Water Research 140 (2018) 158–166

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

The fate of polar trace organic compounds in the hyporheic zone

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ARTICLE INFO

Article history:
Received 4 December 2017
Received in revised form
14 April 2018
Accepted 17 April 2018
Available online 18 April 2018

Keywords:
Pharmaceuticals
Organic micropollutants
Biotransformation
Urban water cycle
Removal efficiency

ABSTRACT

The hyporheic zone (HZ) is often considered to efficiently remove polar trace organic compounds (TrOCs) from lotic systems, mitigating potential adverse effects of TrOCs on ecosystem functioning and drinking water production. Predicting the fate of TrOCs in the hyporheic zone (HZ) is difficult as the in-situ removal rate constants are not known and the biogeochemical factors as well as hydrological conditions controlling the removal efficiency are not fully understood. To determine the in-situ removal efficiency of the HZ for a variety of TrOCs as a function of the biogeochemical milieu, we conducted a field study in an urban river near Berlin, Germany. Subsurface flow was studied by time series of temperature depth profiles and the biogeochemical milieu of the HZ by concentration depth profiles. These results, in conjunction with a 1D advection-dispersion transport model, were used to calculate first-order removal rate constants of several polar TrOCs in the HZ. For the majority of TrOCs investigated, removal rate constants were strongly dependent on redox conditions, with significantly higher removal rates observed under predominantly suboxic (i.e. denitrifying) compared to anoxic (i.e. Fe and Mn reducing) conditions. Compared to previous studies on the fate of TrOCs in saturated sediments, half-lives within oxic/suboxic sections of the HZ were relatively low, attributable to the site-specific characteristics of the HZ in a stream dominated by wastewater treatment plant effluent. For nine out of thirteen investigated TrOCs, concentrations decreased significantly in the HZ with relative removal percentages ranging from 32% for primidone to 77% for gabapentin. For many TrOCs, removal efficiency decreased drastically as redox conditions became anoxic. For the majority of compounds investigated here, the HZ indeed acts as an efficient bioreactor that is capable of removing TrOCs along relatively short flow paths. Depending on the TrOC, removal capacity may be enhanced by either increasing the magnitude of groundwater-surface exchange fluxes, by increasing the total residence time in the HZ or the exposure time to suboxic zones, respectively.

1. Introduction

Trace organic compounds (TrOCs) derived from wastewater treatment plants (WWTP) are frequently detected in surface waters in which they impair ecosystem functioning (Schwarzenbach et al., 2006) and pose risks for drinking water production, especially in urban areas where water cycles might be partially closed (Pal et al., 2014). The hyporheic zone (HZ), the interface between groundwater and surface water in streams, has often been considered to efficiently remove TrOCs (Lewandowski et al., 2011). Depending on the magnitude and direction of groundwater-surface water exchange and hyporheic exchange fluxes, the HZ may contribute to the overall attenuation of TrOCs in streams (Riml et al., 2013; Writer et al., 2013) and may act as a reactive barrier protecting groundwater from surface water pollution and vice versa (Huntscha et al., 2013).

Quantitative information on the reactivity of TrOCs in saturated sediments, often expressed as first-order removal rate constants, predominantly originates from either laboratory experiments (Burke et al., 2014; Li et al., 2015; Radke and Maier, 2014) or bank filtration studies (Henzler et al., 2014; Huntscha et al., 2013). For many TrOCs, reported removal rate constants were found to be highly site- and experiment specific and varied up to three orders of

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https://doi.org/10.1016/j.watres.2018.04.040
0043-1354/

magnitude among different subsurface environments and experimental setups (Greskowiak et al., 2017). It has further been shown that a variety of physical and biogeochemical factors, such as temperature (Burke et al., 2014), redox conditions (Wiese et al., 2011), concentrations of labile dissolved organic carbon (DOC) (Hoppe-Jones et al., 2012) and the abundance and diversity of microorganisms (Bertelkamp et al., 2016) may influence the reactivity of TrOCs in saturated sediments.

Compared to other subsurface environments, hyporheic zones are typically characterized by intense microbial activity, diverse microbial communities and steep redox gradients (Boano et al., 2014). Field investigations that link the fate of TrOCs to the distinct biogeochemical characteristics in the HZ, are widely lacking and thus, in-situ removal rate constants of TrOCs in the HZ are not known. Removal efficiency of the HZ is generally not only a function of the removal rate constants and thus the biogeochemical milieu, but also of the time over which an attenuation reaction can take place (i.e. the residence time). The spatial distribution of biogeochemical parameters, such as the ambient redox potential in the HZ, is often tightly coupled to flow characteristics. Compared to bank filtration systems, residence times in the HZ are usually much shorter. The in-situ interactions between transport timescales in the HZ and the biogeochemical conditions that control the ambient reactivity of TrOCs in HZ, (i.e. the factors that govern the efficiency of the HZ in removing polar TrOCs) are poorly understood.

The present study had two aims: (i) providing in-situ first-order removal rate constants for several TrOCs for the HZ of an urban lowland stream and (ii) determine the hydrological and biogeochemical factors that limit the efficiency of the HZ in removing TrOCs. To this end, in-situ first-order removal rate constants are determined for a variety of polar WWTP derived TrOCs under different redox conditions.

We hypothesize that in a river that is dominated by WWTP effluent removal rate constants in the hyporheic zone substantially deviate from rates obtained in laboratory studies and bank filtration systems. As reaction rates for many compounds are likely to be redox-dependent, reaction rates are expected to be strongly controlled by redox conditions in the HZ. Consequently, removal efficiency is likely to depend on both the extent of redox zones as well as on the magnitude of groundwater-surface exchange and hyporheic exchange fluxes.

2. Methods

2.1. Site description

River Erpe is an urban lowland river, located at the eastern edge of Berlin, Germany, that receives between 60% and 80% of its discharge from the large municipal WWTP Münchehofe. A detailed description of river morphology and general biogeochemical traits of River Erpe can be found elsewhere (Lewandowski et al., 2011). The study site is located at Heidemühle (Lat: 52.478647, Long: 13.635146) roughly 1 km downstream of the confluence of River Erpe and the WWTP Münchehofe effluent.

Streambed morphology at the field site was dominated by small dunes (crest height < 5 cm) and macrophyte cover during the study period was <10%. Streambed sediment characteristics were determined from one 30 cm long core per station taken in close proximity (<10 cm) to the sampling station using a hand auger (9.0 cm ID). Saturated hydraulic conductivities (K) at 10 °C, measured using a KSAT device (UMS Munich), were found to be log-normally distributed with a mean value of 5.0×10^{-5} m s^{-1} and a standard deviation of 7.4×10^{-5} m s^{-1}. Mean sediment porosity calculated from oven dried samples was 0.39 ± 0.1. Organic carbon content (f_{oc}), determined by loss on ignition, ranged between 0.5 and 6 wt.% and was found to be log-normally distributed with a mean value of 2.4 ± 2.7 wt.%.

2.2. Experimental setup overview and field investigation periods

The experimental setup consisted of six stations (S1 − S6) located close to the south-eastern bank of River Erpe (Fig. 1a). Each sampling station was equipped with a ring enclosure (PVC pipes with a diameter of 15 cm and a height of 32 cm) which was inserted vertically into the sediment, with the top rim of the pipe being level with the sediment surface. Concentrations of TrOCs in effluent-receiving streams are typically variable in time as both concentrations of TrOCs in WWTP effluent itself as well as the relative proportion of WWTP effluent to overall stream discharge may change on a sub-daily and daily basis (Lewandowski et al., 2011). To overcome this challenge, we used dialysis chambers, also called peepers (Hesslein, 1976), a passive sampling technique that integrates porewater solute concentrations over a time span of several days and thus allows the sampling of time integrated, quasi-steady-state concentration depth profiles in the hyporheic zone. A detailed description on the functionality of peepers and their applicability to sample TrOCs in the hyporheic zone is provided in the Supplementary Material (SM). Between December 1st and December 15th, 2015, peepers were used to collect porewater depth profiles in the hyporheic zone (details below, section 2.4). To sample porewater both within the ring enclosure and outside of the ring enclosure, one peeper was inserted into the sediment within the ring enclosure and one inserted directly adjacent to the first one but outside of the ring enclosure (Fig. 1 b). Between December 1st, 2015 and April 15th, 2016, temperature probes (details below, section 2.3) were installed inside and outside the ring enclosures. Vertical seepage flux inside the ring enclosure at S1, S2, S3, S4 and S6 as well as outside ring enclosures at S3 was calculated from field temperature data measured between December 1st, 2015 and December 15th, 2015. Due to a limited availability of temperature probes, vertical seepage fluxes inside ring enclosure at S5 and outside ring enclosures at S1, S2, S4, S5 and S6 were calculated from temperature data collected between January 5th and April 15th, 2016. This approach was justified as (i) head gradients between river stage and the riparian aquifer were close to time invariant on timescales of weeks and months and (ii) flux measurements made at the same station and peeper position between December 2015 and April 2016 showed only little variation. A detailed summary of deployment periods and the respective hydrodynamic conditions of the River Erpe between December 2015 and April 2016 can be found in the SM. The original purpose of the ring enclosures was to limit the influence of potential horizontal subsurface flow in the hyporheic zone. However, flow investigations (sections 2.3.2 and 3.1) did not indicate the presence of strong horizontal flow components outside the ring enclosures. As a result, the same reactive transport model was used to evaluate concentration profiles both inside and outside the ring enclosures. Stream stage, temperature and electrical conductivity (EC) were measured continuously every 5 min between December 1st, 2015 and April 15th, 2016 using a CTD Diver (Van Essen Instruments B.V., Netherlands) installed in a stilling well (SW1, Fig. 1a). Between February 8th and April 15th, additional head measurements were performed using a Pressure Diver (Van Essen Instruments B.V., Netherlands) in a second stilling well (SW2, Fig. 1a) and a groundwater observation well (GW, Fig. 1a). Head measurements were performed to gain general information on groundwater-surface water interactions at the field site and qualitatively confirm the temperature based flux calculations (section 2.3). Stream stage at SW2 during peeper deployment was inferred from correlations of stream stages at SW1 and SW2 between February 8th and April 15th, 2016 (Fig. SM-02).