Biofiltration in Drinking Water Treatment: Reduction of Membrane Fouling and Biodegradation of Organic Trace Contaminants

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The goal of drinking water treatment is to produce and deliver safe water to the consumers. To achieve these objectives water treatment plants are designed based on the concept of the multibarrier approach which combines several drinking water treatment processes in order to increase the reliability of the system. The presence of pharmaceutically active compounds (PhACs), personal care products (PCPs) and endocrine disrupting compounds (EDCs) in drinking water sources is becoming a concern, because of chronic and indirect human exposure to contaminant mixtures at sub-therapeutic levels via drinking water consumption.

Membrane filtration can be an efficient treatment process to remove microorganisms and/or trace organic contaminants from drinking water sources. However, membranes are confronted by a major limitation: membrane fouling. Fouled membranes suffer from a loss in performance either leading to a reduction in flux or a higher pressure requirement. Generally, membrane fouling increases the need for membrane maintenance measures such as backwashing and chemical cleaning which has a negative impact on the operating costs and membrane life time. Severe membrane fouling may even impact permeate quality and/or compromise membrane integrity.

The aim of this study was to establish if biofiltration pretreatment without prior coagulation would be able to control membrane fouling in natural waters. The second objective investigated the removal of trace organic contaminants by individual treatment processes (i.e. biofiltration and membrane filtration). Parallel to this work, the presence and concentration of selected trace organic contaminants in Grand River (Ontario, Canada) were determined. The trace organic contaminants investigated included atrazine, carbamazepine, DEET, ibuprofen, naproxen, and nonylphenol.

Direct biofiltration pretreatment (no coagulation) significantly reduced both reversible and irreversible fouling of ultrafiltration membranes. Results showed that the different degree of reduction of hydraulically reversible fouling was primarily attributed to the absolute concentration of a specific fraction of the dissolved organic matter (i.e. biopolymers) in the biofilter effluent (i.e. membrane feed).

The study also suggests that the composition of biopolymers rather than their absolute concentration is important for the control of irreversible fouling.

High pressure membranes such as nanofiltration membranes are also subjected to fouling. Results showed that biofiltration pretreatment was able to achieve fouling control but membrane characteristics (i.e. molecular weight cut off) influence the efficiency of the pretreatment. This study also showed that not only biopolymers but also humic substances and low molecular weight acids are being rejected by nanofiltration membranes.

Selected trace organic contaminants were detected in Grand River water in the low ng/L range with detection frequencies between 48 to 100%. Seasonal occurrence patterns could be explained by compound use and possible degradation mechanisms. These results confirm the impact of human activities on the Grand River.

This study showed that under the right conditions rapid biofiltration is capable of completely removing biodegradable emerging contaminants at ng/L concentrations. DEET, ibuprofen, and naproxen were biodegradable and therefore amenable to removal while carbamazepine and atrazine were recalcitrant. Factors such as empty bed contact time, influent concentration, and temperature influenced the biodegradation kinetics.

Finally, both membrane and contaminant properties influenced the degree of rejection achieved by nanofiltration membranes. Results showed that steric hindrance and electrostatic repulsion were the major rejection mechanisms.

Several benefits are associated with the use of direct biofiltration for drinking water treatment. These benefits include: the removal of easily biodegradable organic matter leading to biologically stable effluents; the removal of biodegradable trace organic contaminants contributing to the multibarrier approach; the absence of chemicals coagulation which is of advantage for operations in isolated areas; the simple operation and maintenance which is an advantage for locations with limited trained operators; and finally if used prior to membrane filtration biofiltration pretreatment can control membrane fouling.

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List of Acronyms

AFM: Atomic force microscopy
ASA: Acetylsalicylic acid
AOC: Assimilable organic carbon
AOP: Advanced oxidation processes
ATP: Adenosine 5'-triphosphate
BDOC: Biodegradable dissolved organic carbon
BOM: Biodegradable organic matter
BP: Biopolymers
B1: Biofilter with 5 minutes empty bed contact time
B2: Biofilter with 14 minutes empty bed contact time
B3: Control column
CA: Cellulose acetate
DOC: Dissolved organic carbon
DOM: Dissolved organic matter
EBCT: Empty bed contact time
EDCs: Endocrine disrupting substances
EFM: Epifluorescence microscopy
EfOM: Effluent organic matter
EPS: Extracellular polymeric substances
EEM: Excitation/emission matrix
GC/MS: Gas chromatography with mass spectra detector
GAC: Granular activated carbon
H1: High 1 period of spiking contaminants at high concentration of 5 μg/L
H2: High 2 period of spiking contaminants at high concentration of 5 μg/L
H3: High 3 period of spiking contaminants at high concentration of 5 μg/L
HPC: Heterotrophic plate count
HS: Humic substances
IEP: Isoelectric point
L1: Low 1 period of spiking contaminants at low concentration of 500 ng/L
L2: Low 2 period of spiking contaminants at low concentration of 500 ng/L
L3: Low 3 period of spiking contaminants at low concentration of 500 ng/L
L4: Low 4 period of spiking contaminants at low concentration of 500 ng/L
LCOCD: Liquid chromatography with organic carbon detector
Log K_{ow}: Octanol-water partitioning coefficient
LMWA: Low molecular weight acids
LMH: Liter per membrane area per hour
LOD: Limit of detection
LOQ: Limit of quantification
LPM: Low pressure membrane

MF: Microfiltration membrane
MWCO: Molecular weight cut off
NDR: Negligible DOC removal
NF: Nanofiltration membrane
NOM: Natural organic matter
NP: nonylphenol
PA: Polyamide
PhACs: Pharmaceutically active substances
PAH: Poly(amide-hydrazide)
PC: Principal component
PCA: Principal component analysis
PCPs: Personal care products
PES: Polyethersulfone
pKa: dissociation constant
PVDF: Polyvinyl fluoride
RF: Roughing filter
RFSP: Roughing filter spike with trace organic contaminants
RO: Reverse osmosis
SDR: statistically significant DOC removal
SEM: Scanning electron microscopy
SUVA: Specific ultraviolet absorbance
TDCC: Total direct cells count
TOC: Total organic carbon
TMP: Transmembrane pressure
UF: Ultrafiltration membrane
UV: Ultraviolet
UV_{254}: Absorbance of ultraviolet (UV) light at a wavelength of 254 nm
Vs: Specific volume (L/m^2) or (m^3/m^2)
WWTP: Waste water treatment plant
ΔTMP: Difference of TMP during a cycle

Chapter 1

INTRODUCTION

1.1 Problem Statement

The ultimate goal of drinking water treatment is to produce and deliver safe water to the consumers. In North America, in order to achieve this objective, water treatment plants are designed and engineered based on the concept of the multibarrier approach which combines several drinking water treatment processes in order to increase the reliability of the overall system. The objective is to produce drinking water that is colorless, odourless, and free of pathogens and contaminants.

Over the past decade, the development of suitable analytical instruments and methods has allowed the detection of trace organic contaminants at low concentration (i.e. μg/L to ng/L) in drinking water and its sources (Yu *et al.*, 2007; Reemtsma *et al.*, 2006; Ternes, 2001; Kuch and Ballschmiter, 2001; Lopez *et al.*, 1998; Bucheli *et al.*, 1997). The presence of pharmaceutically active compounds (PhACs), personal care products (PCPs) and endocrine disrupting compounds (EDCs) in surface water at low concentration is often observed in industrialized areas and where indirect water reuse is practiced (Loraine and Pettigrove, 2006; Lindqvist *et al.*, 2005; Kolpin *et al.*, 2002). Indirect water reuse happens when sewage effluent is released into streams and rivers that are in turn used as a source of raw water for the production of potable supplies for communities living downstream (van Dijk-Looijaard and van Genderren, 2000). The increasing demands on the fresh water supplies of the world will probably lead to greater incidences of indirect and direct water-reuse situations as the spatial and temporal distances between wastewater and drinking water become further reduced (Jones *et al.*, 2005).

Chronic and indirect human exposure to PhACs, PCPs, and EDCs at sub-therapeutic levels via drinking water consumption is becoming a concern (Sudakin and Trevathan, 2003; Daugthon and Ternes, 1999). In fact, regardless of the absence of any proven risks, drinking water would provide a direct route into the body for any contaminants that might be present. Based on precautionary principles, drinking water should be free of these contaminants to reduce the risk of long term exposure and unpredictable effects on human health (Huber *et al.*, 2003). Most likely, the presence of PhACs, PCPs, and EDCs at the low concentrations reported in North America and Europe would be of little or no consequence in healthy adults. However, if present, effects might be more pronounced for the young, during vulnerable life stages such as pregnancy or in individuals prone to allergic reactions (Webb, 2005; Schwab *et al.*, 2005; Webb *et al.*, 2003; Schulman *et al.*, 2002; Christensen, 1998). In fact, little is known about the exposure of foetuses via transplacental exposure from pregnant women who consume drinking water with low concentrations of contaminants (Pomati *et al.*, 2006). This question attracts research attention because of the growing evidence that these compounds can affect the reproduction and development of humans and fauna (Servos *et al.*, 2001; Christensen, 1998). Another concern with respect to the presence of PhACs, particularly antibiotics, is the possible development of drug resistant pathogens (Jones *et al.*, 2005; Kümmer, 2005).

Membrane filtration is an efficient and economical option to treat contaminated drinking water sources. Depending on the type of membrane, contaminants such as particles, bacteria, viruses, dissolved solids, organic matter, disinfection by-product precursors, inorganic ions, regulated, and unregulated organic compounds can be removed by membrane filtration (Huang *et al.*, 2009; Bellona et al., 2004; Laîné et al.,. 2000; Jacangelo et al., 1998). In fact, high pressure membranes, i.e. nanofiltration (NF) and reverse osmosis (RO), have already been identified to be effective for the removal of PhACs and EDCs (Comerton et al., 2009; Verliefde et al., 2009; Nghiem et al., 2004; Kimura et al., 2003). This is of particular interest given the anticipated increase in involuntary and voluntary water reuse. Moreover, membrane filtration has also other advantages such as a decrease in initial capital cost and a small footprint requirement compared to conventional treatment options (Schäfer *et al.*, 2001). Nowadays space allocated in a city for industrial usage such as a water treatment plant may be limited (Schipper et al., 2004). Thus, the compact nature of a membrane filtration plant may be desirable. Moreover, the operation is relatively simple and can be subjected to a high degree of automation.

However, all categories of membranes are subjected to a major limitation: membrane fouling (Jerman *et al.,* 2007). Fouled membranes suffer from a loss of performance manifesting itself either as a reduction of flux when operating at a constant pressure or a higher pressure requirement to maintain a preset flux. This is due to the deposition of dissolved and/or suspended constituents on the membrane surface, on the pore opening, or within the pore. A decrease in permeate quality and membrane degradation are also potential consequences of membrane fouling (Agenson and Urase, 2007). Moreover, a well known consequence of membrane fouling is an increase in the frequency of hydraulic backwashing and chemical cleaning. This in turn has a negative impact on the operating costs. The most effective way to minimize fouling and to optimize the membrane lifetime depends on the nature of the fouling process (Cheryan, 1986). With certain feed water qualities better results are obtained using pretreatment while for source waters with lower fouling potential optimization of operating conditions may work better. Common membrane pretreatment processes include sand filtration (Huang *et al.*, 2009), coagulation (Ratajczak, 2007; Schäfer *et al.*, 2001; Soffer *et al.*, 2000), or low pressure membrane filtration prior to NF or RO (van der Bruggen *et al.*, 2004).

A novel approach to pretreatment is the use of rapid biofiltration prior to membrane filtration. Rapid biofiltration without prior coagulation represents a "green" and chemical free alternative to the above mentioned pretreatment processes for fouling control. Moreover, the operation of rapid biofilters is relatively simple. Previous bench-scale studies on rapid biofiltration using model solutions have indicated its potential to reduce membrane fouling (Mosqueda and Huck, 2009; Zhang *et al.*, 2007; Basu, 2004; Basu and Huck, 2004). Using the effluent of a biofilter fed with tap water, augmented with easy-biodegradable organics and humic material Basu *et al.* (2004) and Mosqueda *et al.* (2009), suggested that biofiltration pretreatment has the potential to reduce fouling on ultrafiltration (UF) membranes.

Generally, conventional rapid biofiltration is situated in the middle of a treatment train usually following coagulation and ozonation. Typical applications of conventional rapid biofiltration have been used to reduce the potential for microbiological regrowth within the distribution system (Hu *et al.*, 1999), to decrease disinfection by-product formation potential through reduction of organic precursors, to decrease chlorine demand of treated water, and lately to treat water containing taste and odour causing contaminants (Elhadi, 2004). Moreover, biofiltration has also been used for many decades in drinking water treatment via slow sand filtration or ground passage

(Ray *et al.*, 2002; Graham, 1999; Bower and Crowe, 1988). This sustainable water treatment process has demonstrated its efficiency for the removal of particles, pathogens, and organic matter (Ray *et al.*, 2002). However, due to the slow filtration rates these processes are not suitable as membrane pretreatment.

1.2 Objectives

The two main objectives of this research focused on different applications of chemically unassisted rapid biofiltration in drinking water treatment.

The first set of objectives is related to the use of biofiltration as an alternative membrane pretreatment to control fouling of subsequent UF and NF membranes. Encouraged by past research results using model waters this research aimed to establish if this pretreatment process would be able to control foulants in natural waters. If successful this would provide proof of concept, thus bringing the application of chemically unassisted rapid biofiltration closer to being practiced at full-scale.

The second set of objectives investigated the removal of trace organic contaminants by individual treatment processes (i.e. biofiltration and membrane filtration). These contaminants are present in many of the source waters commonly treated by membrane filtration. It was therefore prudent to concurrently investigate the ability of the processes studied in the first objective to remove these contaminants. The two general objectives and associated specific objectives are further defined below:

Application 1 - General objective:

Evaluate the impact of chemically unassisted rapid biofiltration pretreatment on the fouling of UF and NF membranes.

Application 1 - Specific objectives:

1) To characterize the natural organic matter present in surface water causing membrane fouling on NF and UF membranes.

2) To evaluate the seasonal performance of biofiltration pretreatment to control fouling on NF and UF membranes.

Application 2 - General objective:

Evaluate the performance of rapid biofiltration and membrane filtration on the removal of selected trace organic contaminants.

Application 2 - Specific objectives:

1) To determine the seasonal occurrence of selected PhACs and EDCs in the Grand River.

2) To evaluate the ability of rapid biofiltration to degrade selected PhACs and EDCs at two different environmentally relevant influent concentrations.

3) To evaluate the efficiency of NF and UF membranes for the removal of selected PhACs.

1.3 Thesis Structure

The literature review presented in chapter 2 includes an overview of the relevant published information related to this research. Chapter 3 presents general materials and methods employed over the course of this research and also describes the selection of organic trace contaminants studied during this research. More specific methods are being presented in the related results chapter.

Chapter 4 presents the results of the concentration of selected contaminants in industrially and agriculturally impacted surface water. The author acknowledges the important contributions of Bob McPhail for the analysis of selected PhACs and EDCs for the different sub-projects of this research.

Chapter 5 presents the results related to the performance of the rapid biofilters for the removal of selected organic trace contaminants. In this chapter, microbiological analyses of the filter media are described and the author recognizes the significant contributions of Dr. Michele Van Dyke in the implementation of the methods. Estimates of kinetic parameters for the transformation of biodegradable contaminants were determined by the author.

Chapter 6 demonstrates the performance of the biofilters for fouling control of UF and NF membranes. The natural organic matter was characterized through liquid chromatography with organic carbon detector (LCOCD) analyses, a technique which was not available at the University of Waterloo. The author therefore acknowledges Dr. Jens Haberkamp from the Technical University of Berlin for processing the samples. The author also thanks Ramila Peiris from the Department of Chemical Engineering at the University of Waterloo for providing and interpreting the results of the fluorescence spectroscopy analyses.

Chapter 7 shows the ability of UF and two NF membranes to reject the selected contaminants in 5 day long experiments.

The final chapter addresses the overall conclusions and recommendation for further research. It also describes the potential application of the technologies investigated and the contributions to knowledge.

Chapter 2

LITERATURE REVIEW

First, general concepts of and relevant factors in biological filtration for drinking water applications are discussed, followed by a review of membrane filtration. In addition, trace organic contaminants present in the Canadian environment are introduced and removal efficiencies of common water treatment processes for such contaminants are presented.

2.1 General Concept of Biological Filtration for Drinking Water Treatment

The principal objective of biological filtration is to produce drinking water that is biologically stable and thus does not support significant microbiological growth during its distribution (Rittmann, 1995). Although commonly applied in Europe, biological filtration is still an emerging drinking water process in North America. In The Netherlands and Germany, biological treatment is often applied through slow sand filtration, ground passage, bank filtration, or rapid filtration following ozonation (Ray *et al.*, 2002; Kuehn and Mueller, 2000; Bower and Crowe, 1988; Sontheimer, 1980; Sontheimer *et al.*, 1978). In France, biological processes are usually performed in second stage granular activated carbon (GAC) contactors (Urfer *et al.*, 1997; Bablon *et al.*, 1988).

Studies have demonstrated that biological filtration is an effective water treatment process for reducing the amount of electron donors such as biodegradable organic matter (BOM), ammonium, nitrite, ferrous iron, manganese (II), and sulfides causing biological instability in the distribution system (Rittmann and McCarty, 2001). Biological instability in the distribution system can be the source of taste and odour events, consumes dissolved oxygen, accelerates corrosion, and causes an increase of heterotrophic plate counts, regrowth of bacteria, and turbidity (Rittmann and McCarty, 2001). Biological filtration is able to diminish bacterial regrowth within the distribution system and

decrease the formation of disinfection by-products after final disinfection (Weiss *et al.*, 2003; Huck *et al.*, 1998; Urfer *et al.*, 1997; Collins *et al.*, 1992).

Engineered biological filters are designed to optimise BOM removal without compromising particulate removal (Huck *et al.*, 1998). In general, for water treatment, the primary substrate (electron donor) for the biomass is the BOM. The primary substrate sustains the growth and maintains the biomass (Kobayashi and Rittmann, 1982; Stratton *et al.*, 1983). Usually, in surface water, the BOM has low concentrations, has a heterogeneous nature, and can vary seasonally. The major components of BOM include humic substances, amino acids, carbohydrates, and if applicable ozonation by-products (Urfer *et al.*, 1997). Several techniques involving batch incubation have been developed to measure BOM.

1. Using pure strains of bacteria selected by their ability to utilize different types of organic compounds, van der Kooij (1992) developed a method analysing the assimilable organic carbon (AOC). The growth of the pure strains (i.e. Pseudomonas fluorescens strain P17 and a Spirillum species strain NOX) is assayed by plate count and converted in concentration of AOC (van der Kooij, 1992). This method is dependent on the metabolic activity of the organisms tested and estimates only the easily biodegradable organic material. Van der Kooij determined that biologically stable water should contain less than 10 µg acetate-C eq/L and such value can be obtained using biological filtration (van der Kooij, 1992). However, if residual disinfectant is maintained within the distribution system, higher AOC in treated water will not necessarily cause regrowth in the distribution system.

2. Biodegradable dissolved organic carbon (BDOC) is an estimate of the biodegradable fraction of the dissolved organic carbon. In river water, BDOC represents between 17 % to 41 % of the total dissolved organic carbon (DOC) (Servais *et al.*, 1987). BDOC can be evaluated using mixed bacteria culture having the same origin as the sample. Sample pretreatment consist in filtration (0.2 µm) for sterilization purpose. Then an inoculum of the same sample filtered through 2 µm is added to the sterilized sample. Then the sample is incubated in the dark at 20°C for a period of 10-30 days. The BDOC is determined by calculating the rate of bacterial mortality or by measuring the initial and final DOC concentrations (Servais *et al.*, 1987).

For drinking water applications, in order to achieve removal of BDOC, fixed-bed biofilm processes are the most common process employed. The biomass forms a biofilm which consists of an aggregate of microorganisms (i.e. prokaryotic and eukaryotic cells) and extracellular polymeric substances (EPS) (Winkler *et al.*, 2001). The biofilm is attached to a support media such as anthracite and sand in the case of a dual media filter (Rittmann, 1995). The biomass obtains its energy through oxidation and reduction reactions of the primary substrate (Rittmann and McCarty, 2001). However, the redox reactions are often really slow and catalytic reaction is required to increase the kinetics of the reaction to provide the energy to grow and maintain the cells.

The basic phenomena controlling biological filtration are the following: substrate utilization, substrate diffusion inside the biofilm, mass transport between the bulk liquid and the biofilm, growth, and decay (Rittmann, 1995). The fundamental biofilm kinetics are based on the assumption that the rate limiting primary substrate is the electron donor (Rittmann, 1995). Other assumptions are that kinetics are evaluated under steady-state conditions and that biofilm biomass exceeds the suspended biomass. The mass balance of the substrate, the suspended biomass, and the biofilm biomass are described by the following equations (Rittmann, 1995):

Substrate	$0 = Q\left(S^{\circ} - S\right) - KaV$	eq. 2.1
Suspended biomass	$0 = -QX_a + r_{\det}$	eq. 2.2
Biofilm biomass	$0 = \left(KY - bX_f L_f\right)aV - r_{\det}$	eq. 2.3

where (s refers to the substrate and x to the biomass):

Q is the flow rate, m^3 day^{-1},
S° is the influent substrate concentration, gs m^{-3},
S is the concentration of rate limiting substrate in the bulk liquid, gs m^{-3},
K is the substrate flux into the biofilm, gs m^{-2} day^{-1},
a is the specific area of biofilm, m^{-1},
V is the total volume of the reactor, m^3,
X_a is the concentration of active biomass in the bulk liquid, gx m^{-3},
r_{det} is the rate of detachment of biofilm, gx day^{-1},
Y is the true yield of biomass grown per unit of substrate consumed, gx gs^{-1},
b is the endogenous decay rate, $days^{-1}$,
X_f is the density of the biofilm, gx m^{-3},
L_f is the biofilm thickness, m,
$X_f L_f$ is the biofilm accumulation per unit surface area, gx m^{-2}

Equation 2.1 indicates that the substrate removal (S°-S) is proportional to the substrate flux (K). Equation 2.2 indicates that the biomass contained in the effluent (X_a) is proportional to the rate of detachment (r_{det}). Equation 2.3 indicates that the rate of detachment (r_{det}) is also proportional to the biofilm growth rate (KY-b X_f L_f).

The drawing of an idealized biofilm and its penetration profiles are presented in Figure 2.1 (Rittmann, 1995). An idealized biofilm has a smooth surface, a uniform biomass density (X_f), and a uniform thickness (L_f).

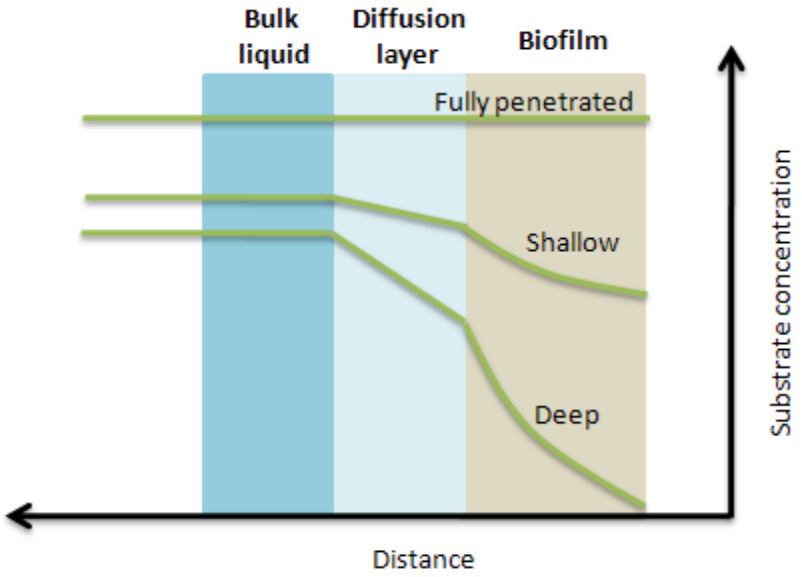


Figure 2-1 Idealized biofilm and different penetration profiles (Adapted from Rittmann, 1995).

A deep biofilm is characterized by a complete reduction of the primary substrate. When the concentration of the substrate does not reach zero, the biofilm is characterized as shallow. Finally, when minimal reduction of substrate occurs the biofilm is considered fully penetrated.

Fick's First Law (equation 2.4) describes the transport of substrate (here defined as K_T) from the bulk liquid to the surface of the biofilm (Rittmann, 1995). At steady state conditions, Fick's First law is described by equation 2.4:

$$K_T = \frac{D}{L}(S - S_s) \qquad \text{eq. 2.4}$$

Where:
D is the substrate molecular diffusion coefficient in the bulk liquid, $m^2\ day^{-1}$,
L is the thickness of the diffusion layer, m
S_s is the substrate concentration at the outer surface of the biofilm, gs m^{-1}.

The simultaneous diffusion and reaction of primary substrate within the biofilm was described by Rittmann (1995). Transport and reaction of substrate into a biofilm in the direction x is described by equation 2.5:

$$\left[N_x A_{yz} - N_{x+\Delta x} A_{yz}\right] + r\Delta xA = \frac{\Delta C(\Delta x A_{yz})}{\Delta t} \qquad \text{eq. 2.5}$$

Where
A_{yz} is the area normal to x direction
N_x is the flux in x direction
r is the reaction rate
C is the concentration of substrate

The one dimensional transport and reaction of substrate into a biofilm for a Δx is then described by equation 2.6:

$$\frac{1}{A_{yz}}\left[\frac{N_x A_{yz} - N_{x+\Delta x} A_{yz+\Delta x}}{\Delta x}\right] + r = \frac{\Delta C}{\Delta t} \qquad \text{eq. 2.6}$$

If both Δx and Δt approach zero the following derivative is obtained:

$$-\frac{1}{A_{yz}}\left[\frac{\partial\left(N_x A_{yz}\right)}{\partial x}\right] + r = \frac{\partial C}{\partial t} \qquad \text{eq. 2.7}$$

Consequently, for steady state conditions and assuming that A_{yz} does not change within the biofilm (x), the transport and reaction rate of substrate into biofilm is given by equation 2.8:

$$N_x = -D\frac{dC}{dx} \qquad \text{eq. 2.8}$$

Then the reaction rate is defined by equation 2.9

$$-\frac{dN_x}{dx} + r = 0 \qquad \text{eq. 2.9}$$

By substitution of diffusive flux for N, the reaction rate is given by the second derivative (equation 2.10):

$$r = \frac{dN}{dx} = D\frac{d^2C}{dx^2} \qquad \text{eq. 2.10}$$

The reaction rate is also influenced by the presence of enzymes. Enzymes are large macromolecule groups of proteins characterised by specific arrangements of amino acids (Rittmann and McCarty, 2001). The enzymes are characterised by their specificity and the rate of the reaction they catalyze. The rate of the reaction may be influenced by pH, temperature, and substrate concentration (Rittmann and McCarty, 2001). The optimal enzymatic activity generally occurs at a specific pH. Some enzymes may have their maxima at lower pH values, while others may benefit from higher pH values. The enzymatic activity is also influenced by temperature. The enzymatic reaction rate can double for each 10°C (Rittmann and McCarty, 2001). However, past their optimal temperature range, enzymes which have complex structures can experience denaturation which causes a decline in the activity which will lead it to eventually cease. Moreover, low water temperature may also influence cell permeability, or the ability of nutrients to be transported into the cell. The substrate concentration also influences the enzymatic reaction rate. The Michaelis-Menten coefficient (K_M) represents the affinity between the substrate and the enzyme (Rittmann and McCarty, 2001) and is influenced by the substrate concentration as shown in Figure 2.2.

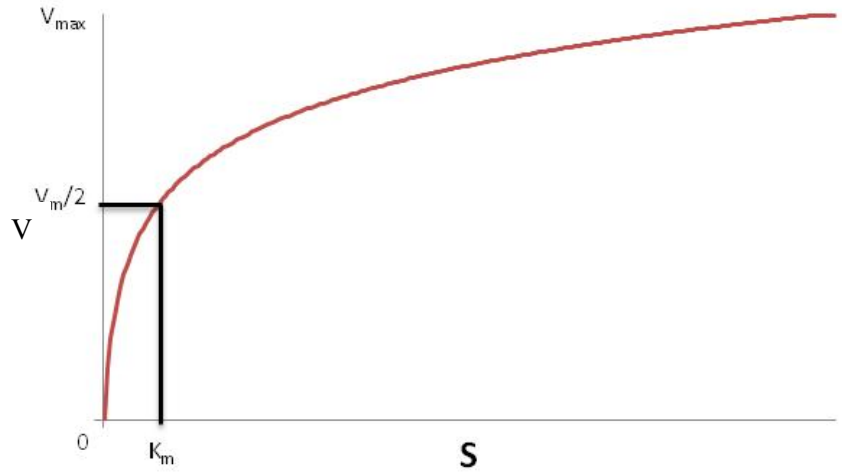


Figure 2-2 Effect of substrate concentration (S) on the enzymatic transformation rate (v). (source: Rittmann and McCarty, 2001)

The first reaction involves the formation of a complex between the enzyme (E) and the substrate (S). Eventually, the complex ES breaks down into the free enzyme (E) and product (P) (equations 2.11 and 2.12).

$$E + S \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} ES \qquad \text{eq. 2.11}$$

$$ES \underset{k_{-2}}{\overset{k_2}{\Leftrightarrow}} E + P \qquad \text{eq. 2.12}$$

Equation 2.13 shows the relation between the ES complex and K_M:

$$ES = \frac{E \times S}{K_M + S} \qquad \text{eq. 2.13}$$

The enzymatic reaction rate (v) or the rate of product formation is given by equation 2.14:

$$v = k_2 ES \qquad \text{eq. 2.14}$$

The activity and the type of enzyme produced by microorganisms are influenced by several factors as cited by Rittmann and McCarty (2001):

> "Microorganisms are able to produce hundreds of different enzymes, and the production of each must be regulated in some coordinated fashion so that the organism can properly respond to changes in substrate types and concentrations, environmental conditions, and its needs of energy for movement, growth, and reproduction."

Microorganisms control the production of enzymes depending on the availability of substrate. Constitutive enzymes are produced at all times in active cells. When a substrate is not present or is present at low concentration, microorganisms may turn off the production of a specific enzyme because the production of enzymes requires energy. Thus, microorganisms will produce certain enzymes intermittently. These are described as inducible enzymes.

Enzymes may be intracellular or extracellular. The task of an extracellular or exoenzyme occurs outside of the cell wall and involves breaking down large nutrients into smaller molecules which are able to pass through the cell wall. In contrast, the action of an intracellular or endoenzyme happens within the cell (Rittmann and McCarty, 2001).

In an engineered biofilter, microbial communities adapt to variable conditions (i.e. nutrient concentration, type of nutrient, or water temperature) using one or several mechanisms such as selective enrichment, enzyme regulation, exchange of genetic information, inheritable genetic change, or alteration of their environment (Rittmann and McCarty, 2001).

Selective enrichment is an important mechanism in environmental processes and generally leads to a significant change in the microbial community. It usually requires a few days to several months for the selective enrichment to happen. Microorganisms called copiotrophs are well suited for the feast and famine lifestyles present in biofilters for drinking water treatment. Copiotrophs use several strategies to handle variation in substrate loading and outgrow the oligotrophs. Generally, copiotrophs have very fast maximum specific growth rates, they can rapidly take up and use substrates, and they can go into dormant states in a period of famine (Rittmann and McCarty, 2001).

A change in the community structure is not required during the enzyme regulation adaptive mechanism and it usually requires a shorter adaptation period (i.e. one hour). In this case, enzyme synthesis starts or stops in response to environmental stresses (Rittmann and McCarty, 2001).

The exchange of genetic material can occur rapidly within hours to days, and in this case the community structure usually stays the same. Exchange of genetic material occurs via conjugation, transformation, and transduction. Inheritable genetic changes come from mutation, duplication, and recombination. This adaptation process is considered as a community evolution because the changes induced in the community are permanent. Usually adaptation by inheritable genetic changes requires a long adaptation period and may not be reproducible.

Finally, microbial communities can alter their environment by using preferred substrates, supply deficient substrate, a change of the redox potential, a change of pH, or eliminate the presence of toxic compounds (Rittmann and McCarty, 2001).

A second objective of engineered biological filters is the removal of trace organic contaminants or secondary utilization. Micropollutants are considered secondary substrates because their concentration is often very low and they are in many cases transient in source water. If a sufficient amount of biomass is accumulated on the media, secondary utilization of biodegradable material is possible (Stratton *et al.*, 1983; Kobayashi and Rittmann, 1982). However, the transformation of secondary substrate does not necessarily support the growth and maintenance of the biomass (Stratton *et al.*, 1983; Kobayashi and Rittmann, 1982).

Very few studies have been performed on the biodegradation of PhACs and EDCs in engineered water treatment processes. Quintana *et al.* (2005) studied the biodegradation of naproxen and ibuprofen in wastewater membrane reactors. They demonstrated that both ibuprofen and naproxen can be transformed at different degrees by co-metabolic degradation in the presence of another carbon source.

2.1.1 Factors Affecting Biofiltration

A considerable amount of research on biological filtration for water treatment has been performed and several factors influencing biofiltration for drinking water treatment will be discussed.

Temperature

As mentioned previously the water temperature will affect the production of enzymes and the transport of nutrients into the biofilm and the microbial cells. Theoretically, BOM removal should increase at higher temperatures (Urfer *et al.*, 1997). For anthracite-sand filters Krasner *et al.* (1993) and Coffey *et al.* (1995) showed that the time required to achieved steady-state removal of glyoxal was shorter at water temperatures between 20-25°C than 10-13°C. Similar conclusions were reported by Daniel and Teffy (1995) for aldehyde removals. Urfer *et al.* (1997) indicated that for BOM removal temperature was an important factor and the amount of biomass on the media was not the rate-limiting factor.

Natural organic matter (NOM) source

NOM is a complex mixture of humic acids, degradation products of humic acids, fulvic acids, small organic acids, and biopolymers such as proteins and polysaccharides. NOM has a molecular weight distribution between 500 and 3000 Da (MWH, 2005) demonstrating its heterogeneous character. The complexity of NOM makes it difficult to measure individual compounds thus the total organic carbon (TOC) is used as a surrogate measure. In general, TOC concentrations of surface waters vary between 1 to 20 mg C/L (MWH, 2005). DOC is the fraction of TOC remaining in solution after filtration through an 0.45 μm filter. Absorbance of ultraviolet (UV) light at a wavelength of 254 nm (UV_{254}) is also a surrogate for NOM concentrations. Chromophores present in the NOM can absorb UV light and a relationship between UV_{254} absorbance and NOM concentration has been established (MWH, 2005). The specific UV absorbance (SUVA) is calculated as the ratio of UV_{254} to DOC. SUVA gives an indication of the unsaturated carbon-carbon bonds of NOM and has been correlated with the hydrophobicity of the NOM. Greater SUVA values are an indication of increased aromaticity and other unsaturated bonds. Larger SUVA values may be associated with a reduced biodegradability of the NOM (Goel *et al.*, 1995; Hosalki *et al.,* 1995). Moreover, Goel *et al.* (1995) determined that biodegradability of NOM increased when larger fractions of low molecular

weight organics are present, because of their lower mass transfer resistance and easier enzymatic attack.

Contact time

The empty bed contact time (EBCT), a key operational parameter, is defined by Hozalski *et al.* (1995) as:

> ‘‘The empty bed volume of the column without media divided by the volumetric flow rate of the feed solution.”

In practice, EBCT is directly influenced by the loading rate and the filter depth. Hozalski *et al.* (1995) indicate that a loading rate less than 5 m/h is ideal for biological filtration to allow the biomass to attach to the media. It also provides enough shear stress to limit excessive accumulation of biomass on the media.

In general, at temperatures above 10°C, the increase in EBCT results in an increase in removals of TOC, DOC, BDOC, AOC, and trihalomethanes (THM) formation potential (Huck *et al.*, 2000; Hosalski *et al.*, 1995; LeChevallier *et al.*, 1992; DeWater and DiGiano, 1990; Servais *et al.*, 1989). However, the increase in removal is less than proportional than the increase in EBCT. Moreover, removal of BDOC plateaued at an EBCT value of 25 minutes (Hozalski *et al.*,1995).

The biodegradability of organic matter fractions differs as demonstrated by Prevost *et al.* (1992) and LeChevallier *et al.* (1992), who showed that shorter EBCTs are required for the removal of AOC compared to BDOC and TOC. Thus higher contact times may be required for the removal of less readily biodegradable organic matter.

However, Zang and Huck (1996) and Zang (1996) demonstrated theoretically and practically that longer contact times will only slightly improve BOM removal. Thus EBCTs between 4 and 25 minutes may be optimal for drinking water treatment depending on the goal to be achieved (Zang and Huck (1996) and Zang (1996).

However, some studies suggested that EBCT does not affect the removal of organics (Krasner *et al.*, 1993). A study performed by Servais *et al.* (1994) pointed out that hydraulic loading

may not be a key parameter in biological removal of BOM. This finding indicates that external mass transfer may not be the main mechanism in BOM removal during biofiltration (Urfer *et al.*, 1997).

Type of media

The selection of filter media has major cost implications and should depend on design objectives and site-specific characteristics (e.g. water temperature). Media commonly used for drinking water treatment to achieve BOM removal are adsorptive media such as GAC and non adsorptive media such as anthracite and sand (Wang *et al.*, 1995; Krasner *et al.*, 1993; LeChevallier *et al.*, 1992). The micropores of GAC (1-100 nm) are not favourable to biogrowth because the typical diameter of bacteria is greater than 200 nm. However, the irregular GAC surface is suitable for bacteria attachment and offers protection against shear stress. Because the effective size of sand is usually smaller than GAC, the specific surface area (i.e. unit surface per unit volume of filter) might be higher in a sand filter (Urfer *et al.*, 1997). Consequently, the total biomass attached as biofilm may be more favourable in a sand filter compared to a GAC filter.

Huck *et al.* (2000) has demonstrated that biofiltration can be effectively implemented in anthracite/sand filters by showing that BOM removals achieved in anthracite/sand filters is similar to removals achieved in GAC/sand filters. GAC/sand filters have advantages such as a faster reestablishment of BOM removal after periods out of service, better recovery from intermittent chlorination, and better tolerance of disinfectant in backwash water (Urfer *et al.*, 1997). GAC/sand filters also showed better TOC and DOC removal than anthracite/sand filters possibly caused by adsorption processes or continuous bioregeneration. However, the cost of GAC is much higher than anthracite.

Backwashing procedure

Optimized backwashing procedures are critical for long term performance of the biofilters (Chipps *et al.*, 1995; Bouwer *et al.*, 1988; Camper *et al.*, 1987) in order to control the accumulation of particulate/colloidal material and biofilm.

Detachment of biofilm from the media is a complex process influenced by shear stress of the bulk liquid, contact between particles, or turbulences caused by pressure fluctuations. Backwashing is therefore necessary to control and prevent excessive detachment of biofilm from the surface of the

media during filtration. Because the biofilters are also used for particle removal, backwashing procedures also restore hydraulic capacity (Hozalski *et al.*, 1995).

The presence of chlorine in the backwash water does decrease the amount of biomass in anthracite/sand filters. Given a sufficient supply of nutrients, the factors influencing the amount of biomass in biological filters are the continuous application of chlorine and the water temperature (particularly under 5°C). The tolerability of chlorine should be determined based on the treatment objectives.

Possibly due to the presence of biomass, biofilters may experience a rapid increase in head loss. Thus, the backwashing strategy should consider the physical performance of the biofilter. Usually, backwash including air-scour provides sufficient media cleaning to mitigate rapid head loss build-up. Ahmad and Amirtharajah (1995) showed that the biomass is attached with a greater force than nonbiological particle to media. Their findings demonstrate that optimized procedures to remove nonbiological material with or without air scour may not lead to a major loss of biomass attached to the media. Moreover, a study on nonbiological filters showed that the best technique to remove particles combined the use of air and water at subfluidization velocities to create collapse pulsing conditions (Amirtharajah, 1993).

In Table 2.1, Huck *et al.* (2000) summarized and rated the degree of control which a utility may have over a parameter and the relative effect of major parameters influencing biological filtration.

Table 2-1 Degree of control (⊗) and effect (♦) of major parameters influencing biological filtration (source: Huck *et al.*, 2000)

Parameter	None	Low	Moderate	High
Media type			♦	⊗
Chlorination			⊗	♦
Filtration rate (EBCT)			⊗♦	
Backwashing method			♦	⊗
BOM loading		⊗	♦	
Temperature	⊗			♦
Time since startup	⊗			♦

Utilities have a high degree of control on the type of media and the employed backwashing method and both parameters have a moderate effect on the biological removal of DOM. The EBCT and BOM loading also have moderate effects on the BOM removal but they can only be controlled to moderate and low degrees. On the other hand, chlorination (i.e. presence of residual chlorine in backwash water), water temperature, and time since start up have high effects on the BOM removal. The concentration of disinfectant in the backwash water can be controlled but utilities have limited control on the temperature and time since start up.

2.1.2 Measurement of Biomass on Media

In addition to biofilter performance, the measurement of biomass on media provides the assurance of colonization of the media. Several approaches are available to characterise biomass on media but below are the most common techniques used for biofilters.

Direct method

Using epifluorescence microscopy (EFM) direct bacterial enumeration has been used to determine the number of microorganisms contained in a sample (Camper *et al.*, 1985; Hobbie *et al.*, 1977). EFM analysis provides a biomass count which includes viable and non-viable cells (Fry, 1988). In order to avoid changes in the number of bacteria, in their size, or in their shape the sample must be fixed immediately after sampling (Fry, 1988). The basic method involves staining bacteria with a chemical fluorochrome, vacuum filtration of the sample onto a non fluorescing polycarbonate membrane filter,

and counting using epifluorescence microscopy (Standard Methods, 2005). While some studies point out the incomplete removal of bacteria from the sediment which can affect the enumeration (Bott and Kaplan, 1985), the method developed by Camper *et al.* (1985) shows a recovery of 90 % of heterotrophic plate count (HPCs) and coliform from GAC particles.

Indirect methods

Adenosine 5'-triphosphate

The energy released from oxidation-reduction reactions is captured by the microorganisms. During these reactions, the electron from the primary donor is transferred to an intracellular electron carrier which transports it to a terminal electron acceptor. An example of a primary electron carrier is Adenosine 5'-triphosphate (ATP). ATP is a useful indicator for biochemical reactions because living organisms use ATP as "currency" for energy exchange; therefore it is a suitable parameter for the quantification of active biomass (Karl, 1980). Figure 2.3 shows the transfer cycle of energy using ATP as an energy carrier (Rittmann and McCarty, 2001).The concentration of ATP is used as a surrogate to measure the active biomass because the ATP synthesized during catabolism is essential for cellular growth.

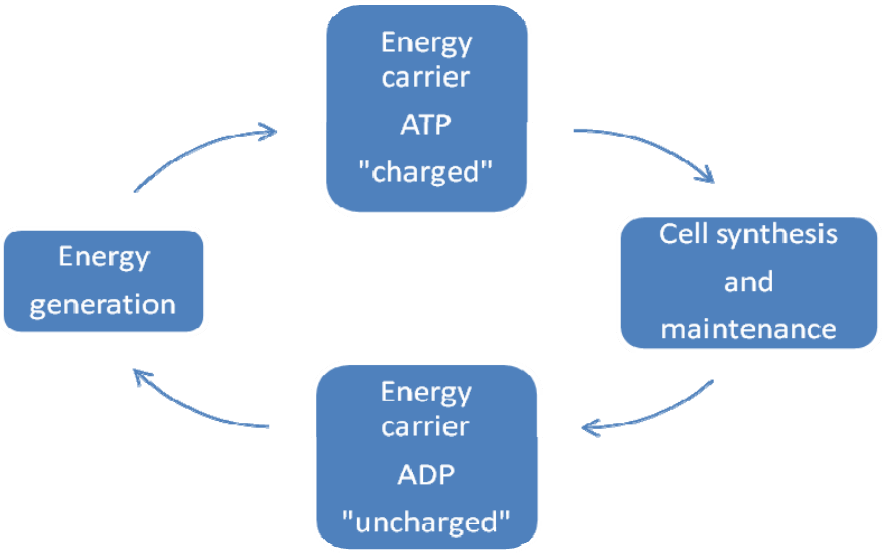


Figure 2-3 Transfer of energy using ATP carrier (adapted from Rittmann and McCarty, 2001)

Phospholipid analysis

Various techniques based on biochemical components of the cell have been developed to measure bacterial biomass in sediment (i.e. ATP or total adenylates, muramic acid, and chlorophylls) (Fry, 1988). However, these techniques have been criticized due to their uncertain recovery of biomass attached to particles or the use of conversion factors to obtain cell numbers or biovolumes of biomass (Fry, 1988; Bakken, 1985; Bratbak, 1985). Thus the need for a simple and accurate technique measuring microbial biomass achieving high recovery was necessary.

Phospholipids constitute approximately 98 % of the bacterial membrane lipid (White, 1983). Upon cell death, lipid phosphate is degraded fairly rapidly (White *et al.*, 1979) and thus phospholipid analysis provides a good indicator of viable microorganisms (Fry, 1999).

Findlay *et al.* (1989) compared the efficacy of phospholipid analysis with the EFM technique and demonstrated that phospholipid analysis presents a more sensitive, accurate, and precise method of phosphate detection leading to a better estimation of the biomass. Replicate and recovery analysis also demonstrated the advantage of the phospholipid analysis approach (Findlay *et al.*, 1989). In phospholipid analysis, lipids-bounded phosphate contained in bacteria can be liberated using a chloroform-methanol extraction in a phosphate buffer. A subsequent extraction using potassium persulfate is used to liberate phosphate from lipids (Findlay *et al.*, 1989). The concentration of phosphate is determined by spectrophotometric analysis by measuring the absorbance at 610 nm.

2.2 Membrane Filtration for Drinking Water Treatment

The purpose of this section is to provide an introduction to membranes processes for drinking water treatment as well as describe the theoretical fundamentals of membrane filtration.

2.2.1 History and Background

Microporous membranes were developed and patented in the USA in the 1920s (Belfort *et al.*, 1994) and their primary usage was for laboratory work such as bacteriological analysis (Lonsdale, 1982). In the 1950s, scientists, engineers, and entrepreneurs realized the potential of membranes in large scale applications. The food industry was one of the first industries to use membranes for clarifying, concentrating, purifying, or sterilizing products such as juice, wine, dairy, and oils (MWH, 2005). Membrane filtration also finds its niche in the treatment of waste such as wastewater and brine recovery (MWH, 2005). Membrane filtration for drinking water applications was first applied in the 1980s to remove microbiological contaminants which were becoming an increased concern for utilities and regulators. Over the last 30 years, advances in membrane design and configurations led to cost reductions thus making membranes an economical option for drinking water treatment. The first membrane filtration plant was commissioned in France in 1988 (Anselme *et al.*, 1999). In North America, the first membrane filtration plants used for drinking water treatment were small capacity and were commissioned between 1991 and 1993 (Lozier and Alspach, 2005). The history and evolution of membrane filtration is summarized in Figure 2.4. As a result of ongoing research, a decrease in the cost of membranes, and more stringent regulations, the use of membrane filtration for the production of drinking water has significantly grown in both Canada and the USA over the past decade.

Several factors have favoured the implementation of membrane filtration plants in Canada, most notably is the serious outbreak of *E.Coli*. in Walkerton in 2000 due to tap water contamination, as well as the declining quality of water sources, and the substantial growth of cities.

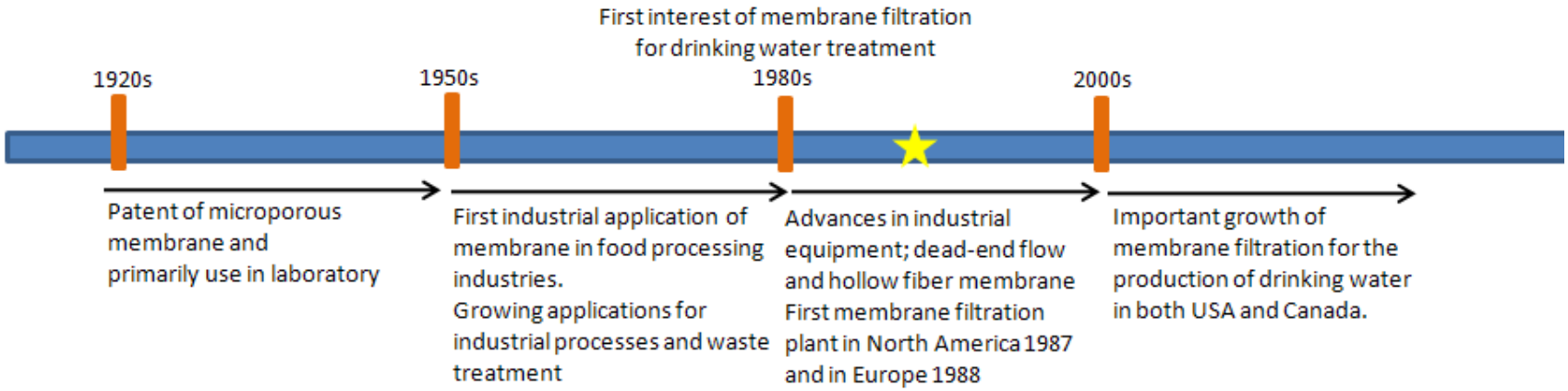


Figure 2-4 Historical timeline of membrane filtration for water treatment

2.2.2 Membrane Processes for Drinking Water

The purpose of membrane filtration is to act as a physical barrier as shown in Figure 2.5. Membrane filtration is a pressurized process where water is pushed through a semi-permeable membrane.

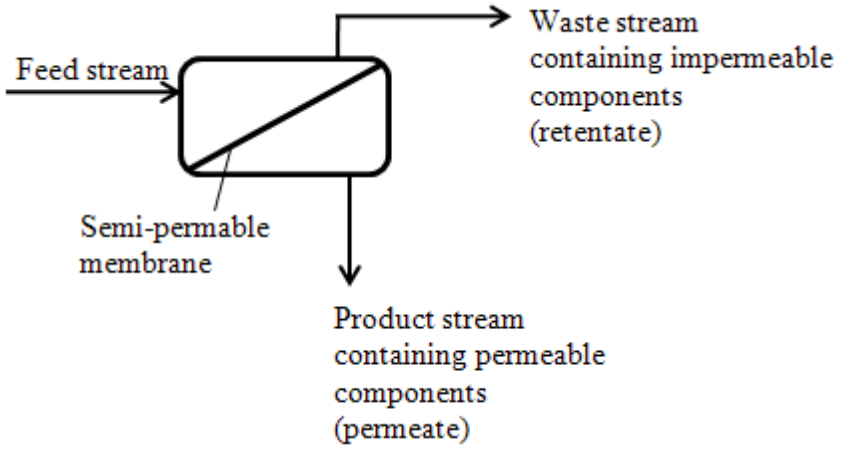


Figure 2-5 Basic membrane filtration process (source: MWH, 2005)

The water that passes through the membrane is called permeate while the water remaining on the feed side is called retentate. The accumulation of material at the surface of the membrane causes a decrease in flux or an increase in the transmembrane pressure. This loss in performance is called fouling and is due to the formation of a cake layer, pore blockage, or pore constriction. Because fouling is the main limitation of membrane filtration for drinking water treatment, further explanations of membrane fouling are provided in section 2.2.4.

Type of membrane

Membrane filtration includes a range of pore sizes with specific removal capacities (Figure 2.6). Microfiltration (MF) has a pore size of approximately 0.1 μm and targets the removal of particles, sediment, algae, protozoa, and bacteria. The pore size of ultrafiltration membranes is around 0.01 μm and targets the removal of small colloids and viruses. Narrower pore sizes of the nanofiltration membrane allow the removal of dissolved organic matter and divalent ions. Finally, reverse osmosis which is a non porous membrane is capable of removing monovalent ions.

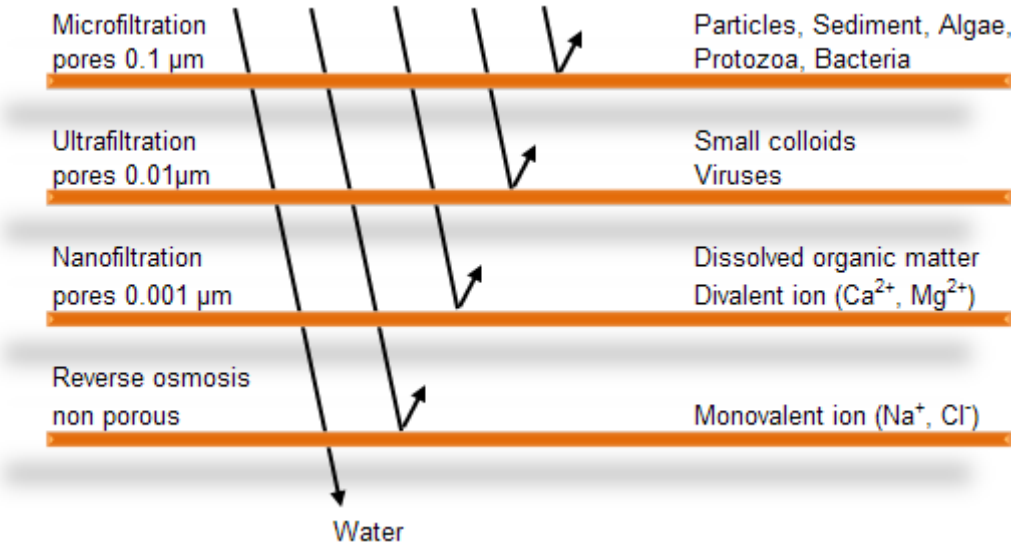


Figure 2-6 Specific removal capacities for each membrane category (source: MWH, 2005)

Low and High Pressure Membranes and Configuration

Membranes can be separated in two sub-categories: low and high pressure membranes. Low pressure membrane includes MF and UF while high pressure membrane includes NF and RO. Low pressure membranes (LPM), considered porous membranes, have experienced an accelerated growth because of the high quality of water produced, the relatively low cost, and the small plant footprint (Freeman *et al.*, 2006).

The typical configurations of LPM for water treatment include hollow fiber and tubular membranes (MWH, 2005). Both configurations allow back flushing of the membrane thus controlling the hydraulically reversible fouling of the membrane caused by particulate and colloidal matter and organic material. Hollow fiber membranes have a higher packing density than tubular membranes. Chemical cleaning is performed at regular intervals to control irreversible fouling.

A recent and major advance in high pressure membrane filtration is the development of a thin-film composite membrane, which consists of a thin film polymer applied over a support layer usually a non-woven polyester film approximately 0.1 mm thick (Figure 2.7).

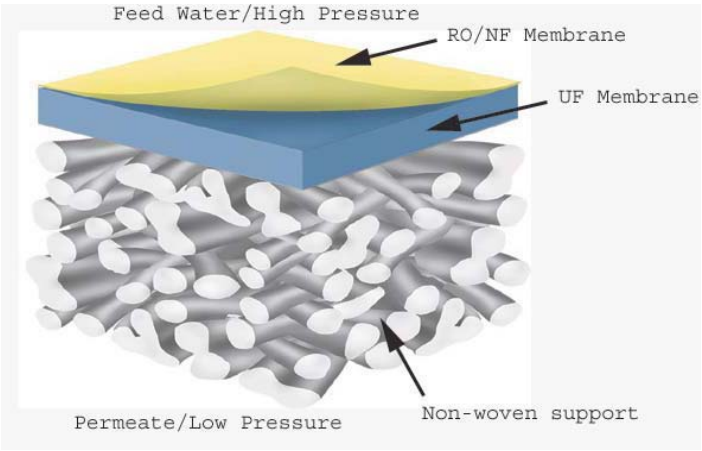


Figure 2-7 Structure of a thin-film composite membrane (source: TriSep Corporation, http://www.trisep.com)

The most common configuration of high pressure membranes is a spiral wound element which provides a high packing density. However, the membrane cannot be back flushed and only chemical cleaning can be performed to remove foulant material accumulated at the surface or within the pores of the membrane.

The membrane configuration will influence the flow regime applied. Cross flow and dead-end filtration are the two common flow regimes used for water treatment (Figure 2.8). Hollow fiber and tubular membranes (i.e. MF and UF) are commonly operated in a dead-end filtration mode while spiral wound membranes (i.e. NF and RO) are usually used in cross-flow mode. The flow regime influences both the permeate flux and the fouling of the membrane.

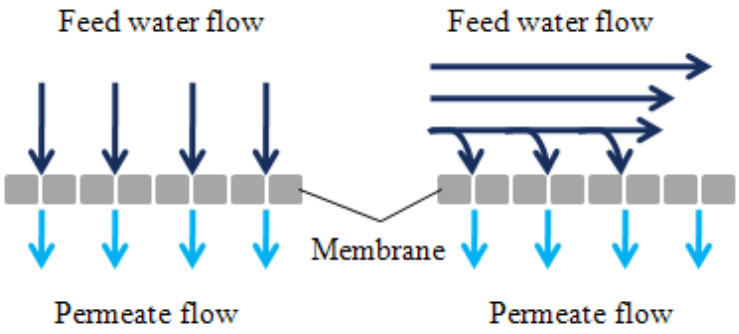


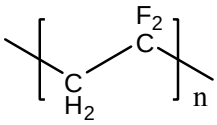
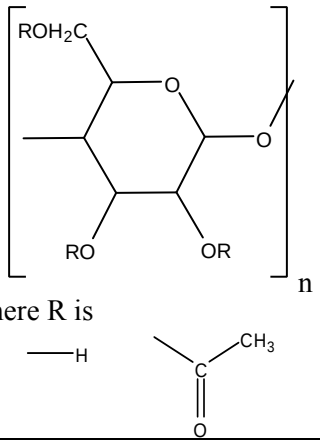
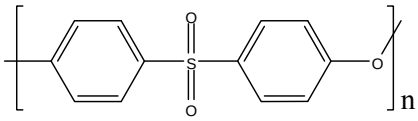
Figure 2-8 Flow regime a) dead-end filtration and b) cross flow filtration (source: MWH, 2005)

In dead-end filtration, the bulk feed water flow is directed perpendicularly towards the membrane. The solids accumulate at the surface of the membrane and are dislodged from the surface of the membrane during backwash. In cross flow filtration, the bulk feed water flows parallel to the membrane surface. Wiesner and Chellam (1992) showed a reduced surface cake formation during cross flow filtration due to the shear forces on the membrane surface. Furthermore, since the solids are carried away from the membrane surface in the retentate, membranes operating with a cross flow filtration regime can usually run at higher fluxes and for longer periods of time.

Membrane properties

Many different polymers can be used to prepare membranes, such as polyvinyl fluoride (PVDF), cellulose acetate (CA), polyamide (PA), poly(amide-hydrazide) (PAH), polyethersulfone (PES). In general, the composition of the polymer is proprietary and the exact structure is not disclosed by manufacturers. Table 2.2 summarizes the generic chemical structure of typical polymers used for membrane production and their main characteristics.

Table 2-2 Chemical structure of membrane material and characteristics (source: MWH, 2005)

Material	Structure	Characteristics
PVDF		Excellent durability Moderately hydrophobic Susceptible to a high degree of fouling Can resist aggressive chemical cleaning Excellent chemical resistance: • Can withstand free chlorine at any concentration • pH between 2 and 10
CA	 where R is 	Susceptible to biological degradation Highly hydrophilic Highly resistant to fouling Cannot resist aggressive chemical cleaning Good chemical resistance: • Can tolerate continuous exposure to 1mg/L of free chlorine and intermittent doses as high as 50 mg/L • pH between 4 and 8.5
PES		Excellent durability Moderately hydrophobic Susceptible to high degrees of fouling High biological resistance Can resist aggressive chemical cleaning Excellent chemical resistance: • up to 200 mg/L of free chlorine and • pH between 1 and 13
PA	[Ar(CONH-)$_2$COOH]	Excellent physical resistance More hydrophobic than CA Susceptible to biological and particulate fouling High biological resistance Not resistant to chlorine Good chemical resistance • pH between 3 and 11

One of the most important surface properties of a membrane is hydrophobicity, which is dependent on the chemical composition of the polymer. Hydrophobicity is measured by the contact angle between the membrane and a drop of water (i.e. contact angle > 50° indicates hydrophobic material; < 50°indicates hydrophilic material). Polymers with ionized functional groups, polar groups, oxygen, or hydroxyl group are usually very hydrophilic (MWH, 2005). Unfortunately, hydrophilic material tends to have a low chemical, mechanical, and thermal resistance which is not desirable for drinking water treatment applications. Moreover, the hydrophobicity reflects the interfacial tension between the water and the membrane material. Soluble, nonpolar, or hydrophobic material contained in water will accumulate on the membrane surface to minimize the interfacial tension between the water and membrane. Therefore, hydrophobic membranes are usually more susceptible to fouling than hydrophilic membranes due to higher interfacial tension (MWH, 2005; Laine *et al.*, 1989).

Other relevant surface characteristics of a membrane consist of surface charge, roughness, and molecular weight cut off. Usually the membrane surface is negatively charged. It is measured by zeta potential analysis and the surface charge can vary with pH (Nghiem and Schafer, 2005). For example, in the case of polyamide membranes, this variation with pH is due to the ionization of the carboxylic and amide functional groups. At a certain pH, which is specific for each membrane material, the zeta potential is null which corresponds to the isoelectric point. Above the isoelectric point (IEP), the membrane is negatively charged whereas below the IEP it carries a positive charge. However, at the pH range for drinking water treatment (6 to 8), membranes are typically negatively charged. Moreover, the zeta potential value is an important factor influencing membrane fouling and rejection of contaminants. The membrane surface charge can influence the significance of electrostatic repulsion in the rejection of contaminants (MWH, 2005). The roughness of the membrane surface is one important factor that can influence the degree of fouling since rougher membranes tend to experience more fouling than smooth membranes (Hobbs et al., 2006).Microporous membranes have a pore size distribution. Thus the average pore radii of the membrane can be determined by filtering inert organic compounds of different molecular weight, measuring the rejection and applying a pore transport model (Nghiem *et al.*, 2004a). The molecular weight cut off (MWCO) is often used to characterize the pore size of a membrane. The MWCO is defined as the molecular weight of a solute corresponding to a 90 % rejection for a given membrane (Koros *et al.*, 1996). Other techniques that can be used to visualize the membrane surface and determine the average pore size by image analysis are scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Flow through porous media

In drinking water treatment the valued product is the permeate. Thus, it is of interest to identify the parameters influencing the flow of water through the porous media. For a porous media such as UF and MF membranes, the flow follows Darcy's Law (MWH, 2005) (equation 2.15). This equation shows that the fluid velocity across the membrane is proportional to the hydraulic permeability coefficient of the membrane and the head loss across the membrane. However, the fluid velocity is inversely proportional to the thickness of the membrane.

$$v = k_p \frac{h_L}{L} \qquad \text{eq. 2.15}$$

where
v is the superficial fluid velocity, m/s
k_p is the hydraulic permeability coefficient, m/s
h_L is the head loss across porous membrane, m
L is the thickness of the porous membrane, m

The standard equation for water flow through a membrane standardised over the membrane area originates from Darcy's Law and is expressed as follows (MWH, 2005):

$$J = \frac{\Delta P}{\mu k_M} \qquad \text{eq. 2.16}$$

where
J is the volumetric water flux, $L/m^2 \bullet h$
ΔP is the differential pressure across the membrane or transmembrane pressure, bar
μ is the viscosity of water, kg/m•s
k_M is the membrane resistance coefficient, m^{-1}

The fluid viscosity is included in eq. 2.16 because it has a significant impact on the flux and can vary drastically with water temperature. Moreover, the membrane thickness influences the membrane resistance coefficient. Nevertheless, it is important to note that the volumetric flux will be primarily influenced by the membrane fouling, rather than the intrinsic resistance of the membrane (MWH, 2005)

The volumetric water flux (J) can be used to determine the recovery of a membrane filtration system. The recovery is defined as the ratio of treated water flow rate (permeate) to feed water flow rate.

2.2.3 Rejection Mechanism for Organic Contaminants

The retention of organic material or contaminants by membranes is attributed to a number of mechanisms; however, the most commonly identified are steric interactions also known as sieving, adsorption to the surface of the membrane or within the pores, charge exclusion and for non-porous membranes i.e. RO solute diffusion. The retention of a contaminant is determined by the coupled interaction between the membrane properties, the contaminants physico-chemical properties, and the constituents present in water (Nghiem *et al.*, 2005). In general, rejection of organic contaminants can only be achieved by high pressure membranes i.e. NF and RO. RO membranes are considered non-porous membranes where concentration driven diffusion governs the transport of a solute through the RO membrane. NF membranes, however, combine properties of porous, low pressure membranes and of high pressure membranes. Hence, rejection mechanisms contributing to contaminant removal can include sieving, adsorption, charge exclusion, and diffusion. Each of these rejection mechanisms are described below.

Steric interaction

Size exclusion is generally the dominant rejection mechanism involved with porous membranes. Theorically, contaminants larger than the membrane pore size are retained. The size of spherical molecules can be estimated by the Stokes radius. The Stokes-Einstein radius (r_s) of a molecule is defined as (Nghiem and Schäfer, 2005):

$$r_s = \frac{kT}{6\pi\eta D_s} \qquad \text{eq. 2.17}$$

Where
k is the Boltzmann constant,
η is viscosity,
T is temperature
D_s is diffusion coefficient

However, molecular weight is the most accessible parameter that indicates the size of a molecule and it can be used to predict the retention of neutral compounds by a membrane. Unfortunately, retention of molecules smaller than the MWCO cannot be predicted. Nonideal performance of retention occurs due to membrane characteristics and membrane-particle interactions. This non-idealism is due to the assumption that membranes consist of a bundle of uniform, cylindrical capillaries and that the solute is spherical in shape. In reality, membranes have a pore size distribution. Consequently, large and flexible molecules (i.e. protein) can be forced through a membrane under pressure.

Adsorption

Solutes can be rejected even when their sizes are an order of magnitude smaller than the membrane pore size. In fact, adsorption can be an important rejection mechanism in the early stages of membrane filtration when the membrane is clean. However, the adsorption capacity can be rapidly reached so it is not an effective removal mechanism in long-term operations.

Usually, organic trace contaminants that can adsorb to the membrane present a high octanol-water partitioning coefficient (Log K_{ow}) or hydrogen bonding capacity and are sparingly soluble in water (Ngheim and Schäfer, 2005). The nature of the interactions during adsorption processes is not fully understood, but hydrophobic or hydrogen bonding interactions may be involved. This is consistent with the fact that the steroid hormone progesterone binds to its receptor via hydrogen bonding (Nghiem *et al.*, 2004a).

The adsorption of contaminants on the membrane surface has important implications. The adsorption of contaminants due to hydrogen bonding can reduce water permeation because water flux across the membrane is thought to be greatly dependent on the formation of hydrogen bonds with the hydrophilic groups on the membrane polymer (Nghiem and Schäfer, 2005). Moreover, the accumulation of organic trace contaminants can lead to membrane structure deteriorative problems. Finally, adsorbed contaminants can diffuse through the membrane during later stages of membrane filtration leading to a decrease in rejection over time (Nghiem *et al.*, 2004a).

Charge exclusion

Higher retention of negatively charged contaminants is often observed compared to the retention of uncharged or positively charged contaminants with similar size for a specific membrane. This behaviour can be attributed to electrostatic repulsion between the contaminants and the negative functional groups present at the surface of the membrane (Nghiem and Schäfer, 2005).

The retention efficiency is a function of the pH of the water due to its influence on the characteristics of the membrane and the charge of the contaminants. As previously explained, the surface charge of a membrane is usually negative but can vary depending on the pH. Thus the amphoteric properties of membranes influence the rejection mechanisms of charged species.

A summary of the important solute and membrane characteristics related to each retention mechanism are presented in Table 2.3.

Table 2-3 Solute and membrane characteristics and their influence on separation processes

	Solute parameters	**Membrane parameters**
Size exclusion	Molecular weight Molecular size	MWCO Pore size
Adsorption	Log K_{ow} Dipole moment	Hydrophobicity
Charge exclusion	pKa	Surface charge

2.2.4 Membrane Fouling

As described by Koros *et al.* (1996), fouling is:

"*the process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores*".

The loss of performance is characterized by a reduction in water flux or by an increase of transmembrane pressure. To evaluate the reduction in flux when filtering natural water, the permeability or clean water flux (J_0) can be determined. For dilute solution, J_0 is defined as:

$$J_0 = \frac{Q}{A} \quad \left(L/\left(m^2 * h\right)\right) \qquad \text{eq. 2.18}$$

Where
η_T is viscosity of water at temperature T
$\eta_{20°C}$ is viscosity of water at 20°C
Q is clean water flow
A is membrane surface area
ΔP is transmembrane pressure difference

For ultrafiltration membrane, the permeate flux can be adjusted in function of the water temperature accordingly to equation 2.19:

$$J_{\left(x^{\circ}C\right)} = \frac{J_{\left(20^{\circ}C\right)}}{1.025^{(20-x)}} \qquad \text{eq. 2.19}$$

From the clean water flux (J_0), the flux reduction (FR) can be calculated as the difference between the flux of the natural water and the clean water flux (equation 2.20):

$$FR = \frac{J_0 - J}{J_0} * 100\% \qquad \text{eq. 2.20}$$

With a virgin membrane, membrane compaction resulting in flux reduction is frequently observed and is not considered as fouling. Therefore, precompaction of the active layer needs to be completed prior to any fouling experiments. Figure 2.9 illustrates the membrane compaction, reversible, and irreversible fouling observed during membrane filtration processes. Reversible fouling corresponds to the loss of flux that can be recovered after water back flush. Irreversible fouling is due to the irreversible binding of material with the membrane and results in permanent loss of flux that cannot

be regained even after appropriate chemical cleaning. Hence, this type of fouling controls the lifetime of the membrane.

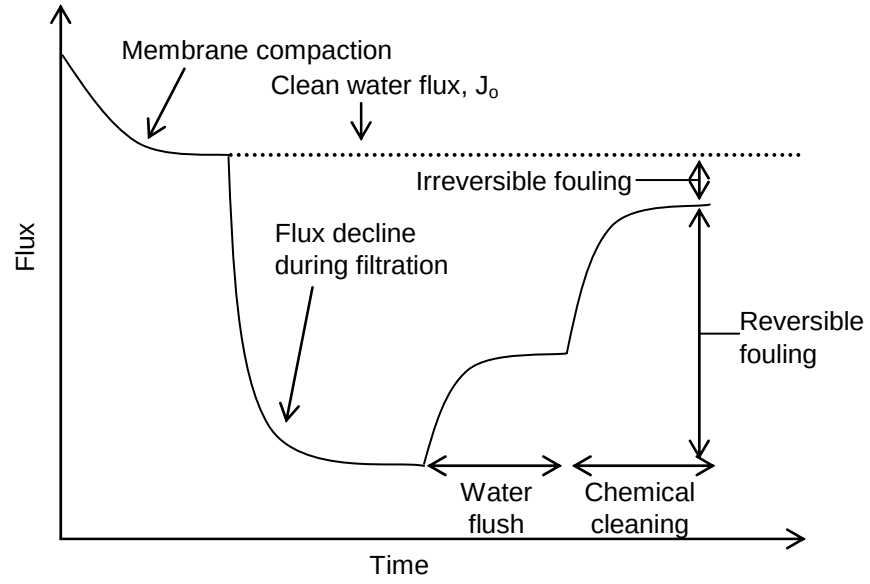


Figure 2-9 Membrane compaction, irreversible fouling, and reversible fouling (source: Schäfer *et al.*, 2005)

Source of fouling

The type of foulants affecting MF and UF membrane is different than foulant affecting NF and RO membranes. The following section identifies the different sources of foulant material for UF and NF membranes encountered during drinking water treatment.

Membrane fouling is the result of several and complex phenomena involving electrostatic and hydrophobic interactions between the surface of the membrane and the components present in the feed water. The main types of fouling are organic, inorganic, biofouling, and colloidal/particulate fouling.

Usually membrane fouling cannot be attributed to a single fouling mechanism but consists of a combination of concentration polarization, deposition of material on the membrane surface, and adsorption on or within the pores of the membrane (Figure 2.10) (MWH, 2005; Yuan and Zydney,

2000). Adsorption often leads to irreversible fouling while concentration polarization and deposition on the surface membrane cause reversible fouling.

After the formation of a cake layer, the pores of the membrane are completely unaffected by the bulk feed water characteristics since the particles causing fouling form a separate layer on top of the membrane. Subsequently, the cake layer increases the resistance to flow which causes a decrease in permeate flow or an increase in transmembrane pressure. Pore constriction occurs when particulates or dissolved material adsorbs within the membrane pores, resulting in a reduction of the cross-sectional area available for filtration. Pore blockage occurs when particles completely seal the pore of the membrane. In this case, the fouling is proportional to the ratio of sealed pores to total pores.

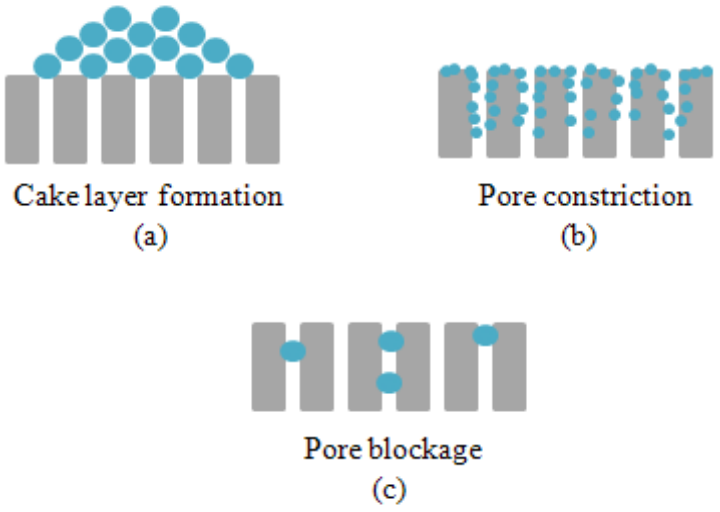


Figure 2-10 Mechanisms of fouling in membrane filtration: (a) cake layer, (b) pore constriction, (c) pore blockage. (source: MWH, 2005)

Organic fouling

Organic fouling is caused by the precipitation and adsorption of colloidal or dissolved NOM on the membrane. NOM is a complex mixture of humic acids, degradation products of humic acids, fulvic acids, small organic acids, and biopolymers such as proteins- and polysaccharides-like substances. Her *et al.* (2007) identified protein- and polysaccharide-like substances as major foulants for NF membranes. Moreover, after ozonation, algae release extracellular biopolymers that are

suspected to accelerate membrane fouling (Her *et al.*, 2007). Amy and Cho (1999) also identified polysaccharides as a principal organic foulant for UF and NF membranes from surface waters.

The solubility of organic acids decreases at lower pH values (i.e. below their pKa values) and increases in the presence of divalent and trivalent cations (i.e. calcium, magnesium, iron, and aluminum). Li and Elimelech (2004) showed that the presence of bivalent ions (Ca^{2+} or Mg^{2+}) in water can also greatly enhance NOM fouling on membranes as it encourages the complexation and formation of bridges within organic foulant molecules.

The type of fouling strongly depends on the characteristics of the organic material as well as their affinity for the membrane material (Schäfer *et al.*, 2005). Organic matter interacts with membranes in several ways:

- The presence of organic compounds at the surface of the membrane changes the surface properties of the membrane
- Organic material can also be a source of nutrients which can encourage the formation of a biofilm

Adsorption mechanisms are not well understood but acid-base interactions and hydrogen bonding between NOM and the membrane surface are the predominantly suggested mechanisms. Adsorption also depends on the pKa of the solute; higher adsorption is observed when compounds are undissociated (Schäfer *et al.*, 2005).

The detection and characterization of NOM causing fouling during drinking water treatment can be performed by two complementary techniques, namely LCOCD and fluorescence analysis (Peiris *et al.*, 2010; Hallé *et al.*, 2009; Peiris *et al.*, 2008; Her *et al.*, 2007; Her *et al.*, 2003). The fluorescence excitation-emission matrix (EEM) allows the characterisation of organic material causing fouling.

Inorganic fouling

During a cross flow regime, if low turbulence in the feed channel occurs or if the concentration of particles and colloids is too high, a concentration polarisation occurs near the membrane surface. Once the solubility of the salt is exceeded precipitation or scaling (i.e. salt crystallization) can occur. The most common inorganic precipitates include calcium carbonate, calcium sulphate, silicon

dioxide, magnesium sulphate, iron hydroxide, and aluminum hydroxides especially if coagulation or oxidation pretreatment is not performed properly. In general, scaling mainly results in flux decline but for high pressure membranes the permeate quality may also deteriorate due to an increase in the passage of salt (Gabelich *et al.*, 2002).

Scaling can pose a serious limitation to membrane filtration systems and severe membrane fouling is expected when natural feed waters contain even moderately elevated concentrations of hardness cations (Hong and Elimelech, 1997).

To prevent or minimize scaling, the water chemistry can be modified and the recovery rate should be decreased to lower the salt concentration below the critical solubility value. Precipitation of inorganic scalants reduces the permeate quality, the permeate flux, and can damage the membrane surface by causing irreversible pore blockage, which shortens the life of the membrane. Some of the parameters affecting scaling are salt concentration, velocity of the water, pH, and membrane composition. SEM is a technique used to identify scaling at the membrane surface.

Colloidal and particulate fouling

Macromolecules and colloids are defined as any aqueous components between 1 nm and 1 μm of size (Buffle and Leppard, 1995). Organic colloids include microorganisms, polysaccharides, organic fibrillar, gel-like material, biological debris, humic acids, and fulvic acids. Inorganic colloids include clay, calcium carbonate, amorphous silica, and iron hydroxides. Fulvic acids, humic acids, and proteins are usually smaller than tens of nanometers while cellular debris, polysaccharides, clay and carbonates are larger than tens of nanometers (Buffle and Leppard, 1995).

Colloidal and particulate materials cause fouling through their accumulation on the membrane surface resulting in reduction of flux and retention. Both colloids and membrane material properties influence the fouling mechanism. Colloidal matter is typically negatively charged in aqueous solutions. The surface charge of a colloid, measured as zeta potential, influences the porosity of the cake structure and its hydraulic resistance. The shape of the colloids can also influence fouling (i.e. the cake structure). Research demonstrates that membrane surface properties such as zeta potential, roughness, pore size, and hydrophobicity influence the rate of colloidal fouling (Hoek *et al.*, 2001).

Previous studies have demonstrated that effluent organic matter (EfOM) from wastewater treatment plants created more fouling than NOM due to a higher content of rigid biopolymers such as polysaccharides and proteins (Laabs *et al.*, 2003; Reichenbach *et al.*, 2001) as well as the presence of soluble microbial products (Drewes and Fox, 1999). Biopolymers are produced by microorganisms during the biological wastewater treatment processes and include cell fragments and macromolecules (i.e. polysaccharides and proteins). Fourier transformed infra-red spectra of the EfOM colloid fraction showed characteristic peaks at 1650 cm^{-1} (C=C, -CO-N; proteins, C-O-C linkage) and at 1080 cm^{-1} (C-O-C: polysaccharides) (Laabs *et al.*, 2003).

The removal of foulant material (down to 1µm in size) by pre-treatment is the best strategy to reduce colloidal fouling. AFM can efficiently identify and characterise colloidal fouling on the membrane surface (Schäfer *et al.*, 2005).

Biological fouling

Bacteria are present in any natural water and since they are not completely removed during pretreatment they can enter the membrane module. NOM may be used by the bacteria as a source of energy and carbon resulting in biological growth at the surface or within the pores of the membrane. Bacteria can attach to the membrane and the spacer by electrostatic interactions, filament and/or slime formation. The formation of a biofilm is enhanced by the production of EPS which form a viscous, slimy, and hydrated gel. When biologically active organisms are involved in fouling, the term biofouling is used. Biofouling generally causes an augmentation in the pressure drop in the feed channel, a decrease in water flux, and a decrease in permeate quality i.e. reduction of salt retention for RO membranes. Biofouling can also cause membrane damage on CA membranes by the excretion of CA hydrolyzing enzymes (Ishigake *et al.*, 2000).

Biofouling is a dynamic process that involves bacterial colonization and proliferation at the membrane surface or within the pores due to the presence of nutrients. In surface water, the limiting nutrient is considered to be biodegradable carbon. EPS which is excreted by bacteria tend to attach well to the membrane surface and may cause pore blockage. In membrane bioreactors, Chang and Lee (1998) have linked fouling and the presence of EPS. They suggest using EPS as a possible feedwater fouling index for wastewater applications. Another source of biofouling can be the chemicals used to

control scaling during RO and NF membrane processes (Vrouwenvelder *et al.*, 2000). Biofilms on the surface of the membrane reduces permeability, causes flux decline, and causes pore blocking.

To prevent biofilm build-up on membranes, pre-treatments such as MF or UF membranes can be effective due to their ability to remove bacteria. However, these pre-treatments do not remove the nutrients that favour microbial growth. Biofiltration is considered as a promising pre-treatment to control biofouling (Uhl *et al.*, 2003). Reducing both bacterial nutrients (i.e. biodegradable carbon) and dissolved and colloidal microbial cell may significantly reduce biofouling. However, very limited investigations have been performed for this usage. The addition of chlorine or chloramines at low concentrations can also be a good strategy to control biofouling if the membrane tolerates chlorine; however, flux decline may be observed as a result. The choice of membrane material also influences the possibility of the attachment of microorganisms. A study performed by Vrouwenvelder *et al.* (1998) demonstrates that to control biofouling the removal of biodegradable matter from the feed water, the utilisation of pure chemicals, and performing an effective cleaning are necessary. Membrane autopsy using scanning electron microscopy (SEM) can confirm the presence of a biofilm on the feed side of the membrane (Vrouwenvelder *et al.*, 1998).

Fouling control

Research and practical experience with membranes for drinking water treatment indicate that UF, NF, and RO are especially susceptible to fouling. Consequently, pretreatment is generally required to control particulate, organic, and biological fouling unless very pristine waters are treated. Efficient pretreatment processes for low and high pressure membranes include: conventional coagulation-sedimentation-filtration, ozonation followed by GAC filtration, slow sand filtration, and river bank filtration.

To meet stringent regulations and forthcoming regulatory requirements related to drinking water treatment (i.e. pathogens removal, reduction of disinfection by-products, removal of trace organic contaminants, and removal of inorganic contaminants), utilities have to fulfill several treatment objectives. An integrated membrane system is defined as the combination of NF or RO with MF or UF which has the goal to reduce fouling of subsequent membrane filtration and other treatment objectives (Schippers *et al.*, 2004).

Comparing two sources of surface water and different coagulants (i.e. alum, ferric chloride, and hydrolysed coagulant SP and SP70), Ratajczak (2007) showed that coagulation followed by direct filtration can significantly reduce the fouling of a PVDF hollow fiber UF membrane. However, the most effective type of coagulant will depend on the quality of the source water.

If the goal of membrane filtration is desalination, the Metropolitan Water District of Southern California, tested the use of a conventional treatment plant prior to RO to reduce fouling (Gabelich *et al.*, 2002). Their pretreatment consisted in coagulation with either alum or ferric chloride followed by sedimentation and filtration. This research showed that severe fouling was caused by alum residuals (e.g. aluminum hydroxide and aluminum silicates). Moreover, alum led to a decrease in salt rejection due to a concentration gradient. In contrast, using ferric chloride, the water flux increased and the salt rejection decreased.

As presented in section 2.1, the principal objective of biological filtration is to produce drinking water that is biologically stable. Thus treated water does not support significant microbiological growth during its distribution (Rittmann, 1995). By achieving this goal, several types of fouling either on UF or NF may be reduced due to the enhanced feed water quality. Gabelich *et al.* (2003) concluded that conventional treatment followed by ozonation and biofiltration produced water suitable for subsequent RO. This pretreatment reduced HPC bacteria and TOC in the membrane feed which resulted in a substantial improvement of RO performance. In The Netherlands, van der Hoek *et al.* (2000) showed that an RO membrane following a complex treatment train, which substantially reduced the biological regrowth potential of the feed water, could be operated at a recovery of 85 % over a period of one year without the need for chemical cleaning providing that scaling was properly controlled.

2.3 Trace Organic Contaminants

2.3.1 Definitions

Concerns about the exposure to xenobiotic compounds such as EDCs are growing because of the possible harmful effects on the endocrine system. In 1998, the Committee on Toxicity, Ecotoxicity and the Environment has defined EDCs as (Vos *et al.*, 2000):

"An exogenous substance or mixture that alters function (s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) population"

The consequences of malfunction of the endocrine system by EDCs are serious and include: interference with the synthesis, secretion, transport, binding action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behaviour (Vos *et al.*, 2000).Various sources of chemicals acting as endocrine disruptors have been identified. Such compounds include some pharmaceuticals such as 17α-ethinylestradiol or tamoxifen, and industrial chemicals such as atrazine, DDT, bisphenol A, and nonylphenol (Snyder *et al.*, 2006; Vos *et al.*, 2005).

PhACs are being extensively used with approximately 3000 different compounds available today (Ternes *et al.*, 2006). Categories of pharmaceuticals detected in the environment includes painkillers, antibiotics, antidiabetics, beta blockers, contraceptives, lipid regulators, antidepressants, contrasting media, etc. Organic trace contaminants are present in the environment either in the form of unaltered parent compounds or if internally administered in the form of metabolites. In fact, many PCPs and PhACs are biotransformed into the body to facilitate excretion. Consequently, metabolites of parent compounds (i.e. glucuronides and conjugates) are also present in the environment (Snyder *et al.*, 2008; Ternes *et al.*, 2006; Daughton and Ternes, 1999; Heberer and Dünnbier, 1999).

The exposure to traces of PhACs and EDCs in drinking water must be considered seriously. However, considering the concentration detected in drinking water and based on a consumption of 2 L/day, Snyder *et al.*, 2008 determined that the exposure to individual compounds is far below any human health risk. However, adverse effects cannot be ruled out especially if the additive effects are

considered. However, research showed that exposure to EDCs at low ng/L concentrations can lead to feminization or masculinisation of aquatic organisms (Ternes *et al.*, 2006).

2.3.2 Organic Trace Contaminants in the Environment

Recently, EDCs and PhACs available over-the-counter has substantially increased (Daughton and Ternes, 1999). The presence of trace organic contaminants in wastewater effluent was first discovered in the 1960s and 1970s in the United States but the issue was initially not perceived as problematic (Hignite and Azarnoff, 1977; Strumm-Zollinger and Fair, 1965).

Wastewater treatment plant processes (WWTP) are able to remove some organic trace contaminants but several reports show that PhACs and EDCs are present at sub μg/L in the WWTPs effluent (Heberer, 2002; Kolpin *et al.*, 2002; Halling-Sorensen *et al.*, 1998). Consequently, the discharge of WWTPs effluent in rivers may lead to further contamination of drinking water sources (Soares *et al.*, 2008). Additionally, the contamination of groundwater by landfill leachate has also been demonstrated (Holm *et al.*, 1995). Despite the lack of data on the human health risks of the exposure to trace levels of PhACs and EDCs from indirect water reuse, the public perception is the driving force to implement advanced drinking water treatment processes (Snyder *et al.*, 2008).

Heberer (2002a), reviewed the sources of PhACs and their possible pathway into environmental compartments. As illustrated in Figure 2.11, groundwater and surface water can easily be contaminated. PhACs employed for human usage can potentially enter into the environment through waste disposal and land fill leachate. Moreover, excretion of PhACs will lead the detection of parent compounds and metabolite in wastewater influent.

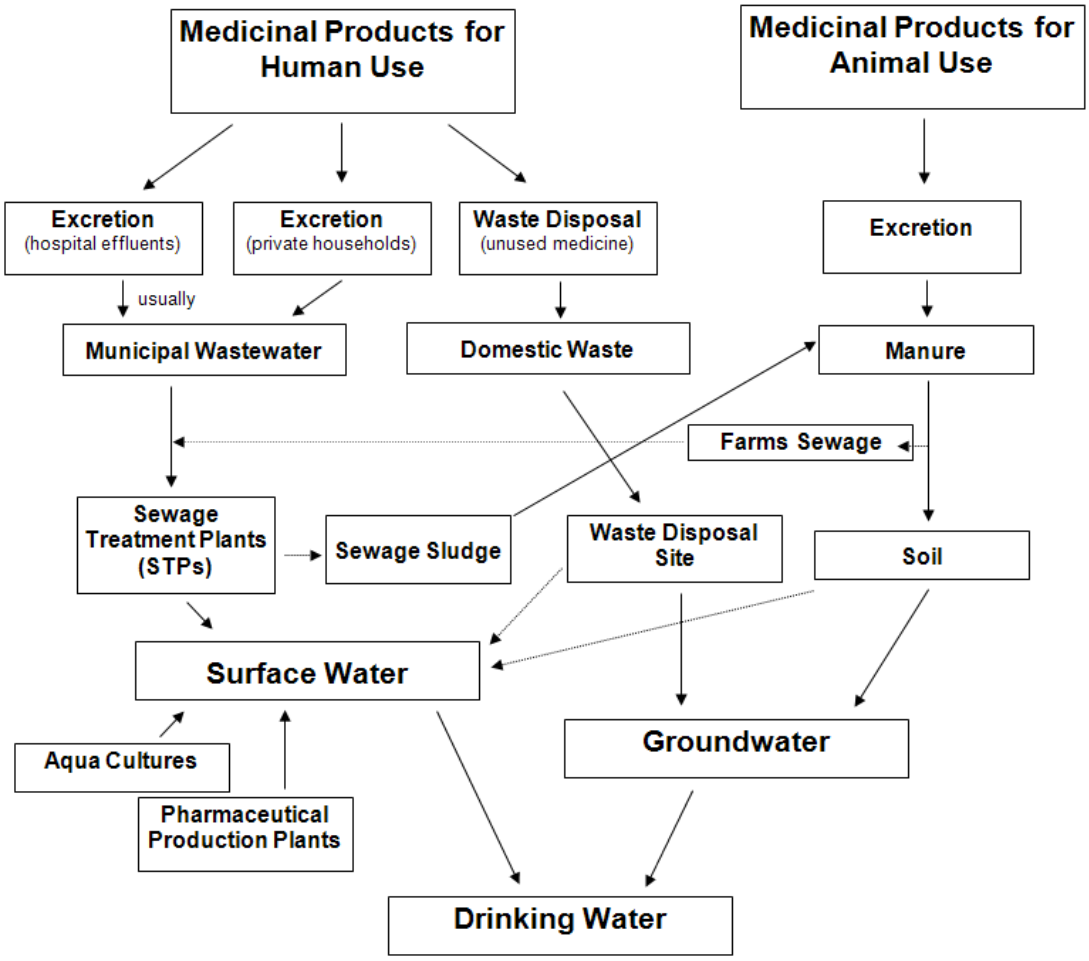


Figure 2-11 Sources of PhACs contamination in the environment (source: Heberer, 2002a)

Occurrence in sewage effluent

Analgesics and anti-inflammatory compounds are often detected in sewage effluent. In fact, ibuprofen, naproxen, and salicylic acid (i.e. metabolite of acetylsalicylic acid (ASA)) can be detected at µg/L concentrations. The very high concentration of ASA in sewage effluent may reflect high usage as a non-prescription drug in Canada. Neutral drugs such as carbamazepine are also widely detected but at a lower concentration range (ng/L). The highest reported concentrations of analgesics and anti-inflammatories in the final effluent of WWTPs in Canada (Metcalfe *et al.*, 2003b) appear to be lower than the ones reported in Germany and Switzerland (Heberer, 2002b; Ternes, 1998). This observation may be the consequence of a different drug usage pattern or due to higher dilution factors

for the particular sites. The frequent detection of carbamazepine in sewage effluent is due to poor removal during sewage treatment (e.g. Metcalfe *et al.*, 2003b).

Natural oestrogens (i.e. 17β-estradiol and estrone) have been commonly detected in Canadian WWTP effluent and their removal rates vary considerably (Servos *et al.*, 2005). Moreover, the synthetic estrogen 17β-ethinyloestradiol has been frequently detected in Canadian WWTP effluent at a concentration range of 1-2 ng/L with a maximum concentration of 20 ng/L (Ternes *et al.*, 1999). While these concentrations are low, they are within the range that can cause feminization of fish (Metcalfe *et al.*, 2001).

Through WWTPs, the removal of different PhACs varies as reported by Vieno *et al.* (2005). The difference in elimination efficiency of PhACs may be influenced by the season. It appears that the elimination process does not work as efficiently during the cold winter months as during other periods of the year. Low water temperature and consequently lower rate of biodegradation, can limit the elimination of contaminants. Although mechanisms for the elimination of PhACs are not well known, biodegradation and sorption are likely the major elimination processes, biodegradation being dominant (Vieno *et al.*, 2005) and both mechanisms are temperature dependent. When the temperature is not a factor for the elimination of contaminant, seasonal variation in influent concentrations may lead to a variable degree of transformation (Loraine and Pettigrove, 2006).

Occurrence in surface water

In Canada, monitoring programs for PhACs detection have been performed in rivers, Lake Ontario, Lake Erie, and the Great Lakes basin (Metcalfe *et al.*, 2003b; Miao *et al.*, 2002). Low concentrations (i.e. 5 to 10 ng/L) of clofibric acid, ketoprofen, and carbamazepine were detected in open locations far from WWTP discharge in Lake Ontario and the Niagara River. Moreover, carbamazepine and one of its metabolites, dihydrocarbamazepine, has been frequently detected in surface water near the WWTP. Lipid regulators from the fibrate class have been detected in surface water near WWTP discharge points at concentrations below 200 ng/L. In Hamilton Harbour and the Little River in Windsor (Ontario), a statin class lipid regulator was detected. Antibiotics were detected in surface water near WWTP discharge points in Peterborough, Burlington, and Windsor (Ontario). Other drugs detected in Canadian surface water are clarithromycin, erythromycin-H_2O,

ciprofloxacin, sulfapyridine, sulfamethoxazole, and tetracycline. This is consistent with antibiotics detected in surface water near WWTP discharge points in Germany (Christensen *et al.*, 2003).

A study performed by Servos *et al.* (2007) in Southern Ontario demonstrates that low concentration of acidic drug such as clofibric acid, ibuprofen, gemfibroxil, naproxen, and triclosan in large lake. However, rivers were more contaminated compared to lake sources. Mean concentration of ibuprofen and naproxen were particularly high with 150 and 176 ng/L, respectively. Other contaminants detected in rivers include gemfibroxil, triclosan, diclofenac, and idomethancin with concentration up to 19, 34, 15, and 6 ng/L respectively.

Several factors can affect seasonal and spatial concentrations of contaminants in surface water. Vieno *et al.* (2005) demonstrate that concentrations of PhACs decrease as the compounds are carried downstream. Dilution of the compounds in river water contributes to the concentration reduction, but also some elimination processes occurred during downstream transportation. The main elimination processes include those identified during WWTP processes such as biodegradation and sorption, but photodegradation must also be considered in the case of surface water because UV light can penetrate the water (Boreen *et al.*, 2003; Buser *et al.*, 1998). Photodegradation is not possible in presence of ice cover, but when photodegradation occurs, it seems to be the most important mechanism of removal for certain PhACs in rivers (Vieno *et al.*, 2005). As mentioned previously, low temperature affects the biodegradation rate and sorption. Thus, during the cold season, PhACs concentrations in rivers may increase, and because biodegradation rates are lower, contaminants are carried further away from the discharge point than in warmer seasons (Vieno *et al.*, 2005).

In Table 2.4, Yoon *et al.* (2002) summarized the most frequently detected EDCs and PPCPs detected in waters in the United States. Table 1.1 also includes the Log K_{ow} value as an indicator of hydrophobicity (i.e. high Log K_{ow} value indicates high hydrophobicity).

Table 2-4 Most frequently detected EDCs and PPCPs in waters in the United States (source: Yoon *et al.*, 2002)

Compound	Use	Log K_{ow}
acetaminophen	analgesic	0.46
atrazine	herbicide	2.61
bisphenol A	plasticizer	3.32
caffeine	stimulant	-0.07
carbamazepine	analgesic (anti-seizure medicine)	2.45
clofibric acid	lipid regulator (metabolite)	2.57
coprostanol	estrogen	8.82
cotinine	notine metabolites	0.07
DEET	mosquitos repellant	2.18
diazepam	muscle relaxant	2.82
diclofenac	analgesic (treatment of arthritis)	0.70
dilantin	anticonvulsant	2.47
17α-ethynylestradiol	estrogen (synthetic birth control)	3.67
erythromycin	antibiotic	3.06
fluoxetine	antidepressant	4.23
galaxolide	musk	Na
gemfibrozil	lipid regulator (antocholesterol)	4.77
glucophage	anti-diabetic	Na
hydrocodone (Loratab)	pain killer	Na
ibuprofen	analgesic (pain reliever)	3.97
iopromide	X-ray contrast reagent	-2.05
meprobamate	anti-anxiety	0.70
musk ketone	fragrance	4.31
naproxen	analgesic	3.18
NDMA	disinfection by-product	-0.57
octylphenol	surfactant	5.50
oxybenzone	sunscreen	3.79
pentoxifylline	blood-viscosity (reducing agent)	0.29
primidone	anticonvulsant	0.91
sulfamethoxazole	antibiotic	0.89
triclosan	antibiotic	4.76
trimethoprim	antibiotic	0.91
tris(2-chloroethyl)phosphate	fire retardant	1.44

Occurrence in drinking water

As demonstrated by several, trace organic contaminants and their metabolites have been identified in WWTP discharges, surface water, and groundwater, but a much smaller number of compounds have been detected above limits of quantification in drinking water (Heberer, 2002a; Heberer, 2002b; Yoon *et al.*, 2002).

Limited information on the PhACs present in Canadian drinking water is available. However, PhACs present in drinking water are likely to be detected at low ng/L concentration. Boyd ***et al.*** (2003) studied the concentrations of selected pharmaceuticals at the A.H. Weeks Water Treatment plant in Windsor (Ontario). After conventional treatment (ozonation, coagulation/flocculation, filtration, and chlorination) only bisphenol A was detected at low concentrations (i.e. below the limit of quantification). Vieno ***et al.*** (2005) studied the removal of PhACs in a drinking water treatment plant using coagulation (ferric coagulant) followed by filtration on granular activated carbon (GAC) and chlorination. Naproxen was well removed, but marginal removal of ibuprofen and ketoprofen (13 % and 8 %, respectively) was observed after coagulation. However, with low influent concentrations between 7 and 17.5 ng/L, the filtration by GAC lowered the concentrations of ibuprofen and ketoprofen below the limit of quantification.

In Berlin, concentration up to 270 ng/L of clofibric acid has been detected in drinking water due to artificial recharge of groundwater located downstream of a sewage treatment plant (Alder ***et al.***, 2006). Also in Germany, concentration of sulfamethoxazole in the range of 13 to 45 ng/L has been detected in 12 % of the samples collected across Bavaria (Alder ***et al.***, 2006).

Servos ***et al.*** (2007) investigated 20 water treatment plants and among them some use source of water containing contaminants. Ibuprofen was the only drug detected in treated water. The concentration was reduced by approximately 23 to 25 % resulting in concentration up to 112 ng/L in finished water. Also trace of triclosan and naproxen were found in few samples.

Loraine and Pettigrove (2006) studied the presence of PhACs and PCPs in finished water in Southern California and contaminants such as di(ethylhexyl)phthalate, benzophenone, ibuprofen, and triclosan were detected. They observed that conventional treatment processes were not able to completely remove all the contaminant except for DEET, clofibrate, and clofibric acid.

Heberer (2002ab) and Servos *et al.* (2007) identified three factors that determine the detectable profile and amounts of PhACs in drinking water: a) the geographical location of the treatment plant, b) the degree of contamination of the water sources, and c) the technologies used to produce drinking water. In fact, as discussed previously, drinking water treatment plants located downstream of a WWTP are more susceptible to receive contaminated surface water. The distance between the installations can also affect the concentrations of contaminants. The degree of contamination of the water sources depends on several factors such as the type of wastewater treatment, the period of the year, and the water temperature. Finally, the type of drinking water treatment influences the amount of PhACs in drinking water.

2.3.3 Elimination of Organic Trace Contaminants During Drinking Water Treatment

Several studies on the removal of PhACs and EDCs during drinking water treatment are available. Therefore, this section briefly introduces the efficiency of the most common water treatment processes.

Destructive drinking water treatment processes such as advanced oxidation or biological filtration can result in complete mineralization (e.g. to CO_2 and water) of organic contaminants. However, in practise this is rarely the case. The more likely outcome is degradation of the contaminants to a variety of lower molecular weight compounds, or minor changes in the chemical structure of the original organic contaminant (Kagle and al., 2009). Therefore, the terminology transformation rather than removal will be employed for these treatment processes as this is deemed more representative of the actual fate of the contaminant. However, with physical treatment processes such as activated carbon or membrane filtration, removal of trace organic contaminants is expressed in terms of adsorption or rejection.

Coagulation/flocculation

Coagulation/flocculation processes can achieve the removal of contaminants attached to particles (Yoon *et al.*, 2002). However, if not associated to particles, low removal (i.e. < 10 %) of EDCs and PCPs is observed using coagulation and flocculation (Yoon *et al.*, 2002). Moreover, as shown in Table 1.1, because most contaminants of concern in drinking water sources are relatively polar and present a Log K_{ow} value less than 3, low removals are expected during coagulation/flocculation

processes. Adams *et al.* (2002) who studied the removal of antibiotics (i.e. carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim) by coagulation/flocculation/sedimentation with alum and iron salts found this treatment relatively ineffective. Zhang and Emary (1999) studied the removal of atrazine using jar tests and determined that neither lime softening nor alum coagulation (conventional or enhanced dosages ranging from 6 to 18 mg/L) can achieve removal. Using natural water and a mixture of 62 EDCs/PCPs, Westerhoff *et al.* (2005) determined that aluminum sulfate, ferric chloride, or chemical lime softening can remove some polyaromatic hydrocarbons but for most contaminants, low removal below 25 % of EDCs and PCPs were observed. However, they observed that in the presence of NOM, enhancement of contaminants removal can occur. Overall, for chemical precipitation processes, the contaminant hydrophobicity is a good indicator for removal potential (Westerhoff *et al.*, 2005).

Oxidation and Advanced oxidation processes

The ultimate goal of oxidation processes is to produce simple and harmless molecules (Parsons and Williams, 2004). The efficiency of several oxidation processes commonly used for drinking water treatment is explored in this section.

Free chlorine (i.e. HOCl and OCl^-) is commonly used for disinfection but is also a strong oxidant. Oxidation by free chlorine can achieve a wide range of removals depending on the chemical structure of the contaminants (Yoon *et al.*, 2002). The presence of functional groups such as secondary amines and thiols increase the rate of reactions (Yoon *et al.*, 2002). Moreover, the oxidant dosage will influence the level of removals. Using four different sources of water and a contact time of 24 mh, Westerhoff *et al.* (2005) show that atrazine, DEET, fluoxetine, iopromide, meprobamate, and TCEP are poorly transformed. However, the same study, demonstrated that several compounds (i.e. trimethoprim, sulfamethoxazole, dilantin, triclosan, and erythromycin) with pKa values between 5.5 and 8.5 are well-oxidized at pH 5.5. In drinking water treatment, it is a common practice to use monochloramine as a secondary disinfectant to reduce the formation of disinfection by-products. Available data with monochloramine, which is a weaker oxidizing agent than free chlorine, show no transformations of PhACs and EDCs (Pinkston and Sedlak, 2003;Yoon *et al.*, 2002). Limited information on the oxidation of PhACs and EDCs by chlorine dioxide (ClO_2) is available in the literature. Yoon *et al.* (2002) show that herbicides, pesticides, and polycyclic aromatic carbons can

be oxidized by ClO_2 but the reactions are more selective than free chlorine. Hoigne and Bader (1994) demonstrated that compounds containing the following functional groups: phenol, tertiary amines, and thiols show higher reactivity than compounds having carbon-carbon double bounds, aromatic carbon, primary or secondary amines, aldehydes, ketones, or carbonydrate.

Alternatively, monochromatic (e.g. 254 nm) and polychromatic (e.g. 200 to 300 nm) UV irradiation can be used for microbial disinfection and for oxidation of contaminants. The presence of chromophores on the contaminants leads to the adsorption of UV light and transformation (Yoon *et al.*, 2002). Typical UV doses for disinfection range from < 5 to 30 mJ/cm^2 but higher dosage ranging from 1000 to 10000 mJ/cm^2 are required for the removal of contaminants (Adams *et al.*, 2002; Yoon *et al.*, 2002).

Ozone is used in water treatment as a disinfectant and also as an oxidant. Ozone reacts via two different pathways: direct molecular reaction or via indirect reaction of hydroxyl radical ($OH^{\bullet}$) (Yoon *et al.*, 2002). Ozone is a selective oxidant that reacts with amines, phenols, and double bounds in aliphatic compounds and thus the efficiency is very compounds-specific (Ternes *et al.*, 2002) while the $OH^{\bullet}$ reacts less selectively. Westerhoff (2005) and his colleagues show transformation greater than 80 % of atrazine, meprobamate, and TCEP using ozone. Adams *et al.* (2002) show a rapid (1.3 min) and high percentage of transformation of antibiotics at typical ozone dosage applied for drinking water treatment. Yoon *et al.* (2002) identify aliphatic methyl and carboxyls functional groups as responsible for the low rate constant with ozone.

The application of ozone is often accompanied by the formation of bromate which is formed over complex pathways involving ozone and $OH^{\bullet}$ from the oxidation bromide (von Gunten and Hoigné, 1994). Many factors such as the pH, the ratio of the ozone/$OH^{\bullet}$ concentration, the alkalinity, the ammonia concentration, and the type of dissolved organic matter (DOM) and its concentration influence the rate and yield of bromate formation. It has been shown that bromate formation is reduced in presence of hydrogen peroxide due to the back reaction of hypobromous acid, an intermediate in bromate formation (von Gunten and Oliveras, 1997 and 1998).

Therefore, advanced oxidation processes (AOP) such as O_3/H_2O_2 or O_3/UV may be beneficial to control bromate formation and also to achieve transformation of micropollutants. Other AOP processes currently applied for drinking water treatment include UV/ H_2O_2 and efficiently remove PCPs such as E2, 17β-ethinyloestradiol, triclosan, ibuprofen, gemfibrozil, and naproxen (Rosenfelt *et al.*, 2007; Crosina, 2006). In AOP processes, the intent is to increase the $OH^{\bullet}$ to improve the oxidation of contaminants (Acero and von Gunten, 2001; Acero, 2000). The concentration $OH^{\bullet}$ are generally higher than the concentration of O_3 and are increased with a rise in temperature, a decrease in NOM concentration, or a lower alkalinity (Elovitz *et al.*, 2000; Elovitz and von Gunten, 1999).

In general, oxidation processes demonstrate a good efficiency of transformation of contaminants but incomplete mineralization can lead to the formation of by-products with unknown human health risks and environmental effects (Rossner *et al.*, 2009; Adams *et al.*, 2002; Yoon *et al.*, 2002).

Activated carbon

Activated carbon has demonstrated its efficiency for the removal of many organic trace contaminants such as pesticides and PhACs in ultrapure water and in competition with NOM (Rossner *et al.*, 2009; Yu, 2007; Yoon *et al.*, 2003; Ternes *et al.*, 2002; Adams *et al.*, 2002; Miltner *et al.*, 1989). The degree of adsorption depends on the properties of the activated carbon (i.e. surface area, pore size distribution, surface charge, and oxygen content) but also on the properties of the contaminants (i.e. shape, size, charge, and hydrophobicity) (Yoon *et al.*, 2002). The main mechanism of removal of organic contaminants is hydrophobic interactions (Yoon *et al.*, 2002). Therefore, contaminants with higher Log $K_{ow} > 2$ value are expected to be removed by activated carbon (Yoon *et al.*, 2002). Because the NOM present in natural water is competing against contaminants for adsorption site, studies performed in ultrapure water may overestimate the percentage adsorption. Consequently, adsorption of contaminants by powder or granular activated carbon should be optimized for a specific plant. Rossner *et al.* (2009) show that a dose of < 10 mg/L of coconut-shell-based activated carbon was sufficient to achieve 2-log removal if adsorption equilibrium is reached. Another example is provided by Snyder *et al.* (2003) who showed the efficient removal of seven antibiotics using powder activated carbon (10-20 mg/L). This study also demonstrates that removals decrease by 10 to 20 % in river water compared to distilled water.

Biofiltration

Some trace organic contaminants biodegrade during biological wastewater processes (Clara *et al.*, 2009; Nghiem *et al.*, 2009; Radjenovic *et al.*, 2009; Kimura *et al.*, 2007; Joss *et al.*, 2005) reducing the risk to contaminate sources of drinking water (Lindqvist *et al.*, 2005). Common biologically active treatment processes for drinking water treatment including slow sand filtration, biologically active carbon filtration, and riverbank filtration may provide some removal of easily biodegradable contaminants. Biodegradation of ibuprofen and clofibric acid was observed in river biofilm systems (Winkler *et al.*, 2001). The EDC amitrol was effectively biodegraded using biologically activated carbon but poorly adsorbed on GAC, while nonylphenol and bisphenol A show a reduced adsorption capacity over time suggesting a limited biodegradability of these compounds (Choi *et al.*, 2005). During conventional wastewater treatment, Radjenovic *et al.* (2009) show high removal (≥ 70 %) of ibuprofen, acetaminophen, naproxen, sulfamethoxazole, ofloxacin, and benzafibrate. Some compounds such as carbamazepine and gemfibroxil are persistent in biological treatment of wastewater and drinking water (Radjenovic *et al.*, 2009; Joss *et al.*, 2005). However, as mentioned for oxidation processes, biological degradation of trace organic contaminants can transform the parent compound into by-products causing environmental concern but further research is needed on this area.

Membrane filtration

Different types of membranes can be used for drinking water treatment but only NF and RO have demonstrated high removal (> 95 %) of organic trace contaminants (Kim *et al.*, 2007; Kimura *et al.*, 2004). UF is less efficient for the removal of organic trace contaminants. Yoon *et al.* (2007) observed a rejection < 30 % by UF membranes except for a few compounds having a Log K_{ow} value > 3. In general, PCPs, PhACs and EDCs have a molecular size between 150 and 500 Daltons (Yoon and al., 2002). Because of the surface membrane properties (i.e. MWCO, material, surface charge, functional group, surface morphology, and hydrophobicity), the contaminants can be rejected via different mechanisms such as size exclusion, adsorption, or electrostatic repulsion. The rejection is not exclusively governed by the membrane properties but also by the compound properties (i.e. molecular weigth, molecular size, pKa, Log K_{ow}, and diffusion coefficient) (Bellona *et al.*, 2004) and the water quality (Comerton *et al.*, 2008).

Comparing RO membranes, Ozaki *et al.* (2008) show that the rejection of undissociated solutes was most likely due to simultaneous adsorption, size exclusion, and diffusion. The research also demonstrates that contaminants with higher hydrophobicity (i.e. K_{ow}) show increased rejection. Adams *et al.* (2002) observed high rejection rates of 99 and 99.9 % using two and three low-pressure reverse osmosis systems in series. Kimura *et al.* (2003) demonstrated the importance of the compound charge in the rejection by NF membrane. The rejection efficiency of charged compounds was always greater than 90 % regardless of the membrane or compound properties. However, the rejections of uncharged compounds vary between 12 % and 87 %.

Overall RO and NF membranes are excellent barriers for the removal of trace organic contaminants except for the lower molecular weight and uncharged compounds (Yoon *et al.*, 2002).

2.4 Summary and Research Gaps

As presented in the review, trace organic contaminants can be detected in drinking water sources at ng/L to low µg/L concentrations. Although studies have shown that treated drinking water usually contains lower numbers of compounds at lower concentrations than in the source water, the presence of these contaminants remains a public concern. A study published by Pomati *et al.* (2006) showed that human embryonic cells may experience physiological and morphological transformations when exposed to a mixture of pharmaceuticals at concentrations typically present in the environment. Therefore, further research on the removal of PhACs, EDCs and PCPs occurring during the water treatment process is needed.

While the removal efficiency of PhACs, EDCs, and PCPs by common water treatment processes has been studied, unconventional processes such as biofiltration remain to be investigated. Wastewater treatment processes utilizing the biological activity of the activated sludge process (Clara *et al.*, 2009; Joss *et al.*, 2005) and biodegradation of ibuprofen and clofibric acid in river biofilms (Winkler *et al.*, 2001) indicate that some compounds are biodegradable. However, the degree of biodegradability of contaminants and also the conditions favoring biodegradation during rapid biofiltration in drinking water applications still needs to be determined.

The efficiency of membrane filtration for the removal of pathogenic microorganisms (MF and UF) and trace organic contaminants (NF and RO) has been demonstrated (Kim *et al.*, 2007; Kimura *et al.*, 2004). But one of the main limitations of membrane filtration remains fouling. Fouled membranes suffer from a loss of performance, reduction of flux, or require higher pressure. Membrane fouling also increases the frequency of backwash and chemical cleaning which has a negative impact on the operating cost. Possible permeate quality decrease and membrane degradation can also be a consequence of membrane fouling.

Consequently, pretreatment processes such as coagulation-sedimentation-flocculation or a variation thereof, integrated membrane systems, or river bank filtration must often be applied to efficiently control membrane fouling on low and high pressure membranes. The application of chemical free, rapid biofiltration as a membrane pretreatment for drinking water applications has only rarely been considered. Thus, determining the performance of rapid biofiltration for fouling control of low and high pressure membranes was one of the main goals of this study.

Chapter 3

MATERIAL AND METHODS

3.1 Feed Water and Experimental Set-up Location

Grand River water was used as source of raw water for this study. Grand River water is representative of municipally and agriculturally impacted surface water used by water treatment plants in North America. The biofiltration and UF membrane set-ups were located at the lowlift pumping station which supplies the raw water for the Mannheim Water Treatment Plant (Kitchener, Ontario, Canada). The location of the pumping station allowed an easy access to a continuous source of fresh water required for continuous operation of the biofiltration set-up. This raw water intake is presented in Figure 3.1. This location is also identified as Doon Station.

a) b)

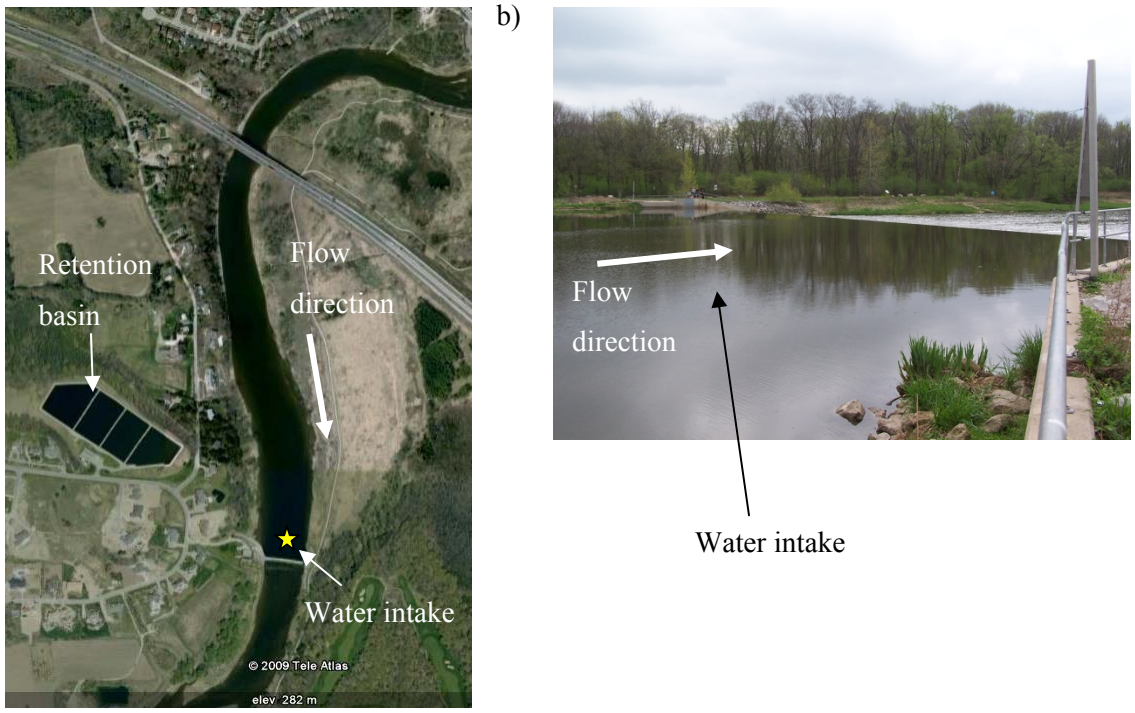


Figure 3-1 Lowlift pumping station intake a) view of Grand River and retention basin (Google Earth Software), and b) view of the dam

3.2 Physico-Chemical Analyses

Weekly parameters measured on Grand River water were TOC, DOC, UV_{254}, SUVA, turbidity, conductivity, pH, and temperature.

The concentration of TOC and DOC were respectively measured using the OI-Analytical TOC analyser (Model 1010, College Station, TX) with the wet-oxidation method as described in Standard Methods 5310C (Standard Methods, 2005). DOC samples were filtered through a 0.45 µm cellulose acetate filter prior to analysis. A new filter was used for each sample and prior to sample filtration, each filter was rinsed with 500 mL of MilliQ water. Samples were preserved by adjusting the pH below 2 using phosphoric acid (1N). Samples were kept at 4°C up to three weeks before analysis.

Turbidity was measured using a Hach 2100P turbidimeter following Standard Methods 2130 (Standard Methods, 2005). Samples were analyzed within 24 h after sampling. The replicability of turbidity measurements was ± 0.1 NTU unit based on 10 analyses the detection limit was 0.2 NTU.

A pH meter Orion 720A and a glass electrode Orion 91-02 were used to measure pH. The replicability of the pH measurement is ± 0.2 pH unit based on 10 analyses.

Conductivity was determined using a conductivity meter (Hach 44600) following Standard Methods 2510 (Standard Methods, 2005). The replicability of the conductivity measurement is ± 1 μS/cm unit based on 10 analyses.

UV_{254} was measured using a spectrophotometer (Hewlett Packard 8453) and a 1cm path length quartz cell following Standard Methods 5910 (Standard Methods, 2005). The replicability of the UV measurement is ± 0.005 cm^{-1} based on 10 analyses.

SUVA is calculated as the ratio of UV_{254} absorbance (κ) to the DOC.

$$SUVA = \frac{\kappa(254)cm^{-1}}{DOC(mgC/L)} \times \frac{100cm}{m} \quad \left(\frac{L}{mgC \cdot m}\right) \qquad \text{eq. 3.1}$$

The water temperature was measured using a general purpose thermometer filled with mineral fluid. The accuracy is ± 0.5°C.

3.3 Roughing Filtration and Biological Filtration

Because of the highly varying and sometimes challenging raw water quality, a roughing filter (RF) was used to reduce peak concentrations of suspended material prior to biofiltration. The RF consisted of three layers (1.2 m total depth) of gravel of decreasing size; the bottom layer was 50 cm depth with media diameter between 12.7-19.1 mm, the middle layer was 40 cm with media diameter between 9.5-12.7 mm, and the top layer was 30 cm depth with media diameter between 4.8-9.5 mm. The RF was operated in an upflow mode (Figures 3.2 and 3.3). The hydraulic loading, 1.1 m/h, was

based on earlier work involving slow sand filtration with this water (Cleary, 2005) and was not optimized for this study. The RF was fed by gravity using a constant head tank. The difference in elevation between the water level of the constant head tank and the water level of the roughing filter was 1.3 m. The roughing filter was back flushed three times at least once a week.

Two biofilters were operated in parallel in down flow mode at 5 m/h. The EBCT of biofilter 1 (B1) was 5 minutes and the column contained 0.2 m of anthracite on top of 0.2 m of sand (Figures 3.2 and 3.3 insert). The EBCT of biofilter 2 (B2) was 14 minutes and the column contained 0.2 m of anthracite on top of 0.97 m of sand (Figures 3.2 and 3.4). Part of the sand layer of B2 was contained in a second column connected in series and fed by gravity, because of site height restrictions within the biofilters' room. Both B1 and B2 contained a layer of support gravel (0.15 m), which was not included in EBCT calculations. On the basis of a sieve analysis, the effective size of the anthracite and sand was 1.07 mm and 0.52 mm, respectively. The uniformity coefficient for both media was 1.5. The biofilters were backwashed weekly using collapse pulsing with air and water for 3 min followed by a 50 % bed fluidization for 8 min. The biofilters were operated for a period of 6 months before experiments were begun and they were operated for a period of 20 months (between December of 2006 and August of 2008). In order to reduce contaminant adsorption, the system was built entirely using Teflon® tubing, glass columns, and stainless steel fittings.

A column without media (B3) was also operated in order to estimate the adsorption of selected PhACs and EDCs on the experimental set-up.

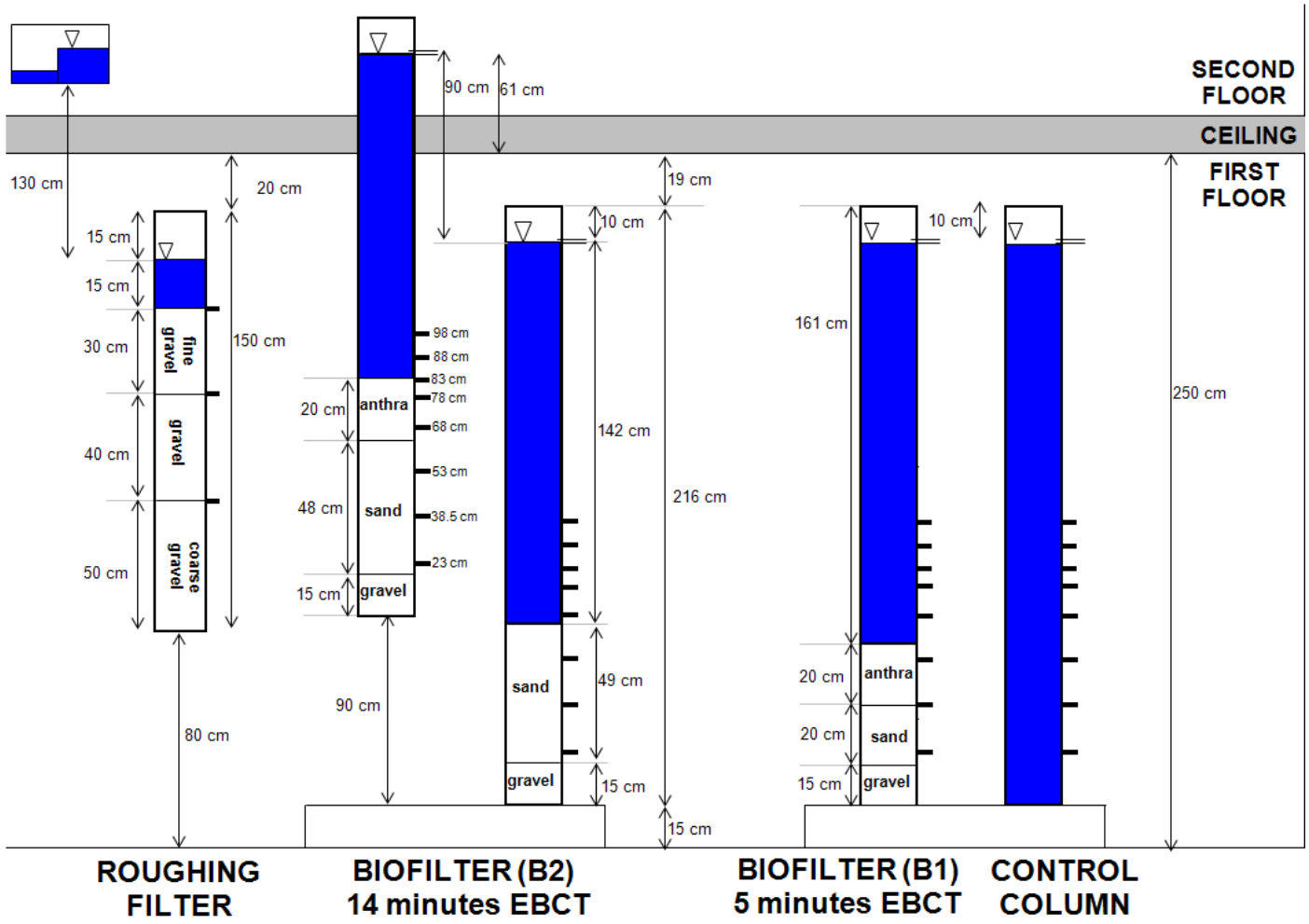


Figure 3-2 Schematic of the rouging filter and biofilters

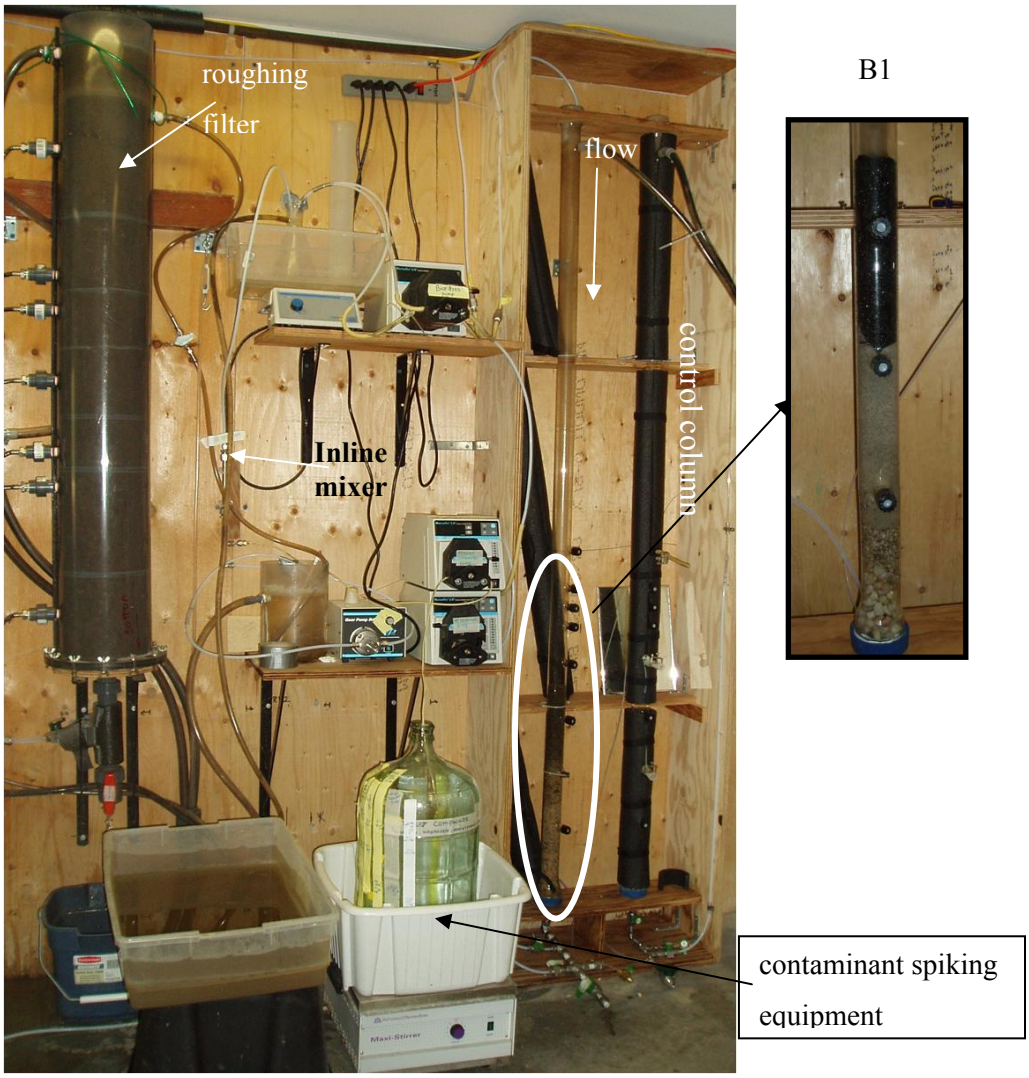


Figure 3-3 View of the biofiltration experimental set-up including roughing filter, contaminant spiking equipment, biofilter B1 (5 minutes EBCT) and control column

Once a month the dissolved oxygen of biofilters influent and effluent was measured to ensure the treatment process was operated under aerobic conditions. The dissolved oxygen was measured using a dissolved oxygen meter following standard methods 4500-OG (Standard Methods 2005). TOC, DOC, UV_{254}, SUVA, and turbidity were also measured on a weekly basis in the effluent of the RF and biofilters.

Figure 3-4 View of biofilter B2 (14 minutes EBCT)

3.4 Membrane Filtration Systems

3.4.1 Ultrafiltration Membrane

The membrane used for this study was the commercially available polyvinylidene fluoride (PVDF) supported ultrafiltration membrane made by GE/Zenon, Oakville, Canada. The Zeeweed - 1® module is built with hollow fiber membranes (500 series) and operated in an outside-in mode. The selection of UF membrane was made to pursue previous work performed within the NSERC Chair in water treatment (Ratajczak, 2007; Basu, 2004).The MWCO provided by the manufacturer is 400 KDa (approximately 20 nm pore size) (Mosqueda and Huck, 2006). The surface charge at pH 7 is -50 mV as shown in Figure 3.5. Membrane zeta potentials were determined in a background solution containing 10 mM KCl using commercially available streaming potential/current equipment (SurPASS, Anton Paar, Graz, Austria). As provided by the manufacturer, the membrane had a nominal surface area of 0.047 m^2 and fibers were 15 cm long.

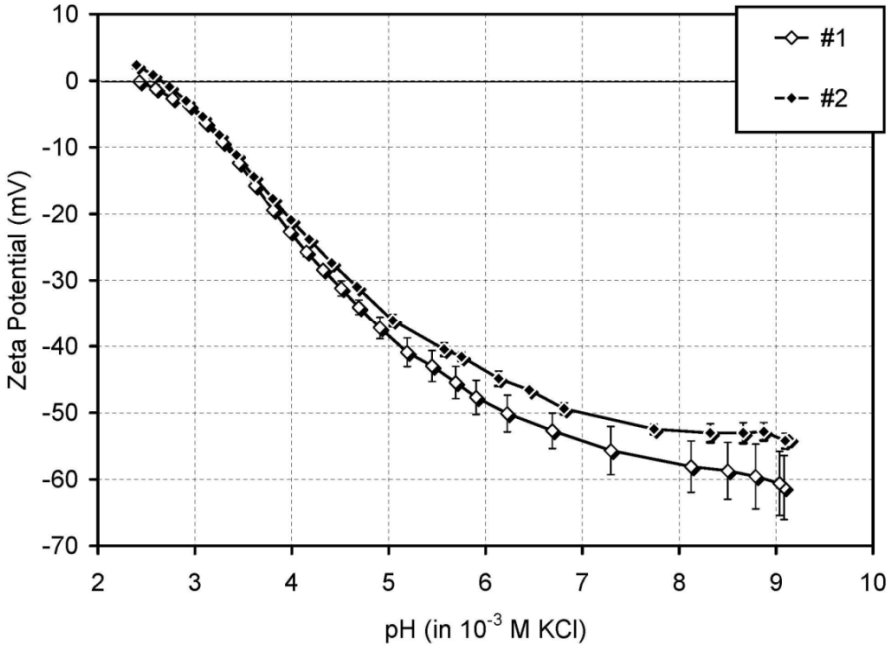


Figure 3-5 Zeta potential of ZeeWeed-1® series 500 membranes as function of pH

Table 3.1 presents the normal operational range of Zeeweed-1® module suggested by the manufacturer.

Table 3-1 Operating range of Zeeweed-1® series 500 modules

Parameters	Range
Flux	30-70 LMH
Permeate flow rate	1.4 – 3.3 L/h
Pressure	0-10 psi
Temperature tolerance	0 – 40°C
Chlorine tolerance	1000 mg/L
pH tolerance	2 -11

LMH: liter per membrane area (m^2) per hour

The virgin membranes were received in a sealed plastic wrap to prevent fiber breakage during transportation and storage. The fibers were preserved by a coating of glycerin to keep the fiber moist. Immediately after unpacking, the membranes were rinsed with tap water for at least 1 h to remove the preservative. The membrane modules were then submerged in a solution of 200 mg/L sodium hypochlorite (NaOCl) for a minimum of 5 h, and then rinsed with tap water for 15 minutes. Following this procedure, the membrane modules were submerged in a solution of 5 g/L citric acid for a minimum of 5 h, and then rinsed with tap water for 15 minutes. Prior to use and after each experiment, the membranes were cleaned in the same manner. Cleaned membranes were kept in tap water in a glass jar at 4°C until usage. Clean water permeability tests were performed after chemical cleaning to confirm the efficiency of the cleaning. During the clean water permeability tests, the flux was adjusted depending on the water temperature and clean water permeabilities vary between 2.05 psi and 3.79 psi depending on the module and applied permeates fluxes. A new UF membrane module was used for each season.

3.4.2 Ultrafiltration Set-up and Operational Conditions

The membrane module was mounted vertically in a cylindrical holder of 1.6 L. The unit was operated at a constant permeate flow at a recovery of 94 %. The automated operational sequence consisted of: 1) permeation for 1 h, 2) back pulse with air sparging for 20 seconds, 3) drain 0.4 L of the tank, and 4) filling of tank for 9 minutes. The transmembrane pressure (TMP) was monitored by a

pressure transducer. The permeate flux was adjusted to correspond to 57.5 LMH at 20°C. Experiments using B1 and B2 effluents as feed water for the UF membrane were performed sequentially since only one UF unit was available. In order to reduce the potential for biofouling, a typical run length of 5 days was used.

The experimental set-up and the sampling locations are presented in Figures 3.6 and 3.7.

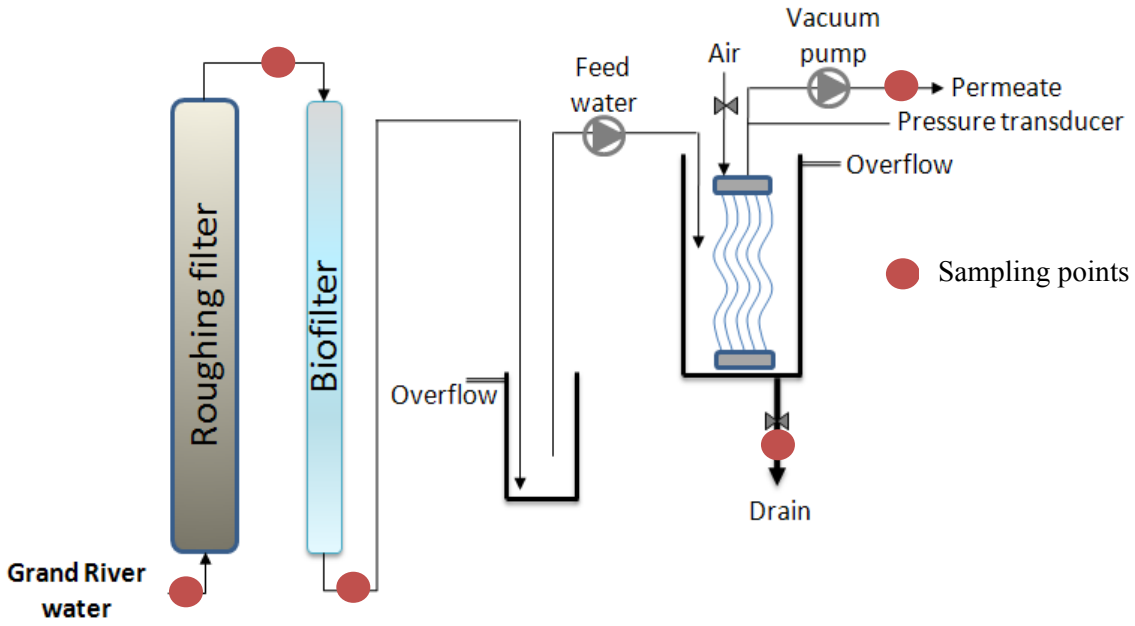


Figure 3-6 Schematic drawing of biofiltration and UF membrane set-ups. The ● indicates sampling locations

Figure 3-7 View of the holding thank and the hollow fiber UF membrane

3.4.3 Nanofiltration Membranes

The membranes used in this study were commercially available nanofiltration membranes: TriSep TS80 and XN45 (TriSep Corp., Goleta, CA, USA). The selection of UF membrane was made to pursue previous work performed with XN45 membrane within the NSERC Chair in water treatment (Mosqueda and Huck, 2009). The second membrane TS80 was selected to compare the performance of the XN45 membrane with a membrane having a similar MWCO as reported by the manufacturer. Both membranes are thin film composite membrane with a cross-linked aromatic polyamide top layer. The membranes were received as flat sheet samples and cut in pieces of 300 cm^2. The experimental membrane surface area of a coupon was 140 cm^2. Following the manufacturer's recommendation, membrane coupons were stored in a solution of 2 % sodium metabisulfite and 18 % glycerin prepared with MilliQ water and stored at 4°C to reduce the chance of microbial growth. The membrane coupons were rinsed for a minimum of 15 minutes with MilliQ water to remove preservation chemicals prior usage.

Prior to the experiments, the virgin membranes were compacted using deionized water until stable permeate flow was achieved typically after 12 hours. Following the compaction period, the deionized water was drained from the feed tank and 20 L of feed water (biofilter effluent) was introduced into the tank.

Table 3.2 presents some important characteristics of the NF membranes selected for this study. The MWCO provided by the manufacturer for both membranes was 200 Da. However, Mandale and Jones (2008) measured a MWCO of 250 Da for the XN45 membrane. The difference between the manufacturer value and the MWCO determined experimentally may be caused by the pore size distribution. As demonstrated by Kosutic *et al.* 2006, pore size is not uniform but varies usually around a mean pore size. Figure 3.8 presents the pore size distribution of the TS80 membrane which is bimodal. It is also expected to observe a pore size distribution for the XN45 membrane.

Table 3-2 Properties of the selected NF membranes

Membrane	**MWCO (Da)**	**Contact angle (°)**	**Roughness (mm)**	**Surface charge at pH 7 (mV)**
TS80	200[b]	48 ± 2[c]	8.8	-14 ± 3[a]
XN45	250[a]	57 ± 1	21	-25[c]

a: Mandale and Jones (2008); b: manufacturer; c: Verliefde *et al.* (2009)

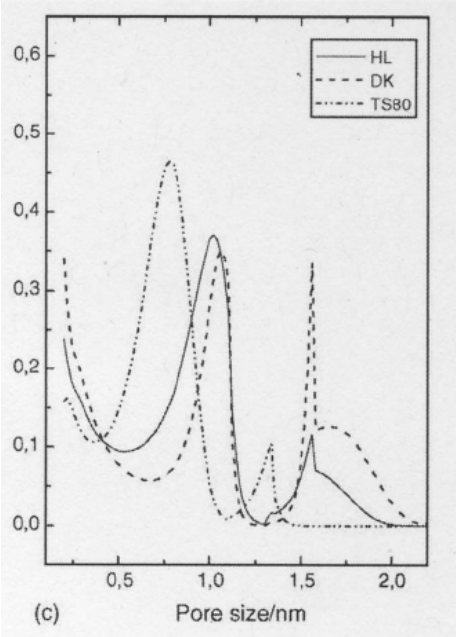


Figure 3-8 Pore size distribution of TS80 membrane (source: Kosutic *et al.*, 2006)

Contact angle gives an indication of the hydrophobicity of the NF membranes. A large contact angle corresponds to a hydrophobic surface. Contact angles of 57.6° and 36.3° for XN45 and TS80 were respectively measured. It indicates that XN45 has a more hydrophobic surface than the TS80 membrane. Membrane hydrophobicity of the XN45 membrane was characterized by sessile drop contact angle measurement by placing a droplet of UP water (5µL) onto the membrane surface. The measurement was performed using a VCA2500 XE instrument (AST). Each contact angle was measured three times and an average value was calculated.

The average roughness values show that the XN45 has a rougher top layer (21 nm) compared to the smoother TS80 membranes (8.8 nm). Membrane surface structure and morphology were characterized by AFM in tapping mode using MultiMode AFM (Veeco). The cantilever was made out of etched silicon with a spring constant of 20-80 N/m and a nominal tip apex radius of 5-10 nm. After scanning, the images were plane fitted and flattened with a second order polynomial approximation to remove AFM scanner-induced curvature and slope from the image. Membrane morphology was characterized as roughness determined through AFM image analysis. Average roughness (arithmetic

average of the absolute values of the surface height deviations measured from the center plane) was determined on three different spots and an average value was calculated.

At a pH below the IEP, polymeric NF membranes have typically a slightly positive charge. Above the isoelectric point, these membranes are negatively charged. The charge of the membrane surface is therefore becoming more negative as the pH increases. The XN45 membrane has an isoelectric point of approximately pH 4 (Mandale and Jones, 2008) and thus is negatively charged at pH values typical for drinking water. The zeta potential of the TS80 membrane at pH 7 is -14 ± 3 mV (Verliefde *et al,*. 2009) again indicating a negative surface charge at a typical drinking water pH.

3.4.4 Nanofiltration Set-up and Operational Conditions

Nanofiltration experiments were performed with a bench scale module (GE SEPA^{TM} CFII) using flat sheet membranes as illustrated in Figure 3.9. The NF experiments with the XN45 and TS80 membranes were operated at a constant pressure of 8.2 bar and 12.4 bar, respectively. The pure water permeability of XN45 and TS80 were 10.4 LMH/bar and 10.0 LMH/bar, respectively. The initial recovery, calculated as the ration of permeate flow to feed flow, was 2% for both membranes. The initial permeate flux of XN45 and TS80 membranes was 85.7 LMH and 124.2 LMH. Throughout the experiments, the temperature was kept constant at 25 ± 2°C through the use of a chiller. The experiments were performed in a recycle mode; both concentrate and permeate were returned to the feed tank. The duration of the experiment varied between 72 h and 144 h. All components of the NF set-up were made of stainless steel and Teflon tubing.

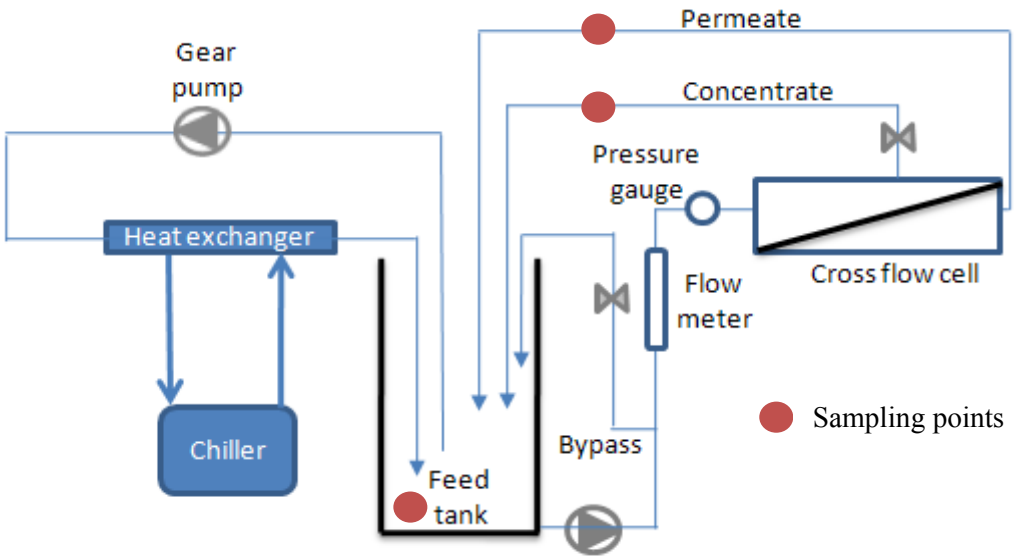


Figure 3-9 Schematic of the nanofiltration experimental set–up. The ● indicates sampling locations

3.5 Selection of Target Compounds

The selection of the target compounds was based on an extensive literature review of PhACs and EDCs in the environment performed by Yu (2007). It is from this literature review that several contaminants were identified as potential candidates.

Target compounds selection for this study was based on three main criteria:

1) Presence in surface waters used as source of drinking water,
2) Differences in physico-chemical properties, and
3) Ability to analyse the contaminants using gas chromatography with mass spectra detector (GC/MS) with detection and quantification limits sufficiently low to represent conditions encountered during drinking water treatment.

The compounds that met these criteria were:

- ibuprofen
- naproxen
- N,N-Diethyl-meta-toluamide (i.e. DEET)
- 2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine atrazine (i.e atrazine)
- carbamazepine
- 4-n-nonylphenol (NP)

The detection and quantification limits for the selected compounds are summarized in Table 3.3.

Table 3-3 Limit of detection (LOD) and limit of quantification (LOQ) for the selected trace organic contaminants

	ibuprofen	**naproxen**	**DEET**	**atrazine**	**carbamazepine**	**NP**
LOD (ng/L)	2	2	5	5	5	7
LOQ (ng/L)	7	6	15	16	16	24

IBUPROFEN

Ibuprofen is a non-steroidal anti-inflammatory drug available over the counter used to relieve the symptoms of arthritis, swelling, and stiffness. The pharmacological effect of ibuprofen is due, almost exclusively, to the S enantiomer. Ibuprofen is negatively charged at neutral pH because the carboxylic group is deprotonated (pKa 4.91). Approximately 15 % of ibuprofen is excreted unchanged or as its glucuronide (Khetan et Collins, 2007). Figure 3.10 presents the metabolic transformation of ibuprofen. The remaining ibuprofen is transformed into other metabolites such as hydroxyl-ibuprofen, carboxy-ibuprofen, carboxy-hydratropic acid and their respective conjugates (Khetan and Collin, 2007).

NAPROXEN

Naproxen is also a non-steroid anti-inflammatory drug available by prescription. The principal photoproducts of naproxen are produced by photoionization and decarboxylation of the parent compounds (Figure 3.11) and those products show higher toxicities than naproxen (Isidori *et al.*, 2005).

DEET

N,N-diethyl-m-toluaminde (DEET) has been used as an active ingredient in most insect repellents since 1946 for military usages and since 1957 for the general public. The o- and p-isomers are effective but the m-isomer is desired for greater efficiency. The acute oral toxicity is 2000 mg/kg for mammals and oral admission can provoke damage to the central nervous system. Less than 20 % of DEET is absorbed through the skin and metabolized. Six metabolites of DEET have been identified and transformation occurs by dealkylation of the n-alkylamide group and by oxidation of the aromatic ring. The aquatic contamination routes are via sewage following washing off and excretion by humans (Costanzo *et al.,* 2007). Studies performed in USA, Germany, and Autralia report high level of detection frequency of DEET in surface water (Costanzo *et al.,* 2007; Schwarzbauer and Heim, 2005; Kolpin *et al.,* 2002).

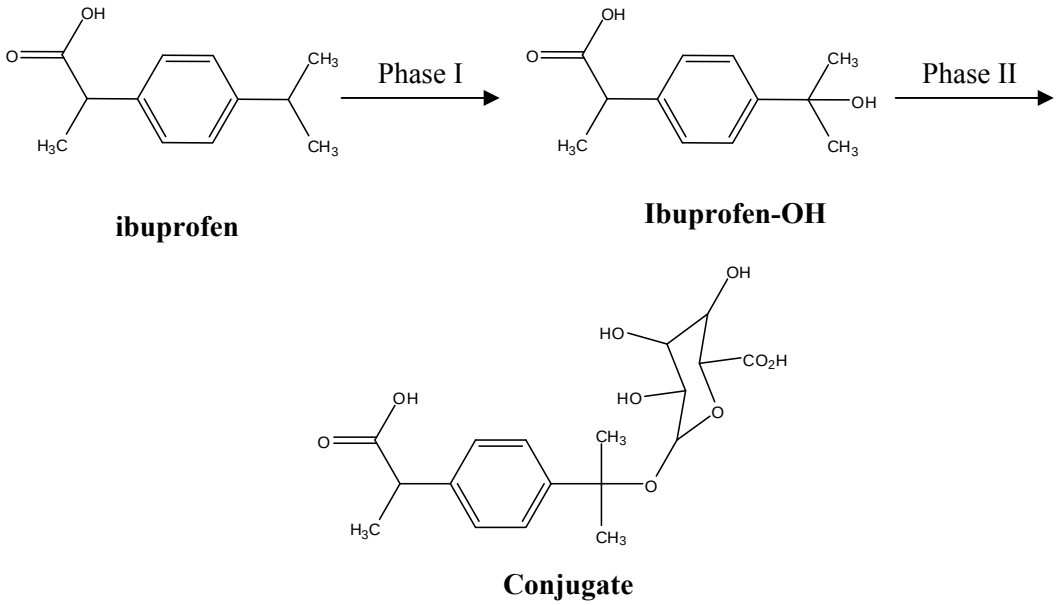


Figure 3-10 Metabolic transformations of ibuprofen (source: Khetan et Collins, 2007)

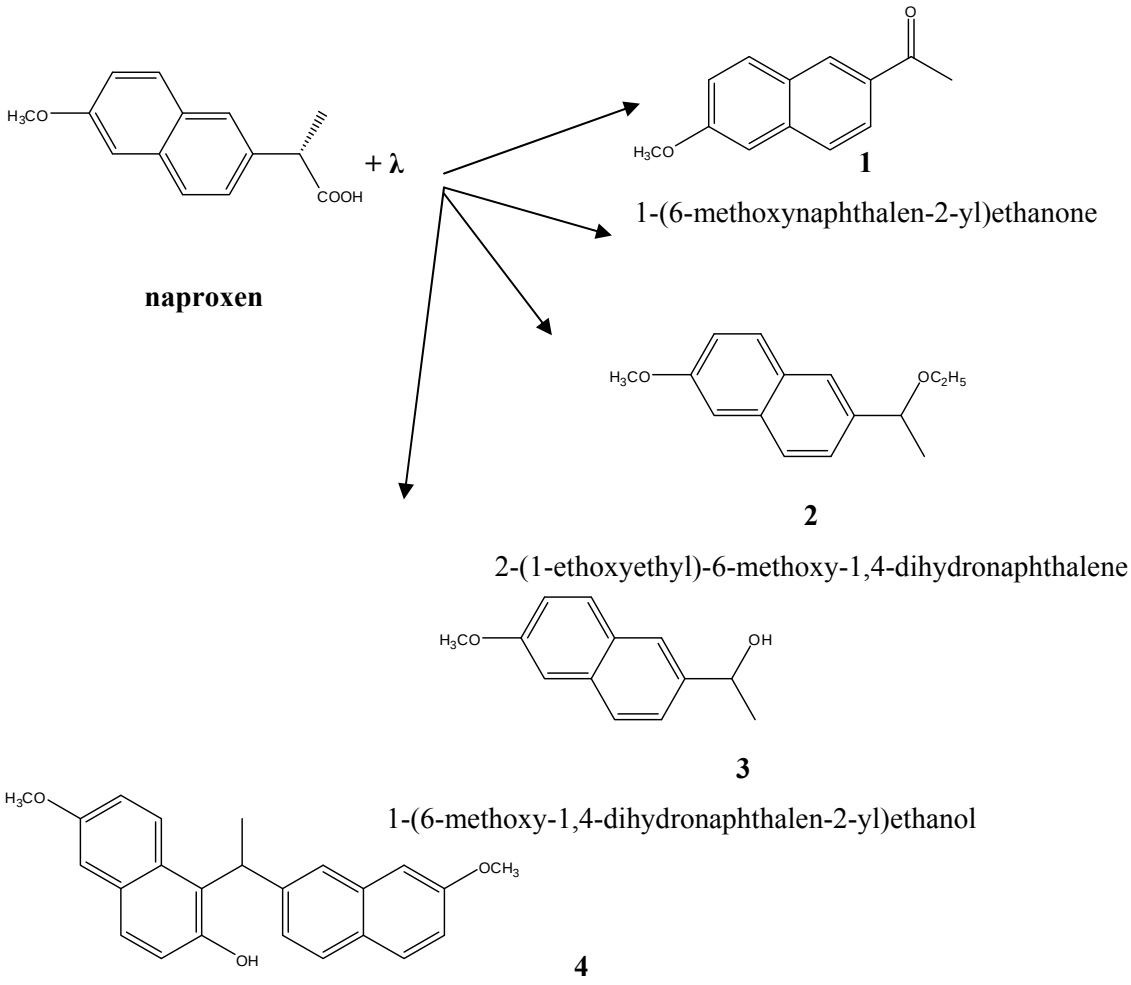


Figure 3-11 Naproxen and photodegradation by-products (source: Isidori *et al.*, 2005 and ChemSketch 12.0 (advanced Chemistry Development Inc., Toronto, Canada))

ATRAZINE

2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine, also known as atrazine, is an agricultural herbicide to control pre and post growth of broadleaf and grass weed in corn fields. First introduced in Canada in 1960, it has been widely used but, due to environmental concern, the usage is now limited due to potency as a EDC. Atrazine is subject to seasonal application and its main entry route into the aquatic environment is through runoff from farm land because the herbicide is soluble. Atrazine or its by-products are the most frequently detected herbicide in surface water and is detected throughout the entire year as reported by Lemieux *et al.* (1995).

CARBAMAZEPINE

Carbamazepine is a neutral drug used for the treatment of epilepsy which is a common central nervous system disease. Also, carbamazepine can be used as a mood stabilizing agent in the treatment of schizophrenia. Carbamazepine is metabolized at a high rate and only 3 % is excreted unchanged. The major metabolic transformation of carbamazepine is via oxidation, hydration, and formation of glucuronide conjugates. The major metabolites are 10,11-dihydro-10,11-dihydroxycarbamazepine and 10,11-dihydro-10,11-epoxycarbamazepine. Carbamazepine and its metabolites have been frequently detected in surface water near WWTP effluent and agricultural fields (Melcalfe *et al.*, 2003a; Lissemore *et al.*, 2006).

NONYLPHENOL

Nonylphenol ethoxylates (NPEs) and its degradation products (i.e. NP2EC, NP1EC, NP2EO, and NP1EO) which are part of a broader group of compounds known as alkylphenol ethoxylate (APEs) degraded to nonylphenol (NP).

The presence of NP in the environment is understood to be solely the consequence of anthropogenic activities because no natural source of NP has yet been identified. From the nonylphenolic compounds, 4-nonylphenol is the most estrogenic and has the greatest tendency to bioaccumulate (Bennie *et al.*, 1997). NP is more lipophilic than NPE and tends to accumulate in sludge and sediments (Bennie *et al.*, 1997). During primary and secondary wastewater treatment, the effluent concentrations of NP are only 3% and 4%, respectively. However, accumulation of NP in the activated sludge and digested sludge has been observed during secondary or tertiary treatments (Giger *et al.,* 1987). Thus, disposal of sludges by landfilling and by use on agricultural fields may cause aquatic contamination. The main mechanisms of removal of NP in the aquatic environment are volatilization and adsorption to suspended solids and sediments, photochemical degradation and transformation, and biodegradation. Limited volatilization of NP is expected out if water due to its low Henry's law constant (3.40×10^{-5} atm-m^3/mol at 25°C from EPI suite). However, Dash *et al.* (1999) confirmed volatilization of NP when high concentrations are detected in surface water. Photochemical degradation of NP is expected to be important in a clear shallow river.
Ahel *et al.* (1994) demonstrated that within a day, 30 % of NP could be photodegraded in the surface layer of natural waters. A photodegradation half–life of 15-20 h at a sunlight intensity of

0.700 kW/m^2 has been determined (Ahel *et al.*, 1994). A biodegradation half -life of 150 days has been estimated for NP in surface water by the U.K. Environment Agency.

A summary of the important properties of the contaminants are presented in Table 3.4. The compounds were purchased from Sigma-Aldrich (Saint Louis, MO) and are reported to have 99 % purity or higher. As seen in Figure 3.12, the selected compounds have quite distinctive functional groups.

The charge of the compounds is governed by the pH of the solution and the compound dissociation constant (pKa) values. The contaminants selected for this study present noticeably different physicochemical properties although they have similar molecular weights: between 191.3 and 236.3 g/mol. Compounds speciate as function of pH so that ibuprofen and naproxen are negatively charged at a neutral pH. Carbamazepine is a base and it exhibits two dissociation constants with a pK_a1 of 2.3 and pK_a2 of 13.9. Thus, it is uncharged at neutral pH. NP is also uncharged at neutral pH. Atrazine is a base with a pKa of 1.7 thus it is also uncharged at neutral pH.

The water solubility and hydrophobicity expressed as Log K_{ow} values of a compound can also be affected by the pH. It is assumed that the value presented in Table 3.3 represents the compounds characteristic in their neutral form. A modified Log K_{ow} value has been suggested by Hu *et al.* (1998) to predict the adsorbability of acidic and basic pesticides (equation 3.2).

$$K'_{ow} = \frac{K_{ow}}{1 + 10^{(pH - pk_a)}} \qquad \text{eq. 3.2}$$

Where K_{ow} represents the octanol–water partition coefficient for the undissociated compound and K'_{ow} represents the coefficient corrected for the dissociated fraction of a compound at a particular pH.

Hydrophilic compounds are capable of forming hydrogen bounds with polar species such as water thus making them very water soluble. Aromatic hydrocarbon molecules tend to be hydrophobic while aliphatic molecules tend to be hydrophilic. With a higher Log K_{ow} value, NP is the most hydrophobic of the selected compounds while naproxen is the most hydrophilic compound at a pH of 8. Thus, it is

expected to observe absorption of NP into organic phase (i.e. NOM, biofilm) and adsorption of NP onto surfaces.

Table 3-4 Physicochemical properties of target compounds

Compound	Class	CAS no.	Molecular formula	Molecular weight (g/mol)	Log K_{ow} / Log K'_{ow}	pKa	Water solubility (mg/L at 25°C)
ibuprofen	PhAC	15687-27-1	$C_{13}H_{18}O_2$	206.3	3.97[a] / 0.88[f]	4.91[a]	21[a]
naproxen	PhAC	22204-53-1	$C_{14}H_{14}O_3$	230.3	3.18[a] /-0.67[f]	4.15[a]	15.9[a]
DEET	PCP	134-62-3	$C_{12}H_{17}NO$	191.3	2.18[a]	na	912[a]
atrazine	EDC	1912-24-9	$C_{18}H_{14}ClN_5$	215.7	2.61[a]	1.7[a]	34.7[a]
carbamazepine	PhAC	298-46-4	$C_{15}H_{12}N_2O$	236.3	2.45[a]	2.3[c], 13.9[a]	17.7[a]
nonylphenol	EDC	104-40-5	$C_{15}H_{24}O$	220.4	5.92[b]	10.25[e]	7[d]

a: Trenholm *et al.* (2006); b:Yoon *et al.* (2002); c :Nghiem *et al.* (2005); d: ChemID Plus Advanced software (http://chem.sis.nlm.nih.gov/chemidplus/); e: USEPA EPI suite program V4.0; f: calculated from eq. 3.2 at pH 8; na: not available

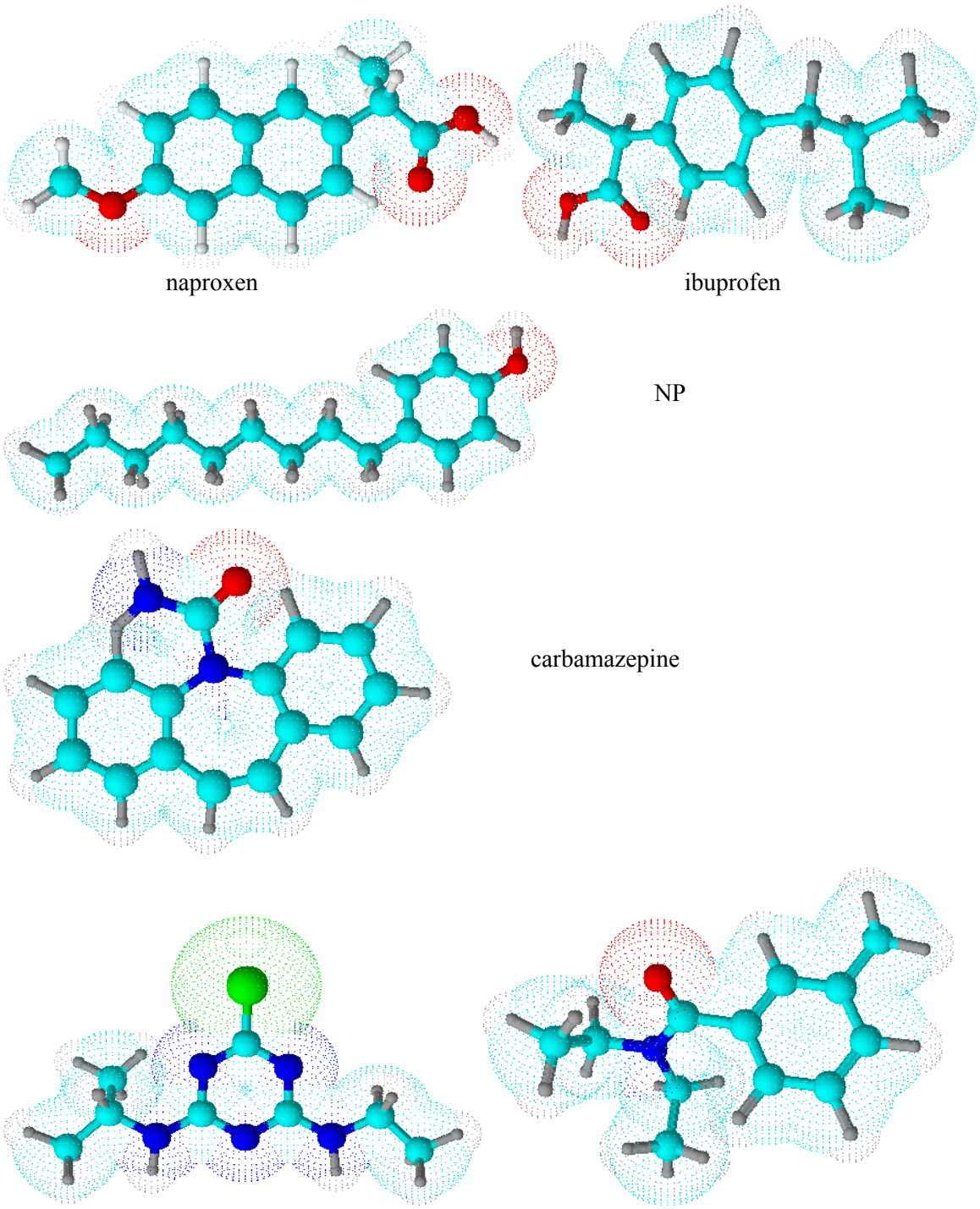


Figure 3-12 Structure of target contaminants using ChemSketch 12.0 (Advanced Chemistry Development Inc., Toronto, Canada). Atom color legend: Pale blue = carbon, dark blue = nitrogen, red = oxygen, grey = hydrogen, green = chloride

3.6 Trace Organic Contaminants Spiking Procedure

The selected contaminants were continuously spiked in the biofilter influent following the acclimation period either at a low concentration of 500 ng/L each or at a high concentration of 5 µg/L each. Stock solution was prepared in batch of 40 L in a stainless steel tank at the UW lab without the use of any solvent. Neat compounds were weighed in and dissolved in MilliQ water. The solution was stirred for one week and transferred into two glass bottles of 20 L. The stock solution was kept at 4°C in the dark until usage. Low and high spiking concentrations, required stock solution concentrations of 0.3 mg/L and 1 mg/L of each compound, respectively. While being used, the stock solution was continuously mixed at the intake using a magnetic stirrer. The spiking equipment is presented in Figure 3.2. After injection, an inline mixer ensured complete mixing of the solution with the RF effluent and the consumption of stock solution was monitored to ensure proper dosing. Influent concentrations to the biofilters were measured at least weekly.

3.7 Other Methods

Several other methods have been used to accomplish this project. Methods used for a specific study are presented in the result chapter as follow:

- The analysis method for the selected PhACs and EDCs (i.e. extraction, GC/MS analysis conditions) and their quantification is described in chapter 4.
- Chapter 5 contains the spiking methodology of PhACs and EDCs in the biofilter influent. The methodologies of analyses performed on the media (i.e. ATP, total direct cell count (TDCC), and phospholipid. Also the media sampling technique is described.
- Chapter 6 include the methodologies of LCOCD analysis, fluorescence spectroscopy analysis, the conditions of operation of UF and NF membranes, the microbiological analyses performed on liquid samples (i.e. HPC, ATP, TDCC).

3.8 Quality Control and Quality Assurance

For TOC, DOC, PhACs and EDCs, turbidity, and UV_{254} analyses blanks and standards were processed alongside all samples. If the results of the quality control and quality assurance were not as expected the sample was reprocessed if possible. The results were not considered for analysis if the sample was not available or store without adequate preservation procedure and could not be reprocessed**.**

Chapter 4

A STUDY OF THE CONCENTRATION OF SELECTED PhACs AND EDCs PRESENT IN SURFACE WATER

4.1 Introduction

As explained in Chapter 2, PhACs and EDCs have been detected in surface water. In general, concentrations lower than 20 ng/L are observed in Canadian surface water close to sewage discharge points (Metcalfe *et al.*, 2004). However, the hydrologic conditions, agricultural activities, industrial activities, and the proportional contribution of sewage effluents to the total flow of receiving water are important factors in determining the degree of contamination present in surface water. It is expected that the highest concentration of contaminants should be detected close to the WWTP effluent discharge but only a few studies have described the spatial distribution of the contaminants near this point (Blackburn and Waldock, 1995). To estimate the expected environmental concentrations of drugs in surface water, the U.S. Food and Drug Administration recommends applying a dilution factor of 10 to the expected concentration of drugs in the WWTP effluent prior to introduction into the receiving water (FDA, 1998). However, data from Little River, Ontario, suggests that this recommended dilution factor is not necessarily a conservative estimate because no dilution of drugs from the WWTP discharge is observed into this low flow system (Metcalfe *et al.*, 2004).

Several factors can affect seasonal and spatial concentrations of contaminants in surface water. The presence of ice cover, water temperature, and solar radiation can influence the concentration of contaminants. Vieno *et al.* (2005) demonstrated that concentrations of PhACs decrease as the

compound is carried downstream from a source of contamination. Dilution of the compounds in river water contributes to the concentration reduction, but there are other elimination processes which may occur during downstream transportation. These elimination processes primarily include those identified during treatment at the WWTP, i.e. biodegradation and sorption. But photodegradation must also be considered because UV light can penetrate the water (Boreen *et al.*, 2003; Buser *et al.*, 1998). Photodegradation is not possible in presence of ice cover, but when photodegradation occurs, it seems to be the most important mechanism for the removal of diclofenac and triclosan from surface water (Vieno *et al.*, 2005; Buser *et al.*, 1998). As mentioned previously, low temperatures affect the biodegradation rate and sorption. Thus, during the cold season, the concentrations of biodegradable PhACs in rivers are expected to be higher. Furthermore, because biodegradation rates are lower, contaminants are carried farther away from the discharge point than in warmer seasons (Vieno *et al.*, 2005).

In general, the active form of pharmaceutical ingredients are metabolised and transformed into a more polar and water soluble metabolite. Usually the metabolite has a reduced pharmacological activity and is rapidly excreted (Cunningham, 2004). Oxidation, reduction, hydrolysis, and conjugation are the main metabolism mechanisms. Conjugation occurs in the presence of hydroxyl, carboxyl, amino, or thiol (SH) groups. Glucuronide formation is the simplest and most common route of metabolism in biological systems due to the general availability of glucose (Cunningham, 2004). The reaction occurs by condensation or biotransformation using the D-glucuronic acid. Thus an ingested compound can be excreted by an organism unchanged, as a glucuronide, as a major metabolite, or as a complex mixture of several metabolites. Metabolized pharmaceuticals can be deconjugated to the parent compound during WWTP processes by the glucuronidase enzyme and sulphatase activity of microorganisms such as *E. Coli* (Ternes *et al.*, 1999). Therefore, if the glucuronide conjugates are the primary metabolites, they have to be considered similar to the parent compound due to possible cleavage during biologically active treatment processes.

4.2 Objectives

The objectives of the study described in this chapter were to:

- Collect information regarding the occurrence of selected PhACs and EDCs present in Grand River water;
- Determine the seasonal variation of selected contaminant concentrations in a natural aquatic environment.

4.3 Material and Methods

4.3.1 Sampling and Sample Preservation

The sampling point for the Grand River raw water has been identified in section 3.1. Grand River water is impacted by municipal activities and several WWTPs effluent are being discharged upstream of our sampling point as further described in section 4.4. The raw water was collected at the entrance of the biofiltration set-up (Figure 3.3). Two clean glass bottles of 0.5 L were rinsed and filled with raw water. One bottle was used for physico-chemical analysis and the other for analysis of selected PhACs and EDCs. The bottles were returned to the UW lab and stored in the dark at 4ºC prior to analysis. The extraction was performed within 24 h after sampling. Sampling of Grand River raw water was performed throughout a period of 20 months with a total of 94 samples between November 2006 and August 2008. Furthermore, 15 duplicate analyses were also performed.

4.3.2 Physico-Chemical Analysis

The weekly parameters measured on Grand River water were TOC, DOC, UV_{254}, SUVA, turbidity, conductivity, pH, and temperature. A description of the methods used is available in section 3.2.

4.3.3 Selected PhACs and EDCs

Selected PhACs and EDCs and their physico-chemical properties are presented in section 3.5.

4.3.4 PhACs and EDCs Analysis Method

The concentrations of selected acidic and neutral PhACs and EDCs were measured simultaneously in the following way. First, a solid phase extraction was performed under acidic conditions. The extract was then derivatized in order to make the extracts less polar, as well as more volatile, and thermally stable. This makes the selected PhACs and EDCs suitable for GC/MS analysis. The method extraction and derivatization processes have been optimized (Yu *et al.*, 2007) using a factorial design.

Extraction

Prior to extraction, raw water samples were pre-filtered using 0.45 μm pore size mixed cellulose esters filters. Filters were rinsed with 0.5 L of ultrapure water before use. Appropriate quality control standards were also processed (i.e. matrix blank, matrix spike, ultra-pure blank, ultra-pure spike). Solid phase extractions were performed using Waters' Oasis HLB cartridges (3 mL, 60 mg). Cartridges were conditioned prior to use by first adding 3 mL of ethyl acetate followed by adding 3 mL of methanol and 3 mL of hydrochloric acid solution (pH 2) together. Samples were acidified to pH 2-3 using concentrated HCl prior to extraction. The sample extraction was performed at a flow of 4 mL/min. The cartridges were dried using a stream of nitrogen. PhACs and EDCs were eluted into labeled disposable 5 mL Kimble centrifuge tubes with two 3 mL aliquots of a 50:50 mixture of ethyl-acetate and acetone. The solvent was evaporated under a low flow of nitrogen. The derivatization was achieved by addition of 200 μL of N-methyl-N-tert-butyl-dimethysilyl-trifluoroacetamide (MTBSTFA). The vials were then capped, swirled, and placed at 60ºC for 90 minutes. Samples were then placed in a freezer for several minutes to stop the reaction. 1,4-bis(pentafluorobenzoyl)benzene (BPFBB) was added to each sample after derivatization as an internal standard. Dihydrocarbamazepine (DCH), meclofenamic acid, and mecoprop-D3 were used as surrogates at a concentration of 50 ng/μL or 10 ng/μL. Samples were kept in a freezer until analysis.

GC/MS Analysis

Samples were analyzed using a GC/MS (Varian 3800 and Varian 4000, respectively) with an autosampler (Varian 8400). The autosampler sample tray was cooled to 7ºC to inhibit any potential further reactions. The injector temperature was maintained at 240ºC and the injection volume was 2 µL, injected at a speed of 50 µL/sec. A fused silica column (DB 1701, 30 m x 0.25 mm) was connected to a deactivated pre-column. The column oven program was the following: 100ºC for 3 minutes, increased to 208ºC at a rate of 20ºC/min and held for 1 minute, increased to 212ºC at a rate of 2ºC/min, increased to 250ºC at a rate of 10ºC/min and held for 2 minutes, and increased to 300ºC at a rate of 5ºC/min and held for 5 minutes. Table 4.1 presents the different compounds in order of elution with their corresponding surrogate, quantification ion, and qualification ion.

Table 4-1 Identification of the quantification and qualification ions for selected compounds and their respective surrogates

Compounds	Surrogate	Quantification ion m/z	Qualification ion m/z
DEET	mecoprop D-3	119	190
ibuprofen	mecoprop D-3	263	N/A
mecoprop D-3 (surrogate)		227	274
atrazine	mecoprop D-3	200	215
nonylphenol	mecoprop D-3	165	277
BPFBB (internal standard)		299	466
naproxen	meclofenamic acid	287	185
DCH (surrogate)		195	295
carbamazepine	DCH	193	293
meclofenamic acid (surrogate)		352	243

Calibration curves for the different compounds are presented in Appendix A.

4.4 Results and Discussion

This section presents the general water quality parameters that were measured on a weekly basis between January 2007 and August 2008 on the Grand River water. The contribution of wastewater effluent to the Grand River is evaluated by comparing their flows. Finally, the concentrations of selected organic trace contaminants are discussed.

Grand River Water Quality

Figure 4.1 represents the TOC and DOC concentrations in Grand River water. The TOC concentrations varied between 5.0 mgC/L and 10.7 mgC/L and the DOC concentrations varied between 4.3 mgC/L to 9.7 mgC/L. In general, higher or similar concentrations of TOC were observed compared to DOC concentrations, as expected. However, when the water temperature increased, the concentration of DOC tended to decrease in relation to TOC. This behavior may have been caused by biodegradation of DOC components in the environment since an increase in water temperature is usually accompanied by increased biological activity.

Figure 4.2 represents the turbidity and pH of Grand River water. The pH was relatively stable throughout the year which is in agreement with the pH usually measured in surface water. The turbidity of Grand River varied between 2 NTU to 300 NTU. The turbidity peaks observed throughout the year were due to rain events or water runoff. Periods of low turbidity were observed during the winter of 2007 due to the presence of ice cover on the river and frozen soil. Frequent high turbidity events in 2008 reflect the high level of precipitation received during this period.

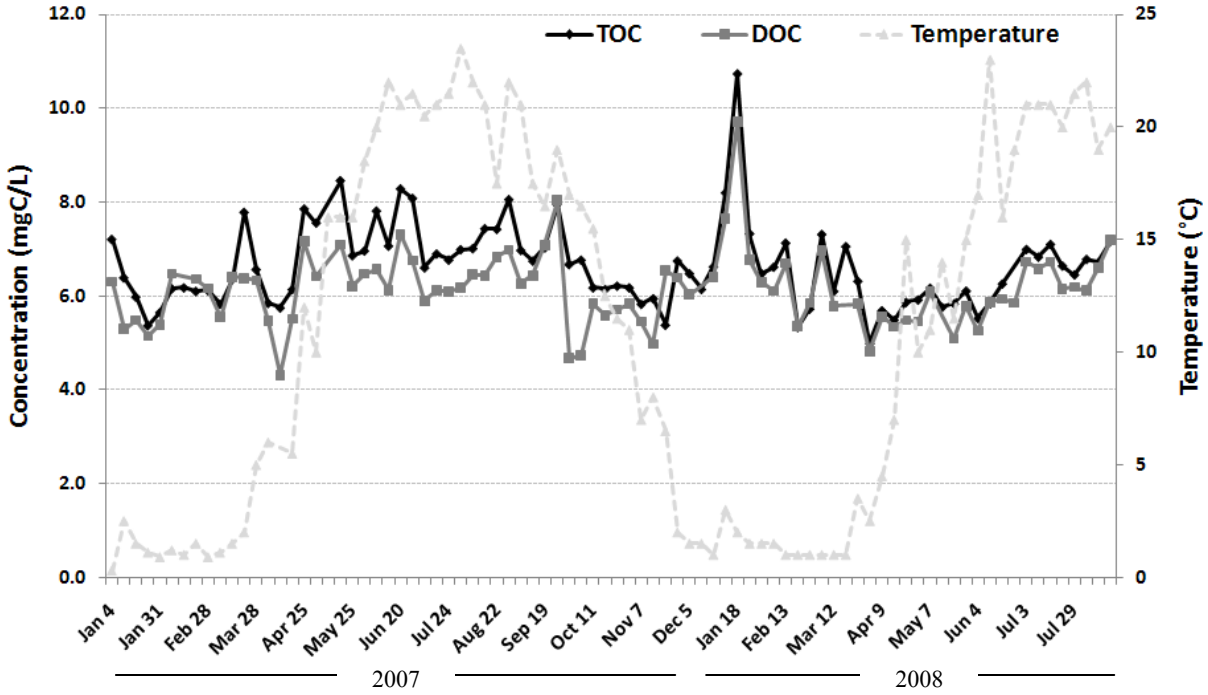


Figure 4-1 Concentration of TOC and DOC and temperature of Grand River water

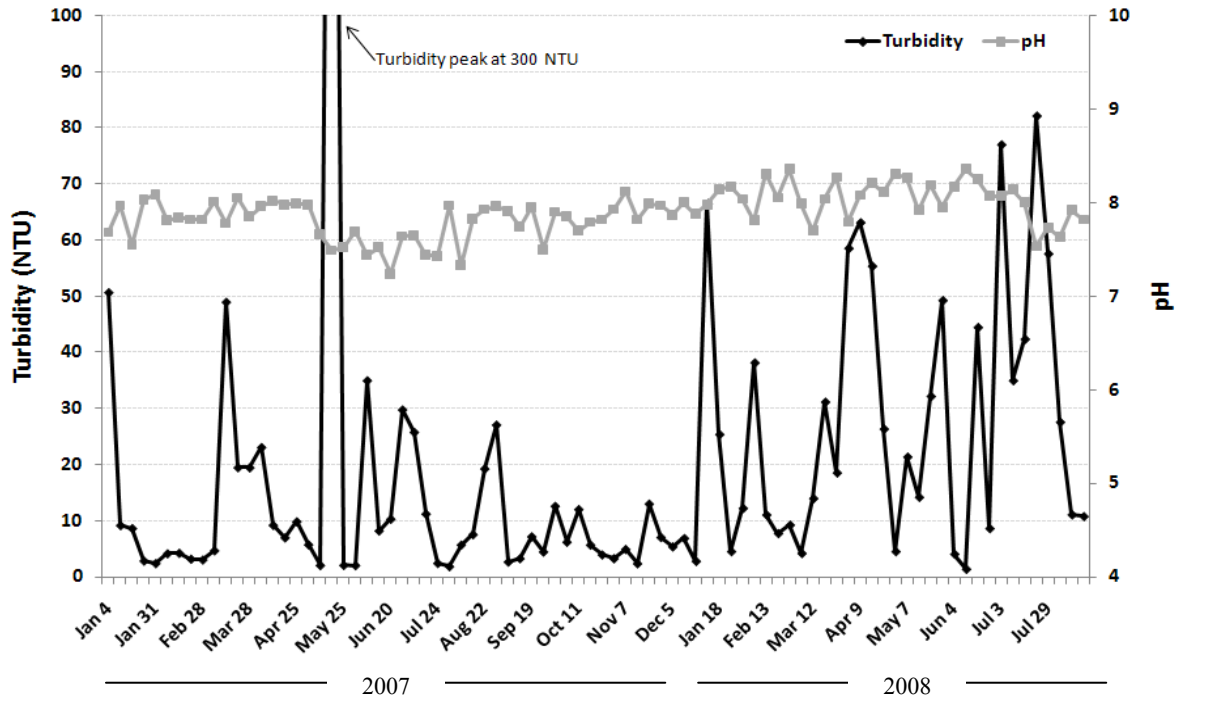


Figure 4-2 Turbidity and pH of Grand River water

Figure 4.3 presents the UV_{254} and SUVA values of Grand River water. UV_{254} is an indication of the non-polar portion (i.e. aromatic) of the NOM (i.e. humic substances). The chromophores of the NOM absorb the UV light, thus, depending on the composition of the NOM, the UV_{254} can vary. The SUVA calculated as the ratio of UV_{254} to the DOC concentration gives an indication of the hydrophobic fraction of the NOM and is often used as an indicator for its treatability. UV_{254} and SUVA values tend to be higher during the winter. Lower UV_{254} and SUVA values were measured during the summer of 2007 but this observation could not be confirmed during the summer of 2008. The greater SUVA value observed during the summer of 2008 was most probably due to several rain fall and storm events experienced during this period.

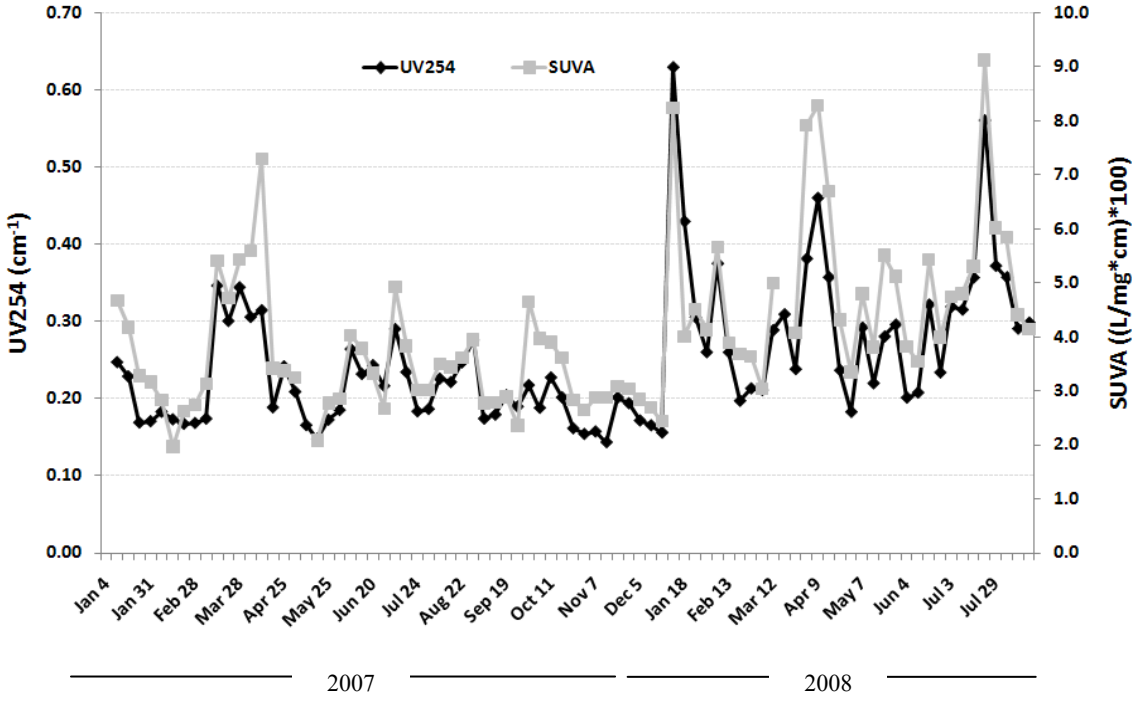


Figure 4-3 UV_{254} and SUVA values of Grand River water

Grand River Water Flow and Waterloo WWTP Flow

Figure 4.4 represents the conductivity of Grand River water. The conductivity level rose during the winter months when deicing salts were being used. Deicing salts were not used during the summer months and the conductivity value decreased as expected. The flow of the Grand River is monitored daily at the plant intake referred to as Doon Station in Chapter 3 by Water Survey Canada. Figure 4.4 shows the flow of the river from May 2006 to August 2008. The summer of 2006 was relatively dry with only a few increases of flow due to storm events. During the fall of 2006 and early winter of 2007 the flow of the river increased significantly reaching a maximum of 300 m^3/sec on December 2nd 2006. Once the ice cover was present and the soil frozen, the flow of the river decreased and stabilized. Then from mid-March to mid-April 2007, during spring runoff, higher river flows were observed. Two storm events can also be identified in late April and mid-May. Summer and fall of 2007 was dry and the Grand River flow was stable and low from late May to mid December 2007. Then the river flow increased due to several rain and snow events. No stable ice cover was observed on the Grand River during winter 2008 and the high and variable flow was representative of this situation. After the spring runoff in late April of 2008 the flow decreased but, for the remainder of the spring and summer of 2008, the flow of the river was high and unstable. This behavior is commonly observed when rainfall exceeds the infiltration rate of the soil since the excess water drains into the river. These conditions are expected to have an impact on the migration of soluble trace contaminants as is discussed later in this chapter.

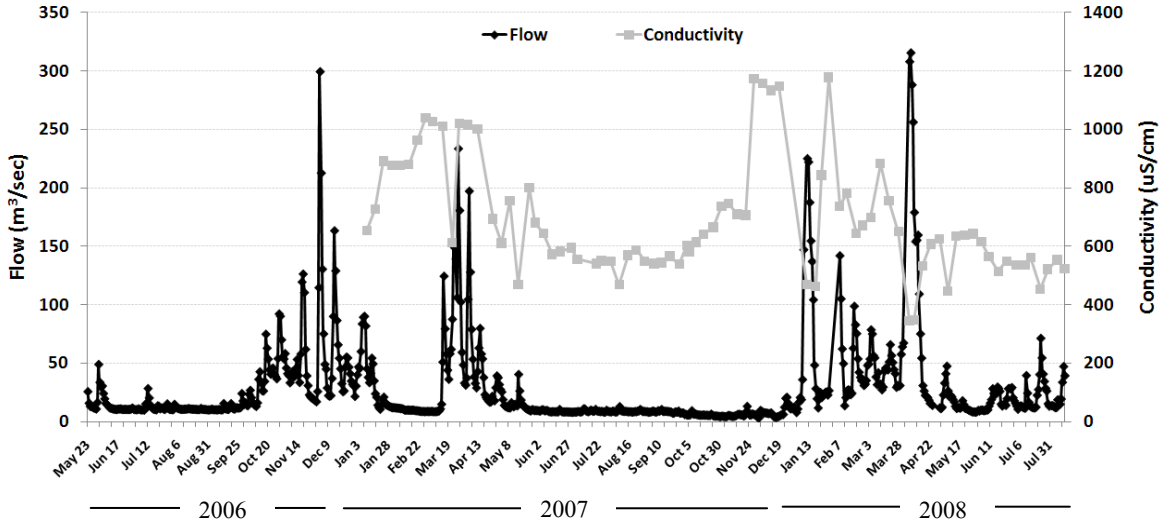


Figure 4-4 Grand River flow and conductivity measured at Doon Station (location: 43° 24' 46" N, 80° 25' 01" W)

Figure 4.5 presents the percentage of wastewater in Grand River water. The Waterloo WWTP effluent discharge point is located 17.2 kilometers upstream of the Doon Station sampling point. (Location: 43° 28' 46" N, 80° 28' 56" W). Some WWTP discharge a comparably small amount of effluent upstream of the Waterloo WWTP and thus the data presented in Figure 4.5 provide a lower bound.

The percentage of WWTP effluent in Grand River varies between 0.2 % and 15.5 % throughout the year. In the Grand River Watershed, 29 WWTP are in operation. From those facility, the following WWTPs discharge upstream of the Waterloo WWTP: Dundalk (serving < 2500 people), Fergus (serving < 20000 people), Elora (serving < 7500 people), Elmira (design flow 7800 m^3/d but running at around 4500 m^3/d), Listowel (serving < 2500 people), St. Jacobs (serving < 2500 people, design flow 1760 m^3/d running around 1100 m^3/d), Alt Heidelberg (running < 100 m^3/d), and Conestogo (running < 100 m^3/d) (Andrews, 2009). Thus the significant WWTP facilities at Doon Station were Waterloo, Fergus, Elora, and Elmira. As expected, the percentage of WWTP effluent was higher during the summer months when the flow of the river was lower. The percentage of WWTP effluent in the Grand River decreased during the winter of 2008. Then it started to increase in April 2008 but it did not achieve levels as high as during the summer of 2007 because of the greater river flow.

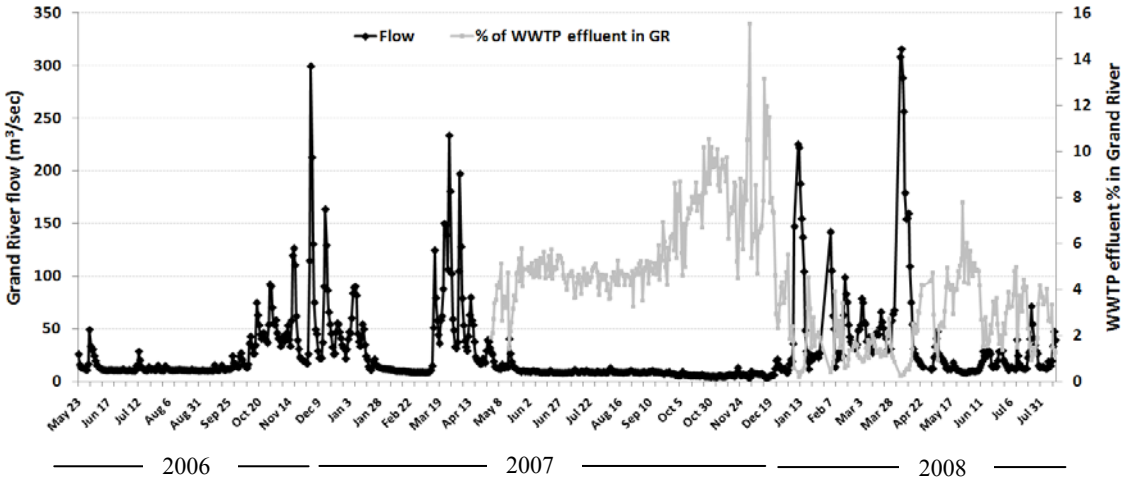


Figure 4-5 Percentage of wastewater in Grand River at Doon Station based on daily Grand River flow at Doon Station and discharge flow of the Waterloo WWTP

Trace organic contaminants

Figure 4.6 shows the concentrations of selected organic trace contaminants in Grand River water. The columns indicate the average concentration measured during a month and the bars represent the maximum and minimum concentrations reported during the same period. The number above each column represents the number of samples taken throughout that month. For all compounds the average concentration in Grand River water was relatively low throughout the year, however, different concentration profiles were observed. Appendix B contains the detailed measurements of selected PhACs and EDCs and the plots of concentration versus time.

Figure 4.6a present the concentration of DEET measured in Grand River water. The frequency of detection of DEET was 98 %. Highest concentrations were always measured during the summer months. Those results are in concordance with the observation made by Knepper (2004). The highest measured concentration was 399 ± 3 ng/L in June 2008. This increase in concentration corresponded to the period of usage of DEET and the concentration slowly decreased afterwards until very low concentrations were measured in late winter.

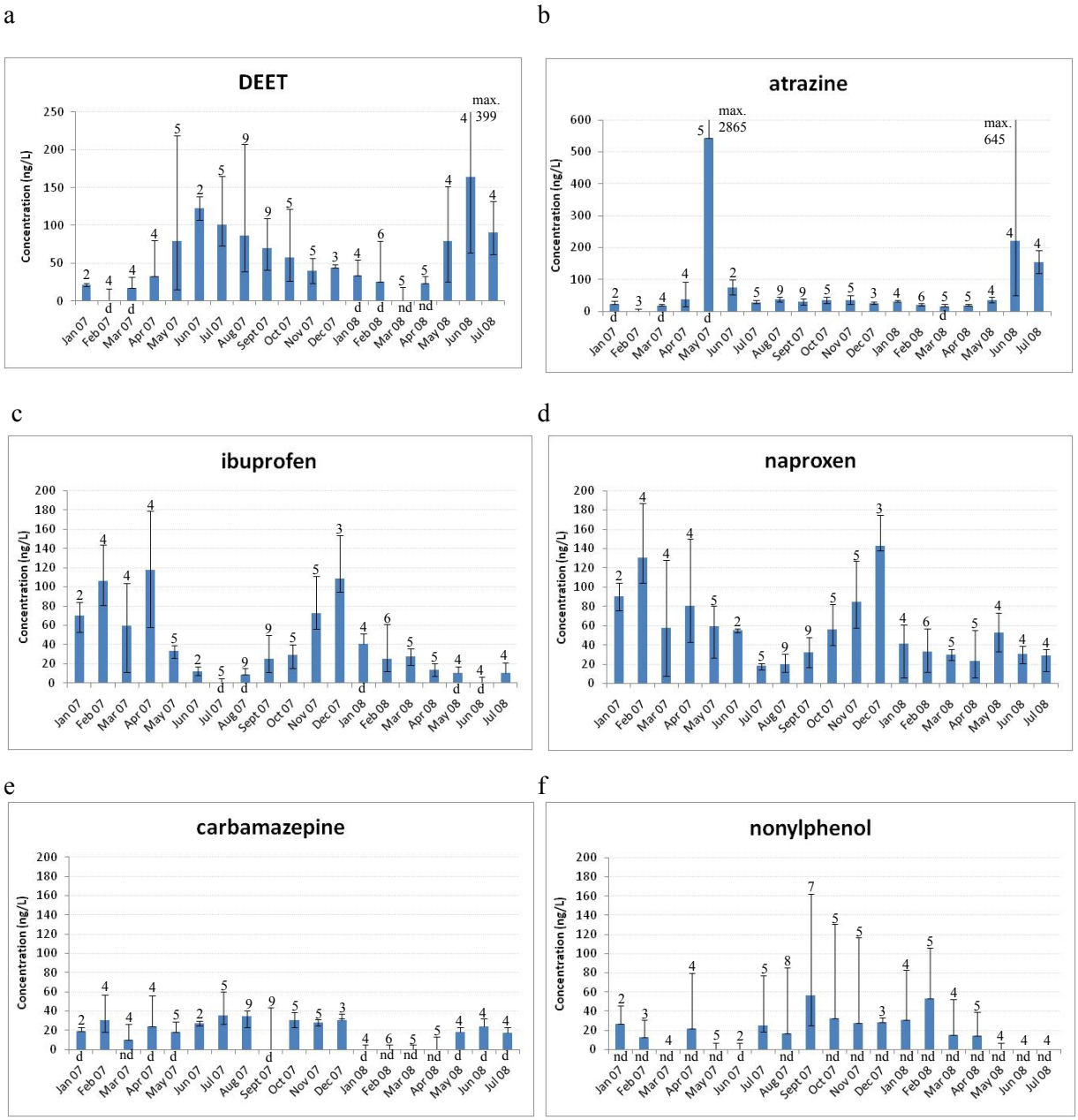


Figure 4-6 Average concentrations (ng/L) of a) DEET, b) atrazine, c) ibuprofen, d) naproxen, e) carbamazepine, and f) nonylphenol in Grand River water between January 2007 and August 2008. The bars present the maximum and minimum concentrations measured during a month. The number above the bars presents the number of analysis performed during a month. If the minimum concentration detected during a month was below the LOQ or below the LOD a "d" or "nd" was respectively added. To calculate the monthly average concentration, a value of 0 ng/L was attributed if the sample concentration was below the limit of detection and the limit of detection (LOD). The LOD value was attributed if the concentration was below the limit of quantification (LOQ) but above the LOD.

The frequency of detection of atrazine was 99%. In the Grand River, a peak of atrazine was detected in May 2007 and June 2008 (Figure 4.6b). Table 4.2 summarizes the peak loading events measured in 2007 and 2008.

Table 4-2 Daily concentration of atrazine in Grand River water prior to and after peak loading events in 2007 and 2008

2007		2008	
Sampling day	atrazine concentration ng/L	Sampling day	atrazine concentration ng/L
April 12	16	April 11	20
April 19	17	April 16	17
April 26	89	April 24	18
May 3	d	April 30	23
May 9	19	May 7	36
May 16	2865	May 14	27
May 23	236	May 21	44
May 30	119	May 28	32
June 13	99	June 4	56
June 20	51	June 10	50
July 5	24	June 19	645
July 18	25	June 25	137
July 20	24	July 10	148
July 24	31	July 25	161
July 26	35	July 23	190

d: detected

Atrazine is an agricultural herbicide use to control weed on corn fields. The usage of atrazine is controlled but seasonal application is still practiced. In 2007, the maximum concentration of 2865 ng/L was measured in Grand River water on May 16th and the concentration decreased rapidly during the following weeks. The spike of atrazine in 2007 corresponded to a rain event, thus the herbicide applied had been flushed from the agricultural land. In 2008, the maximum concentration of 645 ng/L was measured a month later on June 19th. The lower peak concentration of atrazine measured in 2008 compared to 2007 can be explained by a higher dilution factor, because the flow of Grand River water was on average 9% and 51% greater in May and June of 2008, respectively. It is also possible that even higher concentrations may have occurred in between sampling dates. Again the concentration decreased after the peak load. For both years, no peak concentration was observed later on during the year. These results are consistent with the literature which notices a post-application peak load at the end of the spring or early summer (Thurman *et al.,* 1991). For the Grand River, the simultaneous increase of loading and discharge flow in 2008 may explain why the increase of atrazine concentration during the spring is less significant than observed in 2007, as also observed by Thurman *et al.* (1991). The low concentration observed in May 2008 is probably caused by a delay in field spreading. Also, due to the frequency of sampling we may not have captured the maximal concentration in 2008 leading to a lower average concentration.

Figure 4.6c shows the concentration of ibuprofen in the Grand River. The frequency of detection was 99%. Higher concentrations were measured during the winter months and lower concentrations were measured during the summer months. The bars show that in general the variation of concentration within a month was low. Metcalfe *et al.* (2003) detected ibuprofen in surface water at high concentration near the discharge points of WWTPs. The results presented in Figure 4.6c were also in accordance with data collected in a Southern Ontario watershed by Kormos *et al.* (2007). Moreover, other frequently detected compounds in raw water by Kormos *et al.* (2007) included carbamazepine, gemfibrozil, benzafibrate, naproxen, trimethoprim, sulfamethoxazole, and lincomycin HCl . Similar concentrations of ibuprofen have also been detected in the US (Kolpin *et al.*, 2002). Low concentrations during the summer may be due to biodegradation or sorption to particulate matter (Buser *et al.,* 1999; Tixier *et al.*, 2003). Ibuprofen does not absorb sun light thus photodegradation can be neglected; the half life with respect to photodegradation was estimated at 200 h (Lin and Reinhard, 2005; Tixier *et al.*, 2003).

Figure 4.6d shows the concentration of naproxen in Grand River water. Between 6 ± 2 ng/L (July 2007) and 187 ± 2 ng/L (December 2007) of naproxen was measured throughout the year. The standard deviations were calculated from the variation of the monthly average. The frequency of detection was 100%. Higher concentrations were generally measured during the winter months. Lower concentrations measured from January to March 2008 may be explained by a high dilution factor caused by high river flows. Lower concentrations during the summer may be explained by photodegradation and biodegradation of naproxen in surface water (Lin and Reinhard, 2005; Tixier *et al.*, 2003). Direct phototransformation occurs when the compound absorbs sunlight. The half life of naproxen was estimated to be 1.9 h during direct photolysis (Lin and Reinhard, 2005).

The graphs in Appendix B show similar occurrence patterns for ibuprofen and naproxen. The highest concentrations occurred during the winters and the lowest concentrations have been measured during the summers. This behavior suggests similar physico chemical properties of both compounds influencing their behavior in the environment. In fact, ibuprofen and naproxen are both negatively charged (similar pKa value) and are both more hydrophilic than the other three compounds monitored.

Figure 4.6e shows the concentration of carbamazepine in Grand River water. The frequency of detection was 91%. The concentrations measured varied between non detected (Feb – Apr. 08) and 36 ng/L. The average concentration was stable throughout the year except between January 2008 and April 2008 when carbamazepine was not detected. During this period, lower concentrations of carbamazepine may be due to dilution because the flow of Grand River was high. The overall low concentrations of carbamazepine in surface water can be explained by its low water solubility and its tendency to sorb to soil due to its log K_{ow} value of 2.4 which is higher than for the other compounds investigated (with the exception of NP). Only two clear peaks have been observed in April and July of 2007 (see appendix B) and the increase in concentration may be attributed to the application of biosolids on agricultural fields. No peak event was observed in 2008 probably due to the higher dilution factor of Grand River. The concentrations and seasonal trends observed are consistent with previous measurements of carbamazepine performed on Grand River water and in surface water (Lissemore *et al.*, 2006; Metcalfe *et al.*, 2003). Carbamazepine is considered a persistent contaminant in the environment because this compound is not significantly removed during sewage treatment.

Moreover, low removals of carbamazepine in WWTP (7%) and ground passages indicate resistance to biodegradation (Focazio *et al.*, 2008; Ternes, 1998). As demonstrated by Andreozzi *et al.* (2002), the degradation levels of carbamazepine by bioassay progressively increase over 50% after 60 days of experiment. Andreozzi *et al.* (2002) also demonstrate photodegradation of carbamazepine but the degradation level depended strongly on the constituent present in water (i.e. in presence of dissolved humic acid the reaction is inhibited due to an inner filter effect of the NOM). Doll and Frimmel (2003) measured photodegradation of carbamazepine up to 21% in the presence of DOM (up to 7 mg/L) due to indirect photolysis.

Figure 4.6f presents the concentration of NP measured in Grand River water. Due to its low solubility (i.e. log K_{OW} 5.92), NP is generally associated with sediment present in the environment. As expected, low and stable concentrations were observed throughout the year. In Grand River water, the concentration of nonylphenol varied between non-detected to 162 ng/L and the frequency of detection was 50%. A previous study investigating surface waters in Ontario detected concentrations of NP between 10 ng/L and 92 ng/L with a mean of measurable samples of 21 ng/L with higher concentration measured in proximity to WWTP effluent discharge points, large population centers, or industrialized areas (Bennie *et al.*, 1997). When compared to concentrations measured in the US and Europe, the concentration of NP detected in the Grand River was generally lower but the frequency of detection was higher (Kolpin, 2002; Bennie *et al.*, 1997; Blackburn and Waldock, 1995).

4.5 Conclusions

The results obtained by the frequent measurements of six PhACs and EDCs in Grand River water from November 2006 to August 2008 allow the following conclusions to be drawn:

- This study demonstrated that selected PhACs and EDCs were present in Grand River water throughout the year at a sampling point located 17.2 kilometers downstream of a relatively large WWTP effluent discharge point.

- The concentration of DEET in Grand River water increased when the insecticide was being used. The highest concentration of 400 ng/L was detected in June 2008. A high frequency of detection of 97% was observed.

- The concentration of atrazine in Grand River water was generally low except for the period when the herbicide was applied. Peak concentrations of up to 2865 ng/L in 2007 and 645 ng/L in 2008 have been measured in Grand River water. The concentration of atrazine decreased thereafter.

- Concentrations of ibuprofen and naproxen followed similar seasonal patterns. Higher concentrations were measured during the winter months and lower concentrations were measured during the summer months. Biodegradation, sorption, and photodegradation are possible mechanisms causing low concentrations during the summer.

- Carbamazepine was detected at low concentrations but with a high frequency of 91%.

- Nonylphenol was also detected at low concentrations but the detection frequency (50%) was lower than that of the other selected compounds.

Chapter 5

A STUDY ON THE REMOVAL OF SELECTED PhACs AND EDCs PRESENT IN SURFACE WATER BY BIOLOGICAL FILTRATION

5.1 Introduction

Biofiltration for drinking water treatment has been used in North America but is not commonly practiced. Biofilm activity presents on designed filter media could be an efficient alternative in removing organic contaminants from drinking water sources. Biotransformation of organic contaminants during biofiltration can occur by two mechanisms: 1) adsorption of natural organic matter (NOM) into the biofilm structure, and 2) biodegradation. During biodegradation, metabolism is the main mechanism by which biofilm affects organic compounds; the organic compounds are broken down by the enzymes produced by the bacteria. Bacteria in the biofilm require electron-donors (i.e. primary substrate) and electron acceptors to initiate metabolic function. These bacteria are either heterotrophs and/or autotrophs. Heterotrophic bacteria use primarily organic compounds as a source of energy for the growth and maintenance of the biofilm. While autotrophic bacteria can also reduce inorganic carbon for cell synthesis and use inorganic electron donors such as NH_4^+ or Fe^{2+}. Metabolic processes are catalyzed by enzymes. Inducible enzymes are synthesized only when a specific substrate is available at a sufficient concentration. Constitutive enzymes are continuously produced by the cells (Stratton *et al.*, 1983).

For biofiltration processes, primary substrates can biodegrade rapidly or slowly providing the energy for the growth and maintenance of the biofilm. Humic substances are generally considered as recalcitrant to biodegradation but researches have demonstrated that humic substances can serve as a

primary source of carbon to support biofilm in model pipe systems (Camper, 2004) or for biofilm growth in drinking water conditions (Butterfield *et al.*, 2002). Non humic fraction of the BOM include hydrophilic acids, amino acids, carbohydrate, polysaccharides, fatty acids, carboxylic acids, peptides, and hydrocarbons and are recognized to have a high potential for biodegradability (Butterfield *et al.*, 2002)

Furthermore, the composition of the biodegradable organic matter pool varies with the source of water and the seasons. Organic compounds present at a lower concentration which cannot sustain a steady state biomass are considered secondary substrates.

Trace organic contaminants such as PhACs and EDCs present at low concentrations in surface water may be simultaneously metabolized as secondary substrates by microorganisms, while the primary substrate supports the nutritional requirement for the biofilm. The effectiveness of biodegradation of contaminants (i.e. secondary substrate) by biofiltration processes applied for drinking water treatment has been demonstrated for taste and odor compounds (i.e. geosmin) (Ho *et al.*, 2007; Elhadi *et al.*, 2004; Lundgren *et al.,* 1998), pesticides (Headley *et al.*, 1998), PhACs (Kosjek *et al.*, 2009; Winkler *et al.*, 2001), naphthalene and heptaldehydes (Rittmann *et al.*, 1980), chlorinated phenol, and benzenes (Manem and Rittmann, 1992; DeWater and DiGiano, 1990).

However limited data are available regarding the removal of PhACs and EDCs in engineered biofilters for drinking water treatment. In fact, the results presented in this chapter are the first showing the transformation of selected PhACs and EDCs from surface water by rapid biological filtration for drinking water treatment. Thus the results will be compared with previous research performed on slow sand filtration, ground passage, or biological wastewater processes. The literature review introduced the general factors influencing biological filtration performance for BOM removal. Critical variables to consider for the biodegradation of trace organic contaminants are similar, for example, influent concentration of substrate, the mixture effect, and the water temperature. Moreover, environmental factors such as mass transport of substrates and nutrients which are independent of the system configuration and operation will also influence the system performance. Mass transport into biofilms is thought to be a combination of diffusive and advective transport. The dominant functional

groups of EPS forming the biofilm are carboxyl and hydroxyl acids which are ionized at neutral pH producing a negatively charged biofilm surface charge. The negatively charged surface is likely to influence the adsorption and transport of organic compounds through the biofilm. The diffusion of negatively charged molecules may decrease compared to neutral molecules which have a favorable electrostatic interaction with the negatively charged biofilm surface. Carlson and Silverstein (1998) demonstrate that both the molecular size and charge of the target contaminant are important factors influencing mass transport and thus their removal during the biofiltration process.

As explained previously in the literature review, an acclimation period may be necessary to achieve biodegradation of certain compounds. This can be accomplished through a variety of processes. The acclimation period required by the biofilter to achieve statistically significant removal of secondary substrate is important to establish because trace organic contaminants may appear transiently in surface water as demonstrated in Chapter 4.

5.2 Objectives

The objectives of the study described in this chapter were to:

- Demonstrate the biological activity of the media within the biofilters,
- Evaluate the degree of biodegradability of selected PhACs and EDCs by biological filtration for drinking water treatment,
- Identify the impact of EBCT, influent concentration, and water temperature on the biofilters transformation capacity of biodegradable compounds,
- Estimate the acclimation period required to achieve biodegradation of PhACs and EDCs by the biofilters,
- Estimate kinetic parameters and temperature correction factors for the transformation of selected PhACs and EDCs.

5.3 Material and Methods

5.3.1 Rapid Biofiltration

A description of the biofilters used for this study and details regarding their operation and maintenance are available in Chapter 3.

5.3.2 Microbiological Analyses on Media Samples

ATP and phospholipid measurements have been performed on the media to obtain an indication of the amount of biomass present on the media samples. TDCC has also been performed to measure the amount of overall cells present on the media.

ATP measurements were selected because of the rapidity and accuracy of the analysis. ATP analysis is generally used in aquatic microbiology (Magic-Knevez and van der Kooij, 2004; Delahaye *et al.*, 2003; Huck *et al.*, 2000; Webster *et al.*, 1985; Karl, 1980). Moreover ATP is present at a fairly

constant amount in living cells and is rapidly destroyed after the death of the organism (Webster *et al.*, 1985). ATP measurements were performed using a method adapted from Velten *et al.* (2007).

TDCC measurements on media samples were performed using a method adapted from Camper *et al.* (1985).

Phospholipid on the media were extracted and analyzed by a method developed by Findlay *et al.* (1989) and adapted by Urfer-Frund (1998). Details of the procedure for ATP, TDCC, and phospholipid measurements are available in Appendices C, D, and E.

5.3.3 Sampling for Microbiological Analyses

Periodically, media was removed at different depths within the biofilter by core sampling. For the media sample, one sterile test tube of 15 mL with screw cap was collected per sampling point. The column was drained, the port cap was removed, a transversal sample was collected, and the column cap was screwed back in place. Approximately 10 g of media were extracted from the column using a clean plastic spatula. A new spatula was used for each sampling location. Media sampling was always performed before backwash and the filters were in operation for a period of 7 days prior to sampling. After sampling, the equivalent of the volume of media removed was added to the column and a backwash was performed. B1 has two sample ports; one at 5 cm below the bed surface in the anthracite layer and a second sample port was located at 32 cm bed depth in the sand layer. B2 has three sample ports; one located 5 cm below the bed surface in the anthracite layer, a second sample port was located at 15 cm bed depth at the interface of anthracite and sand, and a third sample port was located at 59 cm bed depth in the sand layer (i.e. in the second column).

ATP measurements were performed within 24 h after sampling. TDCC samples were preserved and the analysis was performed within a week. A dry weight measurement was performed on the same day of sampling by drying 1 g of media at 103-105°C overnight. Phospholipid samples were weighed and preserved at -80°C until analysis.

5.3.4 Spiking Trace Organic Contaminants

As presented in Chapter 4, selected PhACs and EDCs are present in the Grand River at low and variable concentrations throughout the year. In order to study the removal efficiency of PhACs and EDCs by the biofilters, a mixture of contaminants were continuously spiked at low and high concentrations in the biofilter influent. Each concentration was spiked alternately for a period varying between 5 to 20 weeks from July 2007 to August 2008 (Table 5.1). The duration of the spiking events are variable because of the membrane filtration experiment schedule.

Table 5-1 Concentration and duration of spiking events and number of samples analyzed during each event.

Spiking event	Year	Duration (# weeks)	# of sample analysed	Spiking event	Year	Duration (# weeks)	# of sample analysed
L1	2007	July 18 - August 18 (4)	10	H1	2007	August 22 - September 27 (5)	13
L2	2007	October 2 - November 1 (4)	6	H2	2007	October 30 - December 5 (5)	8
L3	2008	December 12 - January 23 (5)	6	H3	2008	January 30 - March 12 (6)	10
L4	2008	March 19 - August 6 (20)	19				

Low (L) refers to low spiking concentration of 500 ng/L

High (H) refers to high spiking concentration of 5 µg/L

A low concentration of 500 ng/L was selected to represent the concentration measured in the aquatic environment. A high concentration of 5 µg/ L was chosen to represent extreme conditions such as a spill or an industrial contamination. Low concentration was spiked into the biofilters influent using a stock solution of 0.3 mg/L and the high concentration was obtained using a stock solution of 1 mg/L. The solution was stored in a 20 L glass container and continuously mixed with a magnetic stirrer. The solution was pumped using a peristaltic pump into the feeding line of the biofilters influent. Following the injection point, an inline mixer ensures complete mixing of the solution.

5.3.5 Analysis of Trace Organic Contaminants

The sample extraction and analytical methods are described in section 4.3.4.

5.3.6 Physico-Chemical Analyses

The physico-chemical parameters measured were TOC, DOC, UV_{254}, SUVA, turbidity, pH, and temperature. A description of the methods used is available in section 3.2.

5.3.7 Sampling Locations

For this study, the sampling points were the raw water, the RF effluent, and the effluents of B1 and B2. Sampling was performed once or twice a week. Two clean glass bottles of 0.5 L were rinsed

and filled with the sample. One bottle was used for physico-chemical analyses and the other for the analysis of selected PhACs and EDCs.

5.4 Results and Discussion

This section demonstrates the biological activity of the biofilters through the removal of the primary substrate (i.e. DOC). The biological activity on the rapid filter is also shown by the measurement of biomass attached to the media surface. The performance of the removal of selected PhACs and EDCs due to biofiltration is studied. Finally, an estimation of the kinetic parameter is performed.

5.4.1 Biological Activity of Rapid Biological Filters - Removal of Primary Substrate

The removal of NOM by the biologically active rapid filter may be attributable to adsorption and biodegradation. The DOC present in surface water is the primary substrate for the biomass. The following terminology has been chosen to make operational distinction between periods achieving different removal levels of DOC. Biofilters are defined as "active" when they achieved a statistically significant DOC removal (SDR) and "inactive" for negligible DOC removal (NDR). During the acclimation period and the NDR period, the biofilters achieved less than 5 % removal of DOC. During the SDR periods, the biological filters achieved a DOC percentage removal greater than 5 %. Figure 5.1 presents the acclimation, SDR, and NDR periods of the biofilters between December 2006 and August 2008. During the acclimation period, the percentage removal of DOC was low because the virgin medium requires a period of time to be colonized by the microorganisms present in the raw water. However, during the NDR period loss of biological activity is observed due to low water temperatures which influence kinetics and mass transfer.

The biofilters were commissioned on December 13th, 2006 and the water temperature was 2°C. Usually, the biological filter requires an acclimation period to allow the biomass naturally present in the feed water to colonize the media (Rittmann and McCarty, 2001). Typical acclimation time vary between 2 to 4 months but are influenced by a number of factors such as water temperature. This study shows that a period of acclimation of 4 months was necessary to achieve DOC removal and thus biological activity within the biofilter. A long acclimation period was not surprising due to the

low water temperature at this period of the year. During the acclimation period, statistically non-significant ($\alpha = 0.05$) removal of DOC was achieved by RF and B1 compared to the raw water (Table 5.2). Although the DOC removal achieved by B2 was statistically significant only 4 % removal was achieved which is not sufficient to meet the SDR criteria. The average DOC concentrations of raw water, B1 effluent, and B2 effluent during the acclimation period were 5.84 ± 0.68 mgC/L, 5.78 ± 0.60 mgC/L, and 5.59 ± 0.72 mgC/L, respectively (n= 16).

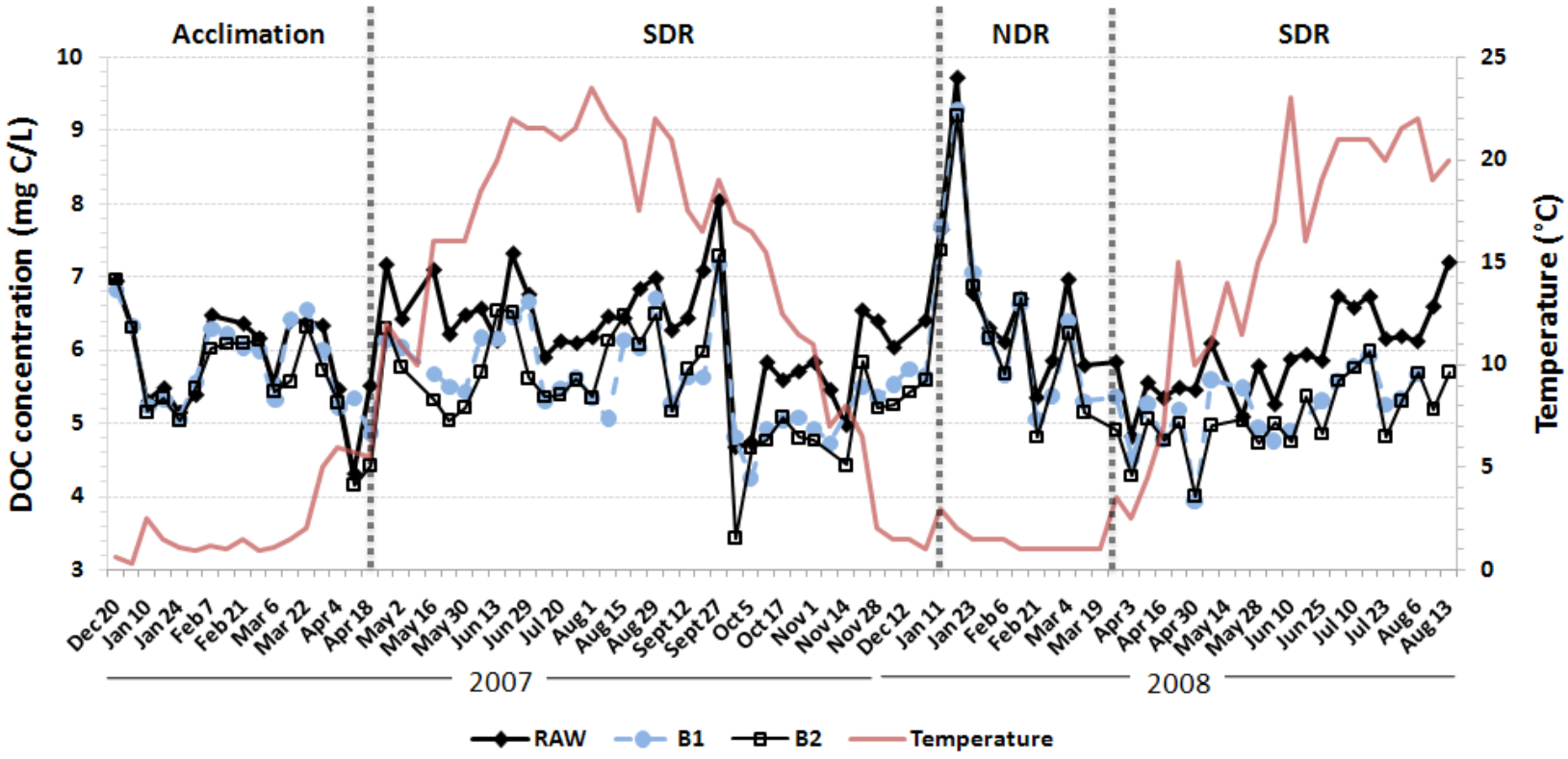


Figure 5-1 Variation in DOC concentrations in raw water and at the effluent of the biofilters at different water temperatures. SDR: period where statistically significant removal of DOC was observed. NDR: period where negligible DOC removal (< 5 %) was observed.

Table 5-2 Average percentage removal of DOC achieved by RF, B1, and B2 during the acclimation, SDR, and NDR periods. The dash represents non-statistically significant removal.

Period	Acclimation	SDR	NDR	SDR
	21/12/06-18/04/07	25/04/07-19/12/07	11/01/08-04/03/08	12/03/08-13/08/08
RAW vs RF	-	4	-	3
RAW vs B1	-	11	3	12
RAW vs B2	4	12	3	14

SDR: significant DOC removal; NDR: negligible DOC removal

Following the period of acclimation, during the first SDR period (occurring between April 25th, 2007 and January 19th, 2007), the biomass achieved a pseudo steady-state removal of DOC. The SDR period started simultaneously with the increase in water temperature. At higher temperatures both microbial kinetics and mass transfer are favoured (Huck et al., 2000). During this period, statistically significant DOC removal was achieved by the RF, B1, and B2. The RF achieved 4 % removal of the DOC itself. An average removal of 11 % and 12 % for B1 and B2 respectively was measured for the first active period (Table 5.2). There was no statistical difference in the DOC effluent of B1 and B2. The average concentration of DOC during the first SDR period for raw water, B1 effluent, and B2 effluent were 6.45 ± 0.72 mgC/L, 5.77 ± 0.62 mgC/L and 5.70 ± 0.74 mgC/L, respectively (n=33).

The first SDR period was observed until January 19th, 2007 even though the water temperature had dropped below 10°C since November 7th, 2007. Thus a lag effect occurred during this period of observation. This phenomenon may be explained by reduced cell growth over time at a colder temperature. However, after several weeks at low temperatures, the microbial kinetics, the mass transfer and the overall removal of DOC are likely to be inhibited by cold temperatures. Thus, at low water temperatures the biofilters achieved negligible DOC removal which is operationally designated as an NDR period (where less than 5 % DOC removal is achieved). However, it is still possible to observe significant removal of readily degradable substrates at these low temperatures (Huck *et al.*, 2000). The average DOC concentration of raw water, B1, and B2 effluents during the NDR period were 6.82 ± 1.27 mgC/L, 6.59 ± 1.30 mgC/L, and 6.63 ± 1.30 mgC/L, respectively (n= 16).

A second SDR period was observed between March 12th, 2008 and August 13th, 2008. Interestingly, the second SDR period started as soon as the water temperature warmed-up a few degrees. This behavior may be due to the presence of acclimated bacteria on the biofilter media as compared with the first SDR. Thus the temperature increases allowed the majority of bacteria already present in the acclimated biofilter to be at their optimal temperature which in turn increased microbiological activity. During the second SDR period, similar DOC removals of 12 % and 14 % were achieved by B1 and B2, respectively. The RF achieved a statistically significant removal of the DOC of 3 %. During this second SDR period, the DOC concentration at the effluent of B2 was statistically lower than the concentration at the effluent of B1. The average concentration of DOC during the second SDR period for raw water, B1, and B2 effluents was 5.93 ± 0.59 mgC/L, 5.21 ± 0.48 mgC/L, and 5.08 ± 0.48 mgC/L, respectively (for B1 n=19 and for raw and B2 n=22).

No statistical difference (paired T-test, $\alpha = 0.05$) in the DOC measurement of the RF and RF spiked (RFSP) was measured during the experimental period. Thus the action of spiking trace organic contaminants at a concentration of 500 ng/L or 5000 ng/L in the RF effluent did not significantly increase the DOC concentrations.

Appendix F presents the concentration of TOC and DOC and turbidity in the raw water, the RF effluent, the RFSP, and the effluent of B1 and B2 between December 2006 and August 2008.

5.4.2 Biological Activity of Rapid Biological Filters – Microbiological Analysis

Phospholipids are a major component of all cellular membranes; therefore, phospholipid analysis was used to measure the biomass attached to the surface of the media. Figure 5.2 presents a typical profile of the phospholipid concentrations of the biofilters at different bed depths in B1 and B2. The phospholipid measurements are expressed in equivalent of nanomole of phosphorus per cm^3 of dry media (nmole P/cm^3). The apparent density of anthracite and sand (i.e. 0.8 and 1.5 g/cm^3) were used to convert the measured values in nmole P/g in a volume basis value. As expected, similar and higher concentrations of phospholipid are measured on the top of both biofilters. The concentration of biomass attached to the media decreased along the bed depth for both filters, and the lowest concentration was measured at the bottom of the filter (Figures 5.2 and 5.3). Similar behavior has

been observed by others (Wang *et al.*, 1995). The decrease of biomass attached to the media can be due to the type of media. Anthracite has a greater potential than sand for biomass attachment due to its larger effective size (d10) than sand (i.e. 1.07 mm vs 0.52 mm). Furthermore, a decrease of the media diameter will increase the external specific area which may explain the difference in biomass attachment between anthracite (ES = 1.04) and sand (ES = 0.46). As indicated in Figure 5.2, the interface between anthracite and sand is located between 15 and 22 cm within the bed depth. For B2, the phospholipid concentration decreased from 148 to 70 nmol PO_4^{3-}/cm^3 within the first 10 cm of bed depth which is entirely located in the anthracite. Phospholipid concentration of 20 nmol PO_4^{3}/cm^3 was measured at 59 cm within the bed depth (sand media). Also the physico-chemical properties of the media surface such as charge may play an important role on the attachment of the biomass. A decrease in availability of primary nutrient deeper in the column can also explain the decrease in phospholipid concentration.

Six phospholipid measurements were performed on the filter media between February 21st, 2008 and July 15th, 2008. The average concentration measured on top of B1 and B2 were 154 ± 10 nmol PO_4^{3}/cm^3 and 157 ± 14 nmol PO_4^{3-}/cm^3, respectively. The results are reproducible as demonstrated in Figure 5.3.The calibration curve and results of phospholipid measurements are presented in Appendix G.

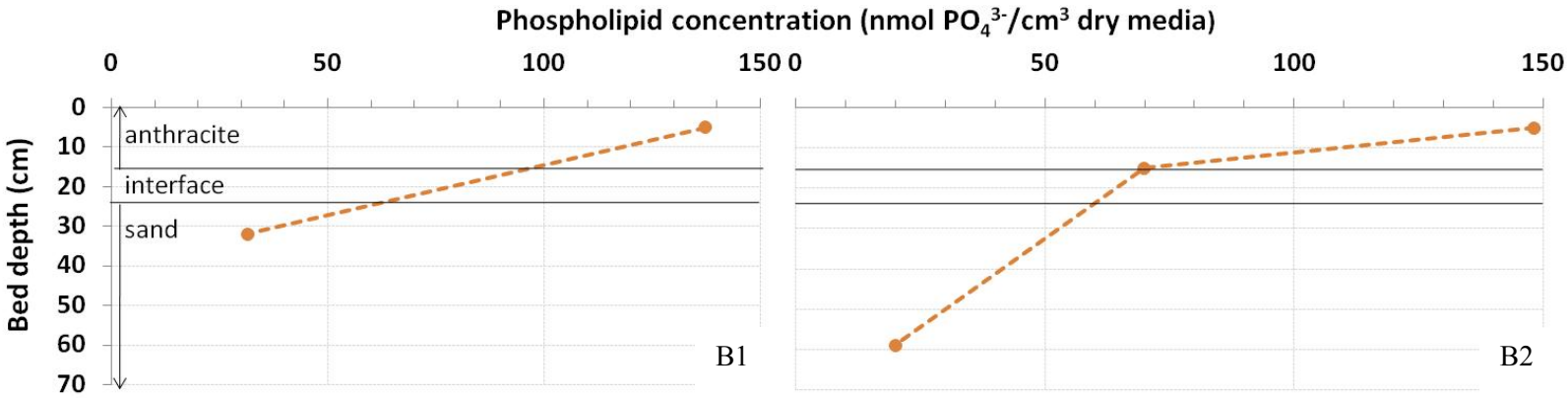


Figure 5-2 Typical concentration profiles of phospholipids (June 15th 2008) on the media at different bed depths

Previous research demonstrated an accumulation of the biomass before reaching a steady state (Wang *et al.*, 1995). Because the phospholipid measurements were performed on the biofilters after 14 months of operation pseudo steady state conditions were assumed. The concentration of phospholipids on top of the filters is higher and independent of the water temperature as shown in Figure 5.3. Those results suggest that the removal of biodegradable organic matter may preferentially occur on top of the biofilter. However, the amount of biomass is not directly related to its activity. As demonstrated by Huck *et al.* (2000), variations in biomass concentration as measured by the phospholipid method were not quantitatively related to the capability of a filter to achieve BOM removal. Thus the sensitivity of the phospholipid measurements may not be high enough to be a good indicator of performance. It may also indicate that the biomass concentration may not be the limiting factor for the removal of biodegradable compounds, except perhaps if the biomass concentration is very low. However, the measurement of phospholipid is very useful to demonstrate the presence of the biofilm on the media surface.

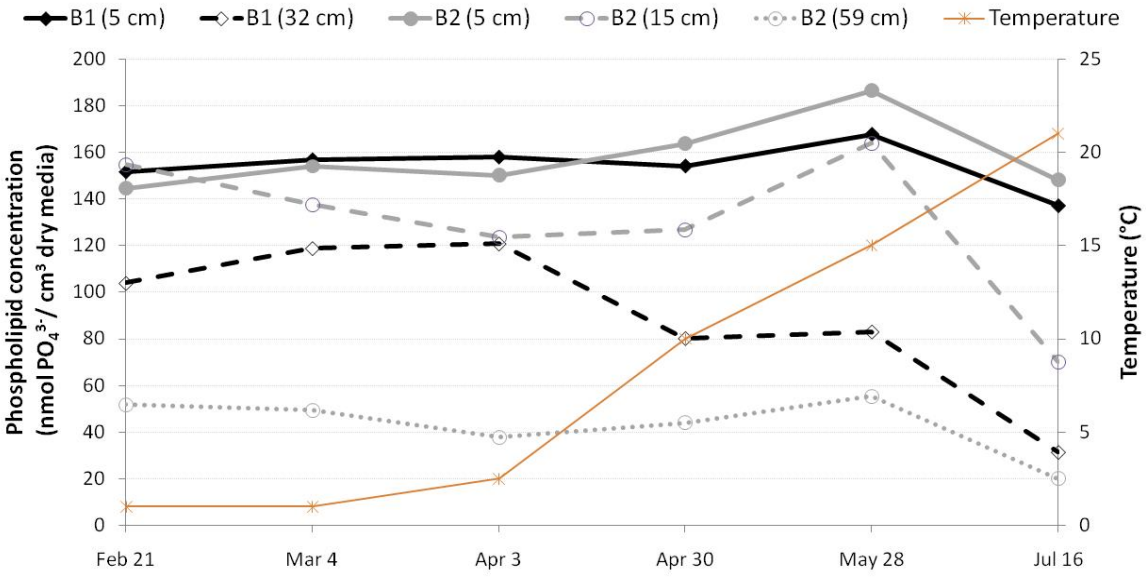


Figure 5-3 Concentration of phospholipids at different bed depths for B1 and B2.

Note: B1 (5 cm) and B2 (5cm) in anthracite; B2 (15 cm) at the interface anthracite and sand; B1 (32 cm) and B2 (59 cm) in sand.

TDCC measurements performed on B1 and B2 at different bed depths are presented in Figure 5.4. TDCC measurements were performed 6 times between February 21st, 2008 and July 15th, 2008. The complete results are presented in Appendix H. The TDCC are expressed in cells per cm^3 of dry media (cells/cm^3 dry media). The apparent density of anthracite and sand (i.e. 0.8 and 1.5 g/cm^3) were used to convert the measured values in cells/g in a volume basis value. Figure 5.4 shows that the cell count per cm^3 of dry media is higher at the top of the bed depth for both biofilters. For B1 and B2 the lowest count occurs on February 21th, and the amount of cells increased until April 3rd, for B1 and May 1st for B2. Then the cell counts stabilized for B1 and the count decreased for B2. Similar cell counts were achieved at 32 cm within B1 and 15 cm within B2. The lowest cell counts were obtained at 59 cm within B2. Biological filtration is a dynamic process involving attachment, detachment, and transport of cells through the bed depth. However, removal of cells was observed when the generation of cells within the biofilter is less than the removal capacity. Consequently, the data presented in Figure 5.4 shows a removal of TDCC by B1 and B2 which increases with the EBCT. Moreover, the removal of TDCC by biofiltration is possible by performing adequate maintenance such as backwash and air scour.

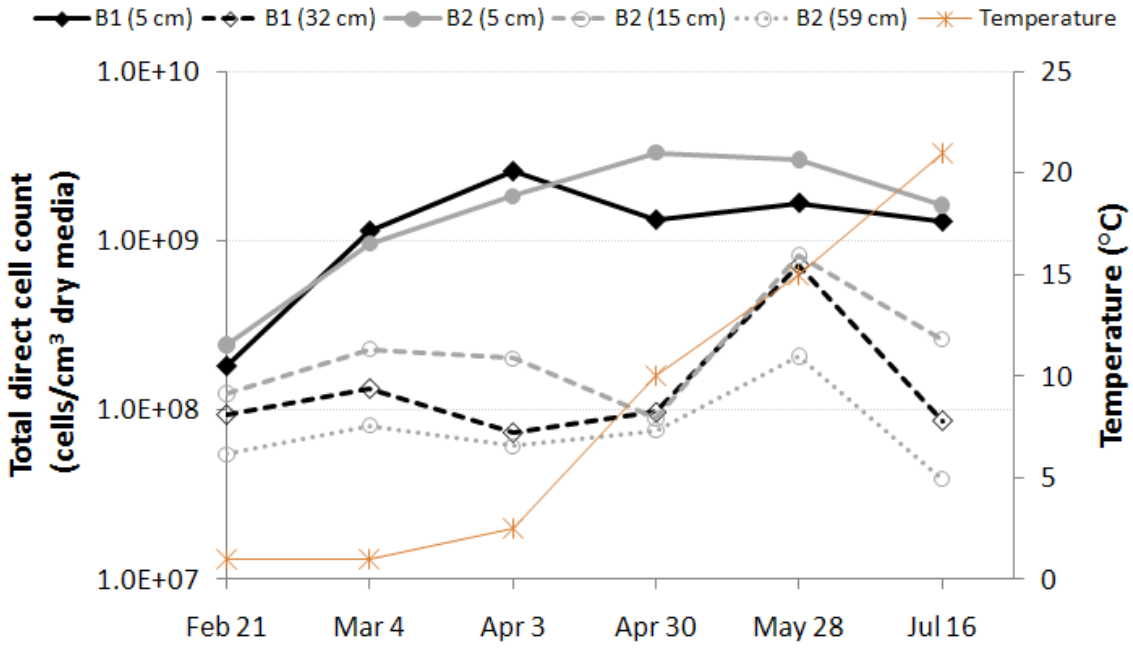


Figure 5-4 TDCC profile for B1 and B2 at different bed depths. B1 (5 cm) and B2 (5cm) in anthracite; B2 (15 cm) at the interface anthracite and sand; B1 (32 cm) and B2 (59 cm) in sand

Phospholipids and TDCC analyses were both performed to measure biomass on the media. By comparing Figures 5.3 and 5.4, the general pattern through the bed depth is similar for both analyses except that the phospholipid measurements in the mid-layer and bottom of B2 seem higher than the TDCC measurements. This could be due to the presence of undegraded phospholipids from dead or non-intact cells from the top layer.

As described in the literature review, ATP measurements provide an indication of the active biomass present in the filter. ATP measurements were performed six times between February 21st, 2008 and July 15th, 2008. The calibration curve and results are presented in Appendix I. This measurement was expressed as ATP per cm^3 of dry media (μmol ATP/cm^3). The bulk densities used to convert the measured value (μmol ATP/g) to volume basis were 0.8 g/cm^3 for anthracite and 1.5 g/cm^3 for sand. At the interface a 50/50 mixture of sand and anthracite was assumed based on visual inspection.

Figure 5.5 presents the average ATP concentration per cm^3 of dry media at different bed depths and the error bar presents the standard deviation based on triplicate analysis. The sampling ports B1-5cm and B2-5cm were located in anthracite, B2-15cm was located at top of the interface anthracite/sand, and B1-32cm and B2-59cm sampling ports were located in the sand. Note that due to site height restriction, biofilter B2 was split in two columns thus media B2-59 cm is not directly in contact with the two sampling ports ahead. This situation may have influenced the colonization of the media in the second part of the biofilter B2. However, as observed in Figure 5.5 the ATP concentrations in B2-15 cm and B2-59 cm were comparable for all measurements.

As expected, the concentration of ATP at 5 cm within B1 and B2 were generally similar. At water temperatures below 10°C lower concentration of ATP were measured at the top of the biofilter and higher ATP concentration were measured deeper within the bed depth (Figure 5.5). However, at intermediate temperature of 10°C to 15°C, the concentrations of ATP along the bed depth were within the same range. At water temperatures above 20°C, the concentrations of ATP were higher at the bottom of the respective biofilters.

Even though the amount of biomass is higher on top of the filter as shown in Figures 5.3 and 5.4, the active biomass seems to be located deeper within the bed depth as demonstrated in Figure 5.5 by ATP analyses.

As mentioned previously, it is also possible that phospholipid and TDCC measurements included dead cells or non-intact cells leading to an apparent higher concentration on top of the filter. The accumulation of debris at the surface of the filter may not offer the optimal growth and attachment conditions for the living biomass explaining the lower concentration ATP concentration on top of the biofilters. However, an increase of ATP concentration on top of the biofilter is consistent with the increase of TDCC overtime. On April 30th and May 28th the concentrations of ATP through the bed depth for both biofilters were similar and may be due to a changeover in the bacterial community occurring at intermediate water temperatures. Finally, at water temperatures greater than 20°C, significantly higher concentrations of ATP were measured at the bottom of their respective bed depth. It is interesting to note that in all cases the concentrations of ATP at the bottom of the respective bed depth were in the same order of magnitude. These results support the observation that longer contact times were generally beneficial for the removal of biodegradable organic contaminants.

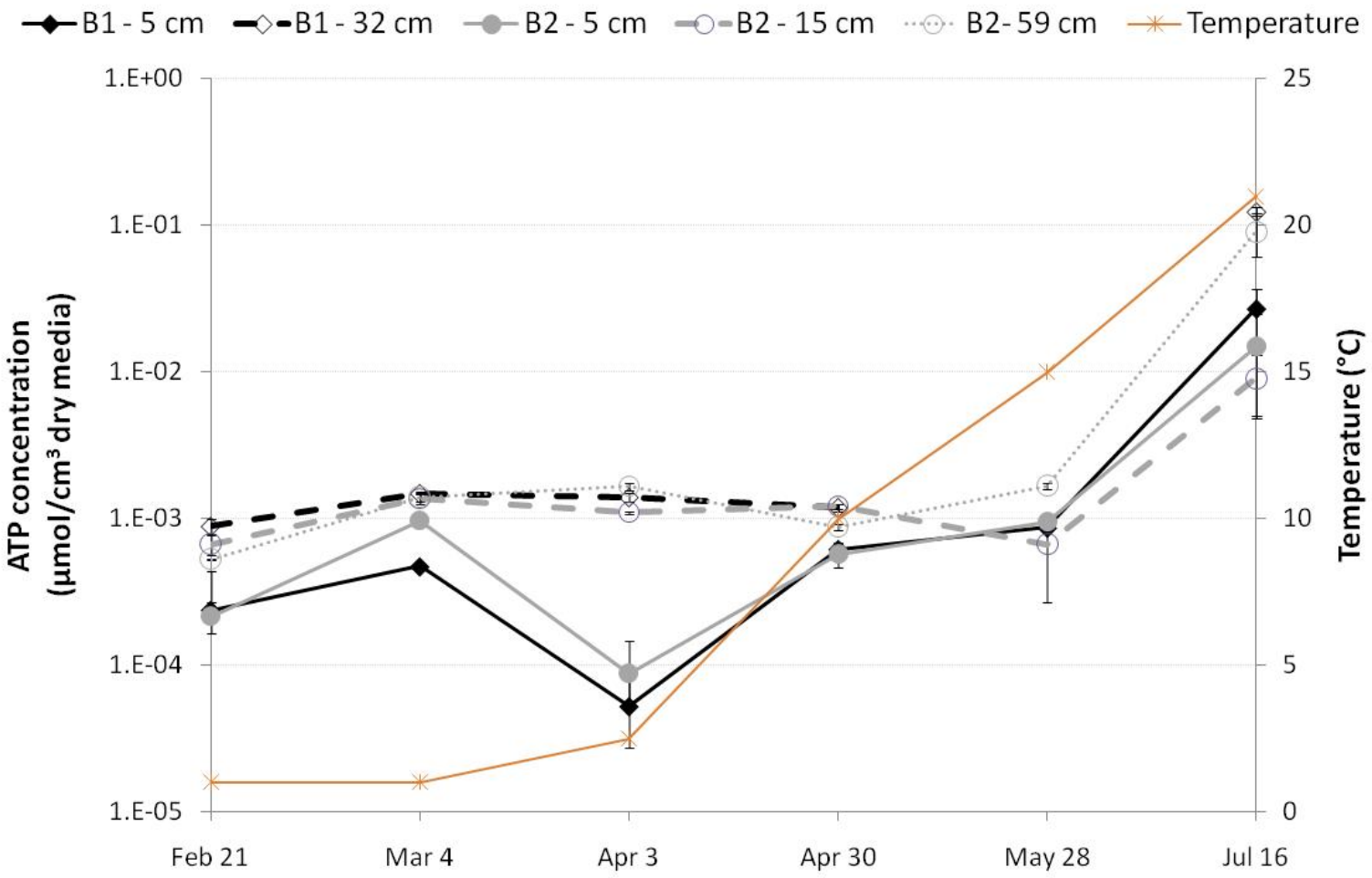


Figure 5-5 ATP concentration attached to the media at different depths in B1 and B2. B1-5cm and B2-5cm were located in anthracite, B2-15cm was at top of the interface anthracite/sand, and B1-32cm and B2-59cm were in the sand

The biological activity of the filter can also be determined by assimilable organic carbon (AOC) measurement of the influent and effluent of the biofilters. The AOC bioassay is based on the capacity of two bacterial species (*Pseudomonas fluorescens* strain P-17 and *Spirillum* strain NOX) ability to grow in a water sample (Magic-Knevez and van der Kooij, 2004). The AOC bioassay is extremely sensitive to organic carbon contamination. Analysis were performed by a commercial laboratory and based on several indications, confidence in the data was not high thus the results are not included.

5.4.3 Biological Activity of Rapid Biological Filters - Removal of Secondary Substrate

In this section, the predicted biodegradability of the selected PhACs and EDCs using the Biodegradation Probability Program for Windows (BIOWIN) software will be presented.

Table 5.3 presents the predicted biodegradability of selected PhACs and EDCs using BIOWIN developed by the U.S. Environmental Protection Agency (U.S. EPA, http://www.epa.gov/oppt/exposure/docs.episuited1.htm). BIOWIN calculates the probability of rapid or slow biodegradation under aerobic conditions with a mixed culture of microorganisms. The program determines the biodegradability of each fragment of a given chemical and the fragment values are summed to calculate the overall biodegradability of a compound. The approach is based on multiple linear and non-linear regressions. BIOWIN uses both the MITI (Ministry of International Trade and Industry) and BIODEG regression models. Also a survey model estimating primary and ultimate biodegradation was developed based on a survey realized with a panel of experts on biodegradation. More details on the BIOWIN models are available in Appendix J.

Table 5-3 Predicted biodegradability of selected PhACs and EDCs by BIOWIN

Contaminant	BIODEG linear model	BIODEG non-linear model	SURVEY primary degradation	SURVEY ultimate degradation	MITI linear model	MITI non-linear model
DEET	+	+	+	+	-	-
ibuprofen	+	+	+	+	-	-
naproxen	+	+	+	+	-	-
atrazine	-	-	-	-	-	-
carbamazepine	+	-	+	+	-	-
nonylphenol	+	+	+	+	-	+

+ biodegrade fast; - do not biodegrade fast

Both MITI linear and non linear models suggest that selected PhACs and EDCs will not be biodegraded with the exception of nonylphenol which is determined biodegradable by the MITI non-linear model. In contrast, the BIODEG linear model suggests that all compounds except for atrazine will be rapidly biodegraded. The BIODEG non-linear model predicts rapid biodegradation for all compounds except for atrazine and carbamazepine. The primary and ultimate degradation of contaminants for the survey models indicates that all selected compounds except atrazine will biodegrade rapidly. This wide range of results emphasizes the need for experimental work to assess the biofiltration performance and to aid further model development. However, the BIODEG non-linear model seems to fit with our experimental data in comparison to the other models.

5.4.4 System Loss Test

The levels of adsorption of the selected PhACs and EDCs on the biofiltration experimental set-up were evaluated at both spiking concentrations. Between July 18th 2007 and August 6th 2008 a column without media (B3) was spiked and the removal due to adsorption could be calculated as:

$$\text{Removal}\ (\%) = \left(\frac{C_0 - C_e}{C_0} \right) x100 \qquad \text{e.q. 5-1}$$

Where
C_e is the concentration at the effluent of column B3
C_0 is the concentration in the influent of column B3

Table 5.4 presents the average percentage of adsorption of selected PhACs and EDCs and standard deviation on the biofiltration experimental set-up. In general, a negligible level of adsorption between 0 % and 7 % of selected PhACs and EDCs occurred on the experimental set-up. The only exception is for NP where up to 16 % of adsorption was observed. Negative percentage removal may be due to analytical error or to the presence of conjugates in the influent acting as a reservoir of the parent compound. In wastewater treatment, studies show that conjugates can be enzymatically cleaved to liberate the parent compounds (Joss *et al.*, 2005; Ternes *et al.*, 2004). Considering the standard deviation, the levels of adsorption at both low and high influent concentrations were comparable. Results of the adsorption tests are available in Appendix K.

Table 5-4 Average adsorption (%) of selected PhACs and EDCs and standard deviation on the biofiltration experimental set-up

	Low spiking concentration	**High spiking concentration**
DEET	0 ± 6	2 ± 6
ibuprofen	5 ± 8	3 ± 9
naproxen	-2 ± 9	5 ± 14
atrazine	-1 ± 6	5 ± 13
nonylphenol	7 ± 57	16 ± 57
carbamazepine	-1 ± 7	7 ± 15

5.4.5 Pilot Scale Experiment – Removal of Selected PhACs and EDCs

As shown by the models of BIOWIN, some organic trace contaminants are more susceptible to biodegradation than others. This section presents the biodegradability results of six contaminants at concentrations of environmental significance. Potential competition among spiked organic trace contaminants and components of dissolved organic matter present in natural water is possible. The identification of sorption and partitioning mechanisms of contaminants in such a complex system are still poorly understood and is out of scope for this research. However, similar processes of sorption and partitioning mechanisms observed for metals can be assumed (Bryers and Characklis, 1982). This study investigated the effect of influent concentration and water temperature on the transformation of selected contaminants by mature biofilms for drinking water treatment.

The spiking periods are temporally represented in Figure 5.6. The biofilters were continuously spiked between July 18th 2007 and August 6th 2008 with alternating high and low influent concentrations. As indicated in Figure 5.6, two spiking events at low concentration have been performed during the first SDR period. The low three (L3) period started during the SDR and finished during the NDR period. The low four (L4) period started during the NDR and finished during the second SDR period. At high concentration, two spiking events happened during the first SDR period of the biofilters and one spiking event happened during the NDR period.

In terms of observed removals, the compounds can be divided into two groups: those that were essentially not removed at all (carbamazepine and atrazine) and those that were removed to a varying extent (DEET, naproxen, ibuprofen).

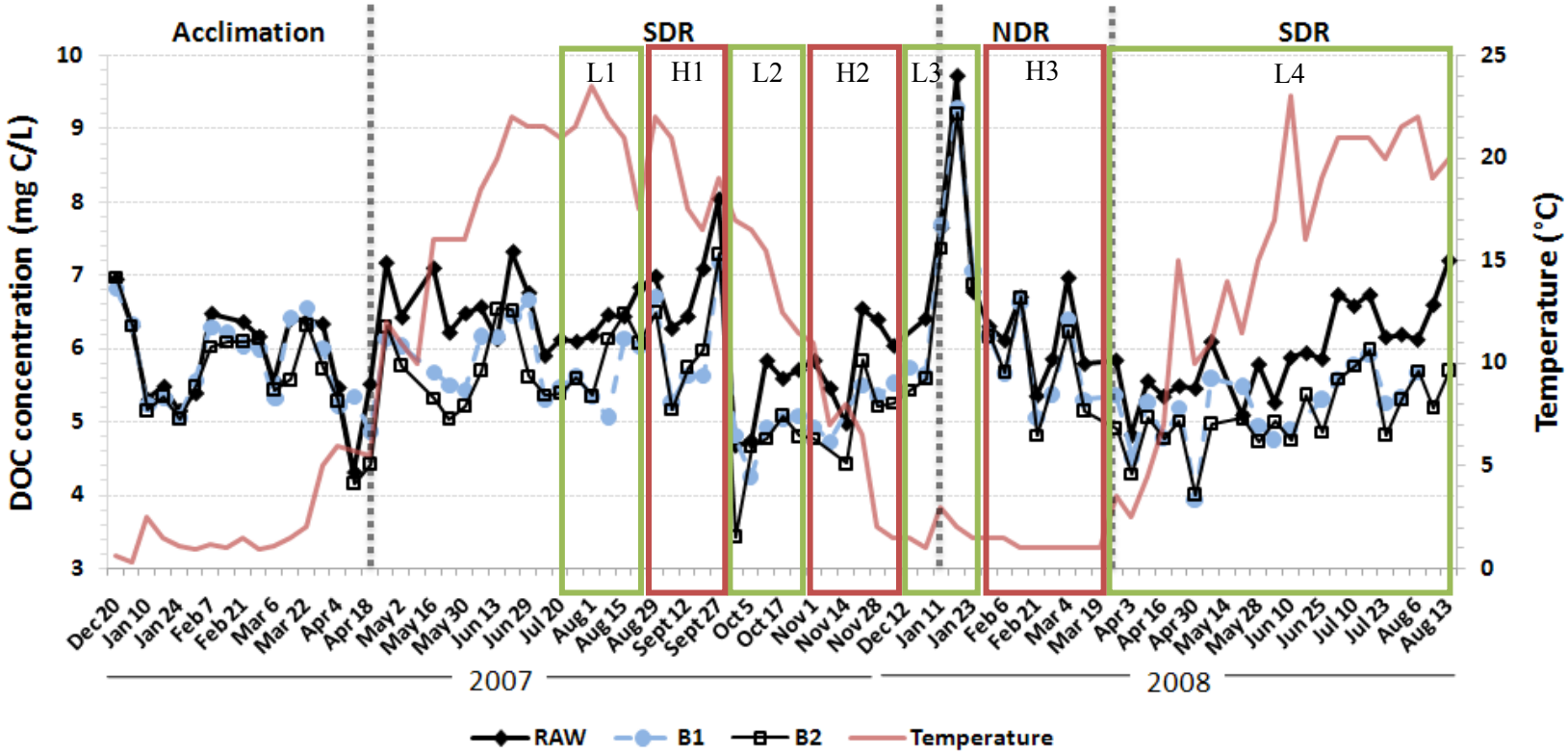


Figure 5-6 Temporal representation of the seven spiking events at low (L1, L2, L3, and L4) and high (H1, H2, and H3) concentrations. Green sections represent low influent concentration (i.e. 500 ng/L) and red sections represent high influent concentration (i.e. 5 µg/L)

Nonylphenol

Figure 5.7 shows the concentrations of NP in the biofilter influent and effluents in function of time during the low 1 period (L1). This figure demonstrates the issue related to spiking NP in the biofilter influent.

The octanol-water partitioning coefficient (Log K_{ow}) is a measure of the equilibrium between octanol and water phases and it indicates the potential of a compound for partitioning into organic matter. A compound with a high log K_{ow} value will preferably partition into organic matter rather than water. With a Log K_{ow} value of 5.92, NP is the most hydrophobic of the selected compounds and NP tends to adsorb to organic surfaces. As demonstrated in Table 5.5, the percentage of adsorption of NP into the instrumental set-up at low and high concentrations was 7 ± 57 % and 16 ± 57 % respectively. Because of near complete adsorption of NP no further evaluation of NP was performed. Appendix K contains the results related to NP for the other spiking periods.

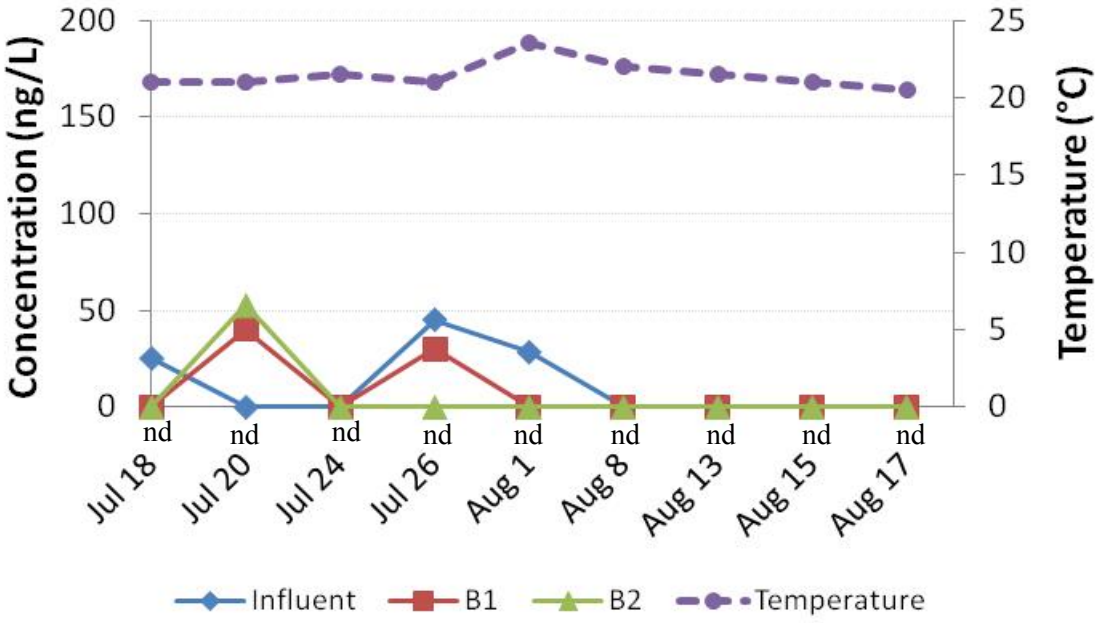


Figure 5-7 Concentration of nonylphenol (NP) in the biofilter influent and effluents and water temperatures

NON-BIODEGRADABLE COMPOUNDS

Carbamazepine

Carbamazepine is ubiquitous in WWTP effluent due to poor removal (i.e. less than 10 %) by the biologically active treatment processes (Heberer *et al.*, 2002; Ternes, 1998). Thus these studies report that carbamazepine was the drug with the highest detection frequency and higher concentration in WWTP (Heberer *et al.*, 2002). Using biodegradation in batch experiments, Ternes *et al.* (2002) determined that the carbamazepine should demonstrate, under real conditions such as slow sand filtration and subsoil passage, low sorption and a high degree of persistence. Heberer *et al.* (2001) also demonstrated the persistence of polar compounds during bank filtration.

Figure 5.8 shows the concentrations of carbamazepine in the biofilters influent and effluent and the water temperature for the spiking events at low (L) and high (H) concentrations. As expected, except for a few data points no statistically significant removal of carbamazepine was observed at low or high spiking concentrations by both biofilters (paired *t*-test analysis).

In Figure 5.8c, on October 4th the concentration measured in the biofilters effluent was higher than the biofilter influent and similar phenomenon was also observed in Figure 5.8 g on April 11th. This discrepancy may be due to analytical error or to enzymatic transformation of carbamazepine metabolite.

Removal of carbamazepine by up to 30 % was measured on April 30th and May 7th (Figure 5.8 g) and on February 8th and 26th (Figure 5.8 f). Although the removals of carbamazepine occurred infrequently and were not consistent with the general trend, the level of transformation was consistent with the maximum removal measured with biological wastewater treatment (Kosjek *et al.*, 2009). Sampling error, analytical error, or sample processing error can all contribute to variability in the data especially at these low concentrations; however, the quality control and quality assurance measures performed were within the expected range. Thus, these data points were not rejected.

In general, Figure 5.8 showed that the biofilter influent concentrations at both low and high concentrations were relatively stable over the duration of the spiking periods. The concentration measured in the effluents of the biofilters demonstrated that carbamazepine is refractory to

biodegradation. The increase in contact time did not reduce the concentration of carbamazepine in the biofilter effluent. Moreover, the water temperature and the SDR and NDR periods of the biofilters had no impact on the removal of carbamazepine.

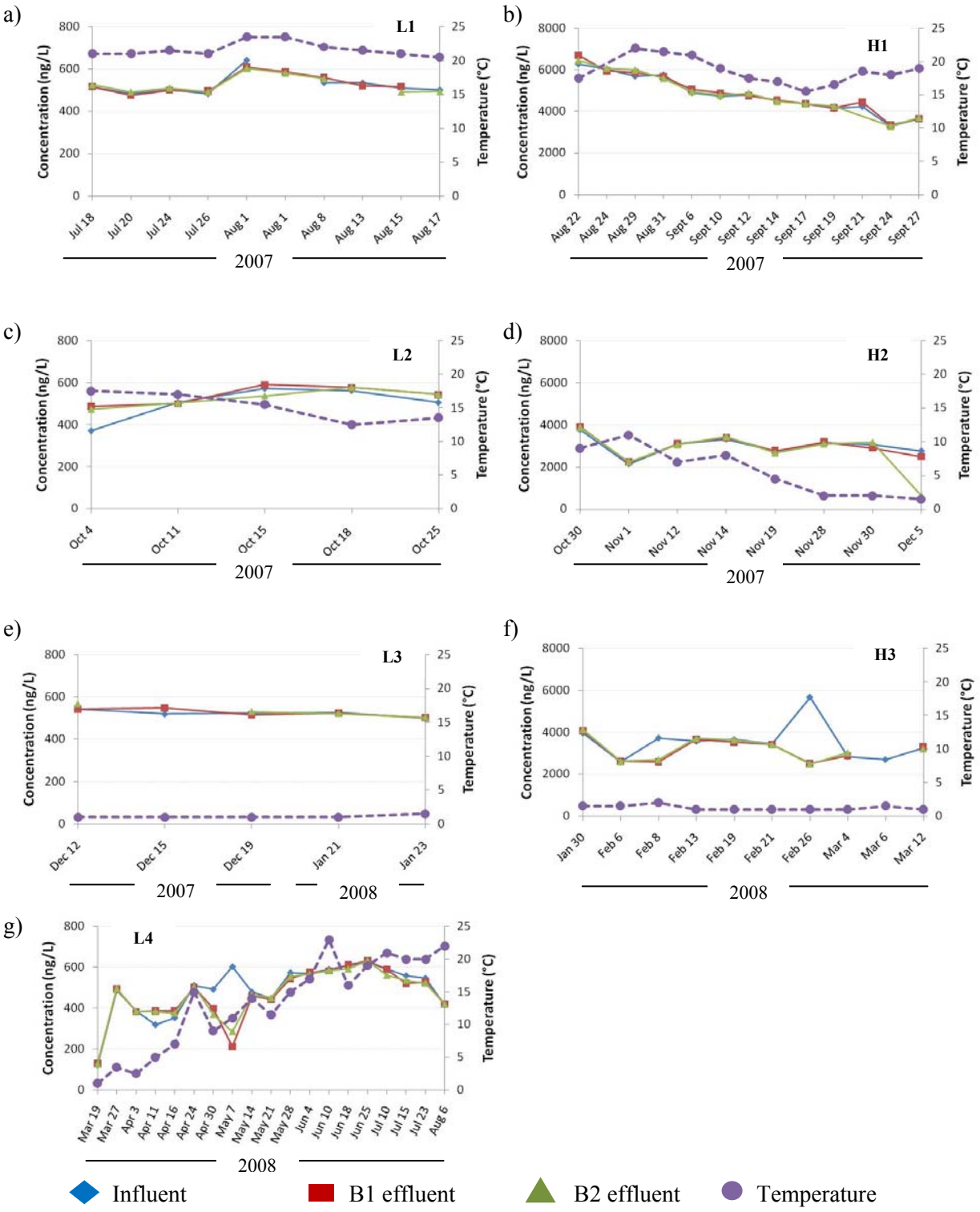


Figure 5-8 Concentration of carbamazepine in the biofilter influent and effluents for spiking periods a) L1, b) H1, c) L2, d) H2, e) L3, f) H3, and g) L4

Atrazine

Atrazine degrades slowly via hydrolysis and n-dealkylation. Atrazine degradation by-products, desethylatrazine, are persistent and mobile while deisopropylatrazine is labile. The half life of atrazine is around 12 weeks at a pH of 5 and at 20°C, but breakdown is negligible in neutral or alkaline solutions with a half life of two years or more (Health Canada 1993). Atrazine was the most common contaminant found in Ontarian farm wells in 1986 and 1987 and has been identified as the most stable herbicide (Thurman *et al.*, 1991; Frank *et al.*, 1990). The high detection frequency of atrazine in groundwater suggests a low degree of biodegradability. Moreover, with a Log K_{ow} value of 2.75, atrazine does not bioaccumulate at any degree in soil.

Figure 5.9 shows the concentrations of atrazine in the biofilter influent and effluents and the water temperature for the spiking events at low (L) and high (H) concentrations. As expected, except for few data points, no statistically significant removal of atrazine was observed at low or high spiking concentrations by both biofilters (paired *t*-test analysis). In general, Figure 5.9 shows that the biofilters influent concentrations were relatively stable over the duration of the spiking periods. The concentration measured in the effluents of the biofilters demonstrated that atrazine is refractory to biodegradation. Moreover, as observed for carbamazepine, the water temperature and the SDR and NDR periods of the biofilters had no impact on the removal of atrazine.

As observed for carbamazepine, the concentration of atrazine in the biofilters effluent was higher than the influent concentration on October 4th of 2007 and April 8th of 2008. At some occasions (e.g. July 24th of 2007, December 5th of 2007, February 8th of 2008, and May 7th of 2008) removals of up to 30 % of atrazine were measured. As mentioned for carbamazepine, sampling error, analytical error, sample processing error, or enzymatic transformation of atrazine metabolites could be the potential reason of this apparent removal or increase in concentration. However, the quality control and quality assurance data that were performed concurrently were within the expected range and thus these data points were not rejected.

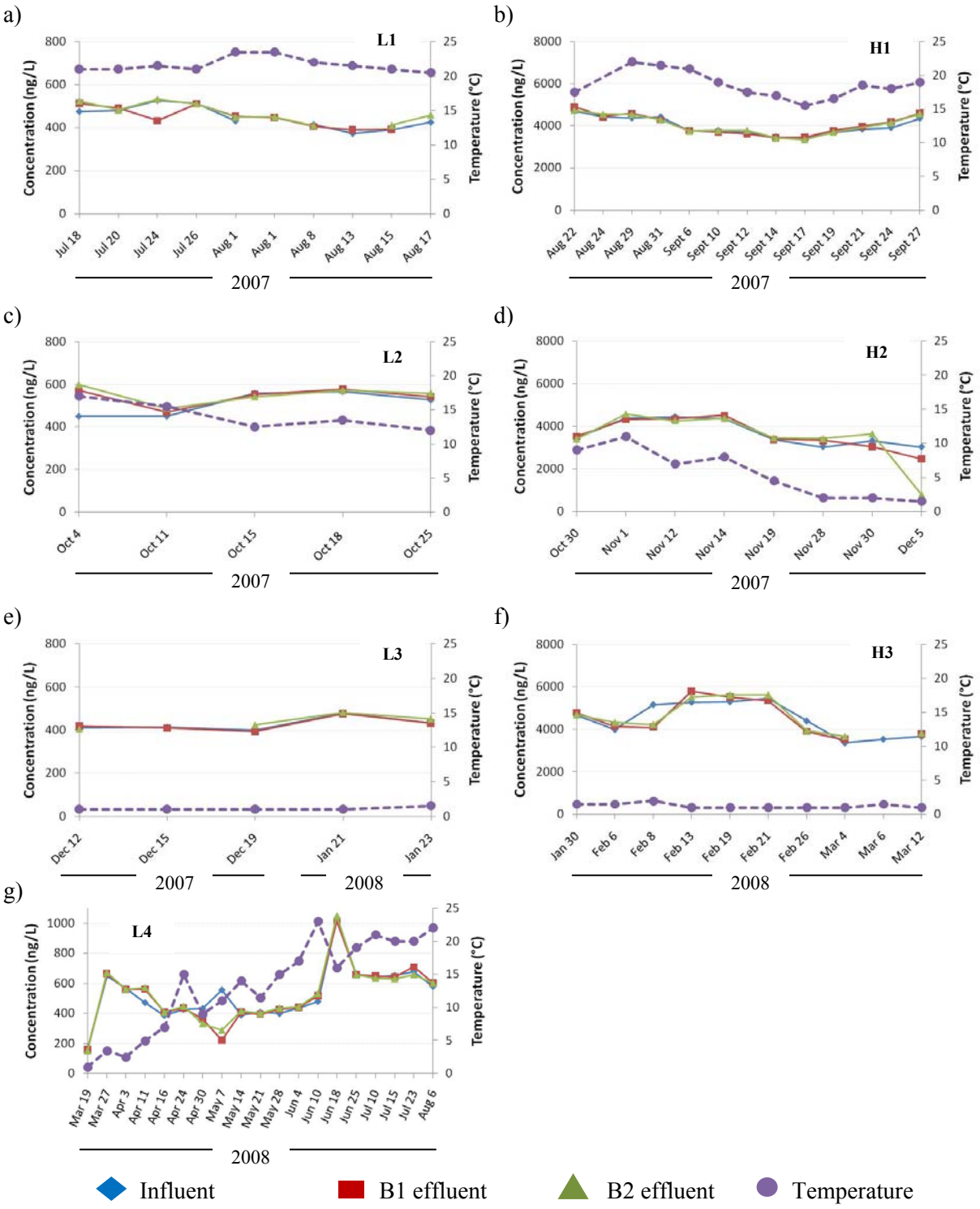


Figure 5-9 Concentration of atrazine in the biofilter influent and effluents for spiking periods a) L1, b) H1, c) L2, d) H2, e) L3, f) H3, and g) L4

BIODEGRADABLE COMPOUNDS

The dataset obtained in this investigation under real-world conditions over an extended period of time indicates that several factors influence the removal of PhACs and EDCs during drinking water biofiltration. The removals of biodegradable PhACs and EDCs depend on the water temperature (i.e. biomass activity for DOC removal), the influent concentration, and the NOM composition of raw water. The results of each biodegradable compound will be interpreted in this section.

Acclimation and pseudo steady state period

As demonstrated by Stratton *et al.* (1983), to be biodegraded, compounds with complex biochemical degradation pathways may require enzymes that are not necessarily constitutively produced by the bacteria. Because of the complex nature of the microbial ecosystem, biological processes can adapt in a very dynamic manner to changes in their environment (Rittmann and McCarty, 2001). As presented in the literature review, biomass acclimation can consist in a variety of processes and are frequently observed during the biological transformation of PCPs in the environment (Kagle *et al.*, 2009). In this study, the biofilters were subjected to several stresses such as change in temperature, raw water quality, and exposure to a mixture of PhACs and EDCs at different concentrations. Despite the real-world conditions of drinking water biofiltration, the microbial community adapted in order to maintain its function. During the acclimation period (i.e. normally ranging from few hours to several months), little or no biotransformation of organic contaminant was observed. When the microbial community was acclimated, organic contaminants could be rapidly transformed and normally this continued until stresses caused changes in the microbial structure.

Figures 5.10, 5.11, and 5.12 show the concentration in the first two spiking events for DEET, naproxen, and ibuprofen, respectively. The spiking event at low concentration (L1) occurred first and immediately afterwards the concentration in the biofilter influent was raised to high concentration (H1). During both events the water temperature was relatively stable at around 20°C.

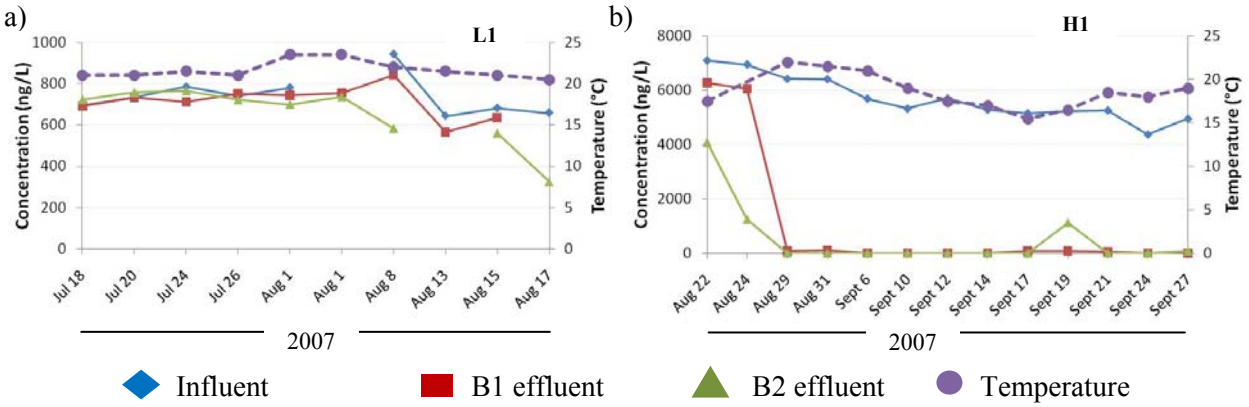


Figure 5-10 Concentration of DEET in the first of spiking period a) L1 and b) H1

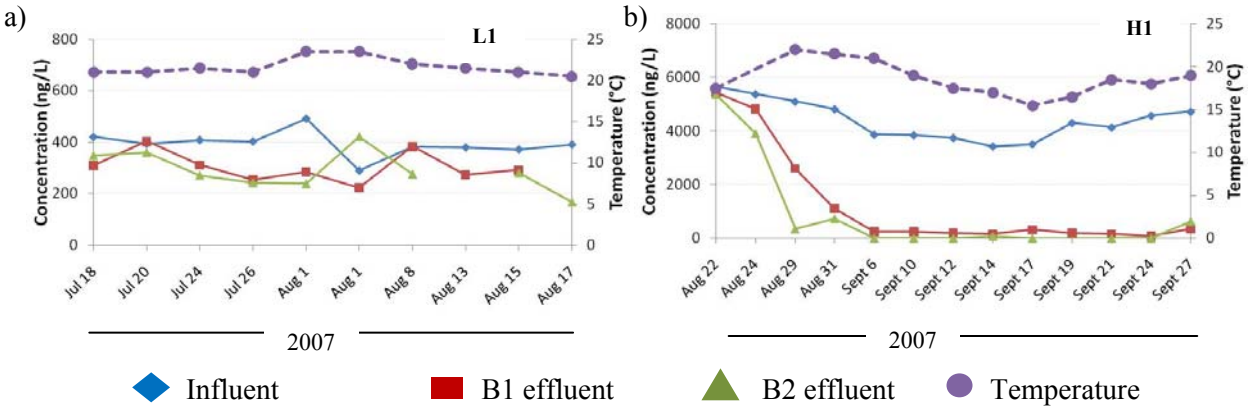


Figure 5-11 Concentration of naproxen in the first of spiking period a) L1 and b) H1

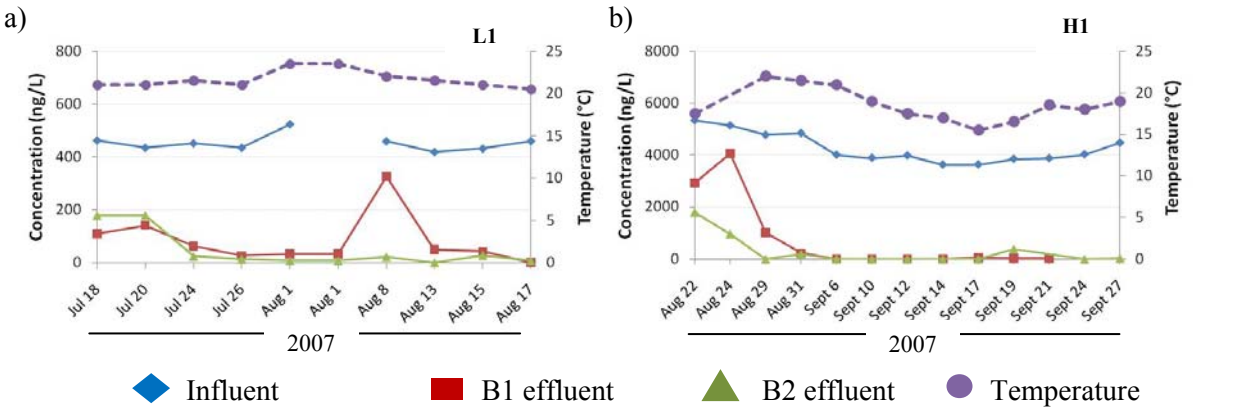


Figure 5-12 Concentration of ibuprofen in the first of spiking period a) L1 and b) H1

At the low concentration initially fed, DEET required several days (i.e. 21 days) before achieving some removal (Figure 5.10a). On August 8th, some removal of DEET by the biofilters was observed for the first time. For the last 4 data points of L1 the average percentage transformation for B1 and B2 were respectively, 10 % and 36 %. During this first spiking period, although the removals were not very high, B2 tends to achieve greater removal than B1. After spiking at 500 ng/L for a period of 4 weeks the influent concentration of PhACs and EDCs was raised to 5000 ng/L.

For DEET, at the high influent concentration, the biofilters required a shorter acclimation period (i.e. approximately one week) (Figure 5.10b). During the first two sampling points in August 22nd and 24th the percentage transformation achieved by both biofilters increased compared to the percentage transformation achieved at the end of the L1 period. During the acclimation period, the impact of the EBCT is noticeable since B2 achieved significantly higher percentage transformation than B1. After the acclimation period, near complete removal was observed for the remaining of the H1 period by both biofilters.

Increasing the influent concentration had a positive impact on the transformation of DEET by the biofilters. Biodegradation of DEET by the biomass was triggered by the increase of influent concentration and one or several mechanisms may have lead to this observation. The biodegradation of DEET was also observed during WWTP but only above a threshold value of 1 µg/L (Knepper *et al.,* 2004). At higher influent concentration, the biomass possibly started the production of the enzyme necessary for the metabolism of DEET. By increasing the influent concentration, the compounds may have been present in sufficient concentration to justify its usage by the biomass. A change in the biomass community may also have been stimulated after a long and continuous exposure to the contaminant. Biodegradation of DEET via metabolization through N-deethylation and N-oxidation at high temperature and at a concentration of 1mM by soil fungi (i.e. C. elegans and M. ramannianus) was also observed by Seo *et al.* (2005). The results suggest that the increase in DEET transformation is caused by the increase in influent concentration as the temperature remained constant during L1 and H1.

As observed for DEET, low removal of naproxen was observed when the contaminant was spiked at low concentration (Figure 5.11a). However, the results showed that naproxen was transformed more easily than DEET. The high concentration of naproxen measured in B2 effluent on August 1st may be due to sampling, sample processing, or analytical error.

When increasing the influent concentration of naproxen, very low removal was initially measured (Figure 5.11b). Thus the change in influent concentration influenced the biomass and the transformation of naproxen. However, shortly after the increase in influent concentration the removal of naproxen constantly improved during the acclimation period which lasted for 15 days. After the acclimation period, near complete removal of naproxen was observed for the remaining H1 period.

Figure 5.12 shows the concentration of ibuprofen in the first two spiking events (i.e. L1 and H1). At low concentration, ibuprofen required an acclimation time of approximately 8 days before achieving high and steady state removal. It is obvious from Figure 5.12a that ibuprofen is easily biodegradable because removals between 60 % and 97 % were achieved by B1 and B2 during the first three sampling points. For the remaining of the L1 spiking period, removals of up to 98 % were observed except for one data point on August 8th of 2007, this data point was considered as aberrant. Both B1 and B2 behaved similarly during the L1 spiking event.

At high concentration, the transformation of ibuprofen required an acclimation time of approximately 9 days. As observed with naproxen, the biofilters were impacted by the change in influent concentration. A major increase in influent concentration reduced temporally the percentage removal of B1 and B2 to 45 % and 66 % respectively. For the remaining of the acclimation period until August 31st of 2007, the removal of both biofilters increased and B2 always outperformed B1. After the acclimation period, near complete removal was observed by both biofilters. Those results are comparable to a study performed by Winkler *et al.* (2001) who studied the biodegradation of ibuprofen by biofilm originating from surface water. They observed rapid degradation up to 90 % of ibuprofen in the water phase when the compound was spiked at 10 µg/L. They also determined that adsorption of ibuprofen and two of its major metabolites (i.e. hydroxyl-ibuprofen and carboxy-ibuprofen) in the biofilm were not significant.

The analysis of the L1 and H1 spiking events and the acclimation periods for the biodegradable compounds showed that the influent concentration influences the degree of removal achieved by the biofilters. For DEET and naproxen low removals were measured at low influent concentration. For ibuprofen, a short acclimation period at both low and high concentrations was observed before achieving almost complete removal. Generally, a major increase in influent concentration temporally reduced the removal but after a short acclimation period, near complete removal of DEET, naproxen, and ibuprofen was observed. After a variable period of acclimation pseudo steady removal was observed. In general, the relatively short period of acclimation shown for DEET, naproxen, and ibuprofen suggests that bacteria present on the media had the necessary constitutive enzymes to achieve biodegradation of those compounds. Figure 5.6 show that both L1 and H1 spiking periods were performed during the SDR period of the biofilters which provided the optimum conditions to achieve biodegradation of trace organic contaminants. Finally, the consistency of the results obtained from the acclimation period demonstrated the quality of the data.

The impacts of water temperature and influent concentration were analyzed during the various spiking events for each biodegradable compounds. Figures 5.13, 5.14, and 5.15 show the various spiking events in sequence (i.e. L2, H2, L3, H3, and L4) for DEET, naproxen, and ibuprofen.

DEET

Figure 5.10 demonstrates that the increase in influent concentration triggers the transformation of DEET by the biofilters. When the concentration of DEET was decreased to 500 ng/L on October 4^{th,} for the L2 period, the percentage removal observed for both biofilters was higher than observed during L1. Between October 11th and 18th, the average removal achieved by B1 and B2 were respectively 53 % and 64 %. Although the temperature was decreasing during this spiking period, the highest percentage removal was measured on October 25th for both biofilters. Thus a lag effect due to temperature was observed during this L2 period.

When transitioning between L2 and H2 periods, the removal achieved by B1 was decreasing. Although the removal achieved by B2 was also diminishing, the biofilter with the longer EBCT was less affected. When the water temperature decreased, the removal achieved by both biofilters also

diminished. This decrease in water temperature is expected to influence the metabolic activity of the biomass. For B1 the transformation of DEET during the last three data points was inhibited. However, at the end of the H2 period, the removal of DEET by B2 unexpectedly increased although the water temperature was colder and this behavior was also observed during the H3 period (i.e. February 6th and 8th) and during the L4 period (i.e. April 3rd and 11th). This increase in removal is difficult to explain considering the low water temperature but changes in water quality may have favored the removal of DEET. Although the H2 period was performed during the SDR period a decline in percentage transformation of DEET was observed. Thus the removal of trace organic contaminant may be more sensitive to water temperature (i.e. biomass activity) than the primary substrate.

During the L3 period, low percentages of removal between 9 % and 24 % were achieved by B1. During the same period, B2 achieved higher percentages of removal (i.e. between 26 % and 53 %). Thus the longer EBCT was beneficial for the removal of DEET at low water temperatures. However, after a long exposure to low temperatures and although influent concentration was raised, the removal of DEET by B1 and B2 was inhibited between February 13th and March 12th (Figure 5.13d). These results were expected because the H3 spiking period was performed during the NDR period of the biofilters.

During the L4 period, except for the first two data points, the removal of DEET was high considering the water temperature was below 10°C until May 7th. As the water temperature rises, the removal of DEET achieved by B1 and B2 also increased. Note that the L4 spiking event started during the NDR period of the biofilter and the increase in DEET transformation on April 11th corresponded with the passage into the SDR period.

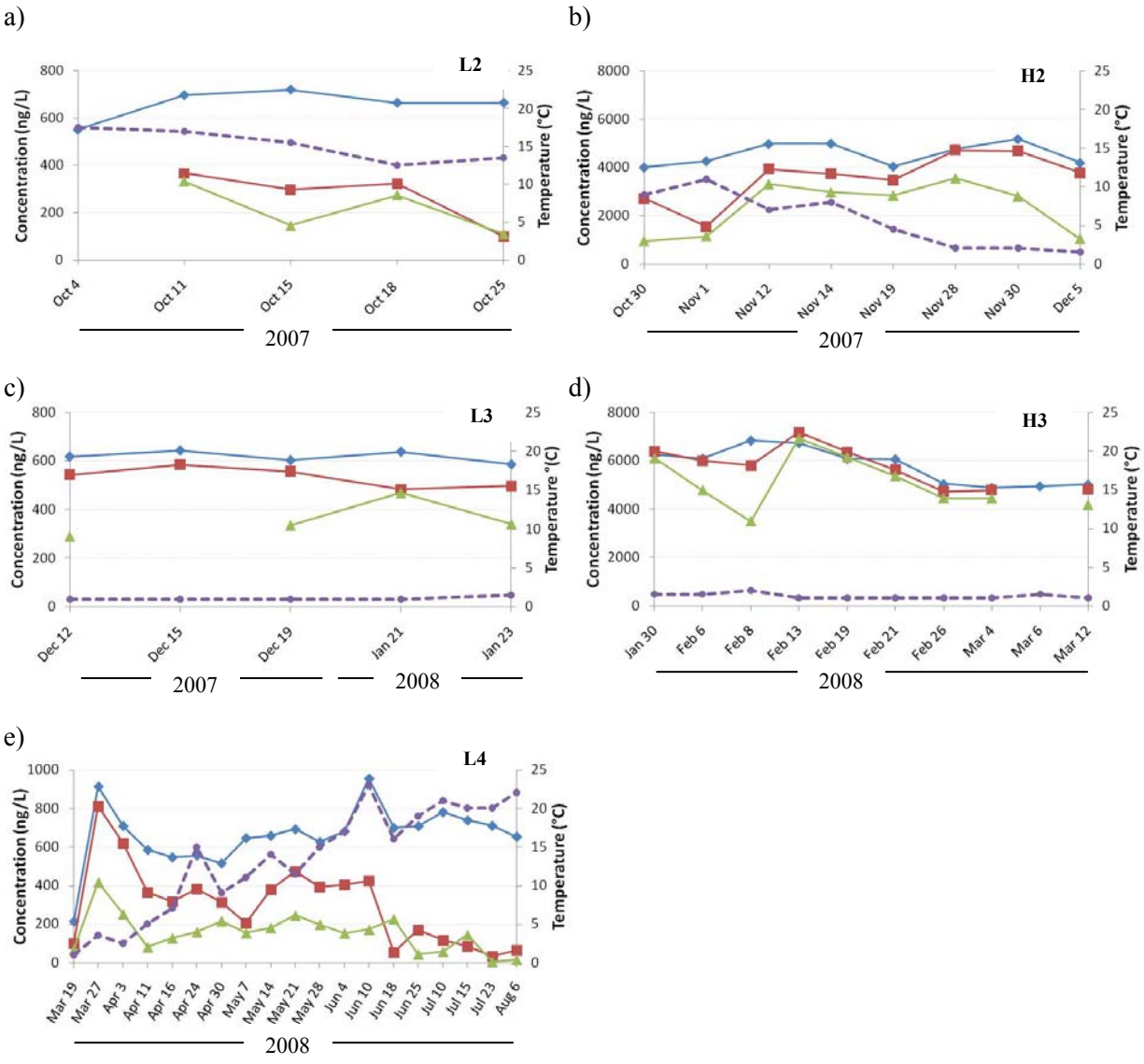


Figure 5-13 Concentration of DEET in the biofilter influent and effluents for the spiking periods at low concentration a, c, and e and for the spiking periods at high concentration b and d

NAPROXEN

As observed for DEET, the transformation of naproxen by the biomass was triggered by the increase of influent concentration. Thus a higher percentage transformation in L2 compared to L1 was expected. In figure 5.14a, the average percentage of removal of naproxen by B1 and B2 was respectively 68 % and 75 %. Except for two data points on October 11th and 15th, both biofilters achieved similar degrees of transformation.

An increase in influent concentration between L2 and H2 caused a decrease in percentage transformation for both biofilters. Because the water temperature was decreasing during this H2 spiking event, the percentage of transformation stayed relatively stable for both biofilters. This phenomenon can be explained by a decrease in microbial activity. As observed for DEET, the percentage transformation increased on December 5th despite the low water temperature.

During the L3 period, lower percentage removals between 55 % and 70 % were achieved by B1. During the same period, B2 achieved a higher percentage removal (i.e. between 71 % and 98 %) over B1. This spiking period demonstrated that naproxen is more easily biodegradable than DEET under cold water conditions after a period of acclimation. It also showed that even if the biofilters achieved non significant removal of DOC, the biomass is still capable of transforming naproxen. The fact that naproxen was biodegradable in cold water was also demonstrated in Figure 5.14d. At high influent concentrations, the percentage transformation initially decreased as previously explained but the trend shows that the percentage transformation tends to improve overtime. At this period of the year the biofilters were defined as NDR. The variation in percentage transformation during H3 may also be due to variation in water quality.

In Figure 5.14e, the percentage transformation achieved by B1 and B2 were similar except for two data points on March 27th and April 3rd. During this period of spiking at low concentration, the water temperature did not improve the percentage of transformation. In fact, for both biofilters the percentage of transformation tended to increase between April 16th and June 4th and a change in water quality due to runoff and rain may be the cause.

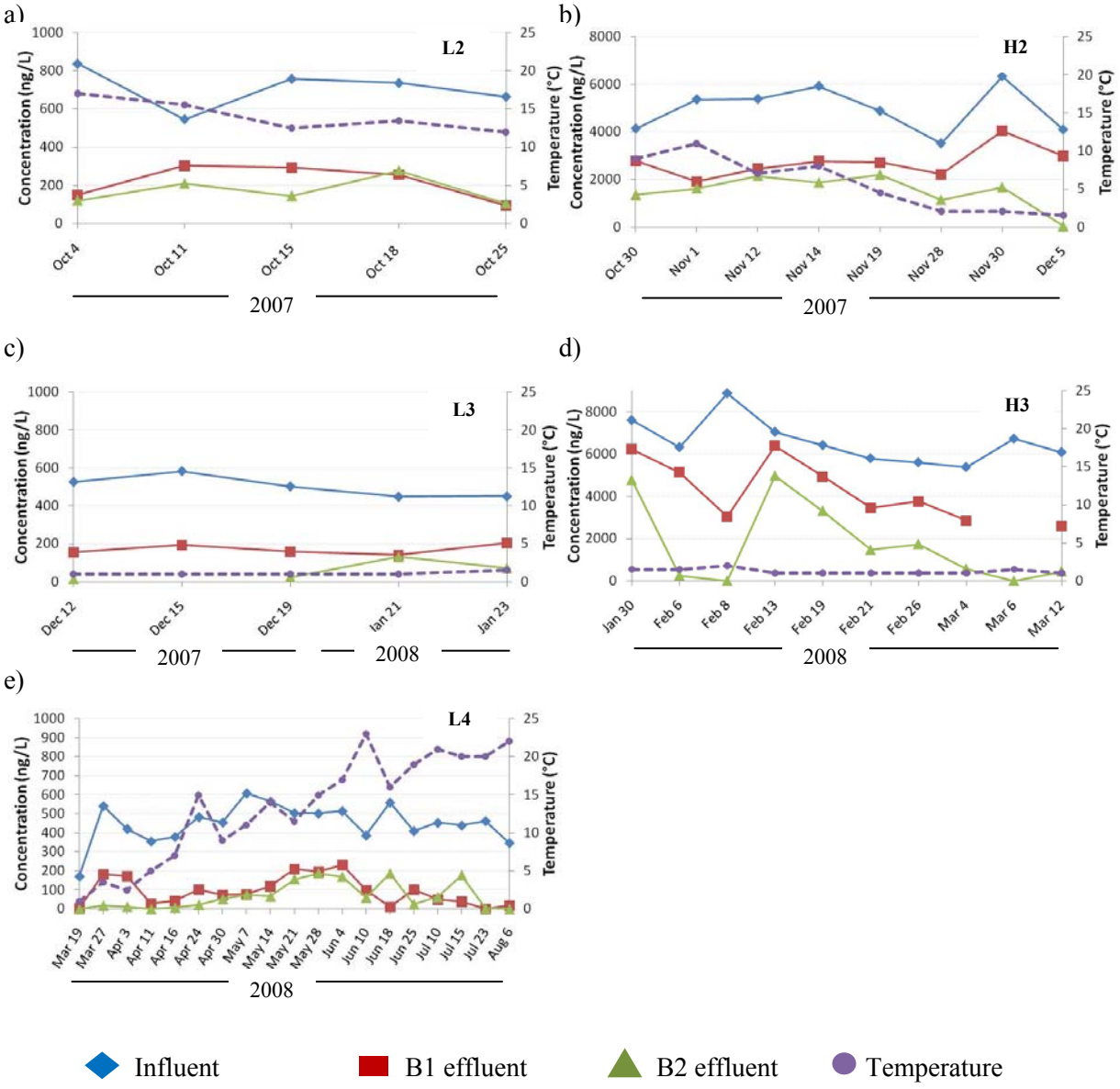


Figure 5-14 Concentration of naproxen in the biofilter influent and effluents for the spiking periods at low concentration a, c, and e and for the spiking periods at high concentration b and d

IBUPROFEN

During the L1 and H1 periods it was observed that ibuprofen was readily biodegradable under drinking water conditions. During the L2 period, very high removal of ibuprofen was also observed even if the water temperature was decreasing. In fact, at the end of the L2 period, the water temperature was 12°C and nearly complete removal of ibuprofen was measured (Figure 5.15a). Thus a temperature lag effect was observed during L2. The influent concentration was raised for a second time on October 30th and at this time of year the water temperature was about 10°C. At the beginning of H2, the removal achieved by B1 decreased most probably due to the change in influent concentration as observed previously during the transition from L1 to H1.The same effect was also observed during the transition between L3 and H3 periods where the performance of B2 was less affected than that of B1. This may be due to the longer contact time. During the H2 event, the effect of water temperature on the removal of ibuprofen was noticeable. As the water temperature decreased the concentration of ibuprofen in the biofilter effluent increased probably due to a decrease in metabolic activity caused by the fall in water temperature. Under those conditions, B2 outperformed B1 possibly due to the longer contact time. After spiking at a high concentration for 36 days, the influent concentration was switched to low concentration (i.e. L3) and the water temperature was stable at around 1°C. At low water temperature during the L3 period, the removals achieved by B1 were reduced compared to the L2 period. Despite the unfavorable temperature conditions in L3, B2 consistently achieved high removal of ibuprofen. Very high removals were also observed during the L4 period despite low water temperature at the beginning of the period. This behaviour may be caused by the previous high concentration spiking event which triggers the transformation of ibuprofen.

In general, these data demonstrated the high level of ibuprofen biodegradability at different water temperatures. This set of data shows that water temperature influenced the transformation of ibuprofen (i.e. higher percentage removal at higher water temperature). The transition between low and high influent concentration also had an impact on the removal.

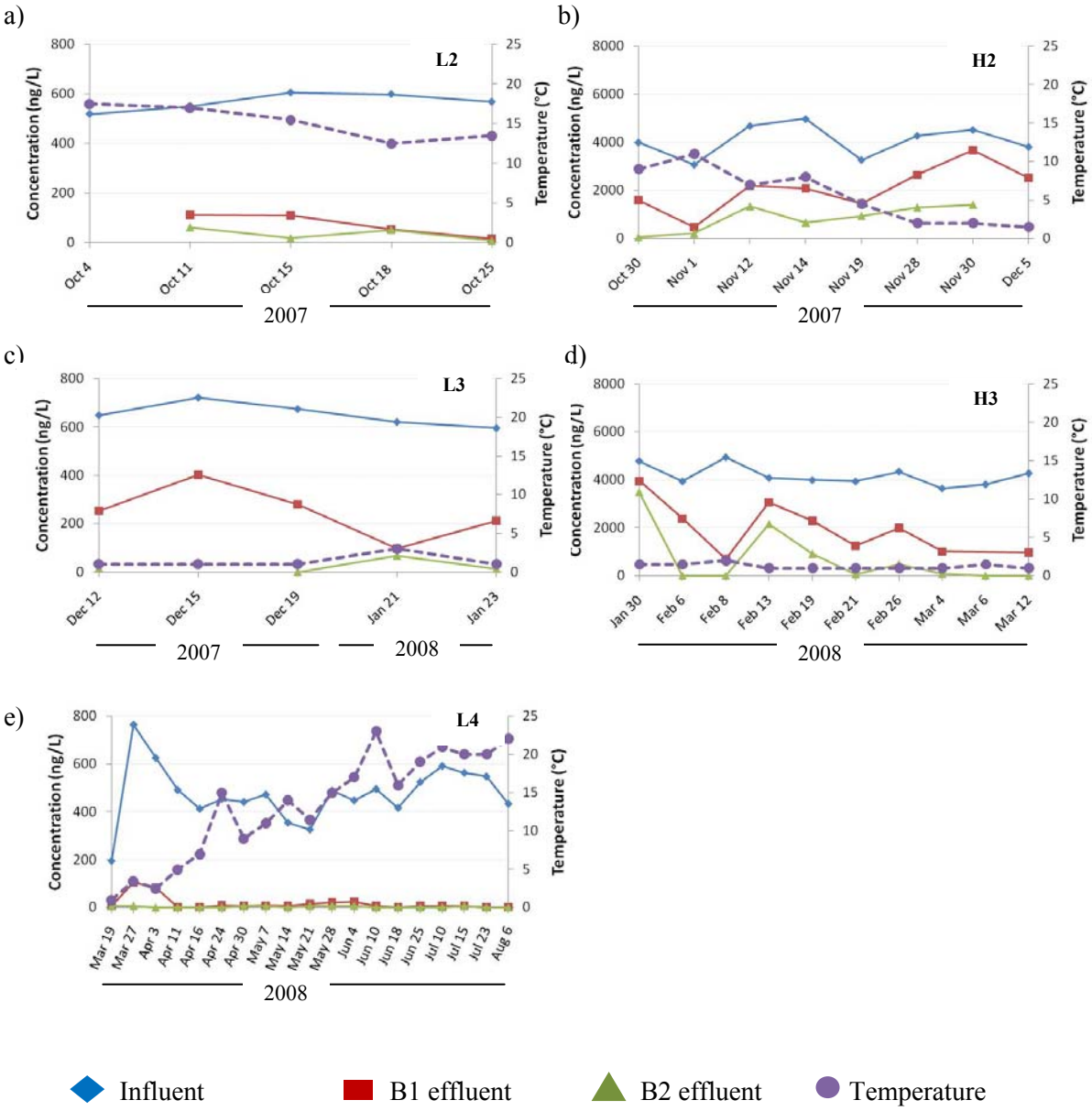


Figure 5-15 Concentration of ibuprofen in the biofilter influent and effluents for the spiking periods at low concentration a, c, and e and for the spiking periods at high concentration b and d

These data on biodegradability of DEET, naproxen, ibuprofen allowed the estimation of kinetic parameters and the results will be presented in the next section.

5.4.6 Kinetic Analysis

Estimation of kinetic parameters describing the degradation of the biodegradable compounds was carried out. The estimated rate constants were calculated for DEET, naproxen, and ibuprofen from selected data points representing pseudo steady-state conditions for both low and high influent concentrations. At low influent concentrations, the rate constants were calculated for four data points (October 15, 2007; December 19, 2007; May 21, 2008; and August 6, 2008). At the high influent concentration, the rate constants were calculated for three data points (September 6, 2007; November 14, 2007; and February 26, 2008). These data points were selected to cover low (1°C), moderate (~10°C), and high (> 20°C) temperatures. At the low influent concentration and intermediate temperature around 12°C, it was possible to select two data points which represented pseudo steady-state conditions. One point was October 15, 2007 when the water temperature was decreasing and another point on May 21, 2008 when the water temperature was increasing. The selection of those two data points enables the comparison of the rate of biodegradation (k_{biol}) under two different conditions that may appear similar.

This study demonstrated that B2 with 14 min EBCT may be overdesigned for the transformation of biodegradable trace organic contaminants particularly at moderate and high water temperatures. However, the results obtained for B2 support the findings observed for B1. Therefore in this section, the rate constants for B1 will be discussed primarily. Complete rate constant calculations are available in Appendix L.

Previous studies performed with natural water have demonstrated that sorption and microbial transformation of pollutants in biofilms observed pseudo first-order kinetics (Smook *et al.*, 2008; Matamoros *et al.*, 2006; Headley *et al.*, 1998; Newton *et al.*, 1990). Therefore, for this study, the biodegradation of DEET, naproxen, and ibuprofen was assumed to be a pseudo first-order reaction. The adjective "pseudo" indicates that first order was considered but other potential parameters, in this study the biomass concentration, were assumed to be present in excess and therefore at constant concentrations. The zero-order reaction was not considered because the removal achieved by the biofilters was not proportionate to their EBCT (see Figures 5.13, 5.14, 5.15). The differential and integrated forms of the first-order equation can be used to estimate rate constants (Sawyer *et al.*, 2003):

$$-\frac{dC}{dt} = kC \qquad \text{eq.5.2}$$

$$\ln\frac{C}{C_0} = -kt \qquad \text{eq. 5.3}$$

$$k = -\frac{\log_{10}\frac{C}{C_0} \times 2.303}{t} \qquad \text{eq. 5.4}$$

where:
C is the concentration of the selected contaminants (ng/L) in the filter effluent
C_0 is the initial concentration of the selected contaminant (ng/L) in the filter influent
k is the pseudo first-order rate constant (d^{-1})
t is the time (d)

The pseudo first-order rate constants (k_{biol}) were estimated by applying equation 5.4. The biofilter influent and effluent concentrations on the above selected dates and the actual contact time were used to estimate k_{biol} for DEET, naproxen, and ibuprofen as shown in Table 5.5. To calculate the actual contact time the EBCT is multiplied by the porosity of the media. The porosity of the media is relative to the fraction of media in a filter.

Table 5.5 shows the impact of water temperature on the rate constant. In general, the estimated rate constants tend to be lower at low water temperatures. In some cases (i.e. naproxen at low influent concentration and ibuprofen at high influent concentration) the rate constant at a low water temperature is similar to the rate constant measured at the intermediate water temperature. As expected in all cases, the higher rate constants were measured at water temperatures greater than 20°C. The trend of these rate constants demonstrates that greater biological transformation of DEET, naproxen, and ibuprofen occurred at higher water temperatures.

Some variability in the k_{biol} estimation is expected because the experiments were not specifically designed to obtain rate constants. However, this set of data indicates that at low influent concentrations, which are representative of environmental concentrations, the degree of biodegradability increases in the following order: DEET, naproxen, and ibuprofen.

At high water temperatures some rate constants represented only a lower bound estimate because the concentrations of trace contaminants measured in the biofilter effluent were below the limit of quantification due to complete degradation of the contaminants. Thus further investigations are necessary to obtain more defined rate constants for these cases.

Table 5-5 Estimated biodegradation rate constant k_{biol} for DEET, naproxen, and ibuprofen for B1

Date	Temp. (°C)	k_{biol} at low influent concentration (min^{-1})			Date	Temp. (°C)	k_{biol} at high influent concentration (min^{-1})		
		DEET	naproxen	ibuprofen			DEET	naproxen	ibuprofen
Dec 19, '07	1	0.03	0.47	0.36	Feb 26, '08	1	0.03	0.16	0.32
Oct 15, '07	13	0.36	0.39	0.70	Nov 14, '07	8	0.12	0.31	0.35
May 21, '08	12	0.15	0.36	1.29					
Aug 6, '08	22	0.94	1.25	≥ 2.20	Sept 6, '07	21	≥ 2.87	1.14	≥ 3.10

≥ indicates lower bound estimation of the rate constant

The rate constants obtained for DEET at intermediate temperatures on October 15th, 2007 and May 21st, 2008 were 0.36 and 0.15 min^{-1}, respectively. A lag effect was observed due to the variation of temperature during these spiking periods. In October, the selected data point was preceded by warmer temperatures, while in May colder temperatures preceded the selected sampling point. Thus at similar water temperatures a higher rate constant was measured when the biofilters were previously exposed to higher water temperature and had therefore higher biological activities. For naproxen, the rate constants measured at intermediate temperatures were similar. However, for ibuprofen a higher rate constant was measured on May 21st 2008. This behaviour may be caused by an extended exposure to the contaminant resulting in greater removal.

In general, at comparable water temperatures, it would be expected to observe similar rate constants at low and high influent concentrations. However, for DEET, naproxen, and ibuprofen some differences in rate constants were observed. The differences in k values may be caused by different biomass compositions at different EBCTs.

At low water temperatures, the rate constants of naproxen at low and high influent concentrations were respectively 0.47 and 0.16 min^{-1}. Although the rate constants were evaluated at similar water temperatures, the rate constant at the low influent concentration was determined prior to the high influent concentration spiking event. This may have caused a continuation of a higher level of biodegradation despite the low influent concentration resulting in an apparent high rate constant. As determined previously, a lag effect was also expected with regards to the impact of water temperature on the percentage of transformation .Thus a less active biomass may also be the cause of the different k_{biol} for naproxen at a low water temperatures.

The rate constant of ibuprofen at the intermediate temperature differs at high and low influent concentrations. Again, the temperature lag effect may be responsible for this variation.

The difference in rate constant at different influent concentrations of PhACs and EDCs was unexpected. No apparent explanation can be provided with this set of data. Consequently, further

research under controlled conditions (e.g. water temperature, constant trace organic contaminant concentrations) is necessary to investigate the effect of influent concentration on the rate constant of biodegradable trace organic contaminants by biofiltration. Also, further investigations will be able to confirm the pseudo-first order kinetics.

The van't Hoff-Arrhenius relationship (equation 5.5), which is commonly used in wastewater treatment to calculate a correction factor for temperature (Metcalf and Eddy, 2003), was used to calculate or estimate the correction temperature coefficient (θ) for DEET, naproxen, and ibuprofen. For conventional biological wastewater processes, typical values are 1.04 for temperatures between 20 and 30°C and 1.12 for temperatures between 10 and 20°C.

$$k_2 = k_1 \theta^{(T_2 - T_1)} \longrightarrow \theta = e^{\frac{1}{(T_2 - T_1)} \ln \frac{k_2}{k_1}} \qquad \text{eq. 5.5}$$

Where
k_1 is the rate constant at temperature T1 (min^{-1})
k_2 is the rate constant at temperature T2 (min^{-1})
θ is the correction temperature coefficient
T1 is the temperature 1 (K)
T2 is the temperature 2 (K)

Table 5.6 presents the θ values calculated for DEET, naproxen, and ibuprofen. These correction temperature coefficients are within the range of reported value for biological wastewater processes which indicates that in general the activation energy required for biodegradation of the selected trace organic contaminants was similar to the activation energy required for the biodegradation of substrate in wastewater. For all compounds, the θ values were smaller at low influent concentrations. This indicates that the transformation of these contaminants by biological filtration was more influenced by temperature at high influent concentrations than at low influent concentrations. At both influent concentrations, naproxen and ibuprofen had a similar value which was expected because these two compounds were more easily biodegradable. However, DEET has a higher θ value at both influent concentrations which indicated that transformation of DEET was more sensitive to water temperature.

Table 5-6 Correction temperature coefficient factor calculated at low and high influent concentrations

Influent concentration	Correction temperature coefficient (θ)		
	DEET	**naproxen**	**ibuprofen**
Low	1.17	1.05	1.09*
High	1.26*	1.10	1.12*

*estimate of correction temperature coefficient factor because these rate constants measured at higher temperatures (22°C) were lower bound estimates (see Table 5.5).

The calculations of rate constant normalized to 20°C (k') were performed using the suitable θ value. Tables 5.7 and 5.8 present a summary of k' at low and high influent concentrations for B1 and the results for B2 are available in Appendix L.

Table 5-7 Summary of correction factor coefficient (θ) and normalized rate constant (k') to 20° for B1 at low influent concentration

Date	Temperature (°C)	DEET		naproxen		ibuprofen	
		θ	k' min^{-1}	θ	k' min^{-1}	θ	k' min^{-1}
Dec 19, '07	1	1.17	0.68	1.05	1.14	1.09	1.85
Oct 15, '07	13	1.17	1.10	1.05	0.54	1.09	1.29
May 21, '08	12	1.17	0.55	1.05	0.52	1.09	2.56
Aug 6, '08	22	1.17	0.68	1.05	1.14	1.09	1.85

Table 5-8 Summary of correction factor coefficient (θ) and normalized rate constant (k') to 20°C for B1 at a high influent concentration

Date	Temperature (°C)	DEET		naproxen		ibuprofen	
		θ	k' min^{-1}	θ	k' min^{-1}	θ	k' min^{-1}
Feb 26, '08	1	1.26*	2.27	1.10	1.03	1.12*	2.77
Nov 14, '07	8	1.26*	1.95	1.10	1.00	1.12*	1.39
Sept 6, '07	21	1.26*	2.27	1.10	1.03	1.12*	2.77

In general, the k' calculated at both influent concentrations are within a factor of 2 indicating a high confidence in the data produced during this study. However, the variations indicate that experiments under controlled conditions must be performed to determinate with certitude the temperature correction factor (θ) and normalized rate constants (k').

5.5 Conclusions

The biofilters were operated for a period of 19 months from December 2006 to August 2008. This study showed that an acclimation period of 4 months was necessary to achieve DOC removal and thus biological activity within the biofilter. The length of this acclimation period was not surprising due to the low water temperatures (2°C) experienced during filter start-up. The following terminology was chosen to operationally distinguish between periods achieving different levels of DOC removal. Biofilters were defined as "active" when they achieved statistically significant DOC removal (SDR) and as "inactive" for negligible DOC removal (NDR). During the acclimation period and the NDR period, the biofilters achieved less than 5 % removal of DOC.

The biomass attached to the media was characterized using phospholipid analyses, total direct cell count (TDCC), and adenosine 5'-triphosphate (ATP) measurements. The results from the evaluation of the microbial activity in the biofilters allow the following conclusions to be drawn:

- The phospholipid measurements were performed on the biofilters after 14 months of operation, thus pseudo steady-state conditions were assumed. This assumption was supported by the fact that the concentration of phospholipids on top of the filters was independent of the water temperature.

- Similar and higher concentrations of phospholipids were measured on top of both biofilters. The concentration of biomass attached to the media decreased along the bed depth for both filters, and the lowest concentration was measured at the bottom of the filter. The decrease of biomass attached to the media can be attributed to the type of media. Moreover, the reduced availability of nutrient further down in the filter may also influence the amount of biomass attached to the media.

- Overall the measurement of phospholipids was very useful in demonstrating the presence of a biofilm on the media surface, but the sensitivity of the phospholipid measurements may not be high enough for it to be a good indicator of biodegradation performance. It also indicates that the biomass concentration may not be the limiting factor for the removal of biodegradable compounds.

- The TDCC per volume of dry media indicated a higher concentration at the top of the bed for both biofilters. Thus a removal of cells was observed and the removal increased with an increase in EBCT.

- Phospholipid and TDCC measurements may take into account dead cells or non-intact cells leading to an apparent higher concentration on top of the filter.

- For both biofilters, the profiles of ATP concentration throughout the bed depth varied depending on the water temperature. Even though the amount of biomass was higher on top of the biofilter as demonstrated by phospholipid and TDCC analyses, higher levels of ATP concentration were measured deeper within the bed depth indicating a more active biomass deeper in the filter.

- Overall these results suggest that longer contact time should be beneficial for the transformation of biodegradable organic contaminants.

These results show that a simple answer cannot be provided to the question, "What removals of a specific PhAC or EDC can be achieved by biofiltration under drinking water conditions?" The results from the removal of selected PhACs and EDCs by biological filtration allow the following conclusions to be drawn:

- Negligible level of adsorption between 0 % and 7 % of the selected PhACs and EDCs occurred in the filter without media which acted as a control. The only exception was nonylphenol where up to 16 % of adsorption was observed.

- Biofiltration can achieve removal of the biodegradable organic compounds. From the selected PhACs and EDCs, the biodegradable compounds were DEET, ibuprofen, and naproxen.

- These experiments demonstrated that carbamazepine and atrazine were refractory to biodegradation.

- The degree of biodegradation of the selected PhACs and EDCs by biologically active filters was the following: ibuprofen > naproxen > DEET >> carbamazepine ~ atrazine.

- A lag phase was observed before biodegradation of DEET, naproxen, and ibuprofen but only for the first spiking event at low and high concentrations.

- For DEET and naproxen, low removals were measured at low influent concentrations. For ibuprofen, a short acclimation period at both low and high concentrations was observed before achieving almost complete removal.

- The results demonstrated that DEET and naproxen require high influent concentrations of 5 μg/L to trigger the usage of those chemicals as a source of nutrient. The exposure to a constant source of PhACs and EDCs may have triggered the transformation of DEET and naproxen during the first spiking event at a high concentration.

- Generally, a major increase in influent concentration temporally reduced the percentage of transformation but after a short acclimation period, near complete removal of DEET, naproxen, and ibuprofen was observed.

- After a variable period of acclimation, pseudo steady state removal was observed for all biodegradable compounds when the water temperature stayed constant. In general, lower percentage transformations were observed at low water temperatures. For DEET and naproxen, the decrease in percentage transformation was observed during the NDR period and the percentage transformation increase during the SDR periods.

- In general, the relatively short acclimation period shown for DEET, naproxen, and ibuprofen suggests that bacteria present on the media probably had the necessary constitutive enzymes to achieve biodegradation of the studied compounds.

- In general, the biofilter with 14 minutes EBCT achieved equal or greater percentage transformation than the biofilter with 5 minutes EBCT.

- During this study biodegradation rate constant were estimated at low (1°C), intermediate (~10° C), and high (~20° C) water temperatures. In general, the rate constants increased with increasing water temperatures. Results obtained at low influent concentration for three temperatures indicated that ibuprofen had the highest rate constant between 0.18 and 1.08 min^{-1} followed by naproxen with rate constants between 0.23 and 0.61 min^{-1}, and DEET with rate constants between 0.02 and 0.46 min^{-1}.

- Rate constants calculated at low and high influent concentrations were in the same order of magnitude. However, further experimentations are necessary under controlled conditions to establish the trend.

- No conclusion can be drawn on the biodegradability of nonylphenol due to the impossibility to spike the compounds in the biofilter influent. A high octanol-water partitioning coefficient favors the portioning of nonylphenol into organic matter.

Chapter 6

PERFORMANCE OF BIOLOGICAL FILTRATION AS MEMBRANE PRETREATMENT TO PREVENT FOULING

Part of this chapter is based on an article published in Environmental Science and Technology:

Hallé, C., P.M. Huck, S. Peldszus, J. Haberkamp, M. Jekel, 2009. Assessing the Performance of Biological Filtration as Pretreatment to Low Pressure Membranes for Drinking Water. Environ. Sci. Technol. 43, 3878-3884.

In addition, information presented in section 6.4.3 summarizes results published in the following two papers, for which the author was second author. This information arose from a fruitful collaboration with a Ph.D. student (R.H.R. Peiris) in the Department of Chemical Engineering at the University of Waterloo and his supervisors.

Peiris, R.H., C. Hallé, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck, R.L. Legge, 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices. Wat. Res. 44(1), 185-194.

Peiris, B.H.R., C. Hallé, J. Haberkamp, R.L. Legge, S. Peldszus, C. Moresoli, H. Budman, M. Jekel, P.M. Huck, 2008. Assessing nanofiltration fouling in drinking water treatment using fluorescence fingerprint and LCOCD analyses. Wat. Sci & Technol. Water Supply. 8(4), 459-465.

6.1 Introduction

Although the use of membrane in drinking water treatment is increasing, fouling still represents an important limitation to the application of this technology. Fouling, a reduction of permeability due to accumulation of material on the surface or within the pores of the membrane, leads to a reduction of flux and/or an increase in transmembrane pressure (TMP), an increase in cleaning frequency, operational costs, and shortened membrane life.

For drinking water treatment and indirect water reuse applications, Amy (2008) identifies three types of bulk organic matter to be considered as potential foulant material: 1. coming from runoff and leaching from surrounding terrestrial vegetable debris allochthonous NOM is dominated by humic substances; 2. the autochthonous or algal organic matter includes extracellular and intracellular macromolecules and cellular debris; and finally, 3. EfOM contains NOM and soluble microbial products coming from wastewater biological treatment. EfOM is primarily composed of NOM and soluble microbial products derived from biological processes (i.e. polysaccharides, proteins, lipids, and carbohydrates) (Shon *et al.*, 2006).

As presented in Chapter 2, different foulant material and fouling mechanisms may be involved during membrane filtration processes. For example Her *et al.* (2007) observed that the major foulants on nanofiltration membranes were protein-like and polysaccharide-like substances. Colloidal and/or high molecular weight macromolecules such as polysaccharides are also suspected to cause irreversible fouling on low pressure membranes (Lee *et al.*, 2004; Kimura *et al.*, 2004a). However, using natural surface water, Howe and Clark (2002) demonstrated that fouling on MF and UF membranes was predominantly caused by small mostly organic colloids (3-20nm) whereas particulate matter and DOM played only minor roles. In addition, wastewater effluent organic matter (EfOM) caused severe but hydraulically reversible fouling on low pressure hollow fibre membranes (Huang *et al.*, 2007). The fouling potential of these biopolymers and/or large humic substances present in secondary wastewater effluents on UF membranes was also demonstrated by Haberkamp *et al.* (2007).

Biofiltration has been used for many decades in drinking water treatment via slow sand filtration, bank filtration, or ground passage (Ray *et al.*, 2002; Graham, 1999; Bouwer and Crowe, 1988). More recently, rapid biological filters have also been used, especially downstream of ozonation. Biofiltration processes can decrease the chlorine demand of treated water and also reduce the potential microbiological re-growth within the distribution system (e.g. Hu *et al.*, 1999). Biofiltration can also be used for the removal of trace contaminants such as geosmin, an odorous compound (Elhadi, 2004).

Various factors affect the removal of BOM during biological filtration (Urfer *et al.*, 1997). Contact time, expressed as EBCT is a key parameter for biofiltration and for a given EBCT the removal of BOM is essentially independent of the hydraulic loading. Zhang (1996) and Zhang and Huck (1996a) developed the concept of an index of dimensionless contact time (X*) that includes the contact time (X) and other factors important for biodegradation: reactor specific surface area, biomass density, substrate diffusivity and kinetic parameters .

For a biofilter, functioning as particle removal step, the backwash procedure has the dual role of removing both biomass and nonbiological material. It has been demonstrated that backwashing for particle removal did not involve excessive loss of biomass (Huck *et al.*, 2000; Amad *et al.*, 1998).

Although the use of biofiltration prior to a membrane has been reported (Persson *et al.*, 2006; Hu *et al.*, 2005), detailed investigations have not been undertaken. This study was undertaken to quantitatively investigate a new concept: chemical-free rapid biofiltration pretreatment to reduce fouling on membranes for drinking water treatment. Since biofiltration also produces soluble and particulate organic matter that can be important for membrane fouling, providing a net reduction of such material in the biofilter effluent becomes an additional biofiltration objective. This study specifically investigates the impact of biological filtration pretreatment on the removal of a specific organic fraction (biopolymers) most implicated in membrane fouling.

6.2 Objectives

The objectives of the study presented in this chapter were to:

- Demonstrate the efficiency of biofiltration as membrane pretreatment to reduce fouling of UF and NF membranes
- Show the seasonal performance of biofiltration as membrane pretreatment
- Demonstrate the efficiency of an integrated membrane system (i.e. biofiltration, UF, and NF) to reduce fouling of NF membranes

6.3 Material and Methods

6.3.1 LCOCD Analysis

LCOCD analyses were performed by Dr. Jens Haberkamp at the Technical University of Berlin. Data analysis and interpretation of the results were performed by the author.

Size exclusion chromatography with continuous organic carbon detection (LCOCD) analyses were performed with a DOC-Labor [Dr. Huber (Karlsruhe/Germany)] system (Huber and Frimmel, 1992; Huber and Frimmel, 1991). This system was characterized by a photochemical oxidation of the sample by a low-pressure mercury-vapor lamp in a Gräntzel rotating thin film reactor (Lankes *et al.*, 2009). The system used a SEC column (length: 250mm; inner diameter: 20 mm filled Toyopearl HW-50S resin as stationary phase (Tosoh Bioscience, Tokyo/Japan)). The column was a nominal molecular weight separation range from 100 g/mol to 18000 g/mol evaluated with polyethylene glycols (Lankes *et al.*, 2009). A phosphate eluent was used for separation (1.5 g/L disodium hydrogen phosphate ($Na_2HPO_4 \cdot 2\ H2O$ + 2.5 g/L potassium dihydrogen-phosphate (KH_2PO_4)). Sample preparation consisted of filtration through a 0.45 µm cellulose acetate filter. Samples were preserved in glass container at 4°C in the dark.

Figure 6.1 represents a typical LCOCD chromatogram obtained for Grand River water and is composed of three peaks. Components of the DOC elute from the SEC column in order of decreasing molecular weight. The first peak, having the largest MW, corresponds to the biopolymers composed of extracellular polymeric substances (EPS) (i.e. protein-like and polysaccharides-like substances), the second peak represents humic substances, and the third peak consists of low molecular weight organic acids (LMWA). The identification of the different NOM fractions was made based on interpretations of the chromatogram described by Haberkamp *et al.* (2007) (2008).

To calculate the concentration in mgC/L of the biopolymers and humic substances of a sample, the total photochemical DOC concentration (pc-DOC), the integration of the specific fractions, and the offline DOC concentration (t-DOC) measured by wet oxidation were used. The pc-DOC was obtained by bypassing the SEC column. Then, the integration ratio for a specific fraction (Ex: integration biopolymers/integration pc-DOC) is calculated. The specific ratio is multiplied by the t-DOC concentration of the sample to obtain the concentration of that fraction (e.g. biopolymers or humic substances) in mgC/L.

During this study, we observe that the t-DOC concentrations were consistently 10 % higher than pc-DOC concentrations, thus a certain amount of carbon were not measured by pc-DOC analysis. Studying DOM in surface water, Lankes *et al.* (2009) also demonstrated a difference between 7 and 24 % between online and offline carbon analysis depending on the nature of the sample. A deficient oxidation efficiency of DOM retains by MF (0.1µm) during pc-DOC analysis was identified as the cause of this difference (Lankes *et al.*, 2009). Consequently, the concentration of large MW organic molecule (i.e. biopolymers) may have been underestimated.

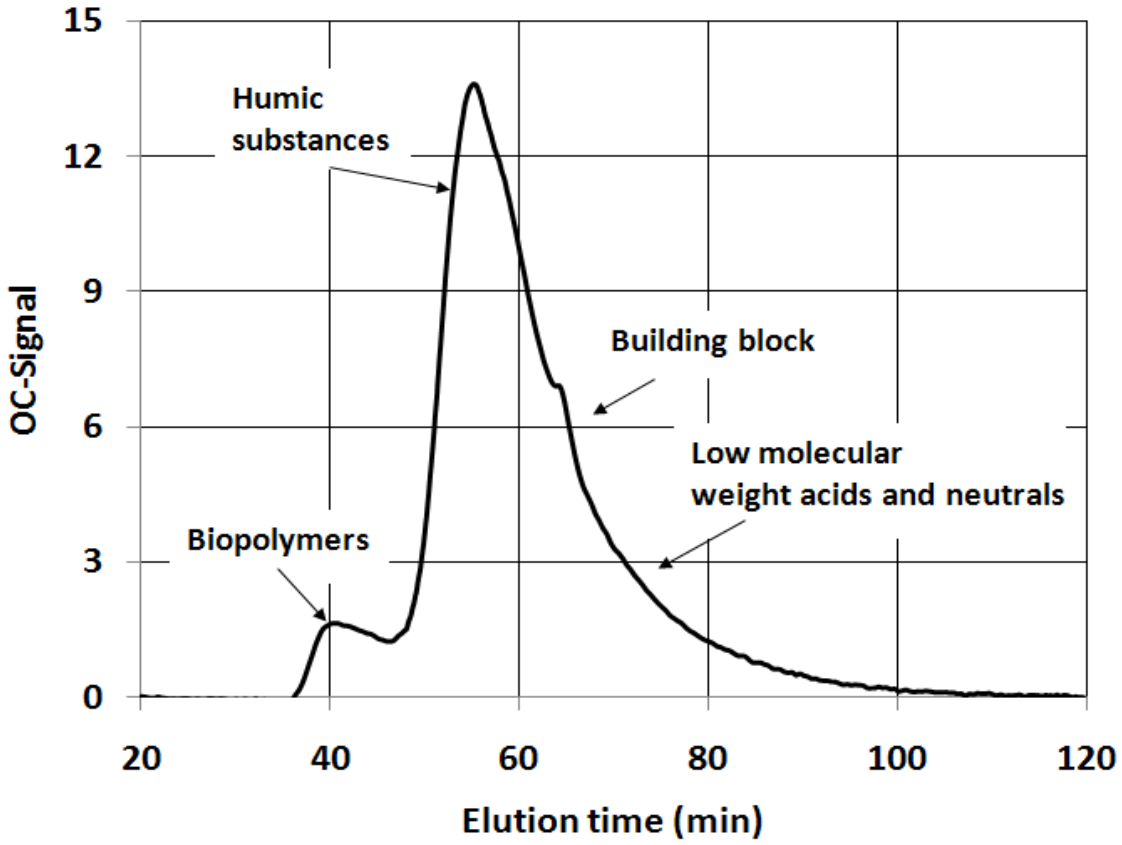


Figure 6-1 Typical LCOCD chromatogram of Grand River water (Ontario, Canada)

Ten LCOCD profiles of the Grand River water, RF effluent, and the biofilter effluents were performed between March 2007 and July 2008.

6.3.2 Fluorescence Analysis

Fluorescence methodology and data analysis procedures were developed by Ramila Peiris Ph.D. candidate in Chemical Engineering at the University of Waterloo. The use of these analyses to interpret the author's data was done jointly by the author and Mr. Peiris.

In this study, fluorescence excitation-emission matrix (EEM) analysis was used for the characterization of NOM. This method is able to capture specific fluorescence features that correspond to humic and protein-like materials into a single matrix in terms of fluorescence intensities. The light scattering regions captured in the fluorescence EEMs can also be used to provide information related the particulate and colloidal matter present in water. In addition, unlike other fluorescence spectroscopic techniques, fluorescence EEM provided a basis to capture the subtle changes in the fluorescence spectra of the water that may occur due to seasonal effects or changes in the water sources.

The fluorescence EEM of each sample was collected using a Varian Cary Eclipse Fluorescence Spectrofluometer (Palo Alto, CA) by scanning 301 individual emission spectra (300 - 600 nm) at sequential 10 nm increments of excitation wavelength between 250 nm and 380 nm. Disposable UV-grade polymethylmethacrylate cuvettes with four optical windows were used in the analyses. The instrument parameters (photomultiplier tube (PMT) voltage = 800 V, scan rate = 600 nm/min, and excitation/emission slit width = 10 nm each) were maintained during the fluorescence signal acquisition. These parameter settings were identified as optimum instrument settings for obtaining reproducible fluorescence signals, especially for the low concentrations seen in NF permeates (Peiris *et al.*, 2009). To eliminate water Raman scattering and to reduce other background noise, fluorescence spectra for Milli-Q water, obtained under the same conditions, were subtracted from all fluorescence spectra. The temperature of all water samples was maintained at room temperature (25°C) during the analyses. Data processing was performed using Matlab 7.3.0 software (The Mathworks Inc., Natick, MA).

6.3.3 Ultrafiltration Experiments

UF membranes and operation conditions

The bench scale UF membrane modules contained commercial outside-in hollow fiber membranes (ZeeWeed – 1 by GE/Zenon, Oakville, Canada). The membrane characteristics are available in section 3.4.1. The membrane module had a nominal surface area of 0.047 m^2 and was mounted vertically in a cylindrical holder of 1.6 L (Figure 3.7). The unit was operated at a constant permeate flow at a recovery of 94 %. The automated operational sequence consisted of: 1) permeation for 1 h, 2) back pulse with air sparging for 20 seconds, 3) drain 0.4 L of the tank, and 4) filling of tank for 9 minutes. The TMP was monitored by a pressure transducer. The permeate flux was adjusted to correspond to 57.5 LMH at 20°C. Experiments using B1 and B2 effluents as feed water to UF membrane were performed sequentially since only one experimental set-up was available. In order to reduce the biofouling, a typical run length was 5 days.

The experimental set-up and the sampling locations are presented in Figure 3.6. For the UF experiments, sampling was normally performed after approximately 1 h, 24 h, 48 h, and 96 h of operation.

Sampling for UF experiments

The parameters monitored were TOC, DOC, UV_{254}, specific UVA (SUVA = UV_{254}/DOC), fluorescence, pH, turbidity, and conductivity. Samples for fluorescence analysis were collected after 1 h, 48 h, and 96 h of operation while the other parameters were measured after 1 h, 24 h, 48 h, and 96 h. The methods used for the measurements of these parameters are described in Chapter 3 section 3.1. Samples for LCOCD analyses were collected after 1 h and 96 h of operation.

6.3.4 Nanofiltration Experiments

NF membranes and operation conditions

Nanofiltration experiments were performed with a bench scale module (GE SEPA^{TM} CFII, GE Water & Process Technologies, Oakville, Canada) using flat sheet membranes as illustrated in Figure 3.9. Two different flat sheet NF membranes (XN45 and TS80) from TriSep Corporation (California, USA) were used for this study. The membrane characteristics are available in section 3.4.3. The nominal surface area of both membranes was 0.0140 m^2. The NF experiments with the XN45 and TS80 membranes were operated at a constant pressure of 8.2 and 12.4 bar, respectively. The pure water permeability of XN45 and TS80 were 10.4 LMH/bar and 10.0 LMH/bar, respectively. The initial recovery was 2 % for both membranes. The initial permeate flux of XN45 and TS80 membranes was 85.7 LMH and 124.2 LMH. Throughout the experiments the temperature was kept constant at 25 ± 2°C through the use of a chiller. The experiments were performed in a recycle mode; both concentrate and permeate were returned to the feed tank. The duration of the experiment varied between 72 h and 144 h.

Sampling for NF experiments

The parameters monitored were TOC, DOC, UV_{254}, pH, fluorescence, turbidity, and conductivity. Samples for LCOCD analysis were collected after 1 h and 96 h of operation, samples for fluorescence measurements were collected after 1 h, 48 h, and 96 h of operation while the others parameters were measured after 1 h, 24 h, 48 h, and 96 h. The methods used for the measurements of these parameters are available in Chapter 3.

The foulant layer accumulated at the surface of the membrane was gently removed from half of the membrane coupon by shaking for 5 minutes in a stomacher bag containing 350 mL of MilliQ water. TOC, DOC, and LCOCD analyses were performed on the solution.

6.3.5 Biodegradable Organic Matter and Microbiological Analyses on Liquid Samples

AOC analyses were performed on the biofilter influent and effluent to determine the removal of AOC achieved by the biofilter. The analyses were performed by an external laboratory (i.e Gelda Scientific) following Standard Methods 9217 (Standard Methods, 2005).

HPC were performed following Standard Methods 9215 (Standard Methods, 2005) using Difco™ R2A agar media (BD). TDCC were measured following Standard Methods 9216 (Standard Methods, 2005) using SYBR gold (Invitrogen) as fluorochrome and a solution of 1,4-diazabicyclo (2,2,2) octane (DABCO) as mounting media.

ATP measurements were performed using the BacTiter-Glo™ Microbial cell viability assay (Promega - Microbial cell viability assay method, cat#: G8231). Details of the procedure for ATP and TDCC measurements are available in Appendices C and D.

6.4 Results and Discussion

6.4.1 Seasonal Variation in Grand River Water Quality

The quality of Grand River water varied substantially throughout the year. Several water quality parameters (i.e. DOC concentration, divalent cations, alkalinity, and temperature) can affect the extent of membrane fouling therefore data demonstrating of the seasonal variation of these parameters is required (Her *et al.*, 2000). In Grand River water, temperature varied from 1°C to 24°C (Figure 6.2). pH varied on a day-to-day fashion and the average measurement was 7.89 ± 0.24. The alkalinity of Grand River water varied seasonally between 150 and 250 mg/L as $CaCO_3$ with lower concentration during the summer due to high water temperature lowering CO_2 solubility. The hardness varied seasonally between 200 and 350 mg/L as $CaCO_3$ with lower concentration during the summer (Mutti, 1995). The average conductivity was 685 ± 197 μS/cm. The highest measurements occurred during the winter months probably due to the use of desalting salt within the watershed. The average TOC and DOC concentrations were 6.65 ± 0.9 mgC/L and 6.19 ± 0.8 mgC/L respectively (Figures 6.3 and 5.1). The concentration of TOC and DOC was subjected to increases during heavy rainfall and runoff (Agren *et al.*, 2008) and decreases in concentration occurs during dry periods. Grand River was subjected to high turbidity events due to heavy rainfall and runoff events as demonstrated by the wide range of turbidity measured throughout the year (Figure 6.2).

A summary of the water quality parameters monitor during the UF experiments (e.g. raw water, RF, B1 or B2 effluent, and membrane permeate) is available in Appendix M.

6.4.2 Impact of Biofiltration on Water Quality

Performance of the roughing filter

The goal of the roughing filter was to stabilize the raw water turbidity by reducing to at least some extent turbidity peaks. The average RF effluent turbidity was 2.84 ± 2.6 NTU. The RF achieved in average 6 % removal of TOC and DOC. The average pH of RF effluent was 7.95 ± 0.2 and the conductivity varied between 450 μS/cm and 970 μS/cm.

The average concentrations of TOC and DOC of B1 effluent were 5.86 ± 0.6 mgC/L and 5.60 ± 0.6 mgC/L respectively. Figures 6.4 and 5.1 and show the seasonal variation of TOC and DOC. On average RF+B1 achieved 13 % and 11 % removal of TOC and DOC. The average turbidity of B1 effluent was 0.47 ± 0.5 NTU (Figure 6.3). The average pH of B1 effluent was 7.94 ± 0.1 and the conductivity varied between 450 μS/cm and 980 μS/cm.

The average concentration of TOC and DOC of B2 effluent were 5.45 ± 0.6 mgC/L and 5.30 ± 0.6 mgC/L respectively. Figures 6.4 and 5.1 and show the seasonal variation of TOC and DOC. On average RF+B2 achieved 19 % and 16 % removal of TOC and DOC. The average turbidity of B2 effluent was 0.38 ± 0.4 NTU (Figure 6.3). The average pH of B2 effluent was 7.79 ± 0.2 and the conductivity varied between 520 μS/cm and 780 μS/cm.

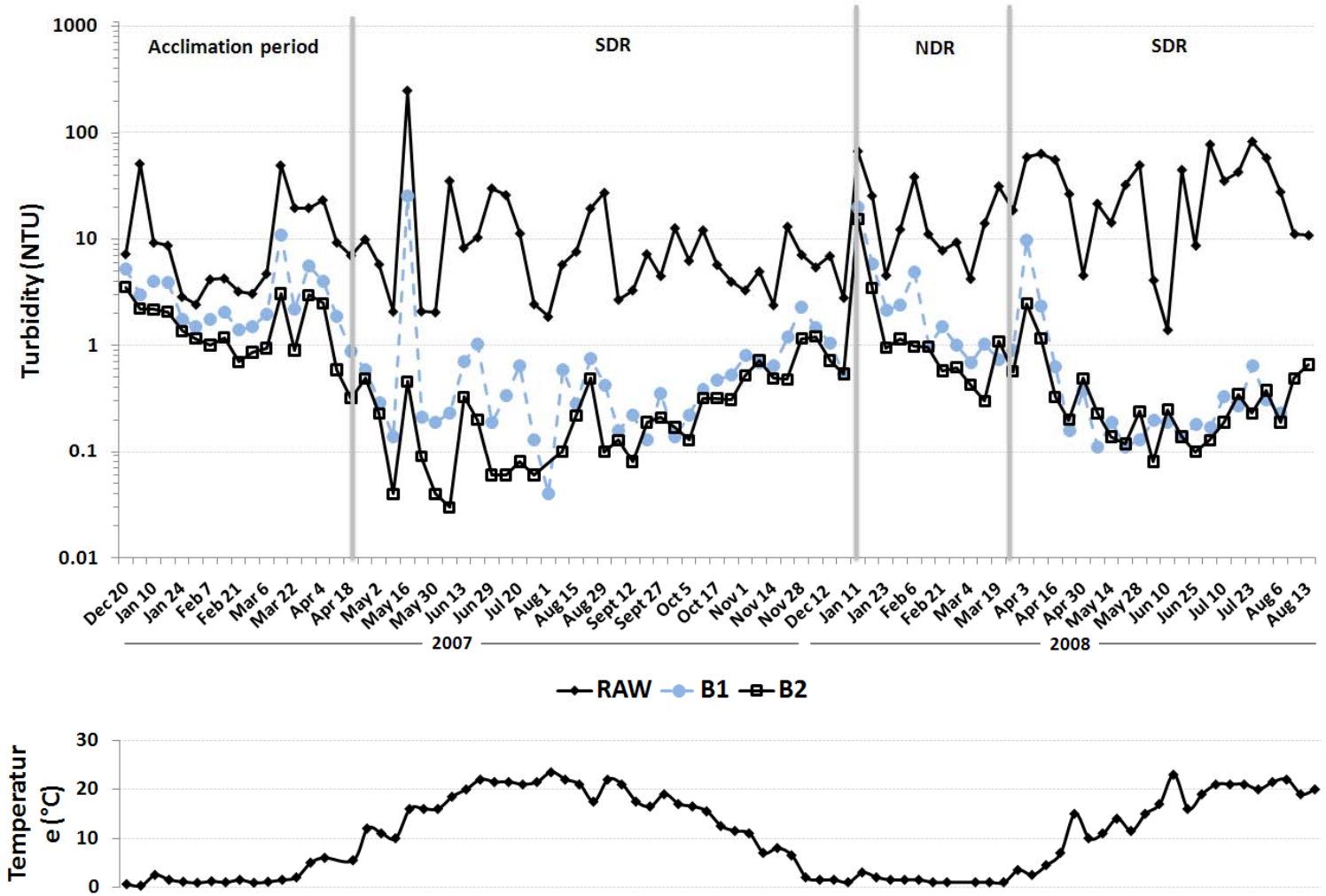


Figure 6-2 Turbidity in raw water and in the biofilter effluents and water temperature

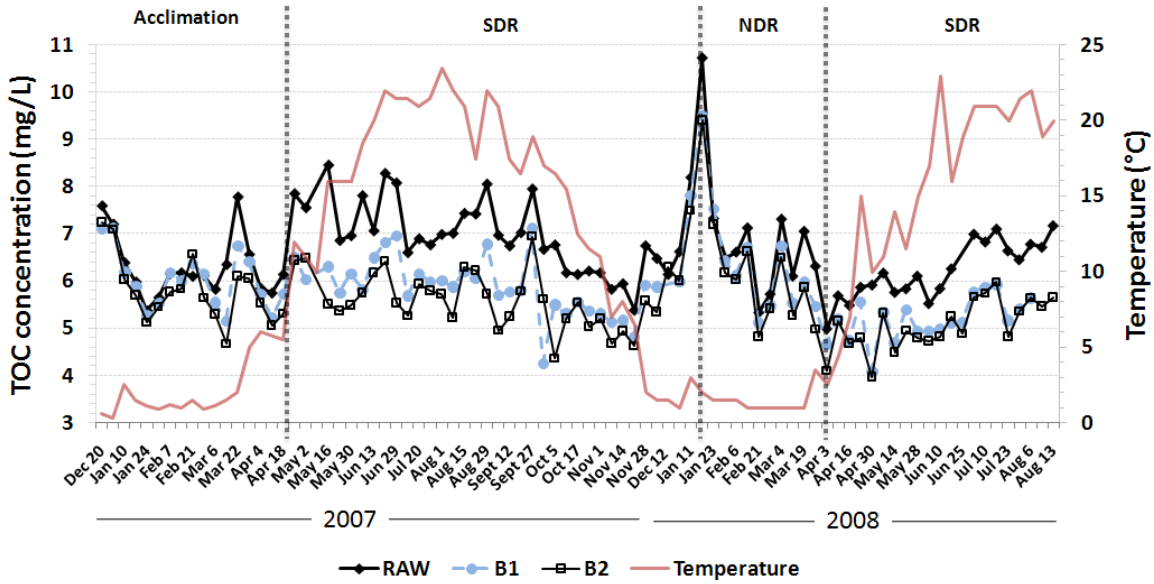


Figure 6-3 TOC concentrations in raw water, in the biofilters effluent, and water temperature

Statistical analysis (paired T-test) showed that the removal of TOC achieved by B1 and B2 were significant for the four periods investigated (Table 6.1). During the acclimation period, B1 and B2 achieved a TOC removal of 4 % and 8 % respectively. Similar percentage removal was observed during the NDR period (i.e. 11/01/08 to 04/03/08) with 5 % and 8 % for B1 and B2 respectively. However, for B1 the removal of TOC increased to 15 % and 16% during the first and second SDR periods. For B2, the removal of TOC increased to 19 % and 18 % during the first and second SDR periods. In general, the removal of TOC achieved by B2 was between 3 % and 5 % higher than the removal achieved by B1.

The RF achieved significant removal of TOC only during the SDR periods. The TOC concentration between RF and RFSP was significantly higher by 4 % during the NDR period (i.e. RFSP higher concentration). Frequent tubing cleaning reduced the chance of developing biofilm on the tubing wall which could increase the TOC concentration on the RFSP effluent.

Table 6-1 TOC removal (%) by the RF, B1 and B2 during the acclimation periods, SDR periods, and NDR period of the biofilters. The dash indicates non-significant TOC removal

Period	Acclimation	SDR	NDR	SDR
	21/12/06-18/04/07	25/04/07-19/12/07	11/01/08-04/03/08	12/03/08-13/08/08
RF	-	7	-	5
B1	4	15	5	16
B2	8	19	8	18

Assimilable Organic Carbon Analysis (AOC)

Several analyses of AOC were performed by a commercial laboratory. However, based on several indicators our confidence in the data was not high. These results were therefore not used but they are available in Appendix N.

6.4.3 LCOCD Analyses of the Raw Water and Biofilter Effluent

Figure 6.4 presents a typical LCOCD chromatogram during the SDR period of the biofilter (i.e. September 2007). Typical fractions of the DOM in Grand River and their removal by roughing filtration and rapid biofiltration are shown. The nature of the first peak in Figure 6.4 inferred to be the biopolymer (i.e. polysaccharides-like material and/or protein-like material) appeared between 36 minutes and 46 minutes. The humic substances peak, the major DOM constituent, appeared between 46 minutes and 63 minutes. The little shoulder after 63 minutes corresponded to low molecular weight acids (LMWA) and was recognized as an indicator for biological activity. Removals of the different DOM fractions were quantified based on these chromatograms.

The inspection of the first portion of the LCOCD UV chromatograms revealed no or very low UV absorption suggesting the absence of chromophores or aromatic structure on this material. This observation does not exclude the possible presence of proteinaceous material but suggests that this fraction consists predominantly of polysaccharides. Muller *et al.* (2000) and Lankes *et al.* (2009) who study surface water with a similar instrument and condition of operation also determined that the first portion of the LCOCD chromatogram was principally made of polysaccharides-like material. Thus,

Figure 6.4 shows that biopolymers were substantially removed during biofiltration, whereas removal of humic substances and LMWA were much lower on a percentage basis. The preferential removal of non-humic substances (i.e. biopolymers) from surface water using biological process (e.g. riverbank filtration) has also been demonstrated by Maeng *et al.* (2008). This study also demonstrated the persistence of humic-like organic matter from surface water and wastewater effluent derived surface water through soil passage. Moreover, Barker *et al.* (1999) demonstrated that aerobic biodegradation of high molecular weight material from secondary effluent was generally easier than lower molecular weight material.

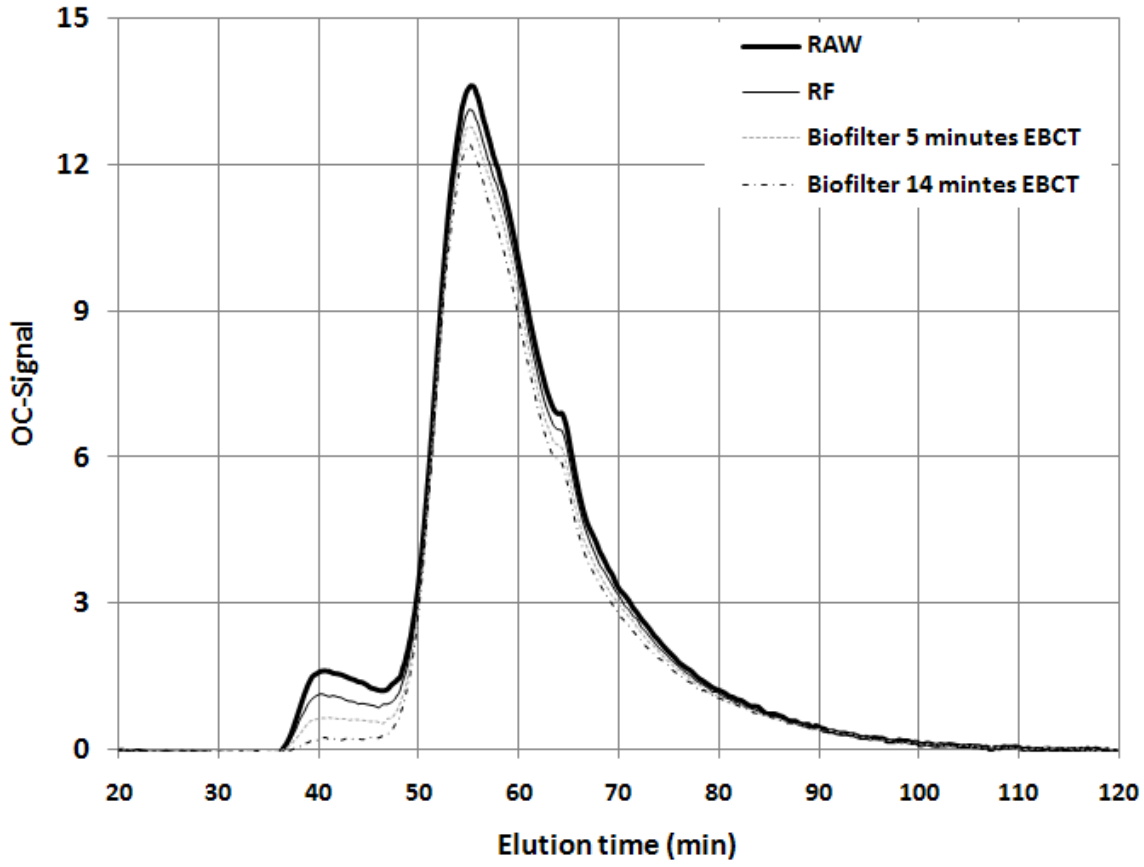


Figure 6-4 Typical LCOCD profile of the biofilters during the SDR period (September 2007)

A total of 10 LCOCD profiles were performed between March 2007 and September 2008. A summary of the concentration and percentage removals of biopolymer and humic substances is available in Appendix O.

The biopolymer concentration in raw water varied from 0.10 mgC/L to 0.53 mgC/L, the highest concentration has been measured during the summer and the lowest concentration during the winter (Figure 6.5). In Grand River, biopolymer may be originated from the wastewater effluent. Since during the summer the flow of Grand River decreased (Figure 4.5) and the wastewater treatment efficiency may change, the percentage of wastewater effluent and its characters can vary throughout the year.

The concentration of biopolymers decreased through the treatment process and in general the lowest concentration was measured at the effluent of B2. The RF itself removed between 10 % and 33 % of the biopolymer contained in raw water. The concentration of biopolymers in B1 effluent varied between 0.02 mgC/L and 0.33 mgC/L and the concentration of biopolymers in B2 effluent varied between 0.01 mgC/L and 0.26 mgC/L. Figure 6.5 show that in general B2 achieved higher removal of biopolymer than B1 with respectively 61 ± 22 % and 40 ± 26 %.

Although humic substances are the main fraction of DOM identified by LCOCD, this fraction was not efficiently removed during the biofiltration (Figure 6.5). The concentration of humic substances in raw water varied between 3.55 mgC/L and 4.92 mgC/L and up to 30 % removals were observed by B1 and B2.

The concentration of LMWA in raw water varied between 0.39 mgC/L and 0.54 mgC/L. As indicated in Appendix O, release of LMWA occurred occasionally leading to negative percentage removal. Otherwise percentage removal between 1 % and 36 % of LMWA has been achieved by B1 and B2.

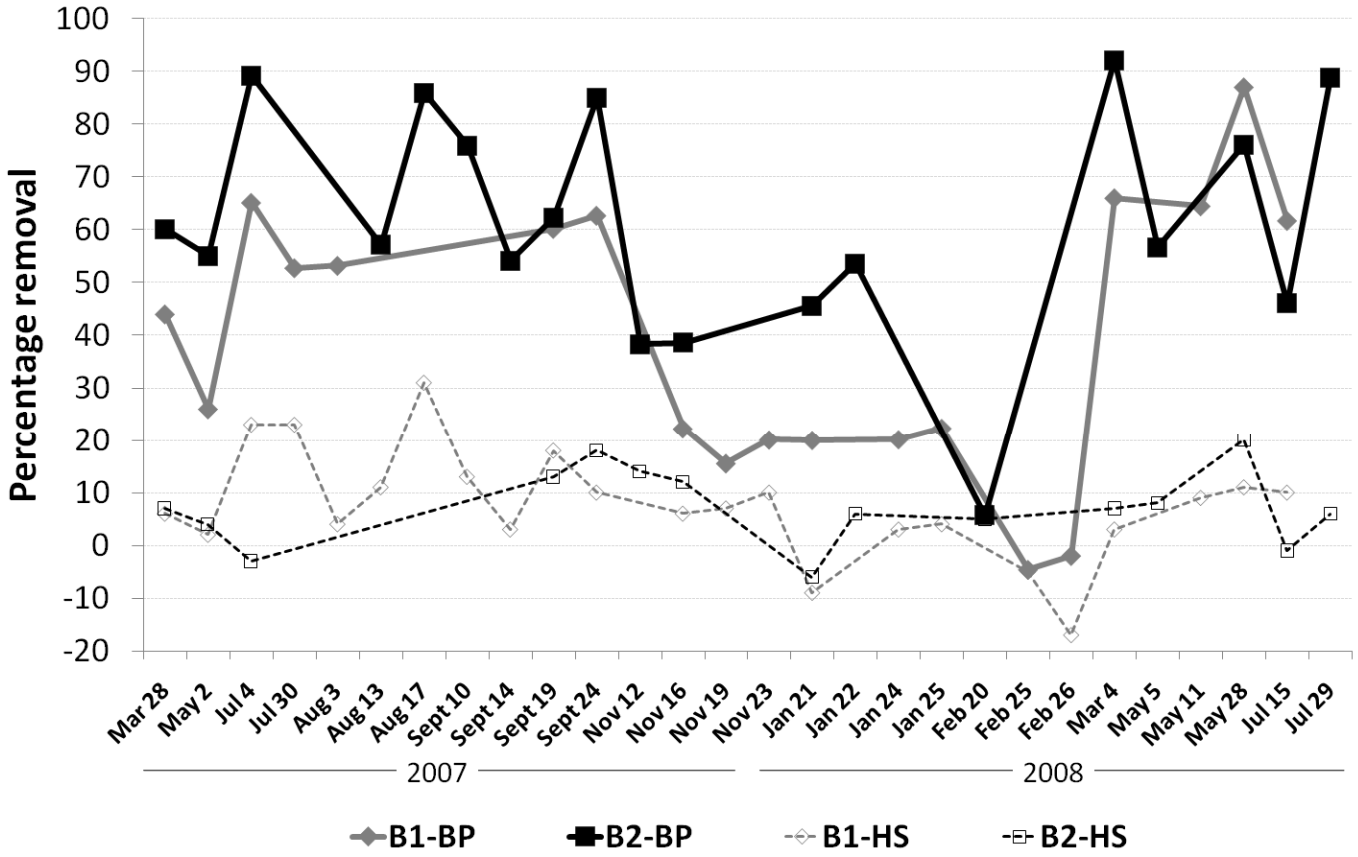


Figure 6-5 Percentage removal of biopolymers (BP) and humic substances (HS) by B1 and B2 (source: Halle *et al.*, 2009)

6.4.4 Fluorescence Excitation/Emission Matrix (EEM)

This section is based on papers published in Water Research and Water Science & Technology: Water Supply. The work presented in here is based on samples obtained from the bench-scale studies. I also provided operational membrane data, water quality data other than fluorescence data, in addition to contributing in the interpretation of the results.

Peiris, R.H., C. Hallé, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck, R.L. Legge, 2010. Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices. Wat. Res. 44(1), 185-194.

Peiris, B.H.R., C. Hallé, J. Haberkamp, R.L. Legge, S. Peldszus, C. Moresoli, H. Budman, M. Jekel, P.M. Huck, 2008. Assessing nanofiltration fouling in drinking water treatment using fluorescence fingerprint and LCOCD analyses. Wat. Sci & Technol. Water Supply. 8(4), 459-465.

Introduction to Fluorescence spectroscopy

Fluorescence spectroscopy is becoming an increasingly popular method for characterizing NOM (Her *et al.*, 2003) as minimal pretreatment and preparation is required and the technique has high sensitivity. Used with LCOCD chromatograms, fluorescence spectroscopy provide complementary information on the nature of NOM.

The fluorescence EEM of Grand River water shows a peak (α) at Ex/Em = 320 nm/415 nm (Figure 6.6a), which corresponds to the range reported for humic substances (Sierra *et al.*, 2005). In addition to the primary peak (α), another secondary peak (β) which also corresponds to humic substances (Peiris *et al.*, 2008; Sierra *et al.*, 2005) appears to be present in the form of a shoulder around Ex/Em = 270 nm/460 nm (Figure 6.6a). The deviations of the fluorescence EEM contours seen in the region (Ex/Em: 280/330 nm) indicated by γ is due to the presence of protein-like substances in the water. The existence of fluorescence EEM peak around the same region (γ) (Figure 6.6) has been previously observed for protein-like substances (Chen *et al.*, 2003; Her *et al.*, 2003). The light scattering regions: first order Raleigh scattering region (F.O.R.S) and second order Raleigh scattering region (S.O.R.S.) captured in the fluorescence EEM of water is also an important area that provides information related to the particulate/colloidal matter present in water (Figure 6.6b). The intensity values of these light scattering regions are related to the

particulate/colloidal matter present in water (i.e. more particulate/colloidal matter generates higher light scattering intensities).

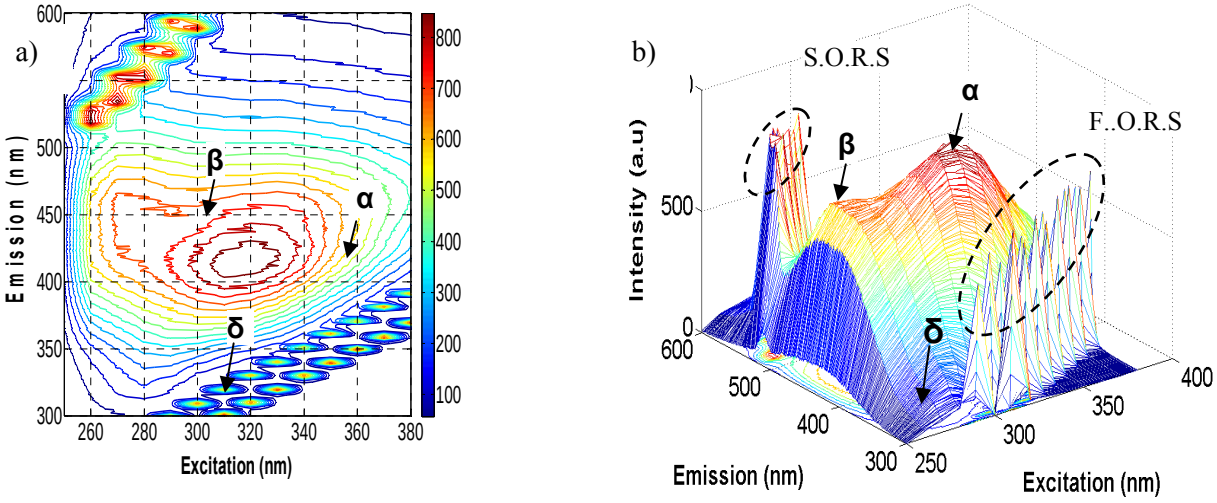


Figure 6-6 Typical fluorescence features seen in the a) fluorescence EEM for Grand River water and b) 3D view of the same EEM. First order Raleigh scattering (F.O.R.S) and Second order Raleigh scattering (S.O.R.S) regions are indicated using dashed-lines (source: Peiris *et al*., 2010)

Introduction to principal component analysis for the fluorescence EEM analysis

Using principal component analysis (PCA) new variables referred as principal components (PCs) were calculated to account for as much of the variance present in a X matrix (Peiris *et al.*, 2010; Wise *et al.*, 2004). Three PCs explained up to 89 % of the cumulative variance during this study. The first PC (PC-1) was related to the content of humic substances, the second PC (PC-2) was related to particulate/colloidal matter, and the third PC (PC-3) was inversely related to the protein-like content in water.

The seasonal variation in raw water quality can also be demonstrated using the score plot of the PCs. Figure 6.7 indicates an important variation of the humic substance (PC-1) throughout the year due to the wide 95 % confidence interval. A seasonal variation in colloidal and particulate matter (PC-2) was also observed for the raw water in Figure 6.7. The removal of humic substances and colloidal and particulate matter through the pretreatment process was also captured by fluorescence analysis. The 95 % confidence interval of RF, B1, and B2 were wide and only shift slightly to the

right. The overlap of the 95 % confidence intervals indicates poor removal of humic substances as demonstrated by the LCOCD analyses. As expected, during filtration process, a reduction of particles and colloidal matter (PC-2) was achieved. The 95 % confidence intervals of B1 and B2 overlap indicating that both biofilter effluents may have similar particulate and colloidal content. Figure 6.8 shows the content of protein-like material (PC-3) in raw water and their removal throughout the treatment process. The large 95 % confidence interval of PC-3 of raw water indicated that the content in protein-like material through the year was variable. The RF achieved some protein-like material removal. However, no removal of protein-like material was achieved by B1. B2 achieved slightly better removal of protein-like material than B1. Overlap of the 95 % confidence intervals of B1 and B2 effluent of PC-3 indicated that the content of protein-like material in the effluent of both biofilters may be similar.

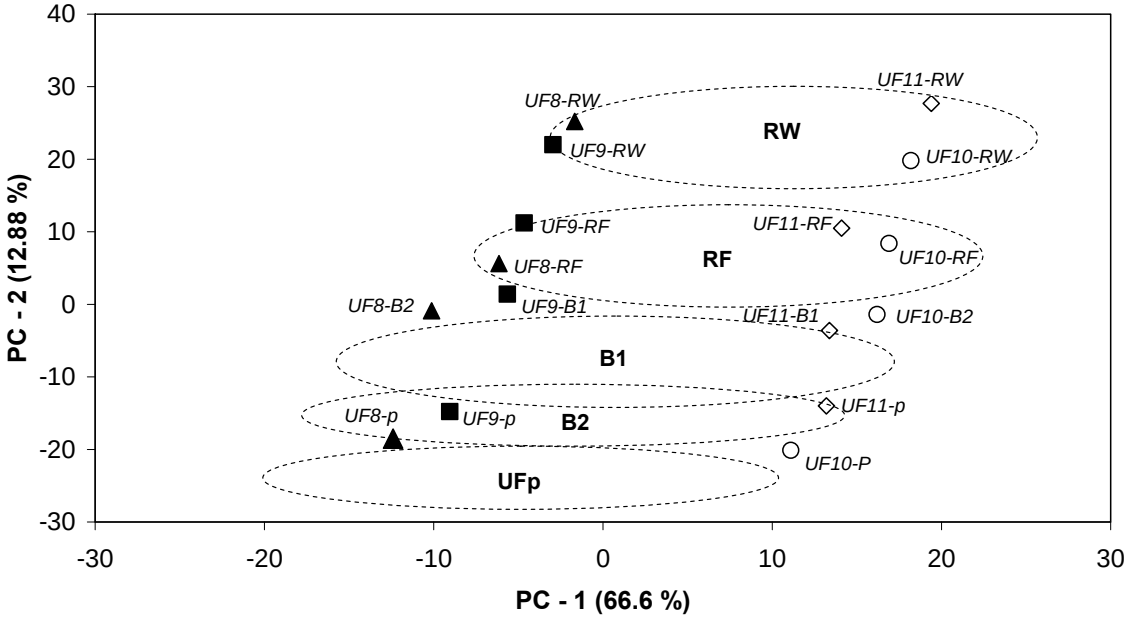


Figure 6-7 Score plot of PC-1 vs PC-2. Scores of PC-1 and PC-2 were grouped and named based on the sampling location. These groups were indicated by dashed-circles based on the 95 % confidence interval regions of the scores in each group. UF8, UF9, UF10 and UF11 indicate the high fouling events captured within a 1 hour of operation of the UF membranes (source: Peiris *et al*., 2010)

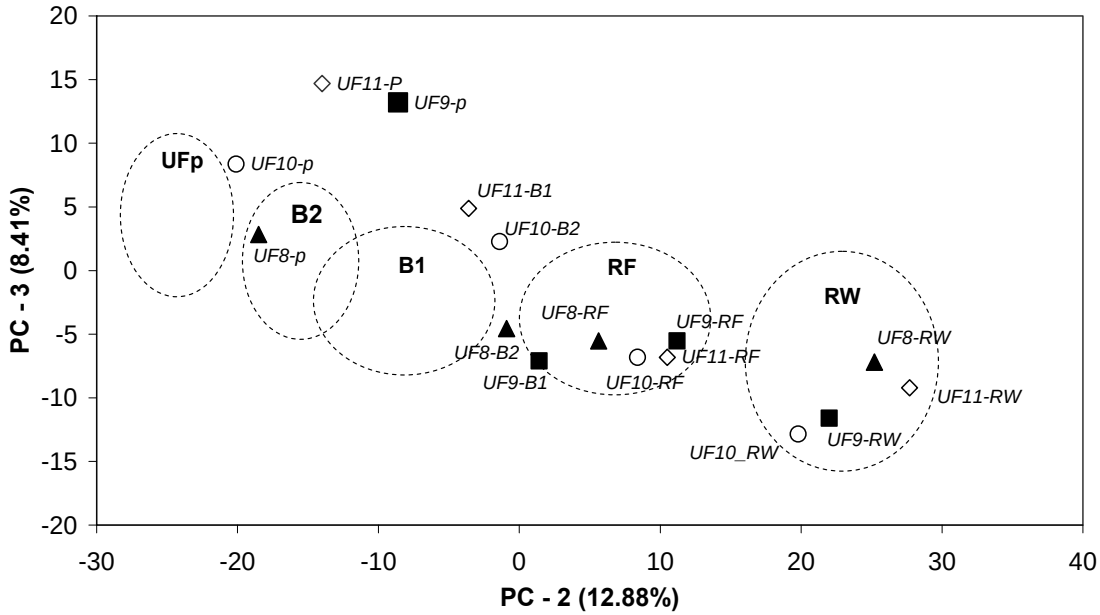


Figure 6-8 Score plot of PC - 3 vs. Pc - 2. Scores of PC - 2 and PC – 3 were grouped and named based on the sampling location. These groups were indicated by dashed-circles based on the 95 % confidence interval regions of the scores in each group. UF8, UF9, UF10 and UF11 indicate the high fouling events captured within a 1 hour of operation of the UF membranes (source: Peiris *et al.*, 2010)

EEM and LCOCD: complementary tools to evaluate membrane fouling

The presence of humic substances in Grand River water can be independently confirmed by both LCOCD and fluorescence EEM analyses (Peiris *et al.*, 2009; Peiris *et al.*, 2008; Sierra *et al.*, 2005). Both LCOCD and EEM analyses also confirmed that humic substances removal during biofiltration pretreatment is substantially less on a percentage basis than the removal of biopolymers.

6.4.5 Impact of Biofiltration on Microorganism Concentrations

Biomass measurements (i.e. ATP, HPC, and TDCC analyses) were performed in the influent and effluent of the biofilters. These results will determine efficiency of the biofilter to reduce the amount of biomass entering the filter. The analyses were performed on the sample collected after 7 days of operation without backwashing.

ATP is a useful indicator for biochemical reaction because living organism used ATP as "currency" of energy exchange; therefore it is a suitable parameter for the quantification of active biomass. ATP measurements were selected because of the rapidity and accuracy of the analysis and its general use in aquatic microbiology (Magic-Knevez and van der Kooij, 2004; Delahaye *et al.*, 2003; Huck *et al.,* 2000; Webster *et al.*, 1985; Karl, 1980). Moreover, ATP is present at a fairly constant concentration in living cell and is rapidly destroyed after the death of the organism (Webster *et al.*, 1985).

ATP measurements of the biofilter influents and effluents were performed from February 21, 2007 until August 15, 2007 (n=21). In general, the data presented in Figure 6.9 demonstrate that the concentration of ATP decreased throughout the treatment process. The ATP concentrations of raw water varied between 3.0×10^{-4} μM to 6.8×10^{-3} μM and the ATP concentration increased with an elevation in water temperature. The ATP removal by the RF improved as the water temperature become warmer except on July 26. The RF achieved up to 1.2 log removal of ATP. RF+B1 and RF+B2 achieved respectively between 0.1 and 2.1 log removal and between 0.2 and 2.4 log removal of ATP. Between February 21 of 2007 and March 22 of 2007, the ATP removal by the RF, B1, and B2 were low and this behaviour is related to the acclimation period of the biofilter. These lower removals of HPC and TDCC were also observed during the acclimation period. Following this period of acclimation, the impact of contact time on the removal of ATP can be observed and longer EBCT achieved higher removal of ATP. The average ATP concentration of B2 effluent (1.5×10^{-4} μM) was lower than the average ATP concentration of B1effluent (2.8×10^{-4} μM).

The effluent of the control column was also analyzed to prove that no biomass was released from the experimental set-up. A difference between -0.1 and 0.6 log was measured between the RF effluent and the control column (B3) effluent.

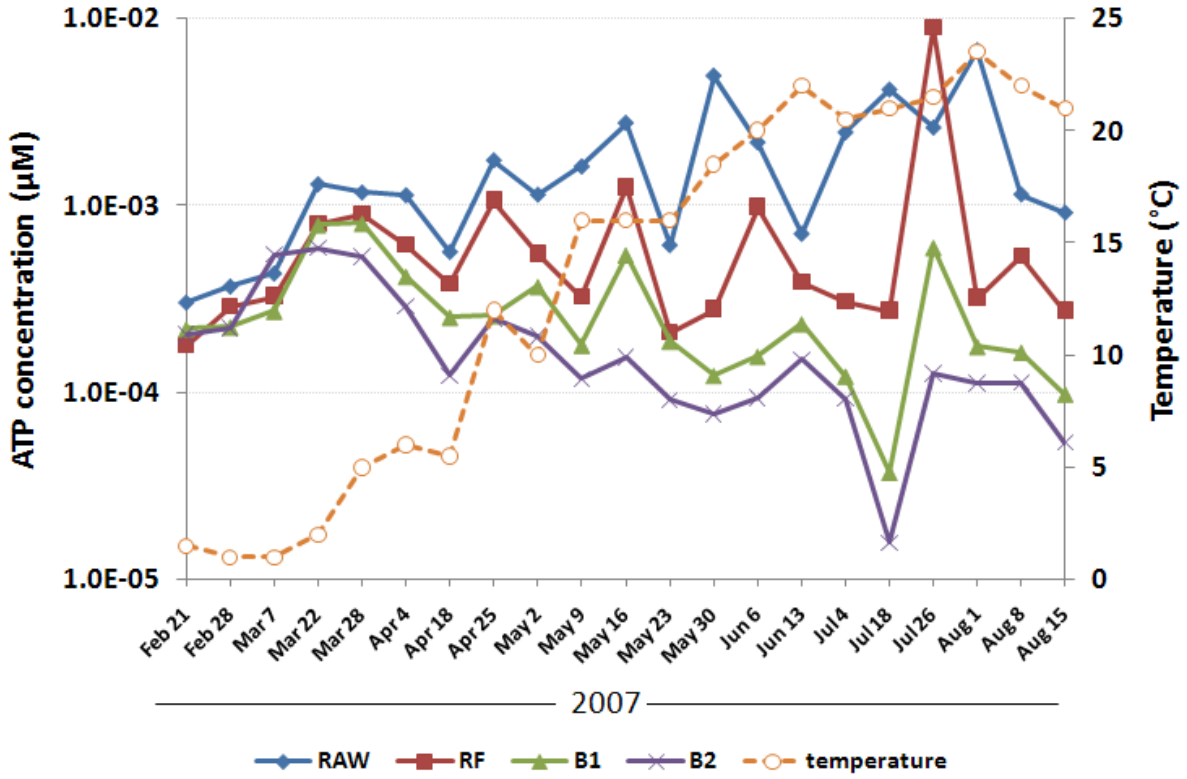


Figure 6-9 ATP concentration in raw water in the effluent of the roughing filter (RF), B1, and B2

The idea of viable plate count procedure such as HPC is that one colony arises from one single monodispersed microorganism (Standard Methods, 1995). This technique has been widely used to monitor water quality.

HPC measurements of the biofilters influent and effluent were performed from January 10, 2007 until July 15 2008 (n=51). The data presented in Figure 6.10 demonstrates that the amount of CFU per mL decreased throughout the treatment process.

The HPC of raw water varied between 7.5 x 10^3 CFU/mL to 2.1 x 10^6 CFU/mL. The RF removes up to 0.9 log of HPC. In general, the RF achieved removal of HPC but at some occasions (n=4) more bacteria were counted in the RF effluent compared to the raw water (Appendix P). Between January 10 and April 25, 2007, the removals of HPC through the treatment process were low due to

the acclimation period of the biofilter. However, when the water temperature rose above 10°C, removal of HPC by B1 and B2 was starting to occur. The impact of EBCT on the removal of HPC was noticeable. After the acclimation period, the average HPC in B2 effluent (1.3×10^5 CFU/mL) was lower than the average TDCC in B1 effluent (5.2×10^4 cells/mL). Figure 6.10 indicates that water temperature did not influence the removal of HPC by the biofilter.

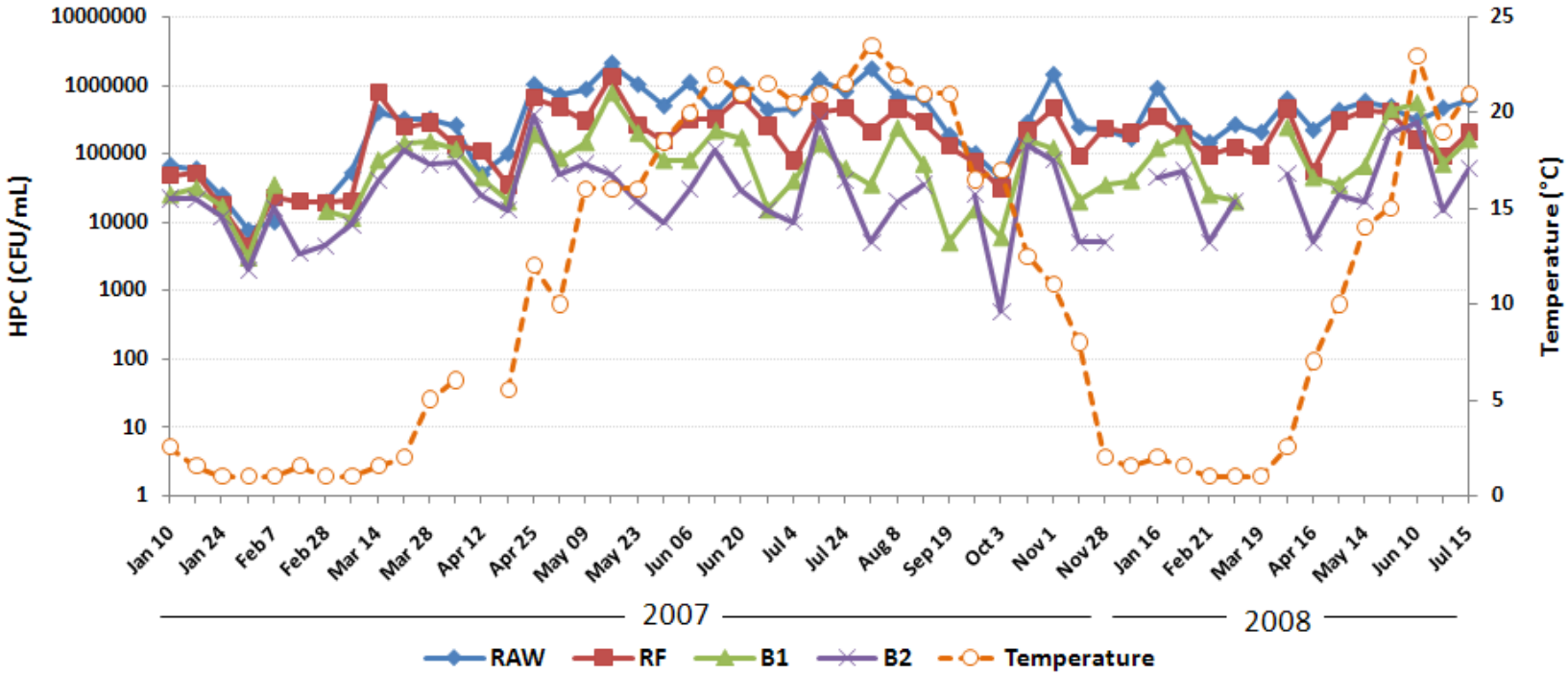


Figure 6-10 HPC concentration in raw water, in the effluent of the roughing filter, and at the effluent of B1 and B2

TDCC utilizes nucleic acid fluorochromes that can be visualized by epifluorescence microscope and provides an indication of the number of cells (active and inactive) present in the biofilter influent and effluent. TDCC is a common method for enumerating the total microbial cells by directly counting cells from a suspension (Langmark *et al.*, 2004).

TDCC measurements of the biofilters influent and effluent were performed from February 21, 2007 until July 15, 2008 (n=45). The data presented in Figure 6.11 indicate that the amount of cells per mL decreases throughout the treatment process after the acclimation period.

The TDCC of raw water varied between 2.2 x 10^5 cells/mL to 8.5 x 10^6 cells/mL. The TDCC in raw water was fairly constant throughout the year. The RF achieved up to 0.7 log removal of the TDCC (n= 45). In general, the RF achieved removal of TDCC but at some occasions (n=7) cells count were higher in the RF effluent than in the raw water (Appendix P). RF+B1 and RF+B2 achieved up to 1.4 log removal of TDCC. Between February 21 and May 2, the removal of TDCC through the treatment process was low due to the acclimation period of the biofilter. However, when the water temperature rose above 10°C, removal of TDCC by B1 and B2 was starting to occur. The impact of EBCT on the removal of TDCC was noticeable. After the acclimation period, the average TDCC in B2 effluent (2.8 x 10^5 cells/mL) was lower than the average TDCC in B1 effluent (4.4 x 10^5 cells/mL). Figure 6.11 also indicates that higher removal of TDCC was achieved at higher water temperature.

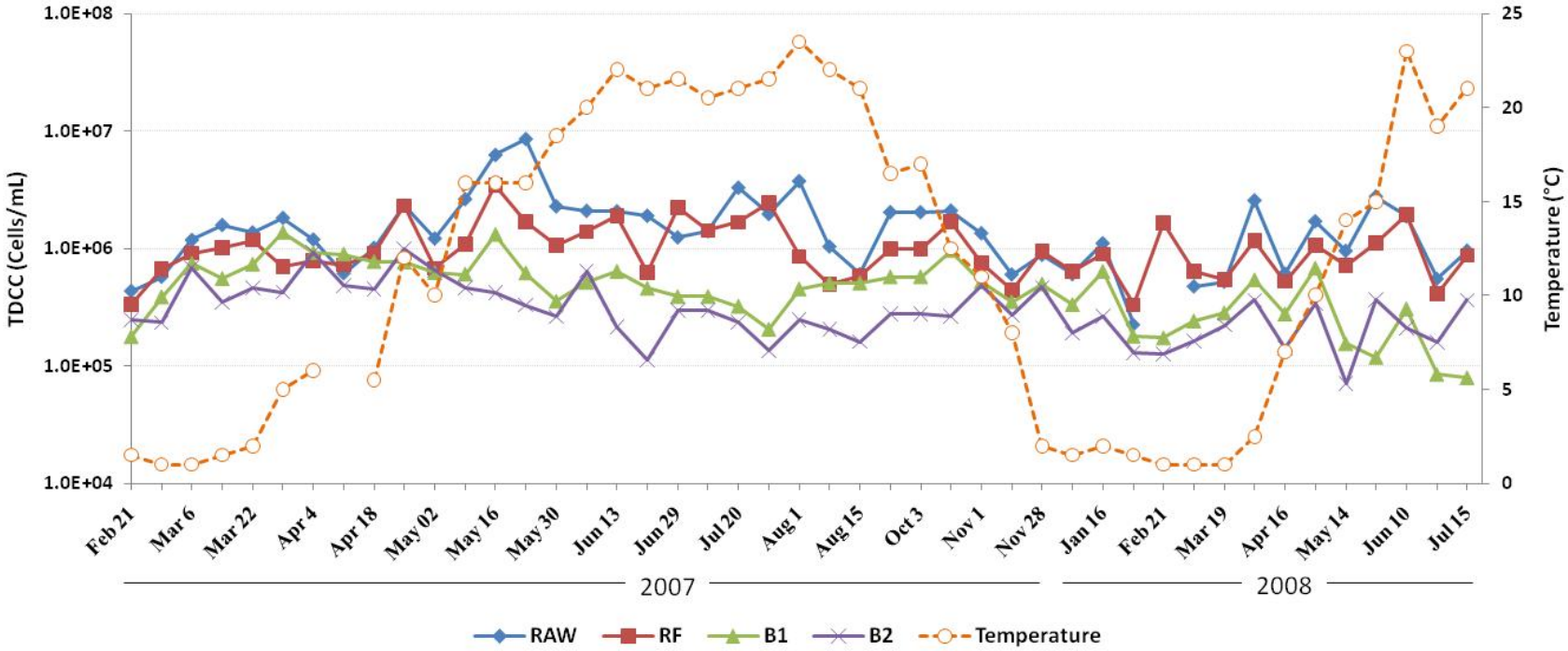


Figure 6-11 TDCC concentration in raw water, at the effluent of the roughing filter, and at the effluent of B1 and B2

From the microbiological results presented, it can be concluded that influent concentrations of active and inactive cells were being reduced by the biofilters. Since ATP measurements is a suitable parameter for the quantification of the microbial activity, a diminution of ATP in the effluent of the biofilter is desirable if subsequent membrane filtration is practiced. If the membrane influent contains a reduced amount of active biomass a diminution of fouling (e.g. organic and biofouling) is expected. Moreover, a reduction of HPC and TDCC concentration in the biofilter effluents indicates that the membrane will be exposed to a reduced number of active and inactive cells and can potentially reduce biofouling, colloidal and particulate fouling, and organic fouling by carrying fewer active microorganisms on the membrane surface. However, to observe a reduction of ATP, HPC, and TDCC an acclimation period of the biofilter was necessary. The duration of the acclimation period may depend on several factors such as the source of water, the water temperature, and the operating conditions of the biofilter. During this study, an acclimation period of 133 days was necessary before removal of HPC and TDCC was observed and an acclimation period of 98 days was necessary before removal of ATP was observed.

6.4.6 Ultrafiltration Membranes

6.4.6.1 Material causing membrane fouling

Figure 6.12a presents a virgin UF membrane prior to experiment. Figure 6.12b presents the smooth fouling layer occurring during the summer using B2 effluent as feed water. The yellowish material was uniformly distributed on the membrane. Figure 6.12c presents severe fouling occurring during the fall of 2007 using the B1 effluent. The brown fouling layer was unevenly distributed on the membrane.

a) b) c)

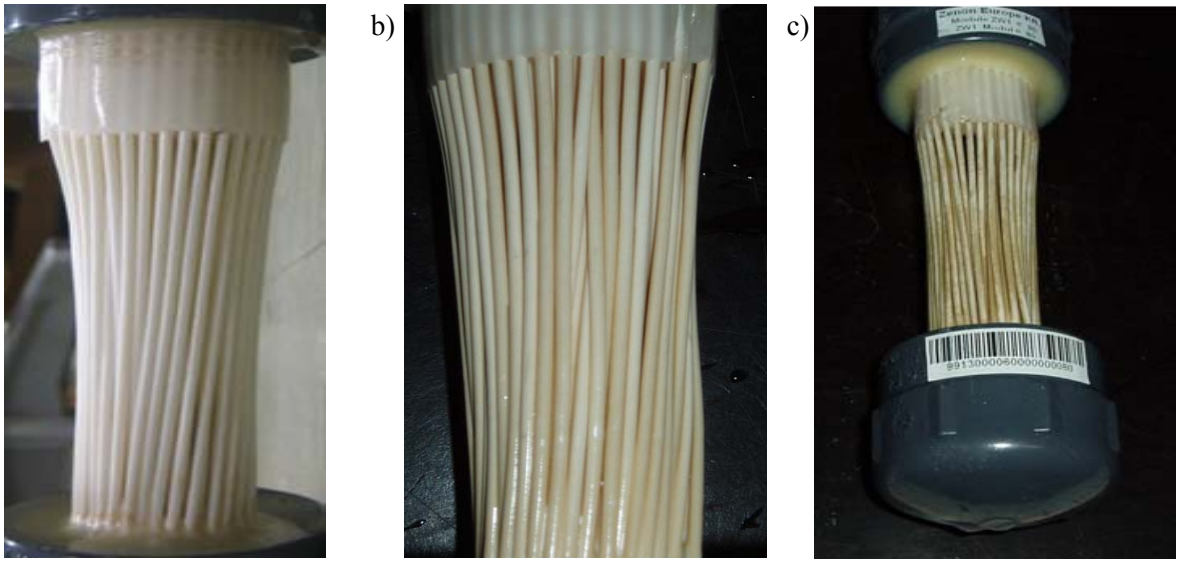


Figure 6-12 Fouling of UF membrane module a) virgin membrane, b) low fouling with B2 effluent summer of 2007, and c) severe fouling with B1 effluent during the fall of 2007

From the 13 experiments performed with the UF membrane, it can be concluded that Zeeweed-1 did not affect the following water quality parameters: pH, conductivity, TOC, DOC, and UV_{254} (Appendix M). However, UF membranes could achieve the removal of turbidity (i.e. particles and colloids). The DOC values of UF membrane feed and permeate were essentially constant indicating that DOC was not removed by UF membrane. However, LCOCD analyses performed on the UF membrane influent and effluent showed that biopolymers were consistently removed (Figure 6.13).

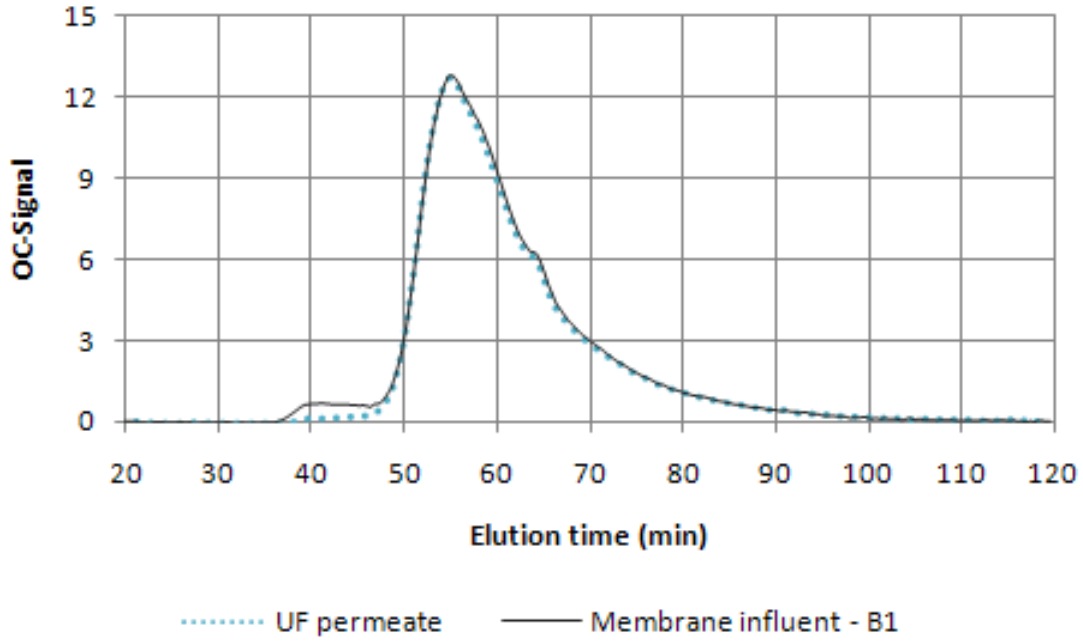


Figure 6-13 Typical LCOCD chromatograms identifying the DOM fraction causing fouling on the UF membrane (Summer 2007) (source: Halle *et al*., 2009)

In Figure 6.13, the biopolymer peak decreased by 86 % in the UF permeate while the humic substances peak decreased by only 7 %. On average, the removal of biopolymers and humic substances by UF membrane from the feed water were 56 ± 22 % and 2 ± 4 % respectively (n=13).

Generally, biopolymer removals increased with increased UF operating time except for one experiment (Table 6.2). The increase removal in biopolymer with longer operation time varied between 9 % and 74 % and was time dependant (i.e. longer operation time achieves higher percentage removal and vice versa). The increase of biopolymer removal can be caused by the accumulation of material on the surface of the membrane thus the surface properties of the membrane were changed. The biopolymers may have a stronger affinity with the accumulated foulant layer on the surface of the membrane than to the virgin membrane surface.

Table 6-2 Increase in biopolymer removal with operating time

Experiment	Sampling time (h)	BP removal (%)	Difference (%)
S07 – B2	1	48	-19
	96	29	
S07 – B2	1	43	34
	96	77	
S07 – B1	1	12	74
	120	86	
F07 – B2	1	56	13
	96*	69	
F07 – B1	1	63	11
	96*	74	
W08 – B1	1	68	11
	24*	79	
W08 – B1	1	31	9
	24*	40	

*UF membrane completely fouled

Fluorescence EEM score plots of PC-1 (i.e. humic substances content) and PC-2 (i.e. colloidal/particulates content) (Figure 6.7) confirmed the low rejection of humic substances by the UF membrane. The 95 % confidence interval of the UF permeate showed a slight shift to the right compare to the 95 % confidence interval of B1 and B2. This was the indication of a very small reduction of humic substances by the UF membrane. However, Figure 6.7 indicates that UF membrane achieved rejection of particulate and colloidal material (i.e. turbidity) as expected. Figure 6.8 shows the score plot of PC-3 (i.e. protein-like substances) and PC-2 indicating that protein-like material was also rejected by the UF membrane.

In conclusion, from LCOCD chromatograms, fluorescence EEM analyses, and PC analysis of the UF membrane influent and permeate, the fractions of DOM contributing to fouling may include: biopolymers, particulate and colloidal matter, and protein-like substances.

6.4.6.2 Impact of biofiltration on the fouling of ultrafiltration membrane

The results presented in this section have been published in Environmental Science and Technology.

> Hallé, C., P.M. Huck, S. Peldszus, J. Haberkamp, M. Jekel, 2009. Assessing the Performance of Biological Filtration as Pretreatment to Low Pressure Membranes for Drinking Water. Environ. Sci. Technol. 43, 3878-3884.

When using the RF effluent as feed for UF membrane, the TMP increase within a cycle of 1 h (Figure 6.14) varied substantially from 1.7 to 4.2 psi indicating a drastic increase in hydraulically reversible fouling. Reversible fouling was caused by material deposited on the surface or within the pore of the membrane but this material could be removed by the hydraulic backwash. The reversible fouling caused an increase in TMP but the permeate flow remained constant. After backwash, the TMP increase could be recovered if the fouling was reversible.

However, hydraulically irreversible fouling caused an average increase of 0.3 psi per cycle. After a specific volume (V_s) of 2000 L/m^2, the maximum TMP of the membrane unit (9 psi) was reached, indicating rapid hydraulically irreversible fouling. Irreversible fouling was also caused by material deposited on the surface or within the pore of the membrane but this material could not be dislodged by the hydraulic backwash. The irreversible fouling also caused an increase in TMP and under sustainable operating conditions the permeate flux remained constant. However, the backwash procedure was not sufficient to recover the TMP increase due to irreversible fouling. Chemical cleaning was necessary to recover membrane performance.

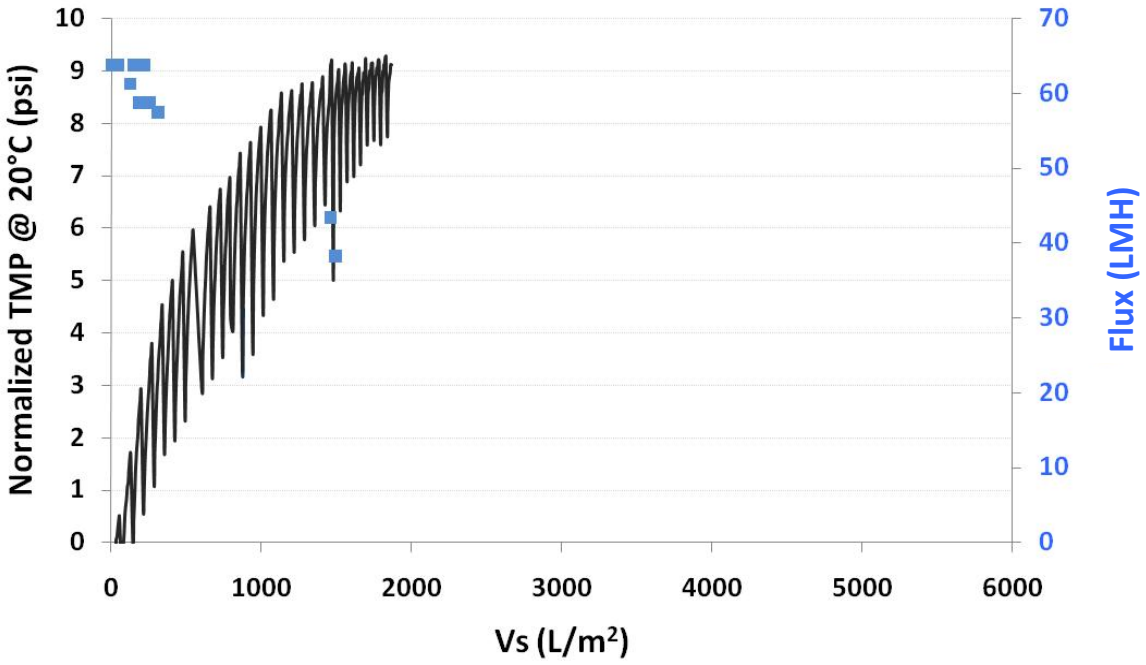


Figure 6-14 Increase of TMP of ultrafiltration membrane using untreated Grand River as feed water. The line represents the normalized TMP at 20°C. The sharp increase was caused by reversible fouling within a cycle of 1 h while the constant increase of TMP was caused by irreversible fouling. As a consequence of irreversible fouling, the initial TMP of a cycle increase gradually to maximum of 9 psi. The squares represent the permeate flux. A non constant permeate flux indicate unsustainable conditions of operation (source: Halle *et al*., 2009)

The experiments were not designed to elucidate exact fouling mechanisms. However, as previously determined it is likely that organic material (DOC 5.79 ± 0.6 mgC/L; biopolymers 0.21 ± 0.02 mgC/L) and also colloidal and particulate material (membrane influent turbidity 1.99 ± 0.6 NTU) contributed to the severe fouling observed. The water quality parameters of membrane feed (i.e. RF effluent) and membrane permeate are available in Appendix M refer to UF3 experiment.

Pre-treatment (roughing filter plus a biofilter with either 5 or 14 minutes EBCT) significantly reduced the TMP required to keep a constant permeate flux (Figures 6.15 and 6.16).

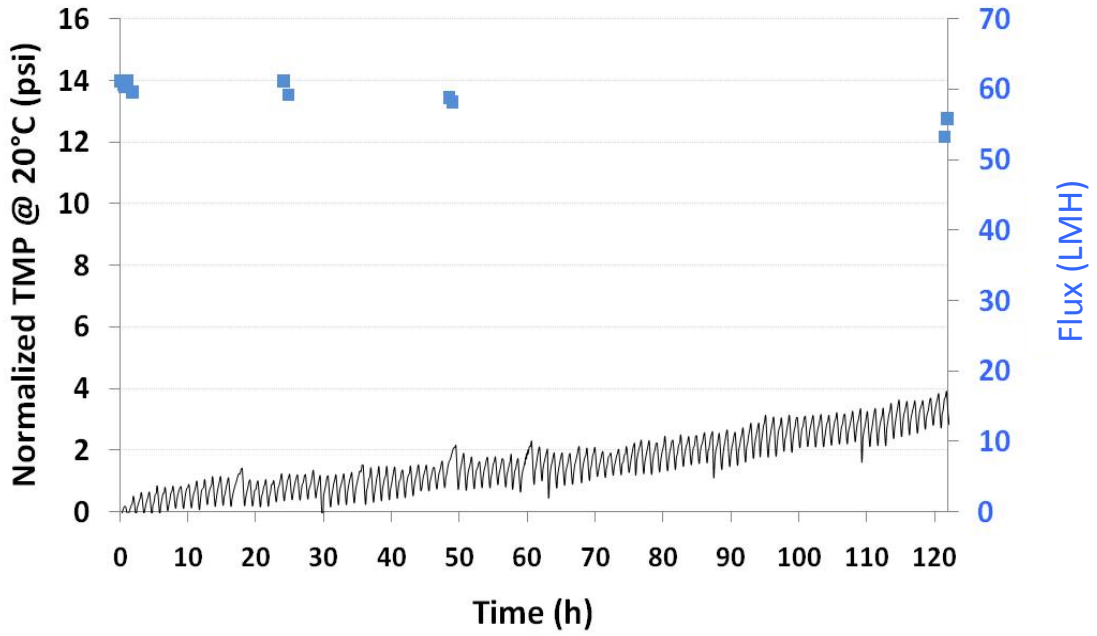


Figure 6-15 Increase of TMP of ultrafiltration membrane using B1 effluent as feed water. The line represents the normalized TMP at 20°C. The squares represent the permeate flux (source: Halle *et al.*, 2009)

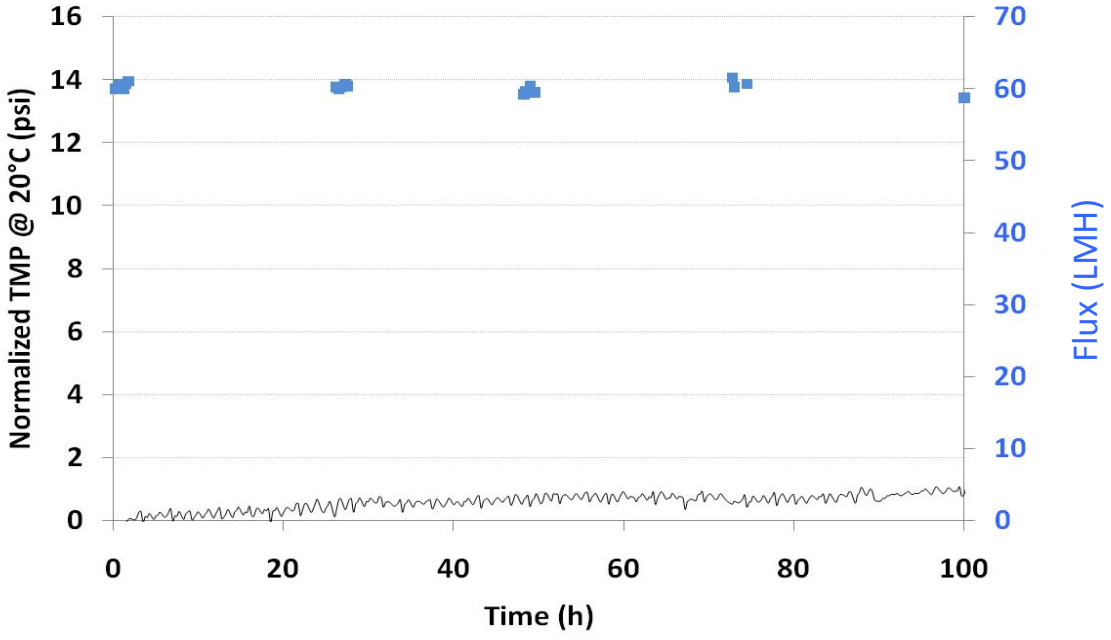


Figure 6-16 Increase of TMP of ultrafiltration membrane using B2 effluent as feed water. The line represents the normalized TMP at 20°C. The squares represent the permeate flux (source: Halle *et al.*, 2009)

Using B1 effluent (Figure 6.15) the TMP increase within a cycle (hydraulically reversible fouling) stayed constant for the entire duration of the experiment (120 h). Irreversible fouling was also reduced as indicated by an overall TMP increase of only 4 psi after Vs of 7500 L/m^2. The desired permeate flux could be maintained for a period of 48 h and only 10 % flux decline was observed within the last 72 h of the experiment.

Using B2 effluent as membrane feed, only very low reversible fouling was observed during any of the 1-hour permeation cycles for the entire period of the experiment of 100 h (Figure 6.16). In addition, very little irreversible fouling was observed as indicated by a TMP increase of only 1 psi after a Vs of 6000 L/m^2. Moreover, the permeate flux stayed constant for the entire duration of the experiment.

LCOCD analyses of the membrane backwash solution showed that biopolymers were detached from the surface of the membrane, as demonstrated by Huang *et al.* (2007), confirming their importance for reversible fouling. For the experiment with B1, the average biopolymer concentration in the backwash water was 16 ± 5 μgC/L compared to an influent concentration of 9 ± 4 μgC/L. For the experiment with B2, the average biopolymer concentration in the backwash water was 11 ± 2 μgC/L compared to an influent concentration of 7 ± 4 μgC/L. These experiments also demonstrated that the rejection and/or detachment of biopolymers increased over time. During the winter 08, using B1 effluent, the concentration of biopolymer in the drain after one hour of operation was 0.16 μgC/L while the biopolymer concentration of B1 effluent was 0.13 μgC/L. After 24 h of operation, the biopolymer concentration of B1 effluent remained the same but the concentration of biopolymer measured in the drain increased to 0.23 μgC/L.

The different degree of reduction of both hydraulically reversible and irreversible fouling achieved by B1 and B2 was primarily attributed to a higher removal of biopolymers by the biofilter with the longer contact time. For the experiments in Figure 6.15 and 6.16, the biopolymer concentrations in the effluent of B1 and B2 were respectively 0.23 mgC/L and 0.14 mgC/L, measured at a time of 1 h (Vs of 57 L/m^2). The turbidities of the B1 and B2 effluents were very similar with 0.16 ± 0.05 NTU and 0.16 ± 0.04 NTU, respectively. These runs were performed back to back, and all water quality parameters remained stable throughout these experiments. Hence, it was inferred that overall particle counts and particle size distribution and therefore their contributions to fouling would have been

similar in both runs. Thus, it is proposed that the measurably improved performance of B2 in terms of fouling control is attributed to its lower effluent concentration of biopolymers. As described earlier, B2 consistently outperformed B1 in terms of biopolymer removal throughout the year and fouling of the UF module was consistently lower using B2 effluent. Although B2 would also be expected to give greater removal of inorganic colloids, the role of colloids warrants further investigation, which was beyond the scope of this study.

Better control of hydraulically irreversible fouling by filter B2 compared to B1 suggests a higher removal of protein-like material, which have only recently been associated with hydraulically irreversible UF membrane fouling (Haberkamp, 2008). Since hydraulically reversible fouling has recently been attributed to larger polysaccharides (Haberkamp, 2008), improvement of hydraulically reversible fouling by B2 compared to B1 may be attributed to better polysaccharide removal. It is possible that some smaller polysaccharides able to enter the pores may also have contributed to hydraulically irreversible fouling. This interpretation is consistent with findings from an MBR study by Metzger *et al.* (2007) who reported that the closest fouling layer to the membrane had a high concentration in proteins, whereas high carbohydrate concentrations were detected in the intermediate fouling layer. The MBR study also employed a PVDF membrane which is generally hydrophobic in nature and therefore prone to protein-like material fouling through interactions of hydrophobic protein segments with the hydrophobic membrane surface.

Figure 6.17 shows the impact of biopolymer concentration in the UF feedwater on hydraulically reversible fouling and the lines in the figure indicate trends only (see also Appendix M). Lower concentrations of biopolymers reduced the increase of TMP during a cycle. In general, lower hydraulically reversible fouling was observed after 1 h than after 24 h or more (the two high ΔTMP values for 1 h in W08 do not follow this general trend and the exact reasons are unknown). It could be postulated that their biopolymer composition (or the nature of the inorganic colloids) differed substantially from that in the other experiments which were all performed in the spring or summer. Figure 6.15 indicates that reversible fouling increases during the first several cycles and then remains relatively constant thereafter, thus the upper line in Figure 6.17 is actually more indicative of membrane behaviour. It is significant that for this line the biopolymer concentration was more important for fouling than is the turbidity – the lowest ΔTMP and biopolymer values were associated with the highest turbidity values.

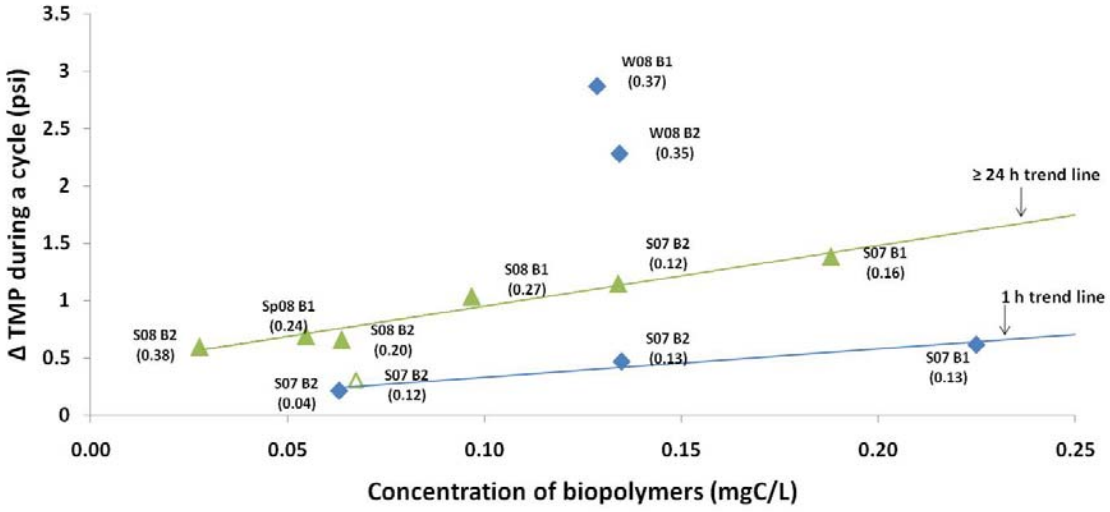


Figure 6-17 Relation between the concentrations of biopolymers and the increase in TMP during a cycle (hydraulically reversible fouling). Data indicate the season and year, type of membrane influent, and in parentheses the membrane influent turbidity. Diamonds represent data collected after 1 h and triangles data collected after 24 h or more. ΔTMP during a cycle indicates the extent of reversible fouling, because backpulsing and sparging between cycles dislodges foulant material. The ΔTMPs shown are an average of the increase in TMP for the 3 cycles before, during and after sampling for LCOCD analysis (source: Halle *et al.*, 2009)

For sustainable membrane operation, irreversible fouling is more important. Although at first glance Figure 6.18 does not seem to show a relationship between irreversible ΔTMP and biopolymer concentration, closer examination reveals an important trend: in general, substantially lower irreversible fouling occurred when the membrane is fed by B2, the biofilter with the longer EBCT. The exceptions to this are two experiments with B2 in F08 and W08 where the turbidity was very high and the membrane was completely fouled during the experiment and one experiment with B1 in S07 when the turbidity was very low (otherwise, no clear effect of turbidity can be seen). The beneficial effect of the longer biofilter EBCT suggests that, for irreversible fouling, the composition rather than the absolute concentration of the biopolymer fraction is important. Haberkamp (2008) identified proteins-like material as being responsible for irreversible fouling. A comparison of the LCOCD chromatograms for B1 and B2 was inconclusive with respect to the biopolymer composition although N- and UV detection was employed simultaneously with the OC detection.

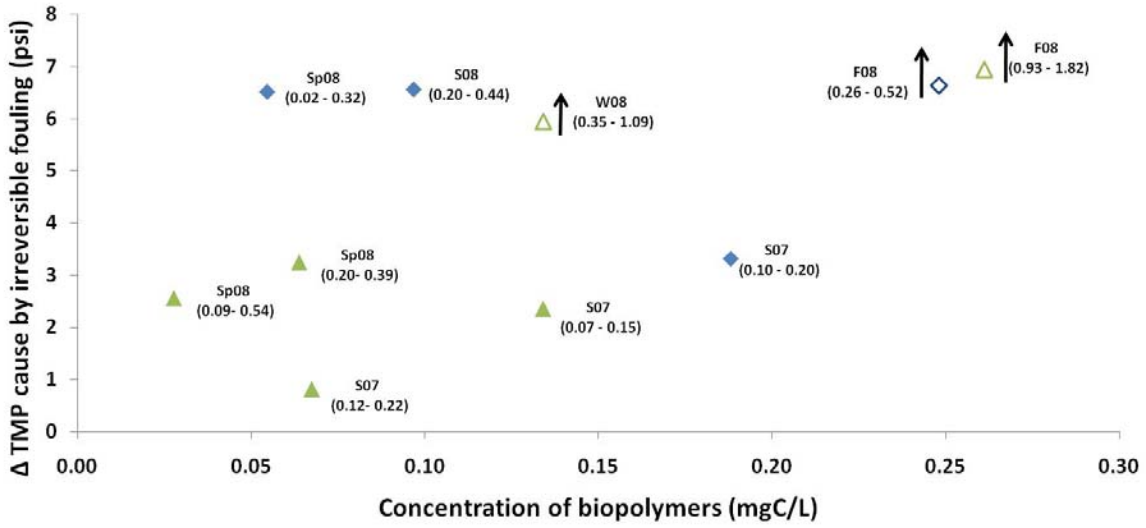


Figure 6-18 Relation between the concentrations of biopolymers and the increase in TMP caused by irreversible fouling. Data indicate the season, the year, and in parentheses the range of membrane influent turbidity. The diamonds represent data from B1 effluent and the triangles data from B2 effluent. The ΔTMPs shown are calculated by subtracting the TMP measured at the end of the first cycle from the TMP measured at the end of the experiment. The upward arrows indicated runs where the membrane was completely fouled during the experiment (source: Halle et al., 2009)

6.4.6.3 Seasonal performance of the biofilters

Impact on irreversible fouling

Figure 6.19 presents the increase of TMP due to irreversible fouling observed during 12 UF experiments. As shown in this figure, the seasonal performance of the biofilters as membrane pretreatment to control hydraulically irreversible fouling can be evaluated. The TMP curves presented in Figure 6.19 are normalized using the clean water TMP of a specific UF membrane unit. The permeate flux was adjusted using a viscosity correction factor except for the experiment performed during the fall were the TMP reading were temperature corrected.

The experiment label RF2007 was performed using the effluent of the roughing filter thus no biological filtration pretreatment was applied. The TMP reaches 8.88 psi within Vs of 1500 L/m^2 indicating rapid hydraulically irreversible fouling as presented in Figure 6.14. As discussed previously, colloidal and organic matter may have caused severe fouling of the UF membrane.

The irreversible fouling on UF membranes was the lowest during the summer of 2007 using B1 and B2 effluents. In fact, using B1 effluent, the TMP reached 3.89 psi after Vs of 7000 L/m^2. An even better performance was observed using B2 effluent where the TMP reached 0.92 psi after Vs of 5675 L/m^2.

The fouling reductions obtained by biofiltration pretreatment during the summer of 2008 were not as pronounced as during the summer of 2007, most likely due to the high turbidity of the raw water in summer 2008. This increased turbidity was caused by frequent heavy rain events. Due to the higher turbidity and possibly higher concentration of particulate and colloidal matter in the biofilter effluent, it is expected to observe higher fouling rates during the summer of 2008. A potentially higher content in protein-like material or different composition of protein-like material in the biofilter effluent may also have caused higher irreversible fouling on UF membrane during the summer of 2008.

During the summer of 2008, using B1 effluent, the TMP reached 7.42 psi after Vs of 5300 L/m^2. At comparative Vs of 5000 L/m^2, the TMP reached due to irreversible fouling was 2.55 psi in 2007. The turbidity of B1 effluent in 2007 was 0.13 NTU compared to 0.44 NTU in 2008. Increase in turbidity and possibly more particulate and colloidal matter may have contributed to higher irreversible fouling.

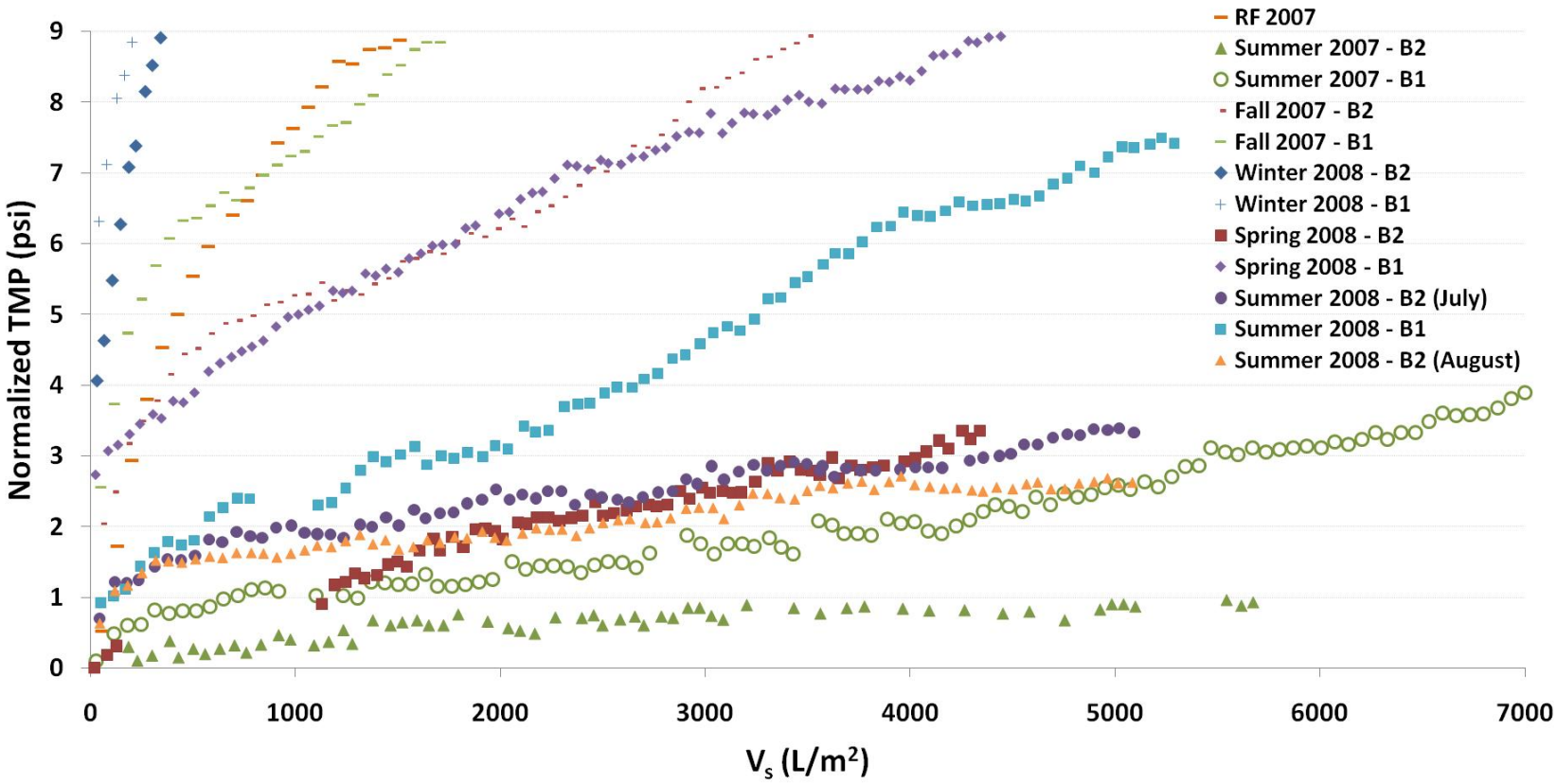


Figure 6-19 Irreversible fouling of UF membrane during different seasons

Two experiments were performed using B2 effluent during the summer of 2008, one in July and the second one in August. Although the initial fouling during the August experiment seems higher at the beginning of the experiment, after Vs of 5000 L/m^2 the TMP increase due to irreversible fouling was lower during the August experiment (2.62 psi) than during the July experiment (3.33 psi). The average turbidity of B2 effluent during July and August experiments were respectively 0.33 ± 0.2 NTU and 0.31 ± 0.2 NTU. Although turbidity is not the ideal parameter to evaluate the particulate and colloidal matter content in a sample, it gives an indication that the biofilter effluents had similar content of light diffracting material (i.e. particulate and colloidal matter).

During the winter, for both B1 and B2 effluents, even if a temperature (viscosity) correction factor was applied to adjust the permeate flux, severe irreversible fouling was observed. The maximal TMP of 9 psi was reached within Vs of 250 L/m^2 and 370 L/m^2 for B1 and B2 respectively. The respective fluxes were 34.5 LMH and 37.0 LMH. The experiments were performed during approximately 24 h before complete fouling occur leading to severe flux decline. The average turbidity of B1 and B2 effluents were relatively high with respectively 1.0 ± 0.04 NTU and 1.3 ± 0.8 NTU. Higher turbidity values, thus potentially high content of particulate and colloidal material, may have lead to severe reversible and irreversible fouling.

During the spring 2008, considerable differences in irreversible fouling were observed between B1 and B2 effluents. The TMP for B1 and B2 after Vs of 4000 L/m^2 were respectively 8.44 psi and 2.97 psi. The irreversible fouling observed with B2 during spring 2008 and July 2008 were similar. During the spring, the average turbidity of B2 was 0.30 ± 0.08 NTU similar to the condition monitor in July 2008. However, with an average turbidity of 0.20 ± 0.1 NTU in B1 effluent, these results show that the content in protein-like substance and not only turbidity may highly influence the extent of irreversible fouling of UF membrane.

The irreversible fouling observed with B1 during the fall 2007 was similar to the fouling measured with the RF effluent. The maximal TMP was reached within Vs of 1950 L/m^2. Using B2 effluent lead to slightly better performance reaching the maximal TMP within Vs of 3700 L/m^2. These results were expected because during these experiments, the fluxes were not adjusted accordingly to the water temperature. The experiment with B1 and B2 were performed at 4.5°C and 7°C respectively. However, the TMP reading plot in Figure 6.21 were corrected using equation (6.2)

$$\text{pressure}_{T2} = \text{pressure}_{T1} * 1.025^{(T1-T2)} \qquad \text{eq. 6.2}$$

These experiments demonstrated the importance of temperature adjusted flux on the fouling reduction when the viscosity increases due to low temperature.

Relationship between reversible and irreversible fouling

Figure 6.20 presents an average of the TMP increase during a cycle indicating the reversible fouling occurring on the UF membrane. The bar presents the standard deviation and the number above the bar indicates the number of cycles analyzed. As concluded previously, the lowest increases of TMP associated to reversible fouling events were correlated with lower concentration of biopolymers in the membrane influent.

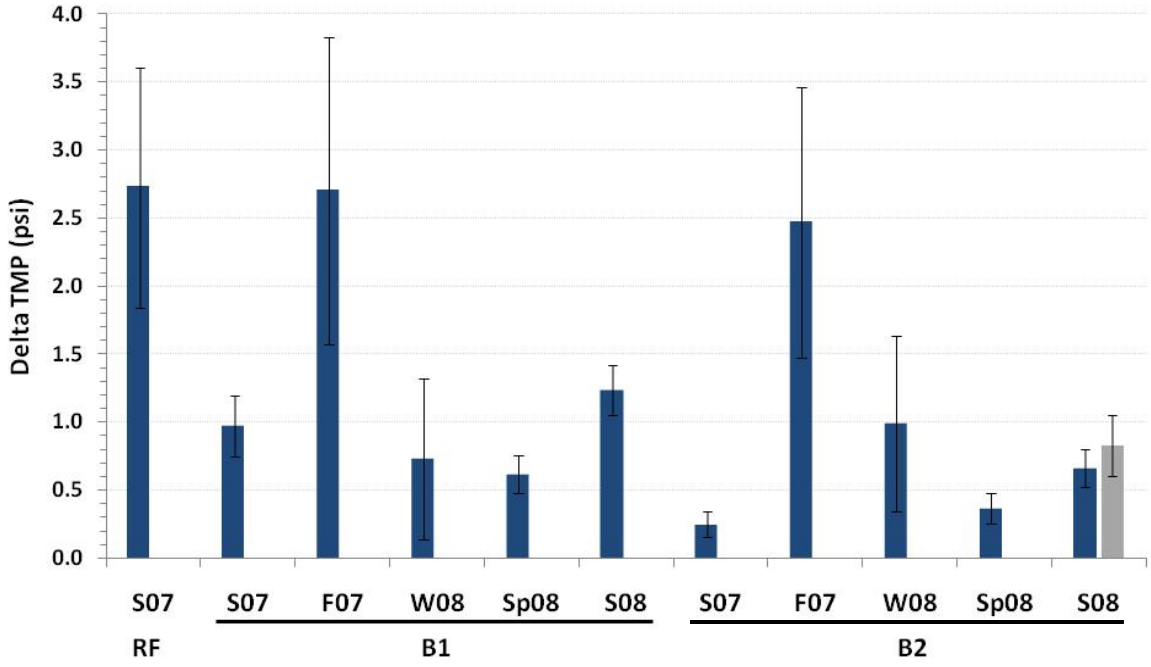


Figure 6-20 Reversible fouling of UF membrane during different seasons. The number above the bar indicates the number of cycles analyzed. For B2, replicate experiment was performed during the summer of 2008. The blue column presents the reversible fouling observed in July and the grey column the reversible fouling observed in August

Furthermore, Figure 6.20 shows that low reversible fouling observed during an experiment is associated with a smaller standard deviation. Low standard deviation indicates that reversible fouling was constant during the experiment which is a sign of sustainable operating conditions. On the contrary, a large standard deviation indicates substantial reversible fouling at the start of the experiment. Figure 6.21 demonstrates the cause of large standard deviation during an event experiencing severe reversible fouling.

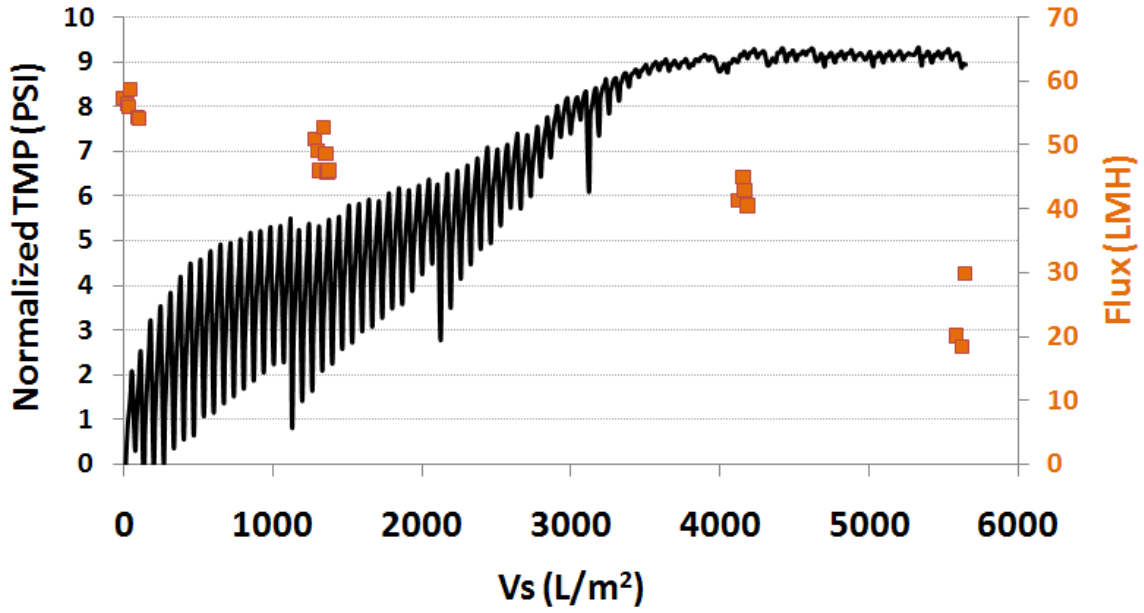


Figure 6-21 Typical increase of TMP during experiment experiencing severe reversible and irreversible fouling (F07 with B2 effluent)

At the beginning of the experiment, during one cycle, the TMP increases significantly due to the accumulation of material on the surface or within the pore of the membrane. During the backflush, some the material causing fouling was dislodged because the TMP significantly decreases at the begging of the following cycle. However, some of the material could not be dislodged since the TMP never went back to the initial value of the previous cycle. The accumulation of material on the membrane surface had two consequences: 1) it increased the resistance for the solute to cross the membrane causing the permeate flux to decrease over time, and 2) the surface properties of the membrane was modified by the accumulation of material. Over time, reversible fouling diminished

probably due to the change in the membrane surface properties but the accumulation of foulant material continue to build up until the maximum TMP of 9 psi was reached.

Figures 6.15 and 6.16 show experiments performed with B1 and B2 effluents during the Summer of 2007 and the reversible fouling was constant over the course of the experiment. Consequently, small variation in standard deviation was observed in Figure 6.20 for those corresponding experiments.

6.4.6.4 Impact of biofilter backwash on the fouling of UF membrane

During the summer of 2007, it was intended to replicate the results obtained with B2 effluent. However, the biofilter had to be backwashed 46 h after the start of the experiment because a storm event caused an increase in the raw water turbidity thus clogging the biofilter.

Figure 6.22 presents the impact biofilter backwash on reversible and irreversible fouling of UF membrane. The reversible and irreversible fouling on UF membrane was low prior to biofilter backwash (i.e. Vs between 0 and 2700 L/m^2). After Vs of 2700 L/m^2, B2 was backwashed. After the backwashing procedure, the effluent of the filter was sent to waste for a period of 30 minutes. Then, the biofilter effluent was used to feed the UF membrane again. After backwash an increase of reversible and irreversible fouling was observed. Before backwash, the average reversible fouling was 0.25 ± 0.08 psi and after backwash the average reversible fouling was 0.96 ± 0.18 psi.

Those results indicate that backwashing strategy may highly influence the performance of the UF membrane. Thus, further operational conditions must be investigated in detail to determine the impact of filter backwash on the fouling of UF membrane.

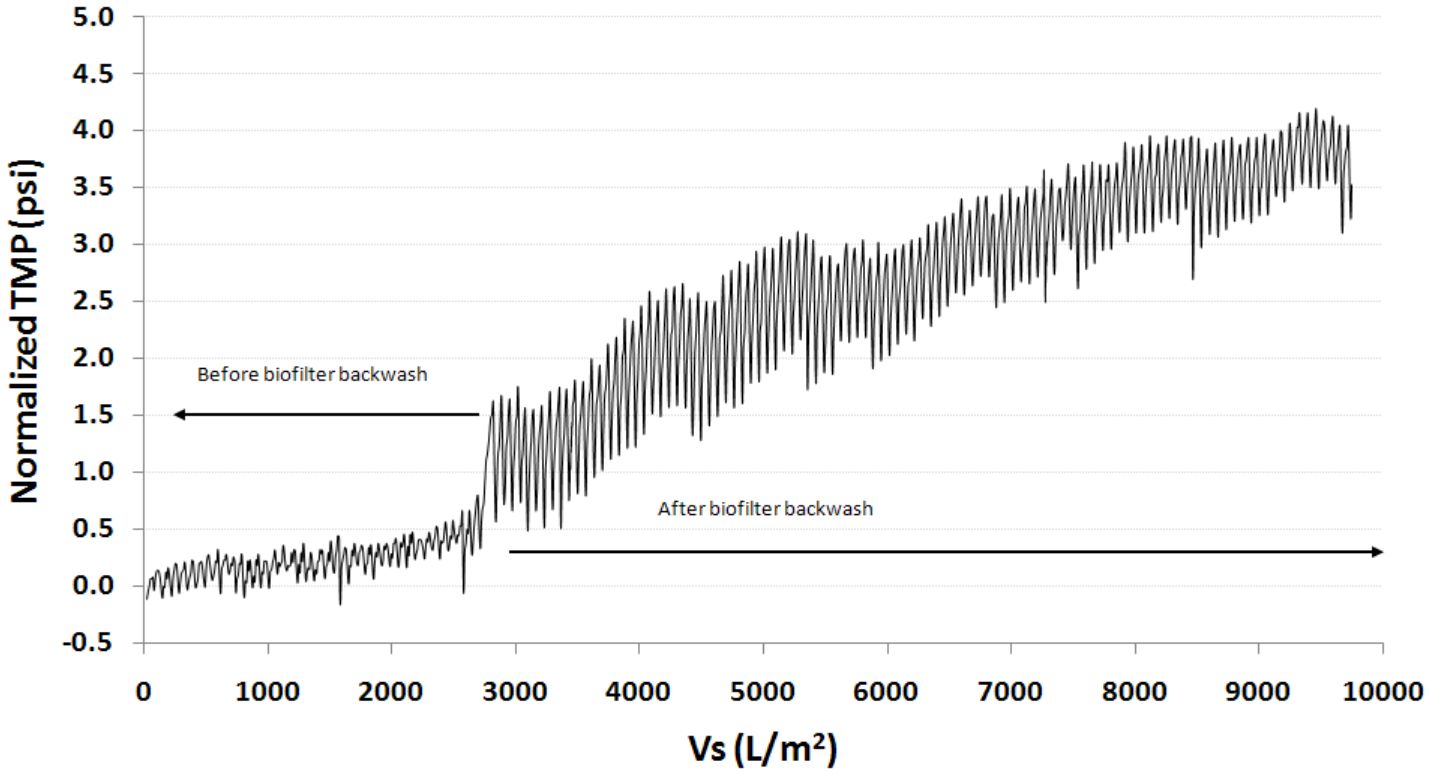


Figure 6-22 Impact of biofilter backwash on the reversible and irreversible fouling of UF membrane

6.4.7 Nanofiltration Membranes

6.4.7.1 Impact of biofiltration on the fouling of nanofiltration membranes

This section presents the impact of biofiltration pretreatment on the fouling of NF membranes. Note that in practice, considering the physico-chemical characteristic of Grand River, NF membranes would likely be preceded by looser membranes to eliminate particulate and colloidal materials as well as microbial materials. However, the results of these experimentations provided useful information on the application of biofiltration as membrane pretreatment.

This section investigates the fouling of XN45 membranes using B1 and B2 effluents. As explained in section 3.4.4, NF membranes were operated at constant pressure. Thus the fouling was monitored by measuring the permeate flux decline over time. Limited results are available for the tight TS80 membrane due to severe fouling as shown in Figure 6.23. These results suggest that biofiltration is not a sufficient pretreatment for TS80 membrane because near complete fouling occurred within 72 h of operation. Consequently, results presented in this section focus on the performance of XN45 membrane.

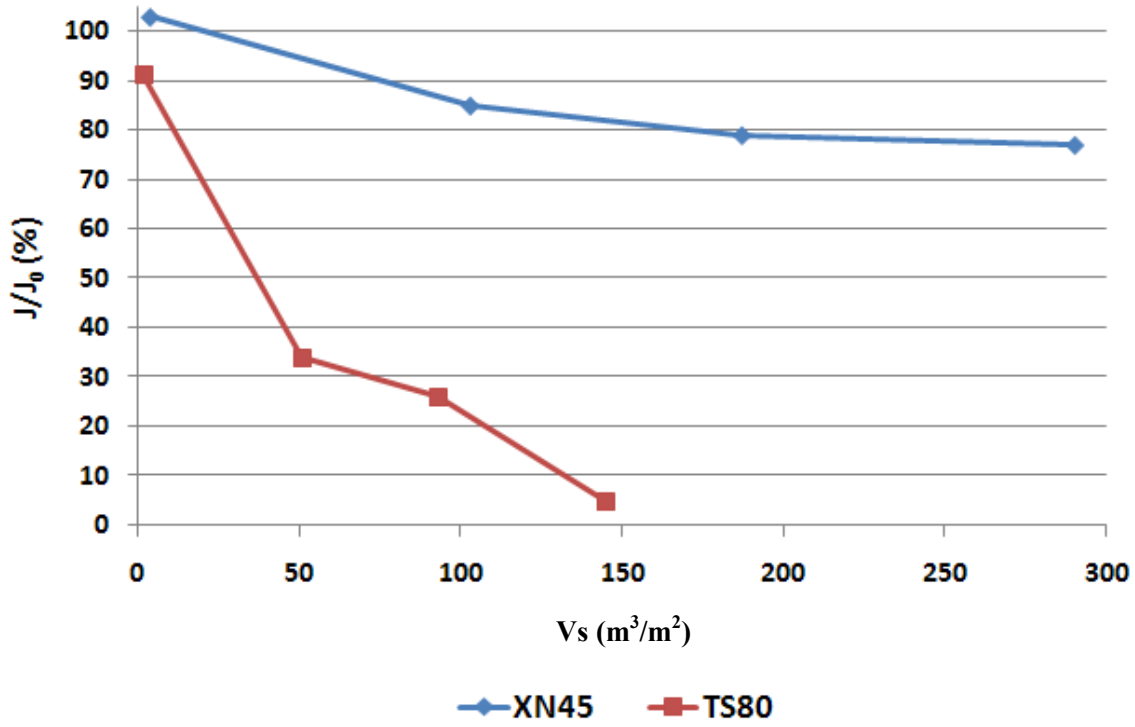
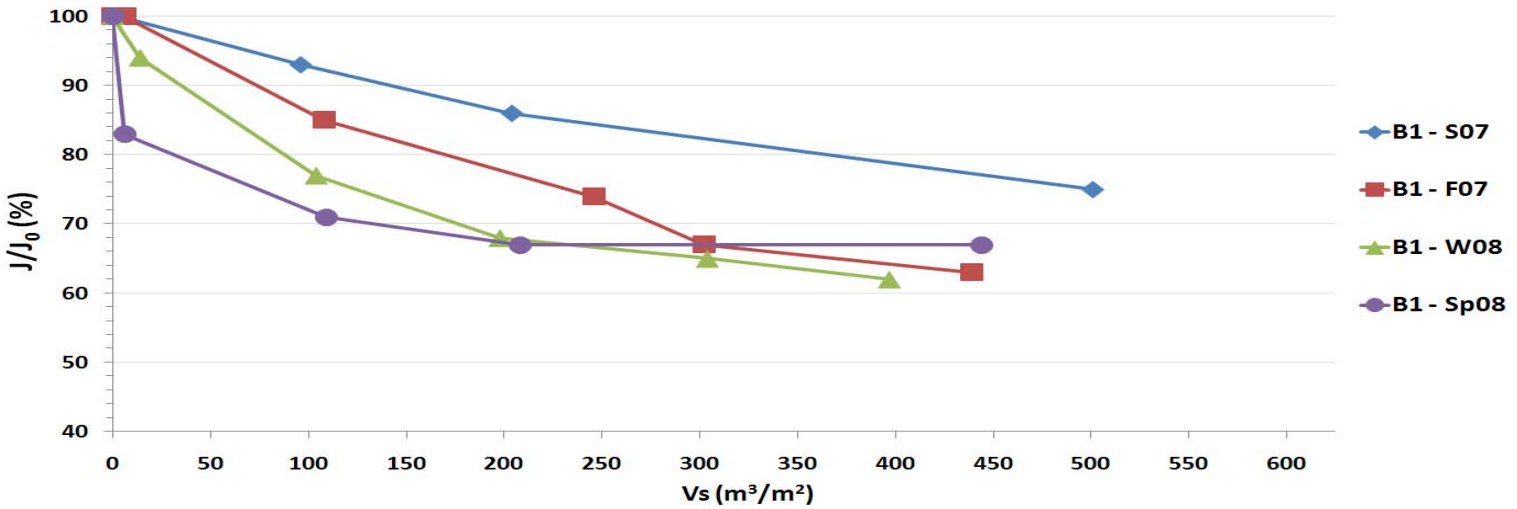


Figure 6-23 Severe flux decline of the TS80 membrane compare to XN45 membrane caused by B2 effluent during summer of 2007

Figure 6.24 presents the flux decline (i.e. flux over initial flux) of the XN45 membrane feed with B1 and B2 effluents at different seasons. The flux decline was measured after 1 h, 24 h, 48 h, 72 h, and 96 h of operation. In Appendix Q, Tables 1 and 2 present the flux decline at corresponding Vs as well as water quality parameters measured during the experiments. In general, except during the fall of 2007, the flux decline using B1 effluent was more severe than using B2 effluent.

a)



b)

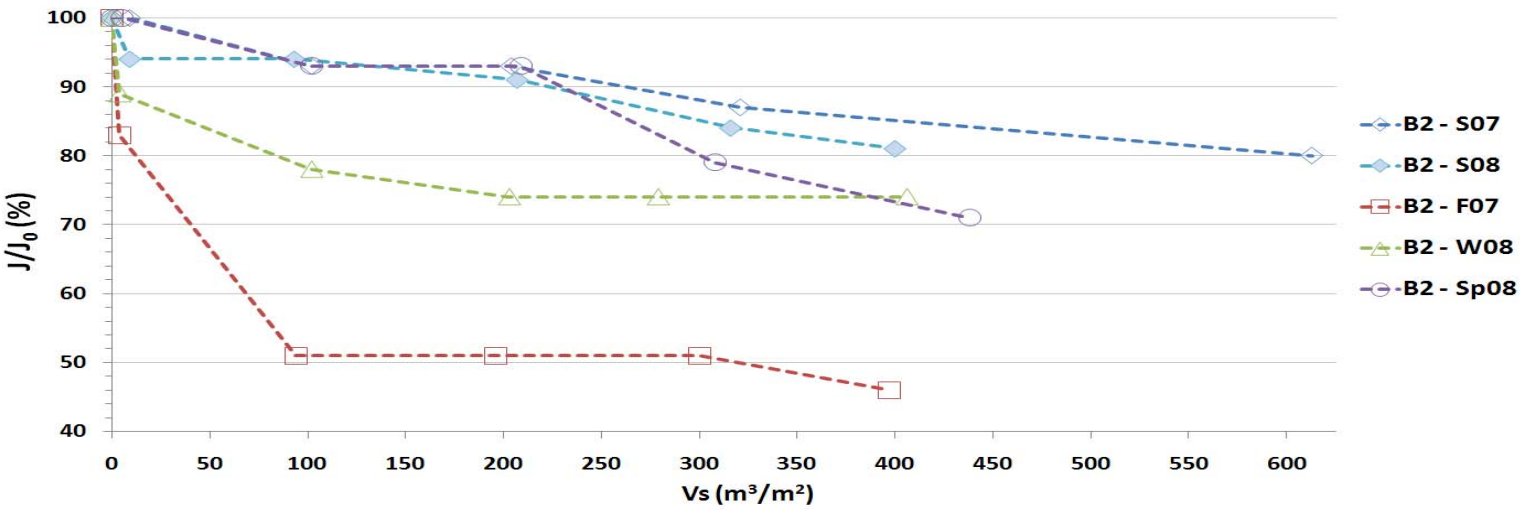


Figure 6-24 Flux decline of XN45 membrane feed with a) B1 effluent and b) B2 effluent at different seasons

The average TOC removals achieved by XN45 using B1 and B2 effluents were respectively 94 ± 4 % and 96 ± 3 %. The average removal of DOC using B1 and B2 effluents were respectively 94 ± 4 % and 95 ± 3 %. High and constant removal of TOC and DOC is an indication of the integrity of the membrane coupon during the experiment duration. As the NF membranes could not be backwashed, rejection TOC and DOC may have caused membrane fouling, leading to flux reduction. The average concentration of TOC and DOC in B1 effluent (e.g. 7.15 ± 1.8 mgC/L and 7.19 ± 1.8 mgC/L) were higher than the average concentration of TOC and DOC in B2 effluent (e.g. 6.17 ± 1.4 mgC/L and 6.19 ± 1.4 mgC/L). Thus higher fouling on NF membrane due to rejection NOM was expected using B1 effluent compared to B2 effluent.

The reductions of SUVA values in membrane permeate also indicate that aromatic molecules (e.g. polysaccharides and humic substances) were being rejected (Appendix Q). The average reduction in SUVA using B1 and B2 effluents were respectively 46 ± 28 % and 37 ± 35 %. The large standard deviation indicates that level of rejection of aromatic molecules changed during the filtration process but no particular trend could be indentified from the results.

As expected, NF membrane achieved rejection of divalent ions. The average reduction in conductivity using B1 and B2 effluents were respectively 23 ± 4 % and 23 ± 3 %. The rejection of ions, may lead to inorganic fouling due to concentration polarization mechanism and cause the precipitation of salt. The reduction of calcium may also indicate the role of the ion in fouling with humic substances.

Particulate and colloidal matter may also be responsible for fouling of NF membranes. The average reduction in turbidity using B1 and B2 effluents were respectively 53 ± 25 % and 54 ± 24 %. The membrane achieved a similar removal percentage of turbidity, however, the average turbidity of B1 effluent was higher (e.g. 0.72 ± 0.6 NTU) than the average turbidity of B2 effluent (e.g. 0.56 ± 0.4 NTU). Thus, the colloidal and particulate fouling of NF membranes is expected to be more pronounced when using B1 effluent as feed, compared to B2 effluent.

The possible mechanisms of fouling occurring on NF due to the rejection of TOC, DOC, turbidity, and ions include: formation of a cake layer, scaling, pore blockage, and/or pore constriction. Further research is necessary to identify the specific fouling mechanism occurring on NF membrane using biofilter effluent.

Figure 6.24a shows that after a short period of operation 24 h, corresponding to a Vs of approximately 100 m^3/m^2, the least flux decline was observed during the summer of 2007 following by fall of 2007, winter of 2008, and spring of 2008. Over a longer period of operation (i.e. approximately 96h or 400 m^3/m^2) the least flux decline was also observed during the summer of 2007 following by spring of 2008, fall of 2007, and winter of 2008. A combination of factors including feed water turbidity, influent TOC and DOC concentrations influenced the flux decline.

In figure 6.24b, at a Vs of 100 m^3/m^2, the least flux decline was observed during the summer of 2007 and 2008 and spring of 2008 following by, winter of 2008, and fall of 2007. Although the fouling experienced during the summer 2008 was slightly more pronounced than the fouling measured during the summer 2007, it remained in the same order of magnitude. This result was expected considering the similar characteristic of the feed water (Appendix Q). However, it is interesting to note that fouling of UF membrane during the summers of 2007 and 2008 were substantially different. During the spring, low fouling was observed at the beginning of the experiment but after Vs of 200 m^3/m^2 the fouling became more pronounced and after Vs of 400 m^3/m^2, the permeate flux decreased by 26 %.

The difference in flux decline between the spring of 2008 and the summer of 2008 experiments can be explained by the higher concentration of BP and HS deposited at the surface of the membrane and further explanation is provided in section 6.4.7.2.

Table 6.3 shows the concentration of DOC, BP, and HS in the membrane influent (e.g. B2 effluent), permeate and foulant material during the summer of 2008 and spring of 2008. Although the DOC was higher during the summer of 2008, the nature of the DOC during the spring of 2008 may have been different and present a greater affinity to the membrane surface causing more fouling. Higher turbidity of the membrane influent during the spring (i.e. 0.7 NTU) compared to 0.4 NTU during the summer of 2008 can also explain the higher rate of flux decline observed during the spring of 2008.

Table 6-3 Comparison of DOC, BP, and HS concentrations during NF experiments during the spring and summer of 2008

	Time	B2 effluent			XN45 permeate			Foulant material		
		DOC	BP	HS	DOC	BP	HS	DOC	BP	HS
	(h)	(mgC/L)								
Sp08	1	4.95	0.08	3.39	0.59	0.00	0.00	na	na	na
NF14	96	na	na	na	na	na	na	5.16	2.25	1.78
S08	1	5.35	0.05	3.66	0.27	0.00	0.00	na	na	na
NF16	96	na	na	na	na	na	na	2.16	0.65	0.76

Using B2 effluent, 74 % of the initial flux was maintained after Vs of 400 m^3/m^2 during the winter of 2008. However, 11 % of the initial flux was lost during the first hour of operation and progressive flux decline was observed. The highest flux decline was observed during the fall of 2007 after Vs of 400 m^3/m^2 where only 48 % of the initial flux was maintained. The rapid flux decline observed during the winter of 2008 and fall of 2007 was attributed to high turbidities of the membrane feed (e.g. 1.70 NTU and 1.21 NTU respectively).

An increase in TOC, DOC, and UV_{254} was observed over time for each NF experiment (Appendix Q). A decrease in turbidity in the feed tank was also measured. This decrease may be explained by the rejection and/or adsorption of particulate and colloidal matter by the membrane. The cause of the change in feed water quality remains uncertain but microbial growth within the set-up and change in the nature of NOM are suspected. The feed water was kept at constant temperature (20 ± 5°C) using a chiller. However, the configuration of the NF set-up contributed to the development of microbial growth because the feed water sits in a tank at approximately 20°C for several days. Moreover, the oversized pump heats the solution momentarily which may alter the nature of the organic matter. During the fall of 2007, HPC measures of B2 effluent and the feed tank were performed after 48 h and 96 h of operation. The results show a slight increase of HPC over time (Table 6.4).

Table 6-4 HPC measurement of B2 effluent (Fall of 2007) and NF feed tank after 48 h and 96 h of operation

Sample	Time (h)	HPC (CFU/mL)	Log increase
B2 – F07	0	$2.45x10^5$	na
Feed tank	48	$3.55x10^5$	0.16
Feed tank	96	$4.00x10^5$	0.21

Moreover, a test was performed to target the cause of organic carbon increase using deionized water as feed water and a fresh and rinsed XN45 membrane coupon (Table 6.5). During this test, an increase in HPCs of 0.22 log was consistent with the increase measured during the Fall 2007 experiment. The TOC and DOC increase were 0.22 mgC/L and 0.09 mgC/L respectively. Lower increase in TOC and DOC may be due to the low initial concentration. No fouling was observed on the membrane surface and similar UV_{254} absorbance was measured after Vs of 398 L/m^2. However, LCOCD analyses showed an increase in humic substances-like material in the feed tank and concentrate but not in the membrane permeate (Figure 6.25). Thus it is suggested that the increase in TOC, DOC, and UV_{254} was due to microbial growth and degradation of the NOM.

Table 6-5 Water quality parameters measured during NF control test with deionized water

Time (h)	Vs (L/m^2)	J/J_0 (%)	TOC (mgC/L)	DOC (mgC/L)	Turbidity (NTU)	UV_{254} (cm^{-1})	HPC (CFU/mL)
1	6	100	0.17	0.23	0.46	$1.32x10^{-3}$	$1.5x10^4$
96	398	100	0.32	0.44	0.44	$1.34x10^{-3}$	$1.0x10^4$

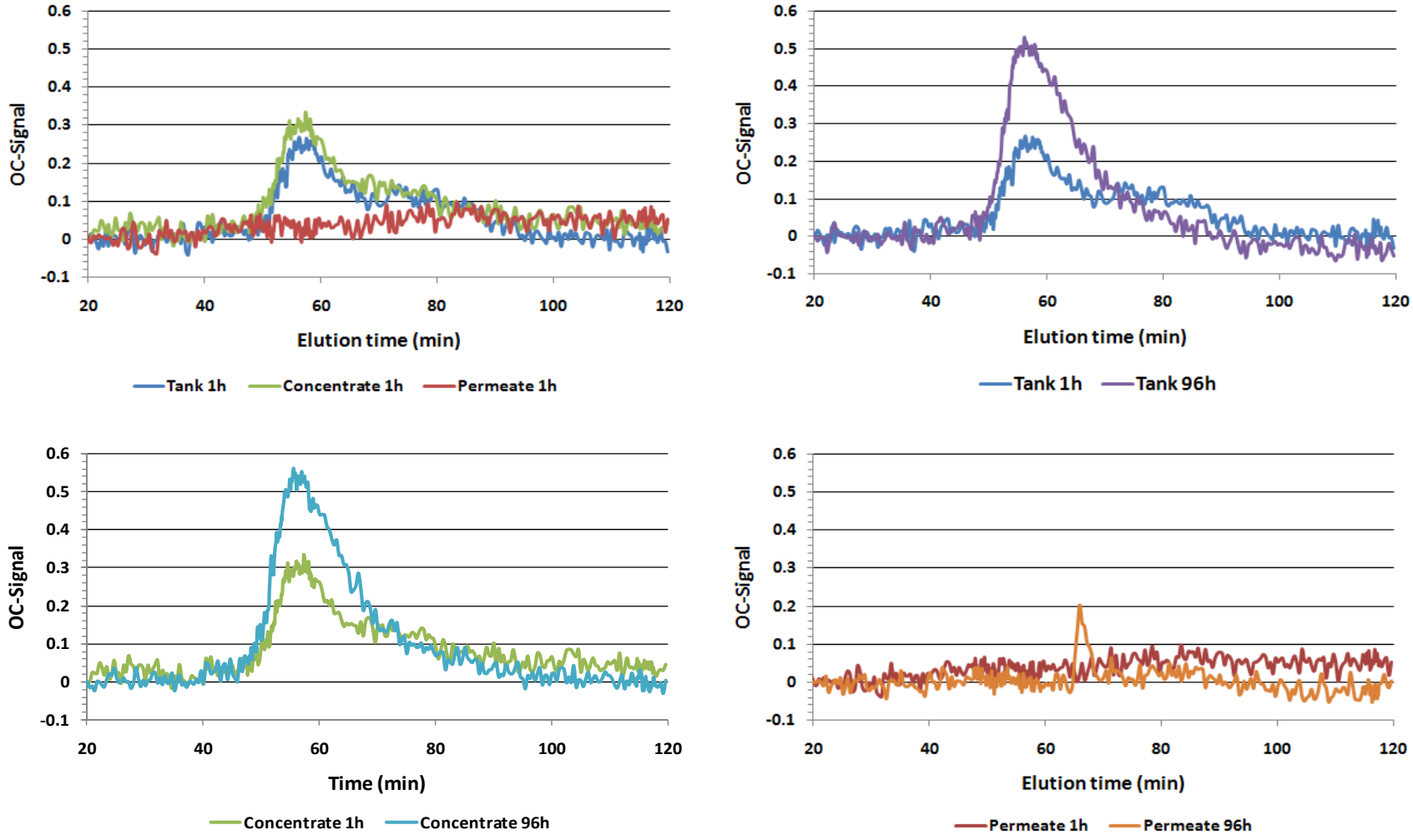
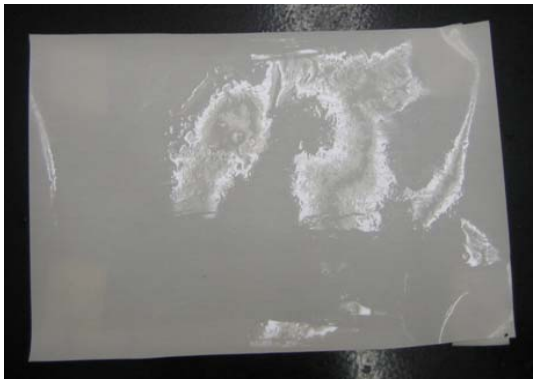


Figure 6-25 LCOCD chromatogram of the NF clean water test

6.4.7.2 Material causing membrane fouling

Figure 6.26a presents a virgin XN45 membrane coupon prior to experiment. Figure 6.26b presents the fouling layer accumulated using B2 effluent during the summer of 2007 (i.e. low fouling). Figure 6.26c presents the fouling layer accumulated using B1 effluent during the fall of 2007 (i.e. high fouling). In Figure 6.26d, the fouling layer deposited during the summer of 2008 using B2 effluent can be visualized. The fouling layer occurring on XN45 membrane was usually brownish and uniformly distributed on the surface of the membrane.

a)



b)

c)

d)

Figure 6-26 Fouling of XN45 membrane a) virgin membrane, b) low fouling using B2 effluent during the summer 2007, c) high fouling using B1 effluent during the fall 2007, and d) low fouling using B2 effluent during the summer 2008

As expected, XN45 and TS80 membranes achieved high rejection of TOC, DOC, ions, and turbidity as shown in Appendix Q.

LCOCD analyses of the membrane feed and permeates shown that during the NF experiments, biopolymers, humic substances, and LMWA were rejected by the membranes (Figure 6.27). High rejection of humic substances was achieved by XN45 and TS80 membranes; however, the TS80 membrane seemed to reject LMWA slightly better than the XN45 membrane as shown in the inset in Figure 6.27. A difference in MWCO of XN45 and TS80 may explain the slightly better rejection of LMWA of TS80 compared to XN45.

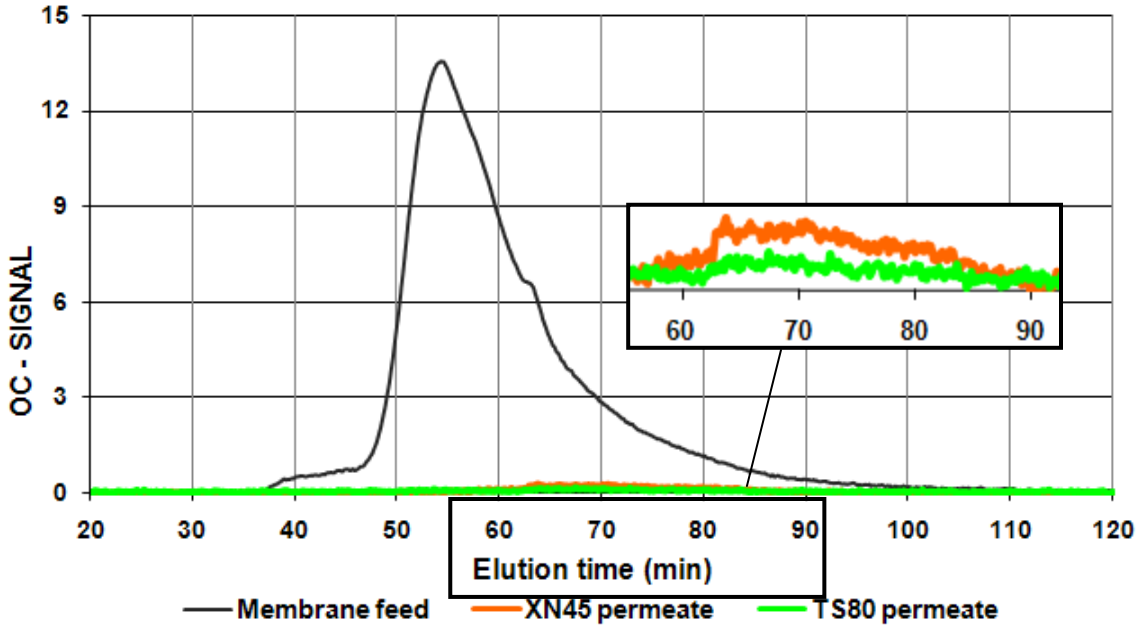


Figure 6-27 Typical LCOCD chromatograms identifying the DOM fraction causing fouling on the NF membranes (NF5)

6.4.7.3 Analysis of the foulant layer

The concentration and accumulation rate of biopolymer and humic substances at the surface of the membrane were calculated during the spring of 2008 (NF 14 and NF15) and summer of 2008 (NF 16A and NF16B) and results are presented in Tables 6.6 and 6.7. The accumulation rate of biopolymer and humic substances on the membrane surface was calculated by dividing the concentrations of biopolymer or humic substances detached from the membrane coupon by the time of operation. The foulant layer was extracted from half of the membrane coupon ($0.014\ m^2 / 2 = 0.007\ m^2$). The coupon was shaken in a stomacher bag with 350 mL of MilliQ water for 5 minutes.

The material detached from to the surface of the membrane coupon was analyzed for TOC, DOC, and LCOCD.

In Table 6.6, the concentration of biopolymer in the membrane influent varied between 0.05 and 0.08 mgC/L. Although the concentration of biopolymer was similar during the Spring and Summer experiments a much higher accumulation rate was observed during the Spring. Using B1 and B2 effluent, the accumulation rate on XN45 membrane were respectively 1.2 and 1.0 mgC/m^2*h during the spring. However, the accumulation rate of biopolymer on XN45 and TS80 membranes during the summer were lower with only 0.3 mgC/m^2*h. These observations indicate that the nature of biopolymer may change seasonally. During spring, the organic matter in Grand River presented a greater affinity for the membrane material than the organic matter present during the summer.

Similarly, the accumulations of humic substances on the membrane surface were calculated (Table 6.7). The concentration of humic substances in the membrane influent during the spring and summer varied between 3.39 to 4.43 mgC/L. As observed for the biopolymers, higher accumulation rate of humic substances on XN45 membrane was observed during the spring compared to the summer.

Moreover during the summer, using B2 effluent with comparable influent concentration of humic substances, higher accumulation rate was measured for TS80 membrane (i.e. 0.7 mgC/m^2•h) compared to XN45 membrane (i.e. 0.4 mgC/m^2*h) which can explain the difference in fouling between the two NF membranes tested.

Table 6-6 Accumulation of biopolymers (BP) on NF membranes

experiment	Membrane	sample	time	LCOCD integration		DOC			Influent conc. of BP	Foulant material	Accumulation rate
			h	TOTAL	BP	mgC/L	mg	mg/m^2	mgC/L	mgC/m^2	mgC/m^2*h
NF14 Fall 08	XN45	B2 Foulant	1 96	3810 3161	63 1381	4.95 5.16	- 1.81	- 258	0.08 na	na 112.7	1.2
NF15 Fall 08	XN45	B1 Foulant	1 96	4939 2780	57 1214	5.82 4.36	- 1.53	- 218	0.07 na	na 95.2	1.0
NF16A Summer08	XN45	B2 Foulant	1 96	4883 1610	42 486	5.35 2.16	- 0.76	- 108	0.05 na	na 32.6	0.3
NF16B Summer08	TS80	B2 Foulant	1 49	5573 623	63 161	5.84 1.04	- 0.36	- 52	0.07 na	na 13.4	0.3

Table 6-7 Accumulation of humic substances (HS) on NF membranes

experiment	Membrane	sample	time	LCOCD integration		DOC			Influent conc. of HS	Foulant material	Accumulation rate
			h	TOTAL	HS	mgC/L	mg	mg/m^2	mgC/L	mgC/m^2	mgC/m^2*h
NF14 Fall 08	XN45	B2 Foulant	1 96	3810 3161	2612 1091	4.95 5.16	- 1.81	- 258	3.39 na	na 89.0	0.9
NF15 Fall 08	XN45	B1 Foulant	1 96	4939 2780	3761 1041	5.82 4.36	- 1.53	- 218	4.43 na	na 81.6	0.9
NF16A Summer08	XN45	B2 Foulant	1 96	4883 1610	3338 568	5.35 2.16	- 0.76	- 108	3.66 na	na 38.1	0.4
NF16B Summer08	TS80	B2 Foulant	1 49	5573 623	3679 394	5.84 1.04	- 0.36	- 52	3.86 na	na 32.9	0.7

Figure 6.28 presents the LCOCD chromatograms of the tank (i.e. feed water), membrane permeate, and foulant material detached from the membrane surface. In general, we observed that BP was the fraction mostly detached from the surface of XN45 membrane. In Figure 6.28a, the OC signal of the first peak suggest the presence of DOC such as particles/biopolymers as foulant material. For the first peak, the UV_{254} pattern shows no absorbance signal suggesting that no aromatic structures were present. Polysaccharides structures are recognized to be linear molecules and therefore do not absorb UV light. Hence, proteins which are likely to contain aromatic amino acids were likely not to be present. The second peak has humic substance-like properties and demonstrated some UV_{254} absorbance.

In Figure 6.28b, the foulant material chromatogram was shifted to the right by approximately 5 minutes. An analytical error may be responsible for this shift because the signal corresponds to the pattern observed for the other analysis. It is reasonable to believe that the peak appearing between 50 and 60 minutes was the BP peak because no UV absorption was observed.

In Figure 6.28 a and b, the influent concentrations of biopolymers were 0.08 mgC/L and 0.07 mgC/L respectively, and the BP accumulation rate were 1.2 mgC/m^2*h and 1.0 mgC/m^2*h. For the same chromatograms, the concentrations of humic substances were 3.39 mgC/L and 4.43 mgC/L respectively and the HS accumulation rate were 0.9 mgC/m^2*h for both experiments. A similar accumulation rate of BP and HS at the surface of the membrane suggests that similar fouling would be observed by the biofilter effluents. In fact, Figure 6.24 shows similar fouling after a Vs of 450 m^3/m^2 the flux declined by 33 % and 29 % using B1 and B2 effluent respectively during the spring.

In Figure 6.28c (summer 2008 using B2), the LCOCD chromatogram shows that less BP was detached from the surface of the membrane than during the spring experiments. This observation supports the fact that a lower accumulation rate of BP was calculated during the summer for XN45 membrane. Similar conclusions could be drawn regarding HS. The accumulation rates of BP and HS during this experiment were respectively 0.3 and 0.4 mgC/m^2*h. The similar accumulation rate for both type of organic material was supported by the comparable LCOCD peak intensity.

The comparison of figure 6.28 c and d show that less BP and HS were detached from TS80 membrane compare to XN45 membrane during the NF16A and NF16B experiments. This result was expected because of the duration of the experiment; 96 h for XN45 membrane compare to 49 h for TS80 membrane. The accumulation rate of BP for both XN45 and TS80 membranes are the same during the summer of 2008. However, higher accumulation rate of HS is observed for TS80 (i.e. 0.7 mgC/m^2*h) compare to XN45 (i.e.0.4 mgC/m^2*h). Thus higher fouling observed on TS80 may be due to larger accumulation of HS rather than BP.

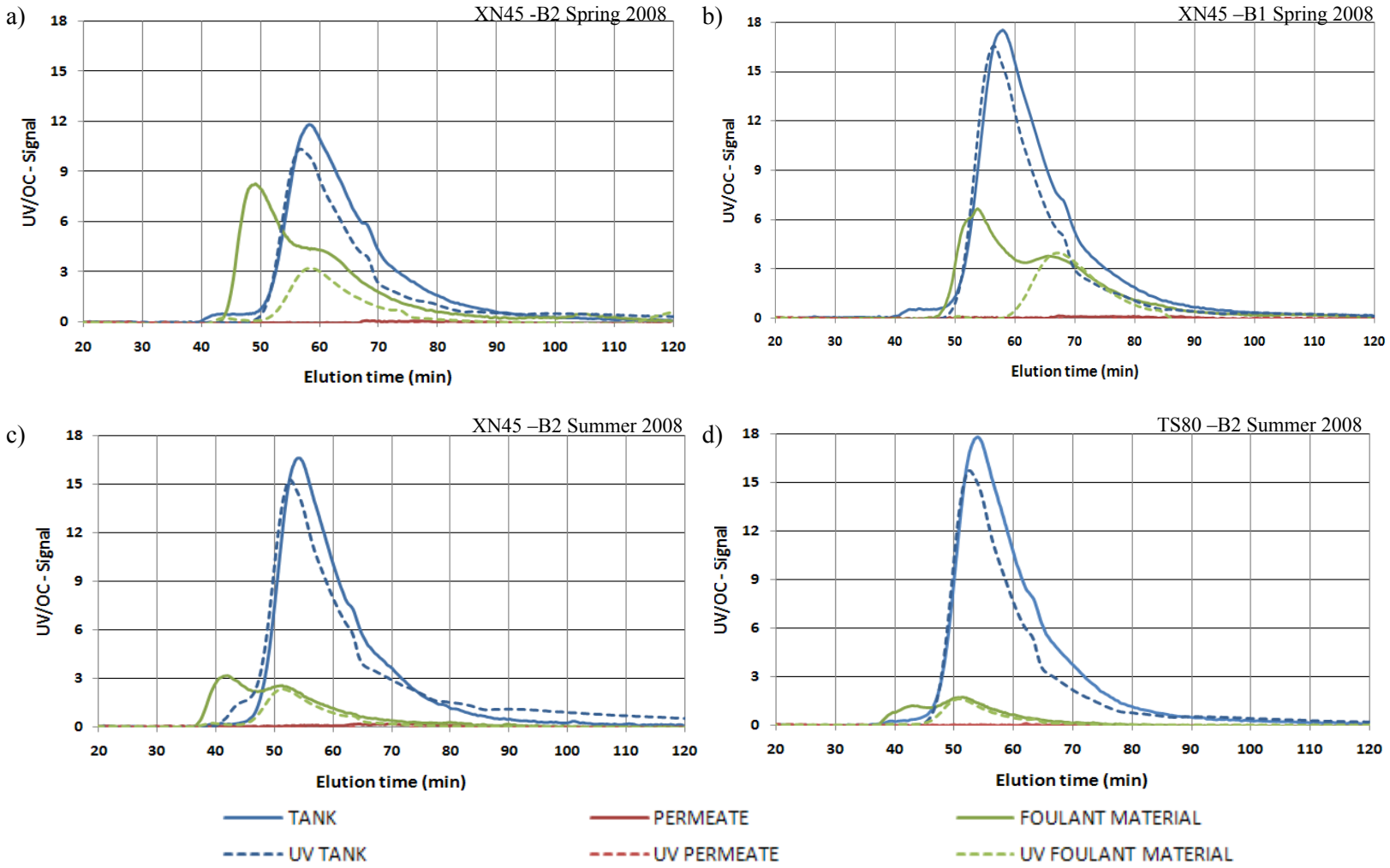


Figure 6-28 Identification of the foulant material during NF experiment a) XN45 feed with B2 effluent during the spring 2008, b) XN45 feed with B1 effluent during the spring 2008, c) XN45 feed with B2 effluent during the summer 2008, and d) TS80 feed with B2 effluent during the summer of 2008

The analysis of NF membrane permeates (i.e XN45 and TS80) with very low level of NOM (between 0.30 and 1.30 mgC/L) demonstrate the strength of EEM analysis. Unlike the weak LCOCD signal, the fluorescence EEM for the permeated of NF membranes contained spectral details demonstrating the sensitivity of the technique at low concentration. For example, in EEM spectra the protein-like substances peak (β) was more clearly noticeable in TS80 permeate than in XN45 permeate. These results show that the composition of NOM in XN45 and TS80 permeates is different (Peiris *et al.*, 2008). Thus EEM is a very sensitive analysis allowing the characterization of low concentration of NOM. Therefore, the use of fluorescence EEM was able to provide warning of high membrane fouling on NF and UF membrane after only one hour of operation (Peiris *et al.,* 2010). In general, a decrease in removal of particulate/colloidal-like material by the biofilters was linked to high membrane fouling events. Conventional turbidity measurements made at the same time did not provide warning of these high fouling events. Finally, in contrast to chromatographic methods, fluorescence EEM can provide a near real-time monitoring.

Using fluorescence EEM, score plots of PC-1 (humic substances) and PC-2 (particulate and colloidal material) confirmed the high rejection of rejection of humic substances by NF membranes (Figure 6.29) (Peiris *et al.*, 2010). The narrow confidence interval of XN45 indicates consistent quality of permeate which is also a sign of test integrity.

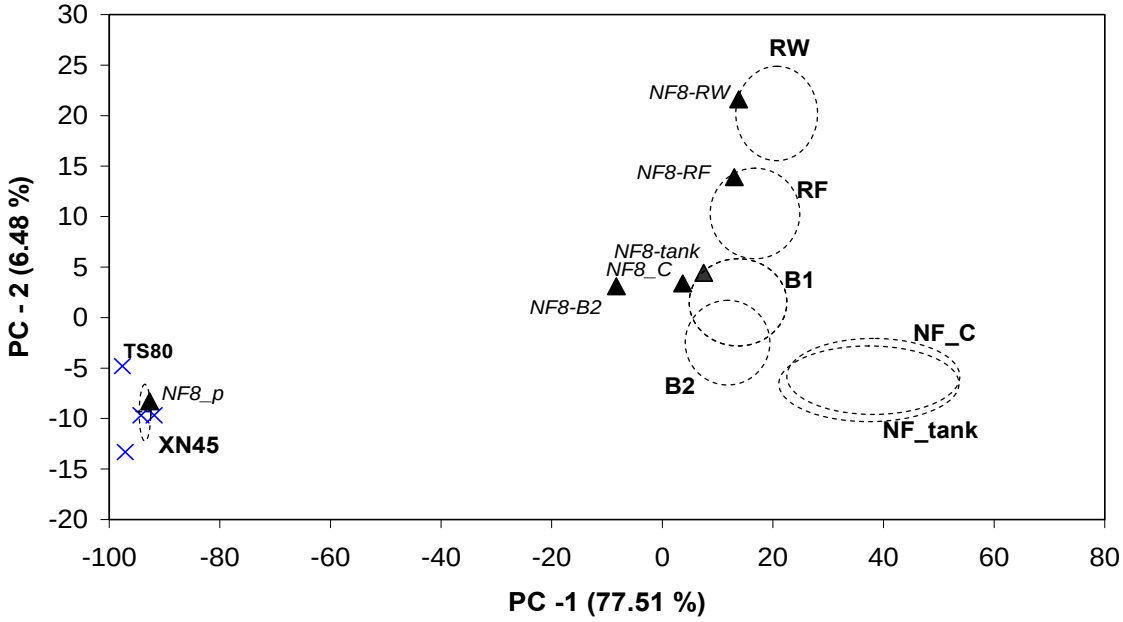


Figure 6-29 Score plot of PC - 2 vs. Pc - 1. Scores of PC - 1 and PC – 2 are grouped and named based on the sampling location. These groups are indicated by dashed-circles based on the 95 % confidence interval regions of the scores in each group. NF8 indicates a high fouling event captured within a 1 hour of operation of the NF membrane (source: Peiris *et al*., 2010)

Score plots of PC-3 (protein-like material) and PC-2 (Figure 6.30) confirms that protein-like materials were rejected by the NF membrane. The small 95 % confidence interval of the NF permeate also indicates a constant permeate quality. From Figure 6.32, the results show that the TS80 membrane tended to reject protein-like material better than the XN45 membrane. This may be due to a greater affinity of protein-like material for the TS80membrane surface or a higher rejection due to a tighter pore size of the TS80 membrane.

Figures 6.29 and 6.30 show that the rejection of particulate and colloidal material by NF membranes was negligible which contradict the turbidity analyses. Further investigations are necessary to explain the differences.

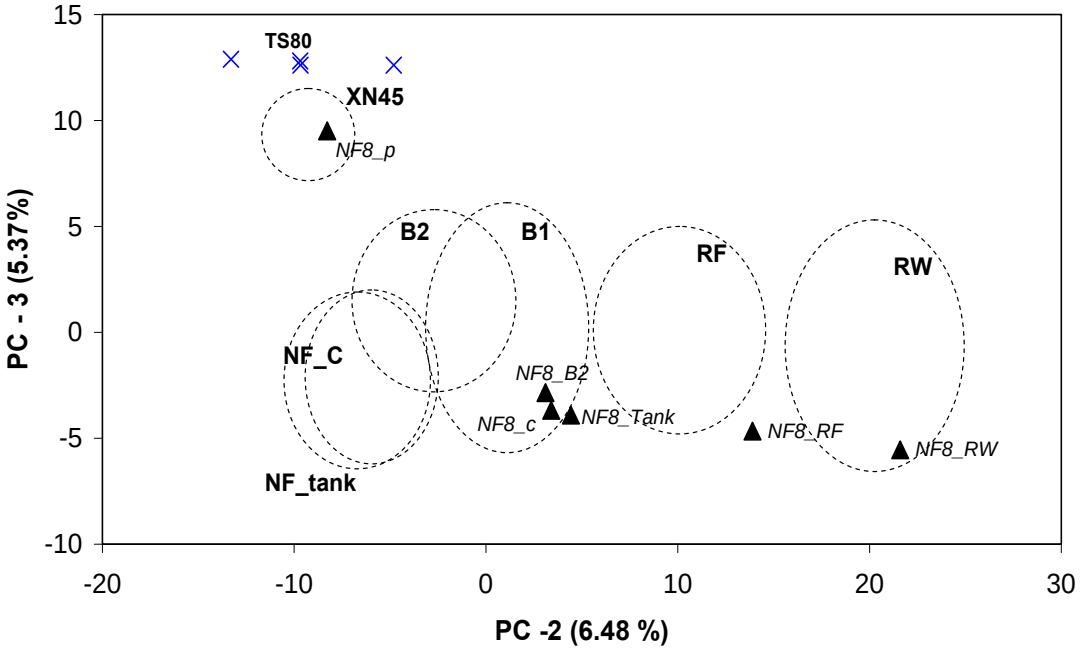


Figure 6-30 Score plot of PC - 3 vs. Pc - 1. Scores of PC - 2 and PC – 3 are grouped and named based on the sampling location. These groups are indicated by dashed-circles based on the 95 % confidence interval regions of the scores in each group. NF8 indicates a high fouling event captured within a 1 hour of operation of the NF membrane (source: Peiris *et al*., 2010)

In summary, based on the finding from LCOCD analysis, biopolymers and humic substances were rejected by XN45 and TS80 membranes. The analysis of the foulant layer shows that both biopolymers and humic substances can be detached from the surface of the membrane. Results also demonstrate that the accumulation of biopolymers and humic substances on the surface of the membrane varied seasonally and the type of membrane may influence the rate of accumulation.

Based on the finding from fluorescence EEM, humic substances and protein-like material were rejected by both NF membranes. However, only a slight reduction of particulate and colloidal matter by NF membranes was observed.

6.4.8 Integrated Membranes System

The performance of an integrated membrane system (e.g. biofiltration-ultrafiltration-nanofiltration) was evaluated during the summer 2008. Table 6.8 summarizes the effect of pretreatment to control the fouling of NF membranes.

Table 6-8 Effect of pretreatment to control fouling of NF membrane

Pretreatment	**Type of fouling**			
	Particulate	Organic	Biological	Scaling
Rapid biological filtration	+	+	+	-
UF	++	+/-	+/-	-
Rapid biological filtration + UF	++	+	++	-

++ very positive; + positive; +/- variable; - no effect

Rapid biological filtration pretreatment presents positive effect on the control of particulate, organic, and biological fouling of NF membranes. In fact, this study shows that biofiltration was an effective pretreatment to remove particulate and colloidal matter. Biofilters can also reduce the concentration of HPC, TDCC, and ATP reducing potential biofouling and organic fouling on subsequent membrane filtration. Furthermore, biofilters can reduce the concentration of biopolymer and protein-like material recognized as foulant. However, no effect on the control of scaling of NF membranes by the rapid biological filtration was observed. UF pretreatment presents very positive effect to control particulate fouling on NF membrane. Variable degree of control of organic and biological fouling was expected depending on the membrane and condition of operation used. No effect on the control of scaling of NF membranes by the UF membrane is expected. Using the combination of rapid biological filtration and UF membrane, very positive or positive control of particulate, organic, and biological fouling was expected. No control of scaling was expected by the combination of both pretreatment.

As demonstrated in section 6.4.7, biofiltration alone may not be an efficient pretreatment for NF to prevent flux decline. Thus, the addition of ultrafiltration prior to nanofiltration had the goal to reduce the flux decline of NF membranes by reducing particulate and colloidal matter in the NF membrane influent. Figure 6.31 presents the flux decline as a function of the specific volume for TS80 and XN45 membranes feed either by B2 effluent or UF permeate.

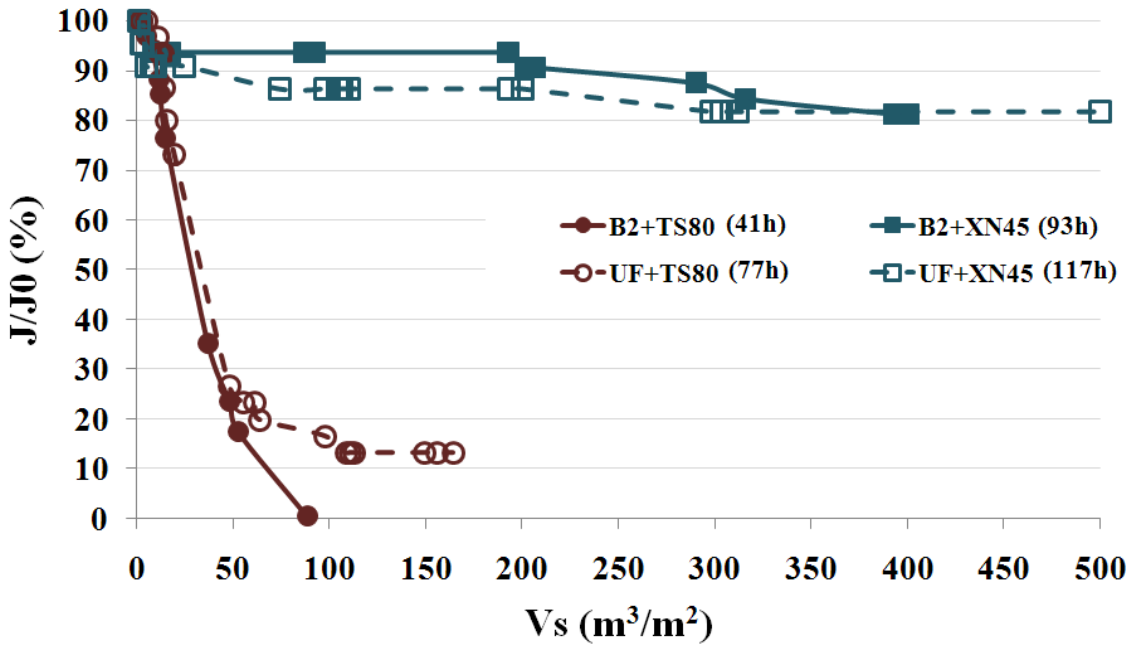


Figure 6-31 Impact of integrated membrane system on the flux decline of XN45 and TS80 membranes

For the TS80 membrane, the flux decline observed using B2 effluent or the UF permeate was similar until a Vs of 50 m^3/m^2. At Vs greater than 50 m^3/m^2, less fouling was observed using the UF permeate as feed water to NF membrane. Using UF permeate as feed, the flux decline stabilized after a Vs of 100 m^3/m^2. These results indicate that for TS80 the removal of biopolymer and turbidity in the membrane feed is not influencing the fouling between a Vs of 0 and 50 m^3/m^2. However, their removal seems to improve long term operation. However, the improvement in flux decline is only 12 % using the combination of pretreatment. These results suggest that two fouling mechanisms occurred for TS80. In the early stage, between Vs of 0 and 50 m^3/m^2 fouling may be dominated by

pore blockage and in the later stage fouling may be dominated by cake formation as observed by Haberkamp *et al.* (2007).

For the XN45 membrane, the flux decline using both B2 effluent and UF permeate were similar. After Vs of 400 m^3/m^2 the flux declined by 20 % using both type of feed water. Thus using a combination of rapid biological filtration and UF membrane for long term operations is not improving flux decline.

6.5 Conclusions

This study demonstrated the application of chemical-free rapid biological filtration pretreatment to reduce fouling of subsequent ultrafiltration and nanofiltration membranes for drinking water applications. The pretreatment consisted in a roughing filter followed by biofiltration. Two biofilters with empty bed contact time (EBCT) of 5 and 14 minutes were investigated over a period of two years. The biofiltration pretreatment demonstrated its capacity to remove organic material which was identified as a membrane foulant:

- The biofilter with 5 minutes EBCT (B1) achieved on average 13 % and 11 % removal of TOC and DOC. Higher removals of TOC and DOC were achieved with the biofilter with 14 minutes EBCT (B2) with respectively 19 % and 16 % removal. The impact of EBCT was also noticeable regarding the removal of turbidity. On average, lower turbidities were measured in the effluent of B2 (0.38 ± 0.4 NTU) compared to B1 (0.47 ± 0.5 NTU).

- LCOCD analyses of Grand River identified three distinct fractions of dissolved organic matter. Biopolymers were the fraction with the highest molecular weight, humic substances were the major constituents of the dissolved organic matter, and low molecular weight acids (LMWA) were also identified. The concentration of biopolymers in Grand River varied seasonally between 0.10 mgC/L to 0.53 mgC/L, with the highest concentration measured during the summers. The concentrations of humic substances varied from 3.55 mgC/L to 4.92 mgC/L. Finally, the concentration of LMWA varied between 0.39 and 0.54 mgC/L.

- LCOCD profiles of the Grand River and biofilter effluents demonstrated that biopolymers were the fraction of dissolved organic matter removed to the greatest extent during biofiltration. Average removals for B1 and B2 were respectively 40 ± 26 % and 61 ± 22 %. Generally, lower removals of humic substances were observed by biofiltration but removals up to 30 % have been measured.

- Fluorescence excitation/emission matrix (EEM) combined with principal component analyses were also shown to be a useful tool to monitor the performance of biofiltration pretreatment. Three principal components (PCs) were able to describe 88.9 % of the variation of data contained in the 3D organic matter EEMs. The first PC was related to humic substances, the second PC was related to particulate and colloidal matter, and the third PC was inversely related to the protein-like content in water. Fluorescence EEM analyses qualitatively showed removal of particulate and colloidal matter during pretreatment. Slight removal of humic substances and protein-like material by biofiltration was also detectable by fluorescence EEM.

Moreover, one of the main concerns with using biological filtration for membrane pretreatment was the release of microbial material by the biofilter. The removal of microbial material content from feed water is crucial to reduce biofouling and organic fouling on subsequent membrane filtration processes. Monitoring of heterotrophic plate count (HPC), adenosine 5'-triphosphate (ATP), and total direct cell count (TDCC) of the biofilter influent and effluent allowed the following conclusions:

- An acclimation period of 133 days was necessary before removal of HPC and TDCC was observed and an acclimation period of 98 days was necessary before removal of ATP was observed.

- The concentration of ATP in Grand River varied between 3.0×10^{-4} to 6.8×10^{-3} μM. The removal of ATP improved as the water temperature became warmer. B1 and B2 removed respectively up to 2.1 and 2.4 log of ATP. The concentration of HPC in Grand River varied between 7.5×10^{3} to 2.1×10^{6} CFU/mL. B1 and B2 removed respectively up to 1.7 and 2.5 log of HPC. Finally, the concentration of TDCC in Grand River was fairly constant but varied between 2.2×10^{5} to 8.5×10^{6} cells/mL. Both B1 and B2 removed up to 1.4 log of TDCC.

- These results indicated that not only were microbial products not released but significant removal of ATP, HPC, and TDCC was achieved by the biofilters. Consequently, biofiltration pretreatment for membrane filtration can potentially control biofouling and organic fouling.

The use of biofiltration pretreatment to control fouling of low pressure membranes e.g. ultrafiltration (UF) membranes allowed the following conclusions to be drawn:

- Using untreated Grand River water (i.e. effluent of the roughing filter) as feed for the UF membrane was not a sustainable approach. Severe reversible and irreversible fouling was observed. The maximum TMP of 9 psi was reached after a specific volume of 1450 L/m^2.

- Pretreatment (i.e. roughing filter followed by biofilter with either 5 or 14 minutes EBCT) significantly reduced the TMP required to keep a constant permeate flux. Using B1 effluent as UF feed, both reversible and irreversible fouling were decreased as indicated by an overall TMP increase of only 4 psi after a specific volume of 7500 L/m^2. Using B2 effluent, only very low reversible fouling was observed during a cycle and very little irreversible fouling was observed as indicated by a TMP increase of only 1 psi after a specific volume of 6000 L/m^2.

- As expected the UF membrane did remove turbidity (i.e. particulates and colloidal matter) but was insufficient for the removal of TOC, DOC, conductivity, and UV_{254}. Moreover, the LCOCD analyses showed that on average biopolymers and humic substances were rejected at 56 % and 2 % respectively. These results suggested that biopolymers constituted the major fraction of dissolved organic matter causing fouling of the UF membrane. Particulates and colloidal matter may have also contributed to UF membrane fouling.

- The different degree of reduction of hydraulically reversible fouling was primarily attributed to the absolute concentration of biopolymers in the biofilter effluent. Consequently, lower hydraulically reversible fouling was measured using B2, the filter with the higher biopolymer capability.

- For sustainable membrane operation the control of irreversible fouling is more important. This study showed that substantially lower irreversible fouling occurred when the UF membrane was fed with B2. These results showed that the composition of the biopolymers rather than their absolute concentration was important for the control of irreversible fouling.

- The performance of the biofilters to control fouling of UF membranes showed seasonal variations. Better performances were generally observed during the summer when the microbial activity within the biofilters was at their maximum which favours the biodegradation of the organic foulant material. Under cold water conditions the performance of the biofilters decreased.

- Further investigations on the impact of biofilter backwash on membrane performance must be performed. Backwash of the biofilter may lead to an increase of reversible and irreversible fouling for example if the filter to waste time is insufficient.

The use of biofiltration pretreatment to control fouling of high pressure membranes e.g. nanofiltration (NF) membranes allowed the following conclusions to be drawn:

- Biofiltration was able to achieve adequate fouling control on the looser NF membrane investigated (XN45). However, biofiltration was not sufficient to control fouling of the tighter NF membrane (TS80).

- As shown by LCOCD analyses both XN45 and TS80 membranes rejected biopolymers, humic substances, and LMWA. However, a difference in MWCO between the XN45 and TS80 membranes may explain the slightly better removal of LMWA by the TS80 compared to the XN45.

- In general, less fouling was observed on the XN45 membrane using the B2 effluent compared to B1 effluent. These results suggest that better removal of turbidity and biopolymers may improve filterability of the XN45 membrane.

- Fluorescence EEM analyses confirmed the rejection of humic substances and protein-like material by the NF membranes. However, negligible removal of particulate and colloidal matter measured by fluorescence EEM contradicted results from the turbidity analysis.

The effect of an integrated membrane system (i.e. rapid biological filtration and UF membrane pretreatment followed by NF) to control fouling of the NF membrane was evaluated as follows:

- For the XN45 membrane, the flux decline was similar when using either the B2 effluent alone or the B2 effluent treated by the UF membrane. These results suggest that humic substances were the main fraction of dissolved organic material causing fouling on the XN45 membrane.

- For the TS80 membrane, flux declines during the early part of the experiment were similar when using either B2 alone or B2 treated by UF. In the later stages, less fouling was observed for the combination of B2/UF. However, only a 12 % improvement in flux was achieved compared to B2 pretreatment alone. This indicated that at the later stages the B2/UF combination was able to control the predominant fouling mechanism to some degree.

Chapter 7

REMOVAL OF PhACs AND EDCs BY MEMBRANE FILTRATION

7.1 Introduction

The presence of contaminants in sources of drinking water has been established and sustainable treatment processes may be required for their removal. Studies show that membrane filtration is an important technology for drinking water treatment and indirect water reuse. Several studies investigated the rejection mechanism of trace organic contaminants by membrane filtration and demonstrated that the main processes are size/steric exclusion, hydrophobic adsorption, and electrostatic repulsion. With charged compounds electrostatic repulsion is the main rejection mechanism while with uncharged compounds steric hindrance is the predominant rejection mechanism (Berg *et al.*, 1997).

Several authors showed that complete or near complete removal of contaminants in secondary effluents can be achieved by NF membranes (Nghiem *et al.*, 2004b; Bellona *et al.*, 2004; Van der Bruggen *et al.*, 2003). Also the removal of 36 PhACs and EDCs by NF and RO membranes at pilot- and full-scale has been demonstrated for the treatment of wastewater and drinking water (Snyder *et al.*, 2007). However, these results should be interpreted carefully and should not be extended to all trace organic contaminants. As observed by Nghiem *et al.* (2004a) natural steroid hormones can adsorb on the membrane surface and subsequently diffuse through the membrane. This process may lead to lower rejection than those predicted based on the steric exclusion mechanism. Moreover, the rejection of trace organic contaminants by membranes is highly dependent on the physicochemical properties of the compounds, which are influenced by the solution chemistry. The separation of ionic

species by NF membranes is controlled by both steric exclusion and electrostatic interactions (Childress *et al.*, 2000). Thus the change on the membrane surface may play a critical role in the rejection charged organic trace contaminants.

Very high removals of organic micropollutants are generally observed with NF membranes since the MWCO values of the membranes are often in the same range or smaller than the molecular weight value of the contaminants. Other mechanisms of rejection such as electrostatic repulsion between the charged solutes and a membrane also occur during membrane filtration (Childress *et al.*, 2000; Xu and Lebrun, 1999; Wang *et al.*, 1997). In general, the negative surface charge of the membrane is favoring the rejection of negatively charged compounds and foulant material (Shim *et al.*, 2002; Xu and Lebrun, 1999). The negative surface charge of the membrane at neutral pH is generally caused by deprotonated sulfonic or carboxylic functional groups (Bellona *et al.*, 2004).

Ultrafiltration membranes are not expected to achieve high rejections of PhACs and EDCs because the MWCO or pore size is larger than the MW of the compound. Consequently, the rejection by size exclusion is not taking place. However, during wastewater treatment, the rejection of estrone from raw sewage and secondary effluent by UF membranes has been demonstrated by Schafer *et al.* (2002).

For drinking water treatment, only a few studies consider the influence of natural water on the rejection of PhACs and EDCs by membranes. Fouling of membranes by NOM may influence the rejection of trace organic contaminants by modifying the surface charge of the membrane, causing pore restriction, and enhance concentration polarization (Nghiem and Hawes, 2009). The characteristic of the source of water (i.e. ionic strength and nature of NOM) can also influence the rejection of organic trace contaminants.

Yoon *et al.* (2006) studied the rejection of 52 EDCs and PhACs by NF and UF membranes and found a decrease in their rejection when NOM concentrations increased due to competition for membrane adsorption sites. However, during this study, filtration tests were run under non-equilibrium conditions and membrane adsorption sites may not have been exhausted. Nghiem *et al.* (2005) demonstrated that the rejection of bisphenol A, nonylphenol, and *tert*-butylphenol increased when 10 mg/L of NOM and 10 mM of NaCl were added to synthetic water. Moreover, membrane

fouling by NOM may result in an apparent increase in trace contaminants rejection due to adsorption on the fouling layer (Agenson *et al.*, 2007; Xu *et al.*, 2006).

Increased rejection may also be the result of the binding of trace organic contaminants to NOM due to hydrogen bounds. Complexation between NOM and contaminants create larger molecule and tend to increase the negative charge of the complex. Consequently, the affinity for adsorption with the membrane compared with the compound itself is modified and rejection of contaminants may increase (Plakas *et al.*, 2006; Devitt *et al.*, 1998).

The presence of cations (i.e. ionic strength) can influence the surface charge of the active layer of the membrane thus change the interaction of compounds and NOM with the membrane surface. Devitt *et al.* (1998) studied the removal of atrazine by NF and UF membranes. They observed that atrazine-NOM complexes decreased in the presence of cations such as Ca^{2+}. (Cho *et al.*, 2000; Devitt *et al.*, 1998; Jucker *et al.*, 1994).

7.2 Objectives

The objectives of the study presented in this chapter were to:

- Demonstrate the rejection of selected PhACs and EDCs by UF and NF membranes using natural water.
- Determine the rejection of selected PhACs and EDCs over a period of 5 days.
- Evaluate the impact of membrane fouling on the rejection of selected PhACs and EDCs.
- Determine and compare the rejection efficiencies of two NF membranes.

7.3 Material and Methods

7.3.1 Feed Water and Contaminant Concentration

The effluent of the biofilters was used in this project as feed water for the UF and NF membranes. Selected contaminants were spiked in the biofilters influent as described in Chapter 5. Consequently the concentration of contaminants in the membrane influent varies depending on their degree of biodegradability. Because of the impossibility to spike nonylphenol into the biofilter influent, this contaminant has been added in NF feed tank prior to the experiment.

7.3.2 Membranes

UF and NF membranes described in Chapter 3 were used for this project. The operating conditions were the same as described in Chapter 6.

Rejection of trace organic contaminants by UF and NF modules is defined as:

$$R = 1 - \frac{c_P}{c_F} \qquad \text{e.q. 7.1}$$

Where
c_P is the concentration in the permeate
c_F is the concentration in the feed

7.3.3 Trace Organic Contaminants Analysis

The analysis of PhACs and EDCs were performed following the method described in Chapter 4.

7.3.4 Sampling

During the UF experiments, the sampling for PhACs and EDCs analysis was performed once, generally after 48 h of operation. Water quality parameters (i.e. pH, turbidity, conductivity, TOC, DOC, UV_{254}, fluorescence, pH, and LCOCD) were performed as presented in chapter 6. For PhACs and EDCs analysis, two clean glass bottles of 0.5 L were rinsed and filled with membrane permeate and biofilter effluent (i.e. membrane feed) . The bottles were returned to the UW lab and stored at 4ºC prior to analysis.

For the NF experiments, the sampling procedure for PhACs and EDCs analysis was the same as for the UF experiments except sampling frequency was increased. Samples were taken after 1 h, 48 h, and 96 h of operation.

7.4 Results and Discussion

7.4.1 System Loss Test

The adsorption of relatively hydrophobic compounds (e.g. Log K_{ow} > 3.0) by NF and UF membranes has been demonstrated in previous study (Nghiem *et al.*, 2004a; Yoon *et al.*, 2004; Kimura *et al.*, 2003a). Because the selected contaminants are being spiked at low concentrations possible loss on the experimental set-up was a concern and was therefore evaluated. The system loss test was performed without the membrane in the set-up in order to avoid adsorption into the membrane.

A 22-hours system loss test was performed on the UF set-up. The concentration of selected PhACs and EDCs at the influent and effluent of the experimental set-up was measured. Data of system loss tests are presented in Appendix R. The results show that DEET, ibuprofen, atrazine, and naproxen were essentially not adsorbed in the UF set-up (the influent and effluent concentrations varied by less than 14 % which may be due to analytical variances). Release of carbamazepine up to 35 % after 8 h of operation has been measured. Nonylphenol was completely adsorbed on the experimental set-up after 8 h of operation. As reported in section 3.3, the Log K_{ow} value of the selected compounds is below 3 except for NP which is 5.92. Thus the system loss test results are consistent with the results previously published (Nghiem *et al.*, 2004a; Yoon *et al.*, 2004; Kimura *et al.*, 2003a).

A 120-hours system loss test was performed on the NF set-up. The concentration of selected PhACs and EDCs in the feed tank were measured every 24 h. The results obtained were inconsistent with the other experimental data. Results for nonylphenol were consistent in that much lower concentrations than expected were measured due to complete loss on the experimental set-up. As a consequence nonylphenol was not further investigated. For the other less hydrophobic compounds,

adsorption was assumed to be minimal since the NF set-up was made exclusively of stainless steel and Teflon.

7.4.2 Ultrafiltration

Figure 7.1 shows the average percentage rejection of selected contaminants achieved by UF membrane. The error bars indicate the standard deviations which vary between 9 and 19%. In most cases, the concentration in the feed and permeate are similar and these results confirm the low level of adsorption on the membrane and instrumental set-up. Moreover, Figure 7.1 indicates that no significant removal of the selected compounds was observed using the Zeeweed-1® membranes. The average removal of naproxen, ibuprofen, and DEET are respectively 5, 4 and 1 %. In average, no removal was observed for both atrazine and carbamazepine. The influent concentration of the contaminant which varied between high and low levels did not statistically influence the removal. Similar results were obtained by Snyder *et al.* (2007) when using fouled UF membrane (Ionics^{TM} and ZeeWeed^{TM} 1000) to treat secondary and tertiary effluents. Yoon *et al.* (2006) who studied the removal of 52 compounds by UF membranes (GM, Desal-Osmonics, USA) having a MWCO of 8000 ± 1000 Da showed that retained compounds were hydrophobic and that the main rejection mechanism was adsorption.

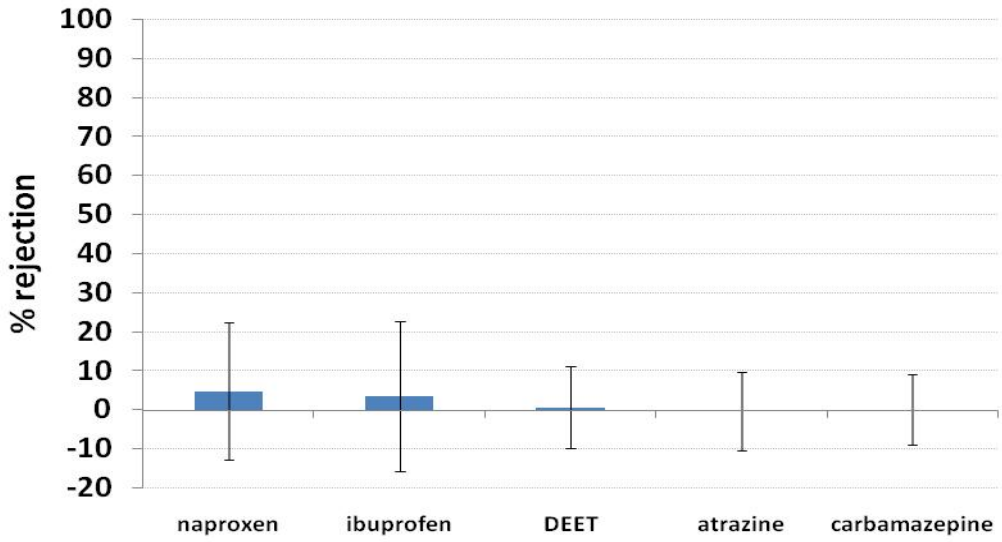


Figure 7-1 Removal of selected PhACs and EDCs by UF membrane

A previous study showed that the retention of trace organic contaminant may vary depending on the feed water properties such as DOC, SUVA, pH, and conductivity (Yoon *et al.*, 2006). They found that UF membranes have better retention of trace contaminants with feed water having relatively low pH and high conductivity, while the worst retention of trace organic contaminant was obtained with a source water having a high DOC and high SUVA value. During our study, the water quality varied depending on the season, thus the relatively large standard deviation may be attributed to variations of the feed water properties.

In this study, the impact of membrane fouling on the rejection of the selected trace contaminant is difficult to establish mainly because of the low level of rejection. No clear trend indicates an increase or decrease of rejection as membrane fouling occurs.

In Appendix S, the influent and permeate concentrations of the selected PhACs and EDCs are available for the 13 experiments performed with the Zeeweed-1 (series 500) membrane.

7.4.3 Nanofiltration

The concentrations of trace contaminants for the NF experiments varied depending on the spiked concentration (i.e. 500 ng/L or 5 µg/L) in the biofilters, the biodegradability of the compounds, and the season. Appendix T presents a table of the average concentration and standard deviation of selected PhACs and EDCs in the membrane feed tank for the duration of the NF experiments.
The rejection potential of a NF membrane can be evaluated by its MWCO, which corresponds to the MW of a solute that is rejected at 90 % (Van der Bruggen *et al.*, 1999). The idea behind the MWCO concept is that the size of the contaminants is proportional to its molecular weight. Consequently, for a membrane with a given MWCO, the sieving effect increases the removal of larger molecule due to steric hindrance (Bellona *et al.*, 2004).

Figure 7.2 presents the percent average rejection and standard deviation of naproxen, ibuprofen, DEET, atrazine, and carbamazepine by XN45 and TS80 membranes. Due to the difference in MWCO of XN45 (250 Da) and TS80 (200 Da) and the pore size distribution (refer to Chapter 3 section3.4.3) only partial rejection via steric hindrance is observed for the selected PhACs and EDCs which vary in MW from 191 to 236 g/mol . Figure 7.2 indicates that XN45 and TS80 membranes achieved different degrees of rejection of selected PhACs and EDCs. For all compounds, the average rejection achieved by TS80 is significantly higher than the rejection achieved by XN45.

For TS80 membrane, the average rejection varied between 78 % and 97 %. For XN45 membrane, the average rejection varied between 27 % and 65 %. The standard deviations for percentage rejection were smaller for the TS80 membrane than the XN45. The larger standard deviations observed with XN45 may be due to the larger number of experiments performed with XN45 and also by the changes in water quality such as the ionic strength (Verliefde *et al.*, 2009a; Nghiem and Hawkes, 2009; Bellona and Drewes, 2005; Boussahel *et al.*, 2002). These experiments suggest that the rejection may be influenced by the water quality of the influent. As suggested by Comerton *et al.* (2009), the presence of NOM in membrane feed can reduce the effective MWCO of NF membranes. Consequently, the interactions and association of the contaminant with organic matter may contribute to an increase in rejection of trace organic contaminants. The rejection measured for all NF experiments are presented in Appendix U.

The difference in percent rejection between TS80 and XN45 membranes presented in Figure 7.2 also support the hypothesis that TS80 is a tighter membrane than XN45. For a given membrane, based on size exclusion solely the rejection of all selected contaminant should be relatively similar because the MW varies between 191 and 236 g/mol.

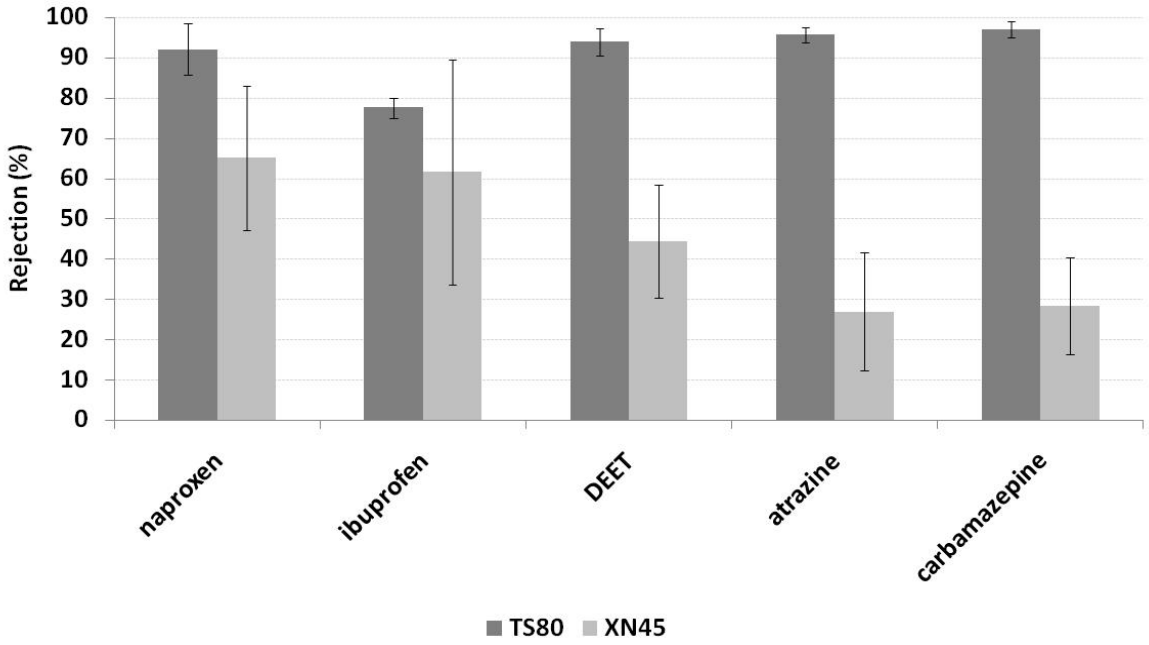


Figure 7-2 Average rejection and standard deviation of selected PhACs and EDCs by XN45 and TS80 membranes. The molecular weight cut off of XN45 and TS80 are respectively 200 Da (Mandale and Jones, 2008) and 250 Da (manufacturer). The molecular weights of naproxen, ibuprofen, DEET, atrazine, and carbamazepine are respectively 230, 206, 191, 216, and 236 g/mol. The error bar indicates the standard deviation of the rejection for all experiments (for TS80 and XN45 the number of experiment performed were respectively 2 and 10).

For TS80 membrane, the charge of the contaminants did not significantly influence the percentage rejection. The negatively charged compounds (i.e. ibuprofen and naproxen) did not exhibit a better rejection than the neutral compounds (i.e. DEET, atrazine, and carbamazepine). This observation indicates that the predominant rejection mechanism of the TS80 membrane is most probably steric exclusion. The rejections measured during this study were similar to the results obtained by Verliefde *et al.* (2008).

However, for the looser XN45 membrane higher percentage rejections were observed for negatively charged compounds (i.e. naproxen and ibuprofen). Intermediate rejection of DEET was measured and the average rejection of the other neutral compounds (i.e. atrazine and carbamazepine) was even lower. These results indicate that not only size exclusion but also electrostatic repulsion mechanisms were involved with XN45 membrane. Moreover, these results suggest that adsorption was not a predominant rejection mechanism for neutral compounds. DEET is most hydrophobic compounds with a Log K_{ow} value of 2.18 and presents a higher rejection value than carbamazepine and atrazine having a Log K_{ow} value of 2.45 and 2.61 respectively. If adsorption was an important rejection mechanism we will expect to observe higher rejection of carbamazepine and atrazine than DEET.

Figures 7.3 and 7.4 show the concentrations of ibuprofen, naproxen, DEET, atrazine, and carbamazepine in permeate and feed as a function of time during an experiment with XN45 membranes at low and high influent concentration to the biofilters. Note that lower concentrations of DEET, naproxen, and ibuprofen in the membrane influent were expected because biodegradation of these compounds occurs during biofiltration process.

Contaminant concentrations in the feed water were fairly constant during the course of the experiments (Figures 7.3 and 7.4). It can be observed that the rejection of contaminant was constant for the duration of the experiment at low and high feed concentration. Several studies showed that rejection of trace organic contaminants depended on feed water chemistry (Yoon *et al.*, 2006; Nghiem *et al.*, 2004; Adams *et al.*, 2002). Verliefde et al. (2008) compared the rejection of neutral and charged compounds in Milli-Q water and surface water by TS80 membrane and show a lower rejection of negatively charged compounds in Milli-Q water compared to surface water containing 6 mg/L of NOM measured as TOC. However, no real trend could be defined for neutral compounds. The difference of rejection of negatively charged compounds could possibly be explained by a decrease of membrane surface charge in Milli-Q water compared to surface water. The change in membrane surface charge may be caused by the deposition of NOM on the membrane surface leading to an increased surface charge (Xu *et al.*, 2006).

Using surface water results indicate that fouling of the XN45 membrane did not significantly affect the rejection of the selected PhACs and EDCs. The J/J0 for the experiments presented in Figures 7.3 and 7.4 were respectively 62 % and 46 %. No decline or increase in the rejection of neutral and charged PhACs and EDCs was observed during the 96 h of the experiment (Figures 7.3 and 7.4). This contradicts the results observed by Kimura and al. (2003) where due to adsorption on the membrane a time dependency was observed for neutral compounds. These different findings may be due to differences in compound characteristics and surface water between Kimura's results and this study.

The retention of the selected trace contaminant depends on the compound properties. For XN45 membrane at both influent concentrations the retention follows this order:

$$\text{ibuprofen} \cong \text{naproxen} > \text{DEET} > \text{carbamazepine} \cong \text{atrazine}$$

The comparison of Figures 7.3 and 7.4 indicates that the percentage of retention of contaminants by the XN45 membrane was increased by 20 % at high influent concentration.

Studying the removal of charged pharmaceuticals at two different concentrations, in the µg/L range, Verliefde *et al.* (2007), showed that the rejection of positively charged compounds is higher at higher feed concentration. These results may be explained by a shield effect. At higher feed concentration, the pharmaceutical created a partial shielding of the negatively charged membrane. Consequently, the attraction between the membrane and the positively charged pharmaceuticals is lower. Because the attraction is reduced, lower concentration polarization occurs thus lower concentration at the surface of the membrane and higher rejection are observed. For negatively charged compounds, Verliefde *et al.* (2007) concluded that the shielding effect is too small to influence repulsive forces between the membrane and compounds negatively charged thus, unlike in this study, rejection values in Verliefde's study are almost equal. This study shows a difference in rejection of negatively charged compounds due to the important difference in influent concentration (i.e. between 200 and 800 ng/L at low concentration compared to 1500 to 4500 ng/L at high feed concentration). Thus a shield effect on the membrane surface may be at the origin of the difference in rejection.

Kimura *et al.* (2003a) who studied the rejection of trace organic contaminants with RO membranes at different feed concentration between µg/L to ng/L also observed an increase in rejection of negatively charged compounds at higher feed concentrations. On the other hand, van der Bruggen *et al.* (1998) and Zhang *et al.* (2004) showed that feed concentrations did not affect the removal of trace organics when spiked at different concentrations (i.e. mg/L to µg/L). However, even the lower concentrations they worked at were significantly above concentrations experienced in the environment.

Other factors such as the concentration of NOM and conductivity may also influence the rejection of trace organics.

Thus, no clear explanations for the decline in rejection efficiency with lower feed concentrations can be drawn. Consequently, further work will be necessary to confirm the trend observed in this study and to suggest mechanistic reasons. These results suggest that studies reporting high rejections of contaminants spiked at µg/L level may overestimate removal efficiencies considering that these contaminants are present at low ng/L concentrations in the membrane influent (Kimura *et al.*, 2003a). Thus previous studies showing rejection results at high feed concentrations must be carefully interpreted.

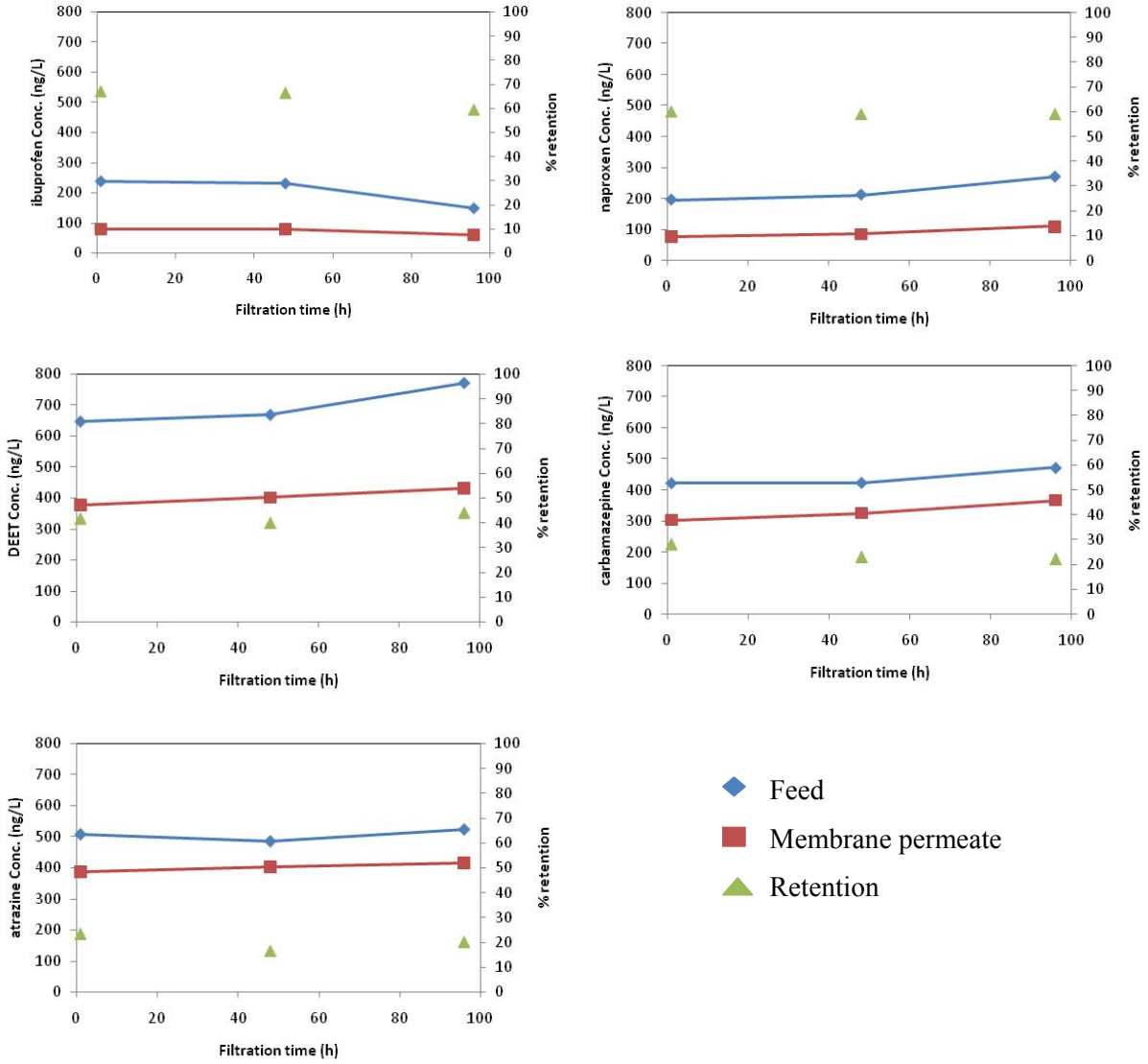


Figure 7-3 Percentage of retention, permeate and feed concentration of ibuprofen, naproxen, DEET, atrazine, and carbamazepine as function of filtration time for XN45 membrane at low influent concentration

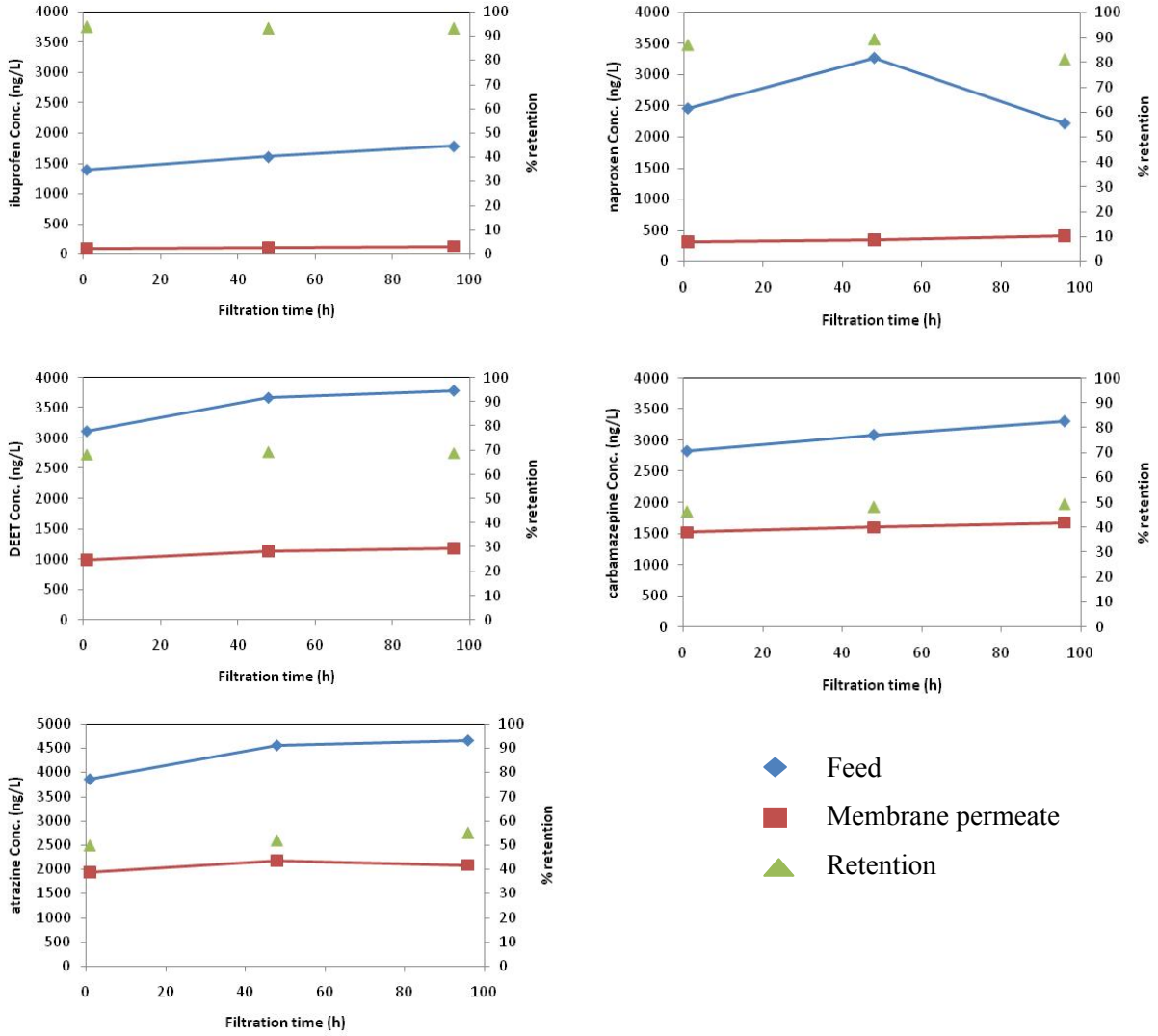


Figure 7-4 Percentage of retention, permeate and feed concentration of ibuprofen, naproxen, DEET, atrazine, and carbamazepine as function of filtration time for XN45 membrane at high influent concentration

The average percent rejection of trace organic contaminants and standard deviations for experiments performed at low concentrations (XN45, n=6 and TS80, n = 3) and at high concentrations (XN45, n = 6) are presented in Table 7.1. Although the rejection within an experiment remained constant, the standard deviations observed in Table 7.1 indicate deviations between experiments. This suggests that fouling between the different experiments may have had an impact on the rejection efficiency of XN45 membrane. Moreover, Table 7.1 shows that TS80 membrane achieved high and constant rejection in all experiments, regardless of differences in fouling between experiments.

Table 7-1 Percentage rejection and standard deviation of select PhACs and EDCs achieve at low and high concentrations by XN45 and TS80 membranes

Rejection	**naproxen**		**ibuprofen**		**DEET**		**atrazine**		**carbamazepine**	
(%)	**low**	**high**	**low**	**high**	**low**	**high**	**low**	**high**	**low**	**high**
XN45	57±11	85±7	43±19	87±6	40±5	56±15	22±6	38±13	23±6	37±9
TS80	92±6	na	78±3	na	94±3	na	96±2	na	97±2	na

na: not available

7.5 Conclusions

This research project studied the removal of PhACs and EDCs by membrane filtration. Several experiments with a duration of 96 h each were performed using biofilter effluent as feed. The results confirmed the low rejection of selected PhACs and EDCs by the ZeeWeed-1 500 series UF membrane. Different degrees of rejection were observed for the two NF membranes namely the XN45 and the TS80 membranes. The results allow the following conclusions to be drawn:

- UF (ZeeWeed-1 500 series) is not an appropriate water treatment process for the removal of selected trace organic contaminants. The average removal of naproxen, ibuprofen, and DEET are respectively 5, 4 and 1 %. In average, no removal was observed for both atrazine and carbamazepine.

- A system loss test was performed for 22 hours on the UF membrane set-up to determine the level of adsorption on the set-up. Nonylphenol was completely adsorbed. Variations of concentration less than 14 % were measured for naproxen, ibuprofen, DEET, and atrazine. An increase in concentration up to 35 % was measured for carbamazepine. Analytical and sampling error may have contributed to slight variations in concentration.

- The percent rejection of selected PhACs and EDCs by NF membranes ranged from 27 to 97 % and was influenced by the membrane characteristics and also the compound properties.

- The TS80 membrane with a molecular weight cut off (MWCO) of 200 Da achieved a much higher percent rejection than the XN45 membrane (MWCO 250 Da). The rejection by the TS80 membrane ranged from 78 to 97 % and was predominantly driven by size exclusion.

- For the XN45 membrane, the rejection of trace organic contaminants depended on the compound properties. Negatively charged compounds (i.e. naproxen and ibuprofen; 47 and 92 % rejection) showed higher rejections than neutral compounds (i.e. DEET, atrazine, and carbamazepine; 10 to 46 % rejection). Thus electrostatic repulsion and size exclusion were two mechanisms governing the rejection by the XN45 membrane.

- Although the rejection within an experiment remained constant, the high standard deviations observed between experiments indicates that rejection between experiments differed and that fouling had an impact on the rejection efficiency of the XN45 membrane.

- For the XN45 membrane the rejection of all compounds increased at high influent concentrations (between 1500 and 4500 ng/L) compared to low concentrations (between 200 and 800 ng/L). An increase of approximately 20 % was measured at high influent concentration. These results may be explained by a shield effect but further research is necessary to confirm these results and put forward mechanistic explanations.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Summary and Conclusions

This study investigated two different applications of chemically unassisted rapid biofiltration in drinking water treatment: a) as pretreatment for fouling control of membrane filtration, and b) for removal of trace organic contaminants.

As a starting point, the seasonal variations in the concentrations of atrazine, carbamazepine, DEET, ibuprofen, naproxen, and nonylphenol in Grand River water, which is highly impacted by agricultural and municipal activities, were evaluated on a weekly basis over a period of 20 months. Then, the ability of rapid biofiltration to degrade PhACs, PCPs, and EDCs was established using Grand River water. Biofiltration experiments were performed at pilot scale using two different contact times of 5 and 14 minutes.

At the same time, the potential of biofiltration pretreatment to prevent fouling of low and high pressure membranes was evaluated. Membrane filtration experiments were performed with bench-scale modules and commercially available membranes.

Finally, the rejection of PhACs, PCPs, and EDCs by high pressure membranes was evaluated. The impacts of membrane fouling and influent concentrations on the rejection of selected contaminants were also evaluated.

The most significant conclusions related to fouling control of ultrafiltration (UF) and nanofiltration (NF) membranes using chemically unassisted rapid biofiltration pretreatment were as follows:

1. Pretreatment (i.e. roughing filtration followed by a biofilter with either 5 or 14 minutes EBCT) was able to control fouling of the UF membrane. It significantly reduced the transmembrane pressure required to keep a constant permeate flux.

2. Biopolymers, a fraction of the dissolved organic matter determined by LCOCD analyses, were found to contribute substantially to UF membrane fouling. In average, biopolymer was rejected at 56 % by UF membrane.

3. This study found that hydraulically reversible fouling of the UF membrane was correlated to the absolute concentration of biopolymers in the membrane feed. Consequently, lower hydraulically reversible fouling was observed when using B2 effluent (i.e. the biofilter with the longer EBCT of 14 min) as feed since it provided a higher removal of biopolymers and therefore a lower absolute biopolymer concentration.

4. For sustainable UF membrane operation the control of irreversible fouling is more important. It could be shown that hydraulically irreversible fouling was substantially lower when the UF membrane was fed with effluent from B2 (14 min EBCT) which had lower biopolymer concentrations. There is also some indication that the composition of biopolymers rather than their absolute concentration play an important role in irreversible fouling.
5. Adequate fouling control of high pressure nanofiltration membranes was related to molecular weight cut off of the membrane. It was found that biofiltration pretreatment was able to achieve adequate fouling control for the looser XN45 membrane, whereas it was insufficient for the tighter TS80 membrane.

The most significant conclusions related to removal of trace organic contaminants by chemically unassisted rapid biofiltration were as follows:

1. The degree of biodegradability of selected contaminants was the following:

   ibuprofen > naproxen > DEET

   An increase in influent concentration temporally reduced the percentage removal but after a short acclimation period near complete removals of ibuprofen, DEET, and naproxen were observed.

2. This study also showed that carbamazepine and atrazine were refractory to biodegradation. No conclusion can be drawn for nonylphenol due to spiking issues.

3. In general, the estimated biodegradation rate constants increased with an increase in water temperature. Results obtained at low influent concentrations indicated that ibuprofen had the highest rate constants between 0.36 and 2.20 min^{-1} followed by naproxen with rate constants between 0.47 and 1.25 min^{-1}, and DEET with rate constants between 0.03 and 0.94 min^{-1}.

The most significant conclusions related to removal of trace organic contaminants by nanofiltration were as follows:

1. The rejection of selected trace organic contaminants by two commercially available high pressure NF membranes i.e. XN45 and TS80 was influenced by membrane characteristics and the compounds properties. The tighter TS80 membrane (MWCO 200 Da) achieved higher rejections than the XN45 membrane (MWCO 250 Da). For the TS80 membrane, the rejection was predominantly driven by size exclusion. For the XN45 membrane, the rejection was also influenced by electrostatic repulsion as negatively charged compounds (i.e. naproxen and ibuprofen) showed higher rejections than neutral compounds (i.e. DEET, atrazine, and carbamazepine).

2. Interestingly, it was also found that rejections at high influent concentrations (between 1500 and 4500 ng/L) were approximately 20 % higher than rejections measured at low influent concentrations (between 200 and 800 ng/L). These results may potentially be explained by a shield effect but further investigations with other membranes and contaminants are necessary to identify underlying mechanisms.

Other relevant conclusions are grouped by theme:

A) Trace Organic Contaminants in Surface Water

Selected PhACs and EDCs measured in Grand River were present throughout the year at low concentration in the ng/L range. This demonstrated the impact of human activities on our environment. Although the concentrations were low, high detection frequencies between 91 and 100 % were observed for atrazine, carbamazepine, DEET, ibuprofen, and naproxen. Nonylphenol had a lower detection frequency (i.e. 50 %). DEET and atrazine are being used for specific purposes at a particular time of the year. Consequently, concentration spikes in the Grand River were identified for both contaminants. Relatively constant concentrations throughout the year were observed for carbamazepine and nonylphenol.

B) Biological Filtration for Drinking Water Treatment

DOM Characterisation and its Reduction by Biofiltration

LCOCD analysis demonstrated that DOM in the Grand River consists of four distinctive fractions; biopolymers, humic substances, building blocks, and low molecular weight acids (LMWA). The predominant fractions were biopolymers (0.10 mgC/L to 0.53 mgC/L) and humic substances (3.55 mgC/L to 4.92 mgC/L). Seasonal variations in biopolymer concentrations have been observed with the highest concentrations detected during the summers.

In general the biofilter with the higher contact time (B2: 14 min EBCT) achieved higher DOM removals than the biofilter with the shorter contact time (B1: 5 min EBCT). The most biodegradable fraction of the DOM was the biopolymers. The average percentage removal of biopolymers observed by B1 and B2 were respectively 40 ± 26 % and 61 ± 22 %. Humic substances were less readily biodegradable and up to 30 % removal was observed for B1 and B2.

Fluorescence EEM analyses was used as a complementary technique. Fluorescence EEM found that particulate and colloidal matter was well removed during biofiltration while only low removals of humic substances were observed. These results were consistent with those obtained by LCOCD analyses and turbidity measurements. Finally, fluorescence EEM showed that protein-like substances may be removed by biofiltration which is an observation unique to this technique.

Biomass Attached to Filter Media

Phospholid analysis is useful to demonstrate the presence of biomass on the media but it was not a good indicator for biodegradation performance. Phospholipids did not vary substantially throughout the seasons and were therefore not indicative of the seasonal trends observed in the performance of the biofilters.

Overall, ATP concentrations, which are an indication of cell activity, tended to increase with increasing bed depth and with rising water temperatures. This temperature dependence suggests that ATP may be a more sensitive indicator for biodegradation performance. Higher concentrations of ATP deeper in the bed also imply that the biomass present on top of the biofilter may be less active and therefore composed of dead cells or non-active cells as suggested by concurrent phospholipid and TDCC analyses. These results also suggest that longer contact times may be beneficial for the transformation of BOM and organic trace contaminants because the contaminants are exposed to biomass for a longer period.

Removal of Microbial Material by Biofiltration

The investigated pretreatment (roughing filtration followed by biofiltration) was able to significantly reduce microbial product contents as the ATP, HPC, and TDCC content were all significantly lower in the biofilter effluents than in the raw water. It is anticipated that this should be

beneficial with respect to a reduction in biofouling of subsequent membrane filtration but further investigations are necessary to confirm this hypothesis.

Biofiltration Pretreatment to Control Fouling on Low and High Pressure Membranes

Using untreated Grand River water it became apparent that direct UF was an unsustainable approach for this water source. But when applying biofiltration pretreatment UF became a sustainable treatment option. Hence, biofiltration pretreatment makes it possible to treat more challenging waters with UF membranes. This should be confirmed with other raw water sources and also for other commercially available membranes.

Particulate and colloidal materials are thought to contribute to reversible and/or irreversible fouling. Reduction of these materials by biofiltration pretreatment, which was confirmed by turbidity and fluorescence EEM data, was therefore likely to contribute to reduce fouling of the UF membrane.

LCOCD and fluorescence EEM analyses of UF membrane feed and permeate showed that 56 % of biopolymers but only 2 % of humic substances were rejected. However, only little or no removal of protein-like substances was achieved as demonstrated by the fluorescence EEM data.

Due to their much smaller pore size, NF membranes not only rejected biopolymers completely but also humic substances. LCOCD analyses also showed that the tighter TS80 membrane achieved a slightly better removal of LMWA than the XN45.

Fluorescence EEM analyses of NF feed and permeate confirmed the complete rejection of humic substances and protein-like substances. However, there were differences between turbidity measurements and fluorescence results in that a decrease in turbidity after NF was not consistent with fluorescence analyses indicating only little removal of particulate and colloidal matter. Further investigations are necessary to elucidate these differences which may be due to different measurement principles.

Integrated Membrane Systems (Biofiltration-Ultrafiltration-Nanofiltration)

For the looser XN45, no improvement in fouling resistance was observed by using BF-UF pretreated water compared to biofiltration alone. This suggests that humic substances were the main DOM fraction causing fouling.

For the tighter TS80 membrane, the flux decline was initially similar using either biofiltration alone or BF-UF as pretreatment. In the later stages, less fouling using the combination BF-UF was observed indicating that the predominant fouling mechanism may be controlled to some degree by this combined pretreatment.

Removal of Organic Trace Contaminants by Biofiltration

The water temperature influenced the percentage removal of biodegradable contaminants since at lower temperatures biological activity generally decreases. For DEET and naproxen, removals decreased during the negligible DOC removal (NDR) period (low water temperatures) and their removals increased during the statistically significant DOC removal (SDR) periods (higher water temperatures).

C**) Removal of Organic Trace Contaminants by High Pressure Membranes**

During the experiments different degrees of membrane fouling i.e. flux declines were observed. However, the rejection of trace organic contaminant stayed constant for the entire period of each individual experiment.

8.2 Recommendations for the Water Industry

Based on the experimental work from pilot-scale biofilters and bench-scale membrane filtration, the following recommendations for the water industry are made:

- The roughing filtration/biofiltration tandem pretreatment is recommended to diminish reversible and irreversible fouling of UF hollow fiber membranes. However, utilities must consider the decrease in performance of the pretreatment at water temperature below 10°C. It is thus recommended to implement this pretreatment in utilities experiencing warm and intermediate water temperatures.

- Implementing proper biofilter backwash procedures and filter-to-waste times is critical for successful membrane fouling control. Breakthrough of turbidity and/or excessive release of microbial products may lead to an increase in membrane fouling.

- Biofiltration pretreament for UF membrane filtration may be a competitive option to other pretreatments such as coagulation or microfiltration. Maintenance and operation of rapid biofilters is simple. However, the footprint of a plant using rapid biofiltration may be larger than a plant using coagulation pretreatment, consequently this option should be considered where space is not an issue.

- Biofiltration is recommended as part of a multi barrier approach for the removal of biodegradable organic trace contaminants. An acclimation period may be necessary before removal is observed.

8.3 Future Research

- Investigate irreversible fouling of hollow fiber UF membranes and determine how the composition of biopolymers rather than their concentration affects fouling.

- Determine the material causing reversible and irreversible fouling on NF membranes using fluorescence EEM analysis data produced during this study.

- Perform fundamental research on biofiltration to identify and quantify the microbial community attached on the media. Direct and more efficient measurements of the active biomass are needed because biomass quantification is primordial in understanding biodegradation of organic carbon and trace organic contaminants.

- Determine the rate limiting factors for different biofiltration objectives (i.e. removal of foulant material or trace organic contaminants).

- Determine the adaptation mechanism of the biomass to achieve biodegradation of secondary substrate such as trace organic contaminants.

- Biodegradation kinetic parameters must be established under controlled conditions (i.e. steady-state, water temperature, constant influent concentration).

- Investigate in detail the influence of PhACs and EDCs influent concentration on the rejection by high pressure NF membranes.

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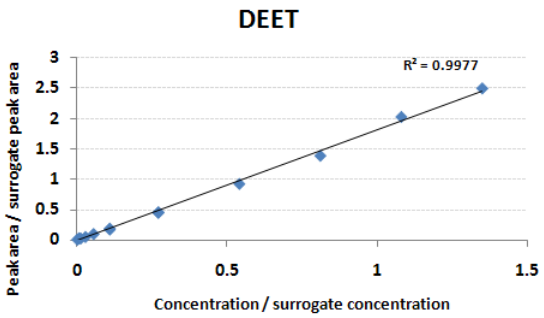
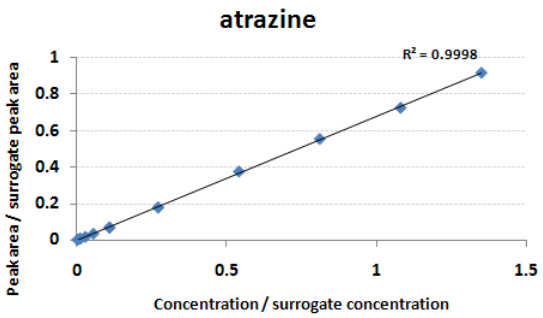
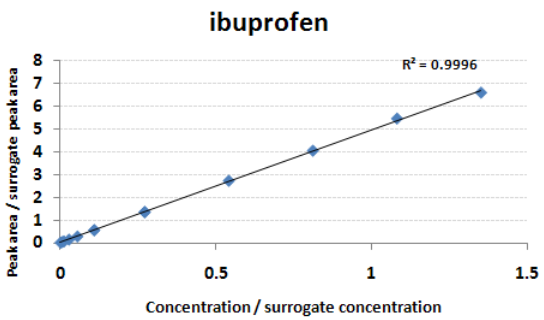
Appendix A

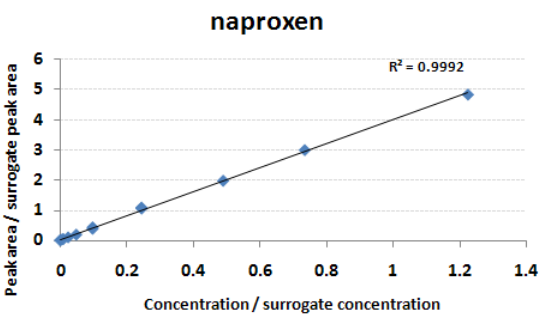
GC/MS Calibration Curves

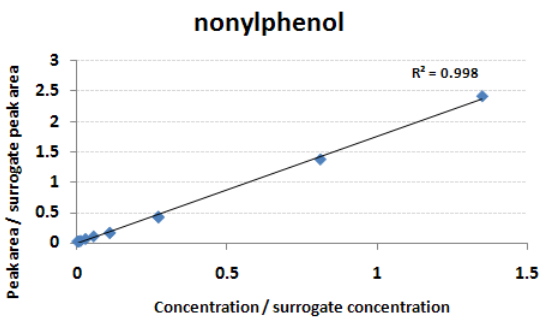
Concentrations range from 0 ng/L to 1250 ng/L

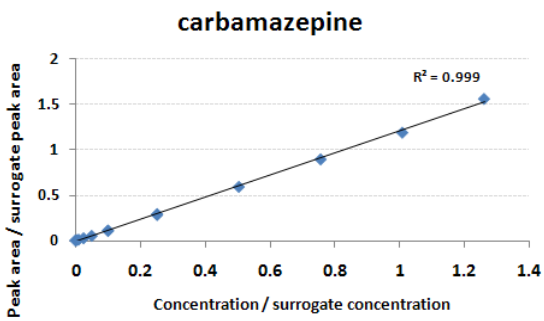












Appendix B

Measurements of selected PhACs and EDCs in Grand River

year	Date	DEET	ibuprofen	atrazine	nonyphenol	naproxen	carbamazepine
2006	November 13	21	8	119	nd	13	d
2006	November 27	53	10	30	nd	17	d
2007	January 24	22	84	23	d	104	18
2007	January 31	23	60	19	46	91	23
2007	February 7	16	107	d	31	108	18
2007	February 14	d	144	nd	nd	147	57
2007	February 21	16	100	d	na	104	26
2007	February 28	d	81	d	d	187	30
2007	March 6	16	91	d	nd	126	26
2007	March 14	32	104	23	nd	70	d
2007	March 22	d	32	d	nd	27	nd
2007	March 28	d	11	17	nd	8	nd
2007	April 5	19	58	23	d	43	d
2007	April 12	16	111	16	nd	59	d
2007	April 19	d	114	17	nd	66	d
2007	April 26	80	179	89	80	143	56
2007	May 3	16	39	d	d	50	d
2007	May 9	34	35	19	nd	74	21
2007	May 16	41	26	2865	nd	27	d
2007	May 23	219	36	236	d	78	24
2007	May 30	154	30	119	nd	81	29
2007	June 13	138	8	99	d	53	30
2007	June 20	107	17	51	d	57	25
2007	July 5	165	d	24	d	21	60
2007	July 18	97	d	25	28	18	33
2007	July 20	73	7	24	77	14	26
2007	July 24	133	d	31	d	19	32
2007	July 26	101	d	35	d	19	27
2007	August 1	105	d	37	nd	13	38
2007	August 8	208	15	38	nd	17	23
2007	August 13	86	d	44	nd	19	32
2007	August 15	133	11	37	nd	31	32
2007	August 17	62	9	30	nd	27	31
2007	August 22	45	7	36	na	24	40
2007	August 24	54	15	39	nd	21	35
2007	August 29	52	9	37	46	14	37
2007	August 31	39	8	29	85	12	40
2007	September 6	49	11	36	37	17	33
2007	September 10	50	18	40	42	19	33
2007	September 12	41	17	34	na	18	28
2007	September 14	72	33	21	na	42	35
2007	September 17	69	12	27	25	30	26
2007	September 19	44	22	26	55	34	44
2007	September 21	106	33	24	162	48	30
2007	September 24	109	50	29	44	45	29
2007	September 27	94	31	29	31	40	29
2007	October 2	122	44	25	d	40	30
2007	October 4	92	38	26	nd	82	34
2007	October 11	58	15	35	131	40	23
2007	October 15	45	40	43	d	79	39
2007	October 18	27	22	45	nd	57	26
2007	October 25	30	24	32	nd	52	32
2007	October 30	28	22	37	82	43	30

continue next page

year	Date	DEET	ibuprofen	atrazine	nonyphenol	naproxen	carbamazepine
2007	November 1	44	22	37	39	54	33
2007	November 12	23	111	42	d	58	31
2007	November 14	38	56	32	117	72	28
2007	November 19	38	56	50	nd	77	25
2007	November 28	57	95	22	nd	118	25
2007	November 30	42	95	25	nd	127	27
2007	December 5	41	51	23	79	88	18
2007	December 12	48	95	29	33	175	37
2007	December 15	44	154	27	nd	138	32
2007	December 19	45	134	23	nd	170	34
2008	January 16	d	d	35	40	6	d
2008	January 21	39	42	30	83	56	d
2008	January 23	54	51	31	nd	61	d
2008	January 30	34	30	d	nd	36	d
2008	February 6	19	21	20	nd	15	nd
2008	February 8	d	13	21	106	57	nd
2008	February 13	79	61	23	nd	48	d
2008	February 19	12	12	25	59	44	d
2008	February 21	d	15	19	na	12	nd
2008	February 26	20	29	18	48	25	d
2008	March 4	d	31	17	52	25	nd
2008	March 6	d	22	17	na	28	d
2008	March 12	nd	30	d	nd	36	d
2008	March 19	18	19	d	na	24	d
2008	March 27	16	36	23	d	36	d
2008	April 3	nd	9	18	34	6	nd
2008	April 11	na	7	20	nd	11	nd
2008	April 16	26	20	17	39	31	d
2008	April 24	21	18	18	nd	46	d
2008	April 30	33	9	23	nd	55	18
2008	May 7	26	9	36	d	33	d
2008	May 14	42	d	27	nd	73	21
2008	May 21	96	11	44	nd	60	19
2008	May 28	152	17	32	na	43	23
2008	June 4	128	8	56	nd	39	20
2008	June 10	399	d	50	nd	32	30
2008	June 19	65	d	645	nd	21	d
2008	June 25	64	nd	137	na	32	32
2008	July 10	78	7	148	nd	36	23
2008	July 15	71	d	161	nd	32	18
2008	July 23	62	8	190	na	13	d
2008	August 6	152	21	118	nd	35	22

LOD	**5**	**2**	**5**	**7**	**2**	**5**
LOQ	**15**	**7**	**16**	**24**	**6**	**18**

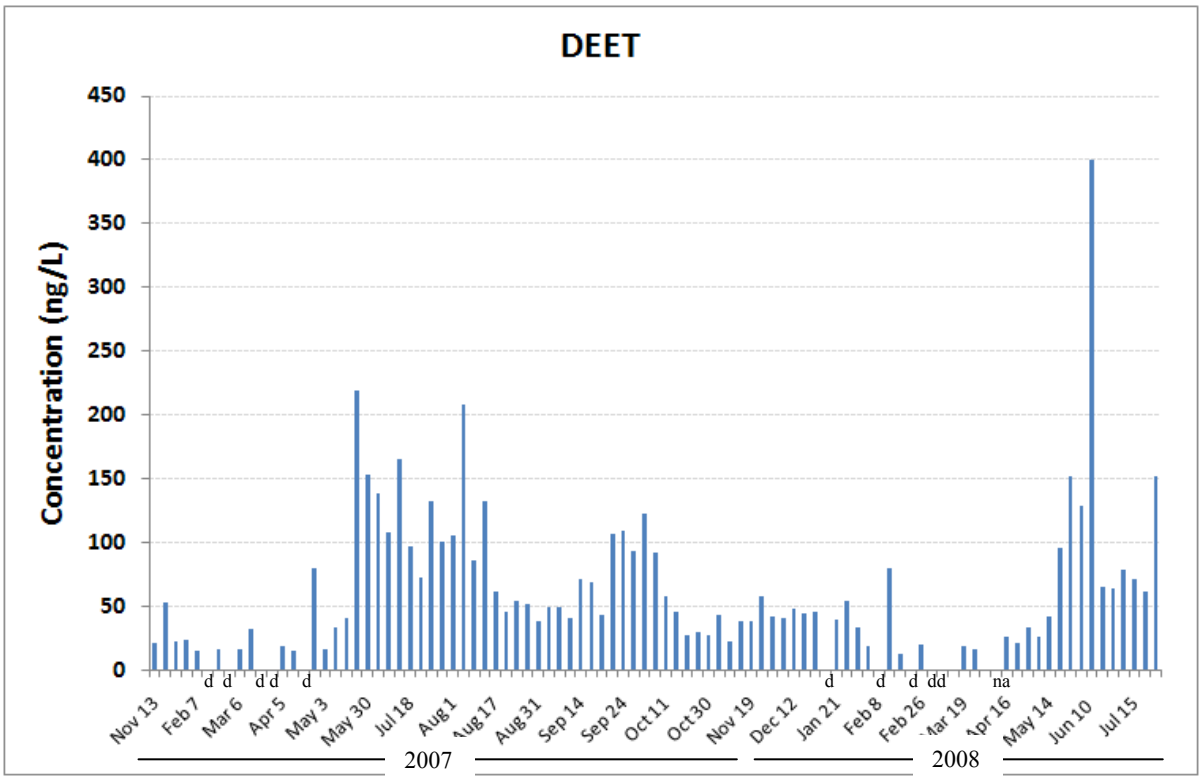
number of measurements	93	94	94	84	94	94
Frequency of detection (%)	98	99	99	50	100	91

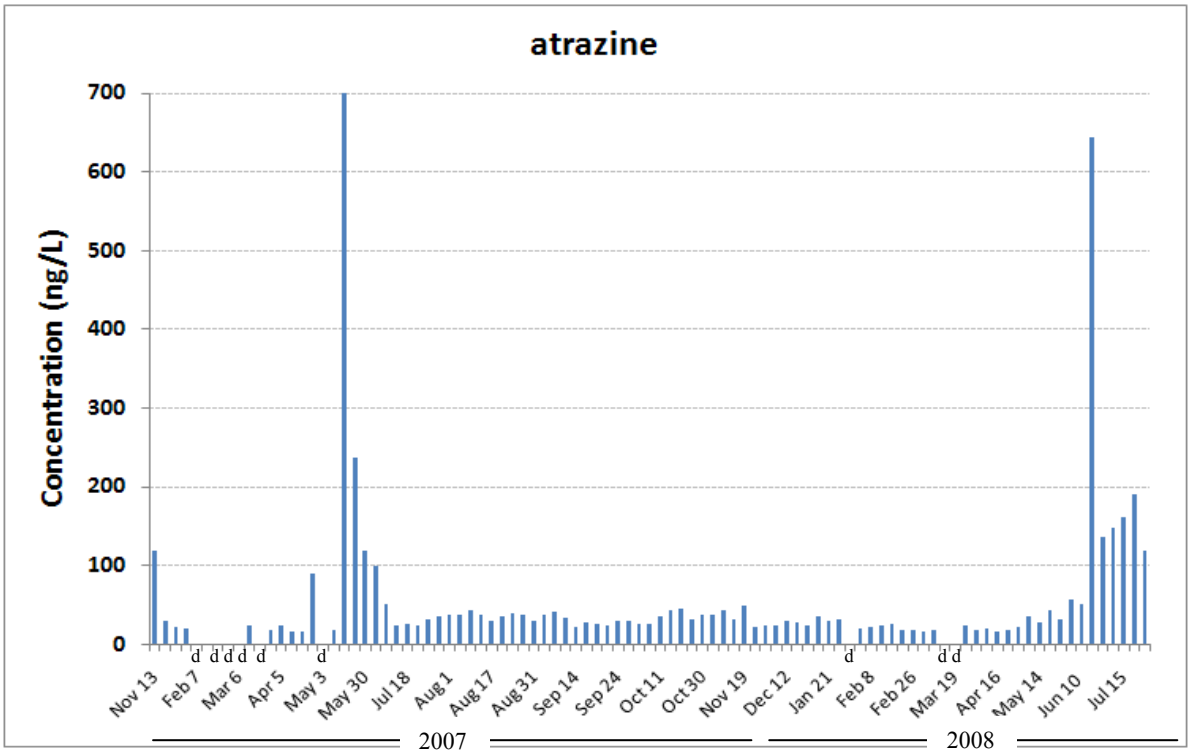
d= detected; nd= not detected; na= not available

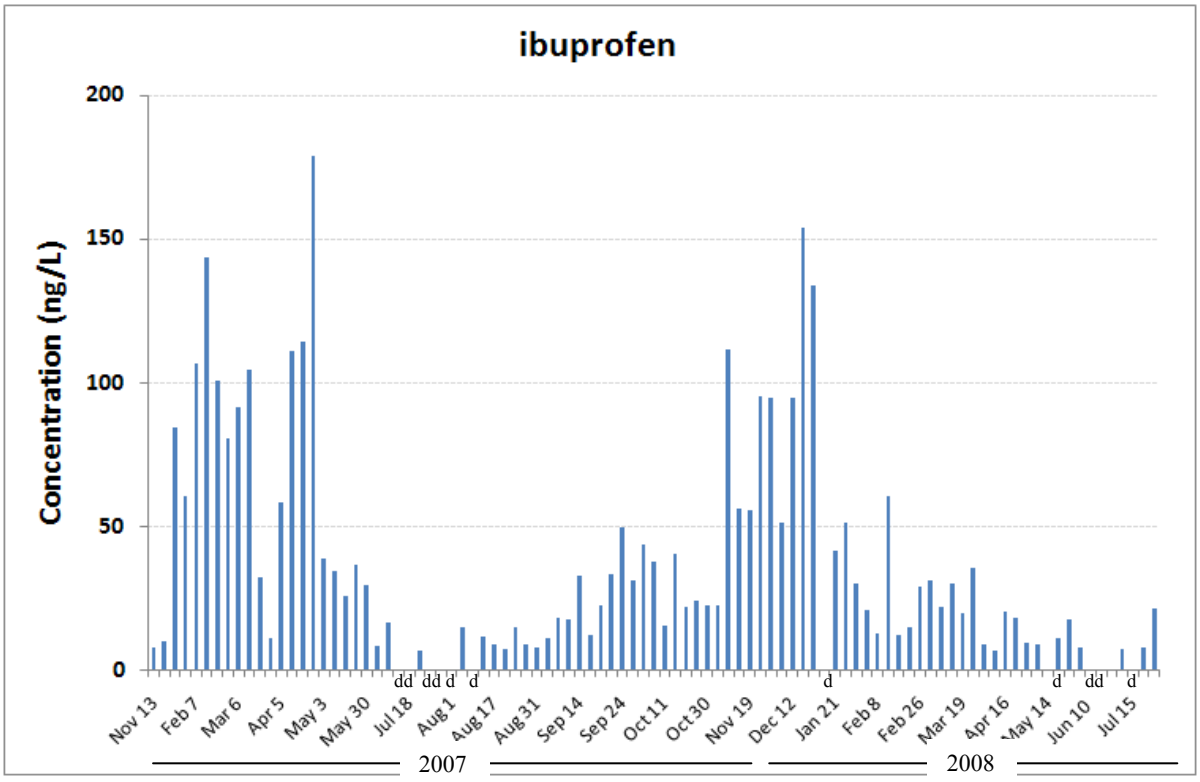
Concentration of trace organic contaminants in Grand River water between November of 2006 and July of 2008

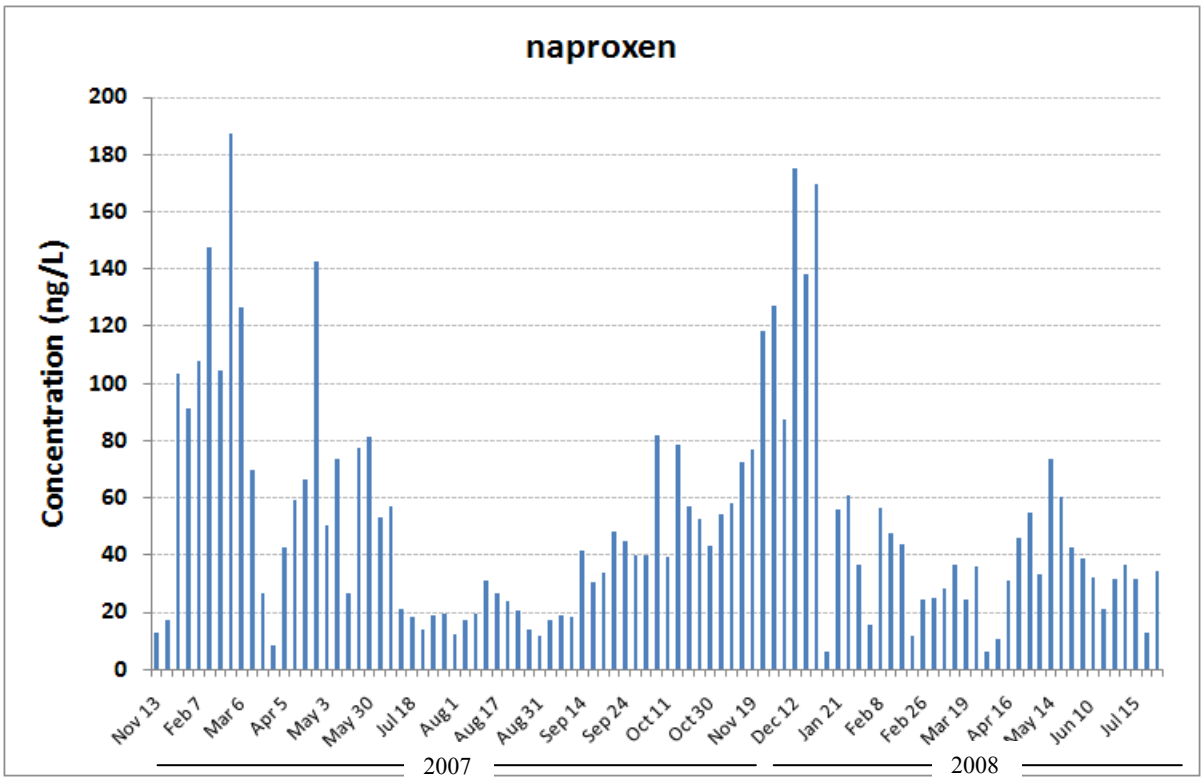
d: indicates that the contaminant was detected but the concentration was below the LOQ,

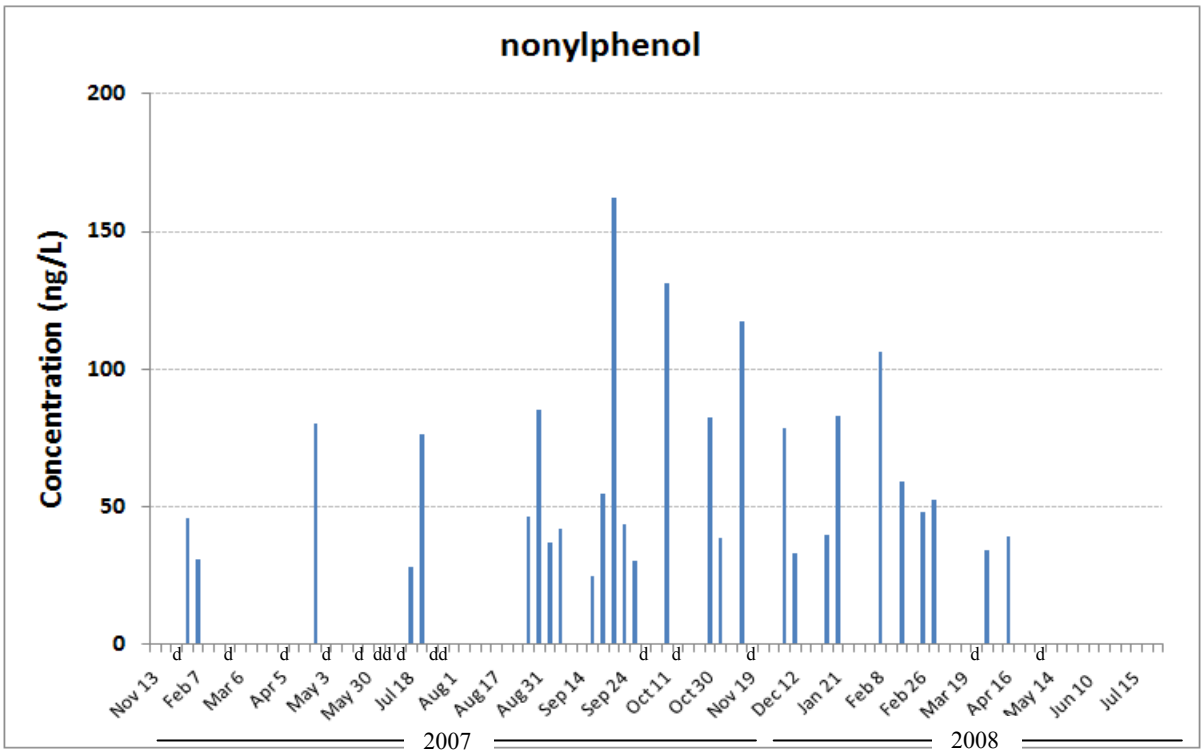
a blank: indicates that the compounds was not detected (i.e. below the LOD)

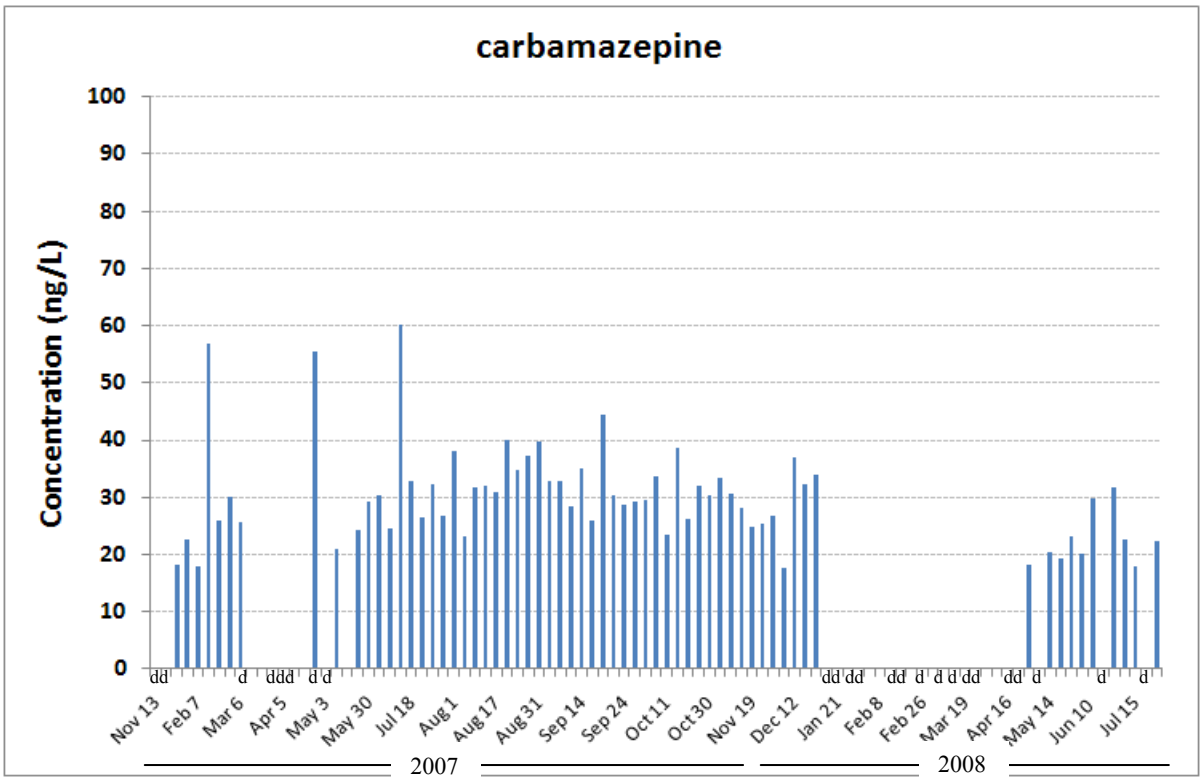



atrazine
Concentration (ng/L)
700
600
500
400
300
200
100
0
d d d d d d d d
Nov 13
Feb 7
Mar 6
Apr 5
May 3
May 30
Jul 18
Aug 1
Aug 17
Aug 31
Sep 14
Sep 24
Oct 11
Oct 30
Nov 19
Dec 12
Jan 21
Feb 8
Feb 26
Mar 19
Apr 16
May 14
Jun 10
Jul 15
2007
2008


ibuprofen
Concentration (ng/L)
200
150
100
50
0
dd dd d d d d d
Nov 13
Feb 7
Mar 6
Apr 5
May 3
May 30
Jul 18
Aug 1
Aug 17
Aug 31
Sep 14
Sep 24
Oct 11
Oct 30
Nov 19
Dec 12
Jan 21
Feb 8
Feb 26
Mar 19
Apr 16
May 14
Jun 10
Jul 15
2007
2008

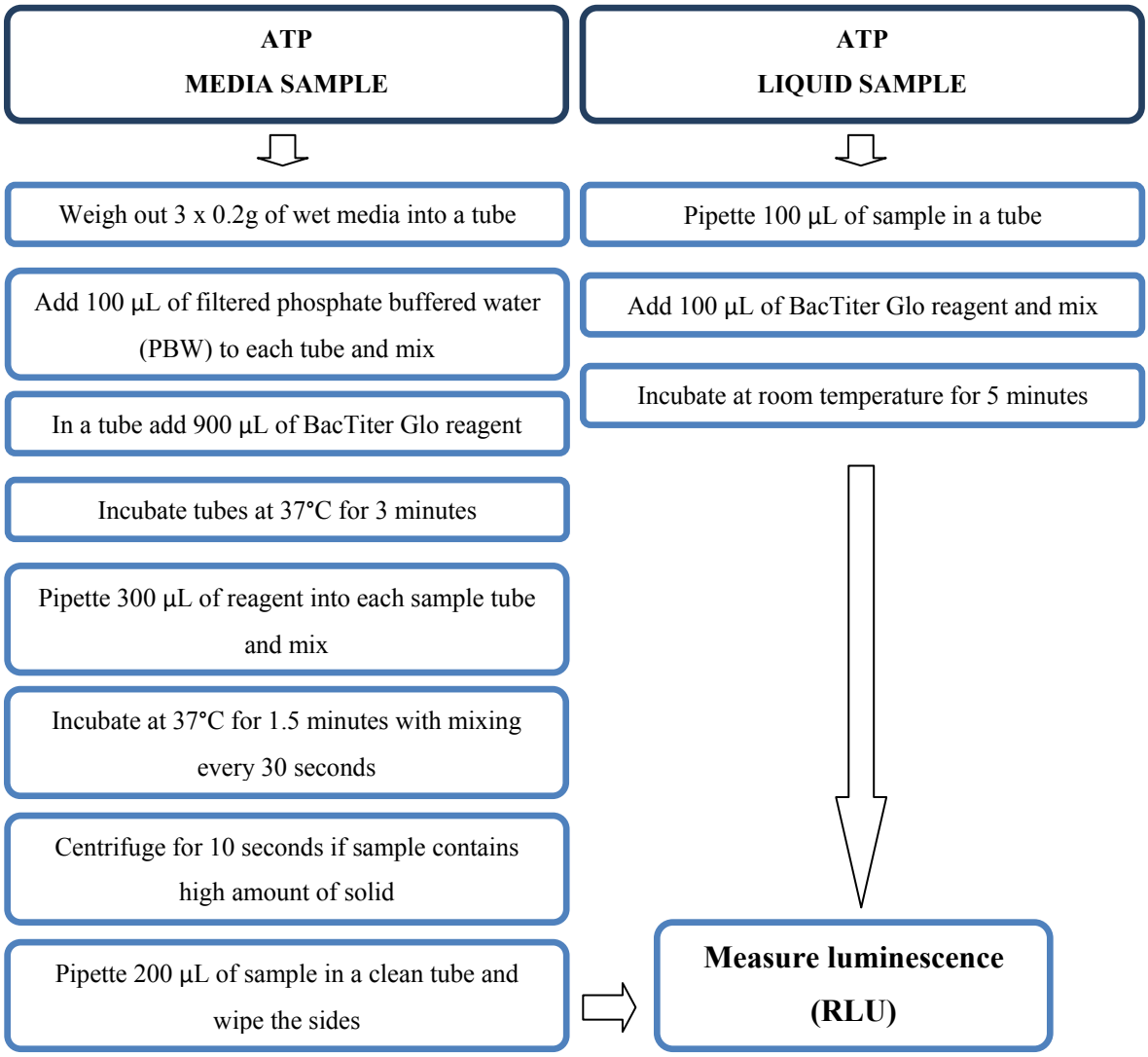

naproxen
Concentration (ng/L)
200
180
160
140
120
100
80
60
40
20
0
Nov 13
Feb 7
Mar 6
Apr 5
May 3
May 30
Jul 18
Aug 1
Aug 17
Aug 31
Sep 14
Sep 24
Oct 11
Oct 30
Nov 19
Dec 12
Jan 21
Feb 8
Feb 26
Mar 19
Apr 16
May 14
Jun 10
Jul 15
2007
2008


nonylphenol
Concentration (ng/L)
200
150
100
50
0
Nov 13
Feb 7
Mar 6
Apr 5
May 3
May 30
Jul 18
Aug 1
Aug 17
Aug 31
Sep 14
Sep 24
Oct 11
Oct 30
Nov 19
Dec 12
Jan 21
Feb 8
Feb 26
Mar 19
Apr 16
May 14
Jun 10
Jul 15
2007
2008


carbamazepine
Concentration (ng/L)
100
90
80
70
60
50
40
30
20
10
0
dd
d
ddd
d d
d
dd dd
dd d d d dd
dd d
d
d
Nov 13
Feb 7
Mar 6
Apr 5
May 3
May 30
Jul 18
Aug 1
Aug 17
Aug 31
Sep 14
Sep 24
Oct 11
Oct 30
Nov 19
Dec 12
Jan 21
Feb 8
Feb 26
Mar 19
Apr 16
May 14
Jun 10
Jul 15
2007
2008

Appendix C

Methods Flow Chart – ATP measurements

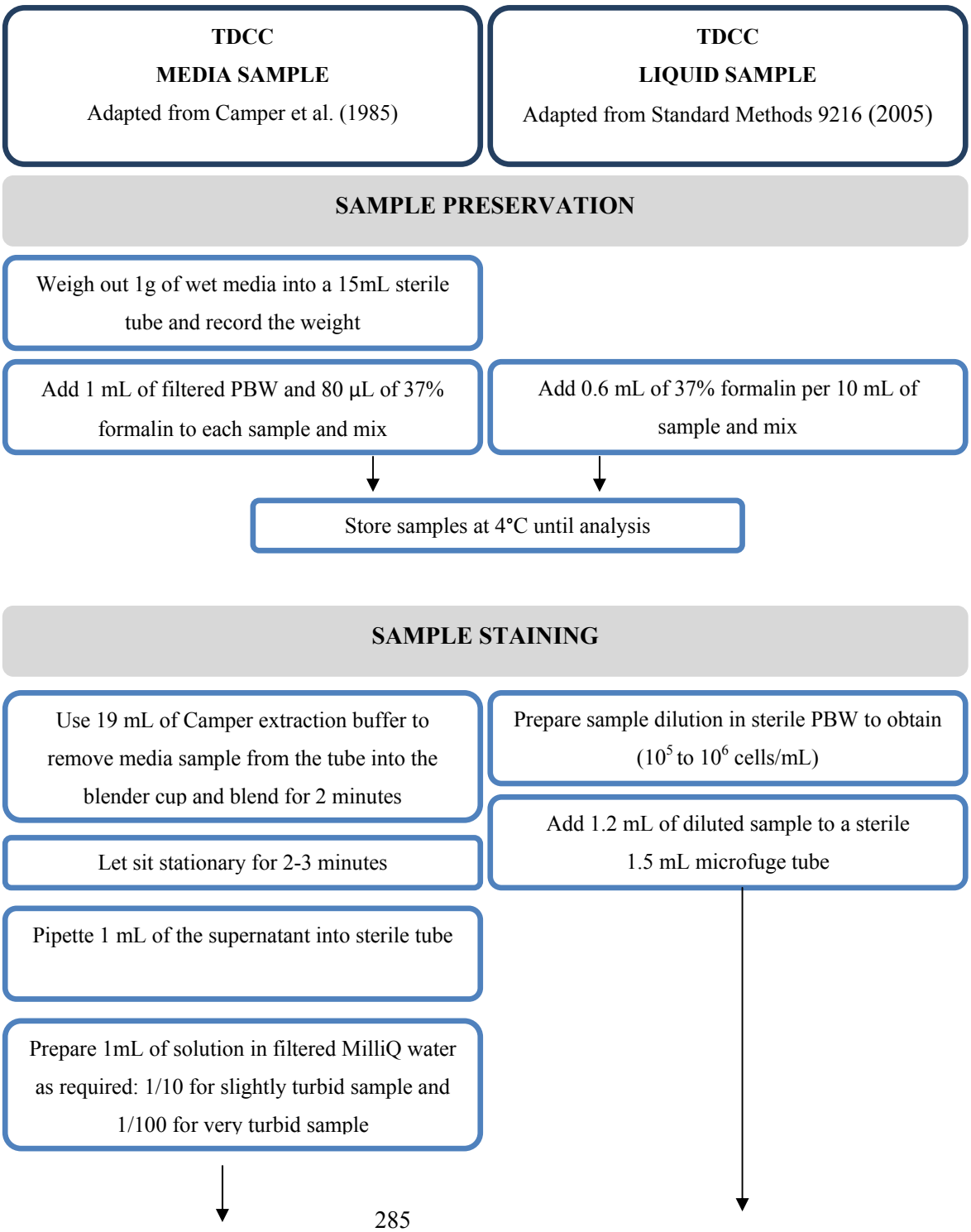


For liquid samples: calibration curve was performed with ATP standard of 0 µM, $1x10^{-2}$ µM, $1x10^{-3}$ µM, $1x10^{-4}$ µM, and $1x10^{-5}$ µM. Used 100 µL of standard and 100 µL of BacTiter Glo reagent and incubated at room temperature for 1 minute.

For media samples: calibration curve was performed with ATP standard of 0 µM, $1x10^{-2}$ µM, $1x10^{-3}$ µM, $1x10^{-4}$ µM, and $1x10^{-5}$ µM. Used 100 µL of standard, 100 µL of PBW, and 200 µL of BacTiter Glo reagent and incubated at 37°C for 4.5 minutes. 200 µL of solution was analysed for RLU.

Appendix D

Methods Flow Chart – Total Direct Cells Count (TDCC)



Pipette 1 µL of SYBR Gold (10000X) solution into each sample

Prepare a negative control using 1 µL of SYBR Gold + 1 mL of filtered PBW

Incubate at room temperature for at least half an hour

Place a 25 mm black filter (0.22 µm) on a glass membrane filter

Pipette 2 mL of PBW on the filter, let sit for 5 minutes and vacuum

Add 1 mL of stained sample onto the filter and vacuum

Wash filter with 10mL of filtered MilliQ water and repeat 3 times

Add a drop of DABCO on glass slide and place the filter on it. Add another drop of DABCO on top and place a cover slip over

CELLS COUNTING

Turn on the microscope lamp and warm up for 15 minutes

Use 100x objective lens

Add non fluorescing immersion oil to the cover slip

Count control sample

Bacteria and protozoa cells stained with SYBR Gold appear green. Count bacteria and protozoa separately.

Count a minimum of 10 fields of view per sample

Appendix E

Methods Flow Chart – Phospholipid measurements

Extraction

Transfer between 0.1 and 1g of media to a 20 mL EPA vial (the amount of sampled media must yield an amount of lipid phosphate ≤ 40 nmol)

Add 1.8 mL of ultrapure water, 5 mL of methanol, and 2.5 mL of chloroform, in this order (final solution must be a single phase)

Mix at low speed on a shaker table for about 10 minutes, let stand overnight for extraction

Add 2.5 mL of chloroform and 2.5 mL of ultrapure water in this order and let stand for phase separation (approximately 30 minutes)

Remove upper layer (MeOH-H_2O) with a pasteur pipette

Transfer the lower layer (chloroform) to Hach vial with pasteur pipette

Remove solvent (chloroform) under a stream of nitrogen

Digestion

Add 1.1 mL of potassium persulfate solution
(5% potassium persulfate in 0.36 N sulphuric acid)

Close tightly and digest at 95-100°C overnight on a heating plate

Quantification

Let cool than add 0.2 mL of ammonium molybdate solution (2.5% $NH_4)_6Mo_7O_{24}$-$4H_2O$ in 5.72 N sulphuric acid) and wait 10 minutes

Add 0.9 mL of malachite green solution (0.011% malachite green oxalate in 0.0111% polyvinyl alcohol solution) and wait 30 minutes

Measure absorbance at 610 nm, use reagent blank (potassium persulfate, ammonium molybdate and malachite green) to zero the instrument

Convert to nmol of lipid phosphate using a standard curve established using inorganic phosphate (K_2PO_4)

Dry extracted media and weigh out. Convert nmol of phosphate to nmol of lipid phosphate per gram of dried media

Appendix F

Measurement of turbidity, TOC, and DOC in raw water, RF effluent and biofilters effluents

Date 2006-2007	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
20-Dec	0.6	RAW	7.60	6.94	7.19
		RF	7.29	6.80	5.14
		B1	7.12	6.82	5.16
		B2	7.25	6.96	3.53
04-Jan	0.3	RAW	7.21	6.30	50.7
		RF	7.22	6.44	5.42
		B1	7.14	6.34	2.97
		B2	7.10	6.30	2.21
10-Jan	2.5	RAW	6.39	5.29	9.19
		RF	6.26	5.35	7.44
		B1	6.19	5.23	3.95
		B2	6.04	5.15	2.17
17-Jan	1.5	RAW	5.99	5.48	8.65
		RF	5.79	5.41	6.57
		B1	5.89	5.33	3.92
		B2	5.70	5.35	2.07
24-Jan	1.1	RAW	5.38	5.14	2.85
		RF	5.27	5.03	2.48
		B1	5.29	5.06	1.76
		B2	5.13	5.04	1.36
31-Jan	0.9	RAW	5.65	5.39	2.41
		RF	5.36	5.56	2.03
		B1	5.54	5.56	1.51
		B2	5.46	5.48	1.16
07-Feb	1.2	RAW	6.16	6.47	4.16
		RF	6.13	6.32	2.53
		B1	6.19	6.29	1.76
		B2	5.79	6.01	1.01
14-Feb	1	RAW	6.18	8.79	4.24
		RF	5.97	6.59	2.68
		B1	6.01	6.22	2.04
		B2	5.84	6.08	1.18
21-Feb	1.5	RAW	6.11	6.36	3.20
		RF	6.21	6.04	2.16
		B1	6.38	6.04	1.40
		B2	6.58	6.09	0.70
28-Feb	0.9	RAW	6.12	6.16	3.05
		RF	6.13	6.31	2.53
		B1	6.16	6.00	1.5
		B2	5.65	6.13	0.86

Date 2007	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
06-Mar	1.1	RAW	5.83	5.54	4.69
		RF	5.80	5.43	2.57
		B1	5.56	5.32	1.94
		B2	5.30	5.43	0.94
14-Mar	1.5	RAW	6.36	6.40	49.00
		RF	7.35	5.83	29.20
		B1	5.16	6.43	10.80
		B2	4.68	5.57	3.06
22-Mar	2	RAW	7.79	6.38	19.50
		RF	7.17	6.70	6.61
		B1	6.76	6.56	2.20
		B2	6.11	6.32	0.90
28-Mar	5	RAW	6.57	6.33	19.48
		RF	6.51	6.13	9.88
		B1	6.42	6.01	5.55
		B2	6.07	5.73	2.97
04-Apr	6	RAW	5.85	5.46	23.10
		RF	5.56	4.95	7.59
		B1	5.74	5.22	4.02
		B2	5.54	5.28	2.48
12-Apr	na	RAW	5.75	4.31	9.22
		RF	5.39	4.02	4.43
		B1	5.22	5.34	1.89
		B2	5.07	4.16	0.59
18-Apr	5.5	RAW	6.14	5.51	6.98
		RF	6.17	5.67	1.9
		B1	5.74	4.87	0.88
		B2	5.32	4.41	0.32
25-Apr	12	RAW	7.86	7.16	9.86
		RF	6.37	6.46	2.2
		B1	6.52	6.13	0.59
		B2	6.44	6.29	0.49
02-May	11	RAW	7.56	6.42	5.75
		RF	6.44	5.23	1.02
		B1	6.05	6.04	0.29
		B2	6.49	5.76	0.23
09-May	10	RAW	na	na	2.07
		RF	na	na	0.35
		B1	na	na	0.14
		B2	na	na	0.04

Date 2007	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
16-May	16	RAW	8.46	7.09	246.9
		RF	7.32	6.22	89.1
		B1	6.31	5.68	25.2
		B2	5.52	5.31	0.46
25-May	16	RAW	6.86	6.21	2.08
		RF	7.94	5.67	0.47
		B1	5.75	5.50	0.21
		B2	5.37	5.04	0.09
30-May	16	RAW	6.97	6.47	2.04
		RF	6.94	6.14	0.87
		B1	6.16	5.43	0.19
		B2	5.49	5.21	0.04
06-Jun	18.5	RAW	7.81	6.56	35
		RF	6.34	6.85	1.4
		B1	5.83	6.17	0.23
		B2	5.76	5.69	0.03
13-Jun	20	RAW	7.07	6.12	8.22
		RF	7.71	7.08	2.12
		B1	6.50	6.16	0.7
		B2	6.19	6.54	0.33
20-Jun	22	RAW	8.29	7.31	10.31
		RF	7.79	8.05	2.72
		B1	6.83	6.44	1.03
		B2	6.43	6.51	0.2
29-Jun	21.5	RAW	8.08	6.75	29.8
		RF	7.04	6.02	1.32
		B1	6.97	6.66	0.19
		B2	5.54	5.61	0.06
04-Jul	21.5	RAW	6.61	5.90	25.8
		RF	na	na	na
		RFSP	5.92	5.74	1.9
		B1	5.70	5.30	0.34
		B2	5.28	5.35	0.06
20-Jul	21	RAW	6.90	6.12	11.23
		RF	na	na	na
		RFSP	6.43	5.87	2.73
		B1	6.17	5.48	0.65
		B2	5.95	5.39	0.08
24-Jul	21.5	RAW	6.77	6.09	2.43
		RF	na	na	na
		RFSP	6.47	5.99	2.89
		B1	5.99	5.63	0.13
		B2	5.81	5.59	0.06
01-Aug	23.5	RAW	6.99	6.17	1.85
		RF	6.52	6.21	0.73
		RFSP	6.53	6.07	0.86
		B1	6.02	5.34	0.04
		B2	5.74	5.35	0.00
08-Aug	22	RAW	7.01	6.46	5.71
		RF	na	na	na
		RFSP	6.46	5.86	2.26
		B1	5.89	5.07	0.59
		B2	5.23	6.12	0.10
15-Aug	21	RAW	7.44	6.43	7.56
		RF	na	na	na
		RFSP	6.73	6.25	2.06
		B1	6.21	6.14	0.28
		B2	6.30	6.48	0.22
22-Aug	17.5	RAW	7.42	6.83	19.28
		RF	6.47	6.43	3.55
		RFSP	6.59	6.24	3.06
		B1	6.07	6.03	0.75
		B2	6.23	6.08	0.49
29-Aug	22	RAW	8.06	6.98	27.1
		RF	7.22	7.14	1.19
		RFSP	7.17	6.71	1.48
		B1	6.79	6.71	0.42
		B2	5.73	6.49	0.10

Date 2007	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
06-Sep	21	RAW	6.98	6.27	2.68
		RF	6.17	6.02	0.72
		RFSP	6.10	5.90	0.73
		B1	5.71	5.27	0.16
		B2	4.96	5.16	0.13
12-Sep	17.5	RAW	6.75	6.43	3.28
		RF	6.51	5.62	1.31
		RFSP	6.37	5.90	1.2
		B1	5.78	5.63	0.22
		B2	5.25	5.74	0.08
19-Sep	16.5	RAW	7.03	7.08	7.18
		RF	6.30	6.03	0.86
		RFSP	6.29	6.31	0.85
		B1	5.81	5.63	0.13
		B2	5.80	5.97	0.19
27-Sep	19	RAW	7.96	8.03	4.47
		RF	7.54	7.90	1.11
		RFSP	7.68	8.10	0.84
		B1	7.12	7.17	0.35
		B2	6.95	7.28	0.21
03-Oct	17	RAW	6.68	4.67	12.61
		RF	6.55	4.59	1.25
		RFSP	5.65	5.98	0.78
		B1	4.27	4.81	0.14
		B2	5.63	3.43	0.17
05-Oct	16.5	RAW	6.77	4.74	6.21
		RF	4.71	5.83	0.73
		RFSP	6.59	4.85	0.77
		B1	5.51	4.26	0.22
		B2	4.37	4.66	0.13
11-Oct	15.5	RAW	6.18	5.83	12.05
		RF	5.89	5.35	1.06
		RFSP	5.80	5.59	2.16
		B1	5.32	4.93	0.39
		B2	5.21	4.76	0.32
17-Oct	12.5	RAW	6.15	5.58	5.7
		RF	6.04	5.40	1.82
		RFSP	6.09	5.23	1.87
		B1	5.57	5.04	0.47
		B2	5.56	5.08	0.32
25-Oct	11.5	RAW	6.22	5.70	3.95
		RF	6.02	5.42	1.87
		RFSP	5.95	5.32	1.85
		B1	5.38	5.08	0.53
		B2	5.04	4.80	0.31
01-Nov	11	RAW	6.18	5.83	3.28
		RF	5.89	5.35	1.93
		RFSP	5.80	5.59	1.99
		B1	5.32	4.93	0.8
		B2	5.21	4.76	0.52
07-Nov	7	RAW	5.83	5.45	4.93
		RF	5.59	5.19	2.8
		RFSP	5.85	5.40	2.75
		B1	5.13	4.74	0.69
		B2	4.69	na	0.72
14-Nov	8	RAW	5.95	4.97	2.38
		RF	5.62	4.94	1.74
		RFSP	5.52	4.99	1.63
		B1	5.18	na	0.64
		B2	4.95	4.43	0.49
21-Nov	6.5	RAW	5.39	6.54	13.02
		RF	5.26	6.20	na
		RFSP	5.25	6.13	3.61
		B1	4.83	5.50	1.21
		B2	4.63	5.83	0.48

Date 2007-2008	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
28-Nov	2	RAW	6.75	6.39	7.06
		RF	6.56	6.21	5.59
		RFSP	6.50	5.95	6.51
		B1	5.93	5.36	2.31
		B2	5.59	5.20	1.16
05-Dec	1.5	RAW	6.48	6.03	5.39
		RF	6.47	5.73	3.86
		RFSP	6.22	5.68	3.42
		B1	5.89	5.53	1.48
		B2	5.36	5.25	1.21
12-Dec	1.5	RAW	6.15	na	6.88
		RF	6.07	6.06	3.47
		RFSP	6.03	5.91	3.87
		B1	na	5.74	1.05
		B2	6.30	5.42	0.72
19-Dec	1	RAW	6.63	6.40	2.79
		RF	6.32	na	1.7
		RFSP	6.21	6.09	1.49
		B1	6.00	5.64	0.54
		B2	6.02	5.58	0.54
11-Jan	3	RAW	8.20	7.64	66.58
		RF	8.46	8.20	47.68
		RFSP	8.28	7.98	51.98
		B1	7.83	7.69	19.68
		B2	7.50	7.36	15.18
18-Jan	2	RAW	10.73	9.71	25.40
		RF	9.79	9.49	15.7
		RFSP	10.06	9.56	15.5
		B1	9.50	9.28	5.87
		B2	9.41	9.20	3.45
23-Jan	1.5	RAW	7.33	6.77	4.53
		RF	7.50	7.04	4.74
		RFSP	7.50	7.03	3.88
		B1	7.54	7.06	2.15
		B2	7.21	6.87	0.95
30-Jan	1.5	RAW	6.48	6.29	12.25
		RF	6.60	6.21	9.74
		RFSP	6.57	6.40	9.35
		B1	6.44	6.17	2.37
		B2	6.18	6.16	1.15
06-Feb	1.5	RAW	6.62	6.11	38.19
		RF	6.49	5.91	23.89
		RFSP	6.35	5.97	19.19
		B1	6.12	5.66	4.86
		B2	6.05	5.67	0.98
13-Feb	1	RAW	7.13	6.70	11.07
		RF	6.94	6.56	3.13
		RFSP	6.80	6.64	2.28
		B1	6.74	6.63	0.99
		B2	6.64	6.69	0.97
21-Feb	1	RAW	5.34	5.35	7.76
		RF	5.35	4.96	3.38
		RFSP	5.71	5.37	3.72
		B1	5.13	5.06	1.49
		B2	4.84	4.81	0.58
26-Feb	na	RAW	5.73	5.85	9.27
		RF	5.89	5.74	3.79
		RFSP	5.92	5.56	3.26
		B1	5.49	5.38	1.01
		B2	5.42	7.40	0.62
04-Mar	1	RAW	7.32	6.96	4.21
		RF	6.92	6.93	1.85
		RFSP	6.95	7.02	1.72
		B1	6.76	6.40	0.69
		B2	6.50	6.23	0.43

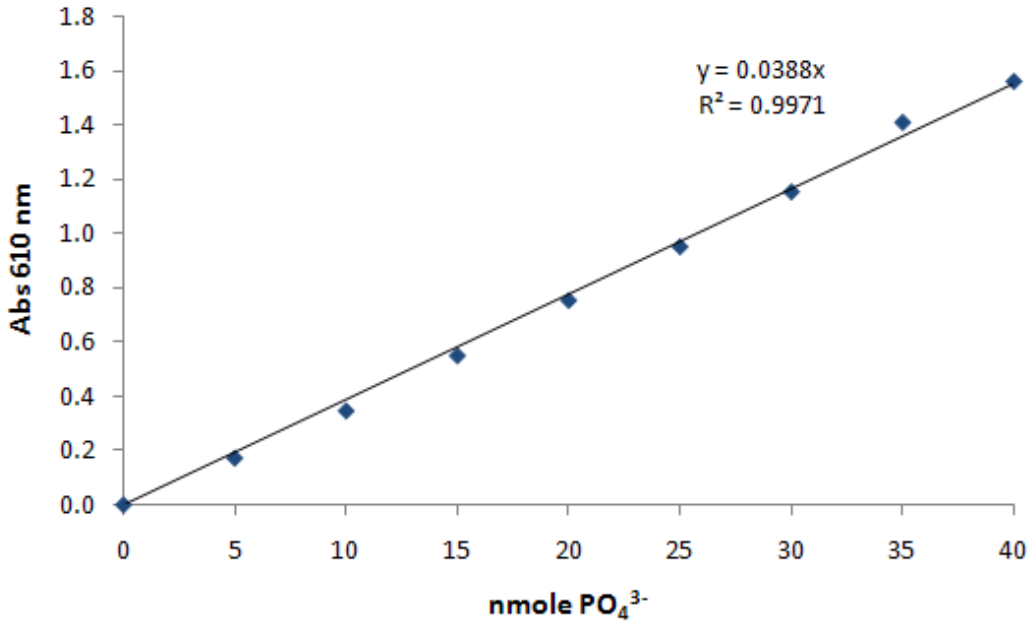
Date 2008	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
12-Mar	1	RAW	6.11	5.79	14.00
		RF	5.77	5.67	7.53
		RFSP	5.78	5.70	8.31
		B1	5.55	5.30	1.02
		B2	5.29	5.15	0.3
19-Mar	1	RAW	7.06	na	31.19
		RF	6.98	na	6.57
		RFSP	6.95	na	5.51
		B1	5.98	na	0.74
		B2	5.87	na	1.09
27-Mar	3.5	RAW	6.32	5.83	18.56
		RF	6.01	5.80	3.76
		RFSP	6.27	5.56	3.44
		B1	5.47	5.36	0.9
		B2	4.99	4.90	0.57
03-Apr	2.5	RAW	4.99	4.82	58.58
		RF	4.98	4.54	37.98
		RFSP	5.04	4.70	62.38
		B1	4.67	4.52	9.79
		B2	4.11	4.27	2.47
09-Apr	4.5	RAW	5.69	5.55	63.17
		RF	5.71	5.60	9.32
		RFSP	5.75	5.73	9.01
		B1	5.21	5.27	2.36
		B2	5.17	5.06	1.17
16-Apr	7	RAW	5.49	5.34	55.4
		RF	5.29	5.26	3
		RFSP	5.39	5.23	2.79
		B1	4.75	4.78	0.63
		B2	4.68	4.76	0.33
23-Apr	15	RAW	5.87	5.48	26.37
		RF	5.95	5.50	1.17
		RFSP	5.80	5.74	1.11
		B1	5.56	5.18	0.16
		B2	4.80	5.00	0.2
30-Apr	10	RAW	5.92	5.45	4.53
		RF	5.82	5.36	1.05
		RFSP	4.71	4.70	0.97
		B1	4.10	3.94	0.38
		B2	3.98	4.00	0.49
07-May	11	RAW	6.17	6.09	21.4
		RF	5.94	6.01	2.02
		RFSP	6.09	5.99	1.25
		B1	5.35	5.60	0.11
		B2	5.34	4.96	0.23
14-May	14	RAW	5.77	na	14.21
		RF	5.59	na	0.71
		RFSP	5.47	na	0.98
		B1	4.70	na	0.19
		B2	4.49	na	0.14
21-May	11.5	RAW	5.84	5.09	32.21
		RF	5.68	5.45	0.88
		RFSP	5.67	5.50	0.82
		B1	5.40	5.49	0.11
		B2	4.96	5.04	0.12
28-May	15	RAW	6.11	5.78	49.31
		RF	5.84	5.45	1.2
		RFSP	5.61	5.37	0.55
		B1	4.96	4.96	0.13
		B2	4.81	4.73	0.24
04-Jun	17	RAW	5.53	5.26	4.08
		RF	5.33	5.21	0.62
		RFSP	5.53	5.22	0.7
		B1	4.95	4.77	0.2
		B2	4.74	5.00	0.08

Date 2008	Temperature °C	sample	TOC mgC/L	DOC mgC/L	turbidity NTU
10-Jun	23	RAW	5.85	5.87	1.39
		RF	5.62	5.78	2.09
		RFSP	5.43	5.48	2.55
		B1	5.00	4.90	0.19
		B2	4.83	4.74	0.25
18-Jun	16	RAW	6.26	5.93	44.5
		RF	5.69	5.57	1.15
		RFSP	5.66	5.52	1.41
		B1	5.13	na	0.14
		B2	5.27	5.36	0.14
25-Jun	19	RAW	na	5.85	8.65
		RF	5.70	5.56	1.17
		RFSP	5.72	5.54	1.2
		B1	5.14	5.32	0.18
		B2	4.90	4.85	0.1
03-Jul	21	RAW	7.00	6.73	77.07
		RF	6.34	6.04	1.37
		RFSP	6.30	5.99	1.38
		B1	5.77	5.59	0.17
		B2	5.67	5.58	0.13
10-Jul	21	RAW	6.83	6.57	35.01
		RF	6.52	6.20	1.6
		RFSP	6.37	6.19	1.52
		B1	5.88	5.79	0.33
		B2	5.74	5.76	0.19
15-Jul	21	RAW	7.11	6.73	42.4
		RF	6.69	6.35	3.94
		RFSP	6.54	6.39	4.67
		B1	5.93	5.92	0.27
		B2	5.98	5.98	0.35
23-Jul	20	RAW	6.65	6.15	82.19
		RF	6.24	6.08	27.19
		RFSP	6.21	6.11	28.49
		B1	5.17	5.25	0.64
		B2	4.83	4.82	0.23
29-Jul	21.5	RAW	6.46	6.18	57.62
		RF	6.16	6.00	4.5
		RFSP	6.12	5.95	4.14
		B1	5.42	5.34	0.31
		B2	5.37	5.31	0.38
06-Aug	22	RAW	6.78	6.12	27.61
		RF	6.42	5.74	3.36
		RFSP	6.31	5.71	5.92
		B1	5.65	5.68	0.23
		B2	5.65	5.68	0.19
13-Aug	19	RAW	6.72	6.59	11.1
		RF	6.44	6.20	5.03
		RFSP	na	na	na
		B1	na	na	na
		B2	5.48	5.18	0.49

Appendix G

Calibration Curve – Phospholipid measurements

Calibration curve used to convert absorbance @ 610 nm to nmole of phosphate (phospholipid biomass measurements)



Results – Phospholipid measurements

Phopholipid results, February 21, 2008 (Day 435)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.8898	74.48	0.393	190	152
B1-3	32	1.3391	34.51	0.499	69	104
B2-1	5	2.835	73.07	0.405	181	144
B2-2	15	2.2679	58.45	0.434	135	155
B2-3	59	0.69247	17.85	0.518	34	52

Phopholipid results, March 4, 2008 (Day 443)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.5677	75.967	0.3876	196	157
B1-3	32	1.0998	32.538	0.4109	79	119
B2-1	5	2.5796	76.320	0.3968	192	154
B2-2	15	1.6552	48.970	0.4102	119	137
B2-3	59	0.5521	16.334	0.4963	33	49

Phopholipid results, April 3, 2008 (Day 475)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.5677	75.967	0.3876	196	158
B1-3	32	1.0998	32.538	0.4109	79	121
B2-1	5	2.5796	76.320	0.3968	192	150
B2-2	15	1.6552	48.970	0.4102	119	123
B2-3	59	0.5521	16.334	0.4963	33	38

Phopholipid results, April 30, 2008 (Day 502)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.9357	75.662	0.3927	192.672	154
B1-3	32	0.92834	23.926	0.4475	53.467	80
B2-1	5	2.9338	75.613	0.3695	204.637	164
B2-2	15	1.6997	43.807	0.3973	110.261	127
B2-3	59	0.56637	14.597	0.4985	29.282	44

Phopholipid results, May 28, 2008 (Day 530)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.9281	75.466	0.3602	209.513	168
B1-3	32	0.99645	25.682	0.464	55.348	83
B2-1	5	2.8729	74.044	0.3177	233.062	186
B2-2	15	2.3171	59.719	0.4193	142.426	164
B2-3	59	0.69348	17.873	0.485	36.852	55

Phopholipid results, July 15, 2008 (Day 578)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B1-1	5	2.5184	64.907	0.3784	171.531	137
B1-3	32	0.40265	10.378	0.496	20.923	31
B2-1	5	2.6595	68.544	0.3699	185.304	148
B2-2	15	1.0618	27.366	0.4495	60.881	70
B2-3	59	0.24461	6.304	0.4708	13.391	20

Phopholipid results, July 24, 2008 (Day 587)

Sample	Depth cm	Abs 610 nm	nmoles PO_4^{3-}	weight media g	nmoles PO_4^{3-} / g of media	Average nmoles PO_4^{3-} / cm3 media
B2-1	5	2.6669	68.735	0.3606	190.612	152
B2-2	15	1.0464	26.969	0.4285	62.938	72

Type of media of the samples: B1-1 anthracite; B1-3 sand; B2-1 anthracite; B2-2 mix of anthracite and sand; B2-3 sand.

The apparent densities of anthracite and sand are 0.8 g/cm^3 and 1.5 g/cm^3.

Appendix H

Results – Total Direct Cell Count (TDCC)

Sampling date **21-Feb-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	1.0512	0.7951	0.636
B1-3	1.0081	0.9202	1.380
B2-1	1.0963	0.8146	0.652
B2-2	1.0702	0.9348	1.075
B2-3	1.0453	0.9852	1.478

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/10	1.16E+08	1.45E+08	1.82E+08
B1-3	1/10	1.30E+08	1.42E+08	9.44E+07
B2-1	1/10	1.58E+08	1.94E+08	2.43E+08
B2-2	1/10	1.35E+08	1.44E+08	1.25E+08
B2-3	1/10	8.15E+07	8.27E+07	5.51E+07
Control		0.00E+00		

Sampling date **04-Mar-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	1.0093	0.7838	0.627
B1-3	1.008	0.9537	1.430
B2-1	1.0015	0.8206	0.656
B2-2	0.9955	0.8962	1.031
B2-3	1.0193	0.9686	1.453

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/100	7.15E+08	9.12E+08	1.14E+09
B1-3	1/10	1.92E+08	2.02E+08	1.34E+08
B2-1	1/10	6.33E+08	7.72E+08	9.65E+08
B2-2	1/10	2.37E+08	2.64E+08	2.29E+08
B2-3	1/10	1.18E+08	1.22E+08	8.10E+07
Control		0		

Sampling date **03-Apr-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	1	0.7531	0.602
B1-3	1	0.9080	1.362
B2-1	1	0.7794	0.624
B2-2	1	0.8882	1.021
B2-3	1	0.9413	1.412

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/100	1.55E+09	2.05E+09	2.56E+09
B1-3	1/10	1.01E+08	1.11E+08	7.38E+07
B2-1	1/100	1.15E+09	1.47E+09	1.84E+09
B2-2	1/10	2.07E+08	2.33E+08	2.03E+08
B2-3	1/10	8.69E+07	9.24E+07	6.16E+07
Control		na		

Sampling date **30-Apr-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	0.998	0.7630	0.610
B1-3	1.03	0.9584	1.438
B2-1	1.04	0.7791	0.623
B2-2	1.06	0.9288	1.068
B2-3	1.02	0.9701	1.455

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/100	8.10E+08	1.06E+09	1.33E+09
B1-3	1/10	1.40E+08	1.46E+08	9.74E+07
B2-1	1/100	2.08E+09	2.67E+09	3.33E+09
B2-2	1/10	9.56E+07	1.03E+08	8.95E+07
B2-3	1/10	1.10E+08	1.14E+08	7.59E+07
Control		na		

Sampling date **28-May-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	1.0079	0.7539	0.603
B1-3	1.0598	0.9899	1.485
B2-1	1.0151	0.7057	0.565
B2-2	1.2096	0.9865	1.134
B2-3	1.0534	0.9787	1.468

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/100	1.01E+09	1.34E+09	1.67E+09
B1-3	1/100	1.07E+09	1.08E+09	7.19E+08
B2-1	1/100	1.71E+09	2.42E+09	3.02E+09
B2-2	1/100	9.31E+08	9.44E+08	8.21E+08
B2-3	1/10	3.07E+08	3.14E+08	2.09E+08
Control		0		

Sampling date **16-Jun-08**

location	wet weight (g)	dry media (g)	cm3 of media
B1-1	1.0226	0.7626	0.610
B1-3	1.039	0.9862	1.479
B2-1	1.007	0.7317	0.585
B2-2	1.0033	0.8621	0.991
B2-3	1.014	0.9440	1.416

Sample	dilution	cells count	Cell/g dry media	Cells/cm3
B1-1	1/100	7.91E+08	1.04E+09	1.30E+09
B1-3	1/100	1.29E+08	1.30E+08	8.69E+07
B2-1	1/100	9.55E+08	1.30E+09	1.63E+09
B2-2	1/100	2.59E+08	3.01E+08	2.62E+08
B2-3	1/10	5.54E+07	5.87E+07	3.91E+07
Control		0		

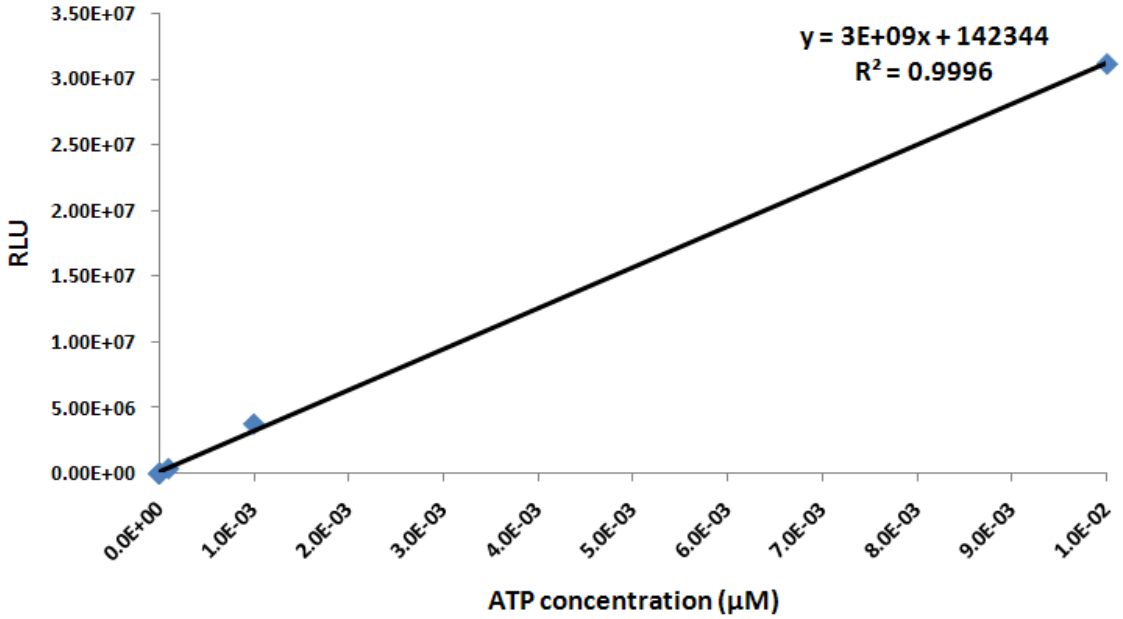
Type of media of the samples: B1-1 anthracite; B1-3 sand; B2-1 anthracite; B2-2 mix of anthracite and sand; B2-3 sand.

The apparent densities of anthracite and sand are 0.8 g/cm^3 and 1.5 g/cm^3.

Appendix I

Calibration Curve – ATP measurements

Representative calibration curve used to convert the relative light unit (RLU) to the concentration of ATP (µM)



Results –ATP media samples

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
21-Feb-08	0	0	0	2661	B1-1 A	1993814	1.25E-05	0.2	0.1513	8.25E-05	6.60E-05	2.37E-04	2.E-04
	0	0	0	2703	B1-1 B	10801069	7.12E-05	0.2	0.1513	4.71E-04	3.77E-04		
	0	0	0	2389	B1-1 C	7774867	5.10E-05	0.2	0.1513	3.37E-04	2.70E-04		
	10-6	1E-4	1E-08	7240	B1-3 A	18280204	1.21E-04	0.2	0.1826	6.63E-04	9.95E-04	8.83E-04	1.E-04
	10-6	1E-4	1E-08	6944	B1-3 B	16700657	1.11E-04	0.2	0.1826	6.05E-04	9.08E-04		
	10-6	1E-4	1E-08	11042	B1-3 C	13756136	9.09E-05	0.2	0.1826	4.98E-04	7.47E-04		
	10-5	1E-3	1E-07	49690	B2-1 A	4856118	3.16E-05	0.2	0.1486	2.12E-04	1.70E-04	2.16E-04	5.E-05
	10-5	1E-3	1E-07	51317	B2-1 B	7509709	4.93E-05	0.2	0.1486	3.31E-04	2.65E-04		
	10-5	1E-3	1E-07	48774	B2-1 C	6057157	3.96E-05	0.2	0.1486	2.66E-04	2.13E-04		
	10-4	1E-2	1E-06	395246	B2-2 A	17906118	1.19E-04	0.2	0.1747	6.79E-04	7.80E-04	6.62E-04	1.E-04
	10-4	1E-2	1E-06	388138	B2-2 B	14759649	9.76E-05	0.2	0.1747	5.59E-04	6.42E-04		
	10-4	1E-2	1E-06	405527	B2-2 C	12957455	8.56E-05	0.2	0.1747	4.90E-04	5.63E-04		
	10-3	1E-1	1E-05	3978046	B2-2 A*	17906118	1.19E-04	0.2	0.1747	6.79E-04	8.28E-04	7.02E-04	1.E-04
	10-3	1E-1	1E-05	4130418	B2-2 B*	14759649	9.76E-05	0.2	0.1747	5.59E-04	6.81E-04		
	10-3	1E-1	1E-05	4213636	B2-2 C*	12957455	8.56E-05	0.2	0.1747	4.90E-04	5.98E-04		
	10-2	1	1E-04	29273132	B2-2 A**	17906118	1.19E-04	0.2	0.1747	6.79E-04	7.33E-04	6.22E-04	1.E-04
	10-2	1	1E-04	29401746	B2-2 B**	14759649	9.76E-05	0.2	0.1747	5.59E-04	6.03E-04		
	10-2	1	1E-04	29638124	B2-2 C**	12957455	8.56E-05	0.2	0.1747	4.90E-04	5.29E-04		
					B2-3 A	9961095	6.56E-05	0.2	0.1889	3.47E-04	5.21E-04	5.25E-04	1.E-05
					B2-3 B	10315449	6.80E-05	0.2	0.1889	3.60E-04	5.40E-04		
					B2-3 C	9861066	6.49E-05	0.2	0.1889	3.44E-04	5.16E-04		

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
4-Mar-08	0	0	0	953	B1-1 A	13384789	8.88E-05	0.2	0.1553	5.71E-04	4.57E-04	4.70E-04	1.E-05
	0	0	0	916	B1-1 B	13802565	9.15E-05	0.2	0.1553	5.89E-04	4.72E-04		
	0	0	0	1049	B1-1 C	14086020	9.34E-05	0.2	0.1553	6.02E-04	4.81E-04		
	10-6	1E-4	1E-08	4432	B1-3 A	28094216	1.87E-04	0.2	0.1892	9.87E-04	1.48E-03	1.48E-03	3.E-05
	10-6	1E-4	1E-08	4856	B1-3 B	27511524	1.83E-04	0.2	0.1892	9.67E-04	1.45E-03		
	10-6	1E-4	1E-08	4552	B1-3 C	28619626	1.90E-04	0.2	0.1892	1.01E-03	1.51E-03		
	10-5	1E-3	1E-07	36868	B2-1 A	28626402	1.90E-04	0.2	0.1639	1.16E-03	9.29E-04	9.63E-04	3.E-05
	10-5	1E-3	1E-07	36498	B2-1 B	29908842	1.99E-04	0.2	0.1639	1.21E-03	9.71E-04		
	10-5	1E-3	1E-07	47927	B2-1 C	30489212	2.03E-04	0.2	0.1639	1.24E-03	9.90E-04		
	10-4	1E-2	1E-06	404841	B2-2 A	33215854	2.21E-04	0.2	0.1801	1.23E-03	1.41E-03	1.36E-03	1.E-04
	10-4	1E-2	1E-06	382577	B2-2 B	29274194	1.95E-04	0.2	0.1801	1.08E-03	1.24E-03		
	10-4	1E-2	1E-06	381301	B2-2 C	33386452	2.22E-04	0.2	0.1801	1.23E-03	1.42E-03		
	10-3	1E-1	1E-05	3898446	B2-2 A*	33215854	2.21E-04	0.2	0.1801	1.23E-03	1.50E-03	1.44E-03	9.E-05
	10-3	1E-1	1E-05	3765595	B2-2 B*	29274194	1.95E-04	0.2	0.1801	1.08E-03	1.32E-03		
	10-3	1E-1	1E-05	3668113	B2-2 C*	33386452	2.22E-04	0.2	0.1801	1.23E-03	1.50E-03		
	10-2	1	1E-04	31129088	B2-2 A**	33215854	2.21E-04	0.2	0.1801	1.23E-03	1.33E-03	1.28E-03	9.E-05
	10-2	1	1E-04	30915128	B2-2 B**	29274194	1.95E-04	0.2	0.1801	1.08E-03	1.17E-03		
	10-2	1	1E-04	31357436	B2-2 C**	33386452	2.22E-04	0.2	0.1801	1.23E-03	1.33E-03		
					B2-3 A	24742202	1.64E-04	0.2	0.1901	8.65E-04	1.30E-03	1.40E-03	1.E-04
					B2-3 B	26098726	1.74E-04	0.2	0.1901	9.13E-04	1.37E-03		
					B2-3 C	29016468	1.93E-04	0.2	0.1901	1.02E-03	1.52E-03		

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
3-Apr-08	0	0	0	2719	B1-1 A	1196360	6.45E-06	0.2	0.1506	4.28E-05	3.43E-05	5.25E-05	3.E-05
	0	0	0	2928	B1-1 B	2709178	1.65E-05	0.2	0.1506	1.10E-04	8.78E-05		
	0	0	0	2012	B1-1 C	1224504	6.64E-06	0.2	0.1506	4.41E-05	3.53E-05		
	10-6	1E-4	1E-08	6690	B1-3 A	24360034	1.61E-04	0.2	0.1816	8.86E-04	1.33E-03	1.39E-03	1.E-04
	10-6	1E-4	1E-08	6849	B1-3 B	24120720	1.59E-04	0.2	0.1816	8.77E-04	1.32E-03		
	10-6	1E-4	1E-08	7260	B1-3 C	28123284	1.86E-04	0.2	0.1816	1.02E-03	1.54E-03		
	10-5	1E-3	1E-07	54450	B2-1 A	1199142	6.47E-06	0.2	0.1559	4.15E-05	3.32E-05	8.75E-05	6.E-05
	10-5	1E-3	1E-07	50721	B2-1 B	4445290	2.81E-05	0.2	0.1559	1.80E-04	1.44E-04		
	10-5	1E-3	1E-07	57803	B2-1 C	2711439	1.66E-05	0.2	0.1559	1.06E-04	8.50E-05		
	10-4	1E-2	1E-06	472380	B2-2 A	22267802	1.47E-04	0.2	0.1559	9.43E-04	1.08E-03	1.10E-03	2.E-05
	10-4	1E-2	1E-06	453573	B2-2 B	22323482	1.47E-04	0.2	0.1559	9.45E-04	1.09E-03		
	10-4	1E-2	1E-06	462990	B2-2 C	23033858	1.52E-04	0.2	0.1559	9.75E-04	1.12E-03		
	10-3	1E-1	1E-05	5452319	B2-2 A*	22267802	1.47E-04	0.2	0.1559	9.43E-04	1.15E-03	1.16E-03	2.E-05
	10-3	1E-1	1E-05	4885158	B2-2 B*	22323482	1.47E-04	0.2	0.1559	9.45E-04	1.15E-03		
	10-3	1E-1	1E-05	5346901	B2-2 C*	23033858	1.52E-04	0.2	0.1559	9.75E-04	1.19E-03		
	10-2	1	1E-04	30328935	B2-2 A**	22267802	1.47E-04	0.2	0.1559	9.43E-04	1.02E-03	1.03E-03	2.E-05
	10-2	1	1E-04	32367478	B2-2 B**	22323482	1.47E-04	0.2	0.1559	9.45E-04	1.02E-03		
	10-2	1	1E-04	27118668	B2-2 C**	23033858	1.52E-04	0.2	0.1559	9.75E-04	1.05E-03		
					B2-3 A	28593846	1.89E-04	0.2	0.1883	1.00E-03	1.51E-03	1.65E-03	1.E-04
					B2-3 B	33302576	2.20E-04	0.2	0.1883	1.17E-03	1.76E-03		
					B2-3 C	32002072	2.12E-04	0.2	0.1883	1.13E-03	1.69E-03		

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
30-Apr-08	0	0	0	928	B1-1 A	15643718	1.03E-04	0.2	0.1529	6.76E-04	5.41E-04	6.16E-04	7.E-05
	0	0	0	810	B1-1 B	18200822	1.20E-04	0.2	0.1529	7.87E-04	6.30E-04		
	0	0	0	991	B1-1 C	19613181	1.30E-04	0.2	0.1529	8.49E-04	6.79E-04		
	10-6	1E-4	1E-08	4133	B1-3 A	23330760	1.55E-04	0.2	0.1861	8.31E-04	1.25E-03	1.19E-03	7.E-05
	10-6	1E-4	1E-08	4548	B1-3 B	22747868	1.51E-04	0.2	0.1861	8.10E-04	1.21E-03		
	10-6	1E-4	1E-08	5113	B1-3 C	20683840	1.37E-04	0.2	0.1861	7.36E-04	1.10E-03		
	10-5	1E-3	1E-07	42663	B2-1 A	19129900	1.27E-04	0.2	0.1498	8.45E-04	6.76E-04	5.66E-04	1.E-04
	10-5	1E-3	1E-07	39862	B2-1 B	13894053	9.17E-05	0.2	0.1498	6.12E-04	4.89E-04		
	10-5	1E-3	1E-07	47490	B2-1 C	15081980	9.96E-05	0.2	0.1498	6.65E-04	5.32E-04		
	10-4	1E-2	1E-06	411365	B2-2 A	28619426	1.90E-04	0.2	0.1753	1.08E-03	1.25E-03	1.21E-03	4.E-05
	10-4	1E-2	1E-06	419855	B2-2 B	26982378	1.79E-04	0.2	0.1753	1.02E-03	1.17E-03		
	10-4	1E-2	1E-06	534285	B2-2 C	27471446	1.82E-04	0.2	0.1753	1.04E-03	1.20E-03		
	10-3	1E-1	1E-05	5453534	B2-2 A*	28619426	1.90E-04	0.2	0.1753	1.08E-03	1.32E-03	1.28E-03	4.E-05
	10-3	1E-1	1E-05	4372680	B2-2 B*	26982378	1.79E-04	0.2	0.1753	1.02E-03	1.25E-03		
	10-3	1E-1	1E-05	4446898	B2-2 C*	27471446	1.82E-04	0.2	0.1753	1.04E-03	1.27E-03		
	10-2	1	1E-04	33462802	B2-2 A**	28619426	1.90E-04	0.2	0.1753	1.08E-03	1.17E-03	1.13E-03	3.E-05
	10-2	1	1E-04	33324896	B2-2 B**	26982378	1.79E-04	0.2	0.1753	1.02E-03	1.10E-03		
	10-2	1	1E-04	33727348	B2-2 C**	27471446	1.82E-04	0.2	0.1753	1.04E-03	1.12E-03		
					B2-3 A	17212264	1.14E-04	0.2	0.1902	5.98E-04	8.97E-04	8.71E-04	4.E-05
					B2-3 B	15816969	1.04E-04	0.2	0.1902	5.49E-04	8.24E-04		
					B2-3 C	17119936	1.13E-04	0.2	0.1902	5.95E-04	8.92E-04		

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
28-May-08	0	0	0	620	B1-1 A	29616986	1.96E-04	0.2	0.1496	1.31E-03	1.05E-03	8.63E-04	2.E-04
	0	0	0	621	B1-1 B	26785396	1.78E-04	0.2	0.1496	1.19E-03	9.50E-04		
	0	0	0	na	B1-1 C	16680105	1.10E-04	0.2	0.1496	7.37E-04	5.89E-04		
	10-6	1E-4	1E-08	5663	B1-3 A	saturation	na	0.2	0.1868	na	na	na	na
	10-6	1E-4	1E-08	5453	B1-3 B	saturation	na	0.2	0.1868	na	na		
	10-6	1E-4	1E-08	6475	B1-3 C	saturation	na	0.2	0.1868	na	na		
	10-5	1E-3	1E-07	43666	B2-1 A	27804926	1.84E-04	0.2	0.1390	1.33E-03	1.06E-03	9.49E-04	1.E-04
	10-5	1E-3	1E-07	40787	B2-1 B	22692572	1.50E-04	0.2	0.1390	1.08E-03	8.65E-04		
	10-5	1E-3	1E-07	39033	B2-1 C	24157866	1.60E-04	0.2	0.1390	1.15E-03	9.21E-04		
	10-4	1E-2	1E-06	767243	B2-2 A	saturation	na	0.2	0.1606	na	na	6.66E-04	4.E-04
	10-4	1E-2	1E-06	707567	B2-2 B	8749690	5.74E-05	0.2	0.1606	3.57E-04	4.11E-04		
	10-4	1E-2	1E-06	731672	B2-2 C	19436560	1.29E-04	0.2	0.1606	8.01E-04	9.21E-04		
	10-3	1E-1	1E-05	6624226	B2-2 A*	saturation	na	0.2	0.1606	na	na	7.06E-04	4.E-04
	10-3	1E-1	1E-05	6485966	B2-2 B*	8749690	5.74E-05	0.2	0.1606	3.57E-04	4.36E-04		
	10-3	1E-1	1E-05	6659212	B2-2 C*	19436560	1.29E-04	0.2	0.1606	8.01E-04	9.77E-04		
	10-2	1	1E-04	na	B2-2 A**	saturation	na	0.2	0.1606	na	na	6.25E-04	3.E-04
	10-2	1	1E-04	na	B2-2 B**	8749690	5.74E-05	0.2	0.1606	3.57E-04	3.86E-04		
	10-2	1	1E-04	na	B2-2 C**	19436560	1.29E-04	0.2	0.1606	8.01E-04	8.65E-04		
					B2-3 A	32042770	2.13E-04	0.2	0.1858	1.14E-03	1.72E-03	1.67E-03	9.E-05
					B2-3 B	29189400	1.94E-04	0.2	0.1858	1.04E-03	1.56E-03		
					B2-3 C	32033902	2.13E-04	0.2	0.1858	1.14E-03	1.72E-03		

	original std conc. µM	original std conc. µM	calibration curve conc. µmoles	RLU	samples	RLU	ATP conc. µmol	Mass wet media g	Mass dry media g	µmol ATP / g dry media	µmol ATP / cm^3 dry media	average µmol ATP / cm^3 dry media	Standard deviation µmol ATP /cm^3
16-Jul-08	0	0	0	0	B1-1 A	12157847	8.00E-03	0.2	0.1492	5.36E-02	4.29E-02	2.68E-02	1.E-02
	0	0	0	0	B1-1 B	6386569	4.15E-03	0.2	0.1492	2.78E-02	2.23E-02		
	0	0	0	0	B1-1 C	4412976	2.83E-03	0.2	0.1492	1.90E-02	1.52E-02		
	10-6	1E-4	1E-08	1128	B1-3 A	25459950	1.69E-02	0.2	0.1898	8.88E-02	1.33E-01	1.24E-01	8.E-03
	10-6	1E-4	1E-08	1653	B1-3 B	22579278	1.49E-02	0.2	0.1898	7.87E-02	1.18E-01		
	10-6	1E-4	1E-08	1701	B1-3 C	22995988	1.52E-02	0.2	0.1898	8.02E-02	1.20E-01		
	10-5	1E-3	1E-07	1556	B2-1 A	1194110	6.88E-04	0.2	0.1453	4.74E-03	3.79E-03	1.49E-02	1.E-02
	10-5	1E-3	1E-07	2131	B2-1 B	2710264	1.70E-03	0.2	0.1453	1.17E-02	9.35E-03		
	10-5	1E-3	1E-07	2011	B2-1 C	8720988	5.71E-03	0.2	0.1453	3.93E-02	3.14E-02		
	10-4	1E-2	1E-06	5948	B2-2 A	2617704	1.64E-03	0.2	0.1719	9.53E-03	1.10E-02	9.02E-03	4.E-03
	10-4	1E-2	1E-06	8238	B2-2 B	2694983	1.69E-03	0.2	0.1719	9.83E-03	1.13E-02		
	10-4	1E-2	1E-06	7060	B2-2 C	1240604	7.19E-04	0.2	0.1719	4.19E-03	4.81E-03		
	10-3	1E-1	1E-05	51350	B2-2 A*	2617704	1.64E-03	0.2	0.1719	9.53E-03	1.16E-02	9.57E-03	4.E-03
	10-3	1E-1	1E-05	64499	B2-2 B*	2694983	1.69E-03	0.2	0.1719	9.83E-03	1.20E-02		
	10-3	1E-1	1E-05	63741	B2-2 C*	1240604	7.19E-04	0.2	0.1719	4.19E-03	5.11E-03		
	10-2	1	1E-04	495479	B2-2 A**	2617704	1.64E-03	0.2	0.1719	9.53E-03	1.03E-02	8.48E-03	3.E-03
	10-2	1	1E-04	680889	B2-2 B**	2694983	1.69E-03	0.2	0.1719	9.83E-03	1.06E-02		
	10-2	1	1E-04	609038	B2-2 C**	1240604	7.19E-04	0.2	0.1719	4.19E-03	4.52E-03		
	10-1	10	1E-03	3904371	B2-3 A	15979072	1.05E-02	0.2	0.1862	5.66E-02	8.50E-02	9.03E-02	3.E-02
	10-1	10	1E-03	4848134	B2-3 B	23028818	1.52E-02	0.2	0.1862	8.19E-02	1.23E-01		
	10-1	10	1E-03	6879807	B2-3 C	11913024	7.83E-03	0.2	0.1862	4.21E-02	6.31E-02		
	1	100	1E-02	29861584									
	1	100	1E-02	32107888									
	1	100	1E-02	31256570									

Type of media of the samples: B1-1 anthracite; B1-3 sand; B2-1 anthracite; B2-2 mix of anthracite and sand; B2-3 sand.

Triplicate analysis are indicated by A, B, and C. na = not available

The apparent densities of anthracite and sand are 0.8 g/cm^3 and 1.5 g/cm^3 respectively.

For the second sampling locations of B2 (i.e. B2-2), the sample collected was a mix of sand and anthracite media. The concentration of ATP per cm3 of dry media have been calculated using a 50 sand /50 anthracite ratio (i.e. B2-2), a 40 sand / 60 anthracite ratio (i.e. B2-2*), and a 60 sand / 40 anthracite ratio (i.e. B2-2**)

Appendix J

BIOWIN Models

Additional information on BIOWIN models for the estimation of biodegradable compounds

Depending on the chemical structure of organic chemicals, the aerobic degradability can be evaluated using BIODEG, survey or MITI models. Details about the development of the models allowing semi-quantitative prediction of biodegradation rates are presented. The approach using fragments of compounds to evaluate biodegradability of organic compound is rather simplistic and do not account for interactions between functional groups. However, the method provides a quantitative or semi-quantitative estimate of the biodegradation rates.

BIODEG models

BIODEG models use a training set of 291 organic compounds to evaluate their probability of rapid biodegradation (Boethling *et al.*, 1994). The level of biodegradability of each compound was evaluated based on experimental mixed-culture biodegradation data. This model takes into consideration several factors influencing biodegradation such as acclimation, microbial toxicity, and temperature. The probability of rapid biodegradation of a contaminant is based on 36 preselected substructures (i.e. independent variable) and molecular weight using linear and non-linear models. The preselected substructures or fragments are described in Boethling *et al.* (1994). The addition of the molecular weight as a continuous variable allows the prediction of biodegradability even if the compounds do not contain any of the 36 preselected substructures. However, the prediction based solely on molecular weight is fairly low except if the compound has a very low or high molecular weight. To decide of a molecule contain a specific fragment, an atom can be included in only one fragment.

The linear model is defined as:

$$Y_j = a_0 + a_1 f_1 + a_2 f_2 + ... + a_{36} f_{36} + a_m M_w + e_j \qquad \text{eq. 1}$$

Where Y_j is the probability that a compound j will biodegrade fast, f_n is the number the nth substructure in the jth compounds, a_0 is the equation constant, a_n is the regression coefficient of the nth structure, M_w is the molecular weight, a_m is the regression coefficient for M_w, and e_j is the error term.

The regression coefficients were calculated using the method of lest squares.

The non-linear model is defined as:

$$Y_j = \frac{\exp(a_0 + a_1 f_1 + a_2 f_2 + ... + a_{36} f_{36} + a_m M_w)}{1 + \exp(a_0 + a_1 f_1 + a_2 f_2 + ... + a_{36} f_{36} + a_m M_w)} \qquad \text{eq. 2}$$

The regression coefficients were estimated using the maximum likelihood method because the model is not a linear function of the variable.
For both linear and non linear model a probability (Y_j) equal or greater than 0.5 indicates fast biodegradation and a probability less than 0.5 indicates that the compound does not biodegrade fast.

Performance of the linear and non-linear model is available in Boethling *et al.* (1994) for both models, the rapidly degraded compounds were classified more accurately than the slowly degraded compounds.

For some fragments such as aromatic F, N-nitroso, and aliphatic Br fragments the confidence in the regression coefficient is not high because only few compounds having these structures have been tested. The confidence into those regression coefficients could eventually be raised by testing additional contaminants.

MITI models

The Ministry of International Trade and Industry (MITI)-I test is a protocol approved by the Organization for Economic Cooperation and Development (OECD) to determined ready biodegradability (EPA, 2009). The data set used to develop this model contains 884 organic compounds (Tunkel *et al.*, 2000). The fragment library used for the development of BIODEG model have been modified to better describe the compounds back bone, functional group, and substitution pattern (Tunkel *et al.*, 2000). The final fragment library of the MITI models contains 42 fragments plus molecular weight as independent variables.

The linear and non-linear models presented in equations 1 and 2 were also used to define MITI models.

AS determined for the BIODEG model, for both linear and non linear model a probability (Y_j) equal or greater than 0.5 indicates fast biodegradation and a probability less than 0.5 indicates that the compound does not biodegrade fast.

Survey models

BIODEG and MITI models are based on experimental data and the validity of the models are limited to structure classification. A survey involving 22 biodegradation experts was performed to estimate rates and biodegradation by-products of 200 organic compounds (Boethling *et al.*, 1989). Each compound was evaluated by 17 different experts. The experts were asked to estimate the rate of primary and ultimate degradation under aerobic conditions. Primary degradation is recognized as the loss of parent compound while the ultimate degradation is the conversion to CO_2 and water.

A semi-quantitative scale (i.e. hours, days, weeks, months, or longer than months) was used to evaluate the primary and ultimate biodegradability. The arithmetic mean score for each compound were calculated after assigning numerical score to the semi-quantitative scale (e.g. 5= hours, 4= days, 3=weeks, 2=months, or 1= longer than months).

The primary and ultimate biodegradability of each compound is estimated by summing the time required for biodegradation times its regression coefficient, plus the equation constant, and the product of the molecular weight and its coefficient are added.
The regression coefficients were estimated by the least square method.

The assessment of the accuracy was performed by reviewing 13 compounds that had been tested in the BIODEG data base. From the examination, it was evident that the expert estimations were consistent with the experimental data.

To allow direct comparison between the survey models and BIODEG or MITI models the following criteria were used:

- rapid primary biodegradation was attributed to a biodegradability score ≥ 3.5 corresponding to days-weeks
- rapid ultimate biodegradation was attributed to a biodegradability score > 2.5 corresponding to weeks-months.

Appendix K

Adsorption of selected contaminants on the biofiltration experimental set-up at low and high spiking concentration

Low spiking concentration

water temp. °C	Year	Date	DEET RFSP ng/L	DEET B3 ng/L	DEET removal %	ibuprofen RFSP ng/L	ibuprofen B3 ng/L	ibuprofen removal %	naproxen RFSP ng/L	naproxen B3 ng/L	naproxen removal %
21	2007	July 18	695	689	1	463	450	3	420	388	8
21	2007	July 20	735	760	-3	435	447	-3	393	441	-12
22	2007	July 24	785	815	-4	452	426	6	408	390	4
21	2007	July 26	741	758	-2	435	422	3	403	449	-11
24	2007	August 1	781	752	4	524	441	16	491	419	15
24	2007	August 1 replicate	781	788	-1	524	435	17	290	na	na
22	2007	August 8	943	889	6	460	416	10	382	390	-2
1	2007	December 12	619	635	-3	648	647	0	526	570	-8
1	2007	December 15	644	654	-2	721	710	2	582	603	-4
1	2007	December 19	604	632	-5	674	663	2	503	522	-4
1	2008	January 21	638	586	8	620	588	5	448	444	1
4	2008	March 27	915	863	6	764	687	10	541	568	-5
3	2008	April 3	710	697	2	626	581	7	421	436	-4
5	2008	April 11	585	696	-19	492	568	-15	355	429	-21
7	2008	April 16	547	548	0	413	406	2	378	409	-8
15	2008	April 24	557	538	3	454	391	14	483	463	4
9	2008	April 30	516	492	5	442	386	13	455	422	7
		Average			0			5			-2
		Standard deviation			6			8			9

water temp. °C	Year	Date	atrazine RFSP ng/L	atrazine B3 ng/L	atrazine removal %	nonylphenol RFSP ng/L	nonylphenol B3 ng/L	nonylphenol removal %	carbamazepine RFSP ng/L	carbamazepine B3 ng/L	carbamazepine removal %
21	2007	July 18	476	475	0	25	d	na	516	512	1
21	2007	July 20	481	498	-4	d	d	na	484	497	-3
22	2007	July 24	528	544	-3	d	d	na	502	551	-10
21	2007	July 26	514	495	4	45	na	na	484	495	-2
24	2007	August 1	432	422	2	28	na	na	642	607	6
24	2007	August 1 replicate	432	448	2	na	na	na	642	599	7
22	2007	August 8	414	410	1	nd	nd	na	536	529	1
1	2007	December 12	411	403	2	75	52	31	542	553	-2
1	2007	December 15	415	422	-2	91	122	-34	519	548	-6
1	2007	December 19	401	407	-2	42	54	-28	523	499	5
1	2008	January 21	480	454	5	108	61	44	525	522	1
4	2008	March 27	651	651	0	97	27	72	487	493	-1
3	2008	April 3	567	583	-3	nd	d	na	385	389	-1
5	2008	April 11	472	568	-20	nd	d	na	319	379	-19
7	2008	April 16	387	398	-3	47	26	45	353	373	-6
15	2008	April 24	429	429	0	d	d	na	511	503	2
9	2008	April 30	433	413	5	51	95	-86	492	440	11
		Average			-1			7			-1
		Standard deviation			6			57			7

na: not available; nd : below limit of detection; d: below limit of quantification

High spiking concentration

water temp. °C	Year	Date	DEET RFSP ng/L	DEET B3 ng/L	DEET removal %	ibuprofen RFSP ng/L	ibuprofen B3 ng/L	ibuprofen removal %	naproxen RFSP ng/L	naproxen B3 ng/L	naproxen removal %
9	2007	October 30	4004	3877	3	4008	3896	3	4135	4217	-2
11	2007	November 1	4264	4275	0	3081	3183	-3	5362	4111	23
7	2007	November 12	4973	4886	2	4691	4610	2	5382	4672	13
8	2007	November 14	4990	4886	2	4984	4849	3	5926	6182	-4
4.5	2007	November 19	4037	3802	6	3280	3233	1	4880	5429	-11
2	2007	November 28	4756	4851	-2	4285	4302	0	3515	3363	4
2	2007	November 30	5176	5170	0	4528	4633	-2	6334	5423	14
1.5	2007	December 5	4186	3432	18	3823	3013	21	4095	3534	14
1.5	2008	January 30	6251	6215	1	4786	4685	2	7603	6576	14
1.5	2008	February 6	6083	6146	-1	3944	3938	0	6323	6699	-6
2	2008	February 8	6839	6324	8	4947	3790	23	8876	7027	21
1	2008	February 13	6740	7204	-7	4082	4363	-7	7050	6645	6
1	2008	February 19	6072	6225	-3	3996	4070	-2	6415	7188	-12
1	2008	February 26	5038	4711	6	4351	3831	12	5605	4223	25
1	2008	March 4	4875	4832	1	3645	3799	-4	5381	5886	-9
1	2008	March 12	5015	5196	-4	4279	4354	-2	6084	7059	-16
		Average			2			3			5
		Standard deviation			6			9			14

water temp. °C	Year	Date	atrazine RFSP ng/L	atrazine B3 ng/L	atrazine removal %	nonylphenol RFSP ng/L	nonylphenol B3 ng/L	nonylphenol removal %	carbamazepine RFSP ng/L	carbamazepine B3 ng/L	carbamazepine removal %
9	2007	October 30	3481	2054	41	873	699	20	3773	3654	3
11	2007	November 1	4392	4503	-3	260	255	2	2138	2191	-2
7	2007	November 12	4448	4316	3	454	333	27	3102	3058	1
8	2007	November 14	4361	4423	-1	527	454	14	3315	3309	0
4.5	2007	November 19	3397	3387	0	256	174	32	2776	2720	2
2	2007	November 28	3046	3086	-1	122	100	18	3152	3158	0
2	2007	November 30	3326	3291	1	447	96	79	3078	3241	-5
1.5	2007	December 5	3034	2199	28	468	d	na	2758	2106	24
1.5	2008	January 30	4664	4511	3	352	301	15	3963	4034	-2
1.5	2008	February 6	3998	4108	-3	105	182	-74	2595	2575	1
2	2008	February 8	5171	4410	15	315	253	20	3731	2883	23
1	2008	February 13	5286	5596	-6	337	755	-124	3573	3565	0
1	2008	February 19	5306	5526	-4	161	97	39	3662	3401	7
1	2008	February 26	4408	3921	11	592	d	na	5670	2552	55
1	2008	March 4	3371	3506	-4	624	35	94	2848	2789	2
1	2008	March 12	3672	3848	-5	560	178	68	3251	3229	1
		Average			5			16			7
		Standard deviation			13			57			15

na: not available; nd : below limit of detection; d: below limit of quantification

Appendix L

Kinetic analysis

Calculation of biodegradation rate constant (k) achieved by B1 and B2 for DEET, naproxen, and ibuprofen at low influent concentration. k values presented in red indicate lower bound since the effluent concentrations were below the method limit of detection.

DEET

Date	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time porosity*EBCT (min)	k (min^{-1})
Dec 19 07	1	604	557	2.45	0.03	1	604	335	6.03	0.10
Oct 15 07	13	721	297	2.45	0.36	13	721	145	6.03	0.27
May 21 08	12	693	475	2.45	0.15	12	693	245	6.03	0.17
Aug 6 08	22	654	66	2.45	0.94	22	654	16	6.03	0.62

naproxen

Date	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})
Dec 19 07	1	503	159	2.45	0.47	1	503	23	6.03	0.51
Oct 15 07	13	758	292	2.45	0.39	13	758	144	6.03	0.28
May 21 08	12	503	208	2.45	0.36	12	503	156	6.03	0.19
Aug 6 08	22	346	16	2.45	1.25	22	346	2	6.03	0.85

ibuprofen

Date	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})
Dec 19 07	1	674	279	2.45	0.36	1	674	2	6.03	0.97
Oct 15 07	13	607	108	2.45	0.70	13	607	19	6.03	0.57
May 21 08	12	327	14	2.45	1.29	12	327	7	6.03	0.64
Aug 6 08	22	434	2	2.45	2.20	22	434	2	6.03	0.89

porosity sand =0.4; porosity anthracite = 0.58

Calculation of biodegradation rate constant (k) achieved by B1 and B2 for DEET, naproxen, and ibuprofen at high influent concentration. k values presented in red indicate lower bound since the effluent concentrations were below the method limit of detection

DEET

Date	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time porosity*EBCT (min)	k (min^{-1})
Feb 26 08	1	5038	4722	2.45	0.03	1	5038	4450	6.03	0.02
Nov 14 07	8	4990	3745	2.45	0.12	8	4990	2967	6.03	0.09
				2.45					6.03	
Sep 6 07	21	5695	5	2.45	2.87	21	5695	5	6.03	1.17

naproxen

Date	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})
Feb 26 08	1	5605	3770	2.45	0.16	1	5605	1737	6.03	0.19
Nov 14 07	8	5926	2770	2.45	0.31	8	5926	1866	6.03	0.19
				2.45					6.03	
Sep 6 07	21	3861	237	2.45	1.14	21	3861	2	6.03	1.25

ibuprofen

Date	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time porosity*EBCT (min)	k (min^{-1})
Feb 26 08	1	4351	2001	2.45	0.32	1	4351	481	6.03	0.37
Nov 14 07	8	4984	2094	2.45	0.35	8	4984	673	6.03	0.33
				2.45					6.03	
Sep 6 07	21	4017	2	2.45	3.10	21	4017	2	6.03	1.26

porosity sand =0.4; porosity anthracite = 0.58

Determination of correction temperature coefficient factor and calculation of temperature normalized at 20°C rate constant (k') at low influent concentration for B1 and B2

DEET

Date	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time (min)	k ng/L min^{-1}	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Dec 19 07	1	604	557	2.45	0.03	1.17	0.68	1	604	335	6.03	0.10	1.09	0.52
Oct 15 07	13	721	297	2.45	0.36		1.10	13	721	145	6.03	0.27		0.49
May 21 08	12	693	475	2.45	0.15		0.55	12	693	245	6.03	0.17		0.35
Aug 6 08	22	654	66	2.45	0.94		0.68	22	654	16	6.03	0.62		0.52

naproxen

Date	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Dec 19 07	1	503	159	2.45	0.47	1.05	1.14	1	503	23	6.03	0.51	1.02	0.81
Oct 15 07	13	758	292	2.45	0.39		0.54	13	758	144	6.03	0.28		0.33
May 21 08	12	503	208	2.45	0.36		0.52	12	503	156	6.03	0.19		0.24
Aug 6 08	22	346	16	2.45	1.25		1.14	22	346	2	6.03	0.85		0.81

ibuprofen

Date	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Dec 19 07	1	674	279	2.45	0.36	1.09	1.85	1	674	2	6.03	0.97	1.00	0.90
Oct 15 07	13	607	108	2.45	0.70		1.29	13	607	19	6.03	0.57		0.56
May 21 08	12	327	14	2.45	1.29		2.56	12	327	7	6.03	0.64		0.62
Aug 6 08	22	434	2	2.45	2.20		1.85	22	434	2	6.03	0.89		0.90

porosity sand =0.4; porosity anthracite = 0.58

Determination of correction temperature coefficient factor and calculation of temperature normalized at 20°C rate constant (k') at high influent concentration for B1 and B2

DEET

Date	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc (ng/L)	effluent conc (ng/L)	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Feb 26 08	1	5038	4722	2.45	0.03	1.26	2.27	1	5038	4450	6.03	0.02	1.22	
Nov 14 07	8	4990	3745	2.45	0.12		1.95	8	4990	2967	6.03	0.09		0.08
Sep 6 07	21	5695	5	2.45	2.87		2.27	21	5695	5	6.03	1.17		

naproxen

Date	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Feb 26 08	1	5605	3770	2.45	0.16	1.10	1.03	1	5605	1737	6.03	0.19	1.10	
Nov 14 07	8	5926	2770	2.45	0.31		1.00	8	5926	1866	6.03	0.19		0.37
Sep 6 07	21	3861	237	2.45	1.14		1.03	21	3861	2	6.03	1.25		

ibuprofen

Date	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})	water temp. (°C)	influent Conc	effluent conc	time (min)	k (min^{-1})	θ	k' at 20°c (min^{-1})
Feb 26 08	1	4351	2001	2.45	0.32	1.12	2.77	1	4351	481	6.03	0.37	1.06	
Nov 14 07	8	4984	2094	2.45	0.35		1.39	8	4984	673	6.03	0.33		0.56
Sep 6 07	21	4017	2	2.45	3.10		2.77	21	4017	2	6.03	1.26		

porosity sand =0.4; porosity anthracite = 0.58

Appendix M

Water quality parameters for UF experiments

	RAW							RF							B1							B2							permeate							Drain						
	TOC	DOC	UV254	SUVA	Turb	pH	cond.	TOC	DOC	UV254	SUVA	Turb	pH	cond.	TOC	DOC	UV254	SUVA	Turb	pH	cond.	TOC	DOC	UV254	SUVA	Turb	pH	cond.	TOC	DOC	UV254	SUVA	Turb	pH	cond.	TOC	DOC	UV254	SUVA	Turb	pH	cond.
	mg/L	mg/L	cm^{-1}	L/mgC*m	NTU		uS	mg/L	mg/L	cm^{-1}	/mgC*r	NTU		uS	mg/L	mg/L	cm^{-1}	/mgC*r	NTU		uS	mg/L	mg/L	cm^{-1}	/mgC*r	NTU		uS	mg/L	mg/L	cm^{-1}	/mgC*r	NTU		uS	mg/L	mg/L	cm^{-1}	/mgC*r	NTU		uS
UF3 - RF																																										
1h								7.04	6.02	0.1800	3.0	1.35	7.64	589															5.96	7.17	0.1669	2.3	0.07	7.91	na							
24h								6.87	5.67	0.1810	3.2	1.53	7.78	na															5.90	5.54	0.1600	2.9	0.01	8.01	na							
48h								6.93	6.42	0.1878	2.9	2.49	7.91	795															5.32	4.99	0.1586	3.2	0.05	8.00	705							
72h								5.70	5.04	0.1779	3.5	2.25	8.06	598															5.65	4.81	0.1572	3.3	0.00	7.08	593							
UF4 - B1																																										
1h	6.59	6.43	0.1952	3.0	6.66	7.83	na	6.93	6.13	0.1746	2.8	1.80	7.99	na	5.85	5.53	0.1577	2.9	0.57	7.91	na								5.33	5.65	0.1494	2.6	0.29	7.95	na							
24h	na	na	na	na	na	na	na	6.69	5.96	0.1690	2.8	0.85	8.07	na	5.94	5.21	0.1568	3.0	0.26	7.92	na								7.08	5.46	0.1633	3.0	0.23	7.98	na							
48h	6.99	6.17	0.1864	3.0	1.87	7.97	548	6.52	6.21	0.1714	2.8	0.75	7.97	546	6.02	5.34	0.1553	2.9	0.06	7.88	499								5.95	5.76	0.1569	2.7	0.07	7.95	548							
72h	7.54	6.52	0.1910	2.9	1.61	8.42	na	6.93	6.25	0.1783	2.9	0.93	8.27	na	6.44	5.89	0.1625	2.8	0.15	8.07	na								6.07	5.71	0.1628	2.9	0.14	7.94	na							
96h	7.25	7.41	0.2026	2.7	2.31	7.92	na	6.93	6.69	0.1888	2.8	0.93	7.90	na	7.29	6.17	0.1682	2.7	0.41	7.80	na								6.12	6.25	0.1682	2.7	0.18	7.85	na							
UF5 - B2																																										
1h	7.14	6.65	0.1982	3.0	3.19	7.75	577	6.36	6.09	0.1724	2.8	0.73	7.72	579								6.03	5.74	0.1590	2.8	0.13	7.62	573	7.37	6.35	0.1605	2.5	0.10	7.65	574							
24h	7.03	6.74	0.2009	3.0	4.05	7.83	579	6.83	na	0.1670	na	0.88	7.79	576								6.06	6.00	0.1557	2.6	0.17	7.72	576	6.10	5.58	0.1554	2.8	0.09	7.79	575							
48h	7.44	6.43	0.2212	3.4	7.56	7.83	570	7.00	6.07	0.1742	2.9	1.22	7.80	565								6.30	5.77	0.1566	2.7	0.22	7.80	562	6.15	5.62	0.1553	2.8	0.15	7.85	560							
72h	7.30	6.70	0.2047	3.1	7.48	7.72	562	6.64	6.67	0.1717	2.6	1.01	7.68	535								5.94	6.18	0.1523	2.5	0.15	7.64	569	6.28	6.61	0.1547	2.3	0.12	7.72	569							
96h	7.62	7.32	0.2024	2.7	4.75	7.86	564	6.52	6.48	0.1710	2.6	0.87	7.80	563								6.37	5.81	0.1540	2.4	0.12	7.69	559	5.98	6.07	0.1531	2.5	0.12	7.79	544							
UF6 - B2																																										
1h	7.17	6.32	0.2087	3.3	9.35	8.17		6.70	6.09	0.1658	2.7	0.77	7.80									5.36	5.37	0.1485	2.8	0.04	7.67		5.22	5.48	0.1450	2.6	0.01	7.74							
24h	7.25	6.38	0.3241	5.1	47.99	7.99		6.64	6.03	0.1550	2.6	1.01	7.85									5.74	5.04	0.1329	2.6	0.04	7.64		5.61	5.90	0.1309	2.2	0.05	7.61							
48h	6.75	6.43	0.1791	2.8	3.27	7.74		6.51	5.62	0.1596	2.8	1.30	7.71									5.25	5.63	0.1335	2.4	0.07	7.63		5.12	4.89	0.1337	2.7	0.09	7.70							
72h	na	na	na	na	na	na		na	na	na	na	na	na									na	na	na	na	na	na		na	na	na	na	na	na							
96h	6.50	6.03	0.1726	2.9	2.09	7.82		6.20	5.86	0.1545	2.6	0.96	7.73									5.60	5.60	0.1344	2.4	0.15	7.65		5.18	5.40	0.1334	2.5	0.04	7.69							
UF7 - B1																																										
1h	7.03	7.08	0.2043	2.9	7.18	7.95	566	6.30	6.03	0.1506	2.5	0.86	7.95	569	5.81	5.63	0.1405	2.5	0.13	7.89	565								5.69	6.18	0.1378	2.2	0.05	7.86	556							
24h	7.63	8.03	0.2549	3.2	15.43	7.77	565	6.86	6.67	0.1539	2.3	1.01	7.77	559	6.02	7.03	0.1372	2.0	0.10	7.86	531								5.25	6.66	0.1337	2.0	0.01	7.89	560							
48h	7.53	6.98	0.2032	2.9	6.43	7.86	574	6.47	6.06	0.1539	2.5	0.76	7.81	571	5.75	5.64	0.1390	2.5	0.20	7.77	570								5.43	5.30	0.1357	2.6	0.14	7.78	559							
120h	7.68	6.95	0.1992	2.9	8.12	7.87	567	6.82	6.20	0.1583	2.6	0.74	7.86	562	6.92	5.94	0.1382	2.3	0.16	7.82	501								4.94	5.11	0.1361	2.7	0.16	7.86	552							
UF8 - B2																																										
1h	5.84	5.78	0.1589	2.7	5.74	7.67	749	5.73	5.38	0.1365	2.5	1.21	7.68	761								5.37	5.01	0.1238	2.5	0.26	7.75	769	6.01	7.31	0.1225	1.7	0.08	7.79	771							
24h	5.68	5.18	0.1469	2.8	2.72	7.82	796	5.63	4.96	0.1381	2.8	1.99	7.82	801								5.02	4.56	0.1236	2.7	0.57	7.82	777	7.75	7.65	0.1178	1.5	0.07	7.80	793							
48h	5.95	4.97	0.1433	2.9	2.46	7.82	710	5.62	4.94	0.1369	2.8	1.83	7.74	742								4.95	4.43	0.1201	2.7	0.47	7.84	770	7.05	6.73	0.1188	1.8	0.30	7.91	758							
96h	6.64	6.34	0.1643	2.6	2.76	7.76	763	6.50	6.24	0.1551	2.5	1.91	7.72	761								5.70	5.46	0.1369	2.5	0.52	7.85	751	6.23	5.80	0.1346	2.3	0.41	8.02	740							
UF9 - B1																																										
1h	6.64	6.18	0.1599	2.6	2.67	8.11	730	6.33	5.99	0.1532	2.6	1.73	8.05	737	5.70	5.70	0.1402	2.5	0.93	8.00	735								5.71	5.76	0.1309	2.3	0.15	8.04	734							
24h	6.34	5.39	0.1530	2.8	3.14	8.23	733	6.29	5.39	0.1461	2.7	2.16	8.24	691	5.94	5.20	0.1330	2.6	1.00	8.26	767								5.43	5.20	0.1295	2.5	0.55	8.30	755							
48h	6.54	5.39	0.2013	3.7	13.02	7.99	707	6.13	5.25	0.1601	3.1	3.61	8.28	726	5.50	4.83	0.1316	2.7	1.21	7.99	754								5.68	4.79	0.1287	2.7	0.67	8.28	729							
96h	6.54	5.96	0.2078	3.5	12.22	8.22	956	6.38	5.67	0.1869	3.3	5.97	8.09	972	5.89	5.51	0.1537	2.8	1.82	8.15	977								5.81	5.79	0.1424	2.5	0.71	8.24	986							
UF12 - B2																																										
1h	6.64	6.22	0.2780	4.5	15.61	7.98	618	6.46	6.09	0.2501	4.1	10.71	7.95	622								5.72	5.52	0.1962	3.6	2.22	7.86	610	5.28	5.42	0.1796	3.3	0.35	7.94	619	5.44	5.08	0.1787	3.5	1.96	8.00	692
24h	5.97	5.54	0.2818	5.1	24.11	8.01	622	5.97	5.52	0.2416	4.4	9.89	8.04	627								5.05	5.19	0.1787	3.4	1.09	7.98	646	4.91	4.99	0.1643	3.3	0.12	7.93	628							
48h	5.34	5.35	0.1970	3.7	7.80	8.05	644	5.71	5.37	0.1800	3.4	3.76	8.03	624								4.84	4.81	0.1526	3.2	0.62	7.97	620	4.79	5.12	0.1459	2.8	0.43	8.05	613	5.17	5.03	0.1530	3.0	1.32	8.08	634
UF13 - B1																																										
1h	5.60	5.43	0.3235	6.0	7.45	8.03	652	5.95	5.47	0.1241	2.3	10.77	8.01	672	5.55	5.28	0.2381	4.5	1.04	7.93	683								5.34	5.26	0.2669	5.1	0.37	7.98	646	5.57	5.37	0.2534	4.7	1.23	7.98	684
24h	5.73	5.85	0.2131	3.6	9.25	8.36	672	5.89	5.74	0.1989	3.5	3.77	8.35	664	5.49	5.56	0.1825	3.3	0.99	8.00	660								5.46	5.26	0.1682	3.2	0.23	8.21	621	5.87	5.71	0.1749	3.1	1.33	8.23	661
UF14 - B2																																										
1h	5.99	5.53	0.2027	3.7	18.90	8.40	651	4.74	4.75	0.1634	3.4	1.34	8.37	651								4.14	4.11	0.1511	3.7	0.29	8.30	650	10.62	9.04	0.1528	1.7	0.23	8.26	650							
24h	6.42	5.92	0.2011	3.4	13.50	8.30	663	4.70	4.65	0.1624	3.5	1.08	8.19	663								4.10	4.13	0.1475	3.6	0.39	8.30	660	5.04	5.55	0.1455	2.6	0.31	8.25	664							
48h	6.29	6.00	0.2107	3.5	7.24	8.33	662	4.99	4.84	0.1849	3.8	3.19	8.23	669								4.26	3.93	0.1533	3.9	0.33	8.02	670	4.97	5.35	0.1512	2.8	0.28	8.11	668							
96h	7.57	6.93	0.2633	3.8	11.76	8.04	526	6.98	6.87	0.2240	3.3	1.54	8.02	530								5.23	5.15	0.2058	4.0	0.20	7.82	539	5.13	6.19	0.2094	3.4	0.21	7.90	540							
UF15 - B1																																										
1h	6.17	6.09	0.2920	4.8	21.40	8.26	446	6.09	5.99	0.2251	3.8	1.25	8.14	446	5.35	5.60	0.2120	3.8	0.23	7.69	447								6.61	6.66	0.2062	3.1	0.00	7.80	397							
24h	7.21	6.56	0.2815	4.3	23.71	8.21	575	5.49	6.24	0.2008	3.2	2.12	8.17	576	4.72	4.62	0.1803	3.9	0.32	7.82	575								4.91	5.79	0.1767	3.1	0.03	7.70	558							
48h	5.73	5.40	0.3126	5.8	27.70	8.30	602	5.63	5.66	0.1943	3.4	1.26	8.17	600	4.82	4.98	0.1754	3.5	0.02	8.08	603								4.96	na	0.1757	na	0.08	7.97	597							
96h	6.21	5.69	0.3316	5.8	52.81	8.40	541	5.85	5.86	0.2029	3.5	1.36	8.41	540	5.27	5.13	0.1898	3.7	0.24	8.25	541								5.05	4.95	0.1886	3.8	0.05	8.21	542							
UF16 - B2																																										
1h	6.71	6.38	0.3974	6.2	50.02	7.96	542	6.30	6.35	0.2647	4.2	5.75	7.96	540								5.84	5.77	0.2256	3.9	0.30	7.85	540	5.83	5.88	0.2327	4.0	0.24	7.85	534							
24h	6.61	6.31	0.3282	5.2	36.62	7.92	524	6.26	6.13	0.2617	4.3	6.71	7.85	526								5.61	5.62	0.2169	3.9	0.54	7.75	528	5.71	5.57	0.2205	4.0	0.18	7.73	530							
48h	6.38	na	0.3820	na	63.52	8.00	515	5.95	5.95	0.2516	4.2	7.65	7.94	514								5.39	na	0.2079	na	0.09	7.74	519	5.45	5.33	0.2063	3.9	0.30	7.78	528							
96h	6.46	6.18	0.3720	6.0	57.62	7.73	522	6.12	5.95	0.2469	4.1	4.14	7.75	520								5.37	5.31	0.2105	4.0	0.38	7.60	523	5.38	5.32	0.2082	3.9	0.26	7.72	524	5.73	5.71	0.2145	3.8	0.48	7.92	527
UF17 - B1																																										
1h	7.12	6.76	0.4259	6.3	60.20	8.02	556	6.77	6.43	0.2727	4.2	7.84	7.90	556	6.97	6.97	0.2366	3.4	0.44	7.84	552								7.68	7.70	0.2308	3.0	0.08	7.85	554							
24h	7.11	6.73	0.3568	5.3	42.40	8.00	562	6.54	6.39	0.2519	3.9	4.67	7.95	561	5.93	5.92	0.2176	3.7	0.27	7.83	560								7.24	7.16	0.2179	3.0	0.32	7.84	556							
48h	6.60	6.28	0.4568	7.3	98.26	8.18	548	6.24	6.01	0.2219	3.7	3.35	8.16	545	5.71	5.55	0.1958	3.5	0.18	8.02	544								5.68	5.53	0.2248	4.1	0.17	7.84	543							
96h	6.63	6.35	0.5476	8.6	132.9	7.95	540	6.23	5.98	0.2168	3.6	2.20	7.98	543	5.80	5.53	0.1992	3.6	0.19	7.87	541								6.17	6.29	0.2145	3.4	0.21	7.94	542	6.37	6.02	0.2087	3.5	0.43	7.99	541
UF18 - B2																																										
1h	7.36	6.94	0.3192	4.6	17.75	7.89	521	7.10	6.86	0.2671	3.9	3.36	7.82	522								6.69	6.47	0.2378	3.7	0.59	7.58	524	na	na	0.2283	na	0.14	7.60	523							
48h	6.57	6.52	0.2794	4.3	13.07	7.75	568	6.52	6.37	0.2419	3.8	4.53	7.64	569								5.51	5.56	0.2034	3.7	0.14	7.59	546	6.45	6.87	0.2034	3.0	0.19	7.55	549	5.82	5.87	0.2090	3.6	0.40	7.75	550
88h	7.18	7.19	0.2984	4.1	10.80	7.82	509	6.97	6.78	0.2830	4.2	5.98	7.74	510								5.66	5.70	0.2148	3.8	0.20	7.57	524	na	na	0.2142	na	0.17	7.62	523							

Appendix N

Summary of the AOC measurements performed in B1 and B2 influents and effluents

Date	04/03/2008		03/04/2008		30/04/2008		28/05/2008		15/06/2008		15/07/2008
temperature (°C)	1		3.5		10		15		21		21
sample	B1	B2	B1	B2	B1	B2	B1	B2	B1	B2	B2
concentration (µg/L)											
Influent	282	267	240	335	109	93	405	368	215	172	302
Effluent	228	219	161	198	118	96	370	284	144	129	444

Appendix O

Summary of the concentration and percentage removal of biopolymers, humic substances and LMWA in raw water, at the effluent of RF and at the effluent of B1 and B2 for the 10 profiles

Profile	Activity	Sample	LCOCD integration				DOC	concentration (mg/L)			%removal			
			Total	BP	HS	LMWA	mg/L	BP	HS	LMWA	Total	BP	HS	LMWA
March	acclimation	raw	4380	169	2916	267	6.33	0.24	4.21	0.39				
28/03/2007		RF	4390	149	2905	343	6.13	0.21	4.06	0.48	0	12	0	-28
5°C		B1	3930	95	2731	288	6.01	0.15	4.18	0.44	10	44	6	-8
		B2	4120	68	2725	339	5.73	0.09	3.79	0.47	6	60	7	-27
May	active	raw	4077	86	2921	242	6.42	0.14	4.60	0.38				
02/05/2007		RF	4032	77	2858	274	5.23	0.10	3.71	0.36	1	10	2	-13
10°C		B1	4146	64	2871	217	6.04	0.09	4.18	0.32	-2	26	2	10
		B2	3842	39	2810	271	5.76	0.06	4.21	0.41	6	55	4	-12
July	active	raw	4791	223	3025	367	5.90	0.27	3.73	0.45				
04/07/2007		RFSP	4800	162	2910	346	5.74	0.19	3.48	0.41	0	27	4	6
20.5°C		B1	5090	92	2770	298	5.30	0.10	2.88	0.31	-6	59	8	19
		B2	3737	21	2682	236	5.35	0.03	3.84	0.34	22	91	11	36
September	active	raw	4314	322	2675	323	7.08	0.53	4.39	0.53				
19/09/2007		RFSP	4151	256	2550	292	6.31	0.39	3.88	0.44	4	20	5	10
16.5°C		B1	3932	147	2511	279	5.93	0.22	3.79	0.42	9	54	6	14
		B2	3889	130	2478	283	5.97	0.20	3.80	0.43	10	60	7	12
September	active	raw	4638	286	2765	360	6.95	0.43	4.14	0.54				
24/09/2007		RFSP	4370	202	2683	307	6.30	0.29	3.87	0.44	6	29	3	15
18°C		B1	4046	109	2541	305	5.94	0.16	3.73	0.45	13	62	8	15
		B2	3971	46	2440	310	5.56	0.06	3.42	0.43	14	84	12	14
November	active	raw	4758	326	2662	359	6.34	0.43	3.55	0.48				
16/11/2007		RFSP	4577	283	2626	296	6.11	0.38	3.51	0.40	4	13	1	18
7°C		B1	4492	253	2570	314	5.86	0.33	3.35	0.41	6	22	3	13
		B2	4249	201	2529	300	5.46	0.26	3.25	0.39	11	38	5	16
January	active	raw	5848	123	3593	358	7.46	0.16	4.58	0.46				
21/01/2008		RFSP	5460	109	3668	364	7.71	0.15	5.18	0.51	7	11	-2	-2
1°C		B1	5358	91	3630	362	7.39	0.13	5.01	0.50	8	26	-1	-1
		B2	5312	63	3595	339	7.21	0.09	4.88	0.46	9	49	0	5
March	inactive	raw	4958	74	3389	284	6.96	0.10	4.76	0.40				
04/03/2008		RFSP	4808	50	3405	280	7.02	0.07	4.97	0.41	3	32	0	1
1°C		B1	4678	26	3370	255	6.40	0.04	4.61	0.35	6	65	1	10
		B2	4518	6	3222	307	6.23	0.01	4.44	0.42	9	92	5	-8
May	active	raw	5233	115	3713	399	6.93	0.15	4.92	0.53				
05/05/2008		RFSP	5001	77	3593	329	6.87	0.11	4.94	0.45	4	33	3	18
11°C		B1	4642	15	3405	327	5.22	0.02	3.83	0.37	11	87	8	18
		B2	4901	31	3388	405	5.15	0.03	3.56	0.43	6	73	9	-2
July	active	raw	5774	232	3602	382	6.73	0.27	4.20	0.45				
15/07/2008		RFSP	5929	196	3541	437	6.39	0.21	3.82	0.47	-3	16	2	-14
20°C		B1	5373	94	3426	386	5.92	0.10	3.77	0.43	7	59	5	-1
		B2	5395	103	3474	364	5.98	0.11	3.85	0.40	7	56	4	5

Appendix P

Microbiological analyses

Summary of the ATP measurements performed in the effluent of B1 and B2 and at the effluent of the control column B3

Date 2007	Days Since Start up	Temperature °C	Calibration curve µM 0	1E-05	1E-04	1E-03	1E-02	RAW 1st repl RLU	RAW 2nd repl RLU	RAW 1st repl µM	RAW 2nd repl µM	RAW average µM	RAW average log µM	RF 1st repl RLU	RF 2nd repl RLU	RF 1st repl µM	RF 2nd repl µM	RF average µM	RF average log µM	RF log removal
February 21	63	1.5	162	na	na	52768	649241	15357	na	3.0E-04	na	3.0E-04	-3.5	6626	na	1.8E-04	na	1.8E-04	-3.7	0.2
February 28	70	1.0	1314	na	na	63120	852125	22725	23578	3.7E-04	3.8E-04	3.7E-04	-3.4	17318	14229	3.1E-04	2.7E-04	2.9E-04	-3.5	0.1
March 7	77	1.0	343	757	705	58126	786317	29867	26405	4.6E-04	4.1E-04	4.3E-04	-3.4	15989	23466	2.8E-04	3.8E-04	3.3E-04	-3.5	0.1
March 22	92	2.0	1193	1679	8240	60393	828758	94460	104516	1.2E-03	1.4E-03	1.3E-03	-2.9	68211	51417	9.1E-04	7.0E-04	8.1E-04	-3.1	0.2
March 28	98	5.0	1286	2062	9133	66156	919276	99760	101270	1.2E-03	1.2E-03	1.2E-03	-2.9	79355	71914	9.4E-04	8.6E-04	9.0E-04	-3.0	0.1
April 4	105	6.0	582	1054	6816	57500	754050	86966	86646	1.1E-03	1.1E-03	1.1E-03	-2.9	47695	42803	6.5E-04	5.9E-04	6.2E-04	-3.2	0.3
April 18	119	5.5	179	3879	7586	59964	759082	42950	42051	5.7E-04	5.6E-04	5.7E-04	-3.2	28687	26800	3.9E-04	3.7E-04	3.8E-04	-3.4	0.2
April 25	126	12.0	1634	1785	9062	67164	871158	171490	137609	1.9E-03	1.6E-03	1.7E-03	-2.8	98558	88389	1.1E-03	1.0E-03	1.1E-03	-3.0	0.2
May 2	133	10.0	1052	1687	7060	51476	668218	73194	81287	1.1E-03	1.2E-03	1.1E-03	-2.9	33721	38036	5.2E-04	5.9E-04	5.5E-04	-3.3	0.3
May 9	140	16.0	1362	1895	7421	89909	909707	127902	163675	1.4E-03	1.8E-03	1.6E-03	-2.8	29608	28969	3.3E-04	3.2E-04	3.3E-04	-3.5	0.7
May 16	147	16.0	1292	1479	6748	78115	778131	210585	232899	2.6E-03	2.9E-03	2.8E-03	-2.6	91067	111098	1.1E-03	1.4E-03	1.3E-03	-2.9	0.3
May 23	154	16.0	1205	1397	6280	69278	720606	38107	47397	5.5E-04	6.8E-04	6.2E-04	-3.2	13173	15404	1.9E-04	2.3E-04	2.1E-04	-3.7	0.5
May 30	161	18.5	1875	2772	10824	88796	845146	338174	458297	4.2E-03	5.7E-03	4.9E-03	-2.3	27078	22910	3.1E-04	2.5E-04	2.8E-04	-3.6	1.2
June 6	168	20.0	1368	2474	9316	65881	719541	118447	186740	1.7E-03	2.7E-03	2.2E-03	-2.7	67409	70936	9.6E-04	1.0E-03	9.9E-04	-3.0	0.3
June 13	175	22.0	1222	2409	11004	99540	1025359	70806	71304	7.1E-04	7.1E-04	7.1E-04	-3.1	35626	42899	3.5E-04	4.3E-04	3.9E-04	-3.4	0.3
July 4	196	20.5	2448	4408	11273	86076	882753	193312	254174	2.1E-03	2.8E-03	2.5E-03	-2.6	30899	27875	3.2E-04	2.9E-04	3.1E-04	-3.5	0.9
July 18	210	21	34062	36485	45274	117215	825157	330658	409180	3.7E-03	4.7E-03	4.2E-03	-2.4	60382	56199	3.0E-04	2.5E-04	2.7E-04	-3.6	1.2
July 26	218	21.5	12545	12692	18047	82568	730068	138917	250100	1.8E-03	3.4E-03	2.6E-03	-2.6	579212	706316	8.1E-03	9.9E-03	9.0E-03	-2.0	-0.5
August 1	224	23.5	12088	12414	19788	94919	825795	549145	556723	6.7E-03	6.8E-03	6.8E-03	-2.2	44407	31437	4.0E-04	2.4E-04	3.2E-04	-3.5	1.3
August 8	231	22	21572	22877	55594	126365	838868	133249	118519	1.2E-03	1.1E-03	1.1E-03	-2.9	80716	72909	5.9E-04	4.9E-04	5.4E-04	-3.3	0.3
August 15	238	21	2086	5850	12399	89862	802743	79726	77976	9.3E-04	9.1E-04	9.2E-04	-3.0	20884	33554	1.9E-04	3.5E-04	2.7E-04	-3.6	0.5

Date 2007	Days Since Start up	Temperature °C	B1 1st repl RLU	B1 2nd repl RLU	B1 1st repl µM	B1 2nd repl µM	B1 average µM	B1 average log µM	B1 log removal	B2 1st repl RLU	B2 2nd repl RLU	B2 1st repl µM	B2 2nd repl µM	B2 average µM	B2 average log µM	B2 log removal	B3 1st repl RLU	B3 2nd repl RLU	B3 1st repl µM	B3 2nd repl µM	B3 average µM	B3 average log µM	B3 log removal
February 21	63	1.5	9382	na	2.2E-04	na	2.2E-04	-3.7	0.1	8320	na	2.0E-04	na	2.0E-04	-3.7	0.2	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
February 28	70	1.0	10691	9201	2.3E-04	2.2E-04	2.2E-04	-3.7	0.2	9961	9231	2.2E-04	2.2E-04	2.2E-04	-3.7	0.2	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
March 7	77	1.0	15157	na	2.7E-04	na	2.7E-04	-3.6	0.2	36978	na	5.4E-04	na	5.4E-04	-3.3	-0.1	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
March 22	92	2.0	69350	47635	9.3E-04	6.6E-04	7.9E-04	-3.1	0.2	45640	38853	6.3E-04	5.5E-04	5.9E-04	-3.2	0.3	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
March 28	98	5.0	70275	63960	8.4E-04	7.7E-04	8.1E-04	-3.1	0.2	38089	46165	4.8E-04	5.7E-04	5.3E-04	-3.3	0.3	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
April 4	105	6.0	30760	27720	4.4E-04	4.0E-04	4.2E-04	-3.4	0.4	18465	19225	2.8E-04	2.9E-04	2.9E-04	-3.5	0.6	54779	49787	7.4E-04	6.7E-04	7.1E-04	-3.2	-0.1
April 18	119	5.5	17524	17135	2.6E-04	2.5E-04	2.5E-04	-3.6	0.4	6012	7898	1.1E-04	1.3E-04	1.2E-04	-3.9	0.7	22960	34735	3.2E-04	4.7E-04	4.0E-04	-3.4	0.0
April 25	126	12.0	21120	19543	2.7E-04	2.5E-04	2.6E-04	-3.6	0.8	16357	22564	2.1E-04	2.8E-04	2.5E-04	-3.6	0.8	46452	51102	5.5E-04	6.0E-04	5.7E-04	-3.2	0.3
May 2	133	10.0	23448	22204	3.8E-04	3.6E-04	3.7E-04	-3.4	0.5	12454	9427	2.2E-04	1.8E-04	2.0E-04	-3.7	0.8	27365	22829	4.3E-04	3.7E-04	4.0E-04	-3.4	0.1
May 9	140	16.0	12691	19348	1.4E-04	2.2E-04	1.8E-04	-3.7	1.0	8321	12796	9.3E-05	1.4E-04	1.2E-04	-3.9	1.1	19116	19883	2.1E-04	2.2E-04	2.2E-04	-3.7	0.2
May 16	147	16.0	41171	46738	5.1E-04	5.8E-04	5.5E-04	-3.3	0.7	14076	11107	1.7E-04	1.3E-04	1.5E-04	-3.8	1.3	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
May 23	154	16.0	13646	11879	2.0E-04	1.8E-04	1.9E-04	-3.7	0.5	6245	5679	9.5E-05	8.7E-05	9.1E-05	-4.0	0.8	18645	18332	2.7E-04	2.7E-04	2.7E-04	-3.6	-0.1
May 30	161	18.5	10487	14467	9.8E-05	1.5E-04	1.2E-04	-3.9	1.6	6107	11380	4.3E-05	1.1E-04	7.6E-05	-4.1	1.8	24103	21751	2.7E-04	2.4E-04	2.5E-04	-3.6	0.0
June 6	168	20.0	12468	9245	1.8E-04	1.3E-04	1.6E-04	-3.8	1.1	6653	6366	9.6E-05	9.2E-05	9.4E-05	-4.0	1.4	20084	18385	2.9E-04	2.6E-04	2.8E-04	-3.6	0.6
June 13	175	22.0	22718	24156	2.3E-04	2.4E-04	2.3E-04	-3.6	0.5	14574	15682	1.4E-04	1.6E-04	1.5E-04	-3.8	0.7	40117	44327	4.0E-04	4.4E-04	4.2E-04	-3.4	0.0
July 4	196	20.5	12279	13065	1.2E-04	1.3E-04	1.2E-04	-3.9	1.3	10228	9826	9.5E-05	9.0E-05	9.2E-05	-4.0	1.4	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
July 18	210	21	39283	na	3.7E-05	na	3.7E-05	-4.4	2.1	39920	35224	4.5E-05	-1.4E-05	1.6E-05	-4.8	2.4	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
July 26	218	21.5	82526	24163	1.0E-03	1.8E-04	6.0E-04	-3.2	0.6	19661	21030	1.2E-04	1.4E-04	1.3E-04	-3.9	1.3	na	na	na	na	#DIV/0!	#DIV/0!	#DIV/0!
August 1	224	23.5	26760	25761	1.8E-04	1.7E-04	1.8E-04	-3.8	1.6	22329	19924	1.3E-04	9.7E-05	1.1E-04	-4.0	1.8	28381	31599	2.0E-04	2.4E-04	2.2E-04	-3.7	0.2
August 8	231	22	49980	44049	2.0E-04	1.3E-04	1.6E-04	-3.8	0.8	43692	42176	1.2E-04	1.0E-04	1.1E-04	-3.9	1.0	43870	46029	1.2E-04	1.5E-04	1.4E-04	-3.9	0.6
August 15	238	21	11417	14810	7.7E-05	1.2E-04	9.8E-05	-4.0	1.0	10433	8770	6.4E-05	4.4E-05	5.4E-05	-4.3	1.2	34346	45764	3.6E-04	5.1E-04	4.3E-04	-3.4	-0.2

Summary of the HPC measurements performed in the effluent of B1 and B2 and at the effluent of the control column B3

Date	Days since Start up	Temperature °C	RAW CFU/ml	log RAW CFU/ml	RF CFU/ml	log RF CFU/ml	RF log removal	B1 CFU/ml	log B1 CFU/ml	B1 log removal	B2 CFU/ml	log B2 CFU/ml	B2 log removal	B3 CFU/ml	log B3 CFU/ml	B3 log removal
10-Jan-07	21	2.5	67000	4.8	47500	4.7	0.1	25000	4.4	0.4	22000	4.3	0.5	na	#VALUE!	#VALUE!
17-Jan-07	28	1.5	59500	4.8	52000	4.7	0.1	31500	4.5	0.3	21500	4.3	0.4	na	#VALUE!	#VALUE!
24-Jan-07	35	1.0	24500	4.4	17500	4.2	0.1	17000	4.2	0.2	12000	4.1	0.3	na	#VALUE!	#VALUE!
31-Jan-07	42	1.0	7500	3.9	4500	3.7	0.2	3000	3.5	0.4	2000	3.3	0.6	na	#VALUE!	#VALUE!
07-Feb-07	49	1.0	10000	4.0	23000	4.4	-0.4	35000	4.5	-0.5	16000	4.2	-0.2	na	#VALUE!	#VALUE!
21-Feb-07	63	1.5	na	#VALUE!	20000	4.3	#VALUE!	na	#VALUE!	#VALUE!	3500	3.5	#VALUE!	na	#VALUE!	#VALUE!
28-Feb-07	70	1.0	19500	4.3	19000	4.3	0.0	14500	4.2	0.1	4500	3.7	0.6	na	#VALUE!	#VALUE!
06-Mar-07	76	1.0	52000	4.7	20500	4.3	0.4	11500	4.1	0.7	9000	4.0	0.8	na	#VALUE!	#VALUE!
14-Mar-07	84	1.5	400000	5.6	785000	5.9	-0.3	80000	4.9	0.7	40000	4.6	1.0	na	#VALUE!	#VALUE!
22-Mar-07	92	2.0	320000	5.5	245000	5.4	0.1	140000	5.1	0.4	110000	5.0	0.5	na	#VALUE!	#VALUE!
28-Mar-07	98	5.0	320000	5.5	285000	5.5	0.1	150000	5.2	0.3	70000	4.8	0.7	na	#VALUE!	#VALUE!
04-Apr-07	105	6.0	260000	5.4	135000	5.1	0.3	115000	5.1	0.4	75000	4.9	0.5	115000	5.1	0.1
12-Apr-07	113		50000	4.7	110000	5.0	-0.3	45000	4.7	0.0	25000	4.4	0.3	95000	5.0	0.1
18-Apr-07	119	5.5	100000	5.0	35000	4.5	0.5	20000	4.3	0.7	15000	4.2	0.8	35000	4.5	0.0
25-Apr-07	126	12.0	1030000	6.0	665000	5.8	0.2	190000	5.3	0.7	360000	5.6	0.5	360000	5.6	0.3
02-May-07	133	10.0	720000	5.9	485000	5.7	0.2	85000	4.9	0.9	50000	4.7	1.2	350000	5.5	0.1
09-May-07	140	16.0	875000	5.9	300000	5.5	0.5	145000	5.2	0.8	70000	4.8	1.1	165000	5.2	0.3
16-May-07	147	16.0	2100000	6.3	1320000	6.1	0.2	765000	5.9	0.4	50000	4.7	1.6	na	#VALUE!	#VALUE!
23-May-07	154	16.0	1025000	6.0	265000	5.4	0.6	200000	5.3	0.7	20000	4.3	1.7	320000	5.5	-0.1
30-May-07	161	18.5	500000	5.7	155000	5.2	0.5	80000	4.9	0.8	10000	4.0	1.7	215000	5.3	-0.1
06-Jun-07	168	20.0	1110000	6.0	315000	5.5	0.5	80000	4.9	1.1	30000	4.5	1.6	235000	5.4	0.1
13-Jun-07	175	22.0	410000	5.6	320000	5.5	0.1	215000	5.3	0.3	115000	5.1	0.6	280000	5.4	0.1
20-Jun-07	182	21.0	1030000	6.0	710000	5.9	0.2	170000	5.2	0.8	30000	4.5	1.5	880000	5.9	-0.1
29-Jun-07	191	21.5	435000	5.6	255000	5.4	0.2	15000	4.2	1.5	15000	4.2	1.5	295000	5.5	-0.1
04-Jul-07	196	20.5	450000	5.7	80000	4.9	0.8	40000	4.6	1.1	10000	4.0	1.7	170000	5.2	-0.3
20-Jul-07	212	21.0	1225000	6.1	415000	5.6	0.5	140000	5.1	0.9	295000	5.5	0.6	250000	5.4	0.2
24-Jul-07	216	21.5	815000	5.9	465000	5.7	0.2	60000	4.8	1.1	40000	4.6	1.3	55000	4.7	0.9
01-Aug-07	224	23.5	1740000	6.2	210000	5.3	0.9	35000	4.5	1.7	5000	3.7	2.5	210000	5.3	0.0
08-Aug-07	231	22.0	670000	5.8	455000	5.7	0.2	235000	5.4	0.5	20000	4.3	1.5	350000	5.5	0.1
15-Aug-07	238	21.0	635000	5.8	290000	5.5	0.3	70000	4.8	1.0	35000	4.5	1.3	260000	5.4	0.0
06-Sep-07	260	21.0	185000	5.3	130000	5.1	0.2	5000	3.7	1.6	na	#VALUE!	#VALUE!	na	#VALUE!	#VALUE!
19-Sep-07	273	16.5	100000	5.0	75000	4.9	0.1	15000	4.2	0.8	25000	4.4	0.6	na	#VALUE!	#VALUE!
03-Oct-07	287	17.0	44500	4.6	31000	4.5	0.2	6000	3.8	0.9	500	2.7	1.9	na	#VALUE!	#VALUE!
17-Oct-07	301	12.5	285000	5.5	215000	5.3	0.1	155000	5.2	0.3	130000	5.1	0.3	na	#VALUE!	#VALUE!
01-Nov-07	316	11.0	1440000	6.2	470000	5.7	0.5	120000	5.1	1.1	80000	4.9	1.3	600000	5.8	-0.1
14-Nov-07	329	8.0	245000	5.4	90000	5.0	0.4	20000	4.3	1.1	5000	3.7	1.7	130000	5.1	-0.2
28-Nov-07	343	2.0	225000	5.4	235000	5.4	0.0	35000	4.5	0.8	5000	3.7	1.7	240000	5.4	0.0
12-Dec-07	357	1.5	165000	5.2	200000	5.3	-0.1	40000	4.6	0.6	0	#NUM!	#NUM!	na	#VALUE!	#VALUE!
16-Jan-08	392	2.0	900000	6.0	345000	5.5	0.4	120000	5.1	0.9	45000	4.7	1.3	na	#VALUE!	#VALUE!
30-Jan-08	406	1.5	255000	5.4	190000	5.3	0.1	180000	5.3	0.2	55000	4.7	0.7	130000	5.1	0.2
21-Feb-08	428	1.0	145000	5.2	95000	5.0	0.2	25000	4.4	0.8	5000	3.7	1.5	na	#VALUE!	#VALUE!
04-Mar-08	440	1.0	265000	5.4	125000	5.1	0.3	20000	4.3	1.1	20000	4.3	1.1	na	#VALUE!	#VALUE!
19-Mar-08	455	1.0	205000	5.3	95000	5.0	0.3	0	#NUM!	#NUM!	0	#NUM!	#NUM!	na	#VALUE!	#VALUE!
03-Apr-08	470	2.5	630000	5.8	455000	5.7	0.1	240000	5.4	0.4	50000	4.7	1.1	na	#VALUE!	#VALUE!
16-Apr-08	483	7.0	220000	5.3	55000	4.7	0.6	45000	4.7	0.7	5000	3.7	1.6	80000	4.9	-0.2
30-Apr-08	497	10.0	430000	5.6	300000	5.5	0.2	35000	4.5	1.1	25000	4.4	1.2	360000	5.6	-0.1
14-May-08	511	14.0	585000	5.8	445000	5.6	0.1	65000	4.8	1.0	20000	4.3	1.5	na	#VALUE!	#VALUE!
28-May-08	518	15.0	490000	5.7	410000	5.6	0.1	435000	5.6	0.1	205000	5.3	0.4	na	#VALUE!	#VALUE!
10-Jun-08	538	23.0	305000	5.5	160000	5.2	0.3	545000	5.7	-0.3	280000	5.4	0.0	na	#VALUE!	#VALUE!
25-Jun-08	553	19.0	465000	5.7	90000	5.0	0.7	70000	4.8	0.8	15000	4.2	1.5	na	#VALUE!	#VALUE!
15-Jul-08	573	21.0	625000	5.8	205000	5.3	0.5	160000	5.2	0.6	60000	4.8	1.0	na	#VALUE!	#VALUE!

Summary of the TDCC measurements performed in the effluent of B1 and B2 and at the effluent of the control column B3

Date	Days since Start up	Temperature °C	RAW Cells/ml	log RAW Cells/ml	RF Cells/ml	log RF Cells/ml	RF log removal	B1 Cells/ml	log B1 Cells/ml	B1 log removal	B2 Cells/ml	log B2 Cells/ml	B2 log removal	B3 Cells/ml	log B3 Cells/ml	B3 log removal
21-Feb-07	63	1.5	4.9E+05	5.7	3.8E+05	5.6	0.1	2.0E+05	5.3	0.4	2.8E+05	5.4	0.2	na	#VALUE!	#VALUE!
28-Feb-07	70	1.0	6.5E+05	5.8	7.6E+05	5.9	-0.1	4.4E+05	5.6	0.2	2.6E+05	5.4	0.4	na	#VALUE!	#VALUE!
06-Mar-07	76	1.0	1.3E+06	6.1	1.0E+06	6.0	0.1	8.4E+05	5.9	0.2	7.7E+05	5.9	0.2	na	#VALUE!	#VALUE!
14-Mar-07	84	1.5	1.8E+06	6.3	1.2E+06	6.1	0.2	6.2E+05	5.8	0.5	3.9E+05	5.6	0.7	na	#VALUE!	#VALUE!
22-Mar-07	92	2.0	1.5E+06	6.2	1.3E+06	6.1	0.1	8.3E+05	5.9	0.3	5.2E+05	5.7	0.5	na	#VALUE!	#VALUE!
28-Mar-07	98	5.0	2.0E+06	6.3	7.9E+05	5.9	0.4	1.5E+06	6.2	0.1	4.8E+05	5.7	0.6	na	#VALUE!	#VALUE!
04-Apr-07	105	6.0	1.3E+06	6.1	8.9E+05	5.9	0.2	1.0E+06	6.0	0.1	1.0E+06	6.0	0.1	7.7E+05	5.9	0.1
12-Apr-07	113		6.9E+05	5.8	8.1E+05	5.9	-0.1	1.0E+06	6.0	-0.2	5.4E+05	5.7	0.1	8.7E+05	5.9	0.0
18-Apr-07	119	5.5	1.1E+06	6.1	1.0E+06	6.0	0.0	8.7E+05	5.9	0.1	5.1E+05	5.7	0.4	9.3E+05	6.0	0.0
25-Apr-07	126	12.0	2.6E+06	6.4	2.6E+06	6.4	0.0	8.6E+05	5.9	0.5	1.1E+06	6.0	0.4	1.3E+06	6.1	0.3
02-May-07	133	10.0	1.4E+06	6.1	7.6E+05	5.9	0.3	7.0E+05	5.8	0.3	7.3E+05	5.9	0.3	7.7E+05	5.9	0.0
09-May-07	140	16.0	3.0E+06	6.5	1.2E+06	6.1	0.4	6.8E+05	5.8	0.6	5.2E+05	5.7	0.8	9.1E+05	6.0	0.1
16-May-07	147	16.0	7.0E+06	6.8	3.9E+06	6.6	0.3	1.5E+06	6.2	0.7	4.7E+05	5.7	1.2	na	#VALUE!	#VALUE!
23-May-07	154	16.0	9.6E+06	7.0	1.9E+06	6.3	0.7	6.9E+05	5.8	1.1	3.7E+05	5.6	1.4	1.6E+06	6.2	0.1
30-May-07	161	18.5	2.6E+06	6.4	1.2E+06	6.1	0.3	4.0E+05	5.6	0.8	3.0E+05	5.5	0.9	3.7E+05	5.6	0.5
06-Jun-07	168	20.0	2.4E+06	6.4	1.6E+06	6.2	0.2	5.8E+05	5.8	0.6	7.3E+05	5.9	0.5	1.1E+06	6.0	0.1
13-Jun-07	175	22.0	2.3E+06	6.4	2.1E+06	6.3	0.0	7.2E+05	5.9	0.5	2.4E+05	5.4	1.0	1.9E+06	6.3	0.1
20-Jun-07	182	21.0	2.1E+06	6.3	7.0E+05	5.8	0.5	5.2E+05	5.7	0.6	1.3E+05	5.1	1.2	2.5E+06	6.4	-0.6
29-Jun-07	191	21.5	1.4E+06	6.1	2.5E+06	6.4	-0.3	4.4E+05	5.6	0.5	3.3E+05	5.5	0.6	2.2E+06	6.3	0.1
04-Jul-07	196	20.5	1.4E+06	6.1	1.6E+06	6.2	-0.1	4.4E+05	5.6	0.5	3.3E+05	5.5	0.6	9.6E+05	6.0	0.2
20-Jul-07	212	21.0	3.7E+06	6.6	1.9E+06	6.3	0.3	3.6E+05	5.6	1.0	2.6E+05	5.4	1.1	1.2E+06	6.1	0.2
24-Jul-07	216	21.5	2.2E+06	6.3	2.8E+06	6.4	-0.1	2.3E+05	5.4	1.0	1.5E+05	5.2	1.2	3.9E+05	5.6	0.9
01-Aug-07	224	23.5	4.2E+06	6.6	9.6E+05	6.0	0.6	5.1E+05	5.7	0.9	2.8E+05	5.4	1.2	1.1E+06	6.0	-0.1
08-Aug-07	231	22.0	1.2E+06	6.1	5.5E+05	5.7	0.3	5.7E+05	5.8	0.3	2.3E+05	5.4	0.7	5.4E+05	5.7	0.0
15-Aug-07	238	21.0	6.8E+05	5.8	6.5E+05	5.8	0.0	5.7E+05	5.8	0.1	1.8E+05	5.3	0.6	7.2E+05	5.9	0.0
06-Sep-07	260	21.0	1.0E+05	5.0	6.8E+04	4.8	0.2	5.3E+04	4.7	0.3	3.4E+04	4.5	0.5	na	#VALUE!	#VALUE!
19-Sep-07	273	16.5	2.3E+06	6.4	1.1E+06	6.1	0.3	6.4E+05	5.8	0.6	3.1E+05	5.5	0.9	na	#VALUE!	#VALUE!
03-Oct-07	287	17.0	2.3E+06	6.4	1.1E+06	6.1	0.3	6.4E+05	5.8	0.6	3.1E+05	5.5	0.9	na	#VALUE!	#VALUE!
17-Oct-07	301	12.5	2.4E+06	6.4	1.9E+06	6.3	0.1	1.1E+06	6.0	0.3	3.0E+05	5.5	0.9	na	#VALUE!	#VALUE!
01-Nov-07	316	11.0	1.5E+06	6.2	8.5E+05	5.9	0.3	5.9E+05	5.8	0.4	5.5E+05	5.7	0.4	9.1E+05	6.0	0.0
14-Nov-07	329	8.0	6.7E+05	5.8	5.0E+05	5.7	0.1	4.0E+05	5.6	0.2	3.0E+05	5.5	0.3	na	#VALUE!	#VALUE!
28-Nov-07	343	2.0	9.9E+05	6.0	1.1E+06	6.0	0.0	5.6E+05	5.7	0.2	5.3E+05	5.7	0.3	7.7E+05	5.9	0.1
12-Dec-07	357	1.5	6.8E+05	5.8	7.2E+05	5.9	0.0	3.8E+05	5.6	0.3	2.1E+05	5.3	0.5	5.1E+05	5.7	0.1
16-Jan-08	392	2.0	1.2E+06	6.1	1.0E+06	6.0	0.1	7.2E+05	5.9	0.2	3.0E+05	5.5	0.6	na	#VALUE!	#VALUE!
30-Jan-08	406	1.5	2.5E+05	5.4	3.7E+05	5.6	-0.2	2.0E+05	5.3	0.1	1.4E+05	5.2	0.2	4.2E+05	5.6	-0.1
21-Feb-08	428	1.0	na	#VALUE!	1.9E+06	6.3	#VALUE!	2.0E+05	5.3	#VALUE!	1.4E+05	5.2	#VALUE!	na	#VALUE!	#VALUE!
04-Mar-08	440	1.0	5.4E+05	5.7	7.2E+05	5.9	-0.1	2.7E+05	5.4	0.3	1.8E+05	5.3	0.5	na	#VALUE!	#VALUE!
19-Mar-08	455	1.0	5.9E+05	5.8	6.1E+05	5.8	0.0	3.2E+05	5.5	0.3	2.5E+05	5.4	0.4	na	#VALUE!	#VALUE!
03-Apr-08	470	2.5	2.9E+06	6.5	1.3E+06	6.1	0.3	6.1E+05	5.8	0.7	4.1E+05	5.6	0.8	na	#VALUE!	#VALUE!
16-Apr-08	483	7.0	6.9E+05	5.8	5.9E+05	5.8	0.1	3.1E+05	5.5	0.3	1.6E+05	5.2	0.6	4.6E+05	5.7	0.1
30-Apr-08	497	10.0	1.9E+06	6.3	1.2E+06	6.1	0.2	7.6E+05	5.9	0.4	3.8E+05	5.6	0.7	1.0E+06	6.0	0.1
14-May-08	511	14.0	1.1E+06	6.0	8.1E+05	5.9	0.1	1.7E+05	5.2	0.8	8.0E+04	4.9	1.1	na	#VALUE!	#VALUE!
28-May-08	525	15.0	3.1E+06	6.5	1.2E+06	6.1	0.4	1.3E+05	5.1	1.4	4.1E+05	5.6	0.9	na	#VALUE!	#VALUE!
10-Jun-08	538	23.0	2.1E+06	6.3	2.2E+06	6.3	0.0	3.4E+05	5.5	0.8	2.3E+05	5.4	1.0	na	#VALUE!	#VALUE!
25-Jun-08	553	19.0	6.2E+05	5.8	4.6E+05	5.7	0.1	9.6E+04	5.0	0.8	1.8E+05	5.3	0.5	na	#VALUE!	#VALUE!
15-Jul-08	573	21.0	1.1E+06	6.0	9.8E+05	6.0	0.0	9.0E+04	5.0	1.1	4.1E+05	5.6	0.4	na	#VALUE!	#VALUE!

Appendix Q

Water quality parameters for NF experiments using B1 effluent

				B1 effluent							Concentrate (XN45)							Permeate (XN45)						
	time (h)	Vs (L/m^2)	J/J_0 (%)	TOC mg/L	DOC mg/L	turbidity NTU	UV_{254} cm^{-1}	SUVA L/mgC*m	pH	cond. uS	TOC mg/L	DOC mg/L	turbidity NTU	UV_{254} cm^{-1}	SUVA L/mgC*m	pH	cond. uS	TOC mg/L	DOC mg/L	turbidity NTU	UV_{254} cm^{-1}	SUVA L/mgC*m	pH	cond. uS
S07	1	4	100	5.75	5.78	0.67	0.14874	2.6	8.06	522	6.04	5.44	0.57	0.14054	2.6	8.04	500	0.96	0.49	0.22	6.3E-03	1.3	7.96	398
	24	96	93	6.34	8.72	0.32	0.15351	1.8	8.32	523	6.60	7.19	0.31	0.15510	2.2	8.34	539	0.23	1.68	0.09	3.5E-03	0.2	8.26	389
	48	204	86	6.80	6.91	0.32	0.15903	2.3	8.13	537	6.45	6.20	0.35	0.16356	2.6	8.16	545	0.26	0.52	0.3	6.2E-03	1.2	7.83	412
	72	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	120	501	75	8.66	8.76	0.22	0.21219	2.4	8.32	585	9.02	9.02	0.24	0.21226	2.4	8.26	551	0.49	0.31	0.14	5.4E-03	1.7	8.09	414
F07	1	6	100	5.71	5.23	2.13	0.14846	2.8	8.31	778	5.68	5.24	2.07	0.14900	2.8	8.36	778	0.30	0.19	0.37	6.2E-03	3.3	8.26	605
	24	108	85	5.69	5.13	1.08	0.14509	2.8	8.5	772	5.36	5.94	1.15	0.14632	2.5	8.51	781	0.32	0.42	0.21	4.5E-03	1.1	8.51	564
	48	246	74	5.49	5.03	0.74	0.15454	3.1	8.59	780	5.89	5.34	0.99	0.15602	2.9	8.59	795	0.27	0.27	0.38	3.9E-03	1.4	8.57	618
	72	302	67	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	439	63	7.16	7.40	0.48	0.18646	2.5	8.29	784	7.34	7.33	0.63	0.19256	2.6	8.36	827	0.13	0.31	0.44	6.8E-03	2.2	8.28	641
W08	1	14	94	7.29	7.29	1.96	0.2452	3.4	8.42	813	7.96	7.45	1.74	0.2894	3.9	8.36	817	0.43	0.22	0.35	1.7E-02	7.6	8.40	697
	24	104	77	8.37	8.37	0.78	0.27695	3.3	8.74	815	8.68	8.51	0.78	0.28075	3.3	8.73	818	1.24	0.29	0.32	1.3E-02	4.3	8.71	681
	48	198	68	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	72	304	65	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	397	62	12.50	12.13	0.49	0.39962	3.3	8.39	869	12.48	12.22	0.59	0.40742	3.3	8.42	894	0.93	0.32	0.37	1.6E-02	5.0	7.92	653
Sp08	1	6	83	5.84	5.82	0.53	0.22612	3.9	8.63	468	5.78	5.88	0.50	0.22514	3.8	8.66	470	0.15	0.29	0.26	7.8E-03	2.7	8.35	353
	24	109	71	6.11	5.89	0.47	0.24126	4.1	8.67	472	6.03	6.76	0.40	0.24295	3.6	8.75	473	0.18	0.24	0.15	3.1E-03	1.3	8.62	380
	48	208	67	7.11	6.7	0.30	0.26693	4.0	8.45	480	6.71	6.75	0.33	0.26913	4.0	8.55	482	0.15	0.26	0.15	3.6E-03	1.4	8.41	366
	72	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	444	67	8.37	8.63	0.35	0.33726	3.9	8.79	515	8.53	8.61	0.35	0.33838	3.9	8.85	514	0.32	0.32	0.13	4.6E-03	1.5	8.85	385
S08	1	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	24	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	48	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	72	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na

na: data not available

Water quality parameters for NF experiments using B2 effluent

				B2 effluent							Concentrate(XN45)							Permeate (XN45)						
		Vs	J/J_0	TOC	DOC	turbidity	UV_{254}	SUVA	pH	cond.	TOC	DOC	turbidity	UV_{254}	SUVA	pH	cond.	TOC	DOC	turbidity	UV_{254}	SUVA	pH	cond.
	time (h)	(L/m^2)	(%)	mg/L	mg/L	NTU	cm^{-1}	L/mgC*m		uS	mg/L	mg/L	NTU	cm^{-1}	L/mgC*m		uS	mg/L	mg/L	NTU	cm^{-1}	L/mgC*m		uS
S07	1	9	100	5.70	5.13	0.31	0.15004	2.9	7.82	546	5.88	5.33	0.44	0.15538	2.9	7.87	557	0.14	0.14	0.08	4.0E-03	2.9	7.85	422
	24	102	93	6.43	6.48	0.29	0.16868	2.6	8.15	590	6.89	6.39	0.23	0.16804	2.6	8.23	584	0.19	na	0.07	-6.8E-06	na	8.14	434
	48	204	93	6.85	6.52	0.25	0.18058	2.8	8.23	592	6.82	7.20	0.18	0.18112	2.5	8.25	590	0.30	0.39	0.17	7.4E-03	1.9	8.13	408
	72	321	87	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	120	613	80	8.24	8.79	0.2	0.23374	2.7	8.3	635	8.66	8.73	0.2	0.23603	2.7	8.27	628	0.29	0.19	0.21	1.2E-02	6.0	8.3	485
F07	1	4	83	4.88	4.89	1.21	0.12204	2.5	8.03	737	4.96	4.92	1.21	0.12269	2.5	8.05	731	0.28	0.29	0.44	2.9E-03	1.0	8.00	556
	24	94	51	5.02	4.82	1.05	0.12502	2.6	8.1	720	5.07	4.67	0.74	0.12449	2.7	8.12	731	0.26	0.29	0.16	2.0E-03	0.7	8.12	542
	48	196	51	5.52	5.09	0.62	0.1349	2.7	8.26	755	5.45	4.95	0.56	0.13354	2.7	8.27	698	0.23	0.37	0.19	1.3E-03	0.3	8.20	556
	72	300	51	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	397	46	7.07	7.14	0.43	0.17705	2.5	8.33	794	7.09	7.16	0.27	0.17698	2.5	8.35	797	0.17	0.37	0.19	6.9E-03	1.9	8.35	568
W08	1	4	89	5.48	5.36	1.7	0.17678	3.3	8.09	908	5.47	5.28	1.76	0.18141	3.4	8.28	872	0.08	0.21	0.35	9.5E-03	4.6	8.20	714
	24	102	78	5.81	5.88	0.61	0.17307	2.9	8.49	932	5.90	5.74	0.72	0.17237	3.0	8.39	919	0.02	0.11	0.28	5.2E-03	4.6	8.49	724
	48	203	74	6.31	6.46	0.37	0.20207	3.1	8.54	953	6.41	6.46	0.31	0.19251	3.0	8.4	969	0.14	0.15	0.22	1.5E-03	1.0	8.54	784
	72	279	74	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	406	74	9.56	9.36	0.41	0.17520	1.9	8.57	1013	9.29	9.55	0.34	0.25149	2.6	8.5	1615	0.09	0.31	0.35	7.1E-03	2.3	8.50	751
Sp08	1	5	100	4.2	4.95	0.7	0.15263	3.1	8.71	643	na	4.93	0.93	0.16207	3.3	8.69	646	0.33	0.59	0.32	5.0E-03	0.8	8.72	509
	24	102	93	4.42	5.37	0.61	0.16282	3.0	9.03	648	4.45	4.35	0.52	0.16043	3.7	9.02	651	0.57	0.28	0.49	8.1E-03	2.9	8.82	516
	48	209	93	4.78	4.85	0.48	0.17191	3.5	9.00	655	5.51	5.63	0.49	0.17419	3.1	8.98	657	0.16	0.35	0.29	7.6E-03	2.2	8.93	522
	72	308	79	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	438	71	6.03	6.19	0.67	0.23703	3.8	8.77	692	6.31	6.23	0.62	0.23923	3.8	8.74	692	0.21	0.21	0.22	7.8E-03	3.7	8.76	527
S08	1	9	94	5.32	5.35	0.4	0.20541	3.8	8.05	511	4.99	na	0.35	0.20902	na	8.04	516	0.15	0.27	0.14	5.1E-03	1.9	8.1	423
	24	93	94	5.9	5.94	0.37	0.23203	3.9	8.25	506	6.07	na	0.25	0.23663	na	8.23	517	0.06	0.08	0.09	4.2E-03	5.1	8.25	403
	48	207	91	6.89	na	0.21	0.27040	na	8.24	533	na	6.89	0.55	0.27796	4.0	8.25	529	0.19	0.38	0.11	5.6E-03	1.5	8.28	410
	72	316	84	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
	96	400	81	9.05	9.08	0.24	0.34019	3.7	8.21	535	9.12	9.15	0.23	0.34676	3.8	8.2	533	0.23	0.32	0.08	3.8E-03	1.2	8.2	419
S08	1	1607	100	6.12	5.84	0.76	0.22969	3.9	8.05	538	5.81	4.78	0.39	0.23157	4.8	8.04	548	0.26	0.18	0.18	7.6E-03	4.2	6.74	24
TS80	24	52500	18	6.23	6.31	0.30	0.24083	3.8	8.43	562	6.27	na	0.41	0.24298	na	8.45	563	0.12	0.16	0.12	3.2E-03	1.9	7.46	54
	48	88393	0.1	6.38	6.19	0.41	0.24452	4.0	8.48	564	6.18	na	0.51	0.24578	na	8.50	563	na	na	na	na	na	na	na

Appendix R

System loss test data of UF experimental set-up

Time	naproxen			ibuprofen			DEET			atrazine			carbamazepine			nonylphenol		
(h)	influent ng/L	effluent ng/L	% adsorption	influent ng/L	effluent ng/L	% adsorption	influent ng/L	effluent ng/L	% adsorption	influent ng/L	effluent ng/L	% adsorption	influent ng/L	effluent ng/L	% adsorption	influent ng/L	effluent ng/L	% adsorption
1	1926	1842	4	2308	2321	-1	1434	1348	6	1371	1267	8	2297	2663	-16	71	80	-13
8	1835	1887	-3	2287	2372	-4	1458	1251	14	1381	1283	7	2292	3101	-35	nd	nd	na
22	1934	1908	1	2207	2198	0	1384	1366	1	1388	1395	-1	2226	2308	-4	nd	nd	na

Appendix S

Concentrations (ng/L) of selected PhACs and EDCs in the UF membrane feed and permeate

Experiment -	Time	DEET		%removal	ibuprofen		%removal	atrazine		%removal	nonylphenol		%removal	naproxen		%removal	carbamazepine		%removal
influent	(h)	influent	permeate		influent	permeate		influent	permeate		influent	permeate		influent	permeate		influent	permeate	
UF4 - B1	48h	756	798	-6	34	32	5	446	455	-2	na	na	na	na	na	na	na	na	na
UF5 - B2	1h	564	628	-11	49	38	22	389	404	-4	nd	na	na	275	245	11	521	491	6
	48h	559	564	-1	29	26	11	412	432	-5	na	na	na	283	289	-2	491	517	-5
	96h	314	288	8	d	d	na	444	417	6	na	na	na	155	155	0	493	479	3
UF6 - B2	1h	nd	na	na	nd	na	na	3774	na		nd	na	na	nd	na	na	4790	na	na
	48h	nd	nd	na	nd	nd	na	3787	3513	7	141	132	6	nd	nd	na	4886	4678	4
	96h	nd	nd	na	nd	nd	na	3406	3350	2	1375	nd	na	73	64	13	4477	4443	1
UF7 - B1	1h	89	88	1	33	28	16	3781	3693	2	nd	nd	na	196	191	3	4175	4084	2
	96h	na	na	na	na	na	na	4181	4456	-7	115	nd	na	77	51	34	3342	3563	-7
UF8 - B2	1h	3313	3267	1	1351	1255	7	4259	3388	20	32	na	na	2156	2198	-2	3052	2966	3
	48h	2967	2996	-1	673	696	-3	4372	4446	-2	d	201	na	1866	1974	-6	3443	3335	3
	96h	2544	2284	10	253	204	19	4510	4152	8	26	d	na	893	640	28	3335	3316	1
UF9 - B1	1h	3471	3479	0	1451	1622	-12	3392	3321	2	na	na	na	2721	3080	-13	2774	2657	4
	48h	3590	3355	7	1748	1607	8	3384	3405	-1	na	147	na	2747	2562	7	2654	2733	-3
UF10 - B2	1h	470	454	3	67	57	15	481	502	-4	nd	52	na	130	128	1	522	504	3
UF12 - B2	1h	6143	5276	14	912	668	27	5614	4913	12	nd	784	na	3313	3146	5	3640	3166	13
	48h	5367	5514	-3	64	69	-7	5622	5832	-4	219	48	78	1466	1622	-11	3410	3398	0
UF13 - B1	24h	4450	4708	-6	481	na	na	3943	3971	-1	na	na	na	1737	na	na	2471	2393	3
UF14 - B2	48h	309	325	-5	19	20	-10	485	508	-5	d	28	na	160	152	5	507	471	7
UF15 - B1	1h	205	253	-23	8	12	-49	223	295	-32	nd	d	na	77	102	-32	211	279	-32
UF16 - B2	1h	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
UF17 - B1	24h	85	64	24	d	d	na	644	641	0	nd	nd	na	40	24	40	522	534	-2

na: not available; nd: not detected; d:detected

Appendix T

Average concentrations of trace organic contaminant and their standard deviation in the membrane influent for the NF experiments

Experiment	Season year	Membrane	Feed	n	ibuprofen ng/L	naproxen ng/L	DEET ng/L	atrazine ng/L	nonylphenol ng/L	carbamazepine ng/L
NF5	S07	XN45	B2 - low	2	9 ± 2	194 ± 11	394 ± 66	388 ± 29	na	527 ± 28
NF5	S07	TS80	B2 - low	2	9 ± 2	194 ± 11	394 ± 66	388 ± 29	na	527 ± 28
NF6	S07	XN45	B2 - high	3	nd	89 ± 62	nd	3720 ± 181	na	4618 ± 30
NF7	S07	XN45	B1 - high	3	na	165 ± 20	na	4471 ± 465	32812 ± 47879	3766 ± 645
NF8	F08	XN45	B2 - high	3	1593 ± 193	2651 ± 550	3526 ± 357	4358 ± 432	1392 ± 1145	3070 ± 237
NF9	F08	XN45	B1 - high	3	1010 ± 681	1714 ± 1016	2650 ± 979	2755 ± 658	942*	2314 ± 565
NF11	W08	XN45	B1 - low	3	206 ± 49	226 ± 39	696 ± 66	505 ± 19	59*	440 ± 28
NF12	W08	XN45	B2 - high	3	1634 ± 335	3641 ± 693	5167 ± 1912	6250 ± 567	1467*	3933 ± 497
NF13	W08	XN45	B1 - high	3	1025 ± 620	4286 ± 733	2057 ± 2397	5029 ± 1224	733*	2907 ± 716
NF14	Sp08	XN45	B2 - low	3	29 ± 7	191 ± 20	377 ± 49	448 ± 19	45*	494 ± 22
NF15	Sp08	XN45	B1 - low	3	22 ± 4	199 ± 28	439 ± 34	472 ± 10	na	490 ± 12
NF16A	S08	XN45	B2 - low	3	d	28 ± 3	75 ± 38	710 ± 23	na	563 ± 26
NF16B	S08	TS80	B2 - low	1	nd	53*	59*	713*	na	551
NF17A	S08	XN45	UF perm	3	d	23 ± 1	157 ± 39	644 ± 25	46 ± 20	479 ± 18
NF17B	S08	TS80	UF perm	2	9*	13 ± 1	124 ± 38	648 ± 67	26*	514 ± 41

* one measurement available

Appendix U

Rejection of trace organic contaminants by XN45 and TS80 NF membranes

	DEET			%	ibuprofen			%	atrazine			%	nonylphenol			%	naproxen			%	carbamazepine			%
Experiment	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection
NF5 - B2 low																								
XN45																								
1h Aug 12 07	441	296	na	33	8	d	na	13	367	326	na	11	na	na	na	na	187	115	na	38	507	421	na	17
48h Aug 14 07	348	209	na	40	10	d	na	30	409	366	na	10	nd	na	na	na	202	138	na	32	546	497	na	9
TS80																								
1h Aug 12 07	441	d	na	99	8	nd	na	75	367	d	na	96	na	na	na		187	d	na	97	507	d	na	96
48h Aug 14 07	348	19	na	95	10	nd	na	80	409	28	na	93	nd	na	na	na	202	d	na	97	546	28	na	95
72h Aug 1507	na	54	na		na	nd	na		na	123	na		na	nd	na		na	31	na		na	178	na	
NF6 - B2 high																								
1h Sept 11 07	nd	nd	nd	na	nd	nd	nd	na	3513	2042	3489	42	na	599	na	na	133	nd	50	98	4623	3191	4623	31
48h Sept 13 07	nd	nd	nd	na	nd	nd	nd	na	3799	2449	3814	36	na	na	na	na	116	nd	36	98	4586	3318	4673	28
144h Sept 17 07	nd	nd	55	na	nd	nd	10	na	3848	2471	3702	36	na	266	170	na	18	nd	85	89	4644	3761	4265	19
NF7 - B1 high																								
1h Sept 19 07	na	na	na	na	na	na	na	na	4222	2492	4192	41	88087	3007	90517	97	168	32	178	81	3366	2130	3368	37
48h Sept 21 07	na	na	na	na	na	na	na	na	4184	2631	4288	37	4269	2342	4582	45	184	29	168	84	3421	2214	3395	35
120h Sept 24th	na	na	na	na	na	na	na	na	5007	3408	4986	32	6079	460	5517	92	143	44	154	69	4510	2898	4395	36
NF8 - B2 high																								
1h Nov 12 07	3119	990	3048	68	1394	86	1354	94	3863	1932	3863	50	2198	61	2591	97	2461	320	2177	87	2827	1520	2787	46
48h Nov 14 07	3671	1125	3429	69	1604	108	1494	93	4555	2180	4347	52	1896	nd	1599		3270	348	2216	89	3083	1600	3127	48
96h Nov 16 07	3788	1179	3798	69	1780	121	1778	93	4656	2086	4723	55	81	102	d	-26	2222	418	1905	81	3301	1674	3420	49
NF9 - B1 high																								
1h Nov 23 07	3343	1329	3281	60	1505	246	1634	84	3215	1814	3183	44	942	na	871	na	2327	462	2603	80	2568	1619	2611	37
48h Nov 25 07	1530	na	1324	na	234	na	177	na	2001	na	2032	na	d	na	na	na	540	na	579	na	1667	na	1686	na
96h Nov 27 07	3078	2725	2743	11	1292	1094	1171	15	3048	3211	3167	-5	na	na	na	na	2274	1792	2122	21	2708	2730	2732	-1
NF11 - B1 low																								
1h Jan 24 08	648	377	615	42	238	78	227	67	508	388	480	24	59	na	75	na	195	78	199	60	423	304	425	28
24h Jan 25 08	669	401	665	40	230	77	230	66	486	405	495	17	na	na	na	na	212	86	224	59	424	326	429	23
96h Jan 28 08	772	431	779	44	149	60	152	59	523	417	524	20	na	na	na	na	270	110	279	59	472	366	476	22
NF12 - B2 high																								
1h Feb 19 08	6025	2091	5921	65	1788	230	1872	87	5703	2853	5733	50	1467	na	1173	na	3692	351	4095	90	3373	1787	3340	47
48h Feb 21 08	6499	2490	6409	62	1864	287	1864	85	6213	3432	6162	45	d	nd	56	na	2924	549	4297	81	4103	2234	3711	46
96h Feb 23 08	2976	1258	2788	58	1249	191	1265	85	6834	3952	6684	42	nd	nd	55	na	4306	644	2720	85	4322	2534	4700	41

	DEET			%	ibuprofen			%	atrazine			%	nonylphenol			%	naproxen			%	carbamazepine			%
Experiment	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection	tank	perm	conc	rejection
NF13 - B1 high																								
1h Feb 25 08	4703	2978	4750	37	1552	368	1604	76	4243	3567	4298	16	733	na	847	na	3681	675	3725	82	2453	1726	2413	30
48h Feb 27 08	1438	1112	1458	23	1180	266	1233	77	4404	4016	4791	9	na	na	175	na	4333	761	3968	82	2536	1911	4746	25
96h Feb 29 08	30	d	29	50	342	27	331	92	6439	4496	6305	30	na	na	114	na	5144	1127	6016	78	3732	2445	3488	34
NF14 - B2 low																								
1h May 1 08	332	199	361	40	21	11	22	47	433	312	462	28	45	36	36	22	171	52	177	70	480	343	477	29
48h May 3 08	372	231	379	38	33	17	36	47	442	334	452	24	d	nd	d	na	190	66	201	65	482	379	491	21
96h May 5 08	428	289	455	33	34	29	37	16	469	397	521	15	nd	nd	nd	na	211	67	249	68	520	381	567	27
NF15 - B1 low																								
1h May 7 08	408	247	412	39	18	9	19	53	463	342	465	26	d	nd	53	na	181	57	185	69	482	363	462	25
48h May 10 08	435	279	435	36	21	11	21	50	469	362	458	23	nd	nd	d	na	185	65	188	65	482	385	473	20
96h May 12 08	475	321	486	32	27	20	26	25	483	399	494	17	nd	nd	34	na	232	80	221	66	504	412	511	18
NF16 - B2 low XN45																								
1h July 28 08	39	22	38	45	d	d	d	na	684	496	678	27	na	na	na	na	28	13	27	53	538	390	529	28
48h July 30 08	71	37	73	47	d	d	d	na	717	514	712	28	na	na	na	na	32	13	26	60	560	389	574	31
96h Aug 1 08	115	61	118	47	d	d	d	na	728	530	758	27	na	na	na	na	26	11	26	59	591	415	587	30
TS80																								
1h July 26 08	59	nd	65	92	nd	nd	nd	na	713	d	735	98	na	na	na		53	nd	54	96	551	nd	562	99
NF17 - Ufp low XN45																								
1h July 15 08	121	75	124	38	d	d	d	na	616	489	611	21	60	N/A	64	na	22	12	23	46	473	371	463	22
48h July 17 08	150	97	155	36	d	d	d	na	654	501	637	23	<MDL	<MDL	<MDL	na	24	12	25	51	466	382	486	18
96h July 19 08	199	113	191	43	d	d	d	na	663	509	670	23	31	<MDL	N/A	na	22	12	24	44	499	385	494	23
TS80																								
1h July 21	97	nd	97	95	d	nd	d		601	d	591	97	26	N/A	44		13	nd	12	84	485	nd	478	99
48h July 23	150	d	146	90	9	nd	8	78	695	36	679	95	<MDL	N/A	69	na	14	nd	12	86	543	23	547	96