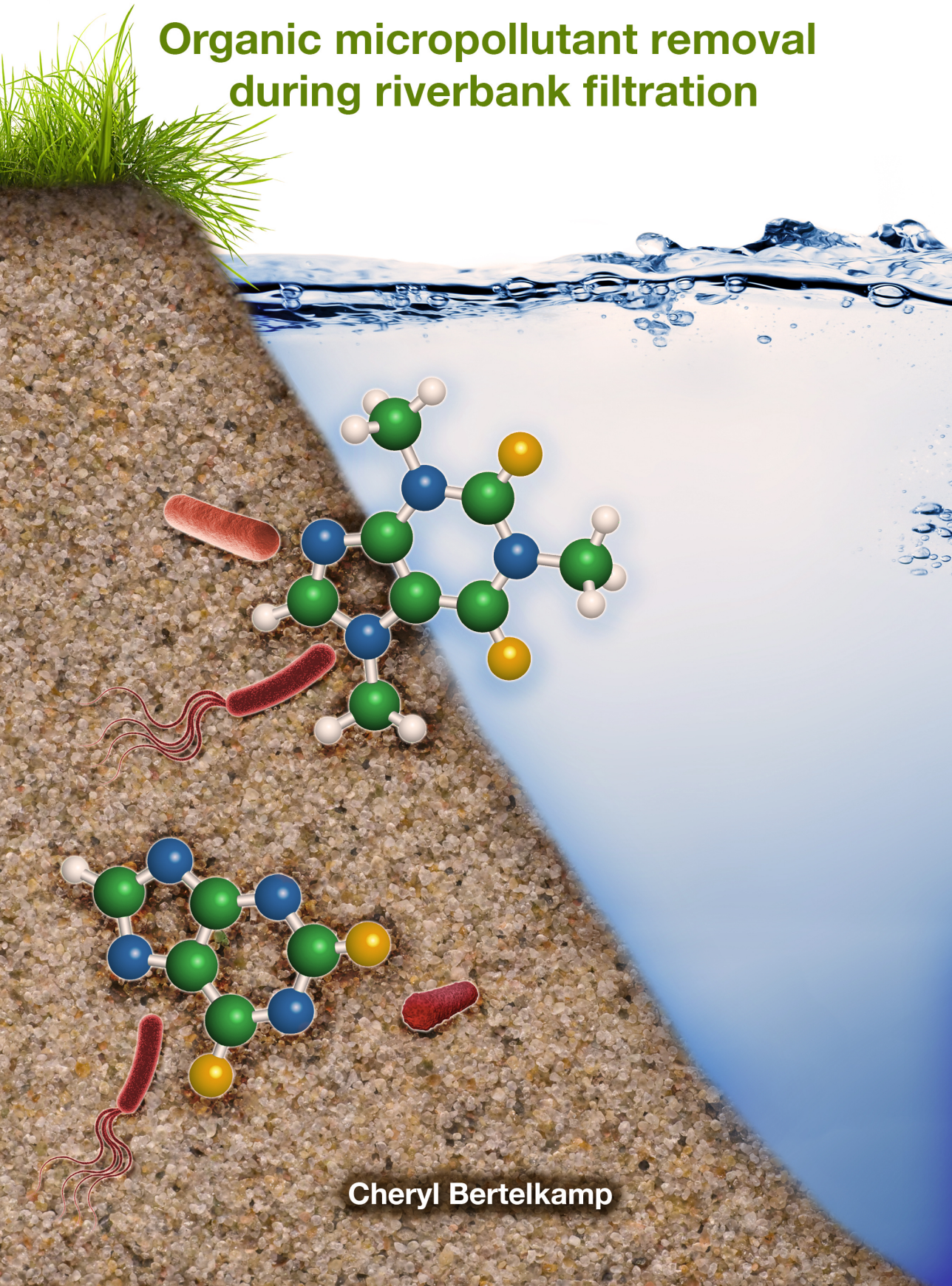
Organic micropollutant removal during riverbank filtration



Cheryl Bertelkamp

Organic Micropollutant Removal during River Bank Filtration

Proefschrift

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In loving memory of my grandmother, Ida Bertelkamp
For Robbin and Phelin

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Samenvatting

Deze studie heeft onderzocht welke factoren van invloed zijn op de twee belangrijkste verwijderingsmechanismen (adsorptie en biodegradatie) voor organische microverontreinigingen (OMV's) tijdens oeverfiltratie (RBF). Tevens heeft deze studie gekeken of het mogelijk is een voorspellend model te ontwikkelen voor OMV-verwijdering tijdens oeverfiltratie.

Hoofdstuk 2 heeft het sorptie- en biodegradatiegedrag van 14 OMV's onderzocht in kolommen gevuld met technisch zand (representatief voor de eerste meter bodempassage in oeverfiltratiesystemen onder oxische omstandigheden). Om een onderscheid te kunnen maken tussen OMV-sorptie en OMV-biodegradatie, zijn doorbraakcurves gemodelleerd op basis van de advectie-dispersievergelijking. Retardatiefactoren (indicatie voor OMV-sorptie) waren voor de meeste stoffen gelijk of ongeveer gelijk aan 1, wat aangeeft dat deze stoffen mobiel gedrag kunnen vertonen tijdens bodempassage. Het effect van actieve en inactieve biomassa (bio-sorptie), zandkorrels en de watermatrix op OMV-sorptie waren verwaarloosbaar klein voor de onderzochte condities in dit hoofdstuk. Hoewel trends werden waargenomen tussen lading, of hydrofobiciteit, van geladen OMV's en hun biodegradatiesnelheid, kon er geen statistisch significante lineaire relatie voor dit OMV-mengsel verkregen worden op basis van deze fysisch-chemische eigenschappen. Echter kon er wel een statistisch significante relatie worden waargenomen tussen de biodegradatiesnelheid van de OMV's en de functionele groepen aanwezig in de moleculaire structuur ervan. De aanwezigheid van ethers en carbonylgroepen verhoogde de biodegradatiesnelheid, terwijl de aanwezigheid van aminen, ringstructuren, alifatische ethers en zwavel de biodegradatiesnelheid verlaagde.

Hoofdstuk 3 onderzocht de relatie tussen functionele groepen in de moleculaire structuur van een mengsel van 29 OMV's (waarvan er 11 hetzelfde waren als in hoofdstuk 2) en hun biodegradatiesnelheid verkregen uit laboratoriumschaal bodemkolommen. Op basis hiervan werd een multilineair regressiemodel ontwikkeld dat vervolgens werd gevalideerd met veldgegevens. In tegenstelling tot hoofdstuk 2, waarbij technisch zand werd gebruikt voor het vullen van de kolommen, werden de laboratoriumschaal kolommen in dit hoofdstuk gevuld met bodemmateriaal van een operationele oeverfiltratie-locatie. Er werd een statistisch significante relatie gevonden tussen de biodegradatiesnelheid van de OMV's en de functionele groepen in de moleculaire structuur ervan. De biodegradatiesnelheid werd verhoogd in de aanwezigheid van carbonzuren, hydroxylgroepen en carbonylgroepen, maar daalde in aanwezigheid van ethers, halogenen, alifatische ethers, methylgroepen en ringstructuren. Verschillen tussen de voorspellende modellen verkregen in hoofdstuk 2 en 3 kunnen worden verklaard door de gebruikte bodemtypen en waterkwaliteiten (water uit het Schie-kanaal en technisch zand in hoofdstuk 2, water uit de Lek-rivier en bodemmateriaal van een oeverfiltratie-locatie in hoofdstuk 3). Het voorspellende model verkregen in hoofdstuk 3 gaf een goede kwalitatieve indicatie van de biodegradeerbaarheid voor ongeveer 70% van de in het veld onderzochte OMV's (voor ongeveer 80% wanneer de glymen werden uitgesloten). Het model was minder betrouwbaar wanneer de voorspelde biodegradatiesnelheid kleiner of gelijk was aan de standaardfout ($s = 0.77\ d^{-1}$) of wanneer de OMV amide- of aminegroepen bevatte.

Aangezien er in de literatuur gerapporteerd is dat waterkwaliteit een belangrijke factor is in OMV-verwijdering tijdens bodempassage, heeft hoofdstuk 4 onderzocht of dit de enige belangrijke factor is, of dat het effect van type bodemmateriaal ook een belangrijke rol speelt in de verwijdering van OMV's

tijdens bodempassage. Sorptie- en biodegradatiegedrag van 20 OMV's werd onderzocht in laboratoriumschaal kolommen gevuld met twee verschillende types bodemmateriaal en gevoed met dezelfde waterkwaliteit. De kolommen simuleerden het oeverfiltratieproces onder oxische omstandigheden. Verschillen in retardatiefactoren en biodegradatiesnelheden van de OMV's waren statistisch niet significant voor de twee bodemtypes, hoewel zij werden gekenmerkt door verschillen in kationische uitwisselingscapaciteit, organische stof en zandgehalte / slib / klei. Dit resultaat werd ondersteund door de samenstelling van de microbiële gemeenschap (rijkheid, gelijkheid) van de twee types bodemmaterialen, die meer vergelijkbaar werd tijdens de experimenten doordat beide kolommen gevoed werden met dezelfde waterkwaliteit. Dit geeft aan dat de samenstelling van de microbiële gemeenschap en daardoor OMV-verwijdering in oevers voornamelijk wordt bepaald door de waterfase (hoeveelheid en kwaliteit organische stof, voedingsstoffen) in plaats van de bodemfase. Deze resultaten impliceren dat verschillende oeverfiltratie-locaties gelegen langs dezelfde rivier vergelijkbare OMV-verwijdering kunnen tonen (in het geval van vergelijkbare waterkwaliteit en verblijftijd).

Hoofdstuk 5 onderzocht het effect van de waterkwaliteit diepgaander, en meer specifiek het effect van verschillende organische koolstoffracties verkregen uit rivierwater (hydrofiel, hydrofoob, transfiel en het totaal aan organische koolstof in het rivierwater) op de biodegradatiesnelheid van de OMV. Bovendien werd het effect van een korte-termijn OMV- en DOC-shock-load (vervierdubbeling van de concentratie OMV en verdubbeling van de concentratie opgelost organische koolstof (DOC)) onderzocht op de biodegradatiesnelheid van de OMV om te beoordelen hoe robuust RBF-systemen zijn ten gevolge van bijvoorbeeld klimaatverandering. De resultaten impliceren dat, in tegenstelling tot wat wordt waargenomen voor bodemsystemen die gevoed worden met afvalwater-effluent, de biodegradatiesnelheid van de OMV's tijdens oeverfiltratie niet wordt beïnvloed door het type organisch koolstoffractie (verkregen uit rivierwater) gevoed aan de kolommen, bij stabiele operatie. Er werd geen effect van een korte-termijn DOC-shock-load op de biodegradatiesnelheid van de OMV's waargenomen tussen de verschillende organische koolstoffracties. Dit betekent dat de oeverfiltratie-locatie onderzocht in dit hoofdstuk veerkrachtig is met betrekking tot voorbijgaande hogere DOC-concentraties in het rivierwater (bijvoorbeeld na een afname van de rivierafvoer als gevolg van seizoensinvloeden). Echter, een tijdelijke OMP-shock-load verhoogd de biodegradatiesnelheden van de OMV's voor de totale organische koolstof- en de hydrofiele organische koolstoffracties verkregen uit rivierwater. Deze verhoogde biodegradatiesnelheden konden niet worden verklaard door één van de parameters onderzocht in dit hoofdstuk (adenosine triphosphate (ATP), DOC-verwijdering, Specific UltraViolet Absorbance (SUVA), rijkdom / gelijkheid van de microbiële populatie of OMV-categorie (hydrofobiciteit / lading).

Het effect van de redoxconditie op de biodegradatiesnelheid van de OMV's en adaptief gedrag van een mengsel van 15 OMV's in laboratoriumschaal bodemkolommen gevoed met rivierwater werd geanalyseerd in hoofdstuk 6. Dimethoaat, diuron en metoprolol toonde redox-afhankelijk verwijderingsgedrag met grotere afbraaksnelheden in de oxische zone dan in de suboxische / anoxische zone. OMV's die persistent gedrag vertoonden in de oxische zone (atrazine, carbamazepine, hydrochloorthiazide en simazine) werden ook niet verwijderd onder meer gereduceerde omstandigheden. Adaptief gedrag werd waargenomen voor vijf OMV's: dimethoaat, chloridazon, lincomycine, sulfamethoxazol en fenazon. Nieuw te ontwikkelen of bestaande oeverfiltratie-locaties die voor het eerst blootgesteld worden aan deze OMV's kunnen na opstarten tot 9 maanden nodig

hebben om de volledige verwijderingscapaciteit bereiken. Voor sommige OMV's, zoals dimethoaat, kunnen zelfs langere opstarttijden nodig zijn, omdat de volledige verwijderingscapaciteit zelfs na 15 maanden nog niet was bereikt voor de onderzochte condities in dit hoofdstuk. Het adaptieve gedrag dat werd waargenomen voor sommige OMV's kon niet worden verklaard door hun fysisch-chemische eigenschappen (hydrofobiciteit, lading, moleculair gewicht) of functionele groepen. Adaptief gedrag van de biomassa richting OMV's bleek een belangrijke factor te zijn die moet worden meegenomen in voorspellende modellen voor OMV-verwijdering tijdens RBF.

Hoofdstuk 7 presenteert de conclusies, gevolgen voor de praktische toepassing en aanbevelingen voor toekomstig onderzoek.

Summary

This study investigated the factors influencing the main removal mechanisms (adsorption and biodegradation) for organic micropollutant (OMP) removal during river bank filtration (RBF) and the possibility of developing a predictive model of this process for OMP removal during RBF.

Chapter 2 analysed the sorption and biodegradation behaviour of 14 OMPs in soil columns filled with technical sand (representative of the first meter of oxic conditions in RBF systems. Breakthrough curves were modelled, based on the advection-dispersion equation, to differentiate between OMP sorption and biodegradation. Retardation factors (indicators for OMP sorption) for most compounds were close to 1, indicating little sorption of these compounds and thus the mobile behaviour of these compounds during passage in soils. The influence of active and inactive biomass (bio-sorption), sand grains and the water matrix on OMP sorption was found to be negligible under the conditions investigated in this chapter. Although trends were observed between charge or hydrophobicity of charged OMPs and their biodegradation rates, 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 OMP biodegradation rates and the functional groups present in the molecular structure of the OMPs. The presence of ethers and carbonyl groups increased biodegradability, while the presence of amines, ring structures, aliphatic ethers and sulphur decreased biodegradability.

Chapter 3 examined relationships between functional groups present in the molecular structure of a mixture of 29 OMPs (of which 11 were the same as in Chapter 2) and their biodegradation rates obtained from lab-scale soil columns and constructed a multi-linear regression model for biodegradation rate prediction based on this. This model was then validated with field data. In contrast to Chapter 2, where technical sand was used to fill the columns, lab-scale columns here were filled with soil from an operational RBF site. A statistically significant relationship was found between OMP biodegradation rate and the functional groups present in the molecular structures of the OMPs. OMP biodegradation rate increased in the presence of carboxylic acids, hydroxyl groups, and carbonyl groups, but decreased in the presence of ethers, halogens, aliphatic ethers, methyl groups and ring structures in the molecular structure of the OMPs. Differences between the predictive models obtained in Chapter 2 and 3 could be explained by the different soil types and water qualities used (Schie Canal water and technical sand in Chapter 2, Lek River water and soil from an operational RBF site in Chapter 3). The predictive model obtained from the lab-scale soil column experiment in Chapter 3 gave a good indication of biodegradability for approximately 70% of the OMPs monitored in the field (80% excluding the glymes). The model was found to be less reliable for the more persistent OMPs (OMPs with predicted biodegradation rates lower or around the standard error = 0.77 d^{-1}) and OMPs containing amide or amine groups. These OMPs should be carefully monitored in the field, to determine their removal during RBF.

Water quality was reported to be an important factor in OMP removal during soil passage, however it is unclear if this is the only important factor and therefore Chapter 4 explored the effect of soil type on OMP removal. Sorption and biodegradation behaviour of 20 OMPs was investigated in lab-scale columns filled with two different soil types and fed with the same water quality - the columns were simulating RBF under oxic conditions.

Differences in retardation factors and OMP biodegradation rates were statistically not significant between the two soil types, although these soil types were characterized by a different cationic exchange capacity, organic matter and sand/silt/clay content. This result was supported by the microbial community composition (richness, evenness) of the two soils that became more similar during the course of the experiments as a result of feeding both columns with the same water quality. This indicates that microbial community composition and thereby OMP removal in soils is primarily determined by the aqueous phase (organic matter quantity and quality, nutrients) rather than the soil phase. These results imply that different RBF sites located along the same river may show similar OMP removal (in case of similar water quality and residence time).

Chapter 5 investigated the effect of the water quality in more detail, and more precisely the effect of different organic carbon fractions (hydrophilic, hydrophobic, transphilic and the complete river water organic carbon) obtained from river water on the OMP biodegradation rate. Additionally, the effect of short-term OMP and DOC shock-loads (e.g. quadrupling the OMP concentrations and doubling the DOC concentration) on OMP biodegradation rates was investigated to assess the resilience of RBF systems to, for example, climate change. The results imply that – in contrast to what is observed for soil systems operating on wastewater effluent - OMP biodegradation rates during RBF are not affected by the type of organic carbon fraction (obtained from river water) fed to the soil column, in case of stable operation. No effect of a short-term DOC shock-load on OMP biodegradation rates was observed, for none of the different organic carbon fractions dosed. This means that the RBF site investigated in this chapter is resilient towards transient higher DOC concentrations in the river water (e.g. following a decrease in river discharge due to seasonal effects). However, a temporary OMP shock-load increased OMP biodegradation rates for the river water organic matter and hydrophilic organic carbon fractions. These increased biodegradation rates could not be explained by any of the parameters investigated in this chapter (ATP, DOC removal, SUVA, richness/evenness of the soil microbial population or OMP category (hydrophobicity/charge).

The effect of redox condition on OMP biodegradation rate as well adaptive behaviour of a mixture of 15 OMPs (largely similar to the OMP mixtures used in Chapter 3, 4, and 5) in laboratory-scale soil columns fed with river water was analysed in Chapter 6. Dimethoate, diuron, and metoprolol showed redox dependent removal behaviour with degradation rates larger for the oxic zone compared to the suboxic/anoxic zone. OMPs that showed persistent behaviour in the oxic zone (atrazine, carbamazepine, hydrochlorothiazide and simazine) were also not removed under more reduced conditions. Adaptive behaviour was observed for five OMPs: dimethoate, chloridazon, lincomycin, sulfamethoxazole and phenazone. Newly developed, or existing, RBF sites exposed to these OMPs for the first time may require up to 9 months following start-up to reach full removal capacity. For some chemicals, such as dimethoate, even longer start-up times could be required since full removal capacity was not reached in our tests even after 15 months. The adaptation time observed for some OMPs could not be explained by their physico-chemcial properties (hydrophobicity, charge, molecular weight) or functional groups. Finally, adaptive behaviour of the biomass towards OMPs was found to be an important factor that should be incorporated in predictive models for OMP removal during RBF.

Chapter 7 presents the conclusions, implications for the practical application and recommendations for future research.

Table of contents

Chapter 1

A review on how to develop a predictive model for organic micropollutant removal during river bank filtration

1 Introduction

1.1 RBF as a special case of MAR

Managed Aquifer Recharge (MAR) technologies such as: infiltration basins/ponds, soil aquifer treatment (SAT), dune filtration, percolation tanks, river bank filtration (RBF) etc. have received a lot of attention in the past years as possible treatment processes for the removal of organic micropolluants (OMPs). MAR has several advantages over other treatment processes capable of OMP removal (e.g. membrane filtration and/or advanced oxidation): it is a low cost and robust process, does not require chemical supplementation and is low in energy demand. The different MAR technologies show some important differences with respect to operational parameters such as feed water quality. SAT uses treated wastewater effluent while RBF uses river water. Feed water organic carbon quantity and quality (composition) were shown to play a major role in shaping the microbial community composition and thus OMP removal (Li *et al.*, 2014). Therefore, result obtained from SAT studies cannot be easily translated to RBF processes.

RBF is the natural treatment of river water by means of soil passage. Pumping wells located along the river create a hydraulic gradient which enables the flow of river water through the bank. RBF is a common pre-treatment technique adopted by Dutch drinking water companies using river water as drinking water source (van der Hoek *et al.*, 2014). Originally, RBF was used for the removal of pathogens, bacteria, protozoa, natural organic matter (NOM) and turbidity. However, more recent studies on RBF demonstrated that this process could act as possible barrier for a wide variety of OMPs as well (Benotti *et al.*, 2012, Hoppe-Jones *et al.*, 2010, Storck *et al.*, 2010).

1.2 Organic micropollutants

OMPs are a diverse group of chemical compounds that include pesticides, personal care products, pharmaceuticals, and industrial waste products. These compounds enter aquatic environments, like rivers, by different pathways such as agricultural run-off, discharges from wastewater treatment plants and industry, as well as illegal spills. (Municipal) wastewater treatment plants are not specifically designed for OMP removal, and thus OMPs have been detected in wastewater treatment plant effluents discharged to rivers (Paxéus, 1996). Run-off and/or leaching from agricultural land results in the presence of pesticides as well as veterinary pharmaceuticals in surface and/or ground waters (Kemper, 2008, Willis *et al.*, 1982). Although the effect of trace levels of OMPs on human health is still largely unknown, ingesting low concentrations of OMPs for a prolonged period of time as well as the effect of ingesting OMP mixtures could pose a potential health risk (Jones *et al.*, 2004, Sonnenschein *et al.*, 1998). Therefore, it is important to remove these compounds from drinking water.

As a result of improved analytical techniques, nowadays more and more OMPs can be detected in the river water. RBF has been shown to be an effective barrier for many OMPs, however, some OMPs (e.g. atrazine, carbamazepine) were seen to persist (Benotti *et al.*, 2012, Storck *et al.*, 2012). Due to the lack of insight into why certain OMPs are removed whilst others show persistent behaviour, drinking water companies are challenged to predict if those newly discovered OMPs will be removed during RBF or not. Ideally, the behaviour of every newly discovered OMP would be tested under controlled conditions in the laboratory simulating the RBF process, but this is unrealistic given the financial and time investments associated. Therefore, the development of a predictive model for OMP removal during RBF is desirable for drinking water companies operating RBF. Predictive models based on

Quantitative Structure Activity Relationships (QSARs), could enable drinking water companies to predict the removal of OMPs based on their physico-chemical properties and/or structural fragments (e.g. functional groups). Based on the outcome of such predictive models, drinking water companies using RBF could adjust their post-treatment to prevent the presence of OMPs in the drinking water. In addition, a predictive model should provide drinking water companies with more insight into the parameters that influence OMP removal during RBF.

1.3 Main mechanisms affecting fate of OMPs during RBF

The fate of OMPs during the RBF process is affected by a number of processes including: adsorption, microbial degradation, photodegradation, hydrolysis, oxidation-reduction, volatilization, phytodegradation, and dilution with native groundwater (Gravilescu, 2005, Hiscock *et al.*, 2002, Storck *et al.*, 2012, Verstraeten *et al.*, 2003) (Figure 1).

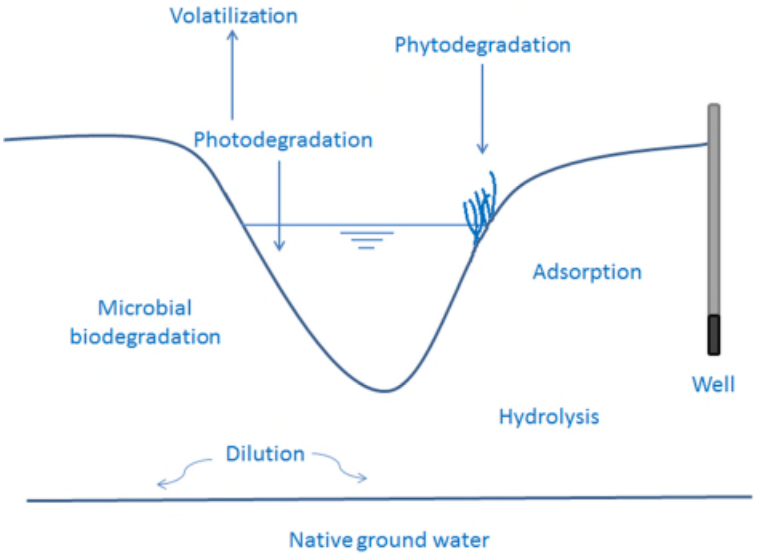

Figure 1 - OMP removal mechanisms during RBF

Photodegradation (photolysis) describes the process of OMP degradation as a result of the reaction with sunlight. Two types of photolysis can be distinguished: direct photolysis and indirect photolysis. Direct photolysis refers to the absorbance of photons (sunlight) by the OMP resulting in bond cleavage or rearrangement to form a new stable product (Mill, 1999). Indirect photolysis describes the process by which soil constituents such as dissolved organic matter (DOM) react with photons to form reactive oxidants such as singlet oxygen ($^1O_2$) or hydroxyl radicals (·OH) (Remucal, 2014). These oxidants can subsequently react with the OMPs.

Hydrolysis is the reaction of an OMP with water (Gavrilescu, 2005, Shonnard *et al.*, 2007). Some functional groups, such as monohalogenated hydrocarbons, polyhalogenated hydrocarbons, carboxylic acid esters, dialkyl phthalates, amides, carbamates, phosphoric acid triesters and thiophosphoric acid triesters, epoxides, lactones, phosphoric acid esters, and sulfonic acid ester, were demonstrated to be susceptible towards hydrolysis (Gavrilescu, 2005, Shonnard *et al.*, 2007). Hydrolysis is a primary degradation pathway for carbamate pesticides (e.g. carbosulfan, pirimicarb) (Wei *et al.*, 2001) and organophosphate pesticides (e.g. parathion, diazinon) (Cowart *et al.*, 1971).

In contrast to activated sludge and membrane bioreactor (MBR) processes, OMP removal facilitated by phytodegradation is typically observed in MAR systems such as RBF, artificial recharge, constructed wetlands. Phytodegradation is defined by Salt *et al.* (1998) as "the use of plants and associated microorganisms to degrade organic pollutants". Riparian vegetation can play an important role in the removal of some OMPs, especially the ones which are not removed by other removal mechanisms. Dordio *et al.* (2011) reported a 82% removal of carbamazepine by the macrophyte *Typha* spp. in a hydroponic solution with an initial concentration of 0.5 mg L^{-1}. Carbamazepine is known to be very persistent during RBF and thus phytodegradation might be the sole removal mechanism for this OMP, indicating the importance of this removal mechanism for certain OMPs.

Volatilization is the tendency of an OMP to move from the water phase into the air and is usually expressed by the Henry's law constant. The Henry's law constant is described by the following equation:

$k_H = p / c$

In which:

k_H	= Henry's law constant	[L · atm/mol]
p	= partial pressure	[atm]
c	= concentration of the dissolved gas	[mol/L]

A high Henry's law constant implies a high tendency of an OMP to move from the water phase into the air.

The extent of dilution with native ground water depends on site specific geo-hydrological conditions. De Vet *et al.* (2010) reported that dilution mainly occurs in the wells as opposed to the aquifer. Although dilution can lead to significantly lower OMP concentrations in the abstracted water, it cannot be regarded as a pure removal mechanism.

Sorption of OMPs onto soil matrices was found to be an important removal mechanism for a number of pharmaceuticals (e.g. ofloxacin, propranolol, diclofenac), pesticides (e.g. oxyfluorfen) and hormones (e.g. progesterone) (Drillia *et al.*, 2005, Hall *et al.*, 2015, Sangster *et al.*, 2015). In general, two types of adsorption can be distinguished: physical and chemical adsorption (Bailey *et al.*, 1964). Physical adsorption is the adsorption of an OMP to soil by means of Van der Waals forces as a result of interactions such as: orientation or dipole-dipole, polarization or induced dipole, dispersion, and ion-dipole in addition to Born repulsion (Bailey *et al.*, 1964). Chemical adsorption is the adsorption of an OMP to the adsorbent (soil constituents) as a result of covalent bonding (Bailey *et al.*, 1964).

OMP sorption in soil is usually indicated by the soil sorption coefficient K_d which is defined by Eq .1.

$$K_D = \frac{C_S}{C_w} \qquad \text{Eq.1}$$

In which:

K_D	=	soil sorption coefficient	[mL/kg]
C_S	=	concentration of the OMP in the soil phase	[µg/kg]
C_W	=	concentration of the OMP in the water phase	[µg/mL]

A high K_D values indicates strong sorption of the OMP to the soil constituents, while a low K_D indicates weak sorption of the OMP to the soil constituents.

Based on the soil sorption coefficient, a retardation factor the OMP can be determined using Eq. 2.

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad \text{Eq.2}$$

In which:

R	=	retardation factor	[-]
ρ_b	=	soil bulk density	[kg m^{-3}]
K_d	=	distribution coefficient	[kg^{-1} m^3]
θ	=	volumetric water content	[m^3 m^{-3}]

The higher the retardation factor, the more strongly an OMP is sorbed to the soil and retarded with respect to the ground water velocity. If an OMP does not sorb onto the soil (or only very weakly), the retardation factor is equal or close to 1.

Microbial degradation is the breakdown of OMPs facilitated by the soil microbial population and was proven an important removal mechanism for OMP removal during soil passage in many studies (Bertelkamp *et al.*, 2014, Maeng *et al.*, 2011a). Microbial degradation does not necessarily mean complete mineralization since it is often defined as loss of the parent compound.

As described by Grady (1985), an OMP can be biodegraded if the following pre-requisites are met: (1) an organism should be present that is capable of degrading the OMP, (2) it should be possible to synthesize the required enzymes and (3) the appropriate environmental conditions should be present to enable the degradation of an OMP at a significant rate. Persistence of an OMP is difficult to prove since it is often the result of inappropriate experimental conditions (Grady, 1985).

Although a number of mechanisms contribute to the overall removal of OMPs as discussed in the previous sections, some processes will play a more important role than others. Photolysis of OMPs was reported to be limited to the first few mm in the soil (Frank *et al.*, 2002, Hebert *et al.*, 1990), thus OMP removal as a result of photodegradation is expected to be small in RBF. McCutcheon *et al.* (2003) showed that for a number of OMPs (carbontetrachloride, hexachloroethane, tetrachloroethylene, triaminotoluent and benzonitrile) half-lives for the hydrolysis reaction were in the order of years, while half-lives for the phyto- and microbial transformation ranged from hours to days. This implies that phyto- and microbial transformation will play a more important role in OMP removal during RBF than hydrolysis. However, since the rizosphere is usually limited to the river bank/initial infiltration phase, phytodegradation can thus only contribute to a small extent to OMP removal in the RBF process. Moreover, OMP losses due to volatilization were reported to be generally negligible (Gavrilescu, 2005, Verstraeten *et al.*, 2003). A large number of studies indicated that sorption and biodegradation were the two main removal mechanisms during soil passage for most OMPs (Gavrilescu, 2005, Hiscock *et al.*, 2002, Hoppe-Jones *et al.*, 2012, Maeng *et al.*, 2011a, Maeng *et al.*, 2011b, Surampalli *et al.*, 2004). Therefore, the remainder of this review will focus on these two removal mechanisms.

1.4 Other biological treatment processes

Besides MAR systems, other biological treatment processes, such as: activated sludge (AS), membrane bioreactors (MBR), bioremediation, biological activated carbon and slow sand filters, have been reported to be capable of (partial) OMP removal (D'Alessio *et al.*, 2015a, Magan *et al.*, 2010, Radjenović

et al., 2009, Rattier *et al.*, 2014). However, process parameters (e.g. residence time, redox conditions, feed water quality (e.g. BDOC concentration and composition), biomass quantity, initial OMP concentration) that were demonstrated to affect OMP removal (Li *et al.*, 2014, Storck *et al.*, 2012), can significantly differ between these processes and RBF (Table 1). Hence, results obtained from other biological treatment processes cannot be easily translated to RBF. However, underlying mechanisms facilitating OMP removal might be comparable and in addition results obtained from other biological treatment process might improve our understanding of OMP removal during RBF. Therefore, this review will refer to studies that investigated other biological treatment processes wherever possible or useful and will indicate major differences.

1.5 Objectives

To enable the development of a predictive model for OMP removal during RBF, more insight is required in the factors influencing the two main OMP removal mechanisms and how these two mechanisms are related to each other.

The objective of this review paper is to: (1) identify the key soil, OMP, and water quality parameters influencing OMP sorption and biodegradation, (2) present currently available QSAR models for OMP sorption and biodegradation, (3) identify knowledge gaps that need to be addressed before a predictive model for OMP removal during RBF can be developed, and (4) formulate research questions to fill these knowledge gaps.

Table 1 - Biological treatment processes and their main differences in process parameters (residence time, redox condition, feed water quality and biomass quantity)

Process	Residence time	Redox condition	Feed water quality	Biomass quantity	Initial OMP concentration
Activated sludge	days	O_2,NO_3^-	Raw wastewater	High	ng/L - µg/L
Membrane bioreactor	days	O_2, NO_3^-	Raw wastewater	High	ng/L - µg/L
Bioremediation	years	O_2, NO_3^-, Fe(III), Mn(IV), SO_4^{2-}, CO_2	Groundwater		mg/L
Biological activated carbon	minutes	O_2	Treated groundwater, surface water or wastewater	Low	ng/L - µg/L
Slow sand filters	hours	O_2, NO_3^-	Treated groundwater, surface water or wastewater	Low	ng/L - µg/L
River bank filtration	weeks - years	O_2, NO_3^-, Fe(III), Mn(IV), SO_4^{2-}	Surface water		ng/L - µg/L

2 Adsorption during RBF

2.1 Highly loaded versus lowly loaded systems

Sorption onto sludge in wastewater treatment processes was demonstrated to be an important removal mechanism for a number of OMPs such as mefenamic acid, propranolol, loratidine, amitriptyline, fluoxetine, triclosan and triclocarban in biological wastewater treatment processes (Hyland *et al.*, 2012, Radjenović *et al.*, 2009). If a compound is recalcitrant towards biodegradation, it is possible that sorption is even the only removal mechanism.

Since OMP sorption onto sludge (biomass) was found to play an important role for some OMPs, it is expected that OMP sorption onto biomass for some OMPs could also be an essential removal mechanism in the RBF process. In natural systems such as MAR, biofilms will develop which could also affect OMP sorption. (Soil) bacteria excrete extracellular polymeric substances (EPS) which create a biofilm in the soil that (partly) covers the soil grains (Flemming, 1995). Since the biofilm can cover the soil grain, a new larger surface area will develop. This newly developed surface area could potentially 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.

2.2 Factors affecting OMP sorption

OMP sorption during soil passage is affected by three categories of parameters: (1) soil properties (e.g. specific surface area, organic carbon content), (2) water quality parameters (e.g. pH, temperature, biodegradable dissolved organic carbon (BDOC)) and (3) solute properties (e.g. hydrophobicity, charge).

2.2.1 Soil parameter affecting sorption

Several batch studies demonstrated that soil properties such as organic carbon content, Cationic Exchange Capacity (CEC), pH and/or composition (e.g. amount of clay, silt, sand) affect OMP sorption (Fingler *et al.*, 2004, Hiller *et al.*, 2009, Hiller *et al.*, 2012). In general sorption increases for an increase in organic carbon content of the soil (Gao *et al.*, 2014, Milinovic *et al.*, 2015), at least for nonpolar OMPs (Delle Site, 2001).

Similarly, if the soil consist of a larger amount of fines, the specific surface area will be larger and this could positively influence OMP sorption. However, Sangster *et al.* (2015) concluded that the effect of the soil organic carbon content on OMP sorption was larger comparted to particle size for steroid hormones. While CEC can directly affect the sorption of charged compounds (Calvet, 1989), pH determines the charge of ionisable OMPs and can thereby potentially affect their sorption behaviour. Sorption of triazines which are weakly bases was reported to decrease for increasing pH (Gao *et al.*, 1998). This was explained by the fact that for a higher pH, the fraction of cationic species present in solution is smaller resulting in less sorption. All of these parameters as well as the solute properties, could explain the often contradictory results observed with different effects reported for different OMPs (Bedmar *et al.*, 2011, Fingler *et al.*, 2004, Hiller *et al.*, 2009, Hiller *et al.*, 2012, Zhang *et al.*, 2011)

OMP sorption is expected to be higher in activated sludge/MBR processes since both organic carbon content and biomass quantity are higher compared to RBF and these factors were positively correlated

with OMP sorption. However, the residence time in RBF systems is much higher which could make up for the lower organic carbon content and biomass quantity.

2.2.2 Feed water parameters affecting sorption

An increase in Dissolved Organic Carbon (DOC) present in the aqueous phase can either decrease sorption of OMPs (e.g. DDT, atrazine, triadimenol, fluroxypyr, anilazine, terbutylazine, and bifenox) or have no effect (e.g. lindane) (Caron *et al.*, 1985). In general, an increase in temperature, results in a decrease in OMP sorption (Delle Site, 2001). The effect of pH has been discussed in "2.2.1 Soil parameters affecting sorption".

2.2.3 Solute parameters affecting sorption

Solute properties that can affect OMP sorption are: hydrophobicity, charge and solubility. Hydrophobicity of neutral OMPs is expressed by Log K_{ow}, while for charged OMPs this is Log D (in which the effect of charge is accounted for). Hydrophobic OMPs will sorb more easily to the soil, than their hydrophilic counterparts. For charged OMPs ion-exchange interactions could also play an important role (Calvet, 1989). Soil constituents such as clay have a negative charge and could therefore interact with charged OMPs. Similarly, the biofilm in the soil consists of functional groups with different charges that could play a role in the sorption of charged OMPs (Flemming, 1995). On the other hand, solubility of an OMP describes its tendency to be present in the aqueous phase. OMPs with high solubility prefer to be present in the aqueous phase rather than the solid phase and therefore sorption onto soil constituents is less likely.

2.3 Existing OMP sorption models

Doucette (2003) wrote an excellent review on the many existing QSAR models for OMP sorption onto soil and concluded that these models can be divided in roughly two categories: (1) QSAR sorption models based on the hydrophobicity or solubility of the OMP and (2) QSAR sorption models based on molecular connectivity indices. Predictive models for OMP sorption onto soil are usually limited to a specific class or property of OMPs (e.g. hydrophobic, non-hydrophobic, carbamates, PAHs, chlorinated hydrocarbons) (Chiou *et al.*, 1983, Gerstl, 1990, Sabljić *et al.*, 1995) and models developed for a wide variety of OMPs are more scarce (Baker *et al.*, 1997, Gerstl, 1990). In contrast to the models based on molecular connectivity indices, those based on hydrophobicity and solubility are easy to use since these properties are widely available. However, their disadvantage is that they are generally less predictable for the more polar OMPs.

2.4 Knowledge gaps

In order to develop a predictive model for OMP removal during RBF, the first step is to assess if both sorption and biodegradation contribute to the same extent towards OMP removal or if one of these removal mechanisms is more dominant than the other. While adsorption plays an important role for some specific OMPs, it is unclear if sorption is equally contributing to overall OMP removal for the majority of the OMPs. Besides, it remains uncertain if sorption is a pre-requisite in both intra- and extracellular OMP degradation.

In addition, adsorption can also significantly influence OMP biodegradation, since OMPs need to be available in the aqueous phase before biodegradation can occur (Ou, 1998). Strongly sorbed OMPs are therefore less bioavailable and thus less susceptible to biodegradation. However, it remains unclear if sorption is a pre-requisite for biodegradation.

Biosorption (OMP sorption onto sludge) was found to be an important factor for OMP removal in biological wastewater treatment processes. 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 *et al.*, 2012) or OMP sorption onto the sand medium (Maeng *et al.*, 2011a, Maeng *et al.*, 2011b). 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 *et al.*, 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 combination of these factors on OMP sorption has not been investigated. Furthermore, since a number of sorption studies are performed with tap water, the effect of the water matrix on OMP sorption should be established to gain insight into how transferable these results are to field conditions

Likewise, a number of studies used silica sand as filter medium in the columns (Maeng *et al.*, 2011a, Rauch-Williams *et al.*, 2010), which excludes the effect of soil properties (e.g. clay content) on OMP sorption. Thus, currently, the effect of the solid phase on OMP sorption is unknown.

An overview of the research questions deduced from these knowledge gaps is presented in section 4.

3 OMP biodegradation during RBF

Microbial degradation in the soil is facilitated by the soil microbial community and the enzymes they synthesize, both of which can vary as a result of prevailing redox condition. First the differences in microbial degradation between highly loaded and lowly loaded systems is discussed. Subsequently, the role of redox environment and soil microbial population is considered and this section concludes with considering the different parameters affecting OMP biodegradation. Roughly three categories of parameters can be distinguished that affect OMP biodegradation: (1) soil properties (e.g. pH, cationic exchange capacity, organic carbon content), (2) water quality parameters (e.g. temperature, biodegradable dissolved organic carbon (BDOC)) and (3) solute properties (e.g. hydrophobicity, charge, molecular weight).

3.1 Highly loaded versus lowly loaded systems

River bank filtration is distinctly different from other biological processes such as conventional activated sludge systems and membrane bioreactors in a number of aspects including: initial OMP concentration in the feed, prevailing redox condition, biodegradable dissolved organic carbon quantity and composition (Table 1). All these parameters were demonstrated to affect OMP biodegradation (Baumgarten *et al.*, 2011, Li *et al.*, 2014, Storck *et al.*, 2012)

Since treated wastewater is discharged on the river, significant dilution of OMPs can be expected. However, other pathways such as agricultural run-off (e.g. pesticides, veterinary pharmaceuticals) and leaching could result in higher concentrations of these OMPs in the river water. Therefore the initial OMP concentration in RBF is expected to be more or less in a similar range to conventional

activated sludge (CAS)/MBR. In contrast, initial OMP concentrations in bioremediation technologies used to clean-up polluted aquifers/sites (through the use soil bacteria) deal with significantly higher initial pollutant concentrations (mg/L) compared to the RBF process (EPA, 1995).

CAS and MBR in general receive raw wastewater which is still high in the amount of biodegradable organic carbon. Total Organic Carbon (TOC) removals of 60 - 99% have been reported (Nguyen *et al.*, 2012, Radjenovic *et al.*, 2007). In contrast, TOC removal in RBF systems is somewhat lower ranging from 35 -67% (Grünheid *et al.*, 2005, Hoppe-Jones *et al.*, 2010, Ludwig *et al.*, 1997). Recent studies reported that OMP removal improved for more humic like (refractory) substrate (Alidina *et al.*, 2014b, Li *et al.*, 2014). Since biodegradability of the organic carbon in river water can be expected to be lower compared to organic carbon in the wastewater entering CAS/MBR, OMP removal will most likely be higher in the RBF process compared to the CAS/MBR processes.

The major difference between CAS/MBR and RBF, however, is the prevailing redox environment. While redox conditions in CAS or MBR are usually limited to oxic and/or NO_3 reducing conditions (Nguyen *et al.*, 2012, Radjenovic *et al.*, 2007, Tadkaew *et al.*, 2010), redox in RBF systems can range from oxic, to NO_3, and Fe(III)-, Mn(IV)-and possibly even SO_4-reducing conditions.

3.2 Redox-controlled degradation

A number of studies identified redox condition as a crucial factor in OMP removal during RBF (Regnery *et al.*, 2015b, Schmidt *et al.*, 2007, Storck *et al.*, 2012). RBF sites are characterized by different redox environments which are created by oxidation-reduction reactions catalysed by the enzymes of soil micro-organisms (MOs). The most important electron donor in soil is organic carbon, although other electron donors are present (e.g. Mn^{2+}, Fe^{2+}, S^{2-}, CH_4, and H_2) as well (DeLaune *et al.*, 2005). Thus, the organic carbon present in the river water and the prevailing redox conditions in the soil system are closely connected.

Soil MOs oxidize soil organic carbon and simultaneously reduce oxygen (or another electron acceptor). The electron that is obtained by oxidizing carbon is used to reduce oxygen. While river water contains a large amount of dissolved oxygen, this is rapidly depleted by soil MOs during the initial infiltration phase. In the absence of oxygen other electron acceptors found in soil such as: NO_3, Mn(IV), Fe(III), SO_4 and CO_2 can be used. The electron acceptors are used in this specific order since MOs obtain the most energy from the reduction of oxygen and the least amount of energy from the reduction of CO_2. The succession of election acceptors for oxidation-reduction reactions in soil is presented in Figure 2.

Different redox conditions are characterised by specific redox potentials. McBride (1994) demonstrated that oxic conditions are characterised by a redox potential between 350 – 600 mV, nitrate reducing conditions between 200 and 400 mV, manganese reducing conditions between -50 and 300 mV and iron reducing conditions between -100 and 100 mV; sulphate reducing conditions and methanogenesis are characterised by redox potentials of -150 mV or lower.

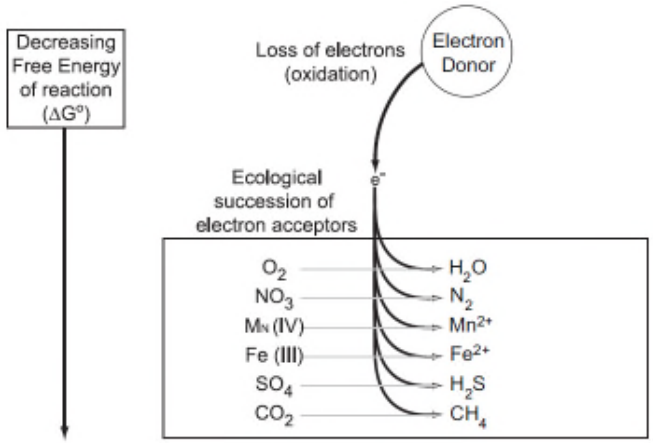

Figure 2 – Succession of electron acceptors in soil aquifer (adapted from (McMahon *et al.*, 2008))

DOC removal is faster under oxic conditions compared to anoxic/anaerobic conditions (Abel *et al.*, 2012, Baumgarten *et al.*, 2011, Grünheid *et al.*, 2005, Maeng *et al.*, 2012), but this statement is not generally applicable to OMPs. While OMPs such as clofibric acid, dichlorprop, mecoprop, phenazone-type pharmaceuticals, 1,7-NSA, 2,7-NSA and NDMA are removed better under oxic conditions compared to anoxic conditions, the opposite is observed for X-ray contrast media and sulfamethoxazole (Baumgarten *et al.*, 2011, Grünheid *et al.*, 2005, Hoppe-Jones *et al.*, 2012, Maeng *et al.*, 2011c, Patterson *et al.*, 2012). This redox dependent behaviour of certain OMPs underpins the importance of assessing the effect of (separate) redox conditions on OMP removal during RBF.

Studies investigating the effect of redox on OMP removal during RBF are scarce and terms as "anoxic" and "anaerobic" are often not well defined which makes it extremely difficult to compare results between different studies. A better approach would be to determine OMP removal under different redox conditions for the specific electron acceptor, thus nitrate reducing conditions, or iron/manganese reducing conditions or to measure the redox potential during an experiment.

Some field studies on OMP removal during RBF have tried to assess OMP removal for different redox zones. Although field studies are very useful in validating lab-scale experimental results, it is a daunting task to assess OMP removal for different redox zones since redox conditions in the field are difficult to separate and subject to seasonal variations. Assessing the effect of redox on OMP removal can therefore be better investigated in controlled laboratory column systems which makes it easier to control and separate various redox conditions.

Most soil column studies investigating anoxic/anaerobic conditions in soil systems (both soil aquifer treatment and river bank filtration) deplete the oxygen present in the feed water by purging it with nitrogen gas or adding ethanol/starch (Abel *et al.*, 2012, Baumgarten *et al.*, 2011, Hoppe-Jones *et al.*, 2012, Maeng *et al.*, 2012, Patterson *et al.*, 2011). These artificially created reduced conditions do not adequately represent real reduced environments as found in the field. Since many studies reported that easily degradable organic carbon (BDOC) is removed already for the largest part in the initial infiltration phase, it is obvious that oxic water made anoxic by purging with N_2 gas is not adequately simulating a real anoxic feed water since all BDOC is still present. Thus, it is questionable whether the developed microbial population in artificially reduced systems is representative of the microbial populations present under reduced conditions at a field site.

3.3 Soil microbial population

3.3.1 Metabolism versus co-metabolism

Metabolism is the degradation of an OMP in which the carbon and energy obtained from this reaction is used by the micro-organism for cell replication (growth). Co-metabolism is "the transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound" as defined by (Dalton *et al.*, 1982). Since the dissolved organic carbon (DOC) concentration is usually a few mg/L and OMPs are present in concentrations six orders of magnitude smaller (ng/L) in surface water, co-metabolic degradation of OMPs is the more likely mechanism as has been suggested in a number of studies (Alidina *et al.*, 2014a, Maeng *et al.*, 2011a, Rauch-Williams *et al.*, 2010). While metabolic degradation is often related to full mineralization of the OMP, co-metabolic degradation in general results in partial degradation or transformation of the OMP (Janke *et al.*, 1985).

Although co-metabolic OMP degradation has been suggested in a number of studies, the mechanism is often not explicitly proven. Proving the metabolic or co-metabolic degradation of OMPs is extremely difficult since OMPs are most likely degraded by bacterial consortia instead of one single species (Aislabie *et al.*, 1995, Dalton *et al.*, 1982, Grady, 1985). Therefore, it is possible that the first step in the degradation process is co-metabolic transformation performed by a one type of bacteria and a subsequent step is metabolically driven by another type of bacteria (Janke *et al.*, 1985). Thus, the degradation of a specific OMP could also be a combination of metabolic and co-metabolic processes. This further complicates the assessment of whether OMPs are degraded metabolically or co-metabolically.

Besides, different bacteria are capable of degrading one and the same OMP. Yu *et al.* (2007) identified 14 types of bacteria capable of 17ß-estradiol degradation in the activated sludge of a wastewater treatment plant (WWTP). Since the strains showed differences in degradation behaviour of the transformation product estrone (only 3 strains could degrade estrone), it was hypothesized that some strains were more likely involved in the metabolic degradation of 17ß-estradiol, while other strains are possibly linked to co-metabolic degradation. Thus, even for one and the same OMP, different bacteria could show different metabolic capabilities. The fact that multiple bacteria are capable of degrading 17ß-estradiol could explain the large differences in OMP removal observed between different treatment processes as suggested by (Yu *et al.*, 2007). Since different bacteria have different metabolic capacities with respect to OMP degradation and not all species are present in the same composition for a specific treatment process this could result in different OMP removal.

Another factor determining metabolic/co-metabolic OMP degradation is the class of bacteria involved (e.g. heterotrophic, autotrophic). Heterotrophic bacteria use organic substrate, while autotrophic bacteria use inorganic substrate for cell growth. As reported by Tran *et al.* (2013) and Ou (1998), ammonia oxidizing bacteria (AOB) degrade OMPs most likely only by co-metabolism since the substrate used is always ammonia, while heterotrophic bacteria could theoretically degrade OMPs both by metabolism and co-metabolism.

3.3.2 Microbial community composition

A study of Janssen (2006) described the most abundant phyla of soil bacteria and their average contribution to the overall soil microbial community: proteobacteria (39%, 10-77%), acidobacteria (20%, 5-46%), actinobacteria (13%, 0-34%), verrucomicrobia (7%, 0-21%), bacteroidetes (5%, 0-18%),

chloroflexi (3%, 0-16%), planctomycetes (2%, 0-8%), gemmatimonadetes (2%, 0-4%), and firmicutes (2%, 0-8%).

Information on the composition of the soil microbial population in RBF systems (or MAR technologies in general) is scarce. Medihala *et al.* (2012) examined the soil microbial community composition of a river bank in relation to well clogging and found Fe-oxidizing bacteria (*Rhodobacter spp.*), S-oxidising bacteria (*Sulfuricurvum spp.*), NO_3-reducing bacteria (*Acidovorax spp.*), Fe(III)-reducing bacteria (*Ferribacterium*), and SO_4-reducing bacteria (*Desulfobrio sp.*). Recently, a study of Alidina *et al.* (2014a) investigated the microbial community composition from soil in a laboratory soil column fed with synthetic wastewater (simulating the SAT process). Major phyla of bacteria were the (*γ-, δ-, ß-, α-*) *proteobacteria, firmicutes, bacteroidetes, actinobacteria* and *acidobacteria*. Similarly, Onesios-Barry *et al.* (2014) identified *proteobacteria, bacteriodetes, actinobacteria* and *firmicutes* as major phyla present in a soil column simulating a SAT site and in soil samples obtained from the SAT field site. However, these studies were unable to link specific phyla or species of bacteria responsible for the degradation of certain OMPs.

Studies exploring the role of bacterial species in OMP degradation are very limited for specifically the RBF process. However, numerous studies have focused on identifying bacteria responsible for OMP degradation in pure cultures. A number of studies showed that both *proteobacteria* and *actinobacteria* are involved in the aerobic degradation of nitrobenzoates, nitrotoluene, polycyclic aromatic hydrocarbons (PAHs) (Bamforth *et al.*, 2005, Ye *et al.*, 2004). Toluene, benzoate, bezaldehyde, benzylacohol, *p*-hydroxybenzoate, *p*-hydroxybenzaldehyde, *p*-hydroxybenzylalcohol, phenol, and *p*-cresol were degraded by a Fe-reducing bacterial strain belonging to the phylum *proteobacteria*. A sulfate-reducing bacterial strain belonging to the *proteobacteria* was reported to degrade 2,4,6-trinitrotoluene (TNT) (Boopathy *et al.*, 1998). Polychlorinated biphenyls (PCBs) were anaerobically degraded by the phylum *firmicutes*, while the phylum *chloroflexi* was responsible for the anaerobic degradation of dioxins (Bunge *et al.*, 2003, Wiegel *et al.*, 1999). The list of bacteria degrading specific OMPs is exhaustive and this review does not attempt to give a comprehensive overview of these bacteria. However, it is tried to convey that the bacterial phyla identified in the previous mentioned RBF and SAT studies possess bacterial strains that are capable of degrading certain OMPs. Nevertheless, it is unclear which bacterial strains will be present in the RBF process and how these are linked to the degradation of specific OMPs.

Moreover, a number of studies concluded that Ammonia Oxidizing Bacteria (AOBs) are an important class of autotrophic bacteria involved in the degradation of OMPs. The nitrification process describes the conversion of ammonia to nitrite performed by AOBs and the subsequent nitrite conversion to nitrate facilitated by Nitrate Oxidising Bacteria (NOBs). The removal of atenolol, 17*α*-ethinylestradiol (EE2) and halogenated hydrocarbon fumigants (methyl bromide, 1,2-dichloropropane, and 1,2-dibromo-3-chloropropane) was reported to be facilitated by AOBs present in processes such as activated sludge systems, fixed bed reactors, and MBRs. As described by Zhang *et al.* (2010) ammonia in the soil can be present as a result of organic carbon degradation and it can thus be expected that AOBs play an important role in OMP removal during RBF as well. However, the role of AOBs in the removal of OMPs during RBF is not yet unveiled, making it an interesting topic for future research.

Redox conditions were found to be an important factor influencing the soil microbial population. Röling *et al.* (2001) made an attempt to correlate microbial community structure to prevailing redox

condition in landfill leachate-polluted aquifer. ß-*proteobacteria* were the dominant species in a sample obtained from the nitrate reducing zone. Two samples obtained from beneath the landfill and downstream of the landfill (both iron(III) reducing conditions) showed differences with respect to abundant bacterial species. The sample taken beneath the landfill was dominated by low-G+C-content gram positive group and high-G+C-content gram positive group bacteria, while the sample taken downstream of the landfill was abundant in ß- and γ-*proteobacteria*. Thus, shifts in the soil microbial community structure as a result of changing redox conditions can be expected.

3.3.3 Role of enzymes

Soil enzymes play an important role in the degradation of OMPs, since they catalyse the oxidation-reduction reactions involved in OMP degradation. Soil enzymes can be divided in two categories: intracellular and extracellular enzymes. OMPs that need to be degraded should fit on the active site of the enzyme before the product can be taken into cell for further degradation. However, some OMPs might be too large to penetrate through the cell. In this case, extracellular enzymes will break down the OMP in smaller pieces which can pass through the cell membrane. An example of OMPs that are too large to penetrate directly into the bacterial cell, and thus need to be broken down in smaller pieces first by extracellular enzymes, are PAHs and PCBs (Burns *et al.*, 2010). The separate contributions of intra- and extracellular enzymes towards OMP biodegradation are currently unclear. In general, soil enzymes constitute of roughly 6 classes: oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases. A number of oxidoreductases (e.g. cytochrome P_{450}, dioxygenase), transferases (e.g. glutathione S-transferase), and hydrolases (e.g. esterases) were reported to be involved in the degradation of OMPs such as PAHs, polyester polyurethane (Bamforth *et al.*, 2005, Cavalca *et al.*, 2007, Kay *et al.*, 1993). These results are just an indication of which enzymes are possibly involved in OMP degradation and by no means try to cover the exhaustive list of studies that investigated this aspect.

Although it would be possible to determine the types of enzymes present at RBF sites, there are a few important aspects to consider: (1) at the moment it is unknown which enzymes are present in RBF systems and most likely it is also impossible to determine all of them, (2) it is unknown how the presence and distribution of enzymes in RBF systems is affected by factors such as DOC composition/concentration of the river water, spatial/temporal variability, prevailing redox conditions and the presence of OMPs, (3) even if the types of enzymes present in the RBF process are known, it is difficult to determine which enzymes are responsible for the degradation of a specific OMP since this is usually a combination of the enzymes provided by the microbial consortium.

An extensive study on the types of soil bacteria and enzymes present in the soil will definitely provide more insight in the degradation of OMPs. However, it will be challenging and potentially impossible to engineer RBF systems with respect to the soil microbial population and the enzymes they synthesize.

3.3.4 Adaptation

OMPs are degraded by the soil microbial community, but if a new (unfamiliar) OMP is detected in the river, the soil microbial population might not be capable of instantly degrading the compound. Newly detected OMPs sometimes require a certain adaptation time (or lag-phase) before degradation is initiated. This adaptation time has been reported for a number of OMPs such as sulfamethoxazole, naproxen, gemfibrozil, clofibric acid, bisphenol A, 17β-estradiol, isononylphenole, bisphenol F,

trimethoprim, bezafibrate, and iohexol in MAR and RBF systems (Baumgarten *et al.*, 2011, Hoppe-Jones *et al.*, 2012, Lim *et al.*, 2008, Patterson *et al.*, 2011, Storck *et al.*, 2012).

Spain *et al.* (1980, 1983) identified three mechanisms by which the soil microbial community can adapt to a new OMP: (1) genetic changes, (2) enzyme induction and (3) population changes (Spain *et al.*, 1980, Spain *et al.*, 1983). Genetic changes as a result of gene transfer or mutations can result in bacteria capable of degrading certain OMPs. Secondly, the presence of specific OMPs can initiate the expression of enzymes appropriate to degrade OMPs. Thirdly, the number of bacteria capable of degrading a particular OMP can be minimal at initial exposure, but can increase when subjected to the OMP.

Recently, a study of (Alidina *et al.*, 2014a) concluded that adaptation of the soil microbial community towards OMPs is not necessary if the soil microbial community is adapted to the primary substrate in the feed. However, it is possible that bacteria (and thus the enzymes) required for degradation of the investigated OMPs (bisphenol A, carbamazepine, gemfibrozil, ibuprofen, methylparaben, oxybenzone, sulfamethoxazole and triclocarban) were already present in the aquifer material used to fill the columns. Another explanation could be that these OMPs have similar structures to the natural substrates used by the soil microbial population present in the column. Since the study was limited to only 8 OMPs, it cannot be concluded that adaptation will not occur for any of OMPs encountered in the environment.

Results on adaptation behaviour of OMPs are thus inconclusive. The main difference between the studies that observed adapting behaviour and the one not, is the feed water quality. Adaptive behaviour was observed in studies using natural waters, while the study of Alidina et al. (2014a) used synthetic water. It could be hypothesized that the adaptation observed in the studies using natural water, was caused by the presence of already low concentrations of these OMPs in the natural water (in the order of low ng/L). When higher OMP concentrations are spiked in the laboratory, but the number of bacteria capable of degrading this OMP is still limited, an increase in this/these specific type(s) of bacteria is expected and thus a lag-phase could be observed.

The adaptation of OMPs is also an important aspect with respect to the development of a predictive model for OMP removal during RBF. The question arises if a predictive model should incorporate the immediate (unadapted) OMP degradation rate or the adapted OMP degradation rate and how different these predictive models will be. First, more insight is required in the adaptation behaviour of a large mixture of OMPs for RBF systems to investigate if similarities in physico-chemical properties and/or functional groups can be found for OMPs characterised by an adaptation time. Once we are able to better explain why certain OMPs require an adaptation time, while others show instant degradation, a decision on whether or not and how to incorporate adaptation behaviour in predictive models can be made.

3.4 Factors affecting OMP biodegradation

3.4.1 Soil properties affecting biodegradation

Soil properties such as pH, texture/grain size distribution, water content, Cationic Exchange Capacity (CEC), nutrient availability, and organic carbon content can all influence OMP biodegradation (Fingler *et al.*, 2004, Hiller *et al.*, 2009, Hiller *et al.*, 2012, Picton *et al.*, 2004, Schroll *et al.*, 2006). These properties are site specific and therefore it can be expected that OMP removal at various RBF sites is different.

To gain more insight in the effect of certain soil properties on the microbial community composition, for each soil property the range of values prevailing at the RBF site was determined from several studied full-scale RBF sites. The results are presented in Table 2.

Table 2 – Soil properties and the range in which they are prevailing at RBF sites

Soil property	Full-scale RBF site	References
pH river water	7.4 – 8.5	(Benotti *et al.*, 2012, Bertelkamp *et al.*, 2015b, Henzler *et al.*, 2014, Shamrukh *et al.*, 2008, Stepien *et al.*, 2013)
pH well water	6.6 – 8.0	(Henzler *et al.*, 2014, Shamrukh *et al.*, 2008, Stepien *et al.*, 2013)
Organic carbon content [%]	0.01 – 0.1	(Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010, Regnery *et al.*, 2015a, Schwarzenbach *et al.*, 1983, Stepien *et al.*, 2013)
Temperature river water[°C]	0 – 31.5	(Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010, Lee *et al.*, 2009, Regnery *et al.*, 2015a, Schubert, 2002, Schwarzenbach *et al.*, 1983, Sheets *et al.*, 2002)
Temperature wells [°C]	2 - 30	(Grünheid *et al.*, 2005, Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010, Lee *et al.*, 2009, Regnery *et al.*, 2015a, Schwarzenbach *et al.*, 1983, Sheets *et al.*, 2002)
Sand [%]	94	(Regnery *et al.*, 2015a)

pH

A number of studies reported an increase in pesticide/fungicide/insecticide biodegradation for an increase in soil pH (more alkaline environments) (Awasthi *et al.*, 2000, Höllrigl-Rosta *et al.*, 1999, Singh *et al.*, 2003). Although an increase in soil pH seems to increase OMP biodegradation, the range of pH investigated in these studies was very broad (4.7 – 8.4). Soil pH for RBF sites usually ranges between 6.6 and 8.5 (Table 1) thus covering a much smaller range in pH near neutral conditions.

Awasthi *et al.* (2000) reported that for an increase in pH from 7.5 to 8.5, α-endosulfan removal increased with 2% and β-endosulfan removal decreased with 3%. Singh *et al.* (2003) reported identical half-lives ($t_{1/2}$ = 16 d) for chlorpyrifos for pH 7.7 and pH 8.4, while Karpouzas *et al.* (2000) demonstrated that the difference in residual ethoprophos between the soil sample with pH = 8.3 and pH = 6.8 was approximately 5-6% after 13 days. These results imply that for the pH range prevailing at RBF sites, the differences in OMP biodegradation rate or percentage removal as a result of pH variations are expected to be rather small.

Soil texture/grain size distribution

Soil texture/grain size distribution can affect the soil permeability and thus the water flow through the soil media as well as the space available for the soil microorganisms. Low permeability soils are characterised by a longer contact time between the OMPs and the soil phase which increases the chance of OMP sorption and/or biodegradation. High permeability soil on the other hand are characterized by shorter contact times which will reduce the chance of OMP sorption and biodegradation. Höllrigl-Rosta *et al.* (1999) investigated two soil types with different textures in a batch-study. Although the two soil types were similar in sand content, but different in silt and clay content, no difference in prochloraz mineralization was found. Since RBF sites require a certain permeability, sand will always be the largest fractions and extreme variations in the silt and clay are therefore not expected.

Water content
A number of studies investigated the effect of water content on OMP biodegradation. In general, OMP biodegradation rate increased for increasing water content of the soil (Chatterjee *et al.*, 2013, Karpouzas *et al.*, 2000, Wang *et al.*, 2014). This can be explained by the fact that OMPs need to be bioavailable to enable biodegradation. If the water content of the soil is high, OMPs can be transported through the medium by means of the water flow thus increasing their bioavailability.

Cationic exchange capacity
Cationic exchange capacity (CEC) is determined by the amount of clay and organic carbon in the soil, their correlation is presented in Eq.4 (Appelo *et al.*, 2005, Breeuwsma *et al.*, 1986):

$$CEC_{calc} = 7 \cdot (\% \text{ clay}) + 35 \cdot (\% \text{ C}) \qquad \text{(Eq. 4)}$$

In which:

CEC_{calc}	= calculated cationic exchange capacity	[meq / kg dry weight]
% clay	= clay content (fraction < 8 μm from grain size distribution)	[% dry weight]
% C	= organic carbon content	[% dry weight]

Soils characterised by a higher CEC are able to sorb more cationic OMPs, thereby reducing their bioavailability and degradation in the soil. In addition, soils with a high CEC are better able to retain nutrients (Ca^{2+}, Mg^{2+}, K^{+}, etc.) which can improve OMP biodegradation.

RBF soils are characterised by low organic carbon contents (0.01 – 1%) (Bertelkamp *et al.*, 2015a, Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010, Regnery *et al.*, 2015a, Schwarzenbach *et al.*, 1983, Stepien *et al.*, 2013) and low contributions of clay (0.5- 4%) (Bertelkamp *et al.*, 2015a). This is not surprising since RBF soils need a certain permeability and clay is impermeable. Thus extreme variations in cationic exchange capacity are not expected at RBF sites.

Organic carbon content
A higher organic carbon (OC) or organic matter (OM) content in soil can result in an increased sorption of OMPs, thereby decreasing the bioavailability of OMPs and thus biodegradation of these compounds. Although several studies showed that the soil with lowest organic carbon/matter resulted in the highest OMP biodegradation, a general trend between soil organic carbon/matter and OMP biodegradation could not be observed (Höllrigl-Rosta *et al.*, 1999, Karpouzas *et al.*, 2000). Karpouzas *et al.* (2000) investigated three soils (0.3% OM, 2.3% OM and 8.5% OM). The difference in residual ethoprophos after 13 days between the best (0.3% OM) and worst degrading soil type (2.3% OM) was approximately 12%. OM content typically found at RBF sites ranges from 0.01 – 0.1% (Table 2) which suggests that the differences in OMP biodegradation found at these sites as a result of variations in OM content will be small.

Extreme variations in the aforementioned parameters (pH, soil texture/grain size distribution, water content, cationic exchange capacity, and organic carbon content) between different RBF sites are not expected (Table 2). At the same time (Alidina *et al.*, 2014b) demonstrated that the soil microbial community composition in soil aquifer treatment systems was largely influenced by BDOC concentration and composition in the feed water (with the composition found to be even more important than concentration). Therefore it was hypothesized that different RBF soil types fed by a similar water quality (and thus BDOC concentration and composition) will lead to similar microbial community compositions and thus OMP retardation factors and biodegradation rates. This would

imply that RBF sites located along the same river may show similar OMP removal (in case of similar water quality and redox configuration) and one predictive model can be used for both sites.

3.4.2 Feed water parameters affecting biodegradation

Since the aqueous phase is expected to play a more important role compared to the solid phase, the effect of aqueous phase parameters (pH, nutrients (carbon, nitrogen and phosphorus), OMP concentration, temperature) on OMP removal needs to be investigated.

pH

River water pH can affect the charge of the OMPs which could possibly affect OMP biodegradation. However, pH variations in river water bodies do not show large variations (Table 2) and are usually near neutral conditions. As hypothesized for soil pH, the small changes in river water pH are not expected to greatly affect OMP biodegradation.

Temperature

Several studies investigated the effect of temperature on OMP biodegradation (Chatterjee *et al.*, 2013, Grünheid *et al.*, 2008, Northcott *et al.*, 2014a). In general, OMP removal increased for an increasing temperature (Chatterjee *et al.*, 2013, D'Alessio *et al.*, 2015b, Karpouzas *et al.*, 2000, Northcott *et al.*, 2014b, Regnery *et al.*, 2015a, Wang *et al.*, 2014). An increase in temperature in the range from 5°C to 25°C resulted in a decrease in OMP half-life by a factor of ~2 – 4.5 for batch experiments (Chatterjee *et al.*, 2013, Northcott *et al.*, 2014b). River water temperature can fluctuate between 0 and about 30°C (Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010, Lee *et al.*, 2009, Regnery *et al.*, 2015a, Schubert, 2002, Schwarzenbach *et al.*, 1983, Sheets *et al.*, 2002), but this effect is dampened by RBF (Gruenheid *et al.*, 2008, Schoenheinz *et al.*, 2011). As described by Schoenheinz *et al.* (2011) the temperature fluctuation of approximately 25°C in the river is already reduced to 13°C in a well located 60 m from the river. A further reduction in temperature fluctuation to 5°C and 4°C is obtained in wells located 120 m and 250 m from the river, respectively. This was also supported by a study of Grünheid *et al.* (2008) that showed a temperature variation of 7°C in a well located about 90 m from the river (residence time 3.9 Months).

While a temperature fluctuation of 30°C in the river seems valid, for RBF the fluctuations are smaller and in the range of 5 - 10°C in the first part of the aquifer and even smaller 1-2°C in the deeper part of the aquifer. Temperature will play a more important role in the initial infiltration phase (first few metres) compared to the deeper parts of the aquifer. Thus the differences in OMP half-life for the deeper parts of the aquifer as a result of temperature variations are expected to be significantly smaller than the factor 2 – 4.5 previously mentioned. This reasoning is supported by a study of (Alidina *et al.*, 2015) who reported no significant change in OMP removal for a temperature variability in the range of 4 – 30 °C for most OMPs in a managed aquifer recharge (MAR) system. Exceptions were the OMPs that showed moderate biodegradability (diclofenac, gemfibrozil, ketoprofen, naproxen, oxybenzone, and trimethoprim).

Although temperature does not seem to have a large effect on OMP removal (biodegradation) during MAR and likely RBF, a rise in temperature in the initial infiltration phase can lead to increased activity and thus oxygen consumption of the microbial population which can result in a different configuration of the prevailing redox conditions (Burke *et al.*, 2014). In this respect, temperature will have a significant influence on OMP degradation, but this aspect will be discussed in more detail in section 5.6.

OMP concentration

An increase in spiked OMP influent concentration (factor 14 -18) resulted in a higher biodegradation rate and a decrease in lag-phase (adaptation time), at least for the degradable OMPs (Baumgarten *et al.*, 2011, Storck *et al.*, 2012). As reported by Storck *et al.* (2012) more persistent OMPs did not show (or only minor) differences in biodegradation potential and lag-phase for an increase in spiked OMP influent concentration. This underpins the importance of dosing OMPs in concentrations similar to those detected in river waters (ng/L - μg/L) when determining their fate in soil column systems simulating the RBF process. Dosing higher OMP concentrations than present in the river will lead a severe underestimation regarding the time necessary to remove these compounds during RBF.

Nutrients (micro- and macro)

Nutrients such as carbon, nitrogen and phosphorus enter the soil via the river water and are indispensable for microbial degradation. The effect of CEC on nutrient retention in soil was already mentioned in section 3.4.1. Lewis *et al.* (1986) investigated the effect of nutrient limitation on the lag phase for *p*-cresol removal and concluded that lag-phases decreased in case samples that received additional nitrogen and phosphorus. Since river water is subject to variations in nutrients, a (temporarily) limitation cannot always be prevented. A possible solution is the enrichment of soils with nutrients (e.g. nitrogen and phosphorus) to enhance OMP biodegradation. This process is known as bioremediation, but falls outside the scope of this study.

BDOC concentration and composition

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.*, 2011a, Maeng *et al.*, 2012, Onesios *et al.*, 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.*, 2014a, 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. Shonnard *et al.* (2007) 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.

3.4.3 Solute parameters affecting biodegradation

Physico-chemical properties

Enzymes have an active site in which the substrate should be captured for a reaction to occur. Thus, OMP properties such as shape and charge as well as the configuration of the functional groups of the OMP are important for reaction with the enzyme. For intracellular enzymes it is important that the OMP can penetrate through the cell membrane to reach the enzyme. Solute properties such as: hydrophobicity, molecular weight, and charge are therefore important.

Paris *et al.* (1984) demonstrated good correlation between biodegradation rate and the octanol-water partition coefficient Log K_{ow} for 2,4-D esters (R^2 = 0.94), while this correlation was weaker for the chloro-ring-substituted phenoxyacetic ethyl esters (R^2 = 0.47). A correlation between hydrophobicity (Log K_{ow}) and degradation rate could be expected since hydrophobicity determines movement through the cell membrane prior to degradation. An explanation given in this study for the difference in correlation between the two groups of compounds was that the movement of OMPs through the cell membrane was possibly not the rate limiting step for biodegradation of the latter compounds. Paris *et al.* (1984) suggested that for the chloro-ring-substituted phenoxyacetic ethyl esters the fit to the active site of the enzyme was potentially rate limiting, implying that hydrophobicity is not the only important factor in determining biodegradation rate.

Another important correlation found in the study of Paris *et al.* (1982) was that between OMP biodegradation rate and van der Waals radii (R^2 = 0.96, no values excluded) for phenols. In a later study, Paris *et al.* (1987) reported that despite the fact that phenols and anilines were degraded by different types of enzymes (monooxygenases and dioxygenases, respectively), steric effects (van der Waals radii) showed high correlations with the degradation rate of both compounds.

Although previous mentioned studies provided valuable information regarding the correlation between biodegradation rate and physico-chemical properties, they are mostly limited to certain classes of compounds (phenols, esters of chlorinated carboxylic acids, anilines). Studies trying to develop predictive models for OMP biodegradability based on physico-chemical properties for a wide range of different classes of OMPs are scarce. Since different classes of compounds can cover different ranges in physico-chemical properties, it is important to investigate a broader range of compounds.

Degner *et al.* (1991) concluded that predictive models based on physico-chemical properties were more suitable for specific classes of OMPs (with similar degradation pathways), while predictive models based on electronic/steric parameters were more suitable for a group of different classes of OMPs (since multiple and different degradation pathways could be described based on these parameters). This reasoning was supported by a study of Okey *et al.* (1996) who suggested that OMP biodegradation rate was mainly determined by electronic effects. These electronic and steric properties of the OMPs can be well described by molecular connectivity indices and using a combination of structural fragments and molecular connectivity indices reduced the amount of structural fragments needed to describe the different OMPs. Besides, Damborsky *et al.* (1997) reported

that in contradiction to predictive toxicity models in which the hydrophobicity was the main predictor, for biodegradability models the electronic and steric properties were more important.

Structural fragments

Enzyme attack can be hindered as a result of steric effects (the location of a functional group), electronic effects (functional groups increasing or decreasing the electron density of the OMP) or polar/a-polar interactions (Miller et al., 1997). The shape/geometry of an OMP is mainly determined by the type of structural fragments (e.g. branches, rings) and their location within the molecular structure. Moreover, the presence/absence of certain functional groups can affect the electron density of the reactive site on the OMP and thus the reaction with the enzyme. Hence, the presence of certain functional groups on the OMP structure can play an important role in the OMP biodegradation process. Enzymes can only catalyse a reaction with an OMP if the reaction site of the OMP fits in the slot of the reactive site of the enzyme.

Several studies found a correlation between certain functional groups present in the OMP molecular structure and OMP degradability in biological processes. However, these studies were often limited to a certain class of OMPs or did not specifically focus on the RBF process but on other biological treatment processes such as activated sludge and/or membrane bioreactors which are usually characterized by higher biomass quantities (Alexander et al., 1966, Okey et al., 1996, Pitter, 1985, Tadkaew et al., 2011).

A number of studies demonstrated that OMP structure, substitute position and type of substitute played an important role in the biodegradation potential of OMPs (Alexander *et al.*, 1961, Alexander *et al.*, 1966, Pitter, 1985, Tabak *et al.*, 1964). Structural fragments such as carboxyl, hydroxyl and methyl groups enhanced a compounds' biodegradability, while fragments such as nitro, sulfonate, amine, cyano and halogens decreased a compounds' biodegradability (Alexander *et al.*, 1966, Degner *et al.*, 1991, Klopman *et al.*, 1997, Okey *et al.*, 1996, Pitter, 1985, Tabak *et al.*, 1964).

Similar to the physico-chemical property studies, most of the studies on structural fragments focused on OMP biodegradability obtained from batch experiments inoculated with micro-organisms from wastewater treatment processes (Klopman *et al.*, 1997, Okey *et al.*, 1996, Pitter, 1985) or the study was limited to a certain class of OMPs (Alexander *et al.*, 1966, Degner *et al.*, 1991, Tabak *et al.*, 1964). Thus, these results cannot be easily translated to the RBF process in which a different feed water quality is used and a wide variety of different classes of OMPs.

Evidently, the methodology of relating biodegradation rate to physico-chemical properties and/or functional groups is not new, however, it was never applied to soil passage processes such as RBF. Although the quantity and species of micro-organisms prevalent in soil might be different compared to wastewater treatment processes, the biological breakdown of OMPs is expected to be of a similar nature.

3.5 Existing OMP biodegradation models

Tools such as BIOWIN and CATABOL can be used to determine the biodegradability potential of OMPs based on the structural fragments present in the molecular structure. These tools are not limited to a specific group or class of OMPs, but biodegradation potential for these OMPs is determined in tests that use a mixture of sludge, surface soil, and water from a variety of sites such as sewage treatment plants, industrial wastewater treatment works, rivers, lakes and seas as inoculum (OECD,

1981, 1992). Biomass density and quality can differ significantly between for example sewage treatment plants and natural treatment systems such as RBF which questions the applicability of these models for RBF systems. Moreover, the tests used to determine these biodegradation rates are often spiked with much higher concentrations of OMPs than naturally present in river water bodies. This can lead to shorter adaptation times and higher biodegradation rates and as a consequence it provides less realistic results (Baumgarten et al., 2011). Consequently, there is a lack of OMP biodegradation rates representative for the RBF system which can be used to develop a predictive model based on the functional groups present in the OMP molecular structure.

3.6 Knowledge gaps

Based on this review, a number of knowledge gaps regarding OMP biodegradation are identified. It is unclear which bacterial phyla (and types of strains) and enzymes are present at RBF sites and how they are linked to OMP biodegradation. In other words, which soil bacteria are capable of degrading OMPs under field conditions? What is the role of AOBs in the removal of OMPs during RBF? Also, do intra- and extracellular enzymes contribute to the same extent towards OMP removal? How do both BDOC concentration and composition and redox conditions affect the soil microbial community? Are OMPs degraded metabolic, co-metabolic or by a combination of both?

An extensive study on the types of soil bacteria and enzymes present in the river bank will definitely provide more insight in the degradation pathways and mechanism of OMPs. However, it will be challenging and potentially impossible to engineer RBF systems with respect to the soil microbial population and the enzymes they synthesize.

A number of knowledge gaps need to be addressed before the development of predictive models for OMP removal during RBF can be initiated. First of all, the separate contributions of sorption and biodegradation to overall OMP removal should be determined. Which of these two removal mechanisms is more dominant, or do they equally contribute to overall OMP removal? The approach in recent soil column studies to determine the role of biodegradation is to compare OMP removal in a biotic column to an abotic column and attribute the difference to biodegradation. However, since these percentage removals are often determined based one point in time, it could potentially lead to underestimations of the biodegradation potential if stable effluent concentrations are not reached yet. This limitation can be tackled by determining breakthrough curves that will provide the OMP biodegradation rate and a retardation factor (as indicator for sorption). These biodegradation rates are not only essential in developing a predictive model for OMP removal during RBF, they will also enable a comparison between different studies.

Both physico-chemical properties and structural fragments were found to show good correlations with OMP biodegradability in other biological process (e.g. activated sludge, membrane bioreactors). While some of these descriptors are easily obtained from online chemical databases others require software programmes (e.g. Qikprop, HyperChem) that are able to calculate a diverse range of extremely complicated OMP properties and characteristics. Although sometimes a correlation can be found between biodegradability and these generated variables, their physical explanation is often difficult to find. The development of a predictive model for OMP removal during RBF should provide more insight into the underlying removal mechanisms instead of randomly correlating predictor variables with response variables. Therefore, a predictive model should focus was on physico-chemical properties (e.g. hydrophobicity, molecular weight, charge) and structural fragments (e.g.

functional groups). The role of these properties in the enzyme catalysed degradation can be physically explained as discussed in "3.4.3 Solute parameters affecting biodegradation". This would also be beneficial for the end-users of the model (the drinking water companies) since OMP properties such as molecular weight, charge, hydrophobicity and types of functional groups present in the molecular structure can be easily obtained from online databases, while descriptors such as molecular connectivity indices are not readily available.

Therefore, the first step towards the development of a predictive model is to correlate the OMP retardation factor and/or biodegradation rate to appropriate predictor variables. This is only possible when the retardation factors and biodegradation rates of a large OMP mixture covering different classes of OMPs (e.g. pharmaceuticals, industrial waste products, pesticides). This is another limitation of previous studies: most studies investigating OMP sorption and biodegradation focused on only 1 to 3 OMPs (Baumgarten *et al.*, 2011, Scheytt *et al.*, 2004), or a certain class of OMPs (Maeng *et al.*, 2011a, Onesios *et al.*, 2012). This makes it impossible to develop predictive models that can predict OMP removal based on, and thus applicable to, a wide variety of distinct classes of OMPs.

Secondly, the aqueous phase and then specifically the organic carbon composition and concentration was found to play an important role in OMP removal (Alidina *et al.*, 2014b, Li *et al.*, 2014). It was observed that for columns fed with more refractory carbon, OMP removal improved. Since carbon limited conditions result in a strong pressure on mutants capable of attacking the OMP as reported by (Grady, 1985), this could explain the improved OMP removal observed in the study of (Alidina *et al.*, 2014b, Li *et al.*, 2014). Moreover, it is unclear if the organic carbon composition and concentration is the only important factor shaping the microbial community and thus OMP removal. A number of soil properties have been reported to influence OMP biodegradation and these properties can greatly differ between different RBF sites. Therefore, the role of the solid phase (soil) on OMP biodegradation should be determined.

In addition, river water organic carbon composition can change as a result of seasonal variations (Alberts *et al.*, 2001, Frehse *et al.*, 2013). The effect of variations in the contribution of different fractions (hydrophilic, transphilic, hydrophobic) to the overall river water organic carbon on OMP removal is unknown and should thus be investigated.

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 (Cowart *et al.*, 1971, Hoppe-Jones *et al.*, 2010, Regnery *et al.*, 2015a). 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. Also, 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.

Moreover, while many OMPs have shown persistent behaviour in oxic soil column systems or in field studies which are always representative of a combination of redox condition, their removal under

more reduced and separate conditions needs to be investigated. Theoretically, it would be possible to develop a predictive model for every single redox condition. Combining the predictive models for redox conditions that prevail at a specific site, would result in a model that could predict overall OMP removal during RBF. In this way, drinking water companies are provided with insight into the OMPs that persist during RBF and thus need additional treatment processes.

Finally, the adaptive behaviour of the soil microbial population towards some OMPs should be investigated for a large mixture of OMPs covering a wide range of physico-chemical properties and functional groups. Both these parameters can be used to try to find an explanation for why adaptive behaviour is observed for certain OMPs, but not for others.

4 Research questions

This review attempted to provide a broad overview of the knowledge gaps that need to be addressed before a predictive model for OMP removal during RBF can be developed.

The following research questions will be addressed in this thesis:

1. Are sorption and biodegradation equally contributing to overall OMP removal? (Chapter 2)

i. What is the effect of (in)active biomass on OMP sorption?
ii. What is the effect of clean filter sand on OMP sorption?
iii. What is the effect of the water matrix as a whole on OMP sorption?

2. Is it possible to develop a predictive model for OMP removal during RBF? (Chapter 2, 3)

i. Is it possible to correlate the OMP retardation factor and/or biodegradation rate to the physico-chemical properties (charge, molecular weight, and hydrophobicity) and/or functional groups of the OMPs in a soil column experiment simulating the RBF process under oxic conditions?
ii. Can the model accurately predict field site removals?

3. What is the effect of soil type on microbial community composition and OMP removal? (Chapter 4)

i. What is the effect of soil type on OMP sorption?
ii. What is the effect of soil type on OMP biodegradation?

4. How is the soil microbial community composition (and thus OMP biodegradation rate) affected by organic carbon fractions obtained from river water? (Chapter 5)

5. How is the soil microbial community composition (and thus OMP biodegradation rate) affected by an OMP or DOC shock-load? (Chapter 5)

6. What is the effect of redox condition on OMP removal? (Chapter 6)

i. Is it possible to design a laboratory-scale column system that simulates the separate redox conditions or the RBF process in a natural manner?
ii. Which OMPs show redox dependent behaviour and is it possible to determine their biodegradation rates for the separate redox conditions?

iii. Are the OMPs that show persistent behaviour under oxic conditions, removed under more reduced conditions (nitrate reducing conditions and iron/manganese reducing conditions)?
iv. Which OMPs show persistent behaviour under all redox conditions?

7. How important is adaptive behaviour of the soil microbial community towards OMPs? (Chapter 6)

i. Which OMPs show adaptive behaviour?
ii. Is it possible to explain adaptive behaviour based on the OMP physico-chemical properties or functional groups?
iii. How should adaptation be incorporated in to predictive models?

References

Abel, C.D.T., Sharma, S.K., Malolo, Y.N., Maeng, S.K., Kennedy, M.D. and Amy, G.L. (2012) Attenuation of Bulk Organic Matter, Nutrients (N and P), and Pathogen Indicators During Soil Passage: Effect of Temperature and Redox Conditions in Simulated Soil Aquifer Treatment (SAT). Water Air Soil Pollut 223, 5205-5220.

Aislabie, J. and Lloyd-Jones, G. (1995) A Review of Bacterial Degradation of Pesticides. Aust. J. Soil Res. 33, 925-942.

Alberts, J.J., Takács, M., McElvaine, M. and Judge, K. (2001) Humic Substances, Structures, Models and Functions. Ghabbour, E.A. and Davies, G. (eds), pp. 179-190, The Royal Society of Chemistry, Cambridge, UK.

Alexander, M. and Aleem, M.I.H. (1961) Effect of Chemical Structure on Microbial Decomposition of Aromatic Herbicides. Agricultural and Food Chemistry 9(1), 44-47.

Alexander, M. and Lustigman, B.K. (1966) Effect of Chemical Structure on Microbial Degradation of Substituted Benzenes. J. Agr. Food Chem. 14(4), 410-413.

Alidina, M., Li, D. and Drewes, J.E. (2014a) Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Research 56, 172-180.

Alidina, M., Li, D., Ouf, M. and Drewes, J.E. (2014b) Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. Journal of Environmental Management 144, 58-66.

Alidina, M., Shewchuk, J. and Drewes, J.E. (2015) Effect of temperature on removal of trace organic chemicals in managed aquifer recharge systems. Chemosphere 122, 23-31.

Appelo, C.A.J. and Postma, D. (2005) Geochemistry, Groundwater and Pollution, Taylor & Francis.

Awasthi, N., Ahuja, R. and Kumar, A. (2000) Factors influencing the degradation of soil-applied endosulfan isomers. Soil Biology & Biochemistry 32, 1697-1705.

Bailey, G.W. and White, J.L. (1964) Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity. Agricultural and Food Chemistry 12(4), 324-332.

Baker, J.R., Mihelcic, J.R., Luehrs, D.C. and Hickey, J.P. (1997) Evaluation of Estimation Methods for Organic Carbon Normalized Sorption Coefficients. Water Environment Research 69(2), 136-145.

Bamforth, S.M. and Singleton, I. (2005) Review Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions. J Chem Technol Biotechnol 80, 723-736.

Baumgarten, B., Jährig, J., Reemtsma, T. and Jekel, M. (2011) Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Research 45, 211-220.

Bedmar, F., Daniel, P.E., Costa, J.L. and Giménez, D. (2011) Sorption of acetochlor, s-metolachlor, and atrazine in surface and subsurface soil horizons of argentina. Environmental Toxicology and Chemistry 30(9), 1990-1996.

Benotti, M.J., Song, R., Wilson, D. and Snyder, S.A. (2012) Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Science & Technology: Water Supply 12(1), 11-23.

Bertelkamp, C., Reungoat, J., Cornelissen, E.R., Singhal, N., Reynisson, J., Cabo, A.J., van der Hoek, J.P. and Verliefde, A.R.D. (2014) Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study. Water Research 52, 231-241.

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Callewaert, C., Boon, N., Singhal, N., Van der Hoek, J.P. and Verliefde, A.R.D. (2015a) A laboratory scale column study comparing organic micropollutant removal and microbial diversity for two soil types. Science of the Total Environment 536, 632-638.

Bertelkamp, C., van der Hoek, J.P., Schoutteten, K., Hulpiau, L., Vanhaecke, L., Vanden Bussche, J., Cabo, A.J., Callewaert, C., Boon, N., Löwenberg, J., Singhal, N. and Verliefde, A. (2015b) The effect of feed water dissloved organic carbon concentration and composition on organic micropollutant removal and microbial diversity during river bank filtration. Submitted to Chemosphere.

Boopathy, R., Kulpa, C.F. and Manning, J. (1998) Anaerobic biodegradation of explosives and related compounds by sulfate-reducing and methanogenic bacteria: a review. Bioresource Technology 63, 81-89.

Breeuwsma, A., Wösten, J.H.M., Vleeshouwer, J.J., van Slobbe, A.M. and Bouma, J. (1986) Derivation of Land Qualities to Assess Environmental Problems from Soil Surveys. Soil Sci. Soc. Am. J. 50, 186-190.

Broznić, D. and Milin, Č. (2012) Effects of temperature on sorption-desorption processes of imidacloprid in soils of Croatian coastal regions. J. Environ. Sci. Health Part B 47, 779-794.

Bunge, M., Adrian, L., Kraus, A., Opel, M., Lorenz, W.G., Andreesen, J.R., Görisch, H. and Lechner, U. (2003) Reductive dehalogenation of chlorinated dioxins by an anaerobic bacterium. Nature 421(357-360).

Burke, V., Greskowiak, J., Asmuß, T., Bremermann, R., Taute, T. and Massmann, G. (2014) Temperature dependent redox zonation and attenuation of wastewater-derived organic micropollutants in the hyporheic zone. Science of The Total Environment 482-483, 53-61.

Burns, R.G. and Wallenstein, M.D. (2010) Microbial extracellular enzymes and natural and synthetic polymer degradation in soil: current research and future prospects 1 - 6 August, Brisbane, Australia.

Calvet, R. (1989) Adsorption of Organic Chemicals in Soils. Environmental Health Perspectives 83, 145-177.

Caron, G., Suffet, I.H. and Belton, T. (1985) Effect of dissolved organic carbon on the environmental distribution of nonpolar organic compounds. Chemosphere 14(8), 993-1000.

Cavalca, L., Guerrieri, N., Colombo, M., Pagani, S. and Andreoni, V. (2007) Enzymatic and genetic profiles in environmental strains grown on polycyclic aromatic hydrocarbons. Antonie van Leeuwenhoek 91, 315-325.

Chatterjee, N.S., Gupta, S. and Varghese, E. (2013) Degradation of metaflumizone in soil: Impact of varying moisture, light, temperature, atmospheric CO2 level, soil type and soil sterilization. Chemosphere 90, 729-736.

Chiou, C.T., Porter, P.E. and Schmedding, D.W. (1983) Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17(227-231).

Cowart, R.P., Bonner, F.L. and Epps, E.A. (1971) Rate of Hydrolysis of Seven Organophosphate Pesticides. Bulletin of Environmental Contamination & Toxicology 6(3), 231-234.

D'Alessio, M., Yoneyama, B., Kirs, M., Kisand, V. and Ray, C. (2015a) Pharmaceutically active compounds: Their removal during slow sand filtration and their impact on slow sand filtration bacterial removal. Science of The Total Environment 524-525, 124-135.

D'Alessio, M., Yoneyama, B. and Ray, C. (2015b) Fate of selected pharmaceutically active compounds during simulated riverbank filtration. Science of The Total Environment 505, 615-622.

Dalton, H. and Stirling, D.I. (1982) Co-metabolism. Phil. Trans. R. Soc. Lond. B 297, 481-496.

Damborsky, J. and Schultz, T.W. (1997) Comparison of the QSAR models for toxicity and biodegradability of anilines and phenols. Chemosphere 34(2), 429-446.

De Vet, W.W.J.M., van Genuchten, C.C.A., van Loosdrecht, M.C.M. and van Dijk, J.C. (2010) Water quality and treatment of river bank filtrate. Drinking Water Engineering and Science 3, 79-90.

Degner, P., Nendza, M. and Klein, W. (1991) Predictive QSAR models for estimating biodegradation of aromatic compounds. The Science of the Total Environment 109/110, 253-259.

DeLaune, R.D. and Reddy, K.R. (2005) Redox Potential.

Delle Site, A. (2001) Factors Affecting Sorption of Organic Compounds in Natural Sorbent/Water Systems and Sorption Coefficients for Selected Pollutants. A review. J. Phys. Chem. Ref. Data 30(1), 187-439.

Dordio, A.V., Belo, M., Martins Teixeira, D., Palace Carvalho, A.J., Dias, C.M.B., Picó, Y. and Pinto, A.P. (2011) Evaluation of carbamazepine uptake and metabolization by *Typha* spp., a plant with potential use in phytotreatment. Bioresource Technology 102, 7827-7834.

Doucette, W.J. (2003) Quantitative structure-activity relationships for predicting soil-sediment sorption coefficients for organic chemicals. Environmental Toxicology and Chemistry(22), 1771-1788.

Drillia, P., Stamatelatou, K. and Lyberatos, G. (2005) Fate and mobility of pharmaceuticals in solid matrices. Chemosphere 60, 1034-1044.

EPA (1995) Bioremediation of Hazardous Wastes - Research, Development, and Field Evaluations, U.S. Environmental Protection Agency.

Fingler, S., Stipičević, S. and Drevenkar, V. (2004) Sorption behaviour of chlorophenols and triazine herbicides in reference euro-soils. International Journal of Environmental Analytical Chemistry 84(1-3), 83-93.

Flemming, H.-C. (1995) Sorption sites in biofilms. Water Sci. Technol. 32(8), 27-33.

Flores-Céspedes, F., González-Pradas, F., Fernández-Pérez, M., Villafranca-Sánchez, M., Socías-Viciana, M. and Ureña-Amate, M.D. (2002) Organic compounds in the environment - effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. J. Environ. Qual. 31, 880-888.

Frank, M.P., Graebing, P. and Chib, J.S. (2002) Effect of Soil Moisture and Sample Depth on Pesticide Photolysis. J. Agric. Food Chem. 50, 2607-2614.

Frehse, H. and Anderson, J.P.E. (2013) Pesticide Chemistry: Human Welfare and the Environment: Pesticide Residues and Formulation Chemistry. Miyamoto, J., Kearney, P.C. and Greenhalgh, R. (eds), Elsevier.

Gao, J.P., Maguhn, J., Spitzauer, P. and Kettrup, A. (1998) Sorption of pesticides in the sediment of the Teufelsweiher Pond (Southern Germany). I: equilibrium assessments, effect of organic carbon content and pH. Water Research 32(5), 1662-1672.

Gao, M., Li, Y., Yang, H. and Gu, Y. (2014) Sorption and desorption of pymetrozine on six Chinese soils. Front. Environ. Sci. Eng.

Gavrilescu, M. (2005) Fate of pesticides in the environment and its bioremediation. Eng. Life Sci. 5(6).

Gerstl, Z. (1990) Estimation of organic chemical sorption by soils. Journal of Contaminant Hydrology 6, 357-375.

Grady, C.P.L. (1985) Biodegradation: Its Measurement and Microbiological Basis, John Wiley and Sons, Inc.

Gravilescu, M. (2005) Review Fate of Pesticides in the Environment and its Bioremediation. Eng. Life Sci. 5(6), 497-526.

Gruenheid, S., Huebner, U. and Jekel, M. (2008) Impact of temperature on biodegradation of bulk and trace organics during soil passage in an indirect reuse system. Water Science & Technology - WST 57(7), 987-994.

Grünheid, S., Amy, G. and Jekel, M. (2005) Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. Water Research 39, 3219-3228.

Grünheid, S., Huebner, U. and Jekel, M. (2008) Impact of temperature on biodegradation of bulk and trace organics during soil passage in an indirect reuse system. Water Science & Technology 57(7), 987-994.

Hall, K.E., Ray, C., Ki, S.J., Spokas, K.A. and Koskinen, W.C. (2015) Pesticide sorption and leaching potential on three Hawaiian soils. Journal of Environmental Management 159, 227-234.

Hebert, V.R. and Miller, G.C. (1990) Depth Dependence of Direct and Indirect Photolysis on Soil Surfaces. J. Agric. Food Chem. 38, 913-918.

Henzler, A.F., Greskowiak, J. and Massmann, G. (2014) Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). Journal of Contaminant Hydrology 156, 78-92.

Hiller, E., Čerňanský, S., Krascsenits, Z. and Milička, J. (2009) Effect of soil and sediment composition on acetochlor sorption and desorption. Environmental Science and Pollution Research 16, 546-554.

Hiller, E., Tatarková, V., Šimonovičová, A. and Bartal', M. (2012) Sorption, desorption, and degradation of (4-chloro-2-methylphenoxy)acetic acid in representative soils of the Danubian Lowland, Slovakia. Chemosphere 87, 437-444.

Hiscock, K.M. and Grischek, T. (2002) Attenuation of groundwater pollution by bank filtration. Journal of Hydrology 266, 139-144.

Höllrigl-Rosta, A., Kreuzig, R. and Bahadir, M. (1999) Investigations on the metabolic fate of prochloraz in soil under field and laboratory conditions. Pesticide Science 55, 531-538.

Hoppe-Jones, C., Dickenson, E.R.V. and Drewes, J.E. (2012) The role of microbial adaptation and biodegradable dissolved organic carbon on the attenuation of trace organic chemicals during groundwater recharge. Science of The Total Environment 437, 137-144.

Hoppe-Jones, C., Oldham, G. and 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.

Hyland, K.C., Dickenson, E.R.V., Drewes, J.E. and Higgins, C.P. (2012) Sorption of ionized and neutral emerging trace organic compounds onto activated sludge from different wastewater treatment configurations. Water Research 46, 1958-1968.

Janke, D. and Fritsche, W. (1985) Review Nature and significance of microbial cometabolism of xenobiotics. J. Basic Microbial 25(9), 603-619.

Janssen, P.H. (2006) Minireviews Identifying the Dominant Soil Bacterial Taxa in Libraries of 16S rRNA and 16S rRNA Genes. Applied and Environmental Microbiology 72(3), 1719-1728.

Jones, O.A.H., Voulvoulis, N. and Lester, J.N. (2004) Potential Ecological and Human Health Risks Associated With the Presence of Pharmaceutically Active Compounds in the Aquatic Environment. Critical Reviews in Toxicology 34(4), 335-350.

Karpouzas, D.G. and Walker, A. (2000) Factors influencing the ability of *Pseudomonas putida* epI to degrade ethoprophos in soil. Soil Biology & Biochemistry 32, 1753-1762.

Kay, M.J., McCabe, R.W. and Morton, L.H.G. (1993) Chemical and Physical Changes Occurring in Polyester Polyurethane during Biodegradation. International Biodeterioration & Biodegradation 31, 209-225.

Kemper, N. (2008) Review - Veterinary antibiotics in the aquatic and terrestrial environment. Ecological indicators 8, 1-13.

Klopman, G. and Tu, M. (1997) Structure-Biodegradability Study and Computer-Automated Prediction of Aerobic Biodegradation of Chemicals. Environmental Toxicology and Chemistry 16(9), 1829-1835.

Lee, J.H., Hamm, S.Y., Cheong, J.Y., Kim, H.S., Ko, E.J., Lee, K.S. and Lee, S.I. (2009) Characterizing riverbank-filtered water and river water qualities at a site in the lower Nakdong River basin, Republic of Korea. Journal of Hydrology 376, 209-220.

Li, D., Alidina, M. and 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. Applied Microbiology and Biotechnology 98, 5747-5756.

Lim, M.H., Snyder, S.A. and 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 Research 42, 2943-2952.

Ludwig, U., Grischek, T., Nestler, W. and Neumann, V. (1997) Behaviour of Different Molecular-weight Fractions of DOC of Elbe River Water during River Bank Infiltration. Acta hydrochim. hydrobiol. 25(3), 145-150.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A. and Amy, G.L. (2011a) 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 Research 45, 4722-4736.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Song, K.G. and 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. Journal of Contaminant Hydrology 140-141, 139-149.

Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K. and Amy, G.L. (2011b) Occurence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: a review. Water Research 45(10), 3015-3033.

Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K. and Amy, G.L. (2011c) Occurence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: A review. Water Research 45, 3015-3033.

Magan, N., Fragoeiro, S. and Bastos, C. (2010) Environmental Factors and Bioremediation of Xenobiotics Using White Rot Fungi. Mycobiology 38(4), 238-248.

McBride, M.B. (1994) Environmental Chemistry of Soils, Oxford University Press, New York.

McCutcheon, S.C. and Schnoor, J.L. (2003) Overview of Phytotransformation and Control of Wastes, John Wiley & Sons, Inc., Hoboken, NJ, USA.

McMahon, P.B. and Chapelle, F.H. (2008) Redox Processes and Water Quality of Selected Principal Aquifer Systems. Ground Water 46(2), 259-271.

Medihala, P.G., Lawrence, J.R., Swerhone, G.D.W. and Korber, D.R. (2012) Spatial variation in microbial community structure, richness, and diversity in an alluvial aquifer. Can. J. Microbiol. 58, 1135-1151.

Milinovic, J., Lacorte, S., Vidal, M. and Rigol, A. (2015) Sorption behaviour of perfluoroalkyl substances in soils. Science of The Total Environment 511, 63-71.

Mill, T. (1999) Predicting photoreaction rates in surface waters. Chemosphere 38(6), 1379-1390.

Nguyen, L.N., Hai, F.I., Kang, J., Price, W.E. and Nghiem, L.D. (2012) Removal of trace organic contaminants by a membrane bioreactor–granular activated carbon (MBR–GAC) system. Bioresource Technology 113, 169-173.

Northcott, G., Jensen, D., Ying, L. and Fischer, P. (2014a) Degradation rate of sodium fluoroacetate in three New Zealand soils. Environmental Toxicology and Chemistry 33(5), 1048-1058.

Northcott, G., Jensen, D., Ying, L. and Fisher, P. (2014b) Degradation rate of sodium fluoroacetate in three New Zealand soils. Environmental Toxicology and Chemistry 33(5), 1048-1058.

Okey, R.W. and Stensel, H.D. (1996) A QSAR-based Biodegradability Model - A QSBR. Water Research 30(9), 2206-2214.

Onesios-Barry, K.M., Berry, D., Proescher, J.B., Ashok Sivakumar, I.K. and Bouwer, E.J. (2014) Removal of pharmaceuticals and personal care products during water recycling: microbial community structure and effects of substrate concentration. Appl. Environ. Microbiol.

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

Ou, L.T. (1998) Enhanced Degradation of the Volatile Fumigant-Nematicides 1,3-D and Methyl Bromide in Soil. Journal of Nematology 30(1), 56-64.

Patterson, B.M., Pitoi, M.M., Furness, A.J., Bastow, T.P. and McKinley, A.J. (2012) Fate of *N*-Nitrosodimethylamine in recycled water after recharge into anaerobic aquifer. Water Research 46, 1260-1272.

Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T. and Toze, S. (2011) Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122, 53-62.

Paxéus, N. (1996) Organic pollutants in the effluents of large wastewater treatment plants in Sweden. Water Research 30(5), 1115-1122.

Picton, P. and Farenhorst, A. (2004) Factors Influencing 2,4-D Sorption and Mineralization in Soil. Journal of Environmental Science and Health Part B B39(3), 367-379.

Pitter, P. (1985) Correlation of Microbial Degradation Rates with the Chemical Structure. Acta hydrochim. hydrobiol. 13(4), 453-460.

Radjenovic, J., Petrovic, M. and Barceló, D. (2007) Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Anal Bioanal Chem 387, 1365-1377.

Radjenović, J., Petrović, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43, 831-841.

Rattier, M., Reungoat, J., Keller, J. and Gernjak, W. (2014) Removal of micropollutants during tertiary wastewater treatment by biofiltration: Role of nitrifiers and removal mechanisms. Water Research 54, 89-99.

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

Regnery, J., Barringer, J., Wing, A.D., Hoppe-Jones, C., Teerlink, J. and 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. and Drewes, J.E. (2015b) Biotransformation of trace organic chemicals during groundwater recharge: How useful are first-order rate constants? Journal of Contaminant Hydrology In press.

Remucal, C.K. (2014) The role of indirect photochemical degradation in the environmental fate of pesticides: a review. Environ. Sci. : Processes Impacts 16, 628-653.

Röling, W.F.M., van Breukelen, B.M. and Braster, M. (2001) Relationships between Microbial Community Structure and Hydrochemistry in a Landfill Leachate-Polluted Aquifer. Applied and Environmental Microbiology 67(10), 4619-4629.

Sabljić, A., Güsten, H., Verhaar, H. and Hermens, J. (1995) QSAR modelling of soil sorption. Improvements and systematics of Log K_{OC} vs. Log K_{OW} correlations. Chemosphere 31(11/12), 4489-4514.

Salt, D.E., Smith, R.D. and Raskin, I. (1998) Phytoremediation. Annu. Rev. Plant Physiol. Plant Mol. Biol. 49, 643-668.

Sangster, J.L., Oke, H., Zhang, Y. and Bartelt-Hunt, S.L. (2015) The effect of particle size on sorption of estrogens, androgens andprogestagens in aquatic sediment. Journal of Hazardous Materials 299, 112-121.

Scheytt, T.J., Mersmann, P., Leidig, M., Pekdeger, A. and Heberer, T. (2004) Transport of Pharmaceutically Active Compounds in Saturated Laboratory Columns. Ground Water 42(5), 767-773.

Schmidt, C.K., Lange, F.T. and Brauch, H.-J. (2007) Characteristics and evaluation of natural attenuation processes for organic micropollutant removal during riverbank filtration. Water Science & Technology: Water Supply 7(3), 1-7.

Schoenheinz, D. and Grischek, T. (2011) Riverbank Filtration for Water Security in Desert Countries, Series C: Environmental Security. Ray, C. and Shamrukh, M. (eds), Springer, The Netherlands.

Schroll, R., Becher, H.H., Dörfler, U., Gayler, S., Grundmann, S., Hartmann, H.P. and Ruoss, J. (2006) Quantifying the Effect of Soil Moisture on the Aerobic Microbial Mineralization of Selected Pesticides in Different Soils. Environmental Science & Technology 40, 3305-3312.

Schubert, J. (2002) Hydraulic aspects of riverbank filtration-field studies. Journal of Hydrology 266, 145-161.

Schwarzenbach, R.P., Giger, W., Hoehn, E. and Schnelder, J.K. (1983) Behavior of Organic Compounds during Infiltration of River Water to Groundwater. Field studies. Environ. Sci. Technol. 17, 472-479.

Shamrukh, M. and Abdel-Wahab, A. (2008) Riverbank filtration for sustainable water supply: application to a large-scale facility on the Nile River. Clean Techn Environ Policy 10, 351-358.

Sheets, R.A., Darner, R.A. and Whitteberry, B.L. (2002) Lag times of bank filtration at a well field, Cincinatti, Ohio, USA. Journal of Hydrology 266, 162-174.

Shonnard, D., Lindner, A., Nguyen, N., Ramachandran, P.A., Fichana, D., Hesketh, R., Slater, C.S. and Engler, R. (2007) Chapter 6 Green Engineering-Integration of Green Chemistry, Pollution Prevention, and Risk-Based Considerations.

Singh, B.K., Walker, A., Morgan, J.A.W. and Wright, D.J. (2003) Effects of Soil pH on the Biodegradation of Chlorpyrifos and Isolation of a Chlorpyrifos-Degrading Bacterium. Applied and Environmental Microbiology 69(9), 5198-5206.

Sonnenschein, C. and Soto, A.M. (1998) An Updated Review of Environmental Estrogen and Androgen Mimics and Antagonists. The Journal of Steroid Biochemistry and Molecular Biology 65(1-6), 143-150.

Spain, J.C., Pritchard, P.H. and Bourquin, A.W. (1980) Effects of Adaptation on Biodegradation Rates in Sediment/Water Cores from Estuarine and Freshwater Environments. Applied and Environmental Microbiology 40(4), 726-734.

Spain, J.C. and van Veld, P.A. (1983) Adaptation of Natural Microbial Communities to Degradation of Xenobiotic Compounds: Effects of Concentration, Exposure, Time, Inoculum, and Chemical Structure. Applied and Environmental Microbiology 45(2), 428-435.

Stepien, D.K., Regnery, J., Merz, C. and Püttmann, W. (2013) Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany. Science of The Total Environment 458-460, 150-159.

Storck, F.R., Schmidt, C.K., Lange, F.T., Henson, J.W. and Hahn, K. (2012) Factors controlling micropollutant removal during riverbank filtration. Journal - American Water Works Association.

Storck, F.R., Schmidt, C.K., Lange, F.T., Henson, J.W. and Hahn, K. (2010) Removal and Fate of EDCs and PPCPs in Bank Filtration Systems.

Surampalli, R.Y., Ong, S.K., Seagren, E., Nuno, J. and Banerji, S. (eds) (2004) Natural attenuation of hazardous wastes, American Society of Civil Engineers, Virgina, USA.

Tabak, H.H., Chambers, C.W. and Kabler, P.W. (1964) Microbial metabolism of aromatic compounds. Journal of Bacteriology 87(4), 910-919.

Tadkaew, N., Sivakumar, M., Khan, S.J., McDonald, J.A. and Nghiem, L.D. (2010) Effect of mixed liquor pH on the removal of trace organic contaminants in a membrane bioreactor. Bioresource Technology 101, 1494-1500.

Tran, N.H., Urase, T., Ngo, H.H., Hu, J. and Ong, S.L. (2013) Review Insight into metabolic and cometabolic activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging trace organic contaminants. Bioresource Technology 146, 721-731.

van der Hoek, J.P., Bertelkamp, C., Verliefde, A.R.D. and Singhal, N.S. (2014) Drinking water treatment technologies in Europe: State of the art - Challenges - Research needs. Journal of Water Supply: Research and Technology - AQUA 63(2), 124-130.

Verstraeten, I.M., Heberer, T. and Scheytt, T.J. (2003) Riverbank filtration. Ray, C., Melin, G. and Linsky, R.B. (eds), Kluwer Academic Publishers, Netherlands.

Wang, H.Z., Zuo, H.G., Ding, Y.J., Miao, S.S., Jiang, C. and Yang, H. (2014) Biotic and abiotic degradation of pesticide Dufulin in soils. Environ Sci Pollut Res 21, 4331-4342.

Wei, J., Furrer, G., Kaufmann, S. and Schulin, R. (2001) Influence of Clay Minerals on the Hydrolysis of Carbamate Pesticides. Environ. Sci. Technol. 35, 2226-2232.

Wiegel, J., Zhang, X. and Wu, Q. (1999) Anaerobic Dehalogenation of Hydroxylated Polychlorinated Biphenyls by Desulfitobacterium dehalogenans. Applied and Environmental Microbiology 65(5), 2217-2221.

Willis, G.H. and McDowell, L.L. (1982) Review: pesticides in agricutural runoff and their effects on downstream water quality. Environmental Toxicology and Chemistry 1, 267-279.

Ye, J., Singh, A. and Ward, O.P. (2004) Biodegradation of nitroaromatics and other nitrogen-containing xenobiotics. World Journal of Microbiology & Biotechnology 20, 117-135.

Yu, C.P., Roh, H. and Chu, K.H. (2007) 17ß-Estradiol-Degrading Bacteria Isolated from Activated Sludge. Environ. Sci. Technol. 41, 486-492.

Zhang, L.M., Offre, P.R., He, J.Z., Verhamme, D.T., Nicol, G.W. and Prosser, J.I. (2010) Autotrophic ammonia oxidation by soil thaumarchaea. PNAS 107(40), 17240-17245.

Zhang, Q., Yang, C., Dang, Z. and Huang, W. (2011) Sorption of Tylosin on Agricultural Soils. Soil Science 176(8), 407-412.

Chapter 2

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

This chapter is based on: Bertelkamp *et al.* (2014), Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study, Water Research 52, 231 - 241

1 Introduction

As a first step towards a predictive model for OMP removal, a better understanding of the contribution of the two main removal mechanisms towards overall OMP removal is required. Only a few studies have attempted to distinguish sorption from biodegradation. The contribution of biodegradation towards overall OMP removal was determined 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.*, 2011, 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 compounds. To enable a fair comparison of OMP biodegradability a more accurate parameter would be the biodegradation rate. The biodegradation rate can be determined from the OMP breakthrough curve. In addition, modeling 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, Scheytt *et al.*, 2004, Scheytt *et al.*, 2006), making it impossible to link physico-chemical properties to OMP removal behavior 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.*, 2011, 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 - µg/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 (Baumgarten *et al.*, 2011). 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.

Some studies indicated that sorption onto sludge can be an important removal mechanism in wastewater 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. Since biofilms are present in the soil and these contain both anionic and cationic groups (Flemming, 1995), biosorption of OMPs could also play an important role in RBF. In addition, the formation of a biofilm in soil can increase the specific surface area thereby possibly increasing OMP sorption. However, the effect of biofilm present in soil on OMP retardation is still largely unknown.

Soil column studies investigating biodegradation behavior 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.*, 2011). 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 and temperature 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.

In this chapter sorption and biodegradation behavior of OMP mixtures at concentrations representative of those in RBF systems is studied. 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. Modeling 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 modeling 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 ($CH_3COONa.3H_20$, 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 (NaN_3, Sigma-Aldrich, The Netherlands) to inactivate the developed biomass. UV_{254} 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 NaN_3 to suppress biological activity in this column from the start of the experiment. Column 6 was fed with demineralized water and 400 mg/L NaN_3 to suppress biological activity in this 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 followed by a 3% HCl solution and flushed with demineralized water before refilling to prevent biofilm formation. The feed solutions were pumped through the columns by a peristaltic multichannel 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 black polyethylene tubing (d_i = 4 mm, Festo, The Netherlands). The hydraulic loading rate applied on the columns was 1 L/d, which equals a filtration rate of 1 m/d. The pore velocities and porosity in the six columns were determined using a tracer (5 g/L, NaCl). NaCl concentration was measured with a conductivity meter (Tetracon probe, Cond340i, WTW, Germany). Pore velocity ranged from 2.4 – 3.2 m/d and porosity varied between 0.31 and 0.42.

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.

Table 1 – Feed water qualities for the columns experimental period

Column	Feed water	$CH_3COONa.3H_2O$ [µg/L]	NaN_3 [mg/L]	Biomass condition	Objective
1	Schie Canal	200	NA	Active biomass	Sorption active biomass + biodegradation
2	Schie Canal	200	NA	Active biomass	Sorption active biomass + biodegradation
3	Schie Canal	NA	400	Inactivated biomass	Sorption inactive biomass
4	Schie Canal	NA	400	Inactivated biomass	Sorption inactive biomass
5	Schie Canal	NA	400	No biomass	Sorption on sand grains, no biomass present (Water matrix effect)
6	Demineralized water	NA	400	No biomass	Sorption on sand grains, no biomass present (Water matrix effect)

NA = Not applicable

Table 2 – Physico-chemical properties OMPs, decay rates and half-lives

						This study	This study	Other studies
Compound	**MW**	**pKa**	**Charge (pH 7)**	**Log P[1]**	**Log D[7] (pH 7)**	**µ [d^{-1}]**	**$t_{1/2}$ [hours]**	**$t_{1/2}$ [days]**
Ibuprofen	206.3	4.91[1]	-1	3.97	1.74	15.8	1	2 minutes[8]
Ketoprofen	254.3	4.45[1]	-1	3.12	0.82	13.5	1	4.6 – 27.6[9]
Gemfibrozil	250.3	4.7[4]	-1	3.40	1.93	12.7	1	4 minutes[8], 17.8; 20.6 [10]
Acetaminophen	151.2	9.38[1]	0	0.46	0.86	17.1	1	6 minutes[8], 2.1[11]
Trimethoprim	290.3	7.12[1]	0	0.91	0.98	11.5	1	3 minutes[8]
Caffeine	194.2	10.4[1]	0	-0.07	-0.58	9.5	2	5 minutes[8], 1.5[11]
Propranolol	259.3	9.42[1]	+1	3.48	0.21	3.6	5	0.4; 1.8[12], 2.2[11]
Metoprolol	267.4	9.4 [2]	+1	1.88	-0.58	1.4	12	4.1; 8.7[12]
Atrazin	215.7	<2 (1.6)[4]	0	2.61[6]	2.26	0	-	
Carbamazepine	236.3	- [2]	0	2.45	2.64	0	-	
Phenytoin	252.3	8.33[1]	0	2.47	1.59	0	-	
Sulfamethoxazole	253.3	1.83; 1.85; 5.57; 5.60; 5.65[5]	0	0.89	0.62	0	-	
Hydrochlorothiazide	297.7	7.9[1]	0	-0.07	-0.71	0	-	
Lincomycin	406.5	7.6[3]	+1	0.56	-1.34	0	-	

[1] Obtained from Drugbank (http://www.drugbank.ca), [2] Chiang and Hu, 2009, [3] Wang *et al.*, 2011, [4] Westerhoff *et al.*, 2005 calculated with SPARC, [5] Babić *et al.*, 2007, [6] Exp. value from chemspider database (http://www.chemspider.com), [7] Obtained from calculated value ChemAxon (http://www.chemspider.com), [8] Zearley and Summers, 2012, [9] Xu *et al.*, 2009, [10] Fang *et al.*, 2012, [11] Yu-Chen Lin *et al.*, 2010, [12] Ramil *et al.*, 2010

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 experiments. 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 2x5 mL of methanol and 2x5 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_2O (25/75, v/v) and spiked with 50 µL of a 200 µg/L mix of matching labeled 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) (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 extraction and after reconstitution in triplicate.

Influent and effluent concentrations were measured at six different time points during a period of one month (T = 10h, 34h, 58.5h, 80h, 1wk and 4wks). 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-$V_{CPH/CPN}$ 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. UV_{254} 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 meter (Cellox 325 probe, Oxi340i, WTW, Germany) 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 columns, to determine adenosine triphosphate (ATP) concentrations 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 sonication the supernatant was decanted and 10 mL fresh demineralized water was added and sonication was repeated until the difference in ATP concentration measured in the supernatant was smaller than 10%. Four HES treatments of 2 minutes 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 kit (Aqua tools, France). The test kit measures the concentration 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 hours 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 difference between columns (e.g. DOC removal between biologically 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 equilibrium convection-dispersion equation (CDE). Concentration mode was set to resident concentration (third type inlet), c_r.

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

$$R\frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} - \mu c_r \qquad \text{Eq. 1}$$

In which:

R	=	retardation factor	[-]
c_r	=	volume-averaged or resident concentration of the liquid phase	[kg · m^{-3}]
t	=	time	[min]
D	=	dispersion coefficient	[m^2 · min^{-1}]
x	=	distance	[m]
v	=	average pore water velocity	[m · min^{-1}]
μ	=	first-order decay coefficient for biodegradation of the solute	[min^{-1}]

Average pore water velocity (υ) and the dispersion coefficient (D) for the columns were obtained from fitting the breakthrough curves of the tracer experiment in CXTFIT (results are presented in Table 1 of the SI).

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

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad \text{Eq. 2}$$

In which:

ϱ_b	=	soil bulk density	[kg · m^{-3}]
K_d	=	distribution coefficient	[kg^{-1} · m^3]
θ	=	volumetric water content	[m^3 · m^{-3}]

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

$$D = \alpha v + \frac{D_0}{\tau} \qquad \text{Eq. 3}$$

In which:

D	=	dispersion	[m^2 · s^{-1}]

α	=	dispersivity	[m]
v	=	average pore water velocity	[$m \cdot s^{-1}$]
D_0	=	fluid phase diffusion coefficient	[$m^2 \cdot s^{-1}$]
τ	=	factor accounting for the tortuosity of the porous medium	[-]

Dispersivity (α) was determined from the tracer curves. The fluid phase diffusion coefficient (D_0) for NaCl (3 g/L) is equal to $1.53 \cdot 10^{-9}$ m^2s^{-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 (D_0) of the OMPs was calculated according to Eq. 4 (Verliefde, 2008):

$$D_0 = \frac{k_B T}{6\pi\eta R_H} \qquad \text{Eq. 4}$$

In which:

R_H	=	Stokes radius	[m]
k_B	=	Boltzmann constant = $1.3806488 \cdot 10^{-23}$ JK^{-1}	[JK^{-1}]
T	=	Temperature = 293.15 K	[K]
η	=	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 dispersion coefficients for the OMPs are shown in Table 2 of the SI.

Half-life of the compound was defined as:

$$t_{1/2} = \frac{\ln(2)}{\mu} \qquad \text{Eq. 5}$$

In which:

$t_{1/2}$	=	half-life	[min]
μ	=	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 = $4.56 \cdot 10^{-15} < 0.05$). In addition, the difference in UV_{254} absorbance decrease between the biologically active and inactive columns was statistically significant (p-value is $< 2 \cdot 10^{-16} < 0.05$),

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 = $8.3 \cdot 10^{-5} < 0.05$), 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.

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

	ATP [ng/cm^3 of sand]		
Column	**Influent side**	**Effluent side**	**Average**
1	47 ± 6	2 ± 1	24.5 ± 6.1
2	70 ± 8	3 ± 1	36.5 ± 8.1
3	5 ± 1	1 ± 0	3 ± 1
4	4 ± 1	1 ± 0	2.5 ± 1
5	3 ± 3	0 ± 0	1.5 ± 3
6	<DL*	<DL*	< DL*

* Below detection limit

Maeng et al. (2011) 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 (Maeng *et al.*, 2011). 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 et al. (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 (Magic-Knezev and van der Kooij, 2004). From the ATP, UV_{254} and DOC results it was concluded that the abiotic/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 = $2.37 \cdot 10^{-4} < 0.05$). 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 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 μ. 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.

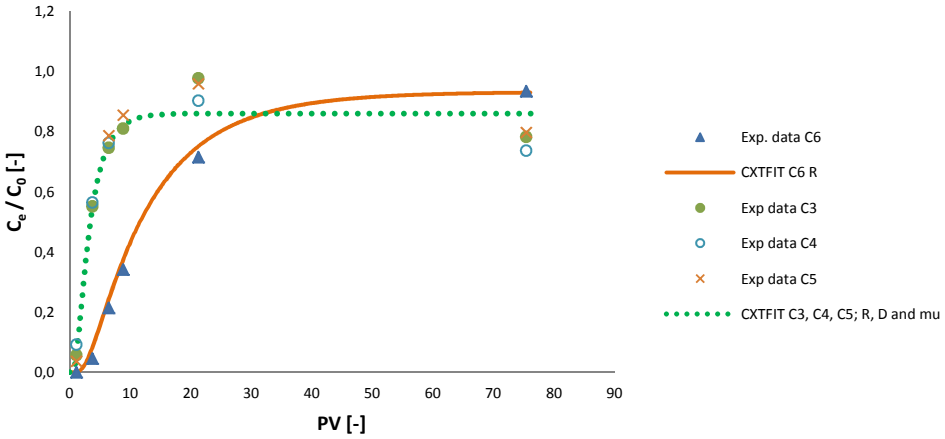

Figure 1 – Experimental data and modelled breakthrough curve metoprolol (PV = Pore Volumes)

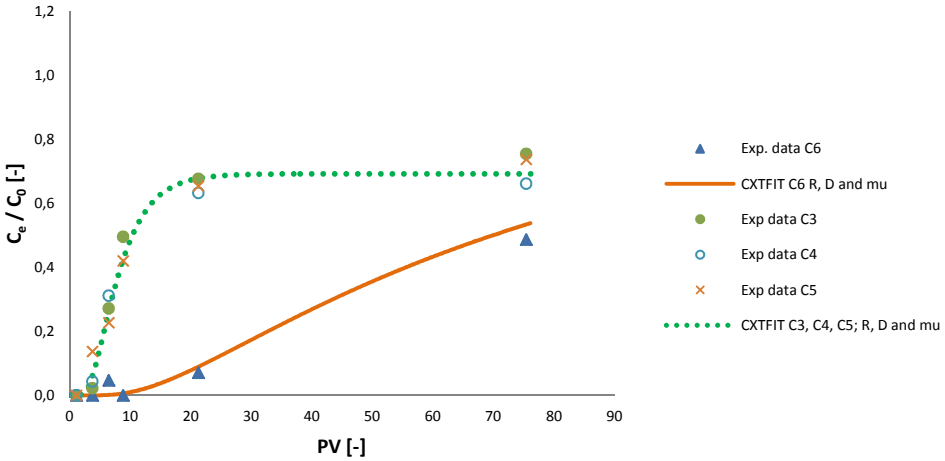

Figure 2 –Experimental data and modelled breakthrough curve propranolol

The experimental breakthrough data as well as the modeled fits for metoprolol and propranolol are shown in Figures 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, Figure 2, clearly shows that the retardation factor of propranolol for column 6 (demineralized water + NaN_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 ($K_{D,\ soil\ 7}$ = 199 L/kg, $K_{D,\ soil\ 1}$ = 16.3 L/kg) compared to carbamazepine ($K_{D,\ soil\ 7}$ = 37 L/kg, $K_{D,soil\ 1}$ = 0.49 L/kg) and sulfamethoxazole [$K_{D,\ soil\ 7}$ = 37.6 L/kg, $K_{D,\ soil\ 1}$ = 0.23 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 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 μ 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^3 compared to 24.5 - 36.5 ng/cm^3 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 modeled by fitting μ 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, μ 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 μ 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 behavior. 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 behavior 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 – 16.3 d^{-1}, while half-lives range from 0.0 – 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 μ 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. As was observed for the distribution coefficient, half-lives can differ by four orders of magnitude between different studies. 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.*, 2011, Maeng *et al.*, 2012, Scheytt *et al.*, 2006, Zearley and Summers, 2012). Hydrochlorothiazide showed recalcitrant behavior in a conventional activated sludge system as well as two pilot MBR systems (Radjenović *et al.*, 2009). Phenytoin was poorly removed (±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) (Baumgarten *et al.*, 2011). This could explain the

more persistent behavior 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, lincomcyin, 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 μ 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 exo-enzymes 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 = $8.87 \cdot 10^{-4}$). 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 = $8.48 \cdot 10^{-3}$). 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 to 0.98) were more biodegradable, while neutral compounds characterized by higher Log D values (1.59 to 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 = $1.26 \cdot 10^{-4}$, $R^2 = 0.96$) for all OMPs was obtained explaining biodegradation behavior using functional groups present within the chemical structure of the OMP:

$$\mu = 22.797 - 7.357 \cdot Am - 7.360 \cdot RS + 6.045 \cdot Et - 6.690 \cdot Al.Et + 5.443 \cdot Ca - 6.766 \cdot S \qquad \text{Eq. 6}$$

In which:

μ	=	biodegradation rate	[d^{-1}]
Am	=	number of amines (primary and secondary)	[-]
RS	=	number of ring structures	[-]
Et	=	number of ethers	[-]
Al.Et	=	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. 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 (Kawasaki, 1980), 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 behavior 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 behavior 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 behavior 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.

References

Babić, S., Horvat, A.J.M., Pavlović, D.M. and Kaštelan-Macan, M. (2007) Determination of pKa values of active pharmaceutical ingredients. TrAC Trends in Analytical Chemistry 26(11), 1043-1061.

Banzhaf, S., Nödler, K., Licha, T., Krein, A. and Scheytt, T. (2012) Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. Science of the Total Environment 438, 113-121.

Baumgarten, B., Jährig, J., Reemtsma, T. and Jekel, M. (2011) Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Research 45, 211-220.

Benotti, M.J., Song, R., Wilson, D. and Snyder, S.A. (2012) Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Science & Technology: Water Supply 12(1), 11-23.

Boethling, R.S., P.H., H., Meylan, W., Stiteler, W., Beauman, J. and Tirado, N. (1994) Group Contribution Method for Predicting Probability and Rate of Aerobic Biodegradation. Environ. Sci. Technol. 28, 459-465.

Broznić, D. and Milin, Č. (2012) Effects of temperature on sorption-desorption processes of imidacloprid in soils of Croatian coastal regions. Journal of Environmental Science and Health, Part B 47, 779-794.

Brusseau, M.L. (1994) Transport of reactive contaminants in heterogeneous porous media. Reviews of Geophysics 32(3), 285-313.

Chiang, P.C., Hu, Y. (2009) Simultaneous Determination of LogD, LogP, and pK_a of Drugs by Using a Reverse Phase HPLC Coupled with a 96-Well Plate Auto Injector. Combinatorial Chemistry & High Throughput Screening 12, 250-257.

Cremasco, M.A., Hritzko, B.J., Xie, Y. and Wang, N.H.L. (2001) Parameters Estimation for Amino Acids Adsorption in a Fixed Bed by Moment Analysis. Brazilian Journal of Chemical Engineering 18(2).

Fang, Y., Karnjanapiboonwong, A., Chase, D.A., Wang, J., Morse, A.N. and Anderson, T.A. (2012) Occurence, fate and persistence of gemfibrozil in water and soil. Environmental Toxicology and Chemistry 31(3), 550-555.

Flemming, H.-C. (1995) Sorption sites in biofilms. Wat. Sci. Tech. 32(8), 27-33.

Flores-Céspedes, F., González-Pradas, E., Fernández-Pérez, M., Villafranca-Sánchez, M., Socías-Viciana, M. and Ureña-Amate, M.D. (2002) Organic Compounds in the Environment - Effects of Dissolved Organic Carbon on Sorption and Mobility of Imidacloprid in Soil. J. Environ. Qual. 31, 880-888.

Gao, J.P., Maguhn, J., Spitzauer, P. and Kettrup, A. (1998) Sorption of Pesticides in the Sediment of the Teufelsweiher Pond (Southern Germany). I: Equilibrium Assessments, Effect of Organic Carbon Content and pH. Water Research 32(5), 1662-1672.

Geudens, P.J.J.G. (2012) Dutch Drinking Water Statistics 2012, VEWIN.

Gruenheid, S., Huebner, U. and Jekel, M. (2008) Impact of temperature on biodegradation of bulk and trace organics during soil passage in an indirect reuse system. Water Science & Technology 57(7), 987-994.

Kawasaki, M. (1980) Experiences with the Test Scheme under the Chemical Control Law of Japan: An Approach to Structure-Activity Correlations. Ecotoxicology and environmental safety 4, 444-454.

Keuten, M.G.A., Schets, F.M., Schijven, J.F., Verberk, J.Q.J.C. and van Dijk, J.C. (2012) Definition and quantification of initial anthropogenic pollutant release in swimming pools. Water Research 46, 3682-3692.

Loonen, H., Lindgren, F., Hansen, B., Karcher, W., Niemelä, J., Hiromatsu, K., Takatsuki, M., Peijnenburg, W., Rorije, E. and Struijś, J. (1999) Prediction of biodegradability from chemical structure: modeling of ready biodegradation test data. Environmental Toxicology and Chemistry 18(8), 1763-1768.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A. and 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 Research 45, 4722-4736.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Song, K.G. and 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. Journal of Contaminant Hydrology 140-141, 139-149.

Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K., Amy, G.L. (2011) Occurence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: A review. Water Research 45(10), 3015-3033.

Magic-Knezev, A. and van der Kooij, D. (2004) Optimisation and significance of ATP analysis for measuring active biomass in granular activated carbon filters used in water treatment. Water Research 38, 3971-3979.

Okey, R.W. and Stensel, H.D. (1996) A QSAR-based biodegradability model - A QSBR. Water Research 30(9), 2206-2214.

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

Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T. and Toze, S. (2011) Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122, 53-62.

R Development Core Team (2008). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, Vienna, Austria.

Radjenović, J., Petrović, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43, 831-841.

Ramil, M., El Aref, T., Fink, G., Scheurer, M. and Ternes, T.A. (2010) Fate of Beta Blockers in Aquatic-Sediment Systems: Sorption and Biotransformation. Environ. Sci. Technol. 44, 962-970.

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

Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W. and Keller, J. (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. Water Research 46(3), 863-872.

Schaffer, M., Boxberger, N., Börnick, H., Licha, T. and Worch, E. (2012a) Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. Chemosphere 87, 513-520.
Schaffer, M., Börnick, H., Nödler, K., Licha, T. and Worch, E. (2012b) Role of cation exchange processes on the sorption influenced transport of cationic ◎◎blockers in aquifer sediments. Water Research 46, 5472-5482.

Scheytt, T., Mersmann, P., Leidig, M., Pekdeger, A. and Heberer, T. (2004) Transport of Pharmaceutically Active Compounds in Saturated Laboratory Columns. Ground Water 42(5), 767-773.

Scheytt, T.J., Mersmann, P. and Heberer, T. (2006) Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83, 53-69.

Ternes, T.A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H. and Joss, A. (2004) A rapid method to measure the solid-water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge. Water Research 38, 4075-4084.

Toride, N., Leij, F.J. and van Genuchten, M.T. (1995) The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.0, Research Report No. 137, U.S. Salinity Laboratory, USDA, ARS, Riverside, CA.

Verliefde, A., Cornelissen, E., Amy, G., Van der Bruggen, B. and van Dijk, H. (2007) Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. Environmental Pollution 146, 281-289.

Verliefde, A.R.D. (2008) Rejection of organic micropollutants by high pressure membranes (NF/RO), Delft University of Technology, Delft.

Wang, C., Teppen, B.J., Boyd, S.A. and Li, H. (2011) Sorption of Lincomycin at Low Concentrations from Water by Soils. Soil Sci. Soc. Am. J. 76, 1222-1228.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environ. Sci. Technol. 39, 6649-6663.

Xu, J., Chen, W., Wu, L. and Chang, A.C. (2009) Adsorption and Degradation of Ketoprofen in Soils. J. Environ. Qual. 38(1177-1182).

Yu-Chen Lin, A., Lin, C.A., Tung, H.H. and Sridhara Chary, N. (2010) Potential for biodegradation and sorption of acetaminophen, caffeine, propranolol and acebutolol in lab-scale aqueous environments. Journal of Hazardous Materials 183, 242-250.

Zearley, T.L. and Summers, R.S. (2012) Removal of Trace Organic Micropollutants by Drinking Water Biological Filters. Environmental Science and Technology 46, 9412-9419.

Chapter 3

A predictive multi-linear regression model for organic micropollutants, based on a laboratory-scale column study simulating the river bank filtration process

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1 Introduction

Although several studies have indicated that RBF is an effective treatment process for many OMPs (Benotti *et al.*, 2012, Henzler *et al.*, 2014, Hoppe-Jones *et al.*, 2010), a few OMPs (e.g. carbamazepine, primidone) have been seen to be very persistent during soil passage (Benotti *et al.*, 2012, Rauch-Williams *et al.*, 2010). Drinking water companies are now faced with a lack of insight into why certain OMPs are removed during RBF while others show persistent behaviour. This makes it difficult to provide appropriate post-treatment after RBF to create an adequate or even absolute barrier against OMPs in drinking water treatment plants. While insight could be obtained by experimentally determining the removal of newly detected OMPs, this is practically not possible due to the high cost of analysis and the associated time investment. Therefore, alternative approaches are needed. Developing a quantitative-structure-activity-relationship (QSAR) for the prediction of OMP removal during RBF could satisfy such requirements. This type of model should enable drinking water companies to a-priori predict whether an OMP is removed during RBF based on its structural fragments (functional groups).

To develop a predictive model for OMP removal during RBF, first a parameter that enables a quantitative comparison in biodegradability between different OMPs should be determined. While most soil column studies on OMP removal report total OMP removal in percentage, such data cannot be used to quantitatively compare biodegradability potential for a group of OMPs - a similar percentage removal at the end of a column does not necessarily mean that the OMPs are biodegraded at the same rate. For example, imagine two soil columns (A and B, length is 1m) that are compared with regard to ketoprofen removal and both columns are characterised by a ketoprofen removal of 80%. It is possible that 80% ketoprofen removal in column A is reached after 10 cm soil passage, while column B requires the full column length/residence time for a similar removal percentage. A more adequate parameter to quantitatively compare biodegradability potential of a group of OMPs would therefore be the biodegradation rate. Although a number of studies investigated OMP biodegradation rates in soil column studies (Patterson *et al.*, 2011, Scheytt *et al.*, 2006, Scheytt *et al.*, 2007), these studies only focused on a limited number of OMPs, a certain class of OMPs (e.g. pharmaceuticals) and/or did not try to link these OMP biodegradation rates to the OMP functional groups.

OMPs are biodegraded by the microbial community present in the soil. Soil bacteria excrete enzymes which can attack the reactive site of the OMP. However, this enzyme attack can be hindered as a result of steric effects (the location of a functional group), electrical effects (functional groups increasing or decreasing the electron density of the OMP) or polar/a-polar interactions (Miller *et al.*, 1997). Therefore, the presence of certain functional groups on the OMP structure can play an important role in the OMP biodegradation process. Several studies found a correlation between certain functional groups present in the OMP molecular structure and OMP degradability in biological processes. However, these studies were often limited to a certain class of OMPs or did not specifically focus on the RBF process but on other biological treatment processes such as activated sludge and/or membrane bioreactors which are usually characterized by higher biomass quantities (Alexander *et al.*, 1966, Okey *et al.*, 1996, Pitter, 1985, Tadkaew *et al.*, 2011).

In addition, tools such as BIOWIN and CATABOL can be used to determine the biodegradability potential of OMPs based on the structural fragments present in the molecular structure. These tools are not limited to a specific group or class of OMPs, but biodegradation potential for these OMPs is

determined in tests that use a mixture of sludge, surface soil, and water from a variety of sites such as sewage treatment plants, industrial waste water treatment works, rivers, lakes and seas as inoculum (OECD, 1981, 1992). Biomass density and quality can differ significantly between for example sewage treatment plants and natural treatment systems such as RBF which questions the applicability of these models for RBF systems. Moreover, the tests used to determine these biodegradation rates are often spiked with much higher concentrations of OMPs than naturally present in river water bodies. This can lead to shorter adaptation times and higher biodegradation rates and as a consequence it provides less realistic results (Baumgarten *et al.*, 2011). Thus, there is a lack of OMP biodegradation rates representative for the RBF system which can be used to develop a predictive model based on the functional groups present in the OMP molecular structure.

A first step towards a predictive model for OMP removal during RBF was proposed in Chapter 2, that described a relation between OMP biodegradation rate and the functional groups present in the OMP molecular structure. However, a limitation of this study was that the RBF lab-scale columns were filled with clean filter sand. Since the soil microbial community is responsible for the OMP biodegradation, and this community is affected by environmental factors such as soil organic carbon content, nutrient availability, and OMP sorption, OMP biodegradation rates may differ, especially between clean filter sand and soil from an operational RBF site. In addition, a relatively small number (14 in total) of OMPs were tested in the previous study and the use of technical sand made it impossible to validate the developed model with field data.

To overcome the aforementioned limitations, a larger set of OMPs (representing various classes of OMPs, e.g. pesticides, pharmaceuticals, industrial waste products) should be investigated and biodegradation rates for these OMPs should be obtained from lab-scale columns filled with soil from an operational RBF site. Subsequently, the model should be validated with field data to test its applicability for drinking water companies.

Therefore, this study investigates: (1) if a correlation exists between OMP biodegradation rates obtained from a lab-scale oxic soil column system filled with soil from an operational RBF site and the functional groups present in the OMP molecular structure (2) the general applicability of the developed model for OMP removal data obtained from the RBF field site that the column is trying to mimic. Laboratory scale columns were filled with oxic soil from RBF site Engelse Werk of drinking water company Vitens (The Netherlands), and were used to simulate the oxic zone of the RBF process at this site. The OMP mixture dosed in the columns was carefully selected to cover different classes of OMPs (e.g. pharmaceuticals, pesticides, industrial agents, food/beverage additives) and a wide variety of functional groups (e.g. aryl-aliphatic ethers, aliphatic ethers, amide, carboxylic acids, carbonyl, esters, ethers, fosfor, halogens, hydroxyl, methyl, primary/secondary/tertiary amines, phosphine oxide, rings, sulphonamide, sulfur), thus representative for a large number of OMPs present in the environment. In addition, some of the selected OMPs have been reported to be detected frequently or in high concentrations in the Dutch surface waters (ter Laak et al., 2014, van der Hoek et al., 2014, Verliefde et al., 2007). OMP biodegradation rates were determined by fitting the convection-dispersion equation to the experimental data. Multi-linear regression was then used to correlate the OMP biodegradation rates obtained in the column study to the functional groups present in the OMP molecular structure. Finally, the developed model was used to predict biodegradation rates of an OMP mixture monitored in the field to validate the model.

2 Materials and Methods

2.1 Experimental set-up

The experimental set-up consisted of 2 transparent PVC columns (L = 1 m, D = 36 mm) in series. Both columns were filled with oxic soil from RBF site Engelse Werk of drinking water company Vitens (52°29'39" N, 6°3'40.4" E). Columns were filled with soil in increments of 4-5 cm while tapping on the column, to prevent layering in the columns. To prevent leaching of soil grains, the top and bottom of the column were fitted with perforated PVC plates (30 holes, d = 0.8 mm) that were covered with filter cloth (45 μm, Top7even net & mesh, The Netherlands). A flow from bottom to top was maintained in both columns to prevent air entrapment and the system was operated in a temperature controlled room (12 °C) in the dark (to prevent algae growth and/or OMP loss due to photolysis).

The pilot was fed from a jerrycan filled with Lek river water and an OMP mixture. River water was refreshed every two weeks and was filtered (d = 0.4 mm), prior to use as feed, to prevent twigs and larger particles from clogging the pump tubes. After every replacement feed jerrycans were washed twice with acetone and flushed several times with demineralized water before refilling to prevent biofilm formation. The feed solution was pumped through the columns by a peristaltic multichannel 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 dark polyamide tubing (d_i = 2.9 mm, Festo, The Netherlands). The hydraulic loading rate applied on the columns was 0.5 L/d, which equals a filtration rate of 0.5 m/d. Pore velocity and porosity in the pilot was determined using deuterium (^2H) as tracer. Deuterium concentrations were determined with laser absorption spectroscopy using a DLT-100 Liquid-Water Isotope Analyzer (Los Gatos Research, USA); precision ±0.56‰ for ^2H. A quantity of 0.19 mL of 99% pure Deuterium was added to the feed solutions (20 L), resulting in an approximate 60 ‰ increase in δ-^2H. Pore velocity and porosity were 1.48 m/d and 0.33, respectively.

2.2 Organic micropollutants

A mixture of 31 OMPs was dosed into the feed solutions of the columns (500 ng/L of each OMP). All compounds used 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 experiments. The OMP mixture analysed in the in- and effluent of the oxic pilot was measured on a monthly basis for about 7 months.

Table 1 presents an overview of all OMPs investigated in this study (in both the lab-scale columns and the field), their physico-chemical properties and the method used to analyse the compound. The OMP mixture was analysed using four different methods. Some OMPs were measured with two different methods as a way of quality control. OMP removal (C_e/C_0) for compounds measured with different methods was compared by means of an ANOVA test, to cross-check results between different analytical methods. No statistical significant differences in C_e/C_0 values were found for any of the OMPs (p-value < 0.05 for all OMPs).

Functional groups were identified for every molecule and the results are presented in Table 1 of the SI.

Method 1: Samples of 100 mL of the influent and effluent from the columns were collected in glass bottles. A mixture of mass labelled internal standards (atrazine-d_5, acetaminophen-d_4, ketoprofen-d_3,

metoprolol-d_7, diuron-d_6 and sulfamethoxazole-$^{13}C_6$) was added to every sample or calibration standard to a final concentration of atrazine-d_5: 50 ng/L, metoprolol-d_7: 1500 µg/L, sulfamethoxazole-$^{13}C_6$: 600 ng/L, ketoprofen-d_3: 600 ng/L, diuron-d_6: 200 ng/L, acetaminophen-d_4: 500 ng/L. The OMPs in solution were extracted using Oasis HLB cartridges (200 mg, 6 cc) (Waters, USA), which had been conditioned with 3 mL of methanol (≥99.9%, Sigma Aldrich) and 5 mL Milli-Q water. Following extraction of the OMPs, cartridges were flushed with 2 x 2.5 mL Milli-Q water to remove salts after which the cartridges were dried under vacuum for 10 minutes. The OMPs on each cartridge were eluted with 2 x 4 mL of methanol, which was subsequently evaporated with N_2 gas to a volume of 100 µL (200 µL for the increased OMP concentration in experimental module 2).

OMPs were analysed with UHPLC-HR-Orbitrap-MS. A benchtop Exactive™ Orbitrap mass spectrometer (Thermo Fisher Scientific, USA) was coupled to an Accela autosampler (maintained at 15 °C), Accela degasser and an Accela 1250 pump, which pumped the injected extract (10 µL) and solvents at a flow rate of 300 µL/min over the column. The injected extract was segregated on a Nucleodur C18 Pyramid column (100 mm × 2.1 mm, 1.8 µm, Macherey-Nagel, PA, USA) at 25 °C. Solvent A (0.08% HCOOH dissolved in ultra-pure water) and solvent B (MeOH) were used according to the following gradient: starting from 98% A and 2 % B, which was held for 1 minute; in 0.5 min the contribution of solvent B increased to 90%; the percentage of B was increased further to 100% in 3 minutes and held for 1 minute; equilibration at initial conditions was done for 1.5 minutes. After segregation of the extract on the column, components were ionised with a HESI-II (Heated Electrospray Ionisation) interface. The HESI-II interface was set to a spray voltage of 4000 V, a capillary temperature of 250 °C and a capillary voltage of 82.50 V. The sheath gas flow rate was set to 30 arbitrary units, no auxiliary or sweep gas were used. The tube lens and skimmer voltage were set to 120 V and 20 V respectively. The vaporizer heater temperature was set to 350 °C. Ionized components were sent to an Orbitrap™-HRMS (Thermo Fisher Scientific, USA) at a polarity alternating from negative to positive ion mode, and operating in a scan range of 80.0 – 800.0 m/z. A resolution of 50 000 FWHM (full width at half maximum) and an automatic gain control (AGC) target of 5.10^5 were used for detection. The High Energy Collision Dissociation (HCD) cell was turned off. Data interpretation was performed with the Thermo Xcalibur 2.1.0.1140 software package (Thermo Fisher Scientific, USA). Every analyte was detected based on the accurate mass of the precursor ions: $[M+H]^+$ and $[M-H]^-$. The maximum mass tolerance was set to 5.0 ppm.

Method 2: Pharmaceutical compounds were analysed using HPLC-MS/MS (API 5500 AB-Sciex. USA). Before injecting the OMP sample (1000 µL) onto the column, 80 µL internal standard and 0.1% formic acid was added to the sample. The injected extract was segregated on a Atlantis T3 (150 mm x 4.6 mm. 3 µm) column (Waters. USA) at 25 °C. Solvent A: Milli-Q water with 0.1% formic acid (HCOOH. Boom. The Netherlands); solvent B: Acetonitrile (C_2H_3N. Lab-scan. Ireland). Solvent A and B were used according to the following gradient for positive ionisation: starting with 99.5% A and 0.5% B for 1.5 minutes; increasing the contribution of solvent B to 95% B. 5% A in 32.5 minutes which was then held for 6 minutes; and 1 minute decreasing the contribution of solvent B to 0.5% B. 99.5% A. For negative ionisation. solvent A and B were used according to the following gradient: starting with 99.5% A and 0.5% B for 1.5 minutes; increasing the contribution of solvent B to 95% B. 5% A for 18.5 minutes which was held for 5 minutes; decrease the contribution of solvent B to 0.5% B. 99.5% A for 2 minutes. The flow was 1 mL/min. After segregation of the extract on the column, analytes were ionised with Turbo Ion Spray. Curtain gas was set to 20 psi. the Nebulizer gas was set to 50 psi and

the Turbo gas was set to 50 psi. The Ionspray voltage was set to 5000 V (-3000 V for negative ionisation), temperature of the heaters equalled 600 °C and collisionally activated dissociation was set to 7 psi. An API 5500 (AB-Sciex. USA) was used for detection. Analyses of the analytes was performed with the AB-Sciex Analyst 1.5.2 software package (AB-Sciex. USA). The analyte was detected based on product ion (daughter) of the precursor ion (parent): [M-H^+] or [M-H^-].

AMPA was analysed in the same manner as the pharmaceutical compounds, only the sample preparation was different. Before injecting the OMP sample (1000 µL) onto the column, 2.5 mL Boraxbuffer and 400 µL titriplex(III)-solution was added to 30 mL of the sample. The titriplex(III)-solution was added to bind amongst others copper(II) and iron(II) to improve derivatisation. After storing the samples overnight in the fridge, 6.5 mL of the sample is collected in a vial and internal standard (52 µL) and 1000 µL FMOC-Cl reagens in acetonitrile added. After 2 hours the derivatisation is ended by adding 80 µL formic acid.

Method 3: Pesticides were analysed using HPLC-MS/MS (API 4000 AB-Sciex. USA). Before injecting the OMP sample (1000 µL) onto the column. 80 µL internal standard . 10 mmol ammonium acetate and 0.1% formic acid was added to the sample. The injected extract was segregated on a Polaris 3 C18-A (1500 mm x 4.6 mm. 3 µm) column (Varian. USA) at 35 °C. Two solvents were used: A and B. Solvent A was Milli-Q water with 10 mmol ammonium acetate (Boom. The Netherlands). 0.1% formic acid (Boom. The Netherlands) and 1% acetonitrile (Lab-scan. Ireland). Solvent B was Acetonitrile with 10 mmol ammonium acetate. 0.1% formic acid and 10% Milli-Q water. Solvent A and B were used according to the following gradient for positive ionisation: starting with 0% B. 100% A for 2 minutes. increasing the contribution of solvent B to 100% B. 0% A for 31 minutes which was then held for 2 minutes. decrease the contribution of solvent B back to 0% B. 100% A for 1 minute. For the negative ionisation. solvent A and B were used according to the following gradient: starting with 0% B. 100% A for 2 minutes. increase the contribution of solvent B to 100% B. 0% A for 8 minutes which was held for 10 minutes. decrease the contribution of solvent B back to 0% B. 100% A for 1 minute. The flow was 1 mL/min. After segregation of the extract on the column, analytes were ionised with Turbo Ion Spray. Curtain gas was set to 30 psi. the Nebulizer gas was set to 80 psi (60 psi for negative ionisation) and the Turbo gas was set to 50 psi (40 psi for negative ionisation). The Ionspray voltage was set to 3000 V (-3000 V for negative ionisation). temperature of the heaters equalled 500 °C and collisionally activated dissociation was set to 8 psi. Analyses of the analytes was performed with the AB-Sciex Analyst 1.5.2 software package (AB-Sciex. USA). The analyte was detected based on product ion (daughter) of the precursor ion (parent): [M-H^+] or [M-H^-].

Method 4 : Volatile hydrocarbons were analysed using GC-MS (Thermo, Interscience, USA). Analytes were purged from the water phase with helium, after which they were retained on a trap (Teledyne Tekmar Analytical Vocarb 3000). The temperature of the cold trap was reduced to -165 ° C using liquid nitrogen. The Vocarb 3000 is rapidly heated to 250 °C to enable desorption of the analyte to the cold trap. When all components were moved from the Vocarb 3000 to the cold trap, the cold trap was heated to 250 °C and by means of thermal desorption the analytes were placed on-line on a capillary column (J & W DB-624, 60m x 0.32 mm, df = 1.8 mm, 40°C). Interpretation of the data was performed with the Thermo Xcalibur 2.2 software package (Thermo Scientific, USA).

2.3 Water quality and soil parameters

The dissolved organic carbon (DOC) concentration was measured with a Shimadzu TOC Analyser after filtering the aqueous samples through 0.45 μm filters (Whatman, Germany); these filters were flushed twice with demineralized water prior to use. Oxygen and temperature were measured with an oxygen meter (FDO® 925 IDS probe, Oxi340i, WTW, Germany) and pH was measured with a multimeter (SenTix® 940 IDS probe, Multi 340i, WTW, Germany) directly in the feed or in a flow through cell connected to the effluent tubes of the columns. Ions were analysed with an ProfIC 15 – AnCat ion chromatograph (Metrohm 881 anion (suppressed) and 883 cation system) (Metrohm, Switzerland) after filtering the aqueous samples through 0.45 μm filters (Whatman, Germany); these filters were flushed twice with demineralized water prior to use. For the anions an A Supp 150/4.0 anion column was used with 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ eluent. For the cations a C5 cation column with 3 mM HNO_3 eluent was used. Regenerant for the suppressor was 50 mM H_2SO_4.

ATP analysis was performed at the end of the experiment. Sand samples (10 g) were obtained from both oxic pilot systems at the influent and effluent side, to determine adenosine triphosphate (ATP) concentrations 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 (2 minutes, amplitude 20%, Boom BV Meppel). After sonication the supernatant was decanted and 10 mL fresh demineralized water was added. Sonication was repeated until the difference in ATP concentration measured in the supernatant was smaller than 10%. Three HES treatments of 2 min were found to be sufficient. From every supernatant sample 667 μL was collected to obtain a mixture of 2 mL in total. From this mixed sample, 200 μL was subjected to ATP analysis. ATP analysis was performed with a Quench-Gone Aqueous™ test kit (Aqua tools, France). The test kit measures the concentration 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 at least 24 hours to determine the dry weight.

Soil pH was measured by adding 40 mL demineralized water to a soil sample (16 g). The mixture was shaken manually every hour and pH of the solution was measured the following day. This pH value is referred to as pH-H_2O. To determine the long-term exchange capacity of H_3O^+ ions, pH was also measured after addition of KCl. After analysing the pH in the water solution, 1.8 g KCl was added. The mixture was shaken manually every 15 minutes and again the pH of the solution was measured. This pH is referred to as pH-KCl.

Grain size distribution of the soil was determined with laser diffraction (Helium-Neon Laser Optical System, KR). Organic matter content of the soil was determined from thermo gravimetric analysis (TGA-601, Leco Corporation). The soil sample was heated to 550 °C and weight loss was determined (LOI550) to obtain an indication for the total organic matter content of the soil. This value was corrected by 7% of the clay content which equals the cumulative value of 8 μm from the grain size distribution (Hagen, 2014). This correction is necessary for Dutch soils to compensate for the loss of crystallization water (Hagen, 2014). According to Eq. 1 (Hagen, 2014):

$$SOM = LOI\ 550 - 0.07 \cdot L \qquad \text{(Eq. 1)}$$

In which:

SOM = Soil Organic Matter [% dry weight]

LOI550	=	Loss of Ignition at 550°C	[% dry weight]
L	=	clay content (fraction < 8 μm from grain size distribution)	[% dry weight]

Soil organic matter was converted to organic carbon by Equation 2 (Hieltjes *et al.*, 1983, van den Berg, 1998, van Reeuwijk, 1992):

$$SOM = 2 \cdot SOC \qquad \text{(Eq. 2)}$$

In which:

SOC	=	Soil Organic Carbon	[% dry weight]

Cationic exchange capacity (CEC) was calculated according to Equation 3 (Appelo *et al.*, 2005, Breeuwsma *et al.*, 1986):

$$CEC_{calc} = 7 \cdot (\%\ clay) + 35 \cdot (\%\ C) \qquad \text{(Eq. 3)}$$

In which:

CEC_{calc}	=	calculated cationic exchange capacity	[meq / kg dry weight]
% clay	=	clay content (fraction < 8 μm from grain size distribution)	[% dry weight]
% C	=	organic carbon content	[% dry weight]

DGGE analysis was performed on soil samples from the in- and effluent of both columns to gain more insight into the microbial community composition as characterized by richness and evenness. Total DNA extraction was performed as previously described (Boon *et al.*, 2000). The 16S rRNA gene regions were amplified by PCR using 338F and 518R primers targeting the V3 region (Muyzer *et al.*, 1993, Øvreås *et al.*, 1997). A GC clamp of 40 bp was added to the forward primer. The PCR program consisted of 10 min. 95°C; 30 cycles of 1 min. 94°C, 1 min. of 53°C, 2 min. of 72°C; and a final elongation for 10 min. at 72°C. Amplification products were analysed by electrophoresis in 1.5% (wt/vol) agarose gels stained with ethidium bromide. DGGE was performed as previously described (Callewaert *et al.*, 2013). The normalization and analysis of DGGE gel patterns was done with the BioNumerics software 5.10 (Applied Maths, Belgium). The community richness (R) was analysed by means of quantification of the total number of bands present on the DGGE gel. This gives an indication of the richness and genetic diversity of species within the bacterial community. A high richness indicates the presence of many types of bacteria. The community evenness was analysed by means of the Gini coefficient (Read *et al.*, 2011). A low evenness indicates an unequal community (1 dominant bacteria), while a high evenness indicates an equal community (no dominant bacteria). A low evenness is characterised by a high Gini coefficient, while a high evenness is characterised by a low Gini coefficient.

2.4 Statistical analysis

The statistical software package IBM SPSS Statistics for Windows version 20.0 was used to perform all statistical analyses (IBMCorp., 2011).

2.5 Modelling

CXTFIT (Toride *et al.*, 1995a) was used to obtain the biodegradation rate (μ) of the OMPs in the columns by fitting the experimental data using the inverse problem based on the deterministic equilibrium convection dispersion equation (CDE) as described in Chapter 2.

Several studies as well as Chapter 2 investigating OMP sorption demonstrated that retardation factors were close or equal to 1 for most OMPs (Burke *et al.*, 2013, Henzler *et al.*, 2014). Therefore the retardation factor was set to 1 in this study for OMPs for which the breakthrough curve was not determined. In addition, data acquisition for the 7 month period showed that C_e/C_0 values obtained steady state conditions, which indicates that the biodegradation rate will not be underestimated as a result of incomplete breakthrough.

The diffusion and dispersion coefficients for the OMPs are shown in Table 3 of the SI.

2.6 RBF field site

Removal behaviour of a mixture of 23 OMPs (pesticides, pharmaceuticals, x-ray contrast media, food/beverage ingredients and industrial compounds) was investigated at RBF site Engelse Werk of drinking water company Vitens, The Netherlands (Table 1). A detailed description of the analytical techniques used to measure the OMP concentrations in the field is presented in the SI.

RBF site Engelse Werk is located along the river IJssel, a tributary of the river Rhine. The oxic monitoring well (94-61, Figure 1) from which the samples for OMP analysis were taken, is situated approximately 10 meter from the river and is characterised by a travel time from the river of about 1 – 3 months. The water abstracted from this well is solely river water (no dilution with groundwater occurring). The oxic monitoring well consists of five mini filters (diameter = 3 cm) located at a height of 10, 15, 20, 25 and 30 m below the average river water level. While OMP concentrations in the river were monitored for more than 20 years in a measuring campaign of the Dutch drinking water companies (Stoks *et al.*, 2013), the mini filters were sampled on only three consecutive events. Since it is almost impossible to obtain OMP biodegradation rates from field data, OMP removal for the 23 compounds was classified as full removal, partial removal or no removal. If an OMP was removed till below its detection level, it was assigned "full removal". In case an OMP was not removed till below its detection level, but the removal was more than 10%, "partial removal" was assigned to the OMP. "No removal" was assigned to an OMP if the OMP concentration in the oxic monitoring well was similar to that in the river or when OMP removal was smaller than 10%.

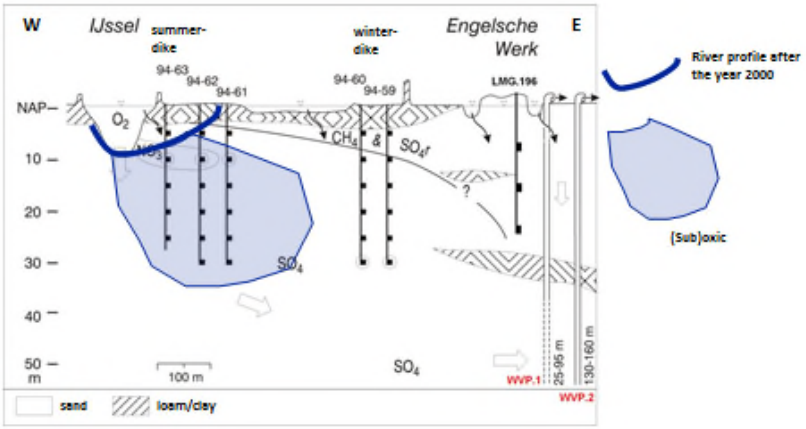

Figure 1 - Cross section of RBF field site Engelse Werk

Table 1 – Organic micropollutants, their physico-chemical properties and analytical method used

OMP	MW	pK_a	Charge at pH 8	Log D at pH 8[1]	Analytical method column study	Analytical method field study
2,4-Dichlorophenoxyacetic acid (2,4-D)	221.04	2.6[a]	-1	-0.69	3	
Acetaminophen	151.16	9.3[b]	0	0.85	1	
(Aminomethylphosphonic acid) AMPA	111.04	1.8, 5.4, 10.0[c]	0	-3.51		2
Atrazine	215.68	<2 (1.6)[d]	0	2.26	1, 3	
Bentazone	240.28	3.3[e]	0	0.57	3	
1H-benzotriazole	119.12	8.57[f]	0	1.25		3
Bisphenol A	228.29	9.9-11.3[g]	0	4.05		4
Caffeine	194.19	10.4[h]	0	-0.58		2
Carbamazepine	236.27	-[b]	0	2.64	1, 2	2
Chloridazon	221.64	3.4[i]	0	1.05	1, 3	
Clofibric acid	214.65	3.2[j]	-1	-0.18	1, 2	
Diatrizoic acid	613.91	3.4[k]	-1	-0.21		2
Dichlorprop	235.06	2.7[l]	-1	-0.12	3	
Diclofenac	296.15	4.2[j]	-1	1.21	1, 2	
Diglyme	134.17	~4[m]	0	0.10	1, 3	3
Dimethoate	229.26	2.0[n]	0	0.21	1	
1,4-Dioxane	88.11	-	0	-0.04		4
Diuron	233.09	13.6[i]	0	2.49	1, 3	
ETBE	102.17	-	0	1.61		4
Hydrochlorothiazide	297.74	7.9[o]	0	-0.72	1	
Ibuprofen	206.28	4.3[b], 4.9[j]	-1	1.01	2	
Iomeprol	777.09	11.7, 12.6, 13.6[i]	0	-1.39	2	
Iopamidol	777.08	10.7[p]	0	-0.66		2
Ketoprofen	254.28	4.7[b]	-1	0.49	1, 2	
Lincomycin	406.54	7.6[q]	+1	-1.22	1	
MCPA	200.62	3.1[r]	-1	-0.77	3	
MCPP	214.65	3.1[i]	-1	-0.22	3	
Metoprolol	267.36	9.4[b], 9.7[o]	1	0.14	1	2
MTBE	88.15	-3.7[s]	0	1.25		4
Phenazone	188.23	1.4[o]	0	1.11	1, 2	
Pindolol	248.32	9.3[o]	+1	0.10	2	
Pirimicarb	238.29	4.5[t]	0	1.74	1	
Propranolol	259.34	9.4[b]	+1	0.95	2	
Prosulfocarb	251.39	-	0	4.19	3	
Simazine	201.66	1.6[n]	0	1.83	1	
Sotalol	272.36	9.44[u]	+1	-1.52		2
Sulfamethoxazole	253.28	1.8, 5.8[i]	0	0.39	1, 2	
Terbutaline	225.28	8.8, 9.5, 10.5[v]	+1	0.18	1, 2	
4-Tertoctylphenol	206.33	10.39[w]	0	4.71		4

Tetraglyme	222.28	-	0	0.06		3
Theophylline	180.16	8.6[b]	0	-1.09	1	
Triglyme	178.23	-	0	0.08		3
Triphenylphosphine oxide (TPPO)	278.28	-	0	4.76	3	3
Triclopyr	256.47	2.7[x]	-1	-0.53	1	

[1] http://www.chemicalize.org

[a] (Celis *et al.*, 1999), [b] (Chiang *et al.*, 2009), [c](Chen *et al.*, 2009), [d](Westerhoff *et al.*, 2005), [e](Boivin *et al.*, 2005), [f](Albert *et al.*, 1948), [g](Rykowska *et al.*, 2006), [h]Obtained from Drugbank (http://www.drugbank.ca), [i](Margot *et al.*, 2013), [j](Packer *et al.*, 2003), [k](Crowley *et al.*, 1986), [l](Loffhagen *et al.*, 2003), [m](Su, 1979), [n](Yang et al., 2013), [o](Ferreira da Silva et al., 2011), [p](Felder et al., 1988), [q](Wang et al., 2011), [r](Vione *et al.*, 2010), [s](Pletcher *et al.*, 1967),[t]http://pubchem.ncbi.nlm.nih.gov, [u](de Ridder *et al.*, 2011), [v](Shalaeva *et al.*, 2007), [w](Błędzka *et al.*, 2009), [x](Petty *et al.*, 2003)

3 Results and Discussion

3.1 Soil and water quality parameters

Soil pH was 7.90/8.23 [pH-KCl/pH-H_2O], soil organic matter content was 0.92 % dry weight and cationic exchange capacity (CEC) was 42.13 meq/kg dry weight. DOC removal of the soil column system was equal to 30.7 ± 14.3%. Oxygen was reduced to low concentrations (1.1 ± 0.8 mg/L, n = 12) in the effluent, but no nitrate removal was observed (see SI, Table 4). This implies that oxic conditions were maintained in the pilot during the experiment. ATP concentrations in the column and at the field site were in the same order of magnitude (547 and 235 ng/cm^3 for the column and the field site, respectively).

3.2 OMP biodegradation rates

OMP biodegradation rates determined from fitting the convection-dispersion equation (Eq. 1) to the experimental data are presented in Table 2 (confidence intervals are presented in Table 5 and 6 of the SI). To get an indication of how well the experimental data fitted the convection-dispersion equation, Figure 1 (SI) shows a plot of the experimental versus the modelled C_e/C_0 values. In case an OMP rapidly degraded (e.g. pindolol), a statistically significant retardation factor could not be determined. To be able to determine the degradation rate, the retardation factor for these OMPs was set equal to 1. This assumption is justified since a number of previous studies as well as Chapter 2 showed that retardation factors of OMPs are close or equal to 1 (Burke *et al.*, 2013, Henzler *et al.*, 2014). Exceptions were metoprolol and propranolol which are well known to show strong sorption affinities with soil and are in general characterized by higher retardation factors than 1 (Chapter 2, Burke et al., 2013). It was expected that given the long operational period in this study, breakthrough would be observed for both these OMPs. However, this was not the case and thus biodegradation rate of these two specific OMPs could not be determined.

Table 2 – OMP degradation rates (μ) for oxic pilot

OMP	Vitens soil Biodegradation rate μ [d^{-1}]
2,4-D	3.00
Acetaminophen	2.30
Atrazine	0.03 ± 0.04[3]
Bentazone	0
Carbamazepine	0.11 ± 0.16[3]
Chloridazon	2.58 ± 0.33[1,3]
Clofibric acid	1.00 ± 0.25[1,3]
Dichlorprop	1.82
Diclofenac	2.06 ± 0.33[3]
Diglyme	0.00 ± 0.00[3]
Dimethoate	0.37[1]
Diuron	0.92 ± 0.50[3]
Hydrochlorothiazide	0
Ibuprofen	2.84
Iomeprol	2.23
Ketoprofen	2.53 ± 0.23[3]
Lincomycin	0.34[1]
MCPA	2.50
MCPP	2.10
Metoprolol	ND[2]
Phenazone	2.67 ± 0.04[1,3]
Pindolol	2.23
Pirimicarb	0.14
Propranolol	ND[2]

Prosulfocarb	2.57
Simazine	0
Sulfamethoxazole	1.44 ± 0.01[1,3]
Terbutalin	1.79 ± 0.50[3]
Theophylline	1.43
TPPO	0
Triclopyr	0.33[1]

[1] For these OMPs an increase in biodegradation rate over time (adaptation) was observed and therefore the adapted biodegradation rate was determined.
[2] ND = Not Determined; It was not possible to determine the retardation factor and biodegradation rate for these OMPs since breakthrough was not observed and no abiotic column was operated.
[3] For OMPs analysed with two methods, an average degradation rate (± st dev) is presented

In general, the magnitude of the biodegradation rates, as well as the spread in biodegradation rates found in the current chapter was lower ($\mu = 0 – 3.24$ d^{-1}) compared to Chapter 2 ($\mu = 0 – 15.8$ d^{-1}). This is remarkable since more active biomass (ATP = 547 ng/cm^3) was present in the soil columns of the current study and a higher DOC removal (30.7 ± 14.3%) was observed compared to the previous study (ATP = 59 ng/cm^3, DOC removal = 5 - 10%). Since the previous study used lab-scale columns filled with technical sand and the current study obtained soil from a RBF site, higher OMP biodegradation rates would be expected (more bacteria present and more substrate available). However, the lower OMP biodegradation rates obtained in the current study could be explained by the higher concentration of easily degradable carbon present in the feed water compared to the previous study. This trend of improved OMP removal in water with lower biodegradable substrate was also observed in other studies (Alidina *et al.*, 2014b, Tiehm *et al.*, 2011).

The obtained degradation rates provide drinking water companies with more insight in the required residence time of river water in the RBF process under oxic conditions necessary to obtain a certain extent of removal of specific pollutants. To the best of the authors knowledge, degradation rates of dichlorprop, iomeprol, MCPA, MCPP, pindolol and prosulfocarb were determined for the first time in the current study.

Most OMPs are removed for >90% ($= 4 \cdot t_{1/2}$, with $t_{1/2} = \ln(2) / \mu$) after about 3 days, while >99% ($= 7 \cdot t_{1/2}$) is removed after about 5 days residence time. Depending on the local geo-hydrological settings a substantial to complete removal of these OMPs can be expected.

Dimethoate, lincomycin, triclopyr, carbamazepine, pirimicarb and atrazine were characterized by much longer half-lives ($t_{1/2}$ = 1.9 - 6.3 days) and thus require a longer residence time in the aquifer to show some extent of removal (required residence time = 13.1 - 44.1 days for 99% removal).

The persistent OMPs ($\mu \approx 0$) atrazine, diglyme, hydrochlorothiazide, simazine, bentazone, and TPPO are most likely not degraded during RBF. This indicates that additional research is required towards the removal of these compounds under other redox environments or possible post-treatment techniques to remove these compounds at drinking water treatment locations using RBF.

3.3 Correlation between OMP biodegradation rate and functional groups

Multi-linear regression was used to determine a relation between OMP biodegradation rates and functional groups present in the OMP molecular structures.

The relation between OMP biodegradation rate and functional groups for the complete OMP mixture is presented by the following equation ($R^2 = 0.65$, p-value = 0.003 < 0.05):

$$\mu = 3.269 + 1.199 \cdot CA + 0.470 \cdot OH + 1.253 \cdot CO - 1.478 \cdot Et - 0.794 \cdot H - 0.827 \cdot AE - 0.894 \cdot Ring - 0.393 \cdot Me \quad \text{Eq. 4}$$

In which:

μ	=	biodegradation rate	[d^{-1}]
CA	=	number of carboxylic acids	[-]
OH	=	number of hydroxyl groups	[-]
CO	=	number of carbonyl groups	[-]
Et	=	number of ethers	[-]
H	=	number of halogens	[-]
AE	=	number of aliphatic ethers	[-]
Me	=	number of methyl groups	[-]
Ring	=	number of ring structures	[-]

The experimental and predicted biodegradation rates μ are presented in Figure 1.

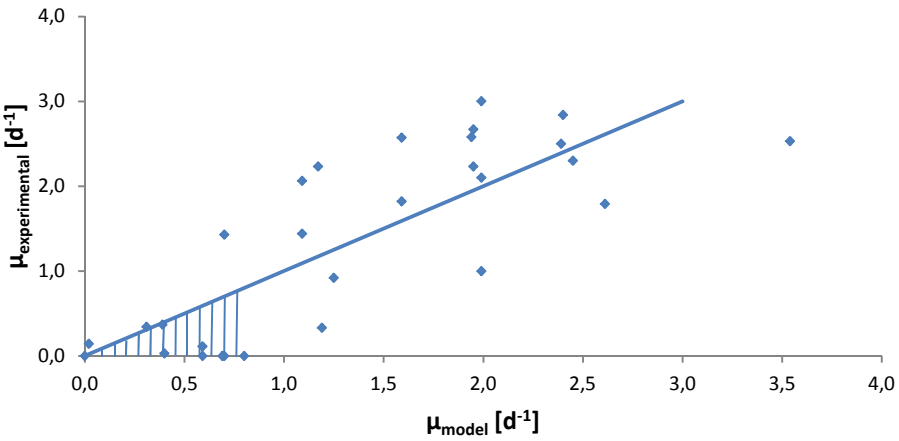

Figure 1 – Predictive model μ versus experimental μ

The predictive model was validated according to the guidelines described by the OECD for validating QSAR models (OECD, 2007). The regression coefficient shows whether the functional group will increase or decrease the OMP biodegradation rate. Carbonyl, carboxylic acids, and hydroxyl groups increase the biodegradation rate and ethers, halogens, aliphatic ethers, rings and methyl groups decrease the biodegradation rate. To determine the relative importance of each of these descriptors, the standardized beta coefficients should be determined (Figure S2). Standardized beta coefficients were all more or less in a similar range (0.42 - 0.70) which implies that the quantitative contribution of the different functional groups are roughly equally distributed, with the contribution of the carbonyl group being the smallest and the contribution of the halogen group being the largest. The statistical significance of the descriptor variables was also tested and these values were <0.05 for all descriptors (see column "Sig" in lowest Table of Figure S2), indicating that these values are statistical significant. To asses if the descriptor variables were not strongly correlated to each other, collinearity was tested with the variation of inflation factor (VIF) which should be lower than 5. This was the case for all descriptor variables.

R^2 is used to determine the goodness-of-fit. $R^2 = 0.65$ for the developed model which demonstrates that 65% of the variance in biodegradation rate can be explained by the functional groups presented in this model . R^2 adjusted is used to determine if the model is not over-fitted. When adding the descriptors stepwise, R^2 adjusted increases to a maximum value of $R^2 = 0.50$, thus the added descriptor reduces the unexplained variance (i.e., the model is not over-fitted).

The standard error of the estimate s = 0.77 d^{-1}, thus predicted OMP biodegradation rates lower or equal to this value are not reliable. These values are indicated in the striped triangle in Figure 1 and represent the persistent OMPs (atrazine, carbamazepine, bentazone, simazine and hydrochlorothiazide). For these compounds (false-positives) the predicted biodegradation rates (μ = 0.40 - 0.80 d^{-1}) are higher compared to the biodegradation rates observed in the columns study (for almost all of these OMPs close to 0 d^{-1}). Thus, OMPs with predicted biodegradation rates lower or around 0.77 d^{-1}, should be carefully monitored in the field, to determine their removal during RBF.

The *F*-value tests the null hypothesis that the coefficients in the multi linear regression equation are equal to 0, implying that the corresponding group does not have a significant effect on the biodegradation rate. Given the degrees of freedom of the experiment and the required confidence level (usually α = 0.05), critical values for the *F*-value can be found in standardized tables. For the experimental conditions investigated in this study, the *F*-value should be > 2.57 (Fischer *et al.*, 1974). The determined *F*-value in this study is 4.56 > 2.57, thus indicating that the null hypothesis can be rejected and that the probability that the regression coefficients are by chance unequal to 0 is <5%.

Eq. 4 shows that the presence of carboxylic acids, hydroxyl and carbonyl functionalities, positively contribute to the OMP biodegradation rate. This result was supported by several other studies that also reported enhanced biodegradability when carboxylic acid (Okey *et al.*, 1996, Pitter, 1985), hydroxyl (Loonen *et al.*, 1999, Pitter, 1985) or carbonyl groups (Loonen *et al.*, 1999) were present in the molecular structure. Ethers, halogens, aliphatic ethers, methyl groups and ring structures were found to negatively affect the OMP biodegradation rate. This more persistent behaviour for molecular structures that contain halogens, ring structures or aliphatic ethers was also observed is a number of other studies (Boethling *et al.*, 1994, Loonen *et al.*, 1999, Okey *et al.*, 1996, Pitter, 1985).

A few discrepancies in contribution of certain functional groups towards OMP biodegradation rate between the current and the previous chapter were observed. The predictive model developed in the previous study did not contain carboxylic, hydroxyl, halogens and methyl groups and the effect of ethers on the biodegradation rate was negative compared to positive in the Eq. 4. In addition, the model obtained in the previous study contained amines and sulphur; both of these functional groups were not represented in Eq. 4. These discrepancies were likely caused by the different range in OMP data sets used, the different water qualities (BDOC quantity/quality, nutrients) and/or soils (technical sand versus field site sand) investigated.

This also directly shows the limitations of the model. A predictive model is influenced by the number and type of OMPs included in the development and calibration of the model. The OMPs selected in the current study were carefully chosen based on the wide range of functional groups they cover. However, based on solely this lab-scale column study it is impossible to predict the degradation rate of all OMPs present in the environment. It is known from literature that the microbial community composition in for example activated sludge systems can differ significantly from those in soil systems (Alidina *et al.*, 2014a, Hu *et al.*, 2012). Possibly different enzymes are produced that react with different functional groups to degrade OMPs. Since the relation between BDOC (quantity and quality) and the breakdown of certain functional groups is not unveiled yet, this shows the importance of using water and soil from the studied RBF field site to develop a predictive model that can adequately predict OMP removal at this site.

Future research should elucidate how microbial populations and their enzymes are related to the breakdown of certain functional groups in RBF systems. In addition, the effect of parameters found to be important in OMP removal during soil passage, for example, redox conditions, biodegradable dissolved organic carbon concentration and composition and the effect of adaptation of the soil microbial population towards certain OMPs should be further explored. The effect of soil type on the predictive model is expected to be small as Chapter 3 demonstrates that soil microbial diversity and thus OMP removal was similar in laboratory-scale columns filled with soil from two different RBF sites. Furthermore, it should be investigated if the metabolic/co-metabolic breakdown of OMPs in RBF systems results in different or similar predictive models. Nevertheless, the developed predictive model can be used to provide a rough estimate of OMP biodegradability in the field.

3.4 Testing the applicability of the predictive model with field data

The applicability of the developed predictive model (Eq. 4) was tested for a mixture of 23 OMPs monitored in the field (see Table 1). OMP removal that is measured in the field unfortunately is an overall removal and consists of several removal mechanisms such as sorption, dilution, volatilization and biodegradation. Although many studies showed that biodegradation is probably the major factor contributing to OMP removal, the comparison between the predictive model and field data is only indicative. OMP removal in the field was classified as full, partial or no removal and results are presented in Table 3. This implies that if the predictive model results in a degradation rate larger than 0, the field site removal should be characterised as "partial" or "full", in order for the predicted degradation rate to be considered a correct prediction. Similarly, if a degradation rate of 0 d^{-1} is obtained from the predictive model, the field site removal should indicate "no" removal to be considered a correct prediction. Based on this reasoning, the model predicts the biodegradation behaviour of 16 out of 23 OMPs (= 70%) correctly.

In total there are 8 overlapping OMPs for the soil column and field study (chloridazon, diglyme, MCPP, sulfamethoxazole, TPPO, bentazone, carbamazepine, diuron). For these 8 OMPs, the biodegradability of 5 OMPs is predicted correctly which equals 63%. For the OMPs which are not overlapping between the column study and the field site, the percentage of correct predicted biodegradability's is 73%. This is explained by the fact that the percentage persistent OMPs is higher for the overlapping OMPs (38%) compared to the non-overlapping OMPs (20%) and the biodegradation rate is difficult to predict for these persistent OMPs since these biodegradation rates or often close to or below the standard error of the estimated biodegradation rate.

From Table 3 it can be observed that diglyme, triglyme and tetraglyme, are characterised by persistent behaviour based on the model prediction, but showed partial removal in the field. However, a field study of (Stepien *et al.*, 2013) also showed persistent behaviour of the three glymes during RBF. Thus, the partial removal observed at the field site was possibly the result of a measurement artefact. Considering the possible measurement artefact in the field data for these three compounds, the exclusion of these OMPs from the validation data set would be justified. Excluding these three OMPs in the comparison of modelled data to field data, results in an increase in percentage of correctly predicted biodegradation rates to 80%.

Bentazone, 1H-benzotriazole, carbamazepine and diatrizoic acid seem to biodegrade based on the predictive model but showed persistent behaviour in the field. The persistent behaviour of these compounds was also observed in other studies which supports the field site data (Drewes *et al.*, 2002,

Grossberger *et al.*, 2014, Lai *et al.*, 2014, Lin *et al.*, 2011, Stuyfzand *et al.*, 2011). The incorrect predictions of the model for these OMPs could possibly be explained by the presence of -amide and -amine groups in the molecular structure of these compounds. Previous studies have reported that -amide and -amine groups decrease the degradation rate of OMPs (Chapter 2, Eggen, 2015, Loonen *et al.*, 1999, Okey *et al.*, 1996). Although the OMP mixture used to develop the predictive model contained OMPs with these -amide and -amine functional groups, their relation with the biodegradation rate was statistically not significant and thus the negative effect of these functional groups was not taken into account for 1H-benzotriazole, carbamazepine and diatrizoic acid. This emphasizes the importance of developing predictive models with an even larger data set covering hundreds of OMPs and a wide range of functional groups.

Since this study was limited to oxic conditions, future research should focus on the development of predictive models for more reduced conditions (NO_3^- reducing, Fe/Mn reducing). By combining these predictive models for separate redox zones, an overall model for the whole RBF process can be obtained.

Table 3 – Predicted biodegradation rates and field site removal

OMP	Predicted biodegradation rate μ of model [d^{-1}]		Field site removal [-]
Degradable			
AMPA	3.27		Partial
Bisphenol A	1.64		Full
Caffeine	0.30		Partial
Chloridazon	0.69		Full
DEET	1.20		Partial
Diglyme	0*	≠	Partial
ETBE	0.22		Full
Iopamidol	2.34		Partial
MCPP	1.99		Full
Metoprolol	0.84		Full
MTBE	0.22		Full
Sotalol	1.67		Full
Sulfamethoxazole	1.09		Partial
Tetraglyme	0*	≠	Partial
4-tertoctylphenol	0.88		Full
TPPO	0.59		Partial
Triglyme	0*	≠	Partial
Non-degradable			
Bentazone	0.70	≠	No
1H-benzotriazole	1.48	≠	No
Carbamazepine	0.59	≠	No
Diatrizoic acid	0.41	≠	No
1,4-dioxane	0*		No
Diuron	0.00		No

* For these OMPs the predictive model gave negative biodegradation rates and were therefore set equal to 0

4 Conclusions

This study investigated relationships between OMP biodegradation rates and the functional groups present in the chemical structure of a mixture of 31 OMPs. The OMP biodegradation rates were determined from lab-scale columns filled with oxic soil from a RBF site in The Netherlands. A statistically significant relationship was found between OMP biodegradation rates and the functional

groups of the molecular structures of OMPs in the mixture. OMP biodegradation rate increased in the presence of carboxylic acids, hydroxyl groups, and carbonyl groups, but decreased in the presence of ethers, halogens, aliphatic ethers, methyl groups and ring structures in the chemical structure of the OMPs.

Applicability of the predictive model was tested with OMP data from the field. In three consecutive measurement campaigns, removal of 23 OMPs in the field was determined. The predictive model was able to give an accurate prediction of biodegradability for approximately 70% of the OMPs monitored in the field (80% excluding the glymes). Incorrect predictions were mainly observed for OMPs that contained amide or amine groups – functional groups that were represented in the OMP mixture used to create the predictive model but did not show a statistically significant relation with the OMP biodegradation rate.

The current study shows it is possible to mimic the RBF process with laboratory scale soil columns and that the biodegradation rates obtained with these soil columns can be used to develop a predictive model for OMP removal during RBF that can fairly accurately predict OMP biodegradation in the field. Exceptions are the OMPs that have predicted OMP biodegradation rates below or close to the standard error of the estimate (most persistent OMPs) and OMPs containing amine or amide groups. The removal of these OMPs should be carefully monitored at the field site to determine their fate. Although the OMP mixture used in this study was carefully selected to cover a wide variety of functional groups, it is possible that the degradation rate of OMPs having functional groups other than the ones tested in this manuscript are not accurately predicted. Nevertheless, the predictive model can be used by the drinking water company operating this RBF site to obtain a first estimate on the OMP biodegradability.

References

Albert, A., Goldacre, R. and Phillips, J. (1948) The strength of heterocyclic bases. Journal of the Chemical Society, 2240-2249.

Alexander, M. and Lustigman, B.K. (1966) Effect of Chemical Structure on Microbial Degradation of Substituted Benzenes. J. Agr. Food Chem. 14(4), 410-413.

Alidina, M., Li, D. and Drewes, J.E. (2014a) Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Research 56, 172-180.

Alidina, M., Li, D., Ouf, M. and Drewes, J.E. (2014b) Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. Journal of Environmental Management 144, 58-66.

Baumgarten, B., Jährig, J., Reemtsma, T. and Jekel, M. (2011) Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Research 45, 211-220.

Benotti, M.J., Song, R., Wilson, D. and Snyder, S.A. (2012) Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Science & Technology: Water Supply 12(1), 11-23.

Błędzka, D., Gryglik, D. and Miller, J.S. (2009) Photolytic degradation of 4-tert-octylphenol in aqueous solution. Environment Protection Engineering 35(3), 235-247.

Boethling, R.S., Howard, P.H., Meylan, W., Stiteler, W., Beauman, J. and Tirado, N. (1994) Group Contribution Method for Predicting Probability and Rate of Aerobic Biodegradation. Environ. Sci. Technol. 28, 459-465.

Boivin, A., Cherrier, R. and Schiavon, M. (2005) Bentazone adsorption and desorption on agricultural soils. Agron. Sustain. Dev. 25, 309-315.

Brusseau, M.L. (1994) Transport of reactive contaminants in heterogeneous porous media. Reviews of Geophysics 32(3), 285-313.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J. and Massmann, G. (2013) Sorption behavior of 20 wastewater originated micropollutants in groundwater - Column experiments with pharmaceutical residues and industrial agents. Journal of Contaminant Hydrology 154, 29-41.

Celis, R., Hermosín, M.C., Cox, L. and Cornejo, J. (1999) Sorption of 2,4-Dichlorophenoxyacetic Acid by Model Particles Simulating Naturally Occuring Soil Colloids. Environ. Sci. Technol. 33, 1200-1206.

Chen, Z., He, W., Beer, M., Megharaj, M. and Naidu, R. (2009) Speciation of glyphosate, phosphate and aminomethylphosphonic acid in soil extracts by ion chromatography with inductively coupled plasma mass spectrometry with an octopole reaction system. Talanta 78, 852-856.

Chiang, P.C. and Hu, Y. (2009) Simultaneous Determination of LogD, LogP, and pKa of Drugs by Using a Reverse Phase HPLC Coupled with a 96-Well Plate Auto Injector. Combinatorial Chemistry & High Throughput Screening 12, 250-257.

Crowley, R. and Kacprzak, J. (1986) The Determination of Commonly Used Iodinated Contrast Media in Postmortem Samples Using HPLC and TLC. Journal of Analytical Toxicology 10, 53-55.

de Ridder, D.J., Verliefde, A.R.D., Heijman, S.G.J., Verberk, J.Q.J.C., Rietveld, L.C., van der Aa, L.T.J., Amy, G.L. and van Dijk, H. (2011) Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. Water Science & Technology 63(3), 416-423.

Drewes, J.E., Heberer, T. and Reddersen, K. (2002) Fate of pharmaceuticals during indirect potable reuse. Water Science & Technology 46(3), 73-80.

Eggen, T., Vogelsang, C. (2015) Persistent Organic Pollutants (POPs): Analytical Techniques, Environmental Fate and Biological Effects. Zeng, E. (ed).

Felder, E., Grandi, M., Pitrè, D. and Vittadini, G. (1988) Analytical Profiles of Drug Substances, Academic press, inc., United States of America.

Ferreira da Silva, B., Jelic, A., López-Serna, R., Mozeto, A.A., Petrovic, M. and Barceló, D. (2011) Occurence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain. Chemosphere 85, 1331-1339.

Fischer, R.A. and Yates, F. (1974) Statistical Tables for Biological, Agricultural and Medical Research, Longman Group Ltd., London.

Grossberger, A., Hadar, Y., Borch, T. and Chefetz, B. (2014) Biodegradability of pharmaceutical compounds in agricultural soils irrigated with treated wastewater. Environmental Pollution 185, 168-177.

Henzler, A.F., Greskowiak, J. and Massmann, G. (2014) Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). Journal of Contaminant Hydrology 156, 78-92.

Hoppe-Jones, C., Oldham, G. and 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. and 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. Science of The Total Environment 496, 54-62.

Hu, M., Wang, X., Wen, X. and Xia, Y. (2012) Microbial community structures in different wastewater treatment plants as revealed by 454-pyrosequencing analysis. Bioresource Technology 117, 72-79.

IBMCorp. (2011) IBM SPSS Statistics for Windows, Version 20.0. Armonk, NY: IBM Corp. .

Lai, H.J., Ying, G.G., Ma, Y.B., Chen, Z.F., Chen, F. and Liu, Y.S. (2014) Occurrence and dissipation of benzotriazoles and benzotriazole ultraviolet stabilizers in biosolid-amended soils. Environ Toxicol Chem 33(4), 761-767.

Lin, K., Bondarenko, S. and Gan, J. (2011) Sorption and persistence of wastewater-borne psychoactive and antilipidemic drugs in soils. J Soils Sediments 11, 1363-1372.

Loffhagen, N., Härtig, C. and Babel, W. (2003) Energization of *Comamonas testosteroni* ATCC 17454 for Indicating Toxic Effects of Chlorophenoxy Herbicides. Arch. Environ. Contam. Toxicol. 45, 317-323.

Loonen, H., Lindgren, F., Hansen, B., Karcher, W., Niemelä, J., Hiromatsu, K., Takatsuki, M., Peijnenburg, W., Rorije, E. and Struijś, J. (1999) Prediction of Biodegradability from Chemical Structure: Modelling of Ready Biodegradation Test Data. Environmental Toxicology and Chemistry 18(8), 1763-1768.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M. and Barry, D.A. (2013) Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Science of The Total Environment 461-462, 480-498.

Miller, R.M. and Herman, D.C. (1997) Soil Ecotoxicology. Tarradellas, J., Bitton, G. and Rosell, D. (eds), CRC Press, Inc., United States of America.

OECD, P., France (2007) Guidance document on the validaion of (quantitative) structure -activity relationships [(Q)SAR] models.

OECD, P., France (1992) Organisation for Economic Cooperation and Development, OECD Guideline for testing of chemicals-ready biodegradability. No 301.

OECD, P., France (1981) Organistion of Economic Cooperation and Develoment, OECD Guideling for testing of chemicals No 302 C.

Okey, R.W. and Stensel, H.D. (1996) A QSAR-based Biodegradability Model - A QSBR. Water Research 30(9), 2206-2214.

Packer, J.L., Werner, J.J., Latch, D.E., McNeill, K. and Arnold, W.A. (2003) Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibric acid, and ibuprofen. Aquatic Sciences 65, 342-351.

Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T. and Toze, S. (2011) Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122, 53-62.

Petty, D.G., Getsinger, K.D. and Woodburn, K.B. (2003) A Review of the Aquatic Environmental Fate of Triclopyr and its Major Metabolites. Journal of Aquatic Plant Management 41, 69-75.

Pitter, P. (1985) Correlation of Microbial Degradation Rates with the Chemical Structure. Acta hydrochim. hydrobiol. 13(4), 453-460.

Pletcher, T. and Cordes, E.H. (1967) The Basicity and C^{13}-H Coupling Constants of Certain Acetals, Ketals, and Ortho Esters. J Org Chem 32, 2294-2297.

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

Rykowska, I. and Wasiak, W. (2006) Properties, threats, and methods of analysis of Bisphenol A and its derivatives. Acta Chromatographica 16(7-27).

Scheytt, T.J., Mersmann, P. and Heberer, T. (2006) Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83, 53-69.

Scheytt, T.J., Mersmann, P., Rejman-Rasinski, E. and These, A. (2007) Tracing Pharmaceuticals in the Unsaturated Zone. Journal of Soils and Sediments 7(2), 75-84.

Shalaeva, M., Kenseth, J., Lombardo, F. and Bastin, A. (2007) Measurement of Dissociation Constants (pKa Values) of Organic Compounds by Multiplexed Capillary Electrophoresis Using Aqueous and Cosolvent Buffers. Journal of Phamaceutical Sciences, 1-24.

Stepien, D.K., Regnery, J., Merz, C. and Püttmann, W. (2013) Behavior of organophosphates and hydrophilic ethers during bank filtration and their potential application as organic tracers. A field study from the Oderbruch, Germany. Science of The Total Environment 458-460, 150-159.

Stoks, P.G.M., van de Haar, G., Bannink, A. and Zwamborn, C.C. (2013) Jaarrapport 2012 De Rijn.

Stuyfzand, P.J., Segers, W. and van Rooijen, N. (2011) Behavior of pharmaceuticals and other emerging pollutants in various artificial recharge systems in The Netherlands.

Su, A.C.L. (1979) Advances in Organometallic Chemistry - Catalytic Codimerization of Ethylene and Butadiene, Academic Press, Inc.

Tadkaew, N., Hai, F.I., McDonald, J.A., Khan, S.J. and Nghiem, L.D. (2011) Removal of trace organics by MBR treatment: The role of molecular properties. Water Research 45, 2439-2451.

ter Laak, T.L., Kooij, P.J.F., Tolkamp, H. and Hofman, J. (2014) Different compositions of pharmaceuticals in Dutch and Belgian rivers explained by consumption patterns and treatment efficiency. Environ Sci Pollut Res 21, 12843-12855.

Tiehm, A., Schmidt, N., Stieber, M., Sacher, F., Wolf, L. and Hoetzl, H. (2011) Biodegradation of Pharmaceutical Compounds and their Occurence in the Jordan Valley. Water Resour Manage 25, 1195-1203.

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

van der Hoek, J.P., Bertelkamp, C., Verliefde, A.R.D. and Singhal, N.S. (2014) Drinking water treatment technologies in Europe: State of the art - Challenges - Research needs. Journal of Water Supply: Research and Technology - AQUA 63(2), 124-130.

Verliefde, A., Cornelissen, E., Amy, G., Van der Bruggen, B. and van Dijk, H. (2007) Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. Environmental Pollution 146, 281-289.

Verliefde, A.R.D. (2008) Rejection of Organic Micropollutants by High Pressure Membranes (NF/RO), Delft University of Technology, Delft.

Vione, D., Khanra, S., Das, R., Minero, C., Maurino, V., Brigante, M. and Mailhot, G. (2010) Effect of dissolved organic compounds on the photodegradation of the herbicide MCPA in aqueous solution. Water Research 44, 6053-6062.

Wang, C., Teppen, B.J., Boyd, S.A. and Li, H. (2011) Sorption of Lincomycin at Low Concentrations from Water by Soils. Soil Science Society of America Journal 76, 1222-1228.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environmental Science & Technology 39, 6649-6663.

Yang, X.J., Qu, Y., Yuan, Q., Wan, P., Du, Z., Chen, D. and Wong, C. (2013) Effect of ammonium on liquid- and gas-phase protonation and deprotonation in electrospray ionization mass spectrometry. Analyst 138, 659-665.

Chapter 4

A laboratory-scale column study comparing organic micropollutant removal and microbial diversity for two soil types

This chapter is based on: Bertelkamp *et al.* (2015), A laboratory-scale column study comparing organic micropollutant removal and microbial diversity for two soil types, Science of the Total Environment 536, 632-638, 2015

1 Introduction

The effect of soil type on OMP sorption and biodegradation has been investigated in several batch studies, but so far not in columns. The batch studies demonstrated that soil characteristics such as organic carbon content, Cationic Exchange Capacity (CEC), pH and/or composition (amount of clay, silt, sand) significantly affect OMP sorption (Fingler *et al.*, 2004, Hiller *et al.*, 2009, Hiller *et al.*, 2012). However, the results are often contradictory with different effects reported for different OMPs (Bedmar *et al.*, 2011, Fingler *et al.*, 2004, Hiller *et al.*, 2009, Hiller *et al.*, 2012, Zhang *et al.*, 2011). OMP biodegradation in soil is influenced by factors such as OMP sorption, moisture content, nutrient availability and organic carbon content (Guo *et al.*, 2000, Picton *et al.*, 2004, Schroll *et al.*, 2006, Si *et al.*, 2009). Since OMPs sorbed to soil particles are less bioavailable to soil microorganisms, sorption can also hamper OMP biodegradation (Guo *et al.*, 2000). The aforementioned factors (soil parameters) can vary significantly between different RBF sites and it could therefore be expected that OMP removal via biodegradation will therefore also considerably differ.

Batch studies do not always accurately describe the results obtained from soil column and field studies (Limousin *et al.*, 2007, Murillo-Torres *et al.*, 2012, Piatt *et al.*, 1996, Rocio Estrella *et al.*, 1993). Sorption is usually overestimated in batch studies as a result of equilibrium conditions which are not always reached in column studies. In addition, OMP concentrations dosed in batch studies are often much higher (mg/L) than those normally detected in rivers (ng/L - μg/L) and the continuous feeding of nutrients and OMPs in column and field studies compared to the one time dosage in batch studies can cause results in these systems to differ. Thus, it is questionable whether the results on OMP sorption and biodegradation from batch studies can actually be translated to lab-scale columns and/or real RBF sites. Therefore there is a clear need for column investigations on the effect of soil type on the sorption and biodegradation of a large mixture of OMPs at concentrations similar to those found at RBF sites.

Since OMP biodegradation during RBF is carried out by soil microorganisms, characterizing the soil microbial community composition could improve our understanding of the underlying mechanisms of OMP removal during soil passage. However, this aspect has been largely ignored in past studies on OMP removal during RBF, with only a few studies having investigated relationships between microbial community composition and OMP removal in soil systems (Alidina *et al.*, 2014a, Li *et al.*, 2014b). Substrate concentration and composition was found to play an important role in shaping the soil microbial community composition (Alidina *et al.*, 2014b, Li *et al.*, 2013, Li *et al.*, 2012). However, it remains unclear if the aqueous phase is the only important factor in determining the soil microbial population or that the soil composition also has a strong effect. This aspect requires more attention to be able to understand the influence of soil characteristics on microbial communities, as well as their effect on OMP sorption and biodegradation. Investigating microbial community composition of soils from two different RBF sites operated with the same river water could provide a better understanding of the role that the solid phase plays in determining the soil microbial community composition and OMP removal.

The main objective of the study described in this chapter was to assess the influence of the solid phase on microbial community composition (richness and evenness) and OMP removal. To overcome the aforementioned limitations, this study investigated OMP removal and soil microbial community composition in laboratory-scale columns filled with oxic soils (with different silt/clay/sand fractions,

organic matter content and cationic exchange capacity) obtained from two RBF-sites. Both soil columns were fed with a similar water quality to determine the role of the solid phase with respect to OMP removal. Modelling the breakthrough curves for OMPs in these columns with a contaminant transport model enabled a differentiation between OMP sorption (retardation factor) and biodegradation (biodegradation rate), in contrast to earlier studies that only reported percentage removals. The modelling provided retardation factors and biodegradation rates along with their 95% confidence intervals to include the error in parameter estimation in analysis and interpretation and to avoid experimental bias. This study was carried out using a large mixture of OMPs, with wide ranging physico-chemical properties, dosed at concentrations similar to those encountered in real RBF systems (i.e. ng/L). Microbial community composition was determined at both RBF field sites as well as in both column systems to assess differences/similarities in richness and evenness between the two communities.

2 Materials and Methods

2. 1 Experimental set-up

The experimental set-up consisted of 2 oxic pilots (A and B) and each pilot consisted of 2 transparent PVC columns (L = 1 m, D = 36 mm) in series. Pilot A was filled with oxic soil from RBF site Engelse Werk of drinking water company Vitens (52°29'39" N, 6°3'40.4" E). Pilot B was filled with oxic soil sampled near the RBF site Bergambacht of drinking water company Oasen (51° 55' 0.4" N, 4° 47' 5.4" E). Columns were filled with soil in increments of 4-5 cm while tapping on the column, to prevent layering in the columns. To prevent leaching of soil grains, the top and bottom of the column were fitted with perforated PVC plates (30 holes, d = 0.8 mm) that were covered with filter cloth (45 μm, Top7even net & mesh, The Netherlands). A flow from bottom to top was maintained in all columns to prevent air entrapment and both pilots were operated in a temperature controlled room (12 °C) in the dark (to prevent algae growth and/or OMP loss due to photolysis).

The pilots were fed from jerry cans filled with Lek river water and an OMP mixture. Prior to dosing the OMP mixture, columns were acclimated on Lek river water (without OMPs, to enable the development of similar microbial populations in the columns) until DOC removal stabilized indicating a stable biomass in both column systems. OMP samples were taken more frequently in the beginning to determine the breakthrough curve. Once this breakthrough curve was established, OMP samples were taken monthly. The running time of the experiment was 7 months in total (excluding the acclimation period). River water was refreshed every two weeks and was filtered (d = 0.4 mm), prior to use as feed, to prevent twigs and larger particles from clogging the pump tubes. After every replacement feed jerry cans were washed twice with acetone and flushed several times with demineralized water before refilling to prevent biofilm formation. The feed solutions were pumped through the columns by a peristaltic multichannel 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 dark polyamide tubing (d_i = 2.9 mm, Festo, The Netherlands). The hydraulic loading rate applied on the columns was 0.5 L/d, which equals a filtration rate of 0.5 m/d. Pore velocity and porosity in both pilots were determined using deuterium (^2H) as tracer. Deuterium concentrations were determined with laser absorption spectroscopy using a DLT-100 Liquid-Water Isotope Analyzer (Los Gatos Research, USA) with a precision of ±0.56‰ for ^2H. A quantity of 0.19 mL

of 99% pure Deuterium was added to the feed solutions (20 L), resulting in an approximate 60 ‰ increase in δ-^{2}H. Pore velocity was 1.48 m/d for the Vitens pilot and 1.40 m/d for the Oasen pilot. Porosity varied between 0.33 (Vitens pilot) and 0.35 (Oasen pilot).

2.2 Organic micropollutants

A mixture of 20 OMPs was dosed into the feed solutions of the columns (500 ng/L of each OMP), Table 1. OMPs were analysed with U-HPLC-HR-Orbitrap-MS, see Method 1 Chapter 3.

Table 1 – Organic micropollutants and their physico-chemical properties

OMP	MW	pKa	Charge at pH 8	Log D at pH 8[1]
Acetaminophen	151.16	9.3[a]	0	0.85
Atrazine	215.68	<2 (1.6)[b]	0	2.26
Carbamazepine	236.27	-[a]	0	2.64
Chloridazon	221.64	3.4[c]	0	1.05
Clofibric acid	214.65	3.2[d]	-1	-0.18
Diclofenac	296.15	4.2[d]	-1	1.21
Diglyme	134.17	~4[e]	0	0.10
Dimethoate	229.26	2.0[f]	0	0.21
Diuron	233.09	13.6[c]	0	2.49
Hydrochlorothiazide	297.74	7.9[g]	0	-0.72
Ketoprofen	254.28	4.7[a]	-1	0.49
Lincomycin	406.54	7.6[h]	+1	-1.22
Metoprolol	267.36	9.4[a], 9.7[g]	1	0.14
Phenazone	188.23	1.4[g]	0	1.11
Pirimicarb	238.29	4.5[i]	0	1.74
Simazine	201.66	1.6[f]	0	1.83
Sulfamethoxazole	253.28	1.8, 5.8[c]	0	0.39
Terbutaline	225.28	8.8, 9.5, 10.5[j]	+1	0.18
Theophylline	180.16	8.6[a]	0	-1.09
Triclopyr	256.47	2.7[k]	-1	-0.53

1 http://www.chemicalize.org

a (Chiang et al., 2009), b (Westerhoff et al., 2005), c (Margot et al., 2013), d (Packer et al., 2003), e (Su, 1979), f (Yang et al., 2013), g (Ferreira da Silva et al., 2011), h (Wang et al., 2011),i http://pubchem.ncbi.nlm.nih.gov, j (Shalaeva et al., 2007), k (Petty et al., 2003),

2.3 Water quality and soil parameters

Dissolved organic carbon (DOC), oxygen, temperature, pH, and ions were measured in the aqueous phase. Adenosine triphosphate (ATP), pH, grain size distribution and organic matter (SOM) were measured in the solid phase (soil). Cationic exchange capacity of the soil was determined from the organic carbon content. DGGE analysis was performed on soil samples from the field sites as well as the influent of both columns to gain more insight into the microbial community composition as characterized by richness and evenness. A detailed description on these analyses is provided in the Chapter 3.

2.6 Statistical analysis

The statistical software package IBM SPSS Statistics for Windows version 20.0 was used to perform all statistical analyses (IBMCorp., 2011). One way ANOVA tests were used to determine if the retardation factors and biodegradation rates between the two soil columns were statistically significant (p-value < 0.05).

2.7 Modelling

CXTFIT (Toride *et al.*, 1995a) was used to obtain the retardation factors (R) and biodegradation rates (μ) of the OMPs in the columns by fitting the experimental breakthrough curves, for a detailed description see Chapter 2.

3 Results and Discussion

3.1 Soil and water quality parameters

Soil from the two RBF sites was characterised for the parameters depicted in Table 2. The parameter "ATP field site (0 – 5 cm)" refers to the ATP concentration measured in the soil samples taken from the RBF field sites at a depth of 0 – 5 cm, which represents the initial conditions of the two soils. The parameter "ATP column (0 – 5 cm)" represents the ATP concentration measured at the influent side (0 – 5 cm) of the lab scale column at the end of the experiment when both soil types are fed by the same influent water quality.

Table 2 – Soil parameters column experiment

	Units	Oasen RBF soil	Vitens RBF soil
ATP field site (0 – 5 cm)	ng/cm^3	109	235
ATP column (0 – 5 cm)	ng/cm^3	135	547
Clay (< 8 μm)	v/v %	0.50	3.72
Silt (8 – 63 μm)	v/v %	0.52	3.58
Sand (63 – 2000 μm)	v/v %	98.98	92.69
d_{median}	μm	330.62	380.38
LOI550	% dry weight	0.36	1.18
SOM	% dry weight	0.33	0.92
pH – H_2O	-	8.04	8.23
pH – KCl	-	7.83	7.90
CEC	meq/kg dry weight	9.19	42.13

Since RBF sites require a certain hydraulic permeability, soils from these sites are usually characterized by a large sand fraction, and extreme variations in the clay, silt and sand content are not expected (Burke *et al.*, 2013, Hoppe-Jones *et al.*, 2012, Scheytt *et al.*, 2006). Although the differences in silt and clay for the soil types investigated in this study are not extreme, they do show a clear difference. In addition, the two soil types differ in ATP concentration, soil organic matter (SOM) content and cationic exchange capacity (CEC). The 4 times higher ATP concentration determined in the Vitens soil (compared to the Oasen soil column) indicated that more active biomass was present in this soil. This could be explained by the larger percentage of small particles in the Vitens soil which results in a larger specific surface area for the biomass to attach to.

ATP results were not in agreement with the DOC removal since no statistical significant difference (*p*-value = 0.065 > 0.05) in DOC removal was observed between the two soil types (Table 3 shows the average DOC removal for both soil types). The ATP concentrations measured in this study were higher than the values reported in other studies. (Maeng *et al.*, 2011) demonstrated ATP concentrations of 91 and 102 ng ATP/cm^3 sand for columns fed with Meuse river water. Chapter 2 reported ATP concentrations of 24.5 and 36.5 ng ATP/cm^3 sand for columns fed with Schie canal water. The higher ATP concentrations reported in the current study are attributed to the fact that RBF-site (and thus biologically active) soil was used, whereas both other studies used clean filter sand to start up new columns.

Table 3 shows the average DOC removal and NO_3^-, PO_4^{3-} concentrations (± standard deviation) in the influent as well as both effluents. Oxygen was reduced to low concentrations (1.1 ± 0.8 mg/L, n=12) in the effluent of both pilots and no nitrate removal was observed. This implies that oxic conditions were maintained in both pilots during the experiment. Water quality parameters of the feed water in the column experiment are presented in the Table S3.

Table 3 – DOC, nitrate and phosphate removal in oxic pilots

	Units	Feed water	Oasen RBF soil	Vitens RBF soil
Δ DOC	[%]		24.2 (± 12.9)	30.7 (±14.3)
NO3-	[mg/L]	9.07 (±3.34)	7.90 (±3.37)	8.65 (±2.24)
PO43-	[mg/L]	0.07 (±0.08)	0.11 (±0.04)	0.10 (±0.03)

3.2 DGGE analysis

Soil samples from the RBF sites (at a depth of 0 – 5 cm) were obtained to characterize the microbial population. These soil samples represented the initial conditions. At the end of the experiment the soil microbial population was characterized again by soil samples that were obtained from both column systems (at the influent side, 0 – 5 cm). The microbial community composition in both soil types was compared in terms of richness and evenness by means of DGGE. The results are presented in Table 4. The microbial DGGE pattern of the different samples is presented in Figure S1 and S2.

Table 4 – Richness and evenness (Gini) results for the soil samples

Field site samples (0 – 5 cm)			Column samples (0 – 5 cm)		
Sample	Richness (# of bands)	Gini (evenness)	Sample	Richness (# of bands)	Gini (evenness)
Vitens	50	0.32	Vitens	35	0.41
Oasen	34	0.56	Oasen	42	0.42

DGGE fingerprinting analysis indicated that richness (determined as total bacterial bands present on gel) and evenness (calculated as Gini coefficient) of the soil microbial community became more similar as a result of feeding the columns with the same river water. The difference in richness and evenness between the Oasen and Vitens soil was much larger at the field sites (representative of the initial conditions when both soil types were fed with different water qualities) (Δ Richness = 16, Δ Evenness = 0.24) than for the columns at the end of the experiments (Δ Richness = 7, Δ Evenness = 0.01). For both soil column systems, a rich bacterial community was found (Table 4, Figure 2 SI) at the end of the experiment when compared to literature (Lyautey *et al.*, 2005). A rather even bacterial community with very few abundant species present was observed (Table 4, Figure 2 SI). Again, the evenness was very comparable for both pilots at the end of the experiment. The soil microbial diversity for both soil column systems was comparable at the end of the experiment, indicating that the microbial community composition present in both soil column systems was similar. This confirms the hypothesis that a similar microbial community composition was achieved, as both pilots were fed with the same water quality.

3.3 Influence of soil type on OMP retardation factors

The OMP retardation factor (R) is based on the solid-water distribution coefficient (K_d) according to Eq. S5. Normalizing this K_d value to the soil organic carbon content gives the soil organic carbon-water partitioning coefficient $K_{OC} = K_d / f_{OC}$. A correlation between K_{OW} and K_{OC} (Log K_{OC} = Log K_{OW} – 0.21) was demonstrated by (Karickhoff *et al.*, 1979). This should make it theoretically possible to determine retardation factors from K_{ow} values of the different OMPs. However, several studies demonstrated that this correlation does not always hold for ionisable OMPs (Burke *et al.*, 2013, Carballa *et al.*, 2008). Therefore, this study determined the retardation factors for all OMPs from experimental data by fitting the convection-dispersion equation (Eq. S4, SI) to the experimentally determined breakthrough curves. The modelled retardation factors are presented in Table 5 (confidence intervals for both soil columns are presented in Table S4 and S5).

Table 5 – OMP retardation factors (R) for both oxic pilots

OMP	Charge	Oasen soil Retardation factor [-]	Vitens soil Retardation factor [-]	References Retardation factor [-]
Lincomycin	1	1.4	1.7	1.1[b]
Metoprolol	1	ND[1]	ND[1]	3.1[b], >9.0[e]
Terbutalin	1	ND[1]	ND[1]	
Acetaminophen	0	ND[1]	ND[1]	
Atrazine	0	1.4	1.7	1.0[b], 1.5 – 6.1[f]
Carbamazepine	0	1.4	1.9	1.8[a], 1.1[b], 1.9[d], 1.0[g]
Chloridazon	0	ND[1]	ND[1]	
Diglyme	0	1.0	0.7	
Dimethoate	0	1.1	1.1	
Diuron	0	ND[1]	ND[1]	
Hydrochlorothiazide	0	1.3	1.7	1.1[b]
Phenazone	0	1.0	0.9	1.0[e]
Pirimicarb	0	1.4	1.5	
Simazine	0	1.3	1.4	2.1 – 5.4[f]
Theophylline	0	ND[1]	ND[1]	
Clofibric acid	-1	ND[1]	ND[1]	1.1[c]
Diclofenac	-1	ND[1]	ND[1]	4.8[a], 1.4[d]
Ketoprofen	-1	ND[1]	ND[1]	
Sulfamethoxazole	-1	1.0	0.5	1.0[b]
Triclopyr	-1	1.1	1.1	

[1] A statistically significant retardation factor could not be determined for these readily degradable OMPs
[a] (Scheytt et al., 2006), [b] (Chapter 2), [c] (Scheytt et al., 2007), [d] (Rauch-Williams et al., 2010), [e] (Burke et al., 2013), [f] (Sakaliene et al., 2007), [g](Patterson et al., 2011)

For the rapidly degradable OMPs a statistically significant retardation factor could not be obtained as these compounds were removed to below the detection level in the effluent right from the start of experiment. An ANOVA test was performed for the less degradable OMPs to determine if there was a statistical significant difference in OMP retardation factors between the two soil types. No statistically significant difference in OMP retardation factors was found for the less degradable OMPs between the two soil types (p-value = 0.63 > 0.05). The ANOVA test indicates that the effect of soil type is insignificant for OMP retardation for the two soil types investigated in this study. Previously mentioned batch studies reported that parameters such as CEC, organic carbon content and/or composition (amount of clay, silt, sand) could each affect OMP sorption. Although the soils investigated in this study show differences with respect to these parameters, no effect on OMP sorption was observed. However, it needs to be mentioned that in soil columns, in contrast to batch studies, sorption is usually limited (Murillo-Torres *et al.*, 2012), resulting in very low retardation factors. As such, the influence of soil parameters on sorption will be more limited in column studies. This is also shown by the fact that in Table 5, the retardation factors for most OMPs were close to 1, indicating that these OMPs are very mobile during soil passage. Similar OMP retardation factors were demonstrated in other studies (Table 5). This implies that, for removal of OMPs during RBF, biodegradation is probably the more dominant removal mechanism compared to sorption, at least for the biodegradable OMPs. To the best of the authors knowledge, retardation factors for diglyme, dimethoate, pirimicarb and triclopyr for the RBF process have not been reported previously and were thus determined for the first time in the current study.

3.4 Influence of soil type on OMP biodegradation rates

OMP biodegradation rates determined from fitting the convection-dispersion equation (Eq. S4) to the experimentally determined breakthrough curve data are presented in Table 6 (confidence intervals for both soil columns are presented in Table S4 and S5). For the OMPs for which a retardation factor

could not be determined, the retardation factor was set to 1. This assumption is justified since several studies reported, and also the results presented in Table 5 show, that retardation factors were close or equal to 1 for most OMPs (Chapter 2, Burke *et al.*, 2013, Henzler *et al.*, 2014). Figures S3 and S4 show a plot of the modelled C_e/C_0 values versus the experimentally obtained C_e/C_0 values for both pilots, representing the "goodness of fit" for the model.

Table 6 – OMP degradation rates (μ) for both oxic pilots

OMP	Oasen soil Biodegradation rate μ [d^{-1}]	Vitens soil Biodegradation rate μ [d^{-1}]
Acetaminophen	2.70	2.30
Ketoprofen	2.68	2.36
Diclofenac	2.28	2.29
Theophylline	2.14	1.43
Phenazone	2.10	2.69
Terbutalin	ND[1]	1.43
Clofibric acid	1.89	1.17
Chloridazon	1.65	2.35
Diuron	1.38	1.27
Sulfamethoxazole	0.98	1.44
Dimethoate	0.42	0.37
Carbamazepine	0.29	0.22
Triclopyr	0.27	0
Pirimicarb	0.21	0.14
Hydrochlorothiazide	0.18	0
Atrazine	0.17	0.05
Simazine	0.13	0
Lincomycin	0	0
Diglyme	0	0
Metoprolol	ND[1]	ND[1]

[1] A statistically significant biodegradation rate could not be determined

For a small number of OMPs (sulfamethoxazole, lincomycin, phenazone, dimethoate, triclopyr, chloridazon, and clofibric acid) an increase in biodegradation rate over time (adaptation) was observed during the 7 months of operation. For these OMPs, the adapted biodegradation rate was determined. An adaptation time of more than 2 years for at least one of the aforementioned OMPs, namely sulfamethoxazole, has been reported in a previous study (Baumgarten *et al.*, 2011). The adaptation time required for these OMPs could be caused by the differences in OMP concentration between the river water and the OMP concentration dosed in the feed water used in this study. The microbial community possibly needs a certain time to adjust itself to the variation in concentration of these OMPs.

An ANOVA test was performed to determine if there was a statistically significant difference in OMP biodegradation rate between the two soil types. No statistically significant difference in OMP degradation rate between the two soil types was found (p-value = 0.82 > 0.05). This implies that for the soil types used in this study, the effect of soil type on OMP biodegradation is insignificant and that OMP biodegradation rate is mainly influenced by the aqueous phase as opposed to the solid phase (since both pilots were fed with the same river water). This was unexpected given the initial differences in physico-chemical and initial microbial community soil characteristics, yet is supported by the comparable microbial community in both columns at the end of the experiment, as shown by the DGGE data.

Although the current study only investigated two specific soil types, the results found are supported by a batch study of Kasozi *et al.* (2010) who investigated the effect of different soil groups (carbonatic

soils, histosoils, oxisoils and spodosoils) on the degradation of diuron; no statistical significant difference in average half-life of diuron was found between the different soil groups. However, the study of Kasozi *et al.* (2010) determined diuron half-lives in batch experiments using aqueous solutions of diuron standard. Along with the previously discussed scale-effects, this approach does not appropriately simulate RBF systems (water matrix effects are not included). Moreover, the study of Kasozi *et al.* (2010) was limited to one specific OMP, namely diuron, which is a neutral OMP with a relatively high Log D of 2.49. The results of the current column study show that soil type does not affect the biodegradation rate of a large mixture of different OMPs covering neutral and charged OMPs with a wide range in hydrophobicity.

Since the Biodegradable Dissolved Organic Carbon (BDOC) concentration of the aqueous phase (mg/L) is typically 6 orders of magnitude larger than the OMP concentration (ng/L), co-metabolic degradation of OMPs during soil passage was suggested by several studies (Maeng *et al.*, 2011, Rauch-Williams *et al.*, 2010). Considering this co-metabolic degradation of OMPs, it is not surprising that operating the RBF soil columns filled with different soil types but with one type/quantity of BDOC in the aqueous phase, results in similar OMP removal.

Half of the OMPs (italics, Table 5) biodegraded very well (biodegradation rate = 1.00 d^{-1} or higher) and most OMPs (17 out of 20) biodegraded at least to a certain extent in one or both pilots. Chapter 2 reported OMP biodegradation rates for ketoprofen and acetaminophen of 13.5 d^{-1} and 17.1 d^{-1}, respectively. These biodegradation rates are higher than observed in the current study which could be explained by the different water types and thus water qualities (BDOC quantity/quality, nutrients) used in both studies resulting in different soil microbial populations. (Henzler *et al.*, 2014) reported degradation rates of 0.01 d^{-1}, 0.02 d^{-1}, 0.01 d^{-1} and 0.03 d^{-1} for carbamazepine, diclofenac, phenazone and sulfamethoxazole, respectively. These degradation rates are much lower than observed in the current study. This could be explained by the fact that Henzler *et al.* (2014) determined OMP biodegradation rates at the field site itself, which makes it extremely difficult to determine OMP removal under a specific redox condition and thus can easily lead to over- or underestimations. Sulfamethoxazole degraded relatively well in this study compared to other studies where no sulfamethoxazole removal was observed in the first nine months of operation (Baumgarten *et al.*, 2011). This could be explained by the fact that Baumgarten *et al*. (2011) used clean filter sand while in the current study soil from an operational RBF site was used. The microbial population present in the soil from the RBF site was probably already adapted to the presence of sulfamethoxazole and/or the BDOC in the river water (average sulfamethoxazole concentration in the Rhine river was 0.02 μg/L (Stoks *et al.*, 2014)). This shows the importance of using soil and river water from RBF locations when rapid data acquisition on OMP removal by RBF is needed.

Close *et al.* (2008) reported OMP biodegradation rates of 0.004 d^{-1}, 0.004 – 0.043 d^{-1} and 0.008 d^{-1} for triclopyr, atrazine and simazine, respectively. In the current study biodegradation rates were 0 - 0.27d^{-1} for triclopyr, 0.05 - 0.17 d^{-1} for atrazine and 0 - 0.13 d^{-1} for simazine. These low biodegradation rates indicate the more persistent behaviour of these OMPs. Persistent behaviour (biodegradation rates of $\mu = 0$ d^{-1}) of carbamazepine, atrazine, hydrochlorothiazide and lincomycin was also reported in Chapter 2. The persistent behaviour of the aforementioned OMPs, dimethoate, pirimicarb and diglyme (Table 6) clearly indicates that more research on these compounds is required to determine if they can be removed under other redox environments or that additional treatment is necessary to prevent them from ending up in the drinking water.

To the best of the authors knowledge, biodegradation rates of terbutalin, theophylline, chloridazon, clofibric acid, diuron, dimethoate, pirimicarb, and diglyme in RBF systems were determined for the first time in the current study. These results provide important information with respect to required residence times under oxic conditions for removal of these OMPs. If the OMP concentrations need to be reduced to less than 1% of their original concentration, the required residence time is about 7 times the half-life of the OMP (OMP half-life $t_{1/2} = \ln(2) / \mu$). This means that theoretically a residence time of 1.8 to 97.0 days under oxic conditions is required to obtain OMP concentrations of less than 1% of their original concentration at the RBF sites and for the OMPs investigated in this study. An oxic zone in the RBF process with a residence time of 97.0 days is not realistic since the oxic zone in general provides a residence time of a couple of hours to days (depending on site specific water quality and hydrogeological conditions), after which oxygen is used up for different biological processes. This implies that in practical situations, the removal of some of the OMPs might be less than 99% in the oxic zone. Further research on OMP removal under specific redox conditions (e.g. NO_3 reducing, Fe/Mn reducing) should therefore elucidate to what extent the OMPs are removed in these redox environments. This will enable the modelling of OMP removal in field conditions and can provide estimates on the extent of removal for the complete RBF process and insight into the required post-treatment processes.

4 Conclusions

This study investigated the effect of two different soil types from operational RBF-sites on soil microbial community composition and OMP removal. DGGE fingerprinting analysis was used to assess the richness and evenness of the microbial community for the soil at the field site (representative of the initial conditions when the soils were fed with different water qualities) as well as for the soil in the columns operated with the same influent water quality (determined during autopsy at the end of the experiment). Retardation factors and biodegradation rates for a large mixture of different types of OMPs (20 in total) were determined by fitting the convection-dispersion equation to the experimentally obtained breakthrough curves.

While richness and evenness of the soil microbial community was very different in the soil samples obtained from the RBF sites, both parameters became more similar as a result of feeding the columns with the same influent water quality. The soil microbial diversity (measured as richness and evenness) for both soil column systems was comparable at the end of the experiment, indicating that the microbial community composition present in both soil column systems was similar.

Retardation factors were close to 1 for all OMPs, indicating mobile behaviour of these OMPs during soil passage. Most OMPs require a residence time of 1.8 to 97.0 days under oxic conditions to obtain a removal of more than 99%. These conditions are in general not present at RBF sites, implying that OMP removal may be less than 99% and further research into the removal of these OMPs under more reducing redox conditions is required. Diglyme, atrazine, hydrochlorothiazide, lincomycin, dimethoate, carbamazepine, triclopyr, pirimicarb and simazine showed relative persistent behaviour with OMP biodegradation rates close or equal to 0, implying that these OMPs should be removed either under more reducing redox conditions, or adequate post-treatment should be provided for their removal.

The results clearly indicated that soil type did not have a significant effect on OMP sorption and biodegradation rate in this study. This result was supported by the similar microbial community composition (richness, evenness) found in both soil types at the end of the experiment, despite the differences in soil characteristics and the differences in microbial community composition at the start of the experiment. This implies that the microbial community composition in the soil and thus OMP removal are mainly determined by the aqueous phase (BDOC quantity/quality, nutrients), rather than the solid phase (the soil). The results of the current study indicate that RBF sites located along the same river will thus most likely show similar OMP removal (in case no significant changes in the water quality occur between the two sites and residence times in the different redox zones are more or less comparable)).

References

Alidina, M., Li, D. and Drewes, J.E. (2014a) Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Research 56, 172-180.

Alidina, M., Li, D., Ouf, M. and Drewes, J.E. (2014b) Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. Journal of Environmental Management 144, 58-66.

Baumgarten, B., Jährig, J., Reemtsma, T. and Jekel, M. (2011) Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Research 45, 211-220.

Bedmar, F., Daniel, P.E., Costa, J.L. and Giménez, D. (2011) Sorption of acetochlor, s-metolachlor, and atrazine in surface and subsurface soil horizons of argentina. Environmental Toxicology and Chemistry 30(9), 1990-1996.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J. and Massmann, G. (2013) Sorption behavior of 20 wastewater originated micropollutants in groundwater - Column experiments with pharmaceutical residues and industrial agents. Journal of Contaminant Hydrology 154, 29-41.

Carballa, M., Fink, G., Omil, F., Lema, J.M. and Ternes, T. (2008) Determination of the solid-water distribution coeffcient (K_d) for pharmaceuticals, estrogens and musk fragrances in digested sludge. Water Research 42, 287-295.

Chiang, P.C. and Hu, Y. (2009) Simultaneous Determination of LogD, LogP, and pKa of Drugs by Using a Reverse Phase HPLC Coupled with a 96-Well Plate Auto Injector. Combinatorial Chemistry & High Throughput Screening 12, 250-257.

Cleuvers, M. (2004) Mixture toxicity of the anti-inflammatory drugs diclofenac, ibuprofen, naproxen, and acetylsalicyclic acid. Ecotoxicology and environmental safety 59, 309-315.

Close, M.E., Lee, R., Sarmah, A.K., Pang, L., Dann, R., Magesan, G.N., Watt, J.P.C. and Vincent, K.W. (2008) Pesticide sorption and degradation characteristics in New Zealand soils - a synthesis from seven field trails. New Zealand Journal of Crop and Horticultural Science 36, 9-30.

Ferreira da Silva, B., Jelic, A., López-Serna, R., Mozeto, A.A., Petrovic, M. and Barceló, D. (2011) Occurence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain. Chemosphere 85, 1331-1339.

Fingler, S., Stipičević, S. and Drevenkar, V. (2004) Sorption behaviour of chlorophenols and triazine herbicides in reference euro-soils. International Journal of Environmental Analytical Chemistry 84(1-3), 83-93.

Geudens, P.J.J.G. (2012) Dutch Drinking Water Statistics 2012. VEWIN.

Guo, L., Jury, W.A., Wagenet, R.J. and Flury, M. (2000) Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. Journal of Contaminant Hydrology 43, 45-62.

Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P.F., Ingerslev, F., Holten Lützhøft, H.C. and Jørgensen, S.E. (1998) Occurrence, Fate and Effects of Pharmaceutical Substances in the Environment - A review. Chemosphere 36(2), 357-393.

Henzler, A.F., Greskowiak, J. and Massmann, G. (2014) Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). Journal of Contaminant Hydrology 156, 78-92.

Hiller, E., Čerňanský, S., Krascsenits, Z. and Milička, J. (2009) Effect of soil and sediment composition on acetochlor sorption and desorption. Environmental Science and Pollution Research 16, 546-554.

Hiller, E., Tatarková, V., Šimonovičová, A. and Bartal', M. (2012) Sorption, desorption, and degradation of (4-chloro-2-methylphenoxy)acetic acid in representative soils of the Danubian Lowland, Slovakia. Chemosphere 87, 437-444.

Hoppe-Jones, C., Dickenson, E.R.V. and Drewes, J.E. (2012) The role of microbial adaptation and biodegradable dissolved organic carbon on the attenuation of trace organic chemicals during groundwater recharge. Science of The Total Environment 437, 137-144.

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

Houtman, C.J., Kroesbergen, J., Lekkerkerker-Teunissen, K. and 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. Science of The Total Environment 496, 54-62.

IBM Corp. (2011) IBM SPSS Statistics for Windows, Version 20.0. Armonk, NY: IBM Corp.

Karickhoff, S.W., Brown, D.S. and Scott, T.A. (1979) Sorption of hydrophobic pollutants on natural sediments. Water Research 13, 241-248.

Li, D., Alidina, M. and 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. Applied Microbiology and Biotechnology 98, 5747-5756.

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

Li, D., Sharp, J.O., Saikaly, P.E., Ali, S., Alidina, M., Alarawi, M.S., Keller, S., Hoppe-Jones, C. and Drewes, J.E. (2012) Dissolved Organic Carbon Influences Microbial Community Composition and Diversity in Managed Aquifer Recharge Systems. Applied and Environmental Microbiology 78(19), 6819-6828.

Limousin, G., Gaudet, J.-P., Charlet, L., Szenknect, S., Barthès, V. and Krimissa, M. (2007) Sorption isotherms: A review on physical bases, modeling and measurement. Applied Geochemistry 22, 249-275.

Lyautey, E., Lacoste, B., Ten-Hage, L., Rols, J.L. and Garabetian, F. (2005) Analysis of bacterial diversity in river biofilms using 16S rDNA PCR-DGGE: methodological settings and fingerprints interpretation. Water Research 39, 380-388.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A. and Amy, G.L. (2011a) 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 Research 45, 4722-4736.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Song, K.G. and 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. Journal of Contaminant Hydrology 140-141, 139-149.

Maeng, S.K., Sharma, S.K., Lekkerkerker-Teunissen, K. and Amy, G.L. (2011b) Occurence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: a review. Water Research 45(10), 3015-3033.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M. and Barry, D.A. (2013) Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Science of The Total Environment 461-462, 480-498.

Murillo-Torres, R., Durán-Álvarez, J.C., Prado, B. and Jiménez-Cisneros, B.E. (2012) Sorption and mobility of two micropollutants in three agricultural soils: A comparative analysis of their behavior in batch and column experiments. Geoderma 189-190, 462-468.

Packer, J.L., Werner, J.J., Latch, D.E., McNeill, K. and Arnold, W.A. (2003) Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibric acid, and ibuprofen. Aquatic Sciences 65, 342-351.

Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T. and Toze, S. (2011) Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122, 53-62.

Petty, D.G., Getsinger, K.D. and Woodburn, K.B. (2003) A Review of the Aquatic Environmental Fate of Triclopyr and its Major Metabolites. Journal of Aquatic Plant Management 41, 69-75.

Piatt, J.J., Backhus, D.A., Capel, P.D. and Eisenreich, S.J. (1996) Temperature-Dependent Sorption of Naphthalene, Phenanthrene, and Pyrene to Low Organic Carbon Aquifer Sediments. Environmental Science & Technology 30, 751-760.

Picton, P. and Farenhorst, A. (2004) Factors Influencing 2,4-D Sorption and Mineralization in Soil. Journal of Environmental Science and Health Part B B39(3), 367-379.

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

Rocio Estrella, M., Brusseau, M.L., Maier, R.S., Pepper, I.L., Wierenga, P.J. and Miller, R.M. (1993) Biodegradatio, Sorption, and Transport of 2,4-Dichlorophenoxyacetic Acid in Saturated and Unsaturated Soils. Applied and Environmental Microbiology 59(12), 4266-4273.

Sakaliene, O., Papiernik, S.K., Koskinen, W.C. and Spokas, K.A. (2007) Sorption and predicted mobility of herbicides in Baltic soils. Journal of Environmental Science and Health Part B 42, 641-647.

Scheytt, T., Mersmann, P., Leidig, M., Pekdeger, A. and Heberer, T. (2004) Transport of Pharmaceutically Active Compounds in Saturated Laboratory Columns. Ground Water 42(5), 767-773.

Scheytt, T.J., Mersmann, P. and Heberer, T. (2006) Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. Journal of Contaminant Hydrology 83, 53-69.

Scheytt, T.J., Mersmann, P., Rejman-Rasinski, E. and These, A. (2007) Tracing Pharmaceuticals in the Unsaturated Zone. Journal of Soils and Sediments 7(2), 75-84.

Schroll, R., Becher, H.H., Dörfler, U., Gayler, S., Grundmann, S., Hartmann, H.P. and Ruoss, J. (2006) Quantifying the Effect of Soil Moisture on the Aerobic Microbial Mineralization of Selected Pesticides in Different Soils. Environmental Science & Technology 40, 3305-3312.

Shalaeva, M., Kenseth, J., Lombardo, F. and Bastin, A. (2007) Measurement of Dissociation Constants (pKa Values) of Organic Compounds by Multiplexed Capillary Electrophoresis Using Aqueous and Cosolvent Buffers. Journal of Phamaceutical Sciences, 1-24.

Si, Y., Takagi, K., Iwasaki, A. and Zhou, D. (2009) Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils. Pest Management Science 65, 956-962.

Sonnenschein, C. and Soto, A.M. (1998) An Updated Review of Environmental Estrogen and Androgen Mimics and Antagonists. The Journal of Steroid Biochemistry and Molecular Biology 65(1-6), 143-150.

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

Su, A.C.L. (1979) Advances in Organometallic Chemistry - Catalytic Codimerization of Ethylene and Butadiene, Academic Press, Inc.

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

van der Hoek, J.P., Bertelkamp, C., Verliefde, A.R.D. and Singhal, N.S. (2014) Drinking water treatment technologies in Europe: State of the art - Challenges - Research needs. Journal of Water Supply: Research and Technology - AQUA 63(2), 124-130.

Verliefde, A., Cornelissen, E., Amy, G., Van der Bruggen, B. and van Dijk, H. (2007) Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. Environmental Pollution 146, 281-289.

Wang, C., Teppen, B.J., Boyd, S.A. and Li, H. (2011) Sorption of Lincomycin at Low Concentrations from Water by Soils. Soil Science Society of America Journal 76, 1222-1228.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environmental Science & Technology 39, 6649-6663.

Yang, X.J., Qu, Y., Yuan, Q., Wan, P., Du, Z., Chen, D. and Wong, C. (2013) Effect of ammonium on liquid- and gas-phase protonation and deprotonation in electrospray ionization mass spectrometry. Analyst 138, 659-665.

Zhang, Q., Yang, C., Dang, Z. and Huang, W. (2011) Sorption of Tylosin on Agricultural Soils. Soil Science 176(8), 407-412.

Chapter 5

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

This chapter is based on: Bertelkamp *et al.* (2016), The effect of feed water dissolved organic carbon concentration and composition on organic micropollutant removal and microbial diversity in soil columns simulating river bank filtration, Chemosphere, 144, pp. 932-939

1 Introduction

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.*, 2014b, Maeng *et al.*, 2011, Maeng *et al.*, 2012a, Onesios *et al.*, 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.*, 2014b). 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.*, 2012a). 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.*, 2014a, Li *et al.*, 2014b, 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. Shonnard *et al.* (2007) 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, Frehse *et al.*, 2013), 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 (Cowart *et al.*, 1971, Hoppe-Jones *et al.*, 2010, Regnery *et al.*, 2015a). 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, the study described in this chapter investigated 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 to 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 Chapter 3 (Method 1). Detection limits are provided in Table S3.

Table 1 – Physico-chemical properties of OMPs

OMP	Class	MW	Charge (pH 8)	Log D (pH 8)[1]	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

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

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 Labor Huber, Germany). The analysis was performed for phase 3 for the unfractioned river water and the different organic carbon fractions fed to the columns. Measurement was performed as described elsewhere (Seybold *et al.*, 2001, Stuyfzand *et al.*, 2011).

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 UltraViolet Absorbance (SUVA) was then calculated as indicator for the aromaticity of the organic carbon according to Eq. 1:

$$SUVA = \frac{UVA_{254nm}}{DOC} \cdot 100 \qquad \text{Eq. 1}$$

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 Chapter 4.

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 Chapter 2). 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 Chapter 4.

2.6 Statistical analysis

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

2.7 Modelling

CXTFIT (Toride *et al.*, 1995b) 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 convection-dispersion equation (for a detailed description see Chapter 2).

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 organic carbon composition of the four organic carbon fractions was indeed different.

Table 2 - Aromaticity of the different fractions

Fraction	Aromaticity (L $mg^{-1} \cdot m^{-1}$) (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)

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 4). 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 to 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.

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 4, 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.

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

	Effect of organic carbon fraction				
Phase	**DOC removal [%]**	**SUVA removal [%]**	**ATP concentration [pg/g]**	**Richness**	**Evenness**
	***p*-value**	***p*-value**	***p*-value**	***p*-value**	***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 [%]**	**SUVA removal [%]**	**ATP concentration [pg/g]**	**Richness**	**Evenness**
	***p*-value**	***p*-value**	***p*-value**	***p*-value**	***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

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 (Chapter 2, Burke *et al.*, 2013, Henzler *et al.*, 2014). Hence, the retardation factor in Eq. S3 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.

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 (Wei *et al.*, 2001). However, for the more degradable OMPs (acetaminophen, chloridazon, clofibric acid, diclofenac, ketoprofen, and phenazone), biodegradation rates were slightly lower compared to our previous study (Wei *et al.*, 2001). 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.*, 2014a, 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.

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		

An increase in OMP biodegradation rate as a result of an increase in initial OMP concentration has been reported before (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 termed 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 and richness/evenness of the soil microbial population/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.

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[1]	0.26	0.13[1]	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[1]	0.89	0.00	0.00	0.25[1]	1.48	0.00	0.38[1]
Clofibric acid	0.50	0.43	0.37	0.51	0.53	0.36[1]	0.06[1]	0.22[1]	0.46	0.48[1]	0.00	0.26
Diclofenac	0.31[1]	0.23[1]	0.09[1]	0.37	0.91	0.52[1]	0.39	0.71[1]	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[1]	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[1]	0.36[1]	0.24	ND	0.26[1]	0.23	0.00
Ketoprofen	0.83	0.34[1]	0.26	0.26	ND	ND	ND	ND	ND	ND	1.16	ND
Lincomcyin	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[1]	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[1]
Simazine	0.00	0.00	0.00	0.00	0.18[1]	0.06[1]	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[1]	1.83	2.09	0.12[1]	0.98[1]
Triclopyr	0.55[1]	0.22	1.25	ND	1.00	0.91	0.73[1]	1.79	0.37[1]	0.37[1]	0.12[1]	0.72[1]
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

[1] Confidence interval through 0, result statistically not significant

[2] $\mu \leq 0.05$ was set to $\mu = 0$

[3] 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.

References

Alberts, J.J., Takács, M., McElvaine, M. and Judge, K. (2001) Humic Substances, Structures, Models and Functions. Ghabbour, E.A. and Davies, G. (eds), pp. 179-190, The Royal Society of Chemistry, Cambridge, UK.

Alidina, M., Li, D. and 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. and 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. and Snyder, S.A. (2012) Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Sci. & Technol. 12, 11-23.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J. and 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) Pharmaceuticals in the Environment. Kümmerer, K. (ed), Springer, Berlin.

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

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

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

Hoppe-Jones, C., Oldham, G. and 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. and 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. and 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. and 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. and 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. and 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. and 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. and 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. and 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. and Amy, G.L. (2008) Adv. Environ. Monit. Kim, Y.J. and Platt, U. (eds), pp. 259-270.

Onesios, K.M. and 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. and 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. and 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. and Drewes, J.E. (2015b) Biotransformation of trace organic chemicals during groundwater recharge: How useful are first-order rate constants? J. Cont. Hydrol. In press.

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

Storck, F.R., Schmidt, C.K., Wülser, R. and 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.

Team, R.D.C. (2008) R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, ISBN: 3-900051-07-0.

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

Chapter 6

The effect of redox conditions and adaptation time on organic micropollutant removal during river bank filtration: A laboratory-scale column study

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1 Introduction

Chapter 2, 3, 4 and 5 have demonstrated that a number of OMPs (e.g. atrazine, carbamazepine, chloridazon, clofibric acid, diclofenac, dimethoate, diuron, hydrochlorothiazide, ketoprofen, lincomycin, metoprolol, phenzone, pirimicarb, simazine and sulfamethoxazole) showed incomplete removal or persistent behaviour under oxic conditions and combined oxic/nitrate reducing conditions. Other studies, however, have demonstrated that some OMPs showing no or only partial removal under oxic conditions sometimes show enhanced removal under more reduced conditions (anoxic, anaerobic) (Grünheid *et al.*, 2005, Storck *et al.*, 2012, 2010). Thus, for drinking water companies operating RBF systems, it is important to investigate if the OMPs showing persistent behaviour under oxic conditions are removed under more reduced and separate redox conditions (e.g. NO_3^- and Fe^{3+}/Mn^{4+}). If knowledge is obtained with respect to OMP removal for separate redox conditions, the results of certain redox conditions prevailing at a specific RBF site could be combined to estimate the overall removal. When OMP biodegradation rates and residence times are known for the different and separate redox conditions, it is possible to determine to what extent these OMPs are removed at field sites. This will provide drinking water companies with more insight into the required residence time of an OMP in a specific redox zone to achieve a certain extent of OMP removal. If the investigated OMPs are not eliminated during the complete RBF process, drinking water companies should implement or adjust post-treatment processes to prevent the presence of these compounds in the produced drinking water.

The removal of some of the previously mentioned OMPs has been investigated in a number of wastewater treatment processes exhibiting different redox conditions such as soil aquifer treatment (in which treated wastewater is infiltrated in, and treated by, the soil), constructed wetlands and conventional activated sludge systems (Matamoros *et al.*, 2007, Patterson *et al.*, 2011, Rauch-Williams *et al.*, 2010, Suarez *et al.*, 2010). However, these results cannot be directly translated to the RBF system, since waste water treatment systems are usually characterized by much higher biomass quantities and a notably different organic carbon composition and concentration in the feed water compared to river water. Higher biomass quantities can lead to higher biodegradation rates while the feed water organic carbon composition and concentration was reported to play an important role in shaping the microbial community responsible for OMP removal and can thus greatly differ for river water compared to wastewater (Alidina *et al.*, 2014b, Frehse *et al.*, 2013, Li *et al.*, 2013).

For some OMPs, such as phenazone, redox dependent removal was identified in RBF field studies (Massmann *et al.*, 2008, Massmann *et al.*, 2006). While field studies can be useful to identify redox dependent removal of OMPs, biodegradation rates for the separate redox conditions cannot be easily determined directly in the field. The reason why OMP removal for a specific redox condition is difficult to determine in the field, is the seasonal variability of the redox zones due to for example river water temperature. Therefore studies investigating OMP removal under controlled redox conditions generally use batch or laboratory scale soil column studies to mimic the RBF process.

The removal behaviour of the formerly mentioned OMPs for separate and more reduced redox conditions in RBF systems is largely unknown. Few batch studies investigated the fate of atrazine, lincomycin, pirimicarb and metoprolol (Barbieri *et al.*, 2012, DeLaune *et al.*, 1997, Gu *et al.*, 2003, Kah *et al.*, 2007, Sara *et al.*, 2013, Taboada *et al.*, 1994), but these either focused on combined redox conditions

or one specific redox condition. Thus the fate of these OMPs for separate and/or other redox conditions remains unclear.

The fate of carbamazepine, clofibric acid, diclofenac, ketoprofen, and sulfamethoxazole has been investigated under different redox conditions in soil column studies simulating soil passage (Baumgarten *et al.*, 2011, Hoppe-Jones *et al.*, 2012, Maeng *et al.*, 2012a). However, these studies used nitrogen gas and/or starch to deplete the feed water from oxygen to create reduced redox conditions. The major drawback of these artificially created redox conditions is that the biodegradable dissolved organic carbon (BDOC) composition entering the nitrate reducing zone is similar to the oxic zone, which is a factually incorrect simulation of what occurs at full-scale operational RBF sites where the easily degradable organic carbon is usually removed in the oxic infiltration zone and thus only the more refractory organic carbon will enter the nitrate reducing zone. BDOC concentration and composition have been reported to have a strong effect on microbial community composition and diversity (Alidina *et al.*, 2014b, Li *et al.*, 2013) and therefore OMP removal can be different for artificially created nitrate reducing conditions (with an oxic BDOC composition) compared to naturally derived nitrate reducing conditions. Besides, most studies reported percentage removals which make it difficult to determine how long an OMP needs to reside in the subsurface to obtain a certain extent of removal. Therefore, OMP biodegradation rates are more appropriate since these can be converted to half-lifes which can be used to determine how long an OMP needs to reside in the subsurface to achieve a 90% or 99% removal.

Another important aspect that has been largely underexposed in previous studies is that of adaptive behaviour. OMPs are degraded by the soil microbial community, but if a new OMP is detected in the river the soil microbial population might not be capable of instantly degrading the compound if, for example, the appropriate enzymes cannot be expressed (Spain *et al.*, 1980, Spain *et al.*, 1983). Therefore, newly detected OMPs sometimes require a certain adaptation time (or lag-phase) before biodegradation is initiated (Storck *et al.*, 2012). This phenomenon is especially important for new developed RBF sites or RBF sites that have never been exposed to certain OMPs, since it will provide important information with respect to the required start-up time before full OMP removal capacity is obtained for the RBF site

An adaptation time (or lag-phase) has been reported for a number of OMPs such as sulfamethoxazole, naproxen, bisphenol A, 17β-estradiol, trimethoprim, bezafibrate, and iohexol during soil passage (Baumgarten *et al.*, 2011, Patterson *et al.*, 2011, Storck *et al.*, 2012). However, recently, a study of Alidina *et al.* (2014a) concluded that adaptation of the soil microbial community towards OMPs is not necessary if the soil microbial community is adapted to the primary substrate in the feed. Thus, results on adaptation behaviour of OMPs are inconclusive. Additionally, it remains unclear why certain OMPs require an adaptation time while others do not.

Furthermore, Baumgarten *et al.* (2011) demonstrated that the adaptation time of sulfamethoxazole could be more than 2 years. This explains why adaptive behaviour is not discussed in most studies since these usually describe experimental periods of a few months or OMP removal for a specific point in time which makes it impossible to capture adaptive behaviour. The studies of Baumgarten *et al.* (2011) and Storck *et al.* (2012) were limited to soil column studies filled with either technical sand or glass beads. The use of these clean filter media could potentially overestimate the required adaptation time, since no biomass is present at the start of the experiment.

Besides, understanding the adaptive behaviour of OMPs is necessary in relation to predictive models for OMP removal during RBF. Such a predictive model enables drinking water companies to predict if an OMP that is detected in a river for the first time will be removed during RBF of not based on for example the functional groups present in its molecular structure. To date it is unclear if and how adaptive behaviour of OMPs should be included in predictive models.

To tackle the aforementioned limitations, the research described in this chapter investigated (1) the fate of a large OMP mixture (15 in total, dosed in a concentration of 500 ng/L), that showed partial or persistent removal under oxic conditions, for more reduced conditions (e.g. oxic, nitrate reducing and almost complete nitrate removal) that were developed in a natural manner, (2) if redox dependent OMP removal could be explained by physico-chemical properties and/or functional groups (3) adaptation behaviour of a large OMP mixture in a long-term column experiment simulating the RBF system (oxic conditions) to examine if adaptation behaviour could be explained by physico-chemical properties and/or functional groups, and (4) how the adaptive behaviour of OMPs could be incorporated in predictive models.

To study the effect of redox condition on OMP removal, a unique set-up was used. To the best of the authors knowledge, an experimental set-up like this has never been used before. Three laboratory-scale RBF pilots were operated in parallel. Each of these pilots mimicked extended travel times: an oxic, an oxic + suboxic (nitrate reducing) and an oxic + suboxic + anoxic installation (nitrate almost completely removed). All three pilots were fed with oxic river water and increasing the number of columns (residence time) resulted in a natural development of the different reduced redox conditions. Three separate installations were required for two reasons: (1) each installation was only sampled at the influent and effluent side (not in between), to prevent oxygen from entering the columns during sampling, which could negatively impact the stable redox conditions inside the columns, (2) to provide sufficient sampling volume for each “redox condition”, despite the low flows . Columns were filled with RBF site soil and fed with river water from the same site. Biodegradation rates were determined from the experimental results by fitting the experimental data to the convection-dispersion equation.

2 Materials and Methods

2.1 Experimental set-up

Three independent RBF pilot installations were used in this research: pilot A, pilot B, pilot C. Pilot A consisted of two transparent PVC columns (L = 1 m, D = 36 mm) in series. Both columns were filled with oxic soil from RBF site Engelse Werk of drinking water company Vitens (52°29’39" N, 6°3’40.4" E). Pilot B consisted of 10 columns in series, the first four columns were transparent PVC (L = 1 m, D = 36mm) filled with oxic soil from RBF site Engelse Werk and the last six columns were stainless steel (L = 1 m, D = 36 mm) filled with soil obtained from anoxic/anaerobic soil drillings (52°29'25.3" N, 6°3'56.0" E) from the same RBF site. Pilot C consisted of 22 columns in series, the first four columns were transparent PVC (L = 1 m, D = 36mm) filled with oxic soil from RBF site Engelse Werk and the last eighteen columns were stainless steel (L = 1 m, D = 36 mm) filled with soil obtained from anoxic/anaerobic soil drillings from the same RBF site. Operational parameters of the three installations are presented in Table 1.

Since the first two columns of all three pilots and columns three till ten of pilot B and C were filled with the same soil material and fed with the same feed water, it is assumed that these columns will show similar OMP removal.

Columns were filled with soil in increments of 4-5 cm while tapping on the columns, to prevent layering in the columns. The anoxic/anaerobic soil columns were filled in a similar manner to the stainless steel column, but the whole filling process took place in a glove box depleted from oxygen. To prevent leaching of soil grains, the top and bottom of the columns were fitted with perforated PVC plates (30 holes, d = 0.8 mm for each hole) that were covered with filter cloth (45 μm, Top7even net & mesh, The Netherlands). A flow from bottom to top was maintained in all columns to prevent air entrapment and the whole system was operated in a temperature controlled room (12°C) in the dark (to prevent algae growth and/or OMP loss due to photolysis).

The pilots were fed from a jerrycan filled with Lek river water (the same water that was feeding the RBF sites from which the soil was taken) and an OMP mixture. River water was refreshed every two weeks and was filtered (d = 0.4 mm), prior to use as feed, to prevent twigs and larger particles from clogging the pump tubes. After every replacement feed jerrycans were washed twice with acetone and flushed several times with demineralized water before refilling to prevent biofilm formation. The feed solution was pumped through the columns by a peristaltic multichannel pump (205S, Watson Marlow, The Netherlands) using Marprene® pump tubing (d = 0.63 mm, Watson Marlow, The Netherlands). The hydraulic loading rate applied on the columns was 0.5 L/d, which equals a filtration rate of 0.5 m/d. Pore velocity and porosity in the pilot was determined using deuterium (^2H) as tracer. Deuterium concentrations were determined with laser absorption spectroscopy using a DLT-100 Liquid-Water Isotope Analyzer (Los Gatos Research, USA); precision ± 0.56 ‰ for ^2H. A quantity of 0.19 mL of 99% pure Deuterium was added to the feed solutions (20 L), resulting in an approximate 60 ‰ increase in δ-^2H. Empty bed contact time (EBCT) and porosity determined in the pilots are presented in Table 1.

Table 1 – Experimental characteristics of the three pilot installations

Pilot	Nr. of columns	Redox conditions	Terminal electron acceptor	EBCT [d]	Porosity [-]	ΔDOC [%]	ΔNO_3^- [%]
A	2	Oxic	O_2, no NO_3 removal	4.1	0.33	24.1 ± 11.9 (n = 13)	~ 0 (n = 13)
B	10	Oxic + Suboxic	Partial NO_3 removal	20.4	0.39	18.1 ± 23.9 (n = 12)	21.3 ± 23.1 (n = 14)
C	22	Oxic + Suboxic + Anoxic	NO_3 almost completely removed	44.8	0.43	19.4 ± 16.6 (n = 14)	98.7 ± 2.5 (n = 14)

2.2 Organic micropollutants

The OMP mixture used in this study and their physico-chemical properties are presented in Table 2. OMP samples were taken from the influent and effluent, more frequently in the beginning to determine the breakthrough curve and once the breakthrough curve was established samples were taken monthly.

Preparation of the stock solution and analysis of the OMP samples was performed as described in (Chapter 3, Method 1).

Table 2 – Organic micropollutants investigated in this study and their physico-chemical properties

OMP	MW	pK_a	Charge at pH 8	Log D at pH 8[1]
Atrazine	215.68	<2 (1.6)[b]	0	2.26
Carbamazepine	236.27	-[a]	0	2.64
Chloridazon	221.64	3.4[c]	0	1.05
Clofibric acid	214.65	3.2[d]	-1	-0.18
Diclofenac	296.15	4.2[d]	-1	1.21
Dimethoate	229.26	2.0[e]	0	0.21
Diuron	233.09	13.6[c]	0	2.49
Hydrochlorothiazide	297.74	7.9[f]	0	-0.72
Ketoprofen	254.28	4.7[a]	-1	0.49
Lincomycin	406.54	7.6[g]	+1	-1.22
Metoprolol	267.36	9.4[a], 9.7[f]	+1	0.14
Phenazone	188.23	1.4[f]	0	1.11
Pirimicarb	238.29	4.5[h]	0	1.74
Simazine	201.66	1.6[e]	0	1.83
Sulfamethoxazole	253.28	1.8, 5.8[c]	0	0.39

[1] http://www.chemicalize.org

[a](Chiang *et al.*, 2009), [b](Westerhoff *et al.*, 2005), [c](Margot *et al.*, 2013), [d](Packer *et al.*, 2003), [e](Yang *et al.*, 2013), [f](Ferreira da Silva *et al.*, 2011), [g](Wang *et al.*, 2011), [h]http://pubchem.ncbi.nlm.nih.gov

2.3 Water quality parameters

Water quality parameters were measured more frequently in the beginning in parallel to the measuring frequency used for the OMP breakthrough curves and biweekly once the breakthrough curves were established (except for UV_{254} which was measured only at the end of the experiment for the OMP samples as function of residence time). The dissolved organic carbon (DOC) concentration was measured with a Shimadzu TOC Analyser after filtering the aqueous samples through 0.45 μm filters (Whatman, Germany); these filters were flushed twice with demineralized water prior to use. UV_{254} 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 meter (FDO® 925 IDS probe, Oxi340i, WTW, Germany) and pH was measured with a multimeter (SenTix® 940 IDS probe, Multi 340i, WTW, Germany) directly in the feed or in a flow through cell connected to the effluent tubes of the columns. Ions were analysed with an ProfIC 15 – AnCat ion chromatograph (Metrohm 881 anion (suppressed) and 883 cation system) (Metrohm, Switzerland) after filtering the aqueous samples through 0.45 μm filters (Whatman, Germany); these filters were flushed twice with demineralized water prior to use. For the anions an A Supp 150/4.0 anion column was used with 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ eluent. For the cations a C5 cation column with 3 mM HNO_3 eluent was used. Regenerant for the suppressor was 50 mM H_2SO_4.

2.4 Soil parameters

Soil pH, grain size distribution, organic matter content and cationic exchange capacity were determined according to the protocols described in (Chapter 4).

2.5 Modelling

CXTFIT (Toride *et al.*, 1995a) was used to obtain the biodegradation rates (μ) of the OMPs in the columns by fitting the experimental breakthrough curves using the inverse problem based on the convection dispersion equation (CDE) as described in (Chapter 2). Average pore water velocity, dispersion coefficient and dispersivity α of the three installations are presented in Table S1 of the Supplemental Information (SI).

For the oxic pilot, breakthrough curves of the complete experimental period of 15 months were used to determine the biodegradation rate. Since it was impossible to determine the OMP biodegradation rates for the separate redox conditions in the suboxic and anoxic pilot by fitting the breakthrough curves of these pilots (this would result in a biodegradation rate for combined redox conditions), both these pilots were sampled along the height at the end of the experimental period (15 months after OMP spiking started) when stable effluent OMP concentrations were obtained. This final sampling campaign was performed to determine the OMP concentrations as a function of residence time for all three pilots and data was used to determine the biodegradation rates of the OMPs that showed redox dependent behaviour for the different redox conditions.

It is assumed that the first two columns in all three installation will behave similarly with respect to OMP removal since these are filled with similar soil and fed with the same feed water quality. Likewise, columns three till ten (representative of nitrate reducing conditions) from pilot B and C are expected to behave similarly with respect to OMP removal. Therefore, OMP biodegradation rates under nitrate reducing conditions were determined by combining the data from column three till ten of pilot B and C (the influent concentration of the suboxic zone was determined as the average of column 2 from both the oxic and suboxic pilot). OMP biodegradation rates under anoxic conditions (nitrate almost completely removed) were determined based on data from columns ten till twenty two of the anoxic pilot (the influent concentration of the anoxic zone was determined as the average of the effluent of column ten from both the suboxic and anoxic pilot).

3 Results and Discussion

3.1 Water quality and soil parameters

Feed water quality parameters are presented in Table 3.

Table 3 – Water quality parameters feed water

Parameter	Units	Value ± st dev
pH	[-]	8.01 ± 0.28 (n=16)
DOC	mg/L	3.81 ± 0.74 (n=64)
NO_3^-	mg/L	8.60 ± 3.05 (n=54)
PO_4^{3-}	mg/L	0.07 ± 0.07 (n=34)
Cl^-	mg/L	56.32 ± 18.74 (n=53)
SO_4^{2-}	mg/L	46.95 ± 9.63 (n=54)
NH_4^+	mg/L	0.08 (min. 0.04, max. 0.13, n=12)[a]
K^+	mg/L	3.71 ± 0.80 (n=54)
Mg^{2+}	mg/L	10.79 ± 1.79 (n=54)
Ca^{2+}	mg/L	52.63 ± 14.69 (n=49)

[a](Stoks *et al.*, 2014)

Soil parameters for the oxic and the suboxic/anoxic soil drillings are presented in Table 4. While grain size distributions are similar, soil organic matter and cationic exchange capacity are lower in the suboxic/anoxic soil drillings.

Table 4 - Soil parameters

	Units	Vitens oxic soil	Vitens sub oxic/deep anoxic soil
Clay (< 8 μm)	v/v %	3.72	1.71
Silt (8 – 63 μm)	v/v %	3.58	2.50
Sand (63 – 2000 μm)	v/v %	92.69	95.79
d_{median}	μm	380.38	394.84
LOI550	% dry weight	1.18	0.24
SOM	% dry weight	0.92	0.12
pH – H_2O	-	8.23	NA
pH – KCl	-	7.90	NA
Cationic Exchange Capacity (CEC)	meq/kg dry weight	42.13	14.07

NA = Not analyzed

3.2 DOC concentration

DOC removal is more or less similar for all three pilot installations (Table 1), which is mainly attributed to the fact that the largest part of the DOC is removed in the first 2 – 3 meters of the soil which has been observed in other studies as well (Maeng *et al.*, 2012a, Möller *et al.*, 2011). This first part of the RBF soil columns is the most active and therefore the largest DOC removal is expected in this zone. For suboxic (2 – 10 m) and anoxic conditions (10 – 22 m), the DOC concentration remains relatively stable and no additional removal was observed. Figure S1 shows the DOC concentrations as a function of soil depth for the oxic, suboxic and anoxic pilot installations combined.

To identify the prevailing redox conditions in the three installations, oxygen and nitrate were measured. Nitrate removal is presented in Table 1 (yearly trends are presented in Figure S2). For the oxic pilot, no nitrate removal was observed and thus oxic conditions prevailed. For the suboxic pilot, partial nitrate removal was observed (average NO_3^- removal = 21.3 ± 23.1 %, n = 14), while for the anoxic pilot practically complete nitrate removal was observed (average NO_3^- removal = 98.7 ± 2.5 %, n = 14). These results show that indeed different redox conditions were created in the three pilot installations.

3.3 OMP removal – redox dependent behaviour

Retardation factors for the different OMPs were all close to 1 with maximum values for the retardation factor equal to 2.6 (Table 5), thus indicating weak sorption and mobile behaviour of these OMPs in the soil environment. These low retardation factors for most OMPs were confirmed by other studies (Burke *et al.*, 2013, Patterson *et al.*, 2011, Scheytt *et al.*, 2004b). OMP biodegradation rates were determined for the complete OMP mixture in all three pilots and the results are depicted in Table 5.

Chloridazon, clofibric acid, diclofenac, ketoprofen, lincomycin, phenazone, and sulfamethoxazole were rapidly degraded in the oxic pilot and therefore their removal could not be determined for the more reduced redox conditions. Biodegradation rates for these OMPs ranged between μ = 1.16 - 3.12 d^{-1} ($t_{1/2}$ = 0.19 - 0.60 d) and thus a 90% removal (= 7 · $t_{1/2}$) can be expected for most OMPs after 1.3 - 4.2 days residence time in the soil. High removal of diclofenac, ketoprofen, phenazone and clofibric acid was also observed in other studies (Chapter 2, Maeng *et al.*, 2012a, Massmann *et al.*, 2006, Storck *et al.*, 2012, Zearley *et al.*, 2012). For sulfamethoxazole a half-life of 9 days was determined (after 27 months of operation time) in a study of Baumgarten *et al.* (2011), which is much higher than the half-life of $t_{1/2}$ = 0.32 days determined in the current study. This discrepancy is most likely the result of the use of technical sand without biomass in the study of Baumgarten *et al.* (2011) and the use of sand obtained from a RBF site in the current study. Lincomycin showed good removal in the current study, while it was found to be persistent in a previous study (Chapter 2). This persistent behaviour of lincomycin is most likely the result of insufficient adaptation time in the previous study in which columns were operated for 6 months compared to 15 months in the current study. For chloridazon a half-life of $t_{1/2}$ = 10 days was reported for an aerated fixed bed bioreactor fed with wastewater treatment plant effluent (Buttiglieri *et al.*, 2009). The half-life demonstrated in the current study was much lower which could be explained by the difference in organic carbon composition and concentration between the wastewater effluent in the study of (Buttiglieri *et al.*, 2009) and the river water used in the current study (Alidina *et al.*, 2014b, Li *et al.*, 2014b). Depending on the local hydraulic and geochemical conditions which determine the length of the oxic zone at the RBF site, a significant to complete removal of these OMPs can be expected. The rapid removal of chloridazon, lincomycin and sulfamethoxazole under oxic conditions was the result of an adaptation time which will be further discussed in section "3.3 OMP removal – adaptative behaviour".

Atrazine, carbamazepine, hydrochlorothiazide and simazine showed persistent behaviour under oxic conditions and thus their removal under more reduced redox zones was investigated in this study. No removal of the four OMPs was observed in any of the redox environments investigated in this study, even after 15 months of operation (Table 5). Apparently, if the OMP is persistent under oxic conditions, it does not tend to be removed under more reduced conditions either, at least for the four persistent OMPs and redox conditions investigated in this study. Atrazine, hydrochlorothiazide and simazine were present in the Lek river in concentrations below the detection limit and therefore it is possible that the microbial population present in the soil obtained from the RBF site fed with Lek river water was never previously exposed to these OMPs and appropriate enzymes to degrade these OMP were not expressed.

The persistent behaviour of atrazine, carbamazepine and hydrochlorothiazide is confirmed by other studies. Benotti *et al.* (2012) demonstrated that atrazine and carbamazepine were not eliminated in two full-scale RBF systems, however the specific prevailing redox conditions were unclear. This study shows that – in oxic, suboxic and anoxic conditions - there is no biodegradation. In addition, both

carbamazepine and hydrochlorothiazide were not removed (<10%) in a conventional activated sludge system (denitrification/nitrification) (Radjenović *et al.*, 2009).

Although atrazine and simazine were not degraded under the redox conditions investigated in the current study, biodegradation of these compounds has been observed under more reduced conditions (DeLaune *et al.*, 1997, Seybold *et al.*, 2001, Shareef *et al.*, 2014). Atrazine biodegradation was observed for a redox potential of -200 mV to +169 mV, covering a number of electron acceptors, namely Mn^{4+}, Fe^{3+} and SO_4^{2-} (Cronk *et al.*, 2001, DeLaune *et al.*, 1997, Seybold *et al.*, 2001). Simazine biodegradation was investigated in batch tests simulating a wetland fed with storm water under nitrate reducing conditions and reported half-lives were $t_{1/2}$ = 26-30 days (Shareef *et al.*, 2014). For both atrazine and simazine high initial spiking concentrations were used (atrazine: 55 - 70 μg g^{-1} soil, simazine 120 μg/L) compared to the current study (500 ng/L). Baumgarten *et al.* (2011) demonstrated that higher initial OMP concentrations lead to shorter lag-phases and higher biodegradation rates. Thus, the reported biodegradation of atrazine and simazine in those studies, is most likely the result of the higher initial dosed concentrations compared to the current study and it is questionable if atrazine and simazine would be biodegraded, in the concentrations used in the current study, when more reduced conditions were examined.

The persistent behaviour of atrazine, carbamazepine, hydrochlorothiazide and simazine implies that RBF alone (with oxic, suboxic and anoxic redox conditions) cannot provide an adequate barrier for all OMPs, thus additional treatment is required to prevent their presence in drinking water.

Dimethoate, diuron, metoprolol and pirimicarb showed redox dependent removal (Table 5, Figure S3). Dimethoate, diuron and metoprolol were characterised by higher biodegradation rates under oxic conditions compared to suboxic and anoxic conditions which has been reported previously (Fritsche *et al.*, 2000, Tran *et al.*, 2013). The higher biodegradation rates of metoprolol under oxic conditions ($t_{1/2}$ = 1.02 d) compared to suboxic (partial nitrate removal, $t_{1/2}$ = 6.29 d) confirm the results found for metoprolol in a study of Burke *et al.* (2014), with half-lives of $t_{1/2}$ = 1 h and $t_{1/2}$ = 37 h for oxic/penoxic/suboxic (oxygen almost depleted, partial nitrate removal) and transition conditions (relatively constant nitrate concentration, manganese reduction), respectively. However, half-lives reported in the study of Burke et al. (2014) were much lower compared to the half-lives reported in the current study. Since feed water quality (surface water) and initial metoprolol concentrations were similar in both studies (130 ng/L in the study of Burke et al. (2014) and 500 ng/L in the current study), it is expected that the difference in half-lives is a result of different biomass quantity and composition present in the column systems or temperature (19.7°C in the study of Burke et al. (2014) compared to 12°C in the current study).

Shareef *et al.* (2014) reported much higher half-lives for diuron of $t_{1/2}$ = 35 – 41 days (oxic conditions) and $t_{1/2}$ = 91 days (nitrate reducing conditions) than observed in the current study ($t_{1/2}$ = 1.33 – 7.49 d). However, as a result of the much higher initial diuron concentration used in the study of Shareef *et al.* (2014) (120 μg/L) compared to the current study (500 ng/L), shorter half-lives would be expected since higher OMP concentration lead to short adaptation times and higher degradation rates as reported in (Baumgarten *et al.*, 2011, Storck *et al.*, 2012). However, it is possible that the higher initial diuron concentration had a toxic effect on (part) of the soil microbial population present in the wetland sediment, which resulted in a reduced biodegradation rate of the compound.

Table 5 – OMP biodegradation rates and half-lives for the oxic, suboxic and anoxic pilot

	Oxic pilot	Oxic pilot	Suboxic pilot	Anoxic pilot
OMP	Retardation factor [-]	Oxic conditions μ [d^{-1}] (CI) / $t_{1/2}$ [d]	NO_3 reducing conditions μ [d^{-1}] (CI) / $t_{1/2}$ [d]	Almost complete NO_3 removal μ [d^{-1}] (CI) / $t_{1/2}$ [d]
Atrazine	1.7	0 / -	0 / -	0 / -
Carbamazepine	1.9	0 / -	0 / -	0 / -
Chloridazon	1.0[a]	2.77[c] (2.22;3.33) / 0.25	ND[d]	ND
Clofibric acid	1.0[a]	1.16 (1.02;1.30) / 0.60	ND	ND
Diclofenac	1.0[a]	2.60 (2.28;2.92) / 0.27	ND	ND
Dimethoate	1.2	0.39[c] (0.31;0.48) / 1.78	0.06 (0.02;0.10) / 11.52	0.11 (0.10;0.12) / 6.05
Diuron	2.6	0.52 (0.37;0.67) / 1.33	0.09 (0.05;0.13) / 7.49	0.11 (0.03;0.19) / 6.36
Hydrochlorothiazide	1.7	0 / -	0 / -	0 / -
Ketoprofen	1.0[a]	2.81 (2.35;3.26) / 0.25	ND	ND
Lincomycin	1.9	2.69[c] (1.97;3.41) / 0.26	ND	ND
Metoprolol	10[b]	0.68 (0.58;0.77) / 1.02	0.11 (0.00;0.22) / 6.29	0.16 (-0.03;0.36)[e]/ 4.22
Phenazone	1.3	3.70[c] (3.42;3.99) / 0.19	ND	ND
Pirimicarb	1.6	0.06 (0.00;0.11) / 11.55	0.04 (0.02;0.06) / 18.80	0.08 (-0.13;0.29)[e] / 8.48
Simazine	1.5	0 / -	0 / -	0 / -
Sulfamethoxazole	0.8	2.19[c] (2.02;2.36) / 0.32	ND	ND

[a] Impossible to determine R since OMP was rapidly biodegraded, assumed to be 1 to enable the determination of μ, [b] Retardation factor was assumed to be 10 based on previous studies (Chapter 2, Burke *et al.*, 2013), [c] Show increase in OMP biodegradation rate over time, adapted biodegradation rate is presented in Table 4, [d] ND = Not determined since OMP was rapidly degraded in oxic pilot

[e] Note that the biodegradation rate of metoprolol and pirimicarb in the anoxic pilot is statistically not significant (confidence interval is going through zero) which means that this obtained biodegradation rate is not the only possible solution when fitting the experimental data to the advection-dispersion equation. This could be explained by the fact that the retardation factor was assumed to be 10 based on previous studies (Chapter 2, Burke *et al.*, 2013). However, since no abiotic control was operated in the current study this assumption could not be verified. A study of (Barbieri *et al.*, 2012) indicated that sorption was more important than biodegradation in the removal of metoprolol and therefore retardation factors higher than 10 are not unlikely.

Biodegradation rates of dimethoate increased from suboxic to anoxic conditions. This trend was also observed for acetaminophen and sulfamethoxazole in other RBF and soil aquifer treatment systems that created anoxic conditions by purging the aqueous phase with nitrogen has (Baumgarten *et al.*, 2011, Regnery *et al.*, 2015b). Fetzner (1998) also demonstrated higher biodegradation rates for quinolone for more reduced conditions (sulphate reducing and methanogenic conditions) compared to denitrifying conditions. An explanation for this higher biodegradation rate under more reduced redox conditions could be the change in soil microbial community diversity. Li *et al.* (2014a) reported that the diversity of the microbial community composition increased as a function of soil depth. Possibly bacteria are present in these more reduced zones that are capable of degrading pirimicarb more effectively than the bacteria in the shallower zones (with higher redox potentials).

In contrast, for pirimicarb, the biodegradation rates for oxic, suboxic and anoxic conditions were approximately similar. Apparently, pirimicarb removal is not redox dependent, but the result of a longer residence time in the soil.

It was not possible to explain the redox dependent removal of diuron, dimethoate and metoprolol based on their physico-chemical properties or functional groups. While diuron and dimethoate are neutral OMPs, metoprolol is positively charged, thus charge does not explain the redox dependent behaviour. Similarly, other neutral OMPs with Log D ranging between those of diuron and dimethoate do not show redox dependent behaviour, implying that hydrophobicity (Log D) also cannot explain the redox dependent behaviour.

To the best of the authors knowledge biodegradation rates for dimethoate, diuron, and metoprolol for suboxic and anoxic conditions in RBF systems were reported for the first time in the current study. This provides drinking water companies using RBF with important information regarding required residence times for these OMPs under the investigated redox conditions. If more than 99% removal of the OMPs is required, the residence time of the suboxic and anoxic zones should range from 1 to 5 months. Although redox zones and their accompanying residence times can vary from site to site and also seasonally, residence times of 1 to 5 months or longer for suboxic (nitrate reducing) and anoxic reducing conditions are not uncommon at RBF field sites in The Netherlands. Therefore these OMPs are not expected to pose a problem in RBF processes.

3.4 OMP removal – adaptative behaviour

Five OMPs, dimethoate, chloridazon, phenazone, lincomycin, and sulfamethoxazole, showed an increase in removal under oxic conditions during the 15 months of operation (Figure 1). Dimethoate showed a sharp increase in removal after about 2 pore volumes (PV), followed by a slower increase which seems to continue even after 330 PV (approximately 15 Months). For lincomycin, complete removal was not observed until after about 200 PV (approximately 9 months). After about 100 PV (approximately 5 months) the removal of sulfamethoxazole and phenazone stabilized and was almost complete. For chloridazon the increase in removal was relatively quick and almost complete removal was observed after about 27 PV (approximately 1 month).

Thus, a certain time was required to enable biodegradation of the aforementioned OMPs in the oxic pilot installation. This could be explained by an adapting soil microbial population and is referred to as adaptation time or lag phase. Table 6 shows the lag phases, the unadapted and adapted biodegradation rates. To the best of the authors knowledge no adaptation time (lag phase) for

dimethoate, chloridazon, phenazone and lincomycin in a RBF system has been previously reported and thus was determined for the first time in the current study.

In Figure 1, the orange striped line represents the tracer (which does not biodegrade). The difference between the tracer and the yellow striped line indicates the non-adapted biodegradation rate of phenazone (the breakthrough curve shows an initial peak at C_e/C_0 = 0.78. The green arrow (difference between tracer and final C_e/C_0 value of phenazone) is the adapted biodegradation rate of phenazone.

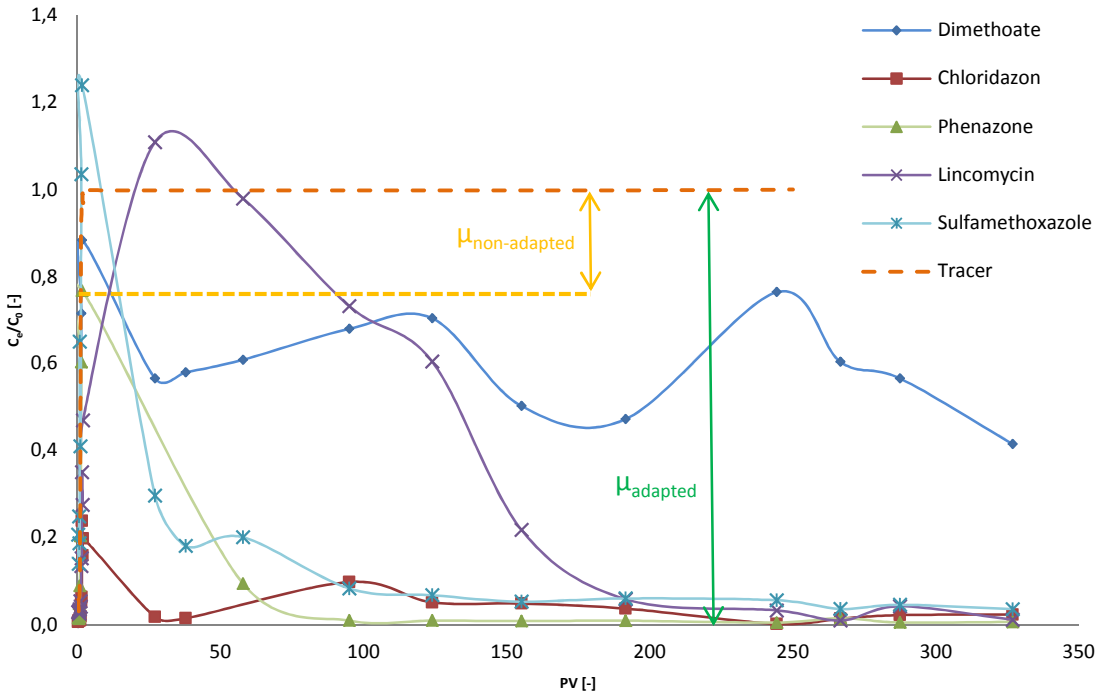


Figure 1 – Adaptive behaviour of dimethoate, chloridazon, phenazone, lincomycin, and sulfamethoxazole

Table 6 – Lag phases, non-adapted and adapted biodegradation rates

OMP	Lag phase [d]	$\mu_{non\text{-}adapted}$ (CI) [d^{-1}]	$\mu_{adapted}$ (CI) [d^{-1}]	Max. concentration river Lek [ng/L]
Chloridazon	2.6	1.85 (1.25;2.45)	2.77 (2.22;3.33)	14
Dimethoate	2.1	0.04 (0.00;0.08)	0.39 (0.31;0.48)	Below detection limit (= 10 ng/L)
Lincomycin	36.4	0.00 (0.00;0.00)	2.69 (1.97;3.41)	1
Phenazone	2.1	0.00 (-0.03;0.19)	3.70 (3.42;3.99)	12
Sulfamethoxazole	2.1	0.00 (-0.26;0.27)	2.19 (2.02;2.36)	36

CI = confidence interval

Spain *et al.* (1980, 1983) identified three mechanisms by which the soil microbial community can adapt to a new OMP: (1) genetic changes, (2) enzyme induction and (3) population changes (Spain *et al.*, 1980, Spain *et al.*, 1983). Genetic changes as a result of gene transfer or mutations can result in bacteria capable of degrading certain OMPs. Secondly, the presence of specific OMPs can initiate the expression of enzymes appropriate to degrade OMPs. Thirdly, the number of bacteria capable of degrading a particular OMP can be minimal at initial exposure, but can increase when subjected to the OMP.

Since all OMPs (except dimethoate) that showed adaptive behaviour were detected in the Lek river water in concentrations ranging from 1 - 36 ng/L (Table 6), it is most likely that the number of bacteria

capable of degrading these OMPs was relatively small at the start of the experiment, but increased as a result of the higher initially dosed OMP concentration (500 ng L^{-1}) in the column experiment. However, genetic changes or enzyme induction cannot be completely ruled out. To determine which of the three mechanisms or combination of mechanisms is responsible for the adaptive behaviour of chloridazon, dimethoate, lincomycin, phenazone and sulfamethoxazole, more in depth microbial analysis towards the type of bacteria/enzymes/genes present in the soil column are required. These analysis should be performed at the start of the experiment and at several points in time during the experimental period to see how the type of bacteria/enzymes/genes evolve over time.

In Chapter 2, persistent behaviour of lincomycin and sulfamethoxazole was observed for a 6 month experimental period. Based on the results of the current study, the observed persistent behaviour of lincomycin and sulfamethoxazole in the previous study was more likely the result of insufficient adaptation time. This demonstrates the importance of running soil columns experiments for a long time (preferably more than 1 year) if adaptive behaviour needs to be captured.

Improved lincomycin removal was also observed in an anthracite biofilter after 30,000 BV (Rattier *et al.*, 2014). Baumgarten *et al.* (2011) reported that sulfamethoxazole biodegradation did not start until after 1 year (initial concentration 0.25 μg/L) after operation started, and was not stabilized after 2 years of operation. The much longer adaptation time observed in that study (1 year versus 3 days in the current study) could be attributed to the use of clean filter sand in which no biomass was present at the start of the experiment. In the current study soil from an operational RBF site was obtained to fill the columns, thus the biomass was already present and sulfamethoxazole biodegradation started almost instantly. The maximum sulfamethoxazole concentration in the Lek river was 36 ng/L and thus it is possible that the biomass present in the soil columns (which was obtained from the RBF site fed with river Lek water) contained certain types of bacteria already capable of expressing enzymes able to catalyse the biodegradation of sulfamethoxazole. Since the spiked concentration of sulfamethoxazole was 500 ng/L, it seems likely that the bacteria capable of degrading this OMP were increasing during the first 5 months.

This shows that when rapid data acquisition is required in lab-scale simulation of RBF, soil from an operational RBF site is preferred over clean filter sand. In addition, when information is required with respect to the operational RBF site (e.g. start-up time required to obtain full OMP removal capacity in case of newly detected OMP) the use of clean filter sand can lead to serious underestimations.

3.5 The role of OMP adaptive behaviour in predictive models

To gain an understanding of why only chloridazon, dimethoate, lincomycin, phenazone and sulfamethoxazole were characterised by an adaptation time, their physico-chemcial properties (charge, molecular weight, hydrophobicity) and functional groups present in the molecular structure were compared with the OMPs that did not show an adaptation time. Larger molecules for examples are more difficult to degrade and need to be broken down in smaller pieces first to enable penetration though the cell membrane for further intracellular degradation. Functional groups can also affect adaptation since some complex functional groups which are not familiar to the soil bacteria, require genetic mutations before the appropriate enzymes can be expressed. Physico-chemical properties of all OMPs investigated in this study are presented in Table 2 and functional groups identified for the OMPs are depicted in Table S2 of the SI.

Dimethoate, sulfamethoxazole, chloridazon and phenazone are all four neutral OMPs with Log D ranging from 0.21 to 1.11, but OMPs that did not show adaptive behaviour were also neutral and characterized by a Log D in the range of -0.72 to 2.64 (carbamazepine, hydrochlorothiazide, pirimicarb, simazine, atrazine and diuron). Similarly, the molecular weight and charge of the OMPs showing adaptive behaviour were in the same range of the OMPs that did not show adaptive behaviour. Thus, the adaptive behaviour observed for the five OMPs could not be explained by these physico-chemical properties.

Multi-linear regression analysis was performed to investigate if a correlation existed between the OMP biodegradation rate and the functional groups present in their molecular structure for the complete OMP mixture (Table 2 SI). First, the regression analysis was performed with the non-adapted biodegradation rates of the complete OMP mixture followed by a regression analysis including the adapted OMP biodegradation rates for the complete OMP mixture (for non-adapted and adapted biodegradation rates see Table 6 and Figure 1).

Although for the non-adapted OMP biodegradation rates no correlation was found, a statistical significant correlation existed between the OMP biodegradation rate (including the adapted OMP biodegradation rate) and the functional groups for the complete OMP mixture (R^2 = 0.93, p-value = $2.80 \cdot 10^{-4} < 0.05$):

$$\mu = 3.21 - 1.46 \cdot SA - 3.01 \cdot AM + 1.0 \cdot Hy - 2.06 \cdot AAE - 0.90 \cdot SuA - 1.51 \cdot TA \quad \text{Eq. 1}$$

In which:

μ	=	biodegradation rate	[d^{-1}]
SA	=	number of secondary amines	[-]
AM	=	number of amides	[-]
Hy	=	number of hydroxyl groups	[-]
AAE	=	number of aryl-aliphatic ethers	[-]
SuA	=	number of sulphonamides	[-]
TA	=	number of tertiary amines	[-]

This correlation differs to a large extent from the relationship found in a previous study for OMP removal under aerobic conditions (Chapter 3). This discrepancy in contributing functional groups could be explained by the limited number and type of OMPs (pharmaceuticals, pesticides) investigated in this study and their more persistent behaviour in oxic zones (the most easily degradable OMPs were not included in the assessment).

Although this study was limited to pesticides and pharmaceuticals that showed persistent behaviour or only partial biodegradation under oxic or combined oxic/nitrate reducing conditions, the found correlation indicates that adaptive behaviour is an important factor that should be incorporated in predictive models for OMP removal during RBF.

4 Conclusion

Based on this study, the following conclusions can be drawn:

- Dimethoate, diuron, and metoprolol showed redox dependent removal behaviour with biodegradation rates larger for the oxic zone compared to the suboxic/anoxic zone. In contrast,

for pirimicarb, the biodegradation rates for oxic, suboxic and anoxic conditions were approximately similar. Apparently, pirimicarb removal is not redox dependent, but the result of a longer residence time in the soil.

- OMPs that showed persistent behaviour in the oxic zone (atrazine, carbamazepine, hydrochlorothiazide and simazine) were also not removed under more reduced conditions (suboxic, anoxic) which indicates that additional treatment processes are required to remove these OMPs from the water and that RBF alone cannot provide an adequate barrier for all OMPs;
- Adaptive behaviour was observed for five OMPs in this study: dimethoate, chloridazon, lincomycin, sulfamethoxazole and phenazone. This implies that new developed RBF sites or existing RBF sites exposed towards chloridazon, lincomycin, sulfamethoxazole, and phenazone for the first time require about 9 months of start-up time to reach full removal capacity. For dimethoate, full removal capacity was not reached after 15 months, thus even longer start-up times are required for this specific OMP.
- Adaptive behaviour of OMPs is an important factor that should be incorporated in predictive models for OMP removal during RBF. However, adaptation could not be explained based on the physico-chemical properties investigated in this study (charge, hydrophobicity, molecular weight).
- When rapid data acquisition is required, soil from an operational RBF site is preferred over clean filter sand and when information is required with respect to the operational RBF site (e.g. start-up time required to obtain full OMP removal capacity in case of newly detected OMP) the use of clean filter sand can lead to serious underestimations.

References

Alidina, M., Li, D. and Drewes, J.E. (2014a) Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Research 56, 172-180.

Alidina, M., Li, D., Ouf, M. and Drewes, J.E. (2014b) Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. Journal of Environmental Management 144, 58-66.

Barbieri, M., Licha, T., Nödler, K., Carrera, J., Ayora, C. and Sanchez-Vila, X. (2012) Fate of ß-blockers in aquifer material under nitrate reducing conditions: Batch experiments. Chemosphere 89, 1272-1277.

Baumgarten, B., Jährig, J., Reemtsma, T. and Jekel, M. (2011) Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Research 45, 211-220.

Benotti, M.J., Song, R., Wilson, D. and Snyder, S.A. (2012) Removal of pharmaceuticals and endocrine disrupting compounds through pilot- and full-scale riverbank filtration. Water Science & Technology: Water Supply 12(1), 11-23.

Burke, V., Greskowiak, J., Asmuß, T., Bremermann, R., Taute, T. and Massmann, G. (2014) Temperature dependent redox zonation and attenuation of wastewater-derived organic micropollutants in the hyporheic zone. Science of The Total Environment 482-483, 53-61.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J. and Massmann, G. (2013) Sorption behavior of 20 wastewater originated micropollutants in groundwater - Column experiments with pharmaceutical residues and industrial agents. Journal of Contaminant Hydrology 154, 29-41.

Buttiglieri, G., Peschka, M., Frömel, T., Müller, J., Malpei, F., Seel, P. and Knepper, T.P. (2009) Environmental occurence and degradation of the herbicide n-chloridazon. Water Research 43, 2865 - 2873.

Chiang, P.C. and Hu, Y. (2009) Simultaneous Determination of LogD, LogP, and pKa of Drugs by Using a Reverse Phase HPLC Coupled with a 96-Well Plate Auto Injector. Combinatorial Chemistry & High Throughput Screening 12, 250-257.

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H. (2005) Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Research 39, 4797-4807.

Cronk, J.K. and Fennessy, M.S. (2001) Wetland Plants: Biology and Ecology, CRC Press LLC, United States of America.

DeLaune, R.D., Devai, I., Mulbah, C., Crozier, C. and Lindau, C.W. (1997) The influence of soil redox conditions on atrazine degradation in wetlands. Agriculture, Ecosystems and Environment 66, 41-46.

Ferreira da Silva, B., Jelic, A., López-Serna, R., Mozeto, A.A., Petrovic, M. and Barceló, D. (2011) Occurence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain. Chemosphere 85, 1331-1339.

Fetzner, S. (1998) Bacterial degradation of pyridine, indole, quinoline, and their derivatives under different redox conditions. Appl Microbiol Biotechnol 49, 237-250.

Frehse, H. and Anderson, J.P.E. (2013) Pesticide Chemistry: Human Welfare and the Environment: Pesticide Residues and Formulation Chemistry. Miyamoto, J., Kearney, P.C. and Greenhalgh, R. (eds), Elsevier.

Fritsche, W. and Hofrichter, M. (2000) Biotechnology: Environmental Processes II. Rehm, H.J. and Reed, G. (eds), Wiley-VCH Verlag GmbH, Weinheim, Germany.

Grünheid, S., Amy, G. and Jekel, M. (2005) Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. Water Research 39, 3219-3228.

Gu, J.G., Fan, Y. and Gu, J.D. (2003) Biodegradability of Atrazine, Cyanazine and Dicamba under methanogenic condition in three soils of China. Chemosphere 52, 1515-1521.

Hoppe-Jones, C., Dickenson, E.R.V. and Drewes, J.E. (2012) The role of microbial adaptation and biodegradable dissolved organic carbon on the attenuation of trace organic chemicals during groundwater recharge. Science of The Total Environment 437, 137-144.

Houtman, C.J., Kroesbergen, J., Lekkerkerker-Teunissen, K. and 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. Science of The Total Environment 496, 54-62.

Kah, M. and Brown, C.D. (2007) Prediction of the Adsorption of Ionizable Pesticides in Soils. J. Agric. Food Chem. 55, 2312-2322.

Li, D., Alidina, M. and Drewes, J.E. (2014a) Role of primary substrate composition on microbial community structure and function and trace organic chemical attenuation in managed aquifer recharge systems. Applied Microbiology and Biotechnology 98, 5747-5756.

Li, D., Alidina, M. and Drewes, J.E. (2014b) 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. and Drewes, J.E. (2013) Microbial community evolution during simulated managed aquifer recharge in response to different biodegradable dissolved organic carbon (BDOC) concentrations. Water Research 47, 2421-2430.

Maeng, S.K., Sharma, S.K., Abel, C.D.T., Magic-Knezev, A., Song, K.G. and 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. Journal of Contaminant Hydrology 140-141, 139-149.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M. and Barry, D.A. (2013) Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? Science of The Total Environment 461-462, 480-498.

Massmann, G., Dünnbier, U., Heberer, T. and Taute, T. (2008) Behaviour and redox sensitivity of pharmaceutical residues during bank filtration – Investigation of residues of phenazone-type analgesics. Chemosphere 71, 1476-1485.

Massmann, G., Greskowiak, J., Dünnbier, U., Zuehlke, S., Knappe, A. and Pekdeger, A. (2006) The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. Journal of Hydrology 328, 141-156.

Matamoros, V., Puigagut, J., García, J. and Bayona, J.M. (2007) Behavior of selected priority organic pollutants in horizontal subsurface flow constructed wetlands: A preliminary screening. Chemosphere 69, 1374-1380.

Möller, P., Knappe, A., Dulski, P. and Pekdeger, A. (2011) Behavior of Gd-DTPA in simulated bank filtration. Applied Geochemistry 26, 140-149.

Packer, J.L., Werner, J.J., Latch, D.E., McNeill, K. and Arnold, W.A. (2003) Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibric acid, and ibuprofen. Aquatic Sciences 65, 342-351.

Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T. and Toze, S. (2011) Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. Journal of Contaminant Hydrology 122, 53-62.

Radjenović, J., Petrović, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43, 831-841.

Rattier, M., Reungoat, J., Keller, J. and Gernjak, W. (2014) Removal of micropollutants during tertiary wastewater treatment by biofiltration: Role of nitrifiers and removal mechanisms. Water Research 54, 89-99.

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

Regnery, J., Wing, A.D., Alidina, M. and Drewes, J.E. (2015) Biotransformation of trace organic chemicals during groundwater recharge: How useful are first-order rate constants? Journal of Contaminant Hydrology In press.

Sara, P., Giuliana, D., Michele, P., Maurizio, C., Luca, C. and Fabrizio, A. (2013) Effect of veterinary antibiotics on biogas and bio-methane production. International Biodeterioration & Biodegradation 85, 205-209.

Scheytt, T.J., Mersmann, P., Leidig, M., Pekdeger, A. and Heberer, T. (2004) Transport of Pharmaceutically Active Compounds in Saturated Laboratory Columns. Ground Water 42(5), 767-773.

Seybold, C.A., Mersie, W. and McNamee, C. (2001) Anaerobic degradation of atrazine and metolachlor and metabolite formation in wetland soil and water microcosms. J. Environ. Qual. 30(4), 1271-1277.

Shalaeva, M., Kenseth, J., Lombardo, F. and Bastin, A. (2007) Measurement of Dissociation Constants (pKa Values) of Organic Compounds by Multiplexed Capillary Electrophoresis Using Aqueous and Cosolvent Buffers. Journal of Phamaceutical Sciences, 1-24.

Shareef, A., Page, D., Vanderzalm, J., Williams, M., Gupta, V.V.S.R., Dillon, P. and Kookana, R. (2014) Biodegradation of Simazine and Diuron Herbicides under Aerobic and Anoxic Conditions Relevant to Managed Aquifer Recharge of Storm Water. Clean-Soil, Air, Water 42(6), 745-752.

Spain, J.C., Pritchard, P.H. and Bourquin, A.W. (1980) Effects of Adaptation on Biodegradation Rates in Sediment/Water Cores from Estuarine and Freshwater Environments. Applied and Environmental Microbiology 40(4), 726-734.

Spain, J.C. and van Veld, P.A. (1983) Adaptation of Natural Microbial Communities to Degradation of Xenobiotic Compounds: Effects of Concentration, Exposure, Time, Inoculum, and Chemical Structure. Applied and Environmental Microbiology 45(2), 428-435.

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

Storck, F.R., Schmidt, C.K., Lange, F.T., Henson, J.W. and Hahn, K. (2012) Factors controlling micropollutant removal during riverbank filtration. Journal - American Water Works Association.

Storck, F.R., Schmidt, C.K., Lange, F.T., Henson, J.W. and Hahn, K. (2010) Removal and Fate of EDCs and PPCPs in Bank Filtration Systems.

Su, A.C.L. (1979) Advances in Organometallic Chemistry - Catalytic Codimerization of Ethylene and Butadiene, Academic Press, Inc.

Suarez, S., Lema, J.M. and Omil, F. (2010) Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. Water Research 44, 3214-3224.

Taboada, E.R., Dekker, A., van Kammen-Polman, A., Smelt, J.H., Boesten, J.J.T.I. and Leistra, M. (1994) Adsorption, degradation and leaching of pirimicarb in orchard soils. The Science of the Total Environment 153, 253-260.

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

Tran, N.H., Urase, T., Ngo, H.H., Hu, J. and Ong, S.L. (2013) Review Insight into metabolic and cometabolic activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging trace organic contaminants. Bioresource Technology 146, 721-731.

Verliefde, A., Cornelissen, E., Amy, G., Van der Bruggen, B. and van Dijk, H. (2007) Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. Environmental Pollution 146, 281-289.

Wang, C., Teppen, B.J., Boyd, S.A. and Li, H. (2011) Sorption of Lincomycin at Low Concentrations from Water by Soils. Soil Science Society of America Journal 76, 1222-1228.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environmental Science & Technology 39, 6649-6663.

Yang, X.J., Qu, Y., Yuan, Q., Wan, P., Du, Z., Chen, D. and Wong, C. (2013) Effect of ammonium on liquid- and gas-phase protonation and deprotonation in electrospray ionization mass spectrometry. Analyst 138, 659-665.

Zearley, T.L. and Summers, R.S. (2012) Removal of Trace Organic Micropollutants by Drinking Water Biological Filters. Environmental Science and Technology 46, 9412-9419.

Chapter 7

Conclusions and recommendations

Conclusions

The main objective of this research was to investigate the main removal mechanisms (sorption, biodegradation) for OMPs during RBF in more detail, in order to establish the role of the factors influencing these mechanisms (physico-chemical properties, functional groups, soil type, river water organic carbon, redox zones and adaptive behaviour of the soil microbial population towards OMPs). Based on this information the possibility to develop a predictive model for OMP removal during river bank filtration (RBF) was studied. As a first step, the contribution of OMP sorption and biodegradation on overall OMP removal needed to be determined. OMP sorption onto soil grains and developed (in)active biomass was found to be negligible for most OMPs and therefore the predictive model was only focused on biodegradation. While the relation between physico-chemical properties (hydrophobicity, charge, molecular weight) and biodegradation rate of the OMPs under oxic conditions showed some trends, a statistical significant correlation was not found.

However, a statistical significant relation between OMP biodegradation rate and functional groups was observed for laboratory columns mimicking RBF filled with either technical sand or RBF site soil. A validation with field data showed that the model could give a correct qualitative indication of the biodegradability of an OMP in the field for 70% of the OMPs (80% when excluding di-, tri- and tetra-glyme). The model was less reliable for the persistent OMPs that were characterised by biodegradation rates below or close to the standard error and OMPs containing amide and amine groups. Nevertheless, the drinking water company operating this RBF site can use the developed predictive model as a first estimate to determine if an OMP will be biodegraded or not.

Subsequently, the effect of soil type on OMP removal was investigated. OMP retardation factors and biodegradation rates in soil columns filled with soil from two different RBF sites, but fed with the same water quality were determined and compared. Soil type did not have a statistical significant effect on OMP biodegradation rate which implies that the microbial community composition and thus OMP removal are mainly determined by the aqueous phase (BDOC quantity/quality, nutrients) rather than the solid phase, at least for the soils and water investigated in this study. This result was supported by a similar final microbial community composition (richness and evenness) for the two different soils as a result of feeding both soil types with the same water quality, despite an initial difference. Thus, it is expected that similar predictive models for RBF sites located along the same river can be used (in case no significant changes in water quality occur between the two sites and residence times in the oxic zones are more or less comparable).

Since the aqueous phase was shown to play an important role in the formation of the soil microbial population and thus OMP removal, OMP biodegradation rates were compared between soil columns fed with different organic carbon fractions (hydrophilic, hydrophobic, transphilic and the complete river water organic carbon) present in the river water. OMP biodegradation rate was not affected by the type of organic carbon fraction (obtained from river water) fed to the soil column – in contrast to what has been described in literature for managed aquifer recharge systems operating on wastewater effluent. Hence, variations in the organic carbon fractions of the river water investigated in this study will most likely not affect the OMP biodegradation rates observed at the RBF site investigated. However, the organic carbon composition of other rivers might contain organic material that was not captured in the organic material from the river investigated in this thesis (e.g. in case of a larger contribution of wastewater effluent) and results may be different.

Furthermore, since no effect of a DOC shock-load on OMP biodegradation rate was observed, the investigated RBF site seems to be resilient towards a temporary higher DOC concentration in the river water. Additionally, a temporary OMP shock-load resulted in an increase in OMP biodegradation rate for the river water organic matter (RWOM) and the hydrophilic fraction. As a result, OMPs will be eliminated more rapidly during RBF fed with river water that contains a large portion of these two specific fractions. An explanation for the increase in OMP biodegradation for specifically these OMPs was not found based on the parameters measured in this study (biomass quantity, biomass richness and evenness, and DOC). An increase in OMP biodegradation rate as a result of an increase in initial OMP concentration was reported in other studies, but never linked to a certain organic carbon fraction. The resilience of RBF systems towards a DOC/OMP shock-load was not investigated previously and provides important information for the drinking water company that operates the RBF site that was simulated with the laboratory scale columns in this study.

Redox zones have been stated in literature to have an effect on removal of OMPs. Dimethoate, diuron, and metoprolol showed redox dependent removal behaviour with degradation rates larger for the oxic zone compared to the suboxic/anoxic zone. The redox dependent removal of these OMPs could not be explained by their physico-chemical properties (hydrophobicity, charge, or molecular weight) or the functional groups present in their molecular structure. OMPs that showed no removal in the oxic zone (atrazine, carbamazepine, hydrochlorothiazide and simazine) were also not removed under more reduced conditions (suboxic, anoxic) which indicates that additional treatment processes are required to remove these OMPs from the water and that RBF alone cannot provide an adequate barrier for all OMPs.

Adaptive behaviour was observed for five OMPs: dimethoate, chloridazon, lincomycin, sulfamethoxazole and phenazone. Adaptive behaviour of sulfamethoxazole and lincomycin has been reported in previous studies, one simulating the RBF process and the other investigating OMP removal in biological anthracite filters. For sulfamethoxazole, adaptation time was much shorter in this thesis (using RBF site soil) compared to another study in which technical sand was used as filter medium. Thus, when rapid data acquisition is required, soil from an operational RBF site is preferred over clean filter sand and when information is required with respect to the operational RBF site (e.g. start-up time required to obtain full OMP removal capacity in case of newly detected OMP) the use of clean filter sand can lead to serious underestimations. It is known that the soil microbial population can adapt to new OMPs by means of genetic changes, inducing appropriate enzymes or increasing the number of bacteria present capable of removing the OMP. The five OMPs showing adaptive behaviour were present in the investigated surface water in concentrations ranging from 1 - 36 ng/L. Therefore it is expected that a small number of bacteria was already capable of degrading these OMPs. The spiked OMP concentration in the column study was equal to 500 ng/L and the most likely mechanism to explain the adaptive behaviour in this study would thus be an increase in the number of bacteria present capable of removing these OMPs, although the other two mechanisms cannot be fully excluded.

Since adaptive behaviour was also observed for two of these OMPs (lincomycin and sulfamethoxazole) in other studies, the chance that adaptive behaviour was observed as a result of an experimental artefact seems small. Therefore, the observed adaptive behaviour implies that new developed RBF sites or existing RBF sites exposed towards chloridazon, lincomycin, sulfamethoxazole, and phenazone for the first time require most likely about 9 months of start-up time

to reach full removal capacity (in case of similar flow rate). For dimethoate, full removal capacity was not reached after 15 months and as a result even longer start-up times are required for this specific OMP. These results indicate that adaptive behaviour of OMPs is in an important factor that should be incorporated in predictive models for OMP removal during RBF.

The next question is then how adaptive behaviour of OMPs should be incorporated in a predictive model for OMP removal during RBF. For the OMPs showing adaptive behaviour an increase in biodegradation rate was observed over time. The initial biodegradation rate is referred to as un-adapted biodegradation rate, while the biodegradation rate at the end of the experiment is referred to as the adapted biodegradation rate. This study attempted to develop a predictive model for OMP removal during RBF based on the un-adapted biodegradation rates and adapted biodegradation rates. Correlating the OMP functional groups to the un-adapted biodegradation rates was impossible, but a statistical significant relationship between the OMP functional groups and the adapted biodegradation rates was observed.

Recommendations for future research

This thesis provided insight in the development of a predictive model for OMP removal during RBF. However, some aspects need further research clarification and therefore recommendations for future research are presented in this section.

This study demonstrated for the first time that it was possible to develop a predictive model for OMP removal during RBF under oxic conditions based on a lab-scale soil column study. The correlation between OMP biodegradation rate and the presence of certain functional groups in the OMP molecular structure for the RBF process was not found previously. The validation with field data showed that the model could give a correct qualitative indication of OMP biodegradability in the field for 70% of the OMPs (for the investigated RBF site under oxic conditions).

A limitation of the model was that it was less reliable for persistent OMPs since these were characterized by degradation rates lower than or close to the standard error and OMPs containing amide or amine groups. These OMPs require careful monitoring in the field to determine their fate.

A larger data set could possibly reduce the standard error. This emphasises the importance of developing predictive models with an even larger data set covering hundreds of OMPs with a wide range of functional groups and physico-chemical properties. Although, OMP biodegradation rates have been determined in a some past studies, they cannot be easily compared due to the different experimental approaches. Therefore, it would be useful to develop a standard protocol to determine OMP biodegradation rates during RBF. In this way a database (containing OMP biodegradation rates for specifically RBF conditions) can be established that can be used to develop a predictive model.

A standard protocol would not only be useful to determine OMP biodegradation rates during RBF, but also for the inactivation of biomass. Most soil passage studies use NaN_3 to inactivate the biomass. However, the effectiveness of NaN_3 in inactivating the biomass was investigated in a study of Bellemans (2013). This study showed that the addition of NaN_3 (10%) and metals (5 mM $NiCl_2$ and 5 nM $BaCl_2$) resulted in a 80-85% decrease in biological activity, while dosing γ-irradiation (25 kGy) resulted in a 99.79 - 99.98% decrease in biological activity (measured as ATP). Thus, using γ-irradiation to inactivate the biomass is much more effective than using NaN_3.

Although the OMP mixture used to develop the model contained OMPs with amide and amine functional groups, the relation of these functional groups with the biodegradation rate was statistically not significant. An OMP mixture of 29 OMPs is already quite large for lab-scale studies and the mixture was carefully chosen to cover a wide range in physico-chemical properties and functional groups. However, (predictive) models and their outcome depend on their input. It is possible that when more OMPs with these functional groups were present in the data set to develop the model, this relation would have been more pronounced. In the current data set only 8, 2, 9 and 3 OMPs had amide, primary amine, secondary amine and tertiary amine groups in their molecular structure, respectively.

Although the developed model showed promising results and provided a lot of insight in functional groups increasing/decreasing the biodegradation rate, the effect of different factors on the model, such as water quality (e.g. BDOC), redox conditions and adaptive behaviour of the soil microbial community towards OMPs, should be further investigated to determine its general applicability.

The effect of the water quality can be investigated by feeding columns (filled with a similar type of RBF soil) with different types of river water (representative for different RBF sites) spiked with an OMP mixture. The predictive models obtained for each of these water qualities can then be compared. By characterising the organic carbon content of the different water qualities (e.g. SUVA, LC-OCD, Fluorescence excitation-emission matrix) a relation might be found between the contribution of certain functional groups and the organic carbon characteristics.

Based on the four OMPs that showed redox dependent removal in the RBF pilot installation investigated in this research, it is impossible to develop a predictive model for more reduced redox zones. Thus, additional spiking before each redox zone is required to determine the OMP biodegradation rates of the OMPs that are already removed in the previous redox zone. Although it seems unnecessary to investigate OMP removal in the nitrate reducing zones when these OMPs are almost completely removed in the oxic zone, this is crucial to develop predictive models for these more reduced redox conditions (e.g. NO_3-, Fe-, Mn-, SO_4-reducing conditions).

Thus, future studies should determine OMP biodegradation rates in the separate more reduced conditions and try to correlate these with the functional groups present in the molecular structure. This could potentially result in predictive models (OMP biodegradation rates) for the separate redox conditions which are useful since it is know from literature that some OMPs (e.g. sulfamethoxazole, iopamidol, amidotrizoic acid, 2-, 3- and 4-nitrotoluene, trichloroethene, metazachlor) are removed more effectively under more reduced redox conditions (anaerobic/anoxic) compared to oxic conditions (Storck *et al.*, 2012). Based on the biodegradation rates, half-lives can be determined. About seven half-lives are required for more than 99% removal of an OMP. Thus, an assessment of the prevailing redox conditions at the site and the residence times of these specific redox conditions is then required to determine the extent of removal of a certain OMP for the complete RBF process.

Furthermore, future studies should elucidate why adaptive behaviour is only observed for specific OMPs and what the responsible mechanism is: (1) mutations, (2) enzyme induction or (3) the increase of a small number of bacteria capable of removing the OMP. This will make it possible to predict if a newly discovered OMP will be characterised by an adaptation time or not.

Biodegradation was found to be the dominant removal mechanism for most OMPs. However, the role of OMP sorption as a pre-requisite for OMP biodegradation is still unclear and requires further examination. An enzyme can only catalyse a reaction if the OMP fits the slot of the reactive site, therefore sorption could potentially play an important role. While extracellular enzymes are present in the aqueous phase, intracellular enzymes are encapsulated in the extracellular polymeric substances (EPS) and OMPs needs to sorb onto the cell wall first before they can partition in the cell where it can be degraded. In addition, the contribution of intra- and extracellular enzymes towards overall OMP removal needs further exploring.

Moreover, the soil microbial population in the columns fed with different organic carbon fractions obtained from river water should be studied with more in-depth microbial analysis (e.g. next generation sequencing, metagenomics) to determine the types of bacteria and enzymes present. This should provide insight into why OMP degradation rates are increasing for the river water organic matter and hydrophilic fraction as a result of a temporary OMP shock-load for the RBF site investigated in this study. The river water used in this research was only slightly impacted by treated wastewater. The effect of larger contributions of wastewater in the river water on OMP removal in columns fed with different organic carbon fractions obtained from this river water should be investigated. Does a threshold exist for the amount of wastewater contributing to the overall river flow, above which an effect on OMP removal can be observed? Similarly, the effect of feeding soil columns with different organic carbon fractions on OMP removal under more reduced conditions should be examined and the seasonal variation in composition of the different fractions and the soil microbial population should be explored.

Most OMPs are removed entirely under oxic conditions and only a few persisted even under the more reduced redox environments which shows that RBF is an effective treatment process for many OMPs. However, the persistent OMPs should be removed by additional post-treatment. RBF can be used effectively in a multi-barrier treatment concept in combination with for example membrane filtration and granular activated carbon. However, it is questionable whether the combination of these three processes is an adequate barrier for the removal of all OMPs.

References

Storck, F.R., Schmidt, C.K., Lange, F.T., Henson, J.W. and Hahn, K. (2012) Factors controlling micropollutant removal during riverbank filtration. Journal - American Water Works Association.

Appendix A - Supplementary material Chapter 2

Table SI1 – Dispersion, dispersivity, average pore water velocity and porosity in the columns determined from the tracer study

Column	v_{mean} [m min^{-1}]	Porosity [-]	D [m^2 min^{-1}]	α [m]
1	$2.25 \cdot 10^{-3}$	0.31	$4.48 \cdot 10^{-6}$	$1.95 \cdot 10^{-3}$
2	$2.19 \cdot 10^{-3}$	0.32	$4.07 \cdot 10^{-6}$	$1.81 \cdot 10^{-3}$
3	$2.02 \cdot 10^{-3}$	0.34	$3.95 \cdot 10^{-6}$	$1.91 \cdot 10^{-3}$
4	$1.96 \cdot 10^{-3}$	0.35	$3.23 \cdot 10^{-6}$	$1.60 \cdot 10^{-3}$
5	$1.73 \cdot 10^{-3}$	0.40	$2.84 \cdot 10^{-6}$	$1.59 \cdot 10^{-3}$
6	$1.67 \cdot 10^{-3}$	0.42	$2.93 \cdot 10^{-6}$	$1.70 \cdot 10^{-3}$

Table SI2 – Calculated diffusion coefficients (D_0) and dispersion coefficients (D) per column

OMP	D_0 [m^2 min^{-1}]	D [m^2 min^{-1}] Column 1	D [m^2 min^{-1}] Column 2	D [m^2 min^{-1}] Column 3	D [m^2 min^{-1}] Column 4	D [m^2 min^{-1}] Column 5	D [m^2 min^{-1}] Column 6
Caffeine	$3.79 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.79 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$
Carbamazepine	$3.49 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Metoprolol	$3.20 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.79 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Propanolol	$3.27 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Acetaminophen	$4.02 \cdot 10^{-8}$	$4.43 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.90 \cdot 10^{-6}$	$3.18 \cdot 10^{-6}$	$2.79 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$
Trimethoprim	$3.25 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Lincomycin	$2.86 \cdot 10^{-8}$	$4.41 \cdot 10^{-6}$	$4.00 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.16 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Sulfamethoxazole	$3.53 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Phenytoin	$3.44 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Atrazine	$3.61 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$
Ibuprofen	$3.49 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Ketoprofen	$3.37 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Gemfibrozil	$3.28 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$
Hydrochlorothiazide	$3.50 \cdot 10^{-8}$	$4.42 \cdot 10^{-6}$	$4.01 \cdot 10^{-6}$	$3.89 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$2.87 \cdot 10^{-6}$

Table SI3 – Average DOC removal and decrease in UV_{254} absorbance between influent and effluent for columns in the experimental period

Column	Average DOC removal [mg/L] (Average ± standard deviation, n = 7)	Average Δ UV_{254} [cm^{-1}] Average ± standard deviation, n = 7)
1	1.19 ± 0.58	0.041 ± 0.016
2	1.34 ± 0.20	0.042 ± 0.013
3	0.19 ± 0.36	0.003 ± 0.006
4	0.11 ± 0.14	0.002 ± 0.006
5	0.09 ± 0.10	0.004 ± 0.004
6	0.00 ± 0.00	0.000 ± 0.000

Table SI4 – Fitted retardation factor for OMPs in the biologically inactive columns

	Retardation factor [-]	95% Confidence interval		Decay rate [min^{-1}]	95% Confidence interval		Decay rate [d^{-1}]	Dispersion [m^2min^{-1}]	95% Confidence interval	
Compound	**R**	**Lower**	**Upper**	**μ**	**Lower**	**Upper**	**μ**	**D**	**Lower**	**Upper**
Acetaminophen	1.1	1.1	1.2							
Atrazine	1.0	1.0	1.1							
Caffeine	1.1	1.1	1.2							
Carbamazepine	1.1	1.1	1.1							
Gemfibrozil	1.1	1.1	1.1							
Hydrochlorothiazide	1.1	1.0	1.1							
Ibuprofen C3, C4, C5	1.1	1.0	1.1							
Ketoprofen	1.0	0.4	1.5							
Lincomycin	1.1	1.1	1.1							
Metoprolol C6	10.4	9.9	11.0	$8.3 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	0.1	$7.4 \cdot 10^{-4}$	$5.4 \cdot 10^{-4}$	$9.4 \cdot 10^{-4}$
Metoprolol C3, C4, C5	3.1	2.5	3.6	$2.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	0.3	$5.6 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$10.0 \cdot 10^{-4}$
Phenytoin	1.0	1.0	1.1							
Propranolol C6	62.6	-524.6	649.8	$2.1 \cdot 10^{-7}$	$-3.1 \cdot 10^{-2}$	$3.1 \cdot 10^{-2}$	0.0	$9.6 \cdot 10^{-4}$	$-2.0 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
Propranolol C3, C4, C5	8.3	7.4	9.1	$6.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$	0.9	$3.3 \cdot 10^{-4}$	$8.9 \cdot 10^{-5}$	$5.7 \cdot 10^{-4}$
Sulfamethoxazole	1.0	1.0	1.1							
Trimethoprim	1.3	0.3	2.3							

Table SI5 – Fitted degradation rates for OMPs in the biologically active columns

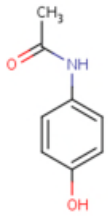
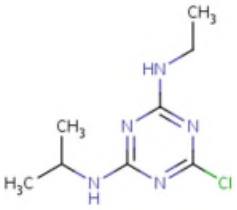
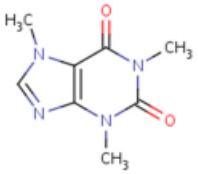
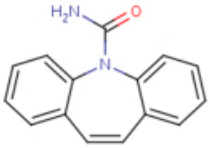
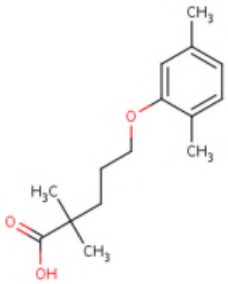
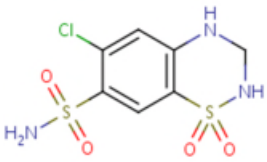
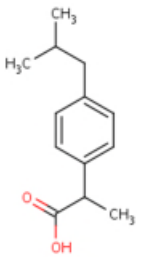
	Retardation factor [-]	Decay rate [min^{-1}]	95% Confidence interval		Decay rate [d^{-1}]	Decay $rate_{sorp}$ [d^{-1}]	Decay $rate_{eff}$ [d^{-1}]	Half life [hours]
Compound	**R**	**μ**	**Lower**	**Upper**	**μ**	**μ**	**μ**	**$t_{1/2}$**
Acetaminophen	1.1	$1.2 \cdot 10^{-2}$	$9.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$	17.1		17.1	1
Atrazine	1.0	$1.0 \cdot 10^{-10}$	$-1.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	0		0.0	-
Caffeine	1.1	$6.6 \cdot 10^{-3}$	$5.7 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	9.5		9.5	2
Carbamazepine	1.1	$1.0 \cdot 10^{-10}$	$-3.4 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	0		0.0	-
Gemfibrozil	1.1	$8.8 \cdot 10^{-3}$	$6.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	12.7		12.7	1
Hydrochlorothiazide	1.1	$1.2 \cdot 10^{-5}$	$-1.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	0		0.0	-
Ibuprofen (C3,C4,C5)	1.0	$1.1 \cdot 10^{-2}$	$8.7 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	15.8		15.8	1
Ketoprofen	1.0	$9.4 \cdot 10^{-3}$	$8.7 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	13.5		13.5	1
Lincomycin	1.1	$7.8 \cdot 10^{-5}$	$-2.0 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	0		0.0	-
Metoprolol (C3,C4,C5)	3.1	$1.2 \cdot 10^{-3}$	$9.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	1.7	0.3	1.4	12
Phenytoin	1.0	$1.0 \cdot 10^{-10}$	$-2.1 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	0		0.0	-
Propranolol (C3,C4,C5)	8.3	$3.1 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	4.5	0.9	3.6	5
Sulfamethoxazole	1.0	$1.8 \cdot 10^{-5}$	$-2.2 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	0		0.0	-
Trimethoprim	1.3	$8.0 \cdot 10^{-3}$	$6.4 \cdot 10^{-3}$	$9.6 \cdot 10^{-3}$	11.5		11.5	1

Table SI6 – Modelled degradation rates for the 1 Month period and the 6 Month period

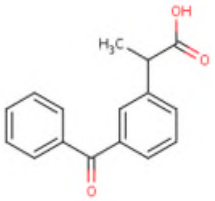
Compound	1 Month period μ_{eff} [d^{-1}]	6 Month period μ_{eff} [d^{-1}]
Acetaminophen	17.1	9.4
Atrazine	0.0	0.0
Caffeine	9.5	8.6
Carbamazepine	0.0	0.0
Gemfibrozil	12.7	12.5
Hydrochlorothiazide	0.0	0.0
Ibuprofen	15.8	ND
Ketoprofen	13.5	ND
Lincomycin	0.0	0.0
Metoprolol	1.4	1.3
Phenytoin	0.0	0.0
Propranolol	3.6	3.1
Sulfamethoxazole	0.0	0.0
Trimethoprim	11.5	10.3

ND = Not determined

Table SI7 – Functional groups

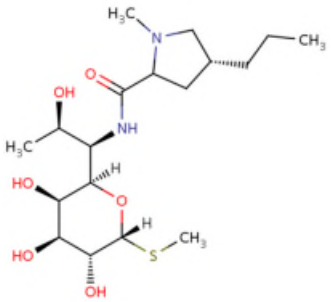
Compound	Structure	Functional groups
Acetaminophen		- 1 Amide - 1 Ring structure - 1 Hydroxyl - 1 Methyl
Atrazine		- 1 Halogen - 2 Secondary Amines - 1 Ring structure - 3 Methyl groups
Caffeine		- 2 Amides - 2 Ring structures - 3 Methyl
Carbamazepine		- 1 Amide - 3 Ring structures
Gemfibrozil		- 1 Carboxylic Acid - 4 Methyl - 1 Aryl-aliphatic Ether - 1 Ring structure
Hydrochlorothiazide		- 2 Sulphonamides - 1 Halogen - 1 Secondary Amine - 2 Ring structures
Ibuprofen		- 1 Carboxylic acid - 3 Methyl - 1 Ring structure

Ketoprofen



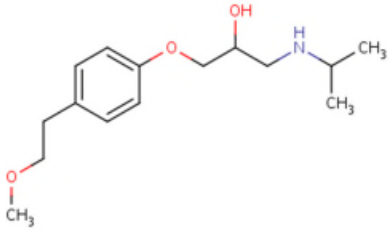
- 1 Carbonyl
- 1 Carboxylic Acid
- 1 Methyl
- 2 Ring structures

Lincomycin



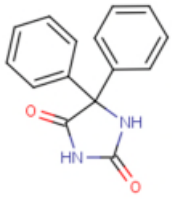
- 1 Amine
- 1 Amide
- 1 Sulphur
- 4 Hydroxyl
- 4 Methyl
- 2 Ring structures
- 1 Ether

Metoprolol



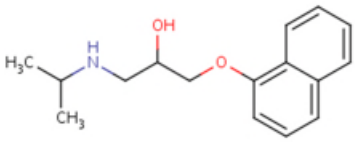
- 1 Aliphatic Ether
- 1 Aryl-aliphatic Ether
- 1 Hydroxyl
- 1 Secondary Amine
- 3 Methyl
- 1 Ring structure

Phenytoin



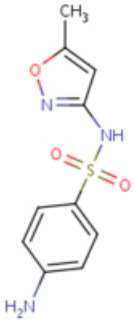
- 3 Ring structures
- 2 Amides

Propranolol



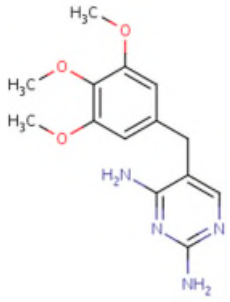
- 1 Aryl-aliphatic Ether
- 1 Hydroxyl
- 1 Secondary Amine
- 2 Methyl
- 2 Ring structures

Sulfamethoxazole



- 1 Methyl
- 1 Sulphonamide
- 1 Primary Amine
- 2 Ring structures

Trimethoprim



- 2 Ring structures
- 3 Ethers
- 2 Amine

Structural fragment / Compound	Ether	Hydroxyl	Methyl	Amines (Primary and secondary)	Amide	Sulphon-amide	Sulphur	Halogen	Aryl-aliphatic Ether	Aliphatic-Ether	Carboxylic Acid	Carbonyl	Ring structures
Propranolol	0	1	2	1	0	0	0	0	1	0	0	0	2
Metoprolol	0	1	3	1	0	0	0	0	1	1	0	0	1
Lincomcyin	1	4	4	1	1	0	1	0	0	0	0	0	2
Atrazine	0	0	3	2	0	0	0	1	0	0	0	0	1
Phenytoin	0	0	0	0	2	0	0	0	0	0	0	0	3
Carbamazepine	0	0	0	0	1	0	0	0	0	0	0	0	3
Trimethoprim	3	0	0	2	0	0	0	0	0	0	0	0	2
Acetaminophen	0	1	1	0	1	0	0	0	0	0	0	0	1
Hydrochlorothiazide	0	0	0	1	0	2	0	1	0	0	0	0	2
Caffeine	0	0	3	0	2	0	0	0	0	0	0	0	2
Gemfibrozil	0	0	4	0	0	0	0	0	1	0	1	0	1
Ibuprofen	0	0	3	0	0	0	0	0	0	0	1	0	1
Ketoprofen	0	0	1	0	0	0	0	0	0	0	1	1	2
Sulfamethoxazole	0	0	1	1	0	1	0	0	0	0	0	0	2

Appendix B - Supplementary material Chapter 3

Table S1 – Functional group assessment OMP mixture

OMP	AAE	AE	Amide	CA	CO	Ester	Ethers	Fosfor	H	Hy	Me	PA	PO	Ring	SA	SuA	Sulfur	TA	μ_{pred} [d^{-1}]
2.4-D	1	0	0	1	0	0	0	0	2	0	0	0	0	1	0	0	0	0	1.99
Acetaminophen	0	0	1	0	0	0	0	0	0	1	1	0	0	1	0	0	0	0	2.45
Atrazine	0	0	0	0	0	0	0	0	1	0	3	0	0	1	2	0	0	0	0.40
Bentazon	0	0	1	0	0	0	0	0	0	0	2	0	0	2	0	1	0	0	0.70
Carbamazepine	0	0	1	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0.59
Chloridazon	0	0	0	0	1	0	0	0	1	0	0	1	0	2	0	0	0	0	1.94
Clofibric acid	1	0	0	1	0	0	0	0	1	0	2	0	0	1	0	0	0	0	1.99
Dichlorprop	1	0	0	1	0	0	0	0	2	0	1	0	0	1	0	0	0	0	1.59
Diclofenac	0	0	0	1	0	0	0	0	2	0	0	0	0	2	1	0	0	0	1.09
Diglyme	0	3	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0.00
Dimethoate	0	0	1	0	1	0	2	0	0	0	3	0	0	0	0	0	2	0	0.39
Diuron	0	0	0	0	1	0	0	0	2	0	2	0	0	1	1	0	0	1	1.25
Hydrochlorothiazide	0	0	0	0	0	0	0	0	1	0	0	0	0	2	1	2	0	0	0.69
Ibuprofen	0	0	0	1	0	0	0	0	0	0	3	0	0	1	0	0	0	0	2.40
Iomeprol	0	0	3	0	0	0	0	0	3	5	1	0	0	1	0	0	0	0	1.95
Ketoprofen	0	0	0	1	1	0	0	0	0	0	1	0	0	2	0	0	0	0	3.54
Lincomycin	0	0	1	0	0	0	1	0	0	4	4	0	0	2	0	0	1	1	0.31
MCPA	1	0	0	1	0	0	0	0	1	0	1	0	0	1	0	0	0	0	2.39
MCPP	1	0	0	1	0	0	0	0	1	0	2	0	0	1	0	0	0	0	1.99
Metoprolol	1	1	0	0	0	0	0	0	0	1	3	0	0	1	1	0	0	0	-
Phenazone	0	0	0	0	1	0	0	0	0	0	2	0	0	2	0	0	0	0	1.95
Pindolol	1	0	0	0	0	0	0	0	0	1	2	0	0	2	1	0	0	0	1.17
Pirimicarb	0	0	0	0	0	1	0	0	0	0	6	0	0	1	0	0	0	2	0.02
Propranolol	1	0	0	0	0	0	0	0	0	1	2	0	0	2	1	0	0	0	-

Prosulfocarb	0	0	1	0	0	0	0	0	0	0	2	0	0	1	0	0	1	0	1.59
Simazine	0	0	0	0	0	0	0	0	1	0	2	0	0	1	2	0	0	0	0.80
Sulfamethoxazole	0	0	0	0	0	0	0	0	0	0	1	1	0	2	0	1	0	0	1.09
Terbutalin	0	0	0	0	0	0	0	0	0	3	3	0	0	1	1	0	0	0	2.61
Theophylline	0	0	2	0	0	0	0	0	0	0	2	0	0	2	0	0	0	0	0.70
TPPO	0	0	0	0	0	0	0	1	0	0	0	0	1	3	0	0	0	0	0.59
Triclopyr	1	0	0	1	0	0	0	0	3	0	0	0	0	1	0	0	0	0	1.19

AAE = Aryl Aliphatic Ether, AE = Aliphatic Ether, CA = Carboxylic Acid, CO = Carbonyl, H = Halogens, Hy = Hydroxyl, Me = Methyl, PA = Primary Amines, PO = Phosphine Oxide, SA= Secondary Amines, SuA = Sulphonamides, TA = Tertiary Amines

Table S2 – Porosity, velocity (v), dispersion (D), and dispersivity (α) for oxic pilot

Parameter	Units	Vitens oxic pilot
Porosity	[-]	0.33
Pore velocity	[m/d]	1.48
Dispersion	[m^2min^{-1}]	$3.04 \cdot 10^{-5}$
α	[m]	$2.94 \cdot 10^{-2}$

Table S3 – Diffusion (D_0) and dispersion coefficient (D) for OMPs for oxic pilot

OMP	D_0 [m^2min^{-1}]	Vitens D [m^2min^{-1}]
2.4-Dichlorophenoxyacetic acid (2.4-D)	$2.96 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Acetaminophen	$3.14 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Atrazine	$2.82 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Bentazon	$2.77 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Carbamazepine	$2.73 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Chloridazon	$2.89 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Clofibric acid	$2.85 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Dichlorprop	$2.87 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Diclofenac	$2.62 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Diglyme	$3.12 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Dimethoate	$2.85 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Diuron	$2.83 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Hydrochlorothiazide	$2.73 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Ibuprofen	$2.72 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Iomeprol	$2.15 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Ketoprofen	$2.63 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Lincomycin	$2.23 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
MCPA	$2.95 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
MCPP	$2.85 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Mebendazole	$2.57 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Metoprolol	$2.50 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
MTBE	$3.43 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Naproxen	$2.71 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Phenazone	$2.90 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Pindolol	$2.60 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Pirimicarb	$2.65 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Propranolol	$2.55 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Prosulfocarb	$2.57 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Salicyclic acid	$3.30 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Simazine	$2.90 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Sulfamethoxazole	$2.75 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Terbutalin	$2.68 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Theophylline	$3.07 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Triphenylphosphine oxide (TPPO)	$2.57 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$
Triclopyr	$2.91 \cdot 10^{-8}$	$3.04 \cdot 10^{-5}$

Table S4 – DOC, nitrate and phosphate removal in oxic pilot

	Units	Feed water	Vitens RBF soil
Δ DOC	[%]		30.7 (± 14.3)
NO_3^-	[mg/L]	7.32 (±2.30)	8.65 (±2.24)
PO_4^{3-}	[mg/L]	0.05 (±0.02)	0.10 (±0.03)

Table S5 – Modelled μ for Vitens pilot determined with analytical method 1 and 2

OMP	R	μ [min^{-1}]	Lower	Upper	μ [d^{-1}]
2.4-D	1.0	$2.08 \cdot 10^{-3}$	$2.04 \cdot 10^{-3}$	$2.13 \cdot 10^{-3}$	3.0
Atrazine	1.0	$6.12 \cdot 10^{-5}$	$-3.95 \cdot 10^{-5}$	$1.62 \cdot 10^{-4}$	0.0
Bentazon	1.0	$3.40 \cdot 10^{-6}$	$-1.95 \cdot 10^{-5}$	$2.63 \cdot 10^{-5}$	0.0
Carbamazepine	1.0	$3.14 \cdot 10^{-5}$	$-1.48 \cdot 10^{-4}$	$2.10 \cdot 10^{-4}$	0.0
Chloridazon	1.0	$1.95 \cdot 10^{-3}$	$1.42 \cdot 10^{-3}$	$2.48 \cdot 10^{-3}$	2.8
Clofibric acid	1.0	$5.69 \cdot 10^{-4}$	$3.78 \cdot 10^{-4}$	$7.60 \cdot 10^{-4}$	0.8
Diclofenac	1.0	$1.27 \cdot 10^{-3}$	$4.71 \cdot 10^{-4}$	$2.06 \cdot 10^{-3}$	1.8
Diglyme	1.0	$9.39 \cdot 10^{-6}$	$-5.74 \cdot 10^{-6}$	$2.45 \cdot 10^{-5}$	0.0
Diuron	1.0	$3.89 \cdot 10^{-4}$	$1.10 \cdot 10^{-4}$	$6.68 \cdot 10^{-4}$	0.6
Ibuprofen	1.0	$1.97 \cdot 10^{-3}$	$1.84 \cdot 10^{-3}$	$2.11 \cdot 10^{-3}$	2.8
Iomeprol	1.0	$1.55 \cdot 10^{-3}$	$1.24 \cdot 10^{-3}$	$1.87 \cdot 10^{-3}$	2.2
Ketoprofen	1.0	$1.87 \cdot 10^{-3}$	$1.37 \cdot 10^{-3}$	$2.38 \cdot 10^{-3}$	2.7
MCPA	1.0	$1.73 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$2.43 \cdot 10^{-3}$	2.5
MCPP	1.0	$1.46 \cdot 10^{-3}$	$6.87 \cdot 10^{-4}$	$2.23 \cdot 10^{-3}$	2.1
Metoprolol	1.0	ND	ND	ND	ND
Phenazone	1.0	$1.84 \cdot 10^{-3}$	$1.44 \cdot 10^{-3}$	$2.23 \cdot 10^{-3}$	2.6
Pindolol	1.0	$1.55 \cdot 10^{-3}$	$1.34 \cdot 10^{-3}$	$1.77 \cdot 10^{-3}$	2.2
Propranolol	1.0	ND	ND	ND	ND
Prosulfocarb	1.0	$1.79 \cdot 10^{-3}$	$1.58 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$	2.6
Sulfamethoxazole	1.0	$7.21 \cdot 10^{-4}$	$8.68 \cdot 10^{-5}$	$1.36 \cdot 10^{-3}$	1.0
Terbutaline	1.0	$1.49 \cdot 10^{-3}$	$1.01 \cdot 10^{-3}$	$1.96 \cdot 10^{-3}$	2.1
TPPO	1.0	$1.26 \cdot 10^{-4}$	$-1.08 \cdot 10^{-4}$	$3.59 \cdot 10^{-4}$	0.0

Table S6 – Modelled R and μ for Vitens pilot determined with analytical method 3

OMP	R	Lower	Upper	μ [min^{-1}]	Lower	Upper	μ [d^{-1}]
Acetaminophen	1.0	-	-	$1.60 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$1.92 \cdot 10^{-3}$	2.3
Atrazine	1.7	1.6	1.7	$3.21 \cdot 10^{-5}$	$6.54 \cdot 10^{-7}$	$6.35 \cdot 10^{-5}$	0.1
Carbamazepine	1.9	1.7	2.1	$1.50 \cdot 10^{-4}$	$5.81 \cdot 10^{-5}$	$2.42 \cdot 10^{-4}$	0.2
Chloridazon	1.0	-	-	$1.29 \cdot 10^{-3}$	$1.03 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$	1.9
Clofibric acid	1.2	1.0	1.5	$7.64 \cdot 10^{-4}$	$6.38 \cdot 10^{-4}$	$8.89 \cdot 10^{-4}$	1.1
Diclofenac	1.0	-	-	$1.59 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$	$1.97 \cdot 10^{-3}$	2.3
Diglyme	0.7	0.6	0.8	$4.59 \cdot 10^{-5}$	$-3.96 \cdot 10^{-5}$	$1.31 \cdot 10^{-4}$	0.0
Dimethoate	1.1	0.9	1.2	$2.14 \cdot 10^{-4}$	$1.52 \cdot 10^{-4}$	$2.75 \cdot 10^{-4}$	0.3
Diuron	1.0	-	-	$8.84 \cdot 10^{-4}$	$6.27 \cdot 10^{-4}$	$1.14 \cdot 10^{-3}$	1.3
Hydrochlorothiazide	1.7	1.5	1.8	$4.77 \cdot 10^{-5}$	$-1.83 \cdot 10^{-5}$	$1.14 \cdot 10^{-4}$	0.0
Ketoprofen	1.0	-	-	$1.64 \cdot 10^{-3}$	$1.19 \cdot 10^{-3}$	$2.09 \cdot 10^{-3}$	2.4
Lincomycin	1.7	1.5	2.0	$1.83 \cdot 10^{-4}$	$6.70 \cdot 10^{-5}$	$3.00 \cdot 10^{-4}$	0.3
Metoprolol	ND	ND	ND	ND	ND	ND	ND
Phenazone	0.9	0.3	1.5	$4.21 \cdot 10^{-4}$	$6.59 \cdot 10^{-5}$	$7.77 \cdot 10^{-4}$	0.6
Pirimicarb	1.5	1.5	1.6	$9.46 \cdot 10^{-5}$	$5.57 \cdot 10^{-5}$	$1.34 \cdot 10^{-4}$	0.1
Simazine	1.4	1.3	1.5	$3.70 \cdot 10^{-5}$	$-7.77 \cdot 10^{-6}$	$8.17 \cdot 10^{-5}$	0.0
Sulfamethoxazole	0.5	0.1	0.8	$5.97 \cdot 10^{-4}$	$2.67 \cdot 10^{-4}$	$9.28 \cdot 10^{-4}$	0.9
Terbutalin	1.0	-	-	$9.95 \cdot 10^{-4}$	$7.28 \cdot 10^{-4}$	$1.26 \cdot 10^{-3}$	1.4
Theophylline	1.0	-	-	$9.93 \cdot 10^{-4}$	$6.91 \cdot 10^{-4}$	$1.29 \cdot 10^{-3}$	1.4
Triclopyr	1.1	0.9	1.3	$2.35 \cdot 10^{-4}$	$1.36 \cdot 10^{-4}$	$3.34 \cdot 10^{-4}$	0.3

ND = A statistically significant retardation factor and biodegradation rate could not be determined for this OMP

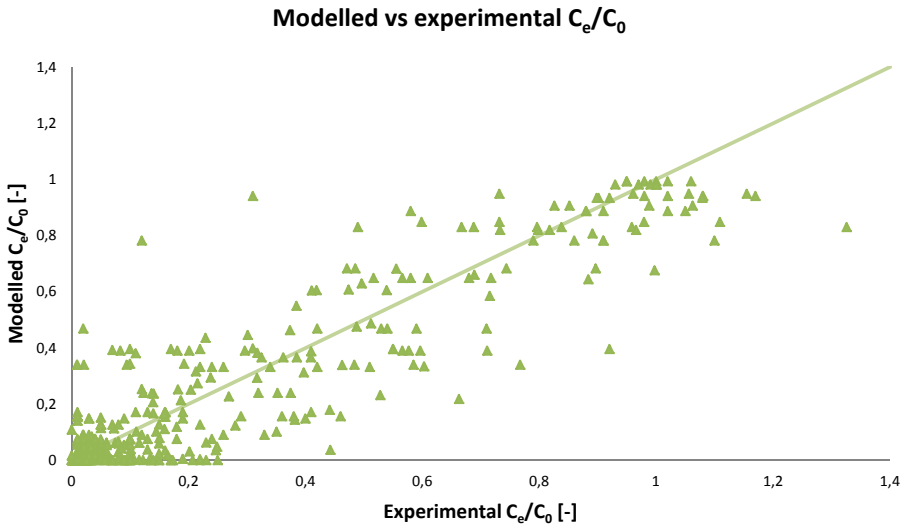


Figure S1 – Goodness of fit for determination of μ with the convection-dispersion equation

Variables Entered/Removed[a]

Model	Variables Entered	Variables Removed	Method
1	Me, CO, AE, OH, CA, Ethers, H, Ring[b]	.	Enter

a. Dependent Variable: DegrRate

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	,804[a]	,646	,504	,77053

a. Predictors: (Constant), Me, CO, AE, OH, CA, Ethers, H, Ring

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	21,658	8	2,707	4,560	,003[b]
	Residual	11,874	20	,594		
	Total	33,532	28			

a. Dependent Variable: DegrRate

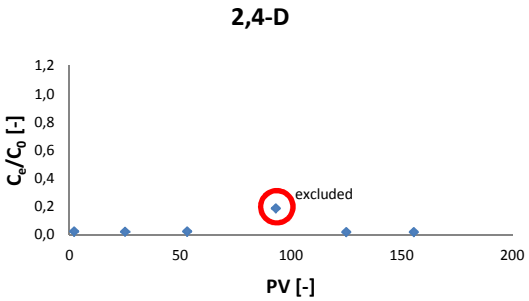
b. Predictors: (Constant), Me, CO, AE, OH, CA, Ethers, H, Ring

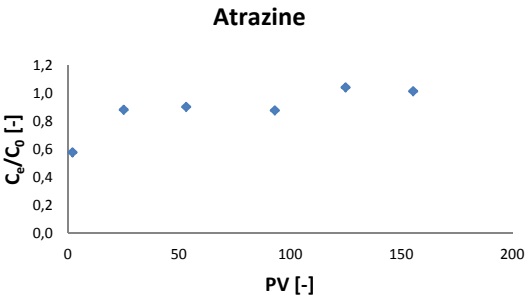
Coefficients[a]

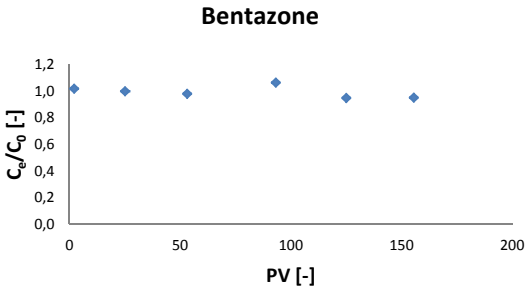
Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.	Collinearity Statistics	
		B	Std. Error	Beta			Tolerance	VIF
1	(Constant)	3,269	,821		3,981	,001		
	CA	1,199	,384	,516	3,120	,005	,647	1,545
	OH	,470	,138	,546	3,404	,003	,689	1,451
	CO	1,253	,427	,440	2,936	,008	,788	1,269
	Ethers	-1,478	,441	-,553	-3,353	,003	,651	1,535
	H	-,794	,236	-,696	-3,367	,003	,414	2,414
	AE	-,827	,327	-,421	-2,533	,020	,641	1,561
	Ring	-,894	,318	-,598	-2,812	,011	,391	2,557
	Me	-,393	,156	-,502	-2,523	,020	,448	2,233

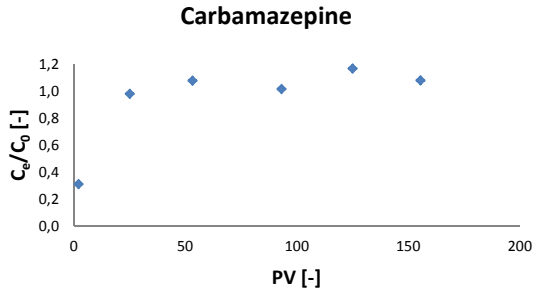
Figure S2 - Multi linear regression model output

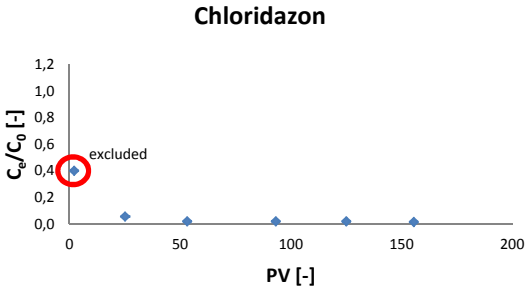
OMP breakthrough curves for the oxic pilot

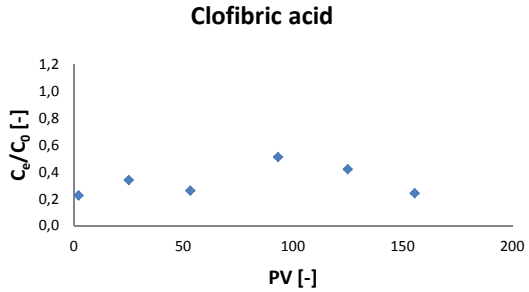


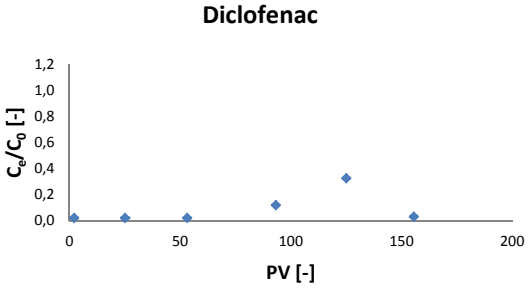


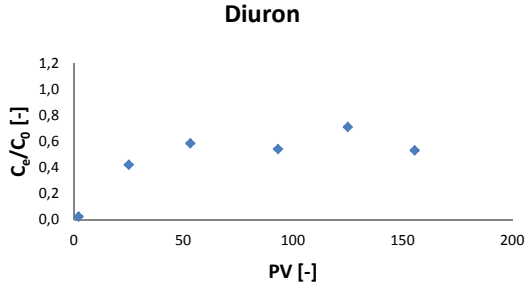


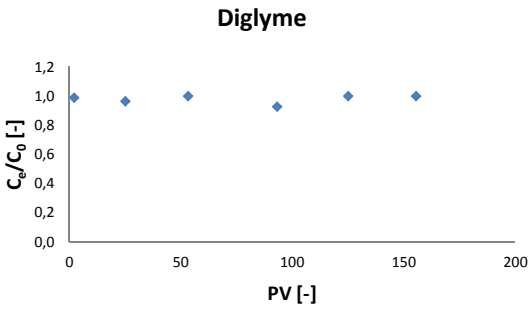











Diglyme
Ce/C0 [-]
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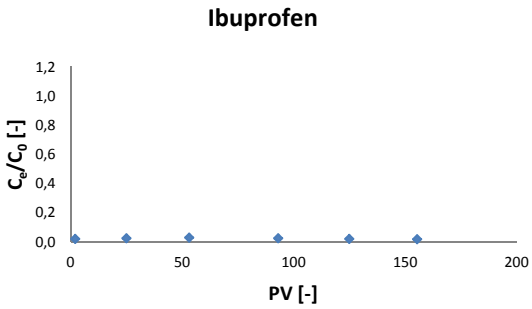
1,0
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]


Ibuprofen
Ce/C0 [-]
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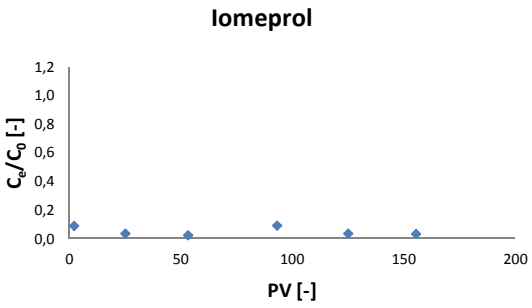
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]


Iomeprol
Ce/C0 [-]
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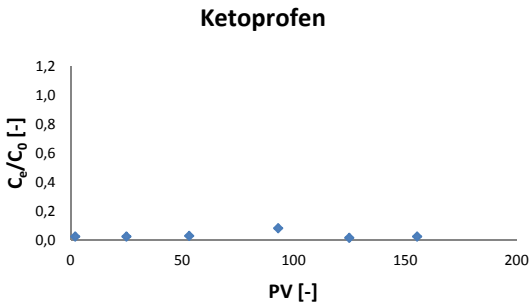
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]


Ketoprofen
Ce/C0 [-]
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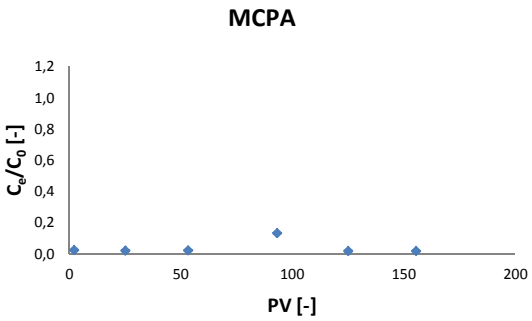
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]


MCPA
Ce/C0 [-]
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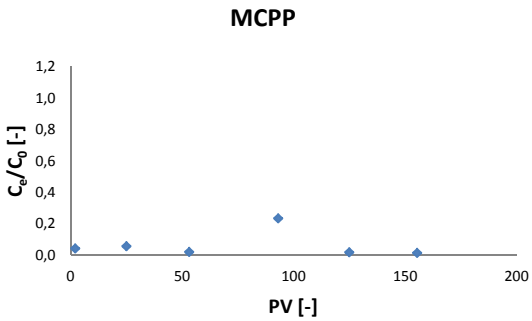
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]


MCPP
Ce/C0 [-]
1,2
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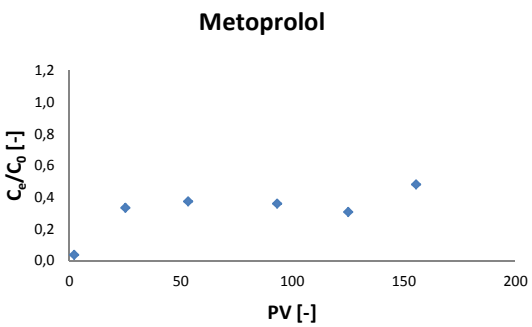
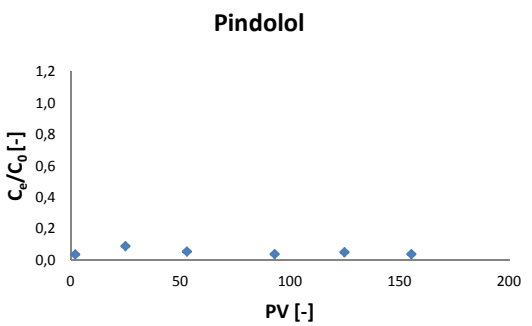
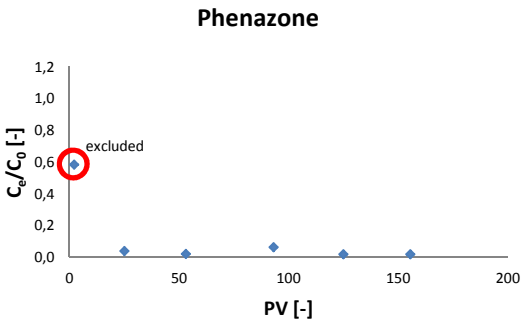
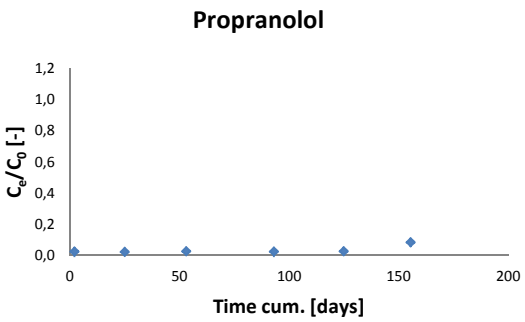
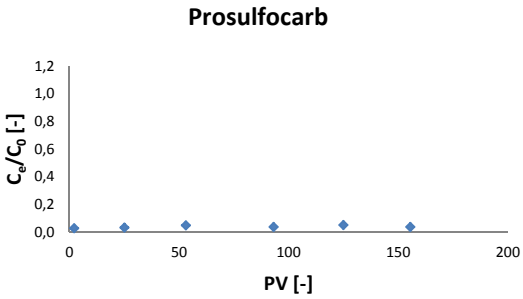
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]

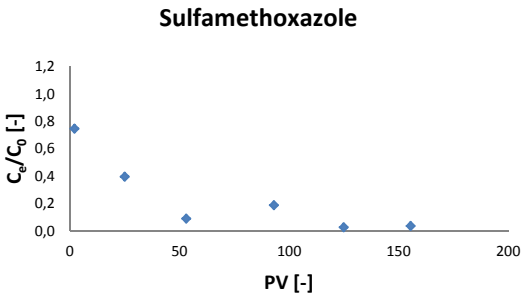

Metoprolol
Ce/C0 [-]
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]

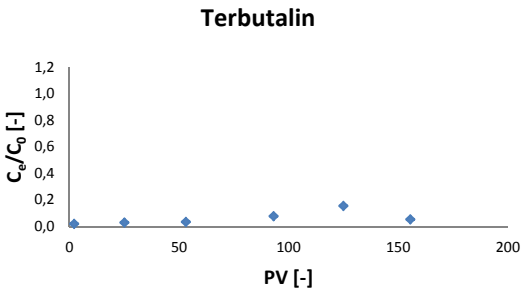

Pindolol
Ce/C0 [-]
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
50
100
150
200
PV [-]

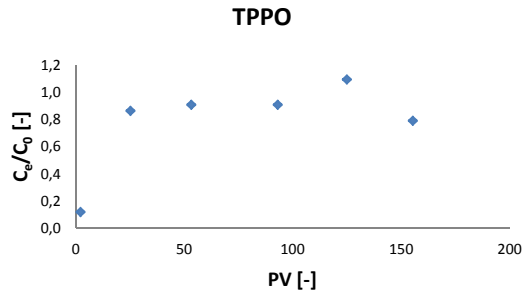

Phenazone
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
excluded
0
50
100
150
200
PV [-]


Propranolol
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
0
50
100
150
200
Time cum. [days]


Prosulfocarb
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
0
50
100
150
200
PV [-]


Sulfamethoxazole
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
0
50
100
150
200
PV [-]


Terbutalin
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
0
50
100
150
200
PV [-]


TPPO
1,2
1,0
0,8
0,6
0,4
0,2
0,0
C_e/C_0 [-]
0
50
100
150
200
PV [-]

Appendix C - Supplementary material Chapter 4

Table S1 – Porosity, velocity (v), dispersion (D), and dispersivity (α) for oxic pilots

Parameter	Units	Vitens oxic pilot	Oasen oxic pilot
Porosity	[-]	0.33	0.35
Pore velocity	[m/d]	1.48	1.40
Dispersion	[m^2min^{-1}]	$3.04 \cdot 10^{-5}$	$2.59 \cdot 10^{-6}$
α	[m]	$2.94 \cdot 10^{-2}$	$2.60 \cdot 10^{-3}$

Table S2 – Diffusion (D_0) and dispersion coefficient (D) for OMPs for both pilot systems

OMP	D_0 [m^2min^{-1}]	Vitens D [m^2min^{-1}]	Oasen D [m^2min^{-1}]
Acetaminophen	$3.13630 \cdot 10^{-8}$	$3.03611 \cdot 10^{-5}$	$2.56315 \cdot 10^{-6}$
Atrazine	$2.81531 \cdot 10^{-8}$	$3.03579 \cdot 10^{-5}$	$2.55994 \cdot 10^{-6}$
Carbamazepine	$2.72584 \cdot 10^{-8}$	$3.03570 \cdot 10^{-5}$	$2.55904 \cdot 10^{-6}$
Chloridazon	$2.88536 \cdot 10^{-8}$	$3.03586 \cdot 10^{-5}$	$2.56064 \cdot 10^{-6}$
Clofibric acid	$2.84981 \cdot 10^{-8}$	$3.03583 \cdot 10^{-5}$	$2.56028 \cdot 10^{-6}$
Diclofenac	$2.62016 \cdot 10^{-8}$	$3.03560 \cdot 10^{-5}$	$2.55799 \cdot 10^{-6}$
Diglyme	$3.11811 \cdot 10^{-8}$	$3.03610 \cdot 10^{-5}$	$2.56297 \cdot 10^{-6}$
Dimethoate	$2.84759 \cdot 10^{-8}$	$3.03583 \cdot 10^{-5}$	$2.56026 \cdot 10^{-6}$
Diuron	$2.83444 \cdot 10^{-8}$	$3.03581 \cdot 10^{-5}$	$2.56013 \cdot 10^{-6}$
Hydrochlorothiazide	$2.73048 \cdot 10^{-8}$	$3.03571 \cdot 10^{-5}$	$2.55909 \cdot 10^{-6}$
Ketoprofen	$2.63139 \cdot 10^{-8}$	$3.03561 \cdot 10^{-5}$	$2.55810 \cdot 10^{-6}$
Lincomycin	$2.23031 \cdot 10^{-8}$	$3.03521 \cdot 10^{-5}$	$2.55409 \cdot 10^{-6}$
Metoprolol	$2.49508 \cdot 10^{-8}$	$3.03547 \cdot 10^{-5}$	$2.55674 \cdot 10^{-6}$
Phenazone	$2.90126 \cdot 10^{-8}$	$3.03588 \cdot 10^{-5}$	$2.56080 \cdot 10^{-6}$
Pirimicarb	$2.65325 \cdot 10^{-8}$	$3.03563 \cdot 10^{-5}$	$2.55832 \cdot 10^{-6}$
Simazine	$2.90399 \cdot 10^{-8}$	$3.03588 \cdot 10^{-5}$	$2.56082 \cdot 10^{-6}$
Sulfamethoxazole	$2.75106 \cdot 10^{-8}$	$3.03573 \cdot 10^{-5}$	$2.55930 \cdot 10^{-6}$
Terbutalin	$2.67601 \cdot 10^{-8}$	$3.03565 \cdot 10^{-5}$	$2.55854 \cdot 10^{-6}$
Theophylline	$3.07362 \cdot 10^{-8}$	$3.03605 \cdot 10^{-5}$	$2.56252 \cdot 10^{-6}$
Triclopyr	$2.90728 \cdot 10^{-8}$	$3.03589 \cdot 10^{-5}$	$2.56086 \cdot 10^{-6}$

Table S3 – Water quality parameters influent column experiment

	Units	Feed water
pH	-	8.1 ± 0.2 (n = 6)
O_2	[mg/L]	9.7 ± 0.7 (n = 5)
DOC	[mg/L]	3.86 ± 0.80 (n = 40)
NO_3^-	[mg/L]	7.49 ± 2.66 (n = 37)
PO_4^{3-}	[mg/L]	0.08 ± 0.08 (n = 37)
SO_4^{2-}	[mg/L]	45.19 ± 9.30 (n = 37)
Cl^-	[mg/L]	60.00 ± 15.31 (n = 37)
NH_4^+	[mg/L]	0.08 ± 0.03 (n = 12)[1]
Mg^{2+}	[mg/L]	10.25 ± 1.76 (n = 37)
Ca^{2+}	[mg/L]	48.67 ± 8.43 (n = 37)

[1] (Stoks *et al.*, 2014)

Figure S1 - Microbial DGGE pattern of the soil samples at the real RBF sites clustered according to Pearson correlation, unweighted pair group with mathematical averages dendrogram type (Oasen 0-5 cm = Oasen RBF site at depth 0 – 5 cm , Vitens Engelse werk 0-5 cm = Vitens RBF site at depth 0-5 cm)

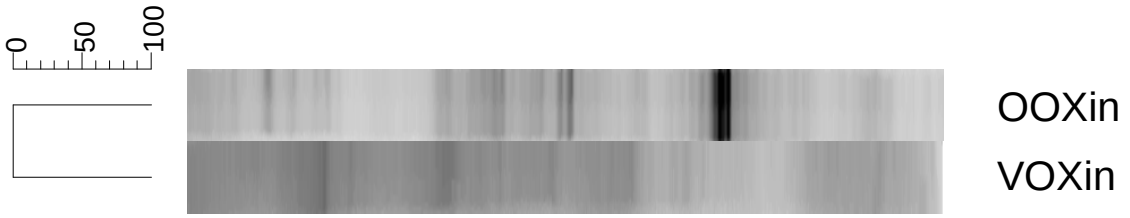


Figure S2 - Microbial DGGE pattern of the soil samples obtained at the influent side of both oxic soil column systems clustered according to Pearson correlation, unweighted pair group with mathematical averages dendrogram type (OOXin = Oasen soil influent side, VOXin = vitens soil influent side)

Table S4 – Modelled R and μ for Vitens pilot

OMP	R	Lower	Upper	μ [min^{-1}]	Lower	Upper	μ [d^{-1}]
Diclofenac	1.00	-	-	$1.59 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$	$1.97 \cdot 10^{-3}$	2.29
Ketoprofen	1.00	-	-	$1.64 \cdot 10^{-3}$	$1.19 \cdot 10^{-3}$	$2.09 \cdot 10^{-3}$	2.36
Chloridazon	1.00	-	-	$1.63 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	$2.16 \cdot 10^{-3}$	2.35
Acetaminophen	1.00	-	-	$1.60 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$1.92 \cdot 10^{-3}$	2.30
Theophylline	1.00	-	-	$9.93 \cdot 10^{-4}$	$6.91 \cdot 10^{-4}$	$1.29 \cdot 10^{-3}$	1.43
Diuron	1.00	-	-	$8.84 \cdot 10^{-4}$	$6.27 \cdot 10^{-4}$	$1.14 \cdot 10^{-3}$	1.27
Terbutalin	1.00	-	-	$9.95 \cdot 10^{-4}$	$7.28 \cdot 10^{-4}$	$1.26 \cdot 10^{-3}$	1.43
Clofibric acid	1.00	-	-	$8.15 \cdot 10^{-4}$	$3.10 \cdot 10^{-4}$	$1.32 \cdot 10^{-3}$	1.17
Phenazone	0.90	$2.75 \cdot 10^{-1}$	$1.53 \cdot 10^{0}$	$1.87 \cdot 10^{-3}$	$6.62 \cdot 10^{-4}$	$3.07 \cdot 10^{-3}$	2.69
Metoprolol	ND	ND	ND	ND	ND	ND	ND
Sulfamethoxazole	0.45	$6.23 \cdot 10^{-2}$	$8.35 \cdot 10^{-1}$	$1.00 \cdot 10^{-3}$	$6.24 \cdot 10^{-4}$	$1.38 \cdot 10^{-3}$	1.44
Carbamazepine	1.89	$1.65 \cdot 10^{0}$	$2.13 \cdot 10^{0}$	$1.50 \cdot 10^{-4}$	$5.81 \cdot 10^{-5}$	$2.42 \cdot 10^{-4}$	0.22
Dimethoate	1.06	$9.25 \cdot 10^{-1}$	$1.19 \cdot 10^{0}$	$2.55 \cdot 10^{-4}$	$1.89 \cdot 10^{-4}$	$3.21 \cdot 10^{-4}$	0.37
Triclopyr	1.07	$8.79 \cdot 10^{-1}$	$1.25 \cdot 10^{0}$	$2.32 \cdot 10^{-4}$	$-5.72 \cdot 10^{-5}$	$5.20 \cdot 10^{-4}$	0.00
Pirimicarb	1.53	$1.47 \cdot 10^{0}$	$1.60 \cdot 10^{0}$	$9.46 \cdot 10^{-5}$	$5.57 \cdot 10^{-5}$	$1.34 \cdot 10^{-4}$	0.14
Diglyme	0.70	$5.71 \cdot 10^{-1}$	$8.23 \cdot 10^{-1}$	$4.59 \cdot 10^{-5}$	$-3.96 \cdot 10^{-5}$	$1.31 \cdot 10^{-4}$	0.00
Atrazine	1.66	$1.60 \cdot 10^{0}$	$1.72 \cdot 10^{0}$	$3.21 \cdot 10^{-5}$	$6.54 \cdot 10^{-7}$	$6.35 \cdot 10^{-5}$	0.05
Hydrochlorothiazide	1.69	$1.54 \cdot 10^{0}$	$1.83 \cdot 10^{0}$	$4.77 \cdot 10^{-5}$	$-1.83 \cdot 10^{-5}$	$1.14 \cdot 10^{-4}$	0.00
Lincomycin	1.72	$1.46 \cdot 10^{0}$	$1.97 \cdot 10^{0}$	$2.39 \cdot 10^{-4}$	$-4.18 \cdot 10^{-5}$	$5.19 \cdot 10^{-4}$	0.00
Simazine	1.43	$1.34 \cdot 10^{0}$	$1.51 \cdot 10^{0}$	$3.70 \cdot 10^{-5}$	$-7.77 \cdot 10^{-6}$	$8.17 \cdot 10^{-5}$	0.00

Table S5 – Modelled R and μ for Oasen pilot

OMP	R	Lower	Upper	μ [min^{-1}]	Lower	Upper	μ [d^{-1}]
Terbutalin	ND	-	-				
Acetaminophen	1.00	-	-	$1.88 \cdot 10^{-3}$	$1.28 \cdot 10^{-3}$	$2.48 \cdot 10^{-3}$	2.70
Ketoprofen	1.00	-	-	$1.86 \cdot 10^{-3}$	$1.48 \cdot 10^{-3}$	$2.24 \cdot 10^{-3}$	2.68
Diclofenac	1.00	-	-	$1.58 \cdot 10^{-3}$	$1.35 \cdot 10^{-3}$	$1.81 \cdot 10^{-3}$	2.28
Theophylline	1.00	-	-	$1.48 \cdot 10^{-3}$	$1.29 \cdot 10^{-3}$	$1.68 \cdot 10^{-3}$	2.14
Diuron	1.00	-	-	9.57E-04	$4.87 \cdot 10^{-4}$	$1.43 \cdot 10^{-3}$	1.38
Metoprolol	ND	ND	ND	ND	ND	ND	ND
Chloridazon	1.00	-	-	$1.14 \cdot 10^{-3}$	$4.95 \cdot 10^{-4}$	$1.79 \cdot 10^{-3}$	1.65
Phenazone	1.04	$8.10 \cdot 10^{-1}$	$1.26 \cdot 10^{0}$	$1.46 \cdot 10^{-3}$	$7.17 \cdot 10^{-4}$	$2.20 \cdot 10^{-3}$	2.10
Clofibric acid	1.00	-	-	$1.31 \cdot 10^{-3}$	$9.15 \cdot 10^{-4}$	$1.71 \cdot 10^{-3}$	1.89
Sulfamethoxazole	0.99	$8.15 \cdot 10^{-1}$	$1.17 \cdot 10^{0}$	$6.78 \cdot 10^{-4}$	$1.32 \cdot 10^{-5}$	$1.34 \cdot 10^{-3}$	0.98
Carbamazepine	1.37	$1.23 \cdot 10^{0}$	$1.50 \cdot 10^{0}$	$2.01 \cdot 10^{-4}$	$8.80 \cdot 10^{-5}$	$3.13 \cdot 10^{-4}$	0.29
Dimethoate	1.05	$9.65 \cdot 10^{-1}$	$1.13 \cdot 10^{0}$	$2.92 \cdot 10^{-4}$	$9.76 \cdot 10^{-5}$	$4.86 \cdot 10^{-4}$	0.42
Lincomycin	1.39	$1.21 \cdot 10^{0}$	$1.58 \cdot 10^{0}$	$3.43 \cdot 10^{-4}$	$-1.76 \cdot 10^{-4}$	$8.63 \cdot 10^{-4}$	0.00
Triclopyr	1.13	$1.07 \cdot 10^{0}$	$1.19 \cdot 10^{0}$	$1.84 \cdot 10^{-4}$	$1.35 \cdot 10^{-4}$	$2.33 \cdot 10^{-4}$	0.27
Hydrochlorothiazide	1.29	$1.25 \cdot 10^{0}$	$1.34 \cdot 10^{0}$	$1.27 \cdot 10^{-4}$	$8.49 \cdot 10^{-5}$	$1.69 \cdot 10^{-4}$	0.18
Pirimicarb	1.39	$1.26 \cdot 10^{0}$	$1.53 \cdot 10^{0}$	$1.48 \cdot 10^{-4}$	$5.00 \cdot 10^{-5}$	$2.47 \cdot 10^{-4}$	0.21
Simazine	1.33	$1.26 \cdot 10^{0}$	$1.39 \cdot 10^{0}$	$8.70 \cdot 10^{-5}$	$2.04 \cdot 10^{-5}$	$1.54 \cdot 10^{-4}$	0.13
Atrazine	1.40	$1.27 \cdot 10^{0}$	$1.53 \cdot 10^{0}$	$1.16 \cdot 10^{-4}$	$2.84 \cdot 10^{-5}$	$2.04 \cdot 10^{-4}$	0.17
Diglyme	0.98	$9.30 \cdot 10^{-1}$	$1.03 \cdot 10^{0}$	$3.51 \cdot 10^{-5}$	$-1.13 \cdot 10^{-5}$	$8.15 \cdot 10^{-5}$	0.00

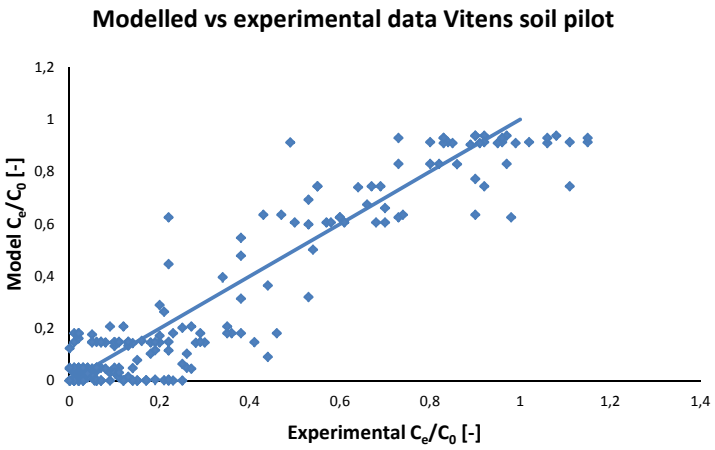


Figure S3 – Modelled versus experimentally obtained C_e / C_0 values for the Vitens soil pilot

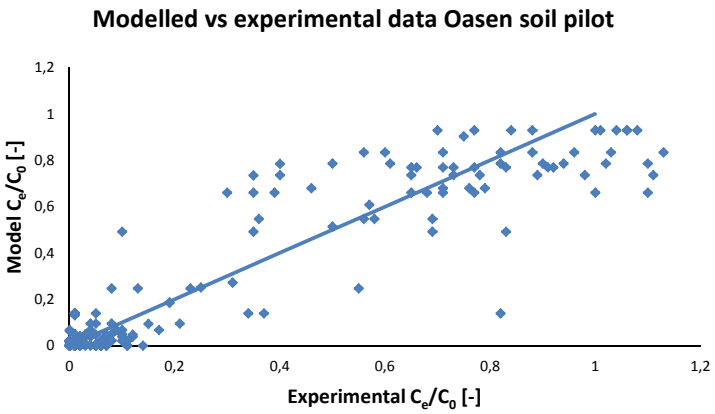


Figure S4 – Modelled versus experimentally obtained C_e / C_0 values for the Oasen soil pilot

References

Appelo, C.A.J. and Postma, D. (2005) Geochemistry, Groundwater and Pollution, Taylor & Francis.

Boon, N., Goris, J., De Vos, P., Verstraete, W. and Top, E.M. (2000) Bioaugmentation of Activated Sludge by an Indigenous 3-Chloroaniline-Degrading *Comamonas testosteroni* Strain, I2*gfp*. Applied and Environmental Microbiology 66(7), 2906-2913.

Breeuwsma, A., Wösten, J.H.M., Vleeshouwer, J.J., van Slobbe, A.M. and Bouma, J. (1986) Derivation of Land Qualities to Assess Environmental Problems from Soil Surveys. Soil Sci. Soc. Am. J. 50, 186-190.

Brusseau, M.L. (1994) Transport of reactive contaminants in heterogeneous porous media. Reviews of Geophysics 32(3), 285-313.

Callewaert, C., Kerckhof, F.M., Granitsiotis, M.S., Van Gele, M., Van de Wiele, T. and Boon, N. (2013) Characterization of *Staphylococcus* and *Corynebacterium* Clusters in the Human Axillary Region. PLoS ONE 8(8), 1-8.

Hagen, M. (2014) Sediment Analysis Laboratory Free Univeristy of Amsterdam, *personal communication*.

Hieltjes, A.H.M. and Breeuwsma, A. (1983) Chemische bodemonderzoekmethoden voor bodemkenmerken en anorganische stoffen, Staatsuitgeverij

Keuten, M.G.A., Schets, F.M., Schijven, J.F., Verberk, J.Q.J.C. and van Dijk, J.C. (2012) Definition and quantification of initial anthropogenic pollutant release in swimming pools. Water Research 46, 3682-3692.

Muyzer, G., De Waal, E.C. and Uitterlinden, A.G. (1993) Profiling of Complex Microbial Populations by Denaturing Gradient Gel Electrophoresis Analysis of Polymerase Chain Reaction-Amplified Genes Coding for 16S rRNA. Applied and Environmental Microbiology 59(3), 695-700.

Øvreås, L., Forney, L., Daae, F.L. and Torsvik, V. (1997) Distribution of Bacterioplankton in Meromictic Lake Saelenvannet, as Determined by Denaturing Gradient Gel Electrophoresis of PCR-Amplified Gene Fragments Coding for 16S rRNA. Applied and Environmental Microbiology 63(9), 3367-3373.

Read, S., Marzorati, M., Guimarães, B.C.M. and Boon, N. (2011) Microbial Resource Management revisited: succesful parameters and new concepts. Appl Microbiol Biotechnol 90, 861-871.

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

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

van den Berg, J. (1998) Organische stof: normering van meetmethoden dringende noodzaak. H2O 22, 30-34.

van Reeuwijk, L.P. (1992) Procedures for soil analysis, International Soil Reference and Information Centre Wageningen - The Netherlands.

Verliefde, A.R.D. (2008) Rejection of Organic Micropollutants by High Pressure Membranes (NF/RO), Delft University of Technology, Delft.

Appendix D - Supplementary material Chapter 5

S1.1 Organic carbon fractionation

Lek river water from the RBF site of drinking water company Oasen (51° 55' 0.4'' N, 4° 47' 5.4'' E, The Netherlands) was used for fractionation. The Lek river is a tributary of the river Rhine and the amount of treated wastewater discharged on the river Rhine is relatively small, 5 to 10% (Hoppe-Jones *et al.*, 2010). Prior to separating the organic carbon fractions, the river water was concentrated by a factor 10 by means of nanofiltration (NF90, Dow-Filmtec, The Netherlands) with a recovery of 90%. The NF-concentrate was placed in an oven at 45°C which reduced the volume of the NF-concentrate by a further 30%. The concentrated river water was then filtered (20 μm, Whatmann, Germany) to remove larger particles before fractionation was initiated. The organic matter in the concentrated river water was fractionated into three fractions: hydrophilic, transphilic, and hydrophobic, by means of XAD-8 and XAD-4 resins based on (Leenheer *et al.*, 2000). The definition of hydrophilic, transphilic and hydrophobic in this study is based on the variation in polarity of the different fractions. A mass balance (mg DOC) was set-up to check for losses during the fractionation. Organic matter in the Lek river water consisted of 41% hydrophilic, 25% transphilic and 37% hydrophobic organic material resulting in a total of 103%. This indicates that the fractionation did not lead to significant loss of organic material.

Each organic carbon fraction (hydrophilic, RWOM, transphilic and hydrophobic) was then diluted into Milli-Q water in the desired concentration and fed to two soil columns each (duplicate measurements). Micro- and macronutrients were added to all feed solutions. The micronutrient solution was based on a study of (Vishniac and Santer, 1957). 10 mL aliquots of the micronutrient solution ($ZnSO_4 \times 7\ H_2O$) (22.00 g), $CaCl_2 \times 2\ H_2O$ (5.54 g), $MnCl_2 \times 4\ H_2O$ (5.06 g), $FeSO_4 \times 7\ H_2O$ (5.00 g), $(NH_4)6Mo_7O_{24} \times 4\ H_2O$ (1.10 g), $CuSO_4 \times 5\ H_2O$ (1.57 g), $CoCl_2 \times 6\ H_2O$ (1.61 g) in 1000 mL distilled water; pH adjustment to pH = 6 with KOH) were added to each feed solution. Macronutrients phosphate (0.2 ppm PO_4^{3-}) and nitrate (11.4 ppm NO_3^-) were dosed in each feed solution in the same order of magnitude as observed from a yearly monitoring programme that analysed both macro nutrients in the field for the river water used in this study (Stoks *et al.*, 2011). pH of the feed solutions for the hydrophilic, transphilic and hydrophobic fractions was corrected with NaOH and H_2SO_4 to a pH similar to the river water. The columns fed with the different fractions were also compared to two duplicate columns fed with original river water, which served as a control that contained all OM fractions at once.

S1.2 Tracer experiments with deuterium

Pore velocity and porosity in all columns were determined using deuterium (^2H) as a tracer. The feed solution was labelled with 150 μL deuterium oxide (^2H_2O) per litre, resulting in a doubling of the natural deuterium abundance (i.e. $\delta^2H \approx 1000$ ‰). Deuterium oxide concentrations were determined by wavelength-scanned cavity ring-down spectroscopy using a L2201-i (Picarro Inc., Sunnyvale, CA USA) equipped with a vaporizer and micro pyrolysis unit. Effluent samples were distilled cryogenically (West *et al.*, 2006) to remove salts and exclude matrix effects.

S1.3 Soil parameters

ATP analysis of soil samples at the influent and effluent side of the columns was performed at the end of each experimental phase according to the method described in (Chapter 2) with the following

exceptions: (1) Sand samples were 2 - 5 g instead of 10 g, (2) From every supernatant sample 333 µL was collected to obtain a mixture of 1 mL in total. This 1 mL mixture was subjected to ATP analysis.

Table S1 – Hydro chemical data Lek river water

Parameter	Units	Average value ± standard deviation
Temperature	°C	20.1 ± 1.4 (n = 8)
pH	-	7.9 ± 0.3 (n = 8)
O_2	mg/L	7.8 ± 1.2 (n = 4)
DOC	mg/L	4.0 ± 0.9 (n = 8)
NO_3^-	mg/L	14.0 ± 0.3 (n = 5)
PO_4^-	mg/L	0.44 (min. = 0.25; max. = 0.60)*

* Obtained from yearly monitoring programme (Stoks *et al.*, 2014)

Table S2 – Characteristics of the experimental phases of the soil columns

Phase	Experimental condition	OMP dosed [µg/L]	DOC feed [mg/L]	Duration [weeks]
1	Stable operation	0.5	4	6
2	OMP shock-load	2	4	3
3	DOC shock-load	2	8	3

Table S3 – Detection limits for analysed OMPs

OMP	LOD (ng/L)
Lincomycin	2.8
Acetaminophen	3.3
Hydrochlorothiazide	2.4
Metoprolol	0.4
Phenazone	0.1
Sulfamethoxazole	0.2
Pirimicarb	0.04
Dimethoate	0.1
Chloridazon	0.1
Simazine	0.2
Carbamazepine	0.03
Atrazine	0.3
Diuron	0.1
Ketoprofen	0.4
Naproxen	16
Clofibric acid	0.04
Diclofenac	0.2
Triclopyr	0.2
Gemfibrozil	0.4

Table S4 – Carbon fractions compared by organic carbon constituents

	Biopolymers [ppb-C] (95% CI)	Humics [ppb-C] (95% CI)	Building blocks [ppb-C] (95% CI)	LMW acids & neutrals [ppb-C] (95% CI)
RWOM	96 (24-168)	4266 (4194-4338)	901 (829-973)	1673 (1601-1745)
Hydrophobic	42 (0-114)	4048 (3976-4120)	1182 (1110-1254)	1451 (1379-1523)
Transphilic	89 (17-161)	4134 (4062-4206)	1064 (992-1136)	1107 (1035-1179)
Hydrophilic	155 (83-227)	3762 (3690-3834)	1591 (1519-1663)	2366 (2294-2438)

Table S5 – pH values in column in- and effluent for all experimental phases

Hydrophilic	**Phase 1**	**Phase 2**	**Phase 3**
Influent	6.54 ± 0.20 (n = 8)	6.81 ± 0.09 (n = 3)	7.41 ± 0.17 (n = 3)
Effluent	7.61 ± 0.68 (n = 16)	7.94 ± 0.57 (n = 6)	8.07 ± 0.23 (n = 6)
RWOM	**Phase 1**	**Phase 2**	**Phase3**
Influent	7.87 ± 0.34 (n = 8)	8.15 ± 0.11 (n = 3)	8.31 ± 0.04 (n = 3)
Effluent	8.04 ± 0.30 (n = 16)	8.15 ± 0.19 (n = 6)	8.41 ± 0.14 (n = 6)
Transphilic	**Phase 1**	**Phase 2**	**Phase 3**
Influent	8.09 ± 0.31 (n = 8)	8.02 ± 0.21 (n = 3)	8.96 ± 0.01 (n = 3)
Effluent	8.46 ± 0.38 (n = 16)	8.67 ± 0.30 (n = 6)	8.86 ± 0.08 (n = 6)
Hydrophobic	**Phase 1**	**Phase 2**	**Phase 3**
Influent	7.85 ± 0.34 (n = 8)	8.05 ± 0.15 (n = 3)	8.61 ± 0.07 (n = 3)
Effluent	8.51 ± 0.45 (n= 16)	8.66 ± 0.33 (n = 6)	8.91 ± 0.12 (n = 6)

Table S6 – Nitrate (NO_3^-) concentrations (mg/L) in column in- and effluent for all experimental phases

	Phase 1	**Phase 2**	**Phase 3**
Hydrophilic	**NO_3^-**	**NO_3^-**	**NO_3^-**
Influent	47.1 ± 7.2 (n=4)	6.3 (n=1)	76.7 (n=1)
Effluent	25.8 ± 16.0 (n=12)	13.6 ± 8.0 (n=4)	71.3 ± 2.6 (n=4)
RWOM			
Influent	11.2 ± 5.5 (n=4)	14.4 (n=1)	28.2 (n=1)
Effluent	1.0 ± 2.1 (n=11)	8.5 ± 3.8 (n=4)	21.7 ± 3.7 (n=4)
Transphilic			
Influent	19.0 ± 5.9 (n=4)	12.3 (n=1)	20.1 (n=1)
Effluent	2.8 ± 3.1 (n=12)	3.7 ± 3.3 (n=4)	7.9 ± 5.3 (n=4)
Hydrophobic			
Influent	16.7 ± 3.1 (n=4)	11.0 (n=1)	9.2 (n=1)
Effluent	8.1 ± 3.2 (n=12)	8.0 ± 3.6 (n=3)	5.4 ± 3.5 (n=4)

Table S7 – Average richness and evenness (± st dev.) in soil samples from the in- and effluent of the duplicate columns

Influent side	Module 1		Module 2		Module 3	
	Gini	Richness	Gini	Richness	Gini	Richness
Hydrophilic	0.75 ± 0.09	38.0 ± 9.9	0.54 ± 0.17	54.5 ±13.4	0.90 ± 0.04	36.0 ± 4.2
RWOM	0.62 ± 0.04	52.0 ± 4.2	0.93 ± 0.01	20.5 ± 0.7	0.65 (-)*	57.0 (-)*
Transphilic	0.55 ± 0.04	56.5 ± 6.4	0.70 ± 0.13	40.5 ± 12.0	0.93 ± 0.01	29.0 ± 0.0
Hydrophobic	0.80 ± 0.08	35.0 ± 5.7	0.58 ± 0.20	52.5 ± 20.5	0.78 ± 0.12	45.0 ± 12.7

Effluent side	Module 1		Module 2		Module 3	
	Gini	Richness	Gini	Richness	Gini	Richness
Hydrophilic	0.58 ± 0.33	50.5 ± 26.2	0.64 ± 0.12	45.0 ± 5.7	0.56 ± 0.33	56.5 ± 26.2
RWOM	0.38 ± 0.12	67.0 ± 2.8	0.62 ± 0.07	45.0 ± 7.1	0.88 (-)*	33.0 (-)*
Transphilic	0.50 ± 0.26	57.0 ± 17.0	0.65 (-)*	41.0 (-)*	0.70 ± 0.05	52.5 ± 9.2
Hydrophobic	0.56 ± 0.04	57.5 ± 2.1	0.50 ± 0.28	55.0 ± 19.8	0.58 (-)*	64.0 (-)*

Avg. influent + effluent	Module 1		Module 2		Module 3	
	Gini	Richness	Gini	Richness	Gini	Richness
Hydrophilic	0.66 ± 0.22	44.3 ± 17.7	0.59 ± 0.13	49.8 ± 10.0	0.73 ± 0.28	46.3 ± 19.3
RWOM	0.50 ± 0.16	59.5 ± 9.1	0.77 ± 0.18	32.8 ± 14.7	0.77 ± 0.16	45.0 ± 17.0
Transphilic	0.52 ± 0.16	56.8 ± 10.5	0.68 ± 0.09	40.7 ± 8.5	0.81 ± 0.14	40.8 ± 14.6
Hydrophobic	0.68 ± 0.15	46.3 ± 13.5	0.54 ± 0.20	53.8 ± 16.5	0.71 ± 0.14	51.3 ± 14.2

* Gini/richness measured only in one of the duplicate columns

Table S8 – Average ATP concentration measured at the column influent and effluent of duplicate columns

	ATP concentrations [pg/g] - Phase 1		
	Average influent ± st. dev.	Average effluent ± st. dev.	Average influent and effluent ± st. dev.
Hydrophilic	40244 ± 47574	12171*	41635 ± 45605
RWOM	22525 ± 17906	10994 ± 8173	16759 ± 4867
Transphilic	14407 ± 8116	12755 ± 1850	13581 ± 4983
Hydrophobic	28175 ± 27739	15478 ± 3612	21826 ± 12063

	ATP concentrations [pg/g] - Phase 2		
	Average influent ± st. dev.	Average effluent ± st. dev.	Average influent and effluent ± st. dev.
Hydrophilic	8770 ± 5183	3898 ± 2514	6334 ± 3849
RWOM	6092 ± 3147	3849 ± 263	4971 ± 1442
Transphilic	5522 ± 1188	8430 ± 5853	6976 ± 3520
Hydrophobic	12802 ± 3126	4632 ± 257	8717 ± 1692

	ATP concentrations [pg/g] - Phase 3		
	Average influent ± st. dev.	Average effluent ± st. dev.	Average influent and effluent ± st. dev.
Hydrophilic	22956 ± 205	8394 ± 3240	15675 ± 722
RWOM	11102 ± 576	5974 ± 1961	8538 ± 693
Transphilic	9204 ± 487	4800 ± 1220	7002 ± 854
Hydrophobic	9876 ± 855	6666 ± 1144	8271 ± 144

* ATP measured only in one of the duplicate columns

Table S9 – Average DOC removal (%) (± st dev) of the columns

	DOC concentrations [mg/L] - Phase 1		
	Average influent ± st. dev.	**Average effluent ± st. dev.**	**Removal [%] ± st.dev.**
Hydrophilic	4.97 ± 0.68 (n = 7)	2.93 ± 0.52 (n = 14)	40.81 ± 9.47 (n = 14)
RWOM	3.78 ± 0.66 (n = 7)	2.53 ± 0.51 (n = 13)	31.64 ± 14.23 (n = 13)
Transphilic	4.67 ± 1.16 (n = 7)	2.91 ± 0.58 (n = 13)	35.80 ± 20.65 (n = 13)
Hydrophobic	5.25 ± 0.92 (n = 7)	3.66 ± 0.89 (n = 13)	31.20 ± 17.68 (n = 13)

	DOC concentrations [mg/L] - Phase 2		
	Average influent ± st. dev.	**Average effluent ± st. dev.**	**Removal [%] ± st.dev.**
Hydrophilic	4.24 ± 0.85 (n = 4)	2.29 ± 0.63 (n = 7)	45.27 ± 7.21 (n = 7)
RWOM	3.45 ± 0.61 (n = 4)	2.51 ± 0.29 (n = 8)	26.40 ± 6.75 (n = 8)
Transphilic	4.85 ± 0.88 (n = 4)	2.73 ± 0.55 (n = 8)	43.72 ± 5.59 (n = 8)
Hydrophobic	3.70 ± 1.14 (n = 4)	2.32 ± 0.66 (n = 8)	36.47 ± 10.98 (n = 8)

	DOC concentrations [mg/L] - Phase 3		
	Average influent ± st. dev.	**Average effluent ± st. dev.**	**Removal [%] ± st.dev.**
Hydrophilic	8.03 ± 0.38 (n = 3)	5.91 ± 0.99 (n = 6)	26.72 ± 9.19 (n = 6)
RWOM	7.61 ± 0.45 (n = 3)	4.89 ± 0.62 (n = 6)	35.87 ± 5.50 (n = 6)
Transphilic	7.90 ± 0.63 (n = 3)	5.73 ± 0.44 (n = 6)	27.09 ± 7.94 (n = 6)
Hydrophobic	8.36 ± 0.46 (n = 3)	5.66 ± 0.47 (n = 6)	32.21 ± 6.71 (n = 6)

Table S10 – Average SUVA removal (%) (± st dev) of the columns

	Phase 1	**Phase 2**	**Phase 3**
	SUVA removal [%]	**SUVA removal [%]**	**SUVA removal [%]**
Hydrophilic	-15.62 ± 76.51	66.41 ± 12.51	17.71 ± 1.86
RWOM	-57.64 ± 48.23	-2.58 ± 19.58	-5.77 ± 8.43
Transphilic	-46.95 ± 70.46	-5.00 ± 28.33	-8.14 ± 3.43
Hydrophobic	14.49 ± 31.31	28.62 ± 23.01	-22.24 ± 7.48

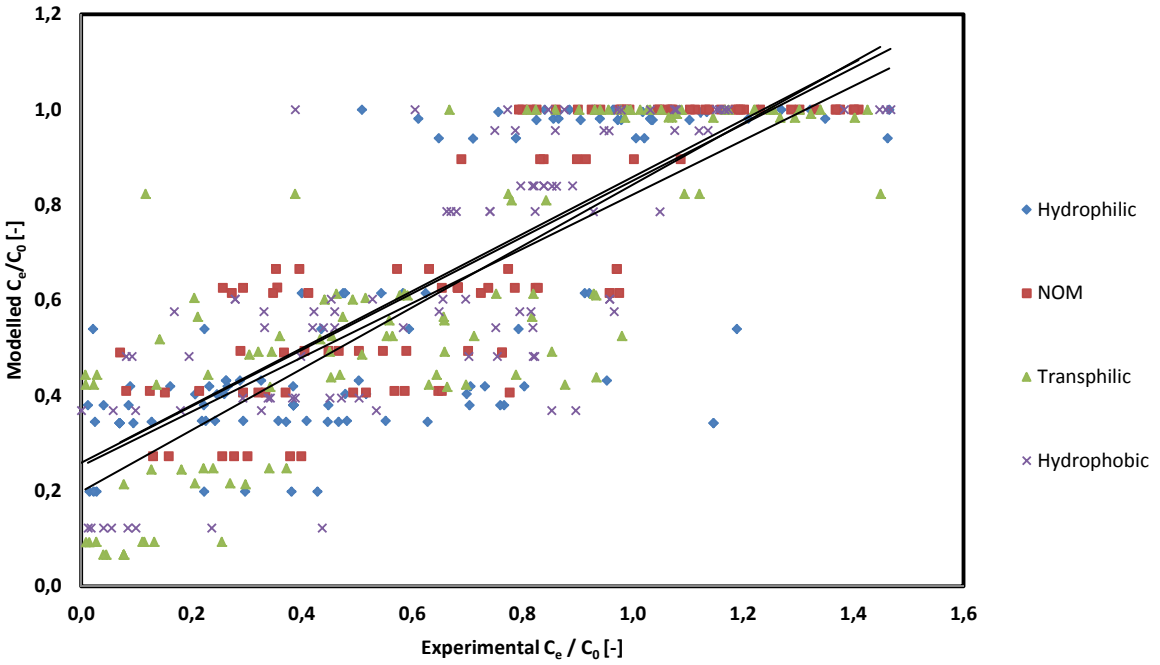


Figure S2 – Experimental versus modelled data points Phase 1[a]

[a] Experimental C_e/C_0 values higher than 1 were mostly observed for the persistent OMPs (e.g. carbamazepine, simazine, atrazine, chloridazon, pirimicarb). However, modelled OMP biodegradation rates were not greatly affected for these OMPs are therefore these data points have not been excluded from the Figure.

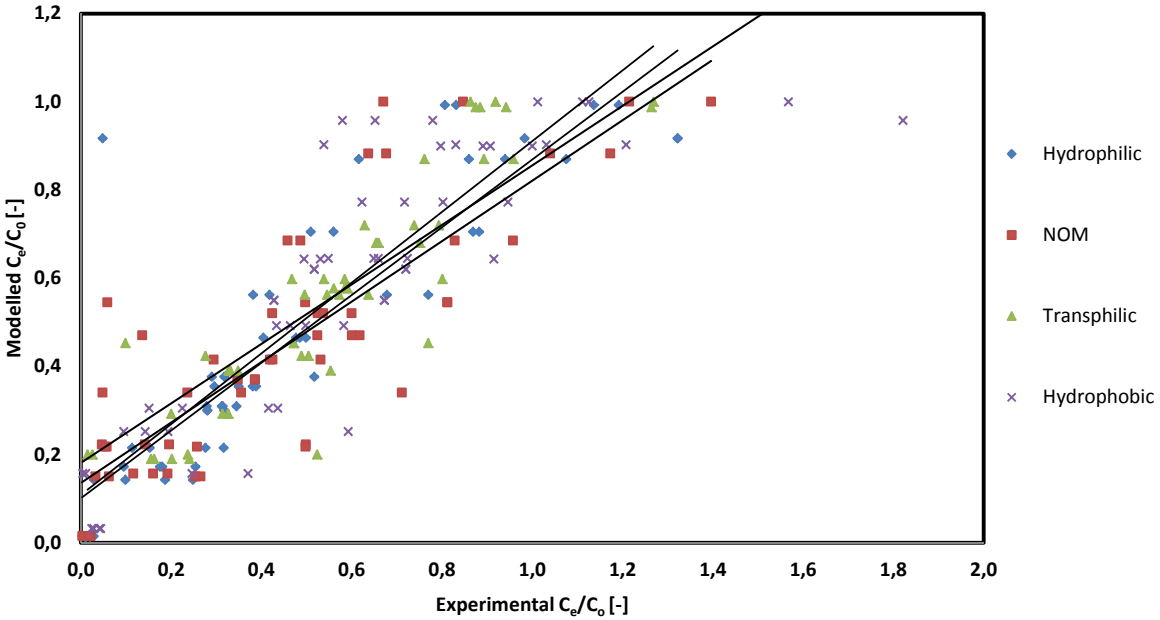


Figure S3 – Experimental versus modelled data points Phase 2[a]

[a] Experimental C_e/C_0 values higher than 1 were mostly observed for the persistent OMPs (e.g. carbamazepine, simazine, atrazine, chloridazon, pirimicarb). However, modelled OMP biodegradation rates were not greatly affected for these OMPs are therefore these data points have not been excluded from the Figure.

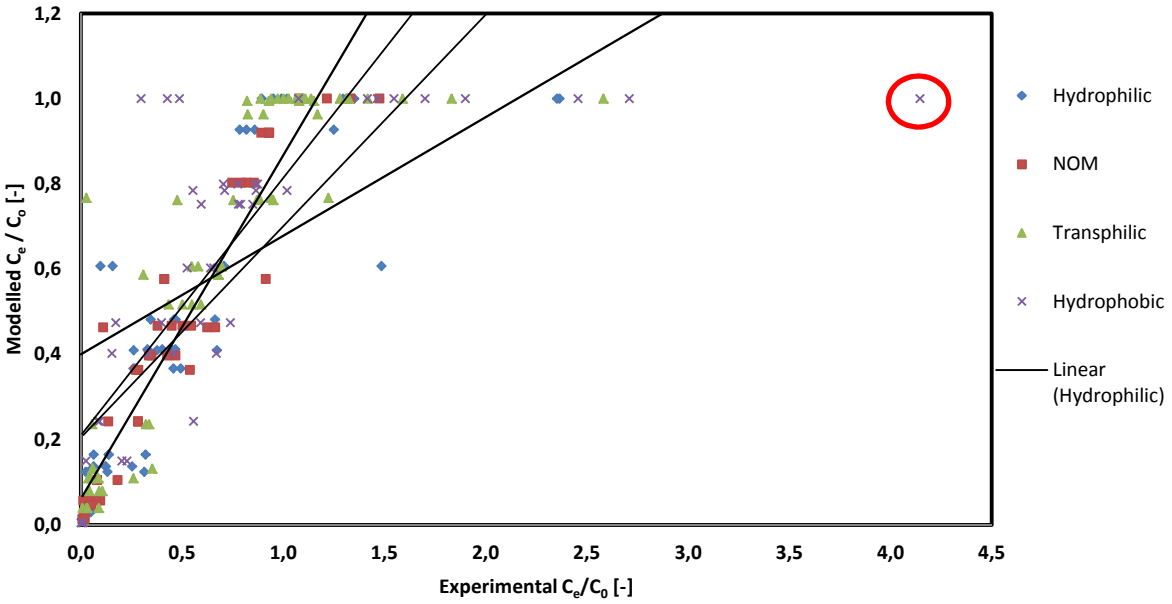


Figure S4 – Experimental versus modelled data points Phase 3[a]

[a] Experimental C_e/C_0 values higher than 1 were mostly observed for the persistent OMPs (e.g. carbamazepine, simazine, atrazine, chloridazon, pirimicarb). However, modelled OMP biodegradation rates were not greatly affected for these OMPs are therefore these data points have not been excluded from the Figure.

Table S11 – Trend lines and R^2 for experimental versus modelled data points (Figures S2, S3 and S4)

	Phase 1		Phase 2		Phase 3	
	Trend line	R^2	Trend line	R^2	Trend line	R^2
Hydrophilic	y = 0.5695x + 0.2519	0.5769	y = 0.768x + 0.1012	0.7685	y = 0.4961x + 0.2047	0.6552
RWOM	y = 0.5987x + 0.2599	0.7035	y = 0.6854x + 0.135	0.6969	y = 0.8051x + 0.0615	0.9014
Transphilic	y = 0.6438x + 0.1987	0.7155	y = 0.8017x + 0.1088	0.8093	y = 0.604x + 0.2098	0.7267
Hydrophobic	y = 0.5919x + 0.2587	0.6253	y = 0.6744x + 0.181	0.7184	y = 0.2782x + 0.3998	0.4425

References

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 Research, 44, pp 4643-4659

Leenheer, J.A., Croué, J.P., Benjamin, M., Korshin, G.V., Hwang, C.J., Bruchet, A. and Aiken, G.R. (2000) Natural Organic Matter and Disinfection By-Products - Characterization and Control in Drinking Water. Barrett, S.E., Krasner, S.W. and Amy, G.L. (eds), American Chemical Society, Washington DC, United States of America.

Stoks, P.G.M., van de Haar, G., Bannink, A. and Zwamborn, C.C. (2011) Jaarrapport 2011 De Rijn.

Vishniac, W., Santer, M. (1957) The Thiobacilli, Bacteriological reviews, 21 (3), pp. 195-213

West, A.G., Patrickson, S.J. and Ehleringer, J.R. (2006) Water extraction times for plant and soil materials used in stable isotope analysis. Rapid Commun. Mass Spectrom. 20, 1317-1321.

Appendix E - Supplementary material Chapter 6

Table S1 – Average pore water velocity, dispersion coefficient and dispersivity α of the three installations

Pilot	Average pore water velocity (υ) [m min^{-1}]	Dispersion coefficient (D) [m^{2}min^{-1}]	Dispersivity α [m]
A	$1{,}03 \cdot 10^{-3}$	$3{,}04 \cdot 10^{-5}$	$2{,}94 \cdot 10^{-2}$
B	$8{,}92 \cdot 10^{-4}$	$1{,}04 \cdot 10^{-4}$	$1{,}16 \cdot 10^{-1}$
C	$8{,}00 \cdot 10^{-4}$	$5{,}10 \cdot 10^{-5}$	$6{,}36 \cdot 10^{-2}$

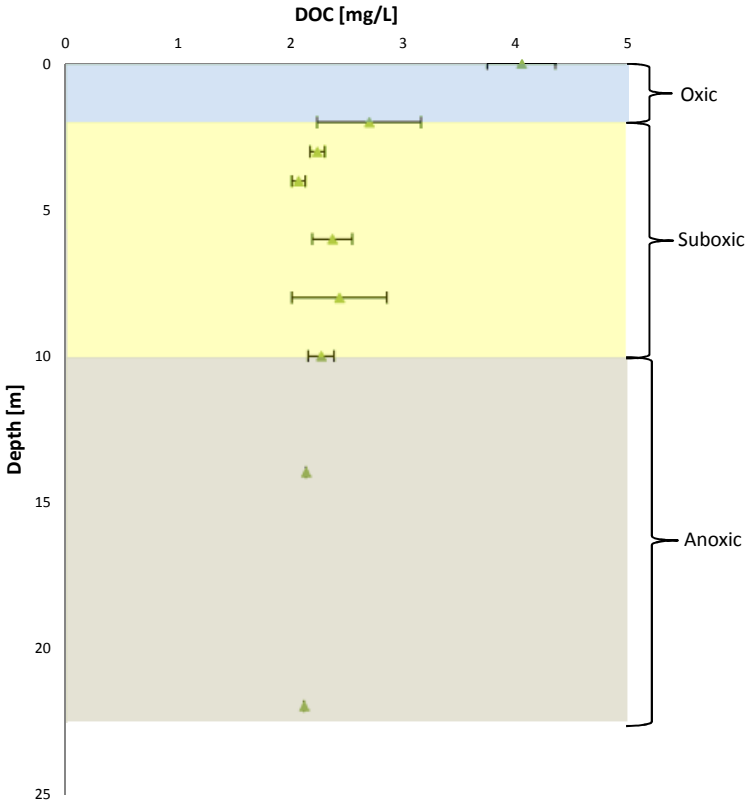


Figure S1 – DOC concentration in suboxic and anoxic pilot

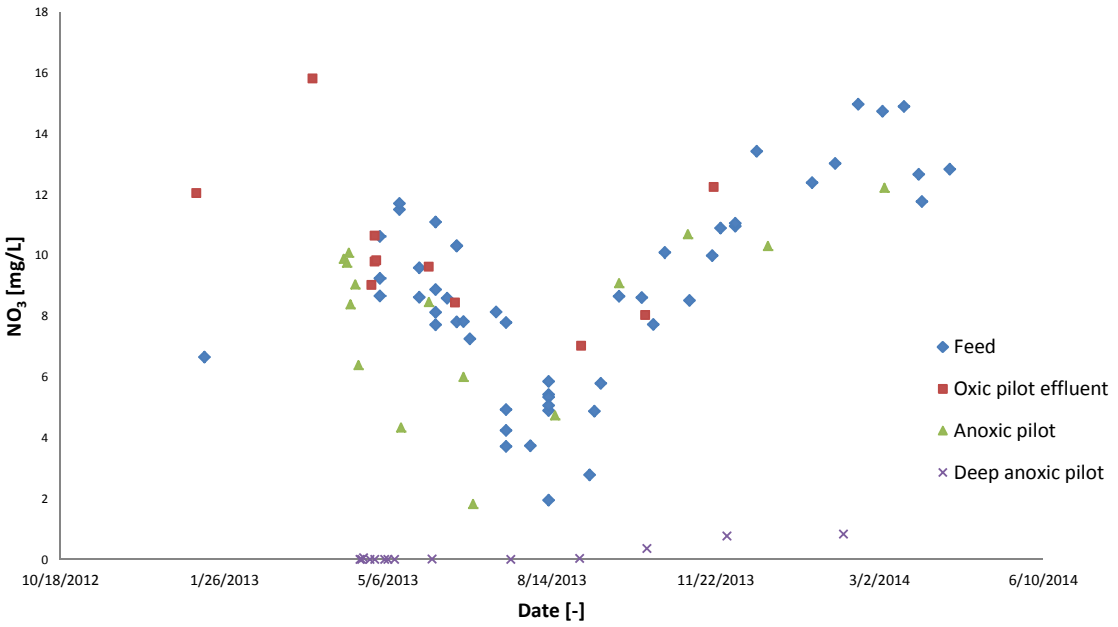


Figure S2 – NO_3 concentrations in the feed and effluent of the oxic, suboxic and anoxic pilot

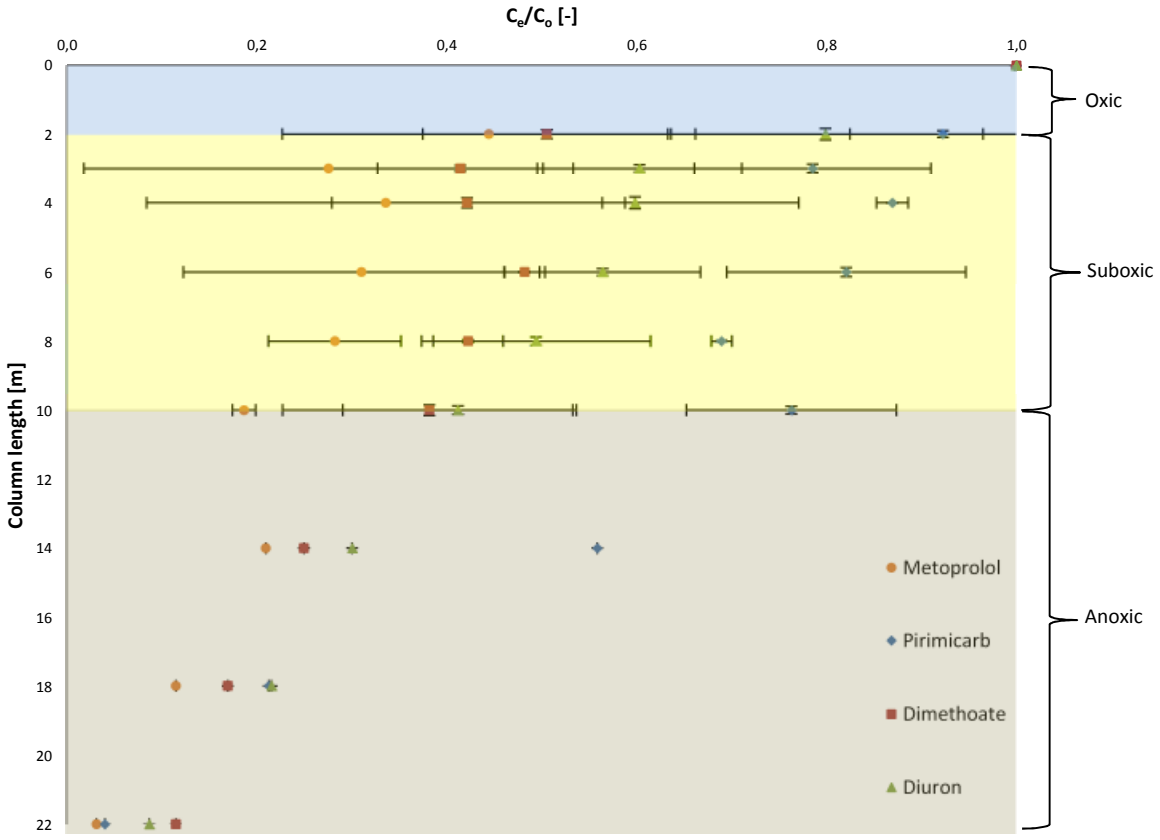


Figure S3 – C_e/C_0 values of metoprolol, pirimicarb, dimethoate and diuron in the different redox zones

Table S2 – Functional groups of the OMPs

OMP	Me	AE	TA	H	SA	Ring	PA	CO	Ethers	Sulfur	Amide	Ester	CA	AAE	Hy	SuA
Dimethoate	3	0	0	0	0	0	0	1	2	2	1	0	0	0	0	0
Sulfamethoxazole	1	0	0	0	0	2	1	0	0	0	0	0	0	0	0	1
Chloridazon	0	0	0	1	0	2	1	1	0	0	0	0	0	0	0	0
Phenazone	2	0	0	0	0	2	0	1	0	0	0	0	0	0	0	0
Lincomycin	4	0	1	0	0	2	0	0	1	1	1	0	0	0	4	0
Atrazine	3	0	0	1	2	1	0	0	0	0	0	0	0	0	0	0
Carbamazepine	0	0	0	0	0	3	0	0	0	0	1	0	0	0	0	0
Clofibric acid	2	0	0	1	0	1	0	0	0	0	0	0	1	1	0	0
Diclofenac	0	0	0	2	1	2	0	0	0	0	0	0	1	0	0	0
Diuron	2	0	1	2	1	1	0	1	0	0	0	0	0	0	0	0
Hydrochlorothiazide	0	0	0	1	1	2	0	0	0	0	0	0	0	0	0	2
Ketoprofen	1	0	0	0	0	2	0	1	0	0	0	0	1	0	0	0
Metoprolol	3	1	0	0	1	1	0	0	0	0	0	0	0	1	1	0
Pirimicarb	6	0	2	0	0	1	0	0	0	0	0	1	0	0	0	0
Simazine	2	0	0	1	2	1	0	0	0	0	0	0	0	0	0	0

Me = Methyl, AE = Aliphatic Ether, TA = Tertiary Amines, H = Halogens, SA= Secondary Amines, PA = Primary Amines, CO = Carbonyl, CA = Carboxylic Acid, AAE = Aryl Aliphatic Ether, Hy = Hydroxyl, SuA = Sulphonamides

List of publications

International refereed journals

Bertelkamp, C., Verliefde, A.R.D., Reynisson, J., Singhal, N., de Jonge, M., van der Hoek, J.P., A predictive multi-linear regression model for organic micropollutants based on a laboratory-scale column study simulating the river bank filtration process, Journal of Hazardous Materials. *In press.*

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., The effect of redox conditions and adaptation time on organic micropollutant removal during river bank filtration: A laboratory-scale column study, Science of the Total Environment. *In press*.

Bertelkamp, C., van der Hoek, J.P., Schoutteten, K., Hulpiau, L., Vanhaecke, L., Vanden Bussche, J., Cabo, A.J., Callewaert, C., Boon, N., Löwenberg, J., Singhal, N., Verliefde, A.R.D. (2016) The effect of feed water dissolved organic carbon concentration and composition on organic micropollutant removal and microbial diversity during river bank filtration. Chemosphere, 144, pp. 932-939

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Callewaert, C., Boon, N., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., A laboratory scale column study comparing organic micropollutant removal and microbial diversity for two soil types. Science of the Total Environment, 536, pp. 632-638, 2015

Bertelkamp, C., Reungoat, J., Cornelissen, E.R., Singhal, N., Reynisson, J., Cabo, A.J., van der Hoek, J.P., Verliefde, A.R.D., Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study, Water Research, 52, pp. 231-241, 2014

Van der Hoek, J.P., Bertelkamp, C., Verliefde, A.R.D., Singhal, N.S., Drinking Water Treatment Technologies in Europe: State of the Art – Vulnerabilities – Research Needs, AQUA, Vol. 63, No. 2, pp. 124-130, 2014

Bertelkamp, C., Reungoat, J., Botton, S., Cornelissen, E., Ghadiri, E., de Jonge, M., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., Transformation of organic micropollutants during river bank filtration: laboratory versus field data, Water Practice & Technology Vol 7 No 4, 2012

Schoutteten, K., Hennebel, T., Dheere, E., Bertelkamp, C., de Ridder, D., Maes, S., Chys, M., Van Hulle, S., Vanden Bussche, J., Vanhaecke, L., Verliefde, A., Effect of oxidation and catalytic reduction of trace organic contaminants on their activated carbon adsorption, Submitted to Water Research

Publications in preparation

Bertelkamp, C., A. Verliefde, N. Singhal, J.P. van der Hoek, Organic micropollutant removal during river bank filtration: How to develop a predictive model? *In preparation*

Conferences and proceedings

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Hulpiau, L., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., The effect of organic carbon composition and concentration on OMP removal and microbial diversity in RBF systems, **Oral presentation**, Ninth International Symposium on Subsurface Microbiology, 5-10 October 2014, Pacific Grove, California, USA

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Singhal, N., Verliefde, A.R.D., van der Hoek, J.P., Organic micropollutants Removal During River Bank Filtration: A Pilot-Scale Study, **Poster presentation**, Ninth International Symposium on Subsurface Microbiology, 5-10 October 2014, Pacific Grove, California, USA

Bertelkamp, C., Sorptie en Biodegradatie van Organische Microverontreinigingen tijdens Bodempassage, **Oral presentation,** Vakantiecursus 2014: K3 in de Watertechnologie, Section Sanitary Engineering, Delft University of Technology, 10 January 2014 Delft, The Netherlands

Bertelkamp, C., Schoutteten, K., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., Sorption and Degradation of Chloridazon and the Formation of its Metabolites under Different Redox Conditions in a River Bank Filtration Pilot, **Oral presentation and proceedings**, YWP Benelux Conference, 2 – 4 October 2013, Luxemburg.

Bertelkamp, C., Kramer, F.C., Reungoat, J., Singhal, N., Cornelissen, E.R., Verliefde, A.R.D., van der Hoek, J.P., Organic micropollutant removal during river bank filtration: Batch studies, **Oral presentation and proceedings**, Water Quality Technology Conference, 4 – 8 November 2012, Toronto, Canada

Van der Hoek, J.P., Bertelkamp, C., Verliefde, A.R.D., Singhal, N.S., Drinking Water Treatment Technologies in Europe: State of the Art – Vulnerabilities – Research Needs, Proceedings 9th International Symposium on Water Supply Technology, 20-22 November 2012, Yokohama, Japan

Bertelkamp, C., Reungoat, J., Botton, S., Cornelissen, E., Ghadiri, E., de Jonge, M., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., Transformation of organic micropollutants during river bank filtration: laboratory versus field data, **Oral presentation and proceedings**, Singapore International Water Week, 1 – 5 July 2012, Singapore

Bertelkamp, C., Reungoat, J., Botton, S., Cornelissen, E., Ghadiri, E., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., Sorption and Biodegradation of Organic Micropollutants During Riverbank Filtration, **Oral presentation**, AWRA Summer Specialty Conference – Contaminants of Emerging Concern in Water Resources II, 25-27 June 2012, Denver, Colorado, USA

Bertelkamp, C., Verliefde A.R.D., van der Hoek, J.P., ESTAB: Emerging Substances Towards an Absolute Barrier, **Oral presentation**, NWO-JSTP Seminar on Micro-pollutants Removal from Urban Water Cycle, 27 June 2012, Delft, The Netherlands

Bertelkamp, C., van der Hoek, J.P., Cornelissen, E., Verliefde, A.R.D., RBF-NF-GAC as absolute barrier for organic micropollutants, **Poster presentation**, 20 – 22 September 2011, Young Water Professionals Conference Leuven, Belgium

Bertelkamp, C., Cornelissen, E.R., Verliefde, A.R.D., Removal of organic micropollutants by riverbank filtration – An overview of (recent) research data, **Oral presentation**, Indo-German Workshop on Bank Filtration for Sustainable Drinking Water Supply, 29 April – 1 May 2011, Dehradun, India

Bertelkamp, C., Lekkerkerker-Teunissen, K., Knol, A.H., Verberk, J.Q.J.C., van Dijk, J.C., Houtman, C.J., Granular Activated Carbon Filtration or Ion Exchange as Pre-Treatment Option for the Advanced Oxidation Process; Advantages and Limitations, **Oral presentation and proceedings**, Water Quality Technology Conference, 14 – 18 November 2010, Savannah, Georgia, USA, AWWA

National publications

Bertelkamp, C., Emerging Substances: Towards an Absolute Barrier (ESTAB), Vakantiecursus 2014: K3 in de Watertechnologie, Sectie Gezondheidstechniek Technische Universiteit Delft, 10 Januari 2014 Delft, Nederland

Editorship

Executive Editor of the online journal Drinking Water Engineering and Science (2013 – 2015)

Biography

Cheryl Bertelkamp was born in 1986 in Naarden, the Netherlands. She obtained her BSc degree in Civil Engineering at Delft University of Technology in 2008 after which she started her MSc Water Management at the same university. She did a three month internship in Australia at Deakin University in collaboration with Coliban Water. She investigated possible causes of high ammonia levels in the wastewater treatment plant effluent, resulting in problems for the subsequent additional treatment processes used to recycle treated wastewater further to a class A water, and received an award from the faculty for this internship. For her MSc thesis, she was involved in a project on organic micropollutant removal with the advanced oxidation process (UV/H_2O_2) at drinking water company Dunea Duin en Water, the Netherlands. She investigated different pre-treatment techniques for the UV/H_2O_2 process regarding their energy savings as well as the effect on the water quality (e.g. scavengers) in the subsequent UV/H_2O_2 process.

In 2010 she graduated *cum laude* and started her PhD research under the supervision of Professor Jan Peter van der Hoek (Delft University of Technology, The Netherlands) and Professor Arne Verliefde (Ghent University, Belgium). Her PhD thesis focused on organic micropollutant removal during river bank filtration and was part of the InnoWater project "Emerging Substances Towards an Absolute Barrier (ESTAB)" and the Topsector Water TKI Watertechnologie project "River bank filtration and organic micropollutant removal". As part of a research exchange, she was a visiting researcher at the University of Auckland, New Zealand for three months under the supervision of Professor Naresh Singhal. She presented/published her research at many international workshops, conferences and in peer reviewed journals.