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

Bertelkamp, C; van der Hoek, JP; Schoutteten, K; Hulpiau, L; Vanhaecke, L; Vanden Bussche, J; Cabo, AJ; Callewaert, C; Boon, N; Lowenberg, J

DOI
10.1016/j.chemosphere.2015.09.017

Publication date
2016

Document Version
Final published version

Published in
Chemosphere

Chemosphere 144 (2016) 932–939

Contents lists available at ScienceDirect

Chemosphere

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

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

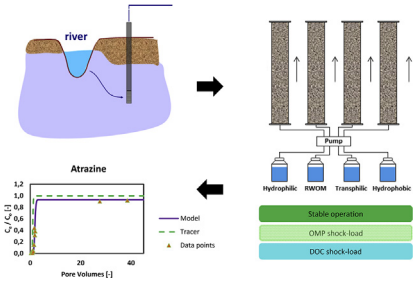
C. Bertelkamp[a,b,*], J.P. van der Hoek[a,c], K. Schoutteten[b], L. Hulpiau[b], L. Vanhaecke[d], J. Vanden Bussche[d], A.J. Cabo[e], C. Callewaert[f], N. Boon[f], J. Löwenberg[g], N. Singhal[h], A.R.D. Verliefde[b]

[a] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Department of Water Management, PO Box 5048, 2600 GA, Delft, The Netherlands
[b] Ghent University, Faculty of Bioscience Engineering, Particle and Interfacial Technology Group, Coupure Links 653, B-9000, Ghent, Belgium
[c] Strategic Centre, Waternet, Korte Ouderkerkerdijk 7, 1096 AC, Amsterdam, The Netherlands
[d] Ghent University, Faculty of Veterinary Medicine, Department of Veterinary Public Health and Food Safety, Laboratory of Chemical Analysis, Salisburylaan 133, B-9820, Merelbeke, Belgium
[e] Delft Institute of Applied Mathematics (DIAM), Faculty EEMCS, Mekelweg 4, 2628 CD, Delft, The Netherlands
[f] Ghent University, Faculty of Bioscience Engineering, Laboratory of Microbial Ecology and Technology (LabMET), Coupure Links 653, B-9000, Ghent, Belgium
[g] University of Applied Sciences and Arts Northwestern Switzerland, School of Life Sciences, Institute for Ecopreneurship, Gründenstrasse 40, CH-4132, Muttenz, Switzerland
[h] The University of Auckland, Department of Civil and Environmental Engineering, Private Bag 92019, Auckland, 1142, New Zealand

HIGHLIGHTS

- RBF is resilient towards variations in the organic carbon fractions.
- RBF is resilient towards a DOC shock-load.
- RBF is not resilient towards an OMP shock-load.
- An OMP shock-load increases OMP biodegradation rates for river water organic matter.
- An OMP shock-load increases OMP biodegradation rates for hydrophilic organic matter.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 May 2015
Received in revised form 22 August 2015
Accepted 5 September 2015
Available online 30 September 2015

Handling editor: Jörg E. Drewes

ABSTRACT

This study investigated organic micropollutant (OMP) biodegradation rates in laboratory-scale soil columns simulating river bank filtration (RBF) processes. The dosed OMP mixture consisted of 11 pharmaceuticals, 6 herbicides, 2 insecticides and 1 solvent. Columns were filled with soil from a RBF site and were fed with four different organic carbon fractions (hydrophilic, hydrophobic, transphilic and river water organic matter (RWOM)). Additionally, the effect of a short-term OMP/dissolved organic carbon (DOC) shock-load (e.g. quadrupling the OMP concentrations and doubling the DOC concentration) on OMP biodegradation rates was investigated to assess the resilience of RBF systems. The results obtained

* Corresponding author. Delft University of Technology, Faculty of Civil Engineering and Geosciences, Department of Water Management, PO Box 5048, 2600 GA, Delft, The Netherlands..
E-mail address: c.bertelkamp@tudelft.nl (C. Bertelkamp).

http://dx.doi.org/10.1016/j.chemosphere.2015.09.017

Keywords:
River bank filtration
Organic micropollutants
Biodegradation
Organic carbon fractions
Microbial community composition

in this study imply that – in contrast to what is observed for managed aquifer recharge systems operating on wastewater effluent - OMP biodegradation rates are not affected by the type of organic carbon fraction fed to the soil column, in case of stable operation. No effect of a short-term DOC shock-load on OMP biodegradation rates between the different organic carbon fractions was observed. This means that the RBF site simulated in this study is resilient towards transient higher DOC concentrations in the river water. However, a temporary OMP shock-load affected OMP biodegradation rates observed for the columns fed with the river water organic matter (RWOM) and the hydrophilic fraction of the river water organic matter. These different biodegradation rates did not correlate with any of the parameters investigated in this study (cellular adenosine triphosphate (cATP), DOC removal, specific ultraviolet absorbance (SUVA), richness/evenness of the soil microbial population or OMP category (hydrophobicity/charge).

1. Introduction

Organic micropollutants (OMPs) such as pharmaceuticals, pesticides and industrial waste products have been detected in Dutch surface waters in the ng/L to μg/L range (Houtman et al., 2014; Stoks et al., 2014). River bank filtration (RBF) can effectively remove various of these OMPs (Benotti et al., 2012; Henzler et al., 2014; Hoppe-Jones et al., 2010), but a few OMPs have also shown rather persistent behaviour (e.g. carbamazepine, primidone) (Maeng et al., 2012; Rauch-Williams et al., 2010). The mechanisms responsible for differences in OMP removal are not yet fully unveiled, but it is apparent that a number of processes are responsible for OMP removal during soil passage, such as sorption, biodegradation, and mixing (Hiscock and Grischek, 2002). Amongst these, biodegradation was found to be the most important mechanism (Bertelkamp et al., 2014; Henzler et al., 2014; Maeng et al., 2011).

Several lab-scale studies have investigated the effect of different dissolved organic carbon (DOC) sources in the feed water (concentration and composition) on OMP removal during soil passage (Li et al., 2014; Maeng et al., 2011, 2012; Onesios and Bouwer, 2012; Rauch-Williams et al., 2010). While some studies reported a positive correlation between biodegradable dissolved organic carbon (BDOC) concentration in the feed water and OMP removal (Lim et al., 2008), others demonstrated a negative correlation (Li et al., 2014). The correlation between the BDOC composition and the removal of OMPs reported in different studies also shows contradictory results (Lim et al., 2008; Maeng et al., 2012). Although not explicitly shown in these previous studies, a possible explanation for the difference in OMP removal with different BDOC concentration/composition, is the difference in microbial growth and speciation as a result of organic carbon composition. This explanation was further supported by a study performed by Rauch-Williams et al. (2010), who investigated OMP removal in soil columns fed with different fractions of organic carbon obtained from wastewater effluent thereby mimicking a managed aquifer recharge system. The soil column fed with hydrophobic acids (refractory carbon) was characterised by the lowest soil biomass, but showed equal or better OMP removal compared to the soil columns fed with other organic carbon fractions. It was hypothesized that an oligotrophic community developed in this column, which was well capable of removing OMPs.

Most previous lab-scale studies involving the effect of BDOC concentration and composition on OMP removal during soil aquifer treatment, have used synthetic wastewater or organic carbon fractions obtained from wastewater effluent as feed (Alidina et al., 2014; Li et al., 2014; Rauch-Williams et al., 2010). Translating the results of these wastewater studies to RBF systems is difficult since the composition and characteristics of organic matter in treated wastewater and natural surface water can greatly differ. Nam et al. (2008) demonstrated for example that river water (more representative of natural organic matter (NOM)) upstream from a wastewater treatment plant was characterised by a higher hydrophobic and lower hydrophilic fraction of organics, compared to a sample obtained from the wastewater treatment plant effluent (representative of Effluent Organic Matter (EfOM)). In addition, the river water sample was also characterised by a lower fraction of humic substances and a higher fraction of low molecular weight acids. These differences emphasize the need to investigate the effect of organic carbon fractions obtained from river water on OMP removal during RBF.

Additionally, it is necessary to gain further insight into the effect of variations in the organic carbon fractions in the feed water matrix on OMP biodegradation rates, because this aspect has not been investigated in previous studies. Since the character of organic matter present in the river is subject to seasonal variations (Alberts et al., 2001; Dong et al., 2014), a larger contribution of a specific organic carbon fraction towards the overall organic matter concentration present in the river could possibly influence the soil microbial population and therefore the removal of (certain) OMPs during RBF.

Finally, another important aspect that has received very little attention in past studies, is the effect of temporary OMP/DOC shock-loads on OMP removal during RBF. These shock-loads could occur as a result of, for example, industrial spills, dry weather conditions (low discharge of the river) in combination with concentrated discharge from wastewater treatment plants, or the seasonal/temporal use of pesticides/veterinary medicines on agricultural land. Few field studies tried to elucidate the effect of seasonal variations in DOC concentration as well as the contribution of wastewater on the RBF systems' capability to remove OMPs (Hoppe-Jones et al., 2010; Regnery et al., 2015a; Storck et al., 2012). However, in field studies the sole effect of seasonal DOC variations or OMP/DOC shock-loads is difficult to determine since the effect of other parameters (e.g. temperature) that influence OMP removal cannot be excluded. In addition, it is practically infeasible to determine OMP biodegradation rates in the field and these are useful when comparing different RBF sites or assessing the removal potential of a specific OMP for a RBF site.

To tackle aforementioned knowledge gaps, this study investigates OMP biodegradation rates in laboratory soil columns simulating the initial infiltration phase of a RBF process under oxic/subanoxic conditions. The objectives of this study were (i) to investigate the effect of feeding different organic carbon fractions obtained from river water (hydrophilic, hydrophobic, transphilic and river water organic matter (RWOM)) to soil columns on OMP biodegradation rates, and (ii) to investigate the effect of a short-term OMP/DOC shock-load on OMP biodegradation rates during

soil passage to determine the resilience of RBF systems towards these loads.

2. Materials and methods

2.1. Soil columns

The experimental set-up consisted of 8 transparent PVC columns (L = 1 m, D = 36 mm) filled with soil from the RBF site of drinking water company Oasen (51° 55′ 0.4″ N, 4° 47′ 5.4″ E). Three different OM fractions (hydrophilic, hydrophobic, transphilic) and the river water were fed in duplicate to one of the 8 columns each. A detailed description of the fractionation of the organic carbon is provided in the Supplemental Information (SI). The RBF soil used was characterised by the following soil fractions: sand 98.98 v/v %, clay 0.50 v/v % and silt 0.52 v/v%. The columns were filled with soil in increments of 4–5 cm until completely full to prevent layering. Top and bottom of the columns were fitted with perforated PVC plates (30 holes, d = 0.8 mm per hole) that were covered with filter cloth (45 μm, Top7even net & mesh, The Netherlands) to prevent leaching of sand grains. Water was fed to the columns from bottom to top to prevent air entrapment at room temperature (20 °C). Columns and feed solutions were packed with aluminium foil to prevent algae growth and/or OMP loss due to photolysis. Feed solutions were pumped through the columns by a peristaltic multi-channel pump (205S, Watson Marlow, The Netherlands) using Marprene® pump tubing (d = 0.63 mm, Watson Marlow, The Netherlands). The pump tubes were connected to the columns by grey polyamide tubing (d_i = 2.9 mm, Festo, The Netherlands). The hydraulic loading rate applied on the columns was 0.2 L/d, implying a residence time of 1 [m]/0.2 [m d^{-1}] = 5 days. Pore velocity and porosity in all columns were determined using deuterium (^2H) as a tracer (SI). Pore velocity in the columns varied between 0.45 and 0.52 m/d, while porosity varied between 0.37 and 0.40.

2.2. Experimental phases

The columns were adapted to river water from the RBF site for approximately 2.5 months, until stable DOC removal was observed, prior to feeding the columns with the organic carbon fractions. Hydro chemical data of the river water is presented in Table S1.

Three experimental phases were distinguished in this study: phase 1, phase 2 and phase 3. In phase 1, the columns were fed with the different fractions (RWOM, hydrophilic, transphilic and hydrophobic) in a concentration of 4 mg/L DOC each. At the same time, OMPs were dosed in a concentration of 0.5 μg/L. Phase 1 is further referred to as “stable operation”. In phase 2, the fractions were dosed in a concentration identical to phase 1 (4 mg/L DOC), but the OMP dosing was increased to 2 μg/L to mimick an OMP shock-load as a result of for example an accidental OMP spill upstream in the river. Phase 2 is referred to as “OMP shock-load”. In phase 3, the OMP dosing was identical to phase 2 (2 μg/L), but the concentration of the organic carbon fractions dosed to the columns was increased to 8 mg/L DOC to mimick a temporarily lower discharge of the river which will result in a higher DOC concentration. Phase 3 is referred to as “DOC shock-load”. Operational characteristics of the three experimental phases are presented in Table S2. In phase 1, four OMP samples were taken from the effluent of each column. Duplicate columns were operated for each fraction, thus eight data points were obtained. For phases 2 and 3, two OMP samples were taken from the effluent of each column, implying that four data points were obtained for each fraction since duplicate columns were operated. Water quality parameters were analysed at the same frequency.

2.3. Organic micropollutants

The OMP mixture fed to the different columns consisted of 20 OMPs covering a wide range of physico-chemical properties (Table 1). All OMPs were of analytical grade and purchased from Sigma Aldrich, Belgium. OMPs were analysed with UHPLC-HR-Orbitrap-MS, a detailed description of the analysis is provided in a previous study (Bertelkamp et al., 2015a). Detection limits are provided in Table S3.

2.4. Water quality parameters

Characterisation of the different DOC fractions (hydrophilic, hydrophobic, transphilic) was performed by means of Liquid Chromatography – Organic Carbon Detection (LC–OCD) to identify differences in DOC, organic nitrogen concentration and UV absorption (DOC Labour Huber, Germany). The analysis was performed for phase 3 for the unfractionated river water and the different organic carbon fractions fed to the columns. Measurement was performed as described elsewhere (Huber et al., 2011; Löwenberg et al., 2014).

Total organic carbon was measured with a TOC-5000 analyser (Shimadzu, USA). Samples (25 mL) were filtered over 20 μm filters (Whatmann, Germany) prior to DOC analysis. UV_{254} was analysed with a spectrophotometer (UV-1600PC, VWR, USA). Specific Ultra-Violet Absorbance (SUVA) was then calculated as indicator for the aromaticity of the organic carbon according to Eq. (1):

$$SUVA = \frac{UVA_{254nm}}{DOC} \cdot 100 \quad (1)$$

In which:
SUVA = specific ultraviolet absorbance [L mg^{-1} m^{-1}].
UVA = ultraviolet absorbance at 254 nm [cm^{-1}].
DOC = dissolved organic carbon concentration [mg L^{-1}].
100 = conversion factor [cm m^{-1}].

Oxygen, temperature, pH and ions were measured as described in Bertelkamp et al. 2015a.

2.5. Soil microbial activity and composition

Cellular adenosine triphosphate (cATP) concentrations in the soil samples were determined as an indicator for active biomass (for a detailed description see SI). Denaturing Gradient Gel Electrophoresis (DGGE) analysis was performed on soil samples from the in- and effluent of all columns at the end of each experimental phase to gain more insight into the microbial community composition as characterized by richness and evenness. A detailed description is provided in (Bertelkamp et al., 2015a).

2.6. Statistical analysis

The statistical software package R was used to perform all statistical analyses (R Development Core Team, 2008). A p-value <0.05 was defined as statistical significant.

2.7. Modelling

CXTFIT (Toride et al., 1995) was used to obtain the OMP degradation rates (μ) in the columns fed with different organic carbon fractions by fitting the experimental data to the advection–dispersion equation (for a detailed description see (Bertelkamp et al., 2015a)).

Table 1
Physico-chemical properties of OMPs.

OMP	Class	MW	Charge (pH 8)	Log D (pH 8)[a]	OMP category
Acetaminophen	Pharmaceutical	151.16	0	0.85	Neutral – hydrophilic
Atrazine	Herbicide	215.68	0	2.26	Neutral – transphilic
Carbamazepine	Pharmaceutical	236.27	0	2.64	Neutral – transphilic
Chloridazon	Herbicide	221.64	0	1.05	Neutral – transphilic
Clofibric acid	Herbicide	214.65	−1	−0.18	Charged – hydrophilic
Diclofenac	Pharmaceutical	296.15	−1	1.21	Charged – transphilic
Diglyme	Solvent	134.17	0	0.10	Neutral – hydrophilic
Dimethoate	Insecticide	229.26	0	0.21	Neutral – hydrophilic
Diuron	Herbicide	233.09	0	2.49	Neutral – transphilic
Gemfibrozil	Pharmaceutical	250.3	−1	1.36	Charged – transphilic
Hydrochlorothiazide	Pharmaceutical	297.74	0	−0.72	Neutral – hydrophilic
Ketoprofen	Pharmaceutical	254.28	−1	0.49	Charged – hydrophilic
Lincomycin	Pharmaceutical	406.54	+1	−1.22	Charged – hydrophilic
Metoprolol	Pharmaceutical	267.36	+1	0.14	Charged – hydrophilic
Naproxen	Pharmaceutical	230.26	−1	0.10	Charged – hydrophilic
Phenazone	Pharmaceutical	188.23	0	1.11	Neutral – transphilic
Pirimicarb	Insecticide	238.29	0	1.74	Neutral – transphilic
Simazine	Herbicide	201.66	0	1.83	Neutral – transphilic
Sulfamethoxazole	Pharmaceutical	253.28	0	0.39	Neutral – transphilic
Triclopyr	Herbicide	256.47	−1	−0.53	Charged – hydrophilic

[a] Obtained from calculated value ChemAxon (http://www.chemspider.com).

3. Results and discussion

3.1. Liquid chromatography – organic carbon detection (LC–OCD)

LC–OCD analysis was performed to determine if the organic fractions obtained after fractionation were actually showing differences with respect to organic carbon composition (e.g. aromaticity and carbon constituents). Decreasing aromaticity of the humics fraction was observed in the order of hydrophobic, transphilic and hydrophilic (Table 2). The hydrophobic, transphilic and hydrophilic fraction showed a statistically significant difference in aromaticity. Although aromaticity of the transphilic fraction and the river water (RWOM) was similar, a statistically significant difference in carbon constituents such as building blocks was observed for these fractions (Table S4). This implies that the composition of the four organic carbon fractions was indeed different.

3.2. Water quality parameters & soil microbial activity and composition

Most columns showed no, or only slight changes in pH between influent and effluent (Table S5) and nitrate reducing conditions prevailed for all organic carbon fractions (Table S6) in all three experimental phases.

The microbial populations in all columns showed a very rich and even community (with an average richness of 47 (±14) bands and an average evenness of 0.66 (±0.18)) (Table S7). The soil microbial population composition (richness and evenness, average in- and effluent side) and concentration (ATP, average in- and effluent side, Table S8) it not greatly affected by either the four organic carbon fractions or an OMP or DOC shock-load (Table 3). Since soil microbial population composition and concentration are not greatly affected by an OMP or DOC shock-load, it apparently needs a longer time to adapt to the new DOC/OMP shock-load than was provided in the current study (3 weeks). Li et al. (2013) observed that the soil microbial population in a column representative of a managed aquifer recharge system reached steady state conditions only after 3–4 months which confirms the observed behaviour in the current study. Thus, RBF seems to be quite resilient against these shock-loads in the sense that the microbial population is not strongly affected as long as the "shock-loads" are only applied for a limited time.

Table 2
Aromaticity of the different fractions.

Fraction	Aromaticity (L mg^{-1} m^{-1}) (95% confidence interval)
Hydrophobic	4.36 (3.94–4.78)
Transphilic	3.38 (2.96–3.80)
RWOM	3.07 (2.65–3.49)
Hydrophilic	2.02 (1.60–2.44)

No statistically significant difference in average DOC removal (Table 3, Table S9) was observed between the four fractions within experimental phase 1 and 3 or for a specific organic carbon fraction in the case of a temporary OMP or DOC shock-load (except the hydrophilic fraction for which the evenness of the microbial population was altered as a result of OMP or DOC shock-load). DOC removal within phase 2 was statistically significant smaller for the river water compared to the hydrophilic and transphilic fractions, but similar to the hydrophobic fraction. Thus, the type of organic carbon fraction or an OMP/DOC shock-load does not seem to affect DOC removal. This could be explained by the similar soil microbial population composition and concentration.

A statistically significant difference in SUVA removal (Table 3, Table S10) was observed between the four organic carbon fractions for each experimental phase. This could be explained by the difference in aromaticity of the four fractions in the feed waters as indicated by the LC–OCD analysis.

3.3. OMP removal

Several studies have indicated that OMP sorption is small compared to OMP biodegradation with retardation factors close or equal to 1 for most OMPs (Bertelkamp et al., 2014; Burke et al., 2013; Henzler et al., 2014). Hence, the retardation factor in the advection-dispersion equation was set to 1 and only the biodegradation rate (μ) was determined. Table 4 provides the modelled degradation rates of the OMPs for the columns fed with different fractions for all experimental phases. Plots of experimental data versus modelled data points ($C_{effluent}/C_{influent} = C_e/C_0$) are presented in Figures S2, S3 and S4. Coefficients of determination for the linear fits as well as the equations describing these fits are presented in Table S11.

Table 3
p-Values (one-way ANOVA) for water quality parameters in the columns between the different fractions for a specific phase and for a specific fraction between different phases.

Phase	Effect of organic carbon fraction DOC removal [%] *p*-value	SUVA removal [%] *p*-value	ATP concentration [pg/g] *p*-value	Richness *p*-value	Evenness *p*-value
1 – Stable operation	0.37	$5{\cdot}10^{-3}$	0.84	0.31	0.37
2 – OMP shock-load	$2.39{\cdot}10^{-4}$	$6.03{\cdot}10^{-7}$	0.63	0.17	0.25
3 – DOC shock-load	0.14	0.03	0.10	0.87	0.90

Effect of OMP/DOC shock-load Fraction	DOC removal [%] p-value	SUVA removal [%] p-value	ATP concentration [pg/g] p-value	Richness p-value	Evenness p-value
Hydrophilic	$3.00{\cdot}10^{-3}$	0.015	0.43	0.89	0.68
River water OM	0.29	0.005	0.15	0.06	0.11
Transphilic	0.15	0.163	0.06	0.16	$4.80{\cdot}10^{-2}$
Hydrophobic	0.71	0.082	0.18	0.78	0.40

For the persistent OMPs (atrazine, carbamazepine, diglyme, dimethoate, diuron, lincomycin, pirimicarb, simazine, and sulfamethoxazole), OMP biodegradation rates were comparable to those observed in a previous study in which similar soil and river water were used (Bertelkamp et al., 2015b). However, for the more degradable OMPs (acetaminophen, chloridazon, clofibric acid, diclofenac, ketoprofen, and phenazone), biodegradation rates were slightly lower compared to our previous study (Bertelkamp et al., 2015b). This could be explained by either the lower active biomass on the soil in the current study (ATP = 70 ng cm^{-3}) compared to the previous study (ATP = 109–135 ng cm^{-3}), the different redox conditions (nitrate reducing versus oxic conditions in the previous study), or a combination of both. Regnery et al. (2015b) demonstrated that acetaminophen removal was not affected by redox conditions, thus the most plausible explanation for the lower OMP biodegradation rates observed in this study is the lower quantity of active biomass.

3.3.1. OMP removal – effect of different organic carbon fractions within an experimental phase on OMP biodegradation rate

No statistically significant difference in OMP biodegradation rate between the different organic carbon fractions within Phase 1 and Phase 3 was observed (Table 5). This implies that variations in the organic carbon fractions present in the river are not likely to affect the OMP biodegradation rate at the RBF site simulated in this study in case of stable operation and for a DOC shock-load. RBF thus seems robust and resilient towards variations in organic carbon composition during stable operation which is contradictory to the results found for wastewater whereby the hydrophobic acids fed column was characterized by the lowest biomass quantity, but showed similar or even better OMP removal (Rauch-Williams et al., 2010). Since similar DOC feed concentrations were used in that study compared to this study, the differences in observed OMP removal could be explained by the different character (e.g. biodegradability) of the organic carbon. Depending on the extent of wastewater treatment, biodegradability of wastewater derived organic matter can be significantly higher than the organic matter found in river waters. Organic matter from river water (with a low impact of wastewater) typically has a more refractory character, which could possibly lead to less distinct differences in biodegradability between fractions. The river water investigated in this study is only slightly impacted by treated wastewater (5–10%) and it is possible that river streams more heavily impacted by wastewater lead to different results. Future research should elucidate if there is a threshold for which OMP degradation rates are affected as a result of impacts of wastewater organics on the river water.

However, a statistically significant difference in OMP biodegradation rate between the different organic carbon fractions was observed within experimental Phase 2 (OMP shock-load). For an OMP shock-load, the columns fed with the hydrophilic and RWOM fraction were characterised by higher average OMP biodegradation rates than the transphilic and hydrophobic fraction. These results indicate that in case of an OMP shock-load river waters consisting mainly of hydrophilic organic carbon could demonstrate much larger OMP biodegradation rates.

The observed differences in OMP biodegradation rates could not be explained by the differences in DOC removal, average ATP concentration, richness/evenness, or SUVA removal. Possibly, the higher average OMP biodegradation rates observed for the RWOM and hydrophilic fraction are caused by the presence of specialised soil bacteria and/or enzymes due to the nature of the organics fed. However, more in-depth analyses of the microbial community composition (e.g. genomic analyses) should be performed to test this hypothesis.

3.3.2. OMP removal – effect of OMP/DOC shock-load on OMP biodegradation rate for a specific organic carbon fraction

A DOC shock-load did not significantly affect OMP biodegradation rates in the columns fed with the different fractions (Table 5) which could be explained by the similar DOC removal and biomasses (e.g. quantity and composition) observed in the different columns for phase 3.

However, an OMP shock-load resulted in a statistically significant difference in OMP biodegradation rate for the hydrophilic and RWOM fraction (Table 5). The average OMP biodegradation rate for the hydrophilic and RWOM fraction increased clearly between Phase 1 and Phase 2. Thus, as a result of an OMP shock-load, average OMP biodegradation rates in the initial infiltration phase can differ depending on the quantity of certain organic carbon fractions (hydrophilic) in the river water contributing to overall RWOM.

In general an increase in OMP biodegradation rate as a result of an increase in OMP concentration is suggestive of metabolic degradation, however, in the current study an increase in biomass is not observed. Therefore the increase in OMP biodegradation rate as a result of an OMP shock-load is most likely due to co-metabolic degradation. The co-metabolic degradation of OMPs during soil passage has been suggested in previous studies as well (Alidina et al., 2014; Rauch-Williams et al., 2010). A further characterisation of the soil microbial population should provide more insight in the role that (specialized) bacteria and/or enzymes play in co-metabolic OMP removal.

An increase in OMP biodegradation rate as a result of an increase in initial OMP concentration has been reported before

Table 4
OMP degradation rates (μ) for different experimental phases and organic carbon fractions.

OMP	Phase 1 – μ [d^{-1}]				Phase 2 – μ [d^{-1}]				Phase 3 – μ [d^{-1}]			
	Hydrophilic	RW OM	Transphilic	Hydrophobic	Hydrophilic	RWOM	Transphilic	Hydrophobic	Hydrophilic	RWOM	Transphilic	Hydrophobic
Acetaminophen	ND	ND	0.63	ND	ND	ND	ND	ND	ND	ND	ND	ND
Atrazine	0.00	0.00	0.00	0.09	0.29	0.18[a]	0.26	0.13[a]	0.00	0.10	0.00	0.14
Carbamazepine	0.00	0.00	0.00	0.12	0.50	0.31	0.23	0.22	0.37	0.36	0.00	0.00
Chloridazon	0.00	0.00	ND	0.00	0.07[a]	0.89	0.00	0.00	0.25[a]	1.48	0.00	0.38[a]
Clofibric acid	0.50	0.43	0.37	0.51	0.53	0.36[a]	0.06[a]	0.22[a]	0.46	0.48[a]	0.00	0.26
Diclofenac	0.31[a]	0.23[a]	0.09[a]	0.37	0.91	0.52[a]	0.39	0.71[a]	0.93	1.08	0.93	ND
Diglyme	0.00	0.00	0.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND
Dimethoate	0.55	0.22	0.39	ND	0.60	0.42	0.43	0.36	0.45	ND	1.01	ND
Diuron	0.25	0.62	0.29	0.47	0.79	0.73[a]	0.76	0.61	0.51	0.44	0.30	0.46
Gemfibrozil	0.50	ND	ND	ND	0.62	0.48	0.56	0.30	ND	0.68	0.24	ND
Hydrochlorothiazide	ND	ND	ND	ND	0.00	0.29[a]	0.36[a]	0.24	ND	0.26[a]	0.23	0.00
Ketoprofen	0.83	0.34[a]	0.26	0.26	ND	ND	ND	ND	ND	ND	1.16	ND
Lincomycin	0.43	0.00	0.70	0.28	ND	ND	ND	ND	ND	ND	ND	ND
Metoprolol	0.44	0.43	1.09	1.08	2.20	ND	ND	ND	1.02	1.37	1.49	2.81
Naproxen	ND	ND	0.22	ND	ND	ND	ND	ND	ND	ND	0.66[a]	ND
Phenazone	0.46	0.19	0.22	ND	0.39	0.72	0.25	0.00	1.07	1.98	0.00	0.00
Pirimicarb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12[a]
Simazine	0.00	0.00	0.00	0.00	0.18[a]	0.06[a]	0.17	0.00	0.00	0.04	0.00	0.11
Sulfamethoxazole	0.54	0.34	0.32	0.31	2.26	2.03	0.15	0.95[a]	1.83	2.09	0.12[a]	0.98[a]
Triclopyr	0.55[a]	0.22	1.25	ND	1.00	0.91	0.73[a]	1.79	0.37[a]	0.37[a]	0.12[a]	0.72[a]
Average	0.30	0.18	0.36	0.27	0.78	0.72	0.29	0.35	0.60	0.87	0.38	0.47
St dev	0.28	0.21	0.38	0.30	0.71	0.61	0.23	0.54	0.57	0.77	0.53	0.96

ND = No Data.
$\mu \leq 0.05$ was set to $\mu = 0$.
In case a row contained two or more "ND" values, the row was omitted from the statistical analysis. OMP biodegradation rates with a confidence interval through zero were also omitted from the statistical analysis.
[a] Confidence interval through 0, result statistically not significant.

Table 5
p-Values (multi-factorial ANOVA) for the effect of organic carbon fraction or OMP/DOC shock-load on the OMP biodegradation rate.

	OMP biodegradation rate, *p*-value		OMP biodegradation rate, *p*-value	
Phase	Effect organic carbon fraction	Fraction	Effect OMP shock-load	Effect DOC shock-load
1 – Stable operation	0.09	Hydrophilic	$4.94 \cdot 10^{-2}$	0.24
2 – OMP shock-load	$1.73 \cdot 10^{-2}$	RWOM	0.03	0.13
3 – DOC shock-load	0.07	Transphilic	0.09	0.62
		Hydrophobic	0.19	0.22

	OMP biodegradation rate, *p*-value		OMP biodegradation rate, *p*-value
OMP category	Effect organic carbon fraction within phase 2	Fraction	Effect OMP shock-load
Hydrophilic-charged	0.20	Hydrophilic	0.07
Hydrophilic-neutral	0.50	RWOM	0.37
Transphilic-charged	0.59		
Transphilic-neutral	0.10		

(Baumgarten et al., 2011), but was never linked to certain organic carbon fraction as in the current study. Again, an explanation for the increase in OMP biodegradation rate as a result of an OMP shock-load for specifically the RWOM and hydrophilic fraction cannot be given based on the DOC removal, average ATP concentration and richness/evenness analyses. However, further characterisation of the organic carbon fractions removal along the height of the column as well as the microbial community composition (quantity and quality), is required to be able to provide a solid explanation for the observed behaviour.

3.3.3. OMP removal – effect of OMP category on OMP biodegradation rate

A statistically significant difference in average OMP biodegradation rate was found between the four different organic carbon fractions within experimental Phase 2. Additionally, a temporary OMP shock-load affected OMP biodegradation rates in the columns fed with the RWOM and hydrophilic fraction (Table 5). To determine if these effects were caused by the OMP category, a multi-factorial ANOVA was used.

OMPs were categorized according to charge (charged and neutral) and hydrophobicity (hydrophilic, transphilic, hydrophobic). According to the definition of (Cunningham, 2008) OMPs with a Log D < 1 were classified as hydrophilic, while OMPs with a log D ≥ 3 were classified as hydrophobic. Any OMP with a log D between 1 and 3 was categorized as transphilic (Table 1).

No statistically significant difference in average OMP biodegradation rate was observed between the four fractions for a specific OMP category within phase 2 (Table 5). Similarly, no statistically significant difference in OMP biodegradation rate as a result of OMP category between Phase 1 and 2 was observed for the hydrophilic and RWOM fraction (Table 5). Therefore it is concluded that the statistically significant difference in average OMP biodegradation rate observed between the four different organic carbon fractions within experimental phase 2 and the difference in average OMP biodegradation rate as a result of the OMP shock-load for the hydrophilic and RWOM fraction could not be explained by the OMP category (charge and hydrophobicity) as investigated in this study.

4. Conclusion

From this study it is concluded that OMP biodegradation rate is not affected by either the type of organic carbon fraction obtained from river water fed to the soil column (in contrast to what is observed for managed aquifer recharge systems operating on wastewater effluent) or a DOC shock-load. Thus, the RBF site simulated in this study is most likely resilient towards variations in the organic carbon composition of the river water and a temporary higher DOC concentration in the river water.

Finally, a temporary OMP shock-load resulted in an increase in OMP biodegradation rate for the columns fed with river water organic matter and the hydrophilic fraction of the river water organic matter. The increase in OMP biodegradation rate for specifically the columns fed with these fractions could not be explained by the parameters investigated in this study (ATP, DOC removal, SUVA, richness/evenness of the soil microbial population, or OMP category). Future research should focus on the changes in organic carbon composition (for example, by LC–OCD and F-EEM analysis) as well as the microbial community composition (quantity and quality, for example by genomic analysis) along the column to provide an explanation for the increase in OMP biodegradation rate as a result of an OMP shock-load for these two fractions and to elucidate the role of metabolic/co-metabolic OMP degradation.

Acknowledgements

The activities and results of this study are part of the project “Emerging Substances Towards an Absolute Barrier (ESTAB)” which is subsidized by the InnoWator program of the Dutch Ministry of Economic Affairs, The Netherlands. The authors would like to acknowledge all project partners involved: Berliner Wasserbetriebe, De Watergroep, EPAS, KWR Watercycle Research Institute, KompetenzZentrum Wasser Berlin, Oasen, Pentair, Veolia Water Solutions and Vitens.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.09.017.

References

Alberts, J.J., Takács, M., McElvaine, M., Judge, K., 2001, Humic Substances, Structures, Models and Functions. In: Ghabbour, E.A., Davies, G. (Eds.). The Royal Society of Chemistry, Cambridge, UK, pp. 179–190.
Alidina, M., Li, D., Drewes, J.E., 2014. Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Res. 56, 172–180.
Baumgarten, B., Jährig, J., Reemtsma, T., Jekel, M., 2011. Long term laboratory column experiments to simulate bank filtration: factors controlling removal of sulfamethoxazole. Water Res. 45, 211–220.
Benotti, M.J., Song, R., Wilson, D., Snyder, S.A., 2012. Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Sci. Technol. 12, 11–23.
Bertelkamp, C., Reungoat, J., Cornelissen, E.R., Singhal, N., Reynisson, J., Cabo, A.J., van der Hoek, J.P., Verliefde, 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., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Callewaert, C., Boon, N., Singhal, N., Van der Hoek, J.P., Verliefde, A.R.D., 2015a. A laboratory scale column study comparing organic micropollutant removal and microbial diversity for two soil types. Sci. Total Environ. 536, 632–638.

Bertelkamp, C., Verliefde, A.R.D., Reynisson, J., Singhal, N., de Jonge, M., van der Hoek, J.P., 2015b. A predictive multi-linear regression model for organic micropollutant removal during river bank filtration. J. Haz. Mat. (submitted for publication).

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J., Massmann, G., 2013. Sorption behavior of 20 wastewater originated micropollutants in groundwater – column experiments with pharmaceutical residues and industrial agents. J. Cont. Hydrol. 154, 29–41.

Cunningham, V.L., 2008. In: Kümmerer, K. (Ed.). Pharmaceuticals in the Environment. Springer, Berlin.

Dong, Q., Li, P., Huang, Q., Abdelhafez, A.A., Chen, L., 2014. Occurrence, polarity and bioavailability of dissolved organic matter in the Huangpu River, China. J. Environ. Sci. 26, 1843–1850.

Henzler, A.F., Greskowiak, J., Massmann, G., 2014. Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). J. Cont. Hydrol. 156, 78–92.

Hiscock, K.M., Grischek, T., 2002. Attenuation of groundwater pollution by bank filtration. J. Hydrol. 266, 139–144.

Hoppe-Jones, C., Oldham, G., Drewes, J.E., 2010. Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems. Water Res. 44, 4643–4659.

Houtman, C.J., Kroesbergen, J., Lekkerkerker-Teunissen, K., van der Hoek, J.P., 2014. Human health risk assessment of the mixture of pharmaceuticals in Dutch drinking water and its sources based on frequent monitoring data. Sci. Total Environ. 496, 54–62.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography-organic carbon detection-organic nitrogen detection (LC–OCD–OND). Water Res. 45, 879–885.

Li, D., Alidina, M., Drewes, J.E., 2014. Role of primary substrate composition on microbial community structure and function and trace organic chemical attenuation in managed aquifer recharge systems. Appl. Microbiol. Biotechnol. 98, 5747–5756.

Li, D., Alidina, M., Ouf, M., Sharp, J.O., Saikaly, P., Drewes, J.E., 2013. Microbial community evolution during simulated managed aquifer recharge in response to different biodegradable dissolved organic carbon (BDOC) concentrations. Water Res. 47, 2421–2430.

Lim, M.H., Snyder, S.A., Sedlak, D.L., 2008. Use of biodegradable dissolved organic carbon (BDOC) to assess the potential for transformation of wastewater-derived contaminants in surface waters. Water Res. 42, 2943–2952.

Löwenberg, J., Zenker, A., Baggenstos, M., Koch, G., Kazner, C., Wintgens, T., 2014. Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: process performance and removal efficiency. Water Res. 56, 26–36.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Amy, G.L., 2011. Role of biodegradation in the removal of pharmaceutically active compounds with different bulk organic matter characteristics through managed aquifer recharge: Batch and column studies. Water Res. 45, 4722–4736.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Song, K.G., Amy, G.L., 2012. Effects of effluent organic matter characteristics on the removal of bulk organic matter and selected pharmaceutically active compounds during managed aquifer recharge: column study. J. Cont. Hydrol. 140–141, 139–149.

Nam, S.N., Krasner, S.W., Amy, G.L.Kim, Y.J., Platt, U. (Eds.), 2008. Adv. Environ. Monit. 259–270.

Onesios, K.M., Bouwer, E.J., 2012. Biological removal of pharmaceuticals and personal care products during laboratory soil aquifer treatment simulation with different primary substrate concentrations. Water Res. 46, 2365–2375.

Rauch-Williams, T., Hoppe-Jones, C., Drewes, J.E., 2010. The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. Water Res. 44, 449–460.

Regnery, J., Barringer, J., Wing, A.D., Hoppe-Jones, C., Teerlink, J., Drewes, J.E., 2015a. Start-up performance of a full-scale riverbank filtration site regarding removal of DOC, nutrients, and trace organic chemicals. Chemosphere 127, 136–142.

Regnery, J., Wing, A.D., Alidina, M., Drewes, J.E., 2015b. Biotransformation of trace organic chemicals during groundwater recharge: how useful are first-order rate constants? J. Cont. Hydrol. 179, 65–75 3128.

Stoks, P.G.M., van de Haar, G., Bannink, A., Zwamborn, C.C., 2014. Jaarrapport 2013 De Rijn.

Storck, F.R., Schmidt, C.K., Wülser, R., Brauch, H.J., 2012. Effects of boundary conditions on the cleaning efficiency of riverbank filtration and artificial groundwater recharge systems regarding bulk parameters and trace pollutants. Water Sci. Technol 66, 138–144.

R Development Core Team, 2008. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Toride, N., Leij, F.J., van Genuchten, M.T., 1995. The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments. Version 2.0. U.S. Salinity Laboratory, USDA, ARS, Riverside, CA Research report no. 137.