

# Spatial and Temporal Variability in Attenuation of Polar Organic Micropollutants in an Urban Lowland Stream

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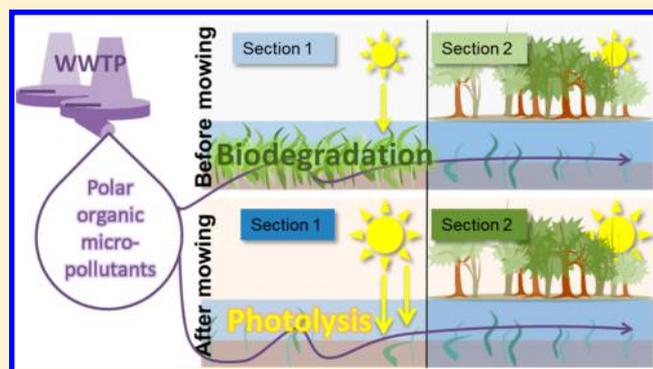
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## Supporting Information

**ABSTRACT:** Contamination of rivers by trace organic compounds (TrOCs) poses a risk for aquatic ecosystems and drinking water quality. Spatially- and temporally varying environmental conditions are expected to play a major role in controlling in-stream attenuation of TrOCs. This variability is rarely captured by in situ studies of TrOC attenuation. Instead, snap-shots or time-weighted average conditions and corresponding attenuation rates are reported. The present work sought to investigate this variability and factors controlling it by analysis of 24 TrOCs over a 4.7 km reach of the River Erpe (Berlin, Germany). The factors investigated included sunlight and water temperature as well as the presence of macrophytes. Attenuation rate constants in 48 consecutive hourly water parcels were tracked along two contiguous river sections of different characteristics. Section 1 was less shaded and more densely covered with submerged macrophytes compared to section 2. The sampling campaign was repeated after macrophyte removal from section 1. The findings show, that section 1 generally provided more favorable conditions for both photo- and biodegradation. Macrophyte removal enhanced photolysis of some compounds (e.g., hydrochlorothiazide and diclofenac) while reducing the biodegradation of metoprolol. The transformation products metoprolol acid and valsartan acid were formed along the reach under all conditions.



## INTRODUCTION

Polar trace organic compounds (TrOCs), such as pharmaceuticals and personal care products, as well as their transformation products (TPs) are frequently detected in urban streams receiving wastewater treatment plant (WWTP) effluent.<sup>1–5</sup> TrOCs may impair aquatic ecosystem functioning and pose a risk to drinking water quality, particularly in semi-closed urban water cycles.<sup>6–8</sup> Despite their widespread occurrence, TrOCs remain mostly unregulated, and knowledge about their fate in streams is still limited.<sup>4,9–11</sup>

Biodegradation, photolysis and sorption are among the key processes controlling TrOC fate in freshwaters. These processes are usually studied in laboratory experiments under controlled conditions.<sup>12–17</sup> The occurrence of processes in situ, however, depends on a diverse set of environmental

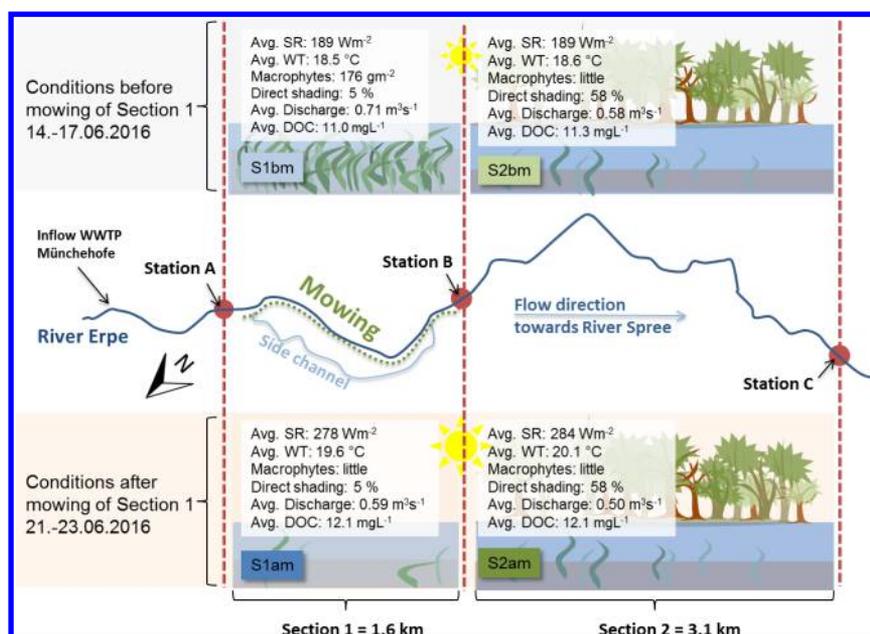
conditions.<sup>18</sup> Biodegradation is driven by factors such as the composition of the microbial community, water temperature, redox zonation and availability of ecohydrological interfaces.<sup>15,19–21</sup> Likewise, photolysis is not only controlled by intensity of solar radiation but also by, for example, shading and concentration of dissolved organic carbon (DOC).<sup>22,23</sup> Sorption depends on availability of binding sites on organic matter, sediment particles or biofilm, for example.<sup>24,25</sup> On one hand, this multitude of environmental conditions may vary temporally, for example, diurnal and annual fluctuations in

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**Figure 1.** Map of the 4.7 km study reach of River Erpe, located in the east of Berlin, Germany. The three sampling stations A, B, and C, downstream of the WWTP inflow, determine the two study sections 1 and 2. The mowing area is shown in a green-dashed line. Graphics below and above depict comparison of attenuation conditions between sections and before and after mowing of section 1. Avg. SR = average solar radiation; Avg. WT = average water temperature; Avg. DOC = average dissolved organic carbon.

temperature. On the other hand, conditions may vary spatially within a river, for example, in transient storage zones where water is delayed in its downstream transport and contact with ecohydrological interfaces is increased. Examples for transient storage zones are hyporheic zones, groyne fields, dead zones behind obstacles and vegetation, and near-shore pools of stagnant water.<sup>26,27</sup>

Submerged macrophytes are an important factor which controls environmental conditions in rivers. They provide a range of ecosystem services, such as creating diverse habitats for fish and invertebrates. They influence oxygen and nutrient concentrations and can change flow velocities and sediment morphology.<sup>28,29</sup> Macrophytes also alter shading and thermal regimes and create transient storage zones.<sup>26,27</sup> Furthermore, they are known to have a direct removal function for TrOCs through biodegradation on epiphytic biofilm or plant uptake.<sup>30</sup> Despite their important role for river ecosystems, removal of aquatic vegetation from rivers is a common management technique for flood prevention.<sup>29</sup> Some rivers are even mowed several times a year.<sup>28</sup> Due to their intense impact on in-stream conditions and their pollutant removal functions, we expect that macrophytes play a major role in in-stream attenuation of TrOCs and that their removal changes the fate of TrOCs drastically.<sup>26,29–31</sup>

The spatial and temporal heterogeneity of factors controlling attenuation processes makes in situ investigation of TrOC in-stream fate generally challenging. Some important in-stream attenuation studies have been conducted previously in single rivers implementing different methods. Some followed a single water parcel in a Lagrangian sampling scheme.<sup>32–34</sup> In those cases snap-shots of attenuation conditions and corresponding attenuation values are reported. Others investigate attenuation over longer periods, mostly resulting in time-integrated single attenuation values.<sup>35–37</sup> While such studies provide important quantitative information about attenuation or potential persistence of TrOCs in streams, the identification of processes

and environmental drivers remains difficult due to a low comparability between studies. Two studies attempted to enhance comparability by conducting the same sampling methods and measuring the same set of parameters at four different rivers.<sup>38,39</sup> However, the boundary conditions between rivers, such as discharge, sediment characteristics or portion of effluent differed to a point where it hindered the identification of distinct processes and responsible drivers.

The objective of the present study was to investigate within-stream variability of TrOC fate, that is the change of TrOC attenuation or transformation in time or space within one single stream. We suggest that this approach has two major advantages: First, for each compound a distribution of rate constants is obtained as opposed to a single value, making the result more realistic and promoting comparability to other studies. Second, it facilitates identification of processes and related drivers that influence the fate of individual compounds due to a higher conformity in the remaining boundary conditions within one stream than between different streams. Hanamoto et al.<sup>40</sup> are to our knowledge the first to demonstrate diurnal changes of in-stream attenuation in an hourly resolution leading to the identification of diurnal fluctuation in solar radiation as a major control for attenuation of certain compounds in situ.

In the present work we studied the in-stream fate of a set of 24 TrOCs and TPs. We expected that temporally and spatially varying environmental conditions would lead to a variation in attenuation rate constants of compounds that undergo biodegradation, photolysis or sorption and attempted to identify the underlying processes. We hypothesized that TrOC attenuation will (a) differ between two adjacent sections of different characteristics; (b) change after removal of macrophytes from the first section; (c) depend on diurnal fluctuations in environmental conditions, such as water temperature or solar radiation.

**Table 1. List of Compounds with Average Concentrations and Loads at Station A, Median Attenuation Rate Constant  $k_{att}$ , Kruskal-Wallis Test and Conover Test Results and Spearman Correlation Values<sup>a</sup>**

compound (parent compounds are highlighted in bold, related TPs are listed below)	avg. concentrations st. A (max, min)[ $\mu\text{g L}^{-1}$ ]	avg. loads st. A [g day <sup>-1</sup> ]	median $k_{att}$ [ $\text{h}^{-1}$ ]				Kruskal-Wallis test (KW) and Posthoc test: Conover with Benjamini, Krueger and Yekutieli correction * $p < 0.05$				Spearman correlation coefficient $\rho$					
			S1am $n = 47$		S2bm $n = 47$		S1bm vs S1am		S2bm vs S2am		solar radiation and $k_{att}$		water temperature and $k_{att}$			
			S1am $n = 48$	S1bm $n = 48$	S1am $n = 47$	S2bm $n = 47$	KW	S1am vs S1bm	S2am vs S2bm	S1am vs S1bm	S2am vs S2bm	S1-am	S2-am	S1-bm	S2-bm	
<b>acesulfame</b>	2.90 (4.9, 1.4)	174	0.0010	0.0082	0.0027	0.0061	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>1H-benzotriazole</b>	10.7 (18, 5.5)	633	(-0.0057)	0.0059	(-0.0031)	0.0051	*	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>bezafibrate</b>	0.564 (0.88, 0.37)	34	0.0141	0.0251	0.0071	0.0045	*	ns	ns	*	ns	ns	ns	ns	ns	ns
<b>carbamazepine</b>	1.53 (1.9, 1.0)	91	0.0021	0.0074	0.0060	0.0035	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>10,11-dihydro-10,11-dihydroxy carbamazepine</b>	2.84 (4.1, 1.7)	168	0.0033	0.0064	0.0085	0.0013	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>carbamazepine-10,11-epoxide</b>	0.063 (0.11, 0.029)	4	0.0113	0.0097	(-0.0028)	0.0190	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>diclofenac</b>	3.36 (5.0, 1.7)	199	0.0190	0.0428	(-0.0031)	0.0198	*	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>4-hydroxydiclofenac</b>	0.585 (1.5, 0.13)	34	0.0134	0.2102	(-0.0427)	0.0291	*	*	*	*	ns	ns	ns	ns	ns	ns
<b>hydrochlorothiazide</b>	5.68 (7.6, 3.4)	338	0.0074	0.0393	0.0079	0.0214	*	ns	ns	*	ns	ns	ns	ns	ns	ns
<b>chlorothiazide</b>	0.173 (0.24, 0.078)	10	(-0.0162)	(-0.0089)	0.0179	(-0.0005)	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>irbesartan</b>	1.74 (2.3, 0.96)	103	(-0.0063)	0.0109	(-0.0014)	0.0094	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>metformin</b>	1.74 (4.39, 1.73)	105	0.0028	0.0162	0.0052	0.0052	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>guanylurea</b>	68.8 (90, 46)	4107	0.0058	0.0263	0.0137	0.0067	*	ns	ns	*	ns	ns	ns	ns	ns	ns
<b>metoprolol</b>	4.40 (5.9, 2.1)	262	0.0392	0.0256	0.0062	0.0105	*	*	*	*	ns	ns	ns	ns	ns	ns
<b><math>\alpha</math>-hydroxy-metoprolol</b>	0.503 (0.73, 0.31)	30	0.0330	0.0464	0.0272	0.0238	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>metoprolol acid</b>	0.245 (0.41, 0.10)	14	(-0.0461)	(-0.0253)	(-0.0072)	(-0.0170)	*	*	*	*	ns	ns	ns	ns	ns	ns
<b>sitagliptin</b>	3.57 (4.5, 1.9)	213	0.0059	0.0151	0.0159	0.0037	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>sotalol</b>	0.221 (0.29, 0.13)	13	(-0.0059)	0.0183	0.0050	0.0068	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>sulfamethoxazole</b>	0.066 (0.14, 0.018)	4	0.0248	0.0313	(-0.0613)	(-0.0035)	*	ns	*	*	ns	ns	ns	ns	ns	ns
<b>tramadol</b>	0.847 (1.0, 0.50)	50	(-0.0006)	0.0129	0.0029	0.0045	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>valsartan</b>	28.5 (38, 17)	1693	0.0289	0.0206	0.0130	0.0161	*	ns	ns	*	ns	ns	ns	ns	ns	ns
<b>valsartan acid</b>	5.41 (8.3, 2.4)	319	(-0.0319)	(-0.0307)	(-0.0211)	(-0.0091)	*	ns	ns	*	ns	ns	ns	ns	ns	ns
<b>venlafaxine</b>	0.325 (0.46, 0.16)	19	0.0102	0.0046	-0.0003	0.0057	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
<b>O-desmethylvenlafaxine</b>	1.58 (2.0, 0.95)	94	0.0050	0.0077	-0.0004	0.0019	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

<sup>a</sup>ns = no significant correlation. Details on the statistics are shown in SI Table S2, half-lives and relative attenuation in SI Table S6 and  $k_{att}$  uncertainties in SI Table S9.

## MATERIAL AND METHODS

**Study Site.** The experiment was conducted in the River Erpe, a lowland stream located east of Berlin, Germany. The study reach was 4.7 km in length, starting 0.7 km downstream of the outlet of WWTP Münchehofe and ending 0.8 km prior to the mouth of the River Erpe into the River Spree (Figure 1). During the study period, the WWTP discharged on average ( $\pm$ SD)  $0.44 \pm 0.22 \text{ m}^3 \text{ s}^{-1}$  treated wastewater into the river (data provided by WWTP Münchehofe, Berlin) increasing its discharge to  $0.69 \pm 0.21 \text{ m}^3 \text{ s}^{-1}$  at the start of the study reach in daily fluctuations (Supporting Information (SI) Figure S1). The effluent strongly influences the hydrological regime and the chemical composition of the study reach.<sup>41</sup> It was divided into two sections (S1 and S2) of 1.6 km and 3.1 km length, respectively, by three sampling stations (stations A, B, and C; Figure 1). Google-maps satellite images showing maximum foliage were used to obtain the portions of shading of the river surface in the different sections. S1 was almost continuously exposed to solar radiation (5% direct shading). Consequently, macrophytes completely covered the channel of S1 with a total dry biomass ( $\pm$ SD) of  $176 \pm 87.3 \text{ g m}^{-2}$  (80% *Stuckenia pectinata*, 12% *Callitriche* sp., 8% *Sparganium emersum*). The channel of S2, in contrast, was 58% directly shaded by adjacent trees and thus the abundance of macrophytes was generally low. Due to patchiness it was not feasible to measure the average biomass. However, since macrophyte biomass is highly sunlight dependent,<sup>42</sup> we estimated that the difference in macrophyte biomass density was similar to the difference in sunlight-exposed channel area between the sections (S1 95%: S2 42%). Thus, we speculate that the average dry biomass density in S2 was roughly 0.44 of the dry biomass in S1 ( $\sim 78 \text{ g m}^{-2}$ ). Most of the river's sediment has a high organic matter content, and thus low hydraulic conductivity. Only in the first 400 m of S1, the river is connected to the fine sandy aquifer and characterized as a losing stream.<sup>43</sup> Infiltration of river water to the hyporheic zone in this stretch was previously measured by means of vertical temperature profiles.<sup>44</sup> Although re-exfiltration of hyporheic water to the river has not been examined, hyporheic exchange flow is probable where dunes form and at the two fish ladders in this stretch. Additionally, a small side channel diverts from the main channel in S1 40 m downstream of station A and re-enters the river at two locations: 641 and 176 m upstream of station B. Similar to the effect of the potential hyporheic zone, its effect is accounted to a lumped transient storage zone of unknown extent. The channel of S2 in contrast is predominantly muddy, and thus mostly confined.<sup>43</sup> The size of the transient storage zone was not quantified, but due to the side channel, the macrophytes and the sediment characteristics described above, it is expected to be larger in S1 than in S2. Detailed information about background data, such as discharge, water chemistry and meteorological data are shown in the SI.

**Sampling.** Autosamplers (ISCO 3700 portable sampler, Teledyne Isco, Lincoln, NE) were installed at stations A, B, and C collecting surface water from the center of the stream cross-section. Samples were continuously cooled inside the autosamplers by ice-packages. A set of 48 hourly samples was taken twice at each station: before (*bm*) and after (*am*) removal of macrophytes from the riverbed of S1. A delay of a daily reoccurring electrical conductivity (EC) trough served as an approximation for travel times between stations. We estimated the travel times from time series in EC of the day

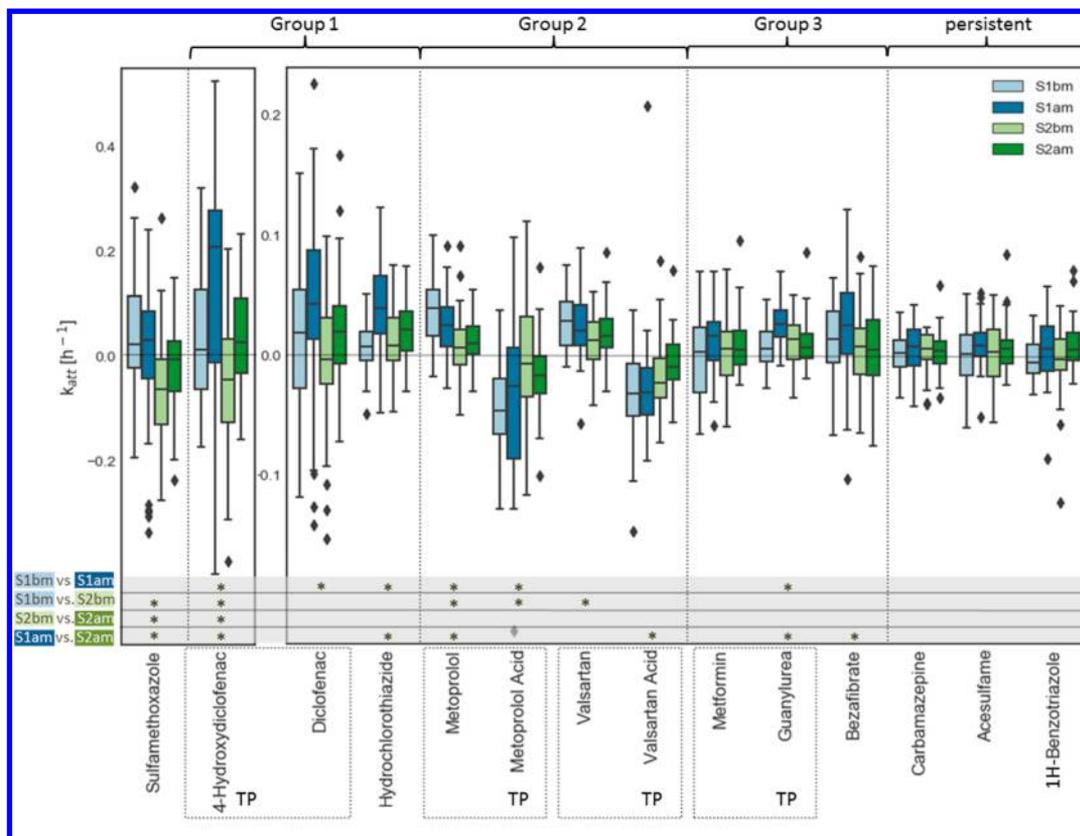
before sampling, both *am* and *bm*. Hence, to capture the water parcels most efficiently, the autosampler at station A started sampling at 23:00 on the 14.06.2016 (*bm*), while sampling at stations B and C followed 4 and 8 h later, respectively. On the 17.06.2016, S1 was mowed to clear the water body from macrophytes. Trucks with mowing shovels cut the plants off the streambed and shoveled them to the shore (SI Figure S2). The delay of the EC trough after mowing showed that the travel time in S1 was reduced by roughly 1 h, while the travel time in section 2 remained similar to before mowing. Hence, the first sample after mowing was taken at station A on the 21.06.2016 at 14:00, followed by station B and C, 3 and 7 h later, respectively. All water samples were split into subsamples for respective analytical methods and stored accordingly until processing. In addition to autosamplers, Chemcatcher passive samplers in polar configuration were deployed in duplicates at all stations *bm* (11 days, 05.06. to 16.06.2016) and *am* (10 days, 20.6. to 30.6.2016).<sup>45</sup> Details on the passive sampling procedure can be found in the SI.

**Collecting of Meteorological, Biomass, Shade Cover, and Electrical Conductivity Data.** Global solar radiation and precipitation data were recorded continuously at a weather station (IGB Berlin) located approximately 2.6 km southeast of sampling station B. At each sampling station data-loggers (CTD-Diver, van Essen Instruments, Delft, The Netherlands) were set up close to the sampling-tubes to track EC, water stage and water temperature continuously (5 min intervals). Background data during the sampling periods are shown in SI Figure S1. To estimate the average biomass of macrophytes *bm* in S1, plants from three representative  $4 \text{ m}^2$  sites ca. 200 m downstream of station A were manually collected. The species were identified and separately dried to obtain dry biomasses.

**Quantitative Determination of TrOCs and Boron.** TrOC analysis of all water samples was conducted at Stockholm University, Sweden.<sup>46</sup> Prior to analysis samples were defrosted, vortexed, combined with MeOH and an internal standard mix, vortexed again and finally filtered ( $0.45 \mu\text{m}$ , PES membrane). Concentrations of 24 TrOCs (a full list is provided in Table 1) were determined by direct injection ultrahigh performance liquid chromatography tandem mass spectrometry as described by Posselt et al.<sup>46</sup> Intermediate precision was good (repeatability <24% RSD and reproducibility <18% RSD) and method accuracy excellent for most compounds.<sup>46</sup> Details on quality control of TrOC analysis are described in the SI and further data including spike/recovery experiments with Erpe water can be found in Posselt et al.<sup>46</sup> Concentrations of all target compounds in all Erpe samples were above the limit of detection. Values below limit of quantification (LOQ) were only found for  $\alpha$ -hydroxymetoprolol, carbamazepine-10,11-epoxide and sulfamethoxazole and were replaced by  $\text{LOQ} \cdot 2^{-0.5}$  (<25% of samples).

Subsamples for analysis of boron were filtered immediately after sampling ( $0.45 \mu\text{m}$  cellulose acetate), acidified with HCl, stored at  $4 \text{ }^\circ\text{C}$  and measured by inductively coupled plasma optical emission spectrometry (ICP iCAP 6000series, Thermo-Fisher-Scientific Inc.).

Analysis of TrOCs collected in the passive samplers was conducted at EAWAG Zurich, Switzerland, by an established liquid chromatography high-resolution tandem mass spectrometry method for passive samplers (see SI for details). It included 17 out of the 24 compounds measured in the water samples (SI Table S4).<sup>45</sup> Concentrations were calculated using experimentally determined sampling rates (data not shown).



**Figure 2.** Distributions of attenuation rate constants ( $k_{att}$ ) of all compounds in the different sampling situations that showed significant differences between sampling situations as well as metformin, carbamazepine, acesulfame, and 1H-benzotriazole for comparison. Boxes indicate quartiles, while whiskers show the rest of the distribution without outliers and diamonds represent outliers. S1bm:  $n = 48$ ; S1am:  $n = 47$ ; S2bm:  $n = 47$ ; S2am:  $n = 46$ . The bottom four lines show significant differences between sampling situations in Conover tests (\*:  $p < 0.05$ ). Dashed boxes indicate pairs of parent compounds and TPs. Compounds were allocated to the groups according to their attenuation patterns.

**Travel Times Estimated by Deconvolution of Intrinsic Electrical Conductivity Signals.** The daily dynamics of the WWTP discharge cause a relatively regular diurnal fluctuation in electrical conductivity (EC) in the river downstream of the wastewater outlet (e.g.: station A *bm*:  $811\text{--}1170 \mu\text{S cm}^{-1}$ ; *am*:  $994\text{--}1150 \mu\text{S cm}^{-1}$ ; SI Figure S4). EC is assumed to behave conservatively in the surface water, that is the signal is not affected by biological or chemical processes but merely by advection and dispersion.<sup>47,48</sup> Thus, EC can serve as tracer for solute transport and allows determination of travel times between sampling stations. Water residence time distributions between pairs of sampling stations were estimated using a nonparametric deconvolution method for EC time series (see SI).<sup>49,50</sup> Given the strong daily periodicity of the input EC signals, the estimation of the transfer function was limited to 1 day. The duration was sufficient to capture the bulk of the transfer function and to prevent secondary peaks resulting from the 24 h periodicity of the input EC signal. A period of 4 days from 13.06.16 8:00 to 17.06.16 7:55 and from 21.06.2016 14:00 to 25.06.2016 13:55 was considered (i.e., *bm* and *am*) to estimate the residence time distributions. Peak travel times were estimated to be 4.4 h in S1bm, 3.1 h in S1am, 4.5 h in S2bm and 5.4 h in S2am.

**Calculation of TrOC Attenuation Rate Constants.** In order to track changes in solute concentration along a river section hourly consecutive water parcels were monitored following the idea of a Lagrangian sampling scheme.<sup>33,47</sup> The concentration at the start time of the parcel ( $p$ ) of a solute ( $x$ )

at the upstream station ( $C_{p,x,in}$ ) is compared to the concentration at the start time plus the travel time ( $t_p$ ) at the downstream station ( $C_{p,x,out}$ ). To account for the possible influence of dilution during the travel period of a parcel, the change of concentration is corrected by the change of concentration in a conservative WWTP-derived reference compound, in this case boron.<sup>51</sup> Low changes in boron concentrations between stations revealed that dilution was generally of minor importance (SI Figure S5). The concentrations and the  $C_x:C_{ref}$  ratios in each sample are assumed to represent the concentrations during the passing-time of one parcel (1 h) at each station. To calculate the attenuation rate constants ( $k_{att,p,x}$ ), pseudo first-order reactions were assumed for all compounds.<sup>17,18,39,40</sup>

$$k_{att,p,x} = \ln \left( \frac{\frac{C_{p,x,in}}{C_{p,x,out}}}{\frac{C_{p,ref,in}}{C_{p,ref,out}}} \right) / t_i \quad (1)$$

Consequently,  $k_{att}$  in S1 were calculated from concentrations at stations A ( $C_{in}$ ) and B ( $C_{out}$ ), whereas  $k_{att}$  in S2 were calculated from concentrations at stations B ( $C_{in}$ ) and C ( $C_{out}$ ). In order to assess the influence of spatial and temporal differing environmental conditions on  $k_{att}$  of individual compounds, we compared the distributions of  $k_{att}$  temporally, that is *bm* and *am*, and spatially, that is in S1 and in S2. This led to a division into four different conditions: S1bm ( $n = 48$ ), S1am ( $n = 47$ ), S2bm ( $n = 47$ ), and S2am ( $n = 46$ ), which we refer to as “sampling situations” in the present work. The

calculation of average solar radiation during a water parcel's travel period and the average water temperature a water parcel was exposed to is shown in the SI.

**Statistical Methods.** Since environmental conditions are often not linearly related to  $k_{\text{att}}$ ,<sup>22</sup> Spearman rank correlations ( $\rho$ ) were applied to determine the correlation of  $k_{\text{att}}$  with solar radiation and water temperature. Kruskal–Wallis tests in combination with Conover tests<sup>52</sup> (posthoc pairwise test for multiple comparisons of mean rank sums) including two-stage linear step-up p-value correction as described by Benjamini et al.<sup>53</sup> were implemented to identify significant differences in distributions of  $k_{\text{att}}$  between sampling situations (SI Table S2). This ranked nonparametric test was used, because according to Shapiro-Wilk tests normality was not given in all distributions (SI Table S2). The significance levels ( $p$ ) for the correlations and the comparisons were set to 5%.

## RESULTS AND DISCUSSION

**TrOC Concentrations and Attenuation Rate Constants.** In general, TrOC concentrations at station A followed the discharge dynamics of the WWTP and showed diurnal fluctuations: For most TrOCs, low concentrations were observed around 7:00 am. Highest concentrations were usually observed in the afternoon (SI Figure S5). Generally concentrations found in River Erpe were comparably high. Average concentrations at station A exceeded the average concentrations measured in an EU-wide survey of 90 WWTP effluents for 1H-benzotriazole, carbamazepine, venlafaxine, irbesartan, tramadol, and the maximum measured concentrations for bezafibrate and diclofenac.<sup>4</sup> Guanylurea, valsartan, and 1H-benzotriazole were the most abundant compounds with average concentrations (min-max) of 68.8 (46–90)  $\mu\text{g L}^{-1}$ , 28.5 (17–38)  $\mu\text{g L}^{-1}$  and 10.7 (5.5–18)  $\mu\text{g L}^{-1}$  at station A ( $n = 96$ ), respectively (Table 1). These compounds were measured in the  $\mu\text{g}$ -range in river water previously.<sup>3,39,54</sup> Concentrations of the 17 TrOCs estimated by passive samplers (10- and 11-day time-weighted averages) were in the same order of magnitude as those measured by active sampling (SI Table S4). As expected, the medians and the distributions of  $k_{\text{att}}$  are compound-specific and may vary significantly between sampling situations. The highest median  $k_{\text{att}}$  was found for 4-hydroxydiclofenac in S1am (0.14  $\text{h}^{-1}$ , interquartile range (IQR) 0.30  $\text{h}^{-1}$ ). Continuous formation along the river sections was observed for metoprolol acid and valsartan acid as median net- $k_{\text{att}}$  values were negative in all situations (Figure 2).

The most persistent compounds were acesulfame, 1H-benzotriazole, carbamazepine, 10,11-dihydro-10,11-dihydroxycarbamazepine and O-desmethylvenlafaxine, all of them showing median  $k_{\text{att}} > -0.01 \text{ h}^{-1}$  and  $<0.01 \text{ h}^{-1}$  (IQR  $<0.04 \text{ h}^{-1}$ ) in all four situations (Table 1). Persistence of carbamazepine, acesulfame, and 1H-benzotriazole was reported previously and carbamazepine and acesulfame were used as conservative wastewater tracers in former studies.<sup>12,18,33,38,55</sup> Writer et al.<sup>33</sup> measured a  $k_{\text{att}}$  ( $\pm\text{SE}$ ) of  $0.033 \pm 0.009 \text{ h}^{-1}$  of carbamazepine in Boulder Creek, Colorado, which is slightly above the IQRs of  $k_{\text{att}}$  distributions measured in River Erpe (3rd Quartiles: 0.012–0.022  $\text{h}^{-1}$ ). Aymerich et al.<sup>37</sup> even found a slight increase in carbamazepine concentration in a receiving river in Spain reporting a  $k_{\text{att}}$  ( $\pm\text{SD}$ ) of  $-0.4 \pm 0.7 \text{ d}^{-1}$ , equivalent to  $-0.017 \text{ h}^{-1}$ , which is lower than the IQRs of  $k_{\text{att}}$  distributions in River Erpe (1st Quartiles:  $-0.010 - -0.003 \text{ h}^{-1}$ ). In contrast, Acuña et al.<sup>39</sup> reported a

carbamazepine half-life ( $\pm\text{SD}$ ) of  $4.1 \pm 2.4 \text{ h}$  measured as an average of four rivers in Spain, which converts to a  $k_{\text{att}}$  of  $0.17 \text{ h}^{-1}$ , that is an order of magnitude higher than the IQRs of  $k_{\text{att}}$  measured in the present study. This value is exceptional, also because many laboratory studies found low degradation of carbamazepine. No decay of carbamazepine was observed in a 30 day river-simulating flume study.<sup>38</sup> Also in a river sediment batch experiment carbamazepine was not significantly removed within 30 days.<sup>18</sup>

Acesulfame concentrations were relatively constant ( $-2.9 - 0.8\%$  relative attenuation) in four different rivers in Europe,<sup>38</sup> which compares well to  $0 - 3\%$  attenuation in the present study. However, interestingly acesulfame persistence in WWTPs was found to have decreased within the past decade because acesulfame degrading bacteria have evolved in WWTPs.<sup>56</sup> This effect is also conceivable for bacterial communities in rivers and might lead to observations of higher acesulfame in-stream  $k_{\text{att}}$ s in the future.

Although the corrosion inhibitor 1H-benzotriazole shows high concentrations in WWTP effluents in Europe,<sup>4</sup> to the best of our knowledge its in-stream attenuation has not been studied prior to our study. However, poor removal has been found in laboratory studies and in bank filtration.<sup>55,57</sup>

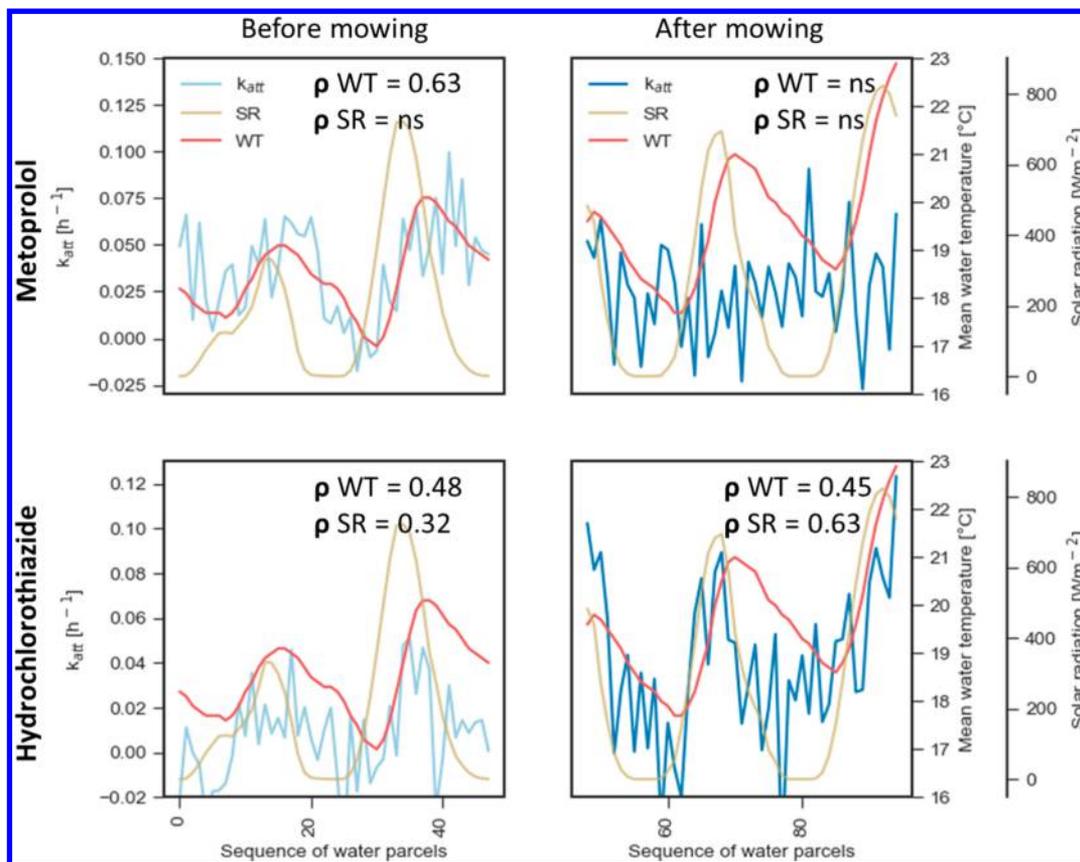
Relative attenuation and half-lives of all TrOCs are shown in SI Table S6. It has been reported previously, that passive samplers are a useful means to accompany in-stream attenuation studies and lead to similar results as obtained through high-resolution sampling.<sup>38</sup> A comparison of  $k_{\text{att}}$  for 11 (*bm*) and 10 days (*am*) obtained from passive samplers to median  $k_{\text{att}}$  in the 2-day sampling periods indicates the same trends between S1bm and S1am for 13 out of 17 compounds (SI Figure S6). Thus, differences in  $k_{\text{att}}$  attributed to macrophyte removal are not only a short-term phenomenon, but are also valid over an extended time period. A detailed discussion is provided in the SI.

**Environmental Conditions and Implications for Processes in the Sampling Situations.** In order to allow appropriate interpretation of the results, the differences in environmental conditions and implications for attenuation processes between the sampling situations have to be taken into account. Photolysis of TrOCs (both direct and indirect) is expected to be mainly driven by diurnal fluctuations of solar radiation within sampling-periods, changes in intensity of solar radiation between sampling periods and differences in shading between sections.<sup>22,40</sup> Biodegradation is more complex due to the variable nature of microbial communities and (co-) metabolic degradation processes.<sup>58</sup> However, the composition of communities is assumed to be relatively constant in diversity and in processing intensity due to the constantly high proportion of treated wastewater in the River Erpe. Hotspots of biodegradation occur mainly at ecohydrological interfaces, that is in biofilms at the surface of submerged macrophytes or in the hyporheic zone.<sup>20</sup> Hence, biodegradation is spatially variable, due to heterogeneous flow regimes and sediment properties and also temporally due to changing presence of macrophytes. In addition, microbial activity is sensitive to daily fluctuations in temperature as respiration and carbon consumption of microbial communities is closely related to temperature.<sup>59,60</sup> Similar to biodegradation, sorption is influenced by the availability of ecohydrological interfaces. Therefore, changes in macrophyte abundance and differences in hyporheic exchange might lead to differences in attenuation of TrOC sensitive to sorption processes, mainly compounds

**Table 2. Qualitative Implications for Biodegradation, Photolysis and Sorption Arising from Differing Spatial and Temporal Conditions in the Four Sampling Situations<sup>a</sup>**

	S1bm vs S1am	S1bm vs S2bm	S2bm vs S2am	S1am vs S2am
implications for biodegradation	higher in S1bm due to the biofilm on macrophytes and potential pumping effect, inducing higher hyporheic flow	higher in S1bm due to higher abundance of macrophytes and better conditions for transient storage	similar	slightly higher in S1am due to higher potential for transient storage
implications for photolysis	higher S1am, due to deeper penetration of the radiation without macrophytes and 47% higher solar radiation	low in both cases, due to in-channel shading by macrophytes in S1 and shading by tree canopies in S2	higher S2am, due to higher solar radiation	higher S1am, due to less shading by canopy
implications for sorption	higher in S1bm due to the biofilm on macrophytes and potential pumping effect, inducing higher hyporheic flow	higher in S1bm due to higher abundance of macrophytes and better conditions for transient storage	similar	slightly higher in S1am due to higher potential for transient storage
behavior of group 1	median $k_{att}$ higher in S1am	median $k_{att}$ higher in S1bm or similar	median $k_{att}$ higher in S2am	median $k_{att}$ higher in S1am
behavior of group 2	absolute value of median $k_{att}$ higher in S1bm	absolute value of median $k_{att}$ higher in S1bm	absolute value of median $k_{att}$ mostly slightly higher in S2am	absolute value of median $k_{att}$ higher in S1am
behavior of group 3	median $k_{att}$ higher in S1am	median $k_{att}$ similar	median $k_{att}$ similar	median $k_{att}$ higher in S1am

<sup>a</sup>S1bm vs S2bm means a spatial comparison under pristine macrophyte abundance. S1bm vs. S1am means a temporal comparison, including the effect of macrophyte removal. S2bm vs S2am means a temporal comparison without change in macrophyte abundance in section 2 but differences in solar radiation and water temperature. S1am vs. S2am means a spatial comparison after macrophyte removal. For comparison the behavior of groups of compounds is added below (group 1 = 4-hydroxydiclofenac, diclofenac, hydrochlorothiazide; group 2 = metoprolol, metoprolol acid, valsartan, valsartan acid; group 3 = metformin, guanylurea, bezafibrate).



**Figure 3.** Exemplary fluctuation in attenuation rate constants ( $k_{att}$ ), average water temperature (WT), and average solar radiation (SR) in the hourly sequence of 48 water parcels S1bm (starting 14.06.2016 23:00) and 47 water parcels S1am (starting 21.06.2016 18:00), respectively, comparing the compounds metoprolol and hydrochlorothiazide.  $\rho$  WT = Spearman correlation coefficient between  $k_{att}$  and average water temperature;  $\rho$  SR = Spearman correlation coefficient between  $k_{att}$  and average solar radiation. ns = no significant correlation.

that are positively charged at the prevailing pH of 7.8.<sup>24,33</sup> A more detailed discussion about the distinct relations between conditions and processes can be found in the SI.

The experimental setup produced two spatial comparisons (S1am vs S2am and S1bm vs S2bm) and two temporal comparisons (S1am vs S1bm and S2am vs S2bm). The differences in attenuation between the sections are expected to have been governed by the aforementioned characteristics: the higher ratio of shading in S2 is expected to generally have impaired photolysis compared to S1, especially *am*, when the macrophytes were not providing additional shading to S1. The higher potential for transient storage, in turn, is generally expected to have promoted biodegradation and sorption, especially *bm* when macrophytes contributed to the transient storage zone and provided more ecohydrological interfaces in S1. The temporal comparison *am* vs *bm* is governed by the removal of macrophytes in S1, but differences might also have been caused by higher solar radiation in the sampling period *am* compared to *bm*. The absence of macrophytes in S1am is expected to have reduced the potential for biodegradation and sorption compared to S1bm due to minimizing the filter-effect of macrophytes. However, as a result of the reduction of in-channel shading, the potential for photolysis was likely increased comparing S1am to S1bm. The abundance of macrophytes was generally low in S2 and no external changes took place, so differences between S2bm and S2am were probably for the most part caused by higher solar radiation *am*. A summary of the comparisons of the distinct environmental

conditions and their implication for the differences in attenuation processes in the four sampling situations is shown in Table 2. Differences in average ( $\pm$ SD) DOC (S1bm:  $11.0 \pm 0.9$  mg L<sup>-1</sup>; S1am:  $12.1 \pm 1.8$  mg L<sup>-1</sup>; S2bm:  $11.3 \pm 0.8$  mg L<sup>-1</sup>; S2am:  $12.1 \pm 1.5$  mg L<sup>-1</sup>), nutrient concentrations (e.g., Nitrate-N: S1bm:  $7.3 \pm 0.9$  mg L<sup>-1</sup>; S1am:  $6.8 \pm 0.6$  mg L<sup>-1</sup>; S2bm:  $7.2 \pm 0.8$  mg L<sup>-1</sup>; S2am:  $6.9 \pm 0.6$  mg L<sup>-1</sup>) and water temperature (S1bm:  $18.5 \pm 0.9$  °C; S1am:  $19.5 \pm 1.4$  °C; S2bm:  $18.6 \pm 0.9$  °C; S2am:  $19.9 \pm 1.8$  °C) between the sampling situations are low and the effects on fate of TrOCs are assumed to be negligible (SI Table S1).

**Influence of Diurnal Fluctuations in Solar Radiation and Water Temperature on TrOC Attenuation.** Environmental conditions may not only have varied between the sampling situations, but also within the single sampling-periods. Some of the high distributions of  $k_{att}$  within single sampling situations (e.g., 4-hydroxydiclofenac in S1am: IQR 0.30 h<sup>-1</sup>) are expected to have been caused by diurnal fluctuations in certain conditions. There were probably a multitude of parameters that controlled attenuation processes which varied within the 2 days of sampling and it remains challenging to capture the full picture. We chose to correlate solar radiation and water temperature to  $k_{att}$  as they are parameters that (1) are potentially strongly related to the fate of TrOCs, (2) vary considerably within hours, and (3) were easy to record continuously and reliably. High, significant correlations ( $\rho > 0.5$ ;  $p < 0.05$ ) were found for solar radiation and  $k_{att}$  of 4-hydroxydiclofenac in S1am ( $\rho = 0.66$ ;  $p < 0.05$ )

and hydrochlorothiazide in S1am ( $\rho = 0.63$ ;  $p < 0.05$ ) and S2am ( $\rho = 0.57$ ;  $p < 0.05$ ) and for water temperature and  $k_{\text{att}}$  of metoprolol ( $\rho = 0.63$ ;  $p < 0.05$ ), tramadol ( $\rho = 0.51$ ;  $p < 0.05$ ), sitagliptin ( $\rho = 0.59$ ;  $p < 0.05$ ), venlafaxine ( $\rho = 0.54$ ;  $p < 0.05$ ) and guanlylurea ( $\rho = 0.51$ ;  $p < 0.05$ ) in S1bm, as well as 4-hydroxydiclofenac ( $\rho = 0.57$ ;  $p < 0.05$ ) in S1am (Table 1, Figure 3).

**Attenuation of Single Compounds.** In this work only attenuation of TrOCs that exhibited significant differences between situations are discussed in detail along with related parent compounds or TPs, since they are most relevant for identification of processes driving attenuation (Table 1). These compounds are allocated to three groups according to their attenuation (median  $k_{\text{att}}$ ) behavior (Figure 2, Table 2). Group 1 (4-hydroxydiclofenac, diclofenac, hydrochlorothiazide) shows highest attenuation and correlation to solar radiation in S1am, additionally higher median  $k_{\text{att}}$  in S2am compared to S2bm. Group 2 (metoprolol, metoprolol acid, valsartan, valsartan acid) shows highest attenuation or formation in S1bm and generally lower attenuation or formation in S2 than S1. Group 3 (metformin, guanlylurea, bezafibrate) shows highest attenuation without high correlation to solar radiation in S1am and similar attenuation in the remaining situations. Sulfamethoxazole does not fit in either of the groups, but has been reported to be affected by both biodegradation and photolysis, including potential back-transformation.<sup>61,62</sup> The combination of processes might explain the high distribution of  $k_{\text{att}}$  of sulfamethoxazole in all situations and back-transformation might be responsible for net-formation in S2.

**Group 1: Diclofenac and Hydrochlorothiazide.** Diclofenac, its TP 4-hydroxydiclofenac and hydrochlorothiazide all behaved in a similar manner (Figure 2). Attenuation of all three compounds significantly increased in S1 following macrophyte removal and higher in S2am at higher average insolation, compared to S2bm. Both diclofenac and hydrochlorothiazide were previously reported to be highly photodegradable relative to other compounds.<sup>16,37,40</sup> The correlation of  $k_{\text{att}}$  in single water parcels with solar radiation confirms this. The highest observed  $\rho$  for correlation between solar radiation and  $k_{\text{att}}$  were found in S1am for diclofenac ( $\rho = 0.49$ ;  $p < 0.05$ ), 4-hydroxydiclofenac ( $\rho = 0.66$ ;  $p < 0.05$ ) and hydrochlorothiazide ( $\rho = 0.63$ ;  $p < 0.05$ ) and in S2am for hydrochlorothiazide ( $\rho = 0.57$ ;  $p < 0.05$ ) (Table 1).

While aerobic biodegradation of diclofenac has been reported and 4-hydroxydiclofenac was found to be its major oxidative biotransformation product,<sup>18,63</sup> several recent studies did not observe biotransformation.<sup>15,16</sup> The high correlation with solar radiation and the fact that 4-hydroxydiclofenac behaves similarly to its parent compound and mostly decreased along the reach suggests that photolysis remained the main degradation process in S1bm, S1am, and S2am. In S2bm, where least penetration of the surface water by solar radiation is expected (Table 2), median  $k_{\text{att}}$  of 4-hydroxydiclofenac were clearly negative indicating formation. This suggests a higher influence of biotic transformation of diclofenac to 4-hydroxydiclofenac in S2bm. To the best of our knowledge, the only other study reporting in-stream fate of both compounds was conducted by Aymerich et al.<sup>37</sup> comparing attenuation rates of a WWTP and its receiving river. They found  $k_{\text{att}}$  ( $\pm$ SD) of  $0.8 \pm 0.9 \text{ d}^{-1}$  ( $0.03 \text{ h}^{-1}$ ) for diclofenac and  $4.4 \pm 1.7 \text{ d}^{-1}$  ( $0.18 \text{ h}^{-1}$ ) for 4-hydroxydiclofenac in a 4 km-reach which compare very well with the median  $k_{\text{att}}$  of  $0.04 \text{ h}^{-1}$

(IQR  $0.08 \text{ h}^{-1}$ ) for diclofenac and  $0.21 \text{ h}^{-1}$  (IQR  $0.30 \text{ h}^{-1}$ ) for 4-hydroxydiclofenac in S1am in the present study.

Hydrochlorothiazide was previously found to transform to chlorothiazide (among other TPs) even under abiotic, dark control conditions by hydrolysis.<sup>17,18</sup> Compared to abiotic transformation, microbial transformation of hydrochlorothiazide plays a minor role.<sup>16,18</sup> Nevertheless, hydrolysis and biotransformation are expected to be of little importance compared to photolysis of hydrochlorothiazide. A river-simulating flume study under dark conditions resulted in a  $k_{\text{att}}$  of  $0.0005 \text{ h}^{-1}$  of hydrochlorothiazide, which is up to 2 orders of magnitude lower than the rate constants in the present study.<sup>17</sup> In addition the high correlation of hydrochlorothiazide with solar radiation in all four situations shows the prevalence of photolysis as major degradation process. In contrast to diclofenac and its TP, the behavior of chlorothiazide does not resemble the attenuation of hydrochlorothiazide and might be a result of more complex transitions of processes. This is in agreement with the suggestion that chlorothiazide is likely an intermediate in the transformation sequence of hydrochlorothiazide and other TPs.<sup>38,63</sup>

The findings for group 1 compounds show that their attenuation was governed by photolysis and their attenuation pattern is in accordance with the expectations for photolysis in Table 2. Interestingly, in S1am all three compounds show significant correlation ( $\rho = 0.44, 0.52, 0.45$ , and  $0.33$  respectively;  $p < 0.05$ ) with water temperature as well, which may be explained by the fact that quantum yield, and thus photolysis rate increases with water temperature.<sup>64</sup> The high correlation of hydrochlorothiazide attenuation with solar radiation (Figure 3) makes it a potential future candidate for tracing intrinsic photolytical processes in contaminated rivers.

**Group 2: Metoprolol and Valsartan.** Metoprolol and valsartan show behavior similar to each other. Despite higher solar radiation and higher water temperature in S1am compared to S1bm, their attenuation was highest in S1bm (significantly in the case of metoprolol) indicating the prevailing role of macrophytes. Their attenuation is generally higher in S1 compared to S2 and in S2 attenuation does not differ considerably *bm* compared to *am* (Figure 2). In several previous studies valsartan and metoprolol were found to be biodegradable.<sup>18,19,36,63,65</sup>

The  $\beta$ -blocker metoprolol is not sensitive to photolysis.<sup>16</sup> It is mostly cationic at ambient pH of 7.8, potentially facilitating sorption via electrostatic interactions to negatively charged surfaces. Both processes can be promoted by hyporheic exchange and by high abundance of biofilm and are normally hard to distinguish in the field.<sup>17–19</sup> Hence, it is conceivable that the higher attenuation in S1 compared to S2 is caused by biodegradation and/or sorption. However, when macrophytes were present in S1bm, where particularly high attenuation was found, a strong correlation of  $k_{\text{att}}$  to water temperature was observed. Since sorption is commonly inversely correlated with temperature, it is likely not the main removal process in this situation.<sup>66,67</sup> In addition, other positively charged compounds (metformin, guanlylurea, tramadol, soatalol, sitagliptin, except for venlafaxine) show comparably low median  $k_{\text{att}}$  ( $<0.01 \text{ h}^{-1}$ ; IQR  $< 0.06 \text{ h}^{-1}$ ) in S1bm and higher median  $k_{\text{att}}$  in S1am. This indicates that higher abundance of epiphytic biofilm and thus negatively charged binding sites generally did not increase the attenuation of positively charged compounds. We can conclude that in S1bm biodegradation is most likely the

governing process for increased metoprolol attenuation caused by the presence of macrophytes. We suspect that epiphytic biofilms are mainly responsible for the degradation and the correlation of degradation with temperature of metoprolol in S1bm. The fact that even after removal of macrophytes, degradation was higher in S1 compared to S2 indicates that a generally larger transient storage zone in S1 contributes to higher attenuation by biodegradation or sorption of metoprolol considerably. In a flume-experiment without macrophytes conducted by Li et al.<sup>17</sup> an average  $k_{att}$  of  $0.005\text{ h}^{-1}$  was measured for metoprolol, which is very close to the median  $k_{att}$  of  $0.006\text{ h}^{-1}$  (IQR  $0.03\text{ h}^{-1}$ ) found in the present study in S2bm.

Metoprolol acid is a biotransformation product<sup>65</sup> and shows a net-negative median  $k_{att}$ , hence, net-formation. “Mirroring” the degradation of metoprolol, median formation was highest in S1bm and lowest in S2bm. However, metoprolol acid is not only formed by metoprolol transformation, but also derives from, for example, atenolol degradation.<sup>68</sup> Despite metoprolol acid being the major TP of metoprolol, metoprolol transforms into a set of other TPs as well.<sup>69</sup> That is why despite the structural resemblance no mass balance between metoprolol degradation and metoprolol acid formation is possible. In contrast to metoprolol, no significant relation of metoprolol acid formation to water temperature was observed. This suggests that formation in the hyporheic zone, which has been reported earlier,<sup>17</sup> may be of higher importance than epiphytic biofilm. Due to temperature dampening, the correlation of water temperature and biodegradation is expected to be less pronounced in the hyporheic zone compared to the surface water.<sup>70</sup> For the second TP of metoprolol,  $\alpha$ -hydroxymetoprolol, attenuation overweighs formation. No significant differences between situations and no significant correlations with temperature or radiation were found, indicating that attenuation pathways are more complex than for metoprolol. Batch experiments indicated that  $\alpha$ -hydroxymetoprolol is less persistent than metoprolol acid.<sup>63,69</sup> In addition, in a field study comparing TrOC fate in four rivers, formation of metoprolol acid was observed in two rivers, whereas attenuation of  $\alpha$ -hydroxymetoprolol was found in all four rivers. These findings are in line with the observation of the present study.

Valsartan did not undergo abiotic transformation or sorption to sludge in batch experiments, neither has it been reported to undergo photolysis.<sup>68,71</sup> Despite its resemblance in behavior to metoprolol, its  $k_{att}$  did not correlate to water temperature and did not differ significantly *bm* and *am*. However, its attenuation was generally higher in S1 than S2, which can be attributed to biodegradation enhanced by the larger transient storage zone in S1. Noedler et al.<sup>71</sup> showed that valsartan biodegradation increased in solutions with higher effluent portion. In contrast, metoprolol biodegradation decreased with higher effluent portion. This confirms the idea that valsartan might be degraded by a different community (e.g., sediment) than metoprolol (e.g., epiphytic biofilm). Despite its high relevance (valsartan concentrations were six times higher than metoprolol concentrations), in-stream fate of valsartan has been rarely studied. Only Acuña et al.<sup>39</sup> measured valsartan concentrations in four different rivers and found average  $k_{att}$  of  $0.32\text{ h}^{-1}$ , which is an order of magnitude higher than the  $k_{att}$  observed in the present study (Table 1). The authors found that the process of valsartan removal is linked to phosphorus

dynamics. However, no correlation to phosphorus attenuation was found in the present study (data not shown).

Similar to metoprolol acid, valsartan acid resembles the degradation of its parent compound in its formation patterns (Figure 2). Higher formation was observed in S1 than S2, no temperature-dependence was found and removal of macrophytes did not impact the formation, indicating again biotransformation in the hyporheic zone. However, the compound has a set of other parent compounds in the sartan-group<sup>12</sup> (e.g., irbesartan) and the transformation sequence deriving from valsartan has at least two intermediates.<sup>68</sup> Therefore, relation between attenuation of valsartan and formation of valsartan acid remains speculative. While metoprolol acid was reported to show limited persistence,<sup>63,65</sup> valsartan acid was found to be more persistent.<sup>12,65</sup> In our experiment, formation of both compounds was generally in the same order of magnitude, indicating that the residence time was too short for an onset of metoprolol acid degradation, and further formation of valsartan acid at longer travel times is conceivable. The environmental relevance of valsartan acid due to its high concentrations, potential formation in ecosystems and high persistence has been highlighted earlier.<sup>12,65,68</sup> However, to the best of our knowledge, this is the first time in-stream formation of valsartan acid was described and studied in situ. The findings for group 2 compounds show that their attenuation and formation were governed by biodegradation and their behavior is in accordance with the expectations for biodegradation in Table 2.

**Group 3: Metformin and Bezafibrate.** Metformin and its biodegradation product guanylurea show generally low attenuation under the studied conditions. Trautwein et al.<sup>72</sup> tested aerobic transformation of both compounds and concluded that most of the transformation from metformin to guanylurea is likely happening in the WWTP and is unlikely in the aquatic environment. Due to the high concentration of guanylurea compared to metformin at station A (approximately 40:1, Table 1), our study confirms high transformation prior to discharge into River Erpe. Also the observed median  $k_{att}$  of both compounds are in the range of those of carbamazepine ( $<0.01\text{ h}^{-1}$ ) and are therefore relatively persistent in S1bm, S2bm, and S2am. However, for both compounds higher attenuation was found in S1am, significantly for guanylurea. In contrast to diclofenac and hydrochlorothiazide, their attenuation is not related to solar radiation and studies show that photolysis does not affect their fate in surface waters.<sup>72</sup> Guanylurea is expected to be a dead-end bio-TP and even breakdown by ozone is limited.<sup>73</sup> Both compounds are positively charged under ambient pH and electrostatic binding to negatively charged soil particles was reported previously.<sup>74</sup> Hence, sorption could be a reason for the increased attenuation in S1am. A possible explanation is a higher contact to specific binding sites caused by disruption of the upper sediment layer by the mowing machines. Bezafibrate again shows similar behavior but is negatively charged. It was found to show abiotic hydrolytic reaction and biotransformation previously.<sup>17,65</sup> The distinct processes causing the attenuation pattern of group 3 remain a subject of speculation and might be of different nature for bezafibrate and metformin/guanylurea. Little research has been done on the environmental fate of guanylurea so far, despite its particularly high concentrations and unknown toxicity.<sup>46</sup> Further studies are needed to elucidate its degradation behavior.

**General Within-Stream Variability.** The methods applied in the present studies are associated with different uncertainties inherent in field experiments and only a selection of possible environmental drivers for the fate of TrOC could be investigated. A discussion about limitations can be found in the SI. Nevertheless, the present study shows that spatially different and temporally changing conditions within a river influence attenuation processes. They result in a range of river-specific  $k_{\text{att}}$  values rather than single values. Although the behavior of TrOCs was compound-specific, some general statements about the differences between sections, the effect of macrophyte removal and the influence of diurnal changes are possible.

- A clear difference between sections was found. Shading by canopy in S2 was seen to clearly reduce breakdown of photosensitive compounds (group 1) compared to S1am. The effect of shading by submerged macrophytes in S1bm showed similar (hydrochlorothiazide) or lower effect (diclofenac) than shading by the canopy in S2bm. Higher potential for transient storage in S1 lead to higher attenuation/formation of the biodegradable/bioformable compounds (group 2) in S1 compared to S2 both *bm* and *am*.
- Macrophyte removal had different effects: The decreased macrophyte-induced shading of the channel increased the photolysis of photosensitive compounds. At the same time, it decreased the attenuation of metoprolol significantly, which has likely occurred on epiphytic biofilm. Other compounds exhibited high correlation of  $k_{\text{att}}$  with water temperature in S1bm even at low  $k_{\text{att}}$  values (guanylurea, sitagliptin, tramadol, venlafaxine) (Table 1). This leads to the assumption that the presence of macrophytes generally promoted the influence of temperature on biodegradation. The impact of macrophytes on drivers of TrOC attenuation is highlighted by the fact, that high correlation with solar radiation is primarily seen in S1am and high correlation with water temperature, in contrast, mostly in S1bm.
- Diurnal changes of solar radiation had significant influence on the breakdown of photosensitive compounds, especially in the situation of least shading (S1am). Water temperature in particular influenced attenuation of metoprolol in the situation of high macrophyte density (S1bm).

In-stream fate of some compounds of high environmental concern, for example, guanylurea, 1H-benzotriazole, and valsartan acid were reported here for the first time. Further studies on their environmental fate are of great importance. Some of the variation in TrOC attenuation in the River Erpe could be explained by changes in environmental conditions and lead to identification of situation-dependent attenuation processes. Therefore, we propose within-stream attenuation studies as opposed to between-streams studies as a valuable means to better identify transformation processes. Eventually better understanding of in-stream attenuation processes of TrOCs will improve the predictability of their environmental fate and benefit both regulatory decision making and river management.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05488.

Background data; deconvolution method; concentration curves of selected TrOCs; discussions on relation of attenuation processes to environmental conditions; passive sampling methods and results; details on  $k_{\text{att}}$  distributions (PDF)

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### Notes

The authors declare no competing financial interest.

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