Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study


A Delft University of Technology, 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 The University of Queensland, Advanced Water Management Centre (AWMC), QLD 4072, Australia
d KWR Watercycle Research Institute, PO Box 1072, 3430 BB Nieuwegein, The Netherlands
e The University of Auckland, Department of Civil and Environmental Engineering, Private Bag 92019, Auckland 1142, New Zealand
f The University of Auckland, School of Chemical Sciences, Private Bag 92019, Auckland 1142, New Zealand
g Delft Institute of Applied Mathematics (DIAM), Faculty EEMCS, Mekelweg 4, 2628 CD Delft, The Netherlands
h Strategic Centre, Waternet, Korte Ouderkerkerdijk 7, 1096 AC Amsterdam, The Netherlands

Abstract

This study investigated sorption and biodegradation behaviour of 14 organic micropollutants (OMP) in soil columns representative of the first metre (oxic conditions) of the river bank filtration (RBF) process. Breakthrough curves were modelled to differentiate between OMP sorption and biodegradation. The main objective of this study was to investigate if the OMP biodegradation rate could be related to the physico-chemical properties (charge, hydrophobicity and molecular weight) or functional groups of the OMPs. Although trends were observed between charge or hydrophobicity and the biodegradation rate for charged compounds, a statistically significant linear relationship for the complete OMP mixture could not be obtained using these physico-chemical properties. However, a statistically significant relationship was obtained between biological degradation rates and the OMP functional groups. The presence of ethers and carbonyl groups will increase biodegradability, while the presence of amines, ring structures, aliphatic ethers and sulphur will decrease biodegradability. This predictive model based on functional groups can be used by drinking water companies to make a first estimate whether a newly detected compound will be biodegraded during the first metre of RBF or that additional treatment is required.

In addition, the influence of active and inactive biomass (biosorption), sand grains and the water matrix on OMP sorption was found to be negligible under the conditions investigated in this study. Retardation factors for most compounds were close to 1, indicating mobile behaviour of these compounds during soil passage. Adaptation of the

* Corresponding author. Delft University of Technology, Department of Water Management, PO Box 5048, 2600 GA Delft, The Netherlands.
E-mail addresses: C.Bertelkamp@tudelft.nl, cherylbertelkamp@hotmail.com (C. Bertelkamp).
1. Introduction

In the Netherlands, 6.5% of the total amount of produced drinking water is obtained from river bank filtrate (Geudens, 2012). Traditionally, river bank filtration (RBF) was used for the removal of pathogens, bacteria, protozoa, disinfection by-product pre-cursors, natural organic matter (NOM), etc., as well as dampening variations in water quality. Since organic micropollutants (OMPs) are increasingly being detected in Dutch surface waters (ng/L range) (Verliefde et al., 2007), interest has risen in the capability of RBF to provide an effective barrier for these compounds. In contrast to other water treatment processes used for OMP removal, such as membranes and advanced oxidation processes, RBF offers natural treatment, low cost, and no requirement for chemical supplementation. These aspects, in combination with the fact that several drinking water companies in the Netherlands already use RBF as a pre-treatment step in their multi-barrier treatment trains, make RBF an attractive option for OMP removal. However, insight into the role that OMP characteristics (functional groups, physico-chemical properties) play in to why certain OMPs are removed during RBF while others, such as carba-mazepine, show very persistent behaviour is lacking. This makes it very difficult for drinking water companies to assess what type of additional treatment is required to prevent OMPs from penetrating through the treatment trains ending up in the drinking water.

Field parameters influencing OMP removal are subject to large variation. Therefore, the general approach to investigate OMP removal during soil passage (and thus also RBF) is mimicking this process in controlled soil columns. Many laboratory column studies have already been performed to mimic OMP removal during soil passage. These studies focused on: OMP removal under specific redox conditions (Banzhaf et al., 2012; Baumgarten et al., 2011), the effect of temperature on OMP biodegradation (Gruenheid et al., 2008), the fate of OMPs under saturated or unsaturated conditions (Scheffter et al., 2004, 2006), the role that cationic exchange capacity of the soil plays in sorption of cationic OMPs (Schaffer et al., 2012b), the influence of pH on sorption of ionizable compounds (Schaffer et al., 2012a), the effect of the initial OMP concentration dosed (Baumgarten et al., 2011), the effect of the amount and type of organic carbon source present in the water (Baumgarten et al., 2011; Maeng et al., 2011a,b; Onesios and Bouwer, 2012; Rauch-Williams et al., 2010) and comparing OMP removal in a pilot column to full scale field conditions (Benotti et al., 2012). However, these studies do not differentiate between OMP removal via sorption and biodegradation. As such, the individual contribution of these underlying mechanisms on OMP removal is not well understood. More insight into these mechanisms is required to enable the development of predictive models for OMP removal during RBF. Such predictive models (e.g. Quantitative Structure Activity Relationship (QSAR) models) can be used by drinking water companies to assess whether a newly detected compound will be effectively removed during RBF or additional treatment is required. A first step towards this better understanding would be to distinguish between the two main removal mechanisms, sorption and biodegradation (Maeng et al., 2011a,b), to assess which mechanism is the dominant contributor to overall OMP removal. Distinguishing between the two removal mechanisms will also provide insight into the sorption and biodegradation potential of the compounds in relation to each other.

Few studies have attempted to determine OMP biodegradation by comparing a biotic (active biomass) sand column to an abiotic (inactive biomass) sand column at a certain time point and allocate the difference in OMP removal between these two systems to biodegradation (Maeng et al., 2011a,b; Onesios and Bouwer, 2012). However, this only gives a rough estimate of the percentage of OMP biodegraded and can lead to an underestimation when stable effluent OMP concentrations have not been obtained yet. In addition, a difference in OMP removal percentage at one time point does not elucidate how fast a compound is degrading, which makes it more difficult to quantitatively compare between compounds. To enable a fair comparison between OMP biodegradability a more accurate parameter would be the biodegradation rate that can be determined from the OMP breakthrough curve. In addition, modelling the OMP breakthrough curves takes into consideration OMP dispersion and allows determining the retardation factor which represents the extent of OMP sorption.

Most column studies on OMP sorption and biodegradation during soil passage involved only one to four compounds (Baumgarten et al., 2011; Gruenheid et al., 2008; Scheffter et al., 2004, 2006), making it impossible to link physico-chemical properties to OMP removal behaviour and observe trends. The behavior of a larger collection of OMPs in soil column systems has been investigated in a few studies (Maeng et al., 2011a,b; Onesios and Bouwer, 2012; Patterson et al., 2011), and was still mainly limited to negatively charged and neutral compounds, thus not covering a wide range of physico-chemical properties. Moreover, many studies dose higher OMP concentrations (10–700 μg/L) (Onesios and Bouwer, 2012; Patterson et al., 2011) than the concentrations found for most compounds to be present in surface water (lower ng/L range) (Verliefde et al., 2007). Baumgarten et al. (2011) reported that increasing the sulfamethoxazole concentration in the influent by one order of magnitude showed significantly better removal of the compound. Thus, dosing higher OMP concentrations than present in the environment could significantly overestimate the biodegradation rates. Therefore it is very important to dose OMPs at concentrations representative of those detected in surface water.
(Soil) bacteria excrete extracellular polymeric substances (EPS) which create a biofilm in the soil that (partly) covers the soil grains (Flemming, 1995). This will increase the available surface area which could possibly increase OMP sorption. Since biofilms contain anionic as well as cationic groups (Flemming, 1995), it is expected that biofilm can influence sorption of charged OMPs (but also neutral OMPs). However, the effect of biofilm present in soil on OMP retardation is still largely unknown. Some studies indicated that sorption onto sludge can be an important removal mechanism in waste water treatment plants for several OMPs (e.g. propranolol) (Radjenović et al., 2009; Ternes et al., 2004). In case the OMP is not biodegradable, sorption onto sludge can even be the only removal mechanism. Therefore it is essential to investigate OMP biosorption for the RBF system. Soil column studies investigating biodegradation behaviour of OMPs often use an abiotic control to correct for OMP sorption (or other abiotic losses such as hydrolysis). The type of abiotic control column used can differ from one study to another. The abiotic control can correct for OMP sorption on to the developed biomass (Onesios and Bouwer, 2012) or OMP sorption onto the sand medium (Maeng et al., 2011a, b). The effect of biomass or sand medium on OMP sorption can be different, but these effects have not been investigated simultaneously yet. Moreover, numerous studies investigated the effect of for example dissolved organic carbon (DOC), pH, temperature, etc., on OMP sorption (Broznić and Milin, 2012; Flores-Céspedes et al., 2002; Gao et al., 1998). While every factor separately can have a positive or negative influence on the sorption, the effect of the water matrix as a whole on OMP sorption has not been investigated.

This study examines sorption and biodegradation behaviour of OMP mixtures at concentrations representative of those in RBF systems. The main objective of this study is to investigate if the OMP biodegradation rate can be related to the physico-chemical properties (charge, hydrophobicity and molecular weight) or functional groups of the OMPs. Modelling OMP breakthrough curves will enable a differentiation between sorption (retardation factor) and biodegradation (biodegradation rate) and it will include OMP dispersion. Multi-linear regression is used to relate OMP biodegradation rates to the physico-chemical properties or functional groups. In addition, this study investigates OMP sorption onto sand grains, active and inactive biomass (biosorption), and assesses the influence of the water matrix on OMP sorption. OMP retardation factors are determined for different experimental conditions (sand grains, (in)active biomass and different water matrices) by modelling the breakthrough curves. Comparing OMP retardation factors for the different experimental conditions provides insight in the effect of the aforementioned factors on OMP sorption.

### 2. Material and methods

#### 2.1. Columns set-up and operation

The experimental set-up consisted of 6 transparent PVC columns (L = 1 m, D = 36 mm) filled with technical sand (d = 1.4–2 mm, d_{50} = 1.83 mm, Filcom, The Netherlands). Columns were filled with sand in increments of 4–5 cm while tapping on the column, to prevent layering in the columns. To prevent leaching of sand grains, the top and bottom of the column were fitted with perforated PVC plates (30 holes, d = 0.8 mm).

The columns were operated from bottom to top in a controlled climate room in the dark (to prevent algae growth and/or OMP loss due to photolysis). During an adaptation period of 4 months, the columns were operated at 15 °C for two months after which the temperature was increased to 20 °C for two months to increase biological activity. After 4 months adaptation time, the biomass reached stable conditions indicated by a stable DOC removal. Subsequently, the experimental period was initiated by dosing of the OMPs. During the whole experimental period the columns were operated at 20 °C.

Columns (1, 2, 3 and 4) were fed with surface water from the local Schie Canal, spiked with 200 μg/L sodium acetate (CH₃COONa·3H₂O, Merck, Germany) to stimulate biological growth. After the adaptation period of 4 months, columns 3 and 4 were fed with Schie Canal water with 400 mg/L sodium azide (NaN₃, Sigma–Aldrich, The Netherlands) to inactivate the developed biomass. UV₂₅₄ absorbance was measured in the influent and effluent, as an indicator for DOC removal, to confirm inactivation of the biomass. After inactivation of the biomass was confirmed, OMP dosing was started in all columns. Column 5 was fed with Schie Canal water and 400 mg/L NaN₃ to suppress biological activity in this column from the start of the experiment. Column 6 was fed with demineralized water and 400 mg/L NaN₃ to suppress biological activity in this

### Table 1 – Feed water qualities for the columns experimental period.

<table>
<thead>
<tr>
<th>Column</th>
<th>Feed water</th>
<th>CH₃COONa·3H₂O [μg/L]</th>
<th>NaN₃ [mg/L]</th>
<th>Biomass condition</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schie canal</td>
<td>200</td>
<td>NA</td>
<td>Active biomass</td>
<td>Sorption active biomass + biodegradation</td>
</tr>
<tr>
<td>2</td>
<td>Schie canal</td>
<td>200</td>
<td>NA</td>
<td>Active biomass</td>
<td>Sorption active biomass + biodegradation</td>
</tr>
<tr>
<td>3</td>
<td>Schie canal</td>
<td>NA</td>
<td>400</td>
<td>Inactivated biomass</td>
<td>Sorption inactive biomass</td>
</tr>
<tr>
<td>4</td>
<td>Schie canal</td>
<td>NA</td>
<td>400</td>
<td>Inactivated biomass</td>
<td>Sorption inactive biomass</td>
</tr>
<tr>
<td>5</td>
<td>Schie canal</td>
<td>NA</td>
<td>400</td>
<td>No biomass</td>
<td>Sorption on sand grains, no biomass present (Water matrix effect)</td>
</tr>
<tr>
<td>6</td>
<td>Demineralized water</td>
<td>NA</td>
<td>400</td>
<td>No biomass</td>
<td>Sorption on sand grains, no biomass present (Water matrix effect)</td>
</tr>
</tbody>
</table>

NA = Not applicable.
Table 2 – Physico-chemical properties OMPS, decay rates and half-lives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>pKa</th>
<th>Charge (pH 7)</th>
<th>Log P&lt;sub&gt;0&lt;/sub&gt;</th>
<th>Log D&lt;sub&gt;0&lt;/sub&gt; (pH 7)</th>
<th>This study μ (d&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>This study t&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>Other studies t&lt;sub&gt;1/2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibuprofen</td>
<td>206.3</td>
<td>4.91±</td>
<td>–1</td>
<td>3.97</td>
<td>1.74</td>
<td>15.8</td>
<td>1</td>
<td>2 min&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>254.3</td>
<td>4.45±</td>
<td>–1</td>
<td>3.12</td>
<td>0.82</td>
<td>13.5</td>
<td>1</td>
<td>4.6–27.6&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>250.3</td>
<td>4.7±</td>
<td>–1</td>
<td>3.40</td>
<td>1.93</td>
<td>12.7</td>
<td>1</td>
<td>4 min&lt;sup&gt;e&lt;/sup&gt;, 17.8; 20.6&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>151.2</td>
<td>9.38±</td>
<td>0</td>
<td>0.46</td>
<td>0.86</td>
<td>17.1</td>
<td>1</td>
<td>6 min&lt;sup&gt;e&lt;/sup&gt;, 2.1&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>290.3</td>
<td>7.12±</td>
<td>0</td>
<td>0.91</td>
<td>0.98</td>
<td>11.5</td>
<td>1</td>
<td>3 min&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
<tr>
<td>Caffeine</td>
<td>194.2</td>
<td>10.4±</td>
<td>0</td>
<td>–0.07</td>
<td>–0.58</td>
<td>9.5</td>
<td>2</td>
<td>5 min&lt;sup&gt;i&lt;/sup&gt;, 1.5&lt;sup&gt;j&lt;/sup&gt;</td>
</tr>
<tr>
<td>Propranolol</td>
<td>259.3</td>
<td>9.42±</td>
<td>+1</td>
<td>3.48</td>
<td>0.21</td>
<td>3.6</td>
<td>5</td>
<td>0.4, 1.8, 2.2&lt;sup&gt;k&lt;/sup&gt;</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>267.4</td>
<td>9.4±</td>
<td>+1</td>
<td>1.88</td>
<td>–0.58</td>
<td>1.4</td>
<td>12</td>
<td>4.1, 8.7&lt;sup&gt;l&lt;/sup&gt;</td>
</tr>
<tr>
<td>Atrazine</td>
<td>215.7</td>
<td>&lt;2 (1.6)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0</td>
<td>2.61&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.26</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>236.3</td>
<td>4.35±</td>
<td>0</td>
<td>2.45</td>
<td>2.64</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Phenytoin</td>
<td>252.3</td>
<td>8.33±</td>
<td>0</td>
<td>2.47</td>
<td>1.59</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>253.3</td>
<td>1.83; 1.85; 5.57; 5.60; 5.65&lt;sup&gt;l&lt;/sup&gt;</td>
<td>0</td>
<td>0.89</td>
<td>0.62</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hydrochlorothiazide</td>
<td>297.7</td>
<td>7.9±</td>
<td>0</td>
<td>–0.07</td>
<td>–0.71</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Lincomycin</td>
<td>406.5</td>
<td>7.6±</td>
<td>+1</td>
<td>0.56</td>
<td>–1.34</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Note:
- a Obtained from Drugbank (http://www.drugbank.ca).
- b Chiang and Hu, 2009.
- c Wang et al. 2011.
- d Westerhoff et al., 2005 calculated with SPARC.
- e Babic et al. 2007.
- f Exp. value from chemspider database (http://www.chemspider.com).
- g Obtained from calculated value ChemAxon (http://www.chemspider.com).
- h Zealley and Summers, 2012.
- i Xu et al. 2009.
- j Fang et al. 2012.
- k Yu-Chen Lin et al. 2010.
- l Ramil et al., 2010.

From column from the start as well. From column 1 and 2 biodegradation rates and retardation factors for active biomass were determined. From the other columns, only retardation factors were determined. Comparing retardation factors of column 1 and 2 to column 3 and 4 and to column 5, provided insight into the effect of (in)active biomass and sand grains on OMP sorption. Comparing OMP removal in column 5 to column 6 provided insight in the effect of the water matrix on OMP sorption. The biologically active columns (1 and 2) and the inactivated columns (3 and 4) were operated in duplicate since a larger variability in results for these biological columns was expected. Table 1 presents the feed water qualities for the columns during the experimental period.

Schie canal water was filtered (d = 0.4 mm), prior to use as feed, to prevent clogging of the pump tubes. The columns were fed from 20 L jerrycans which were replaced three times a week to prevent biological degradation of the OMPs in the feed. The jerrycans were washed with a 3% NaOH solution before refilling to prevent biofilm formation. The feed, to prevent clogging of the pump tubes. The columns were fed from 20 L jerrycans which were replaced three times a week to prevent biological degradation of the OMPs in the feed. The jerrycans were washed with a 3% NaOH solution before refilling to prevent biofilm formation. The feed, to prevent clogging of the pump tubes. The columns were fed from 20 L jerrycans which were replaced three times a week to prevent biological degradation of the OMPs in the feed. The jerrycans were washed with a 3% NaOH solution before refilling to prevent biofilm formation.

2.2. Organic micropollutants (OMPs)

A mixture of 14 OMPS (200 ng/L per solute) was dosed into the feed of the columns. Table 2 depicts the wide variability in physico-chemical properties of the OMPS. All compounds were of analytical grade and purchased from Sigma Aldrich, The Netherlands.

A stock solution of 2 mg/L of OMPS was prepared by adding 20 mg of each compound to 10 L tap water. The OMPS were dissolved in the stock solution by mixing for a minimum of three days before being used as feed solution in the experiment. Samples of 200 mL of the influent and effluent from the columns were collected in glass bottles. The OMPS in solution were extracted using Oasis HLB cartridges (200 mL, 6cc) (Waters, USA), which had been conditioned with methanol (>99.9%, Sigma Aldrich) and demineralized water. The OMPS on each cartridge were eluted with 2 × 5 mL of methanol and 2 × 5 mL of hexane/acetone (1/1, v/v) and the extract was gently blown down to dryness under nitrogen. The extract was reconstituted in 1 mL MeOH/H<sub>2</sub>O (25/75, v/v) and spiked with 50 μL of a 200 μg/L mix of matching labelled internal standards. A volume of 20 μL of extract was injected in a Shimadzu UFLC connected to an AB Sciex 4000QTrap QLIT-MS equipped with a Turbo Spray source. The analysis parameters were as described in Reungoat et al. (2012). The OMPS were quantified by an internal calibration renewed for each batch of samples. Quality control standards were injected regularly.
during the run to ensure the signal intensity did not vary by
more than 10%. The final results were corrected for losses
during extraction using the recovery of the extraction method.
The extraction recoveries were determined for each matrix
and each OMP by spiking samples at 100 ng/L before extrac-
tion and after reconstitution in triplicate.

Influent and effluent concentrations were measured at six
different time points during a period of one month (T = 10 h,
34 h, 58.5 h, 80 h, 1 wk and 4 wks). Samples were taken directly
from the influent and effluent side of the column to correct for
possible sorption losses in the tubing. After one month all
columns were stopped, except column 2 which was operated
for six months in total to investigate if adaptation of the
biomass to degrade OMPs could be observed.

2.3. Other analyses

Dissolved organic carbon (DOC) concentrations were
measured with a Shimadzu TOC-VCPH/CPN Analyser after
filtering the aqueous samples through 0.45 μm filters
(SPARTAN™, Whatman, Germany). These filters were flushed
twice with demineralized water prior to use. UV254 absorbance
was measured using a UV–Vis spectrophotometer (Thermo
Scientific, Genesys 6) and a 1 cm quartz cuvette. Oxygen and
temperature were measured with an oxygen metre (Cellox 325
Scientific, Genesys 6) and pH was measured with a multimeter
(Sentix 41 probe, Multi 340i, WTW, Germany) in a
flow-through cell connected to the influent and effluent tubes
of the columns.

At the end of the experiment, duplicate sand samples
(2–5 g) were taken from the bottom and the top of the col-
UMS, to determine adenosine triphosphate (ATP)
tolutions as a measure of biological activity. The sand sample
with 10 mL of demineralized water was subjected to high
energy sonication (HES) treatment to suspend the biomass in
solution. HES was performed with a Branson digital sonifier,
Model 250 D (amplitude 45%, Boom BV Meppel). After soni-
cation the supernatant was decanted and 10 mL fresh demin-
eralized water was added and sonication was repeated until
the difference in ATP concentration measured in the super-
natant was smaller than 10%. Four HES treatments of 2 min
were found to be sufficient. From every sample 2 mL was
collected and mixed to obtain a total volume of 8 mL. From
this mixed sample, 200 μL was subjected to ATP analysis. ATP
analysis was performed with a Quench-Gone Aqueous test
test kit (Aqua tools, France). The test kit measures the concen-
tration of cellular bound ATP (cATP), which is an indication of
the active biomass. A detailed description of the method is
reported by (Keuten et al., 2012). In this study a LB 9509
luminometer (Aqua tools, France) was used. The sand samples
were subsequently dried in an oven (105 °C) for 24 h to
determine the dry weight.

2.4. Statistical analyses

The statistical software package R was used to perform all
statistical analyses (R Development Core Team, 2008). Two
way ANOVA tests were used to determine if an observed dif-
ference between columns (e.g. DOC removal between biolog-
ically active and inactive columns) was statistically significant
(p-value < 0.05). Multi-linear regression was used to determine
if a statistically significant (p-value < 0.05) relationship existed
between OMP biodegradation rates and their physico-
chemical properties or functional groups.

2.5. Modelling

CXTFIT (Toride et al., 1995) was used to obtain the retardation
factors (R) and biodegradation rates (μ) of the OMPs in the
columns by fitting the experimental breakthrough curves
using the inverse problem based on the deterministic equi-
librium convection–dispersion equation (CDE). Concentration
mode was set to resident concentration (third type inlet), cR.

The CXTFIT model is based on the convection dispersion
equation (CDE) given by Eq. (1) (Toride et al., 1995):

$$R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} - \mu c_r$$  \hspace{1cm} (1)

in which:

- $R$ is retardation factor [-]
- $c_r$ is volume-averaged or resident concentration of the liquid
  phase $[kg \ m^{-3}]$
- $t$ is time $[min]$
- $D$ is dispersion coefficient $[m^2 \ \text{min}^{-1}]$
- $x$ is distance $[m]$
- $v$ is average pore water velocity $[m \ \text{min}^{-1}]$
- $\mu$ is first-order decay coefficient for biodegradation of the sol-
  ute $[min^{-1}]$

Average pore water velocity ($u$) and the dispersion coeffi-
cient ($D$) for the columns were obtained from fitting the
breakthrough curves of the tracer experiment in CXTFIT (re-
ults are presented in Table 1 of the SI).

The retardation factor is defined as (Toride et al., 1995):

$$R = 1 + \frac{\rho_b K_d}{\theta}$$  \hspace{1cm} (2)

in which:

- $\rho_b$ is soil bulk density $[kg \ m^{-3}]$
- $K_d$ is distribution coefficient $[kg^{-1} \ m^3]$
- $\theta$ is volumetric water content $[m^3 \ m^{-3}]$

The dispersion coefficient is defined as (Brusseau, 1994):

$$D = a v + \frac{D_0 \tau}{\rho}$$  \hspace{1cm} (3)

in which:

- $D$ is dispersion $[m^2 \ \text{min}^{-1}]$
- $a$ is dispersivity $[m]$
- $v$ is average pore water velocity $[m \ \text{min}^{-1}]$
- $D_0$ is fluid phase diffusion coefficient $[m^2 \ \text{min}^{-1}]$
- $\tau$ is factor accounting for the tortuosity of the porous medium

Dispersivity ($a$) was determined from the tracer curves. The
fluid phase diffusion coefficient ($D_0$) for NaCl (3 g/L) is equal to
1.53 · 10⁻⁸ $m^2 \ s^{-1}$ as reported by Cremasco et al. (2001)
(Cremasco et al., 2001). Tortuosity (τ) was assumed to be 1. The dispersivity (α) values for the different columns are shown in Table 1 of the SI.

To determine the dispersion coefficient (D) for the OMPs, dispersivity was assumed to be equal to the tracer and average pore water velocity was obtained from the tracer. The diffusion coefficient (D0) of the OMPs was calculated according to Eq. (4) (Verliefde, 2008):

$$D_0 = \frac{k_BT}{6\pi\eta R_h}$$

in which:

- $R_h$ = Stokes radius [m]
- $k_B$ = Boltzmann constant = 1.3806488 $10^{-23}$ [JK$^{-1}$]
- $T$ = Temperature = 293.15 [K]
- $\eta$ = viscosity [kg s$^{-1}$m$^{-1}$]

The Stokes radius was determined from the molecular volume of the OMPs assuming the OMP molecules to be ideal spheres. The OMP volumes were obtained from ChemAxon (www.chemicalize.org). The diffusion and obtained dispersivity coefficients for the OMPs are shown in Table 2 of the SI.

Half-life of the compound was defined as:

$$t_{1/2} = \frac{\ln(2)}{\mu}$$

in which:

- $t_{1/2}$ = half-life [min]
- $\mu$ = first-order decay coefficient for biodegradation of the solute [min$^{-1}$]

3. Results and discussion

3.1. Water quality parameters

Oxic conditions were maintained during the complete experiment. No significant changes in pH were observed between the influent and effluent for the columns. DOC, UV$_{254}$ and ATP were used as indicator parameters to determine if the specific experimental conditions (biotic/abiotic) were obtained in the columns. DOC and UV$_{254}$ values are presented in Table 3 of the SI. Although DOC removal was small (±5–10%) in the biologically active columns, the difference in DOC removal between the biologically active columns and biologically inactive columns was statistically significant (p-value = 4.56 $10^{-15}$ < 0.05). In addition, the difference in UV$_{254}$ absorbance decrease between the biologically active and inactive columns was statistically significant (p-value is < 2 $10^{-16}$ < 0.05), confirming the trend observed with the DOC results. The difference in DOC removal for columns 3 and 4 between the adaptation period and the experimental period was statistically significant (p-value = 8.3 $10^{-5}$ < 0.05), implying that inactivation of the biomass in these columns was obtained.

ATP concentrations were measured in sand samples from the influent and effluent side of the column after finishing the experiment, results are presented in Table 3. ATP concentrations measured at the influent side of the columns were in all cases higher than at the effluent side of the column, indicating most biomass is present at the influent side, due to the largest fraction of biodegradable organic matter present there. The average ATP concentration measured in the biologically active columns 1 and 2 was 24.5 ± 6.1 ng/cm$^3$ and 36.5 ± 8.1 ng/cm$^3$, respectively. Columns 3 and 4, which contained biomass that was inactivated at the start of the study, showed an order of magnitude smaller ATP values of 3 ng/cm$^3$ and 2.5 ng/cm$^3$, respectively. Column 5 (Schie canal water and NaN$_3$ from the start) showed an ATP concentration of 1.5 ng/cm$^3$ which corresponds to, or is slightly less than the ATP concentration measured in column 3 and 4. ATP concentrations in column 6 (fed with demineralized water and NaN$_3$) were below the detection limit, indicating that no biomass developed in the column.

Maeng et al. (2011a) found an average (top and bottom of the column) ATP concentration of 102 ng ATP/cm$^3$ for a column fed with Meuse river water. This value is larger than the ATP concentrations found in this study which could be explained by the higher DOC removal (54%) in their study (compared to 5–10% in this study). However, Magic-Knezev and van der Kooij (2004) reported ATP concentrations of 18–93 ng/cm$^3$ for slow sand filters and this range exactly covers the values reported in this study. From the ATP, UV$_{254}$ and DOC results it was concluded that the abiobiotic/biotic conditions aimed for in the columns were obtained.

3.2. Effect of (in)active biomass and the water matrix on OMP sorption

A statistically significant difference in OMP removal between the biologically active columns (1 and 2) and the biologically inactive columns (3, 4, 5 and 6) for the different time points was observed (p-value = 2.37 $10^{-4}$ < 0.05). In addition, no statistically significant difference in OMP removal was observed for the different time points within the two groups of columns (i.e., between 1 and 2 (p-value = 0.60 > 0.05), or between 3, 4, 5 and 6 (p-value = 0.18 > 0.05), indicating that OMP removal was similar in columns 1 and 2 and similar in columns 3, 4, 5 and 6. Exceptions were metoprolol and propranolol which show a clear difference in retardation behaviour between columns 3, 4, 5 and column 6.

The similar trend in breakthrough curves for column 1 and 2 was expected as well as for column 3 and 4, since these columns were duplicates. For most compounds, however, since no statistically significant difference in removal was

### Table 3 – ATP concentrations measured at the influent and effluent side of the sand columns.

<table>
<thead>
<tr>
<th>Column</th>
<th>Influent side</th>
<th>Effluent side</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47 ± 6</td>
<td>2 ± 1</td>
<td>24.5 ± 6.1</td>
</tr>
<tr>
<td>2</td>
<td>70 ± 8</td>
<td>3 ± 1</td>
<td>36.5 ± 8.1</td>
</tr>
<tr>
<td>3</td>
<td>5 ± 1</td>
<td>1 ± 0</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>4</td>
<td>4 ± 1</td>
<td>1 ± 0</td>
<td>2.5 ± 1</td>
</tr>
<tr>
<td>5</td>
<td>3 ± 3</td>
<td>0 ± 0</td>
<td>1.5 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>&lt;DL*</td>
<td>&lt;DL*</td>
<td>&lt;DL*</td>
</tr>
</tbody>
</table>

* Below detection limit.
measured between columns 3, 4, 5 and 6, it could be assumed that OMP sorption was not affected by the inactivated biomass or the water matrix in the circumstances studied. As such, experimental data of the biologically inactive columns could be lumped and used to model the retardation factor \( R \), while experimental data of the biologically active columns could also be lumped and used to model the biodegradation rate \( \mu \).

In addition, retardation factors for non-degradable compounds were fitted for the biologically active and inactivated columns and no statistically significant difference (p-value = 0.14 > 0.05) was found between the two experimental conditions. This observation implies that also the effect of active biomass on OMP sorption is negligible. The negligible effect of (in)active biomass on OMP sorption is probably caused by the low DOC removal (5–10%) that limited the quantity of developed biomass in the columns. Fitted retardation factors \( R \) of the biologically inactive columns can be found in Table 4 of the SI.

The experimental breakthrough data as well as the modelled fits for metoprolol and propranolol are shown in Figs. 1 and 2. The retardation factor for metoprolol was \( R = 3.1 \) for columns 3, 4 and 5 and \( R = 10.4 \) for column 6. The retardation factor for propranolol was \( R = 8.3 \) for columns 3, 4 and 5 and \( R = 62.6 \) for column 6. The confidence interval of the dispersion and decay coefficient for propranolol (Column 6 data) are both going through zero, indicating the result is not statistically significant. However, Fig. 2, clearly shows that the retardation factor of propranolol for column 6 (demineralized water + Na\( \mathrm{N}_3 \)) is much larger than for the other three columns.

For both metoprolol and propranolol, the retardation factor is smaller for the columns fed with Schie Canal Water compared to the column fed with demineralized water, which could be attributed to competition of metoprolol and propranolol with the DOC (DOC = 16.5 ± 3.2 mg/L, \( n = 27 \)) in the Schie Canal Water for sorption places onto the sand or the inactivated biomass. The higher retardation factors observed with demineralized water for these two compounds in comparison to other OMPs likely arise from metoprolol and propranolol being positively charged, making them strongly sorb to the negatively charged sand compared to the neutral and negatively charged OMPs. Drillia et al. (2005) also reported higher distribution coefficients for propranolol \( (K_D, \text{soil} 7 = 199 \text{ L/kg}, K_D, \text{soil} 1 = 16.3 \text{ L/kg} \) compared to carbamazepine \( (K_D, \text{soil} 7 = 37 \text{ L/kg}, K_D, \text{soil} 1 = 0.49 \text{ L/kg} \) and sulfamethoxazole \( (K_D, \text{soil} 7 = 37.6 \text{ L/kg}, K_D, \text{soil} 1 = 0.23 \text{ L/kg} \). However, one aspect that is not taken into account in the above discussion, is that the solute lincomycin is also positively charged but not retarded \( (R = 1.09 \) for both biologically inactive and active columns). The much stronger retardation for metoprolol and propranolol in all columns could be explained by the lower hydrophilicity of the compounds. Hydrophilic compounds

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**Fig. 1** — Experimental data and modelled breakthrough curve metoprolol (PV = Pore Volumes).

**Fig. 2** — Experimental data and modelled breakthrough curve propranolol.
have good solubility and are thus less likely to sorb. Lincomycin is the most hydrophilic compound ($\log D = -1.34$) followed by metoprolol ($\log D = -0.58$) and propranolol ($\log D = 0.21$). The negligible sorption of lincomycin could thus be explained by its higher hydrophilic character (high solubility) and the partial deprotonation of this solute at the pH at which the experiment was conducted (weaker positive charge).

### 3.3. Organic micropollutant sorption — retardation factors

OMP retardation factors ($R$) were determined by fitting $R$ for the lumped experimental data of the four biologically inactive columns (3, 4, 5 and 6), since these were determined not to be statistically different. The average velocity and dispersion coefficient of the four columns were determined from the tracer experiment and used as input for the CXTFIT model. The biodegradation rate $\mu$ was set to 0 since it was assumed that no biodegradation occurred in these columns (ATP concentrations in the biologically inactive columns were one order of magnitude lower compared to the biologically active columns — in column 6 no biomass was present at all).

In the convection—dispersion equation, retardation is linked to reversible sorption. Losses arising from irreversible sorption or biodegradation of OMPs are included as first-order decay processes. Although no loss of OMPs was observed for most compounds in the biologically inactive columns, losses of metoprolol and propranolol were observed. As acetaminophen and caffeine, both easily degradable compounds (Yu-Chen Lin et al., 2010; Zearley and Summers, 2012), did not show a loss in the inactive columns — consistent with measurements of low ATP concentrations ($2.5-3$ ng/cm$^2$ compared to $24.5-36.5$ ng/cm$^2$ in the biologically active columns), biodegradation of metoprolol and propranolol in the biologically inactive columns does not seem likely. Therefore, the loss of these compounds could be attributed to irreversible sorption possibly as a result of charge interactions; however, further research is required to test this hypothesis. The loss (irreversible sorption) of metoprolol and propranolol was modelled by fitting $\mu$ to correct for the effective biodegradation rate. The effective biodegradation rate is determined as the biodegradation rate from the biologically active columns minus the loss of the compound as a result of irreversible sorption from the biologically inactive columns, thereby obtaining a safe estimate of the biodegradation rate for these two compounds.

### 3.4. Organic micropollutant biodegradation

To determine the biological degradation rates of the different OMPs, $\mu$ was fitted for the experimental data of both biologically active columns 1 and 2. The average velocity and dispersion were obtained from the tracer and used as input for the CXTFIT model. The retardation factor determined from the inactive columns was used to fit the biological degradation rate $\mu$ for the biologically active columns.

The OMPs were separated in two groups: biodegradable and non-biodegradable. Non-biodegradable in this study means that the compound is either non-biodegradable (persistent) or is characterised by a very small biodegradation rate which could not be determined with a statistically significant confidence interval by the model. Acetaminophen, ibuprofen, ketoprofen, gemfibrozil, trimethoprim, caffeine, propranolol and metoprolol were found to be biodegradable, while atrazine, carbamazepine, hydrochlorothiazide, lincomycin, phenytoin and sulfamethoxazole showed more persistent behaviour. These results are in agreement with other studies: biodegradation of acetaminophen, ibuprofen, ketoprofen, gemfibrozil, trimethoprim, caffeine, propranolol, and metoprolol has been reported in many studies (Fang et al., 2012; Ramil et al., 2010; Xu et al., 2009; Yu-Chen Lin et al., 2010; Zearley and Summers, 2012) as well as the more persistent behaviour of compounds such as atrazine, carbamazepine, hydrochlorothiazide, phenytoin and sulfamethoxazole (Benotti et al., 2012; Radjenović et al., 2009; Scheytt et al., 2006; Zearley and Summers, 2012). To the best knowledge of the authors, no biodegradation rates for lincomycin have been reported.

Biodegradation rates in this study range from 1.4 to 16.3 d$^{-1}$, while half-lives range from 0.0 to 0.5 d. Table 2 presents an overview of decay rates, half-lives obtained in this study and reported in other studies for all OMPs. Graphs of the OMPs that show biological degradation ($\mu \neq 0$) are presented in Figures 1 and 2 of the SI. Table 5 of the SI presents the fitted biodegradation rate $\mu$ for the OMPs in the biologically active columns.

From Table 2 it is observed that the half-lives determined in this study for the biodegradable compounds are within the range of half-lives reported in literature. The difference in half-life (biodegradation rate) is probably a result of the specific experimental conditions investigated (initial OMP concentrations, type and quantity of biomass present, experimental scale, soil etc.) in each of the studies.

Atrazine, carbamazepine, hydrochlorothiazide, lincomycin, phenytoin and sulfamethoxazole are not or very poorly biodegraded. Atrazine also showed very poor removal in other soil column studies (Benotti et al., 2012; Zearley and Summers, 2012), and also the persistent behaviour of carbamazepine has been reported in many studies (Benotti et al., 2012; Maeng et al., 2011a, b; Maeng et al., 2012; Scheytt et al., 2006; Zearley and Summers, 2012). Hydrochlorothiazide showed recalcitrant behaviour in a conventional activated sludge system as well as two pilot MBR systems (Radjenović et al., 2009). Phenytoin was poorly removed ($\pm 20\%$) in a pilot RBF system and did not show removal during full-scale RBF treatment (Benotti et al., 2012). Sulfamethoxazole did not show removal in a pilot scale RBF system as well as during full scale RBF treatment (Benotti et al., 2012) or in biological filters (Zearley and Summers, 2012), but was reported to be biodegradable under oxic conditions in two soil column studies (Baumgarten et al., 2011; Gruenheid et al., 2008). Baumgarten et al. (2011) reported a half-life of $t_{1/2} = 9$ d for sulfamethoxazole in oxic conditions, but only after an operational period of 27 months (sulfamethoxazole influent concentration $= 0.25$ µg/L). This could explain the more persistent behaviour of sulfamethoxazole observed in this study, even after the longest operation period, since biologically active column 2 was operated for only 6 Months.

Column 2 was operated for six months to investigate if adaptation of the biomass towards the OMPs would occur. The
fitted biodegradation rates for the one month period and the six month period are presented in Table 6 of the SI. The difference in biodegradation rates for column 2 over the six month period and for column 1 and 2 over the one month period was statistically not significant ($p$-value = 0.71 > 0.05), indicating that OMP biodegradation rates were similar and no adaptation of the biomass towards the OMPs occurred in the six month period. This implies that new developed RBF sites (under oxic conditions) might not be capable of removing OMPs such as atrazine, carbamazepine, hydrochlorothiazide, lincomycin, phenytoin and sulfamethoxazole during the first months of operation.

3.5. Link with physico-chemical properties and functional groups

The main objective of this study was to determine if the OMP biodegradation rate $\mu$ could be related to the OMP physico-chemical properties (MW, charge or hydrophobicity) or functional groups. Table 2 presents an overview of the physico-chemical properties of the OMPs and their biodegradation rates. Table 7 in the SI depicts the functional groups present in their molecular structures. Log P is used as an indication of the hydrophobicity of the non-ionizable compounds, similarly Log D is used for ionizable compounds. Hydrophobicity of the compound is expected to play an important role in penetrating the cell membrane, before the compound can be further degraded by intracellular enzymes, in case no exoenzymes are present. In addition, hydrophobicity of the compound is related to the bioavailability of a compound. Hydrophobic compounds have poor solubility and are therefore more likely to sorb, thereby reducing their mobility (and bioavailability) in soil.

From Table 2 it is observed that all negatively charged compounds are well removed in the biologically active column, and thus characterized by high biodegradation rates (12.74–15.77 d$^{-1}$), while positively charged compounds are characterized by lower biodegradation rates (0–3.61 d$^{-1}$). A statistically significant linear relationship was observed between biodegradation rate and charge for the charged compounds ($R^2 = 0.95$, $p$-value = 8.87 $\times$ 10$^{-4}$ < 0.05). In addition, charged compounds with higher Log D (ibuprofen, ketoprofen and gemfibrozil) showed higher biodegradation rates than charged compounds with lower Log D (propranolol, metoprolol and lincomycin). This was also confirmed by a statistically significant linear relationship ($R^2 = 0.85$, $p$-value = 8.48 $\times$ 10$^{-3}$ < 0.05). A higher Log D indicates larger hydrophobicity of the OMP, thus the compound will be sorbed more easily. The fact that charged OMPs with higher Log D show higher biodegradation rates, could be explained by their increased chance of sorption onto the cell and subsequent penetrating through the cell membrane to be further degraded. However, this increased sorption of the compounds with high Log D could not be observed from the retardation factors. It may be possible that the biological degradation of ibuprofen, ketoprofen and gemfibrozil was so fast that it outcompeted the sorption and thus the retardation effect could not be observed. Future research should elucidate why negatively charged compounds show higher biodegradation rates compared to positively charged OMPs and determine the specific role of sorption as a pre-requisite for biodegradation.

Although charge and hydrophobicity separately played an important role in predicting the biodegradation rate of the charged compounds, no statistically significant relation was observed between biological degradation rate and the physico-chemical properties for the neutral compounds. Neutral compounds characterized by lower Log D values (−0.58–0.98) were more biodegradable, while neutral compounds characterized by higher Log D values (1.59–2.64) showed more persistent behaviour, in contrast to what was observed for the charged compounds. Exceptions were hydrochlorothiazide and sulfamethoxazole. Both compounds have low Log D values, but did not show biodegradation. Although some trends were observed between the biodegradation rates and two physico-chemical properties as explained above (charge and hydrophobicity), a statistically significant relationship for the whole OMP mixture and all three physico-chemical properties considered could not be obtained.

However, a statistically significant relationship ($p$-value = 1.26 $\times$ 10$^{-4}$, $R^2$ = 0.96) for all OMPs was obtained explaining biodegradation behaviour using functional groups present within the chemical structure of the OMP:

$$
\mu = 22.797 – 7.357 \cdot Am – 7.360 \cdot RS + 6.045 \cdot Et – 6.690 \cdot AlEt + 5.443 \cdot Ca – 6.766 \cdot S
$$

(6)

in which:

- $\mu$ = biodegradation rate [d$^{-1}$]
- Am = number of amines (primary and secondary) [-]
- RS = number of ring structures [-]
- Et = number of ethers [-]
- AlEt = number of aliphatic ethers [-]
- Ca = number of carbonyl groups [-]
- S = number of sulphur atoms [-]

Eq. (6) shows that the presence of ethers and carbonyl groups will increase biodegradability, while the presence of amines, ring structures, aliphatic ethers and sulphur will decrease biodegradability.

Several studies concluded that functional groups such as carbonyl positively contribute to the biodegradability of the compound (Loonen et al., 1999), while other functional groups such as ring structures (Loonen et al., 1999), amines (Loonen et al., 1999; Okey and Stensel, 1996), aliphatic ether (Boethling et al., 1994) and sulphur (Okey and Stensel, 1996) negatively contribute to a compounds’ biodegradability. Kawasaki et al. (1980) reported that the presence of ethers in the molecular structure of aliphatic compounds and their derivatives did not show a significant effect on the biodegradability of these compounds, but ethers were found to increase biodegradability rate of the OMPs investigated in this study. The different contribution of ethers to the biodegradation rate in the two studies, could be attributed to the difference in biological system (sludge mixture versus RBF, e.g. differences in biomass concentration and residence time) and/or the difference in type of compounds investigated in the studies.

Further research is required to extend the amount of molecular properties investigated in the predictive model as well.
as the OMP cocktail. For example, molecular properties such as: globularity, ionization potential, electron affinity, and solubility could influence OMP biodegradation during soil passage. A more extensive study is required to elucidate the importance of these molecular descriptors which will be another step towards the development of a QSAR model for OMP removal during soil passage.

4. Conclusion

This study examined sorption and biodegradation behaviour of OMP mixtures, at concentrations representative of those in RBF systems, in lab-scale soil columns under oxic conditions. The main objective of this study was to investigate if the OMP biodegradation rate could be related to the physico-chemical properties (charge, hydrophobicity and molecular weight) or functional groups of the OMPs. In addition, this study investigated OMP sorption onto sand grains, active and inactive biomass (biosorption), and assessed the effect of the water matrix on OMP sorption.

- OMP biodegradation rate of the complete mixture of OMPs investigated in this study can be predicted based on the functional groups present in the OMP chemical structure. The obtained predictive model provides a tool for drinking water companies to make a first estimation whether a newly detected compound may be biodegraded during RBF or if additional treatment is required to prevent the OMP from penetrating through the treatment train ending up in the drinking water.

- Although a clear trend was observed between biodegradation rate and hydrophobicity or charge for the charged OMPs, it was not possible to obtain a statistically significant relation between biodegradation rate and these physico-chemical properties for the complete OMP mixture.

- To distinguish OMP sorption from biodegradation it is imperative to determine breakthrough curves as opposed to measure only influent and effluent concentration at one time point, since they will provide retardation factors as well as decay rates and will take into account OMP dispersion. This makes a comparison of sorption and/or biodegradation behaviour between OMPs possible, which is required to observe trends and to relate OMP removal to the OMP physico-chemical properties or functional groups.

- Retardation factors for most compounds were close to 1, indicating mobile behaviour of these compounds in the soil environment.

- OMP sorption onto sand grains and developed (in)active biomass as well as the effect of the water matrix on OMP sorption were found to be negligible under the conditions investigated in this study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.10.068.

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