

HENRY

Hydraulic Engineering Repository

Ein Service der Bundesanstalt für Wasserbau

Article, Author's Postprint

Munz, Matthias; Oswald, Sascha E.; Schäfferling, Robin; Lensing, Hermann-Josef

Temperature-dependent redox zonation, nitrate removal and attenuation of organic micropollutants during bank filtration

Water Research

Verfügbar unter/Available at: <https://hdl.handle.net/20.500.11970/108896>

Vorgeschlagene Zitierweise/Suggested citation:

Munz, Matthias; Oswald, Sascha E.; Schäfferling, Robin; Lensing, Hermann-Josef (2019): Temperature-dependent redox zonation, nitrate removal and attenuation of organic micropollutants during bank filtration. In: Water Research 2019 (162). S. 225-235.

Standardnutzungsbedingungen/Terms of Use:

Die Dokumente in HENRY stehen unter der Creative Commons Lizenz CC BY 4.0, sofern keine abweichenden Nutzungsbedingungen getroffen wurden. Damit ist sowohl die kommerzielle Nutzung als auch das Teilen, die Weiterbearbeitung und Speicherung erlaubt. Das Verwenden und das Bearbeiten stehen unter der Bedingung der Namensnennung. Im Einzelfall kann eine restriktivere Lizenz gelten; dann gelten abweichend von den obigen Nutzungsbedingungen die in der dort genannten Lizenz gewährten Nutzungsrechte.

Documents in HENRY are made available under the Creative Commons License CC BY 4.0, if no other license is applicable. Under CC BY 4.0 commercial use and sharing, remixing, transforming, and building upon the material of the work is permitted. In some cases a different, more restrictive license may apply; if applicable the terms of the restrictive license will be binding.



Erstveröffentlichung in *Water Research* 162 (2019), S. 225-235.
Verfügbar unter <https://doi.org/10.1016/j.watres.2019.06.041>

Temperature-dependent redox zonation, nitrate removal and attenuation of organic micropollutants during bank filtration

Matthias Munz^a, Sascha E. Oswald^a, Robin Schäfferling^a, Hans-Josef Lensing^b

^a Institute of Environmental Science and Geography, University Potsdam

^b Department of Geotechnical Engineering, Federal Waterways Engineering and Research Institute (BAW)

Keywords: Pharmaceuticals, In-situ degradation rates Denitrification, River-groundwater-interaction, Urban water cycle

Abstract: River bank filtration (RBF) is considered to efficiently remove nitrate and trace organic micropollutants (OMP) from polluted surface waters. This is essential for maintaining good groundwater quality and providing high quality drinking water. Predicting the fate of OMP during RBF is difficult as the biogeochemical factors controlling the removal efficiency are not fully understood. To determine in-situ removal efficiency and degradation rates of nitrate and OMP indicator substances we conducted a field study in a RBF system during a period of one and a half years incorporating temporally and spatially varying redox conditions and temperature changes typically occurring in temperate climates. RBF was analyzed by means of mixing ratios between infiltrated river water and groundwater as well as average residence times of surface water towards the individual groundwater observation wells. These results were used to calculate temperature dependent first order degradation rates of redox sensitive species and several OMP. Five out of ten investigated OMP were completely removed along RBF pathways. We demonstrate that degradation rates of several OMP during bank filtration were controlled by redox conditions and temperature whereby temperature itself also had a significant influence on the extent of the most reactive oxic zone. The seasonal variations in temperature alone could explain a considerable percentage of the variance in dissolved oxygen (34%), nitrate (81%) as well as the OMPs diclofenac (44%) and sulfamethoxazole (76%). Estimated in-situ degradation rates roughly varied within one order of magnitude for temperature changes between 5 °C and 20 °C. This study highlights that temporal variability in temperature and redox zonation is a significant factor for migration and degradation of nitrate and several OMPs.

1 Introduction

The main sources of organic micropollutants (OMP) in the aquatic system are from farm manure on agricultural land and effluents from sewage treatment plants (STP) (Petrie et al., 2015). An important fraction of the OMP are not fully eliminated in the waste water treatment processes and thus released to surface waters such as rivers and lakes (Vieno et al., 2005). Within the surface waters the OMPs are transported substantially downstream while photochemical degradation is likely to be an important loss mechanism (Boreen et al., 2003). OMPs even appear at low concentrations in

groundwater, especially in STP effluent impacted rivers, where surface water is used indirectly for drinking water production via bank filtration (Maeng et al., 2011).

River bank filtration (RBF) is an important, effective and cheap technique for surface water purification due to filtration of suspended solids, bacteria, viruses or parasites, adsorption and biodegradation of inorganic and some organic pollutants (Hamann et al., 2016). Consequently, improved understanding of the environmental fate and transport of wastewater-derived pollutants is essential for effective protection of vital aquatic ecosystem services, environmental health, and drinking water supplies. The potential for attenuation of OMP and corresponding removal rates strongly depend on subsurface residence time, temperature (Burke et al., 2014), redox condition (Wiese et al., 2011), particulate organic carbon content of the substrate (Hebig et al., 2017), labile dissolved organic carbon concentrations (Hoppe-Jones et al., 2012) and the evolving local microbial community (Bertelkamp et al., 2016), all of them are site specific or strongly vary in time. Reported removal rates of OMP varied up to three orders of magnitude among different subsurface environments and experimental setups (Greskowiak et al., 2017).

An increased number of laboratory batch and column studies (Bertelkamp et al., 2014; Burke et al., 2014; Schmidt et al., 2017) as well as modelling studies of artificial groundwater recharge (Greskowiak et al., 2006) and bank filtration systems (Henzler et al., 2014, 2016) revealed that factors including seasonal temperature variations, redox conditions, and physical-chemical properties of OMP had strong impacts on their attenuation and degradation behavior. But natural attenuation and degradation processes of OMP under a wide range of environmental conditions at the field scale are studied rarely (Massmann et al., 2006; Heberer et al., 2008; Schaper et al., 2018) and correlation to factors that are well known to affect the degradation rate may be weak (Greskowiak et al., 2017). Despite the large number of OMP found in natural environments little is known about their transport behavior in groundwater. Rather, many more experimental studies, especially field studies are urgently needed to improve our understanding of degradation mechanisms and controlling factors.

The objectives of this study were: (i) to assess the behavior of representative OMPs under seasonal varying redox states and temperatures present in the aquatic system, and (ii) to quantify in-situ degradation rates and their dependence on environmental conditions during RBF. For this purpose, concentrations of a number of OMPs were measured at the field scale during a period of one and a half years with a high temporal resolution of about four weeks. This unique data set allows a comprehensive assessment of the interlinked processes and controls governing solute attenuation to disentangle the mixed effects of seasonal variations in the redox state, temperature, occurrence of OMPs in the surface water and the hydraulic controls during RBF.

2 Material and methods

2.1 Study site

The study site is located in Potsdam (Brandenburg, Germany), where a bank filtration water works is operated south of the Sacrow-Paretzer-Kanal, which is part of the Havel river system connecting

Berlin with the lower River Havel, sidestepping the city of Potsdam. The Havel is a lowland river with a catchment area of about 24.000 km² located in northeastern Germany, flowing mainly through the federal states of Brandenburg and Berlin. The Havel discharge is strongly regulated by several barrages and large flow-through lakes (e.g. Tegeler See and Wannsee). Mean discharge at the study side was 24 m³ s⁻¹ with a standard deviation of about 14m³ s⁻¹.

The main tributaries of the Havel are the river Spree and the Teltow Canal. Especially by these tributaries the Havel is impacted by sewage treatment plant effluents from the city of Berlin (e.g. Heberer, 2002). In total six relevant STP treat the wastewater of about 3.7 million people. The portion of sewage effluents at the Havel discharge at the study site at mean discharge is about 16% (~4 m³s⁻¹). The distance from the study site to the waste water effluents varies between approximately 14 km (STP Stahnsdorf and Ruhleben), 40 km (STP Wansdorf) and 60 km (STP Münchhofe). For details about the Potsdam/Berlin waterways and the locations of the STP see Heberer (2002).

The aquifer adjacent to the Sacrow-Paretzer-Kanal is formed by quaternary sediments mainly consisting of silica sand and gravels, which are semi-confined aquifers stratified by glacial till layers from the later Pleistocene. The glaciofluvial sediments above the till were deposited during Weichsel glacial period (qsWA), while those below belong to the Saale glacial period (qsD). The aquifer extends from approximately 36 m.a.s.l. to 5 m below average sea-level. The aquifer is underlain by an aquitard of the Holstein interglacial. The hydraulic conductivity of the aquifer sediments varies between 2.9 x 10⁻⁰⁵ms⁻¹ and 1.75 x 10⁻⁰³ms⁻¹ and was slightly higher for the qsWA (6.94 x 10⁻⁴ m s⁻¹) compared to the qsD (2.39 x 10⁻⁴ m s⁻¹) sediments (estimates based on pumping tests).

The monitoring design consisted of six observation points; one located at the northern floodplain of the river, three distributed along the southern river-shoreline and two further in a transect roughly perpendicular to the river aligned along the groundwater flow direction between the river and the pumping well gallery as ascertained by a numerical groundwater flow model (Wang et al., 2019) (Fig. 1a and b). Along this transect (W07-W03-W04) two observation wells each were placed together with different filter screen elevation. The shallow ones are located approximately in the qsWA sediments and the deeper ones are located approximately in the qsD sediments (Fig.1c). Continuous measurements of hydraulic heads and temperatures within the surface water and in the nine groundwater observation wells were automatically recorded with a temporal resolution of 15 min (Rugged TROLL 100: Accuracy, pressure: ±0.1%, temperature: ±0.3 °C). Daily sums of sunshine duration and air temperature was measured at the nearby climate station in Potsdam (52°38'12.9"N, 13°06'22.3"E) of the German weather service DWD.

2.2 Water sampling and analysis

Surface water and groundwater samples were taken once a month between December 2015 and July 2017. Groundwater was pumped from the observation boreholes using the Grundfos MP 1 submersible pump set with a connected, closed flow cell to measure the physicochemical parameters with digital IDS sensors (WTW with an accuracy of temperature: ±0.2%, electrical conductivity ±0,5% and dissolved oxygen ±0,5), in-situ without air contact. Samples were collected after pumping a minimum of one and a half well volumes and once the physicochemical parameters had stabilized. Surface

water samples were taken in about 1.5 m distance to the shoreline of the river bank as grab samples (1 l) in between 0.05 m-0.5 m below the water surface. On May 2016, December 2016, January 2017 and February 2017 surface water samples were taken at three positions along the river-shoreline. Furthermore, on March 2017 surface water samples were collected over the course of one day every 6 h (2 a.m., 8 a.m., 2 p.m., and 8 p.m.).

Water samples were filled in 80 ml and 250 ml brown glass bottles without any air entrapment and brought to the laboratory at the same day or latest one day afterwards. Samples were stored at 4°C and full water analysis was generally performed one day after sampling. Concentrations of major anions were analyzed with an ion chromatograph (Dionex DX-120), cations with an ICP-OES (Thermo iCAP 6300 Duo, Thermo Scientific) and dissolved organic carbon with a TOC analyzer (Shimadzu TOC-5050A) at the Geochemisches Gemeinschaftslabor, Technische Universität Berlin. The limit of detection was 0.75 mg l⁻¹ for NO₃⁻, 10⁻³ mg l⁻¹ for Fe²⁺, and 2 x 10⁻⁴ mg l⁻¹ for Mn²⁺. The selected pharmaceuticals were analyzed using a high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) at PWU Potsdamer Wasser-und Umweltlabor GmbH (commercially accredited laboratory) following the German DIN standard 38407-F36. Details concerning the procedures as well as HPLC-MS/MS analyses can be found in Hebig et al. (2017). The limit of detection was 10 ng l⁻¹ for all OMPs, except for valsartan (20 ng l⁻¹). Non-detects below the detection limit were reported as half the detection limit. The investigated compounds were chosen because of their common occurrence in the Havel catchment and their expected fate and reactivity during bank filtration (Heberer, 2002; Jekel et al., 2015; Schaper et al., 2018) (Table 1).

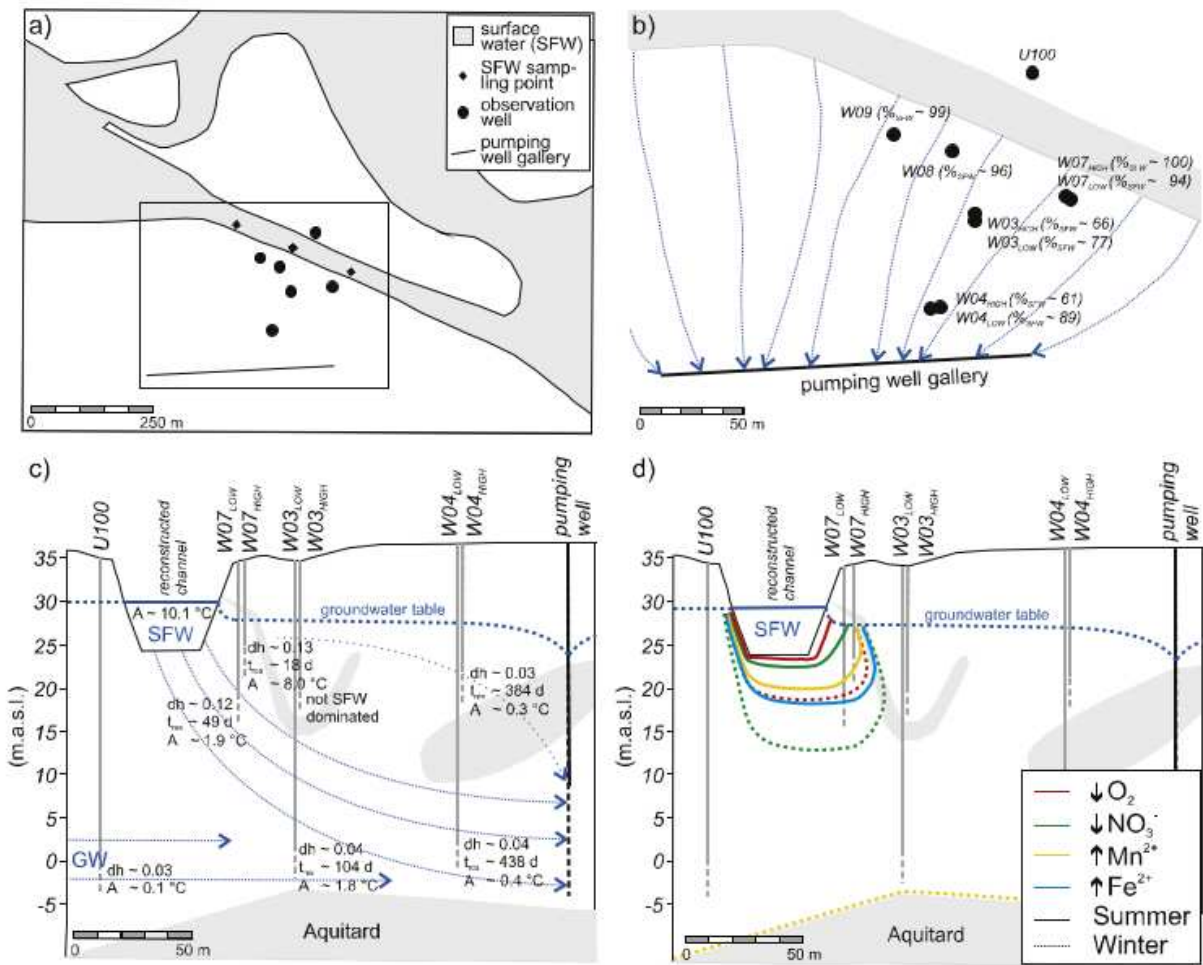


Figure 1: (a&b) Plan view of the study site with groundwater observation wells, groundwater flow lines as ascertained by a numerical groundwater flow model (blue, dotted lines) and calculated mixing ratios. (c&d) Cross section of the bank filtration transect along W07-W03-W04 showing the idealized geological setting, idealized groundwater flow lines and estimated hydraulic head gradients (dh), subsurface residence times (t_{res} and t_{low}) and temperature amplitudes (A) for each groundwater observation well, and the estimated subsurface redox zonation.

Table 1: Studied organic micropollutants along with their occurrence and fate in the river and aquifer and literature values of degradation rates (k) and retardation factors (R) during bank filtration.

Dissolved species	Application/Use	Occurrence and time of the maximum river concentration	Fate and condition of degradation in the aquifer	$k_{literature}[d^{-1}]$ (RBF)	$R_{literature}$ (RBF)
acesulfame	sweetener	summer	conservative	0.000 ^{*1}	1.0 ^{*1}
bezafibrate	lipid regulator	winter	not detected	$>7.1 \cdot 10^{-4}$ ^{*2}	1.0 ^{*2}
carbamazepine	antiepileptic	summer	anoxic	0.011 ^{*3}	1.7 ^{*3} –2.5 ^{*2}
clofibrac acids	lipid regulator	not detected	–	0.038–0.150 ^{*4}	1.3 ^{*4}
diclofenac	analgesic	winter	oxic	0.022 ^{*3}	>26.0 ^{*3}
ibuprofen	analgesic	winter	not detected	$>1.1 \cdot 10^{-3}$ ^{*2}	1.0 ^{*2}
pentoxifylline	vasodilatic	not detected	–	–	–
phenazone	analgesic	no seasonality	oxic	0.012 ^{*3} –0.062 ^{*5}	1.0 ^{*3}
primidone	anticonvulsant	no seasonality	conservative	$8.6 \cdot 10^{-5}$ ^{*3}	1.0 ^{*3}
sulfamethoxazole	antibiotic	no seasonality	anoxic	0.032 ^{*3}	1.0 ^{*3}
valsartan	antagonistic	winter	oxic	–	–

^{*1} Henzler et al. (2014), ^{*2} Hamann et al. (2016), ^{*3} Burke et al. (2014), ^{*4} Wiese et al. (2011), ^{*5} Greskowiak et al. (2006).

2.3 Calculation of mixing ratios and residence times

In order to estimate the mixing ratio between infiltrated surface water and original groundwater (i.e. dilution of effluent impacted river water with groundwater) at each observation well we used naturally occurring solute concentrations, assuming a linear mixing model between independent endmembers. The mixing ratios between the members were evaluated by means of multivariate statistical analysis using the MIX code (Carrera et al., 2004). MIX contains a maximum likelihood method to estimate mixing ratios, while acknowledging uncertainty in endmember concentrations. To improve the quality of computations three species were included in our analyses (acesulfame, Cl^- , Na^+). An essential assumption for the calculation of the mixing ratios is that the included species exhibit a conservative behavior and that their values significantly differ between surface water and groundwater. The values of groundwater endmembers were taken from the deep groundwater observation well U100 assumed to be not affected by infiltration from the Sacrow-Paretzer-Kanal.

Average residence times of surface water towards the individual groundwater observation wells were evaluated based on the propagation of the seasonal temperature signal into the aquifer. The seasonal temperature signal is transported into the saturated sediment via advection and conduction but is retarded to a certain degree depending on heat capacity and thermal conductivity of the saturated sediment (that means the thermal front moves slower than the water particle or conservative solutes itself and the amplitude of the seasonal temperature signal is reduced with increasing transport distance) (Munz and Schmidt, 2017). Nonetheless, seasonal temperature signals can penetrate at least to distances of several tens of meters into the aquifer upon bank filtration and can therefore be detected in equipped, standard observation boreholes in the vicinity of the river (Wang et al., 2019). Aquifer residence times can be assessed based on the time shift of the fitted, sinusoidal temperature oscillation to the measured temperature data. The temperature time lag (difference in temperature time shift between surface water and groundwater observation well) can be converted to an estimate of the aquifer residence time using the thermal retardation factor relating the flow velocity of a water parcel (conservative transport) to that of advective-conductive transport of temperature (Hoehn and Cirpka, 2006). Where the measured groundwater temperature data show a clear sinusoidal pattern and amplitude, the propagation of the river temperature is well applicable. In the last years this concept has also been applied to the more dynamic situation of hyporheic exchange flows and residence times, analytically as well as numerically (e.g. Munz et al., 2016; Munz et al., 2017).

2.4 Potential for pharmaceutical removal - degradation rates

The river-groundwater interface is considered as being a hotspot for microbial activity and biogeochemical reactions, for horizontally dominated exchange within the hyporheic zone (e.g. Trauth et al., 2015) or for groundwater recharge as in river bank filtration (e.g. van Driezum et al., 2018). If concentrations of dissolved substances observed in the groundwater do not agree with the predicted concentrations by means of the mixing ratios, than removal processes must be occurring also, including chemical or biological degradation. The redox zonation within the aquifer is characterized by the disappearance of oxygen ($\downarrow \text{O}_2$), nitrate ($\downarrow \text{NO}_3^-$) or the appearance of manganese ($\uparrow \text{Mn}^{2+}$) and iron

($\uparrow \text{Fe}^{2+}$) as suggested by Massmann et al. (2008) rather than by their redox potential. Sulphate reduction was monitored based on sulphate decrease.

To evaluate the role of aerobic respiration on DOC we used metabolism calculation as proposed by Battin (1999), evaluating the difference in DO concentration between river and groundwater (ΔDO) against the difference in DOC concentration between river and groundwater (ΔDOC). Assuming a molar respiratory quotient of 1 :1, i.e. metabolism of one mole of DOC requires one mole of oxygen (idealized stoichiometry of aerobic, microbially mediated processes: $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) ΔDO in this case is equal to ΔDOC .

The potential for pharmaceutical removal of a given compound during RBF (at the river-groundwater interface and along subsurface flow paths) was quantified by the percentage of removal (PR) for each individual pollutant (Heberer et al., 2008; Massmann et al., 2008) depending on the time of infiltration (temperature and redox condition within the aquifer), their concentration in the recharge sources, the corresponding surface water - groundwater mixing ratios and the subsurface residence times.

The first order degradation rate constant (k) was calculated with respect to the subsurface residence time, the retardation factor and the corresponding mixing ratios, between the river and W07_{HIGH} (oxic), or between W07_{LOW} and W03_{LOW} (anoxic) in respect to the subsurface zone where the observed substances were clearly degraded. For oxic degradation the degradation rate is likely much higher in the immediate vicinity of the streambed then further downgradient (Henzler et al., 2014), and hence the quantified degradation rates potentially underestimate local rates close to the streambed. If dissolved substances were completely degraded along their subsurface flow path (concentration in the observation well is equal to the detection limit) the calculated rate constants have to be regarded as minimum values of degradation rates. If a calculated degradation rate was slightly negative it was set to zero and the difference in concentrations between river and observations well was attributed to be caused by uncertainties in the detected concentrations or underestimated desorption processes.

2.5 Statistical analysis

To assess sampling variability in the source concentrations, all OMP recorded in the river were reported along with their spatial and temporal variations. Therefore we used the average of the standard deviations of all river concentrations per sampling campaign (SD_{space}) and the standard deviation of all concentrations measured during one day (SD_{time}).

Multiple regression models were used to identify the influence of physicochemical aquifer parameters (T, DOC, pH, EC and Eh) on the fate of redox sensitive species and observed OMP. If the reported p-values were smaller than 0.01 the parameter was assumed to have a significant effect on the observed concentration. For all parameters having a significant effect a linear model was fitted to the experimental data and was evaluated in terms of R^2 . To characterize the non-parametric relationships between predictor variables and the observed concentrations we used Spearman's rank correlation coefficient. For the statistical analyses the variables were log-normalized, when bivariate

relations showed a clear nonlinear behavior (e.g. DO versus T). To perform the statistical analyses we used the software environment R (R Development Core Team, 2011).

3 Results

3.1 Hydraulic situation and temperature dynamics

Seasonal variation in river water level at the study site (situated at river kilometer 20-21) ranged between 29.8 m.a.s.l. (February/ March) and 29.4 m.a.s.l. July/August). The yearly water level fluctuation was about only 0.4 m within the observation period between December 2015 and July 2017. Rainfall induced discharge events occurred in July 2017 resulting in a short peak in river water level of about 29.8 m.a.s.l. (Fig. 2a). The boundary condition of river water level, which only varies slightly, in combination with the quasi continuous pumping rates at the waterworks caused an almost temporally constant hydraulic gradient (dh) from the river toward the pumping well gallery ($dh = \frac{\Delta h}{\Delta L}$ where Δh is difference of hydraulic head and ΔL is horizontal distance), yielding to continuous river water infiltration into the aquifer via bank filtration. Based on the hydraulic conditions the RBF system is seen to be fairly stable without pronounced flood events that induce short term variations in mixing ratios and residence times.

Seasonal temperature extremes ranged between a minimum of 1 °C in winter (December-February) and a maximum of 22 °C in summer June-August). Temperature variation in the river could be approximated well by a sinusoidal function ($R^2 = 0.94$) with amplitude of about 10.1 °C (Fig. 2c and d). The seasonal temperature signal (thermal front) penetrates into the aquifer by heat advection and conduction. Sinusoidal temperature oscillations at the groundwater observation wells were reduced in amplitude and shifted towards later times compared to the temperature oscillation in the river (Fig. 2c). The temperature amplitude reduced to 0.4 °C at a distance of about 120 m (W04_{LOW}) from the river shore line. Strong seasonal temperature oscillation with minimum temperatures below 6 °C only occurred within the nearshore aquifer, along the first 10-20 m of the infiltration zone (W07). For a detailed spatial temperature distribution within the aquifer see results of transient 3-D modeling of flow and heat transport of Wang et al. (2019).

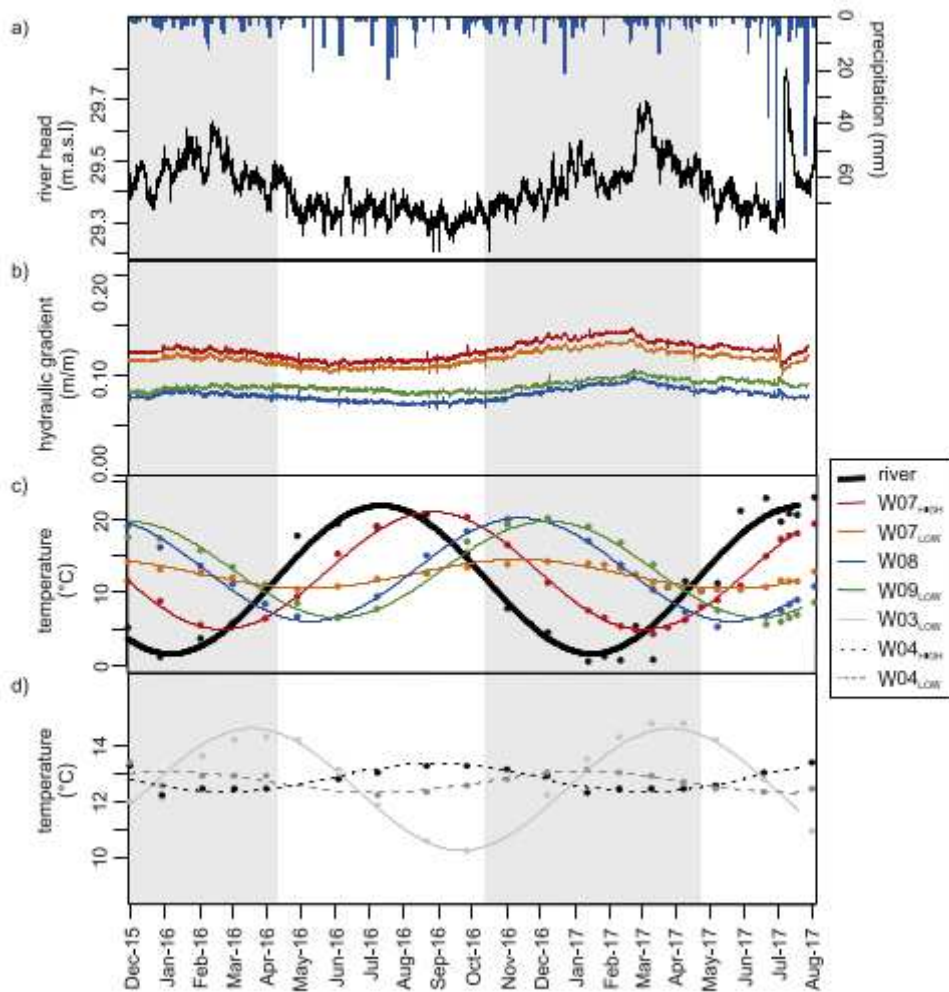


Figure 2: Time-series of (a) river water level and precipitation, (b) hydraulic head gradient between river and groundwater observation well and (c&d) temperatures with fitted sinusoidal function. In all graphs, the grey shaded area denotes times when river temperature was below 11.7 °C (yearly average).

3.2 Mixing ratios and residence times

The concentrations of acesulfame, chloride and sodium in the river tend to vary seasonally with maximum concentrations in october/november 2016 and minimum concentrations in may/june 2016 and 2017 (Fig. SM-1). The seasonal course of these conservative substances at the groundwater observation wells followed the trend observed in the river, but was individually shifted in time. The concentration range at the observation wells was close to the range observed in the river (Fig. SM-1). Average background concentration of deep, lateral groundwater (U100) was about 1224 ng l⁻¹ for acesulfame, 32 mg l⁻¹ for sodium and 46 mg l⁻¹ for chloride.

Generally the groundwater observation wells are dominated by infiltrated surface water throughout the entire observation period. The spatial distribution of the average mixing ratios is illustrated in Fig. 1b. The portion of surface water in the aquifer at the near shore is above 94% whereby the surface water contribution at W07_{HIGH} is 100% (no mixing effects of the source concentrations). Details

about the deviation between measured and calculated concentrations are presented in detail in Table SM-2. The average uncertainty of the mixing ratios of the observation wells dominated by surface water infiltration ranged between -3.0% (W08) and 2.5% (W07_{LOW}) (Tab. SM-2).

The subsurface residence times ranged between 18 d close to the river and 438 d close to the pumping well gallery (Fig. 1c). Residence times of W08 (49d) and W09 (59d) were slightly higher than those of W07_{HIGH}. A temperature retardation factor of 2.4 was used for the analyses, calculated from literature derived values of the heat capacity and thermal conductivity for sandy materials (Stonestrom and Blasch, 2003). Addressing the uncertainty in the temperature retardation factor, which reasonably might vary between 2.1 and 2.7, would end up in variations in the estimated aquifer residence times of ± 2 days for W07_{HIGH} and of ± 15 days for W03_{LOW}.

3.3 Redox condition in the aquifer

The river water was almost saturated with O₂ during the entire observation period varying between 12 mg l⁻¹ in winter and 5 mg l⁻¹ in summer. Mean nitrate concentration in the river was 5.2 mg l⁻¹ with slight seasonal variation with a maximum of 9.4 mg l⁻¹ in winter and a minimum of 4.1 mg l⁻¹ in summer, following the course of the oxygen concentration (Fig. 3a). In comparison to the permanent oxic river water, the groundwater at the observation wells was substantially reduced. In W07_{HIGH} and W07_{LOW}, close to the river shore line (13.5 m) with a depth of 0.1-2.1 m and 5.6-7.6 m below the river bottom, respectively (Fig. 1c), the redox condition displayed strong seasonal variations (Fig. 1d). In summer all oxygen was removed before reaching the first groundwater observation well (W07_{HIGH}). Only when aquifer temperatures were below 11 °C, from December 2015 until June 2016 and from December 2016 until April 2017, oxic conditions were encountered in W07_{HIGH} with maximum concentrations of 3 mg l⁻¹. Shortly after the observed peak in oxygen, also the NO₃⁻ concentration reached its maximum of 6 mg l⁻¹ which was comparable to the corresponding NO₃⁻ concentration within the river at the time of infiltration ($t_{res} \sim 18$ d). Only on 30.08.2016, when temperature at W07_{HIGH} was highest (20.2 °C) the NO₃⁻ concentration decreased to zero. In W07_{HIGH} Mn²⁺ appeared only in autumn, at times when O₂ had been fully depleted and shortly after the NO₃⁻ concentration decreased to zero (Fig. 3b).

At W07_{LOW} Mn²⁺ and Fe²⁺ appeared between June 2016 and January 2017 when the oxygen and nitrate were completely degraded (Fig. 3c). In winter 2017 no O₂ breakthrough was observed and maximum concentration of NO₃⁻ peaked at March 2017 with concentration up to 3 mg l⁻¹ for a short period (roughly half of the corresponding river concentration). Wells W03_{LOW} and W04_{LOW}, far from the shore line, never contained oxygen or nitrate, but iron concentration of up to 1 mg l⁻¹. No sulphate reduction was observed at the observation wells with exception of W07_{LOW}. Average sulfate concentration in the river and W04_{LOW} was about 187 mg l⁻¹ and 194 mg l⁻¹, respectively.

On top of the seasonal variations, the NO₃ concentrations dropped to zero during the rainfall induced discharge events in July 2017. That occasional drop down propagated towards the near shore observation wells. In contrast no substantial event based variation in O₂, Mn²⁺ and Fe²⁺ concentration were observed neither in the river nor in the groundwater observation wells.

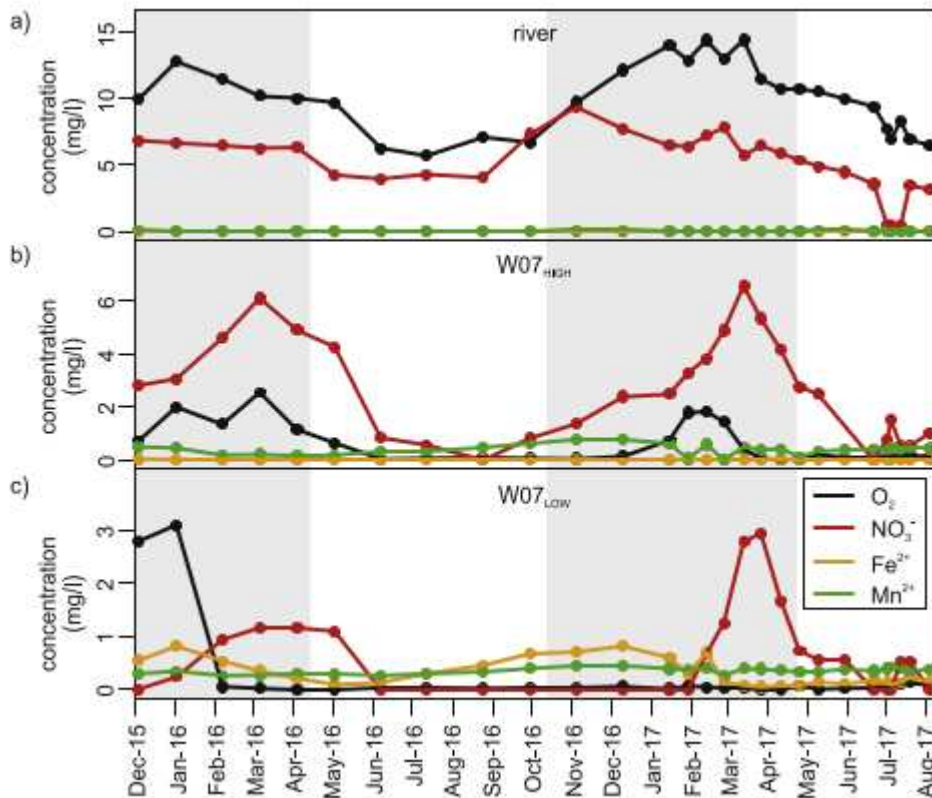


Figure 3: Concentration of the redox indicators (O_2 , NO_3^- , Mn^{2+} , Fe^{2+}) in (a) the river, (b) W07_{HIGH} and (c) W07_{LOW} between December 2015 and July 2017. In all graphs, the grey shaded area denotes times when river temperature was below 11.7 °C (yearly average). Note the decrease in scaling of the y-axes from a-c

3.4 DOC

Throughout the year, river DOC concentrations were quite constant with a mean value of 6.9 mg-C l⁻¹ and a standard deviation of 0.6 mg-C l⁻¹. Average groundwater DOC concentrations were always less than river water concentrations (Fig. SM-3). The DOC concentration from the river towards the observation wells decreased only within the first meters of the infiltration area (oxygenated zone). The DOC concentration between river and W07_{HIGH} decreased in average of about 4.2 mg-C l⁻¹ between April and November 2016 (~64% of the total DOC present) and of about only 1.5 mg-C l⁻¹ between December 2016 and July 2017 (~23%). The degree of DOC removal fluctuated slightly between both periods but did not show any seasonality, nor did it show a clear relation to the hydraulic conditions. Throughout the entire observation period the ΔDO exceeds the ΔDOC . An according metabolism plot for W07_{HIGH} is shown in (Fig. SM-4).

3.5 Concentration of OMP in the river and in the aquifer

Fig. 4 shows the observed OMP concentrations in the river along with the spatial and temporal variations. Observed concentrations were comparable along the river and over the course of one day (cp. SD_{space} and SD_{time} in Figs. 5 and 6). The surface water is well mixed by frequently induced turbulent

water circulation through shipping. Observed concentrations were typically in the higher nanogram per liter level, except valsartan which occur in the mg per liter level (Fig. 4).

The occurrence of OMPs in the river was grouped according to their occurrence and seasonal variation in their concentrations (Fig. 4, Table 1) and their fate and conditions of degradation in the aquifer (Table 1, Figs. 5 and 6). In the deeper, lateral groundwater

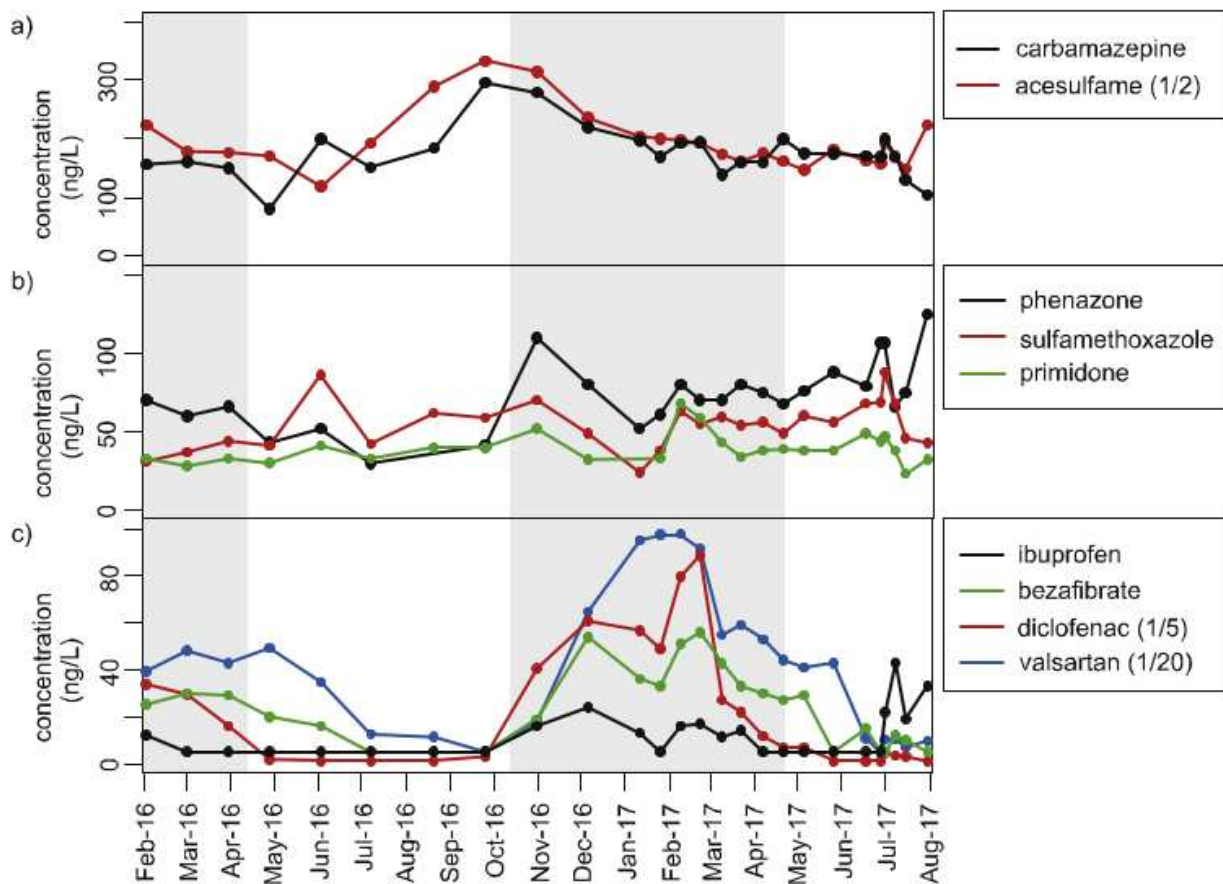


Figure 4: Concentrations of OMP in the river grouped according to their occurrence and seasonal variations (a-c) between February 2016 and July 2017. In all graphs, the grey shaded area denotes times when river temperature was below 11.7 °C (yearly average). Diclofenac, valsartan and gabapentin plotted in different scaling.

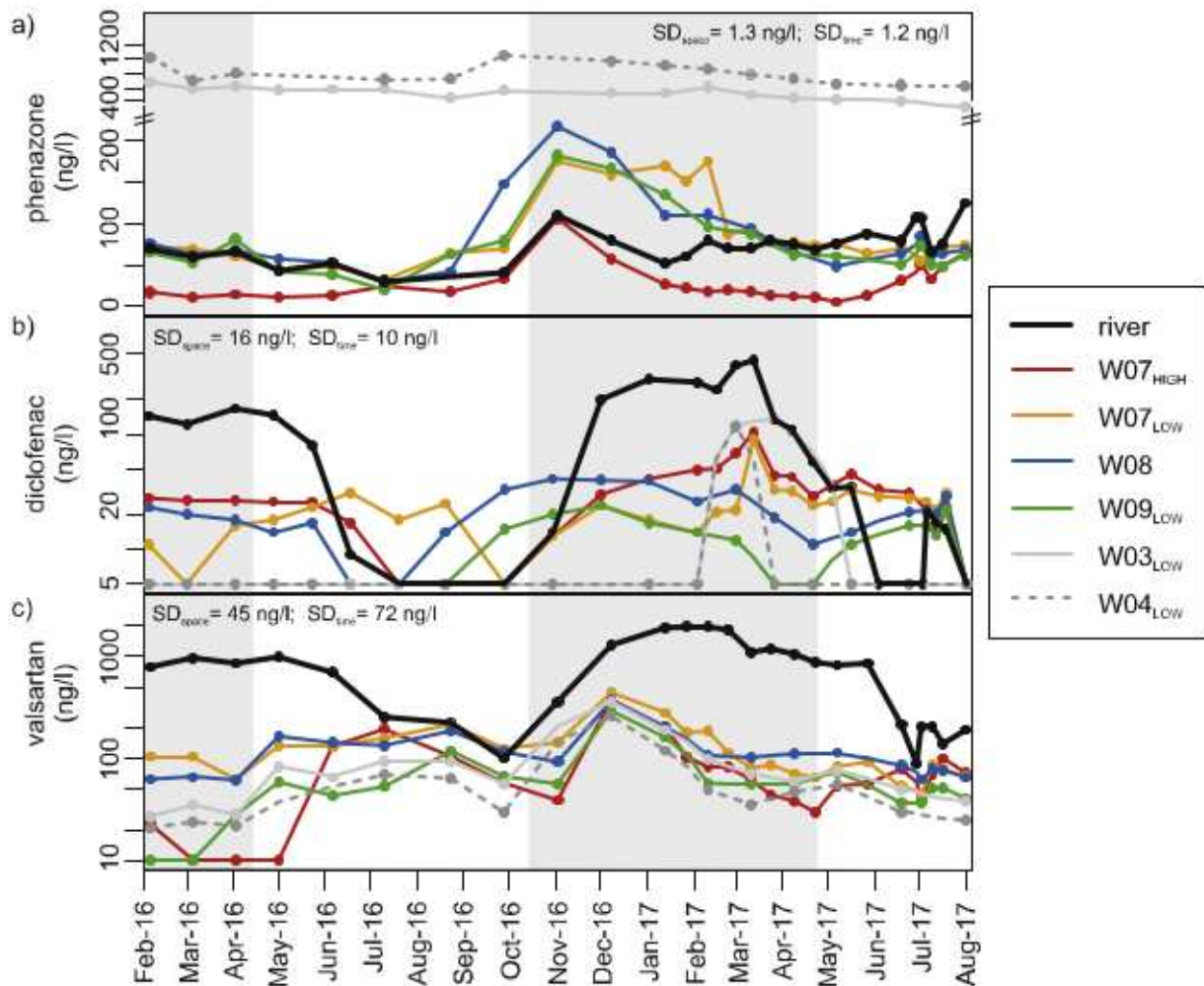


Figure 5: Concentrations of (a) phenazone, (b) diclofenac, and (c) valsartan in the river and groundwater observation wells between February 2016 and July 2017. In all graphs, the grey shaded area denotes times when river temperature was below 11.7 °C (yearly average). Note that the y-axis in b&c is log scaled.

(U100) out of the observed OMPs only acesulfame ($\overline{c_{U100}} = 1224 \text{ ng l}^{-1}$), primidone ($\overline{c_{U100}} = 31 \text{ ng l}^{-1}$) and phenazone ($\overline{c_{U100}} = 935 \text{ ng l}^{-1}$) were detected.

Phenazone, sulfamethoxazole, and ibuprofen substantially varied in their measured concentration between mid-June and mid-July 2017 (Fig. 4) when the water level and discharge in the river quickly raised due to strong precipitation events (Fig. 2). The concentration increased after the rise up of the water level by about 35% (phenazone), 28% (sulfamethoxazole), and 760% (ibuprofen). Afterwards the concentrations of phenazone and sulfamethoxazole decreased below the pre-event concentration, whereas the concentration of ibuprofen stayed above the pre-event concentration (56%).

The results of the degradation rates and the statistical analyses are presented in Table 2. The results highlight the significant effect of seasonal temperature variations on the fate of redox sensitive species and several OMP within the shallow aquifer. Within the thermally active zone (W07_{HIGH}) the

seasonal variations in temperature alone can explain a considerable percentage of the variance in DO (34%), nitrate (81%) as well as diclofenac (44%) and

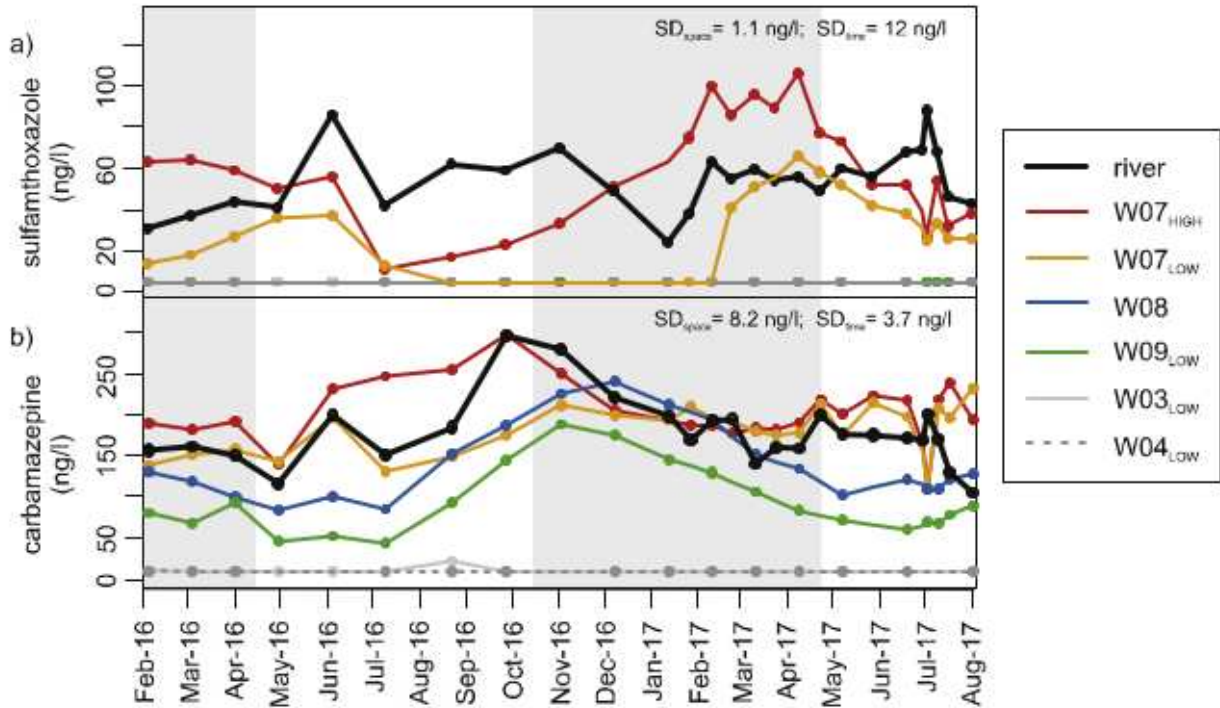


Figure 6: Concentrations of (a) sulfamethoxazole, and (b) carbamazepine in the river and groundwater, observation wells between February 2016 and July 2017. In all graphs, the grey shaded area denotes, times when river temperature was below 11.7 °C (yearly average).

Table 2: First order degradation constant (\pm uncertainty of the calculated rates based on the uncertainties of mixing ratios, residence times and retardation factors), multiple regression p-values and coefficient of determination (R^2) for linear model fits between redox indicators/OMP versus temperature, and Spearman's rank correlation coefficient of OMP versus the redox indicators. Dark colors indicate higher absolute correlations. Red indicates negative, blue positive correlations.

Dissolved species	average k (SD_{Time}) [d^{-1}]	R^2 Solute \sim T	Spearman's rank correlation coefficient				
			T	O ₂	NO ₃ ⁻	Mn ²⁺	Fe ²⁺
oxygen	0.196 ± 0.021 (0.062)	0.34*	-0.45				
nitrate	0.077 ± 0.009 (0.059)	0.81**	-0.89				
manganese(II)	-	-	0.26				
iron(II)	-	-	-0.03				
diclofenac	0.071 ± 0.008 (0.035)	0.44**	-0.68	0.22	0.52	0.08	0.08
phenazone	0.068 ± 0.008 (0.029)	0.28*	0.50	-0.14	-0.48	0.72	-0.38
valsartan	0.128 ± 0.057 (0.072)	0.04	0.57	-0.36	-0.66	0.46	-0.25
sulfamethoxazole	0.036 ± 0.004 (0.028)	0.76**	-0.89	0.30	0.57	0.41	-0.83
carbamazepine	> 0.039	0.28*	0.84	0.33	0.28	0.62	-0.84

** p-value < 0.001; * p-value < 0.01

sulfamethoxazole (76%). For these substances we observed a negative correlation between temperature and concentration in the water sample. In contrast only a minor part of the variance in phenazone and carbamazepine can be explained by seasonal variations in temperature (28%). For these substances we observed a positive correlation between temperature and concentration in the water sample.

4 Discussion

4.1 Redox zonation and nitrate removal

At the river groundwater interface the dissolved organic carbon (DOC) concentrations substantially decrease (SM-3), according to this interface being considered a hotspot for microbial activity and biogeochemical reactions. Along the subsurface flow path of the bank filtrate distinguishable redox zones develop due to the sequential order of terminal electron acceptors such as oxygen, nitrate, manganese- and iron-oxides and hydroxides. The observed redox zonation highly depended on the environmental temperature which can explain 34% of the variance in DO and 81% of the variance in NO_3^- using a simple linear model.

The highest rates of oxygen consumption in the aquifer (PR > 99% at W07) occurred when groundwater temperatures were high (Fig. 3b). In winter, when average temperature in the aquifer falls below 8 °C oxygen consumption rates significantly decreased resulting in a breakthrough of oxygen at W07_{high} (PR = 75%). The decrease in oxygen concentration along the subsurface flow path is presumably caused by intense heterotrophic aerobic respiration of DOC as a river-borne carbon source and particulate organic matter (POC) present in the aquifer. At all times, but particularly in winter, the molecular decrease in oxygen between river and W07_{HIGH} exceeded the decrease in DOC (Fig. SM-4). This indicates that besides dissolved organic carbon, POC present in the aquifer or, more likely, fresh organic matter of the clogging layer may act as an additional electron donor during RBF as has been previously found in riverbank filtration settings (Grunheid et al., 2005).

The percentage of nitrate removal between river and W07 ranged between 6% and 89%. Only for longer flow paths towards W03 the entire nitrate load imported from the river into the aquifer was removed (PR > 99%). Nitrate degradation rates of the near groundwater zone were about 1/5 of first order rate constants of RBF and artificial recharge sites reported for Berlin (Henzler et al., 2016; Greskowiak et al., 2006) and about one order of magnitude smaller than for natural riparian zones (Trauth et al., 2018).

Decreasing DO concentrations favor anaerobic heterotrophic denitrification, limited by the inhibition effect of DO and the temperature dependent degradation rates. Several studies observed a threshold in DO concentrations of about 2 mg l⁻¹ below which denitrification activity strongly increases whereby various nitrogen species can be efficiently assimilated, transformed or permanently removed (Rivett et al., 2008). Finally, temperature is a crucial control on the activity of both, aerobic and anaerobic bacteria, significantly affecting degradation rates in hyporheic zones (Hill et al., 1998), riparian groundwater (Trauth et al., 2018) and RBF systems (this study).

4.2 Concentration of OMP in the river

Seasonal changes in concentrations in the surface water are caused by changes in precipitation and dilution and by changes in elimination rates through photochemical degradation, biodegradation, and/or adsorption processes (Loraine and Pettigrove, 2006). The seasonal course of acesulfame and carbamazepine concentrations, which have been found to be stable in surface aquatic environments (Tixier et al., 2003), were related to changing dilution of effluents with maximum concentrations in October 2016 after a long period of low river discharge. Maximum variation in observed concentrations caused by dilution at the study site is expected to be about $\pm 60\%$ caused by variations in the river discharge to effluent discharge ratio (assuming a constant input by the STP). Clofibric acid was not detected in the surface water during the entire observation period even though it is assumed to exhibit a significant persistence in the aquatic system (Tixier et al., 2003). Some of the compounds observed, e.g. phenazone, primidone, and sulfamethoxazole, seem to show a significant persistence in the surface water though these substances partly are affected by degradation and sorption processes in an aquatic environment (Meierjohann et al., 2016). Seasonal variation in degradation and sorption processes, which tend to increase with increasing temperature, seems to compensate seasonal variations in observed concentrations due to dilution (Fig. 4b).

Concentrations of most OMP in the Havel river system tend to vary seasonally, with higher concentrations in winter and lower concentrations in summer most likely caused by photochemical degradation (Boreen et al., 2003). In winter the global radiation is low (often below 200 W m^{-2}) and the sunshine duration is short (often below 1 h d^{-1}). Under these conditions photo transformation is limited as an elimination pathway. The opposite conditions are prevailing in summer with high global radiation up to 1100 W m^{-2} and daily sunshine duration up to 15 h d^{-1} creating excellent conditions for photochemical degradation of the pharmaceuticals. The observed concentrations of valsartan ($CC = -0.85$, $R^2 = 0.72$), diclofenac ($CC = -0.87$, $R^2 = 0.67$) and bezafibrate ($CC = -0.86$, $R^2 = 0.76$) were found to significantly decrease with sunshine duration of the previous month.

4.3 Concentration of OMP in the aquifer

4.3.1 Persistent OMP

Primidone and acesulfame were detected in the bank filtrate (Fig. SM-1). Especially the artificial sweetener acesulfame is assumed to be persistent in the aquatic environment and thus supposed to act as an ideal wastewater marker (Engelhardt et al., 2013). Recently Burke et al. (2014) demonstrated that acesulfame was not attenuated in laboratory column studies under cold conditions ($6.5 \text{ }^\circ\text{C}$) but displayed slight removal under warm conditions ($19.5 \text{ }^\circ\text{C}$). We found that acesulfame was transported within the aquifer in a conservative manner under anoxic aquifer conditions, quite independent of the temperature conditions (k equal to zero). Only under the oxic conditions between 09/2016 and 04/2017 we observed slight degradation of acesulfame (average $k = 0.009 \text{ d}^{-1}$, $SD_{\text{time}} = 0.005 \text{ d}^{-1}$).

4.3.2 Degradation under oxic aquifer condition

Out of the nine compounds detected in the surface water, bezafibrate ($k > 0.13 \text{ d}^{-1}$), and ibuprofen ($k > 0.09 \text{ d}^{-1}$) were not present any more in the bank filtrate. These substances are well known to be biodegradable under oxic conditions, while the minimum in-situ degradation rates at our site with rather short-distance RBF were substantially higher than previously reported during long-term/long-distance RBF (Table 1). The calculated degradation rates in combination with the low source concentration in the river during summer, when the extent of the oxic zone is narrow, are sufficient for a complete removal of these substances at the nearshore aquifer throughout the entire observation period.

Phenazone, diclofenac and valsartan, were efficiently attenuation under oxic conditions in winter when temperature was low and oxygen was present in the near shore aquifer. The removal rates of these compounds decreased under anoxic conditions up to a persistent behavior in summer when temperatures were high and oxygen did not penetrate into the aquifer. Based on the experimental data alone it is not possible to clearly quantify the single effect of temperature and the redox regime on the degradation rates due to the cross correlation between both effects within the nearshore aquifer. Burke et al. (2014) observed a significant decrease in phenazone degradation rates in saturated laboratory columns under oxic/penoxic conditions at a temperature of $19.4 \text{ }^{\circ}\text{C}$ ($k = 5.53 \text{ d}^{-1}$) and a temperature of 6.5°C ($k = 1.64 \text{ d}^{-1}$). Within that temperature range, the removal rate constant of phenazone decreased by a factor of 3 but was about two orders of magnitude higher than degradation rates found in this study. Average phenazone concentrations at W03 (548 ng l^{-1}) and W04 (779 ng l^{-1}) were predominantly higher than the concentrations in the river (74 ng l^{-1}). About half of these values could be explained by mixing with the lateral groundwater flow constituting an additional source with much higher phenazone concentration ($\overline{c_{U100}} = 935 \text{ ng l}^{-1}$). Desorption seems not to be a suited explanation since phenazone is reported not to be subject to sorption/desorption in an aquifer (Henzler et al., 2014; Massmann et al., 2008).

Average degradation rates of diclofenac of the near groundwater zone were about 0.07 d^{-1} . Generally diclofenac is known to be better attenuated at higher temperatures whereby the temperature effect observed during infiltration was rather low due to the strong variations in river concentrations which were almost zero in summer. However the observed rate constant in laboratory column studies with undisturbed sediment cores from a riverbank filtration site at Lake Wannsee substantially decreased by a factor of 1.6 for the temperature settings of $6.5 \text{ }^{\circ}\text{C}$ ($k = 6.4 \text{ d}^{-1}$) and $19.4 \text{ }^{\circ}\text{C}$ ($k = 10.4 \text{ d}^{-1}$) (Burke et al., 2014), but were about two orders of magnitude higher than degradation rates found in our field study, which is often the case for degradation rates (e.g. Watson et al., 2005). When aquifer conditions turned anaerobic diclofenac behaves persistent (Burke et al., 2014) and can be transported over longer distances within the aquifer. The measured breakthrough of diclofenac at W03 ($t_{res} = 104 \text{ d}$, $R_{diclofenac} \sim 1$) in between 02/2017 and 05/2017 with concentrations of about 200 ng l^{-1} were related to high concentrations in the river paired with anoxic aquifer conditions between 10/2016 and 01/2017, whereas the breakthrough at W04 resulted from the previous year when high river concentrations paired with anoxic aquifer conditions at the nearshore aquifer between December 2015 and March 2016. But it remains unclear why in W03 no breakthrough of diclofenac was observed in spring 2016 under these circumstances.

Average degradation rates of valsartan of the near groundwater zone were about 0.13 d^{-1} . Despite the degradation valsartan was still detected within the aquifer, demonstrating the relevance of this compound for drinking water suppliers. Thus, more information on the environmental behavior of valsartan is needed.

4.3.3 Degradation under anoxic aquifer condition

Carbamazepine was detected in all near shore observation wells caused by low degradation rates of carbamazepine under prevailing oxic condition along the river shore line. In contrast to the generally reported high persistence of carbamazepine in groundwater environments (Heberer, 2002; Schmidt et al., 2017; Wiese et al., 2011) under anoxic conditions we observed high elimination rates up to 100% ($k > 0.039 \text{ d}^{-1}$). Moreover, we found that occurrence of iron reducing conditions dominate carbamazepine degradation in groundwater.

Average degradation rates of sulfamethoxazole were in the range of other bank filtration sites (Grunheid et al., 2005; Henzler et al., 2014), but were found to significantly depend on groundwater temperatures (Fig. 6), likely due to decreased microbial activity at lower temperatures.

5 Conclusion

Greskowiak et al. (2017) reveals a huge natural variability in compound specific first-order degradation rate constants even for similar types of field studies. They clarified some of the tremendous uncertainties about the influencing factors, and how and to what degree they affect the degradation process in a specific environment. Our study is a step forward to quantitatively verify environmental effects on the in-situ variability in degradation rate constants. River and groundwater hydrological and hydrochemical data were analytically and statistically evaluated to quantify the environmental factors that control attenuation efficiency of nitrate and trace organic micropollutants from polluted surface waters during river bank filtration on a row of monitoring wells with groundwater travel times ranging between 18 and 438 days. The presented dataset for RBF at field scale from a monthly sampling campaign during a one and a half year period incorporates temporally and spatially varying redox conditions and temperature changes typically occurring in temperate climates. Our study emphasizes that degradation rates of several OMP during bank filtration are controlled by redox conditions and temperature whereby temperature also has a significant influence on the extent of the most reactive oxic/suboxic zones. We highlight, that temperature plays a crucial role in controlling in-situ degradation rates which were found to vary within one order of magnitude for temperature changes between $5 \text{ }^{\circ}\text{C}$ and $20 \text{ }^{\circ}\text{C}$. Comparing to degradation rates commonly derived from laboratory experiments these in-situ values are more representative with regard to the geological aquifer complexity and biogeochemical conditions of natural systems. Comparing the determined first-order degradation rate constants of this study with those of Greskowiak et al. (2006) and Henzler et al. (2014), who modeled the coupled transport and degradation of several OMP, it seems that at least the magnitudes of rate constants are transferable from one field site to another for comparable hydrogeological and geochemical aquifer conditions. This has important implications for local and catchment scale management strategies aiming to reduce future pollutant concentrations in drinking water production

wells. Especially those substances showing enhanced degradation only under oxic conditions potentially threaten groundwater quality if they infiltrate under anoxic conditions into the aquifer (e.g. diclofenac, phenazone, valsartan). However, for other OMP such as carbamazepine the presence of anoxic conditions seems to yield substantial removal potential decreasing the exposure of downstream pumping wells. To refine the estimation of the degradation parameters presented herein, further investigations as well as simulations including the spatially and temporally variable temperature and redox conditions of the RBF site are needed, especially to support guideline values for OMP in river and groundwater used for drinking water supplies.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Federal Waterways Engineering and Research Institute (BAW) in Karlsruhe, Germany. We also gratefully acknowledge Dorit Tscherner and Karsten Zühlke from Energie und Wasser Potsdam GmbH for supporting this study and Peter Biro for carrying out the river and groundwater sampling. For the laboratory work we would like to thank Iris Pieper and Sabine Dumke from the Biogeochemical Laboratory at TU Berlin for performing the analyses for ions as well as Anke Putschew from the TU Berlin, Institute of Environmental Science and Technology, Department Water Quality Engineering for performing the analyses for DOC.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2019.06.041>.

References

- Battin, T.j.. 1999. Hydrologic flow paths control dissolved organic carbon fluxes and metabolism in an alpine stream hyporheic zone. *Water Resour. Res.* 35, 3159-3169.
- Bertelkamp, C., Reungoat, J., Cornelissen, E.R., Singhai, N., Reynisson, J., Cabo, A.J., van der Hoek, J.P., Verliefe, A.R.D., 2014. Sorption and biodegradation of organic micropollutants during river bank filtration: a laboratory column study. *Water Res.* 52, 231-241.

- Bertelkamp, C., van der Hoek, J.P., Schoutteten, K., Hulpiau, L., Vanhaecke, L., Bussche, J.V., Cabo, A.J., Callewaert, C., Boon, N., Lowenberg, J., Singhai, N., Verliefde, A.R.D., 2016. The effect of feed water dissolved organic carbon concentration and composition on organic micropollutant removal and microbial diversity in soil columns simulating river bank filtration. *Chemosphere* 144, 932-939.
- Boreen, A.L., Arnold, W.A., McNeill, K., 2003. Photodegradation of pharmaceuticals in the aquatic environment: a review. *Aquat. Sci.* 65, 320-341.
- Burke, V., Greskowiak, J., Asmuss, T., Bremermann, R., Taute, T., Massmann, G., 2014. Temperature dependent redox zonation and attenuation of wastewater-derived organic micropollutants in the hyporheic zone. *Sci. Total Environ.* 482, 53-61.
- Carrera, J., Vazquez-Sune, E., Castillo, O., Sanchez-Vila, X., 2004. A methodology to compute mixing ratios with uncertain end-members. *Water Resour. Res.* 40, W12101.
- Engelhardt, I., Prommer, H., Moore, C., Schulz, M., Schuth, C., Ternes, T.A., 2013. Suitability of temperature, hydraulic heads, and acesulfame to quantify wastewater-related fluxes in the hyporheic and riparian zone. *Water Resour. Res.* 49, 426-440.
- Greskowiak, J., Hamann, E., Burke, V., Massmann, G., 2017. The uncertainty of biodegradation rate constants of emerging organic compounds in soil and groundwater - a compilation of literature values for 82 substances. *Water Res.* 126, 122-133.
- Greskowiak, J., Prommer, H., Massmann, G., Nutzmann, G., 2006. Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater. *Environ. Sei. Technol.* 40, 6615-6621.
- Grunheid, S., Amy, G., Jekel, M., 2005. Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. *Water Res.* 39, 3219-3228.
- Hamann, E., Stuyfzand, P.J., Greskowiak, J., Timmer, H., Massmann, G., 2016. The fate of organic micropollutants during long-term/long-distance river bank filtration. *Sci. Total Environ.* 545, 629-640.
- Heberer, T., 2002. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. *J. Hydrol.* 266, 175-189.
- Heberer, T., Massmann, G., Fanck, B., Taute, T., Dunnbier, U., 2008. Behaviour and redox sensitivity of antimicrobial residues during bank filtration. *Chemosphere* 73, 451-460.

- Hebig, K.H., Groza, L.G., Sabourin, M.J., Scheytt, T.J., Ptacek, C.J., 2017. Transport behavior of the pharmaceutical compounds carbamazepine, sulfamethoxazole, gemfibrozil, ibuprofen, and naproxen, and the lifestyle drug caffeine, in saturated laboratory columns. *Sci. Total Environ.* 590, 708- 719.
- Henzler, A.F., Greskowiak, J., Massmann, G., 2014. Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). *J. Contam. Hydrol.* 156, 78-92.
- Henzler, A.F., Greskowiak, J., Massmann, G., 2016. Seasonality of temperatures and redox zonation during bank filtration - a modeling approach. *J. Hydrol.* 535, 282-292.
- Hill, A.R., Labadia, C.F., Sanmugadas, K., 1998. Hyporheic zone hydrology and nitrogen dynamics in relation to the streambed topography of a N-rich stream. *Biogeochemistry* 42, 285-310.
- Hoehn, E., Cirpka, O.A., 2006. Assessing residence times of hyporheic ground water in two alluvial flood plains of the Southern Alps using water temperature and tracers. *Hydrol. Earth Syst. Sci.* 10, 553-563.
- Hoppe-Jones, C., Dickenson, E.R.V., Drewes, J.E., 2012. The role of microbial adaptation and biodegradable dissolved organic carbon on the attenuation of trace organic chemicals during groundwater recharge. *Sci. Total Environ.* 437, 137-144.
- Jekel, M., Dott, W., Bergmann, A., Dunnbier, U., Gnirss, R., Haist-Gulde, B., Hamscher, G., Letzel, M., Licha, T., Lyko, S., Miehe, U., Sacher, F., Scheurer, M., Schmidt, C.K., Reemtsma, T., Ruhl, A.S., 2015. Selection of organic process and source indicator substances for the anthropogenically influenced water cycle. *Chemosphere* 125, 155-167.
- Loraine, G., E Pettigrove, M., 2006. Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. *Environ. Sci. Technol.* 40, 687-695.
- Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K., Amy, G.L., 2011. Occurrence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: a review. *Water Res.* 45, 3015-3033.
- Massmann, G., Dunnoer, U., Heberer, T., Taute, T., 2008. Behaviour and redox sensitivity of pharmaceutical residues during bank filtration - investigation of residues of phenazone-type analgesics. *Chemosphere* 71, 1476-1485.

- Massmann, G., Greskowiak, J., Dunnbier, U., Zuehlke, S., Knappe, A., Pekdeger, A., 2006. The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. *J. Hydrol.* 328, 141-156.
- Meierjohann, A., Brozinski, J.M., Kronberg, L., 2016. Seasonal variation of pharmaceutical concentrations in a river/lake system in Eastern Finland. *Environ. Sci. Proc. Imp.* 18, 342-349.
- Munz, M., Oswald, S.E., Schmidt, C., 2016. Analysis of riverbed temperatures to determine the geometry of subsurface water flow around in-stream geomorphological structures. *J. Hydrol.* 539, 74-87.
- Munz, M., Oswald, S.E., Schmidt, C., 2017. Coupled long-term simulation of reach-scale water and heat fluxes across the river-groundwater interface for retrieving hyporheic residence times and temperature dynamics. *Water Resour. Res.* 53, 8900-8924.
- Munz, M., Schmidt, C., 2017. Estimation of vertical water fluxes from temperature time series by the inverse numerical computer program FLUX-BOT. *Hydrol. Process.* 31, 2713-2724.
- Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. *Water Res.* 72, 3-27.
- R Development Core Team, 2011. R: a language and environment for statistical computing. Vienna, Austria. <http://www.R-project.org/>. ISBN 3-900051-07-0.
- Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water Res.* 42, 4215-4232.
- Schaper, J.L., Seher, W., Nutzmann, G., Putschew, A., Jekel, M., Lewandowski, J., 2018. The fate of polar trace organic compounds in the hyporheic zone. *Water Res.* 140, 158-166.
- Schmidt, N., Page, D., Tiehm, A., 2017. Biodegradation of pharmaceuticals and endocrine disruptors with oxygen, nitrate, manganese {IV}, iron {III} and sulfate as electron acceptors. *J. Contam. Hydrol.* 203, 62-69.
- Stonestrom, D.A., Blasch, K.W., 2003. Determining temperature and thermal properties for heat-based studies of surface-water ground-water interactions. *U. S. Geol. Surv.* 73-80.
- Tixier, C., Singer, H.P., Oellers, S., Muller, S.R., 2003. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. *Environ. Sci. Technol.* 37, 1061-1068.

- Trauth, N., Schmidt, C., Vieweg, M., Oswald, S.E., Fleckenstein, J.H., 2015. Hydraulic controls of in-stream gravel bar hyporheic exchange and reactions. *Water Resour. Res.* 51.
- Trauth, N., Musolff, A., Knaller, K., Kaden, U.S., Keller, T., Werban, U., Fleckenstein, J.H., 2018. River water infiltration enhances denitrification efficiency in riparian groundwater. *Water Res.* 130, 185-199.
- van Driezum, I.H., Derx, J., Oudega, T.J., Zessner, M., Naus, F.L., Saracevic, E., Kirschner, A.K.T., Sommer, R., Farnleitner, A.H., Blaschke, A.P., 2018. Spatiotemporal resolved sampling for the interpretation of micropollutant removal during riverbank filtration. *Sci. Total Environ.* 649, 212-223.
- Vieno, N.M., Tuhkanen, T., Kronberg, L., 2005. Seasonal variation in the occurrence of pharmaceuticals in effluents from a sewage treatment plant and in the recipient water. *Environ. Sci. Technol.* 39, 8220-8226.
- Wang, W., Oswald, S.E., Gräff, T., Lensing, H.-J., Liu, T., Strasser, D., Munz, M., 2019. Impact of river reconstruction on groundwater flow during bank filtration assessed by transient 3-D modelling of flow and heat transport. *Hydrogeol. J.* (in revision).
- Watson, I.A., Oswald, S.E., Banwart, S.A., Crouch, R.S., Thornton, S.F., 2005. Modelling the dynamics of fermentation and respiratory processes in a groundwater phenols plume interpreted from laboratory - to field-scale. *Environ. Sci. Technol.* 39, 8829-8839.
- Wiese, B., Massmann, G., Jekel, M., Heberer, T., Dunnbier, U., Orlikowski, D., Grutzmacher, G., 2011. Removal kinetics of organic compounds and sum parameters under field conditions for managed aquifer recharge. *Water Res.* 45, 4939-4950.

Authors:

Matthias Munz

Institute of Environmental Science and Geography, University Potsdam

Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

E-Mail: munz@uni-potsdam.de

Sascha E. Oswald

Institute of Environmental Science and Geography, University Potsdam

Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

14476 Potsdam, Germany

Robin Schäfferling

Institute of Environmental Science and Geography, University Potsdam

Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

14476 Potsdam, Germany

Hermann-Josef Lensing

Department of Geotechnical Engineering, Federal Waterways Engineering and Research Institute (BAW), Kussmaulstr. 17, 76187 Karlsruhe

E-Mail: hermann.lensing@baw.de.