Hyporheic Exchange Controls Fate of Trace Organic Compounds in an Urban Stream

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Hyporheic exchange controls fate of trace organic compounds in an urban stream

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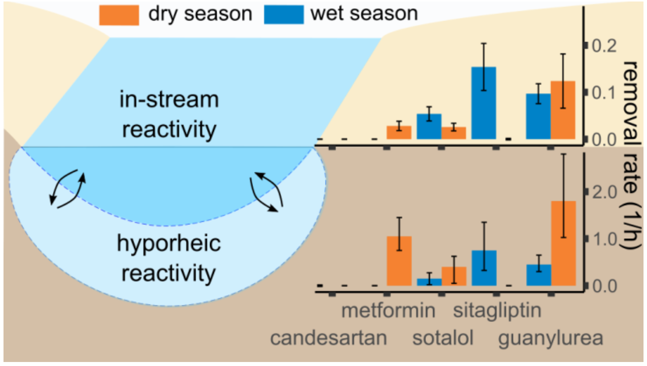
TOC Art


dry season
wet season
in-stream reactivity
hyporheic reactivity
0.2
0.1
0.0
2.0
1.0
0.0
removal rate (1/h)
metformin
sitagliptin
candesartan
sotalol
guanylurea

Abstract

First-order half-lives for 26 trace organic compounds (TrOCs) were determined in the hyporheic zone (HZ) and along a 3 km reach of a first-order stream in South Australia during both, dry and wet seasons. Two salt tracer experiments were conducted and evaluated using a transient storage model to characterize seasonal differences in stream residence time and transient storage. Lagrangian and time-integrated surface water sampling were conducted to calculate half-lives in the surface water. Half-lives in the HZ were calculated using porewater samples obtained from a modified mini-point sampler and hyporheic residence times measured via active heat-pulse sensing. Half of the investigated TrOCs (e.g. oxazepam, olmesartan, candesartan) were not significantly removed along both the investigated river stretch and the sampled hyporheic flow paths. The remaining TrOCs (e.g. metformin, guanylurea, valsartan) were found to be significantly removed in the HZ and along the river stretch with relative removals in the HZ correlating to reach-scale relative removals. Using the modeled transport parameters, it was estimated that wet season reach-scale removal of TrOCs was predominately caused by removal in the HZ when the intensity of hyporheic exchange was also higher. Factors that increase HZ exchange are thus likely to promote in-stream reactivity of TrOCs.

Keywords

Pharmaceuticals, urban water cycle, transient storage, hyporheic zone, metformin

Introduction

Trace organic compounds (TrOCs) originating from wastewater treatment plants (WWTPs) are frequently detected in urban rivers,[1,2] in which they have adverse effects on aquatic ecosystems[3–6] and pose risks for drinking water production.[7] The in-stream removal of TrOCs in rivers is driven by a variety of physio-chemical and biological processes. Some of these removal processes (photolysis and volatilization) are restricted to surface water. Others such as sorption and abiotic and microbially mediated transformation and degradation processes occur predominately at the water-sediment interface, in biofilms growing on stones and macrophytes and river sediments.[8–10] The hyporheic zone (HZ) is defined as the portion of river sediments that acts as an interface and mixing zone between groundwater and surface water. Hyporheic sediments are typically characterized by steep redox gradients, increased reactive surface areas, high microbial turnover rates and diverse microbial communities and are therefore considered to act as efficient bioreactors.[11–13] Compared to other saturated subsurface environments, reactivity of TrOCs in the HZ is relatively high, primarily due to higher chemical turnover rates in the HZ.[14] Both laboratory[15,16] and field studies[14,17] further demonstrated that the HZ is capable of removing TrOCs, even along short (cm) flow paths. A number of studies have consequently attributed a large proportion of the observed in-stream removal at the reach-scale to removal processes in the HZ.[18–20]

The relative contribution of the HZ to in-stream removal of TrOCs, and thus the significance of hyporheic zones, is not only a function of the reactivity of TrOCs in the HZ but is also controlled by physical exchange flows between the HZ and the surface water. In previous studies on the in-stream fate of TrOCs, exchange flows between the HZ and the surface water were either not quantified[19,20] or found to be relatively small.[9,18] Therefore, the relative importance of removal processes in the HZ for reach-scale in-stream removal of TrOCs as a function of the intensity of hyporheic exchange fluxes remains poorly understood. While the fate of some TrOCs such as neuro-active pharmaceuticals,[18] endocrine disruptors[9] and beta blockers,[19] in rivers has been investigated previously, quantitative information on the reactivity of many other TrOCs, such as the antidiabetic drugs metformin and sitagliptin and compounds of the sartan group, and their transformation products in lotic systems is widely lacking.

The aims of the present study were (i) quantify both the in-stream and hyporheic reactivity (i.e. half-lives) of several TrOCs and their respective transformation products in a WWTP effluent dominated stream, and (ii) quantify the relative contribution of hyporheic removal to in-stream (i.e. reach-scale) removal of TrOCs. To this end, we determined stream transport characteristics and both the in-stream and the HZ reactivity of 26 TrOCs including 19 parent compounds and 7 transformation products during wet and dry seasons in a first-order stream in South Australia. We hypothesize that in a small, first-order stream the fate of many TrOCs will be largely controlled by their respective reactivity in the HZ as well as the intensity of hyporheic exchange fluxes.

2. Methods

2.1 Site description and salt tracer experiments

The present study was conducted in a 3 km section of the Sturt River; a first-order stream in South Australia located in the Adelaide Hills (Figure SI-01). The Sturt River originates at the outlet of a small, municipal wastewater treatment plant (WWTP Heathfield). Consequently, at its source (Site A) the Sturt River contains close to 100% WWTP effluent. Several small ephemeral streams contribute water to the Sturt River during the wet season (May to September) but not during the dry season (October to April). Due to the Mediterranean climate in South Australia, surface water and porewater temperatures in the Sturt River are, on average, 5 °C higher during the dry than the wet season (Figure SI-02). Mean (±1 standard deviation, SD) river sediment porosity (θ) determined from 40 oven dried (105 °C, 48h) sediment samples taken using KSAT rings (Meter, Germany) at various locations between Site A and B was 0.4 ± 0.06. Saturated hydraulic conductivities (K) at 10 °C, measured in the same samples using a KSAT device (Meter, Germany), were found to be log-normally distributed with a mean of 1.7×10^{-4} m s^{-1} and a SD of 1.2×10^{-3} m s^{-1}. Mean (1 ± SD) sediment organic matter content (f_{oc}) determined in a subset of 6 samples by loss on ignition was 0.9 ± 0.2 wt.%. Mean surface water pH, measured at Site A using a YSI multiparameter probe (ProDSS YSI, USA) was 7.2 ± 0.1 during the wet and 7.5 ± 0.1 during the dry season experiments.

Two salt tracer experiments were conducted on October 7th 2016 and March 16th 2017 (corresponding to wet and dry seasons, respectively) to estimate hydrological transport characteristics, such as the magnitude of transient storage and hydraulic residence times. During both experiments, a salt tracer solution (75 gL^{-1} NaCl) was injected into the surface water at the WWTP outlet (Site A, Figure SI-01) over a 1 h period at a constant rate using a submersible pump (MP1, Grundfos, Denmark). Breakthrough curves of electrical conductivity (EC) were measured in the surface water at two locations downstream (Site A - after mixing length 0.1 km downstream of the WWTP outlet; Site B - 3 km downstream of Site A) using CTD Loggers

(Aqua TROLL 200, In-Situ, USA). Streamflow during the tracer experiment at Site A was provided by SA Water (owner and operator of the Heathfield WWTP).

2.2. Water Sampling

During the wet season (September 2016) experiment, time-integrated, hourly surface water samples were collected at Sites A and B over the course of 24 h from 00:00 on September 26th to 00:00 on September 27th 2016. All surface water samples were taken using an automatic water sampler (model 3700, Teflon suction line, Teledyne ISCO, Lincoln, NE.). During the March 2017 experiment, 6 and 8 surface water grab samples were collected during tracer breakthrough at Sites A and B, respectively. Samples of hyporheic porewater were collected using self-constructed minipoint samplers.[21,22] Mini-points consisted of HPLC tubes (PEEK, ID 0.03 inch, Sigma Aldrich, USA) inserted into 1.5 m long stainless steel tubes (ID 0.7 mm) with laser-cut, 1-cm long screens at the sealed tips. The HPLC tube was connected to 6-channel syringe pumps (NE-1600 New Era Pump Systems, Inc, Farmingdale, USA) via Swagelok fittings (Swagelok, USA). Ten ml of hyporheic porewater was sampled at a constant sampling rate of 1 ml min^{-1}. Porewater samples were taken along the upper section of the investigated river reach (Figure SI-01) at two depths in the HZ; 10 and 15 cm. During the wet season sampling event, 7 and 5 porewater samples were taken over the course of 3 h from the two depths respectively. Compared to the dry season event where 7 and 4 samples were taken over the course of 4.5 h at the two depths. At every sampling site, porewater velocities were measured via active heat pulse sensing.[23] The instrument injected one-minute heat pulses in the HZ and used the resulting measured temperature breakthrough curves to estimate Darcy flow velocities and thermal properties of the sediment in approximately 7.5 and 15 cm depth. Estimated Darcy flows were subsequently divided by sediment porosity to estimate porewater velocities. During the wet season porewater samples were taken on September 26th and were thus related to surface water samples taken on the same day. During the dry season porewater samples were taken on March 20th and related to surface water grab samples taken hourly over the course of 16 h prior to porewater sampling on the same day. Differences in sampling methodology between the two experiments resulted from the fact that due to field site logistical issues during the wet season, the stream tracer test was conducted 10 days after water sampling took place. Transferability of the transport characteristics was assumed because hydrological conditions on September 27th and October 7th were relatively similar (inferred from stream stage data), particularly when compared to differences in streamflow between the two seasons (see SI for detailed discussion).

All samples were filtered on site using regenerated cellulose filters (0.2 µm, Macherey-Nagel, Germany) for TrOCs and cellulose acetate syringe filters (0.2 µm, Sartorius, Germany) for anion and cation analysis (compare section 2.3). Samples for chloride and cation analysis were stored in polyethylene bottles at 4°C until analysis. Samples for major cation and trace element analyses were acidified with nitric acid (1% v/v HNO_3). Samples for TrOCs were stored in amber glass bottles with Teflon lined caps and were frozen immediately after recovery from the field.

2.3 Analytics

Samples for TrOC analysis were split and analyzed in parallel via high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) at Technical University of Berlin (TUB) following standard protocols,[24,25] and at the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University using a method established previously.[22] Separation was achieved using 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 using linear gradients (ultra-pure water versus 100% methanol; HPLC grade, J.T. Baker, USA). A TSQ Vantage and a Quantiva triple-quadrupole mass spectrometer (Thermo Fisher Scientific, USA) in ESI ± modes were used for MS/MS analysis at TUB and ACES, respectively. We analyzed 54 TrOCs, including 34 parent compounds (PCs) and 20 transformation products (TPs). In both methods, compound identification was achieved using the characteristic ratio of two ion fragments. Quantification was achieved using isotope-substituted standards (Toronto Research Chemicals, Canada) in combination with the most abundant fragment ion (Table SI-01). Calibration standards were measured before and after the sampling sequences in both methods. Details on linear gradients, respective internal standards, limits of detection

(LODs) and quantification (LOQs) for each target compound and a detailed description of the TUB method are provided in the SI. A detailed description of the ACES quantification method can be found in Posselt et al. 2018 (in press). Chloride concentrations in tracer test samples were determined by ion-chromatography (Metrohm, Switzerland, DIN EN ISO 10304-1 & Dionex ICS-2500, Thermo Fisher, USA). Cations and trace metals were analyzed by a Perkin Elmer NexION 350D Inductively Coupled Plasma Mass Spectrometer at Flinders University, Adelaide, South Australia. All ion balances were better than ±5%.

2.4 Relative removal and first-order removal rate constants

The relative removal (%) and first-order removal rate constants in the river between Site A and B and between the surface water and the hyporheic porewater were calculated by normalizing TrOC concentrations to those of a stable reference compound.[19,20] This method requires (i) relatively stable hydrological conditions during the sampling period, (ii) relatively constant compound ratios in the WWTP effluent, and (iii) the absence of other sources of TrOCs in the investigated stream reach. All of these assumptions were met in the present study as river discharge fluctuations at Site B during sampling were relatively small (Figures SI-03 & 04) and concentrations of TrOCs in the WWTP effluent were found to be close to time invariant over the sampling events (Table SI-06). Additional, diffuse inputs of TrOCs from other sources such as septic tanks can be assumed to be negligible because acesulfame (ACS), often associated with this source,[26] behaved conservatively in the surface water and concentrations of ACS did not increase relative to stable reference compounds during both sampling events. We used carbamazepine (CBZ) as a stable reference compound as it has previously been shown to behave highly persistent in lotic systems and saturated sediments[14,19,27] and was used as a stable reference compound previously.[20] Candesartan (CAN), a compound that can also be considered to behave rather persistent in saturated sediments[27] and in streams (present study), was used to cross-validate the approach (Figure SI-10).

For each sampling event, the relative removal for each TrOC ($\mathrm{Rel}_{\mathrm{x}}$) was calculated via:

$$\mathrm{Rel}_{x} = \left(1 - \frac{C_{ref,SiteA}}{C_{ref,SiteB}}\frac{C_{x,SiteB}}{C_{x,SiteA}}\right) x\ 100\% \tag{1}$$

in which $C_{\mathrm{ref,SiteA}}$ and $C_{\mathrm{ref,SiteB}}$ are the mean concentrations of the reference compound CBZ at Site A and Site B and $C_{\mathrm{x,SiteA}}$ and $C_{\mathrm{x,SiteB}}$ are the mean concentrations of a TrOC at Site A and Site B, respectively. For calculation purposes, concentrations of TrOCs larger than their LOD, but smaller than their LOQ, were set to their respective LOQ. Removal of TrOCs was considered significant if the 95% percentile of the relative removal did not include zero. For TrOCs that were significantly removed, first-order in-stream removal rate constants (k) were calculated for from log-transformed normalized concentration ratios:

$$k = -ln\left(\frac{C_{ref,SiteA}}{C_{ref,SiteB}}\frac{C_{x,SiteB}}{C_{x,SiteA}}\right)t_{med}^{-1} \qquad (2)$$

whereby t_{med} denotes the median travel time (h) between Sites A and B. Compound half-lives ($t_{1/2}$) were calculated from first-order removal rate constants via:

$$t_{1/2} = \frac{\ln(2)}{k} \qquad (3)$$

For TrOCs that were not significantly removed, first-order removal rate constants were set to zero and compound half-lives to infinity. Relative removal in the HZ was calculated using equation 1, whereby Site B denotes the porewater sample in the HZ and Site A is the mean surface water concentration. First-order removal rate constants in the HZ were calculated using equation 2, in which t_{med} was replaced with the residence time in the HZ at the respective sampling depth (t_{hz}). Hyporheic residence times were calculated from measured porewater velocities using the respective sampling depths.

2.5 River transport characteristics

River transport characteristics were derived from the measured salt-tracer breakthrough curves using an extended version of the one-dimensional advection-dispersion transient storage model (TSM),[28] which is discussed in detail in the SI. In brief, the original transient storage equations were transformed into a system of ordinary differential equations (ODEs) by eliminating the time derivate using the Laplace Transform Galerkin Technique.[29] The resulting set of ODEs was then solved numerically using a finite element discretization before it was back transformed to real space using the DeHoog algorithm.[30] An evolutionary Monte Carlo Markov chain embedded in the DREAM algorithm[31] was used to minimize the model likelihoods and produce parameter probability density distributions for streamflow at Site A ($Q_{\mathrm{Site\ A}}$), cross-sectional area of the main channel (A_{sw}), and the transient storage zone (A_s), first-order transient storage coefficient (α), dispersion (D) and lateral inflow (Q_L, posterior distributions shown in Figures SI-08 & 09). Measured EC time series were converted into time series of chloride concentration using an EC-chloride correlation curve, which was obtained from serial dilutions using WWTP effluent and NaCl solution from the tracer experiment. Median travel time (t_{med}) between Site A and B was defined as the time for 50% of the chloride mass to pass Site B.[32] The overall magnitude of transient storage in the reach can further be estimated by the fraction of median travel time due to transient storage (F_{med}):[32]

$$F_{med} \cong \left(1 - e^{-L_c\left(\frac{\alpha}{u}\right)}\right)\left(\frac{A_s}{A_{sw} + A_s}\right) \quad (4)$$

in which A_{sw} and A_s denote the cross-sectional area (m^2) of the main channel and the transient storage zone, respectively, α the storage zone exchange coefficient (s^{-1}), L_c the reach length (m) and u ($m\ s^{-1}$) the surface water flow velocity.

2.6 Relative contribution of the HZ to in-stream removal of TrOCs

The relative contribution of the HZ to in-stream removal of TrOCs can qualitatively be assessed by comparing removal percentages in the HZ to in-stream removal in the surface water relative to a theoretical mixing line. The slope of the mixing line can be approximated by the ratio between L_c, the length of the river reach (distance between Site A and B) and L_s, the theoretical reach length water parcels travel downstream before they are exchanged with the storage zone.[32] Following previous formulations,[33] and assuming that transient storage is mainly driven by streambed exchange, L_s can be estimated from transient storage parameters via:

$$L_s = \frac{u}{\theta \alpha} \tag{5}$$

where u is the average reach-scale flow velocity calculated as Q/A_{sw}. After L_s meters, the entire discharge will have spent a mean residence time τ_{hz} (A_s / αA_{sw}) in the transient storage zone. Using the mean residence time of the sampled porewater in the HZ (t_{hz}), L_c/L_s can be corrected for not sampling porewater with a mean age of τ_{hz}:

$$\frac{L_c}{L_s} = \frac{t_{hz}}{\tau_{hz}} \frac{L_c \theta \alpha}{u} \tag{6}$$

See SI for derivation of equations 5 and 6 and a detailed discussion of underlying assumptions.

3. Results & Discussion

3.1 Stream transport characteristics and hyporheic residence times

Streamflow (Q), A_{sw}, A_s, α, D and surface water flow velocity (Q/A) were considerably higher during the wet season (Table 1). Consequently, median travel time (t_{med}) between Sites A and B was more than twice as large during the dry season experiment compared to the wet season experiment. The calculated exchange (α) and dispersion (D) coefficients fall well within the range of values presented in previous studies on streams with similar characteristics.[32,34] Due to the absence of pools and dead zones in the water body, the transient storage in the investigated section of the Sturt River is mainly caused by streambed exchange. Higher flow velocities during the wet season cause dispersion and exchange coefficients to increase[34] and the hyporheic zone to expand,[35] which explains the larger cross-sectional area of the transient storage zone. The fraction of the median travel time due to transient storage (F_{med}) in the wet season (0.50) was more than double that of the dry season (0.20), indicating a higher intensity of hyporheic exchange during the wet season experiment. Fractions of WWTP effluent in the river system at Site B, calculated using carbamazepine as a stable reference compound, were 93 ± 2% in the dry season and 57 ± 2% in the wet season. The fraction of surface water in the HZ ranged from 80 to 100% during the wet season and from 85 to 100% during the dry season, indicating that the contribution of groundwater to hyporheic porewater was relatively small.

Hyporheic porewater velocities, calculated using active heat pulse sensing, ranged from 1.0 to 7.3 m d^{-1} with median values of 2.0 m d^{-1} (n = 11) and 3.4 m d^{-1} (n = 12) during the wet and dry season, respectively (Table SI-01). Assuming a log-normal distribution of the measured hyporheic residence times, mean (± 1 standard deviation) hyporheic residence times (t_{hz}) at the sampling depths were 2.0 h (± 1.3 h) during the wet season, compared to 1.0 h (± 0.6 h) during the dry season. Measured hyporheic porewater velocities compare well to values reported in previous studies.[14,33]

Table 1 Transport characteristics (streamflow at Site A ($Q_{Site\ A}$), stream cross-sectional area (A_{sw}), cross-sectional area of the transient storage zone (A_s), one-dimensional exchange coefficient (α) and fraction of median travel time due to transient storage (F_{med})) of the investigated stream reaches modeled using the one-dimensional advection-dispersion model with transient storage. Additionally, median travel time (t_{med}), mean surface water temperature, the proportion of WWTP effluent at Site B calculated using carbamazepine as a stable reference compound and the mean residence time in the transient storage zone (τ_{hz}) as well as the mean residence time of the sampled porewater in the HZ (t_{hz}) are shown. The length of the investigated reach was 3020 m in both experiments. Calculated dispersion coefficients (D) are provided in the SI.

Experiment	$Q_{Site\ A}$ (L s^{-1})	A_{sw} (m^2)	A_s (m^2)	$Log_{10}(\alpha)$ (s^{-1})	surface water temperature (°C)
dry season	19	0.25 ± 0.01	0.09 ± 0.03	-4.45 ± 0.06	19.6 ± 2.6
wet season	52	0.40 ± 0.00	0.50 ± 0.02	-4.00 ± 0.01	14.9 ± 0.3
	F_{med} (-)	t_{med} (h)	t_{hz} (h)	τ_{hz} (h)	WWTP effluent, Site B (%)
dry season	0.20 ± 0.01	12.2	1.0 ± 0.6	2.8 ± 1.1	93 ± 2
wet season	0.50 ± 0.01	4.9	2.0 ± 1.9	3.4 ± 0.2	57 ± 2

3.2. Occurrence of TrOCs in WWTP effluent

Twenty-five TrOCs, including 19 PCs and 6 TPs were consistently detected above their respective LOQ at the WWTP outlet (Site A) during both the wet and dry season sampling events (Figure 1). 4-Hydroxydiclofenac (HDF), a TP of diclofenac (DCF) was only detected during the wet season. During the wet season, median TrOC concentrations ranged from 0.04 µg/L for epoxy-carbamazepine (EBZ) to 48.3 µg/L for guanylurea (GUA, Table SI-06). TrOCs concentrations in the WWTP effluent during the dry season experiment ranged from 0.04 µg/L EBZ to 15.1 µg/L olmesartan (OLM). For the majority of TrOCs, concentrations at Site A were relatively constant during both porewater and surface water sampling. Relative standard deviations of mean surface water concentrations ranged from 3% for OLM and benzotriazole (BTA) to 21% for EBZ, from 2% for GPL to 68% for HDF and from 2% for VSA to 56% for HDF, during the wet season, dry season tracer and dry season porewater sampling events (Table SI-06).

The concentrations of 14 compounds were significantly higher during the dry season experiments than in the wet season experiments (Kruskal-Wallis tests, p-value < 0.01, Figure 1). For 7 compounds, concentrations were significantly higher during the wet season experiment, while for 5 compounds no significant differences were found. Seasonal differences in TrOC concentrations in WWTP effluents have been described earlier[18,36] and are commonly attributed to changes in consumption patterns, differing proportions of stormwater and wastewater entering the WWTP as well as temperature driven changes in WWTP removal efficiency. For instance, ratios of valsartan (VAL) to its main TP valsartan acid (VSA, compare section 3.3) were significantly higher during the wet season sampling event (Figure SI-11), indicating that with higher temperatures transformation efficiency of VAL in the WWTP increases and thus PC:TP ratios (parent compound to transformation product) decrease. On the contrary, PC:TP ratios for CBZ to two of its TPs EBZ and DBZ and for venlafaxine (VLX) to its main TP *O*-desmethyl-venlafaxine (MLX) remained relatively constant during both sampling events, although concentrations of these compounds were higher in the dry season. As large changes in consumption patterns for these pharmaceuticals between the sampling events are unlikely, we attribute changes in their concentration mainly to dilution.

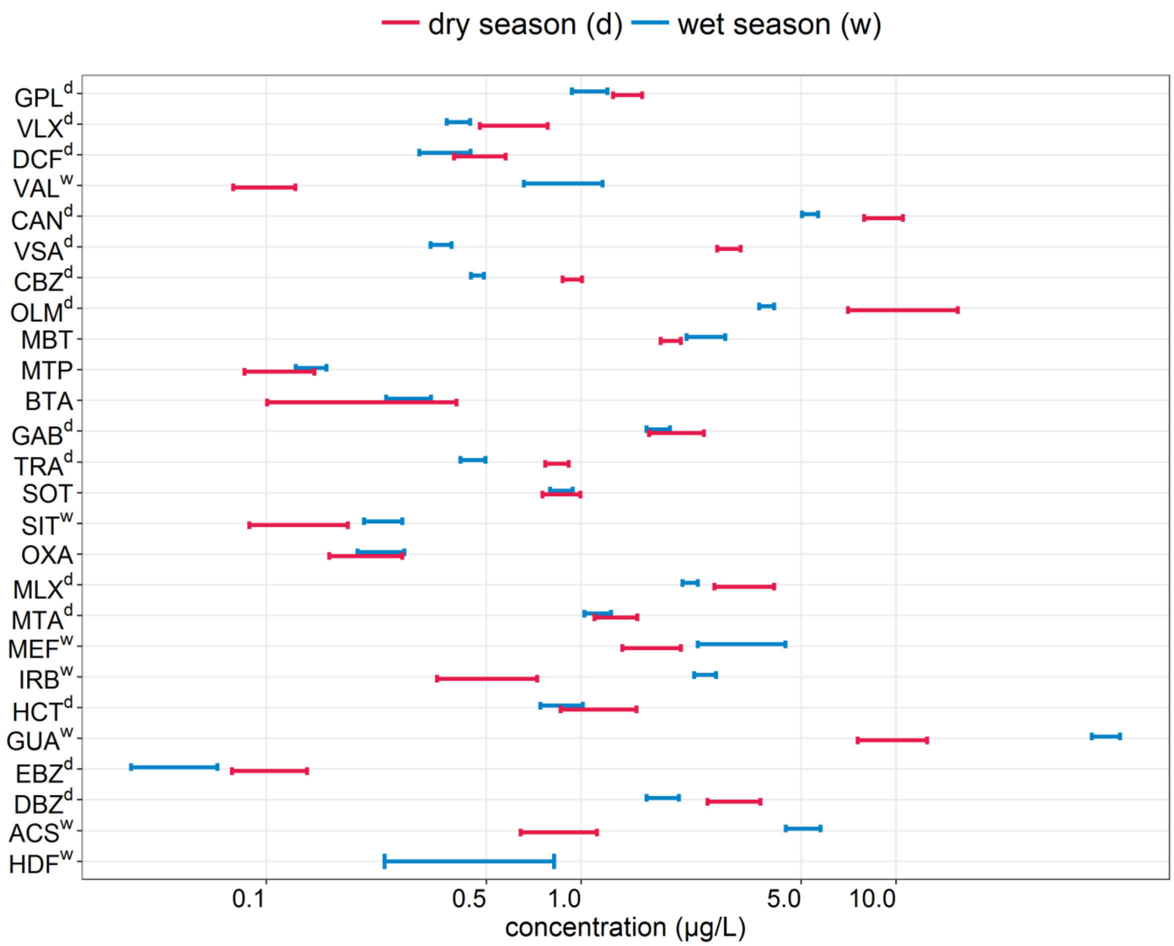


Figure 1 Concentration ranges for the 25 TrOCs that were detected consistently above their respective limit of quantification (LOQ) during the wet and the dry season sampling events at Site A. The concentration range of 4-hydroxydiclofenac (HDF), which was only detected above its LOQ during the wet season is depicted as well. Superscripts indicate whether concentrations were significantly higher (Kruskal-Wallis tests, p value < .01) during the dry season sampling events (d) or wet season sampling events (w). GPL, gabapentin-lactam; VLX, venlafaxine; DCF, diclofenac; VAL, valsartan; CAN, candesartan; VSA, valsartan acid; CBZ carbamazepine; OLM olmesartan; MBT, methylbenzotriazole; MTP, metoprolol; BTA, benzotriazole; GAB, gabapentin; TRA, tramadol; SOT, sotalol; SIT, sitagliptin; OXA, oxazepam; MLX, *O*-desmethylvenlafaxine; MTA, metoprolol acid; MEF, metformin; IRB, irbesartan; HCT, hydrochlorothiazide; GUA, guanylurea; EBZ, epoxy-carbamazepine; DBZ, dihydroxy-carbamazepine; ACS, acesulfame.

3.3 In-stream reactivity of TrOCs

Relative removal (half-lives) in the surface water between Site A and B ranged from 21 ± 5% (14.0 ± 3.9 h) for methylbenzotriazole (MBT) to 53 ± 12% (4.5 ± 1.5 h) for sitagliptin (SIT) during the wet season and from 20 ± 8% (38.9 ± 18.2 h) for VLX to 78 ± 16% (5.6 ± 2.6 d) for GUA during the dry season, respectively (Table 2, Figure 2, Table SI-05). All TrOCs that were detected above their respective LOQ at Site A, were still present above their LOQ at Site B.

The beta blockers, metoprolol (MTP) and sotalol (SOT) as well as diclofenac (DCF) were found to be readily removed in streams in Germany and Sweden (discharge 0.03 - 6 $m^3 s^{-1}$)[19,20] which is in qualitative agreement with the findings in the present study. Li et al.[19] attributed higher removal of SOT and MTP to higher hyporheic exchange fluxes, although the magnitude of transient storage was not assessed in their study. Valsartan, an angiotensin II receptor antagonist, was the only compound of the sartan group that was significantly removed along the investigated river stretch. This finding is in agreement with previous studies that reported that the compound is readily transformed to valsartan acid (VSA) in aquatic environments.[37] The half-lives of VAL calculated in the present study (11.2 – 12.5 h) are an order of magnitude higher than the mean half-life reported in a study conducted along four river stretches in Spain (t_{med} 2.2 h, discharge 0.05 – 2.7 $m^3 s^{-1}$).[38] During the wet season sampling event, concentrations of VSA increased between Site A and B, while during the dry season sampling event concentrations remained relatively constant. Similar to observations in the HZ (compare section 3.4), this finding is likely due to a seasonal shift in PC:TP ratios in the WWTP effluent. During the dry season, VAL was already largely transformed to VSA during wastewater treatment, while during the wet season a larger proportion of VAL leaves the WWTP unchanged, allowing measurable transformation of VAL to VSA along the investigated river reach. Once transformed, VSA was found to be stable in both sampling events, which is supported by studies that reported the widespread occurrence of the compound in urban surface waters and tap water.[37] The antidepressant venlafaxine and its TP *O*-desmethylvenlafaxine were found to be rather stable along a 5 km reach of Boulder Creek, Colorado,[18] while both compounds were significantly removed along the 3 km reach investigated in the present study. However, the magnitude of hyporheic exchange reported for Boulder Creek was an order of magnitude smaller ($F_{med} \approx 0.03$) than in the Sturt River (section 3.1). Quantitative information on the in-stream removal of the anti-corrosive agent 5-methyl-1H-benzotriazole (MBT), the anti-diabetic drugs sitagliptin (SIT) and metformin (MEF) as well as its main TP guanylurea (GUA)[39] in streams is limited and thus a direct comparison of the calculated half-lives is difficult. MEF and GUA have both been detected ubiquitously in surface waters[40] and even in sea water,[41] which raised concerns on their environmental persistence. Previous studies reported that once formed, GUA behaved rather stable in aquatic environments and sediments.[39] Based on the results of the present study, this finding cannot be confirmed as GUA was significantly attenuated in both surface water and hyporheic porewater.

Thirteen out of the 26 TrOCs that were consistently detected above LOQ at Site A were not significantly removed along the investigated river stretch in both sampling campaigns (Table SI-07). Relatively low relative removals (%) as found in the present study have also been reported for the opioid analgesic tramadol (TRA) and the diuretic hydrochlorothiazide (HCT) in the study of Li et al. (2015).[42] The anti-epileptic drug carbamazepine and two of its TPs, epoxy-carbamazepine and dihydroxy-carbamazepine as well as the artificial sweetener acesulfame (ACS), were found to be stable in a German and three Swedish rivers,[19] which is in accordance with the data reported in the present study. Quantitative data on the fate of the three other sartans investigated in the present study, (i.e. irbesartan, olmesartan and candesartan), the anti-corrosive agent benzotriazole (BTA), the antianxiety agent oxazepam (OXA) and the anticonvulsant gabapentin (GAB) and its main TP, gabapentin-lactam (GPL) in lotic environments is limited. OXA was found to be persistent over several decades in a Swedish lake.[43] Given the comparatively short median travel time in the investigated river reach we did not expect significant removal of this compound. The frequent detection of the BTA in urban surface waters[44] and the occurrence of the anticonvulsant GAB and its TP GPL in drinking water[45] indicate that these compounds are rather stable in surface waters.

The only TP that increased along the investigated river stretch was VSA during the wet season. For all investigated PCs (excluding VAL), transformation to TPs seems to be limited to the WWTP. This finding is in agreement with previous observations demonstrating that the majority of PC:TP ratios stayed relatively constant in receiving waters.[19]

For MLX, SIT, SOT, MBT, MTP, VSA, MEF and DCF, half-lives and thus in-stream reactivity differed between the two sampling events, while for GUA, VAL and VLX similar half-lives were calculated for both dry and wet seasons. For half of the TrOCs that were significantly removed between Site A and B (SIT, VLX, MLX, MTP, SOT, MBT), in-stream half-lives ($t_{1/2}$) were considerably lower during the wet season (Table 2) although temperatures and presumably global radiation were higher during the dry season. This finding is in agreement with a larger proportion of the median travel time due to transient storage (F_{med}) during the wet season. It is therefore likely that the higher reactivity of TrOCs during the wet season (i.e. lower half-lives) can be attributed to a higher intensity of hyporheic exchange.

Table 2 Surface water half-lives ($t_{½}$, hours, ± 1 standard deviation) and median (lower quartile– upper quartile) hyporheic half-lives ($t_{½}$, hours, ± 1 standard deviation) of all trace organic compounds that were significantly removed between Site A and B either during the dry or the wet season. Half-lives were set to infinity (inf) if the 95% percentile of their respective relative removal (%) included zero. Negative half-lives indicate compound formation. Note that for HDF, concentrations at Site A during the dry season were largely between its LOD and LOQ and hence reactivity of HDF during the dry season could not be assessed.

TrOC	acronym	in-stream reactivity $t_{½}$ (h)		median hyporheic reactivity $t_{½}$ (h)	
		wet season	dry season	wet season	dry season
metformin	MET	n.s.[a]	24.6 ± 8.7	inf[c]	0.7 (0.5-1.0)
guanylurea	GUA	7.2 ± 1.6	5.6 ± 2.6	1.6 (1.0-2.1)	0.4 (0.2-0.7)
sitagliptin	SIT	4.5 ± 1.5	n.s.	1.1 (0.5-2.3)	inf
diclofenac	DCF	n.s.	35.0 ± 10.8	inf	1.3 (0.5-inf)
4-hydroxydiclofenac	HDF	6.3 ± 3.6	n.q.[b]	2.0 (0.9-Inf)	n.q.
venlafaxine	VLX	14.0 ± 3.8	38.9 ± 18.2	1.5 (0.9-2.7)	inf (1.9-inf)
O-desmethylvenlafaxine	MLX	13.2 ± 4.4	18.1 ± 5.6	3.4 (1.6-6.5)	inf
metoprolol	MTP	12.8 ± 5.0	n.s.	3.3 (1.7-inf)	inf (0.1-inf)
sotalol	SOT	12.9 ± 3.6	26.9 ± 8.4	5.7 (2.8-inf)	2.7 (1.2-inf)
methylbenzotriazole	MBT	14.0 ± 3.9	30.6 ± 8.3	2.1 (1.1-4.1)	1.5 (0.8-inf)
valsartan	VAL	11.2 ± 6.2	12.5 ± 5.2	0.9 (0.5-inf)	0.9 (0.5-inf)
valsartan acid	VSA	-8.5 ± 1.8	n.s.	-1.5 (-1.8- -0.5)	inf

[a] n.s. = not significantly removed; [b] n.q. = not quantified (below LOQ); inf[c] = infinite half-live

3.4 Reactivity of TrOCs in the hyporheic zone

Median removal in the HZ ranged from 23% for sotalol to 69% for sitagliptin during the wet season and from 13% for methylbenzotriazole to 87% for guanylurea during the dry season, respectively (Figure 2, Table SI-08). Similarly, median half-lives in the HZ ranged from 0.9 h for VAL to 5.7 h for SOT during the wet season and from 0.4 h for GUA to 2.7 h for SOT during the dry season (Table 2, Table SI-09). CBZ, its two main transformation products EBZ and DBZ, three compounds of the sartan group OLM, CAN, IRB and BTA, TRA, GAB, its main TP GPL, OXA, and the main TP of MTP, MTA showed a median relative removal (%) of zero in the HZ during both sampling events. Thus these compounds were considered as not significantly removed along the investigated hyporheic flow paths. ACS showed a median relative removal of zero in the wet season, but was slightly removed in some profiles (median removal 27% during the dry season. Reactivity of the TrOCs that were significantly removed in the HZ was in the order of VAL > SIT > VLX ≈ GUA ≈ VSA > HDF ≈ MBT > MTP ≈ MLX > SOT in the wet season and GUA ≈ MEF ≈VAL > DCF > MBT > SOT in the dry season. For some TrOCs half-lives in the HZ were significantly different (Kruskal-Wallis tests, $p < 0.05$, Table SI-9) between the two seasons. For instance, MEF and DCF were removed during the dry season but not during the wet season, while VSA was only formed during the wet but not during the dry season. SIT, MLX and GUA were removed in both seasons with MLX and SIT exhibiting lower half-lives during the wet season while GUA showed lower half-lives during the dry season.

Removal of TrOCs in the HZ is generally a function of the combined effect of physical factors, such as residence time and temperature, and biogeochemical factors, such as microbial transformation and degradation rates, sorption to sediment and biofilms and, depending on the individual TrOC, exposure to favourable redox conditions. For many TrOCs reactivities in the HZ increase with temperature[15] and decrease when redox conditions become increasingly anoxic (i.e. drop to iron and manganese reducing conditions).[14] Redox conditions along the sampled hyporheic flow paths, as judged from total dissolved iron and manganese concentrations (Table SI-02), were relatively similar during both sampling events and predominantly ranged between oxic and suboxic conditions (see SI for detailed discussion). Higher reactivities of MEF, GUA and DCF may therefore be attributed to higher hyporheic temperatures during the dry season. Similarly to findings in the surface water, differences in half-lives of VSA between the two seasons may be related to PC:TP ratios in the WWTP effluent. During the wet season, concentrations of VAL in WWTP effluent and PC:TP ratios of VAL:VSA were larger compared to the dry season (compare section 3.2). It is therefore likely that during the wet season concentrations of VAL were too low to facilitate significant (i.e. measurable) production of VSA in the HZ.

The reactivities of TrOCs in the HZ found in the present study partly differ from compound reactivities reported previously in hyporheic sediments. Removal of DCF, SOT, MBT and MTP in saturated sediments, has been described in laboratory[15] and field experiments.[14,20] MBT and DCF, for instance, showed half-lives of 4.3 h and 3.8 h in the HZ of an urban lowland river in Germany,[14] values that are in the same order of magnitude as the ones calculated for the HZ of the Sturt River (Table 2). The high stability of CAN, OLM and CBZ in saturated sediments has been demonstrated in column experiments[15,46] and a field study.[14] For other compounds such as VLX, MLX or BTA, previous studies found inconsistent behaviour in the HZ. Some studies reported removal of VLX[46] and BTA[14] while others found MLX and VLX[14,18] as well as BTA[15] to be rather stable. Likewise, ACS and GAB showed relatively low half-lives in the HZ of an urban lowland river,[14] while the compounds appear to be rather stable in hyporheic porewater of the Sturt River. Such site-specific variations in TrOC reactivity in the HZ have previously been described and mainly attributed to differences in microbial communities and sediment heterogeneity.[16]

Retardation of TrOCs along hyporheic flow paths due interactions between TrOCs and sediment material and biofilms was not considered in the calculation of removal rate constants. Previous studies found no notable retardation for neutral TrOCs which interact with streambed sediment matrices predominantly through hydrophobic partitioning,[47] even for compounds that are characterized by relatively high $\mathrm{LogK_{ow}}$ values such as CBZ ($\mathrm{logK_{ow}}$ 2.8).[48] Likewise, sorption to sediment matrices and retardation of anionic TrOCs has been found to be rather small.[48–50] We therefore assumed that for TrOCs that are neutral at pH values measured in the Sturt River (e.g. BTA, MBT and CBZ, pH 7.2-7.5) and compounds that are negatively charged (e.g. ACS, VAL and DCF), sorption contribution to removal and retardation is not significant. However, it has been shown that sorption can be important for cationic TrOCs such as MEF and its TP GUA,[51] VLX[18] and MTP[52] and thus, these compounds may have been retarded along hyporheic flow paths. Although sorption and retardation do not influence relative removals (%), and therefore the relative contribution of the HZ to in-stream removal (compare section 3.5), strong retardation would lead to an underestimation of the residence time of TrOCs in the HZ and hence to an overestimation of the removal rate constant. Calculated half-lives of cationic TrOCs should therefore be viewed as estimates and treated with caution. A list of $\log D_{ow}$ and pKa values of the investigated TrOCs can be found in Table SI-05.

3.5 Relative importance of the HZ to in-stream removal of TrOCs

TrOCs that were found to be rather stable in the HZ were also found to be stable in the surface water and vice versa. Median relative removal (%) of TrOCs in the HZ correlated well with in-stream relative removal (%) for all TrOCs that were removed in the surface water in either the wet or the dry season (Figure 2). Values of L_c/L_s (equation 6) were higher during the wet season (0.5 ± 0.3) compared to the dry season (0.2 ± 0.15).

The ratio of L_c/L_s defines a theoretical mixing line that approximates the relative contribution of the hyporheic zone to reach-scale, in-stream removal (%) of TrOCs. During the wet season, the majority of TrOCs plot close to the theoretical mixing line, indicating that hyporheic removal was the main driver of in-stream removal of TrOCs. VAL plots below the mixing line, which might be due to an overestimation of either hyporheic exchange intensity or hyporheic removal percentages. During the dry season, however, the majority of TrOCs plot well above the theoretical mixing line indicating that the in-stream removal is higher than the removal predicted by the mixing model and the hyporheic zone removal. For instance, VLX, MBT and MLX, were only poorly removed in the HZ but showed significant removal in the surface water. It is therefore likely that during the dry season, other removal processes in the main channel, such as photolysis or biotransformation in interstitial biofilms and algae mats growing on stones, submerged macrophytes and riparian vegetation,[8,53] gained importance.

The calculation of the theoretical mixing line is based on a variety of assumptions and thus should be viewed as an estimate. The slope L_c/L_s is calculated from TSM parameters which assumes that the HZ is a well-mixed compartment characterized by an exponentially-shaped residence time distribution (RTD).[28]Although widely used, the TSM is often criticized for its inability to describe longer residence times and hence its tendency to favor shorter flow paths.[54,55] This is often evident by the inability of the exponential RTD model to match late time breakthrough.[56] However, in our study the TSM with an exponential RTD was able to reproduce stream breakthrough curves well (SI section 3.2). Furthermore, it is likely that removal rates of TrOCs are highest in the shallow HZ,[14] where carbon turnover rates are highest and redox conditions are oxic.[12] It is therefore reasonable to assume that short flow paths contributed more to overall reach-scale removal of the reactive TrOCs and hence the use of an exponentially shaped RTD to calculate τ_{hz} is adequate.

The present study demonstrates that, for many TrOCs, in-stream removal and reactivity are to a large extent driven by both compound reactivity (half-lives) in the HZ and the intensity of hyporheic exchange fluxes. We thus conclude that river restoration measures seeking to increase the magnitude of exchange fluxes between surface water and the HZ are likely to increase the reactivity of TrOCs on the reach-scale and the efficiency of rivers to remove TrOCs. However, we also found that some TrOCs were not removed along the 3 km reach during both dry and wet seasons. These compounds may be transported downstream over longer distances with potential consequences for water management, particularly in urban areas where water cycles are partially closed.

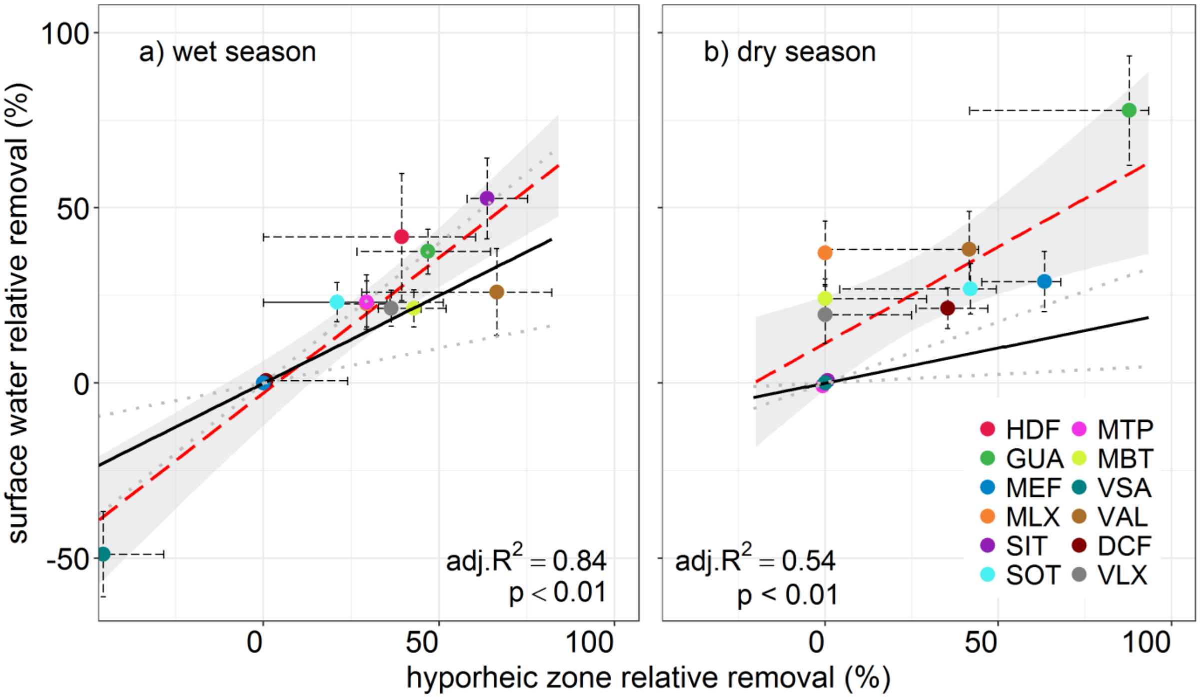


Figure 2 Correlation (red dashed line and associated 95% confidence interval in grey) between the median hyporheic relative removal (%) and the reach-scale relative removal between Site A and Site B during the wet season (a) and the dry season (b). The black line represents a theoretical mixing line with a slope of L_c/L_s that depicts the predicted in-stream removal (%) given a relative removal in the (HZ) after a mean residence time in the transient storage zone of τ_{hz}. Error ranges (± 1 standard deviation) of the theoretical mixing line are shown with a grey dotted line. Regression lines and associated 95% confidence intervals are plotted in red and grey shading, respectively. Note that HDF was only detected above LOQ during the wet season experiments.

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Supporting Information

(1) Map of the field site showing sampling locations (Figure SI-01), description of sediment characteristics, hyporheic and surface water temperatures during sampling campaigns (Figure SI-02), WWTP discharge during the tracer experiments (Figure SI-03), stream stage during the wet season experiments (Figure SI-04), porewater velocities in the HZ measured using active heat pulse sensing (Table SI-01) and total dissolved iron, dissolved manganese and NO_3^--N concentrations in the HZ (Table SI-02, Figure SI-05); (2) Additional information on TrOC analysis (Tables SI-03 & 04); (3) Description of the transient storage model, tracer breakthrough curves and posterior distribution of model parameters (Figures SI-06-09); (4) Details on calculation of L_s/L_c and discussion of approach; (5) LogD_{ow} and pKa values of investigated TrOCs (Table SI-05); (6) Comparison of stable reference compounds (Figure SI-10), mean concentrations of TrOCs, total dissolved iron and manganese and NO_3^--N at Site A (Table SI-06), relative removal (%) of TrOCs not significantly removed between Site A and B (Table SI-07), half-lives and relative removal (%) of TrOC in the HZ (Tables SI-08 & 09) and molar concentration ratios of PCs to their TPs (Figure SI-11).

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