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Seasonal Differences in the Attenuation of Polar Trace Organics in the Hyporheic Zone of an Urban Stream

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Key Points:

- The attenuation of 12 out of 18 trace organic compounds (TrOCs) in the hyporheic zone was higher in winter while three TrOCs were attenuated better in summer
- Residence times in sediment were longer and more diverse in winter
- The extent of the oxic sediment was similar between seasons but the gradient from the oxic to anoxic zone was steeper in winter

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Attenuation of trace organic compounds (TrOCs) in a river occurs to a large extent in its hyporheic zone. A major part of the attenuation of polar TrOCs is of microbial origin. As microbial activity depends on temperature and redox conditions, seasonal differences in TrOC attenuation are likely. We investigated TrOC attenuation at a river influenced by treated wastewater during two sampling campaigns, one in summer and one in winter. In addition to redox conditions and temperature, we also determined residence times of porewater in sediment using three methods: (a) non-parametric deconvolution of electrical conductivity time series, (b) the model VFLUX 2.0 based on temperature time series (only summer), and (c) applying Darcy's law to differences in hydraulic heads (only summer). Contrary to our expectations, we found higher attenuation for 12 out of 18 TrOCs in winter, while three TrOCs were better attenuated in summer. Sediment conditions varied between seasons as more of the top sandy layer with a higher hydraulic permeability accumulated on the river bed in summer. As a result, residence times in the sediment were shorter in summer. In winter, longer residence times, lower temperatures, and a steeper oxygen gradient in sediment coincided with higher TrOC attenuation. Further research is needed to understand our unexpected findings and underlying mechanisms.

1. Introduction

Trace organic compounds (TrOCs) occur widespread in the environment (Barbosa et al., 2016) including freshwaters. They can be harmful for aquatic life and can alter aquatic ecosystems (Malaj et al., 2014). Furthermore, TrOCs are found in drinking water resources (Putschew et al., 2000; Ruff et al., 2015; Troger et al., 2020). TrOCs enter the aquatic environment via different pathways, for example with discharge of treated wastewater to rivers (Petrie et al., 2015). Once in a river, possible attenuation pathways of TrOCs include biodegradation, sorption (de Wilt et al., 2018), hydrolysis, or photolysis (Herrmann et al., 2015).

A hotspot of TrOC attenuation in a stream is the hyporheic zone (Peralta-Maraver et al., 2018; Schaper et al., 2018). We define the hyporheic zone as the part of the streambed which comprises all flow paths beginning and ending at the streambed surface (Lewandowski et al., 2019). Steep hydrological and biogeochemical gradients, a large surface area, and high microbial activity (Lewandowski et al., 2019) characterize this interface between surface water (SW), sediment, and groundwater.

The attenuation of polar TrOCs in a stream is mainly due to biotransformation (Alidina, Li, Ouf, et al., 2014). In general, microbial activity is higher under warmer compared to colder conditions (Kaplan & Bott, 1989). Accordingly, some previous studies on temperature influence on TrOC attenuation showed elevated removal at warmer temperatures, for example, in a wastewater treatment plant (WWTP; Zhang et al., 2018) or in the SW of a river-lake system (Meierjohann et al., 2016). However, other studies, for example, on a managed aquifer recharge system (Alidina et al., 2015) or a membrane bioreactor plant (Trinh et al., 2016), observed increased attenuation under warm conditions for only some TrOCs while other TrOCs were attenuated independent of temperature or even better at colder temperatures.

Besides temperature, redox conditions can also impact the attenuation of TrOCs. Many polar TrOCs are better attenuated under oxic or suboxic (nitrate present) than anoxic conditions (Schaper et al., 2018). Few TrOCs are

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better attenuated under anoxic conditions (El-Athman et al., 2019; Grünheid et al., 2005) and for some TrOCs, attenuation is independent of oxygen availability (Bertelkamp et al., 2016).

Oxygen concentrations in a stream are also temperature dependent: The solubility of oxygen in water increases as water temperature decreases. As a result, a lower oxygen solubility in SW and an increased microbial activity consuming oxygen might lead to a smaller extent of the oxic zone in the streambed during warmer compared to colder temperatures. Therefore, TrOC attenuation in summer could either be reduced due to limited oxygen availability or promoted as a result of higher microbial activity in the hyporheic zone.

Attenuation pathways which are only relevant for some polar TrOCs are sorption or photolysis. While a variety of previous studies found sorption to be negligible or limited for polar TrOCs (Alidina, Li, Ouf, et al., 2014; Drewes et al., 2014; Huntscha et al., 2013), some studies observed retardation (Schaper et al., 2019) of TrOCs in and sorption to sediment (de Wilt et al., 2018; Riml et al., 2013). Photolysis was reported for a few polar TrOCs (Zhang et al., 2018) while the majority showed persistency to photodegradation (Jaeger et al., 2019; Kunkel & Radke, 2012).

Another parameter which can strongly influence TrOC attenuation is residence time of a substance in a system where it can potentially be transformed, such as the hyporheic zone. Longer residence times lead to a more efficient attenuation of TrOCs in previous studies (Drewes, 2009; Grünheid et al., 2005). Seasonal changes in meteorological conditions impact hydrological conditions in a stream, which in turn might influence the residence time of contaminated water in the hyporheic zone. For SW, a dominating effect of seasonal changes in discharge on the attenuation of TrOCs has already been observed (Mandaric et al., 2019).

Previous studies on seasonal differences in TrOC attenuation focused on WWTPs (Kahl et al., 2018), bank filtration (Munz et al., 2019), managed aquifer systems (Alidina et al., 2015), SWs of freshwater systems (Meierjohann et al., 2016), or lab studies such as soil columns (Burke et al., 2014). To the best of our knowledge, the hyporheic zone of a real stream was not among these environments for which seasonal changes in the fate of TrOCs as well as changes in temperature, redox conditions, and residence time were examined. Therefore, the aim of the present study is to close this knowledge gap and investigate seasonal differences in TrOC attenuation in the hyporheic zone of an urban lowland stream. For the highest contrast in environmental conditions, two sampling campaigns following the same protocol were conducted, one in winter and one in summer. We hypothesize that the attenuation of TrOCs in the hyporheic zone of an urban stream is higher in summer than in winter. This hypothesis is based on the assumption that biogeochemical turnover processes are promoted by warmer conditions (Sharma et al., 2012).

2. Materials and Methods

2.1. Study Site

Our study site (52.476437 N, 13.625765 E, Figure S1 in Supporting Information S1) is located at a side channel of the River Erpe, which is a sandy lowland river in the East of Berlin, Germany. A WWTP discharges its effluents to the River Erpe, contributing 60%–80% to the river's discharge (Schaper et al., 2018). Receiving diurnally fluctuating amounts of treated wastewater results in daily fluctuations of discharge, temperature, electrical conductivity (EC), and TrOC concentrations (Schaper et al., 2019) in the river. In contrast to the main river, where TrOC concentrations fluctuate diurnally depending on discharge (Jaeger et al., 2019), there is no clear diurnal pattern of TrOC concentrations in the side channel. Reasons are the long travel time of treated wastewater from the WWTP to the study site, dispersion, temporal retention in stagnant pools, and sorption-desorption processes upstream of the sampling site (Mueller, Schulz, Danczak, et al., 2021).

The side channel branches off the River Erpe 700 m after the outlet of the WWTP. Macrophyte growth strongly decreased the cross sectional area of the side channel in summer while the channel remained almost completely free of plants in winter. Therefore, mean water level was about twice as high in summer than winter although mean discharge and maximum flow velocity of the free flowing SW were higher in winter (Table 1). In addition, emersed macrophytes in the channel created almost stagnant zones in summer. More sand accumulated in the middle of the channel cross section in summer, making the top sandy layer in the center of the channel thicker than in winter. On both sampling days, the weather was mostly sunny with warmer air temperature in summer than winter (Table 1).

Table 1
Hydrological and Meteorological Parameters of the Side Channel Given as Arithmetic Mean (Sample Size n, Minimum-Maximum)

Parameter	Winter	Summer
Water level [cm]	16.1 (1,440, 13.6–17.8)	30.2 (1,440, 26.5–32.8)
Discharge [l/s]	78.6 (1,440, 38.8–105.7)	51.1 (1,440, 28.1–65.0)
Maximum flow velocity [m/s]	0.47 (8, 0.45–0.49)	0.34 (7, 0.32–0.36)
Air temperature [°C]	0.3 (1,440, −2.5–9.3)	20.5 (1,440, 12.9–29.6)
Water temperature [°C]	6.4 (1,440, 4.6–8.0)	21.1 (1,440, 19.6–22.7)

Note. Water level, water temperature, and air temperature continuously measured at the study site between 00:00–23:59 on each sampling day, point measurements of maximum flow velocity and discharge 15 m upstream of study site: 10:30–17:30 during winter sampling, 8:30–12:30 during summer sampling.

2.2. Sampling Campaigns

In order to compare TrOC attenuation between the coldest and warmest season, we conducted a sampling campaign following the same protocol on 31st of January (winter) and 08th of August 2019 (summer). As discharge of the WWTP Münchehofe changes with the day of the week and can be particularly different between working days and weekends, both sampling campaigns were planned for a Thursday.

To sample pore water along a depth profile, HPLC tubes (PEEK, inner diameter 0.76 mm, Sigma-Aldrich) were attached to three metal sticks: Tubes in 2, 8, 14, and 20 cm depth to stick A, tubes in 4, 10, and 16 cm depth to stick B, and tubes in 6, 12 and 18 cm depth to stick C. These sticks were installed vertically in the sediment and arranged in a triangle with 15 cm distance to each other. This setup was chosen to reach a high depth resolution but avoid that sampling impacts neighboring sampling ports and to account for heterogeneous flow paths in the sediment. We took 30 ml pore water samples with a sampling rate of 2 ml/min using syringe pumps attached to the pore water tubes and additional SW samples every hour for 7 hr ($n = 8$). Samples were taken at time points which covered the same part of the fluctuating discharge regime during both seasons. Samples from 6 to 12 cm depth showed signs for preferential flow of SW to the sampling ports in the sediment in winter. Affected samples were therefore either excluded or interpolated between depths, depending on the data analysis method.

2.3. Sediment Analysis

After both sampling campaigns, sediment cores ($n = 3$) were taken at the location of the pore water sampling sticks and of CTD divers ($n = 2$, only in summer, Section 2.4) using 60 cm long PVC pipes (inner diameter = 5.8 cm). From the uppermost part of each of the visually distinguishable layers in each sediment core, undisturbed sediment samples were transferred to a 5 cm high metal ring (inner diameter = 5 cm). Saturated hydraulic conductivities (K_S) of the samples were measured with a KSAT meter (KSAT, Meter Group) and normed to 10°C. Thermal properties needed for VFLUX 2.0 modeling were measured with a thermal properties analyzer (KD2 Pro, Decagon Devices Inc.). Afterward, sediment from the metal rings was dried and grain size distribution was determined by sieving. After grinding and homogenizing, total carbon was analyzed with high-temperature decomposition (vario El III Element Analyzer, Elementar Analysensysteme). Winter sediment data were already reported in Mueller, Schulz, Danczak, et al. (2021).

2.4. Hydrology and Determination of Residence Times

EC, temperature, and pressure were measured with CTD divers (length: 13.5 cm, diameter: 2.1 cm, width of EC measuring chamber: 1.7 cm; Van Essen Instruments B.V., Netherlands), and the latter two parameters with TD divers of the same company. Water level was obtained with two CTD divers fixed in the water column and corrected for atmospheric pressure measured by a Baro diver (Van Essen Instruments B.V.).

A handheld discharge meter (OTT MF Pro, OTT HydroMet) was used to measure discharge and flow velocity repeatedly, covering the whole range of water levels on the sampling day. Discharge measurements were conducted approximately 15 m upstream of the main sampling site where the channel cross section was more suitable

for discharge measurements. Pressure data from divers and discharge data from the discharge meter were used to calculate one rating curve per season.

Residence times of water in the hyporheic zone between SW and different depths of the streambed were calculated with (a) nonparametric deconvolution of EC time series (1 hr moving averages) in both seasons. To check the reliability of this method, we additionally applied the following two methods in summer: (b) VFLUX 2.0 based on temperature time series, and (c) Darcy's law using differences in hydraulic heads.

1. Deconvolution: In order to measure EC in SW and pore water, two (three in summer) CTD divers were installed in the water column and in each of the following sediment depths: 4, 8, 12, 16, and 20 cm. To prevent sediment from entering the measuring chamber, divers were covered with a nylon mesh before inserting them vertically with the tip facing downward in the sediment. Divers were installed randomly in an area of 0.25 m^2 two or seven days before the sampling campaign in winter or summer, respectively. The residence time distribution (RTD) between SW and each depth was determined by applying nonparametric deconvolution to the two respective electrical conductivity time series following Cirpka et al. (2007). In brief, the deconvolution method generates nonparametric RTD function estimates using a geostatistical method for smoothing and Lagrange multipliers for nonnegativity. We generated 250 realizations for each depth investigated. For each of the 250 computed RTDs per depth, temporal moment analysis of the RTD was applied after Cirpka and Kitanidis (2000) to calculate mean pore water velocities and mean residence times from SW to each sediment depth.
2. VFLUX 2.0: A temperature lance (Umwelt- und Ingenieurtechnik GmbH Dresden) with temperature sensors in 0, 5, 20, 22, 25, 30, and 60 cm depth was inserted into the sediment to measure time series of temperature depth profiles in pore water for 17 days. The MATLAB based model VFLUX 2.0 (Gordon et al., 2012) applies a 1D analytical method of the heat transport model by McCallum et al. (2012). This method is based on amplitude and phase shift of temperature time series to calculate vertical seepage fluxes along a vertical flow path. VFLUX 2.0 uses sediment properties, for example, porosity and thermal properties (see 1.4 Sediment analysis) as input parameters. Obtained fluxes were then used to calculate the residence time to each sediment depth investigated.
3. Darcy: Two pressure devices were installed in summer. Tubes with an inner diameter of 4 mm were inserted in 5, 7, 10, 15 (or 12), and 20 cm depth in the sediment and another tube had its opening in the SW. The other end of each tube was attached to a fixed syringe containing a TD diver each. It was assured that all syringes (divers) were located in exactly the same water depth of the side channel. As the syringe-tube systems were completely filled with water, measured pressures represented the pressure in the sediment depth of the corresponding port. Darcy's law was then applied to calculate vertical seepage velocity v_s from SW to each sediment depth x with corresponding hydraulic head h, distance between measuring points l, porosity Φ, and saturated hydraulic conductivity K_s of the sediment (Equation 1). Residence time of infiltrating water was calculated between surface water and each depth investigated using these seepage velocities.

$$v_s = \frac{K_s * \frac{h_{SW} - h_x}{l}}{\Phi} \quad (1)$$

Using three different methods enabled us to compare resulting residence times based on electrical conductivity, temperature, and pressure time series along depth profiles in summer. All methods come with individual uncertainties and using multiple methods allows for clarifying whether calculated residence times are independent of the method. Methods (b and c) assume a vertical flow path through the sediment and result in a mean residence time. In contrast, method (a) uses the whole RTD which considers the heterogeneity of flow paths. Note that applying the temporal moments analysis to the RTDs results in a vertical flow path assumption making the results of (a) comparable to the results of (b and c).

The general flow direction is downwards during both seasons. This is indicated by daily fluctuations of EC in surface water which proceed down to the different pore water depths. As these fluctuations were hardly dampened in the sediment, there was no impact of groundwater down to 20 cm depth. This justifies calculating residence times and TrOC attenuation along downward flow paths.

In summer, accumulation of sediment led to a change of the depth of buried CTD sensors over time. We assume that the accumulation occurred temporally uniform and that residence time estimations are least prone to bound-

ary effects in the middle of analyzed time series. Therefore, the depths of these sensors were corrected with half of the sediment height accumulated in the course of the experiment.

2.5. Chemical Analysis

Water samples were filtered (regenerated cellulose, 0.2 µm) and analyzed for 18 TrOCs using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS, TSQ Vantage, Thermo Fisher Scientific) at the Chair of Water Quality Engineering, Technische Universität Berlin. See Text S1 in Supporting Information S1 for further details.

Oxidation-reduction processes during infiltration are strongly determined by microbial activity and usually lead to a redox zonation of the sediment (Wang et al., 2020). As oxygen availability is one major factor for the attenuation of trace organic compounds (Schaper et al., 2018), redox conditions in surface water and sediment were monitored. Flow through cells with optodes (FTCM-PSt7, PreSens) were attached to the pore water sampling tubes and fixed in the surface water to assure stable temperature conditions. Oxygen concentrations in surface water were measured with a miniDOT data logger (Precision Measurement Engineering, Inc.). Filtered water samples were further analyzed for the redox sensitive parameters dissolved iron and manganese (inductively coupled plasma optical emission spectrometry (ICP-OES) ICP iCAP 6000series, Thermo Fisher Scientific), as well as nitrate and sulphate (samples acidified to pH 2 with 2 M HCl; ion chromatography, Metrohm 930 Compact IC Flex) in the laboratory of the Leibniz Institute of Freshwater Ecology and Inland Fisheries.

Boron can be used as a tracer for treated wastewater in a stream as it is an ingredient in cleaning products (Hyer, 2007). We estimated differences in the proportion of treated wastewater on total stream discharge by comparing TrOC and boron concentrations in surface water between seasons. Boron was analyzed with ICP-OES (ICP iCAP 6000series, Thermo Fisher Scientific Inc., USA). We further analyzed the samples for dissolved organic carbon (DOC, NDIR after combustion (*TOC/TN Analysator, Shimadzu)) and measured absorbance spectra (250–600 nm, interval: 5 nm, UV-2401 PC, Shimadzu). The specific ultraviolet absorbance (SUVA) is a proxy for aromaticity of DOC and was calculated by dividing the absorbance at 254 nm by the DOC concentration (Hansen et al., 2016).

2.6. Data Analysis

TrOC concentrations were normalized in order to be able to compare the occurrence of TrOCs along depth profiles in the hyporheic zone between seasons. We applied the minimum-maximum normalization, which calculates a normalized value $x_{i,\text{normalized}}$ from the ith measured value $x_{i,\text{measured}}$ by using the measured minimum x_{min} and maximum values x_{max} of a single TrOC (Equation 2). Normalized TrOC concentrations were used to plot depth profiles, grouped by TrOC and season.

$$\boldsymbol{x}_{i,\text{normalized}} = \frac{\boldsymbol{x}_{i,\text{measured}} - \boldsymbol{x}_{\text{min}}}{\boldsymbol{x}_{\text{max}} - \boldsymbol{x}_{\text{min}}} \tag{2}$$

To test whether depth profiles of a TrOC are significantly different between seasons, we applied the aligned rank transform (ART) procedure (Hodges & Lehmann, 1962) using the R package ARTool (Kay & Wobbrock, 2020) with subsequent two-way repeated measures ANOVA on measured TrOC concentrations in each sampling depth. The significance level was predefined at 0.05. A non-parametric test was chosen because visual comparison of sample quantiles with theoretical quantiles (quantile-quantile plots) of measured TrOC concentrations at each sampling depth did not reveal normal distribution. To ensure correctness of the ART procedure, the sum of every column of aligned responses was calculated. In case of a correct calculation, this sum should be 0 (Wobbrock et al., 2011). As the ART procedure cannot deal with missing values, concentrations were interpolated between depths if preferential flow was suspected or a sample could not be taken (winter: all samples from 6 to 12 cm depth, sample in 2 cm depth at 12:30, summer: sample in 18 cm depth at 18:00).

In order to compare attenuation of TrOCs between summer and winter, attenuation was calculated as the proportional change a in concentration c between SW and (a) x cm sediment depth (Equation 3), and (b) only 20 cm sediment depth (Equation 3 with $x = 20$ cm).

$$\boldsymbol{a}_{x-\text{SW}} = \frac{\boldsymbol{c}_{\boldsymbol{x}} - \boldsymbol{c}_{\text{SW}}}{\boldsymbol{c}_{\text{SW}}} \tag{3}$$

Table 2
Sediment Parameters in Two Visually Distinguishable Layers (Bright: 0–5 cm and Dark: 12–21/23 cm) Per Season

Sample depth [cm]	K_S (normalized to 10°C) [m/s]	Porosity	Grain size distribution (gravel, sand, silt + clay) [%]	Total carbon [wt%]
Winter				
00–05	1.61E-04 (1.12E-04–3.71E-04)	0.32 (0.32–0.35)	13.7, 85.8, 0.5 (12.9–14.4, 84.8–86.9, 0.4–0.8)	0.5 (0.1–0.9)
12–21	4.53E-05 (9.26E-06–1.16E-04)	0.45 (0.44–0.45)	3.8, 94.7, 1.5 (2.4–5.1, 93.1–96.6, 1.1–2.0)	1.4 (1.1–2.0)
Summer				
00–05	8.37E-05 (4.19E-05–1.48E-04)	0.42 (0.41–0.43)	0.1, 99.8, 0.1 (0.1–0.2, 99.7–99.9, 0.1–0.2)	<0.5 (–)
12–23	1.14E-05 3.01E-06–1.33E-05	0.43 (0.43–0.44)	0.9, 98.7, 0.4 (0.1–1.9, 97.7–99.7, 0.3–0.4)	0.6 (0.5–0.9)

Note. Given are arithmetic mean (minimum – maximum) for each parameter. K_S = saturated hydraulic conductivity. $n = 3$, except for K_S in winter where $n = 2$.

A negative value for $\boldsymbol{a_{x-SW}}$ therefore means a decrease in concentration while a positive value represents an increase in concentration. If the concentration of a TrOC was below detection limit in the surface water and increased to a value above detection limit in the lower depth x, we set the respective attenuation value $\boldsymbol{a_{x-SW}}$ to 100%. For a better overview, we grouped all TrOCs into categories according to seasonal differences in surface water concentrations and $a_{sw-20cm}$. We compared these parameters using a Wilcoxon signed-rank test (significance level = 0.05) as normal distribution could not be assumed for all parameters tested.

The 18 TrOCs we analyzed have different chemical properties which might influence their attenuation. For example, molecular charge and the octanol/water distribution ratio $logD_{OW}$ are important compound properties which affect sorption to sediment (Schaper et al., 2019). Chemical properties of a TrOC could thus be an indicator for the reason of seasonal differences in its attenuation. Therefore, the difference between the mean winter and summer value for $a_{SW-20cm}$ of a TrOC was correlated with the following chemical characteristics of TrOC: molecular charge, acid dissociation constant pKa, octanol/water distribution ratio $logD_{OW}$, van der Waals radius, and molar mass (Detailed overview: Table S1 in Supporting Information S1).

R version 3.6.2 (R Core Team, 2019) was used for the entire data analysis if not indicated differently. All data used in this publication are available open access (Mueller, Schulz, Höhne, et al., 2021).

3. Results

3.1. Sediment

Analysis of streambed sediments revealed a top bright sandy layer with an underlying darker sandy layer. In winter, the top layer was thinner, ranging between 0–4 and 0–9 cm depth (mean: 6.7 cm = 33.5% of the 20 cm depth profile which we took TrOC samples from); in summer it ranged between 0–12 and 0–18 cm depth (mean: 16.3 cm = 81.5% of the sampled depth profile). K_S was higher in the upper layer for both seasons with slightly higher values in winter compared to summer. Porosity of the top layer was lower in winter with a higher proportion of gravel (Table 2). The darker layers contained more carbon for both seasons with slightly higher values in winter.

3.2. Hydrology and Residence Times

Discharge, EC, and surface water temperature fluctuated daily during both seasons (Figures 1a–1f). The proportion of treated wastewater on total discharge was comparable between seasons throughout both sampling campaigns as indicated by similar boron concentrations (Figure S2 in Supporting Information S1). In pore water, EC and temperature fluctuations were delayed compared to fluctuations in surface water. As initial offsets of individual CTD divers varied, absolute values are not comparable between divers. However, fluctuations were not affected by different offsets and could therefore still be used to calculate residence times. Pressure differences between surface water and different sediment depths only showed weak daily fluctuations in 5 cm sediment depth (Figure 1g).

EC, temperature and pressure fluctuations can be used as natural tracers. In order to assess TrOC attenuation during the passage through the hyporheic zone, general flow direction of pore water and residence times are

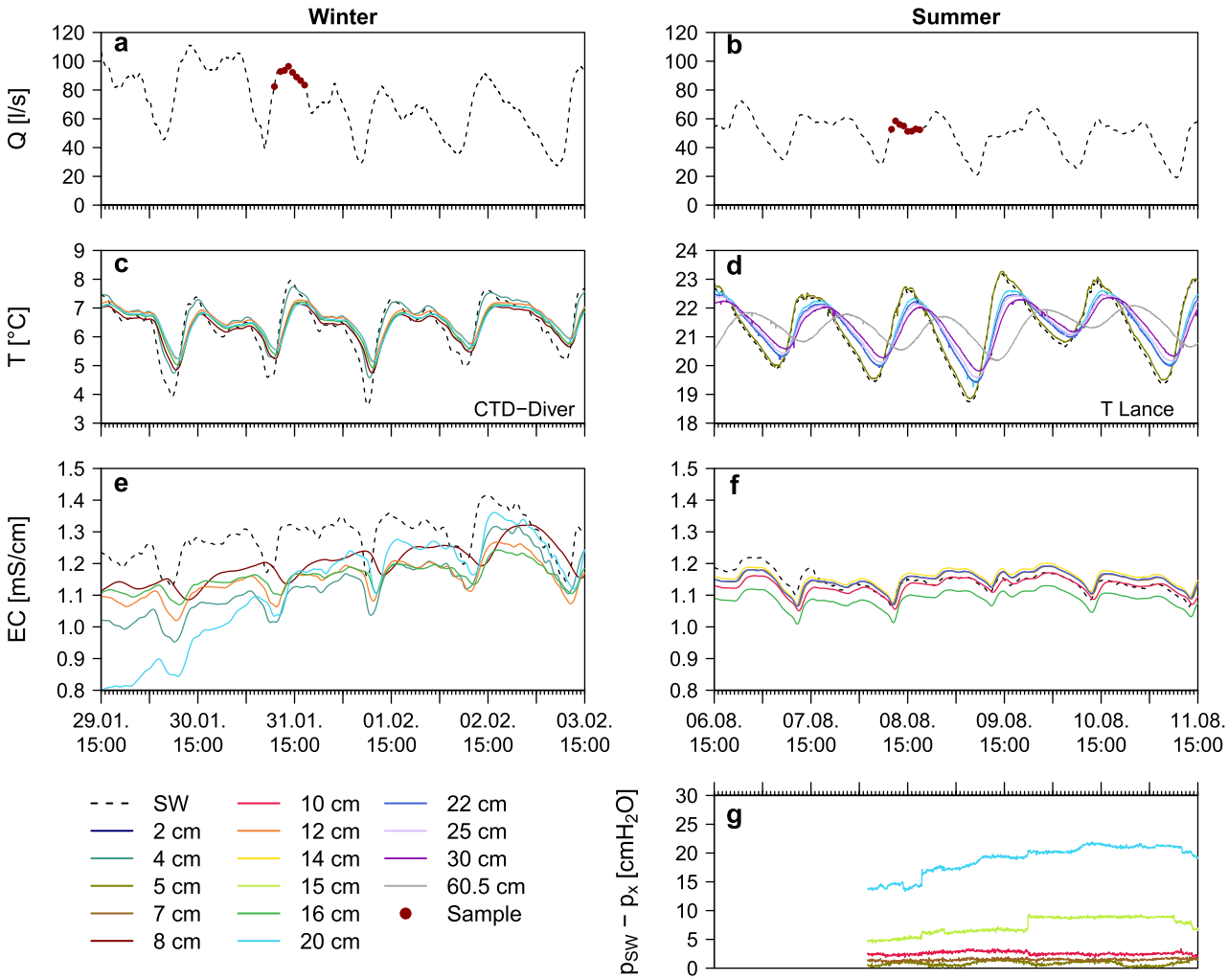

Figure 1. (a and b) Discharge (Q) and sampling times, (c and d) temperature (T), (e and f) electrical conductivity (EC) in surface water (SW) and pore water at different depths in winter, and summer and (g) differences between pressure (p) in SW and pore water at different depths *x*, measured with one of the two pressure devices in summer. For better comparability between time series, Q, EC, and T (in winter) are displayed as 1 hr moving average and EC in 16 cm depth in winter is displayed as original data +0.4 mS/cm.

needed. Using EC, temperature, and pressure data displayed in Figure 1, we applied three methods to calculate general flow direction and residence times (Figure 2): Deconvolution of EC time series, the VFLUX 2.0 model with temperature time series (only summer) and Darcy's law with hydraulic head time series (only summer). The latter two methods further allowed us to evaluate the reliability of deconvolution of EC time series.

Mean residence times obtained by deconvolution of EC time series were in general longer in winter (Figure 2a) than summer (Figure 2b). Calculated infiltration velocities on which these theoretical residence times are based ranged between 3.6 and 74.4 cm/hr (mean = 25.0 cm/hr) in summer and 0.9–15.3 cm/hr (mean = 4.6 cm/hr) in winter. In summer, we also used temperature and pressure time series to calculate residence times in the sediment and to check the reliability of the deconvolution approach. Residence times calculated using these data were in a similar range as those calculated with deconvolution of EC data (Figure 2b). However, data from the second pressure device indicated 2-3 times longer residence times between surface water and each depth compared to the first pressure device. Moreover, VFLUX results revealed residence times in the range of the two pressure devices between surface water and the uppermost depth. In comparison, VFLUX results covered also deeper depths than the other two methods and exhibited longer residence times in larger depths. Generally, mean residence times were approximately the same until down to 20 cm sediment depth and increased from that depth on as shown by VFLUX results. In winter, residence times also remained similar between different depths except for 8 cm where residence time calculated by deconvolution peaks at 6–8 hr.

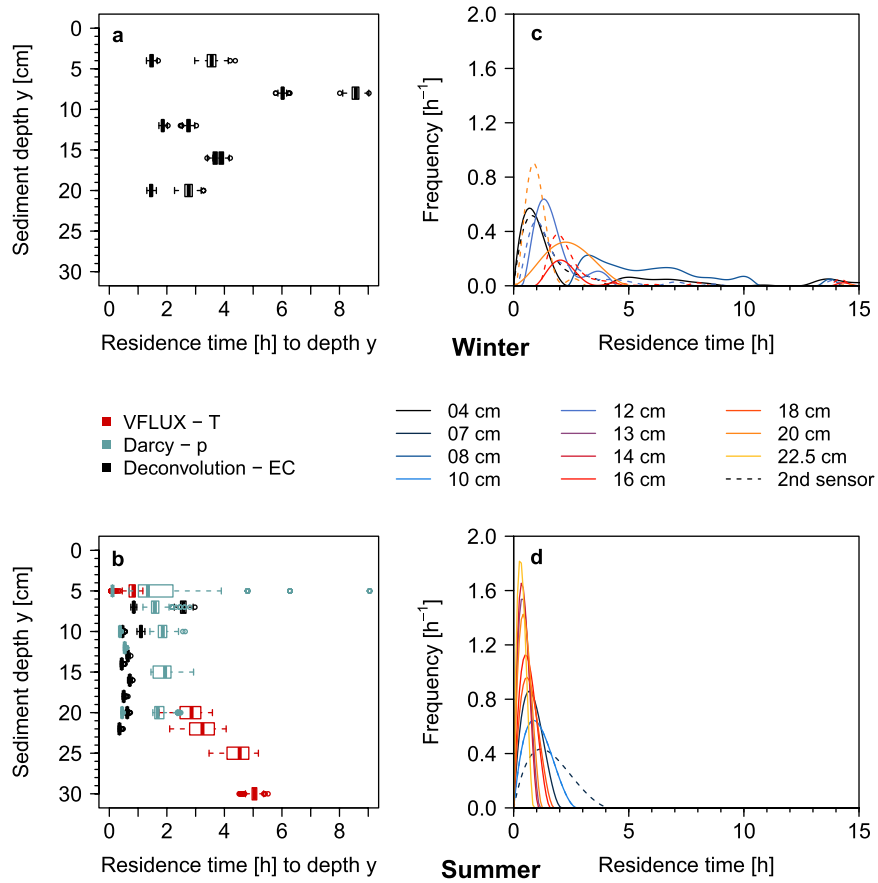

Figure 2. Residence times in the hyporheic zone between surface water and a specific sediment depth y in (a) winter and (b) summer, calculated using differences in hydraulic heads (Darcy) measured as pressure (p, only summer, $n = 828$ per depth), the VFLUX 2.0 model with temperature (T) time series (only summer, $n = 161$ per depth), and temporal moment analysis of residence time distribution (RTDs) based on deconvolution of electrical conductivity EC time series ($n = 250$ means per depth) which gives mean residence times. Multiple boxes in same depth and of same color represent independent repetitions (two divers) in same depths. RTDs are displayed for (c) winter and (d) summer; dashed lines represent a second diver in the same depth.

In contrast, the full RTDs differed significantly between seasons (Figures 2c and 2d). While RTDs were more diverse including a broad range of longer residence times of up to 15 hr in winter (Figure 2c), RTDs were quite homogeneous, consistently short and narrow in summer (Figure 2d).

3.3. Redox Conditions and DOC

We analyzed redox conditions in the streambed as the attenuation of TrOCs is redox sensitive for many compounds (Schaper et al., 2018). The extent of the oxic zone (oxygen >1 mg/l) down to 8–10 cm depth was comparable between summer and winter (Figure 3). However, oxygen concentrations in surface water and within the upper part of the oxic zone were generally 2–5 mg/l lower in summer than in winter. As a result, the gradient of decreasing oxygen concentrations was steeper in winter. Below the oxic zone, we observed less anaerobic conditions in summer than winter: Dissolved iron and manganese concentrations in depths below 8–10 cm were elevated in winter (Figures S3 and S4 in Supporting Information S1) while nitrate and sulphate concentrations throughout the depth profiles were higher in summer compared to winter (Figure S5 and S6 in Supporting Information S1).

DOC concentrations were lower in summer and declined with depth during both seasons (Figure S7a in Supporting Information S1). The mean decrease of DOC between surface water and 20 cm sediment depth was stronger in winter (−3.00 mg/l) than summer (−1.26 mg/l). In contrast, SUVA increased with depth with a stronger mean

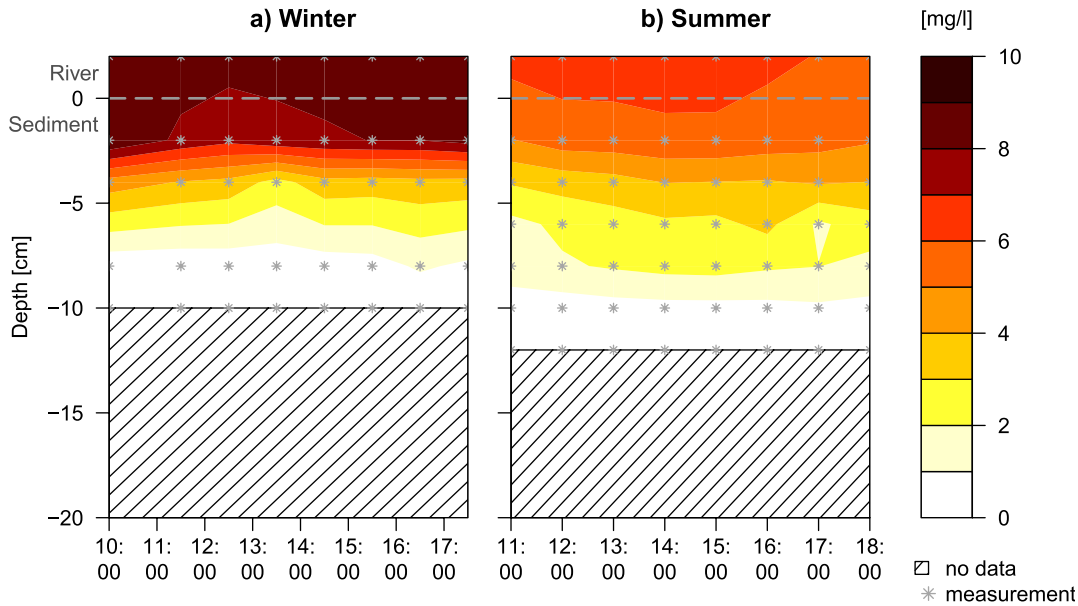

Figure 3. Time series of oxygen depth profiles and time in winter and summer.

difference between surface water and 20 cm sediment depth in winter (+0.88 l/mg C*m) than in summer (+0.09 l/mg C*m, Figure S7b in Supporting Information S1).

3.4. Trace Organic Compounds

We collected surface water and pore water samples along a depth profile in the hyporheic zone during summer and winter. The normalized TrOC concentrations along these depth profiles compared between seasons and grouped by seasonal differences are displayed in Figure 4.

For most TrOCs, concentrations decreased with depth (Figure 4). We observed seven types of depth profiles when comparing surface water concentrations and their attenuation in 20 cm depth in winter and summer. The most abundant type with similar surface water concentration in both seasons but a significantly ($p < 0.05$) stronger decrease of concentration in winter (Figure 5b) is represented by 8 out of 18 TrOCs, for example, carbamazepine and diatrizoate (group No 2). Four other TrOCs, for example, acesulfame (No 1), also showed a stronger decrease of concentration in winter but with significantly higher surface water concentrations occurring in winter compared to summer. Three TrOCs (diclofenac, benzotriazole, and primidone, No 3 and 4) showed similar attenuation with depth between seasons with similar surface water concentrations or higher ones in winter. In contrast, the remaining three TrOCs were better attenuated in summer (No 5–7). Furthermore, the decrease in concentration with depth suddenly decelerates at 8–10 cm depth for 11 out of 18 TrOCs, for example, iopromide or gabapentin, in winter. Such a deceleration from a certain depth was only observed for three TrOCs in summer.

The three transformation products analyzed show diverse patterns. While 4-formylaminoantipyrine decreased with depth during both seasons but stronger in summer, gabapentin-lactam only decreased in winter while its concentration remains approximately the same along the depth profile in summer. In contrast, valsartan acid increased with depth in the upper part of the depth profile in both seasons.

Benzotriazole was the only TrOC whose depth profiles did not significantly differ between summer and winter ($p = 0.653$) as analyzed with ANOVA after ART procedure. For all other TrOCs, the two seasons had a significant impact ($p < 0.05$) on the concentration along the depth profile.

Proportional attenuation from surface water to each depth examined (Figure 5a) was higher (as in the sense of more negative) in winter than in summer for 12 of 18 TrOCs. Similarly, attenuation between surface water and 20 cm sediment depth showed the same seasonal pattern for all TrOCs (Figure 5b). For most TrOCs, for example, diatrizoate, gabapentin-lactam, sulfamethoxazole and valsartan acid, either one or both calculated attenuation

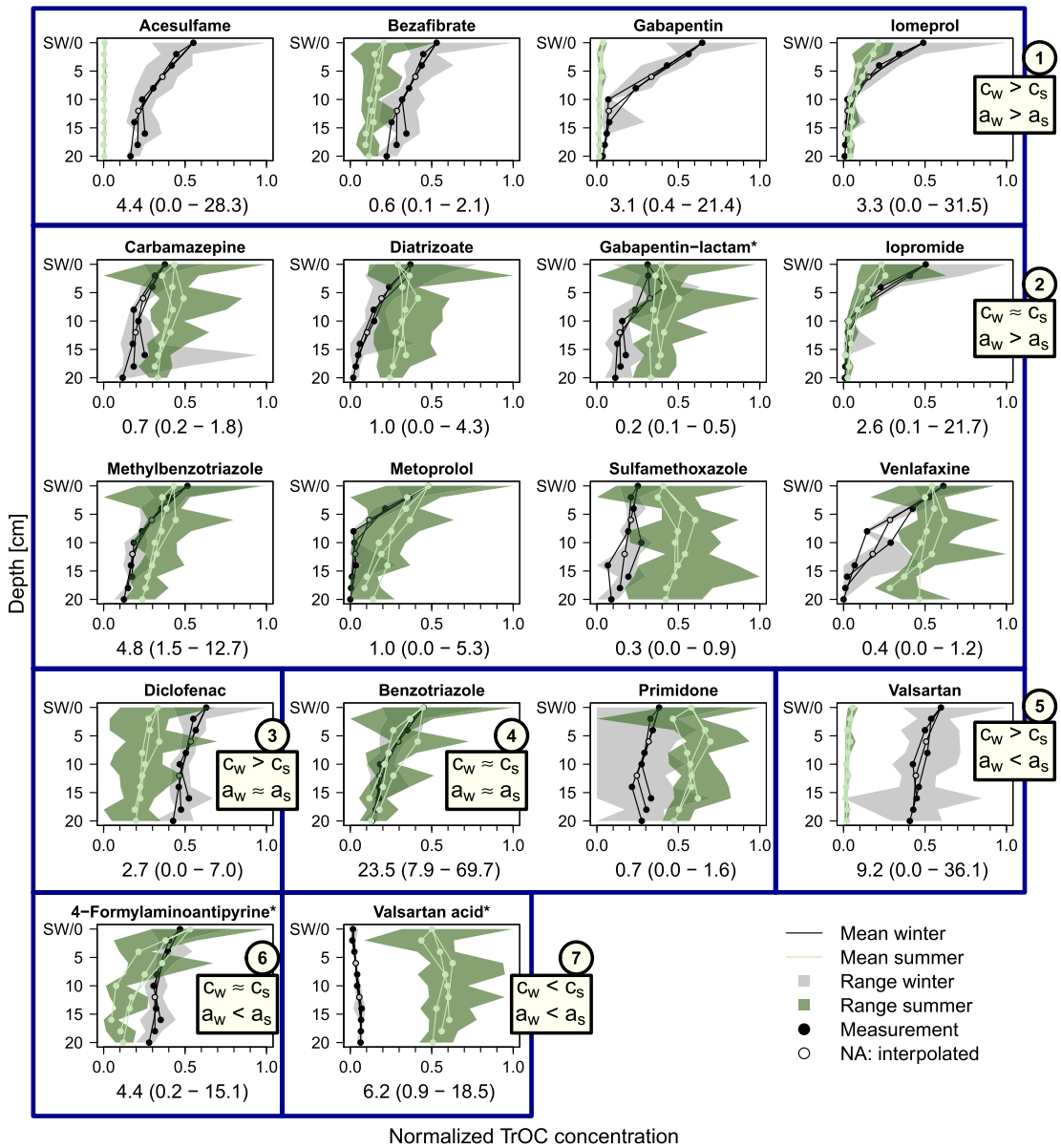

Figure 4. Depth profiles of normalized mean ($n = 8$, time series) concentration of trace organic compounds (TrOCs) in winter and summer including ranges (minimum to maximum) shown as colored areas. Mean (minimum - maximum) values in µg/l are reported below the *x*-axis. Three mean depth profiles per season are displayed according to the three sticks used for sampling of pore water in different depths. Depth of 0 cm ≙ surface water (SW) concentration. * = transformation product. TrOCs are grouped by seasonal difference in SW concentration c (summer: c_s, winter: c_w) and its proportional attenuation in 20 cm sediment depth (summer: a_s, winter: a_w, Figure 5b). Grouping is indicated by bold blue lines and labeled with grouping criteria in small boxes and group number (1–7) in circles. Significance of seasonal difference (significance level = 0.05) for grouping was tested with Wilcoxon signed rank test; if difference significant: > or <, if not significant: ≈.

values were partly also positive, meaning that the TrOC concentration increased between surface water and pore water. This increase with depth is either due to the formation of a daughter compound during infiltration, due to fluctuating TrOC concentrations or is a result of our data analysis procedure. As we set the attenuation to 100% if the concentration of a TrOC was below detection limit in the surface water and above detection limit in the pore water, resulting mean values are increased. This affected 17 of 2,574 attenuation values between surface water and different depths and 1 of 288 attenuation values between surface water and 20 cm. An increase in concentration with depth mostly occurred during summer except for the transformation product valsartan acid, which showed a stronger increase in concentration in winter.

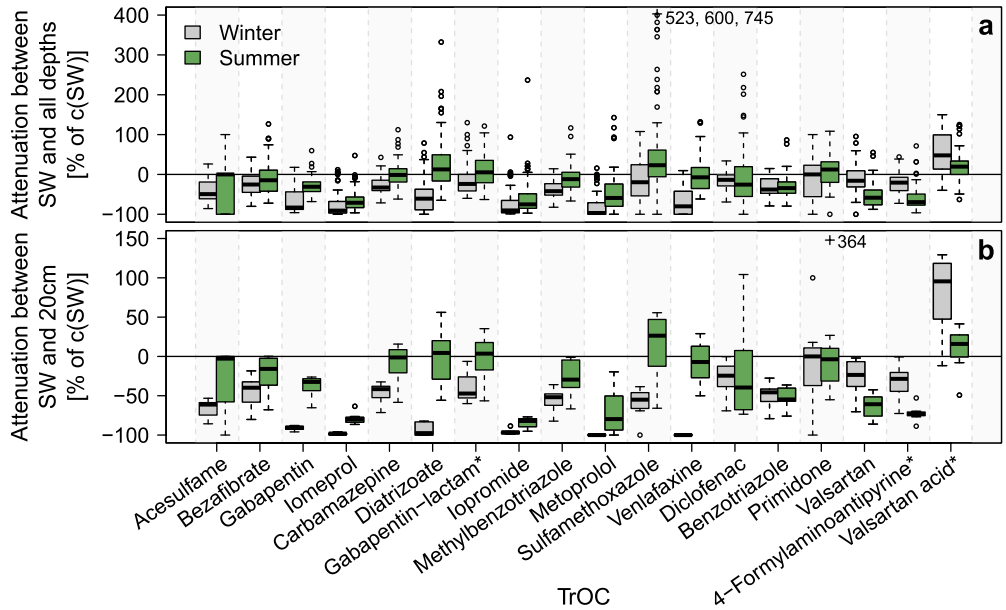

Figure 5. Boxplots, grouped by compound and season, of attenuation as proportional change in concentration between (a) surface water (SW) and each sediment depth ($n_{winter} = 64$, $n_{summer} = 79$); (b) SW and 20 cm sediment depth ($n_{each\ season} = 8$). Positive attenuation indicates increase in concentration, * = transformation product and, + = extreme outlier.

In addition to redox conditions, temperature and residence time, chemical properties of the substances could have played a role for potential seasonal differences in TrOC attenuation. Therefore, we tested whether pK_a, $logD_{OW}$, van der Waals radius, molecular charge, and molar mass of a TrOC influence seasonal differences in attenuation of respective TrOC. All parameters except molecular charge were distributed normally. Due to the nonnormal distribution of charge, correlation was done using Spearman's rho. No correlation between the difference of mean attenuation (SW to 20 cm depth) in summer and winter with neither chemical property of each respective TrOC was significant.

4. Discussion

Attenuation of polar TrOCs in a water-sediment system mainly occurs through biotransformation (Alidina, Li, & Drewes, 2014; Huntscha et al., 2014) but some TrOCs are also influenced by sorption (Schaper et al., 2019) or photodegradation (Zhang et al., 2018). These processes are altered by numerous external parameters and chemical properties of the substance itself (Figure 6). All external parameters can vary with the season, for example, seasonal temperature fluctuations which in turn influence redox conditions in the sediment (Munz et al., 2019). In order to investigate seasonal differences in hyporheic TrOC attenuation and altering parameters, we conducted one winter and one summer sampling campaign at the same study site. Based on preliminary knowledge, we focused on temperature, redox conditions, and residence time as potential parameters determining seasonal differences in TrOC attenuation in the hyporheic zone. We further included photodegradation, chemical properties of TrOCs, sediment composition (Peruchi et al., 2015), and organic carbon (Maeng et al., 2011) in our analysis on seasonal differences in TrOC attenuation as summarized in Figure 6. An overview of the literature for potential sorption/retardation, photodegradation, and redox sensitivity of the TrOCs investigated can be found in Table S2 in Supporting Information S1.

In order to be able to compare hyporheic TrOC attenuation during both sampling campaigns, boundary conditions have to be similar. Although discharge was lower in summer, surface water concentrations of 11 TrOCs and boron, which is a tracer for treated wastewater, were similar between seasons. Thus, the proportion of treated wastewater on total discharge and therefore dilution of TrOCs by natural stream water have been comparable between seasons for all stages of discharge.

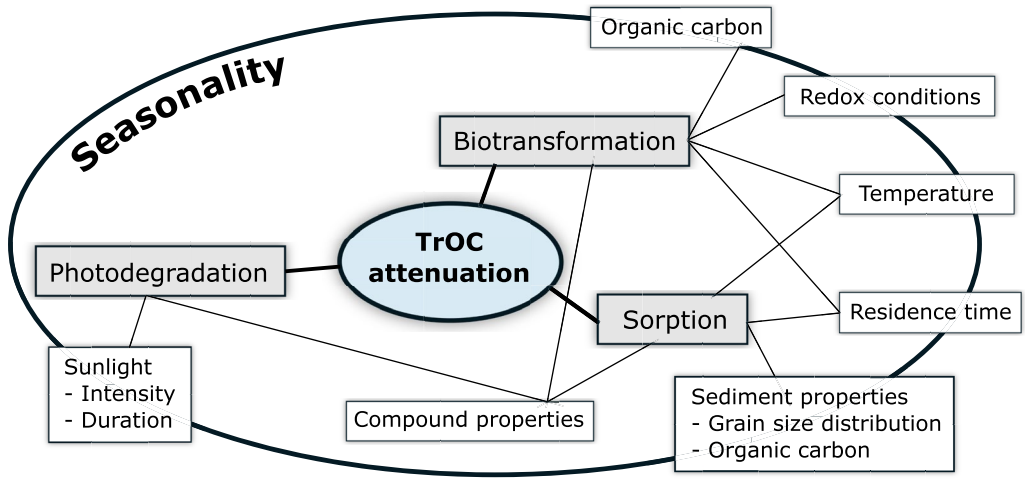

Figure 6. Parameters which are analyzed in the present study and which can influence trace organic compounds attenuation in a stream (links and parameters which are not analyzed in the present study are not shown).

Daily discharge fluctuations or varying wastewater composition can explain the increase in concentration with depth observed for a few parent compounds such as diatrizoate and sulfamethoxazole. Their increase cannot be due to compound formation. This observation could rather be the result of either different proportions of treated wastewater in the stream, which vary with the daily fluctuating discharge or changing wastewater composition over the course of a day. This causes fluctuating TrOC concentrations without attenuation being the underlying process. We tried to compensate for that effect by repeating the sampling eight times over a time period of 7 hr and averaging concentrations.

Despite similar proportions of treated wastewater on total stream discharge and measurement replicates, mean surface water concentrations from 7 of the 18 TrOCs we investigated differed between summer and winter. These differences could be due to seasonal differences (a) in TrOC usage and input to wastewater (Meierjohann et al., 2016), (b) in efficiency of the WWTP, and (c) in TrOC attenuation upstream of the study site.

1. The usage of for example, the antibiotic sulfamethoxazole might be expected to be higher in winter as bacterial infections tend to peak during colder months (Fares, 2013). Higher concentrations of antibiotics in rivers receiving treated wastewater in colder months were observed previously (Castiglioni et al., 2006; Sui et al., 2011; Zhang et al., 2015). However, we observed similar surface water concentrations for sulfamethoxazole in both seasons which makes different input of this substance to wastewater unlikely during our sampling campaigns.
2. In contrast, seasonal temperature variation (Figure 6) seemed to impact the efficiency of the WWTP regarding acesulfame, bezafibrate, diclofenac, gabapentin, iomeprol and valsartan. These TrOCs occurred in higher surface water concentrations in winter than summer (Figure 4). Lower removal efficiencies during wastewater treatment in colder compared to warmer months were observed in previous studies and attributed to temperature-dependent microbial processes: for example, for acesulfame (Kahl et al., 2018), bezafibrate (Castiglioni et al., 2006) and diclofenac (Sui et al., 2011). These results are in accordance with our observations. Lower surface water concentrations in summer might therefore be a result of more efficient attenuation of the six affected TrOCs in the WWTP under warmer temperatures.
3. Seasonal differences in surface water concentrations could also be due to photodegradation (Figure 6, Table S2 in Supporting Information S1) upstream of the study site. Intense vegetation and foliated trees shaded the side channel in summer. However, the photodegradation potential might still have been higher in summer due to a higher intensity and duration of daylight compared to winter. Photosensitivity was previously reported for benzotriazole, methylbenzotriazole (Janssen et al., 2015), gabapentin (Herrmann et al., 2015), venlafaxine (Guillet et al., 2019), and diclofenac (Jaeger et al., 2019; Kunkel & Radke, 2012; Zhang et al., 2018). We measured lower surface water concentrations for gabapentin and diclofenac in summer indicating potential photodegradation. In contrast, concentrations of venlafaxine, benzotriazole, and methylbenzotriazole were similar

between seasons. We therefore assume that the potential for photodegradation of gabapentin and diclofenac was higher in summer and balanced between seasons for venlafaxine, benzotriazole, and methylbenzotriazole.

At the study site itself, we investigated the attenuation of TrOCs in the hyporheic zone. We observed that 12 of the investigated TrOCs were better attenuated in winter. Possible attenuation processes in the sediment are biotransformation and sorption (Figure 6).

Many previous studies found sorption to sediment to be negligible for polar TrOCs (Table S2 in Supporting Information S1), for example, diclofenac and primidone (Alidina, Li, Ouf, et al., 2014), sulfamethoxazole (Drewes et al., 2014), metoprolol (Huntscha et al., 2013), and carbamazepine (de Wilt et al., 2018). Furthermore, sorption to biomass was negligible for for example sulfamethoxazole and diclofenac under winter and summer conditions (Trinh et al., 2016). In contrast, other studies observed sorption (Table S2 in Supporting Information S1) for metoprolol (de Wilt et al., 2018; Li et al., 2015) or retardation for benzotriazole, bezafibrate, carbamazepine, diclofenac, 4-formylaminoantipyrine, methylbenzotriazole, metoprolol, and venlafaxine (Schaper et al., 2019).

Sorption varies with environmental conditions (Figure 6). For example, sorption of an antibiotic increased with clay content (Peruchi et al., 2015). Sorption to clay would be most likely for cationic TrOCs (Xu et al., 2021) such as metoprolol and venlafaxine (Chemicalize by ChemAxon, n.d., Table S1 in Supporting Information S1). In agreement with this assumption, the two mentioned TrOCs were better attenuated at our study site in winter when clay content was slightly higher. Furthermore, sorption can be temperature-dependent but observations vary. While Khazri et al. (2017) observed an increase of adsorption of carbamazepine to clay with decreasing temperature, Liu et al. (2017) found increased sorption of sulfamethoxazole on humic acid at higher temperatures. In comparison, carbamazepine was better attenuated in winter at our study site.

Nevertheless, the stream at our study site has been influenced by treated wastewater and TrOCs for many years. Therefore, we assume that an equilibrium between sorption and desorption has been reached in the sediment. Thus, attenuation by sorption without desorption is likely not important at our study site but retardation (sorption followed by desorption) might still be possible. Schaper et al. (2019) observed retardation, which varied for different compounds, but no permanent retardation for all analyzed TrOCs at the main River Erpe close to our study site.

While retardation might have affected some TrOCs, biotransformation (Figure 6) was identified as the main attenuation process for polar TrOCs in sediment previously (Alidina, Li, & Drewes, 2014; Huntscha et al., 2014). However, biotransformation rates vary strongly between studies (Greskowiak et al., 2017). Lower surface water concentrations of a TrOC in summer than winter likely indicate the importance of temperature-dependent biotransformation in the WWTP for that compound. This temperature effect should also occur in the hyporheic zone for respective compounds. However, we only observed lower surface water concentrations combined with higher attenuation along the depth profile in summer for valsartan. The higher attenuation of most TrOCs in winter is in opposition to a higher potential for microbial metabolism in summer. Furthermore, in winter DOC concentrations decreased stronger with depth with a parallel stronger increase in aromaticity as indicated by increasing SUVA values. Zarnetske et al. (2011) explained this connection with the preference of microbes for more labile, nonaromatic DOC compounds. Thus, DOC and SUVA at our study site indicate a higher microbial turnover of DOC in winter. We therefore conclude that temperature cannot be the main parameter responsible for seasonal differences in TrOC attenuation at our study site. We can further assume that seasonal differences in TrOC attenuation were not influenced by DOC (Figure 6) as DOC concentrations were in a similar range for summer and winter. In agreement with our observations, previous studies found higher attenuation for only a few TrOCs in summer than in winter in a membrane bioreactor plant (Trinh et al., 2016), in soil columns (Alidina et al., 2015) or in a river-lake system (Meierjohann et al., 2016) while the majority of TrOCs was attenuated independent of temperature. In contrast, higher attenuation in summer and autumn than winter was observed for all TrOCs considered in constructed wetlands (Zhang et al., 2018). Our findings, that seasonal patterns in attenuation are different among TrOCs, are therefore similar to general findings in previous studies.

We further tested whether chemical properties (Figure 6) could explain seasonal differences in TrOC attenuation. However, we did not find correlations between pK_a, $logD_{OW}$, van der Waals radius, molecular charge and molar mass of the TrOCs and the difference between mean attenuation in winter and summer. Therefore, these parameters cannot explain seasonal differences in TrOC attenuation either.

Another parameter we investigated are redox conditions in the sediment (Figure 6). Changes in redox conditions affect microbial activity (de Wilt et al., 2018) and the attenuation of many TrOCs (Schaper et al., 2018, Table S2 in Supporting Information S1). Previous studies observed that the oxic zone becomes more shallow under warm compared to cold temperatures in soil columns (Burke et al., 2014) or in a bank filtration system (Munz et al., 2019). In contrast, the extent of the oxic zone at our study site remained approximately the same between seasons. However, we found a stronger gradient of oxygen, nitrate, dissolved iron, and manganese in winter (Figures S3 and S4 in Supporting Information S1). These steeper gradients indicate that turnover processes were increased, similar to DOC turnover, at our study site in winter compared to summer. This observation is in contrast to a generally higher microbial activity under warmer conditions (Kaplan & Bott, 1989). We therefore conclude that seasonal temperature variation cannot explain increased redox processes at our study site in winter.

Seasonal differences in oxygen concentrations in the upper part of the sediment could have influenced attenuation of redox sensitive TrOCs (Table S2 in Supporting Information S1). We observed deceleration of TrOC attenuation in around 8–10 cm depth in winter for 11 TrOCs, in summer for three TrOCs. In approximately this depth, oxygen was depleted (oxygen concentration <1 mg/l). This coincidence indicates redox sensitive degradation of respective TrOCs and was, for example, observed and also previously reported for iomeprol and iopromide (Redeker et al., 2018; Schulz et al., 2008; Zhang et al., 2019). Furthermore, acesulfame, 4-formylaminoantipyrine, metoprolol (Burke et al., 2014), benzotriazole, bezafibrate, gabapentin, and methylbenzotriazole (Schaper et al., 2018) were previously reported to be better attenuated under oxic/suboxic conditions which is in agreement with our findings. However, these studies also observed better attenuation under oxic/suboxic conditions for diclofenac, primidone (Burke et al., 2014; Schaper et al., 2018), and valsartan (Edefell et al., 2021). In contrast, we found redox independent attenuation for diclofenac, diatrizoate, primidone, sulfamethoxazole, valsartan, and venlafaxine. Redox independency was also previously observed for sulfamethoxazole (Filter et al., 2017), diatrizoate, and venlafaxine (Schaper et al., 2018). In general, the oxygen gradient at our study site was stronger along the depth profiles in each season than the difference in redox conditions between seasons. Therefore, differing oxygen concentrations in the upper part of the hyporheic zone can only explain seasonal variation in the attenuation of redox-sensitive TrOCs to a limited extent.

The third main parameter we examined was residence time (Figure 6) in the sediment, which varied between seasons. Residence times derived from the three methods used in summer were, in general, in a similar range with an overlap for most depths. Divergence between results from different methods but in the same depths was inconsistent and can probably be attributed to small-scale sediment heterogeneity. In addition, results from replicates with the same method in the same depth differ sometimes stronger than results of different methods. We therefore assume that partly varying residence times obtained with the three different methods were mainly due to heterogeneous sediment and not a result of differences between methods.

In previous studies, residence time decreased with increasing water level and related surface water flow velocity (Boano et al., 2007; Packman & Salehin, 2003). Surface water flow velocities which we observed at the side channel were on average 28% faster in winter but water level was twice as high in summer. In contrast, mean infiltration velocity was 443% faster (based on deconvolution of EC time series) in summer than in winter. Therefore, seasonal differences in surface water flow velocities could not have been the main driver for differences in residence times between seasons. In comparison, higher water levels could have pushed water into the sediment with more force in summer resulting in faster infiltration.

In addition, water is 1.5 times more viscous for the mean surface water temperature we measured in summer compared to the one we measured in winter (Korson et al., 1969). Thus, lower viscosity of the water due to warmer temperatures could have also promoted faster infiltration in summer (Wu et al., 2020).

We also found changes in sediment composition, which influenced residence time. The thickness of the top layer with its higher hydraulic conductivity was on average 9.6 cm larger in summer. More accumulation of sand might be a result of summer vegetation acting as a sediment trap. Differences in bed migration (Wolke et al., 2019) could also be an explanation for a thicker top sandy layer in summer compared to winter. Due to the larger extent of the top sandy layer, the investigated 20 cm long vertical flow path contained a substantially higher proportion of the more permeable upper sediment layer in summer compared to winter. We therefore assume that sand accumulation promoted faster infiltration and thus shorter residence times in summer.

In general, we would assume an increase of residence time with depth as the direct distance to the surface water gets longer. However, we observed a mixture of increase, constancy, or even decrease of residence time with depth for both seasons (Figure 2). A possible explanation for this irregularity is very heterogeneous hyporheic flow paths (Angermann et al., 2012) in heterogeneous sediment. At our study site, potential lenses of the more conductive upper layer in the lower, less permeable sediment layer might have created preferential flow (Earon et al., 2020). These potential flow paths would reach deeper sediment layers faster than upper parts of the streambed. As a result, sediment and flow path heterogeneity might also explain variance in TrOC concentration between the three depth profiles.

For both seasons, longest residence times were observed in 7 or 8 cm depth. In winter, this depth matched the change from the sediment layer with higher to the one with lower hydraulic conductivity and showed the most diverse RTD. Thus, it is plausible that residence time of TrOCs in the hyporheic zone was extended by a higher proportion of the less permeable, more heterogeneous layer on the investigated depth profile in winter. The diverse RTD in winter indicates some preferential flow paths to deeper depths in addition to mainly frequent shallow hyporheic flow paths. These flow paths repeatedly enter and exit the sediment in the upper part of the hyporheic zone and sum up to long residence times. In contrast, we can assume that the accumulated sand promoted a few dominant and fast infiltration pathways in summer as indicated by rather uniform RTDs (Figure 2d).

Previous studies observed an increase in TrOC attenuation with longer residence time of the contaminated water in soil/sediment (Drewes, 2009; Grünheid et al., 2005). At our study site, longer residence times coincided with higher TrOC attenuation and a stronger oxygen decrease as well as DOC turnover with depth in winter. Longer residence times likely increased the exposure time of TrOCs to favorable conditions for their attenuation in the sediment in winter compared to summer. Schaper et al. (2019) further suggest a more efficient TrOC attenuation along short and shallow flow paths compared to long and deep flow paths. This is in accordance with our findings for most TrOCs. However, the proportion of surface water which flows through the hyporheic zone is probably lower in winter as a result of longer residence times. Therefore, the contribution of the hyporheic zone to in stream attenuation of TrOCs is probably lower in winter compared to summer.

5. Conclusion

Our hypothesis that TrOC attenuation would be more efficient in summer was based on the assumption that microbial activity is higher under higher temperatures. Furthermore, we assumed that these higher temperatures outweigh lower oxygen concentrations in the hyporheic zone. In contrast, the results from the present study show that attenuation in the hyporheic zone was stronger in winter than in summer for the majority of TrOCs during our sampling campaigns. We therefore have to reject our hypothesis of higher attenuation in summer for most TrOCs and can only accept it for valsartan, valsartan acid and 4-formylaminoantipyrine.

TrOC concentrations at the sampling points are a result of all attenuation processes which have occurred along the flow path leading to that sampling point. Thus, TrOC attenuation is a function of processes, determining conditions for these processes and the time in which these processes can take place. Seasonal differences in temperature could not explain variation in TrOC attenuation between seasons while differences in redox conditions could only have contributed to a limited part. In contrast, residence times and the extent of the top sandy layer show strong variation between winter and summer. Residence times of TrOCs in favorable redox conditions have to be sufficiently long for reactive attenuation processes to occur. Therefore, differences in residence times resulting from changes in sediment conditions might have played a role in seasonal differences in TrOC attenuation. However, as the present study is mainly descriptive, we can only report a coincidence of longer residence times, lower temperatures, a steeper oxic gradient, and higher attenuation of the majority of TrOCs in winter compared to summer. Therefore, it would be of interest to conduct similar sampling campaigns which focus on disentangling the parameters and processes leading to seasonal differences in TrOC attenuation. The biogeochemical changes we observed probably have also impacted the microbial community. Microbial degradation is a major attenuation process for polar TrOCs. Thus, analyzing the impact of seasonal changes in the microbial composition and functioning would likely be beneficial for future studies regarding TrOC attenuation in urban streams.

On the scale of the urban water cycle, another parameter is important: the proportion of river water that flows through the hyporheic zone. Longer residence times of contaminated water in the hyporheic zone probably lead to a more efficient TrOC removal along a hyporheic flow path. However, longer residence times, like we measured

in winter, might result from limited hyporheic flux. Consequently, a smaller proportion of surface water flows through the hyporheic zone where the contaminants are potentially attenuated. Such a limited hyporheic zone would only contribute little to the total in stream attenuation of TrOCs. Therefore, analyzing the proportion of surface water flowing through the hyporheic zone would be of interest for studies focusing on the fate of TrOCs on the scale of the urban water cycle.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data used in this study is available via the Freshwater Research and Environmental Database (FRED) of the Leibniz Institute of Freshwater Ecology and Inland Fisheries: doi:10.18728/igb-fred-578.0.

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