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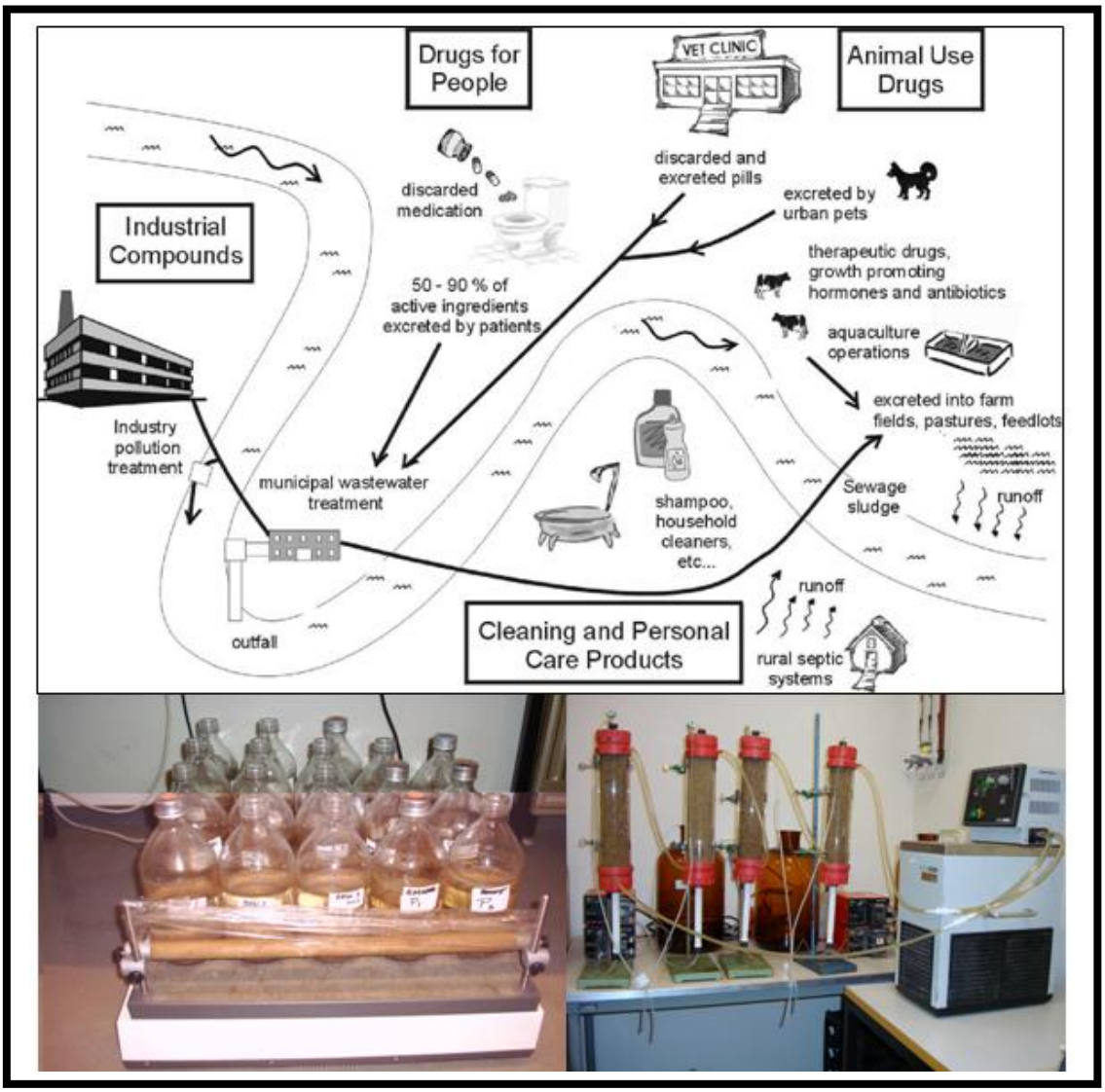

Impact of Biodegradability of Natural Organic Matter and Redox Conditions on Removal of Pharmaceutically Active Compounds during Riverbank Filtration

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Impact of Biodegradability of Natural Organic Matter and Redox Conditions on Removal of Pharmaceutically Active Compounds during Riverbank Filtration

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May 2009

The findings, interpretations and conclusions expressed in this study do neither necessarily reflect the views of the UNESCO-IHE Institute for Water Education, nor of the individual members of the MSc committee, nor of their respective employers.

Dedication

To my sister Aker Deng

Abstract

Riverbank filtration (RBF) is a low cost, robust and sustainable natural filtration process which has been in use for drinking water production for more than a century. During RBF, water filtration is achieved by inducing hydraulic gradient to pass river water through riverbank sediments and recovered from adjacent wells field after mixing with native groundwater. During this soil passage, raw water quality is improved through physical, biological and chemical processes. However, some contaminants in surface water are cleaved and attenuated while some are not eliminated; instead they leach through the subsoil into groundwater aquifers.

Pharmaceutically active compounds (PhACs) are chemicals used in human diseases treatment and animal husbandry. These compounds are not eliminated in human body, but they are conjugated and excreted with urine and feces and are in turn discharged to wastewater treatment plants.

In semi closed urban water cycle where effluent water from wastewater treatment plant is discharged to receiving water bodies and indirectly used as influent water by water treatment facility, a wide range of contaminants such as pharmaceutically active compounds (PhACs) may end up in drinking water. Drinking water treatment works use a wide spectrum of processes, but most of these processes are not designed to remove PhACs.

Laboratory-scale batch and soil column experiments were carried out to simulate attenuation and pathways of pharmaceutically active compounds in riverbank. Maas river water (MRW), secondary effluent (SE) in 50:50 ratio, Maas river water amended with synthetic organic matter (SOM, ozonation BPDs) and plant-derived water were used as influent. Silica sand of size 0.8 – 1.25 mm was used as a filter media. PhACs and odour compounds (geosmin and 2-MIB) measurement was conducted at TZW and TU-Dresden (Germany) respectively.

Most targeted compounds were removed above 90%, in 60 days retention time in laboratory-scale batch experiments. However, gemfibrozil, diclofenac and clofibric acid were less removed in plant-derived water due its less biopolymer fraction of BDOC. Moreover, carbamazepine was persistent. Geosmin and 2-MIB were eliminated in batch experiments in the first 30 days retention time.

Long soil columns were conducted to study effect of redox conditions and addition of secondary effluent to Maas river water on fate of PhACs. Removal of targeted PhACs was similar in both oxic and anoxic conditions, except for carbamazepine which was persistent. Addition of SE reduced removal of gemfibrozil, diclofenac and bezafibrate by more than 15%. Geosmin and 2-MIB were removed above 80% during oxic and anoxic conditions.

In short soil column study conducted to investigate removal mechanisms of PhACs in RBF, removal of bezafibrate, diclofenac, gemfibrozil and ibuprofen decreased by more than 20% in TW (ATP = 15 pg ATP/g) compared to MRW+SOM (ATP = 48 pg ATP/g). Removal of hydrophilic compounds of phenacetine, paracetmamol, pentoxifylline and caffeine from more than 90% in tap water and MRW+SOM to less than 20% in demineralised water spiked with 40 mM sodium azidw (ATP = 0.4 pg ATP/g). Geosmin and 2-MIB were removed above 90% in soil columns with tap water and MRW+SOM (biotic) while their removal decreased to 75.3% for geosmin and 66.6% for 2-MIB in soil column fed with demineralised water spiked with sodium azide (abiotic).

***Keywords**: Riverbank Filtration, Biodegradation, Pharmaceutically Active Compounds, Redox Conditions, Natural Organic Matter.*

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Table of Contents

List of Tables

List of Figures

List of symbols

AOPs	Advanced Oxidation Processes
BDOC	Biodegradable Dissolved organic Matter
DOC	Dissolved Organic Carbon
DW	Demineralised Water
EBCT	Empty Bed Contact Time
EDCs	Endocrine Disrupting Compounds
F-EEM	Fluorescence Emission-excitation Matrix
GAC	Granular Activated Carbon
PDW	Plant-derived water
MRW	Maas River Water
MRL	Method Reporting Limit
NF	Nanofiltration
NOM	Natural Organic Matter
PCPs	Personal Care Products
PhACs	Pharmaceutically Active Compounds
RBF	Riverbank Filtration
MRW	Maas River Water
RO	Reverse Osmosis
SAR	Structure-Activity Relationship
SE	Secondary Effluent
SOM	Synthetic Organic Matter
SP	Sampling Point
TW	Tap Water
UVA	Ultra Voilet Absorbance
WWTPs	Wastewater Treatment Plants

1 INTRODUCTION

1.1 Background

One environmental consequence of growing population is increasing pressure on natural resources. Demand for water is growing rapidly as population and industrial activity expand and irrigated agriculture (the largest use) continues to increase. From 1940 to 1990, for example, withdrawals of freshwater from rivers, lakes, and underground aquifers increased by a factor of four. Many current patterns of water withdrawals are clearly unsustainable, such as pumping from subsoil aquifers at rates far greater than they are recharged. Water shortages are already critical in some regions, posing obstacles and threats to freshwater habitats (UN/WB, 1996). In industrialized and urban areas, surface waters are to a high level exposed to anthropogenic environmental impacts and are therefore often contaminated with a wide spectrum of organic trace compounds (Schmidt et al.,2007). As a result, many cities` waterworks are faced with the challenge to secure unpolluted water sources to provide safe water to inhabitants. Hence, low cost treatment methods such as artificial recharge and riverbank filtration become important to improve the quality of drinking water(Alder et al., 2006).

Riverbank filtration (RBF) is a water treatment process that makes use of surface water that has naturally infiltrated into groundwater through the riverbed or bank(s) and is recovered by a pumping well (Schijven et al., 2002). This is generally performed where the quality of water in the river is not suitable for water supplies due to intermittent or chronic pollution. The streambed sediments and aquifer materials provide 'slow-rate infiltration' and the recovered water is of higher and more consistent quality than water drawn directly from the river (Dillon et al., 2001). Riverbank filtration is a robust barrier, low cost, and multi-objective process which is sustainably used in both developed and developing countries to produce drinking water from raw water sources under influence of wastewater. Furthermore, it is relevant to large and small systems (Amy, 2008).

The effectiveness of bank filtration has long been recognized in Europe. Many utilities in North America are also utilizing this technology. However, their treatment objectives are different. In North America, RBF is considered as only a pre-treatment for microorganisms, particles and some dissolved organic carbon (DOC) in a multiple barrier concept whereas, in Europe, it is often considered as a major part of the overall treatment that produces a biostable, high quality water that can be distributed after little additional treatment without chlorine addition (Grünheid et al., 2005).

In partially closed water cycles, where treated sewage is used indirectly for potable use via managed aquifer recharge such as bank filtration, pharmaceutical residues may even appear at low concentrations in groundwater and drinking water (Reemtsma et al., 2006). Human and veterinary applications are the main sources of pharmaceutically active compounds (PhACs) in the environment that are introduced primarily through excretion and the subsequent transport in sewage, whereas direct disposal of unwanted or expired drugs in the sewage is believed to be of minor importance.

Despite the fact that many researches have been carried out on riverbank filtration, detailed research about the removal of PhACs in relation with biodegradability of natural organic matter (NOM) under prevailing redox dynamics during riverbank filtration is essential, to bridge the knowledge gap between the impact of redox conditions and the fate of organic micro-pollutants during riverbank filtration.

1.2 Problem identification

Consumption of human pharmaceutically active compounds (PhACs) is substantially increasing world wide. Based on the size of country; this consumption is in the range of tones per annum per one PhAC. The amounts consumed are expected to keep increasing due to improvement in health care system (Kujawa-Roeleveld et al., 2007). Pharmaceutically active compounds (PhACs) from human medical care have been detected in sewage water, in surface water and even in groundwater (Heberer, 2002a; Tixier et al., 2003). PhACs in wastewater and surface water can reach groundwater by several ways including riverbank filtration, artificial groundwater recharge, naturally occurring influent groundwater flow conditions, and leaky sewage systems. In the case of wastewater reuse, sewage water irrigation, and application of sewage sludge on agricultural land, the pharmaceuticals pass through the unsaturated zone before reaching an aquifer. Not only excretion but also disposal of pharmaceuticals leads to occurrences in the aquatic system, because pharmaceuticals are either disposed into the toilet or with the garbage (Scheytt et al., 2006).

Many pharmaceuticals do not exhibit an acute aquatic toxicity, but have a significant cumulative effect on the metabolism of non-target organisms and the ecosystem as a whole (Bendz et al., 2005).

Since the processes during RBF are very complex, it is difficult to predict the fate of trace organics during RBF or to estimate important factors that influence their degradation. In addition to redox conditions, factors such as retention time, initial biodegradable organic carbon (BDOC) concentration, soil properties and hydrogeological conditions may affect the final concentration (Grünheid and Jekel, 2004). Holm et al. (1995) stated that a number of pharmaceuticals have shown to be redox sensitive. Redox changes during artificial recharge are of particular importance, since they may cause the appearance of the undesired metals Fe^{2+} and Mn^{2+} (Bourg and Bertin, 1993).

Due to the amounts used and due to the nature of their application, PhACs belong to the environmentally relevant compounds. Because they are produced and administered with the aim of causing biological effect, their occurrence in the groundwater is not only of scientific but also of public interest. To date, many of the possible actions and biochemical ramifications on non-target organisms (aquatic biota) are not fully understood, and many may be completely unknown (Daughton and Ternes, 1999). The presence of anthropogenic substances; including pharmaceuticals, that potentialy can pose risks on human health and affect aquatic organisms' endocrine systems through exposure to contaminated aquatic recreational source or drinking water, is increasing level of concern among scientists and policymakers around the world (Ghijsen and Hoogenboezem, 2000).

Contamination of freshwater sources with emerging micropollutants is one of the driving forces for scientists to conduct more research on the removal of these substances during riverbank filtration.

1.3 Goal and objectives

The overall goal of this research is to conduct an assessment of effectiveness of riverbank filtration for removal of pharmaceutically active compounds (PhACs), with special emphasis on the impact of biodegradable organic matter related to PhACs removal.

The specific objectives of this study are:

1- To study the fate of PhACs during RBF by conducting laboratory-scale experiments.
2- To analyse the impact of natural organic matter present in water and redox conditions on the removal of pharmaceuticals during soil passage.
3- To study biodegradation, sorption and persistence of pharmaceutical active compounds during RBF and the use of microbial activity to assess the potential for biodegradation of contaminants

2 LITERATURE REVIEW

2.1 Pharmaceutically active compounds (PhACs)

2.1.1 PhACs in the environment

The increasing worldwide contamination of freshwater systems with thousands of micropollutants is one of the key environmental problems humanity is facing, even though compounds tend to be present at low concentrations (Schwarzenbach et al., 2006). In the past few years, the detection of pharmaceutically active compounds (PhACs), such as antibiotics, analgesics, blood lipid regulators or contrast agents in the aquatic environment has been recognized as one of the most important emerging concerns in environmental chemistry (Massmann et al., 2005).

Pharmaceuticals are defined as chemicals used for the treatment or prevention of illness. As such, they can range from compounds used for cancer treatment and birth control to antibiotics used to combat infection to compounds used to relief pain (e.g. aspirin and ibuprofen). They are found in personal care products such as fragrances, disinfectants and antiseptics, sunscreen agents, and preservatives. Pharmaceuticals are also used in veterinary health care e.g. antibiotics and growth hormones (Sawyer et al., 2003).

The main sources and emission routes for PhACs and Personal care products (PCPs) to the environment are effluent water from municipal wastewater treatment plants, disposal of unused PhACs, manure containing veterinary pharmaceuticals and industrial wastewater and solid waste from the production of PhACs and PCPs (Kiwa and Stowa, 2004). Schematic drawing of origins and emission routes of PhACs is shown in Figure 2.1.

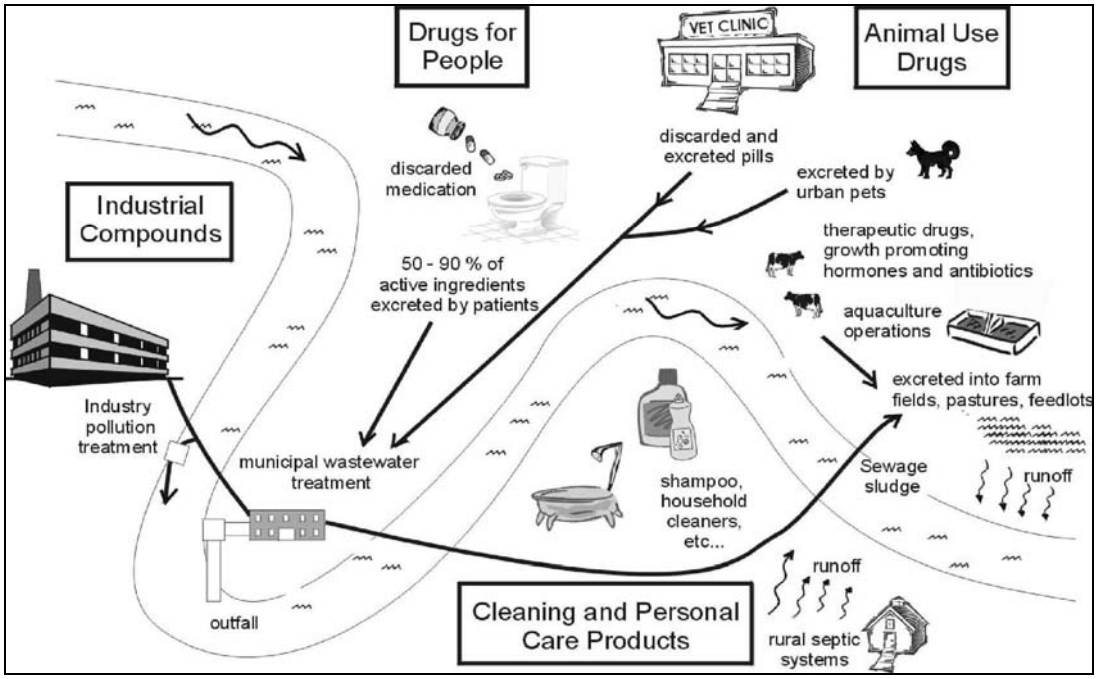


Figure 2.1 Origins and emission routes of PhACs detected in water

Source: (Holtz,2006)

Many pharmaceuticals used in human medical care are not eliminated in the human body. They are excreted by the human body only slightly transformed or even unchanged often conjugated to polar molecules (e.g. as glucoronides) (See Table2.1). These conjugates are easily cleaved during sewage treatment and, thus, several pharmaceutically active compounds (PhACs) are discharged almost unchanged from municipal sewage treatment plants (STPs) into the receiving waters (Daughton and Ternes, 1999; and Heberer, 2002b). Bendz et al., (2005) showed that sewage treatment plants (STPs) play a crucial role in the separation of PhACs into two exposure pathways associated with aquatic and the solid and the subsequent introduction into the environment. In addition to that, partitioning between phases depends in part on the degree of polarity of the particular compound. Furthermore, sludge material and consequently terrestrial environments are likely to be the destination for less polar or non-polar substances, whereas the polar substances are expected to remain primarily in the aqueous phase. He concluded that a large number of PhACs are polar and neither volatile nor biodegradable, thus escaping sedimentation and biological treatment in STPs; these compounds represent the bulk of the load into aquatic environments.

Table2.1 Urinary excretion rates of unchanged active ingredient for selected pharmaceuticals

Compound	Pharmaceutical product group	Parent compound excreted (%)	Reference
Amoxycillin	Antibiotic	60	Bound and Voulvoulis, (2005)
Atenolol	Beta-blocker	90	Bound and Voulvoulis, (2005)
Bezafibrate	Lipid regulator	50	Bound and Voulvoulis, (2005)
Carbamazepine	Antiepileptic	3.0	Bound and Voulvoulis, (2005)
Cetirizine	Antihistamine	50	Bound and Voulvoulis, (2005)
Clofibric acid	Active metabolite	6.0	Alder et al., (2006)
Diclofenac	Anti-inflammatory	15	Alder et al., (2006)
Erythromycin	Antibiotic	25	Bound and Voulvoulis, (2005)
Felbamate	Antiepileptic	40-50	Bound and Voulvoulis, (2005)
Ibuprofen	Analgesic	10	Bound and Voulvoulis, (2005)
Indometacin	Anti-inflammatory	10-20	Alder et al., (2006)
Metoprolol	Beta-blocker	10	Bound and Voulvoulis, (2005)
Paracetamol	Painkiller	4.0	Bound and Voulvoulis, (2005)
Propanolol	Beta-blocker	<1.0	Alder et al., (2006)
Sulfamethoxazole	Antibiotic	15	Bound and Voulvoulis, (2005)

Further investigations of groundwater samples have shown, that polar PhACs detected in the surface waters may also leach through the subsoil into the groundwater aquifers whenever contaminated surface water is used for groundwater recharge. Due to their polar structures some of the persistent PhACs are not significantly adsorbed in the subsoil (Heberer et al., 2001).

A review of research data conducted by Heberer (2002a) to investigations carried out in Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, The Netherlands, and The U.S., revealed that more than 80 compounds, pharmaceuticals and several drug metabolites were detected in the aquatic environment. Several PhACs from various prescription classes have been found at concentrations up to the µg/l-level in sewage influent and effluent samples and also several surface waters located downstream from municipal sewage treatment plants (WWTPs). Table2.2 and Figure 2.2 show the most frequently detected PhACs in WWTPs effluents. The studies show that some PhACs originating from human theraphy are not eliminated completely in the municipal WWTPs and are, thus, discharged as contaminants into the receiving waters (Heberer, 2002a).

Table2.2 Pharmaceuticals and Personal care products concentrations frequently detected in WWTPs effluents

Pharmaceutical class	Median concentration (ng/L)	Maximum concentration (ng/L)	Reference
Analgesics			
Acetylsalicylic acid, Diclofenac, Ibuprofen, Naproxen, Paracetamol and Phenazone	160 - 810	600-6000	(Kiwa and Stowa, 2004)
Antibiotics			
Amoxicillin, Ciprofloxacin, Erythromycin, Roxithromycin Indometacine, Oxytetracyclin, Sulfamethoxazole and Trimethoprim	300 - 2500	6000	(Kiwa and Stowa, 2004)
Fibrates/lipid regulators (Antihyperlipidamics)			
Bezafibrate, Clofibric acid, Fenofibric acid, Pentoxiphylline and Gemfibrozil	400-2200	1000 - 7000	(Kiwa and Stowa, 2004)
Tranquillizers			
Diazpam	—	40	(Kiwa and Stowa, 2004)
X-ray contrast media			
Amidotrizoic acid, Iopamidol, Iopromide and Iomeprol	—	11000	(Kiwa and Stowa, 2004)
Estrogens			
17-α-ethinylestradiol (EE2)	2 to 20	60	(Stumpf et al., 1996)
Personal care products			
Musk ketone and Musk xylene	20	410	(Kanda et al., 2003)
Galaxolide	6600	13300	(Kanda et al., 2003)
Tonalide	2100	4360	(Kanda et al., 2003)
Celestoide	120	210	(Kanda et al., 2003)

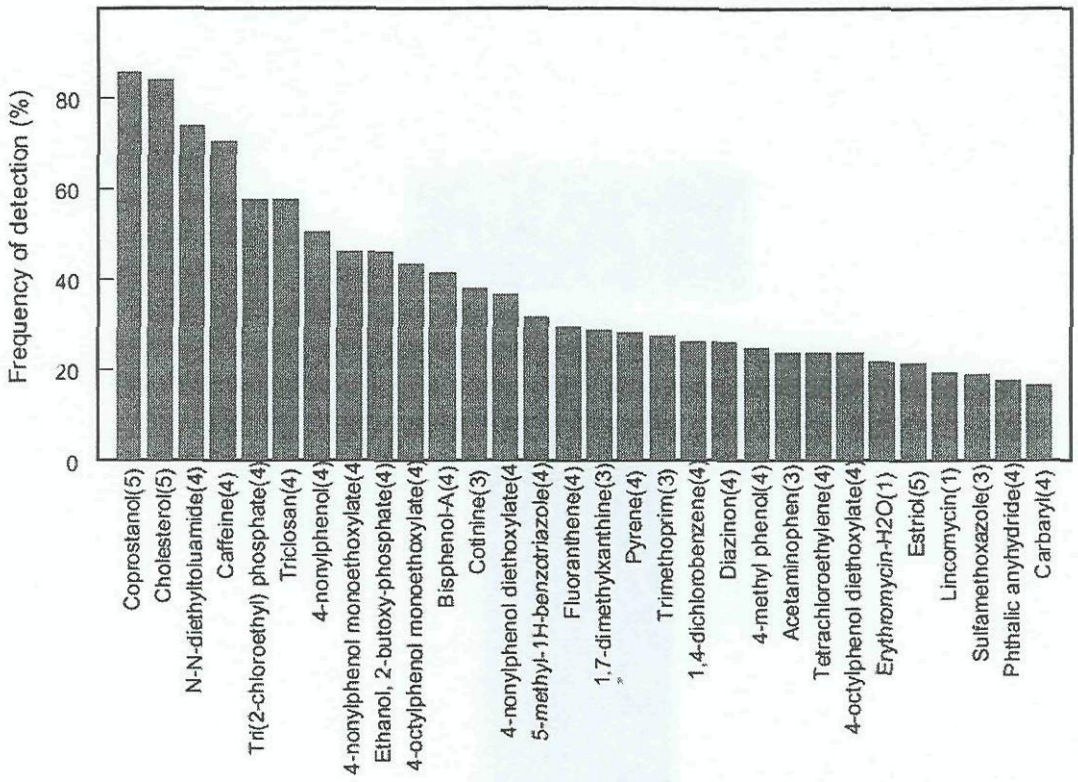


Figure 2.2 Most frequently detected compounds

Source: (USGS, 2002)

2.1.2 Removal of PhACs by water treatment processes

Drinking water treatment works use a wide range of processes, but these processes are not specially designed to remove pharmaceuticals that may be present in source water. However, biodegradation on slow sand filters and/or sorption to particles removed by coagulation may reduce concentration present in the treated effluent for some PhACs (Watts et al., 2007).

a) Removal of PhACs by coagulation process

Coagulation is perceived as a process during which particles in water are destabilized by dosing chemical additives and forming rapidly small flocs. These stable particles have a negative charge which is neutralised through coagulation mechanisms such as double layer compression, charge neutralisation, sweep flocculation and inter particle bridging. However, selection of the mechanism to be used is dominated by factors such as selected coagulant, its dose and water quality (Parsons and Jefferson., 2006). Snyder et al. (2007) studied removal of PhACs, EDCs and PCPs by coagulation process using surface water from four rivers in U.S.A., namely, Colorado river water (CRW), Passaic river water (PRW), Ohio river water (ORW), and Suwannee river water (SRW). Two coagulants, aluminum sulfate (alum, $Al_2(SO_4)_3$) and ferric chloride (ferric, $FeCl_3$), were used in jar tests simulating coagulation, flocculation, and sedimentation. Calcium hydroxide ($Ca(OH)_2$) and soda ash (Na_2CO_3) were used to evaluate chemical softening treatment in separate jar test. Removal likely occurred partitioning onto the particulate matter initially present in the source water or partitioning/adsorbing onto metal (hydro)oxide or carbonate precipitates formed during coagulation, the average percent

removal for the four water studied, was less than 15% for 34 of the 36 compounds. Table2.3 summarizes the removal categories by coagulation for some compounds.

Table2.3 Summary of full-scale occurrence of PhACs and percent removal by coagulation

Target compound	Full-scale utilities detected at 2*MRL (n)	Degree of removal observed			
		< 20%	20-50%	50-80%	> 80%
Acetaminophen	1				1
Atrazine	11	11			
Caffeine	14	12	1	1	
Carbamazepine	11	8	1	1	1
DEET	14	12	2		
Dilantin	11	8	3		
Erythromycin	3	1		2	
Gemfibrozil	7	4	1	2	
Ibuprofen	10	10			
Iopromide	11	8	3		
Meprobamate	9	9			
Metolachlor	6	6			
Naproxen	5	3			2
Oxybenzone	1			1	
Sulfamethoxzole	11	5	1		5
TCEP	14	6	3	3	2
Triclosan	3	1	1	1	
Trimethoprim	2			2	

MRL: Method reporting limit *Source*: (Snyder et al., 2007)

Octanol-water partition coefficient log K_{ow} of compounds provides a rough indication of percent. If the compound of concern has a log K_{ow} greater than 5.0, then some removal could be expected due to particle binding and subsequent settling/filtering (Tolls., 2001).

Vieno et al. (2006) carried out a number of jar test experiments using spiked deionized water, lake water and commercial humic solutions using aluminum (pH 6) and ferric sulphate (pH 4). In dieonized water, less than 10% of the pharmaceuticals were removed by coagulation with the exception of diclofenac, which was removed up to 66% with ferric sulphate. However, diclofenac was the only pharmaceutical removed by ferric sulphate coagulant from the Lake water while the removal of other pharmaceuticals was impaired by the presence of lower molecular weight natural organic matter (NOM). He concluded that neutral pharmaceuticals such as carbamazepine and sulfamethoxazole can not be removed by coagulation (Watts and Maycock, 2007).

d) Removal of PhACs by Filtration

Filtration is often taken to mean passing water (with physical impurities content) through a granular bed of media at a relatively slow velocity. Particles collide and stick to filter grains during water passage allowing water to flow with less particles content (Parsons and Jefferson., 2006).

Filtration provides polishing of a potable water supply and is required for every surface water (Droste, 1997). Removal of the phenazone pharmaceuticals by filtration process (summarized in Table2.4) reported by Reddersen et al. (2002) appears very good. Contrariwise, removal of the phenazone metabolite, AMDOPH was poor.

Table2.4 Removal of phenazone type pharmaceuticals and their metabolites by aeration and filtration

Source water and treatment	Compound	Concentration in source water (ngL^{-1})	Percentage removal by WTP (%)
Polluted groundwater, Germany (aeration followed by biologically active clay and sand filters)	Phenazone	3950	90
	Propiphenazone	1230	90
	Demethylamino-phenazone	400	>90
	AMDOPH	1200	25

Source: (adapted from Reddersen et al., 2002)

c) Removal of PhACs by Activated Carbon

Activated carbon is broadly used in the water industry to remove organic and in organic matter. It effectively removes substances such as natural organic matter, pesticides, taste and odour and algal toxins (Parsons and Jefferson., 2006). During an evaluation carried out by Snyder et al. (2007) for activated carbon facilities, three full-scale drinking water utilities and one water reuse facility were examined, where drinking water facility number one, regenerates regularly its activated carbon, while the other two operate in biological mode. Data indicated that fresh GAC is highly effective for the removal of trace organic contaminants, while GAC that is not regularly replaced/regenerated is relatively ineffective. Table 2.5 and Table 2.6 present the studied water utilities and percent removal by GAC.

Table 2.5 Full-scale GAC facilities investigated

Utility	Carbon type	Carbon source	Biological treatment
Drinking water – 1	Calgon Filtrasorb-400	Bituminous Coal	No
Drinking water – 4	Calgon Filtrasorb-300	Bituminous Coal	Yes
Drinking water – 19	Calgon Filtrasorb-820	Bituminous Coal	Yes
Drinking water – 6	Unknown	Unknown	Yes

Source: (Snyder et al., 2007)

Table 2.6 Results of GAC tests carried out on full-scale drinking water treatment plants

Compound	Drinking water # 1 Percent removal (%)	Drinking water # 2 Percent removal (%)	Drinking water # 3 Percent removal (%)
Atrazine	>99	5.9	NA
Caffeine	>41	36	<1.0
Carbamazepine	>54	NA	<1.0
DEET	>44	38	29
Dilantin	>44	NA	NA
Estradiol	NA	>84	NA
Erythromycin	>44	NA	NA
Galaxolide	NA	>9.0	NA
Gemfibrozil	>16	NA	52
Ibuprofen	>9.0	>58	14
Iopromide	>69	<1.0	16
Meprobamate	>16	NA	NA
Metolachlor	>91	NA	NA
Oxybenzone	<1.0	>58	NA
Sulfamethoxzole	>83	NA	NA
TCEP	NA	NA	40

Source: (Snyder et al., 2007)

Kim et al. (2007) investigated the treatment efficiency of micropollutants, including a number of pharmaceuticals, in drinking water processes using different purification methods. All compounds were reduced to below the analytical reporting limits in the finished drinking water. Table 2.7 shows the investigated compounds.

Table 2.7 Removal of pharmaceuticals by GAC

Source Water	Compound	Concentration in source water (ng/L)	Removal (%)
Paldang Lake	Diclofenac	143	100
	Ibuprofen	15	100
	Meprobamate	4,8	100
	Androstenedione	45	100

Source: (Kim et al., 2007)

d) Removal of PhACs by Chlorine Oxidation

Chlorine reacts selectively with electron rich bonds of organic chemicals (e.g., C=C bonds in aromatic rings). Electron donating substitutes in organic molecules tend to increase reactivity, while electron withdrawing groups decrease reactivity. Phenolic steroids (e.g., estradiol, estrone, estriol, and ethynyl estradiol) can be readily oxidized

(Westerhoff et al., 2004). The rapid reactions of phenolic compounds with free chlorine are mainly through the electrophilic attack of the deprotonated phenolate anion (Gallard and Von Gunten, 2002). This reaction results in sequential chlorine additions to the aromatic ring followed by ring cleavage and subsequent formation of THMs (Greyshock and Vikesland, 2006).

e) Removal of PhACs by Ozone and ozone/hydrogen peroxide oxidation

Ozone is a strong oxidant and disinfectant. Unlike free chlorine or chloramine, ozone decays rapidly within minuets after its addition to water and results in the formation of fewer halogenated disinfection by-products. Ozone reacts with organic contaminants through either the direct reaction with molecular ozone or through the formation of free radicals, including the hydroxyl radicals (HO·). Both molecular ozone (O_3) and hydroxyl radical pathways can lead to transformation of organic compounds (Snyder et al., 2007). In the direct pathway, ozone is a selective electrophile that reacts quickly with amines (phenazone, dimethylaminophenazone, pentoxifylline), phenols, and double bonds (caffeine, propyphenazone) in aliphatic compounds, while the HO· reacts less selectively than ozone and with faster reaction rates, with second order rate constants (k_{OH}) in the order of 10^8 to 10^{10} $M^{-1}s^{-1}$ (Snyder et al., 2007). Carlile et al. (1996) stated that many EDCs/PCPs react directly with ozone resulting in significant decreases in concentrations under conditions used for disinfection. Sacher et al. (2002) pointed out that the use of an advanced oxidation process (AOP) will increase the destruction of target contaminants. They added that clofibric acid could not be as efficiently removed as diclofenac, carbamazepine, and bezafibrate by direct ozonation.

f) Removal of PhACs by Ultraviolet irradiation and ultraviolet/hydrogen peroxide oxidation

Mazellier et al. (2003) studied the photodegradation of 4-tert-octylphenol at 253.7 nm in pure aqueous solution and in simulated lake water. This study determined the photolysis quantum yield as 0.058±0.004 and the HO· rate constant k= $(6.4\pm0.5)\times10^9$. Pereira et al. (2005) compared the degradation kinetics of six pharmaceuticals (ciprofloxican, carbamazepine, iohexol, clofibric acid, naproxen, ketopeofen) in drinking water and wastewater, using low-and medium-pressure collimated beam reactors. The HO· radical rate constants were large for all pharmaceuticals, ranging from 3×10^9 (ciprofloxacin) to 1.2×10^{10} (ketoprofen) $M^{-1}s^{-1}$ (Snyder et al., 2007). When compared with conventional treatment processes such coagulation/flocculation and activated carbon in removing micro-pollutants including PhACs, AOPs and UV processes have great potential in treating the whole range of chemicals, typically better than coagulation with metal salts and comparable with activated carbon (Parsons and Jefferson, 2006). However, UV doses used for treatment of micro pollutants must be several orders of magnitude higher than those used for disinfection (< 30 mJ/cm^2) to obtain an effective removal (Kiwa and Stowa, 2004). Summary of removal of PhACs by some water treatment processes is shown in Table 2.8.

Table 2.8 Unit processes and operations used for micropollutant removal

Classification	GAC	AOP	UV	Cl2/ClO2	Coagulation
Estroids	>90	>90	>90	<20	<20
Industrial chemicals	>90	>90	>90	>90	<20-40
Antibiotics	40-90	20-90	40-90	20-90	20-40
Antidepressants	70-90	20-90	40-90	20-70	20-40
Anti-infalamants	>90	20-90	70-90	20-70	<20
Lipid regulators	>90	—	>90	20-70	<20
X-ray contrast media	70-90	70-90	20-90	20-70	20-40
Synthetic musks	70-90	70-90	>90	20-70	20-40
Antimicrobials	70-90	70-90	40-90	20-70	20-40
Surfactants	>90	>90	40-90	<20	20-40

Source: (Parsons and Jefferson, 2006)

g) Removal of PhACs by Membranes

Membranes filtration separates contaminants from water based upon molecular size and/or electrostatic interactions on the membrane surface. In some cases, organic contaminant adsorb onto membrane surfaces and/or particulates in the water, which impacts the removal of the contaminant by membrane filters. Size, charge, and hydrophobicity of EDCs and PCPs emerge as critical characteristics influencing the removal effectiveness of filtration membranes. Microfiltration and ultrafiltration, both considered low pressure membranes, generally remove only those EDCs/PCPs that adsorb onto colloids or particulates in the water. EDCs/PCPs can be removed by high-pressure membranes, such as reverse osmosis (RO) and tight nanofiltration (NF), commonly used for rejection of inorganic and organic contaminants due to their smaller pore sizes and corresponding lower molecular weight cut-offs (Huang and Sedlak, 2001). Bellona et al. (2004) showed that the removal of organic compounds by RO and NF can be qualitatively predicted based on compound structure and membrane properties. Removal of some pharmaceuticals is shown in Table 2.9.

Table 2.9 Removal of pharmaceuticals by reverse osmosis

Source water	Compound	Concentration in source water (ngl^{-1})	Removal
Tetlowkanal, Germany	Phenacetine	170	>99,4
	Primidone	38	>95,0
	Isoproplantipyrine	329	>99,7
	Sulfamethoxazole	155	>99,4
	Carbamezepine	330	>99,7
	Caffeine	430	>99,8

Source: (Watts and Maycock, 2007)

2.2 Riverbank filtration

2.2.1 Introduction

Riverbank filtration describes the process of extracting groundwater from wells adjacent to river, or horizontal collector beneath a riverbed or within the banks in order to induce infiltration from the river (Dillon et al., 2002). Pumping water induces a continuous flow of surface water towards the wells through the riverbank and/or the riverbed. Typical aquifers used for RBF consist of alluvial sand and gravel deposits with a hydraulic conductivity greater than approximately 10 m/day (Goldschneider et al., 2007). The quality of filtrate at RBF facilities depends upon numerous factors, including the source water characteristics, local geologic settings, distance of the well from the surface water source, and their pumping rates, and ultimately the biogeochemical processes in the aquifer and the sediments at the river-aquifer interface. The source water quality is controlled by land use and climatic conditions (Ray et al., 2002). In a situation where chemical pollution is not serious in river, bank-filtered water can be used directly as drinking water after disinfection (Kim et al., 2003).

Many substances present in surface water including particles, bacteria, viruses, parasites, micropollutants (such as chelating agents, pesticides, amines, pharmaceuticals, and endocrine disrupters),organic and inorganic compounds, are largely and in most cases completely removed by RBF (Shamrukh and Abdel-Wahab, 2007). In fact little is known, either theoretically or through field investigation, about the *in situ* characteristics of the riverbed adjacent to an RBF well and its role in governing flow and transport under normal flow conditions (Schijven et al., 2002).
Figure **2.3** and Figure 2.4 show main components of RBF and well types.

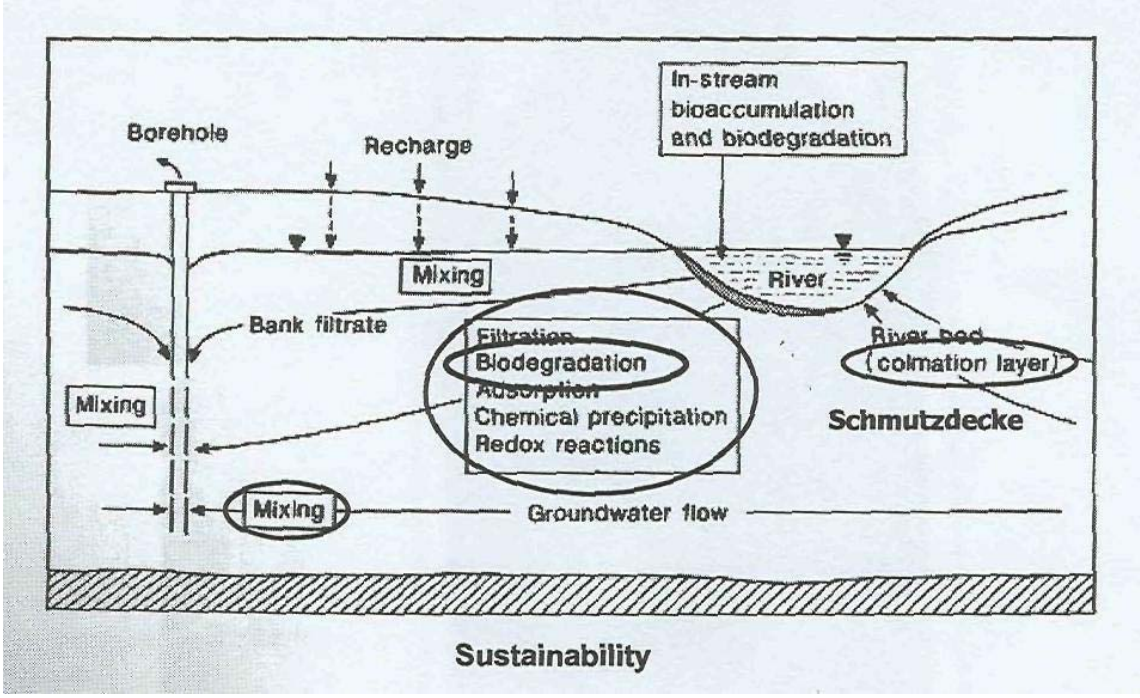


Figure 2.3 Schematic diagram of processes affecting water quality during riverbank filtration.

*Source: (*Amy,2008*)*

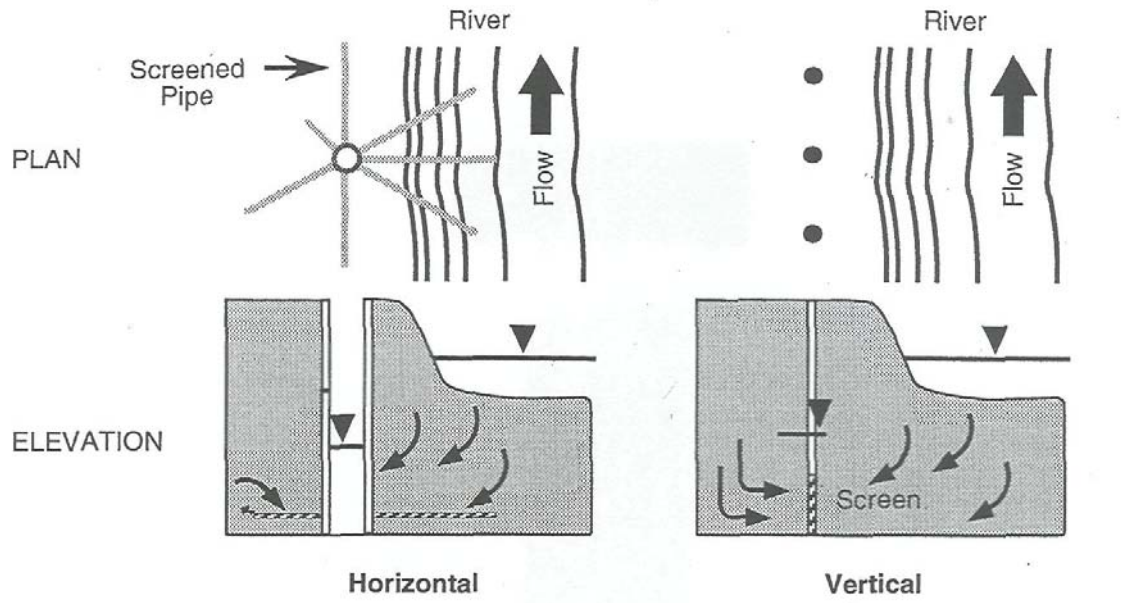


Figure 2.4 Schematic representation of horizontal and vertical wells

*Source: (*Ray, 2002*)*

In Europe, river bank filtration (RBF) has been the primary mode of drinking water production for many cities located along major rivers such as Danube in central Europe (from Austria to Black Sea), Rhine and Elbe in Germany, Lot and Seine in France, and Rhine in the Netherlands, as well as along rivers in Austria, Switzerland, Slovenia, and Spain, see Table 2.10. In the United States, RBF systems are also used for drinking water production (Ray, 2002).

Table 2.10 Percentage of drinking water production from bank filtration in some European countries

No.	Country	Percentage
1	Slovak Republic	50
2	Hungary	45
3	Germany	16 (Berlin 60%)
4	Netherlands	5
5	Finland	48
6	Switzerland	80
7	France	50

*Source: (*Amy, 2008*)*

During soil passage, microorganisms may be removed from the aqueous phase primarily by straining, inactivation, and attachment to the aquifer grains (in combination with inactivation). Other removal processes of uncertain significance are sedimentation in connected pores and trapping in dead-end pores (Ray, 2002).

Inactivation is regarded as a first order process. The most important factors that influence virus inactivation rates during saturated subsurface transport are temperature, adsorption to particulate matter, and soil microbial activity. Temperature is the most important factor that influences virus inactivation (Schijven et al., 2002). Straining is a purely physical removal process governed by the size of pore throats and microbial particles. Settling is more likely to occur where groundwater velocities are lowest, such as in the finer grained riverbed material (Ray, 2002).

The number of infective enteric pathogens will decrease with time and will, eventually, decrease to zero or near zero by natural processes. Pathogens persistency depends on how quickly it will perish outside the host. Various abiotic and biotic environmental factors, as well as the properties of the microbe itself, will determine the elimination rate. Temperature, humidity, pH, the amounts of organic matter in soil and aquifer material, rainfall, sunlight, or competitive microorganisms will all affect the survival of pathogen in water, soil, other unconsolidated material, and within aquifer matrices (Schijven et al., 2002).

2.2.2 Full-scale RBF systems around the world

RBF wells have been used at many riverbank communities in Europe and United States for public and industrial water supply. Louisville Water Company (LWC) in USA estimated the population that could benefit from RBF by correlating metropolitan population centers to areas where potential RBF locations can be found. According to the LWC preliminary estimates over 68.3 million people (>25% of the total US population) could benefit from water quality improvement by the RBF process (Ray et al., 2002). Table 2.11 shows RBF practices in some countries in Europe and North America.

Table 2.11 Selected bank filtration for public water supply in the United States, Canada and Europe

Site location (City)	Country	Well type (horizontal (H); vertical (V))	Number of wells	Design capacity of well field (m^3/s)	River system
Cincinnati, Ohio	USA	V	10	1.750	Great Miami[1]
Columbus, Ohio	USA	H	4	1.750	Scioto/Big Walnut[1]
Galesburg, Illinois	USA	H	1	0.438	Mississippi [1]
Independence, Missouri	USA	H	1	0.656	Missouri[1]
Jacksonville, Illinois	USA	H	1	0.350	Illinois[1]
Kalama, Washington	USA	H	1	0.114	Kalama[1]
Kansas city, Kansas	USA	H	1	1.750	Missouri[1]
Kennewick, Washington	USA	H	1	0.131	Columbia[1]
Lincoln, Nebraska	USA	H and V	2(H)+44 (V)	1.530	Platte[1]
Kearny, Nebraska	USA	-	12	0.095	Platte
Mt Carmel, Illinois	USA	V	1	0.044	Wabash[1]
Sacramento, California	USA	H	1	0.438	Sacramento [1]
Terre Haute, Indiana	USA	H	1	0.525	Wabash[1]
Louisville, Kentucky	USA	H and V	1+1	0.875	Ohio[1]
Cedar Rapids, Iowa	USA	V+H	53+4	1.25	Cedar[4]
British Columbia	Canada	H	14	0.66	Nechao[3]
Maribor	Slovenia	V	13	0.750	Drava[1]
Mockritz,	Germany	V	74	1.260	Elbe[1]
Torgau	Germany	V	42	1.737	Elbe[1]
Düsseldorf	Germany	V and H	12	2	Rhine[2&3]
Csepel Island, Budapest	Hungary	V and H	280 (total)	3.470	Danube[1]

[1] Ray et al., (2002) *Source: (* Ray et al., (2002) and Verstraeten et al., (2002))
[2] Eckert et al., (2006)
[3] Hunt et al., (2002a) and [4] Hunt et al., (2002b)

In the Netherlands, 65% of the drinking water is produced from groundwater and 21% from surface water (by storage reservoirs or direct intake). There are two methods of infiltration, or artificial recharge, in use, namely, Dune infiltration (artificial recharge of groundwater) and bank filtration, 'natural' recharge of groundwater. In 1999 the production of drinking water in the Netherlands from bank infiltrated surface water amounted to 62.4 million m^3/year, which represents 5% of the total Dutch drinking water supply, covered by 13 treatment plants (Weiss et al., 2002).

Currently, there are discussions in Russia about possible installation of RBF systems for cities like Khabarovsk (population 600,000) along the river Amur (Ray, 2008).

Some of the most densely populated countries are located in Asia. Drinking water supplies in large cities in those countries mostly come from surface water. In India, a number of cities have started using RBF for water supply. For example, the city of Hardwar in the state of Uttarakhand uses a number of collector wells to extract water from the Ganga river and its diversion canals. The cities of Faridabad in the state of Haryana and metro Delhi are beginning to experiment with RBF, while the cities of Ahmedabad in the state of Gujarat, and Kota in Rajasthan state have used RBF on a limited scale. The city of Kimhae, along the Nakdong river in Korea is installing a RBF system to extract 200,000 m^3 of water quality for drinking water supply. Many large cities along the major rivers of China can easily use RBF for their water supply (Ray, 2008).

A full-scale RBF plant located along the river Nile to supply potable water to the 30,000 residents of Sidfa city in Egypt was operated in 2004 to replace the old compact surface treatment plant from the Nile due to quality problems of treated water (Sharmukh and Abdel-Wahab, 2007). In addition to that, cities along the Niger river in Nigeria (e.g., Onitsha, with a population of more than 500,000) and cities in other west Africa countries (Niyamey, capital of Niger with a population about one million) could use RBF (Ray, 2008).

2.3 Role of physical - chemical properties of PhACs

In order to achieve proper understanding of the removal of PhACs mechanisms during RBF, the role of physicochemical properties in their fate and behavior in water must be well understood. Some of the important physicochemical properties in removing PhACs for riverbank filtrate drinking water are solubility, hydrophilicity, hydrophobicity and octanol/water partition coefficient (K_{ow}).

2.3.1 Solubility

Solubility of a compound as a solute adverts to its competency to dissolve in a solvent (water in this case). This property contemplates the affinity of this compound for water. Moreover, it tremendously affects its degradation during treatment processes as whole including RBF. Solubility can be predicted by using another physical property namely, polarity. This physical property influences intermolecular forces and therefore leads to some compounds or molecules being labelled as polar or non-polar. While polar molecules dissolve in water due its polar nature, non-polar substances are water insoluble.

2.3.2 Hydrophilicity, hydrophilicity and Octanol/water partition coefficient (Kow)

Hydrophilicity is the affinity of some compounds to aqueous phase. This affinity impairs the removal of some compounds and limits their degradation during treatment processes. A reseach conducted by (Ternes and Joss, 2006), showed that a high number of trace organic compounds are extremely polar compounds and in turn possess limited sorption properties and high chemical and biological persistency in the environment. These compounds are characterised with their high mobility in bank filtration systems and may appear in treated drinking water. Unlike hydrophilicity, hydrophobicity favours the removal of PhACs with low affinity to water during treatment processes. Sorption is one of the significant removal mechanisms for such PhACs. Some of PhACs adsorb to surface of biota or solids because of their nature (non-polar and hydrophobic). The degree of partitioning of a given compound is determined by their solubility and partition coefficient. The solubility of a given compound in water reflects its affinity for water. For those compounds with high solubility in water, they commonly show greater mobility during soil infiltration and often detected in riverbank filtrate water. The affinity of a given compound is expressed by its log K_{ow} value and often used to describe hydrophobicity. Therefore, to enhance association with the solid surface and biota, a compound with low solubility in water and a high K_{ow} is preferred (Maeng, 2007). Physical-chemical properties for PhACs are presented in Table 2.12.

Table 2.12 Physical-chemical properties of some PhACs

Compound	Abb.	MW (g/mol)	Molar volume (cm3/mol)	Log Kow
Atenolol	ATL	184.11	217.81	0.16
Clenbuterol	CBT	277.19	192.77	2.00
Metoprolol	MTP	267.37	241.48	1.88
Pindolol	PDL	248.32	197.74	1.75
Salbutamol	SAB	239.31	180.94	0.64
Sotalol	STL	272.37	194.77	0.24
Terbutaline	TBT	225.29	164.57	0.90
Antipyrine	ANP	188.23	151.90	0.38
Cyclophosphami	CPA	261.09	189.89	0.63
Pentoxifyline	PFL	278.31	205.38	0.29
Bezafibrate	BEF	361.82	249.24	4.25
Diclofenac	DCF	295.14	172.67	4.51
Fenoprofen	FPF	242.27	180.90	3.90
Gemfibrozil	GFB	250.34	221.91	4.77
Ibuprofen	IBP	206.28	188.07	3.97
Ketoprofen	KPF	254.28	187.90	3.12
Naproxen	NPX	230.26	170.60	3.18
Propanolol	PNL	259.35	218.04	3.48
Carbamazepine	CBM	236.27	166.27	2.45

Source: (Adapted from Quintanilla, 2006)

2.4 Removal mechanisms of PhACs in RBF

Filtrate water during riverbank filtration undergos wide range of processes such as dispersion, filtration, biodegradation, adsorption and mixing with groundwater (Worch et al., 2002).

2.4.1 Adsorption

RBF could be complex process with respect to adsorption of organic compounds. The heterogeneous environment and site specific conditions reflect different results of organic compounds removal. PhACs with hydrphobic properties tend to preferentially adsorb onto suspended solids and sediment during infiltration. The K_{ow} values often used to determine the degree of association between the organic compounds and the solid phase. K_{ow} is defined by the concentration ratio at equilibrium of organic compounds partitioned between octanol and water. Among other quantitative physical properties, K_{ow} shows a good correlation with biological activity (Maeng, 2007).

The classification of substances in hydrophobic or hydrophilic responds to the criteria of their log K_{ow} value. When the log K_{ow} value is greater than two, we refer to the substance as hydrophobic, therefore, substances with log K_{ow} less than two are hydrophilic (Quintanilla, 2006). The coefficient K_{oc} is also important when considering adsorption because it is organic-carbon/water partition coefficient. A compound with a high value of K_{oc} will tend to adsorb on organic content such as biomass, whereas a low value remains in liquid phase. Adsorption of organic compounds on biomass and inorganic is important in removing PhACs because this is the first step in biological degradation of these compounds. Table 2.13 summarizes log K_{ow} for some compounds.

Table 2.13 Octanol-water coefficient Log K_{ow} for some compounds

Compound	**Log K_{ow}**
Ibuprofen	3.97
Propanolol	3.48
Naproxen	3.18
Ketoprofen	3.12
Atrazine	2.61
Carbamazepine	2.45
Metoprolol	1.88
Terbutaline	0.9
Sotalol	0.24
Atenolol	0.16

Source: (adapted from Quintanilla et al., 2006)

2.4.2 Biodegradation and transformation

Microbial degradation is known as the biologically catalysed reduction in chemical compound's components. This biotransformation takes place at the biologically active layer within the river bed, where intensive degradation and adsorption occur within a short residence time (Hiscock and Grischek, 2002). Biodegradation by aquatic microorganisms can play an important role in fate of of PhACs, especially for those PhACs compounds that are highly water-soluble with low log K_{ow}. If PhACs have low log K_{ow} values, those compounds will be highly mobile and probably migrate into groundwater easily, and sorption is not significant in this case, therefore biodegradation is major part of reduction (Holm et al., 1995).

Several studies showed a high potential of biodegradation of lipid regulartors and anti-inflammatory drugs during soil filtration, but some antiepileptic drugs such as carbamazepine and primidone were not removed during wastewater treatment and soil infiltration and are known to be very persistent in terms of biodegradation and the adsorption (Drewes and Summers, 2002; Heberer, 2002a; Scheytt et al., 2006).
Biodegradation of PhACs is associated with numerous chemical factors including structure characteristics and environmental factors such as redox conditions. Firstly, in regard to structure characteristics, molecules with highly branched hydrocarbon chain are less favourable to biodegradation than unbranched chains and the long chains are more quickly biodegrade compared to the short chains. Secondly, the extent of biodegradation of PhACs during RBF may be different under oxic and anoxic/anaerobic conditions. Sulfonamides (antibiotic for urinary infections) were degraded strongly under anaerobic conditions and most of its derivatives are attenuated in the characteristics as methanogenic/sulphate-reducing and iron-reducing conditions (Holm et al., 1995). Phenazon-type pharmaceaticals are antipyretic pharmaceuticals that have been detected during routine analysis for groundwater in north-west Berlin (Massmann et al., 2005). Phenazone is a redox sensitive pharmaceutical, and was generally degraded under oxic conditions, however, when temperature increases during summer, which promotes anoxic/anaerobic conditions in the region of aquifer, then the phenazone was not fully eliminated (Maeng, 2007).

2.4.3 Dilution

Unlike surface water, groundwater is known with its relatively good and stable water quality. When surface water is induced through riverbed or riverbank during RBF; it is diluted with groundwater, lowering the weight of solid content of surface water compared to water volume. However, dilution is not a removal mechanism, but may play a role in attenuation of contaminants during riverbank filtration.
RBF has many similarities with slow sand filtration (SSF), often used for water treatment in small systems, with the added benefits of contaminant mixing with background groundwater and multi-dimensional dispersion. However, dilution is possible if the concentrations of the contaminants in the groundwater are lower than in the surface water (Ray et al., 2002).

3 MATERIALS AND METHODS

3.1 Introduction

This chapter elaborates on materials and procedures used for running laboratory scale experimental setups, data collection and analysis. A selected number of pharmaceutically active compounds (PhACs) were spiked into different experimental setups under different operating conditions to investigate the fate of these substances during a certain period of time.

3.2 Selected PhACs, geosmin and 2-MIB

A number of PhACs were used to prepare stock solutions, out of which working solutions were made and spiked into different laboratory scale setups as shown in Table3.1. Moreover, an easy biodegradable synthetic organic matter (simulating ozonation by-product) stock solution (with DOC content of 1.66 mg/L) was prepared from aldehyde compounds, being Formaldehyde (easily biodegradable), and glyoxal (less readily biodegradable) and carboxylic compounds namely Sodium acetate, and Sodium formate, working solutions were then spiked side by side with PhACs.

Table3.1 Properties of selected phACs spiked to different laboratory scale test experiments

No.	Name	CAS No.	MW (g/mol)	pKa	log Kow	Classification
1	Gemfibrozil	25812-30-0	250.34	4.70	4.77	HP - ionic
2	Diclofenac	15307-86-5	296.16	4.15	4.51	HP - ionic
3	Bezafibrate	41859-67-0	361.82	3.61	4.25	HP - ionic
4	Ibuprofen	15687-27-1	206.29	4.91	3.97	HP - ionic
5	Fenoprofen	53-16-7	242.28	4.5	3.9	HP - ionic
6	Naproxen	22204-53-1	230.27	4.15	3.18	HP - ionic
7	Ketoprofen	22071-15-4	254.29	4.45	3.12	HP - ionic
8	Clofibric acid	882-09-7	214.645	3.20	2.88	HP - ionic
9	Carbamazepine	298-46-4	236.28	14	2.45	HP-neutral
10	Phenacetine	62-44-2	179.2182	2.2	1.94	HL - ionic
11	Paracetamol	103-90-2	151.17	9.38	0.46	HL - neutral
12	Pentoxifylline	6493-05-6	278.31	6.00	0.29	HL - ionic
13	Caffeine	58-08-2	194.19	10.40	0.07	HL - neutral

Source: (Quintannilla, 2006)

Selected Odour compounds, namely geosmin and 2-methylisoborneol (2-MIB) were introduced to influent water of the three types of laboratory scale setups, being batches, long soil columns and short soil columns. These compounds implicated in muddy-

musty flavours of water and fish, pose problems on food and water industry (Jelen et al., 2003). Due to their very low odour threshold concentrations, geosmin and MIB are easily detected by human olfactory sense at low levels (Lin et al., 2002). Properties of Geosmin and 2-methylisoborneol (2-MIB) are presented in Table 3.2.

Table 3.2 Physical and chemical characteristics of Geosmin and 2-methylisoborneol (2-MIB)

Characteristics	Geosmin	2-methylisoborneol (2-MIB)
Chemical name	trans-1, 10-Dimethyl-trans-9-decalol	1,2,7,7-Tetramethyl-exo-bicyclo-heptan-2-ol
Molecular formula	$C_{12}H_{22}O$	$C_{11}H_{20}O$
Log K_{ow}	3.57	3.31
Appearance	Light yellow oil	White solid
Organoleptic properties	Earthy-muddy	Musty
Odour threshold concentration (ng/L)	10	29
Human olfactory sense (ng/L)	4	7-15

Source: (Adapted from Watson et al., 2000)

3.3 Experimental setups

3.3.1 Batch experimental setup

Batch experimental setups (1 litre glass bottles) using biologically active silica sand (with grain size ranging from 0.8 to 1.25 mm) were used to assess attenuation of selected odour compounds (Geosmin and 2-MIB) and target PhACs under the influence of different organic matter concentrations, simulating long travelling time during riverbank filtration. Six categories in triplicate (18 in total) batch experimental reactors were fed with Maas river water (MRW), Maas river water spiked with synthetic organic matter (MRW+SOM), secondary effluent (SE, from Hoek van Holland, the Netherlands), plant-derived water (PDW) from basins used for growing plants. In addition to that, three blank reactors packed with fresh silica sand and received Milli-Q, demineralised water (DW) and tap water (TW) were deployed to assess the removal of target PhACs under abiotic conditions, while a set of triplicate reactors was used as control since the glass bottles received only Milli-Q, demineralised and tap water as well as target compounds without addition of sand.

Reactors were exposed to continuous agitation by placing them on a table shaker at 85 rpm frequency under oxic followed by conditions. See
Figure **3.1**. Anoxic conditions were achieved through stripping out oxygen gas by defusing nitrogen stream into the first reactor in each category after one month from introducing PhACs for the first time. However, control and blank reactors using tap water spiked with target compounds were chosen for anoxic conditions.

Figure 3.1 Laboratory-scale batch reactor experimental setups

3.3.2 Long soil column experimental setups

Laboratory scale long soil columns (LSC), constructed and instrumented based on the schematic diagram shown in Figure 3.2 and were used to simulate and investigate the impact of different organic matter characteristics from Maas river water and secondary effluent on odour compounds and PhACs transport and removal under different redox conditions. These setups were constructed from uPVC pipes with an internal diameter of 57 mm, and each column consists of two parts with 2.5 m height each. The first part was running in down flow mode while the second part was connected to the first one and ran in up flow mode to attain saturation conditions in the column. Two soil columns were used to run two experiments with influent waters of MRW and MRW+SE in LSC1 and LSC2 respectively. Silica sand with grain size ranging from 0.8 mm to1.25 mm was used as the filter media, and 200 mm layer of well graded gravel was used as a support layer at the bottom of the column. The setup contains 12 sampling points as could be seen from schematic diagram shown in Figure 3.3.

Figure 3.2 Laboratory-scale long soil columns

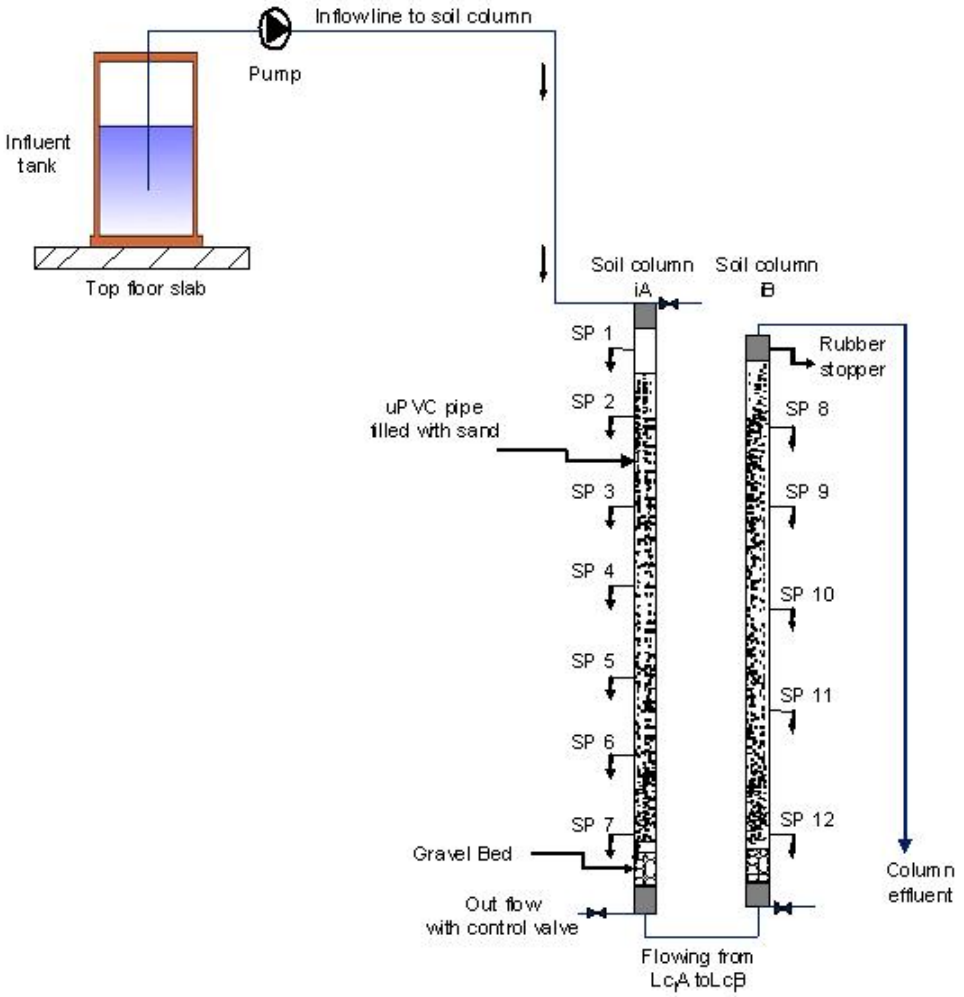


Figure 3.3 Schematic representation for laboratory-scale long soil column

3.3.3 Short soil columns experimental setups

Biologically active silica sand and fresh sand with grain size ranging between 0.8 mm and 1.25 mm were packed into XK 50/30 columns. These columns consist of borosilicate glass tube with 300 mm length and 50 mm inner diameter, in addition to acrylic plastic tube thermstat with threaded ends. The end pieces of the column are made of reinforced acetal plastic and contain O-ring, sealing ring, washer and locking ring. Furthermore, a tubing connector through which water enters or leaves the column is interconnected with the end pieces. Four short soil columns (as shown in Figure 3.4) were deployed to assess the role of biodegradation on odour compounds (Geosmin and 2-MIB) and PhACs removal under different temperatures. Except for the first column (SSC1) which was operated at room/ambient temperature of approximately 25° C, the other three columns were connected to a chiller, whereby operating temperatures were between 19° C to 23° C. SSC1 was filled up with biologically active silica sand (0.8 – 1.25 mm), ripened with MRW for two months, and then fed with tap water containing PhACs during steady state conditions. This practice aimed at assessment of dominant removal mechanism for some of the targeted PhACs, geosmin and 2-MIB (especially biodegradation) by biomass since tap water is believed to have less BDOC content compared with other influent waters used in this research. SOM with DOC content of 1.66 mg/L was added to SSC2 (after two months ripening) and SSC3 (ripened for ten

days). This organic matter (simulates ozononation by-products) was added to influent water to augment the low DOC content of MRW and consequently increase microbial activity which is believed to accelerate PhACs co-metabolism. However, SSC4 was packed with fresh sand, fed with demineralised water spiked with 40 mM sodium azide solution (DW+NaN_3) and used as control for the above mentioned three columns. Sodium azide (NaN_3) was used to inhibit microbial growth since the column was meant to study removal of target PhACs and odour compounds adsorption removal mechanism.

Figure 3.4 Laboratory-scale short soil column experimental setups

3.4 Experimental procedures

MRW was collected from Wester Kade in the vicinity of Rotterdam city centre and wastewater effluent secondary effluent from Hoek van Holland wastewater treatment plant. These influent waters were characterized and their parameters were measured and revealed results which could be seen in chapter 4.

3.4.1 Batch experimental procedures

Batch experiments were carried out under aerobic and anoxic conditions (as shown in Table 3.3) according to the following steps:
1) Influent water (from the above mentioned sources) was stored in cold room under an ambient temperature of 4° C (cold room) before application to batch reactors.
2) Silica sand (0.8 – 1.25 mm size) was biologically activated by placing 3 kg in a 10 litre container, filled with wastewater secondary effluent and left to ripen for one month.

3) A weight of 200 g from the biologically active silica sand was then transferred to each reactor (15 glass bottles, 1 litre volume), deployed in triplicate and filled with influent water as shown in Table 3.3. The bottles were agitated on a table shaker at 85 rpm frequency to bring DOC and oxygen in contact with microorganism (films) on the sand grains.
4) Samples taken from influent and effluent of batch reactors every five days were filtered with 0.45 µm fibreglass filters and measurement of DOC was carried out to quantify their BDOC content.

Table 3.3 Operation conditions for batch experimental setup

No.	Influent water	No. of reactors used	Type of sand	Removal process	Operation conditions
1	MRW+ PhACs	2	Biologically active	Biotic	Oxic
2	MRW+ SOM + PhACs	2	Biologically active	Biotic	Oxic
3	SE + PhACs	2	Biologically active	Biotic	Oxic
4	PDW + PhACs	2	Biologically active	Biotic	Oxic
5	Milli-Q water + PhACs	1	N.A	Abiotic	Oxic
6	DW + PhACs	1	N.A	Abiotic	Oxic
7	TW + PhACs	1	N.A	Abiotic	Oxic
8	MRW + PhACs	1	Biologically active	Biotic	Anoxic
9	MRW + SOM + PhACs	1	Biologically active	Biotic	Anoxic
10	SE + PhACs	1	Biologically active	Biotic	Anoxic
11	PDW + PhACs	1	Biologically active	Biotic	Anoxic
12	TW+ PhACs	1	Fresh	Abiotic	Anoxic (blank)
13	TW + PhACs	1	Without sand	Abiotic	Anoxic (control)

N. A.: not applied

3.4.2 Long soil column experimental procedures

As shown in Table 3.4, different types organic matter were introduced to LSC under oxic and anoxic conditions to assess the influence of these substances on the removal of PhACs according to the following steps:
1) Water from the above stated sources was collected and stored at an ambient temperature of 4° C, prior to application to experimental setups. Low storage temperature was aimed at minimizing microbial activity.
2) The columns' filter media were conditioned with influent water for a period of time, during which DOC at the influent and effluent water was monitored. This biological acclimation of the filter sand was continued until the columns were stabilized (steady removal of DOC was achieved). This phase is known as ripening period, and bio-films of microorganisms' population were believed to exist on sand's grains.
3) After ripening phase, the influent water was applied to soil columns under different operating conditions.
4) Samples were collected from influent and effluent of the columns and filtered with 0.45 µm fibreglass filter.
5) Analysis of various relevant parameters (DOC, UV-scan, pH, and O_2) was performed on the collected samples.

Table 3.4 Operating conditions for long soil column experimental setup

No.	Influent water	Hydraulic loading rate (m/d)	Phase No.	Redox conditions
1	MRW+ PhACs	0.56	1	Oxic
2	MRW + SE (1:1)	0.56	1	Oxic
3	MRW + SOM + PhACs	0.56	2	Oxic
4	MRW + SE + SOM + PhACs	0.56	2	Oxic
5	MRW + SOM + PhACs	0.56	3	Anoxic
6	MRW + SE + SOM + PhACs	0.56	3	Anoxic

3.4.3 Short soil column experimental procedures

Seasonal variation in ground water temperature was simulated by conducting laboratory-scale short soil column experiments. These experiments were carried out under different operating temperatures. Table 3.5 shows process conditions performed to evaluate the fate PhACs during soil column passage. Tests were conducted as stated below:

1) Water from the above stated sources was collected and stored at an ambient temperature of 4° C, prior to application to experimental setups. Low storage temperature aimed at minimizing microbial activity.
2) The columns' filter media were ripened with influent water for two months until DOC removal was stable.
3) After ripening phase, the influent water containing PhACs was applied to soil columns under different operating conditions.
4) Samples were collected from influent and effluent water applied to the columns and filtered with 0.45 µm fibreglass filter.
5) Analysis of various relevant parameters (DOC, UV-scan, pH, and O_2) was performed on the collected samples.

Table 3.5 Operation conditions for short soil column experimental setups

No.	Influent water	Hydraulic loading rate (m/d)	Ripening period (day)	Operation conditions
1	TW + PhACs	0.26	60	Oxic
2	MRW + SOM + PhACs	0.26	60	Oxic
3	MRW + SOM + PhACs	0.26	10	Oxic
4	DW + NaN_3 + PhACs	0.26	□	Oxic

3.4.4 Process conditions

a) Influent water quality

With the intention to scrutinize the impact of influent water quality on organic matter removal during RBF; Maas river water , irrigated plants water, demineralised water, tap water, secondary effluent and Maas river water spiked with synthetic organic matter were fed to batch, long and short soil columns experimental setups. However, application of Maas river water blended with wastewater secondary effluent was performed to assess the impact of discharged effluent wastewater into effluent receiving water bodies on RBF sites downstream of WWTPs, while the collected water from underneath a laboratory scale research plants was used in batch experimental setups to simulate removal of PhACs in wetlands. In addition to that, SOM was added to prevent carbon limitation for microorganisms and provide additional carbon source for co-metabolism process.

Influent waters (containing spiked target compounds and odour compounds) were applied to experimental setups as follows:

i) Batch experiments

- Maas river water (MRW)
- Mass river water spiked with synthetic organic matter (MRW+SOM)
- Irrigated plant water (IPW)
- Wastewater secondary effluent (SE)
- Milli-Q water
- Demineralised water (DW)
- Tap water (TW)

ii) Long soil columns

- Maas river water (MRW)
- Maas river water mixed with Wastewater secondary effluent (MRW+SE, 1:1)

iii) Short soil columns

- Maas riverwater spiked with synthetic organic matter (MRW+SOM)
- Tap water (TW)
- Demineralised water spiked with 40 mM sodium azide solution (DW+NaN_3).

b) Aerobic and anoxic conditions

Aerobic conditions in long soil columns were maintained through aeration of influent water by to enhance aerobic biodegradation of PhACs by inserting aeration tubes connected to fine O_2 diffusers into feed tank.

To achieve anoxic operation conditions, continuous stripping off of O_2 was performed through nitrogen gas diffuser connection to setups' influent containers while DO meter probe was inserted from time to time to read dissolved oxygen concentration. Stripping was stopped at DO-meter measurement of 0.2 mg O_2 /L, the containers were then connected to the setups and sealed.

c) Porosity test for silica sand used

Porosity is the percentage pore volume of void space, or that volume within a media that can contain a fluid.

- Porosity test was carried out by placing a volume of (V_m = 300 mL) clean silica sand (size: 0.8 – 1.25 mm) in a 500 mL glass beaker.
- 250 mL beaker was filled with a known volume of water which was poured into the beaker containing sand by means of measuring cylinder.
- The remaining volume of water in the 250 mL beaker was recorded and used volume was calculated by deducting the remaining volume of water from the initial water volume. This volume was considered as pore volume V_p.

Porosity of silica sand was then calculated using the formula shown in Equation 3.1

$$\text{Porosity } \Phi = \frac{Vp}{V_m} \times 100 \quad \text{..... (3.1)}$$

Moisture content of the media was found to be 0.1%.

d) Tracer tests and empty bed contact time (EBCT)

Empty bed contact time depends on infiltration rate. An increase in infiltration rate through a media will subsequently result in a reduction in retention time, which will in turn impair the removal of contaminants due to less interaction between these contaminants and the media.

Influent water was introduced to batch experiments with retention time of 5 days during ripening period.

Flow through long soil column was maintained at 1 mL/min, short soil columns running at 0.35 mL/minute.

Theoretical EBCT was calculated both for long and short soil columns. Tracer tests were conducted for these setups to relate the removal of PhACs to an exact contact time between the influent water and biomass population. Initial electrical conductivity (EC) of sodium chloride solution which was used as a tracer solution was checked in influent water followed by continuous measurement of EC at the effluent points at constant intervals. This measurement was conducted by inserting the probe of conductivity meter in effluent water while keeping measurement mode at constant intervals.

The following fromulae can were used in theoretical EBCT calculations.

Average detention time in column (days)

$$\tau = EBCT \times \phi \quad \text{..... (3.2)}$$

Where:

EBCT ≡ Empty bed contact time (days)

ϕ ≡ Media porosity

$$\text{EBCT} = \frac{V_v}{Q} = \frac{H}{V} \quad \text{..... (3.3)}$$

Where:

V_v ≡ Column volume (m^3)

V ≡ Flow velocity (m/d)

Q ≡ Flow rate (m^3/day)

H ≡ Height of soil column (m)

The flow rate or infiltration rate is given by:

$$Q = A \times V = A_i \times V_i \quad \text{..... (3.4)}$$

Where:

Q ≡ Flow rate (m^3/day)

V_i ≡ Velocity through the pores (m/d)

A ≡ Media cross sectional are (m^2)

A_i ≡ Cross sectional are of the pore space (m^2)

V ≡ Flow velocity (m/d)

The velocity of flow through the pores or interstitial velocity is given by :

$$V_i = \frac{V}{\phi} \quad \text{..... (3.5)}$$

The hydraulic loading rate (HLR) is consequently calculated as:

$$HLR = \frac{Q}{A} \quad \text{.....(3.6)}$$

3.5 Analytical methods

In an intensify effort to measure parameters of concern, a wide spectrum of methods and equipments were used. These methods and equipments are presented below.

3.5.1 pH, EC and O_2

Samples were collected from batch reactors, influent and effluent of long soil columns, stirred by means of magnetic stirrer to ensure thorough mixing and subsequently uniformity. Moreover, a Sweden made (METROHM-691) pH meter was calibrated, then its probe (electrode) was rinsed with demineralised water and immersed in sample containers. Readings were recorded manually.

Electrical conductivity of influent water was measured by means of WTW cond 330i conductivity meter. The meter's probe was inserted into sample's container, stirred for a while and a stable reading was obtained and recorded.

Measurement of dissolved oxygen was carried out by using HACK HQ10 oxygen meter.

3.5.2 Dissolved organic carbon (DOC)

NOM is used to describe the complex mixture of organic material, such as humic acids, hydrophilic acids, protein, lipids, amino acids, and hydrocarbons. NOM found in natural ecosystems is derived from allochthonous sources, originating outside a water body and autochthonous sources originating from processes within the water body (Sundaramoorthy et al., 2005). NOM is frequently used to represent components of organic material, namely dissolved and particulate. The later form of NOM occurs widely in both surface and groundwater. DOC is practically marked off by filtration through 0.45 µm filter, while particulate organic matter represents colloidal and particulate matter. DOC consists of Humic and non-humic components (Drewes et al., 2002). Humic substances represent the hydrophobic fraction of NOM. These substances are heterogeneous polyfunctional formed through the breakdown of plant and animal tissues or synthesis of the product by chemical and biological processes (Thurman, 1985). Dissolved organic carbon (DOC) concentration in surface water is in three to five orders of magnitudes higher than trace organics which have been detected up to µg/L levels. Hence, used as surrogate indicator for organic micro pollutants biodegradation.
In vast majority of cases, non-pathogenic microorganisms' population rely on dissolved organic carbon (DOC) as primary substrate for growth. In addition to that, removal of trace organics (such as PhACs) is enhanced markedly by co-metabolism process as secondary substrate through reaction with enzymes released by biomass.
Collected samples from both soil columns and batch experimental setups were filtered through 0.45 µm fibreglass filter. However, the filter was rinsed by flushing 20 mL of Milli-Q water through it and then a 50 mL plastic syringe was filled with the sample

and 10 mL was then wasted to rinse the filter thoroughly. The samples were filtered and made ready for analyses in injection vials of 40 mL volume.

DOC of the samples was measured using **TOC-VCPN** Combustion catalytic oxidation/NDIR method (at around 720° C, PC-controlled, standard model (Shimadzu corporation, Japan) as shown in Figure 3.5. The instrument measures up to 68 samples in a single batch and the measurement of each sample takes about 15 minutes with double injection. However, the first three vials were used for Milli-Q water samples. This practice aimed at minimizing any carry over that could occur from previous measurements and works at the same time as a check for accuracy of the machine where DOC concentration of 0.05 mg/L implies that the apparatus is ready for measurement. Data from the machine were saved to PC.

Figure 3.5 Total organic carbon analyzer

3.5.3 Size exclusion chromatography with on-line DOC and UV detection (LC-OCD)

High performance liquid size exclusion chromatography is a technique used to segregate NOM based on the molecular size. The size exclusion column allows high molecular weight compounds flow faster. Elusion time provides a basis for NOM molecular weight distribution approximation. The technique uses bulk water samples and allows for differentiation of organic carbon by integrating chromatograms into five different fractions: (1) humics (HS), (2) humic substances (HS) hydrolysates, (3) low molecular mass acids, (4) low molecular mass neutrals and amphilics and (5) polysaccharides.
Samples with DOC measurement above 5 mg/L were diluted and send to Het Waterlaboratorium in Harlem for LC-OCD measurement.

3.5.4 Fluorescence Excitation-Emission Matrix (FEEM) and protocol

Fluorescence characteristic is function in structure and functional groups in molecules. It provides a wide spectrum of information on chemical nature of NOM (Chen et al., 2003).
When excited by UV visible light, OM fluoresces and the characteristics and intensity of the fluorescence varies depending on fluorophores present. The composition of aquatic OM can be visualised as a pattern of fluorescence peaks within an excitation – emission matrix (EEM). Fluorescence can be attributed to both natural fluorescence (humic – and fulvic – like) and amino acid – like organic matter (tryptophan – and tyrosine – like) fluorescence (Coble, 1996). Fluorescence is influenced by many factors, such as type of solution, interaction with metal ions and organic substances, pH, ionic strength, temperature, redox potential of the medium (Peuravuori et al., 2002).
According to Baker et al. (2003), fluorescence spectrophotometry can be used as an environmental monitoring tool to detect pollution events in surface waters impacted by effluent of WWTPs. Advantages of fluorescence over UV absorbance include reduced interference from inorganic compounds and more opportunities to optimize the signal through the combination of excitation/emission wavelengths. However, fluorescence does not provide information about other substances such as polysaccharides. River and wastewaters posses noticeable light absorption and fluorescence spectrophotometric properties. Dissolved organic matter presents in these waters shows strong absorption in ultra-violet region as well as fluorescing (Baker et al., 2004). Reduction of fluorescence during treatment processes indicates either degradation of fluorescence materials or quenching of DOM fluorescence by organic molecules newly formed. On the contrary, increase in fluorescence indicates formation of new fluorescing materials associated with DOM biodegradation and degradation of certain organic components capable of quenching DOM fluorescence (Saadi et al., 2006). According to Leenheer et al. (2003), various organic components of fluorescence that can be detected by spectrofluorometer, show peaks at specific excitation/emission range. Results showing these components are summarized in Table 3.6.

Table 3.6 Main Fluorescence components in EEM matrix

Range of excitation (nm)	Range of emission (nm)	Type of organic component
330 - 350	420 - 480	Humic-like
250 - 260	380 - 480	Humic-like
310 - 320	380- 420	Marine humic-like
270 - 280	300 - 320	Tyrosine – like,protein-like
270 - 280	320 - 350	Tryptophan-like, protein-like or phenol-like.

Source: (Leenheer et al., 2003)

Results from DOC measurements were used to measure FEEM of influent and effluent samples from soil columns and batch reactors. The samples were diluted with Milli-Q water to attain DOC concentration of 1 mg/L in at least 10 ml measuring sample volume. FluoroMax-3 spectrofluorometer (HORIBA Jobin Yvon Inc., USA) shown in Figure 3.6 was used to measure 3D Fluorescence (excitation-emission matrix) of samples. The entire excitation and emission matrix (EEM) were obtained by measuring the emission spectra in the range of 290-530 nm at 2 nm intervals, with an excitation range of 240 to 450 nm at 10 nm intervals. EEM of the blank (measured using three dimensional spectra) was subtracted from each sample to remove raman scatter peaks. Manufacturer provided instrument correction factors were used. Each sample takes 15 minutes measurement time. Finally, MATLAB software was used to plot contours of each sample. The obtained figures from MATLAB were then used to categorize dissolved organic carbon fractions to protein-like, humic-like and fulvic-like.

Figure 3.6 FluoroMax-3 for fluorescence measurement

3.5.5 UV-Scan

Among others, UV_{254} has proven reliability with respect to aromatic carbon content detection. This parameter is a measure of humic-like components with an aromatic character. Aromatic with saturated bonding structure specifically absorb UV in the range 200 – 300 nm.

Specific ultraviolet absorption (SUVA expressed in L/mg.m) has been used as a water parameter. It adverts to the UV absorption at 254 nm (in 1/m) divided by the dissolved organic carbon (in mg/L). SUVA is used as an indicator of the humic content of water and the ability of the water to be treated for the removal of disinfection byproduct

precursors (Minear and Amy, 1996). Waters with high SUVA values are generally enriched in hydrophobic NOM, such as humic substances, SUVA implies presence of aromatic compounds in the DOC at a given location (Leenheer and Cruoé, 2003).
SUVA is calculated according to equation 4.1 shown below.

$$\text{SUVA (L/mg.m)} = \frac{UV_{254}\,(cm^{-1}) \times 100}{DOC\,(mg/L)} \quad \text{.....(3.7)}$$

SUVA values of samples could be used to get an insight to type of natural organic matter found this samples. Guidelines for SUVA interpretation are show in Table 3.7.

Table 3.7 Guideline values of SUVA and related nature of NOM

SUVA value (L/mg.L)	NOM composition
< 2	Mostly non-humic, low hydrophilicity, low molecular weight
2 - 4	Mixture of aquatic humics and other NOM, Mixture of hydrophobic and hydrophilic NOM, Mixture of molecular weights
> 4	Mostly aquatic –humics, High hydrophobicity, High molecular weight.

Source: (Edzwald and Tobiason, 1999)

Samples from different experimental setups were scanned using spectrophotometer UV-2501PC Shimadzu as shown in Figure 3.7. This instrument measures the characteristics of absorption materials by automatic double beam light scanning. It has performance guaranteed range of 190 nm to 900 nm extendable to 1100 nm with wavelength accuracy of ±0.3 nm, while its wavelength scanning speed contains fast, medium, slow and very slow modes of operation. Furthermore, its light source is 50 W halogen lamp and D2 lamp. Samples were filtered through 0.45 µm fibreglass filter prior to measurement. Two transparent quartz sand cuvettes were used to allow the light to penetrate through the sample and measurement data were obtained through PC connected to the spectrophotometer.

Figure 3.7 UV-2501PC for scanning water samples

3.5.6 Adenosine triphosphate (ATP) measurement

Adenosine triphosphate is used as an indication for biomass concentration. As a result of this correlation, ATP can be used as a soil microbial biomass (Maeng et al. 2008)

Wet sand samples of 2 g to 4 g were collected from batch and soil column laboratory-scale experimental setups. The sand samples were then autoclaved in a tap water volume of about 50 mL, in which the samples were exposed to high energy sonication at a power of 40 W to detach biomass from the sand. Concentration of ATP in suspension obtained through sonication was used to determine biomass concentration. 90% of the attached biomass (expressed as ATP) can be obtained in two minutes sonication. **Figure 3.8** shows apparatus used in ATP concentration measurement.

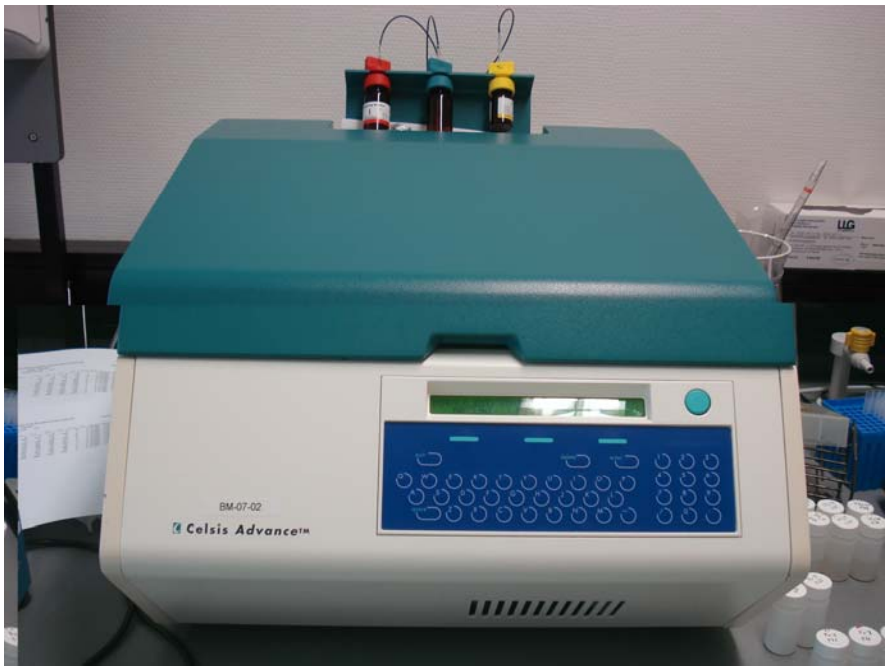


Figure 3.8 ATP analyser

4 RESULTS AND DISCUSSION

4.1 Introduction

This chapter focuses on presentation and interpretation of results obtained from various experimental setups. It consists of four different parts to investigate; i) the effect of different sources of NOM on the removal of PhACs, ii) the effect of redox conditions on the removal of PhACs, iii) the influence of temperature on the removal of PhACs under carbon-limiting conditions during bank filtration.

4.2 Ripening of batch, short soil column and long soil column experimental setups

Silica sand used in this study was acclimated with different sources of water, and samples were taken when columns or batch reactors reached steady state with respect to DOC removal. MRW, MRW+SE (1:1 ratio), and SE were fed into batch reactors at five days intervals for more than two months. Moreover, two LSCs were ripened with MRW and SE water. LSC1 received MRW whilst LSC2 received MRW+SE (1:1 ratio). Furthermore, MRW was used to acclimate SSCs for about two months. Upon development of bioactive sands, biodegradation of DOC in influent water (quantified by taking samples after defined intervals) increased significantly.

4.2.1 Ripening of batch experimental setups

Glass bottles of 1000 mL volume containing 200 g of bioactive silica sand of size 0.8 – 1.25 mm received a 700 mL of water, were used in batch study carried out in triplicate. 12 bottles (reactors) were ripened for two months, during which influent and effluent samples were collected on every first and fifth day respectively. DOC of the collected samples was monitored until the DOC removal efficiency became stable (acclimated).

An average removal efficiency of 6% was attained in batch reactors fed with MRW for an average influent and effluent DOC content of 2.89 ± 0.55 mg/L and 2.73 ± 0.59 mg/L respectively, while an average removal efficiency of about 7.6% was achieved in the reactors that received MRW+SE (1:1) for an average influent and effluent DOC content of 7.80 ± 0.92 mg/L and 7.20 ± 0.67 mg/L respectively. In addition to that, batch reactors that received SE showed an average removal of 11.1 % for influent and effluent DOC concentration of 11.93 ± 1.79 mg/L and 10.65 ± 1.52 mg/L respectively.
DOC measurement during ripening period for laboratory scale batch experimental setups simulating effect of different sources of NOM on the removal of PhACs during RBF are shown in Figure 4.1, Figure 4.2 and Figure 4.3.

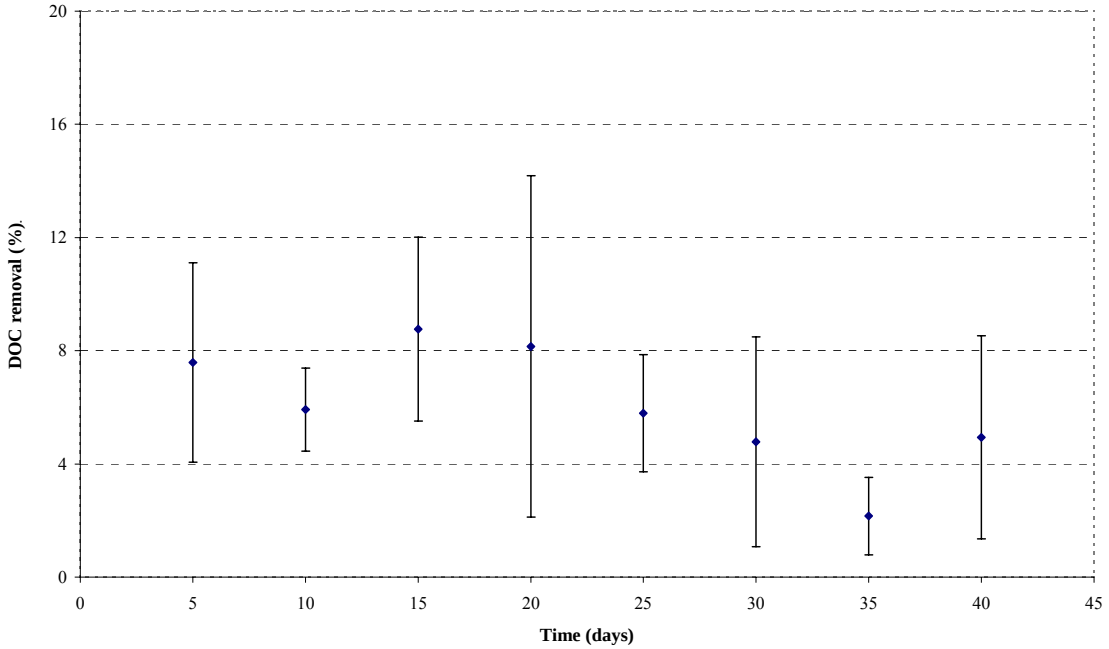


Figure 4.1 DOC degradation during ripening period of batch experimental setup (Influent water: MRW; 200 g of biotic silica sand media size: 0.8 – 1.25 mm, agitated on a shaker table at 85 rpm frequency under oxic conditions)

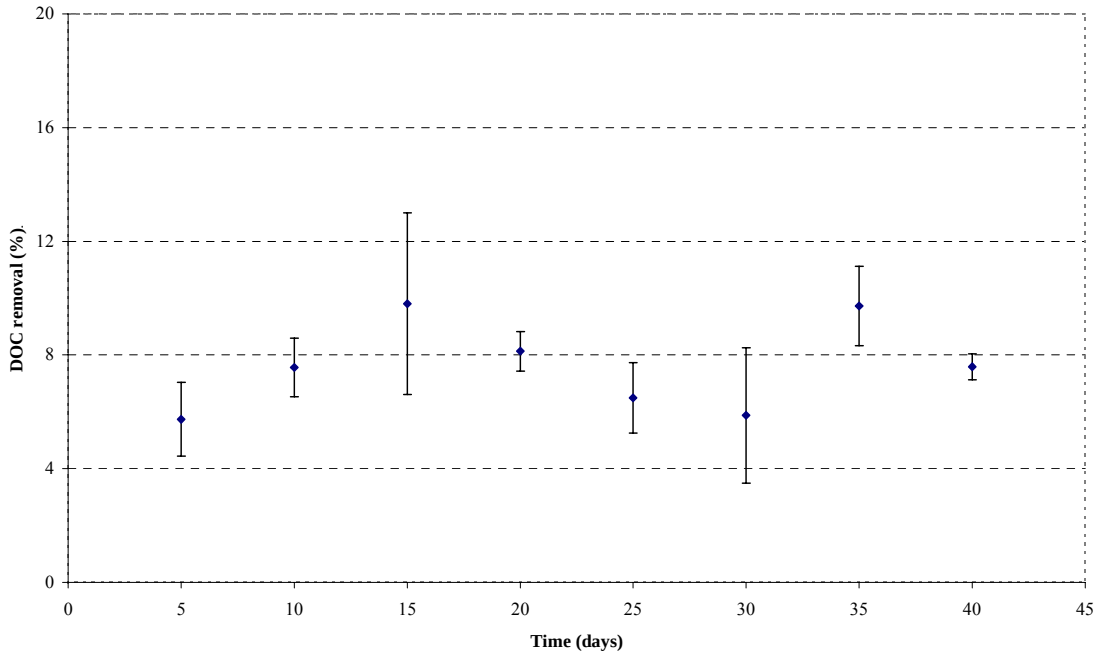


Figure 4.2 DOC degradation during ripening period of batch experimental setup (Influent: MRW+SE; 200 g of biotic silica sand media size: 0.8 – 1.25 mm, agitated on a shaker table at 85 rpm frequency under oxic conditions)

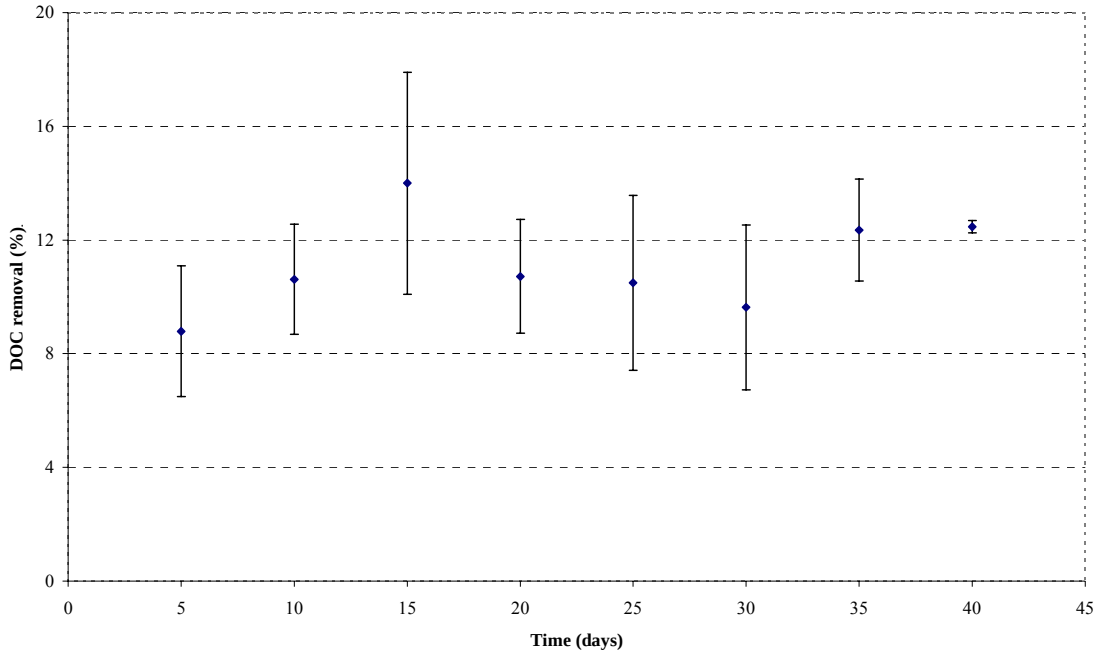


Figure 4.3 DOC degradation during ripening period of batch experimental setup (Influent: SE; 200 g of biotic silica sand media size: 0.8 – 1.25 mm, agitated on a shaker table at 85 rpm frequency under oxic conditions)

DOC removal rate of 11.1% in reactors fed with secondary effluent indicated increase in biomass activity supported by presence of BDOC (being the fraction of DOC that support the growth needs for microorganisms). MRW was observed to have lower DOC content and subsequently low DOC removal rate of 6%, while MRW+SE showed an average removal of 7.6 %.

4.2.2 Ripening of long soil columns

Waters taken from Maas River and Hoek van Holland wastewater treatment plant were percolated through a fixed bed uPVC soil column of 57 mm diameter and 5 m height. Each of these columns comprised two equal parts of 2.5 m height each; both of which were packed with a silica sand media of grain size ranging between 0.8 mm and 1.25 mm and operated at HLR = 0.56 m/d. Based on infiltration rate, tracer tests were conducted to determine interaction time between contaminants contained in influent water and column bed.

- **Tracer tests for long soil columns**

Porosity of silica sand media was first determined by conducting porosity test. Two tests for each LSC were performed. Calculations of porosity and empty bed contact time (EBCT) are presented in Appendix A 2.

Sodium chloride was used to conduct tracer tests to find the exact EBCT of the setup. These tests were conducted twice for each soil column. Figure 4.4 and Figure 4.5 show breakthrough curves for long soil columns tracer tests.

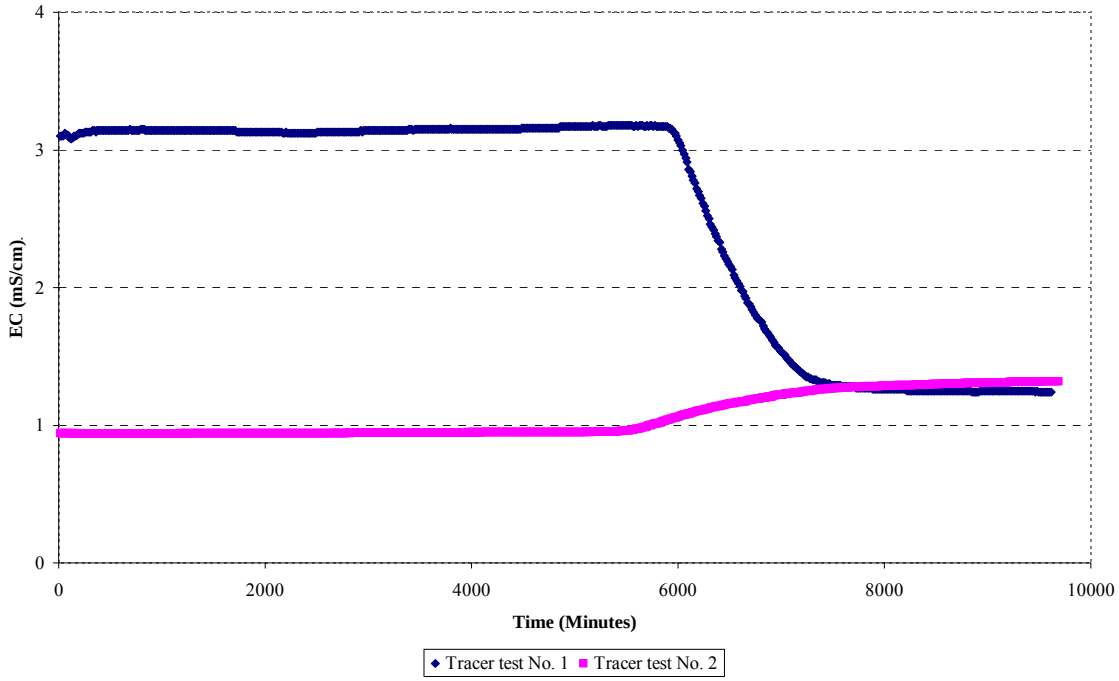


Figure 4.4 Breakthrough curves for sodium chloride used as tracer solution for determination of EBCT in LSC1

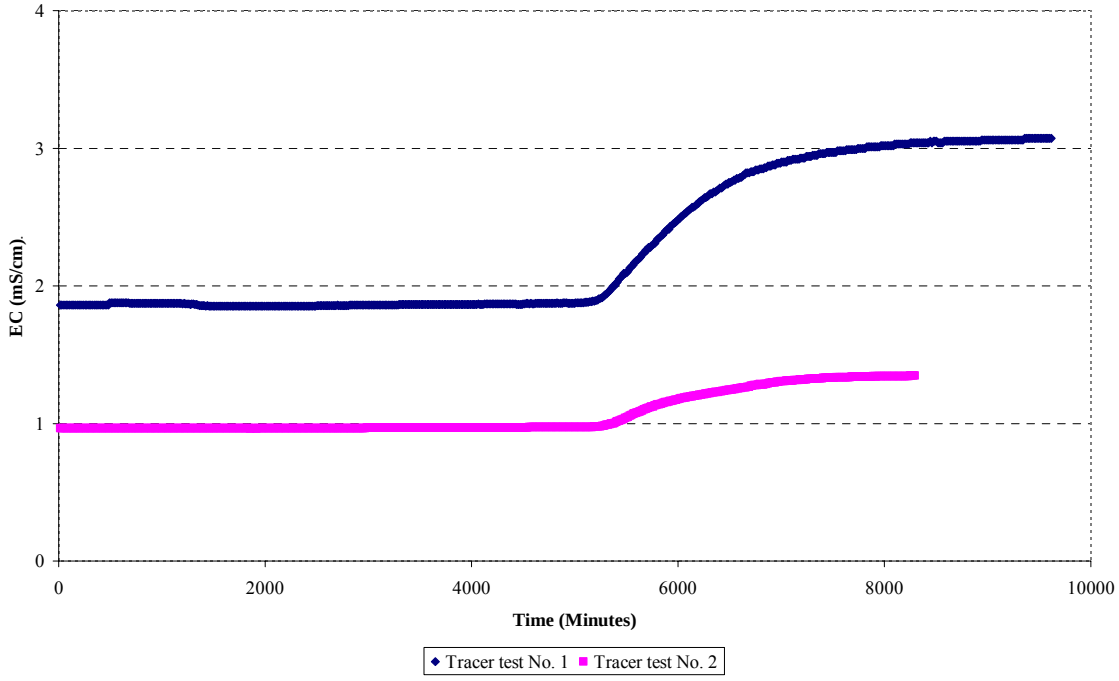


Figure 4.5 Breakthrough curves for sodium chloride used as tracer solution in determination of EBCT for LSC 2

Tracer test No. 1 carried out in LSC1 was performed by introducing influent water less in electrical conductivity compared to the influent water used before conducting tracer test. Initial and Mean EBCT values for tracer test No. 1 were found to be 4 days and 4.6 days respectively, while Nacl was used as a tracer solution (EC increased) for tracer test No. 2 where initial and mean EBCT were found to be 3.8 days and 4.6 days respectively.

In LSC 2, NaCl was used as a tracer for both tracer tests in which test No.1 showed initial EBCT value of 3.6 days and mean EBCT of 4.6 days, while tracer test No. 2 resulted in an initial and mean EBCTs of 3.6 days and 4.5 days respectively.

During ripening process of LSCs, biodegradation of DOC along the columns was determined by DOC of the samples collected from feed and effluent points. LSC1 received MRW, while LSC2 received MRW+SE to elucidate the impact of effluent organic matter (i.e wastewater impact) under different redox conditions on the performance of bank filtration. With respect to DOC removal, LSC1 had an average influent and effluent DOC of 3.17 ± 0.54 mg/L and 2.79 ± 0.46 mg/L respectively and an average removal efficiency of 12.1%. LSC2 had an average influent and effluent DOC content of 7.81 ± 1.52 mg/L and 6.00 ± 0.67 mg/L respectively, and an average DOC removal efficiency of 23.1 %. This higher removal efficiency in LSC2 compared with LSC1 is attributed to high BDOC content of wastewater secondary effluent introduced to the column. Figure 4.6 and Figure 4.7 represent normalized DOC concentration in LSC1 and LSC2 during column ripening process respectively.

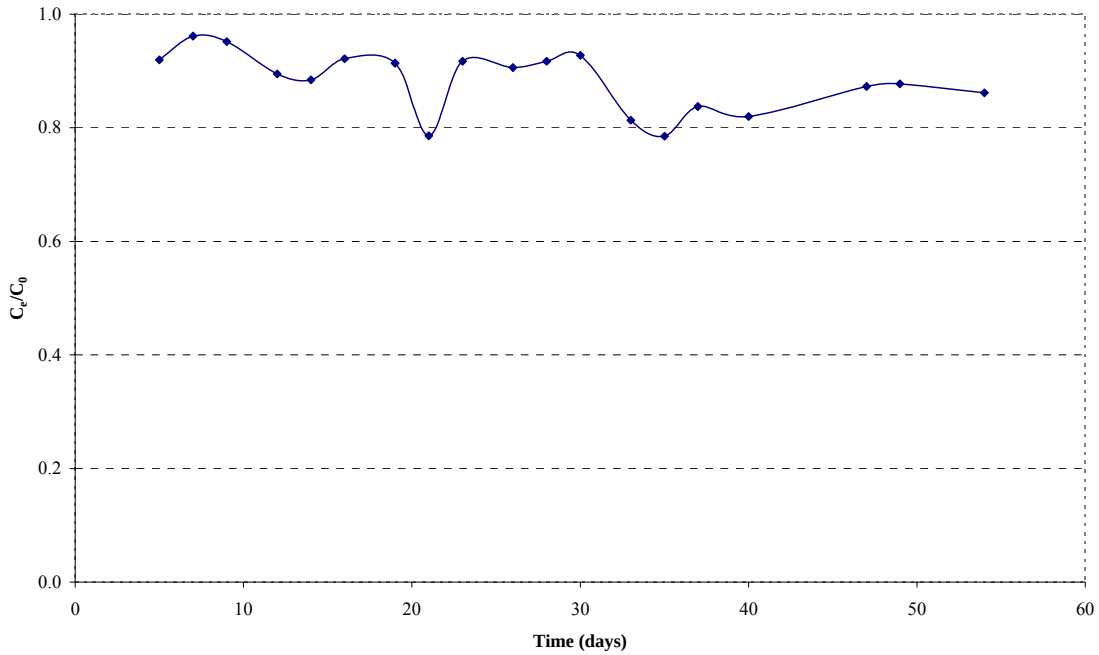


Figure 4.6 Normalized concentration of DOC during ripening period of LSC1 (Influent: MRW, column height = 5 m; media size: 0.8 – 1.25 mm; HLR = 0.56 m/d; EBCT = 3.57 days; oxic conditions)

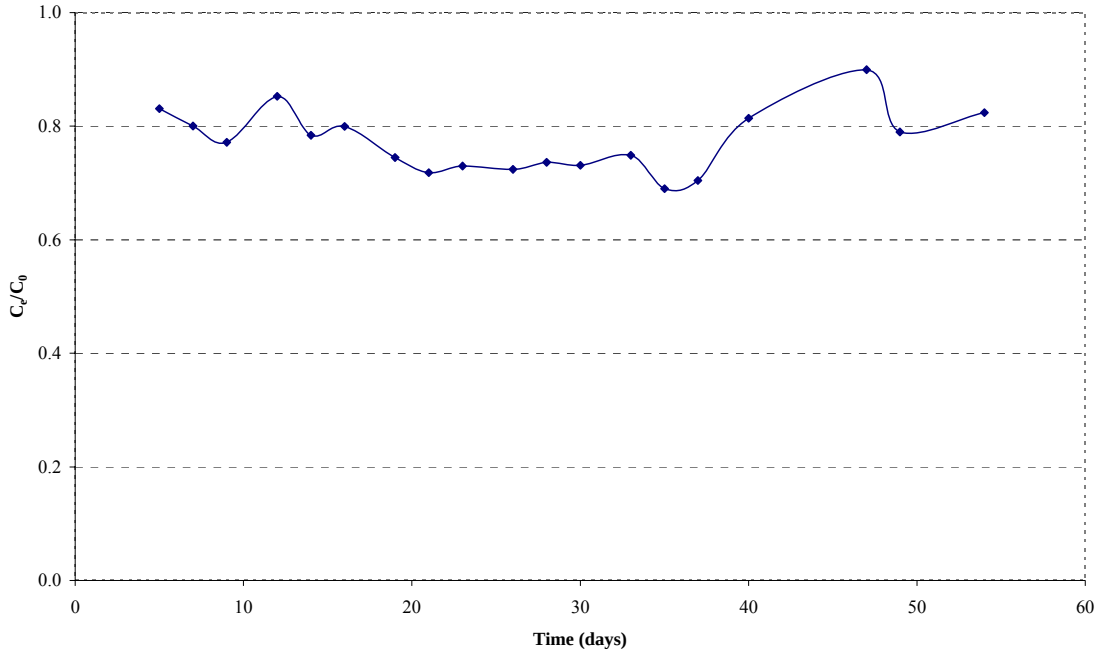


Figure 4.7 Normalized concentration of DOC during ripening period of LSC2 (Influent: MRW+SE; column height = 5 m; media size: 0.8 – 1.25 mm; HLR = 0.564 m/d; EBCT = 3.57 days; oxic conditions)

4.2.3 Ripening of short soil column

Four borosilicate glass columns with internal diameter of 50 mm and 300 mm height were packed with 0.8 mm to 1.25 mm silica sand. The Maas river water (used as influent water) was introduced at HLR = 0.257 m/d to ripen two soil columns under oxic conditions. In order to evaluate effectiveness of sand media in contaminants attenuation, tracer test was carried out to identify empty bed contact time in short soil column (SSC) experimental setups.

- **Tracer tests for short soil columns**

EBCT of short soil columns was determined by conducting tracer tests in two columns. It was found that initial and mean EBCT for SSC1 were 16.92 hours and 23.17 hours, respectively, while 17 hours and 23.88 hours were recorded for SSC2. Breakthrough curves of sodium chloride used as tracer solution are presented in Figure 4.8 and Figure 4.9. Calculations of EBCT for SSCs are presented in Appendix A 4.

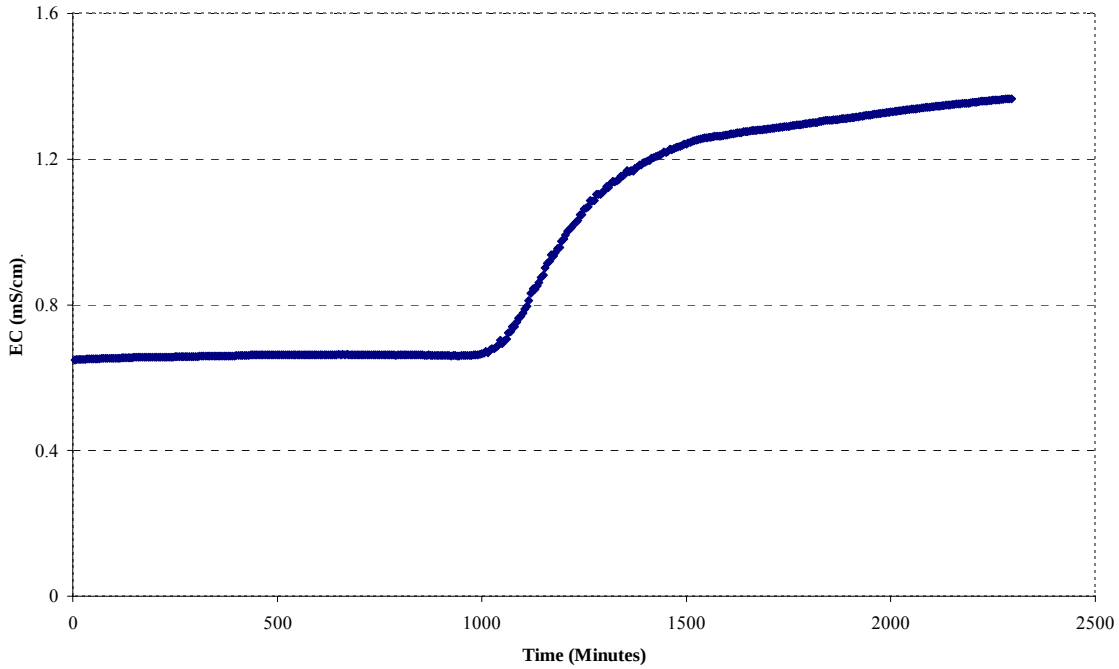


Figure 4.8 Breakthrough curves of sodium chloride used as tracer solution for determination of EBCT in SSC1.

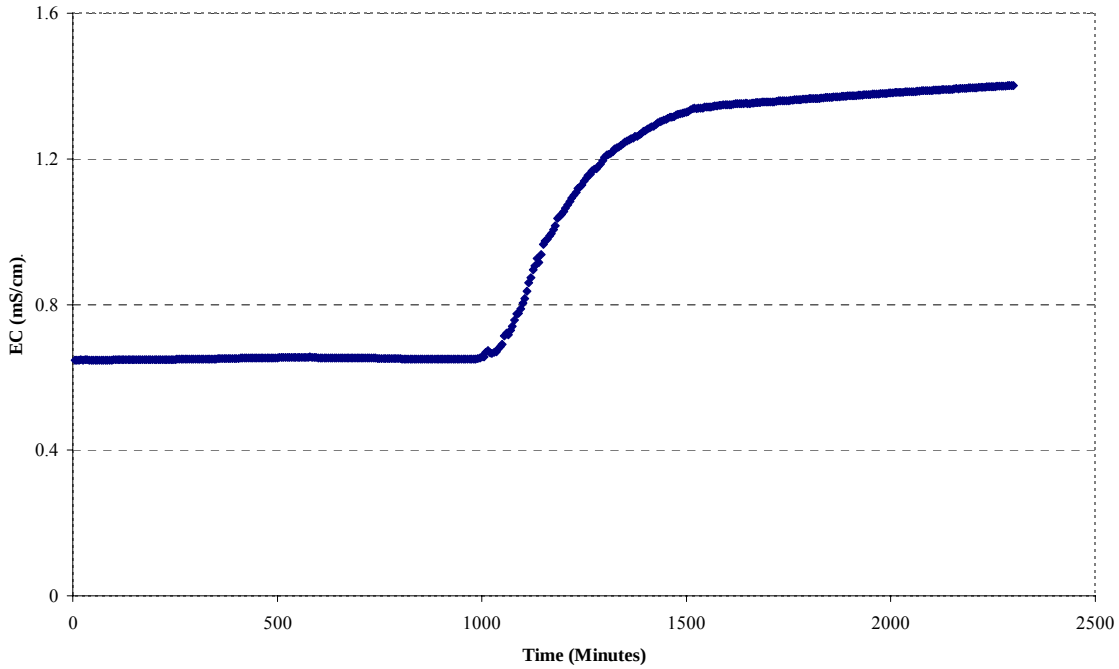


Figure 4.9 Breakthrough curves of sodium chloride used as tracer solution for determination of EBCT in SSC2.

Ripening process was carried out for about two months. DOC was continuously quantified and monitored at influent and effluent points of the columns to affirm steady state conditions with respect to DOC removal. Moreover, influent waters of the two soil columns were supplemented with synthetic organic matter to augment the low BDOC content of Maas river water in order to prevent carbon-limiting conditions during PhACs removal through biodegradation. Also, a control soil column was operated under abiotic conditions using sodium azide (40 mM) to differentiate sorption from biodegradation. The last column was prepared in a short ripening period to compare the ability of individual PhAC removal with respect to acclimation period of microorganisms.

Average DOC contents for influent and effluent water for SSC1 were found to be 2.95 ± 0.80 mg/L and 2.67 ± 0.62 mg/L with an average DOC removal of 9.3 %, while the average DOC content for short soil column No. 2 effluent was 2.64 ± 0.53 mg/L with an average removal of 10.4%. Figure 4.10 and Figure 4.11 show normalized DOC concentrations for SSC1 and SSC2 respectively.

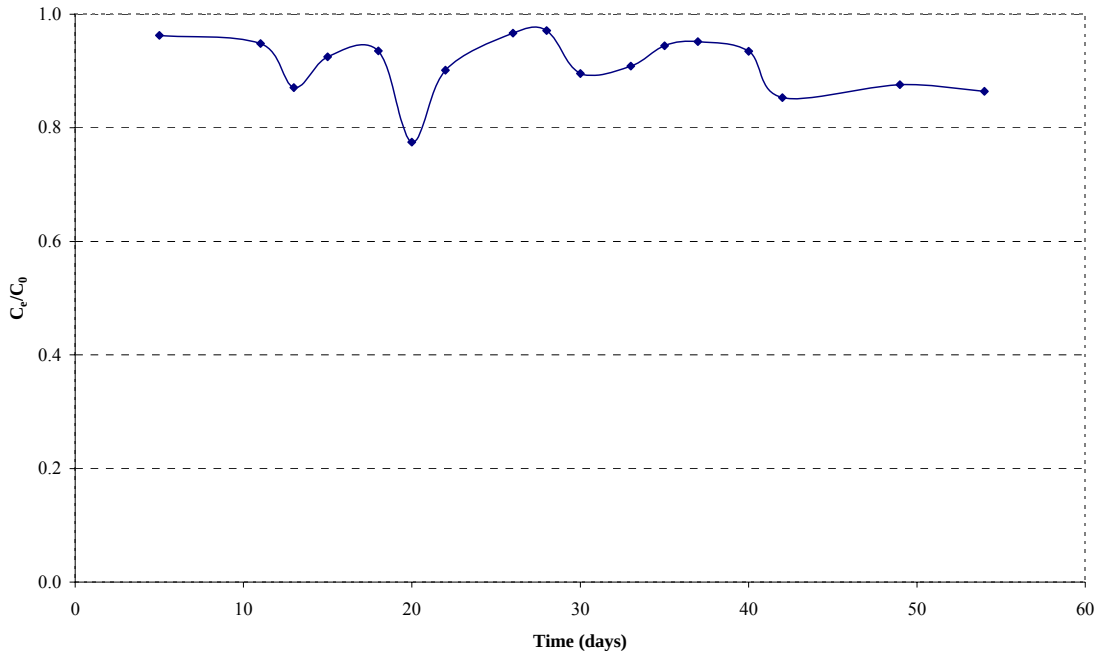


Figure 4.10 Normalized DOC concentration for influent and effluent water during ripening of SSC1 (Influent: MRW; column height = 300 mm; HLR = 0.26 m/d, EBCT = 17 hours; media size: 0.8 – 1.25 mm, oxic conditions)

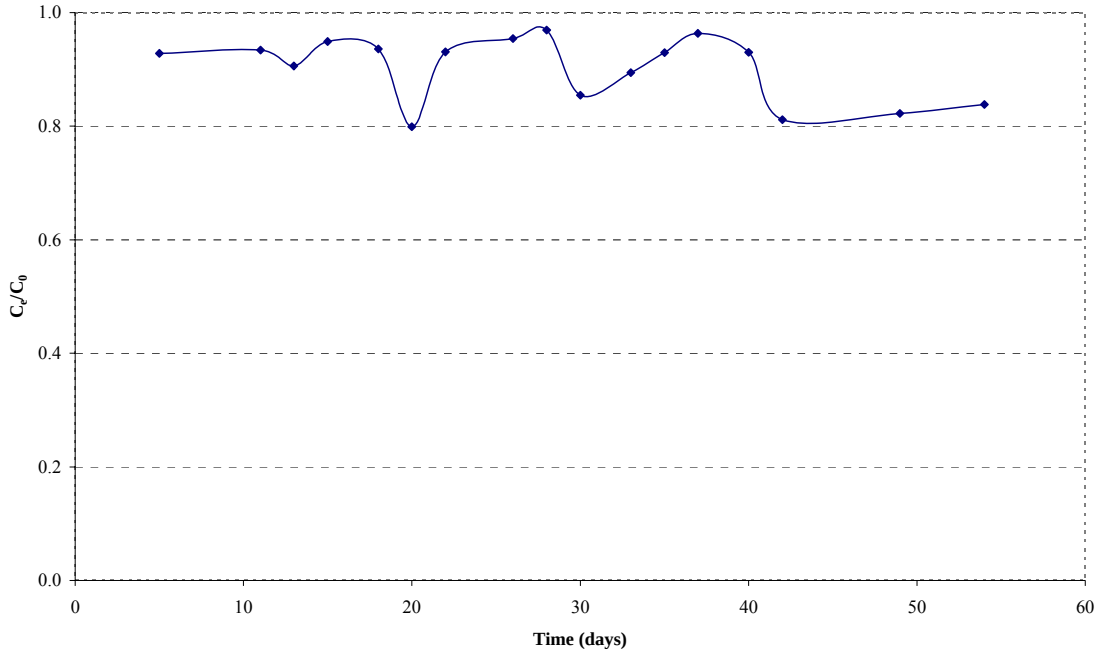


Figure 4.11 Normalized DOC concentration for influent and effluent water during ripening of SSC2 (Influent: MRW; column height = 300 mm; HLR = 0.26 m/d, EBCT = 17 hours; media size: 0.8 – 1.25 mm, oxic conditions)

4.3 Natural attnucation of pharmaceuticals by biodegradation in different water matrices

4.3.1 Characterization of organic matter

Both influent and effluent samples taken from batch reactors were characterized using a number of NOM characterization tool (e.g., DOC, UV254, SUVA, LC-OCD and FEEM) and microbial activity by ATP. First, Table 4.1 shows influent and effluent characteristics of water with respect to pH, DOC, UVA and SUVA used in this study. High SUVA value of (3.613 L/mg.m) of PDW followed by SE (3.407 L/mg.m) and MRW (3.121 mg/L), implies that these three water types posses more humic fraction than the Maas river water combined with synthetic organic matter. Though the same MRW was spiked with SOM at Time = 0-day, the decrease in SUVA value was attributed to the aliphatic nature of this synthetic organic matter.
Incubation period of 60 days in bioactive sand had resulted in increase in UV_{254} and SUVA (Figure 4.12). Increase in SUVA values over the entire experimental period of 60 days retention time is in agreement with previous findings by Cha et al., (2004), which explained that SUVA values increase after a biological reaction due to removal of readily biodegradable matter (i.e, aliphatic structure of NOM). NOM contained in PDW showed to be dominated by humic fraction since less aliphatic compounds were removed in 60-day retention time, manifested by minimal increase in SUVA values.

Table 4.1 Characterization of organic matter in different water matrices

Influent water	Point	pH	DOC (mg/L)	BDOC (mg/L)	UV-254 (ab./cm)	Average SUVA (L/mg. m)
MRW	Influent	7.73 ± 0.06	3.6 ± 0.05	1.52 ± 0.19	0.11 ± 0.002	3.12 ± 0.09
	Effluent	8.33 ± 0.14	2.08 ± 0.23		0.09 ± 0.006	4.26 ± 0.71
MRW+SOM	Influent	7.77 ± 0.01	5.27 ± 0.14	2.79 ± 0.42	0.12 ± 0.002	2.36 ± 0.11
	Effluent	8.42 ± 0.07	2.48 ± 0.37		0.11 ± 0.006	4.72 ± 0.89
SE	Influent	7.62 ± 0.09	14.83 ± 1.57	6.31 ± 0.53	0.50 ± 0.006	3.41 ± 0.37
	Effluent	8.61 ± 0.14	8.52 ± 1.05		0.42 ± 0.019	4.96 ± 0.78
PDW	Influent	7.87 ± 0.03	14.62 ± 0.51	4.60 ± 1.85	0.53 ± 0.007	3.61 ± 0.16
	Effluent	8.48 ± 0.09	10.02 ± 1.37		0.39 ± 0.017	3.94 ± 0.63

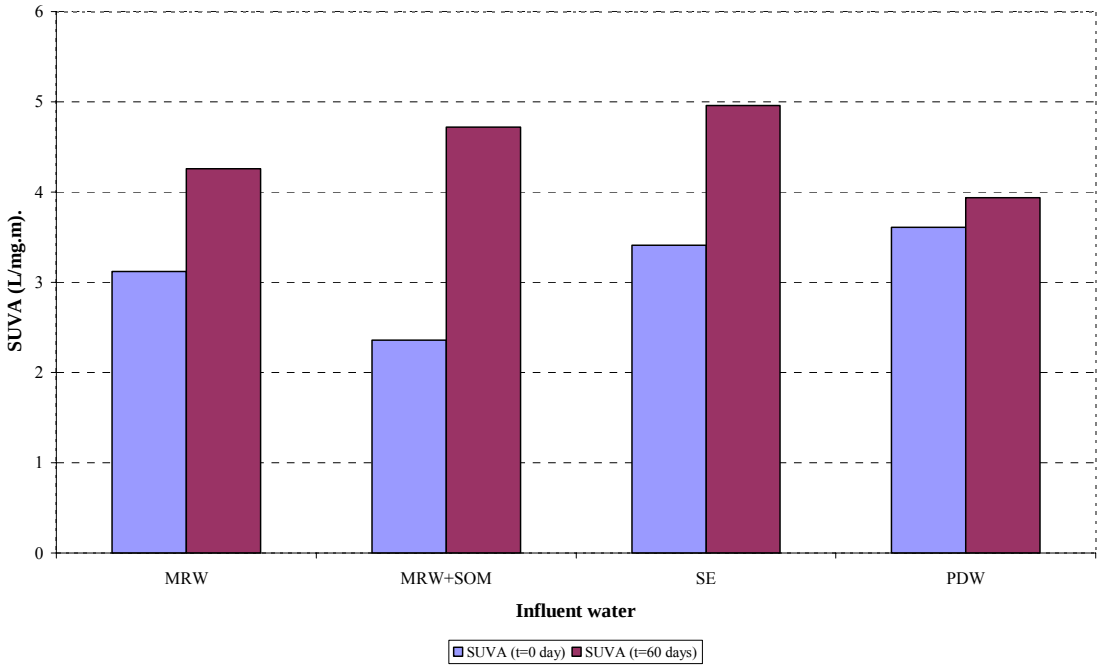
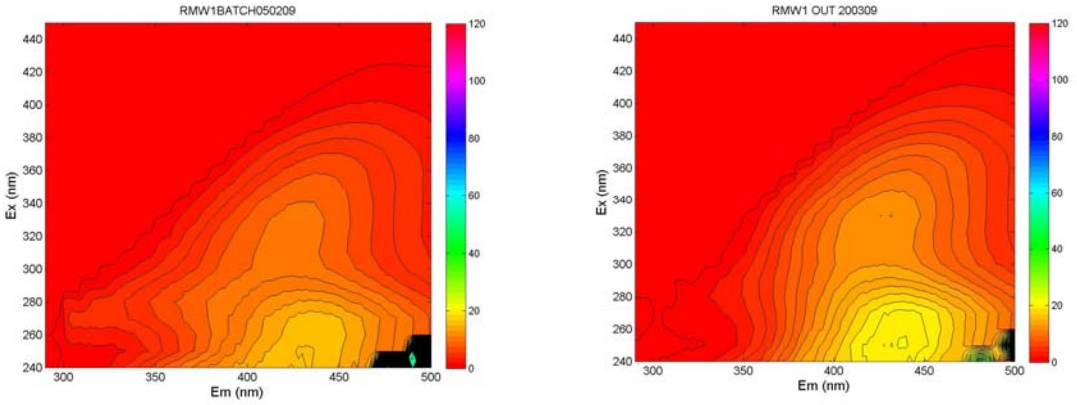


Figure 4.12 Initial and final SUVA values in laboratory batch-scale reactors

4.3.2 Change in Fluorescence EEM during batch studies

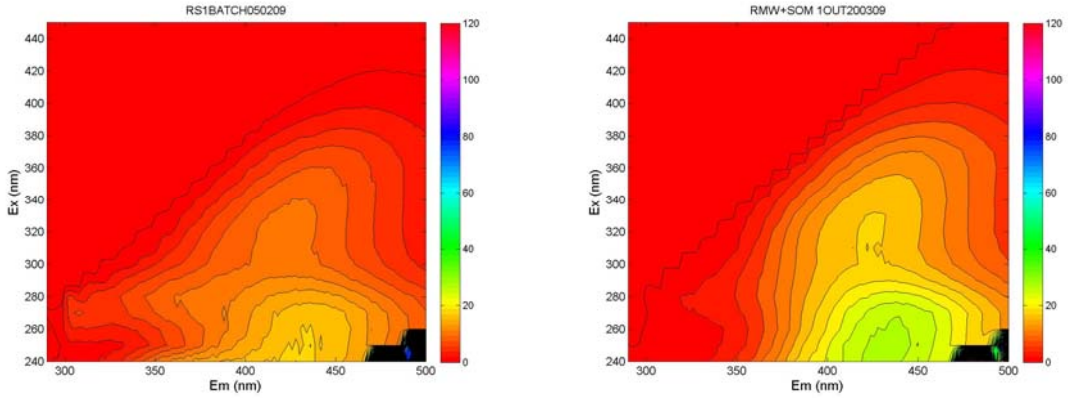
Fluorescence EMM (F-EEM) spectra of influent and effluent samples were measured to investigate NOM characteristics. Contour lines represent the distribution of fluorescence intensity at different excitation-emission wavelength. Three peaks were identified namely, humic/fulvic-like, humic-like and protein-like peaks related to maximum excitation and maximum emission checked. The differences between fluorescence intensities for Time = 0-day and Time = 60-day were identified. Results of F-EEM for different waters are presented in Figure 4.13, Figure 4.14, Figure 4.15 and Figure 4.16.

Fluorescence intensities (FI) for humic/fulvic-like (peak 1) and humic-like (peak 2) increased in effluent samples of MRW, MRW+SOM, SE, and PDW. However, fluorescence intensities for protein-like (peak 3) showed substantial decrease in the same samples. Figure 4.13 exhibited an increase in fluorescence intensities of peak 1 and peak 2 intensities by 27% and 33.6% respectively, whilst 52.4% of peak 3 intensity was removed for MRW. In addition to that, 35.7% of DOC was removed in the batch reactor. This results indicated that FEEm intensities represented humic/fulvic-like and humic-like did not correlate to the reduction in DOC. Figure 4.14 also showed increases in fluorescence intensities by 63.1% and 63.8% for peak 1 and peak 2 respectively for the batch reactor contained MRW+SOM. On the other hand removal of protein-like peak was equal to that of MRW (52.4%) and DOC removal for MRW+SOM was found to be 44.3%. Figure 4.15 presents DOC removal of 33.5%, increase in fluorescence intensity for peak 1 and peak 2 by 32.1% and 25.1% respectively for the sample that contained SE. On the contrary peak3 fluorescence intensity was reduced by 49.3%. Figure 4.16 indicates minimal increase in both peak 1 and peak 2 fluorescence intensities by 2.9% and 6%, respectively for the batch reactor that contained PDW. Moreover, DOC was removed 17.6%, while peak 3 was removed in the reactor. According to Saadi et al. (2006), formation of new fluorescing materials associated with DOM biodegradation and degradation of certain organic components capable of quenching DOM fluorescence can lead to increase in fluorescence during long incubation time (i.e., 60-day).



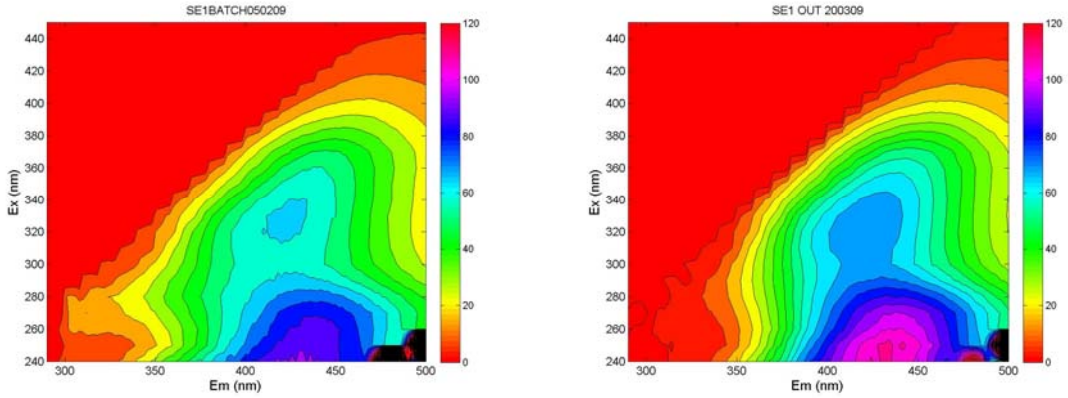
(a) Influent (b) Effluent

Figure 4.13 F-EEM spectra for influent (a), and effluent (b) of Maas river water (Incubation Time = 60-day)



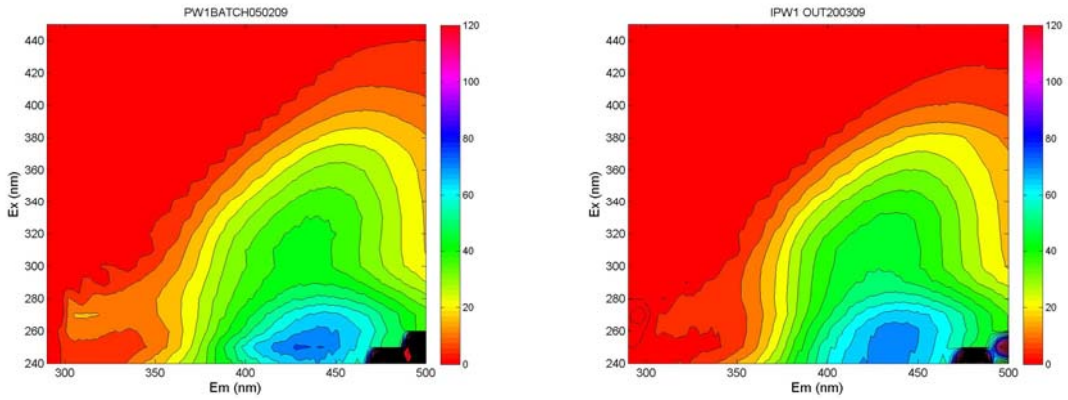
(a) Influent (b) Effluent

Figure 4.14 F-EEM spectra for influent and effluent of MRW+SOM (Incubation Time = 60-day)



(a) Influent (b) Effluent

Figure 4.15 F-EEM spectra for influent and effluent of secondary effluent (Incubation Time = 60-day)



(a) Influent (b) Effluent

Figure 4.16 F-EEM spectra for influent and effluent of PDW (Incubation Time = 60-day)

4.3.3 Removal of PhACs and odour compounds

a) Pharmacetucals

Fate of PhACs was studied in batch experimental setups using different sources of water (i.e, different NOM characteristics). Approximately, a solution with concentration of 4 µg/L of 13 PhACs was prepared and spiked into different influent waters. Sources of water used in batch experiments were, secondary effluent (SE), plant-derived water (PDW), surface water (SW), surface water with synthetic organic matter (SW+SOM), tap water. Ripening period for batch study lasted for almost two months and 15 batch reactors (in triplicate) were spiked with the target PhACs compounds, geosmin and 2-MIB and agitated on a table shaker at 85 rpm during laboratory experiments period. However, batch reactors were incubated for 30-day, and redox conditions were rendered anoxic after being exposed to nitrogen gas stream until dissolved oxygen reached a concentration of 0.2 mg O_2/L. Change of redox conditions in batch study was performed to mimic field conditions in which dissolved oxygen is depleted in the first few meters and anoxic conditions prevails accordingly. In this batch study, various types of water matrices were used to investigate PhACs removals (extent) under different organic matter characteristics and also to correlate between these removals and microbial activity indicated by ATP. In general presence of biomass catalyzes removal of organic micro pollutants through bio-oxidation (co-metabolism). Effluent PhACs samples were collected on day 60 and removal efficiency was then calculated. Figure 4.17 shows removal efficiencies calculated for various water types.

In Figure 4.17, most of the targeted compounds exhibited removal efficiencies greater than 90% of initial concentration found in various influent waters after 60-day retention time. However, hydrophobic (with log $K_{ow} > 2$) compounds of clofibric acid, diclofenac, and gemfibrozil were less removed in PDW which was more humic compared to other influent water types used in this batch experiment. These PhACs were not well removed due to the amount of biodegradable dissolved carbon (BDOC) (i.e., biopolymer) during biotransformation. The concentrations of biopolymer in SE, MRW, MRW+SOM were

greater than in PDW. Previous study done by Lim. et al. (2009) showed that biotransformation of some wastewater-derived contaminants (e.g., diclofenac and gemifibrozil) increased at initial concentration of wastewater BDOC. This implies that the amount of BDOC is related to removal of these pharmaceuticals. Hydrophilic compounds of paracetamol, pentxifylline, phenacetine and caffeine were easily biotransformed in reactors containing even low BDOC (tap water) which reflected by low ATP concentration of 1214 pg/g dry sand compared to SE (4844 pg/g dry sand), MRW (3030 pg/g dry sand) and MRW+SOM (3676 pg/g dry sand) PDW (2070 pg/g dry sand). Carbamazepine was found to be persistent and an average reduction of 3 % in target PhACs concentrations was observed in control reactors. This reduction may be attributed to adsorption of compounds to reactors' walls and/or lost during experiment.

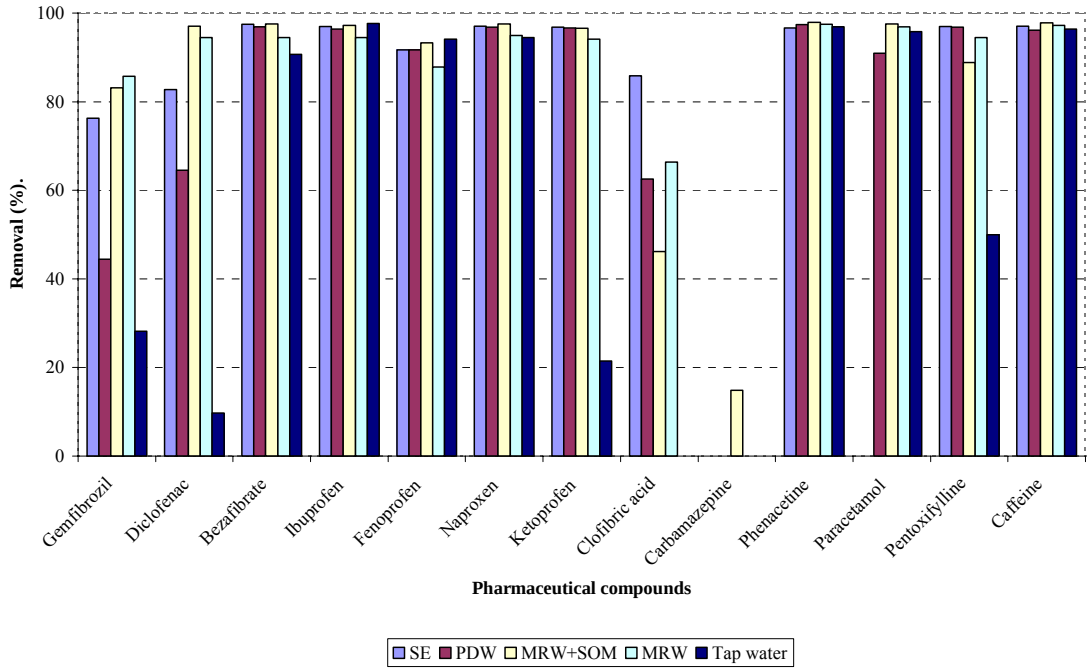


Figure 4.17 Removal of target PhACs from different water sources in batch reactors

b) Odour compounds

Geosmin and 2-MIB were studied in batch experimental setups. Influent waters from MRW, MRW+SOM, SE, PDW, and TW were spiked with 200 ng/L concentrations from geosmin and 2-MIB. Elimination of these two odour compounds was achieved under oxic conditions in the first 30 days of the test period by sorption and biodegradation. Results obtained from tests are presented in Table 4.2.

Table 4.2 Removal of geosmin and MIB in experimental batch studies

Influent water	Geosmin (ng/L)			MIB (ng/L)		
	Influent	Effluent	% removal	Influent	Effluent	% removal
MRW	217.6	N.D[a]	> 99	254.1	N.D	> 99
MRW+SOM	236.7	N.D	> 99	268.4	N.D	> 99
SE	69.6	N.D	> 99	238.5	N.D	> 99
PDW	278.2	N.D	> 99	292.9	N.D	> 99
Blank	226.4	N.D	> 99	273.4	N.D	> 99

N.D[a]: not detected

4.4 Effects of redox conditions and secondary effluent on the removal of PhACs

4.4.1 NOM characteristics

Prior to application to experimental setups, influent water for long soil column was characterized in order to provide an insight correlation between DOC removal and various parameters of influent water.

a) DOC, UV_{254} and SUVA measurement during steady state conditions
5-m soil columns were used to investigate the impact of redox conditions on selected PhACs removal. DOC, UVA-254 and SUVA for each sample were measured and showed in Table 4.3. It showed increase in SUVA values as a result of aliphatic compounds removal in the soil column. However, MRW+SE+SOM showed inconsistency since a decreased SUVA value was observed in effluent water.

Table 4.3 Characteristics of influent and effluent water for long soil column experiments carried out under oxic conditions

Influent water	DOC (mg/L)		UVA-254 (1/cm)		SUVA (L/mg.m)	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
MRW	3.66	2.99	0.09	0.07	2.48	2.38
MRW + SE	9.67	6.43	0.28	0.21	2.85	3.22
MRW + SOM	5.65	2.70	0.11	0.09	1.95	3.30
MRW + SE + SOM	11.55	8.33	0.34	0.23	2.96	2.74

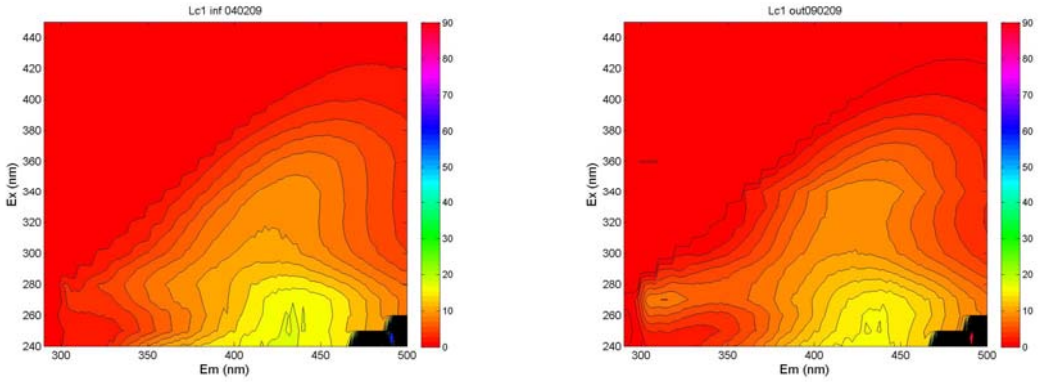
Under anoxic conditions, there was substantial increase in effluent water SUVA value due to removal of readily biodegradable organic matter.

Table 4.4 Characteristics of influent and effluent for 5-meter soil column experiments carried out under anoxic conditions

Influent water content	DOC (mg/L)		UVA-254 (1/cm)		SUVA (L/mg.m)	
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
MRW + SOM	3.15	2.21	0.10	0.08	2.69	5.75
MRW + SE + SOM	9.26	7.01	0.33	0.28	2.75	6.59

b) Change in F-EEM during long soil column studies

F-EEM spectra were measured for river mass water and Maas river water blended with secondary effluent samples under different redox conditions. Fluorescence peaks and corresponding excitation/emission values were obtained (Figure 4.18 to Figure 4.19) Table 4.5 summarizes humic-like, humic/fulvic-like and protein-like intensities and reduction in fluorescence intensity.



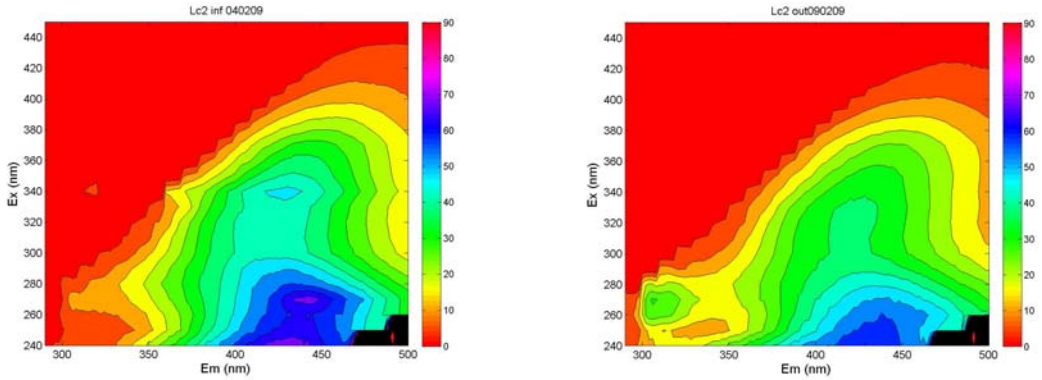
(a) Influent (b) Effluent

Figure 4.18 F-EEM of MRW in influent (a) and effluent (b) (oxic conditions)

Table 4.5 Summary of F-EEM results for long soil column No. 1 operated under oxic conditions

Peak 1 humic/fulvic-like substances		Excitation (nm)	Emission (nm)	Intensity	Reduction in intensity (%)
MRW	Influent	340	432	12.26	11.3
	Effluent	340	432	10.87	
Peak 2 humic-like substances					
MRW	Influent	260	432	17.28	2.8
	Effluent	260	432	16.79	
Peak 3 protein-like substances					
MRW	Influent	270	322	9.47	5.9
	Effluent	270	322	8.91	

Table 4.5 shows high reduction in MRW intensities by 11.3% for peak No. 1, 2.8% for peak No. 2 and 5.9% for peak No. 3.

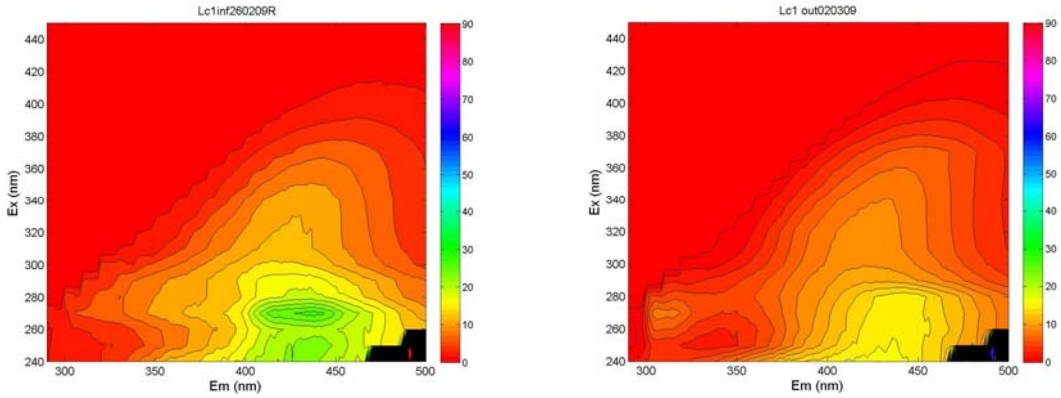


(a) Influent (b) Effluent

Figure 4.19 F-EEM of MRW + SE in influent (a) and effluent (b) (oxic conditions)

Table 4.6 Summary of F-EEM results for long soil column No. 2 operated under oxic conditions

Peak 1 humic/fulvic-like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SE	Influent	340	430	49.11	51.4
	Effluent	340	430	23.85	
Peak 2 humic-like substances					
MRW+SE	Influent	270	442	71.22	49.9
	Effluent	270	442	35.68	
Peak 3 protein-like substances					
MRW+SE	Influent	280	334	16.16	45.5
	Effluent	280	334	8.81	

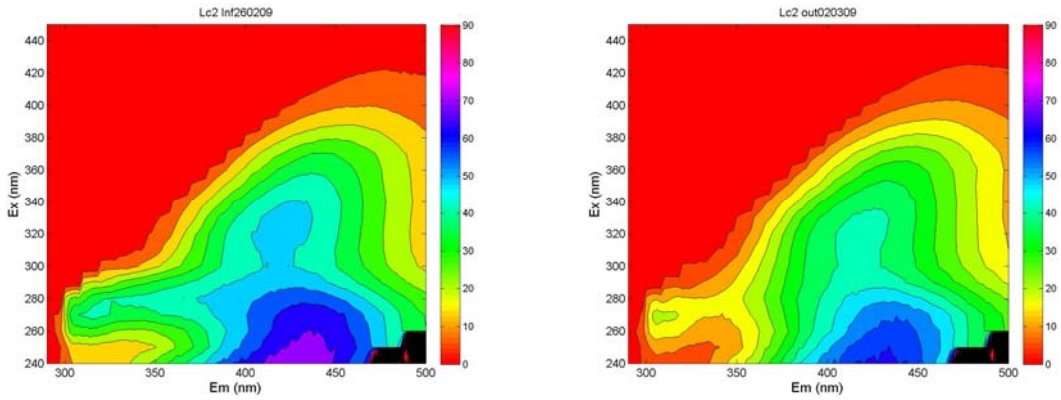


(a) Influent (b) Effluent

Figure 4.20 F-EEM of MRW + SOM in influent (a) and effluent (b) (oxic conditions)

Table 4.7 Summary of F-EEM results for long soil column No. 1 operated under oxic conditions

Peak 1 humic/fulvic-like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SOM	Influent	340	432	12	18.9
	Effluent	340	432	9.73	
Peak 2 humic-like substances					
MRW+SOM	Influent	270	432	27.67	42.3
	Effluent	270	432	15.97	
Peak 3 protein-like substances					
MRW+SOM	Influent	270	324	7.68	5.6
	Effluent	270	324	7.25	

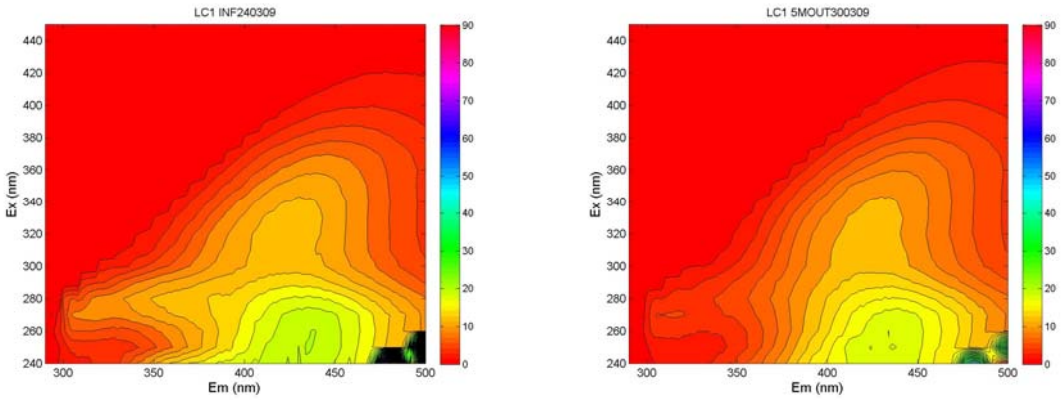


(a) Influent (b) Effluent

Figure 4.21 F-EEM of MRW+SE+SOM in influent (a) and effluent (b) (oxic conditions)

Table 4.8 Summary of F-EEM results for long soil column No. 2 operated under oxic conditions

Peak 1 humic/fulvic-like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SE+SOM	Influent	340	426	49.2	16.6
	Effluent	340	426	41.01	
Peak 2 humic-like substances					
MRW+SE+SOM	Influent	250	434	71.64	21.9
	Effluent	250	434	55.92	
Peak 3 protein-like substances					
MRW+SE+SOM	Influent	270	320	43.39	53.8
	Effluent	270	320	20.04	

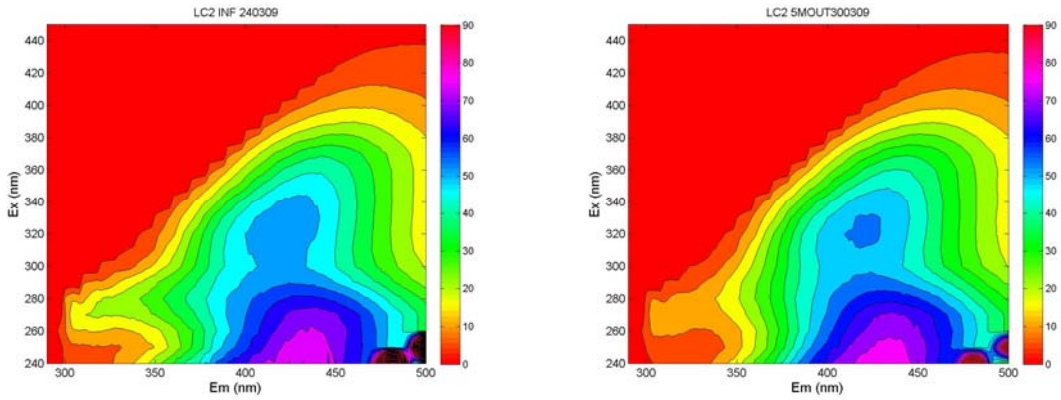


(a) Influent (b) Effluent

Figure 4.22 F-EEM of MRW+SE+SOM in influent (a) and effluent (b) (anoxic conditions)

Table 4.9 Summary of F-EEM results for long soil column No. 1 operated under anoxic conditions

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SOM	Influent	340	432	12	18.9
	Effluent	340	432	9.73	
Peak 2 Humic- like substances					
MRW+SOM	Influent	330	426	12.9	7.8
	Effluent	330	426	11.9	
Peak 3 - Protein-like substances					
MRW+SOM	Influent	280	336	10.7	56.1
	Effluent	280	336	4.7	



(a) Influent (b) Effluent

Figure 4.23 F-EEM of MRW+SE+SOM in influent (a) and effluent (b) (anoxic conditions)

Table 4.10 Summary of F-EEM results for long soil column No. 2 operated under anoxic conditions

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SE+SOM	Influent	330	424	54.7	0.2
	Effluent	330	424	54.6	
Peak 2 Humic- like substances					
MRW+SE+SOM	Influent	250	432	77.0	0.3
	Effluent	250	432	76.8	
Peak 3 - Protein-like substances					
MRW+SE+SOM	Influent	280	330	24.3	42.8
	Effluent	280	330	13.9	

4.4.2 Removal of PhACs and odour compounds

a) PhACs

12 pharmaceuticals (e.g., 8 hydrophobic ionic compounds, one hydrophobic nutral compound and 1 hydrophilic ionic compound and 2 hydrophilic neutral compounds) were studied in laboratory-scale soil column of 57 mm diameter, 5 m length made of uPVC. In this study, two soil column set-ups were used to compare the attenuation of pharmaceuticals between surface water (e.g., Maas river) and wastewater effluent derived-surface water (i.e., surface water containing about 50% wastewater effluent). Also, attenudation of these 12 pharmaceutical compounds under oxic and anoxic conditions in soil columns was conducted in order to investigate redox sensistive compounds in among these compounds.

Figure 4.24 shows removal of PhACs from Maas river water and Maas river water blended with secondary effluent (50;50). Removal of ibuprofen, fenoprofen, naproxen, ketoprofen, clofibric acid, carbamazepine, phenacetine, pentoxifylline and caffeine in

MRW+SE was similar to that of MRW. However, removal of gemfibrozil decreased from 86% in Maas river water (MRW) to 60% in Maas river water blended with secondary effluent (MRW+SE) while removal of diclofenac decreased from 53% in (MRW) to 28% in MRW+SE and removal of bezafibrate decreased from 93% in MRW to 78% in MRW+SE. This result was consistent with a batch study conducted by Lim et al. (2008) which showed a higer removal of diclofenac and gemfibrozil in surface water than secondary effluent. The different biotransformation observed for diclofenac and gemfibrozil in MRW and MRW+SE suggested that BDOC derived from surface water enhanced removal of these compounds as compared to that derived from wastewater effluent. Majority of studied compounds showed removal above 90% in MRW and MRW+SOM under both oxic and anoxic conditions, except for diclofenac and clofibric acid which showed removal less than 80% and 40%, respectively, in both redox conditions (Figure 4.25). Carbamazepine showed a persistent behaviour under oxic and anoxic conditions. This persistence is in agreement with findings of study carried out by (Drewes and Summers, 2002). In MRW+SE, carbamazepine also exhibited a persistent behaviour under oxic and anoxic conditions. Ibuprofen, naproxen, phenacetine and caffeine were removed above 80% from MRW+SE. The rest of the compounds were removed within the range of 10% to 60%.

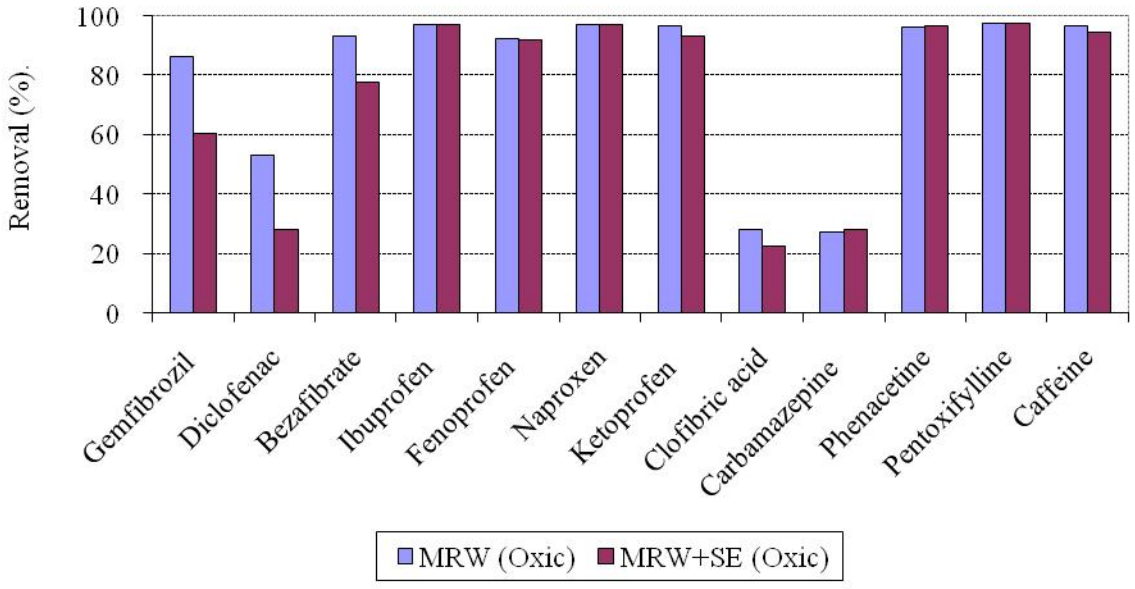


Figure 4.24 Impact of secondary effluent added to MRW (50:50) on removal of PhACs (EBCT = 3.57 days and HLR = 0.56 m/d)

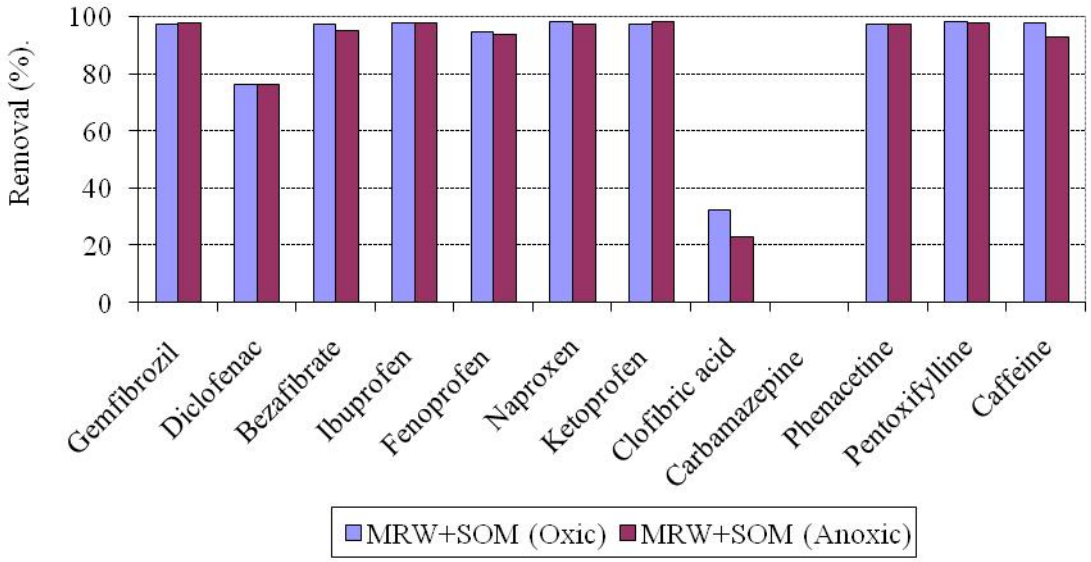


Figure 4.25 Comparison of percent removals of target compounds during oxic and anoxic conditions in Maas river water (EBCT = 3.57 days and HLR = 0.56 m/d)

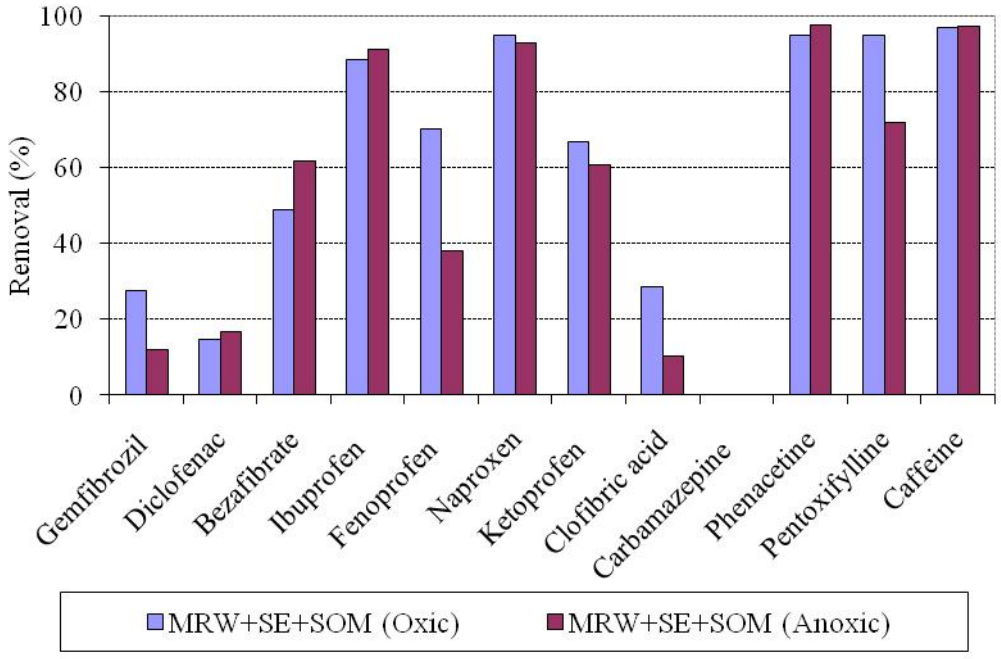


Figure 4.26 Comparison of percent removal of target compounds during oxic and anoxic conditions in Mass river water amended with secondary effluent (EBCT = 3.57 days and HLR = 0.56 m/d)

b) Odour compounds (Geosmin and 2-Methyl isoborneol)

Geosmin and 2-MIB removal was studied in LSC setups to track their removal during oxic and anoxic conditions. Results are presented in Figure 4.27. The initial average concentrations of geosmin and 2-MIB fed to the columns were 415 ng/L and 470 ng/L respectively. Geosmin was removed above 99% in both MRW and MRW+SE columns while 2-MIB was removed by 97.3% and 95% in MRW and MRW+SE respectively. Thus, there was no impact on the removal of geosmin and 2-MIB by secondary effluent.

Geosmin and 2-MIB removed higer under anoxic conditions. On the other hand, 2-MIB removal increased from 80.3% under oxic conditions to 99.2% under anoxic conditions for MRW+SOM. Moreover, an increase in 2-MIB was attained from 67.4% under oxic conditions to 81.6% under anoxic conditions for MRW+SE+SOM. Effluent concentrations for geosmin and 2-MIB under anoxic conditions (influent water: MRW+SOM) were 4 ng/L each. This concentration is the human olfactory sense limit for geosmin and below the human olfactory sense limit for 2-MIB. It could be concluded from the results above that there was some impact by secondary effluent in the removal of geosmin and 2-MIB, while 2-MIB was better removed under anoxic conditions.

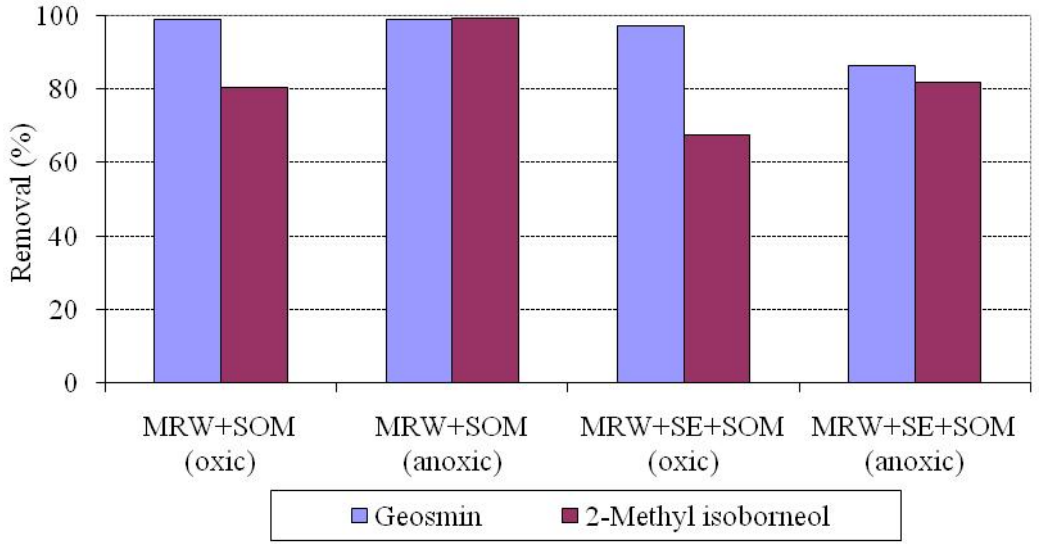


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Figure 4.27 Geosmin and 2-MIB removal in long soil column experiments (EBCT = 3.57 days; HLR = 0.56 m/d)

4.5 Biodegradation, sorption and persistence of PhACs during RBF and the use of microbial activity to assess the potential for biodegradation of contaminants

4.5.1 NOM characteristics

a) EC, pH, dissolved oxygen, DOC, UV_{254}, SUVA measurement

Three water sources were used to carry out SSC experiments. Various parameters such as DOC, UV_{254}, EC, pH and O_2 were measured prior to application of these influent waters. Parameters measured are presented in Table 4.11 and Table 4.12.

Table 4.11 Conductivity, pH and dissolved oxygen concentrations in soil columns

Influent water content	Influent			Effluent			Rippening period
	EC (µS/cm)	pH	O_2 (mg/L)	EC (µS/cm)	pH	O_2 (mg/L)	
Tap water	489	7.63	10.7	498	8.09	8.1	60-day
MRW + SOM	650-716	7.72-8.19	8.6-9.1	645-718	8.15-8.38	8.2-8.4	60-day
MRW + SOM	650-722	7.77-8.19	8.5-9.11	650-720	8.17-8.34	8.18-8.5	30-day
DW + NaN_3	450-455	6.63-6.98	8.9-10.2	462-467	7.17-7.29	8.19-9.4	-

Table 4.12 DOC, UV_{254}, and SUVA of short soil column

Influent water content	DOC (mg/L)		UV-254 (1/cm)		SUVA (L/mg.m)		Rippening period (day)
	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	
TW	2.548-3.175	1.736-1.301	0.226-0.033	0.022-0.031	0.882-1.295	1.691-1.786	60
MRW + SOM	3.173-5.721	2.649-2.861	0.099-0.100	0.079-0.082	1.996-3.120	2.965-3.096	60
MRW + SOM	3.029-6.692	2.635-2.861	0.095-0.106	0.084-0.09	1.584-3.268	2.971-3.188	10
DW + NaN_3	1.618-2.548	1.466-1.736	0.033-0.226	0.031-0232	12.08-13.97	12.33-14.67	-

Table 4.12 shows increase in SUVA for Maas river water spiked with synthetic organic matter. This increase of SUVA indicates removal of easy biodegradable aliphatic compounds found in influent water. However, DW+NaN_3 have shown high value of SUVA in both influent and effluent of the SSC (12 to 14 L/mg.m). This high SUVA value is attributed to double bond of sodium azide's structure.

b) Change in Fluorescence EEM during short soil column studies

F-EEM was measured for various influent and effluent waters of various short soil columns. Figure 4.28 shows reduction in humic-like peak by 9.7%, while humic/fulvic-like peak was reduced by 28.3%. In addition to that, protein-like peak was reduced 3.8%. Low reduction in fluorescence intensities was observed tap water (TW) contains low organic matter. **Error! Reference source not found.** exhibited 9% percent removal for peak No. 1 (humic-like), 34.4% for peak No. 2 and 54.5% in peak No. 3. Figure 4.30 exhibited 7.7% percent removal for peak No. 1 (humic-like), 8.7% for peak No. 2 and 24.5% in peak No. 3. MRW+SOM showed high protein peak compared to the tap water and demineralised water. Figure 4.31 shows low reductions of fluorescence intensities for DW+NaN_3. 28% reduction was recorded for humic-like (Peak No.2), and Peak No. 3 (protein-like) fluorescence was removed substantially (42%). However, intensities observed in demi water were significatlylower than that of River Maas.

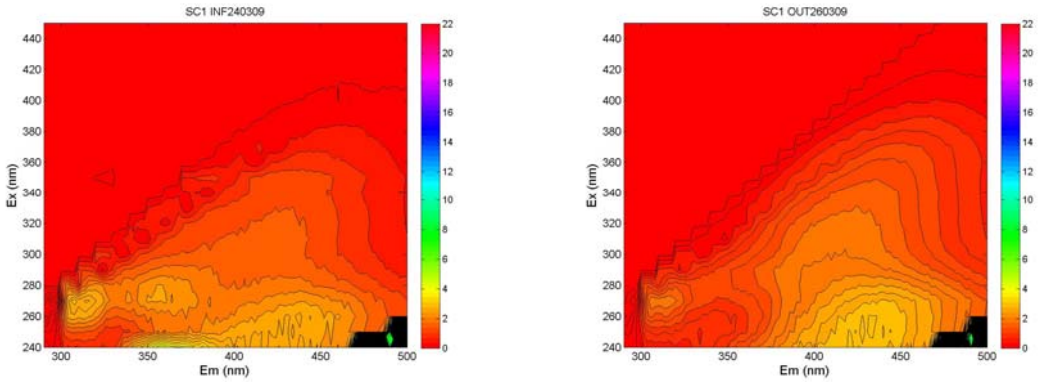
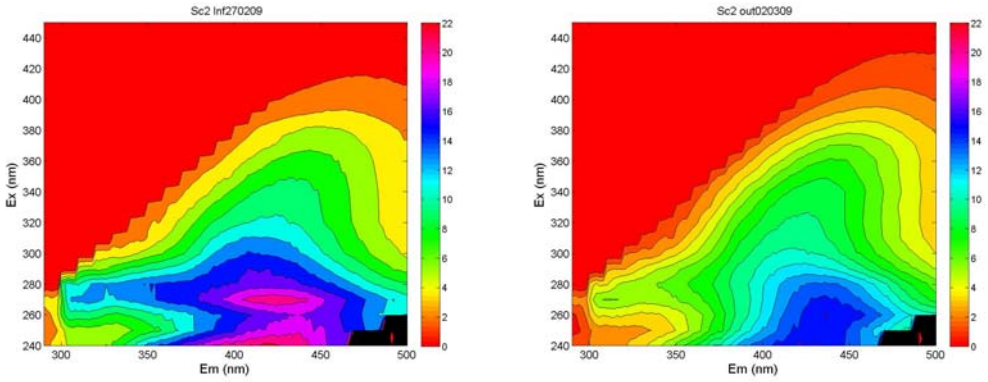


Figure 4.28 F-EEM spectra for influent (a) and effluent (b) of SSC1 (Rippening period=60-day, Maas river water and bioactive sand)

Table 4.13 Reductioin of fluorescence intensity of SSC1 (Tap water and bioactive sand)

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
TW	Influent	340	432	1.335	-
	Effluent	340	432	1.674	
Peak 2 Humic- like substances					
TW	Influent	270	424	2.322	-
	Effluent	270	424	2.840	
Peak 3 - Protein-like substances					
TW	Influent	270	318	3.117	37
	Effluent	270	318	1.963	



(a) Influent (b) Effluent

Figure 4.29 F-EEM spectra for influent (a) and effluent (b) of SC2 (Rippening period=60-day, Maas river water a

Table 4.14 Reductioin of fluorescence intensity of SSC2 (Maas river water and bioactive sand)

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SOM	Influent	340	432	9.82	9.0
	Effluent	340	432	8.94	
Peak 2 Humic- like substances					
MRW+SOM	Influent	270	424	21.5	34.4
	Effluent	270	424	14.1	
Peak 3 - Protein-like substances					
MRW+SOM	Influent	270	318	13.55	54.5
	Effluent	270	318	6.17	

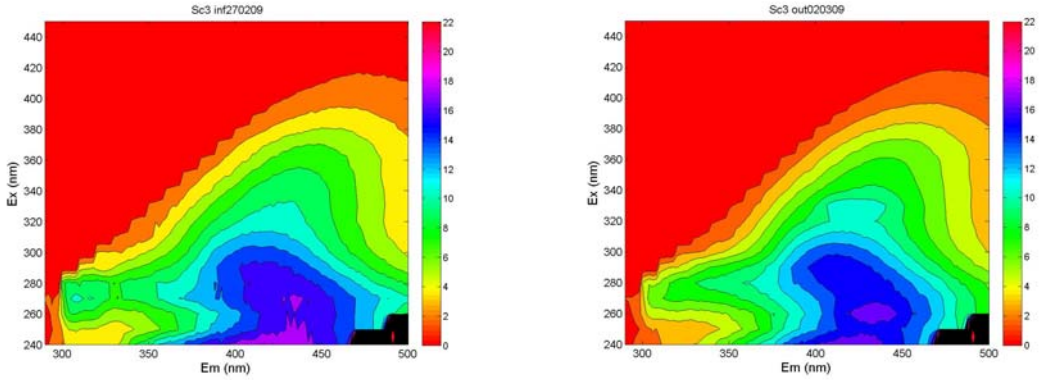


Figure 4.30 F-EEM spectra for influent (a) and effluent (b) of SSC3 (Rippening period=10-day, Maas river water and bioactive sand)

Table 4.15 Reductioin of fluorescence intensity of SSC3 (Maas river water and bioactive sand)

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
MRW+SOM	Influent	340	432	10.01	7.7
	Effluent	340	432	9.24	
Peak 2 Humic- like substances					
MRW+SOM	Influent	270	434	17.67	8.7
	Effluent	270	434	16.13	
Peak 3 - Protein-like substances					
MRW+SOM	Influent	270	314	10.24	24.5
	Effluent	270	314	7.73	

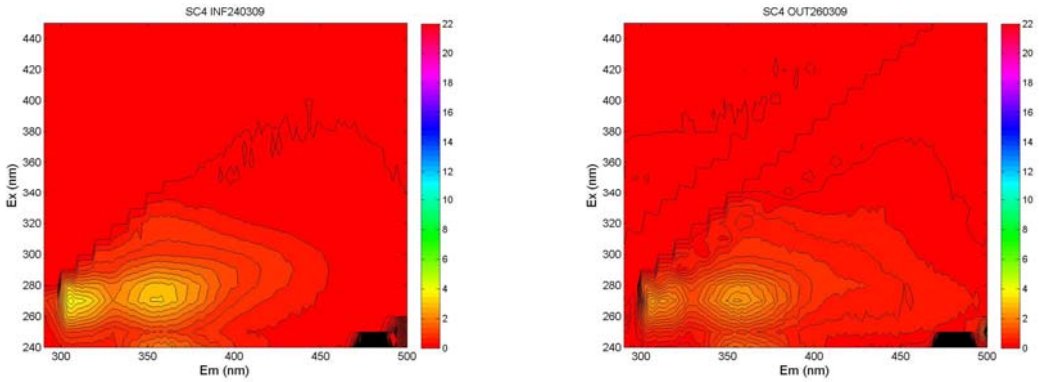


Figure 4.31 F-EEM spectra for influent (a) and effluent (b) of SSC4 (Rippening period=10-day, Demineralised water with sodium azide 40 mM, abiotic)

Table 4.16 Reductioin of fluorescence intensity of SSC4 (Rippening period=10-day, Demineralised water with sodium azide 40 mM, abiotic)

Peak 1 Humic/Fulvic- like substances		**Excitation (nm)**	**Emission (nm)**	**Intensity**	**Reduction in intensity (%)**
$DW+NaN_3$	Influent	340	432	0.10	-
	Effluent	340	432	0.28	
Peak 2 Humic- like substances					
$DW+NaN_3$	Influent	270	434	0.46	28
	Effluent	270	434	0.64	
Peak 3 - Protein-like substances					
$DW+NaN_3$	Influent	270	314	3.81	42
	Effluent	270	314	2.20	

4.5.2 Removal of PhACs and odour compounds

a) PhACs

Soil columns comprise of inner and outer diameters, the inner part was packed with either bioactive (acclimated) for SSC1, SSC2 and SSC3 and fresh sand for SSC4, while the outer one was used to control the prevailing ambient temperature by using a chiller. SSC1 was filled with acclimated silica sand, ripened for two months and ran under temperatures between 19 and 23 °C. The aim of using this setup was to study the effect of microbial activity on the removal of PhACs by lowering microbial activity using tap water (i.e, low BDOC). SC2 and SSC3 were prepared the same way like SSC1, the only difference from SSC1 was influent waters which was MRW+SOM. However, SSC1 and SSC2 were ripened for two months, while SSC3 was spiked with PhACs after ten days of ripening. Finally, SSC4 was fed with sterilized sand and fed with 40 mM NaN_3 with deminearlised water to differentiate sorption. All soil columns were kept in a dark room to minimize any potential effect of photodegradation. Results showing PhACs removal in the above mentioned conditions are presented in Figure 4.32, Figure 4.33 and Figure 4.34.

In Figure 4.32, removal of phenacetine and pentoxifylline (e.g., hydrophilic neutral and ionic compounds respectively) decreased from above 90% in a 2-months ripened column to below 80% in a 10-day ripened short soil column. Bezafibrate and fenoprofen (e.g., hydrophobic ionic compounds) showed 50% and 78% removal in a 2-month rippen column and 38% and 42% in a 10-day rippen column, respectively. Removal of phenacetin, pentoxifylline, bezafibrate and fenoprofen were increased with the time of ripening. This implies that the removal of these compounds increased with microbial activity and soil organic matter associated with sand. Ibuprofen, naproxen and ketoprofen were removed above 90% in both columns.

Figure 4.33 shows two short soil columns (SSC1 and SSC2) which were ripened for two months. During steady state conditions, SSC1 received tap water (BDOC = 0.8 mg/L), while SSC2 received MRW+SOM (BDOC = 2.549 mg/L). Low BDOC in TW resulted in low microbial activity (ATP = 15 pg ATP/g) compared to that of MRW+SOM (ATP = 48 pg ATP/g). Removal of bezafibrate, diclofenac, gemfibrozil and ibuprofen decreased in TW by more than 20% due to low microbial activity as result of low BDOC (i.e., low biodegradation). However, hydrophilic compounds of paracetamol, pentoxifylline, phenacetine and caffeine were biodegraded above 90% in tap water since the biomass measured in the column (ATP = 15 pgATP/g) was still capable of removing these compounds even under low BDOC (e.g., 0.8 mg/L). Carbamazepine again showed a persistent behaviour.

Removal of hydrophilic compounds of paracetamol, pentoxifylline, phenacetine and caffeine significantly decreased in a column fed with demineralised water spiked with 40 mM sodium azide (i.e., abiotic) (ATP = 0.4 ngATP/g). This decrease in percent removal of these compounds is attributed to inactivation of microorganisms. Carbamazepine exhibited a persistent behaviour in biotic and abiotic columns (see Figure 4.34). An average removal of 30% was obserbed for hydrophobic compounds of clofibric acid, fenoprofen, gemfibrozil, ketoprofen and naproxen. This was lower than the expected removal efficiencies because of their hydrophobic chacteristics (i.e., logKow higer than3). pH of influent and effluent water of SSC2 and SSC4 ranged between 7.63 and 8.19 which was higher than pKa of selected acidic PhACs. Thus, acidic compounds remained as ionic compounds under such circumstances and their removals were influenced by ionic interaction between the compounds and silica sand (both with negative charges). However, high removal (> 90%) observed for hydrophobic compounds in MRW+SOM could be attributed to biosorption to the biomass accumulated on sand surface.

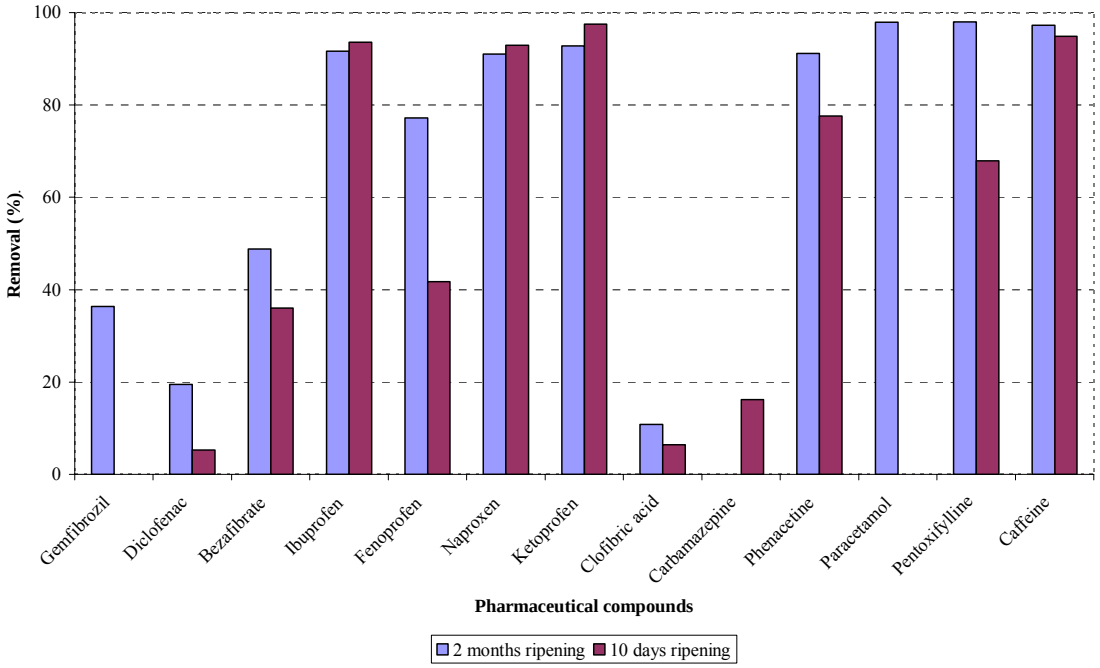


Figure 4.32 Impact of ripening period on PhACs removal in 2-months and 10-days ripened columns (Influent water: MRW+SOM; EBCT = 17 hours, silica sand media size 0.8 – 1.25 mm, HLR = 0.26 m/d)

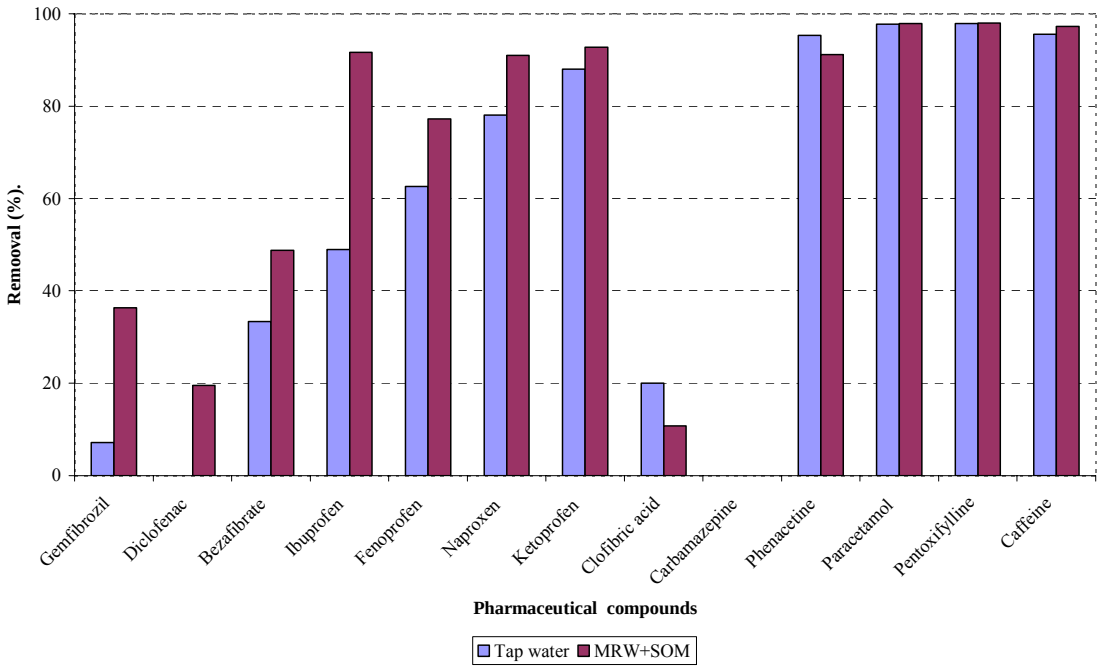


Figure 4.33 Impact of microbial activity on PhACs removal in 2 months ripened columns (T= 25°C, EBCT = 17 hours, silica sand media size 0.8 – 1.25 mm, HLR = 0.26 m/d)

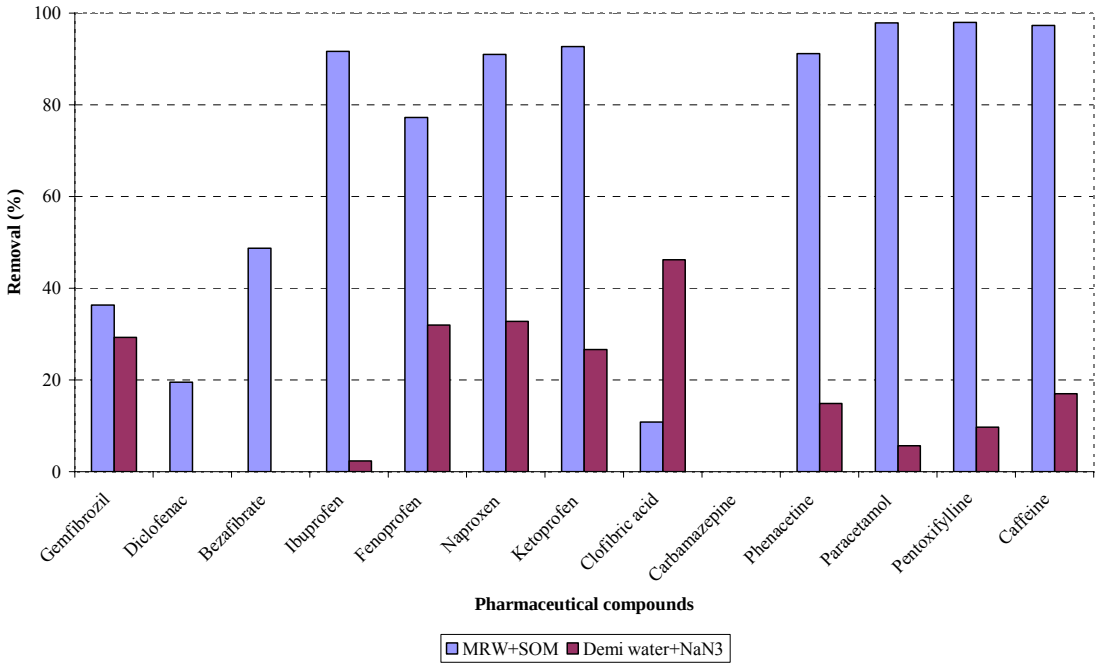


Figure 4.34 Comparative analysis of removal mechanism between biodegradation and adsorption in SSCs, (Silica sand media size 0.8 – 1.25 mm, HLR = 0.26 m/d, EBCT = 17 hours)

b) Odour compounds (Geosmin and 2-Methyl isoborneol)

Geosmin and 2-MIB were spiked into short soil columns fed with TW, MRW+SOM and DW+NaN_3 influent waters at average concentrations of 420 ng/L and 470 ng/L respectively, to study their removal under biodegradation and abiotic conditions. Samples were taken from influent and effluent points to gain insight into effectiveness of RBF with respect to odour compounds removal. Removal of odour compounds in short soil column studies is presented in Figure 3.8 and Figure 4.35.

Geosmin and 2-MIB were eliminated in soil columns fed with TW and MRW+SOM in which a removal of about 99% through biodegradation/sorption was observed in soil columns ripened for two months. However, removal of geosmin and 2-MIB decreased significantly during abiotic conditions to 75.3% and 66.6% respctively. It could be concluded from the above graph that geosmin and 2-MIB were eliminated 51.6% and 33.6% through soption, respectively, while geosmin and 2-MIB were biotranformed 23.7% and 33%, respectively. Thus, the removal of geosmin was more dominated by sorption.

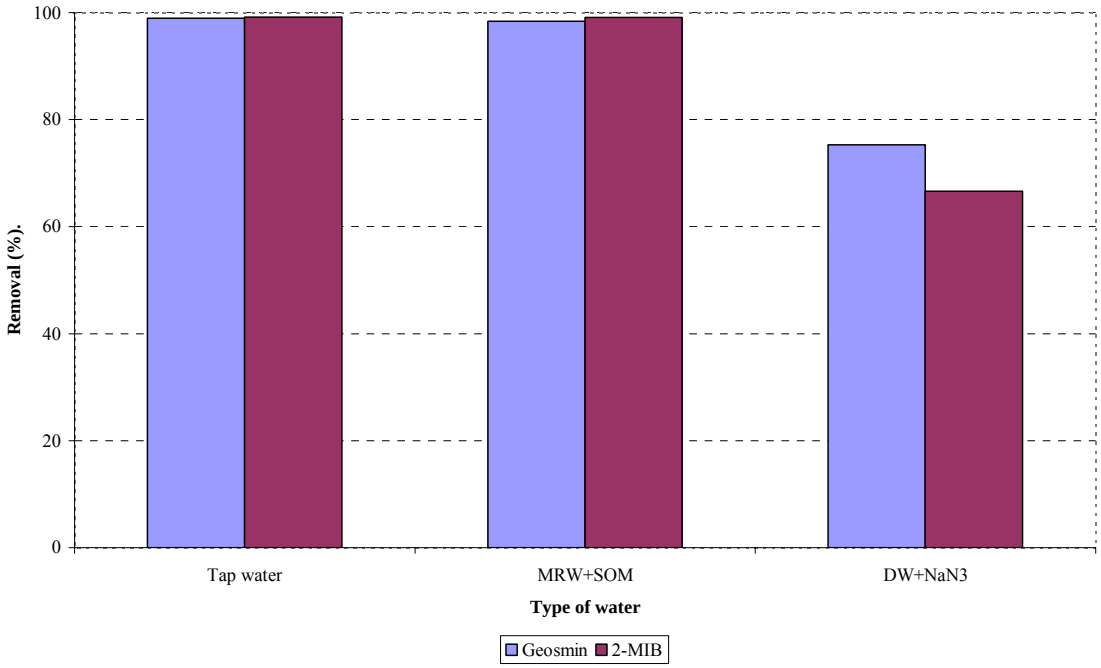


Figure 4.35 Geosmin and 2-Methyl isoborneol removal in short soil column experiments under different conditions (Silica sand media size 0.8 – 1.25 mm, HLR = 0.26 m/d, EBCT = 17 hours, 10ºC)

4.6 Practical implication of the study

Results obtained from laboratory experiments on removal of PhACs and odour compounds during RBF have the following practical implications:

1. Experiments simulating long retention time (60 days) during RBF for different influent water types showed that RBF is viable treatment since above 80% of most of target compounds were removed. In addition to that, geosmin and 2-MIB were eliminated within 30 days retention time.
2. Results collected from oxic and anoxic conditions showed that change in RBF redox conditions does not significantly affect removal of PhACs which was above 80%. Furthermore, results showed that geosmin was well removed under both oxic and anoxic conditions, while anoxic conditions reduce 2-MIB beyond human threshold concentration.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the above experimental results, the following conclusions can be made.

Batch experiments

1. Average DOC reduction during steady state conditions for MRW+SOM was 44.3% for influent and effluent DOC concentrations of 5.204 mg/L and 2.899 mg/L respectively, while MRW had DOC removal of 35.7% for influent and effluent DOC of 3.648 mg/L and 2.347 mg/L respectively. Likewise, SE showed 33.5% removal for DOC influent and effluent concentrations of 14.634 mg/L and 9.729 mg/L respectively and finally, reactors fed with IPW showed DOC removal of 17.6% for influent DOC concentration of 14.052 mg/L and effluent DOC of 11.58 mg/L.
2. SUVA values after sixty days retention time showed increase in various batch reactors, for MRW from 3.12 L/mg.m to 4.26 L/mg.m, while for MRW+SOM 2.36 L/mg.m to 4.72 L/mg.m, for SE 3.41 L/mg.m to 4.96 L/mg.m and for IPW it increased from 3.61 L/mg.m to 3.94 L/mg.m.
3. Most of the targeted compounds exhibited removal efficiencies greater than 90% of initial concentration found in various influent waters after 60-day retention time. However, hydrophobic (with log K_{ow} > 2) compounds of clofibric acid, diclofenac, and gemfibrozil were less removed in PDW which was more humic compared to other influent water types used in this batch experiment. Carbamazepine was persistent.
4. Geosmin and 2-MIB were removed beyond detection limit in the first 30 days retention time in batch experiments.

Long soil column experiments

5. SUVA values for MRW+SOM increased from 2.694 L/mg.m to 5.748 L/mg.m and mixture of MRW +SE+SOM from 2.747 L/mg.m to 6.591 L/mg.m. These SUVA values above 4 L/mg.m for effluent water show that these waters contain mostly aquatic–humics, high hydrophobicity, high molecular weight NOM.
6. Reduction in fluorescence EEM intensities under oxic conditions for MRW+SE were 51.4% for humic-like, 49.9% for humic/fulvic-like intensity and 45.5% for protein-like peak. MRW showed 11.3% reduction in humic-like intensity, 2.8% for fulvic/humic-like, and 5.9% reduction in protein-like intensity.
7. Addition of synthetic organic matter to MRW significantly improved removal of paracetmaol from 0% to 97.8%, while it impaired carbamazepine removal from 27% to persistent. However, Bezafibrate, fenoprofen, gemfibrozil, ibuprofen, ketoprofen, naproxen, pentoxifylline, phenacetine, and caffeine showed over 90% removal in MRW and MRW+SOM under oxic conditions.
8. Majority of targeted PhACs were removed above 90% in MRW, MRW+SE . However, removal of gemfibrozil decreased from 86% in Maas river water (MRW) to 60% in Maas river water blended with secondary effluent

(MRW+SE) while removal of diclofenac decreased from 53% in (MRW) to 28% in MRW+SE and removal of bezafibrate decreased from 93% in MRW to 78% in MRW+SE.

9. Removal of the targeted PhACs was similar (>90%) under oxic and anoxic conditions. Carbamazepine exhibited persistent behaviour under oxic and anoxic conditions,
10. Geosmin was removed above 80% under oxic and anoxic conditions for various waters, while 2-MIB removal increased from 80.3% under oxic conditions to 99.2% during anoxic conditions.

Short soil column experiments

11. SUVA values for MRW+SOM and TW were in the order of 1 L/mg.m to 3 L/mg.m in influent and effluent water samples under various temperatures. On the other hand, demineralised water spiked with sodium azide showed high hydrophobicity and high molecular weight since SUVA values were within the range of 12 L/mg.m to 14 L/mg.m.
12. Fluorescence EEM intensity for protein-like was reduced by 54.5% in the two months ripened column compared to 24.5% in the short column with ten days ripening period.
13. Removal of carbamazepine was not affected by operating temperature and was found to be persistent.
14. Hydrophilic compounds of paracetamol, pentoxifylline, phenacetine and caffeine were biodegraded above 90% in tap water. However, removal of these compounds decreased to less than 20% demineralised water spiked with 40 mM sodium azide.
15. Compared to 2-MIB, removal of geosmin was dominated by sorption.

From results of this study, RBF can be used as a viable treatment method for PhACs and odour compounds.

5.2 Recommendations

1. Detailed batch study should be carried out to examine direct uptake of PhACs by microorganisms as first substrate under nutrients limiting conditions using Milli-Q water with amended pH.
2. Detailed batch and column studies should be conducted including ATP measurement to correlate between biomass in soil media and removal of PhACs and odour compounds.
3. Removal of pharmaceutically active compounds should be investigated and modelled by using Quantitative Structure Activity Relationships (QSARs).

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APPENDICES

Appendix A - Measurement of DOC

A 1 - DOC measurement results during ripening of batch experimental setups

A 2 – Tracer test calculation for long soil columns

A 3 - DOC measurement results during ripening of long soil column setups

A 4 - Tracer test calculation for short soil columns

A 5 - DOC measurement results during ripening of short soil column (SSC) experimental setups

Appendix B - Measurement of ultraviolet absorbance (UVA)

B1- Water characteristics in batch experiments steady state conditions

B2- Water characteristics in long soil column experiments steady state conditions

B3- Water characteristics in short soil column experiments steady state conditions

Appendix C - Influent and effluent concentrations of PhACs and odour compounds

C 1 – PhACs and odour compounds concentrations in batch experiments

C 2 - PhACs and odour compounds concentrations in long soil column experiments.

C 3 – PhACs and odour compounds concentrations in short soil column experiments

Appendix A - Measurement of DOC

A 1 - DOC measurement results during ripening of batch experimental setups

A1 – 1: Batch reactors with influent water: Maas river water (MRW**)**

Time (Days)	Sampling time (Date)	Reactor No.	Inf. water DOC (mg/L)	Eff. water DOC (mg/L)	Removal of BDOC (%)	Average removal 0f BDOC (%)
5	01/11-06/11/2008	1	2.577	2.540	1.4	7.6
	01/11-06/11/2008	2	2.665	2.360	11.4	
	01/11-06/11/2008	3	2.515	2.361	6.1	
	01/11-06/11/2008	4	2.625	2.379	9.4	
	01/11-06/11/2008	5	2.521	2.361	6.3	
	01/11-06/11/2008	6	2.533	2.416	4.6	
10	17/11-22/11/2008	1	2.595	2.46	5.2	5.9
	17/11-22/11/2008	2	2.591	2.478	4.4	
	17/11-22/11/2008	3	2.683	2.500	6.8	
	17/11-22/11/2008	4	2.67	2.482	7.0	
	17/11-22/11/2008	5	2.661	2.455	7.7	
	17/11-22/11/2008	6	2.639	2.524	4.4	
15	22/11-27/11/2008	1	2.754	2.73	0.9	8.8
	22/11-27/11/2008	2	2.776	2.625	5.4	
	22/11-27/11/2008	3	2.787	2.489	10.7	
	22/11-27/11/2008	4	2.811	2.67	5.0	
	22/11-27/11/2008	5	2.787	2.482	10.9	
	22/11-27/11/2008	6	2.806	2.477	11.7	
20	27/11-02/12/2008	1	2.600	2.605	-0.2	8.2
	27/11-02/12/2008	2	2.73	2.503	8.3	
	27/11-02/12/2008	3	2.741	2.761	-0.7	
	27/11-02/12/2008	4	2.768	2.48	10.4	
	27/11-02/12/2008	5	2.834	2.391	15.6	
	27/11-02/12/2008	6	2.757	2.599	5.7	
25	03/12-08/12/2008	1	2.675	2.457	8.1	5.8
	03/12-08/12/2008	2	2.777	2.624	5.5	
	03/12-08/12/2008	3	2.775	2.578	7.1	
	03/12-08/12/2008	4	2.723	2.628	3.5	
	03/12-08/12/2008	5	2.787	2.548	8.6	
	03/12-08/12/2008	6	2.754	2.636	4.3	
30	23/12-29/12/2008	1	3.82	3.453	9.6	4.8
	23/12-29/12/2008	2	3.605	3.51	2.6	

	23/12-29/12/2008	3	3.501	3.539	-1.1	
	23/12-29/12/2008	4	3.457	3.253	5.9	
	23/12-29/12/2008	5	3.593	3.44	4.3	
	23/12-29/12/2008	6	3.545	3.491	1.5	
35	29/12/2008-05/01/2009	1	3.371	3.306	1.9	2.2
	29/12/2008-05/01/2009	2	3.365	3.334	0.9	
	29/12/2008-05/01/2009	3	3.474	3.348	3.6	
40	06/01-12/01/2009	1	2.834	2.806	1.0	4.9
	06/01-12/01/2009	2	3.045	2.802	8.0	
	06/01-12/01/2009	3	2.908	2.738	5.8	

A1 – 2: Batch reactors with influent water: Maas river water mixed with wastewater secondary effluent (MRW+SE)

Time (Days)	Sampling time (Date)	Reactor No.	Inf. water DOC (mg/L)	Eff. water DOC (mg/L)	Removal of BDOC (%)	Average removal of BDOC (%)
5	11/10-16/10/2008	7	7.797	7.308	6.3	5.7
	11/10-16/10/2008	8	7.797	7.275	6.7	
	11/10-16/10/2008	9	7.797	7.465	4.3	
10	27/10-01/11/2008	7	8.160	7.472	8.4	7.6
	27/10-01/11/2008	8	8.459	7.796	7.8	
	27/10-01/11/2008	9	8.185	7.659	6.4	
15	01/11-06/11/2008	7	7.375	6.532	11.4	9.8
	01/11-06/11/2008	8	7.674	6.556	14.6	
	01/11-06/11/2008	9	7.483	6.871	8.2	
20	06/11-11/11/2008	7	7.216	6.604	8.5	8.1
	06/11-11/11/2008	8	7.142	6.619	7.3	
	06/11-11/11/2008	9	7.254	6.631	8.6	
25	22/11-27/11/2008	7	6.996	6.631	5.2	6.5
	22/11-27/11/2008	8	7.094	6.629	6.6	
	22/11-27/11/2008	9	7.408	6.838	7.7	
30	03/12-08/12/2008	7	7.447	7.005	5.9	5.9
	03/12-08/12/2008	8	7.355	6.927	5.8	
	03/12-08/12/2008	9	7.322	7.193	1.8	
35	29/12/2008-05/01/2009	7	8.653	7.942	8.2	9.7
	29/12/2008-05/01/2009	8	8.828	7.944	10.0	
	29/12/2008-05/01/2009	9	8.83	7.863	11.0	
40	06/01-12/01/2009	7	8.183	7.537	7.9	7.6
	06/01-12/01/2009	8	8.158	7.582	7.1	
	06/01-12/01/2009	9	8.545	7.879	7.8	

A1 – 3: Batch reactors with influent water: Wastewater secondary effluent (SE)

Time (Days)	Sampling time (Date)	Reactor No.	Inf. water DOC (mg/L)	Eff. water DOC (mg/L)	Removal of BDOC (%)	Average removal of BDOC (%)
5	11/10-16/10/2008	10	12.850	11.690	9.0	8.8
	11/10-16/10/2008	11	12.850	12.230	4.8	
	11/10-16/10/2008	12	12.850	11.750	8.6	
10	22/10-27/10/2008	10	14.000	12.230	12.6	10.6
	22/10-27/10/2008	11	14.000	12.540	10.4	
	22/10-27/10/2008	12	14.000	12.770	8.8	
15	01/11-06/11/2008	10	12.450	10.620	14.7	14.0
	01/11-06/11/2008	11	13.230	10.740	18.8	
	01/11-06/11/2008	12	12.630	10.950	13.3	
20	06/11-11/11/2008	10	11.040	10.700	3.1	10.7
	06/11-11/11/2008	11	12.030	10.570	12.1	
	06/11-11/11/2008	12	11.600	10.520	9.3	
25	12/11-17/11/2008	10	4.973	4.346	12.6	10.5
	12/11-17/11/2008	11	4.928	4.341	11.9	
	12/11-17/11/2008	12	4.879	4.539	7.0	
30	22/11-27/11/2008	10	11.59	10.58	8.7	9.6
	22/11-27/11/2008	11	11.72	11.15	4.9	
	22/11-27/11/2008	12	12.51	11.19	10.6	
35	27/11-02/12/2008	10	12.14	10.721	11.7	12.4
	27/11-02/12/2008	11	12.22	10.63	13.0	
	27/11-02/12/2008	12	12.34	10.46	15.2	
40	06/01-12/01/2009	10	15.01	13.37	12.3	12.5
	06/01-12/01/2009	11	15.18	13.5	12.4	
	06/01-12/01/2009	12	15.18	13.47	12.7	

A 2 – Tracer test calculation for long soil columns

Water volume (V_m) used to fill soil voids for these three tests were 122 mm, 118 mm, and 124 mm. Equation (3.1) under subsection 3.3 was then used to calculate porosity of the media (Φ). Total soil volume of Vp = 300 mL was used.

$$\Phi = \frac{Vp}{V_m} \times 100$$

$$\Phi_1 = \frac{122}{300} \times 100 = 40.67\%,\ \Phi_2 = \frac{118}{300} \times 100 = 39.33\%,\quad \Phi_3 = \frac{124}{300} \times 100 = 41.33\%$$

Average porosity $\Phi = \frac{40.67 + 39.33 + 41.33}{3} = 40.44\%$

Moisture content of the sand (m.c = 0.1%) was deducted.
Therefore actual sand porosity (Φ) was equal to 40.34%.

Theoretical EBCT was then calculated according to equations (3.2 to 3.6)

Column dimensions: height (h) = 5 m, diameter (D) = 57mm, porosity of the sand Φ = 0.4034

$$Column\ volume\ V_v = \frac{\pi}{4} d^2 \times h = \frac{\pi}{4} \times (0.057)^2 \times 5 = 12.759 \times 10^{-3}\ m^3$$

$$Q = 1 ml / Min. = \frac{60 \times 24}{1000 \times 1000} = 1.44 \times 10^{-3}\ m^3 / d$$

$$EBCT = \frac{V_v}{Q} = \frac{12.759 \times 10^{-3}}{1.44 \times 10^{-3}} = 8.86\ days$$

$$Water\ velocity\ for\ empty\ column\ v = \frac{Q}{A} = \frac{1.44 \times 10^{-3} \times 4}{\pi \times 0.057^2} = 0.5643\ m/d$$

$$Actual\ water\ velocity\ through\ sand\ grains\ in\ the\ column\ v_i = \frac{v}{\phi} = \frac{0.5643}{0.4034} = 1.399\ m/d$$

$$Actual\ EBCT = \frac{V_v}{Q} = \frac{h}{v_i} = \frac{5}{1.399} = 3.57\ days$$

A 3 - DOC measurement results during ripening of long soil column setups

Long soil column No. 1 (LSC1) with influent water Maas river water (MRW) and long soil column No. 2 (LSC2) with influent water Maas river water mixed with wastewater secondary effluent (MRW+SE).

Date	Time	Long soil column No. 1			Long soil column No. 2		
		Influent water (mg/L)	Effluent water (mg/L)	C/C0	Influent water (mg/L)	Effluent water (mg/L)	C/C0
17/11/2008	5	2.896	2.664	0.920	6.862	5.7	0.831
19/11/2008	7	2.862	2.752	0.962	7.455	5.968	0.801
21/11/2008	9	2.866	2.727	0.952	7.933	6.122	0.772
24/11/2008	12	2.744	2.456	0.895	7.474	6.37	0.852
26/11/2008	14	2.753	2.435	0.884	7.968	6.245	0.784
28/11/2008	16	2.659	2.451	0.922	7.613	6.085	0.799
01/12/2008	19	2.805	2.564	0.914	7.913	5.896	0.745
03/12/2008	21	2.946	2.316	0.786	7.874	5.652	0.718
05/12/2008	23	3.011	2.762	0.917	8.613	6.283	0.729
08/12/2008	26	3.062	2.775	0.906	8.408	6.088	0.724
10/12/2008	28	2.964	2.718	0.917	8.127	5.983	0.736
12/12/2008	30	3.058	2.836	0.927	8.238	6.021	0.731
15/12/2008	33	3.57	2.903	0.813	8.798	6.589	0.749
17/12/2008	35	3.629	2.85	0.785	8.869	6.12	0.690
19/12/2008	37	3.609	3.023	0.838	8.859	6.241	0.704
22/12/2008	40	3.725	3.055	0.820	7.777	6.329	0.814
29/12/2008	47	3.688	3.219	0.873	5.834	5.246	0.899
31/12/2008	49	3.681	3.23	0.877	6.890	5.444	0.790
05/01/2009	54	3.736	3.219	0.862	6.890	5.674	0.824

A 4 - Tracer test calculation for short soil columns

Column dimensions: height (h) = 0.3 m, diameter (D) = 50 mm, porosity of the sand Φ = 0.4034

$$Column\ volume\ V_v = \frac{\pi}{4} d^2 \times h = \frac{\pi}{4} \times (0.05)^2 \times 0.3 = 5.89 \times 10^{-4}\ m^3$$

$$Q = 0.35\ ml/Min. = \frac{0.35 \times 60 \times 24}{1000 \times 1000} = 5.04 \times 10^{-4}\ m^3/d$$

$$EBCT = \frac{V_v}{Q} = \frac{5.89 \times 10^{-4}}{5.04 \times 10^{-4}} = 1.1686\ days$$

$$Water\ velocity\ for\ empty\ column\ v = \frac{Q}{A} = \frac{5.04 \times 10^{-4} \times 4}{\pi \times 0.05^2} = 0.2567\ m/d$$

$$Actual\ water\ velocity\ through\ sand\ grains\ in\ the\ column\ v_i = \frac{v}{\phi} = \frac{0.2567}{0.4034} = 0.64\ m/d$$

$$Actual\ EBCT = \frac{V_v}{Q} = \frac{h}{v_i} = \frac{0.3}{0.64} = 0.469\ days \approx 11.25\ hours$$

A 5 - DOC measurement results during ripening of short soil column (SSC) experimental setups

Short soil column No.1 (SSC1) and short soil column No.2 (SSC2) with influent water: Maas river water (MRW)

Date	Time	Short soil column No. 1			Short soil column No. 2		
		Influent water (mg/L)	Effluent water (mg/L)	C/C0	Influent water (mg/L)	Effluent water (mg/L)	C/C0
11/11/2008	5	2.709	2.609	0.963	2.709	2.514	0.928
17/11/2008	11	2.324	2.204	0.948	2.324	2.171	0.934
19/11/2008	13	2.721	2.370	0.871	2.721	2.465	0.906
21/11/2008	15	2.644	2.445	0.925	2.644	2.51	0.949
24/11/2008	18	2.561	2.395	0.935	2.561	2.397	0.936
26/11/2008	20	3.018	2.339	0.775	3.018	2.411	0.799
28/11/2008	22	2.550	2.299	0.902	2.550	2.373	0.931
01/12/2008	26	2.596	2.509	0.966	2.596	2.477	0.954
03/12/2008	28	2.556	2.483	0.971	2.556	2.477	0.969
05/12/2008	30	3.015	2.7	0.896	3.015	2.576	0.854
08/12/2008	33	2.983	2.710	0.908	2.983	2.667	0.894
10/12/2008	35	2.822	2.665	0.944	2.822	2.623	0.929
12/12/2008	37	2.895	2.756	0.952	2.895	2.789	0.963
15/12/2008	40	3.288	3.074	0.935	3.288	3.059	0.930
17/12/2008	42	3.851	3.285	0.853	3.851	3.124	0.811
24/12/2008	49	3.927	3.439	0.876	3.927	3.229	0.822
29/12/2008	54	3.674	3.174	0.864	3.674	3.080	0.838

Appendix B –Measurement of water characteristics during steady state conditions

B1- Water characteristics in batch experiments steady state conditions

B1-1 Influent water

Influent water	Reactors	Parameters					
		pH	Conductivity (µS/cm)	DOC (mg/L)	UV-254 (ab./cm)	SUVA (L/mg.m)	Average SUVA (L/mg.m)
MRW	1	7.70	627	3.648	0.11	3.015	3.121
	2	7.70	631	3.61	0.114	3.158	
	3	7.80	627	3.544	0.113	3.188	
MRW+SOM	1	7.78	638	5.204	0.126	2.421	2.363
	2	7.76	641	5.17	0.126	2.437	
	3	7.78	647	5.424	0.121	2.231	
SE	1	7.72	1135	16.634	0.496	2.982	3.407
	2	7.54	1149	13.764	0.506	3.676	
	3	7.60	1150	14.09	0.502	3.563	
PDW	1	7.88	1182	14.052	0.531	3.779	3.613
	2	7.84	1191	15.038	0.52	3.458	
	3	7.90	1192	14.77	0.532	3.602	

B1-2 Effluent water

Influent water	Reactors	Parameters								
		DO (mg/L)	pH	EC (µS/cm)	Inf. DOC (mg/L)	Eff. DOC (mg/L)	BDOC (mg/L)	UV-254 (ab./cm)	SUVA (L/mg.m)	Average SUVA (L/mg.m)
MRW	1	0.57	8.17	712	3.648	2.347	1.301	0.081	3.451	4.26
	2	8.15	8.40	791	3.61	1.992	1.618	0.091	4.568	
	3	8.32	8.42	788	3.544	1.912	1.632	0.091	4.759	
MRW+SOM	1	0.62	8.34	748	5.204	2.899	2.305	0.108	3.725	4.72
	2	8.25	8.45	833	5.17	2.188	2.982	0.119	5.439	
	3	8.22	8.47	826	5.424	2.347	3.077	0.117	4.985	
SE	1	0.31	8.45	1274	16.634	9.729	6.905	0.395	4.060	4.96
	2	8.25	8.67	1437	13.764	7.865	5.899	0.428	5.442	
	3	8.24	8.70	1416	14.09	7.956	6.134	0.428	5.380	
PDW	1	0.35	8.38	1219	14.052	11.58	2.472	0.372	3.212	3.94
	2	8.30	8.53	1322	15.038	9.489	5.549	0.406	4.279	
	3	8.31	8.54	1295	14.77	8.989	5.781	0.389	4.328	
Blank	1(MQ)	8.02	7.73	60.9	N.M	N.M	N.M	0.034	N.M	2.65
	2(DW)	7.94	7.65	61.6	N.M	N.M	N.M	0.034	N.M	
	3 (TW)	0.48	8.05	547	2.21	1.697	0.513	0.045	0.045	
Control	1(MQ)	8.00	5.72	5.3	N.M	N.M	N.M	0.009	N.M	–
	2(DW)	7.82	6.00	3.5	N.M	N.M	N.M	0.009	N.M	
	3(TW)	0.76	8.02	553	N.M	N.M	N.M	0.037	N.M	

N.M: Not measured

2- Water characteristics in long soil column experiments steady state conditions

Influent water content	DOC (mg/L)			UV-254			SUVA			Operation conditions
	Influent	Effluent (2.5 m)	Effluent (5 m)	Influent	Effluent (2.5 m)	Effluent (5 m)	Influent	Effluent (2.5 m)	Effluent (5 m)	
MRW	3.664	–	2.987	0.091	–	0.071	2.484	–	2.377	Oxic
MRW + SE	9.667	–	6.429	0.275	–	0.207	2.845	–	3.220	Oxic
MRW + SOM	5.645	3.04	2.699	0.11	–	0.089	1.949	–	3.298	Oxic
MRW + SE + SOM	11.55	8.089	8.325	0.342	–	0.228	2.961	–	2.739	Oxic
MRW + SOM	3.13	2.317	2.209	0.099	0.086	0.079	3.163	3.7117	3.576	Anoxic
MRW+ SE + SOM	9.257	7.342	7.005	0.328	0.294	0.281	3.543	4.0044	4.011	Anoxic

Influent water content	Influent			Effluent (2.5 m)			Effluent (5 m)			Operation conditions
	EC (µS/cm)	pH	O2 (mg/L)	EC (µS/cm)	pH	O2 (mg/L)	EC (µS/cm)	pH	O2 (mg/L)	
MRW + SOM	644	7.85	10.9	647	8.09	8.0	653	7.81	7.5	Oxic
MRW + SE + SOM	951	7.5	8.3	943	8.25	7.0	930	7.99	6.0	Oxic
MRW + SOM	715	8.25	0.2	–	–	–	704	7.64	0.9	Anoxic
MRW + SE + SOM	1026	8.16	0.2	–	–	–	1010	7.69	1.2	Anoxic

B3- Water characteristics in short soil column experiments steady state conditions

B3-1 Short soil column NOM characteristics

Sampling period	Short column	Influent water content	DOC (mg/L)			UV-254		SUVA	
			Influent	Effluent	BDOC	Influent	Effluent	Influent	Effluent
18/2-18/03/2009	Sc1	RMW + SOM	5.011	2.506	2.505	0.100	0.082	1.996	3.272
18/2-18/03/2009	Sc2	RMW + SOM	5.011	2.649	2.362	0.100	0.082	1.996	3.096
18/2-18/03/2009	Sc3	RMW + SOM	6.692	2.635	4.057	0.106	0.084	1.584	3.188
04/03-06/03/2009	Sc1	Tap water	3.376	1.704	1.672	0.033	0.031	0.977	1.819
27/02-02/03/2009	Sc2	RMW + SOM	5.721	2.664	3.057	0.101	0.079	1.765	2.965
27/02-02/03/2009	Sc3	RMW + SOM	7.040	2.861	4.179	0.095	0.085	1.349	2.971
27/02-02/03/2009	Sc4	DW + NaN3	1.618	1.882	-0.264	0.226	0.232	13.968	12.327
24/03-26/03/2009	Sc1	Tap water	2.521	1.697	0.824	0.028	0.022	1.111	1.296
24/03-26/03/2009	Sc2	RMW + SOM	3.173	2.851	0.322	0.099	0.09	3.120	3.157
24/03-26/03/2009	Sc3	RMW + SOM	3.029	2.809	0.220	0.099	0.09	3.268	3.204
24/03-26/03/2009	Sc4	DW + NaN3	1.763	1.466	0.297	0.213	0.215	12.082	14.666

B3-2 Short soil column continued

Sampling period	Short column	Influent water content	Influent			Effluent		
			Conductivity (µS/cm)	pH	O2 (mg/L)	Conductivity (µS/cm)	pH	O2 (mg/L)
13/02-18/02/2009	Sc1	MRW + SOM	–	8.14	–	–	8.07	–
13/02-18/02/2009	Sc2	MRW + SOM	–	8.14	–	–	8.11	–
13/02-18/02/2009	Sc3	MRW + SOM	–	8.16	–	–	8.21	–
27/02-02/03/2009	Sc2	MRW + SOM	650	8.19	8.6	645	8.38	8.4
27/02-02/03/2009	Sc3	MRW + SOM	650	8.19	8.5	650	8.34	8.5
27/02-02/03/2009	Sc4	DW + NaN3	455	6.98	10.2	467	7.29	9.4
24/03-26/03/2009	Sc1	Tap water	489	7.63	10.7	498	8.09	8.1
24/03-26/03/2009	Sc2	MRW + SOM	716	7.72	9.1	718	8.15	8.2
24/03-26/03/2009	Sc3	MRW + SOM	722	7.77	9.11	720	8.17	8.18
24/03-26/03/2009	Sc4	DW + NaN3	450	6.63	8.9	462	7.17	8.19

ppendix C - Influent and effluent concentrations of PhACs and odour compounds

C 1 - PhACs and odour compounds concentrations in batch experiments

C1 – 1 PhACs concentrations

Compounds	Carbamazepine	Bezafibrate	Clofibric acid	Diclofenac	Fenoprofen	Gemfibrozil	Ibuprofen	Ketoprofen	Naproxen	Paracetamol	Pentoxifylline	Phenacetine	Caffeine
Inf. MRW	1.8	3.6	2.3	2.2	1.8	0.82	1.9	1.8	1.7	2.0	3.2	1.8	4.0
Eff. MRW	0.1	0.1	2.3	0.74	0.1	0.1	0.27	0.1	0.1	0.1	0.1	0.1	0.1
Inf. MRW+SOM	4.1	4.6	5.4	5.2	3.4	1.5	3.2	3.6	2.9	4.1	4.1	0.90	4.7
Eff. MRW+SOM	0.1	0.1	4.6	2.8	0.1	0.1	0.54	0.1	0.1	0.1	0.1	0.1	0.1
Inf. SE	4.0	3.4	3.9	4.1	3.3	1.2	3.2	3.3	3.1	3.4	0.10	3.3	3.0
Eff. Se	0.1	0.1	5.6	0.58	0.57	0.1	0.76	0.1	0.1	0.1	0.1	0.1	0.1
Inf. IPW	3.2	2.6	4.5	4.0	3.1	1.2	3.6	2.8	3.0	3.1	1.1	3.1	3.8
Eff. IPW	0.1	0.1	4.5	1.5	1.1	0.1	2	0.1	0.1	0.1	0.1	0.1	0.1
Inf. Blank (TW)	3.0	2.8	3.1	3.9	4.1	1.7	3.9	4.3	2.8	1.8	2.4	3.0	3.5
Eff. Blank(TW)	3.3	4.5	5.1	4.3	4.9	1.6	4.1	3.4	2.6	2.4	4.8	3.8	5
Inf. Control(TW)	3.0	2.8	3.1	3.9	4.1	1.7	3.9	4.3	2.8	1.8	2.4	3.0	3.5
Eff. Control(TW)	0.28	0.1	4.6	4.7	3.7	0.1	2.8	0.1	2.2	0.1	0.1	1.5	0.11

C1 – 2 Odour compounds (geosmin and 2-MIB)

Water type	Sampling point	Geosmin	2-Methyl isoborneol	Sampling time (days)
MRW	Influent	217.6	254.1	0
	Effluent	ND	ND	30
MRW+SOM	Influent	236.7	268.4	0
	Effluent	ND	ND	30
SE	Influent	69.6	238.5	0
	Effluent	ND	ND	30
IPW	Influent	278.2	292.9	0
	Effluent	ND	ND	30

C 2 - PhACs and odour compounds concentrations in long soil column experiments

C2 –1 PhACs concentrations (oxic)

Compounds	Gemfibrozil	Diclofenac	Bezafibrate	Ibuprofen	Fenoprofen	Naproxen	Ketoprofen	Clofibric acid	Carbamazepine	Phenacetine	Paracetamol	Pentoxifylline	Caffeine
Influent MRW	3	3	4	3	1	4	3	4	5.0	3	0.1	4	4
Effluent MRW	0.4	1.5	0.3	0.1	0.1	0.1	0.1	2.8	3.7	0.1	0.1	0.1	0.1
Influent MRW+SE	2.1	3.2	3.7	3.4	1.2	3.3	2.6	4.0	5.3	3.1	0.1	3.6	3.7
Effluent MRW+SE	0.83	2.3	0.82	0.1	0.1	0.1	0.18	3.1	3.8	0.1	0.1	0.1	0.20
InfluentMRW+SOM (oxic)	3.5	4.2	3.6	4.5	1.8	5.0	3.9	3.7	4.9	4.0	4.6	5.2	4.6
Effluent MRW+SOM (oxic)	0.10	1.0	0.10	0.10	0.10	0.10	0.10	2.5	5.0	0.10	0.10	0.10	0.10
Influent MRW+SE+SOM (oxic)	4.0	4.1	3.9	4.5	1.6	4.7	4.5	3.5	5.0	2.5	0.10	5.0	3.2
EffluentMRW+SE+SOM (oxic)	2.9	3.5	2.0	0.52	0.48	0.25	1.5	2.5	5.5	0.13	0.10	0.26	0.10
Influent MRW+SOM (anoxic)	4.8	4.6	5	4.1	1.6	3.6	5.2	3.5	5.3	3.9	0.1	4.8	4.1

C2 –2 PhACs concentrations in long soil column (anoxic)

Compounds	Gemfibrozil	Diclofenac	Bezafibrate	Ibuprofen	Fenoprofen	Naproxen	Ketoprofen	Clofibric acid	Carbamazepine	Phenacetine	Paracetamol	Pentoxifylline	Caffeine
Influent MRW+SOM (anoxic)	4.8	4.6	5	4.1	1.6	3.6	5.2	3.5	5.3	3.9	0.1	4.8	4.1
Effluent MRW+SOM (anoxic)	0.1	1.1	0.24	0.1	0.1	0.1	0.1	2.7	7.6	0.1	0.1	0.1	0.3
Influent MRW+SE+SOM (anoxic)	5	4.8	4.7	3.9	1.4	3.2	3.8	2.9	5.4	4.2	0.1	4.6	3.6
Effluent MRW+SE+SOM (anoxic)	4.4	4	1.8	0.35	0.87	0.23	1.5	2.6	5.4	0.1	0.1	1.3	0.1

C2 – 3 Odour compounds (geosmin and 2-MIB)

Water type	Sampling point	Geosmin	2-Methyl isoborneol
MRW	Influent	49.4	277.6
	Effluent	ND	7.4
MRW+SE	Influent	29.3	195.1
	Effluent	ND	9.8
MRW+SOM	Influent	433.9	426.1
	Effluent	ND	3.3
MRW+SE+SOM	Influent	452.2	458.2
	Effluent	12.6	149.2
MRW+SOM (anoxic)	Influent	392.2	473.3
	Effluent	< 4	< 4
MRW+SE+SOM (anoxic)	Influent	378.6	527.5
	Effluent	52.0	97.3

C 3 - PhACs and odour compounds concentrations in short soil column experiments

C3 – 1 PhACs concentrations for SSC (sampling period 13/02/2009 to 18/02/2009)

Compound	Gemfibrozil	Diclofenac	Bezafibrate	Ibuprofen	Fenoprofen	Naproxen	Ketoprofen	Clofibric acid	Carbamazepine	Phenacetine	Paracetamol	Pentoxifylline	Caffeine
Influent MRW+SOM	3.0	3.1	3.1	3.6	1.4	3.7	2.4	4.3	4.3	3.8	3.0	3.3	3.8
Effluent MRW+SOM	2.5	2.9	1.7	0.20	0.57	0.46	0.31	4.5	3.9	0.40	0.1	0.1	0.12
Influent MRW+SOM	3.0	3.1	3.1	3.6	1.4	3.7	2.4	4.3	4.3	3.8	3.0	3.3	3.8
Effluent MRW+SOM	2.2	2.6	1.5	0.14	0.59	0.25	0.20	4.9	3.0	0.29	0.1	0.1	0.1
Influent MRW+SOM	3.1	3.3	3.8	3.7	1.4	3.7	2.3	4.4	4.7	4.3	3.2	3.8	4.2
Effluent MRW+SOM	1.5	2.7	2.0	0.1	0.43	0.1	0.1	4.4	4.3	0.15	0.1	0.18	0.22

C3 – 2 PhACs concentrations for SSCs (sampling period 27/02/2009 to 02/03/2009)

Compound	Gemfibrozil	Diclofenac	Bezafibrate	Ibuprofen	Fenoprofen	Naproxen	Ketoprofen	Clofibric acid	Carbamazepine	Phenacetine	Paracetamol	Pentoxifylline	Caffeine
Influent TW	4.2	4.0	3.9	4.7	1.9	3.1	5.0	4.0	4.4	4.1	4.4	4.8	3.6
Effluent TW	3.9	4.1	2.6	2.4	0.71	0.68	0.60	3.2	5.9	0.19	0.10	0.10	0.16
Influent MRW+SOM	3.3	4.1	4.1	4.8	1.8	4.9	4.0	3.7	4.8	4.2	4.8	5.0	3.7
Effluent MRW+SOM	2.1	3.3	2.1	0.40	0.41	0.44	0.29	3.3	4.9	0.37	0.10	0.10	0.10
Influent MRW+SOM	2.5	3.8	6.1	4.5	1.7	4.8	4.0	3.1	6.8	5.8	0.10	8.1	6.4
Effluent MRW+SOM	3.2	3.6	3.9	0.29	0.99	0.34	0.10	2.9	5.7	1.3	0.10	2.6	0.33
Influent DW+NaN_3	4.7	4.2	8.2	4.6	3.4	5.8	7.7	8.3	8.6	9.1	4.2	3.3	11
Effluent DW+NaN_3	3.6	3.3	3.2	3.9	3.4	5.6	2.6	5.2	3.0	3.4	1.9	3.1	2.6

C3 – 3 PhACs concentrations for SSCs (sampling period 24/02/2009 to 26/03/2009)

Compound	Gemfibrozil	Diclofenac	Bezafibrate	Ibuprofen	Fenoprofen	Naproxen	Ketoprofen	Clofibric acid	Carbamazepine	Phenacetine	Paracetamol	Pentoxifylline	Caffeine
Influent TW	5	4.3	3.9	3.1	1.3	2.4	4	3.2	4.2	4.6	5.2	4.8	4.3
Effluent TW	2.9	4	2	0.1	0.27	0.1	0.1	2.9	4.4	0.32	0.1	0.1	0.1
Influent MRW+SOM	5.4	4.2	3.4	4.1	1.4	3.2	3.6	3	4.6	3.8	0.1	4.1	4.2
Effluent MRW+SOM	3.7	3.8	3.3	0.1	0.81	0.1	0.13	3	4.6	0.82	0.1	2.2	0.1
Influent MRW+SOM	4.2	4.2	4.2	3.9	1.5	3.4	2.7	3.2	4.8	4.8	2.3	4.5	4.5
Effluent MRW+SOM	3.4	4.2	3.1	0.12	0.9	0.1	0.1	3.1	4.7	0.9	0.1	2.9	0.1
Influent DW+NaN_3	5.8	4.0	2.8	4.2	2.5	5.8	3.0	6.7	4.4	4.7	5.3	4.1	4.7
Effluent DW+NaN_3	4.1	4.2	3.3	4.1	1.7	3.9	2.2	3.6	4.4	4.0	5.0	3.7	3.9

C3 – 3 Odour compounds (geosmin and 2-MIB)

Influent water	Geosmin (ng/L)		MIB (ng/L)		Temp. (°C)
	Influent	Effluent	Influent	Effluent	
MRW+SOM	202.7	4.3	256.5	6.4	25
MRW+SOM	202.7	2.3	256.5	2.2	25
MRW+SOM	232.6	8.7	257.3	13.3	25
TW	468.8	4.9	478	4.1	10
MRW+SOM	383.3	6.1	468.3	4.1	10
MRW+SOM	355.4	9.3	443.8	52.1	10
DW+NaN_3	469.1	115.8	493.6	164.9	10
TW	461.9	11.6	477	9.7	5
MRW+SOM	277.7	5	487.3	60.4	5
MRW+SOM	412.4	4	428.4	7.8	5
DW+NaN_3	443.7	116.5	418	139.9	5