 (CBZ); DCF and 1HB were always measured above limit of quantification.

The daily loads (g/d) from STP effluents and the river water were calculated based on analysed concentrations (μg/L) and discharges (m^3/d). For the 24-h composite samples, the concentration was therefore multiplied with the daily discharges (m^3/d). These daily discharges represent the sum of hourly or 2-h discharge values (m^3/h). For time proportional 1-h or 2-h composite samples, first the hourly or 2-h loads were calculated before these loads were summed up to daily loads. Subsequently, mass balances were calculated from daily loads.

2.3. The DWA water quality model

OMP concentrations were simulated with the DWA Water Quality Model (former ATV Water Quality Model, DWA − German Association for Water Wastewater and Waste) (Christoffels, 2001). Daily loads were calculated from simulated river flow data and simulated OMP concentration. The model describes the physico-chemical processes in the river with a deterministic approach. The discharge simulation is one-dimensional and based on the Saint-Vernant-Equation (Müller, 2001). Water quality parameters are calculated in 20 individual modules, that simulate parameters such as temperature, oxygen, solar radiation, phosphorous, nitrogen, biological and chemical oxygen demand, pH, metals but also OMPs. The modules can be used individually, but simulations of some of these modules depend on input from other modules (e.g. data from the oxygen module are needed for the simulation of nitrate in the nitrogen module). We used the module for OMP simulation. Input data from emission sources − both non-point and point sources − can be either fixed values or diurnal concentration curves. In our study, we simulated dry weather scenarios (precipitation < 1 mm on the sampling day itself and <5 mm total precipitation two days before the sampling) exclusively and OMP emissions were limited to the effluent from the four STPs in the catchment. The input data for STP emissions such as effluent discharge, water temperature and pH, were taken directly from STP effluent measurements. Input parameters were based on independent data and not on model calibration data except for the discharge, which was manually calibrated for river sections with a very low water level. The spatial resolution of the simulation was approximately 100 m and the temporal resolution was 1 h.

Relevant characteristics of the DWA Water Quality Model in OMP simulation are (according to Müller (2001)):

- photodegradation is calculated from a specific radiation absorption and quantum yield.
- the calculation of sorption to suspended solids is based on the octanol water partition coefficient with $K_{OC} = K_{OW} \times 0.41$ (Karickhoff, 1981).
- ionisation of molecules is not taken into account.
- sorption is assumed to be independent of the concentration of the OMP and amount of sorbent; sorption equilibrium happens instantaneous compared to other substance conversion processes.
- the biodegradation calculation is based on a single first order rate constant for the full river transect, and this rate is independent of e. g. hydraulics or biocenosis.
- the exchange processes between pore water from the river sediment and the river water are not considered.

Monitoring data were used to validate simulation results. One flow gauge and one water quality station in the catchment (Fig. 1) were measuring continuously water level and quality parameters such as temperature amongst other. For the plausibility analysis measured data were compared to simulation results: river discharge to validate the basic hydraulic model, water temperature

because it influences most OMP removal processes and OMP concentration to validate OMP removal processes.

3. Results and discussion

3.1. Monitoring of OMPs

3.1.1. OMP concentration

Concentrations measured during the four years of sampling at STP effluents and the river are variable (Table 1). Median HHCB concentrations decreased over the sampling years in contrast to the other investigated OMPs. This is possibly due to a decrease in HHCB consumption in the Swist catchment area. In general, the reason for concentration variability for the 4 OMPs might also be related to the different sampling years with different environmental conditions, and different sampling intervals (e. g. 24-h and 2-h composite samples). Nevertheless, STP outflow concentrations in 2015 and 2018 of 1HB, CBZ and DCF were similar.

In the following, river concentrations from the two samplings in 2015 (normal dry weather) and 2018 (exceptional dry weather) were compared (Fig. 2) for evaluating short-term concentration variability in the Swist river. The data show that diurnal concentration patterns vary amongst the OMPs. Concentrations of 1HB and CBZ were highest in 2018, presumably due to the lack of dilution of STP effluent with groundwater, surface runoff or water discharged by tributaries. CBZ and 1HB concentrations have been compared with each other and show a good correlation (coefficient of correlation 0.91). This shows that the diurnal variability of these two compounds is comparable. In contrast to CBZ and 1HB, concentrations of DCF were similar in 2015 and 2018. This indicates removal of DCF in the river, since concentrations of STP outflow were similar in both years (Table 1) and dilution effects in 2015 as found for CBZ and 1HB, not noticeable. HHCB was not detectable in the river in 2018 and thus not comparable with 2015 data. The variation of the concentration of HHCB in 2015 with highest values of 0.46 µg/L at 14:00 is remarkable but cannot be explained. The concentration decreases measured in 2018 at 11:00 for 1HB, CBZ and DCF is presumably due to a short rain event (see section 2.1)

Table 1
Concentrations (µg/L) incl. Median values and standard deviation measured at outflows of STP F, STP R, STP M and STP H as well as in the Swist at the water quality station.

| Year		Sampling strategy	n	1HB Median (Stand.Dev.)	CBZ Median (Stand.Dev.)	HHCB Median (Stand.Dev.)	DCF Median (Stand.Dev.)
2015	STP	2-h composite	48	5.40 (3.24)	0.89 (0.19)	1.33 (0.17)	2.87 (0.85)
	River	1-h composite	24	1.70 (0.29)	0.31 (0.03)	0.14 (0.07)	0.48 (0.14)
2016/2017	STP	24-h composite	28	3.35 (2.31)	0.64 (0.23)	0.79 (0.23)	2.50 (1.53)
	River	24-h composite	7	1.90 (0.81)	0.28 (0.13)	0.22 (0.06)	0.88 (0.36)
2018	STP	24-h composite	4	4.95 (1.25)	1.00 (0.05)	0.36 (0.11)	3.35 (2.84)
	River	2-h composite	12	3.00 (0.34)	0.73 (0.05)	<0.05 (0.00)	0.40 (0.08)
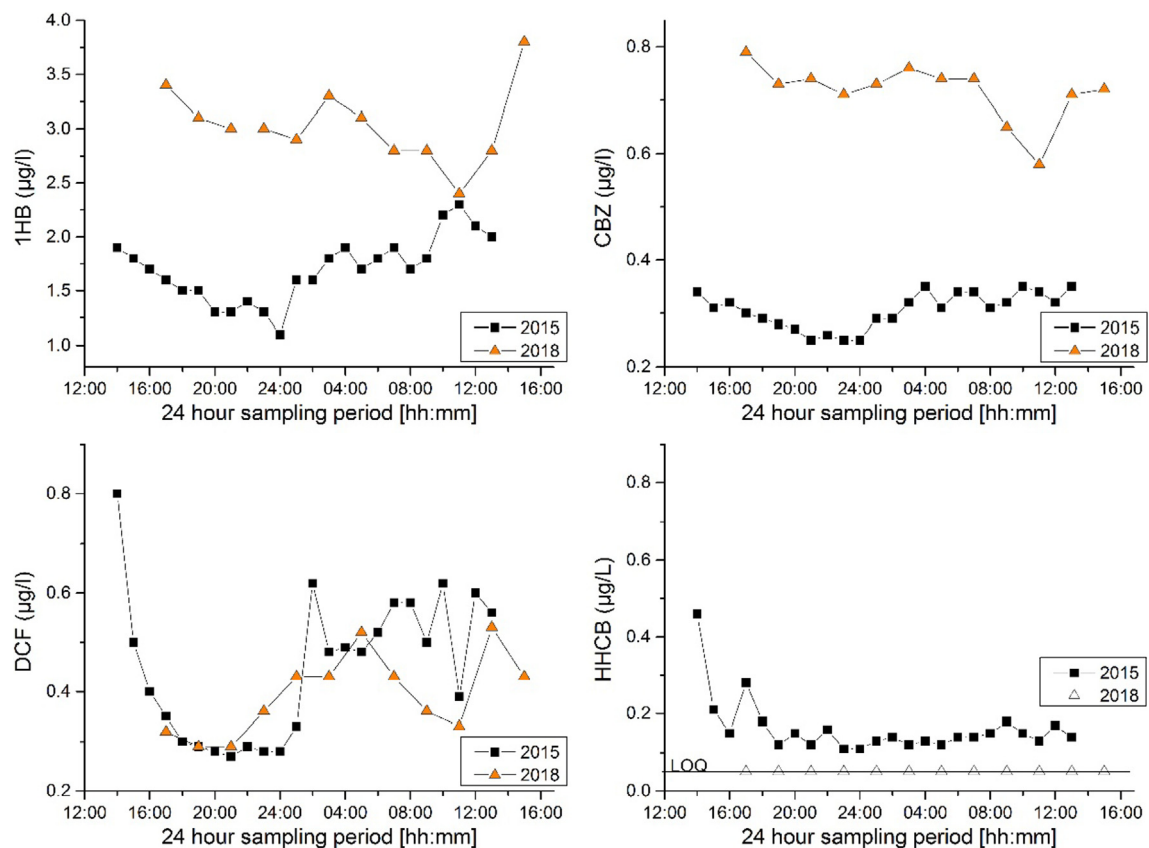
Fig. 2. Daily OMP concentrations measured at the water quality station at the river Swist in 2015 and 2018. Colour-filled symbols = measured above limit of quantification (LOQ); transparent symbols = measured below LOQ.

and subsequent dilution with rain water in the river. Diurnal concentration variabilities of DCF and HHCB show completely different patterns compared to 1HB and CBZ. This illustrates that concentration variability over the day and amongst the samplings is influenced by several factors. For persistent OMPs we can assume that concentration variability in the river (Fig. 2) originates from variable STP effluent volumes. This is a result of, first, typical diurnal variation of STP effluent volumes due to greater water usage during day time and second, steady STP effluent concentration during dry weather (within the 24-h samplings) (Brunsch et al., 2018b). This diurnal concentration pattern of stable compounds in the river can also vary amongst the different samplings as shown by the concentrations and individual effluent volumes of the four STPs observed at the individual sampling day campaign. Another reason for short term concentration variability is removal processes in the river such as sorption, volatilisation, biodegradation or photodegradation. The lowest DCF concentrations were measured between 15:00 and 2:00 in both 2015 and 2018. Given the flow time of 4–5 h from STP R and STP F to the water quality station the water during this time period was mainly influenced by sunlight that promotes photodegradation. The photodegradability of DCF in natural surface waters was already determined by several authors (Bartels and von Tümpling, 2007; Buser et al., 1998; Kunkel and Radke, 2012).

3.1.2. OMP load and mass balance

The load in the river (L_{River}) was compared to the total load from the four STPs (L_{STP}) to be able to create a mass balance and identify removal of OMPs in the river or additional emission sources (Fig. 3). A ratio of 1 would imply neither additional input nor removal.

L_{River}/L_{STP} for 1HB and CBZ and the 2016/2017 campaigns was approximately 1 or higher, which potentially implies that there is additional emission input, for example from diffuse sources or unknown point sources. During the exceptional dry weather campaign in 2018 with no or limited discharge from tributaries and only little influence by groundwater, loads from STPs and river were found to be the same. This suggests that there is no removal of 1HB and CBZ in the river. Persistence of CBZ in rivers was shown in several studies (Kasprzyk-Hordern et al., 2009; Kunkel and Radke, 2012; Lam et al., 2004). The stability of 1HB in rivers was also shown by Reemtsma et al. (2010) and Wolschke et al. (2011). Similarly to our study, these authors also detected increasing 1HB concentrations along the rivers. However, in these studies also large rivers were investigated and it was argued that additional
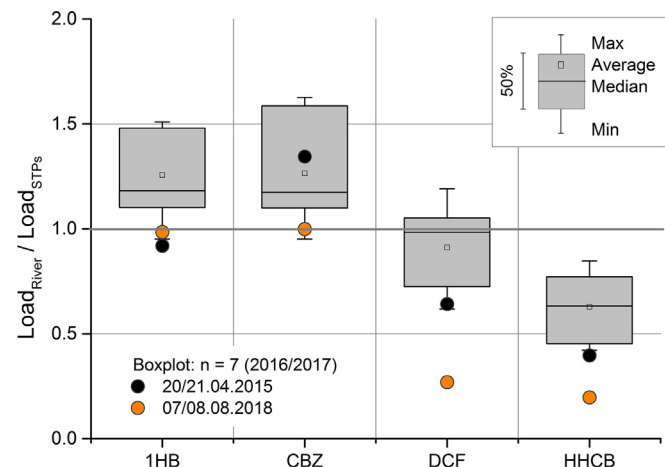
emissions were possibly stemming from water discharges from industries (Wolschke et al., 2011). Moreover, increasing mass flows of 1HB along a river stretch in the Glatt river in Switzerland were identified to originate not only from STPs but also from an airport, where 1HB was used as a de-icing agent (Giger et al., 2006). This shows that 1HB has many applications, and other input pathways besides STPs are possible. However, in our catchment, emissions from direct dischargers such as big industries and airports can be neglected. Moreover, the L_{River}/L_{STP} ratio of loads in the river of both 1HB and CBZ frequently exceeds 1, suggesting additional input of wastewater and need to be further investigated. Another reason for higher CBZ loads in the river might be back transformation of carbamazepine-N-glucuronide to CBZ as determined in STPs by Vieno et al. (2007).

Lower loads in the river compared to that of the STPs have been found for DCF. L_{River}/L_{STP} values were around 1 at four samplings and smaller than 1 at five samplings, demonstrating that occasionally removal occurred in the river. As previously mentioned, in section 3.1.1, sunlight and photodegradation do have influence on DCF concentrations in the Swist river. Here, data of global radiation, i.e. total short-wave radiation, were compared with our DCF mass balance results. The maximum global radiation was greater than 700 W/m² on days with $L_{river}/L_{STP} < 1$, whereas on days with $L_{river}/L_{STP} >/= 1$ the global maximum radiation was below 400 W/m² (Fig. 4). This reinforces the assumption that removal of DCF in the Swist river is influenced by solar radiation triggering photodegradation. The lowest L_{river}/L_{STP} ratio value (0.27) was detected in 2018 during exceptional dry and hot weather with high solar irradiation combined with an exceptionally low flow (0.27 m³/s at the mouth), leading to shallow water, high water temperature and optimal UV exposure. Additionally, high water temperatures and biodegradation may have contributed to the removal of DCF. Schaper et al. (2018) found a half-live of 0.09 d for 1HB and 0.16 d for DCF in the hyporheic zone (i.e. the sediment zone beneath the stream bed with which stream water easily exchanges) of a river in Berlin, Germany. According to these findings, it is likely that removal, and mainly biodegradation, is related to specific conditions of the hyporheic zone. We hypothesize that biodegradation in the hyporheic zone in the Swist river does not contribute significantly to removal, since 1HB was persistent and removal of DCF mainly related to photodegradation with the exception of the data in 2018.

HHCB load in the river was in all samplings lower than load from STPs, implying constant removal of this compound. The underlying process associated to this could not be identified, but did not correlate to variations in temperatures. Musolff et al. (2009) and Lange et al. (2015) showed increased removal of HHCB in surface water with increasing water temperature. Whereas Musolff et al. (2009) could not assign this result to a specific removal process, Lange et al. (2015) concluded that HHCB removal is due to oxidation caused by chemical or microbiological processes. Biodegradation as a contribution to removal of HHCB in rivers was also determined by Schwientek et al. (2016). In contrast to this, Bester (2005) showed that biodegradation of HHCB in the river Ruhr in Germany is negligible. For HHCB volatilisation and sorption are suspected removal processes because of its volatility and hydrophobicity (see Henry constant and K_{ow} values in Table 2). These air-water and water-sediment exchange processes are both related to temperature and flow turbulence. The latter was not part of our study, however, the lower load ratio values in the warmer summer of 2018 with warmer water temperatures in the river thus contribute volatilisation, whereas colder water temperatures induce sorption. Therefore, a combination of both volatilisation and sorption is most likely the reason for the good removal of HHCB in the Swist river. Nonetheless, biodegradation as a possible removal process cannot
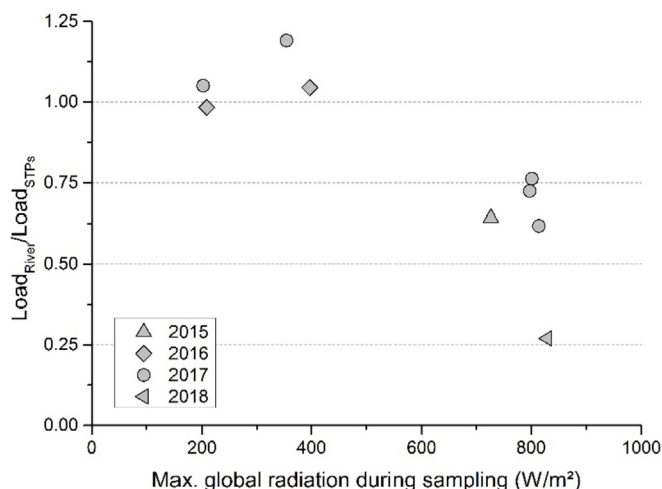

Fig. 3. Ratio of loads in the river to loads from the sewage treatment plant for the three different samplings (indicated by boxplot and two filled circles).

Fig. 4. The ratio of DCF loads in the river Swist to loads from the four STPs, related to global radiation measured at the water quality station.

be excluded, but in order to make a reliable statement, behaviour of transformation products such as HHCB-lactone must be investigated as well. This might be subject of future studies.

A study conducted by Schwientek et al. (2016), determined mass balances for OMPs - as we did in this Swist study - in another small river in Germany. Their results reported for HHCB, DCF and CBZ removal in that river (net removal 32%, 17%, 2.5%) were in very good agreement with our results.

3.2. OMP behaviour determined by modelling

3.2.1. Model input data

To simulate the behaviour of OMPs in the river profile and diurnal variation with the DWA Water Quality Model, input parameters for OMP removal are essential. The most important input parameters for OMP simulation used are presented in Table 2. For the calculation of sorption and volatilisation the K_{OW} value and the Henry constant were used by the model. Both parameters are constants and hence not variable. DCF and 1HB are often described as photodegradable OMPs which is related to their high quantum yield values. Several quantum yield values that were determined under different conditions such as pH, light wavelength and light intensity have been collected (for DCF: Andreozzi et al., 2003; Buser et al., 1998; Keen et al., 2013; Moore et al., 1990; Packer et al., 2003 for 1HB: Andreozzi et al., 1998; Benitez et al., 2013; Borowska et al., 2016; Wang et al., 2000). Three quantum yield values for each DCF and 1HB, representing a minimum, maximum and intermediate value representative for the study conditions were used in our

simulations (Table 2). It is known that under laboratory conditions, photodegradation can only occur at water depths up to 100 cm due to UV quenching (He et al., 2016), hence it is likely that deeper waters with high turbidity do not show significant DCF photodegradation. The river Swist is shallow, especially at dry weather discharges as studied here, with large transects having depths of a few decimetres. Hence, photodegradation is a potential contributor to removal. For biodegradation, data on rates in rivers are rarely reported. Kunkel and Radke (2008) stated that half-live for DCF in the river sediment is 5.5 and 18.6 days at slow and high flow rates. Buser et al. (1998) found out that biodegradation of DCF in a lake (Greifensee) is minimal. Biodegradation of 1HB was detected in activated sludge with a half-live of 23–45 h by Mazioti et al. (2015). According to these data and in consideration of the high uncertainties in biodegradation rate constants adopted from literature to modelling (Greskowiak et al., 2017), a variety of removal factors [1/d] (0.00, 0.03 and 0.30) for biodegradation was used for simulating 1HB and DCF. CBZ is known as a stable compound (Clara et al., 2004), with neither photodegradation (Baena-Nogueras et al., 2017) nor biodegradation to be significant in the river water, river sediment respectively (Löffler et al., 2005). HHCB was detected to be recalcitrant against biodegradation (Bester, 2005) and photodegradation (Buerge et al., 2003) in rivers (see also section 3.1.2). On the other hand, degradation of HHCB was determined in a STP under nitrifying conditions (Suarez et al., 2010). According to that, the removal factors adapted for DCF and 1HB (0.00, 0.03 and 0.30 1/d) have also been applied for the simulation of HHCB.

3.2.2. Simulation results

Two different dry weather scenarios were simulated with the model. In order to validate the simulation results with monitoring data, we selected April 20/21 2015 and August 07, 2018 as simulation periods, representing one normal dry weather and one extreme dry weather scenario. The short rain event at August 8 (see section 2.1) was excluded in the simulation to reduce uncertainties due to surface runoff and dilution. The Nash-Sutcliff model Efficiency coefficient (NSE) (Nash and Sutcliffe, 1970) and the coefficient of determination (R^2) were calculated to compare simulated and measured discharge and temperature data. The NSE for discharge at gauge W was 0.58 for the 2015 campaign and 0.25 for the 2018 campaign. R^2 was calculated with 0.69 and 0.63 respectively. The 2018 campaign data showed higher differences between measured and simulated discharge data. The reason is presumably the extremely low water level and discharge in the river. However, in consideration of the high temporal resolution of the simulation, results for both years are accounted to be satisfactory and the model to be well validated in regard to basic hydrology. Moreover, the measured temperature data validate well the simulated temperature values for the 2015 campaign ($R^2 = 0.81$), whereas the measured temperature data of 2018 did not match the simulated

Table 2
Input parameter for the DWA Water Quality Model.

	Biodegradation Removal factor 1/d	Photodegradation Quantum yield mol/Einstein	Volatilisation Henry constant[f] Pa*m^3/μmol	Sorption K_{OW}[g]
1HB	0.00; 0.03; 0.30	0.0294[a]; 0.0123[b]; 0.00472[b]	1.49E-08	20
CBZ	0.00	0.0000	1.09E-11	589
DCF	0.00; 0.03; 0.30	0.22[c]; 0.094[d]; 0.0375[e]	4.79E-06	18197
HHCB	0.00; 0.03; 0.30	0.0000	1.34E-05	794328

[a] Benitez et al. (2013).
[b] Andreozzi et al., (1998).
[c] Moore et al. (1990).
[d] Packer et al. (2003).
[e] Andreozzi et al. (2003).
[f] www.norman-network.net.
[g] www.chemicalize.com.

data ($R^2 = 0.39$). This is in accordance to the discharge values and illustrates that the extreme dry weather scenario (2018) is more difficult to describe with the model in small rivers in contrast to the normal dry weather scenario (2015). The accuracy of the parameterization of the model i.e. the description of the real conditions of the river and the surrounding environment is most important under extreme conditions with very low water level and consequently uncertainties in simulating such scenarios are growing.

A range of loads in the river was simulated for 1HB and DCF using different input parameters for biodegradation and photodegradation (Table 2). In Fig. 5 simulated and measured loads are presented. A minimum and maximum load were simulated for DCF, 1HB and HHCB, while for CBZ only a single load is simulated. For DCF, 1HB and HHCB, worst removal represents a simulation with the lowest biodegradation rate and quantum yield values, and best removal represents the simulation with the highest biodegradation rates and quantum yields as shown in Table 2. 1HB load in the river could be well described by the model for the campaign in 2015, with a L_{sim}/L_{mon} of 0.9–1.1. In 2018, measured loads are higher than the simulated values (L_{sim}/L_{mon} 0.4–0.7). CBZ loads were slightly underestimated by the model in both years (L_{sim}/L_{mon} ~0.7 in 2015 and 2018 respectively). Reason for higher CBZ and 1HB monitoring loads could be additional unknown sources of emission as discussed in section 3.1.2 that were not considered in the model. Alternatively, photodegradation and biodegradation for 1HB might have been overestimated with modelling. This is in accordance to the results as discussed in section 3.1.2, showing that 1HB is recalcitrant in rivers.

DCF loads from monitoring were both years in the range of the simulated loads (L_{sim}/L_{mon} in 2015 0.5–0.9 and in 2018 0.5–1.3), showing that quantum yields from literature and a biodegradation removal factor of up to 0.3 1/d are able to explain observed losses of DCF loads in the Swist river. Given the fact that the flow time from the two main dischargers, STP F and STP R to the mouth of the river is 4–5 h, the biodegradation factor of 0.3 1/d might have a much lower contribution to the simulated loads in comparison to photodegradation. Moreover, both quantum yield and the

biodegradation factor are fixed values in the model, despite their sensitivity to external factors. Subsequently, in real surface waters these factors might vary, due to redox conditions, conditions in the hyporheic zone, flow properties, or the biocenosis characteristics in different river segments. HHCB loads were slightly overestimated in 2015 with a L_{sim}/L_{mon} of 1.3–1.5 and considerably overestimated in 2018 with a L_{sim}/L_{mon} of 2.5–3.1. Differences in simulated daily loads for worst and best removal with biodegradation removal factor from 0.0 to 0.3 1/d were low (3.1 and 2.5 g/d 2018, 11.7 and 11.6 g/d 2015), leading to the conclusion that sorption and volatilisation were the most relevant removal processes for HHCB as determined by the model. However, it is possible that these processes were underestimated, possibly by inadequate determination of amounts of suspended solids enhancing sorption and removal by sedimentation out of the water column, inadequate determination of sorption to sediment, or higher biodegradation rate that may have occurred. Moreover, uncertainties and variabilities in comparing simulation and field observations are considered to be higher for volatile and hydrophobic compounds, sensitive to temperature variation and flow dynamics than for stable or photodegradable compounds (when known regional lux data are available). As an overall result, OMP behaviour can be reasonably well described with the DWA Water Quality Model, especially at "normal" dry weather conditions as in our example in 2015.

4. Conclusion

Studying the behaviour of OMPs in a real river system, by monitoring OMP concentrations is challenging, due to influences of "uncontrollable" environmental conditions such as weather, varying compositions of microbial communities or hydraulics in the river. For this reason, modelling is a suitable additional approach to the field monitoring results. We combined high resolution monitoring of a river, and a model with a deterministic mechanistic basis that includes a variety of removal processes. This enables to better understand the processes that occur in a river, and to determine the effects of environmental conditions on removal. This combined
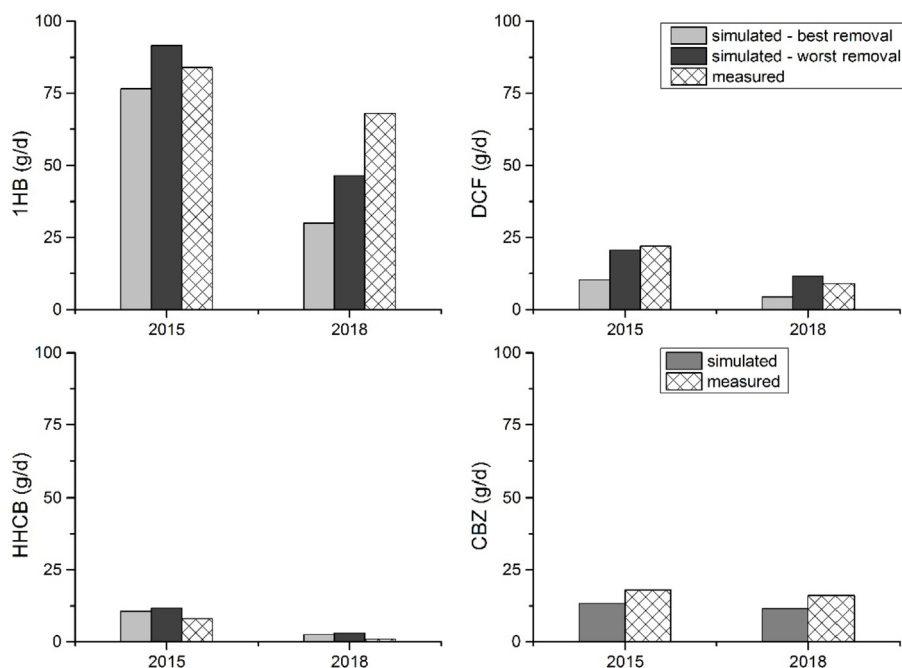

Fig. 5. Daily loads in the river Swist calculated with monitoring data and simulated data for April 2015 and August 2018. Simulated best removal is based on highest quantum yield and biodegradation input data and worst removal is based on lowest quantum yield and biodegradation input data as shown in Table 2.

approach fills the gap between laboratory and mesocosm studies of diverse OMP emissions, and the fate and behaviour of OMPs in river systems.

Generally, our monitoring data revealed that short term concentration variability in a river is at first a result of varying STP effluent volumes and subsequent dilution, and secondly, by action or absence of diverse removal processes occurring in the river. With the DWA Water Quality Model, it was possible to simulate OMP concentration profiles as observed in the river, using a variety of kinetic rate constants for various OMP removal processes as reported in the literature. Modelling results showed, that data on photodegradation as well on sorption and volatilisation, which were determined in laboratory studies, were transferable to the conditions in a shallow natural river system. It can be concluded that the DWA Water Quality Model is well suited for simulating OMP concentrations and loads in rivers as well as for secondary identification of *in situ* removal process for some compounds in rivers. We recommend this model, and included micropollutant module, to be further developed for other conditions and compounds to enhance its use for managing river water quality with respect to OMPs.

In this study different dry weather scenarios were compared, all valuable to determine the behaviour of OMPs in small rivers. Extreme dry weather scenarios, with lowest input on diffuse or other unknown sources, were ideal for studying OMP *in situ* behaviour in rivers through only monitoring data. For modelling hydraulic as well as reactive processes, the "normal" dry weather scenarios appear to be most suitable.

Diclofenac removal was mainly related to high global radiation triggering photolysis. Accordingly, in central Europe's latitudes diclofenac is well removed by photodegradation during summer time. In areas with higher global radiation and/or more hours of sunshine diclofenac removal in rivers can be expected to be better. Galaxolide showed the highest removal, presumably due to a variety of processes working simultaneously such as volatilisation, sorption and biodegradation whereas carbamazepine and 1-H benzotriazole were persistent in the river.

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