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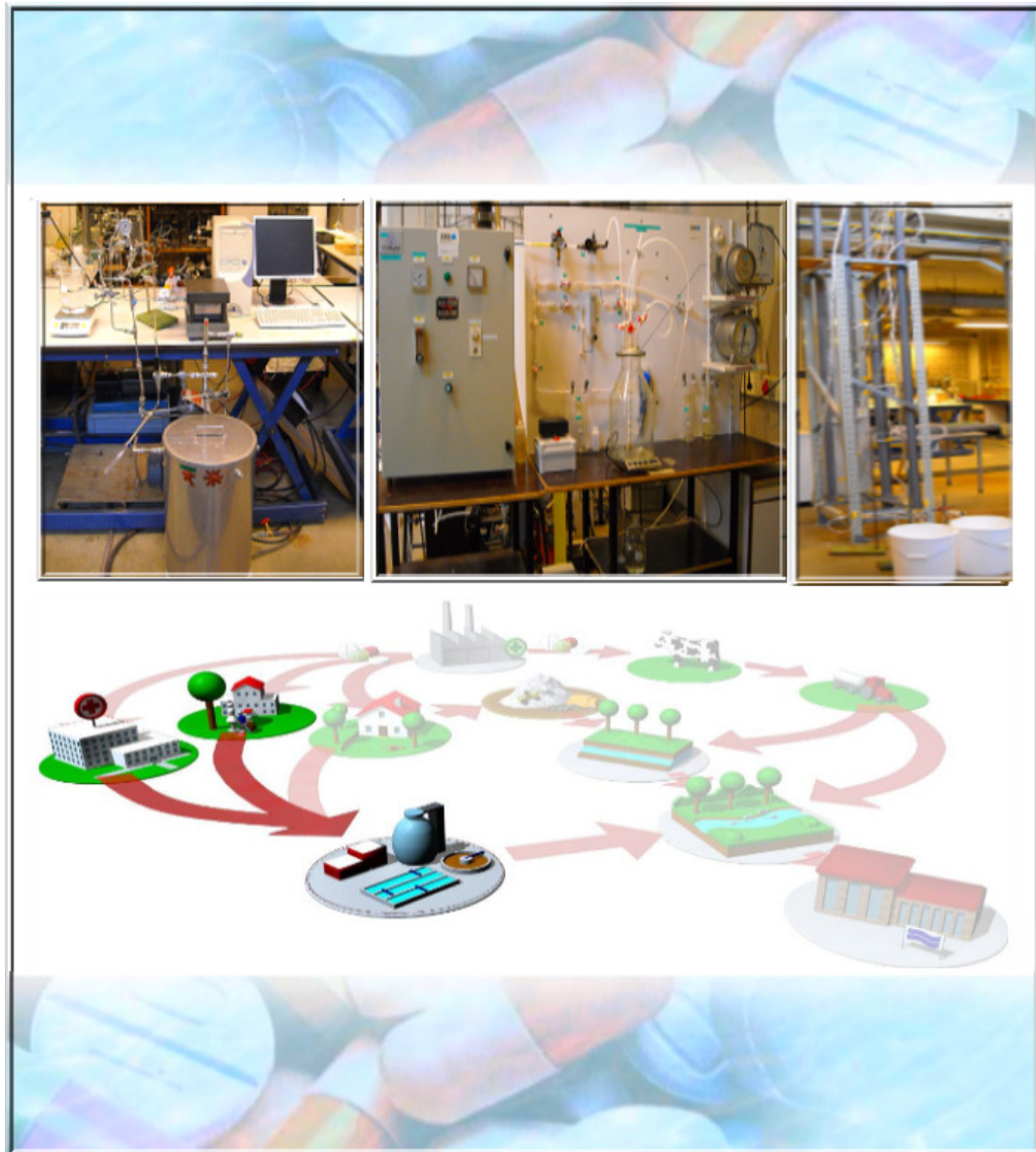
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UNESCO-IHE INSTITUTE FOR WATER EDUCATION



Soil Aquifer Treatment as a Pre-treatment for Organic Micropollutants Removal during Membrane Filtration

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MSc Thesis- MWI-2010/05
April 2010

Soil Aquifer Treatment as a Pre-treatment for Organic Micropollutants Removal during Membrane Filtration

Master of Science Thesis
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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

This thesis is dedicated to my parents, for their love and support. Thanks to mom for encouraging me to follow my dreams and to fight for them. Thanks to my dad for his wisdom, patience and professionalism... I am your biggest fan!

Abstract

Soil Aquifer Treatment (SAT) is an attractive and environmentally sustainable technology for wastewater reclamation and reuse. Its effectiveness under given conditions depends on the effluent qualities, hydrogeologic conditions and process parameters applied. Furthermore, some organic micropollutants may not be completely removed during SAT. In this context, SAT pre-treatment of WWTP effluent followed by membranes for polishing is likely to provide water of required quality. However, the effect of SAT as a pre-treatment on performance of NF is not fully understood.

To assess the effect of SAT as a pre-treatment for persistent organic micropollutants removal during membrane filtration, the removal of target compounds (gemfibrozil, diclofenac, bezafibrate, ibuprofen, fenoprofen, carbamazepine, acetaminophen, naproxen, clofibric acid, phenacetine, caffeine, pentoxifylline, ketoprofen, NDMA and 1,4-dioxane) during soil passage were analyzed in three different types of water samples before using NF membrane.

Laboratory-scale soil columns experiments were conducted at a hydraulic loading rate of 1.25 m/day using secondary effluent as feed water. High removals for most of the target compounds (> 70 %) were observed which can be linked to sorption onto soil particles or transformation through biodegradation. However, some compounds (clofibric acid, diclofenac, carbamazepine, NDMA and 1,4-dioxane) showed a persistent behavior with low removals due to their miscibility with water and resistance to biological degradation. On the other hand, soil passage in combination with ozone showed even higher removals for the majority of target compounds (<0.05 µg/L) in all the samples. Furthermore, an increase was observed in NDMA and 1,4-dioxane removals for pre-ozonated to secondary effluent during column studies (73% and 61% respectively).

Excellent rejections of target compounds by NF-90 were achieved (>98%), which was correlated with their physico-chemical properties and the influence of the amount effluent organic matter (EfOM) in the different water matrices, with the exception of NDMA that was poorly rejected (20%) independently of the water characteristics. However, SAT as a pre-treatment of NF has demonstrated its capability not only on providing significant reductions in emerging contaminants but also in the removal of organic matter content present in wastewater leading to reduction of fouling and an increase of the life-time of the membranes. Furthermore, the improved effect of pre-ozonation on biodegradation of recalcitrant compounds followed by SAT and NF illustrate the benefits of this hybrid system as a promising technology for wastewater effluent reuse applications.

Keywords: Soil aquifer treatment, pharmaceutically active compounds), NDMA, 1,4-dioxane, nanofiltration, ozonation, wastewater reuse.

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List of Symbols

| | |
|-------|---|
| AOPs | Advanced Oxidation Processes |
| DBPs | Disinfection Byproducts |
| DO | Dissolved Oxygen |
| DOC | Dissolved Organic Carbon |
| DWTPs | Drinking Water Treatment Plants |
| EC | Electrical Conductivity |
| EDCs | Endocrine Disrupting Compound |
| EfOM | Effluent Organic Matter |
| FEEM | Fluorescence Excitation and Emission Matrix |
| HL | Hydrophilic |
| HLR | Hydraulic Loading Rate |
| HP | Hydrophobic |
| MW | Molecular Weight |
| MWCO | Molecular Weight Cut-off |
| NOM | Natural Organic Matter |
| NF | Nanofiltration |
| PhACs | Pharmaceutically Active Compounds |
| PCPs | Personal Care Products |
| RO | Reverse Osmosis |
| SAT | Soil Aquifer Treatment |
| SE | Secondary Effluent |
| SMP | Soluble Microbial Product |
| SUVA | Specific Ultraviolet Absorbance |
| THMs | Trihalomethanes |
| TOC | Total Organic Carbon |
| UVA | Ultraviolet Absorbance |
| WWTP | Wastewater Treatment Plant |

1. INTRODUCTION

1.1 Background

The imbalance between availability and demand of water as a consequence of climate change, growing population and competition among agriculture, recreational and industrial sectors reflects the necessity of searching for alternatives water sources in a sustainable, economical and safe manner. According to WHO (2003), within the next fifty years, it is estimated that 40% of the world's population will live in countries facing water stress or water scarcity.

One of the most promising options for water augmentation is the reuse of municipal wastewater for solving the problem of ever increasing water demand. However, the amount of wastewater that can be reclaimed for this purpose is affected by many factors, ranging from technical possibility to socio-economic and institutional aspects (Yang & Abbaspour, 2007).

The use of reclaimed water can be accomplished in two main ways, directly or indirectly. Direct potable reuse for drinking purposes is not a commonly practiced in many countries even when the water requirements fulfill high standards due to concerned issues of society related to health and safety. On the other hand, according to Rodríguez et al. (2009), indirect potable reuse is one of widely applied alternatives for water augmentation mainly because enables the production of recycled water with very high qualities at reasonable costs. Nevertheless, the possibility of water reuse might be affected due to the occurrence of a vast amount of emerging contaminants such as pharmaceutically active compounds (PhACs), personal care products (PPCPs), endocrine disrupter compounds (EDCs) and disinfection by-products (DBPs) in concentrations ranging from nanograms per liter (ng/l) up to micrograms per liter (µg/l) that can pass through conventional and advanced wastewater treatment technologies. As a result, implementation of potential methods for removing organic micropollutants is needed in order to reduce or eliminate this threat.

Pressure-driven membrane technique such as Nanofiltration (NF) and Reverse Osmosis (RO) have proved to be an effective barrier for removing several organic pollutants. Still, some of them can be found in the permeate (NDMA, 1,4-dioxane, among others) even when high rejections could be achieved for the majority of organic micropollutants (Verliefde et al., 2007; Yangalli, 2010). Furthermore, operation might become difficult and costly when secondary effluent (SE) is treated due to the high content of effluent organic matter (EfOM) that can settle on the surface of the membrane leading to fouling and a reduction of the life-time of the NF system. For that reason, would be convenient to use a kind of pre-treatment that minimized the membrane fouling and also contributes to the removal of emerging contaminants for indirect potable reuse of wastewater.

In this context, Soil Aquifer Treatment (SAT) appears as a low cost and efficient technology with the capability of renovating wastewater effluents to high standard levels. SAT has demonstrated to be very effective in removing many organic constituents from wastewater through different biological and chemical mechanisms during soil passage (Amy & Drewes, 2007). However, from a regulatory point of view SAT can not be used as a single treatment for indirect water reclamation purposes.

Therefore, the combination of SAT and nanofiltration as a hybrid system provides a multiple barrier approach for organic micropollutants removal in terms of potable reuse (Jarusutthirak et al., 2003; Yangalli, 2010).

1.2 Problem identification

The increasing demand on finite water sources and water shortage in some regions, create a complex scenario when the water requirement for diverse sectors is certainly not enough. As a consequence, reclamation and reuse applications are growing as supplies solutions in arid regions mainly for irrigation activities. However, the presence of emerging contaminants has been recognized one of the major concerns for water consumers due to the adverse effects on human health.

It has been demonstrated that the existing water and wastewater treatment plants are not effective in the removal of diverse organic compounds bringing as a consequence that after effluent discharges to the environment, these compounds can be found in several water sources. One of the emerging contaminants that have been receiving special attention is a probable human carcinogen Nitrosodimethylamine (NDMA) with a 10^{-6} cancer risk level of 0.7 ng/L (Lee et al., 2007). This unintended by-product is formed during chlorination by a reaction with chloramines and dimethylamine and other compounds that contains nitrogen (Sedkak et al., 2005). The increased concern about NDMA is that after formation results very difficult to remove by conventional treatments such as biodegradation, air stripping, and activated carbon adsorption and even by physical processes like membrane filtration NDMA exhibited very low rejections (Lee et al., 2007). However, recent studies have been shown the potential reduction of NDMA in soils attributed to the microbiological activity of *Pseudomonas* under aerobic conditions (Bradley et al., 2005; Haruta et al, 2009).

Another compound that has raised the interest of researchers is the highly toxic personal care products 1,4 dioxane due to its probable human carcinogenicity. 1,4-dioxane is also hardly to remove by traditional technologies because its miscibility with water, resistance to biological degradation linked to its chemical structure and low rejections by membrane systems due to their low molecular weight and polarity (Abe, 1999; Clara et al, 2003). Nevertheless, previous results demonstrated that this resistant compound can be removed from “shallow subsurface environments” by the use of phytoremediation (Zenker et al., 2003).

Little is known how efficiently many of these emerging compounds are eliminated or transformed in reclaimed water. Although, even when it has been observed that most of them disappears during soil passage through biotransformation and adsorption mechanisms (Yu et al, 2006) hydrophobic compounds such as colifibric acid and carbamazepine can pass through the subsoil and further detected in groundwater due to their persistence (Heberer, 2002).

Soil aquifer treatment (SAT) has demonstrated to be an effective method for achieving substantial reductions in effluent organic matter (EfOM) and organic micropollutants. Nevertheless, the combination of ozonation as a pre-treatment before SAT can enhance the biodegradability of recalcitrant compounds present in the secondary effluent. Ozone has proved to be a powerful oxidant for the transformation of the majority of pharmaceuticals in seconds (Sharma, 2008). Uncertainties, however, exist regarding to

the effectiveness of this strong oxidant before SAT and their impact as a pre-treatment for micro pollutants removal during membrane filtration.

On the other hand, nanofiltration (NF) technology is considered to be an alternative solution for wastewater reuse. Still, the performance of the treatment can be affected by membrane fouling and low rejection of hydrophilic and neutral compounds with low molecular weight such as NDMA. Thus, it is expected that a hybrid system using SAT as pre-treatment followed by NF would be an effective technology not only for increasing membrane productivity but also for removing a vast range of emerging contaminants. The proposed research therefore focuses on the analysis of different types of pre-treatments for persistent organic micropollutants removal during NF.

1.3 Goal and objectives

The main goal of this study is to assess the effect of SAT as a pre-treatment for persistent organic micropollutants removal during membrane filtration.

The specific objectives of this study are:

1. To analyse the effectiveness of SAT on persistent organic micropollutants removal from secondary effluent.
2. To study the effect of pre-ozonation on persistent organic micropollutants from secondary effluent during SAT.
3. To determine the effect of different effluent pre-treatment on the performance of nanofiltration for persistent organic micropollutants removal.

2 LITERATURE REVIEW

2.1 General overview of emerging contaminants in the environment

2.1.1 Presence of PhACs, NDMA and 1,4-dioxane in water sources

The awareness of emerging contaminants such as Pharmaceutically Active Compounds (PhACs) has increased in the last decades linked to the evidence of its persistence and bioaccumulation in the environment where they were discharged after being used by humans and animals (Zhou et al., 2009; Yangalli 2010; Snyder 2003). Pharmaceuticals comprise a wide spectrum of substances with a variety of functionalities (e.g. analgesics, antibiotics, anti-inflammatory and antiepileptic drugs, beta-blockers, blood lipid regulators, among others) that exhibit different physic-chemical properties (Kümmerer, 2009).

Figure 2.1 shows that the main pathway of these pollutants to the aquatic environment is through wastewater effluents as a result of domestic, veterinary and industrial disposal in the sewage (Esplugas et al., 2007; Zhou et al., 2009). However, an incorrect management of these hazard substances in landfills can lead to the production of lixiviates that might infiltrate into groundwater sources. Pharmaceuticals have also been detected in soils for indirect water reuse (Mompelat et al., 2009).

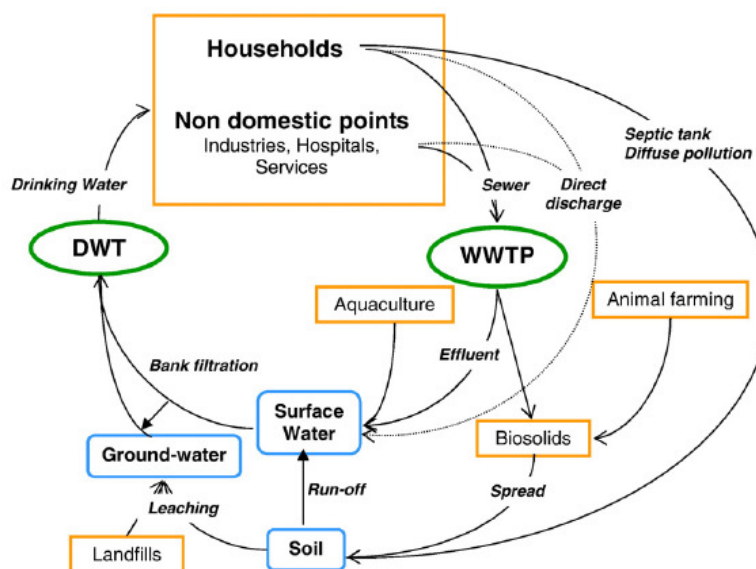


Figure 2.1 Origin and routes of PhACs
Source: Mompelat et al. (2009)

Several researchers have recognized the serious impact that the presence of PhACs causes in water sources mainly because these contaminants can suffer bio-transformations having as a result more harmful by-products. Many of these organic micropollutants used for prevention of illness or treatment are excreted by the human body after metabolization to the environment (Esplugas et al., 2007; Kümmerer, 2009; Abel, 2009) (Figure 2.2).

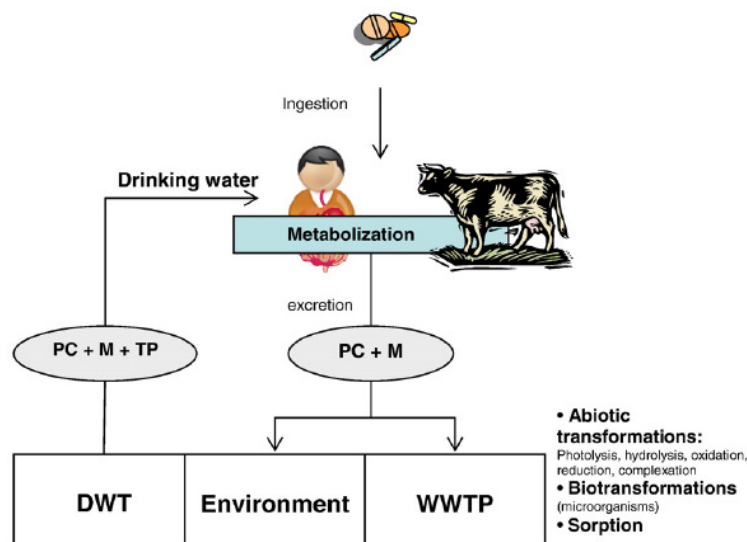


Figure 2.2 Transformation pathways of PhACs (PC: parent compound, M: Metabolite(s), TP: Transformation Product(s), WWTP: Waste Water Treatment Plant; DWT: Drinking Water

Source: Mompelat et al. (2009)

The presence of emerging contaminants in tap water in concentrations of nanograms per liter (ng/L) has been reported by Mompelat et al. (2009) for several countries (Table 2.1). Furthermore, suspected human carcinogens compounds such as NDMA and 1,4-dioxane are broadly studied due to their presence in the aquatic environment. NDMA is formed during chlorination when dimethylamine react and other nitrogen groups react with chloramines. NDMA can be found in median concentrations in untreated wastewater of about 80 ng/L up to 790 ng/L and around 46 ng/L in secondary effluent before disinfection (Sedlak et al., 2005). Thus, the potential leaching of NDMA in soils receiving effluents for wastewater reclamation and reuse is a great concern due to its miscibility in water (Haruta et al., 2008). Yangalli (2010) reported values of 2 ng/L for NDMA detected in drinking waters in The Netherlands.

On the other hand, Abe (1999) investigated the distribution of 1,4-dioxane in surface and groundwater sources, where it was observed that almost all the samples were polluted with this solvent. The main possible pathways for this compound to enter in the water environment is through domestic effluents due to 1,4-dioxane is a by-product of several chemicals frequently used in households. Furthermore, other studies reported contamination with 1,4-dioxane in diverse sites were municipal water supply wells needed to be closed due to the presence of this compound in concentrations of 2,100 µg/L or in natural waters in Japan where 1,4-dioxane exhibited concentrations ranged from 1.9 to 94.8 µg/L in 83 of 95 river, ocean, and groundwater samples (Zenker et. al, 2003).

Table 2.1 Overview of pharmaceutical (and metabolites) concentrations detected in worldwide tap water

| Therapeutic use | Compound | Maximal concentration detected (ng/L) | Country |
|--------------------------------|----------------|---------------------------------------|---------|
| Antibiotics | Triclosan | 734 | USA |
| Anticonvulsants | Carbamazepine | 24 | Canada |
| | | 140-258 | USA |
| | | 43.2 | France |
| | | 60 | Germany |
| | Dilatin | 1.3 | USA |
| | Primidone | 40 | Germany |
| Antidepressants, anti-anxiety | Amitryptilline | 1.4 | France |
| | Diazepam | 10 | UK |
| | | 23.5 | Italy |
| | Meprobamate | 5.9 | USA |
| Antineoplastics | Bleomycin | 13 | UK |
| Iodinated X-ray contrast media | Diatrizoate | 1200 | Germany |
| | Iopromide | <50 | Germany |
| Lipid regulators | Bezafibrate | 27 | Germany |
| | Clofibric acid | 50-270 | Germany |
| | | 5.3 | Italy |
| NSAIDs and analgesics | Gemfibrozil | 70 | Canada |
| | Acetaminophen | 210.1 | France |
| | Diclofenac | 6-35 | Germany |
| | | 2.5 | France |
| | Ibuprofen | 3.0 | Germany |
| | | 0.6 | France |
| | | 8.5 | Finland |
| | | 1350 | USA |
| | Ketoprofen | 8.0 | Finland |
| | | 3.0 | France |
| | Phenazone | 250-400 | Germany |
| | Propyphenazone | 80-240 | Germany |
| Opioidanalgesics | Codein | 30 | USA |
| Psycho-stimulants | Caffeine | 60-119 | USA |
| | | 22.9 | France |

Source: Adapted from Mompelat et. al. (2009)

2.1.2 Physico-chemical properties of organic micropollutants

The classification of organic compounds according to their physicochemical properties leads to a better understanding about the mechanisms that govern the fate of organic micropollutants. Properties such as molecular, octanol-water partition coefficients, solubility and acid dissociation constant constitutes important key parameters to be analyzed before considering any kind of treatment.

2.1.2.1 Molecular weight (MW)

The molecular weight (MW) of a compound is one of the most used properties in membrane applications due to the strong relation with the molecular weight cut-off of the membrane in the rejection of non-charged and non-polar organic micropollutants (Yangalli, 2010). Pharmaceutical Active Compounds (PhACs) are characterized to have molecular weight in the range of 200 to 500/1000 Da (Kümmerer, 2009), which is suitable for further predictions. However, some of them can exhibit molecular weight lower than this interval, for instance acetaminophen (MW 151.17).

2.1.2.2 Octanol-water partition coefficients

The distribution of a compound between water and octanol is used to calculate the octanol-water partition coefficient (K_{ow}). This important property describes the hydrophobic or hydrophilic character of a given compound. Solutes with octanol-water partition coefficient greater or equal to 2 have been classified as hydrophobic and as hydrophilic when this coefficient is less than 2 (Yangalli, 2010). A compound with high K_{ow} and low solubility is an indicator that an association among a surface and the compound may takes place. However, less adsorption will occur in the same proportion at which this coefficient starts to decrease having as a consequence higher mobility through the media (Abel, 2009).

2.1.2.3 Solubility

The solubility of a compound is defined by the affinity of this solute to dissolve in water. Therefore, the more soluble is a given compound the higher mobility will exhibit in the water matrix. Moreover, the polarity can also predict the solubility of a compound due to its polar or non-polar nature mainly because polar compounds tend to dissolve in the aqueous phase as a result of the polar character of the water; while the opposite phenomena occurs with non-polar substances (Yangalli, 2010; Abel, 2009).

2.1.2.4 Acid dissociation constant

The acid dissociation constant (K_a) gives a measure of the ability of an acid to donate protons to a respective base. The greater the value of this equilibrium constant, the stronger an acid is in the solution. The knowledge of the pK_a value (defined as $-\log K_a$) can be used not only for classification of compounds into ionic or neutrals but also together with $\log K_{ow}$ is an efficient tool for estimating the fate of a compound in a system.

2.1.3 Potential treatment technologies in removing or reducing organic micropollutants

In general, conventional wastewater treatment plants have been designed to remove organic constituents and nutrients but can not eliminate completely micropollutants due to their wide range of physic-chemical properties. The persistence of trace compounds requires more advance technologies where the selection of the treatment depends mainly on factors like cost, concentration of the organic pollutants and volume flows to be treated. Depending on the compound, different methods can be employed for its elimination, for instance: physic-chemical treatment, biological degradation, or in some cases for its recuperation: liquid extraction, absorption and membrane processes (Esplugas et al., 2007; Bolong et al., 2009). Table 2.2 summarizes the pharmaceutical removal performance of different treatment processes.

According to Bolong et al (2009), physicochemical treatment as coagulation–flocculation process has demonstrated the inefficacy on removing organic micropollutants such as EDCs and PPCPs. However, other reseachers showed that if a compound has an octanol-water partition coefficient ($\log K_{ow}$) greater than 5, then some removal could be expected but neutral compounds ($pK_a > 7$) such as carbamazepine and sulfamethoxazole can not be removed via coagulation (Abel, 2009).

Furthermore, the use of activated carbon and ozonation has proved the efficacy for the removal of many emerging contaminants in watercourses. Activated carbon adsorption system shows hydrophobic interactions mainly for non polar compounds (with $K_{ow} > 2$) while ozone oxidizes refractory compounds such as carbamazepine with removal higher than 97%. However, the require dose of ozone may increase when high concentrations of colloids are present in the solution, making the process more costly (Bolong et al., 2009).

Table 2.2 Pharmaceuticals removal performance by treatment processes

| Treatment process | Removal performance |
|--|--|
| Coagulation by alum or ferric sulphate | <20% of compound removed, specially associated with particulate matter Presence of hydrophobic dissolved organic carbon enhances removal and provides partitioning |
| Lime softening | <20% of compound concentration was removed at pH 9 -11 |
| Powder activated carbon (PAC) | >90% of many EDCs removed (at 5 mg/L dose PAC of 4 hour contact time) Yet some EDCs (ibuprofen, sulfamethoxazole, meprobamate) had lower removals (40–60%) Hydrophobic compounds (octanol-water partition co-efficient, $\log K_{ow} > 5$) have better removal than polar compounds |
| Biofilm | Removal depends on biodegradability of compounds but removal rate is unclear |
| Chlorination | Able to remove >90% for more reactive compounds containing aromatic structures with hydroxide functional groups Not suitable because it produces chlorine by-product (react with EDCs) and should be avoided |
| Ozonation | Oxidized similar to chlorination but at slightly higher removal rates Addition of hydrogen peroxide during ozone addition slightly increased the EDCs removal |

Source: Bolong et al. (2009)

Bolong et al (2009) also reported that biological degradation can be another way to for removing organic compounds. Unfortunately, biological treatments such as activated sludge systems and biological trickling filters can eliminate only a part of a wide range of emerging contaminants, where polar compounds remain in the aqueous phase and consequently are being discharge into the environment. Nevertheless, it was suggested by having a biological treatment with longer hydraulic retention time (HRT) and sludge retention time (SRT), the removal of these compounds can be increased.

Therefore, advanced treatment technologies such as ultra-violet (UV) photolysis, ion exchange and membrane filtration appears to be alternatives options for removing organic micropollutants. However, even when the first two options can improve the removal of those contaminants, the technology is too expensive for considering as feasible solutions (Bolong et al., 2009).

Nonetheless, high pressure membrane such as reverse osmosis (RO) and nanofiltration (NF) have been receiving special attention due to the effectiveness for eliminating micropollutants (Fernando, 2009). The rejection of both inorganic and organic contaminants is mostly based in physic-chemical properties of the solute and interactions with the membrane (Yangalli, 2010).

Radjenovic' and co-workers (2008) have demonstrated the excellent overall performance of both NF and RO on removing a wide range of pharmaceuticals such as analgesics and anti-inflammatory drugs that were detected in groundwater with rejection percentages greater than 85% for almost all compounds analyzed. Still, compounds with small molecular weight such as acetaminophen, the retention were lowered (44.8–73%). And even though numerous pharmaceuticals can be rejected by the process, their accumulation in the brine stream at concentrations of several hundreds ng/l represent a hazard of this type of treatment at the moment of future disposal.

Natural systems such as Soil Aquifer Treatment are gaining acceptance due to the high potential on removing organic matter and several micropollutants through a variety of physical, chemical and biological process. Soil passage has demonstrated the capability in the elimination of compounds such as NDMA where biodegradation seem to be the dominant mechanism for the reduction of this contaminant in the vadose zone (Bradley et al., 2005). Nonetheless, small traces compounds can resist through soil passage and to enter into groundwater sources causing pollution. Therefore, a combination of SAT as a primary barrier follow by a second barrier such as membrane filtration is proving to be an effective solution for removing emerging contaminants in wastewater effluents. (Jarusutthirak et al., 2003; Abel, 2009; Amy & Drewes, 2007).

SAT as a sustainable solution for wastewater reclamation

2.2.1 General overview of Soil Aquifer Treatment

Soil Aquifer Treatment (SAT) emerged as a natural system not only to solve the problems related to diminishing groundwater level, water intrusion in aquifers and subsidence, but also for playing an important role as a robust multi-barrier for indirect potable reuse due to its great potential on removing diverse classes of contaminants through several physic-chemical processes in the vadose and saturated zone with simplicity in operation and low treatment costs (Fernando, 2009; Amy & Drewes, 2007; Jarusutthirak et al., 2003; Xue, 2009). SAT system consists mainly in spreading wastewater effluents in a recharge basin that infiltrate through the upper layers (unsaturated zone) where several mechanisms take place (chemical precipitation, adsorption, biological degradation, nitrification and denitrification, among others) followed by mixing with groundwater and a subsequent recovery by wells (Amy & Drewes, 2005). Through these mechanisms it is possible to achieve considerable removal rates on organic compounds, pathogens and potentially other contaminants such as pharmaceutical active compounds (PhACs) and endocrine disrupting compounds (EDCs) present in the wastewater (Fernando 2009). Figure 2.3 shows a schematic representation of SAT system.

However, the performance of SAT can be affected by different factors such as the quality of the influent to be infiltrated, wetting/drying cycles and hydro-geological parameters (infiltration rates, retention time, permeability and soil properties) (Sheriff, 2009; Fernando, 2009; Harun, 2007).

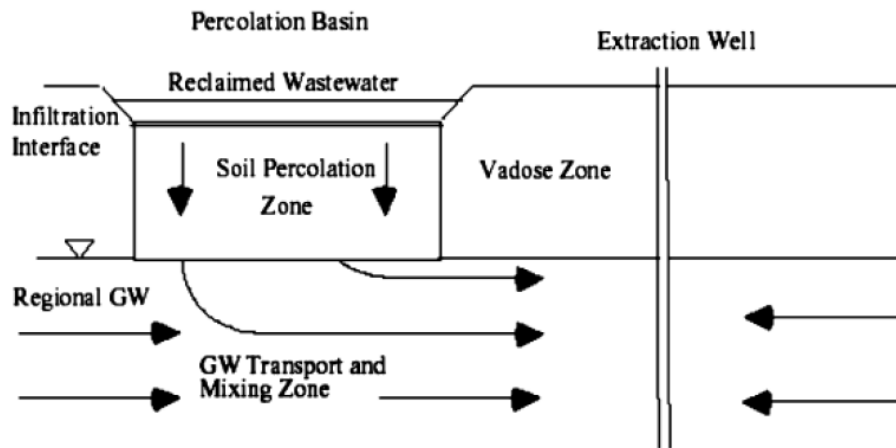


Figure 2.3 Soil Aquifer Treatment (SAT)
Source: Amy and Drewes (2007)

2.2.2 Factors affecting SAT performance

Natural systems (SAT) have shown the great potential for removing many biological and chemical contaminants from wastewater effluents. Nevertheless, as it was mentioned previously, the behavior of SAT systems is strongly dependent on several factors, which are discussed in this section:

▪ **Influent wastewater quality:** Treated wastewater is commonly used for wastewater reclamation and reuse applications. However, the quality of the water plays an important role in the performance of the treatment and in the removal of many compounds. Furthermore, the degree of pre-treatment is also associated to the potential risk of clogging in the surface due to the suspended solids content present in the wastewater. Therefore, the application of secondary effluent rather than primary effluent is more desirable in order to minimize clogging issues (Figueredo, 2007).

Wetting/Drying cycles: One of the main constraints of SAT systems is related to clogging problems. Thus, operation is enhanced by applying alternatively wet/dry cycles. This sequence limits the propensity for forming the *schmutzdecke* layer as results of spreading the reclaimed waters in the recharge basin (Figueredo, 2007; Fernando, 2009). The clogging layer reduces the infiltration rate causing operation problems and therefore, the pond needs to be cleaned by draining, drying and scraping during dry cycles (Fernando, 2009; Harun, 2007).

▪ **Hydro-geological parameters:** Surface infiltration systems require soils with high permeability in which water can infiltrate easily to reduce land requirements. Therefore, key parameters such as infiltration rate, retention time and soil properties are important for determining appropriate sites for artificial recharge of groundwater with this type of systems (Bouwer, 2002).

- **Infiltration rates:** The Green-and-Ampt equation for infiltration into a flooded soil allows determining this parameter by classifying the soil texture using the hydraulic conductivity (K), where typical values vary from <0.1 m/day for clay soils up to >10 m/day for coarse sands (Figure 2.4). Furthermore, infiltration rates can be reduced due to the formation of a clogging zone caused by physical and biological process which tends to decrease permeability and a uniform infiltration having a direct impact on the hydraulic loading (Bouwer, 2002; Harun, 2007; Cuyk et al., 2001).

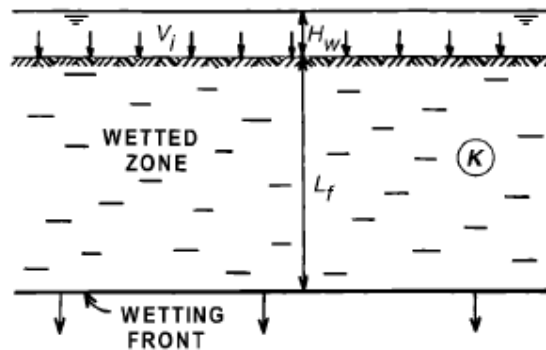


Figure 2.4 Section showing geometry and symbols for Green and Ampt piston-flow model of infiltration
Source: Bouwer (2002)

- **Retention time:** Differences in travel times lead to depletion or partial reduction of organic and inorganic compounds through the vadose and saturated zone. For natural systems (SAT), a travel time of six months (minimum) has to be considered before recovery due to the necessity of nitrate attenuation in the aquifer (Sheriff, 2009).

- Soil properties: Major mechanisms occurring in SAT can be affected by soil properties, where significant removal efficiencies vary depending on the soil type due to biological activity (Fernando, 2009). Furthermore, some studies indicate that differences between soil parameters such as hydraulic conductivity for clay and loam soil has an direct impact in infiltration rates, where remarkable reductions were observed for the first type of soil during wastewater infiltration experiments (Viviany & Iovino, 2004).

2.2.3 Removal mechanisms of organic micropollutants during soil passage

Several studies confirm the effectiveness of natural systems (SAT and soil passage) for improving water quality by removing the majority of organic compounds present in wastewater effluents through different mechanisms such as biodegradation, adsorption, dispersion, filtration and mixing with groundwater, where the first two processes play an important role in the fate and transport of organic micropollutants (Amy & Drewes, 2007; Abel, 2009).

During SAT, trace organic compounds can be affected by sorption process due to the strong dependency between physic-chemical properties of the organic micropollutants and the environment. For instance, if the media and the compound presents opposite charges, it is expected that adsorption is the primary mechanism for the removal of such contaminant (Lorphensri et al., 2007). Hydrophobic and hydrophilic properties of the organic solutes are related with the octanol-water partition ($\log K_{ow}$), where compounds with $\log K_{ow}$ values greater than two can be classified as hydrophobic. This important property allows anticipating the tendency of a compound to adsorb onto suspended solids and sediment during infiltration. On the other side, hydrophilic compounds with $\log K_{ow}$ value less than two remains in aqueous phase due to its affinity with water (Yangalli, 2010; Abel, 2009).

The potential biodegradation of PhACs and EDCs by microbial communities in the surface and vadose zone has been documented in numerous studies (Quanrud et al. 2003; Abel, 2009; Bradley et al., 2009; etc). Biotransformation of organic micropollutants can takes place linked to several factors including redox conditions (aerobic and anoxic/anaerobic conditions) and chemical structures even when, hydrophilic compounds can exhibit high mobility through the soil and might migrates into groundwater (Abel, 2009). One of these studies conducted by Amy & Drewes (2007) in the Northwest Water Reclamation Plant in Mesa, Arizona (Mesa WRP); and the Sweetwater Underground Storage and Recovery Facility in Tucson, AZ (Tucson WRP), showed that target compounds including antiepileptics, analgesics, lipid regulators and X-ray contrast agents were effectively removed by soil passage under oxic/anoxic conditions even though few of them persisted (Table 2.3).

Table 2.3 Removal of selected pharmaceutically active compounds (PhACs) through SAT at Mesa WRP and Tucson (WRP)

| Sample | Antiepileptics (ng/L) | | Analgesics (ng/L) | | Lipid regulators (ng/L) | Wastewater indicators (ng/L) | X-ray contrast agents |
|-------------------|-----------------------|-----------|-------------------|----------|-------------------------|------------------------------|-----------------------|
| | Carbamazepine | Primidone | Ibuprofen | Naproxen | Gemfibrozil | Caffeine | AOI (µg/L) |
| <i>Mesa WRP</i> | | | | | | | |
| Mesa3eff | 175 | 202 | 16 | 8.0 | n.d. | n.d. | 24.9 |
| NW4 | 235 | 120 | n.d. | n.d. | n.d. | n.d. | 8.0 |
| NW2 | 125 | 160 | 16 | n.d. | n.d. | n.d. | 8.9 |
| 2U | 145 | 90 | n.d. | n.d. | n.d. | n.d. | 6.7 |
| 6U | 85 | 100 | n.d. | n.d. | n.d. | n.d. | 12.5 |
| <i>Tucson WRP</i> | | | | | | | |
| Tucson2eff | n.d. | 110 | 3,380 | 6,280 | 1,235 | 15,700 | 16.7 |
| WR199 | 610 | 155 | n.d. | n.d. | n.d. | n.d. | 20.5 |

n.d. = not detected.

Source: Amy & Drewes (2007)

2.2 General overview of nanofiltration technology

2.3.1 Characteristics of NF membranes

Nanofiltration (NF) membrane has been developed and applied as one of promising technologies for the rejection of neutral and charged solutes in aqueous solutions. Some remarkable properties play an important role on how the membrane will reject a target compound, for instance, molecular weight cutoff (MWCO) which ranges from 200 to 2000 Da, pore size, surface charge and hydrophobicity but also solute parameters have to be taken into consideration in the process, such as molecular weight (MW), dissociation constant (pK_a), hydrophobicity/hydrophilic (commonly represented by its log K_{ow}) and its diffusivity (D_p) (Wang et al., 2007; Fernando, 2008; Verliefde, 2008). Table 2.4 presents a qualitative prediction of rejection of organic during NF micropollutants based on their physic-chemical properties.

Table 2.4 Qualitative prediction of rejection of organic micropollutants

| Hydrophobicity (log K _{ow}) | Molecular size parameter | pK _a (-) | Rejection mechanism | Qualitative rejection prediction |
|---------------------------------------|--------------------------|---------------------|--------------------------|----------------------------------|
| <2 (hydrophilic) | *MW<MWCO | >pH (uncharged) | Steric hindrance | - (moderate) |
| | *Size < pore size | | | |
| <2 (hydrophilic) | *MW>MWCO | >pH (uncharged) | Steric hindrance | 0 (moderate to high) |
| | *Size > pore size | | | |
| >2 (hydrophobic) | *MW<MWCO | >pH (uncharged) | Hydrophobic interactions | - - (low) |
| | *Size < pore size | | | |
| >2 (hydrophobic) | *MW>MWCO | >pH (uncharged) | Hydrophobic interactions | - (moderate) |
| | *Size > pore size | | | |
| <2 (hydrophilic) | *MW<MWCO | <pH (charged) | Charge repulsion | + (high) |
| | *Size < pore size | | | |
| <2 (hydrophilic) | *MW>MWCO | <pH (charged) | Charge repulsion | ++ (very high) |
| | *Size > pore size | | | |
| >2 (hydrophobic) | *MW<MWCO | <pH (charged) | Charge repulsion | + (high) |
| | *Size < pore size | | | |
| >2 (hydrophobic) | *MW>MWCO | <pH (charged) | Charge repulsion | + + (very high) |
| | *Size > pore size | | | |

Source: Verliefde et al. (2007)

According to Bolong (2009), three are the dominant mechanisms for transport during NF: convection, diffusion (sieving) and charge effects. The first one happens when pressure difference is applied over the membrane and consequently diffusion occurs due to concentration gradient across the membrane having as a result that the compounds with sizes larger than the membrane pore size are rejected (Fernando, 2009).

After that, an electrostatic repulsion occurs between a charged membrane and a charged organic compound. Table 2.5 shows a summary of the main characteristics of the NF process.

Table 2.5 Characteristics of NF process

| Permeability ($\text{l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$) | Pressure (bar) | Pore Size (nm) | Rejection | Separation Mechanisms | Applications |
|--|-------------------|-------------------|----------------------------|--------------------------|---|
| 1.5 - 30 | 3 - 20 | 0.5 - 2 | Monovalent ions | - | Removal of (multivalent) ions and relatively small organics |
| | | | Multivalent ions | + | |
| | | | Small organic compounds | -/+ | |
| | | | Macromolecules | + | |
| | | | Particles | + | |

Source: Fernando (2009)

2.3.2 NF technology for organic micropollutants removal for water reuse applications

According to Wang et al. (2007), NF technology has been widely applied in the desalination and concentration, separation and purification, drinking water production and wastewater treatment. Besides, NF technology can be applied to separate amphoteric materials (the amino acids, proteins, etc.) since most commercial NF membranes showed diverse rejection performance for solutes at the different pH values.

In water treatment, the separation capacities of NF membrane allow to remove organic micropollutants, color and mineral components (softening hardness, sulphate, nitrate, among others) (Wang et al., 2007; Fernando, 2008). Nowadays, nanofiltration is also been used in the rejection of many emerged compounds such as PhACs, EDCs and PPCPs, since when these ones are in the size range of the MWCO values of NF membranes (Verliefde et al. 2007).

The basic separation principle is due to the sieve and electrostatic effects of a NF membrane. When the molecular weight (MW) of solute is larger than the maximum MWCO, the separation performance of a NF membrane is primarily due to the sieve effect. If the MW of solute falls into the separation range of MWCO, both sieve and electrostatic effects operate (Wang et al., 2007).

Verliefde et al. (2007) offers an overview on how organic micropollutants removal by nanofiltration can be roughly predicted based on the values of key solute and membrane parameters (Table 2.6).

Table 2.6 Qualitative rejection prediction based on log K_{ow}, MW and pK_a-values and experimental rejection values for the priority list organic micropollutants.

| Compounds | log K _{ow} (–) | Molar mass (g/mol) | pK _a (–) | Category | Qualitative rejection prediction | Literature rejection value (%) |
|-----------------------------|-------------------------|--------------------|---------------------|----------|---------------------------------------|---|
| Hormones | | | | | | |
| 17β-Estradiol | 4.01 | 272 | N/A | 4 | Initially high, drop to moderate/high | 85–100 ^a |
| 17α-Ethinylestradiol | 3.67 | 296 | N/A | 4 | Initially high, drop to moderate/high | n.d. |
| Estrone | 3.13 | 270 | N/A | 4 | Initially high, drop to moderate/high | *0–60 ^b *85–100 ^a |
| Progesterone | 3.87 | 314 | N/A | 4 | Initially high, drop to moderate/high | 90–100 ^a |
| Testosterone | 3.32 | 288 | N/A | 4 | Initially high, drop to moderate/high | 80–100 ^a |
| Industrial chemicals | | | | | | |
| Bisphenol A | 3.32 | 228 | N/A | 4 | Initially high, drop to moderate/high | *70–100 ^c *45 ^d |
| p-Dimethylphthalate | 2.25 | 194 | N/A | 3–4 | Initially high, drop to moderate/low | 65–80 ^e |
| p-Diethylphthalate | 3.24 | 222 | N/A | 3–4 | Initially high, drop to moderate | 65–80 ^e |
| Nonylphenol | 4.48 | 220 | 10.25 | 3–4 | Initially high, drop to moderate | 70–90 ^f |
| MTBE | 0.94 | 88 | N/A | 1 | Moderate | 89.6 ^g |
| NDMA | –0.57 | 74 | N/A | 1 | Moderate | n.d. |
| Pesticides | | | | | | |
| Atrazine | 2.61 | 216 | 1.7 (weak base) | 3–4 | Initially high, drop to moderate | *68–98 ^h *95 ^h *81–99 ⁱ * >80 ^j *26–97 ^k *88–93 ^h * >75 ^j *17–96 ^k |
| Simazine | 2.18 | 202 | 1.62 (weak base) | 3–4 | Initially high, drop to moderate | n.d. |
| DDT | 6.91 | 354 | N/A | 4 | High | n.d. |
| Chlorpyrifos | 5.27 | 350 | N/A | 4 | High | >99 ^g |
| Pharmaceuticals | | | | | | |
| Sulfamethoxazole | 0.89 | 253 | N/A | 2 | High | n.d. |
| Primidone | 0.91 | 218 | N/A | 2 | Moderate/high | 72–87 ^d |
| Carbamazepine | 2.45 | 236 | N/A | 4 | Initially high, drop to moderate/high | 93 ^l |
| Ibuprofen | 3.97 | 206 | 4.91 | 7–8 | High | *30–95 below pK _a ^m *70 above pK _a ^{m,n} |
| Iopamidol | –2.42 | 777 | N/A | 2 | Very high | n.d. |
| Amidotrizoic acid | n.d. | 614 | n.d. | – | Very high | n.d. |

N/A, not applicable; n.d., no data; ^aNghiem et al., 2004; ^bChang et al., 2002; ^cWintgens et al., 2002; ^dKimura et al., 2003; ^eKiso et al., 2001; ^fHofman et al., 2006; ^gKiso et al., 2000; ^hChen et al., 2004; ⁱKosutic and Kunst, 2002; ^jBoussahel et al., 2002; ^kVan der Bruggen et al., 1998; ^lXu et al., 2005; ^mBellona and Drewes, 2005; ⁿPark and Cho, 2005.

Source: Verliefde et al. (2007)

Persistent organic micropollutants (NDMA and 1,4-dioxane) are of continuous concern for water consumers due to the low rejection by NF membranes. Still, biodegradation of NDMA can be achieved under aerobic and anaerobic conditions through aquifer recharge and further recovery (Yangalli, 2010; Bradley et al., 2005).

2.3 Ozonation technology

2.4.1 General overview of ozonation processes

The early discovery and application of ozone during the 1980s for primary purposes as strong disinfectant, contributed to spread the use of ozonation as a substitute of disinfection by chlorination in order to avoid the formation of halogenated compounds such as Trihalomethanes (THMs) (Fernando, 2009; Techneau, 2006). Currently, ozone treatment is applied widely for several purposes (eg., reduction and elimination of colour, odour and taste in drinking water facilities) and more recently, it has been demonstrating its potential for degradation of contaminants (Gunten, 2003; Rosal et al., 2010; Fernando, 2009).

Ozone requires a large amount of energy to be formed by passing an electrical discharge in the presence of air or oxygen. After ozone entering in the aqueous solution, two

reactions take place due to its solubility in water. The first one is a direct oxidation but relatively slow and very selective that is favored at low pH and the second basic reaction is the self-decomposition of ozone in hydroxyl radicals (Fernando, 2009; Techneau, 2006).

According to Gunten (2003), the oxidation of many compounds via ozonation can occur through these two paths: direct reaction with ozone or with hydroxyl radicals. However, ozone molecule is highly selective and reacts mainly with double bonds, aromatic rings and non-protonated amines. Due to the unstable character of ozone in aqueous solutions, ozone may dissociates into OH[•] radicals which are stronger oxidizers and less selective than ozone itself. As a consequence, compounds that have resistance to ozone can be oxidized by hydroxyl radicals into more biodegradable and simple structures. Nevertheless, the stability of O₃ is dependent upon several factors; including pH, alkalinity, among other water parameters related to the water composition (Fernando, 2009).

Despite that ozonation is an effective technology for treating polluted waters, some substances exhibit low reactivity to ozone, which can lead to search for more advanced methods by combining ozone with peroxide or ultraviolet light in order to enhance the oxidation level for the removal of emerging compounds like personal care products, endocrine disruptors, pharmaceuticals, disinfection by-products, among others (Techneau, 2006).

2.4.2 Effect of ozone on emerging contaminants during wastewater treatment

The presence of a wide spectrum of organic micropollutants in wastewater effluent has lead to the necessity of searching for effective treatment options for removing those compounds from water. Conventional processes such as coagulation/flocculation, filtration and chlorination have demonstrated their inefficacy in achieving good removals. However, chemical oxidation via ozonation has gained acceptance due to the proved effectiveness of ozone as strong oxidant for degradation of the majority of emerging contaminants as well as for microbial disinfection. Ozonation of organic contaminants is repeatedly proposed in the literature due to its fast kinetic reaction with functional groups such as aromatic rings, neutral alkylamines, double bounds, among others. The oxidation process may occur through direct reaction with ozone or by reacting with free radicals including the hydroxyl radical that is linked with the oxidation of the most recalcitrant compounds produced from ozone in the solution (Wert et al., 2009; Broséus et al., 2009; Fernando, 2009).

According to Esplugas et al. (2007) ozonation is the method most widely applied for removing trace organic micropollutants. Esplugas et al. (2007) reported removals greater than 90% with ozone doses ranged from 0.1 to 30 mg L⁻¹ for a vast range of compounds (pesticides, anti-inflammatories, antiepileptics, antibiotics and natural and synthetic estrogens). Rosal et al. (2010) studied the impact of ozone in 84 pollutants present in a secondary effluent from a conventional wastewater treatment plant. The contaminants analyzed included pharmaceuticals (analgesics, antidepressants, anti-inflammatory, antibiotics, antiepileptics, betablockers and lipid regulators among others), personal care products (sunscreen agents, synthetic musks), stimulants (caffeine, nicotine) and some metabolites (clofibrilic acid, cotinine, several metabolites of

dipyron). The results showed high removals for most all the compounds even at lower ozone doses. However, some personal care products were poorly removed by ozonation treatment like diclofenac.

Other authors also studied the effect of incorporating ozonation in the degradation of eighteen major PhACs (and metabolites) and seven s-triazines herbicides found in raw water intake of a DWTPs in Canada. The drinking water facility uses flocculation-coagulation and dual media filtration as treatment steps. The findings showed that without ozone treatment no decreases in concentrations for the target compounds were observed. However, when ozone treatment was included as part of the water treatment, decreases of 66–100% (below detection limits: 0.05–1 ng/L) were achieved, proving that ozonation is highly effective in reduction of carbamazepine, caffeine, cotinine, and atrazine. Still, concentrations at ng/L levels were found after ozone treatment in the water product mainly because water composition and changes in seasons (Hua et al., 2006).

Moreover, Snyder et al. (2006) proved the effectiveness of ozone on removing organic contaminants in water at doses of 1.25 mg/L or greater were only 6 of 36 compounds were less removed than 50% (Table 2.7).

Table 2.7 Ozone removal summary

| > 80% Removal | 80–50% Removal | 50–20% Removal | < 20% Removal |
|------------------|----------------|----------------|---------------|
| Acetaminophen | Benzo(a)pyrene | Atrazine | TCEP |
| Androstenedione | DDT | Iopromide | Lindane |
| Caffeine | DEET | Meprobamate | Musk Ketone |
| Carbamazepine | Diazepam | | |
| Diclofenac | Dilantin | | |
| Erythromycin | Fluorene | | |
| Estradiol | Ibuprofen | | |
| Estriol | Metolachlor | | |
| Estrone | | | |
| Ethinylestradiol | | | |
| Fluoxetine | | | |
| Galaxolide | | | |
| Gemfibrozil | | | |
| Hydrocodone | | | |
| Naproxen | | | |
| Oxybenzone | | | |
| Pentoxifylline | | | |
| Progesterone | | | |
| Sulfamethoxazole | | | |
| Testosterone | | | |
| Triclosan | | | |
| Trimethoprim | | | |

Source: Snyder et al. (2006)

Lee et al. (2007) demonstrated that even when, ozone is powerful tool for oxidizing refractory compounds; emerging contaminants such as NDMA and 1,4-dioxane showed very little oxidation (less than 25%) with ozone doses of 7.7 mg/L by conventional ozonation due to its low reactivity towards ozone. To enhance NDMA greater than 50%, hydrogen peroxide was added to promote the production of OH radicals in natural waters. Also for 1,4-dioxane, Suh & Mohsen (2004) proved that a direct reaction of 1,4-dioxane with ozone is not significant compared with the combination of O₃/H₂O₂ reaction in which hydroxyl radicals contributes to 1,4-dioxane oxidation.

In addition, ozonation is a viable method for helping micropollutants to break down into smaller fractions at feasible doses of ozone, which can be subsequently, removed by other mechanisms namely adsorption or biodegradation during soil passage.

2.4 SAT as pre-treatment for NF

A study conducted by Fernando (2009), demonstrated the effectiveness of SAT as a pre-treatment before NF membrane for water reuse applications. SAT pre-treatment not only reduces the fouling of NF membranes but also removes other contaminants and allows longer operation of NF system. SAT proved to remove about 24% of DOC from secondary effluent having a substantial reduction on flux decline during nanofiltration. Although the effect of SAT+NF on the removal of organic micropollutants was not investigated, other studies in long soil column experiments have demonstrated that the majority of target PhACs such as analgesics/anti-inflammatories, lipid regulators showed removal efficiencies greater than 90% but antiepileptics like carbamazepine shows a persistent behavior even under oxic and anoxic conditions (Abel, 2009).

Musabe (2007) and Kahawita (2008) have shown that pre-ozonation of secondary effluent before SAT increases DOC removal significantly. Other researchers at UNESCO-IHE also demonstrated that the performance of SAT+NF system improves when ozonation a pre-treatment step is included in the train (Fernando, 2009). However, the effect of pre-treated secondary effluent by using ozonation on organic micropollutants compounds and consequently the impact on SAT+NF process has not been fully investigated. It is expected that the combination of ozonation, SAT and NF will improve the overall efficiency of organic micropollutants removal from wastewater treatment plant effluents.

3 MATERIALS AND METHODS

General description

The materials and methods for experimentally assessing the effect of different effluent pre-treatment on the performance of nanofiltration for persistent organic micropollutants removal are described in this chapter. This research is mainly divided in two parts. The first one was to investigate the SAT performance on the removal of emerging contaminants such as 1,4-dioxane, NDMA and thirteen PhACs spiked into secondary effluent using one soil column set-up (SC1), while the second laboratory scale soil column (SC2) was fed with ozonated secondary effluent that was spiked before ozonation with all the compounds mentioned above.

The second part of this study consists of NF experiments using NF-90 nanofiltration membrane and three different types of water (effluents from both soil columns and secondary effluent without pre-treatment that was spiked with the referred micropollutants).

3.1 Materials

3.1.1 Wastewater source

Secondary effluent from conventional activated sludge of Hoek van Holland WWTP, Netherlands was used. Samples were collected at the discharge point of the second secondary clarifier (Figure 3.1 and Figure 3.2) and later on stored at 4 °C to preserve wastewater characteristics before usage in the experiments.



Figure 3.1 Hoek van Holland wastewater treatment plant

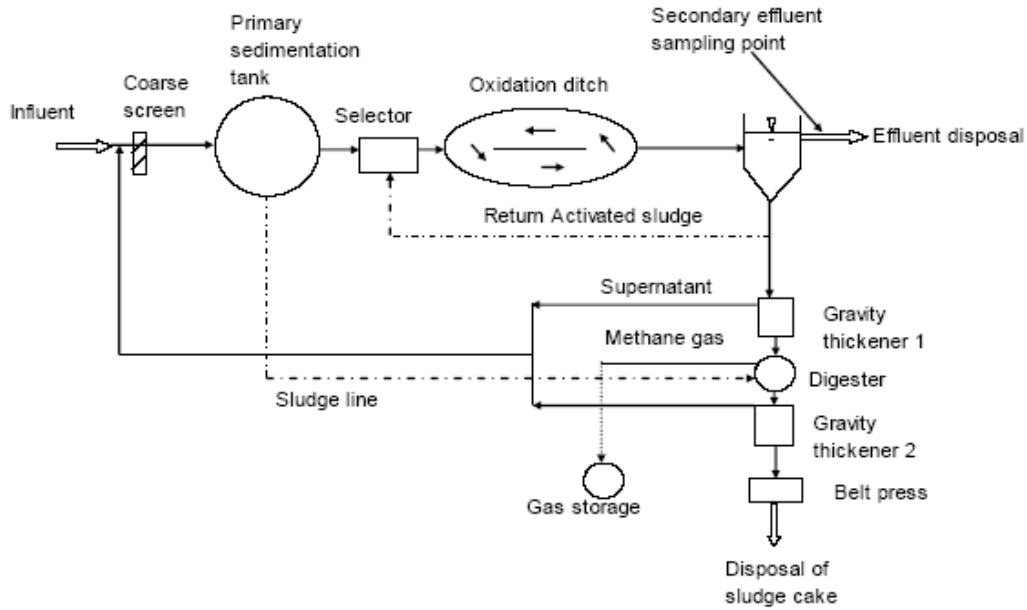


Figure 3.2 Schematic representation of Hoek van Holland WWTP
Source: Fernando (2009)

3.1.2 NF membrane

The membrane used for conducting the experiments was NF-90 and it was supplied by DOW/FilmTec. This membrane was selected mainly because it can reject nearly all of the hydrophobic neutral compounds (95–98%) and it is commonly used Dutch drinking water companies (Fernando, 2008; Yangalli et al., 2009). The membranes were already cut in pieces, stored at 4 °C and immersed in a solution of 1% sodium bisulfphite (Na_2SO_3) to prevent growth activity. Characteristics and properties of the membrane NF-90 are summarized in Table 3.1 and Table 3.2.

Table 3.1 Membrane characteristics (NF-90)

| Characteristics | Units | Value |
|--------------------|-------------------------|-------|
| MWCO | Da | 200 |
| Water permeability | L/m ² -h-bar | 5.2 |
| Contact angle | Degrees | 54 |
| Roughness | Angstrom | |
| 0.5 µm x 0.5 µm | | 108 |
| 1 µm x 1 µm | | 219 |
| 3 µm x 3 µm | | 331 |
| 5 µm x 5 µm | | 388 |
| Zeta potential | mV | |
| pH 3 | | 3.7 |
| pH 12 | | -19.4 |

Source: Adapted from Fernando (2008)

Table 3.2 Membrane properties (NF-90)

| Membrane type | Polyamide |
|-----------------------------------|------------|
| Nominal salt rejection (%) | 98 |
| Nominal flow (m3/day) | 36.1 |
| Element area (m2) | 37.2 |
| Test solution/concentration (ppm) | 2000 MgSO4 |
| Test pressure (bar) | 4.8 |

Source: Adapted from Fernando (2008)

3.1.3 Selected pharmaceutically active compounds (PhACs), NDMA and 1,4-dioxane

Pharmaceutically active compounds (PhACs)

Based on different criteria such as human health risk, possible occurrence of high concentrations of pollutants in the reclaimed water sources due to high production volumes and persistence in the environment, a list of selected pharmaceutically active compounds and their main physicochemical properties such as: molecular weight (MW), water-octanol partition coefficient ($\log K_{ow}$) and acid dissociation constant (pK_a) are shown in Table 3.3 (Verliefde et al., 2007; Yangali-Quintanilla et al., 2008).

PhACs namely Gemfibrozil, Diclofenac, Bezafibrate, Ibuprofen, Fenoprofen and Carbamazepine were purchased from Sigma's Company and Acetaminophen, Naproxen, Clofibric acid, Phenacetine, Caffeine Pentoxifylline, Ketoprofen were obtained from Aldrich.

Table 3.3 also shows the classification of the target compounds. These ones were classified in ionic and neutral according to the acid dissociation constant, where compounds with a $pK_a > 7$ or not available (n.a) are selected as neutral. Furthermore, compounds were also classified as hydrophilic (HL) when $\log K_{ow} < 2$; and as hydrophobic (HP) when $\log K_{ow}$ greater than 2 (Yangali-Quintanilla et al., 2008)

In order to have a practical understanding of the fate of these target compounds, a cocktail with a concentration of 2 $\mu\text{g/L}$ of each compound was prepared, taking into consideration that these PhACs are used in significant amounts and they had been detected in wastewater and river samples (Yu et al., 2006; Zhou et al., 2009). To achieve this dose, a stock solution A was prepared containing a mass of 0.1 g for each PhACs that was taken. The procedure to obtain Stock Solution A is described below:

First, 20 mL of ethanol was used to dissolve selected PhACs. After weight, each PhAC was transferred into a 100 mL of volumetric flask and filled with ethanol up to 100 mL. By using ethanol, 13 selected PhACs were completely dissolved. It was not possible to make stock solution by using MQ water because of some hydrophobic PhACs with very low solubility.

According to this, the relation for concentration of stock solution would be:

$$\frac{0.1 \text{ g}}{100 \text{ mL}} = \frac{1000 \text{ mg}}{1000 \text{ mL}} = 1 \text{ mg/L} \quad (100 \text{ mL of ethanol was used})$$

By using ethanol an external carbon source is added. However, this amount can be considered negligible due to the several dilutions.

Having a concentration of 1 g/L on Stock Solution A, it was necessary to start making dilutions to reach the final desired concentration of 2 µg/L. From Stock Solution A, another Stock Solution B was prepared by taking 1 mL from the first one and transferred to a volumetric flask of 1 L that was initially partially filled with 40 mL of Milli-Q water. Consequently the flask was filled again with 959 mL of Milli-Q water to reach the total volume of 1 L. The following relation can be applied for obtaining the concentration of Stock Solution B:

$$\frac{1 \text{ mg}}{1000 \text{ mL}} = \frac{1000 \text{ µg}}{1000 \text{ mL}} = 1 \text{ µg/L}$$

All the feed waters for the different experiments were prepared by using brown bottles made of glass to prevent the attachment of selected compounds to the container. From Stock Solution B, 2 mL were transferred for each liter of secondary effluent. The procedure to accomplish the final concentration of 2 µg/L was the same that in case for preparing the previous stock solutions.

***N*-Nitrosodimethylamine (NDMA)**

It is known that NDMA concentration in wastewater after chlorination is about 20-100 ng/L and prior to chlorination determined for secondary effluent shows a concentration range of 20-59 ng/L. The maximum concentration of NDMA found in wastewater secondary effluent was 360 ng/L (Sedlak et al. 2005). By considering the average removal efficiency of NDMA during soil passage (80%), 2 µg/L of NDMA was used for this study. With that, at least 400 ng/L of NDMA would likely to remain in the effluent from soil columns for the post-treatment with nanofiltration. Furthermore, according to WHO (2008) the guideline for NDMA in drinking water is 100 ng/L associated to lifetime cancer risk of 10⁻⁵.

NDMA was purchased from Supelco (USA) contained in a bulb with a mass of 100 mg in a pure liquid form and it was preserved in the refrigerator until the bulb was opened. The entire amount was taken from the bulb and transferred into a volumetric flask of 100 mL that was filled partially with Milli-Q water. After transferring NDMA, the remaining volume was filled with Milli-Q until 100 mL (Stock Solution A). From the previous Stock Solution A, it was necessary to make a dilution to achieve a low NDMA concentration. In this case, a volume of 1 mL from Stock Solution A was transferred into a volumetric flask of 1 L. The same procedure was followed by using Milli-Q water to generate another stock solution namely B with a concentration of 1 mg/L.

Same as in case of PhACs, 2 mL of NDMA was transferred from Stock Solution B for each liter of secondary effluent following identical procedures that were explained before for PhACs.

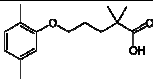
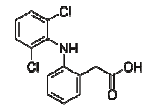
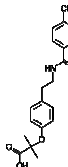
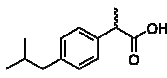
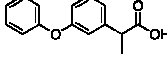
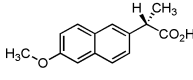
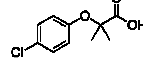
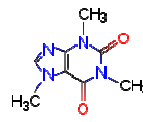
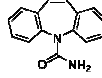
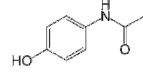
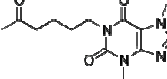
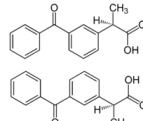
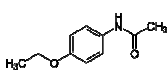
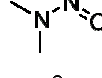

1,4-dioxane

1,4-dioxane has been found in concentrations ranging from <0.1 to $14\text{ }\mu\text{g/L}$ in groundwater and also it has been detected in drinking waters at concentrations up to $0.5\text{ }\mu\text{g/L}$ in The Netherlands (TNO and RIVM, 2002). However, for secondary effluents from an activated sludge treatment system these concentrations can reach values up to $12\text{--}38\text{ mg/L}$ (Zenker et al. 2005). Therefore, a mass of $20\text{ }\mu\text{g}$ of 1,4-dioxane was dosed for each liter of secondary effluent.

1,4-dioxane was purchased from Aldrich and it was contained in a dark bottle stored in a cold room at $4\text{ }^{\circ}\text{C}$ with a concentration of 99.8 g/100 mL . Taking into account that the density of this compound is 1.034 g/mL then the real concentration of 1,4-dioxane would be 103.19 g/100 mL .

Several dilutions were made to achieve a final concentration of $20\text{ }\mu\text{g/L}$. First, Stock Solution (A) was prepared by taking a volume of 1 mL from the initial concentration of 103.19 g/100 mL and transferred to a volumetric flask of 1000 mL that was filled partially with Milli-Q water and later on the remained volume was filled with Milli-Q until 1000 mL . This stock solution presents a concentration of 1031.9 mg/L , therefore, another Stock Solution B was prepared by taking 1 mL from Stock Solution A and transferring into another volumetric flask of 1 L that was also partially filled with Milli-Q water and refilled with Milli-Q until 1000 mL volume. The concentration for this Stock Solution B was $1031.9\text{ }\mu\text{g/L}$. Therefore, to achieve the desired concentration of $20\text{ }\mu\text{g/L}$, 20 mL were transferred from Stock Solution B for each liter of secondary effluent. The final concentration of 1,4-dioxane spiked per liter of secondary effluent was $20.6\text{ }\mu\text{g/L}$.

Table 3.3 Characteristics of selected pharmaceuticals compounds

| Compound | Chemical Formula | Molecular | | Log K_{ow} | Structure | Classification |
|----------------|------------------------|----------------|------|--------------|---|----------------|
| | | Weight (g/mol) | pKa | | | |
| Gemfibrozil | $C_{15}H_{22}O_3$ | 250.34 | 4.70 | 4.77 |  | Hp-ionic |
| Diclofenac | $C_{14}H_{11}Cl_2NO_2$ | 296.16 | 4.15 | 4.51 |  | Hp-ionic |
| Bezafibrate | $C_{19}H_{20}ClNO_4$ | 361.82 | 3.61 | 4.25 |  | HP-ionic |
| Ibuprofen | $C_{13}H_{18}O_2$ | 206.29 | 4.91 | 3.97 |  | HP-ionic |
| Fenoprofen | $C_{15}H_{14}O_3$ | 242.28 | 4.5 | 3.9 |  | HP-ionic |
| Naproxen | $C_{14}H_{14}O_3$ | 230.27 | 4.15 | 3.18 |  | HP-ionic |
| Clofibric acid | $C_{10}H_{11}ClO_3$ | 214.645 | 3.20 | 2.88 |  | HP-ionic |
| Caffeine | $C_8H_{10}N_4O_2$ | 194.19 | 10.4 | -0.07 |  | HL-neutral |
| Carbamazepine | $C_{15}H_{12}N_2O$ | 236.28 | 13.9 | 2.45 |  | HP-neutral |
| Acetaminophen | $C_8H_9NO_2$ | 151.17 | 9.38 | 0.46 |  | HL-neutral |
| Pentoxifylline | $C_{13}H_{18}N_4O_3$ | 278.31 | 6.00 | 0.29 |  | HL - ionic |
| Ketoprofen | $C_{16}H_{14}O_3$ | 254.281 | 5.94 | 0.97 |  | HL-ionic |
| Phenacetine | $C_{10}H_{13}NO_2$ | 179.2182 | 2.2 | 1.94 |  | HL-ionic |
| NDMA | $C_2H_6N_2O$ | 74.08 | 9.3 | -0.57 |  | HL-neutral |
| 1,4-dioxane | $C_4H_8O_2$ | 88.10 | | -0.27 |  | HL |

Sources: Abel (2009); Andrzejewsk et al. (2004); XU et al. (2009); Zenker et al.(2005)

3.2 Experimental set-ups

3.2.1 Soil column set-ups

As stated earlier, two laboratory scale soil columns were used to simulate SAT performance. Constructed using uPVC pipes, both sets have an internal diameter of 57 mm and a total length of 5.0 m (2.5 m each, connected in series). There were a total of 12 sampling points at the spacing of 0.25-0.5 m along the depth of the column as is shown in Figure 3.3. To maintain a static head, a volumetric displacement pumps were used for pumping secondary effluent from glass bottles when the selected compounds were dosed to the secondary effluent into the reactor bottles.

In addition, silica sand with grain size from 0.8 mm to 1.25 mm was used as filter media, a graded gravel of 20 cm thick was used as a support layer at the bottom of the column.

During all the experiments, the secondary effluent from the wastewater treatment plant that was stored in the cold room was let to reach room temperature before feeding the soil columns.

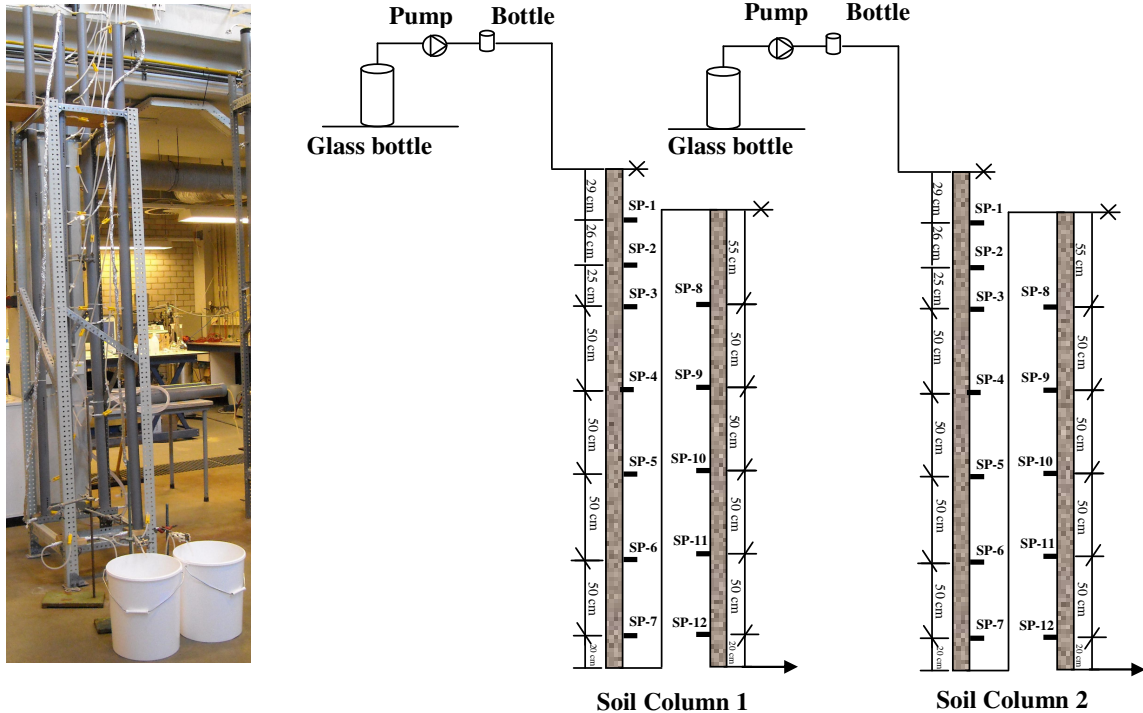


Figure 3.3 Photograph and schematic representation of soil column experimental set-up

3.2.2 Ozonation set-up

Ozone is effective as a strong oxidant for removing majority of trace organic contaminants from water. With the objective of analyzing the impact of ozone in the biodegradability and degradation of the target compounds before SAT process, ozonation of secondary effluent spiked with thirteen PhACs, NDMA and 1,4-dioxane was conducted in the laboratory. The ozonation set-up consisted of four main parts: Ozone generator (Trailigaz Ozonizer, LABO LO Type), flow board, ozone detection alarm and ozone destruction (Figure 3.4 and Figure 3.5).

Ozone was produced and applied to sample contained in an eight liters reactor by using bubble diffuser. A magnetic stirrer was used to enhance the contact between the sample and ozone, allowing the bubbles to disperse in the aqueous phase more efficiently. A ratio of DOC: O₃ of 1mg:1mg was used during this study.

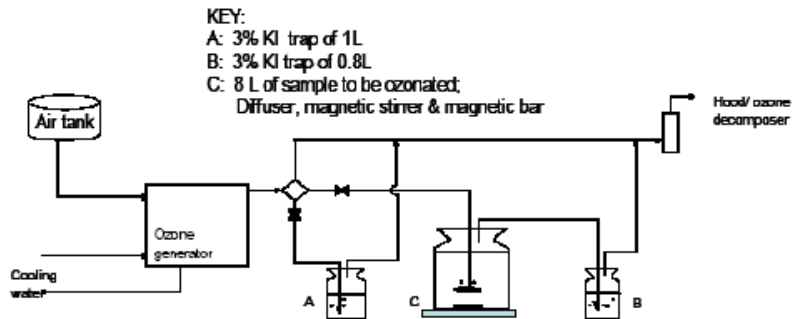


Figure 3.4 Schematic diagram of the ozone generator set-up
Source: Musabe (2007)

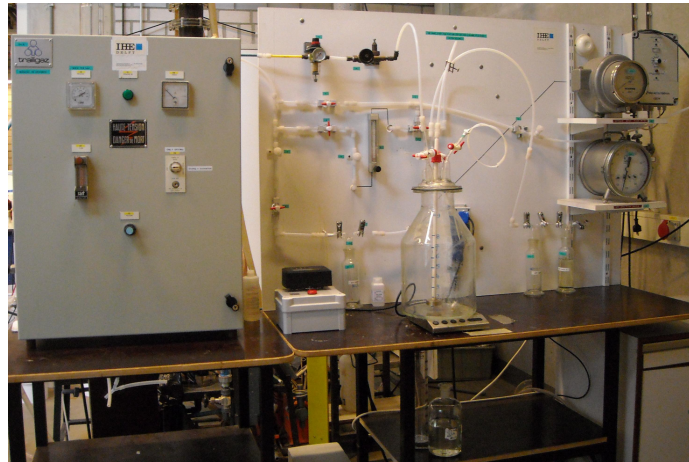


Figure 3.5 Photograph of the ozone generator set-up

3.2.3 Nanofiltration set-up

Nanofiltration experimental set-up is shown on

Figure 3.6 and consists on several parts that are described as follows:

1. Membrane cell and a cell holder
2. Stainless steel tank with a volume of 50 L,
3. A hydraulic pump
4. A variable speed pump,
5. A frequency driver, control needle valves, pressure gauges, flow meters and stainless steel tubing.
6. A digital balance that is connected to the computer to record the permeate weight by using WinWedge software.

The membrane cell has a channel space with dimensions of 14.6 x 9.5 x 0.86 cm, with an effective surface area of 139 cm² and it is made from steel. Also, plastic spacers were used to separate the membrane and the cell walls. The feed flow rate, corresponding cross-flow velocity, and the trans-membrane pressure was regulated either by varying the pump speed, controlling the needle valves in the concentrate stream, or controlling the pressure relief valve on bypass stream. The system flow configuration only had one mode of circulation: One pass: In this case, feed applied to the membrane, concentrate and permeate were collected separately.

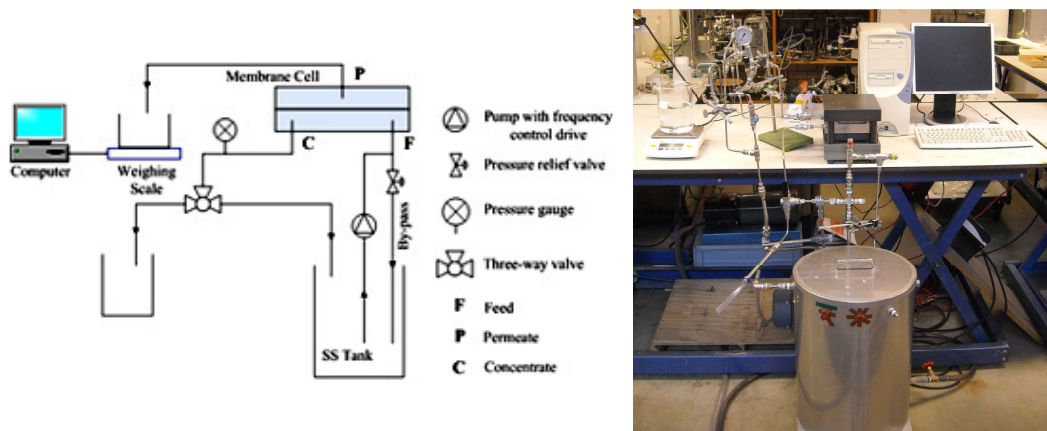


Figure 3.6 Schematic representation and photograph of the NF set-up
 Source of schematic diagram: Fernando (2008)

3.3 Experimental procedures

3.3.1 Soil columns experimental procedures

The two set of columns were ripened or acclimated using the following procedure:

1. First, the secondary effluent collected from the WWTP and stored at 4 °C was allowed to reach room temperature before feeding the columns.
2. The hydraulic loading rate of 1.25 +/- 0.5 m/day was adjusted in each column by manipulating the control device (valve) in the effluent side and flow measurements were taken using a glass cylinder and stop watch to obtain the desired flow rate.
3. Influent and effluent samples were collected from both columns to obtain the dissolved organic carbon (DOC) levels and this process was continued until a steady state removal rate of DOC was reached. This state was taken as an indicator that the bio-film had fully developed on the soil columns.

Once steady state conditions were reached, some water quality parameters namely DO, pH, EC and temperature, were measured at all sampling points to obtain the profile along the soil column depth.

The first experiments started by adding secondary effluent with the cocktail of thirteen PhACs, NDMA and 1,4-dioxane to one set of column (SC1). A hydraulic loading rate of 1.25 m/day was maintained during the experiment using the same procedure explained before. The system was continuously fed with this type of water that was stored in glass bottles and after fourteen days samples were taken in the effluent. In addition, DO, pH, EC and temperatures were also measured in all sampling points. During this period, water samples were also collected from the influent and effluent in the column to measure DOC levels.

The second set of columns (SC2) was fed with pre-ozonated secondary effluent containing the thirteen selected PhACs (NDMA and 1,4-dioxane were excluded) with ozone to DOC ratio of 1mg O₃/mg DOC. Same conditions were maintained for this set of column: a hydraulic loading rate of 1.25 m/day and samples were also collected after fourteen days of feeding. Furthermore, water quality parameters such as DO, pH, EC and temperatures were measured at all sampling points and DOC levels were monitored from influent and effluent in the soil column.

3.3.2 Ozonation experimental procedures

The start-up procedure was followed according to the manual for ozonation set-up:

1. Precautions were taken to not exceed the pressure of 8 bar in the air supply and wash bottles were connected correctly. Special attention was paid to avoid any leakage in the system from joints in the flow lines by using the ozone detector.
2. During the 30 minutes for conditioning, the wash bottles were filled with a solution 200 mL of potassium iodide with the objective of determining the strength of ozone.

3. Later on, the magnetic stirrer was switched on at 400 rpm and power supply up to 7 ampere. All the valves were checked to confirm that they were in the right position and before the experiment start the volumes of gas meters (bypass and off gas) were registered.
4. Ozone was applied to eight liters of secondary effluent spiked with the target compounds through a bubble diffuser during 35 minutes controlled by a stopwatch.
5. At the end of this period, the ozone generation was stopped and the readings from the by-pass and off-gas flow meters were taken.
6. Again, the bypass line was open for 15 minutes to blow off the ozone that was trapped in the sampling bottle and wash bottles were changed for titration.
7. The solutions of potassium iodide trapped in both bottles were transferred into a 250 mL volumetric flask and 2.5 mL of H_2SO_4 was added to each one.
8. Thereafter, 50 mL were transferred into an Erlenmeyer flask to determine the mass of ozone captured in the respective wash bottles by titrating with 0.025 N $\text{Na}_2\text{S}_2\text{O}_3$ until all reddish-orange color disappeared. Subsequently, the mass of ozone used in the experiment was calculated with the help of an excel sheet presented in appendix C. The experiment was repeated until a ratio of 1:1 for DOC and Ozone was reached.

3.3.3 Nanofiltration experimental procedure

The experiments using NF-90 membrane involved the following types of feed water:

- 1) **SE + PhACs + NDMA + 1,4-dioxane**
- 2) **SE + PhACs NDMA + 1,4-dioxane and SAT as a pre-treatment**
- 3) **SE+ PhACs + Ozone and SAT as pre-treatments**

Conducted with feed pressure, pf of 50 psi (3.6 bar), recovery, r of 3 %, Flux from 15-20 $\text{L/m}^2\text{h}$, Flux decline from 20-30 %, room temperature of 20 °C and without recirculation, all the experiments followed the following procedure:

1. First, the feed tank was filled with 40 L of demineralised water and after switching the pump on, the feed pressure was gradually increased to 50 psi (3.6 bar).
2. After approximately two hours running the system with demineralised water with the objective of cleaning the membrane and checking that the flux became stable, the feed tank was quickly draining by opening the drain valve.
3. The Flux was calculated by using the following expression and knowing that the elemental area is 139 cm^2

$$\text{Flux} = \frac{Q_p}{A} \quad [\text{L/m}^2.\text{h}]$$

4. Consequently, the feed tank was filled with 40 L of the selected type of water sample.
5. The feed pressure was maintained to 50 psi (3.6 bar) by adjusting the pressure relief valve on the bypass line and the valve on the concentrate flow line.
6. The filtration was done for six hours under the specified conditions and permeate obtained it was collect in a glass vessel located on a weighing scale connected to the computer. During this period the weight of permeate was recorded automatically every 30 seconds and also the permeate flow rate, Q_p (in mL/min) through a computer using the WinWedge software.

7. The concentrate flow rate (Q_c) was measured using glass cylinder and stop watch.
8. Having then the concentrate flow rate (Q_c) and the permeate flow rate (Q_p), it was possible to obtain the recovery value, r (%):

$$r(\%) = \frac{Q_p}{Q_p + Q_c}$$

When the recovery was not the selected value of 3%, the concentrate flow rate was adjusted by manipulating the valve on the concentrate line and the pressure relief valve on the bypass flow line.

9. Samples were collected from the permeate stream for the analysis of the different compounds (PhACs, NDMA and 1,4-dioxane).

3.4 Analytical Methods

3.4.1 Temperature, Electrical Conductivity (EC), pH and dissolved oxygen (DO)

The temperature and the electrical conductivity (EC) were measured by a WTW cond 330i portable conductivity meter fitted with WTW Tetracon 325 electrode. The electrode was submerged in the water sample, gently stirred and measurements were taken when the reading became stable. The pH measurements were taken by a calibrated Metrohm 691 pH-meter fitted with a WTW SenTix 61 pH electrode. The temperature in the pH meter was set according to the sample temperature. By using a WTW Oxi 340 portable DO, dissolved oxygen (DO) concentrations were measured in all the sampling points. To obtain accurate dissolved oxygen values from the columns, the electrode was introduced into a plastic syringe that was properly covered to avoid air intrusion. All the electrodes were rinsed with demineralised water after every measurement to avoid any pollution from the previous sample (Figure 3.7).



Figure 3.7 Portable pH, EC and DO meters

3.4.2 Dissolved and Total organic carbon (DOC/TOC)

For the total organic carbon (TOC) and dissolved organic carbon (DOC) measurements, a total organic carbon analyzer TOC-VCNP, PC controlled, standard model (from Shimadzu Corporation, Japan) was used (Figure 3.8).

In case of DOC measurements, all the samples were filtered with cellulose acetate filters of 0.45 μm pore size. To avoid that filters contribute to increase DOC values by leaching during the filtration, all the filters were soaked in Milli-Q water during 24 hours and the water was changed three times in this period prior to usage. The samples were arranged in the machine in such a way that the first sample would contain a DOC concentration lower than the next one (from effluent to influent). The objective was to minimize contamination from the previous sample.



Figure 3.8 TOC-VCPN (Shimadzu) total organic carbon analyzer

3.4.3 UV_{254} nm/SUVA

Samples were previously filtered with 0.45 μm cellulose acetate filter before using a Perkin Elmer (Lambda 20 1.11) spectrophotometer to measure UV absorbance at a wavelength of 254 nm (Figure 3.9). Demi-water was used as a blank and the two transparent quartz cuvettes 1 cm wide were rinsed with demi-water before these ones were filled with the samples and later on cleaned with soft laboratory tissue paper to avoid any interference in the measurements.



Figure 3.9 Perkin Elmer (Lambda 20 1.11) spectrophotometer

Specific Ultraviolet Absorption (SUVA) at 254 nm gives an idea about the type of natural organic matter contained in the samples. According to the expression below,

SUVA expressed in L/mg.m can be determined by dividing the sample's UV absorbance at 254 nm by its concentration of dissolved organic carbon in mg/L.

$$SUVA = \frac{UV_{254} \cdot 100}{DOC}$$

3.4.4 Fluorescence Excitation Emission Matrix (F-EEM)

Strict compliance of the procedure was followed for measuring the fluorescence excitation-emission matrix (F-EEM) spectra for different samples by using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer with xenon lamp as the excitation source, with the objective of obtaining information about the chemical nature of NOM (Figure 3.10).

All the samples were first allowed to reach room temperature before measurements and later on filtered with 0.45 µm cellulose acetate filter. In this case, Milli-Q water was used as a blank and samples with high concentration of DOC were diluted to approximately 1.0 mg/L of DOC with Milli-Q water.

Result of each sample was plotted using MATLAB software for categorizing dissolved organic carbon fractions into protein-like, humic-like and fulvic-like (Abel, 2009).



Figure 3.10 Horiba Jobin Yvon FluoroMax-3 spectrofluorometer

4 RESULTS AND DISCUSSION

This chapter presents the results obtained during laboratory experimental part of this research. It is divided in two parts, the first one deals with the use of soil columns set-up, whilst the second one with the impact of different pre-treatments for organic micropollutants removal during NF.

4.1 Wastewater characterization

Secondary effluent collected from the WWTP Hoek van Holland and used during the experiments was characterized by analyzing several water parameters. The results presented in table 4.1 shows typical values for domestic wastewater effluent.

Table 4.1 Average quality parameters of secondary effluent used

| Parameter | Unit | Value |
|-------------------------------|--------|-------|
| Temperature | °C | 12.2 |
| DO | mg/L | 4.1 |
| pH | - | 7.1 |
| EC | µS/cm | 930 |
| TOC | mg/L | 12.2 |
| DOC | mg/L | 10.9 |
| UV ₂₅₄ | Ab/cm | 0.342 |
| SUVA | L/mg-m | 3.175 |
| Cl ⁻ | mg/L | 159.2 |
| NO ₃ ⁻ | mg/L | 1.9 |
| PO ₄ ³⁻ | mg/L | 2.5 |
| SO ₄ ²⁻ | mg/L | 70.9 |

Some parameters were measured in situ such as temperature, dissolved oxygen (DO), pH and electrical conductivity (EC). Even though water temperature was representative for a cold month, the wastewater was allowed to reach room temperature (approximately 20 °C) before application to soil columns. The pH was found in the range suitable for discharge (typically between 6 and 9) and showed less fluctuation than the electrical conductivity with values ranging from 658 up to 1267 µS/cm that were attributed to the weather conditions. SUVA values between 2-4 L/mg-m show that there is a mixture of aquatic humics and other hydrophobic and hydrophilic NOM. The rest of the parameters were consistent with the results presented in previous studies (Abel, 2009; Sheriff, 2009; Fernando, 2009).

The presences of target compounds in secondary effluent were also analyzed during this study as a background check (Figure 4.1). It was observed that some trace organic micropollutants concentrations were present at the range of nanograms per litre (ng/L). Such is the case of NDMA with a value of 5.3 ng/L been considered in the range 5–20 ng/L for sewage treatment plants effluents (Krauss et al., 2009). The formation of NDMA prior chlorination may be possible as results of chemical and biological transformations of alkylamines in the presence of nitrate or nitrite. Studies have also demonstrated that activated sludge treatment can accumulate NDMA due to the increment of the sludge age when processes such as nitrification and denitrification are applied (WHO, 2008).

Analgesics (diclofenac and naproxen) were found in medium concentration range of 160-810 ng/L reported on previous study by Abel (2009). However, acetaminophen and ibuprofen concentrations were much lower than expected for this type of water (50 and 120 ng/L respectively).

Lipid regulators (bezafibrate, clorifibric acid and pentoxifylline) with concentrations less than < 50 ng/L are comparatively far from the values reported in the literature (400-2200 ng/L). On the other hand, the lipid regulator gemfibrozil showed a concentration of 820 ng/L been in agreement with the mentioned range.

The occurrence of 1,4-dioxane is cause of concern due to its miscibility and carcinogenicity and its presence can be linked from commonly used shampoos and detergents in households. The concentration value of 500 ng/L found for 1,4-dioxane in secondary effluent is consistent with the findings of Abe (1999) after analysing domestic effluents where concentrations at 1 µg/L were consistent.

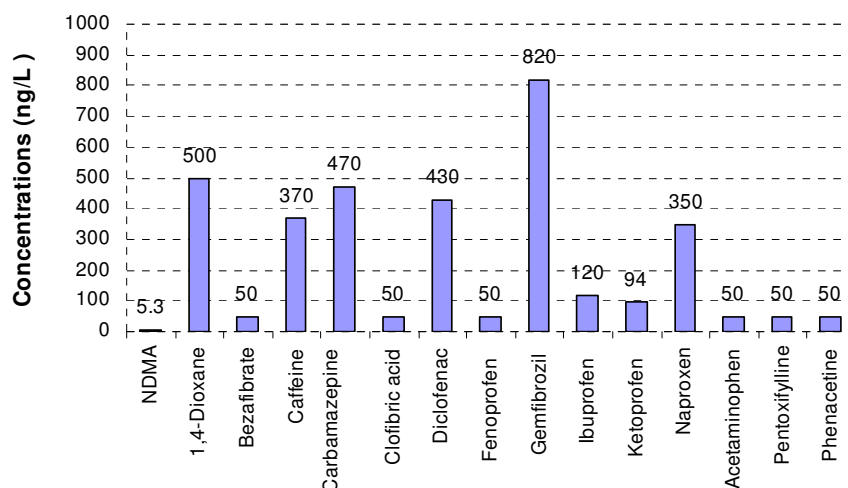


Figure 4.1 Initial concentrations (background) of target compounds found in secondary effluent from the wastewater treatment plant Hoek van Holland

4.2 Soil aquifer treatment for organic micropollutants removal

4.2.1 Ripening of soil columns

Experiments started with the ripening of two soil columns by continuous dosing of secondary effluent at 1.25 m/day, until steady state conditions were achieved with respect to DOC removal. This was an indicator that the biomass was fully developed and the silica sand employed in this research was acclimatized. After 65 days of operation, it was possible to conclude that this state was reached by correlating that the DOC removal along the columns for a certain period of time did not experience significant variations (Figure 4.2). This was also demonstrated previous researchers at UNESCO-IHE that steady state conditions were reached after 50-65 days of ripening period (Abel, 2009; Fernando, 2009).

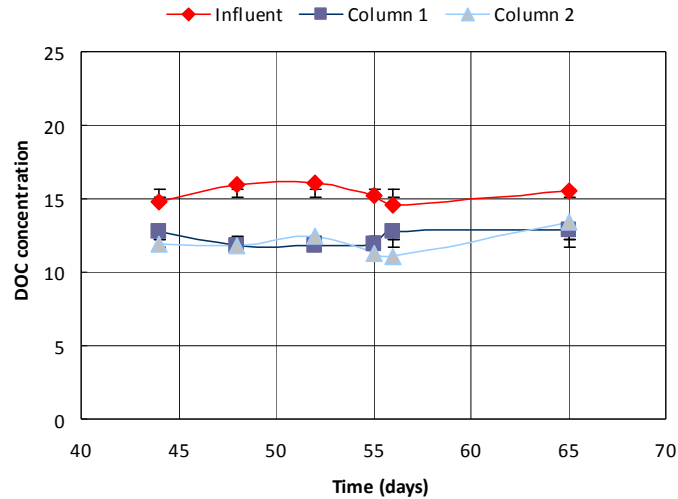


Figure 4.2 Influent and effluent DOC concentrations during ripening period for soil columns

During the course of the study; it was observed that influent DOC ranged from 14.21 to 16.11 mg/L. Meanwhile, effluent DOC ranged in SC1 from 11.54 to 12.96 mg/L and for SC2 from 10.85 to 13.69 mg/L. The variations on DOC for influent have been attributed to introduction of new wastewater that was collected from the WWTP having in some cases lower or higher DOC values and was consequently reflected in the removal efficiencies. Nevertheless, after 48 days DOC removal became more or less stable at the average of 20 % and 22 % for SC1 and SC2 respectively. These percentage removals are in concordance with the values found by Maeng et al. (2008) during their studies with similar set-ups. The results are presented in appendix A and graphically in Figure 4.3.

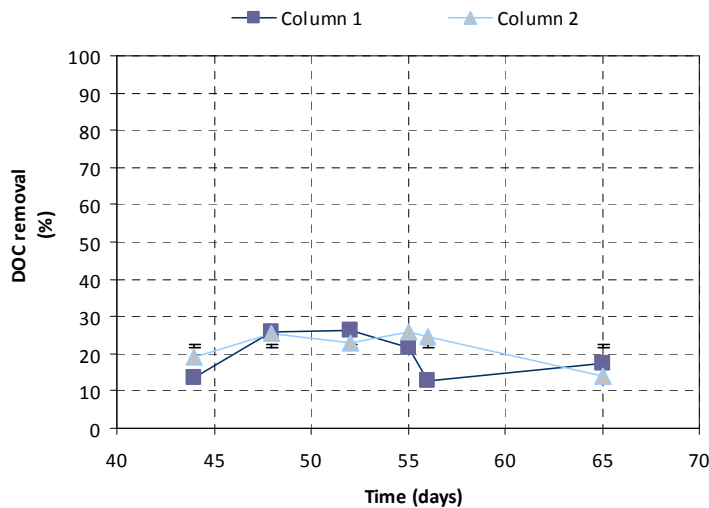


Figure 4.3 DOC removal in SC1 and SC2 using SE alone during ripening period (HLR: 1.25 m/day)

Furthermore, for a comprehensive analysis of performance of the soil columns, DO, DOC and pH values were measured after the ripening period by taking samples along the depth on both columns. Detailed results of DOC, pH, EC and DO profile measurements for SC1 and SC2 are presented in appendix B. Similar removals of DOC were observed on both columns ranging from 13.80 mg/L to 11.36 mg/L (17.7%) in

SC1 and from 13.61mg/L to 11.22 mg/L (17.6%) in SC2. DOC removals were linked to decreased concentration of dissolved oxygen in the first meter of columns depths suggesting that oxygen was used to reduce organic matter through biological process. Even though, dissolved oxygen was consumed from 3.7 mg/L to 1.3 mg/L, both columns were operating under aerobic conditions. Slight reduction of pH was also observed during the measurements, with the pH ranging from 7.8 to 7.6. Soil column 2 (SC2) showed similar behavior as SC1. This can be seen in appendix A and Figure 4.4.

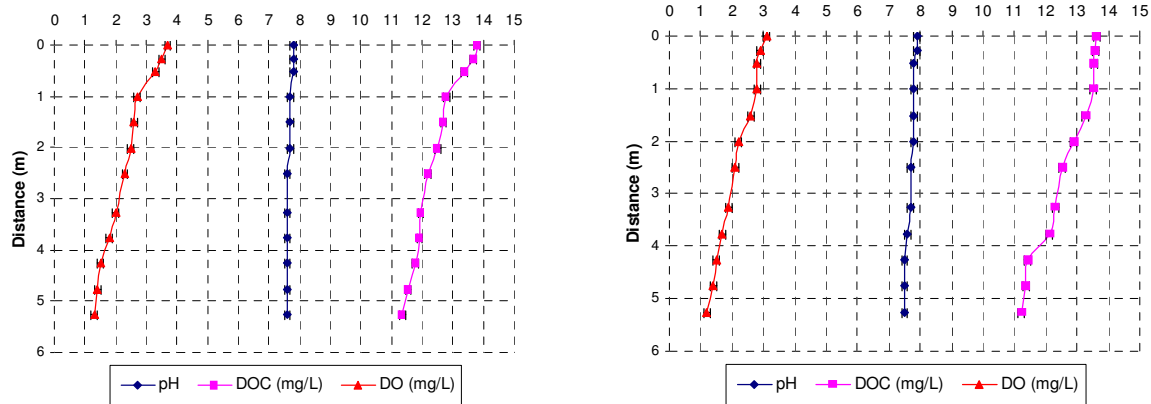


Figure 4.4 pH, DOC and DO profiles of SC1 and SC2 (left to right respectively) after ripening period using secondary effluent at a HLR: 1.25m/day

Tracer tests for soil columns

In order to have an idea on how the selected compounds that were dissolved in secondary effluent migrates through the soil columns, sodium chloride (inert substance) was applied as a conservative tracer to describe the movement on both soil columns by measuring the retardation factor which measures the transport velocity of a reactive solute relative to the fluid that carries it (Feng et al., 2004). Retardation factor can be calculated by using breakthrough curves (BTCs) as is shown in figure 4.5 and figure 4.6 for soil column 1 (SC1) and soil column 2 (SC2) respectively.

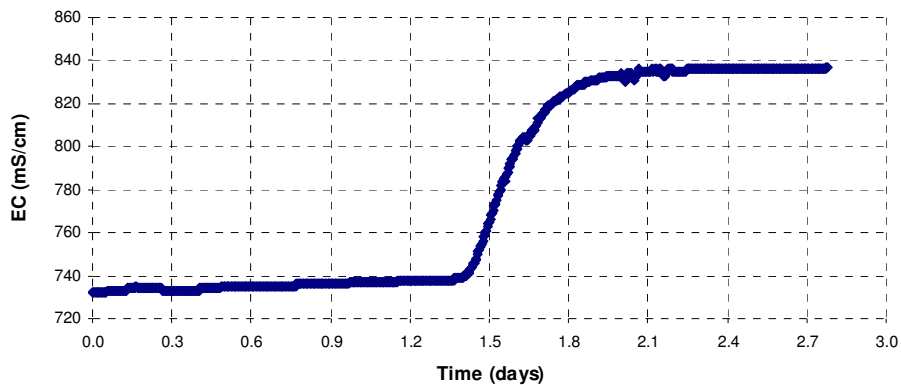


Figure 4.5 Breakthrough curve of sodium chloride with silica sand which shows retardation factor of 1.5 in SC1

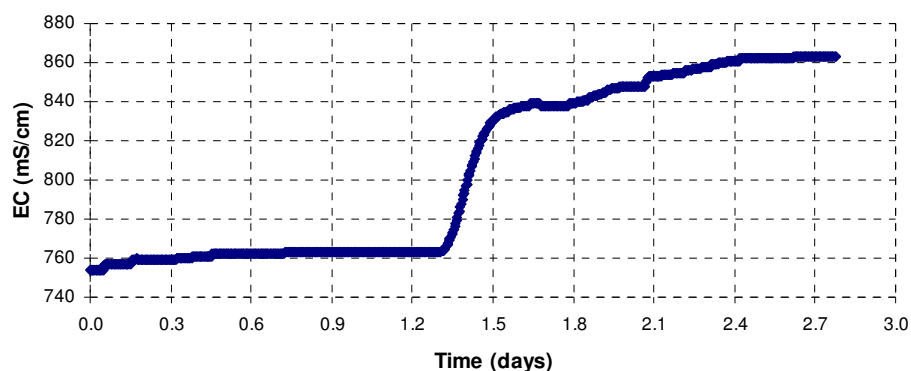


Figure 4.6 Breakthrough curve of sodium chloride with silica sand which shows retardation factor of 1.4 in SC2

The secondary effluent with an initial electrical conductivity of 745 $\mu\text{S}/\text{cm}$ was spiked with sodium chloride until the electrical conductivity reached 845 $\mu\text{S}/\text{cm}$ taking into consideration the range of EC in wastewater.

The breakthrough curves reflect that sodium chloride was similarly retarded on both soil columns (retardation factors of about 1.5 for SC1 and 1.4 for SC2). Nevertheless, it was expected that retardation factor of about 1 as NaCl travels at about the same rate as water. However, because the retardation factor is strongly dependent of different factors such as temperature, organic content, pH, among others; a retardation factor of 1.5 can be considered reasonable for NaCl under the mentioned conditions.

4.2.2 Removal of bulk organic matter from secondary effluent spiked with target compounds

The experiments performed of soil column (SC1) allowed to assess the fate of bulk organic matter from secondary effluent. After steady state conditions were achieved with respect to DOC, samples were taken from sampling point 1 for DOC measurements (influent to the column 1) and after 4 days (according to the adjusted HLR) another sample was taken from effluent to check DOC removals (table 4.2). During this period it was observed that DOC removals ranged from 15-27 %.

Table 4.2 DOC removals after ripening period of soil column (SC1)

| Days | Influent (mg/L) | Effluent (mg/L) | Removal (%) |
|------|--------------------|--------------------|----------------|
| 1 | 9.2 | 6.8 | 26 |
| 5 | 9.2 | 6.9 | 25 |
| 9 | 8.8 | 6.7 | 24 |
| 12 | 8.9 | 7.6 | 15 |
| 26 | 8.1 | 6.9 | 15 |
| 29 | 9.0 | 7.3 | 19 |

UVA₂₅₄, SUVA and DOC results were used as representative bulk EfOM parameters. The decrease in UVA₂₅₄ (ranging from 0.357 to 0.337 /cm) in SC1 indicates a preferential removal of non-humic substances over the slowly biodegradable humic substances. Furthermore, aerobic degradation seemed to be the main responsible for the increased SUVA values from 3.402 up to 3.974 L/mg-m along the SC1 depth due to its preferential reduction of non-aromatic (aliphatic) compounds or formation of aromatic products from the removal of readily biodegradable matter (Figure 4.7). This proved the capacity of SAT for removing bulk organic matter present in the secondary effluent that can serve as precursors for disinfection by-products (DBPs) when the extracted water is chlorinated upon recovery (Abel, 2009; Amy & Drewes, 2007; Xue et al., 2009).

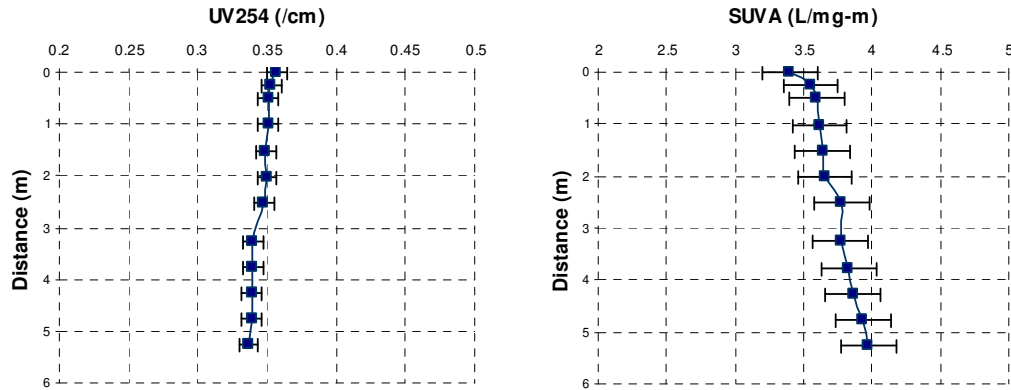


Figure 4.7 UV₂₅₄ and SUVA along the depth of SC1 fed with SE (HLR: 1.25 m/day)

Removal of DOC (more than 75% of the total removal) was observed in the first two meters of the column. In addition, a decreasing in DO concentration accompanied the DOC reductions along the depth of the column (Figure 4.8). This implies that DO was utilized by microbial population (biomass) to transform (degrade) DOC. The results derived from this analysis showed that physico-chemical and biological processes took place in the Schemutzdecke layer of the soil column (SC1). Furthermore, aerobic degradation or sorption could also contribute to the lower DOC concentrations along the soil column depth (Xue et al., 2009).

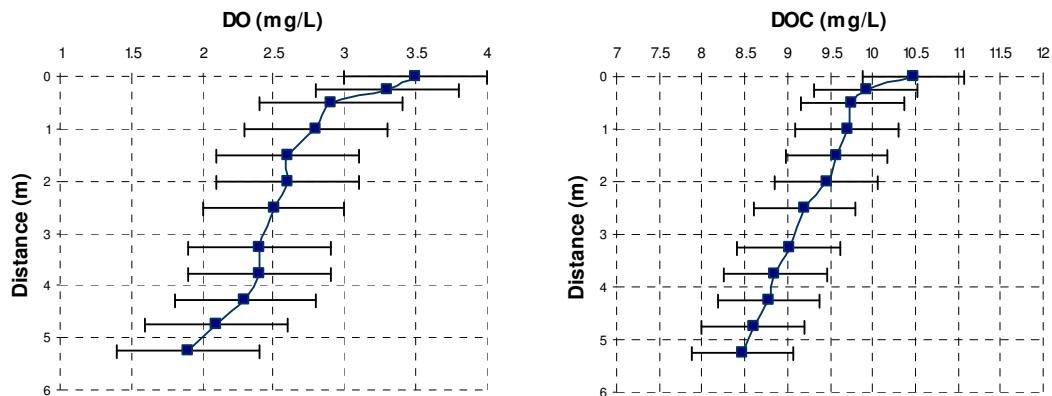


Figure 4.8 DO and DO along the depth of SC1 fed with SE (HLR: 1.25 m/day)

Furthermore, pH and EC were measured as additional information for a better understanding of the bulk organic matter and organic micropollutants removal on SC1 (Figure 4.9). It was found that on average pH decreased along the soil column depth from 8.1 to 7.5. The reason might be due to the development of the biofilm on the surface of the filter media (Sheriff, 2009). Sheriff (2009) explained that this biofilm participates in the degradation of organic matter and as a consequence there is a formation of carboxylic acid which causes a detriment in pH. Electrical conductivity also exhibited slight reductions from 1267 to 1242 $\mu\text{S}/\text{cm}$ in SC1.

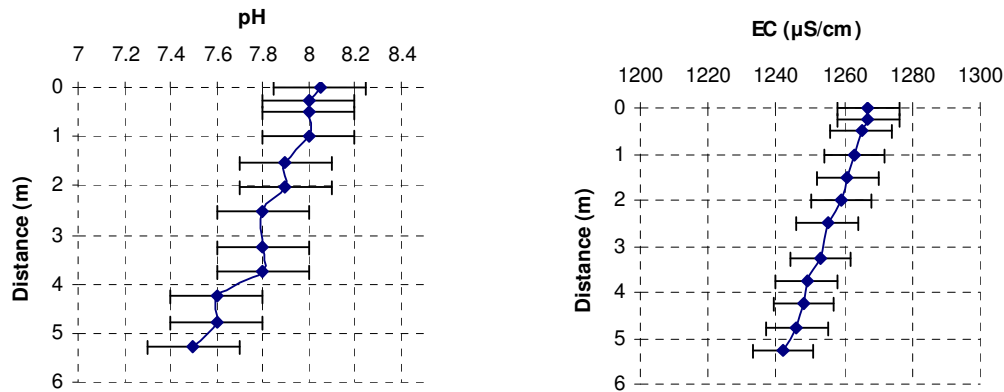


Figure 4.9 pH and EC along the depth of SC1 fed with SE (HLR: 1.25 m/day)

Fluorescence EEM spectra from SC1

F-EEM spectrum measurements were conducted for influent and effluent of both soil column samples according to the sampling program. It is well known that fluorescence intensity peaks have been associated with humic-like, protein-like and soluble microbial by-product-like (SMP-like) organic compounds. Table 4.3 presents the characteristics of organic matter analysed by F-EEM spectra. In general, higher values of excitation and emission wavelengths (Ex/Em 240–260 nm/380–480 nm as well as of Ex/Em 320–350 nm/400–480 nm) are associated to humic-like organic matter and fluorescence intensity peaks at lower values of excitation and emission wavelengths (<250 nm and <350 nm respectively) are related to protein-like organic matter. SMP-like are linked to peaks in the range of Ex/Em 250–280 nm/320–360 nm (Maeng et al., 2008; Chefetz et al., 2008).

Table 4.3 Characteristics of organic matter by F-EEM spectra

| Region | Excitation (nm) | Emission (nm) | Description |
|----------|-----------------|---------------|--------------------|
| Region 1 | 240–260 | 380–480 | Humic-like peaks |
| Region 2 | 320–350 | 400–480 | Humic-like peaks |
| Region 3 | 250–280 | 320–360 | SMP-like peaks |
| Region 4 | <250 | <350 | Protein-like peaks |

Source: Maeng et al., 2008; Chefetz et al., 2008

Figures 4.10 and 4.11 show F-EEM spectra for influent (11 and 30 days) and effluent (14 and 33 days) respectively at a hydraulic loading rate of 1.25 m/day. Table 4.4 and table 4.5 presents a comparison between influent and effluent samples. Samples showed protein-like peak that usually appears at lower values of excitation and emission wavelengths with reductions for influent and effluent ranging from 65-78%. Humic-like substances dominated influent and effluent samples. Nevertheless, changes in the fluorescence intensity between them were observed due to the reduction of humic-like

compounds (vary from 43 – 61%) but not in locations peaks for influent and effluent samples (Maeng et al., 2004).

Table 4.4 Comparison of F-EEM results between influent (11 days) and effluent (14 days) using SE in SC1

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|--------------------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Influent (11 days) | 436 | 250 | 7.54 | 45 |
| | Effluent (14 days) | 438 | 250 | 4.18 | |
| Humic-like 2 | Influent (11 days) | 438 | 340 | 7.44 | 61 |
| | Effluent (14 days) | 428 | 330 | 2.94 | |
| Protein-like | Influent (11 days) | 308 | 270 | 1.88 | 78 |
| | Effluent (14 days) | 320 | 270 | 0.41 | |

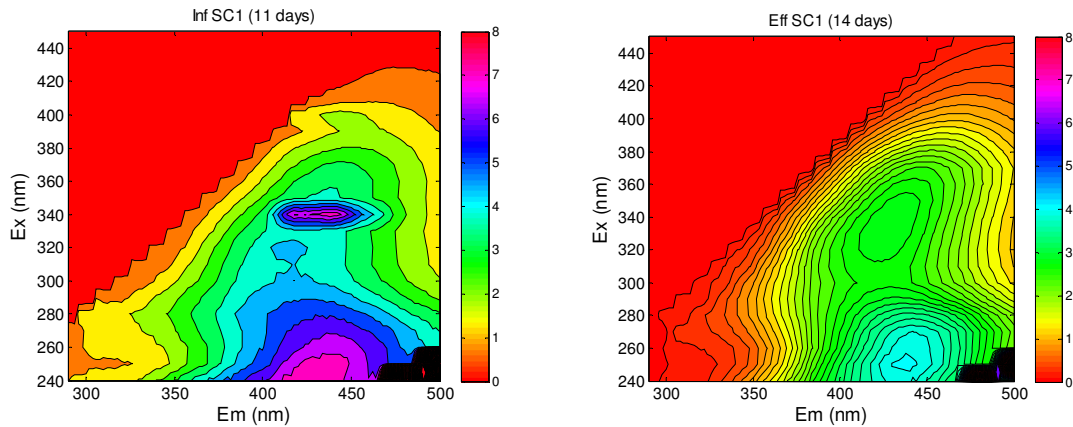


Figure 4.10 F-EEM spectra for SC1 after 11 days fed with SE

Table 4.5 Comparison of F-EEM results between influent (30 days) and effluent (33 days) using SE in SC1

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|--------------------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Influent (30 days) | 436 | 250 | 8.39 | 46 |
| | Effluent (33 days) | 438 | 250 | 4.54 | |
| Humic-like 2 | Influent (30 days) | 424 | 330 | 5.94 | 43 |
| | Effluent (33 days) | 428 | 330 | 3.41 | |
| Protein-like | Influent (30 days) | 320 | 270 | 1.09 | 65 |
| | Effluent (33 days) | 316 | 270 | 0.38 | |

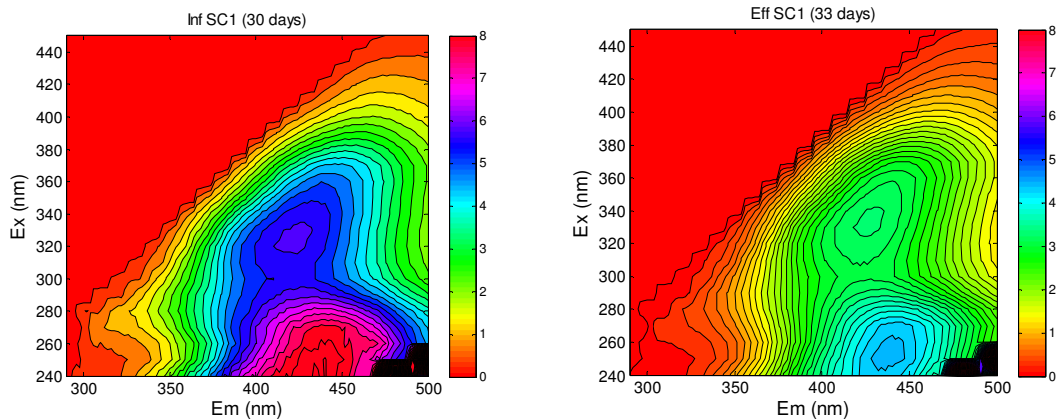


Figure 4.11 F-EEM spectra for SC1 after 30 days fed with SE

4.2.3 Removal of selected PhACs, NDMA and 1,4-dioxane from secondary effluent

Fate of thirteen PhACs, NDMA and 1,4-dioxane was studied in soil columns set-ups. Solution with concentrations of 20 µg/L for 1,4-dioxane, 2 µg/L for each pharmaceuticals and also for NDMA were prepared in glass bottles of 1000 mL volume using secondary effluent as feed water. Samples were collected in the selected sampling points based on previous discussion (Fig 4.12).

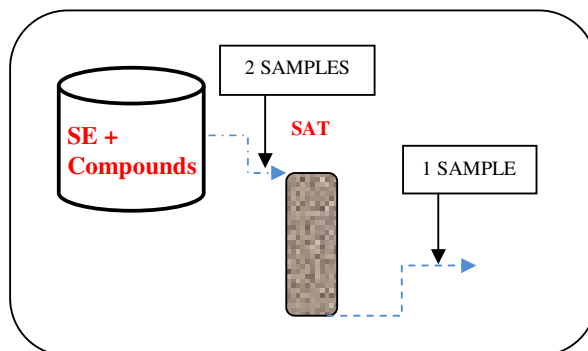


Figure 4.12 Number of samples and sampling points for soil column studies

The first influent's sample was collected on day 11 and four days later the sample from effluent according to the hydraulic loading rate of 1.25 m/day. A second sampling program was performed after 30 days and 33 days for influent and effluent respectively in the same sampling points. The percentages removals obtained for different trace organic compounds are presented on figure 4.13 and the results in table 4.6. The time lag period for collecting the first sample was decided taking into account an acclimatization of the biomass to the new conditions related to the introduction of the mentioned compounds.

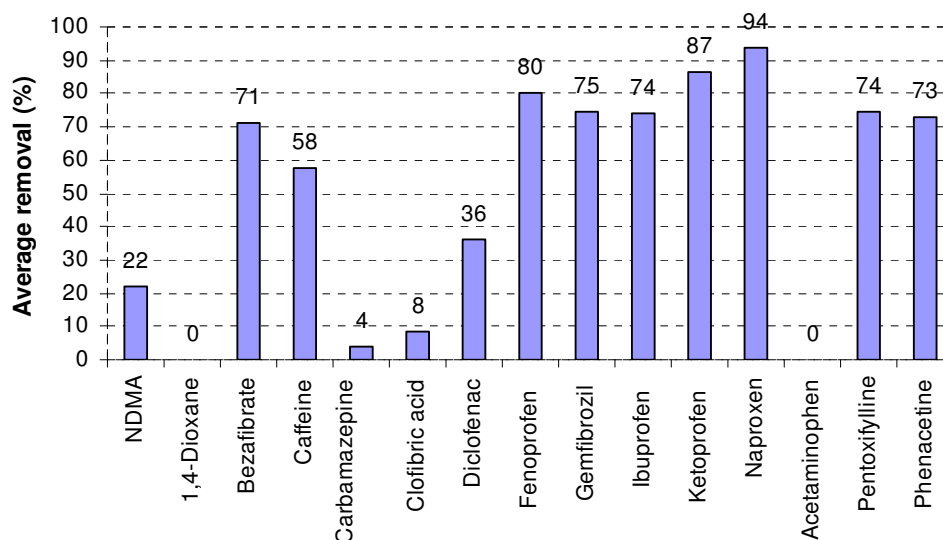
The SC1 exhibited high removals for most of the target compounds (> 70 %). This can be linked to sorption onto soil particles or transformation easily through biodegradation mechanisms leading to the conclusion that soil passage is an effective barrier for many of these organic micropollutants.

However, hydrophobic (with log Kow > 2) compounds such as clofibric acid and diclofenac were removed less in the soil column (8,4% and 36% respectively). This could be attributed to sorption behavior and consequently the mobility of organic acid (clorifibric acid) which is pH dependent. Organic acids usually have the tendency of sorb onto organic matter due to their presence at pH conditions below the pKa-value. However, the mobility of this compound at higher pH significantly increases and this result is in good agreement with the findings reported by Oppel et al. (2004) in which clofibric acid movement during soil columns and riverbank filtration can be reflected as almost a tracer due to its persistent behavior.

Table 4.6 Concentrations of target compounds before and after SC1

| Compound | Unit | Influent Sample 1 | Effluent Sample 1 | Removal (%) | Influent Sample 2 | Effluent Sample 2 | Removal (%) | Average removal (%) |
|----------------|------|-------------------|-------------------|-------------|-------------------|-------------------|-------------|---------------------|
| NDMA | µg/L | 1.3 | 0.99 | 23.8 | 1.2 | 0.95 | 20.8 | 22 |
| 1,4-Dioxane | µg/L | 17 | 17 | 0 | 17 | 17 | 0.0 | 0 |
| Bezafibrate | µg/L | 0.95 | 0.21 | 77.9 | 0.73 | 0.26 | 64.4 | 71 |
| Caffeine | µg/L | 0.43 | < 0.13 | 69.8 | 0.24 | 0.13 | 45.8 | 58 |
| Carbamazepine | µg/L | 2.0 | 2.2 | 0.0 | 2.4 | 2.2 | 8.3 | 4 |
| Clofibric acid | µg/L | 1.3 | 1.2 | 7.7 | 1.1 | 1.0 | 9.1 | 8 |
| Diclofenac | µg/L | 1.8 | 1.0 | 44.4 | 1.3 | 0.94 | 27.7 | 36 |
| Fenoprofen | µg/L | 0.35 | < 0.05 | 85.7 | 0.20 | 0.05 | 75.0 | 80 |
| Gemfibrozil | µg/L | 0.91 | 0.20 | 78.0 | 0.73 | 0.21 | 71.2 | 75 |
| Ibuprofen | µg/L | 0.30 | < 0.05 | 83.3 | 0.14 | 0.05 | 64.3 | 74 |
| Ketoprofen | µg/L | 0.64 | 0.070 | 89.1 | 0.37 | 0.058 | 84.3 | 87 |
| Naproxen | µg/L | 1.4 | < 0.05 | 96.4 | 0.54 | 0.05 | 90.7 | 94 |
| Acetaminophen | µg/L | < 0.05 | < 0.05 | * | < 0.05 | < 0.05 | * | * |
| Pentoxifylline | µg/L | 0.32 | < 0.05 | 84.4 | 0.14 | 0.05 | 64.3 | 74 |
| Phenacetine | µg/L | 0.20 | < 0.05 | 75.0 | 0.17 | 0.05 | 70.6 | 73 |

* Below detection limits before and after SC1

**Figure 4.13** Removal of selected compounds during soil column experiment

Neutral compound carbamazepine had relatively low sorption and elimination of (8.3% in the second sample). This result is consistent with similar studies which reported that this antiepileptic drug is not subjected to any degradation or adsorption and removal rates of 8 % can not be considered as significant (Clara et al., 2004).

Hydrophilic and neutral compounds such as NDMA, 1,4-dioxane and acetaminophen exhibited different behaviors. NDMA was expected to be very persistent due to its miscibility in water. However, removals of approximately 22 % were achieved in SC1 for NDMA indicating that reduction may be attributed to biological activities. Zhou et al. (2009) demonstrated that biodegradation of NDMA under oxic conditions can be attributed to a common soil microorganism namely *Pseudomonas* that use “the quantitative Polymerase Chain Reaction (Q-PCR) to be 4.2×10^6 and 1.8×10^5 cells/g

fresh soil for the NDMA-impacted”. Nevertheless, 1,4-dioxane (hydrophilic and neutral compound) did not experiment the same behavior as NDMA. 1,4-Dioxane was absolutely not removed from secondary effluent (0 % of removal) mainly because for this compound adsorption is not a significant mechanism due to its miscibility with water and its very resistant to biological degradation due to its heterocyclic structure with two ether linkages (Zenker et al., 2003).

In case of acetaminophen very low concentrations were found in influent and effluent (lower than the detection limit). Therefore, it was not possible to analyze whether it is removed or persistent during soil passage.

4.3 Soil aquifer treatment combined with ozonation for organic micropollutants removal

The effect of ozonation as a pre-treatment was investigated to enhance the biodegradability of organic micropollutants in the secondary effluent for its removal during soil passage on SC2. An ozone/DOC ratio of 1 mg O₃/mg DOC was applied taking into account preceding studies for researchers at IHE referring that an increment in the dose of ozone beyond this dose does not cause considerable reductions in DOC. Furthermore, the transfer efficiency for the ozonation system achieved values of 53% ± 2%, which is consistent with previous findings where the transfer efficiency averaged was around 50% +/- 10% using the same set-up, volume of the sample and operational conditions (Fernando, 2009).

4.3.1 Removal of bulk organic matter from secondary effluent using O₃+ SC2

To assess the removal of organic matter from secondary effluent using ozone, samples were taken from SP1 and effluent at a hydraulic loading rate of 1.25 m/day to monitor DOC removals. Table 4.7 shows DOC removals values ranging from 16-26.4 %.

Table 4.7 DOC removals of SC2 fed with SE+O₃

| Day | Influent (mg/L) | Effluent (mg/L) | Removals (%) |
|-----|-----------------|-----------------|--------------|
| 1 | 10.56 | 8.57 | 18.8 |
| 5 | 10.15 | 8.43 | 16.9 |
| 9 | 10.41 | 7.66 | 26.4 |
| 12 | 9.40 | 7.91 | 15.9 |
| 16 | 10.33 | 8.30 | 19.7 |

The potential of ozone in causing structural changes in organic matter particularly to the humic fractions leads to a decrease in UVA₂₅₄ and colour as a consequence of the loss in the aromatic character of the compounds present in wastewaters. Figure 4.14 shows that UVA₂₅₄ samples from SC2 decreased considerably in relation to these from SC1 when secondary effluent without pre-treatment was used (from 0.337 to 0.293 /cm). These changes in UVA₂₅₄ and SUVA values are consistent with previous studies which demonstrated the effectiveness of ozone in converting refractory compounds into more biodegradable ones with a slight reduction in DOC (Fernando, 2009).

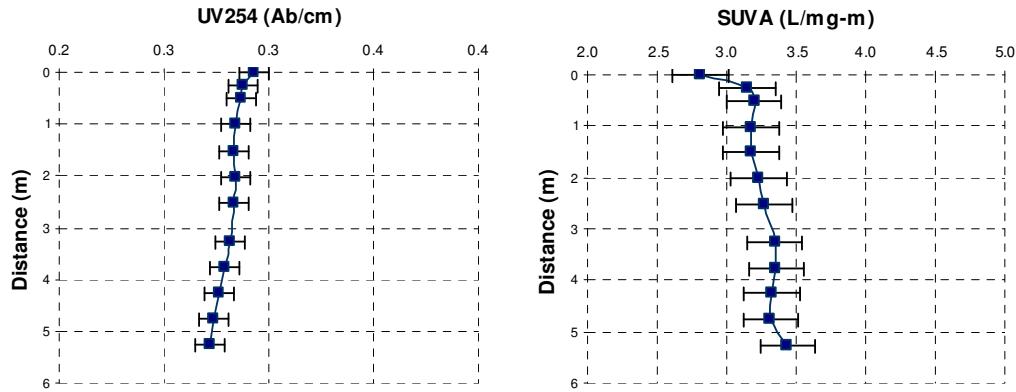


Figure 4.14 UV_{254} and SUVA along the depth of SC2 fed with ozonated secondary effluent (HLR: 1.25 m/day)

After ozonation, the biological activity in soil columns increased due to the increasing in amount of readily available DOC. Figure 4.15 shows the effective utilization of dissolved oxygen as a common electron acceptor for the degradation of DOC in ozonated secondary effluent. This is consistent with previous findings in which it was demonstrated that biodegradation is the dominating mechanism for the removal of DOC from waste in soil column studies (Abel, 2009; Sherif, 2009; Fernando 2009).

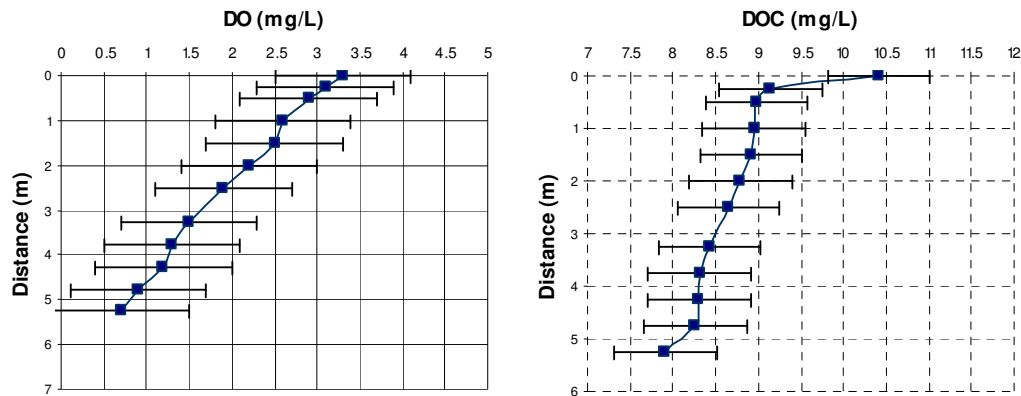


Figure 4.15 DO and DOC along the depth of SC2 fed with ozonated secondary effluent (HLR: 1.25 m/day)

Fluorescence EEM spectra from SC2

Figures 4.16 and 4.17 show F-EEM spectra of influent and effluent from SC2 using secondary effluent combined with ozonation (1:1) at a hydraulic loading rate of 1.25 m/day. Organic compounds were classified according to table 4.3 “Characteristic of organic matter by F-EEM spectra”, were humic-like peaks dominated in all samples. Reductions of humic-like compounds varied from 11 – 22% and also slight change in peaks locations for influent and effluent samples were noticed. Change in the peak position was observed after ozonation compared to the secondary effluent before ozonation. Furthermore, reductions of protein-like peaks ranged from 41-42% were also observed (Table 4.8 and Table 4.9). These findings could be interpreted as derived from the effects of pre-ozonation that can cause a reduction of dissolved organic carbon

(DOC) (including mineralization of small organic molecules) and breaking large molecules. Furthermore, these changes in EEM after oxidation confirm the formation of a significant amount of ozonation by-products, i.e. carboxylic acids, aldehydes and ketones during the oxidation process (Swietlik & Sikorska, 2004; Zhu et al., 2010).

Table 4.8 Comparison of F-EEM results between influent (8 days) and effluent (11 days) using SE+O₃ in SC2

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|--------------------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Influent (8 days) | 438 | 280 | 5.82 | 22 |
| | Effluent (11 days) | 428 | 270 | 4.51 | |
| Humic-like 2 | Influent (8 days) | 428 | 240 | 5.76 | 20 |
| | Effluent (11 days) | 430 | 240 | 4.61 | |
| Protein-like | Influent (8 days) | 316 | 270 | 5.09 | 41 |
| | Effluent (11 days) | 314 | 270 | 3.02 | |

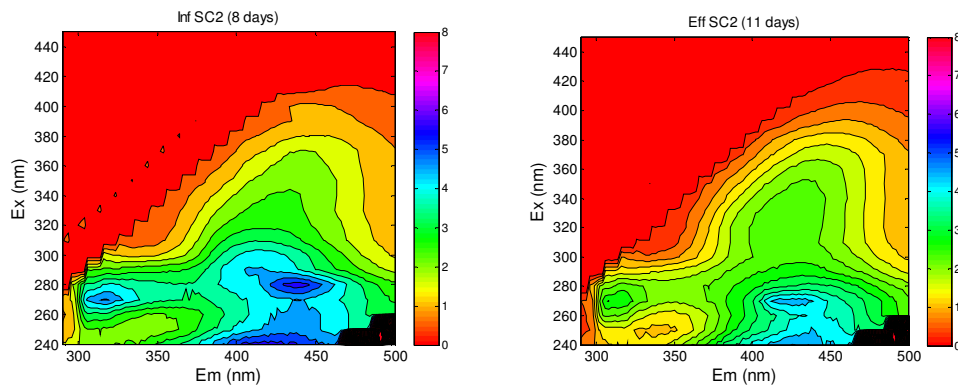


Figure 4.16 F-EEM spectra of SC2 fed with ozonated secondary effluent after 8 days (HLR: 1.25 m/day)

Table 4.9 Comparison of F-EEM results between influent (14 days) and effluent (17 days) using SE+O₃ in SC2

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|--------------------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Influent (14 days) | 434 | 240 | 3.46 | 11 |
| | Effluent (17 days) | 434 | 240 | 3.07 | |
| Humic-like 2 | Influent (14 days) | 420 | 310 | 2.28 | 21 |
| | Effluent (17 days) | 440 | 350 | 1.80 | |
| Protein-like | Influent (14 days) | 318 | 260 | 0.65 | 42 |
| | Effluent (17 days) | 328 | 260 | 0.38 | |

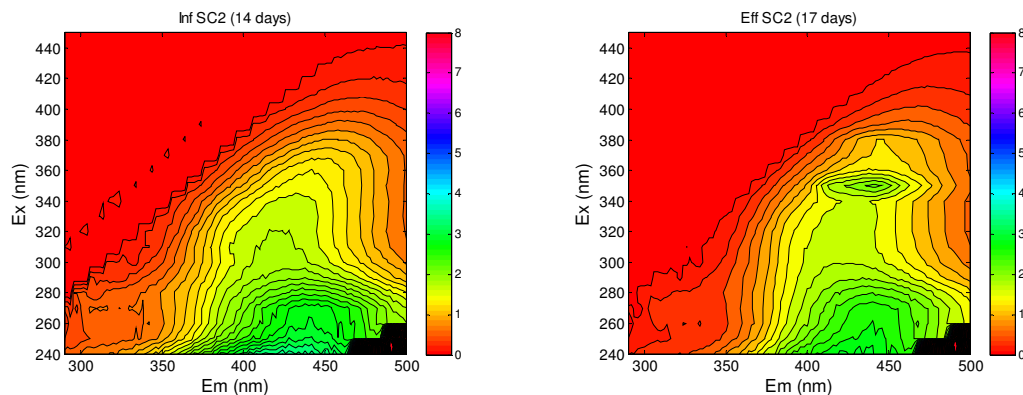


Figure 4.17 F-EEM spectra of SC2 fed with ozonated secondary effluent after 14 days (HLR: 1.25 m/day)

4.3.2 Removal of selected PhACs, NDMA and 1,4-dioxane from secondary effluent

The removal of target compounds from secondary effluent was evaluated by using ozone as a pre-treatment before the use of SC2. The target compound included NDMA, 1,4-dioxane and 13 PhACs that were spiked in glass bottles of 1000 mL volume using secondary effluent in concentrations of (1,4-dioxane: 20 µg/L, PhACs: 2 µg/L each and NDMA: 2 µg/L). Ozonation process took place for 35 minutes for each eight liters of sample until a O₃: DOC ratio of 1 mg: 1 mg was reached. Ozone was used to enhance biodegradation and to transform some refractory organic matters to biodegradable organic ones (Wang et al., 2008). Figure 4.18 shows the schematic of locations from where samples were collected after feeding pre-ozonated secondary effluent to SC2.

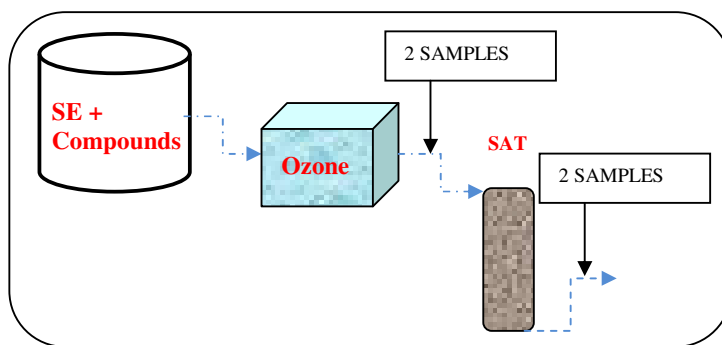


Figure 4.18 Number of samples and sampling points for soil column studies

Two samples were collected for influent and effluent on SC2 on different days at a hydraulic loading rate of 1.25 m/day (same sampling points that for SC1). Table 4.10 and figure 4.19 shows that in both cases, the majority of target compounds were removed lower than detection limit (> 0.05 µg/L) for influent samples, proving that ozone pre-treatment is highly effective in the removal of most of trace organic compounds in wastewater effluent and make them more easy for further biological degradation (Shu et al., 2004; Snyder et al., 2006).

Table 4.10 Concentration of target compounds before and after ozonation (O₃: DOC ratio 1mg: 1mg)

| Compound | Unit | Before O ₃ Sample 1 | After O ₃ Sample 1 | Removal (%) | Before O ₃ Sample 2 | After O ₃ Sample 2 | Removal (%) | Average removal (%) |
|----------------|------|---|--|----------------|---|--|----------------|---------------------------|
| NDMA | µg/L | 2 | 0.88 | 56 | 2 | 0.83 | 58.5 | 57.2 |
| 1,4-Dioxane | µg/L | 20 | 9.4 | 53 | 20 | 6.7 | 66.5 | 59.8 |
| Bezafibrate | µg/L | 2 | 0.25 | 87.5 | 2 | 0.069 | 96.6 | 92 |
| Caffeine | µg/L | 2 | 0.14 | 93 | 2 | < 0.13 | 93.5 | 93.3 |
| Carbamazepine | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Clofibric acid | µg/L | 2 | 0.34 | 83 | 2 | 0.28 | 86 | 84.5 |
| Diclofenac | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Fenoprofen | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Gemfibrozil | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Ibuprofen | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Ketoprofen | µg/L | 2 | 0.078 | 96.1 | 2 | 0.057 | 97.2 | 96.6 |
| Naproxen | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Acetaminophen | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Pentoxifylline | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |
| Phenacetine | µg/L | 2 | < 0.05 | 97.5 | 2 | < 0.05 | 97.5 | 97.5 |

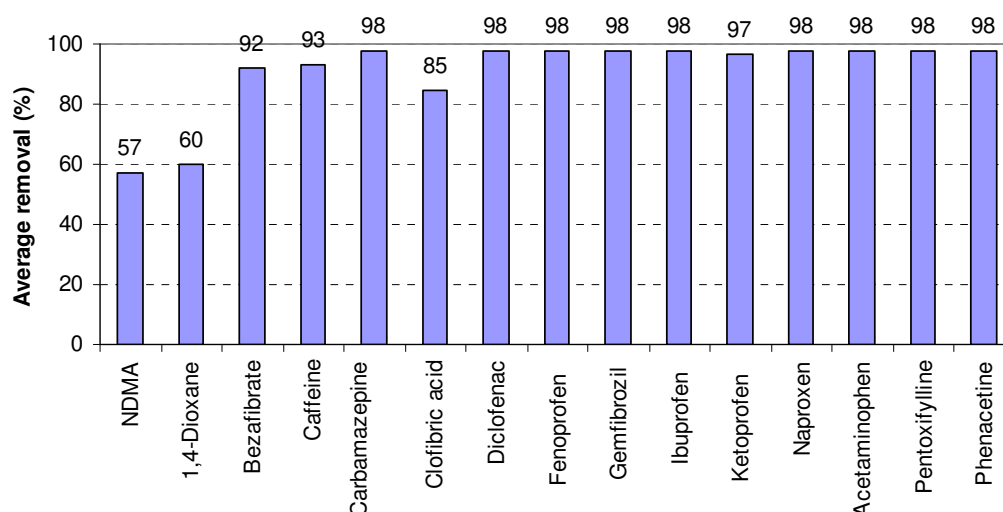


Figure 4.19 Average removals of target compounds before and after ozonation (O_3 : DOC ratio 1mg: 1mg)

However, no single treatment process will eliminate all trace organics to less than the detection limits. The addition of soil passage in combination with ozone as a multiple barrier treatment contributes to the complete elimination of residuals compounds that were not removed by oxidation and it will avoid the necessity for more cost-effective solutions. The results and the percentages removals obtained from this part of the study are presented in table 4.11 and figure 4.20.

Table 4.11 Concentration of target compounds using ozone before and after SC2 (HLR: 1.25 m/day)

| Compound | Unit | Influent Sample 1 | Effluent Sample 1 | Removal (%) | Influent Sample 2 | Effluent Sample 2 | Removal (%) | Average removal (%) |
|----------------|------|-------------------|-------------------|-------------|-------------------|-------------------|-------------|---------------------|
| NDMA | µg/L | 0.88 | 0.64 | 27.3 | 0.83 | 0.44 | 47 | 73 |
| 1,4-Dioxane | µg/L | 9.4 | 10 | -6.4 | 6.7 | 5.8 | 13.4 | 60.5 |
| Bezafibrate | µg/L | 0.25 | < 0.05 | 80 | 0.069 | < 0.05 | 27.5 | 97.5 |
| Caffeine | µg/L | 0.14 | < 0.13 | 7.1 | < 0.13 | < 0.13 | - | 93.5 |
| Carbamazepine | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Clofibric acid | µg/L | 0.34 | 0.082 | 75.9 | 0.28 | 0.24 | 14.3 | 92.0 |
| Diclofenac | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Fenoprofen | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Gemfibrozil | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Ibuprofen | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Ketoprofen | µg/L | 0.078 | < 0.05 | 35.9 | 0.057 | < 0.05 | 12.3 | 97.5 |
| Naproxen | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Acetaminophen | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Pentoxifylline | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |
| Phenacetine | µg/L | < 0.05 | < 0.05 | - | < 0.05 | < 0.05 | - | 97.5 |

(-) Removed below detection limit before SC2

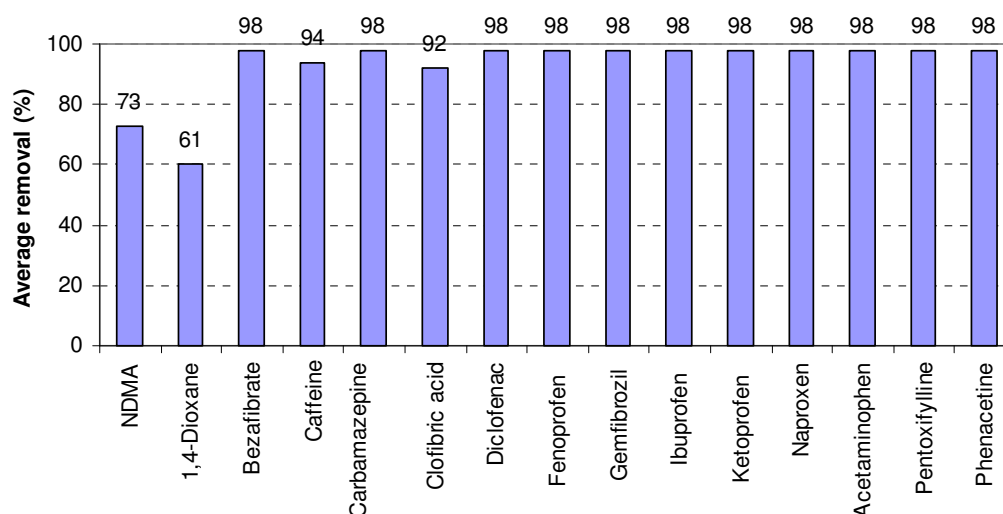


Figure 4.20 Removal of selected compounds from ozonated secondary effluent during soil passage (HLR: 1.25m/day)

The obtained results are in generally good agreement with the findings in several studies that have been demonstrated the efficacy of ozone as powerful oxidizer. Snyder et al., (2006) showed a pilot-scale test in which up to 10 from 11 pharmaceuticals spiked into municipal wastewater effluents were readily oxidized. It was demonstrated that 14 PhACs (Caffeine, Carbamazepine, Diclofenac Ibuprofen, Gemfibrozil, among others) were removed below the detection limit by O_3 doses of 1.25 mg L^{-1} . However, some compounds seem to be more recalcitrant to oxidation such is the case of clofibric acid (Esplugas et. al., 2007). Still, good removal was achieved taking into consideration that it was reduced from an initial concentration of $2 \text{ }\mu\text{g/L}$ to $0.28\text{-}0.34 \text{ }\mu\text{g/L}$ after ozonation (83-86 %) but through soil column (SC2) its persistence was demonstrated once again when it could not be removed completely (removals varied from 14-76%). On the other hand, comparatively with SC1 (removals between 8,4% and 36%), the SC2 shows a better performance enhance by the use of ozonation.

Earlier, it was observed that carbamazepine exhibited a recalcitrant behaviour during SC1 experiment. Meanwhile, ozone reacts rapidly with the double bond in carbamazepine and it is breakdown into simpler and more biodegradable compounds making possible to end up with a final concentration less than $0.05 \text{ }\mu\text{g/L}$ (Hua et al., 2006).

Ozonation proved to be an efficient technique on removing the lipid regulator bezafibrate (Dantas et al., 2007). With initial concentration of $2 \text{ }\mu\text{g/L}$, bezafibrate was eliminated almost completely after 35 minutes of treatment. However, a small part persisted and passed through SC2 from which was reduced below detection limits.

Even though higher removals were achieved for most of all PhACs, two compounds showed persistence in both samples (NDMA and 1,4-dioxane). Reduction was observed for 1,4-dioxane using ozone but not during soil passage due to its low affinity for organic matter and fully miscibility in water. It was unclear fluctuations in the measurements (influent and effluent from $6.7\text{-}9.4$ and $5.8\text{-}10 \text{ }\mu\text{g/L}$ respectively), however it was assumed because of “1,4-dioxane can diffuse into static pore water (the pore fraction does not participate in fluid migration)” and create the appearance of

retardation” (EPA, 2006). It is documented that the resulting mass of 1,4-dioxane stored in this fraction could be so significant that even after controlling or removing the source of dioxane, this one persist due to its physic-chemical properties (EPA, 2006). Although a number of microorganisms can degrade 1,4-dioxane through co-metabolism during growth on propane or tetrahydrofuran, many studies have been demonstrated the recalcitrance of 1,4-dioxane to degradation in microcosms in samples with different soil properties and redox conditions employed (Steffan, et al., 2007). Zenker et al., 2003, also gives references related to the use of ozone for degradation of 1,4-dioxane at neutral pH (7-9), concluding that O₃ alone could not readily oxidized this compound.

On the other hand, NDMA showed higher removals with the combination of ozone and soil passage (73 %). Earlier studies have been proving that NDMA or its precursors do not react with ozone in water and despite the presence of *Pseudomonas* bacteria that degrade NDMA via co- metabolism in soil, no significant losses were observed during soil passage. The reason behind this was linked to complex interactions between dissolved organic nutrients requirements for the growth of this type of microorganism that is able to degrade NDMA (SFPUC, 2007). Nonetheless, Andrzejewski et al., (2005), commented that ozone can react with secondary amines (NDMA precursors) but due to the reaction rate is very fast do not lead to NDMA formation and consequently the risk of an over increasing of NDMA concentration is avoided. Still, recent research by the same authors demonstrated that precursors like DMA could be associated to generation of NDMA as a by-product of ozonation when specific DMA/Ozone ratio is used (Andrzejewski et al., 2008).

4.4 Nanofiltration processes for organic micropollutants removal using SE alone, SE + SAT and SE+O₃ + SAT

Cross-flow membrane experiments were performed by cleaning the membrane (NF-90) for an interval of two hours with demineralized water until the flux became stable. All the tests were conducted in one mode of circulation: one pass (to avoid an increment of temperature in the system), in which feed was applied to the membrane, concentrate and permeate were collected separately under the following operational conditions:

- Feed pressure: 50 psi (3.6 bar)
- Flux: 15-25 L/m².h
- Recovery \approx 3%
- Temperature: 20 °C
- Membrane area (A_m): 139 cm²
- X-sectional area (A_{cross}): 0.665 cm²

Table 4.12 shows the operational parameters obtained for the three water types (SE, SE+SC1 and SE+O₃+SC2) by NF-90. It was noticed that the increment in the feed water concentrations increases the osmotic pressure. Thus, keeping the applied pressure constant, the flux decreased when secondary effluent without pre-treatment contained high concentration of organic matter was used as feed water in comparison with SE+SC1 and SE+O₃+SC2.

Table 4.12 Operational parameters for three types of water feed (SE, SE+SC1 and SE+O₃+ SC2)

| Parameter | Unit | SE | SE+ SC1 | SE+O ₃ + SC2 |
|------------------------------|---------------------|------|---------|-------------------------|
| Cross flow velocity (U or v) | cm/s | 3.41 | 3.86 | 4.51 |
| U or v = Q_c/A_{cross} | | | | |
| Permeate flow (Q_p) | L/h | 0.23 | 0.28 | 0.35 |
| Concentrate flow, Q_c | L/h | 8.16 | 9.24 | 11.1 |
| Flux (J) = Q_p/A_m | L/m ² .h | 16.5 | 20 | 25 |
| Recovery (r) | % | 2.7 | 3.0 | 3.0 |

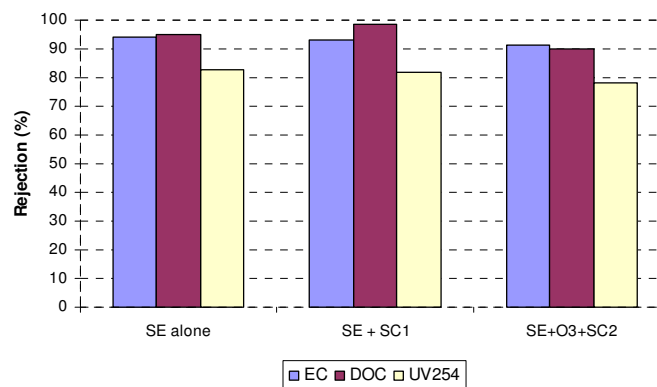
Even though, the flux decline after membrane fouling could not be observed due to the shorter performance of the experiments (around two hours), it was noticed the flux dropped within 10 minutes of starting filtration and gradually decreased. Fernando (2009) found that much higher flux decline was obtained for secondary effluent (50%) than for SE+SC1 (39%) and SE+O₃+SC2 (21%) after six hours of filtration by NF-90 under the same operational conditions.

4.4.1 Removal of bulk organic matter using SE alone, SE+SAT and SE+O₃+SAT

The study revealed rejections for DOC and UVA₂₅₄ greater than 92% and 78% respectively in the three water matrices by NF-90. Table 4.13 and figure 4.21 summarizes EC, DOC and UVA₂₅₄ values for the different scenarios and calculated rejections. Electrical conductivity was measured in the feed tank and permeates flows as a test for checking if the rejections by the membrane were in the order of 85-95% before concluding each experiment.

Table 4.13 Rejection of different water quality parameters during NF experiments

| Type of feed water | EC | | | DOC (mg/L) | | | UVA ₂₅₄ | | |
|------------------------|------|------|------------|------------|------|------------|--------------------|-------|------------|
| | Feed | Qp | Reject (%) | Feed | Qp | Reject (%) | Feed | Qp | Reject (%) |
| SE alone | 1266 | 73.8 | 94 | 11.0 | 0.53 | 95 | 0.359 | 0.062 | 83 |
| SE + SC1 | 1269 | 86.8 | 93 | 7.3 | 0.11 | 98 | 0.320 | 0.059 | 82 |
| SE+O ₃ +SC2 | 1086 | 92.8 | 92 | 8.2 | 0.62 | 92 | 0.256 | 0.056 | 78 |

**Figure 4.21** Rejection of different water quality parameters during NF experiments

Organic compounds (characterized as humic and fulvic acids) with molecular weight (MW) greater than the molecular weight cut-off (MWCO) of the membrane were efficiently rejected by NF-90 due to size exclusion mechanism. However, the remaining percentage that could not be rejected by electrostatic repulsion, steric hindrance or adsorption mechanisms and it was found in permeates comprises, humic hydrolysates, polysaccharides, low molecular weight acids and neutral compounds (Fernando, 2009; Drewes et al., 2003). Table 4.14 and figure 4.22 shows F-EEM spectra results obtained for feed and permeate using SE +NF-90 where high removal for humic-like compounds (99%) and also for proteins-like (94%) were observed.

Table 4.14 Comparison of F-EEM results between feed and permeate using SE +NF-90

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|----------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Feed | 426 | 240 | 7.53 | 99 |
| | Permeate | 422 | 240 | 0.06 | |
| Humic-like 2 | Feed | 420 | 320 | 4.70 | 99 |
| | Permeate | 418 | 320 | 0.03 | |
| Protein-like | Feed | 310 | 270 | 1.38 | 94 |
| | Permeate | 306 | 270 | 0.09 | |

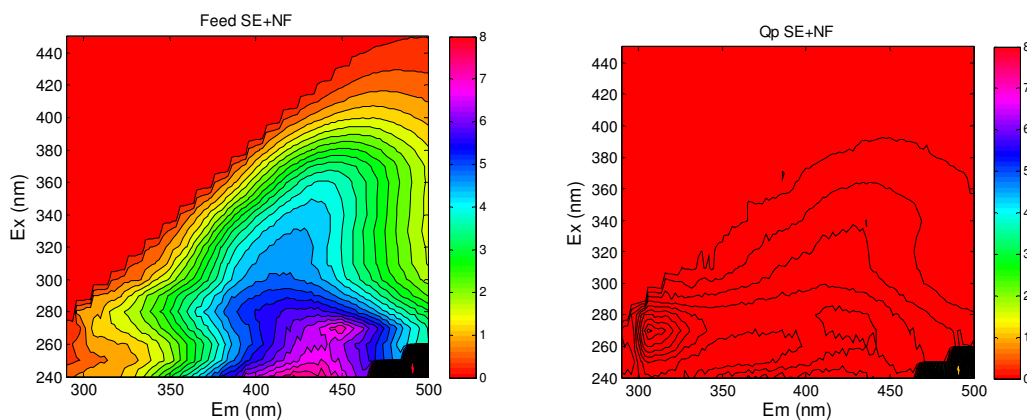


Figure 4.22 F-EEM spectra for feed and permeate using SE +NF-90

On the other hand, F-EEM results obtained between feed and permeate using SE + SC1+ NF-90 showed a high removal for humic-like compounds (98-100%). However, a detriment of 6% was observed for this water matrix in case of protein-like compounds that passed through the membrane (Table 4.15 and figure 4.23).

Table 4.15 Comparison of F-EEM results between feed and permeate using SE + SC1+ NF-90

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|----------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Feed | 436 | 250 | 4.09 | 100 |
| | Permeate | 436 | 250 | 0.009 | |
| Humic-like 2 | Feed | 428 | 330 | 2.89 | 98 |
| | Permeate | 418 | 330 | 0.05 | |
| Protein-like | Feed | 312 | 250 | 0.17 | 88 |
| | Permeate | 306 | 270 | 0.02 | |

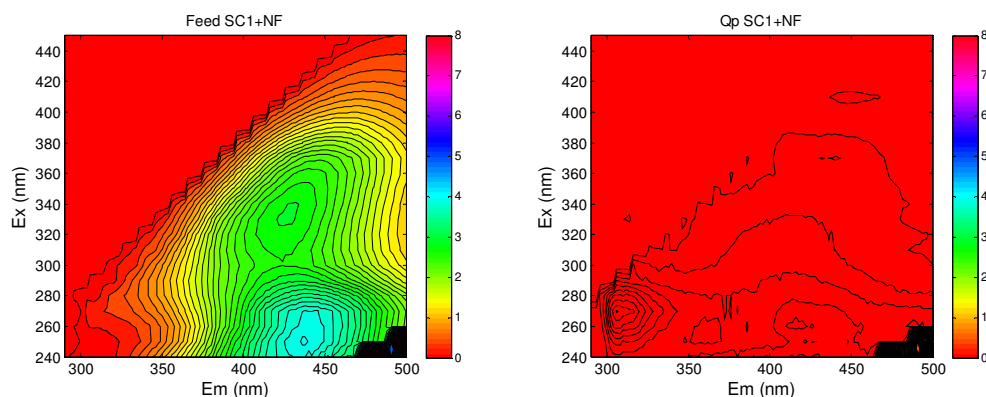


Figure 4.23 F-EEM spectra for feed and permeate using SE +SC1+NF-90

High reductions were also observed when ozonation and soil column were used as a pre-treatment for NF. Table 4.16 and figure 4.24 shows that F-EEM results exhibited high removal for humic-like compounds (99%) and 95% for protein-like compounds, similar values achieved when secondary effluent without pre-treatment was used as feed.

Table 4.16 Comparison of F-EEM results between feed and permeate using SE + O₃+ SC2 + NF-90

| DOC component | | Wavelength (nm) | | Peak Intensity | |
|---------------|----------|-----------------|-----|----------------|-----------|
| | | Em | Ex | (RA unit) | Reduction |
| Humic-like 1 | Feed | 420 | 240 | 5.44 | 99 |
| | Permeate | 424 | 240 | 0.06 | |
| Humic-like 2 | Feed | 432 | 340 | 2.23 | 99 |
| | Permeate | 424 | 340 | 0.02 | |
| Protein-like | Feed | 306 | 270 | 3.02 | 95 |
| | Permeate | 316 | 270 | 0.15 | |

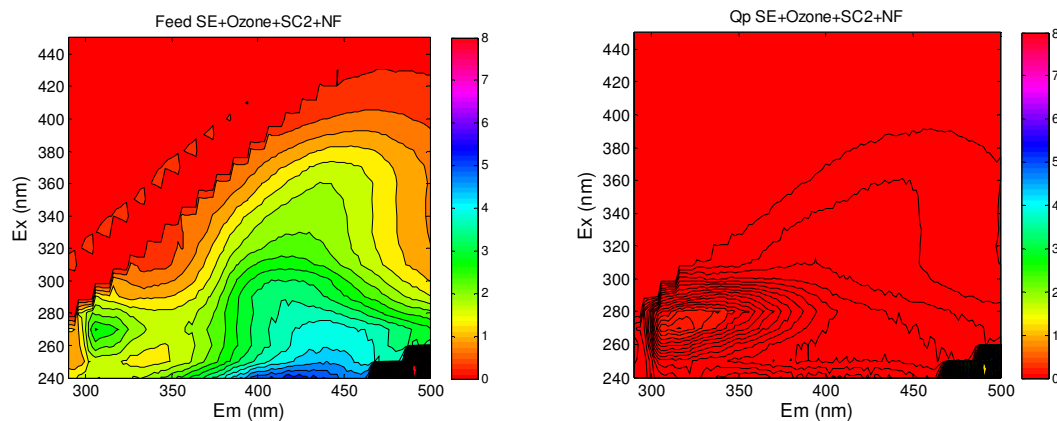


Figure 4.24 Fluorescence F-EEM spectra for feed and permeate using SE +SC2+O₃+NF-90

4.4.2 Rejection of selected PhACs, NDMA and 1,4-dioxane using SE alone.

The feed solution contained a cocktail of target compounds with concentrations ranging from 1,5 to 16 µg/L and its physico-chemical properties are shown on table 4.17. Concentration of acetaminophen of 0.74 µg/L was much lower than the expected of 2 µg/L but differences can be due to inaccuracy in measurements.

Rejection of selected organic micropollutants was investigated by using NF-90. Bellona et al. (2004) recognized that rejections will be affected by different membrane and solute properties. With regards to solutes, these ones can be rejected by three membrane mechanisms: steric hindrance, electrostatic repulsion and adsorptive interactions between solvent, solute and membrane. Several studies report that rejection of neutral compounds is influenced by size exclusion. Meanwhile, for polar compounds are rejected by interactions with charges membranes (Yangalli 2010; Radjenović et al. 2008).

Table 4.17 Physic-chemical properties and initial concentrations of target compounds

| Compound | Initial concentrations (µg/L) | Molecular Weight (g/mol) | pKa | Log K _{ow} | Classification |
|----------------|-------------------------------|--------------------------|------|---------------------|----------------|
| Gemfibrozil | 2.7 | 250.34 | 4.70 | 4.77 | Hp-ionic |
| Diclofenac | 2.5 | 296.16 | 4.15 | 4.51 | Hp-ionic |
| Bezafibrate | 1.9 | 361.82 | 3.61 | 4.25 | HP-ionic |
| Ibuprofen | 2.0 | 206.29 | 4.91 | 3.97 | HP-ionic |
| Fenoprofen | 2.0 | 242.28 | 4.5 | 3.9 | HP-ionic |
| Naproxen | 2.4 | 230.27 | 4.15 | 3.18 | HP-ionic |
| Clofibric acid | 1.7 | 214.645 | 3.20 | 2.88 | HP-ionic |
| Caffeine | 2.2 | 194.19 | 10.4 | -0.07 | HL-neutral |
| Carbamazepine | 2.3 | 236.28 | 13.9 | 2.45 | HP-neutral |
| Acetaminophen | 0.74 | 151.17 | 9.38 | 0.46 | HL-neutral |
| Pentoxifylline | 1.9 | 278.31 | 6.00 | 0.29 | HL-ionic |
| Ketoprofen | 2.0 | 254.281 | 5.94 | 0.97 | HL-ionic |
| Phenacetine | 2.3 | 179.2182 | 2.2 | 1.94 | HL-ionic |
| (NDMA) | 1.5 | 74.08 | 9.3 | -0.57 | HL-neutral |
| 1,4-dioxane | 16 | 88.10 | | -0.27 | HL- |

Table 4.18 present a summary of the rejection of the fifteen target compounds. Trace organic compounds that were present in the feed solution exhibited rejections by NF-90 ranged from 20-98.2%.

Table 4.18 Rejections of target compounds from SE by NF-90

| Compound | Initial concentrations (µg/L) | Permeate Concentrations (µg/L) | Rejections (R) (%) |
|----------------|-------------------------------|--------------------------------|--------------------|
| Gemfibrozil | 2.7 | < 0.05 | 98.2 |
| Diclofenac | 2.5 | < 0.05 | 98.0 |
| Bezafibrate | 1.9 | < 0.05 | 97.4 |
| Ibuprofen | 2.0 | < 0.05 | 97.5 |
| Fenoprofen | 2.0 | < 0.05 | 97.5 |
| Naproxen | 2.4 | < 0.05 | 97.9 |
| Clofibric acid | 1.7 | < 0.05 | 97.1 |
| Caffeine | 2.2 | < 0.13 | 94.1 |
| Carbamazepine | 2.3 | < 0.05 | 97.8 |
| Acetaminophen | 0.74 | 0.36 | 51.4 |
| Pentoxifylline | 1.9 | < 0.05 | 97.4 |
| Ketoprofen | 2.0 | < 0.05 | 97.5 |
| Phenacetine | 2.3 | 0.41 | 82.2 |
| (NDMA) | 1.5 | 1.2 | 20 |
| 1,4-dioxane | 16 | 3.2 | 80 |

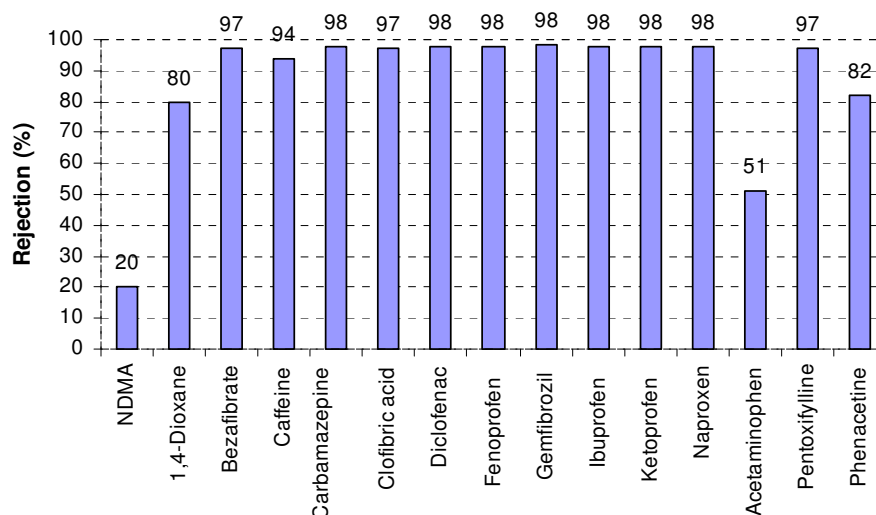


Figure 4.25 Rejections of target compounds from SE by NF-90

According to their physic-chemical properties, hydrophobic ionic compounds were rejected by electrostatic repulsion with the negatively surface charge of the membrane ($R > 97\%$). Radjenović et al. (2008) reported that retention on negatively charged compounds was influenced by the three parameters: degree of deprotonation of the trace organic, the membrane surface charge and presence of divalent cations. Yangalli (2010) also demonstrated that hydrophobic ionic compounds shown relatively stabilized rejections (96-99%) due to electrostatic repulsion by clean NF-90 membranes.

Rejection of hydrophilic neutral compounds (caffeine, acetaminophen, NDMA and 1,4-dioxane) was correlated with their molecular weights (MW) and MWCO (200 Da) of the membrane (Yangalli 2010; Radjenović et al. 2008). It was expected low rejections for those compounds with MW less than 200. The results obtained for NDMA (20%), acetaminophen (51.4%) and caffeine (94.1%), are consistent with the observations made by Yangalli (2010), who reported that NDMA showed low rejection (35%) using NF due to its small MW of 74.08 g/mol avoiding to be completely eliminated by size exclusion mechanism and for caffeine with a MW close to the MWCO of the NF-90 had a rejection of 92 %. Radjenović et al. (2008) referred low rejection for acetaminophen (44.8%) by using NF-90 considering that the MW of this compound (151.17 g/mol) was lower than the MWCO of the membrane for being rejected fully by steric hindrance mechanism. For dioxane, it was expected that due to its low length and effective diameter, the interaction between the membrane and the solute would be low and consequently a poor removal (Yangalli 2010). However, the hydrophilic and neutral compound 1,4-dioxane with a low MW (88 g/mol) exhibited an anomaly rejection of 80% by NF-90. This value differs from the results expressed by Yangalli (2010) where the rejection of 1,4-dioxane was of 46% and 41% by clean and fouled NF-90. On the other hand, the presence of NOM significantly increases the rejection of hydrophilic neutral compounds. This finding is supported by Comerton et al. (2009) after an ANOVA test that showed that NOM statistically increases the rejection of this kind of compounds. Comerton et al. (2009) also showed that in previous studies are reported the enhanced rejection for prepared waters containing NOM as well as for secondary effluent and raw sewage. In addition, Yangalli (2010) found that rejections for hydrophilic neutral compounds increased up to 30% due to fouling of the membrane.

The increased rejections were adjudicated to an enhanced of the sieving effect as a dominated rejection mechanism for this kind of compounds by fouled membranes.

Hydrophobic neutral compound (carbamazepine) was rejected by 97.8% due to the sieving effect (MW 236.28 g/mol). However, rejections of HP-neutral compounds can be also correlated with the adsorption onto the membrane because their moderates to high log K_{ow} (Yangalli, 2010).

Hydrophilic ionic compounds (pentoxifylline, ketoprofen, phenacetine) were rejected by 97.4, 97.5 and 82.17 % respectively. The higher degree of rejection might be attributed not only to electrostatic repulsion but also to the size exclusion mechanism.

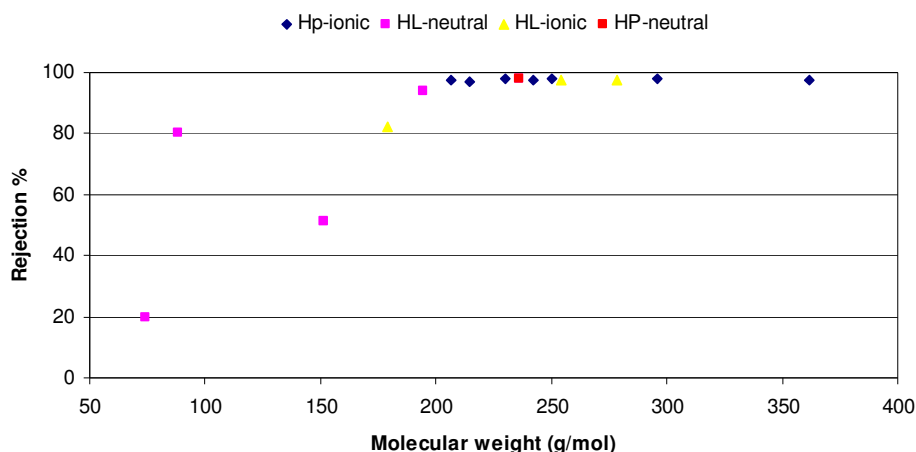


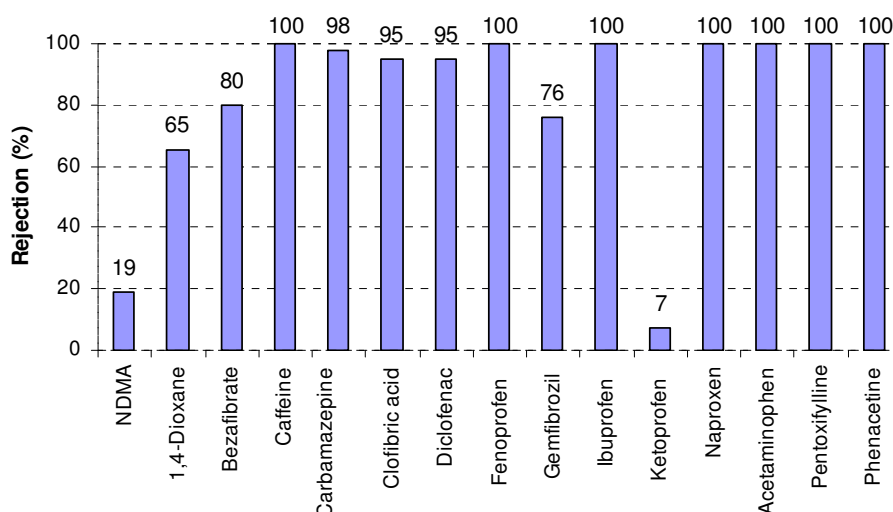
Figure 4.26 Rejection of target compounds in relation with molecular weight by NF-90 (SE alone)

4.4.3 Rejection of selected PhACs, NDMA and 1,4-dioxane using SE + SAT

Soil column study proved the efficiency of soil passage on removing the majority of target compounds. Although, some of these micropollutants remained in the effluent after soil passage in concentrations ranged from 0.21 to 17 $\mu\text{g/L}$; the synergy between SAT and membrane filtration provides excellent removals for emerging contaminants for water reuse purposes (Figure 4.27). A summary of the rejection of the remaining compounds is presented in table 4.19 with values ranged from 7.4% for ketoprofen to 97.5% for carbamazepine.

Table 4.19 Rejections of target compounds from SE+SC1 by NF-90

| Compound | Initial concentrations (µg/L) | Permeate Concentrations (µg/L) | Rejections (R) (%) |
|----------------|-------------------------------|--------------------------------|--------------------|
| Gemfibrozil | 0.21 | < 0.05 | 76.2 |
| Diclofenac | 0.96 | < 0.05 | 94.8 |
| Bezafibrate | 0.25 | < 0.05 | 80 |
| Ibuprofen | < 0.05 | < 0.05 | 100 |
| Fenoprofen | < 0.05 | < 0.05 | 100 |
| Naproxen | < 0.05 | < 0.05 | 100 |
| Clofibric acid | 1.0 | < 0.05 | 95 |
| Caffeine | < 0.13 | < 0.13 | 100 |
| Carbamazepine | 2.0 | < 0.05 | 97.5 |
| Acetaminophen | < 0.05 | < 0.05 | 100 |
| Pentoxifylline | < 0.05 | < 0.05 | 100 |
| Ketoprofen | 0.054 | < 0.05 | 7.4 |
| Phenacetine | < 0.05 | < 0.05 | 100 |
| NDMA | 1.0 | 0.81 | 19 |
| 1,4-dioxane | 17 | 5.9 | 65.3 |

**Figure 4.27** Rejections of target compounds from SE+SC1 by NF-90

Carbamazepine exhibited a very high rejection for secondary effluent without pre-treatment and secondary effluent combined with soil column (98% on both water matrices). As discussed before, rejections of hydrophobic neutral compounds was adjudicated mainly to sieving effects due to high molecular weight of the solute in comparison with the MWCO of the membrane (Comerton et al., 2009).

On the other hand, gemfibrozil, diclofenac, bezafibrate and clofibric acid (hydrophobic ionic compounds) showed deteriorations in rejections by NF-90 for this water matrix. Comerton et al., (2009) investigated the hypothesis related to the influence of cations and NOM on the rejection of PhACs. According to its findings the interactions between NOM and cations have a significant impact on the rejection of compounds such as gemfibrozil, mainly because NOM acquires a more rigid configuration leading to a reduction in NOM-compound association.

During this experiment, the rejection of 1,4-dioxane reduced to 65.3% (approximately 15 % less than for SE). As it was explained on section 4.4.2, the presence of NOM can affect the rejection of organic compounds. During soil passage the amount of NOM decreases, consequently there is a decline in rejections in comparison with the previous results when secondary effluent without pre-treatment was used.

The concentrations found for ketoprofen for influent and permeate were very low (almost below to detection limits for influent). Still, ketoprofen was not completely removed and no reasonable explanation was found.

NDMA was not affected by the difference in water matrices. This persistent compound almost did not experiment any variation in rejections. From 20 % using secondary effluent only slight reduction of 1% showed when effluent collected after soil passage was used as feed for nanofiltration experiment. The results are consistent with the values reported in the literature (35-45%) by using NF and RO. NF-90 has proved its inefficacy on removing this emerging contaminant due to its specific physico-chemical properties (specially its very low MW 74.08 g/mol, neutrality and miscibility). However, field observations and laboratory soil studies demonstrated that NDMA can be biodegraded up to 80% and even disappeared under aerobic and anaerobic conditions (Yangalli, 2010).

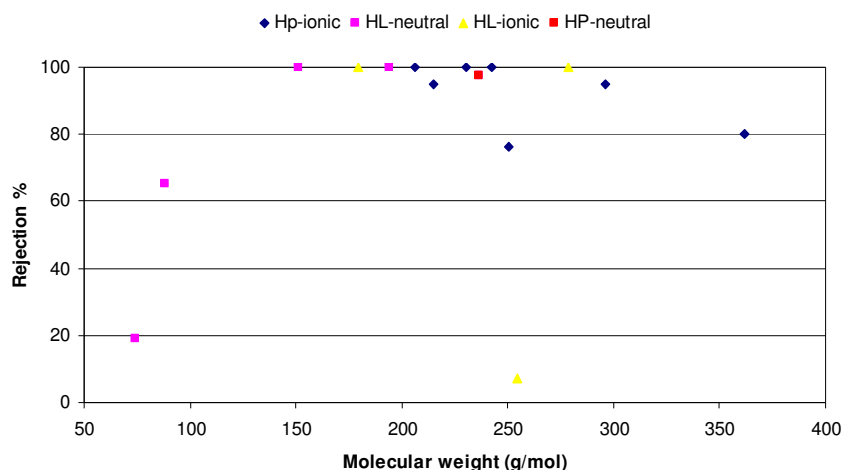


Figure 4.28 Rejection of target compounds in relation with molecular weight by NF-90 (SE+SC1)

4.4.4 Rejection of selected PhACs, NDMA and 1,4-dioxane using SE + O₃ + SC2

The results shown in table 4.20 and figure 4.29 proved the efficacy of the combination of soil passage with ozone on removing the majority of target compounds. Almost all the trace organic micropollutants were eliminated below detection limits before entering as a feed to the nanofiltration experiment. 1,4-dioxane continued exhibiting its persistence in all water matrices. However, rejections of this compound varied depending on water feed from 80% for secondary effluent to the lowest one when ozonation was used as a pre-treatment (63.6%). Small concentrations remained in permeate for compounds such as caffeine. Although, caffeine showed a high rejection for secondary effluent as feed (94%), this hydrophilic-neutral compound with a molecular weight close to the molecular weight cut-off of the membrane was not

eliminated by size exclusion mechanism due to changes in the water matrix (pre-ozonated secondary effluent contains less organic matter that might contribute to higher rejections of PhACs (Comerton et al., 2008).

Hydrophobic-ionic compound (clofibric acid) was rejected below detection limit (>0.05), where the rejection mechanism may be attributed to electrostatic repulsion. Nevertheless, small concentration was found in the feed due to its persistence through the soil as it was explained before.

Table 4.20 Rejections of target compounds from SE+O₃+SC2 by NF-90

| Compound | Initial concentrations (µg/L) | Permeate Concentrations (µg/L) | Rejections (R) (%) |
|----------------|-------------------------------|--------------------------------|--------------------|
| Gemfibrozil | < 0.05 | < 0.05 | 100 |
| Diclofenac | < 0.05 | < 0.05 | 100 |
| Bezafibrate | < 0.05 | < 0.05 | 100 |
| Ibuprofen | < 0.05 | < 0.05 | 100 |
| Fenoprofen | < 0.05 | < 0.05 | 100 |
| Naproxen | < 0.05 | < 0.05 | 100 |
| Clofibric acid | 0.17 | < 0.05 | 70.6 |
| Caffeine | 0.36 | 0.31 | 13.9 |
| Carbamazepine | < 0.05 | < 0.05 | 100 |
| Acetaminophen | < 0.05 | < 0.05 | 100 |
| Pentoxifylline | < 0.05 | < 0.05 | 100 |
| Ketoprofen | < 0.05 | < 0.05 | 100 |
| Phenacetine | < 0.05 | < 0.05 | 100 |
| NDMA | 0.52 | 0.45 | 13.5 |
| 1,4-dioxane | 11 | 4.0 | 63.6 |

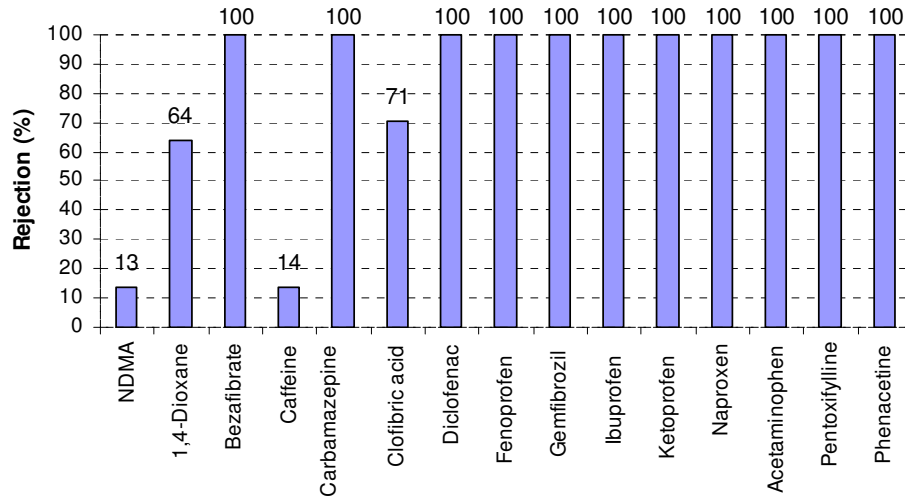


Figure 4.29 Rejections of target compounds from SE+O₃+SC2 by NF-90

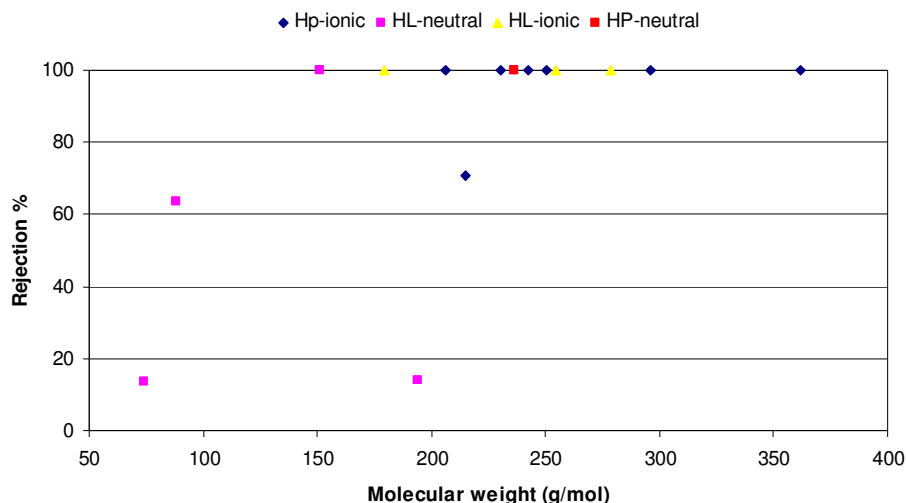


Figure 4.30 Rejection of target compounds in relation with molecular weight for NF-90 fed with SE+O₃+SC2 pre-treatment

Table 4.21 shows a summary of removals of target compounds by different treatments which demonstrated that soil passage in combination with ozonation can eliminate the majority of those contaminants, first by oxidation and further polished using SAT (Figure 4.31). The main advantage of the use of ozonation as pre-treatment is the increment of the degradability of the DOC and trace organic compounds before soil passage. Additionally, compounds such as NDMA and 1,4-dioxane exhibited better removals (73% and 61% respectively) under these conditions than in the rest of the alternatives.

SAT by itself showed a great potential against emerging contaminants; still, some of them persisted in the effluent (NDMA, 1,4-dioxane, carbamazepine, clofibric acid) compared with the rest of treatments. Soil passage is an excellent additional barrier but never can be seen as the unique treatment solution to meet standards for indirect potable reuse.

On the other hand, secondary effluent without pre-treatment showed high rejections for the selected organic micropollutants by NF-90, the inconvenience of small particles (proteins and polysaccharides) retained by the membrane strongly affects the performance of the system in terms of membrane fouling. Furthermore, compounds such as NDMA exhibited better removals during soil passage than in NF experiments.

The last alternative combining ozonation, soil passage and including tight NF as post-treatment demonstrated that the removal capacity increased and consequently the robustness of the treatment train. However, rejections of some compounds (caffeine and NDMA) could be affected due to low content of EfOM in this water matrix. Besides, O&M costs for energy consumption, membrane elements and concentrate streams that require additional treatments, makes this option more expensive and complex for full scale implementations.

In contrast, if SAT were excluded from this train and only ozonation and NF were taken into consideration, the overall removal efficiency of the system might decrease due to ozonation can breakdown compounds into smaller ones making them more easily for

biodegradation but at the same time the presence of these small particles would lead to a rapid increase of membrane fouling.

Table 4.21 Summary of removals of target compounds by different treatments

| Compound | SE+SC1 Removal (%) | SE+O ₃ +SC2 Removal (%) | SE+NF Removal (%) | SE+SC1+NF Removal (%) | SE+O ₃ +SC2+NF Removal (%) |
|----------------|--------------------------|--|-------------------------|-----------------------------|---|
| Gemfibrozil | 75 | 98 | 98 | 76 | 100 |
| Diclofenac | 36 | 98 | 98 | 95 | 100 |
| Bezafibrate | 71 | 98 | 97 | 80 | 100 |
| Ibuprofen | 74 | 98 | 98 | 100 | 100 |
| Fenoprofen | 80 | 98 | 98 | 100 | 100 |
| Naproxen | 94 | 98 | 98 | 100 | 100 |
| Clofibric acid | 8 | 92 | 97 | 95 | 71 |
| Caffeine | 58 | 94 | 94 | 100 | 14 |
| Carbamazepine | 4 | 98 | 98 | 98 | 100 |
| Acetaminophen | 0 | 98 | 51 | 100 | 100 |
| Pentoxifylline | 74 | 98 | 97 | 100 | 100 |
| Ketoprofen | 87 | 98 | 98 | 7.4 | 100 |
| Phenacetine | 73 | 98 | 82 | 100 | 100 |
| NDMA | 22 | 73 | 20 | 19 | 14 |
| 1,4-dioxane | 0 | 61 | 80 | 65 | 64 |

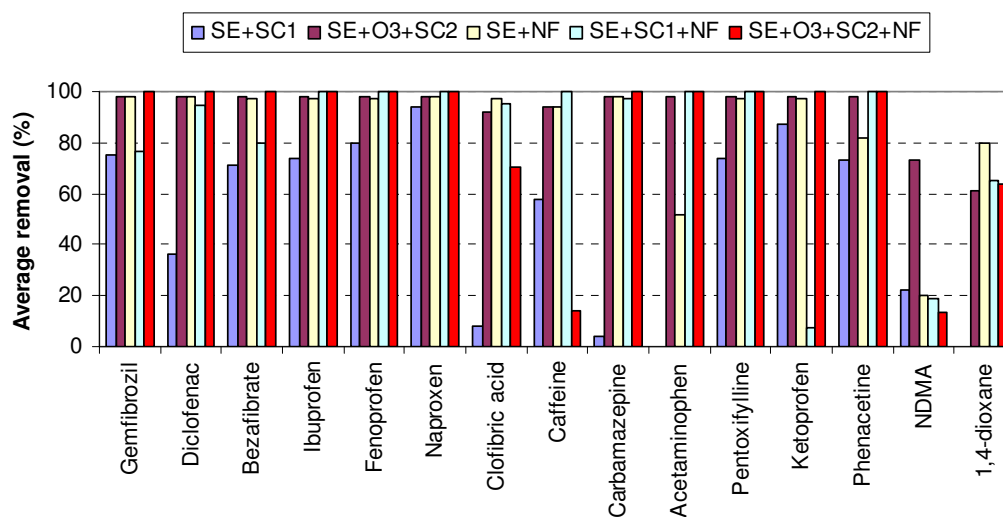


Figure 4.31 Average removals for organic micropollutants by different treatments

Even though, the presence of these contaminants in different types of waters is of very high concern, the majority of those organic micropollutants remain unregulated. Currently there is not federal regulation that controls emerging contaminants in drinking or natural waters and only a pharmaceutical would be evaluated if the concentration in soil or water is expected to exceed 1 mg/L (Yangalli, 2010).

4.5 Practical implications of the study

The research outputs allow suggesting four main wastewater treatment technologies taking into account the unique character of SAT as a multi-barrier approach for water reclamation uses:

- 1. SE + SAT**
- 2. SE+ Ozone and SAT**
- 3. SE + SAT as pre-treatment + NF**
- 4. SE+ Ozone and SAT as pre-treatments + NF**

The first two options under good operating conditions and after evaluation of the hydrogeology of the aquifer can be considered for non potable reuse such as unrestricted irrigation of crops, public parks, golf camps, street cleaning. However, even when the second option is a viable technology for enhancing and reducing recalcitrant compounds below detection limits, cost and feasibility analysis should be done when ozone is included as a pre-treatment step before SAT.

On the other side, the inclusion of NF in the train will lead to highly treated water that can be used for aquifer recharge and recovery for indirect potable reuse. The combination of soil aquifer treatment (SAT) and ozone prior to NF will also contribute to have a substantial minimization of the fouling in membranes due to the reduction of organic matter via soil passage and oxidation and further enhance the scheme for potable reuse.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results discussed in previous sections, the following conclusions can be drawn from this research:

1. Target organic micropollutants were present in the secondary effluent from Hoek van Holland WWTP at concentration ranging from 5.3 ng/L for NDMA up to 820 ng/L for gemfibrozil.
2. Steady state conditions with respect to DOC removal in both soil columns at a hydraulic loading rate of 1.25 m/day were achieved after 65 days of continuous dosing secondary effluent. After steady state, the DOC removal from SE in soil columns ranged from 20 to 22%.
3. Decrease in UVA₂₅₄ values (in SC1 and SC2) during soil passage indicates a preferential removal of non-humic substances over the slowly biodegradable humic substances, demonstrating the capability of SAT in removing many organic compounds that can serve as precursors for disinfection by-products (DBPs).
4. Soil column experiments using secondary effluent as feed water exhibited high removals for most of the target compounds (> 70 %) linked to sorption onto soil particles or transformed easily through biodegradation mechanisms.
5. Hydrophobic compounds such as clofibric acid and diclofenac were less removed in SC1 (8,4% and 36% respectively) due to its strongly pH dependency.
6. Neutral compounds (e.g carbamazepine) showed a persistent behavior during soil passage due to its significantly lower sorption (8.3%).
7. Soil column studies showed the efficacy of ozone on removing the majority of target compounds to lower than detection limit (<0.05 µg/L) for influent samples.
8. Some compounds were more recalcitrant to oxidation (clofibric acid); the combination of ozone with soil passage contributes to the complete elimination of residual compounds that were not removed by ozonation.
9. NDMA and 1,4-dioxane did not exhibit significant reductions during soil passage. An improvement in their removal was achieved (22 to 73% and 0-61% respectively) when ozone was used as a pre-treatment.

Nanofiltration experiments

1. The rejection of target compounds by NF-90 was correlated with their physico-chemical properties and it was influenced by the amount of effluent organic matter (EfOM) in water matrices.

2. Improved rejection of hydrophilic-neutral compounds with molecular weight (MW) lower than the molecular weight cut-off of the membrane (MWCO) was observed for compounds such as 1,4-dioxane (SE+SC1: 65.3% to SE: 80%). However, uncertainties exist in relation with the rejection of this solute by using different water matrixes because of the limited data.
3. NDMA was not affected by the difference in water matrices (rejection of 20 % using SE to a slight reduction of 1% for SE+SC1).
4. Hydrophobic ionic compounds were rejected by electrostatic repulsion with the negatively surface charge of the membrane ($R > 97.4\%$) for SE. However, deteriorations were observed for some compounds gemfibrozil (98.2-76.2%), diclofenac (98.0-94.8%), bezafibrate (97.4-80%) and clofibric acid (97.1-95.0%).
5. Excellent rejections for hydrophobic neutral compound (e.g. carbamazepine) on both water matrices were achieved due to the sieving effect (SE+SC1: 97.5 and SE: 97.8%).
6. High rejections for hydrophilic ionic compounds were highly attributed not only to electrostatic repulsion but also to the size exclusion mechanism.

5.2 Recommendations

1. It was demonstrated that most of the target compounds were well removed using O_3 +SAT. However, other pre-treatment options (AOPs) should be investigated for NDMA and 1,4-dioxane removal during soil passage.
2. Additional investigations should be conducted in order to support the synergy between SAT+NF technology for removing emerging organic contaminants (NDMA and 1,4-dioxane) for potable reuse.
3. More experimental work would be necessary to support the potential biodegradation of NDMA under different redox conditions through soil column study.
4. Further investigation is necessary to verify that the rejection of 1,4-dioxane is influenced by water compositions.
5. Cost-Benefit analyses need to be done in order demonstrate that an integrated SAT+NF system for removal of micropollutants is less expensive and more effective solution than other alternative treatment processes.

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Appendix A. Ripening of soil columns using Secondary Effluent (SE) and profile of soil columns after ripening period

Experimental conditions

Feed water: Secondary effluent from Hoek van Holland

Hydraulic Loading rate: 1.25 m/day

Column depth: 5.0 m

Filter Media: Silica sand

Table A-1 DOC concentrations for SC1 and SC2 during ripening period

| Time (days) | SC1 | | | | SC2 | | |
|----------------|--------------------------|-------------------------|------|-----------------------|-------------------------|------|-----------------------|
| | Co Influent (mg/L) | C Effluent (mg/L) | C/Co | DOC removal (%) | C Effluent (mg/L) | C/Co | DOC removal (%) |
| 44 | 14.57 | 12.96 | 0.87 | 13.44 | 12.07 | 0.81 | 19.09 |
| | 14.96 | 12.61 | | | 11.83 | | |
| 48 | 15.72 | 11.95 | 0.74 | 25.88 | 11.75 | 0.74 | 25.50 |
| | 16.11 | 11.65 | | | 11.97 | | |
| 52 | 15.70 | 12.06 | 0.74 | 26.48 | 11.94 | 0.77 | 22.68 |
| | 16.39 | 11.54 | | | 12.88 | | |
| 55 | 14.78 | 11.80 | 0.78 | 21.62 | 11.23 | 0.74 | 25.94 |
| | 15.56 | 11.98 | | | 11.24 | | |
| 56 | 15.02 | 12.82 | 0.87 | 12.65 | 11.26 | 0.76 | 24.38 |
| | 14.21 | 12.72 | | | 10.85 | | |
| 65 | 15.34 | 12.80 | 0.83 | 17.34 | 13.69 | 0.86 | 14.16 |
| | 15.79 | 12.94 | | | 13.04 | | |
| Average | 15.35 | 12.32 | 0.81 | 19.57 | 11.98 | 0.78 | 21.96 |

Table A-2 pH, DOC and DO values along the depth on both soil columns after ripening period

| Sampling Point | Distance (m) | pH | SC1 | | pH | SC2 | |
|-------------------|-----------------|-----|---------------|--------------|-----|---------------|--------------|
| | | | DOC (mg/L) | DO (mg/L) | | DOC (mg/L) | DO (mg/L) |
| SP-1 | 0.00 | 7.8 | 13.80 | 3.7 | 7.9 | 13.61 | 3.1 |
| SP-2 | 0.26 | 7.8 | 13.67 | 3.5 | 7.9 | 13.58 | 2.9 |
| SP-3 | 0.51 | 7.8 | 13.38 | 3.3 | 7.8 | 13.53 | 2.8 |
| SP-4 | 1.01 | 7.7 | 12.80 | 2.7 | 7.8 | 13.52 | 2.8 |
| SP-5 | 1.51 | 7.7 | 12.70 | 2.6 | 7.8 | 13.27 | 2.6 |
| SP-6 | 2.01 | 7.7 | 12.50 | 2.5 | 7.8 | 12.89 | 2.2 |
| SP-7 | 2.51 | 7.6 | 12.19 | 2.3 | 7.7 | 12.53 | 2.1 |
| SP-8 | 3.26 | 7.6 | 11.96 | 2.0 | 7.7 | 12.31 | 1.9 |
| SP-9 | 3.76 | 7.6 | 11.92 | 1.8 | 7.6 | 12.12 | 1.7 |
| SP-10 | 4.26 | 7.6 | 11.79 | 1.5 | 7.5 | 11.42 | 1.5 |
| SP-11 | 4.76 | 7.6 | 11.55 | 1.4 | 7.5 | 11.37 | 1.4 |
| SP-12 | 5.26 | 7.6 | 11.36 | 1.3 | 7.5 | 11.22 | 1.2 |

Appendix B. Profile of SC1 using Secondary Effluent (SE) and profile of SC2 using ozone combined with Secondary Effluent (SE) spiked with target compounds

Table B-1 Profile of SC1 using SE spiked with target compounds

| Sampling Point | Distance | pH | EC (μS/cm) | DO (mg/L) | DOC (mg/L) | UV ₂₅₄ (Ab/cm) | SUVA |
|----------------|----------|------|------------|-----------|------------|---------------------------|-------|
| SP-1 | 0.00 | 8.05 | 1267 | 3.5 | 10.48 | 0.357 | 3.402 |
| SP-2 | 0.26 | 8.0 | 1267 | 3.3 | 9.92 | 0.353 | 3.553 |
| SP-3 | 0.51 | 8.0 | 1265 | 2.9 | 9.76 | 0.351 | 3.596 |
| SP-4 | 1.01 | 8.0 | 1263 | 2.8 | 9.70 | 0.351 | 3.619 |
| SP-5 | 1.51 | 7.9 | 1261 | 2.6 | 9.58 | 0.349 | 3.638 |
| SP-6 | 2.01 | 7.9 | 1259 | 2.6 | 9.46 | 0.350 | 3.656 |
| SP-7 | 2.51 | 7.8 | 1255 | 2.5 | 9.20 | 0.348 | 3.777 |
| SP-8 | 3.26 | 7.8 | 1253 | 2.4 | 9.02 | 0.340 | 3.769 |
| SP-9 | 3.76 | 7.8 | 1249 | 2.4 | 8.86 | 0.340 | 3.832 |
| SP-10 | 4.26 | 7.6 | 1248 | 2.3 | 8.78 | 0.339 | 3.861 |
| SP-11 | 4.76 | 7.6 | 1246 | 2.1 | 8.60 | 0.339 | 3.936 |
| SP-12 | 5.26 | 7.5 | 1242 | 1.9 | 8.48 | 0.337 | 3.974 |

* (Temperature along the column ≈ 22 °C)

Table B-2 Profile of SC2 using ozone combined with SE spiked with target compounds

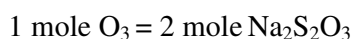
| Sampling Point | Distance | pH | EC (μS/cm) | DO (mg/L) | DOC (mg/L) | UV ₂₅₄ (Ab/cm) | SUVA (L/mg-m) |
|----------------|----------|------|------------|-----------|------------|---------------------------|---------------|
| SP-1 | 0.00 | 8.1 | 1242 | 3.3 | 10.41 | 0.293 | 2.815 |
| SP-2 | 0.26 | 8.01 | 1235 | 3.1 | 9.145 | 0.288 | 3.149 |
| SP-3 | 0.51 | 8.0 | 1223 | 2.9 | 8.978 | 0.287 | 3.197 |
| SP-4 | 1.01 | 7.98 | 1228 | 2.6 | 8.954 | 0.284 | 3.172 |
| SP-5 | 1.51 | 7.94 | 1239 | 2.5 | 8.912 | 0.283 | 3.175 |
| SP-6 | 2.01 | 7.90 | 1230 | 2.2 | 8.793 | 0.284 | 3.230 |
| SP-7 | 2.51 | 7.88 | 1237 | 1.9 | 8.647 | 0.283 | 3.273 |
| SP-8 | 3.26 | 7.86 | 1229 | 1.5 | 8.430 | 0.282 | 3.345 |
| SP-9 | 3.76 | 7.85 | 1252 | 1.3 | 8.311 | 0.279 | 3.357 |
| SP-10 | 4.26 | 7.83 | 1242 | 1.2 | 8.309 | 0.276 | 3.322 |
| SP-11 | 4.76 | 7.81 | 1233 | 0.9 | 8.265 | 0.274 | 3.315 |
| SP-12 | 5.26 | 7.79 | 1223 | 0.7 | 7.913 | 0.272 | 3.437 |

Appendix C. Calculations for Ozone set-up UNESCO-IHE Laboratory

Table C-1 Calculations for ozone set-up UNESCO-IHE Laboratory

| | | | |
|---------------------|--|----------|---------------------|
| By-pass: | | | |
| 1 | Volume gas meter B-15 [end of ozonation]: | 52443.75 | (Liters) |
| 2 | Volume gas meter B-15 [start of ozonation]: | 52440.11 | (Liters) |
| 3 | Volume by-pass [gas meter]: | 3.64 | (Liters) |
| 4 | Titration volume by-pass: | 7.7 | (mL) |
| 5 | Molarity titrant [Na ₂ S ₂ O ₃ ·5H ₂ O]: | 0.1000 | (mol/L) |
| 6 | Mass ozone in by-pass: | 92.4 | mg ozone |
| 7 | Strength of ozone: | 25.4 | |
| Sample line: | | | |
| 8 | Volume gas meter B-16 [end of ozonation]: | 6947.28 | (Liters) |
| 9 | Volume gas meter B-16 [start of ozonation]: | 6941.02 | (Liters) |
| 10 | Volume of ozonation experiment [gas meter]: | 6.26 | (Liters) |
| 11 | Incoming mass of ozone [strength]: | 158.9 | mg ozone |
| 12 | Titration volume of off gas: | 6.2 | (mL) |
| 13 | Outgoing mass of ozone not used [off gas]: | 74.4 | mg ozone |
| 14 | Mass of ozone used in experiment: for total volume of your sample | 84.5 | mg ozone |
| 15 | Efficiency for this sample: [Depends on bottle & sample size, stirring, diffuser etc.] | 53.2 | % |
| 16 | Concentration of ozone in the sample: | 10.56 | mg/L O ₃ |
| 17 | Concentration of DOC in the sample: | 10.75 | mg/L DOC |
| 18 | [O ₃]:[DOC] ratio | 1.0 | |

Reactions:



In titration [2] the iodine (red) is converted into sodium iodide (colorless)

Remarks:

Mass of ozone = Volume titrated · Molarity of titrant · 24 · Ratio of KI used [mg]

Ratio of KI used = total volume of KI relative to the KI used in titration [250/50]

24 = mass of ozone [48]/ mole ratio between thiosulphate and ozone [2]

Appendix D. Concentrations of NDMA, 1,4-dioxane and PhACs compounds in µg/L

Table D-1 Concentrations of target compounds in different water samples

| Water source Compounds | NDMA | 1,4-Dioxane | Bezafibrate | Caffeine | Carbamazepine | Clofibric acid | Diclofenac | Fenoprofen | Gemfibrozil | Ibuprofen | Ketoprofen | Naproxen | Paracetamol | Pentoxifylline | Phenacetine |
|---|--------|-------------|-------------|----------|---------------|----------------|------------|------------|-------------|-----------|------------|----------|-------------|----------------|-------------|
| Stock Solution | 1.7 | 20 | 1.9 | 2.0 | 2.0 | 2.0 | 2.0 | 1.9 | 2.0 | 2.0 | 2.1 | 2.0 | 2.0 | 2.0 | 2.0 |
| Secondary Effluent (Background check) | 0.0053 | < 0.5 | < 0.05 | 0.37 | 0.47 | < 0.05 | 0.43 | < 0.05 | 0.82 | 0.12 | 0.094 | 0.35 | < 0.05 | < 0.05 | < 0.05 |
| SE +SC1 (Influent after 11 days) | 1.3 | 17 | 0.95 | 0.43 | 2.0 | 1.3 | 1.8 | 0.35 | 0.91 | 0.30 | 0.64 | 1.4 | < 0.05 | 0.32 | 0.20 |
| SE +SC1 (Effluent after 14 days) | 0.99 | 17 | 0.21 | < 0.13 | 2.2 | 1.2 | 1.0 | < 0.05 | 0.20 | < 0.05 | 0.070 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| SE +SC1 (Influent after 30 days) | 1.2 | 17 | 0.73 | 0.24 | 2.4 | 1.1 | 1.3 | 0.20 | 0.73 | 0.14 | 0.37 | 0.54 | < 0.05 | 0.14 | 0.17 |
| SE +SC1 (Effluent after 33 days) | 0.95 | 17 | 0.26 | 0.13 | 2.2 | 1.0 | 0.94 | < 0.05 | 0.21 | < 0.05 | 0.058 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| NF Feed (SE alone) | 1.5 | 16 | 1.9 | 2.2 | 2.3 | 1.7 | 2.5 | 2.0 | 2.7 | 2.0 | 2.0 | 2.4 | 0.74 | 1.9 | 2.3 |
| NF Qp (SE alone) | 1.2 | 3.2 | < 0.05 | < 0.13 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.36 | < 0.05 | 0.41 |
| NF Qc (SE alone) | 1.5 | 29 | 1.7 | 2.1 | 2.4 | 1.9 | 2.3 | 2.4 | 2.6 | 1.9 | 1.7 | 2.4 | 0.61 | 1.9 | 2.1 |
| NF Feed (SE + SC1) | 1.0 | 17 | 0.25 | < 0.13 | 2.0 | 1.0 | 0.96 | < 0.05 | 0.21 | < 0.05 | 0.054 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| NF Qp (SE + SAT) | 0.81 | 5.9 | < 0.05 | < 0.13 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| SE + O ₃ + SC2 (Influent after 8 days) | 0.88 | 9.4 | 0.25 | 0.14 | < 0.05 | 0.34 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.078 | < 0.05 | < 0.05 | 0.05 | < 0.05 |
| SE + O ₃ + SAT (Effluent after 11 days) | 0.64 | 10 | < 0.05 | < 0.13 | < 0.05 | 0.082 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| SE + O ₃ + SAT (Influent after 14 days) | 0.83 | 6.7 | 0.069 | < 0.13 | < 0.05 | 0.28 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.057 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| SE + O ₃ + SAT (Effluent after 17 days) | 0.44 | 5.8 | < 0.05 | < 0.13 | < 0.05 | 0.24 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| NF Feed (SE + O ₃ + SAT) | 0.52 | 11 | < 0.05 | 0.36 | < 0.05 | 0.17 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 0.057 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| NF Qp (SE + O ₃ + SAT) | 0.45 | 4.0 | < 0.05 | 0.31 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |
| NF Qc (SE + O ₃ + SAT) | 0.51 | 12 | < 0.05 | 0.31 | < 0.05 | 0.19 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.05 |