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Fate of trace organic compounds in the hyporheic zone: influence of retardation, the benthic bio-layer and organic carbon

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Abstract

The fate of 28 trace organic compounds (TrOCs) was investigated in the hyporheic zone (HZ) of an urban lowland river in Berlin, Germany. Water samples were collected hourly over 17 h in the river and in three depths in the HZ using minipoint samplers. The four relatively variable time series were subsequently used to calculate first-order removal rates and retardation coefficients via a one-dimensional reactive transport model. Reversible sorption processes led to substantial retardation of many TrOCs along the investigated hyporheic flow path. Some TrOCs such as dihydroxy-carbamazepine, O-desmethylvenlafaxine and venlafaxine were found to be stable in the HZ. Others were readily removed with half-lives in the first 10 cm of the HZ ranging from 0.1±0.01 h for iopromide to 3.3±0.3 h for tramadol. Removal rate constants of the majority of reactive TrOCs were highest in the first 10 cm of the HZ, where removal of biodegradable dissolved organic matter was also highest. Because conditions were oxic along the top 30 cm of the investigated flow path we attribute this finding to the high microbial activity typically associated with the shallow HZ. Frequent and short vertical hyporheic exchange flows could therefore be more important for reach-scale TrOC removal than long, lateral hyporheic flow paths.
Keywords
Pharmaceuticals, metformin, guanylurea, urban water cycle, reactive transport modeling

TOC Art
**Introduction**

Many trace organic compounds such as pharmaceuticals are only partially retained in wastewater treatment plants (WWTPs)\textsuperscript{1,2} and thus are ubiquitous in urban surface waters.\textsuperscript{3,4} In rivers, TrOCs are of eco-toxicological concern\textsuperscript{5–7} and the high persistence of some TrOCs in aquatic environments poses issues for drinking water production.\textsuperscript{8} The hyporheic zone (HZ), the portion of the streambed in which surface waters and groundwater mix,\textsuperscript{9} is generally regarded as an effective bioreactor, characterized by steep redox gradients, diverse microbial communities and relatively high microbial turnover rates.\textsuperscript{10,11} Both laboratory\textsuperscript{12,13} and field studies\textsuperscript{14,15} demonstrated that the HZ is able to efficiently remove many TrOCs, even along relatively short flow paths (< 20 cm). Therefore, the HZ may not only act as a filter protecting groundwater form surface water contamination\textsuperscript{16} but also contributes to whole-stream, i.e. reach-scale attenuation of TrOCs.\textsuperscript{17}

The adequate assessment of the in-situ efficiency of the HZ in removing TrOCs requires a sound understanding of both the in-situ reactivity and the exposure time of TrOCs to favorable attenuation conditions. Hyporheic residence times are predominately controlled by transport characteristics such as porewater velocity and dispersion. However, residence times of TrOCs along hyporheic flow paths may also be influenced by sorption and desorption processes, i.e. retardation.\textsuperscript{18–20} Retardation can extend residence times of TrOCs in the HZ and, if not considered in reactive transport modeling, may lead to an overestimation of the in-situ reactivity of TrOCs in the HZ. Although retardation of some TrOCs in saturated sediments has been demonstrated in laboratory studies\textsuperscript{20,21} little is known about its driving factors and its overall importance for transport of TrOCs in hyporheic sediments.

Reactivity of TrOCs in the HZ increases with temperature\textsuperscript{12} and, for many TrOCs, is higher under oxic conditions.\textsuperscript{12,14} However, since microbially mediated degradation and transformation mechanisms are considered to be a main driver of TrOC removal in saturated sediments, it is likely that TrOC reactivity in the HZ is also linked to microbial activity and growth and therefore to turnover of biodegradable dissolved organic matter (BDOC).\textsuperscript{22} It has been shown that microbial activity in the HZ is typically highest in the
shallow HZ (within the so called benthic bio-layer), where BDOC availability is highest and redox conditions are rather oxic. It is therefore reasonable to assume that removal rates of TrOCs may vary substantially along hyporheic flow paths, even if redox conditions are relatively similar. In previous investigations on the fate of TrOCs in the HZ, neither retardation nor the effect of benthic bio-layers and depth-dependent transport characteristics on the fate of TrOCs has been considered. In addition, previous studies have mainly investigated the fate of parent TrOCs in the HZ, while information on the fate of transformation products (TPs) such as guanylurea, the main TP of the antidiabetic drug metformin, valsartan acid, the main TP of compounds of the sartan group, or gabapentin-lactam a main TP of the anticonvulsant gabapentin in the HZ is widely lacking.

The objectives of the present study were to use concentration time series of TrOCs and conservative tracers sampled along a 40 cm long hyporheic flow path to calculate depth-dependent in-situ retardation coefficients and first-order removal rate constants of 28 TrOCs, including 7 transformation products, in the HZ of an urban lowland river in Berlin, Germany. We hypothesize that hyporheic reactivities of TrOCs are highest in the shallow HZ, where redox conditions are rather oxic and microbial activity is highest. We further anticipate that many TrOCs are retarded along hyporheic flow paths, which notably influences their residence times in the HZ and thus the estimation of hyporheic removal rates.
2. Methods

2.1 Site description and experimental overview

River Erpe, an urban lowland river located east of Berlin, Germany, receives 60% to 80% of its discharge from the municipal WWTP Münchehofe. The present study was conducted at Heidemühl (Lat: 52.478647, Long: 13.635146), a section of River Erpe that has been subject to previous investigations on the fate of TrOCs in the HZ due to its sandy streambed sediments.\textsuperscript{14,15,26} Sediment characteristics at the sampling site were determined from one 40 cm long sediment core which was taken using a hand auger (inner diameter 9 cm) in close proximity of the sampling site (< 10 cm) and cut into 8 cm long sections, which were transferred into 5 KSAT rings (Meter, Germany) on site. Saturated hydraulic conductivity at 25 °C was measured using a KSAT device (Meter, Germany) and ranged between $1.6 \times 10^{-5}$ m s\(^{-1}\) and $1.7 \times 10^{-4}$ m s\(^{-1}\). Porosity, determined from oven dried (105 °C, 48h) samples, decreased from 0.5 in the upper 8 cm of the HZ to 0.4 in the last 2 sub-cores (i.e. 24-40 cm depth).

The experimental setup consisted of three self-constructed mini-point samplers\textsuperscript{26} (compare section 2.2) that were installed in the HZ in 10, 30 and 40 cm depth (Figure 1). An additional mini-point sampler was installed in the HZ in 20 cm depth. However, due to clogging, the sampler in 20 cm depth provided only a limited number of samples and was thus excluded from further analysis. To gain additional information on the hydrological conditions at the study site and to cross-check porewater velocities determined by conservative transport modeling (section 2.5), porewater velocities were additionally calculated from temperature time series in the HZ. To this end, a Multi-Level Temperature Stick\textsuperscript{27} (MLTS, UIT, Dresden) was installed adjacent to the minipoint samplers ($\approx$10 cm). Temperature time series were collected over the course of two weeks (14.06.-28.06.2016) in 5, 10, 15, 20, 30 and 50 cm depth in the HZ. Subsequently, vertical seepage fluxes and thermal dispersion coefficients were evaluated via the McCallum method\textsuperscript{28} incorporated in the VFLUX 2.0 program.\textsuperscript{29} The McCallum method simultaneously uses phase shifts ($\Delta \phi$) and amplitude damping ratios ($A_r$) of two sinusoidal temperature time series to calculate both the thermal dispersivity and the Darcy velocity via an analytical solution of the one-
dimensional heat transport equation. In VFLUX, dynamic harmonic regression, a form of harmonic regression in which the spectral coefficients describing a periodic signal can be non-stationary, is used to estimate phase and amplitude information from the measured time series. Vertical seepage fluxes and thermal dispersion coefficients were calculated from measured temperature time series in 5 and 10 cm, 10 and 30 cm and 20 and 50 cm depth in the HZ, yielding parameter estimates at center-of-pair depths of 7.5 cm, 20 cm and 35 cm, respectively, covering the three different model sections in the HZ (compare section 2.5). Further details on the method and its underlying assumptions can be found elsewhere and in the Supporting Information (SI, section SI-01).

Figure 1 Experimental setup showing the three minipoint sampler installed in 10 cm, 30 cm and 40 cm depth in the hyporheic zone (HZ). The samplers were installed in a line (< 1 cm distance) perpendicular to the water flow direction. A Multilevel Temperature Stick (MLTS) was installed in close proximity (≈ 10 cm) next to the minipoint sampler array. Blue arrows indicate surface water and predominant hyporheic flow directions. Minipoint samplers were sampled from an aluminum bridge spanning the river channel (not shown).
2.2 Water sampling

Hyporheic porewater samples were collected hourly between 22:30 on June 15\textsuperscript{th} and 15:30 on June 16\textsuperscript{th} 2016 using self-constructed mini-point samplers.\textsuperscript{26} In brief, the mini-points consisted of HPLC tubes (PEEK, ID 0.03 inch, Sigma Aldrich, USA) that were inserted into 1.5 m long stainless steel tubes (ID 0.7 mm). At the tip of the steel tubes, four 1-cm long laser cut slits (< 0.1 mm) allowed water flow but acted as a filter screen for most sediment particles. The HPLC tubes were connected to a syringe pump (NE-1600 New Era Pump Systems, Inc, Farmingdale, USA) via Swagelok fittings (Swagelok, USA) to allow slow, constant pumping of hyporheic porewater. Thirteen ml of hyporheic porewater were sampled applying a constant sampling rate of 1 ml min\textsuperscript{-1}. In previous investigations conducted at the same site pumping rates of 1 ml min\textsuperscript{-1} have been found to be sufficiently low to maintain the integrity of the hyporheic flow field.\textsuperscript{26} Electrical conductivity (EC) was measured in each sample and in the surface water using handheld EC meters (GMH 3431, Greisinger, Germany). Every four hours, pH was measured in the hyporheic porewater samples and in the surface water using a handheld pH meter (SenTix 41, WTW, Germany), calibrated prior to sampling. Samples in the HZ were related to surface water samples, obtained from an automatic water sampler (model 3700, Teflon suction line, Teledyne ISCO, Lincoln, NE.) located 150 m upstream of the sampling site following procedures described elsewhere.\textsuperscript{31} Samples for TrOC and dissolved organic carbon (DOC) analysis were filtered through regenerated cellulose syringe filters (0.2 µm, Macherey-Nagel, Germany) and stored in amber glass bottles with Teflon lined caps. Samples for TrOC analysis were immediately frozen on site. Samples for DOC analysis were stored at 4° C in the dark and were measured within two weeks after sampling. Samples for NO\textsubscript{3}-N and major cation analysis were filtered through cellulose acetate syringe filters (0.2 µm, Sartorius, Germany) and stored in polyethylene bottles at 4 °C until analysis. Samples for total dissolved iron and dissolved manganese analysis were additionally acidified to pH ≈ 2.0 using HCl. A sampling period of 17 h was considered sufficient as the aim of the present study was to investigate TrOC reactivity and the effect of retardation on TrOC transport along a relatively constrained hyporheic flow path. From previous studies at
the same field site it was known that (i) chemical conditions in River Erpe oscillate on a daily basis
(concentration troughs in the morning, peaks in the afternoon) but are relatively constant over the course
of weeks and (ii) that porewater velocities were in the order of several cm per hour.\textsuperscript{14,31}
2.3 Analytical procedures

To enlarge the number of target compounds, samples were split and analyzed in parallel using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) at the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University and the Chair of Water Quality Engineering at Technical University of Berlin (TUB) following standard protocols established previously.\textsuperscript{26,32,33} In brief, separation of TrOCs was achieved via a XSelect HSS T3 HPLC column (2.5 µm particle size, 2.1 * 50 mm, Waters, USA) at TUB and an Acquity UPLC HSS T3 column (1.8 µm, 2.1 mm × 100 mm, Waters, USA) at ACES. Both protocols used linear gradients (ultra-pure water versus 100% methanol; HPLC grade, J.T. Baker, USA). A TSQ Vantage (Thermo Fisher Scientific, USA) and a Quantiva triple-quadrupole mass spectrometer in ESI ± modes were used for MS/MS analysis at TUB and ACES, respectively. In both methods, TrOC were identified based on the characteristic ratio of two ion fragments and quantified via isotope-substituted standards (Toronto Research Chemicals, Canada) in combination with the most abundant fragment ion (Table SI-01). In both methods, a series of calibration standards was measured before and after each sampling sequence. To assess analytical errors, samples at TUB were measured in triplicate, while at ACES quality control standards were measured during each run. In total, 29 TrOCs, including 22 parent compounds (PCs) and 7 transformation products (TPs), were analyzed in the present study. Ultra-pure water (Maxima UF device, ELGA LabWater, Germany) and tap water were measured as method blank at TUB and ACES, respectively. Limits of detection (LODs) and quantification (LOQs) for each target compound and additional information on the analytical procedures and data evaluation are provided in the SI (section 2). Concentrations of major cations and total dissolved iron and manganese were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, ICP iCAP 6000series, Thermo Fisher). Nitrate-N concentrations were measured via continuous-flow-analysis (SAN ++, Skalar) following DIN EN ISO 13395. Absorbance spectra of dissolved organic matter (DOM, 250–600 nm, every 5 nm) and excitation-emission matrices (EEMs, excitation wavelength ranging from 250 to 600 nm, 5 nm increments; emission range of
250–550 nm 1.64 nm increments) were measured in triplicate at a Horiba Aqualog (Horiba Ltd, Japan) in a 1 cm quartz cuvette. One blank (MiliQ water) was measured for every 9 measurements. Scan speed was 12 000 nm min\(^{-1}\) at a response time of 0.01 s. The Humification Index (HIX), a measure of the degree of humification of DOM,\(^{34}\) was calculated after EEMs were blank-subtracted and corrected for the inner filter effect. DOC concentration was measured in triplicate at a varioTOC cube (elementar Analysensysteme, Germany). Specific UV absorbance at 254 nm (SUVA\(_{254}\)) was calculated by normalizing the decadal absorbance measured at 254 nm to DOC concentration (mg/L).\(^{35}\)

### 2.4 Calculation of relative removal percentages

To assess overall TrOC removal along the investigated hyporheic flow path and to cross-validate calculated removal rate constants (section 2.5), relative TrOC removals were calculated between the surface water and hyporheic water in 40 cm depth and between other pairs of concentration time series, i.e., between the surface water and hyporheic water in 10 cm depth, between hyporheic water in 10 and in 30 cm depth and between hyporheic water in 30 and in 40 cm depth. Because measured concentrations varied with time, relative removal of a given TrOC (x) between two sampling depths (Rel\(_x\)) was calculated using cumulative concentrations of a TrOC normalized to cumulative concentrations of a stable reference compound:\(^{36,37}\)

\[
\text{Rel}_x^{\text{in-out}} = \left(1 - \frac{\sum_i^n c_{x,\text{out},i} \sum_i^n c_{\text{ref,in},i}}{\sum_i^n c_{x,\text{in},i} \sum_i^n c_{\text{ref,out},i}}\right) \times 100\%
\] \hspace{1cm} (1)

whereby \(c_{x,\text{in}}\) and \(c_{x,\text{out}}\) (\(c_{\text{ref,in}}\) and \(c_{\text{ref,out}}\)) are the concentrations of the upper and lower concentration time series of a TrOC (a stable reference compound), respectively, and \(n\) is the number of data points in each time series. In the present study we used O-desmethylvenlafaxine (MLX) as a stable reference compound as it showed low retardation along the hyporheic flow path and was found to be rather stable in the HZ (compare section 3.3). The approach was cross-validated using the diurnal varying EC signal measured in
the surface water and in hyporheic porewater samples as another conservative reference (SI section 4).

Removal of a TrOC was considered significant if the 95% confidence interval of the relative removal, computed using the respective analytical uncertainties of each TrOC (Table SI-02), did not include zero.

The applicability of equation 1 requires either relatively constant flow conditions or a positive correlation between the reference compound and the target TrOC concentrations. Both requirements were likely met in the present study as the study site was characterized by strong downwelling conditions (compare section 3.1) and concentrations of TrOCs (with the exception of acesulfame, metoprolol acid and metformin) were well correlated to \( O\)-desmethylvenlafaxine concentrations (Pearson Product Moment Correlation coefficients > 0.7, p-value < 0.05). Equation 1 is based on the assumption that the transport time scales of both, the target TrOC and the reference compound, are similar. Thus \( \text{Rel} \) calculated for stronglyretarding TrOCs (compare section 3.4) should be treated with caution.
2.5 Reactive transport modeling

Measured concentration time series in the HZ were evaluated using the one-dimensional (1D) advection-dispersion transport equation including first-order degradation and retardation (1D-ADE). Assuming steady and uniform flow in a homogeneous medium, and time invariant dispersion, retardation and first-order decay the 1D-ADE equation can be written as:

$$R \frac{\partial c}{\partial t} = D_h \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x} - \lambda c$$  \hspace{1cm} (2)

where $c$ denotes the concentration of a (reactive) compound, $D_h$ the effective hydrodynamic dispersion coefficient ($\text{m}^2 \text{h}^{-1}$), $\nu$ the vertical porewater velocity ($\text{m h}^{-1}$), $\lambda$ a first-order removal rate constant ($\text{h}^{-1}$) and $R$ the retardation coefficient (-). Equation 2 was implemented in the programming language Python and solved numerically using a finite-difference scheme. The HZ was vertically divided into three sections delimited by each pair of concentration time series: Section 1 between the surface water and 10 cm depth, section 2 between 10 and 30 cm depth and section 3 between 30 and 40 cm depth. For each section in the HZ, equation 2 was solved separately, yielding independent parameter estimates for each section. The upper concentration time series served as an upper boundary condition in equation 2. The lower boundary condition (in 100, 110 and 120 cm depth for sections 1, 2 and 3, respectively) was set to zero. The lower concentration time series in each section was used for parameter estimation.

Parameter estimation was achieved using the DREAM algorithm,\textsuperscript{38,39} a Bayesian parameter optimization method which employs evolutionary Monte Carlo Markov chains to estimate posterior probability density distributions (posteriors) of model parameters. In a first step, posteriors of conservative transport characteristics (i.e. $\nu$ and $D_h$) were estimated from EC time series by setting $\lambda$ to zero and $R$ to unity. In a second step, measured concentrations of TrOCs, DOC and NO$_3$-N were used to derive first-order removal rate constants and, for TrOCs, retardation coefficients using the previously derived posteriors for $\nu$ and $D_h$ as priors. This approach was justified as the relative contribution of molecular diffusion to $D_h$, which at sediment-water interface is commonly described as the sum of molecular, hydrodynamic and turbulent
diffusivities\textsuperscript{40,41} can be considered negligible, because porewater velocities measured in the present study were larger than $10^{-6}$ m s\textsuperscript{-1} (compare section 3.1) and molecular diffusion coefficients ($D_{mol}$) for the investigated TrOCs are generally smaller than $10^{-9}$ m\textsuperscript{2} s\textsuperscript{-1} (Table SI-03, see SI section 3.3 for details on calculation of $D_{mol}$).

Retardation coefficients can only be estimated from measured concentration time series that show a distinct, traceable temporal pattern, i.e., a trough or peak. For TrOCs, parameter optimization via DREAM was therefore conducted using two models, one including ($R \geq 1$) and one excluding the effect of retardation ($R=1$). If retardation coefficients could not be estimated, i.e., if posteriors of $R$ were indifferent from their priors, $\lambda$ was estimated from the model in which $R$ was set to unity. The conceptual model of equation 2 assumes that i) water flows vertically from the surface into the HZ and that ii) mixing with groundwater can be neglected. These assumptions were justified as i) the study site was characterized by strong downwelling conditions (compare section 3.1) and a previous investigation on hyporheic flow fields at the same site found that horizontal flow components were of minor importance\textsuperscript{14} and ii) relative removal of O-desmethylvenlafaxine, a stable reference compound (compare section 2.4), was calculated to be -3 to 4\% (Table 2) indicating that groundwater input along the investigated flow path was negligible. Details on the numerical scheme used to solve equation 2 and the parameter estimation procedure including the prior distributions of model parameters and other DREAM settings are provided in the SI.

\section*{3. Results & Discussion}

\subsection{3.1 Transport characteristics in the hyporheic zone}

Median porewater velocities, estimated from temperature depth profiles using VFLUX, ranged between 0.06 and 0.11 m h\textsuperscript{-1} (Table 1). These strong downwelling conditions (positive flux = downward flow) are in line with values reported previously for the same study site.\textsuperscript{14} As a result of low WWTP discharge during nighttime, EC time series in the surface water of River Erpe follow a saw-toothed pattern with distinct EC troughs in early morning hours.\textsuperscript{14} The EC trough, measured in the surface water between 02:00
and 10:00 on June 16th propagated into the HZ and served as a natural tracer from which conservative
transport parameters were modeled using equation 2 (Figure 2). Porewater velocities derived from EC
time series using the 1D-ADE model ranged from 0.07 m h\(^{-1}\) to 0.17 m h\(^{-1}\) and are thus somewhat higher
than porewater velocities calculated from temperature time series using VFLUX, particularly in the upper
two sections of the HZ (Table 1). Differences in porewater velocities might be the result of erroneous
VFLUX calculations (e.g., due to violations of VFLUX model assumptions) and sediment heterogeneity.
Values for the effective hydrodynamic dispersion coefficient (\(D_h\)) ranged between 10 \(\times 10^{-4}\) and 48 \(\times 10^{-4}\)
m\(^2\) h\(^{-1}\) and are within the same order of magnitude as values of the effective thermal dispersion coefficient
calculated by VFLUX (\(D_t\), Table 1).

Table 1 Mean values (± 1 standard deviation) of porewater velocities (\(v\)) and dispersion coefficients (hydrodynamic dispersion
coefficient \(D_h\), thermal dispersion coefficient \(D_t\)) derived from i) electrical conductivity (EC) time series using eqn. 2 (1D-ADE)
and ii) from temperature time series using VFLUX 2.0 for all three sections in the hyporheic zone. In addition, removal rates of
\(\text{NO}_3^-\)-N (\(k_{\text{nit-N}}\)) and DOC (\(k_{\text{DOC}}\)) are shown.

<table>
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<th>depth</th>
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<th>VFLUX 2.0</th>
<th>NO(_3^-)-N</th>
<th>DOC</th>
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<td>(D_h)</td>
<td>(v)</td>
<td>(D_t)</td>
</tr>
<tr>
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<td>m h(^{-1})</td>
<td>m(^2) h(^{-1}) x 10(^{-4})</td>
<td>m h(^{-1})</td>
<td>m(^2) h(^{-1}) x 10(^{-4})</td>
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<td>0.11 ± 0.02</td>
<td>73 ± 05</td>
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<tr>
<td>10-30</td>
<td>0.17 ± 0.01</td>
<td>10 ± 3</td>
<td>0.07 ± 0.01</td>
<td>34 ± 01</td>
</tr>
<tr>
<td>30-40</td>
<td>0.07 ± 0.01</td>
<td>46 ± 12</td>
<td>0.06 ± 0.01</td>
<td>36 ± 01</td>
</tr>
</tbody>
</table>
3.2 Redox zonation and DOC dynamics in the hyporheic zone

DOC concentrations gradually decreased along the investigated hyporheic flow path, while SUVA$_{254}$ and HIX, measures of the aromaticity and the degree of humification of DOC, respectively increased (Figure SI-04). A general decrease of DOC concentrations and an increase of SUVA$_{254}$ along hyporheic flow paths has been reported previously and was attributed to preferred degradation of non-aromatic, biodegradable DOC fractions in the HZ. The largest removal rate of DOC as well as the largest change in HIX occurred between 0 and 10 cm depth (Table 1, Figure SI-04), suggesting that the largest change in DOC quantity and quality along the investigated hyporheic flow path occurred in the upper 10 cm of the HZ. This finding is in agreement with previous investigations in the HZ, suggesting that the highest carbon turnover rates in the HZ are typically found within the first cm of the HZ in the so called active benthic bio-layer. A more detailed discussion of DOC dynamics in the HZ including information on other EEM indices is provided in the SI (SI section 6).

During the sampling period, nitrate concentrations in the surface water were high (median concentrations 7.0 mg/L NO$_3$-N, Table SI-04). In the HZ, nitrate removal rates were high between 0 and 10 cm depth, low between 10 and 30 cm depth and highest between 30 and 40 cm depth (Figure SI-03, Table 1). Concentrations of total dissolved iron and dissolved manganese in the HZ were relatively low (< 0.05 mg/L, Table SI-04), indicating the redox conditions in the stream sediment were not yet within iron- and manganese-reducing ranges. Removal of nitrate-N in the HZ can be caused by microbial uptake (i.e., assimilation) and denitrification occurring in both anoxic sections of the HZ and in anoxic microzones. Because DOC removal rates were highest in the shallow HZ, it is reasonable to assume that in addition to potential denitrification in anoxic microzones, nitrate-N removal in the upper 10 cm in the HZ was primarily caused by biotic assimilation. The higher nitrate-N removal rate in the deeper HZ (i.e., between 30 and 40 cm depth), however, is presumably attributable to denitrification. It is therefore likely that redox conditions in the bulk porewater were rather oxic in the first 30 cm of the HZ and became suboxic (i.e. denitrifying) thereafter. Redox zonation in the HZ is a function of biogeochemical parameters, such as
microbial turnover rates and the abundance and quality of electron acceptors and donors, physical parameters such as temperature and transport characteristics that control residence time distributions in the HZ. Compared to earlier investigations on redox zonation in the HZ at the same study site, redox zonation in the present study was shifted downwards (i.e. deeper onset of denitrification and iron/manganese reduction). In line with previous studies, we attribute this finding to larger porewater velocities measured in the present study.
3.3 Reactivity of trace organic compounds in the HZ

Out of the 29 investigated TrOCs, relative removals (%) and first-order removal rates could be calculated from measured concentration time series of 28 compounds (Table 2). For epoxy-carbamazepine (EBZ), concentrations were either below LOQ or just slightly above LOQ and thus EBZ was not considered in further analysis (Table SI-04). Modeled and measured concentration time series for valsartan acid (VSA), metformin (MEF) and its TP guanylurea (GUA) and EC are depicted in Figure 2. Measured and modeled concentration time series of the remaining TrOCs are shown in Figures SI 05-32. Twenty-two compounds were significantly removed between the surface water and 40 cm depth with half-lives within the first 10 cm of the HZ ranging between 0.1±0.01 h for iopromide and 3.5±0.3 h for tramadol (Table 2).

The highest removal rate constants were calculated for the iodinated X-ray contrast agents iomeprol (IOM) and iopromide (IOP). Complete de-iodination of both compounds in saturated sediments has only been observed under anoxic redox conditions\cite{45} but both compounds are known to readily loose side chains of the iodinated ring structure under aerobic conditions.\cite{46,47} It is therefore likely that the high removal rates calculated in the present study are due to transformation of both compounds and do not represent complete mineralization. Removal of the artificial sweetener acesulfame (ACS), the lipid-lowering agent bezafibrate (BZF), the anti-corrosive agents benzotriazole and methylbenzotriazole and the anticonvulsant GAB along oxic to suboxic (i.e. denitrifying) flow paths in hyporheic sediments has previously been described in laboratory column experiments\cite{12,48} and observed in the HZ.\cite{14} For ACS, reported half-lives range from 1.2\cite{14} to 5\cite{12} h and for BZF and GAB were calculated to be 1.2 h and 0.96 h in a previous investigation at the same site.\cite{14} Thus, half-lives for ACS, BZF and GAB calculated in the present study match half-lives calculated previously for hyporheic sediments. Removal of gabapentin-lactam, a major TP of GAB,\cite{48} in saturated sediments has previously been reported during bank filtration, with half-lives between 1.2 and 3.7 h.\cite{49} These values match the ones calculated for the first 10 cm of the HZ (2.3±0.2 h), although no further removal of GPL was observed in deeper section of the HZ.
Although the antidiabetic drug metformin and its main TP guanylurea\(^{50}\) have been detected ubiquitously in surface waters,\(^{51,52}\) qualitative information on the fate of the two compounds in saturated sediments is relatively scarce. Both were found to be rather stable in laboratory batch experiments;\(^{50,53}\) a finding that cannot be confirmed in the present study where they show half-lives in the HZ of several hours. Calculated half-lives for the beta-blockers MTP are in line with findings of a laboratory column study reporting half-lives of several hours for oxic/suboxic conditions,\(^{12}\) but contrast results of investigations conducted previously at the same study site, in which MTP was, on average, not significantly removed along a 20 cm long hyporheic flow path.\(^{14}\) Metoprolol acid (MTA), a main TP of MTP, was formed in the HZ, suggesting that removal of MTP in the HZ is at least in part due to transformation into MTA. Quantitative information on the fate of the beta blocker sotalol (SOT) and the opioid analgesic tramadol (TRA) in the HZ is limited. For SOT and TRA, a concentration decrease in the HZ\(^{25}\) and in sediments of a flume study mimicking the HZ,\(^{13}\) respectively, has been reported, but no removal rates were calculated. The antihypertensive drugs olmesartan (OLM), irbesartan (IRB), candesartan (CAN) and valsartan (VAL) were significantly removed along the investigated flow path. Simultaneously concentrations of their common TP valsartan acid\(^{54,55}\) (VSA) increased. At least part of the removal of OLM, CAN, VAL and IRB can therefore be attributed to transformation to VSA. While VAL removal in hyporheic sediments has been described,\(^{17}\) OLM and CAN were found to be rather stable in both, hyporheic sediments and during river bank filtration.\(^{17,49}\) Although removal of VSA has been described in bank filtration systems,\(^{49}\) concentrations of its PCs were likely too high in the HZ and thus net formation rates were higher than potential VSA removal rates. Carbamazepine (CBZ) and one of its TPs dihydroxy-carbamazepine (DBZ), diclofenac (DCF), diatrizoic acid (diatrizoate, DTA) and venlafaxine (VLX) and its TP O-desmethylvenlafaxine (MLX) were not significantly removed and were thus considered to be rather stable along the investigated flow path (Table 2). CBZ is well known for its stability in saturated sediments\(^{56}\) and hitherto, removal has only been observed under iron-reducing conditions after long (several days) residence times.\(^{57}\) Since concentrations
of DBZ remained relatively constant along the investigated flow path it is reasonable to assume that
transformation of CBZ to DBZ along short (<40 cm) and rather oxic flow paths in the HZ is limited.
Laboratory and field studies have demonstrated that VLX, DCF, and DTA can be removed in saturated sediments. It is therefore likely that in the present study exposure times to favorable biogeochemical conditions in the HZ times were likely too short to facilitate significant removal of these compounds.

The anticonvulsant primidone (PRI) and the antibiotic sulfamethoxazole (SMX) showed negative removal indicating a concentration increase in the HZ. To the best of our knowledge, formation of PRI in the HZ has not been reported and we thus attribute the small concentration increase (18±7%) to desorption processes. For SMX however, back-transformation of photo-transformation products into SMX has been observed in water/sediment systems. It is therefore perceivable that back-transformation was responsible for the observed concentration increase of SMX. The TrOC 4-formylaminoantipyrin (FAA), a human metabolite of metamizole (a phenazone-type analgesics not investigated in the present study), was found to be removed between 0 and 30 cm depth but was formed between 30 and 40 cm depth. Removal of FAA in oxic sections of saturated sediments has been described, although a previous investigation at the same site found inconsistent behavior (removal in some profiles, formation in others) of the compound. It remains unclear whether the formation of FAA during suboxic (i.e. denitrifying) redox conditions is due to back-transformation or due to increased transformation of its PC(s).

For some compounds (e.g. OLM), modeled concentration time series could be fitted well over the entire time series. For other compounds such as MTP, VSA or GUA (Figure 1, Figure SI-24), modeled concentrations matched measured concentration time series well in some parts of the time series but deviated in others. Such discrepancies indicate that model assumptions such as time invariant porewater velocities or removal rate constants were not met throughout the sampling event. Time varying removal rate constants could be the consequence of temperature dependent biotransformation rates or varying substrate and TrOC concentrations in the surface water.
Figure 2 Measured (dots) and modeled (solid lines) concentration time series in 10 cm, 30 cm and 40 cm depth in the hyporheic zone (HZ) and measured concentration time series in the surface water (0 cm) of guanylurea (GUA), metformin (MEF), valsartan acid (VSA) and electrical conductivity (EC). For concentration time series measured in the HZ, analytical uncertainty (one standard deviation) is shown in grey. Note that for modeling purposes, concentration time series in the surface water were linearly interpolated (black dashed line) and that for EC no measurement uncertainties were available.
Table 2 Relative removal in the upper 40 cm of the hyporheic zone (Rel$_{0-40}$, %), half-lives (t$_{1/2}$, h) and retardation coefficients (R, dimensionless) of all trace organic compounds investigated in the present study except epoxy-carbamazepine calculated between 0 and 10, 10 and 30 and 30 and 40 cm depth in the hyporheic zone. Note that retardation coefficients could only be estimated from input time series that showed a distinct temporal pattern, i.e. a trough or peak. Half-lives exceeding the sampling period (i.e., 17 h) were set to infinity.

<table>
<thead>
<tr>
<th>TrOC</th>
<th>Rel$_{0-40}$ (%)</th>
<th>t$_{1/2}$ (h)</th>
<th>R (-)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>0-40</td>
<td>0-10</td>
<td>10-30</td>
</tr>
<tr>
<td>acesulfame (ACS)</td>
<td>78±1</td>
<td>0.5±0.0</td>
<td>2.9±0.2</td>
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<td>benzotriazole (BTA)</td>
<td>63±2</td>
<td>0.9±0.0</td>
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<td>bezafibrate (BZF)</td>
<td>69±2</td>
<td>0.8±0.0</td>
<td>3.7±0.1</td>
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<td>candesartan (CAN)</td>
<td>27±4</td>
<td>1.1±0.1</td>
<td>12.9±3.8f*</td>
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<tr>
<td>carbamazepine (CBZ)</td>
<td>9±5*</td>
<td>9.8±1.6</td>
<td>inf</td>
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<tr>
<td>dihydroxy-carbamazepine (DBZ)</td>
<td>-1±6*</td>
<td>3.2±0.4*</td>
<td>11.4±5.3</td>
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<tr>
<td>diclofenac (DCF)</td>
<td>-11±6*</td>
<td>inf</td>
<td>inf</td>
</tr>
<tr>
<td>diatrizoic acid (DTA)</td>
<td>0±9*</td>
<td>6.3±1.4*</td>
<td>inf</td>
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<td>4-formylaminoantipyrine (FAA)</td>
<td>6±4</td>
<td>1.2±0.1</td>
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<td>gabapentin (GAB)</td>
<td>79±1</td>
<td>0.4±0.0</td>
<td>1.5±0.0</td>
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<td>gabapentin-lactam (GPL)</td>
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<td>2.3±0.2</td>
<td>8.9±1.4*</td>
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<td>guanylurea (GUA)</td>
<td>78±1</td>
<td>0.6±0.0</td>
<td>1.4±0.0</td>
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<td>iomeprol (IOM)</td>
<td>98±0</td>
<td>0.1±0.0</td>
<td>0.7±0.0</td>
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<td>iopromid (IOP)</td>
<td>98±0</td>
<td>0.1±0.0</td>
<td>0.8±0.1</td>
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<td>irbesartan (IRB)</td>
<td>37±3</td>
<td>1.0±0.0</td>
<td>7.1±1.3f</td>
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<td>methylbenzotriazole (MBT)</td>
<td>36±3</td>
<td>1.7±0.0</td>
<td>4.1±0.1</td>
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<tr>
<td>metformin (MEF)</td>
<td>66±2</td>
<td>1.1±0.1</td>
<td>1.6±0.0</td>
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<td>O-desmethylvenlafaxine (MLX)</td>
<td>0±6*</td>
<td>14.1±6.8f</td>
<td>12.1±5.6*</td>
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<td>metoprolol acid (MTA)</td>
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<td>metoprolol (MTP)</td>
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<td>olmesartan (OLM)</td>
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<td>1.5±0.1</td>
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<td>-18±7</td>
<td>10.3±3.9f*</td>
<td>inf</td>
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<td>sulfamethoxazole (SMX)</td>
<td>-478±8</td>
<td>6.8±1.4*</td>
<td>4.9±0.4f</td>
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<td>sotalol (SOT)</td>
<td>50±2</td>
<td>0.8±0.0</td>
<td>3.3±0.2</td>
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<td>tramadol (TRA)</td>
<td>12±4</td>
<td>3.5±0.2</td>
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<td>valsartan (VAL)</td>
<td>26±4</td>
<td>1.1±0.0</td>
<td>7.8±0.2</td>
</tr>
<tr>
<td>venlafaxine (VLX)</td>
<td>-5±9*</td>
<td>6.2±2.2*</td>
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<tr>
<td>valsartan acid (VSA)</td>
<td>-205±15</td>
<td>1.2±0.0f</td>
<td>2.4±0.1f</td>
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</table>

inf = half-life > 17 h. * = not significantly removed/formed as indicated by Rel$_{t}$. n.e. = not estimated. f = TrOC formation.
Figure 3 First-order removal rate constants ($\lambda$) as a function of depth of all investigated parent compounds (PCs, shown in red) and transformation compounds (TPs, shown in blue) except, primidone, epoxy-carbamazepine, venlafaxine and O-desmethylvenlafaxine. Error bars indicate one standard deviation. ACS, acesulfame; BTA, benzotriazole; BZF, bezafibrate; CAN, candesartan; CBZ, carbamazepine; DBZ, dihydroxy-carbamazepine; DCF, diclofenac; DTA, diatrizoic acid; FAA, 4-formylaminoantipyrine; GAB, gabapentin; GPL, gabapentin-lactam; GUA, guanylurea; IOM, iomeprol; IOP, iopromide; IRB, irbesartan; MTA, methylbenzotriazole; MEF, metformin; MTA, metoprolol acid; MTP, metoprolol; olmesartan, OLM; SMX, sulfamethoxazole; SOT, sotalol; TRA, tramadol; VAL, valsartan; VSA, valsartan acid.
3.4 Retardation of TrOCs in the HZ

Surface water concentration time series of all 28 TrOCs that were further investigated in the present study showed a pronounced temporal pattern (i.e. a concentration trough) and thus retardation coefficients for all TrOCs except IOP and MTA could be calculated for the first 10 cm in the HZ. However, concentration time series of many TrOCs measured in 10 and 30 cm did no longer exhibit a distinct temporal pattern and thus retardation coefficients could not be estimated between 10 - 30 and 30 - 40 cm for these compounds (Table 2). Calculated retardation coefficients ranged from 1.1±0.1 (i.e., no retardation) for compounds such as ACS, VSA, and DTA to 15.3±2.2 for MEF (Table 2).

Retardation of TrOCs along hyporheic flow paths is due to reversible sorption processes caused by a variety of interaction mechanisms between TrOCs and streambed sediments and biofilms. Neutral TrOCs interact with streambed materials predominately via hydrophobic partitioning, while sorption and retardation of ionizable compounds can additionally be caused by electrostatic interactions and surface complexation. At ambient pH values measured in River Erpe during the sampling campaign (pH ≈ 7.3), 7 of the investigated compounds occur as cations (GUA, MEF, MTP, SOT, VLX, MLX and TRA), 10 TrOCs occur as anions (ACS, BZF, CAN, DCF, DTA, IRB, OLM, SMX, VAL and VSA), 2 occur as a zwitterions (GAB, MTA) and 9 do not carry any charge (BTA, CBZ, DBZ, FAA, GPL, IOM, IOP, MBT, and PRI). To assess the possible influence of hydrophobic partitioning retardation, Pearson Product Moment correlations were calculated between retardation coefficients estimated for the first 10 cm in the HZ and pH-dependent octanol-water partitioning coefficients (logD_{ow}) of the respective TrOCs (obtained from www.chemicalize.com, Table SI-05). Retardation coefficients of positively charged TrOCs were all larger than 1 and did not significantly correlate with logD_{ow} values (Table SI-06), suggesting that the contribution of hydrophobic partitioning to retardation of cationic TrOCs is negligible. This finding is in line with previous observations indicating that sorption of cationic TrOCs, such as MEF, its TP GUA, VLX and beta-blockers such as MTP and SOT to sediment materials can be substantial and occurs predominately via electrostatic interactions. By contrast, logD_{ow} values of negatively charged TrOCs
correlated positively with estimated retardation coefficients (Table SI-06), indicating that retardation of anionic TrOCs in the HZ is at least partially caused by hydrophobic partitioning into sediment organic matter. This finding is in agreement with work that showed that sorption of anionic compounds is driven by their hydrophobicity rather than by electrostatic interactions.\textsuperscript{66} For the neutral TrOCs PRI, CBZ, and DBZ, retardation coefficients found in a laboratory column ($R_{\text{CBZ}} = 2.1$, $R_{\text{DBZ}} = 3.2$, $f_{\text{oc}} = 0.29\%$)\textsuperscript{20} and batch tests ($R_{\text{CBZ}} = 3.6-5.3$, $R_{\text{PRI}} = 1.2$, $f_{\text{oc}} = 0.23\%$)\textsuperscript{21} compared well to values calculated in the present study (sediment $f_{\text{oc}} = 0.5 – 6\%$),\textsuperscript{14} while a field study had found negligible retardation for compounds such as CBZ and BTA during riparian bank filtration ($f_{\text{oc}} = 0.01-0.11\%$).\textsuperscript{16} Such discrepancies are likely attributable to differences in sediment organic matter content and general sediment heterogeneity. We conclude that reversible sorption processes can substantially retard TrOCs along hyporheic flow paths, even for compounds that are negatively charged. Retardation caused by reversible sorption processes increases the residence time of TrOCs relative to the water residence time in the HZ. Neglecting the effect of retardation may lead to erroneous estimates of removal rate constants, particularly when their calculation is based on simple concentration differences\textsuperscript{17} and when sampling periods are relatively short compared to the characteristic time scales over which surface water concentrations fluctuate. Studies that aim at quantitatively investigating the fate of TrOCs in the HZ and along river reaches with significant hyporheic exchange flows should therefore consider retardation and adjust their reactive transport models and sampling schemes accordingly. Some compounds (e.g. CBZ, DBZ, VLX, or DCF) were retarded along the investigated hyporheic flow path but showed only very small removal rates in the HZ. If concentrations of these compounds in surface waters drop considerably over short time scales (e.g. during hydrological events), desorption processes might remobilize TrOCs previously adsorbed to sediment materials and biofilms and hence hyporheic exchange would lead to a concentration increase of these TrOCs in the surface water.
3.5 Influence of benthic bio-layer and DOC on TrOC reactivity

For all TrOCs for which concentration changed significantly between the surface water and 40 cm depth in the HZ (22 out of 28) except SMX, removal rates calculated for the top 10 cm in the HZ were substantially higher compared to removal rate constants calculated between 10 and 30 and 30 and 40 cm depth (Figure 3). Because redox conditions in the top 30 cm of the HZ were predominantly oxic, it is reasonable to assume that the increased reactivity in the top 10 cm of the HZ is due to increased microbial activity in the benthic bio-layers growing in the top cm of the HZ and high chemical turnover rates typically associated with shallow hyporheic flow paths.\textsuperscript{10,11} This finding is further underlined by changes in DOC concentration and quality, suggesting that TrOC turnover within similar redox zones in the HZ is closely coupled to DOC turnover. Studies on managed aquifer recharge reported that TrOC removal rates under oxic conditions were highest when BDOC was limited, an observation that was mainly attributed to the presence of highly adapted microbial communities that developed under oligotrophic conditions.\textsuperscript{22,49,67} However, our results show, that in natural systems such as the HZ, high TrOC removal rates can also be associated with oxic and eutrophic conditions, in which high concentrations of BDOC likely fuel microbial metabolism and serve as a co-substrate for the co-metabolic removal of TrOCs.

Due to practical limitations associated with our sampling approach, the present study investigated a downwelling flow path that is unlikely to return to the surface water. However, our findings should in principle be transferable to hyporheic flow paths that return to the stream and thus have implications for reach-scale removal of TrOCs. Together with earlier investigations showing that for many TrOCs removal rates are higher under oxic compared to anoxic redox conditions,\textsuperscript{12,14} our results suggest that short and shallow flow paths are more efficient in removing TrOCs than long and deep flow paths, along which redox conditions become increasingly anoxic and microbial activity decreases. River restoration measures that promote frequent and short vertical exchange flows through the shallow HZ, such as the construction of engineered hyporheic zone elements\textsuperscript{68–70} or the application of woody debris,\textsuperscript{71} are therefore likely to
contribute more to overall in-stream removal of TrOCs than measures that promote, longer lateral exchange flows such as the installation of meander bends or pool-riffle sequences.
References


(7) Arnok, P.; Singh, R. R.; Burakham, R.; Pérez-Fuentetaja, A.; Aga, D. S. Selective Uptake and


Supporting Information

(1) Additional information on VFLUX 2.0 calculations and (2) TrOC analysis (Tables SI-01 & 02); (3) Description of the reactive transport model, DREAM settings, and molecular diffusion coefficients of TrOCs (Table SI-03); (4) Comparison of table reference compounds (Figure SI-01); (5) Median concentrations of TrOCs, NO$_3^-$-N, dissolved manganese and total dissolved iron in the surface water and in hyporheic porewater; (6) Measured hyporheic temperatures (Figure SI-02) and further discussion on DOC and NO$_3^-$-N dynamics in the HZ (Figures SI-03 & 04); (7) pKa and LogK$_{ow}$ values of investigated TrOCs (Table SI-05); (8) Pearson Product Moment correlations between logD$_{ow}$ and calculated retardation coefficients; (9) Concentration time series and associated model fits (Figures SI-05 - SI-32) of all investigated TrOCs.
Acknowledgements

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Figure 1 Experimental setup showing the three minipoint sampler installed in 10 cm, 30 cm and 40 cm depth in the hyporheic zone (HZ). The samplers were installed in a line (< 1 cm distance) perpendicular to the water flow direction. A Multilevel Temperature Stick (MLTS) was installed in close proximity (≈ 10 cm) next to the minipoint sampler array. Blue arrows indicate surface water and predominant hyporheic flow directions. Minipoint samplers were sampled from an aluminum bridge spanning the river channel (not shown).

200x139mm (300 x 300 DPI)
Measured (dots) and modeled (solid lines) concentration time series in 10 cm, 30 cm and 40 cm depth in the hyporheic zone (HZ) and measured concentration time series in the surface water (0 cm) of guanylurea (GUA), metformin (MEF), valsartan acid (VSA) and electrical conductivity (EC). For concentration time series measured in the HZ, analytical uncertainty (one standard deviation) is shown in grey. Note that for modeling purposes, concentration time series in the surface water were linearly interpolated (black dashed line) and that for EC no measurement uncertainties were available.
First-order removal rate constants (\( \lambda \)) as a function of depth of all investigated parent compounds (PCs, shown in red) and transformation compounds (TPs, shown in blue) except, primidone, epoxy-carbamazepine, venlafaxine and O-desmethylvenlafaxine. Error bars indicate one standard deviation. ACS, acesulfame; BTA, benzotriazole; BZF, bezafibrate; CAN, candesartan; CBZ, carbamazepine; DBZ, dihydroxy-carbamazepine; DCF, diclofenac; DTA, diatrizoic acid; FAA, 4-formylaminoantipyrine; GAB, gabapentin; GPL, gabapentin-lactam; GUA, guanylurea; IOM, iomeprol; IOP, iopromide; IRB, irbesartan; MBT, methylbenzotriazole; MEF, metformin; MTA, metoprolol acid; MTP, metoprolol; olmesartan, OLM; SMX, sulfamethoxazole; SOT, sotalol; TRA, tramadol; VAL, valsartan; VSA, valsartan acid.