

Direct Biofiltration and Nutrient (Phosphorous) Enhancement for Polymeric Ultrafiltration Membrane Fouling Control

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

Membrane filtration is growing in popularity as a viable technology for drinking water treatment to meet high demand and regulatory requirements. While many improvements have been made to the technology in the past decade, fouling continues to be one of the major operational challenges associated with membranes as it increases operating costs and reduces membrane life. Fouling control typically requires some form of pre-treatment. Biofiltration is a “green” technique that can minimize chemical usage and waste during water treatment and is a relatively new application as a pre-treatment for membranes.

Proteins and polysaccharides (biopolymers) have been found to contribute most to fouling of low pressure polymeric membranes. Biofiltration has recently been demonstrated as an effective pre-treatment method for reducing biopolymer-associated fouling of this type of membrane (Hallé *et al.*, 2009). Given that the concentration and composition of organic matter in water is variable, there is an opportunity to explore the applicability of this robust technology for different water types.

The primary goals of this research were to assess the effectiveness of direct biofiltration in minimizing ultrafiltration polymeric (PVDF) membrane fouling and at the same time evaluate the biofilter development, biofilter performance based on organics removal potential, and the effect of phosphorus addition (as a nutrient) to the biofilter influent.

A pilot-scale treatment train was constructed at the Technology Demonstration Facility at the Walkerton Clean Water Centre. It included two parallel dual media (sand/anthracite) biological filters (preceded by roughing filters), followed by an ultrafiltration membrane unit. Experiments were conducted using water from the Saugeen River (Ontario, Canada) whose primary form of carbon is humic material. The biofilters were allowed to acclimate and

biofilter performance and organics removal were tested over a fourteen month period, the last four months of which were dedicated to phosphorus enhancement experiments. The membrane fouling experiments started seven months following the start-up of the biofilters, after confirmation of steady-state operation.

Biofilter water samples were analyzed for natural organic matter constituents along with other water quality parameters, and biomass quantity and activity in the media were measured. Biomass activity in the biofilter media and biopolymer removal through the biofilter indicated a rapid acclimation period, and also demonstrated similar performance of the parallel biofilters during start-up and steady-state operation. The biofilters achieved 21% removal of the biopolymers on average following acclimation, while reduction of the humic fractions was not observed. A linear relationship between biopolymer removal and its concentration in the river water was observed (first-order process).

Membrane fouling experiments were conducted using both untreated and biofiltered river water. The fouling rates were computed by monitoring changes in transmembrane pressure over time. Analysis of the samples with liquid chromatography-organic carbon detection confirmed the significant contribution of biopolymers to irreversible and reversible membrane fouling rates even when only present at low concentrations.

During the phosphorus enhancement phase, two different phosphorus doses were fed into the influent of one of the parallel biofilters in order to achieve a target C:N:P ratio of roughly 100:10:1. Although initially (first month of the dosing period) an increase in the removal of dissolved organic carbon and ultraviolet-absorbance was observed in the phosphorus-enhanced biofilter, this was not sustained. Phosphorus addition did not affect biopolymer

removal or biomass quantity and activity in the biofilter, and the membrane fouling experiments during this period did not show any significant effect of phosphorus addition.

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Dedication

I dedicate this thesis to my loving family

Without you nothing would have been possible

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List of Acronyms

AOC: Assimilable organic carbon

ATP: Adenosine triphosphate

BB: Building blocks

BDOC: Biodegradable dissolved organic carbon

BF1: Biofilter-1, used as control during phosphorus dosing experiment

BF2: Biofilter-2, phosphorus added biofilter

BOM: Biodegradable organic matter

BP: Biopolymers

C:N:P: Carbon, nitrogen, phosphorus ratio

DL: Detection limit

DOC: Dissolved organic carbon

DOM: Dissolved organic matter

EBCT: Empty bed contact time

EPS: Extracellular polymeric substances

FA: Fulvic acid

FDA: Fluorescein diacetate

GAC: Granular activated carbon

HPC: Heterotrophic plate count

HS: Humic substances

LC-OCD: Liquid chromatography with organic carbon detector

LMH: Liter per membrane area per hour

LMW: Low molecular weight

MF: Microfiltration membrane

MWCO: Molecular weight cut off

NOM: Natural organic matter

PVDF: Polyvinyl fluoride

RF: Roughing filter

SUVA: Specific ultraviolet absorbance

TMP: Transmembrane pressure

TOC: Total organic carbon

UF: Ultrafiltration membrane

UV: Ultraviolet

UV₂₅₄: Absorbance of ultraviolet (UV) light at a wavelength of 254 nm

Δ TMP: Difference of TMP during a cycle

Chapter 1

Introduction

1.1 Problem Statement

The well-being of humans can readily be related to the availability of potable water. Water, though abundant on Earth is largely in oceans or trapped in glacial ice caps. The very small percentage that can be used for drinking cannot be ingested directly and is also increasingly being degraded by human development. Diseases and even death by the ingestion of contaminated water is very common all over the world.

The history of water treatment goes back to the times of the ancient Greeks with their simple, yet effective, methods for water treatment (e.g. boiling, sand filtration). With time these methods were refined and new techniques have emerged. One of the newest approaches in this field is the application of membrane filtration processes. Since their first application for drinking water treatment in 1980s, the technology has seen tremendous development and is now an established technology for drinking water treatment (Crittenden *et al.*, 2005).

Membrane filtration has various uses in water treatment including, but not limited to, particle and pathogen removal (Farahbakhsh *et al.*, 2004). Large-scale treatment facilities are increasingly using membranes for treatment purposes. Membranes can be of different types and materials, and membrane modules have various configurations. Regardless of the diversity, one of the major challenges with the use of membranes in water treatment is ‘fouling’. Fouling is an inevitable phenomenon associated with membrane based treatment systems which occurs due to gradual blockage of membrane pores while water being filtered through and thus results in reduction of the filtration efficiency of membrane units. Thus, it

increases the necessity for frequent backwashes and chemical cleanings, which reduce membrane life and increase the cost associated with membrane operation. Hence, various methods have been attempted to reduce or control fouling including pre-treating feed water with chemical coagulants, ozone, adsorbents, ion exchange resins, or filtering the water through granular media. The efficiency of these techniques is highly dependent on water quality and the membrane itself. Of the various pretreatment options, biofiltration is a relatively new and “green” technique that has the potential to minimize chemical usage and wastes during water treatment.

Biopolymers (proteins and polysaccharides) have been demonstrated to contribute most to fouling of low pressure polymeric membranes (Amy, 2008). Recent research by Hallé *et al.* (2009) demonstrated the utility of biofiltration as an effective pre-treatment method for reducing biopolymer-associated fouling of low pressure polymeric membranes. Considering the fact that the concentration and composition of organic matter in different waters is variable (Her *et al.*, 2003), there is an opportunity to explore the applicability of this robust technology for different water types.

The microorganisms in biofilters rely on the nutrients (carbon, nitrogen, phosphorus, iron etc.) in water for growth and activity. Hence, the optimum nutrient conditions in the water for favorable growth of microorganisms have also been a subject of interest. Research with nutrients, especially phosphorus, has shown the potential for reduction of extracellular polymeric substances and corresponding reductions in headloss in the filters and also increases in organics removal potential (Lauderdale *et al.*, 2012). However, it has not yet been thoroughly investigated if nutrient enhancement in biofilters affects the fouling reduction potential of the biofilters. This research aimed at quantifying biofilter development

and assessment of its performance as an ultrafiltration (UF) membrane pretreatment under natural and phosphorus-enhanced conditions using a river characterized by elevated concentrations of humic material as a water source.

1.2 Approach

To achieve the goal of this research a pilot-scale treatment train was built at the technology demonstration facility at the Walkerton Clean Water Centre in Walkerton, Ontario. The set-up included two parallel dual-media (sand/anthracite) biological filters which were preceded by roughing filters to minimize the impact of varying raw water quality. Water treatment experiments were conducted using water from the Saugeen River, Ontario, Canada which is high in TOC with variable turbidity. Experiments with a bench-scale membrane unit to assess the effect of the biofilters on fouling were initiated after an appropriate acclimation period for the biofilters. Later in the project, one of the identical biofilters was dosed with phosphate and the other was used as a control to observe the effect of nutrient addition. Biofilter samples were collected at regular intervals from March, 2012 to May, 2013 and were analyzed for natural organic matter (NOM) constituents using a variety of NOM quantification techniques.

1.3 Objectives

The primary objectives of this research were to –

1. Quantify biofilter acclimation and development by measuring biomass quantity and activity in the filters, and the removal of various natural organic matter (NOM) fractions, especially biopolymers for their role in membrane fouling.

2. Confirm the reproducibility of the performance of the parallel biofilters under identical operating conditions.

3. Assess the performance of biofiltration pretreatment for the improvement of UF membrane performance by conducting comparison membrane experiments with untreated raw water and biofilter effluent as membrane feed waters.

4. Compare the phosphorus-enhanced and control biofilters to assess the effects of phosphorus addition in terms of biomass quantity and activity, NOM removal potentials, and fouling mitigation.

1.4 Thesis Organization

Chapter 1 is the statement of research scope and objectives. Chapter 2 consists of a literature review, provides general information relevant to this research, and identifies research gaps.

Chapters 3 and 4 of this thesis were written in paper format and as such they contain separate literature reviews and experimental methods sections.

Chapter 3 is a summary of the ultrafiltration membrane fouling experiments conducted with untreated and biofiltered water which provide an indication of its performance as membrane pretreatment. This includes the detailed study of the performance of parallel drinking water treatment biofilters during the start-up and steady-state periods focusing mainly on NOM removal. The different water quality parameters of the studied river are also presented here. This chapter was submitted to a scientific journal in August 2013 to be considered for publication.

Chapter 4 contains the results from the biofilter phosphorus enhancement experiments. Raw river water quality in terms of nutrient concentrations is presented here. Biofilter performance in terms of NOM removal and biomass development is compared between the

phosphorus-dosed and control conditions. Finally, the results from the fouling experiments with biofiltered water from the two conditions are compared.

Chapter 5 summarizes the findings from this research and provides recommendations for future work.

Chapter 2

Background Information

2.1 Membrane Filtration in Drinking Water

2.1.1 General overview

A membrane is a thin sheet of synthetic material which is semi-permeable. Membrane treatment processes exploit the properties of membranes as a separation technique for removing chemical and microbial contaminants from water. Though industrial application of this technology started in the 1950s, the use of membranes in drinking water treatment began in the 1980s, mostly for microbial risk mitigation (Crittenden *et al.*, 2005). Since then membrane filtration has evolved tremendously and found novel applications in different water treatment sectors. Membranes can be used for removal of organics, bacteria, viruses, ions, in water re-use applications, and for desalination. As membranes have smaller footprints, require less operator involvement, and can achieve various water treatment goals, they are now considered as viable substitutes for more traditional filtration systems. However, some costs associated with membrane operation (energy, membrane replacement, cleaning, pretreatments, and concentrated waste disposal) are still problematic.

2.1.2 Membrane types and characteristics

Membranes can be classified based on material, pore-size/permeability, surface characteristics, and operating conditions.

Based on their pore size pressure driven membranes can be of the following four types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse-osmosis (RO) membranes (Figure 2.1).

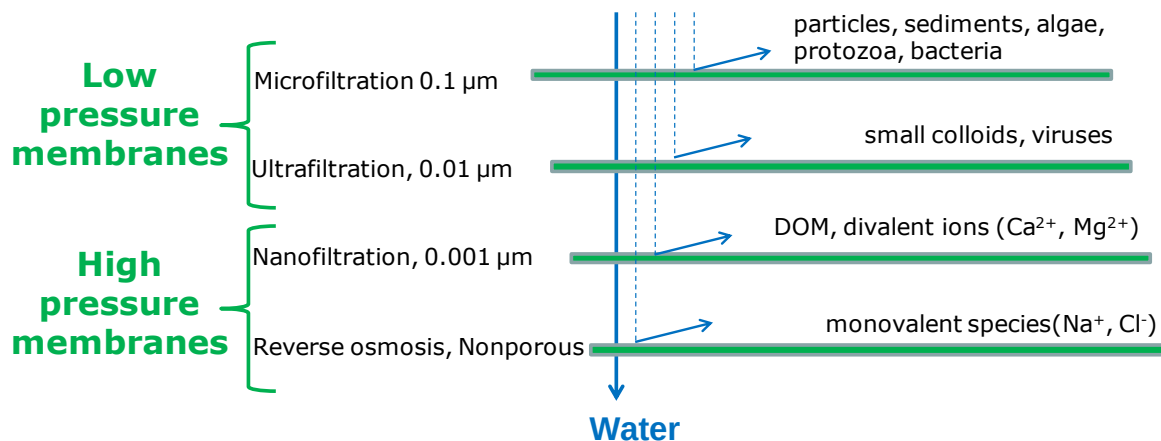


Figure 2.1 Classification of membrane based on pore-size/operating pressure

(Adapted from Crittenden et al., 2005. This material is reproduced with permission of Wiley & Sons, Inc.)

Of these four types, microfiltration membranes have the largest pore size (0.1 μm) and can reject particles, algae, protozoa, and bacteria. Ultrafiltration membranes have a smaller pore size (~0.01 μm) and in addition to the contaminants rejected by MF, will reject viruses and small colloids. UF and MF membranes are classified as “low pressure membranes” and the dominant exclusion mechanism for these two types of membranes is straining (Crittenden *et al.*, 2005).

The NF and RO membranes are classified as “high pressure membranes”. While nanofiltration membranes can remove dissolved organic matter and divalent cations, reverse-osmosis membranes can remove monovalent cations. In these cases, diffusion is the exclusion mechanism (Crittenden *et al.*, 2005).

Membranes are fabricated using variety of materials including cellulose acetate (CA), polysulfone (PS), polyethersulfone (PES), polyamide (PA), polyvinylidene fluoride (PVDF) and polypropylene (PP). Differences in materials produce different membrane properties. A major classification based on materials includes the above membranes (polymeric) and those

which are ceramic-based (e.g. Al_2O_3 , TiO_2 , CeO_2 , SiO_2 , etc.). Historically, polymeric MF/UF membranes have most commonly been used in water treatment. However, ceramic membranes are gaining popularity in this field of water treatment as they are more tolerant to chlorine and ozonation, than polymeric membranes (Lehman and Liu, 2009) and their higher cost can be compensated for by higher flux.

Membranes can be hydrophilic or hydrophobic which influences the permeability of the membrane and the adsorption of the contaminants. Hydrophobic membranes tend to be less permeable hence less prone to fouling (Crittenden *et al.*, 2005). This property can be determined based on contact angle (angle at which water meets membrane surface) , with clean hydrophilic membranes having contact angles less than 20° and hydrophobic membranes having angles greater than 50° . The change in the contact angles after fouling can assist with characterizing the foulants (Lee *et al.*, 2004).

A membrane's surface charge depends on its composition and is usually negative for polymeric membranes. Surface charge and roughness play an important role in fouling. While negative surfaces reduce fouling by repulsing negatively charged particles (Cho *et al.*, 2000), it has been observed that rough surfaces tend to foul more (Lee *et al.*, 2004).

Other classifications of membranes include pore geometries to differentiate between microporous and asymmetric membranes (Hendricks, 2011). And depending on operational configurations membranes are manufactured as flat sheet/tube and can be incorporated into different types of modules like plate and frame, spiral wound, tubular, hollow-fiber, hollow-fine fiber or track etched (Crittenden *et al.*, 2005).

2.1.3 Rejection mechanisms and membrane fouling

Membranes remove or reject particles and organic matter as water passes through it. The following are the important rejection mechanisms associated with membrane filtration:

- Size exclusion- Size exclusion or straining is the principal mechanism associated with membrane filtration. It is the mechanism where larger particles are retained on the membrane surface and smaller particles pass through. However, depending on particle and membrane characteristics and their interactions, particles smaller than the membrane pores may be retained as well, while under some conditions larger flexible particles may pass through the pores under pressure.
- Electrostatic repulsion- As membrane surfaces are normally negatively charged higher removals of negatively charged contaminants than positively charged or neutral contaminants of the same size by electrostatic repulsion are expected (Nghiem *et al.*, 2005). This mechanism depends on solution pH.
- Adsorption- Adsorption can act as a vital rejection mechanism when the membrane is clean. But this capacity diminishes fast and is not good as a long-term process. Accumulation of contaminants in membrane pores can decrease membrane life. Absorbed contaminants can also partially diffuse through the membrane and thus decrease the total rejection by the membrane.
- Fouling- Though fouling is problematic in the context of membrane-based treatment systems, the cake layer formed on the membrane surface can also function as a mechanism for particle removal. As fouling or cake layer obscures the membrane surface characteristics, some particles which would not ordinarily be removed may have affinity to the cake layer formed by fouling.

2.1.4 Types of fouling

Fouling decreases the effectiveness of a membrane by accumulation of material (foulant) within membrane pores and on the membrane surface (Crittenden *et al.*, 2005). Fouling reduces the flux through the membrane and thus increases the transmembrane pressure (AWWA, 2005). Classification of fouling is based on foulant type are:

- Particulate fouling by colloidal particles larger than the membrane pore size which form cake layer on the membrane surface. This type of fouling is backwashable.
- Fouling by dissolved organic matter which depends on the characteristics of the DOM and membrane. This is discussed further in Section 2.2.3.
- Biofouling, which is caused by microbial accumulation on and attachment to a membrane surface. This type of fouling is predominantly associated with wastewater applications and high pressure membranes.

Fouling can also be classified by fouling mechanisms such as i) cake layer formation, ii) pore constriction, and iii) pore sealing (Crittenden *et al.*, 2005) as shown in Figure 2.3 and discussed in Section 2.1.5.

Based on removal of foulant layer, fouling can be classified as i) reversible or ii) irreversible (Figure 2.2). Accumulation of particles and organic matter on a membrane reduces flux and a part of this flux decline can be recovered by backwashing and chemical cleaning. This is known as reversible fouling. The part that cannot be removed during cleaning cycles and leads to permanent degradation of the membrane is termed as irreversible fouling.

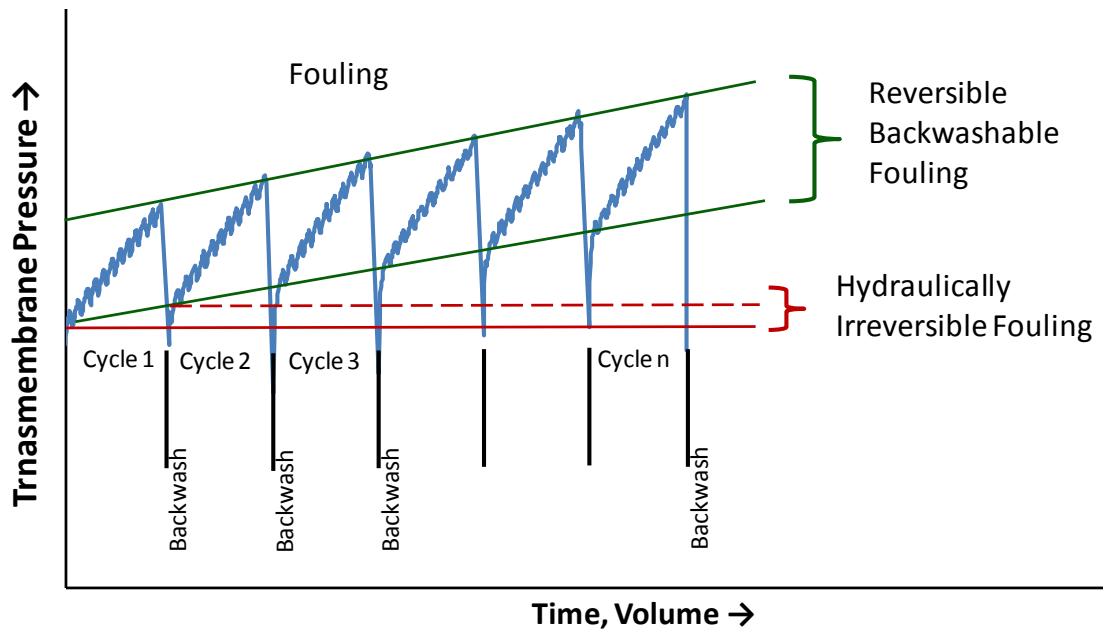


Figure 2.2 Example of reversible and irreversible membrane fouling

2.1.5 Fouling mechanisms

Membrane and foulant properties affect fouling mechanisms. These mechanisms (Figure 2.2) include:

- Pore constriction – reduction in flux due to adsorption of small size particles within the membrane pores decreasing total pore volume,
- Pore sealing– pores get completely blocked by particles of similar size as the pore diameter, and
- Cake layer formation – particles larger than the pore size create a layer of deposited material which increases resistance against flow and the transmembrane pressure.
- Studies have shown that while cake layer formation is more common in UF membranes, MF membranes often foul due to pore constriction (Lee *et al.*, 2004).

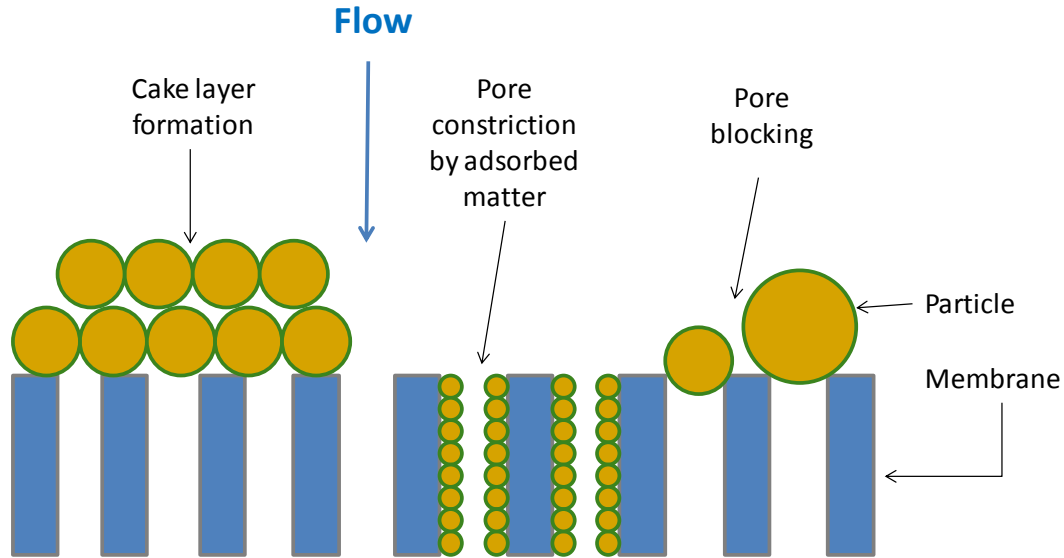


Figure 2.3 Mechanism of fouling of membranes

(Adapted from Crittenden et al., 2005. This material is reproduced with permission from Wiley & Sons, Inc.)

2.2 Membrane Filtration and NOM Fouling

Natural water is abundant in various organic and inorganic constituents which can be ionic or dissolved, colloidal or in a suspended state. Of these different constituents natural organic matter (NOM) has been identified as the major foulant of membranes used for surface water treatment (Rubia *et al.*, 2007). Factors affecting this type of fouling include ionic strength, pH, and divalent cations (e.g. Ca^{2+} , Mg^{2+} , Mn^{2+} etc.) in water.

2.2.1 NOM characteristics and composition

NOM is a mixture of naturally occurring organic chemicals that are found in all water bodies. NOM can cause odour, colour, and taste problems in water and produces disinfection by-products when it reacts with chlorine. It can also increase coagulant demand for removal, affect corrosion and stability of the water, and cause membrane fouling (Juhna and Melin,

2006). NOM comprises living and dead plants, animals, microorganisms, and their degradation products. NOM, in its simplest form can be carbohydrates, lipids, amino acids, nucleic acids, and their combinations with inorganic chemicals in water (Thurman, 1985).

NOM is moderately soluble in water is moderate and its molecular weight varies. NOM, like other organics, consists mostly of carbon, oxygen, hydrogen, and small percentage of nitrogen (Thurman, 1985).

NOM can be classified in various ways. A general classification (based on biodegradability) is as humic substances (less biodegradable) and non-humic substances (carbohydrates, lipids and amino acids, all of which are readily biodegradable). In terms of particle size, NOM can be particulate organic carbon (POC) and dissolved organic carbon (DOC). POC are larger sized organics (bacteria, algae, flocculated organics that are larger than 0.2 or 0.45 μm , while particles smaller than this are considered DOC (Juhna and Melin, 2006, Thurman, 1985).

Based on solubility NOM can be classified as humic acid and fulvic acid. Humic acid remains soluble in alkaline solution and precipitates at low pH, while fulvic acid is soluble in acidic solution. Humic and fulvic acids have complex structures and the presence of stereochemical isomers makes it difficult to acquire comprehensive structural data for them (Jansen *et al.*, 1996). Humic acids have much higher molecular weights (2000-10000 g/mole) than fulvic acid (500-2000 g/mole) (Thurman *et al.*, 1982). Larger sized components of NOM include biopolymers (polysaccharides and proteins) which have been found to be responsible for fouling in membranes (Amy, 2008). NOM also includes fibrils which are linear aggregates of biopolymers (Makdissy *et al.*, 2010), building blocks (degradation products of humics), and colloidal organic molecules.

2.2.2 NOM characterization

Some of the important methods/analyses used to characterize NOM are described below.

- Total and dissolved organic carbons (TOC/DOC) are a measurement of CO₂ produced by oxidation or combustion of organics.
- Visible, UV- absorbance, SUVA, and UV intensity are related to organics in water. High UV absorbance is related to the presence of humic substances.
- SUVA is the indication of aromaticity and treatability of the water (for coagulation treatment). An SUVA value of >4 indicates the presence of highly hydrophobic and higher molecular weight (MW) aquatic humics, while a value of <2 indicates the presence of highly hydrophilic, lower MW humics and SUVA between 2 to 4 signifies a mixture of hydrophobic and hydrophilic, and mixed MW humic and non-humic substances in water (Edzwald and Tobiason, 1999). Smaller SUVA values indicate that the water contains more biodegradable organics (Juhna and Melin, 2006).
- Methods of NOM characterization using size exclusion include the use of high performance size exclusion chromatography HP-SEC. An example of which is liquid chromatography-organic carbon detection (LC-OCD) analysis which uses a chromatographic column and phosphate buffer and includes UV and organic nitrogen detectors (Huber *et al.*, 2011). This technique is sensitive and requires comparatively simple sample preparation and with combined functions of the detectors and elution times can characterize the NOM into the following fractions:
 - Biopolymers (A in Figure 2.4) – hydrophilic fraction with high MW (≥ 10 kDa), including polysaccharides and protein like materials, does not have a UV response.

- Humic substances (B) – includes humic and fulvic acids, where humic acids are eluted earlier (at 43.4 min) than fulvic acids (46.7 min), which are largest peaks in the chromatogram and this fractions absorbs UV.
- Building blocks (C) – these are lower-MW humic-like materials, possibly produced from degradation of humic substances (0.3 – 0.45 kDa)
- Low MW acids (D) – these are anions at neutral pH of the phosphate buffer and may sometimes include small amounts of low MW humics which can be separated by using empirical formulae
- Low MW neutrals (E) – hydrophilic to amphiphilic in nature, includes low MW alcohols, aldehydes, ketones, amino acids and sugars, no/low UV response

Figure 2.4 is an example of an LC-OCD-derived chromatogram.

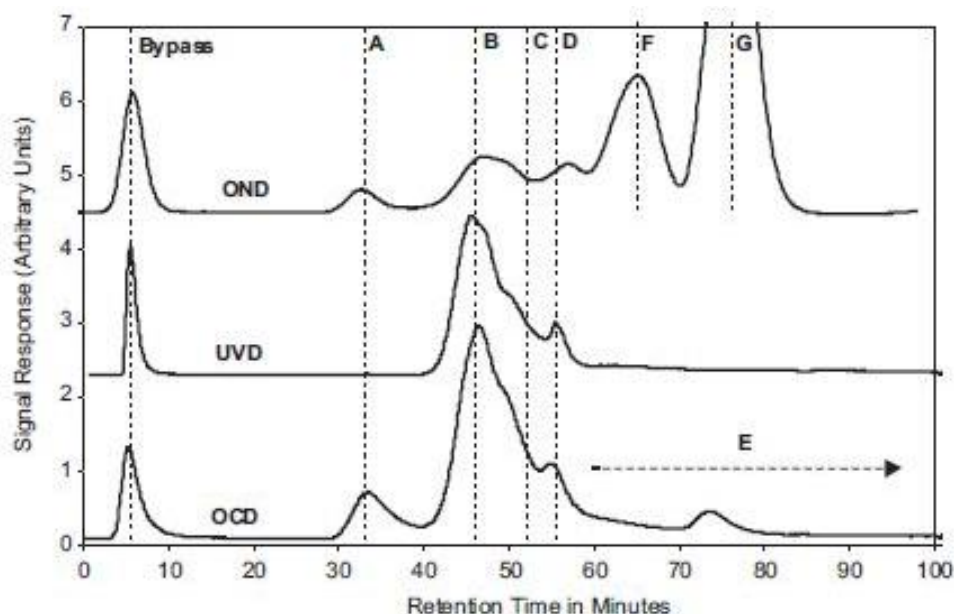


Figure 2.4 LC-OCD chromatogram with organic carbon, UV, and organic nitrogen detector signal responses indicating different NOM fractions elution times for Pfingz River (Germany) water

(Reprinted from Huber et al., 2011, with permission from Elsevier)

Another NOM detection technique in use is fluorescence excitation emission matrix (FEEM) (Peiris *et al.*, 2010). This technique involves excitation of electrons followed by light emission at different wavelengths for NOM characterization.

The above methods and various other methods including pyrolysis gas chromatography-mass spectrometry (Pyr-GC-MS), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and liquid chromatography-mass spectrometry (LC-MS) are described in detail by Matilainen *et al.* (2011).

2.2.3 NOM in membrane fouling

NOM plays an important role in membrane fouling (Hong and Elimelech, 1997). Lee *et al.* (2004) showed that the hydrophilic fraction of NOM can provide a good estimate of fouling for low-pressure membranes. The study also indicated the greater fouling potential of proteins and polysaccharides i.e. biopolymers (Lee *et al.*, 2004).

Hallé *et al.* (2009) observed marked increases in transmembrane pressure after each backwash cycle were associated with biopolymer concentration increases in water. NOM is considered to be the main reason for building up fouling layer on membranes by Cornelissen *et al.*, (2006). However, the effect of polysaccharides and proteins on membrane material is not yet fully established (Huang *et al.*, 2009; Ratajczak *et al.*, 2012).

Ionic strength, pH, and divalent cations in water influence membrane fouling by NOM. Ionic strength and pH affect the surface charge of the membranes and NOM which often results in less repulsion between membrane surfaces and NOM (Cho *et al.*, 2000) and subsequent deposition of NOM on the membrane surface thus causes fouling.

Divalent cations aid NOM fouling by increasing the ionic strength of the particles and also by forming complexes with NOM creating larger compounds which are more likely to be

rejected by a membrane (Sobeck and Higgins, 2002; Farahbakhsh *et al.*, 2004). However, this is dependent on a particular NOM molecule's shape, size, charge density, and aromaticity (Cho *et al.*, 2000).

2.3 Membrane Pre-treatment Methods

Membrane filters are bound to foul to an extent depending on the characteristics of the water. The faster the membranes get fouled, the more expensive it is from an operational point-of-view as chemical cleaning will add to costs and it will also reduce the life of the membrane. To reduce or control membrane fouling, various pretreatment options are currently in practice. However, optimum operating conditions, interactions between chemical pretreatment and membranes, cost, and compatibility are yet to be resolved (Farahbakhsh *et al.*, 2004). A few common pre-treatment techniques for low-pressure membranes are described in the following sections.

2.3.1 Coagulation

Coagulation is the most common and cost effective pretreatment process for low-pressure membranes. It involves the application of chemicals to destabilize and neutralize the charge of the suspended particles (NOM) in water and increase their size by formation of flocs for ease of removal (Gaulinger, 2007). Though coagulants can be available as inorganic metal salts and organic macromolecules, metal salts such as alum, ferric chloride, and sulfate and polyaluminum chloride (PACl) are most commonly used (Huang *et al.*, 2009).

Coagulation occurs by two mechanisms i) charge neutralization or ii) sweep flocculation. Charge neutralization is dominant in the pH range of 5.5-6.5 when metal species of charge opposite to that of particles neutralize the surface charge those particles resulting in removal

as precipitates by forming flocs. Sweep flocculation occurs at higher coagulant doses and higher pH (>6.5). The coagulant metal ions in water form metal hydroxide (aluminum hydroxide) which precipitates due to its low solubility. In this case, suspended particulates get attached to the precipitated metal hydroxides and settle out (Gregory and Duan, 2001; Gao *et al.*, 2011).

Removal of NOM by coagulation can occur through any of the two mechanisms depending on the pH. Humic substances being negative charged can precipitate as metal-humic complexes with positively charged metal coagulants. Or at higher pH humics can absorb on the metal hydroxides. However, it is difficult to distinguish between the mechanisms (Gregory and Duan, 2001).

Coagulation processes can be classified as standard (with sedimentation) and in-line coagulation (Gao *et al.*, 2011). While some researchers acknowledge the benefits of standard coagulation (Liang *et al.*, 2008), others (Dong *et al.*, 2007, Konieczny *et al.*, 2009) using in-line coagulation also found reduction in fouling by increased removal of hydrophilic compounds by getting deposited on the cake layer formed on the membrane surface.

In most studies (Choi and Dempsey, 2004; Howe and Clark, 2002; Ratajczak *et al.*, 2012) coagulation has proved to be a good pretreatment for polymeric membranes (Figure 2.5). An exception is the study by Maartens *et al.* (1999) where higher flux reduction was observed with metal-ion coagulants. However, fouling reduction depends on the coagulant nature and optimum dose (Barbot *et al.*, 2008). Non-optimized coagulant dosages may increase fouling even more than without any pretreatment at all (Howe and Clark, 2002, Choi and Dempsey, 2004, Ratajczak *et al.*, 2012). A higher dose than optimum can also increase irreversible fouling (Meyn *et al.*, 2010).

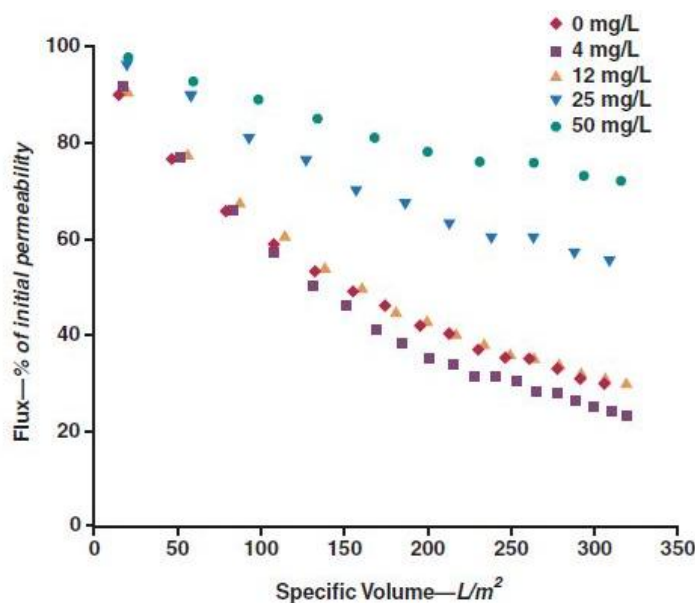


Figure 2.5 Increase in flux for a polypropylene microfiltration membrane with increased alum dose (up to 50 mg/L for enhanced coagulation) for Salt River water
(Reprinted from Howe and Clark, 2006, Journal AWWA by permission)

Coagulation-membrane filtration processes are highly impacted by pH, dose and type of coagulant depending on raw water NOM concentration (Gregory and Duan, 2001, Ratajczak *et al.*, 2012, Konieczny *et al.*, 2009). Removal efficiency and permeate flux also depend on operating conditions and coagulation (Abeynayakaa *et al.* 2010; Lee *et al.*, 2000).

Although coagulation is not too expensive, this process produces solid wastes which require disposal (Huang *et al.*, 2009). Addition of ferric chloride coagulant in the feed water has been seen to cause extensive fouling during MF filtration (Schafer *et al.*, 2001).

2.3.2 Ozonation

Ozone is highly reactive as it has both electrophilic and nucleophilic characteristics. Ozone can react with dissolved NOM directly as molecular ozone or indirectly in free radical form such as hydroxyl radicals ($\text{OH}\cdot$). As a powerful oxidant, ozone can oxidize compounds with

carbon-carbon double bonds and also aromatic compounds (Beltran, 2004). In the reaction of ozone with NOM, oxygenated saturated bonds are formed which can be carboxylic, aldehydic, or ketonic groups that are hydrophilic in nature (von Gunten, 2003a). Also, unsaturated bonds present in humics can be easily broken down by ozone to form low molecular weight compounds (van Geluwe *et al.*, 2009). This reaction may increase membrane flux as the hydrophilic products are less likely to cause fouling (Geluwe *et al.*, 2011). The breaking down of the humic substances is considered to be from the periphery in the “outside-in trimming mechanism” hypothesized by Jansen *et al.* (2006), where the central part of the molecule remains intact with the double bonds and bonds on the outer side break resulting in the degradation into small compounds (<200 Da).

In the case of proteins and polysaccharides, pore constriction or blocking is common in low-pressure membrane because of the size of these molecules. Ozone depolymerises the polysaccharides by oxidizing the in β -D-glycosidic linkages (Wang *et al.*, 1999). In the case of reacting with protein it was seen in the study of Cataldo (2003) that in solid state, proteins are not affected by ozone, but when in solution, ozone oxidizes aromatic amino acids. Ozonation also modifies the secondary and tertiary structures of protein. However, ozonation cannot break the polyamide bond of the main chain of the protein (Cataldo, 2003). By breaking the NOM to smaller particles, ozone facilitates the removal of these particles and hence reduces flux drop through the membranes (Karnik *et al.*, 2005; Lee *et al.*, 2005b). The effect of divalent cations on ozone-induced reduction of membrane flux drop is yet to be elucidated. While some researchers have suggested less flux decline due to secondary removal of small (nano) particles by divalent ion-NOM complexes on fouling layers

(Lohwacharin and Takizawa, 2009), others have suggested the reduction in flux is due to the formation of a dense cake layer (Hong and Elimelech, 1997, Costa *et al.*, 2006).

Studies with model solutions (Mozia *et al.*, 2006), rain water (Sartor *et al.*, 2008), or with natural surface water (Hashino *et al.*, 2001; Song *et al.*, 2010) have all demonstrated reduced fouling and a stable flux with ozonation (Figure 2.6).

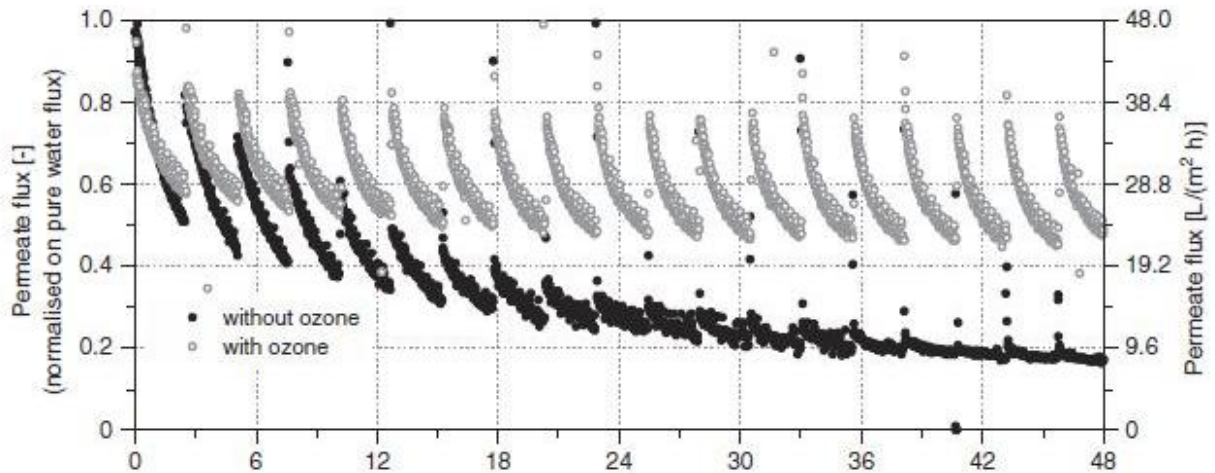


Figure 2.6 Increase in permeate flux with the application of ozonation prior to ultrafiltration at constant transmembrane pressure

(Reprinted from Sartor et al., 2008, with permission from Elsevier)

Ozone breaks down small particles which can easily pass through membrane hence the possibility of having a dense cake layer is lessened and sticky biofilms are also prevented developing (Sartor *et al.*, 2008) thus fouling is reduced. However, DOC of the permeate increases in the process (Hashino *et al.*, 2001).

Ozonation is a good pretreatment to reduce fouling and improve water quality. However, its efficiency varies depending on water quality characteristics and membrane type. Studies of ozonation pretreatment have mostly been conducted using ceramic membranes (Schlichter *et al.*, 2004; Karnik *et al.*, 2005; Kim *et al.*, 2008) as polymeric membranes may degrade in the presence of ozone (Shen *et al.*, 1990, Hashino, 2001). Amongst the polymeric membrane

materials, polyvinylidene fluoride (PVDF) is the least vulnerable to ozone degradation compared to polyethylene, polysulfone, and polycrylonitrile (Mori *et al.*, 1998; Hashino *et al.*, 2001; Farahbakhsh *et al.*, 2004). Optimum dosing is critical based on site specific criteria and the process may not be cost effective. Also the potential formation of bromate, a regulated ozone by-product, needs to be taken into consideration.

2.3.3 Biofiltration

Biofiltration can act as a membrane pretreatment in two ways; as a i) direct biofiltration pretreatment and as ii) biofiltration after ozonation. A detailed description of biofiltration processes and their potential as membrane pretreatment options is explained in detail in Sections 2.4 and 2.5.

2.3.4 Others

Other pretreatment techniques include absorption using PAC (Bérubé *et al.*, 2002), ion exchange, MIEX[®] resin (Kabsch-Korbutowicz *et al.*, 2008), and combinations of different pretreatment techniques (Ødegaard *et al.*, 2010; Gao *et al.*, 2011).

2.4 Biological Filtration in Drinking Water Treatment

Biofiltration is a “green” technique for water treatment. It has been widely used in wastewater treatment applications and its use in drinking water treatment in Europe has been practiced since the 1970’s (Rittmann and Huck, 1989). However, this technique has gained popularity in North America only relatively recently due to its potential to deal with modern water treatment challenges (Brown, 2007).

Drinking water biofiltration is typically in the form of regular slow or rapid filtration with sand or anthracite, biologically active carbon filtration, or filtration with other types of media

in the absence of chlorine. Lack of the presence of a disinfectant allows for growth of biofilms on the filter media which have the potential to remove different organics and contaminants (Huck *et al.*, 2011).

2.4.1 Application of biofiltration

Electron donors in natural water include BOM, NH_4^+ , Fe^{+2} , NO_2^- , Mn^{+2} , and S which are the cause of bio-instability of the water (Rittmann and McCarty, 2001). BOM, with concentration of $<10 \mu\text{g/L}$ when measured as AOC and $<50 \mu\text{g/L}$ when measured as BDOC, is considered a requirement to ensure biostability. The presence of an ozonation process in a treatment train can increase the easily biodegradable portion of NOM even further (Rittmann, 1995). If uncontrolled, this can result in bacterial re-growth in distribution systems, reduced dissolved oxygen levels, problems associated with taste, odour, nitrate, corrosion, and also the formation of disinfection-by-products (such as THMs, haloacetic acids, chlorinated aromatics). Hence, ensuring biostability of the finished water is important, where biofiltration can play an important role.

Biofiltration is a robust process that can be inserted in any stage of a treatment plant. It does not require chemical addition, or pH, temperature, or oxidation potential adjustments like many other treatment processes (Juhna and Melin, 2006). It produces less chemical waste/sludge and thus can be cost effective (Brown, 2007). It can remove trace contaminants and odour causing compounds from water (Elhadi *et al.*, 2006), control bacterial re-growth in the distribution system (Persson *et al.*, 2006), and aid in denitrification (NO_3^- to N_2) of water (Rittmann and McCarty, 2001). The process uses indigenous bacteria which are not harmful to human health, and the filter environment is not favorable for the growth of pathogenic bacteria (Rittmann and McCarty, 2001). Biofiltration is usually followed by some

disinfection/membrane treatment process which makes the treated water safe for human consumption (Brown, 2007).

Biofiltration also has the potential to remove organic foulants of membranes (Peldszus *et al.*, 2011; Filloux *et al.*, 2012) and thus can play a role in fouling control and energy consumption for membrane filtration processes (Mosqueda-Jimenez and Huck, 2006). The role of biofiltration in membrane fouling reduction is further confirmed using advanced liquid chromatography with organic carbon detection (LC-OCD) by Hallé *et al.* (2009).

2.4.2 Biofiltration process

Biofilters are colonized by native bacteria in the water and in the case of drinking water these bacteria are usually heterotrophic (mostly oligotrophs) which use organic compounds as electron donors (Brown, 2007). An ideal environment for the growth of bacteria must include nutrients as well and being oligotrophic, they can survive and achieve substantial removal efficiently in low nutrient conditions which is common in drinking water treatment scenarios (Rittmann and Huck, 1989). Bacteria use red-ox reactions for energy generation and in the process of reducing primary electron donor substrate (BOM) to CO₂ (aided by O₂) secondary removal of contaminants may be achieved (Rittmann, 1995).

The filter becomes biologically active with the “aggregation and attachment” of bacteria to the media (Figure 2.7). Biofilm growth in water may take several months and is mostly dependant on water characteristics (Chaudhury *et al.*, 2003). Microorganisms, (both bacteria and protozoa) attach to the media using extracellular polymer (EPS) which provides habitat and protects bacteria, and ensures significant biofilm retention to achieve a treatment credit (Rittmann, 1995).

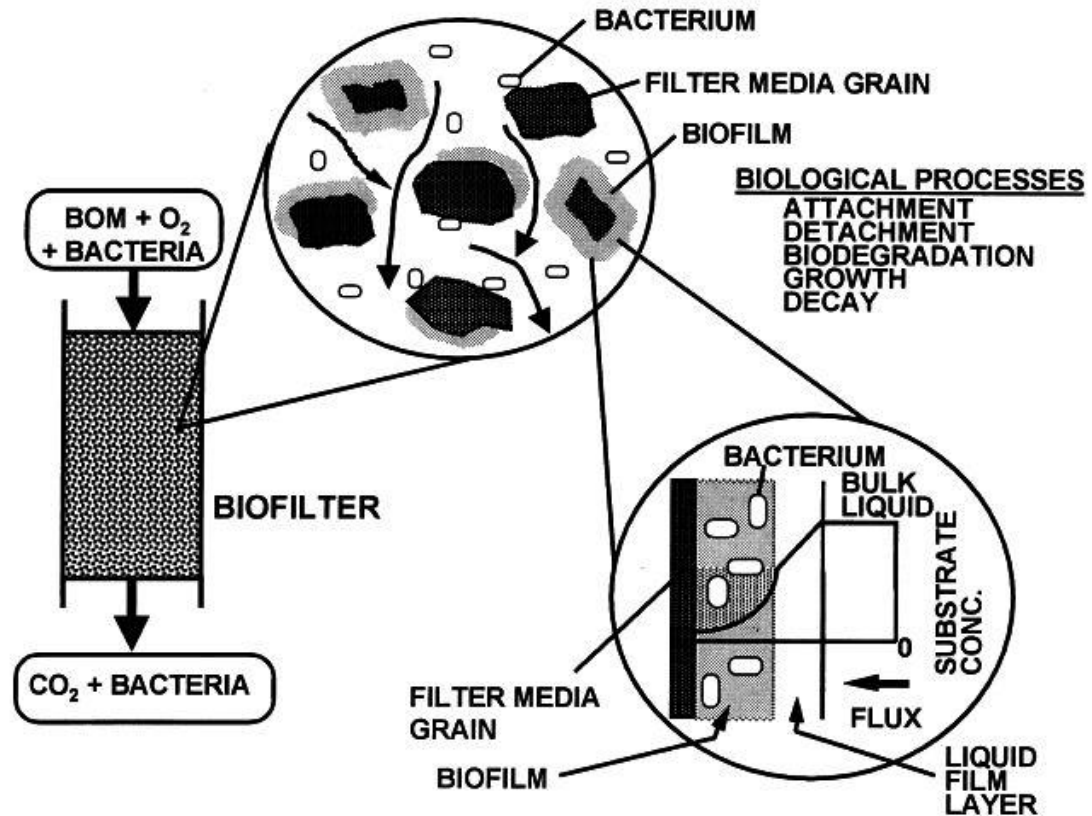


Figure 2.7 Biomass development and biological processes in biofilters

(Reprinted from Hozalski et al., 2001, with permission from Elsevier)

Biofilters can have different configurations such as fixed bed, fluidized bed, membrane bioreactor, or bank filtration (Brown, 2007). Rittmann (1995) further classified slow/rapid biofilters into three configurations, i) small-granule filters (<1 mm ϕ), ii) large-granule filters (4-10 mm ϕ), and iii) fluidized bed biofilm processes. These processes have advantages over one another in different situations. However, the basic principles are the same for different configurations and include:

- a) Utilization and diffusion of organics in the biofilm which can be expressed by Monod kinetics and Fick's second law, respectively, and will help to quantify biofilm accumulation where substrate is rate limiting.

- b) Transfer of mass between liquid and biofilm.
- c) Biofilm development and detachment (due to shear stress, turbulence, abrasion etc.).

During steady-state operation the decay/detachment and growth of bacteria in the filter are in a state of balance (Chaudhury *et al.*, 2003).

2.4.3 Factors affecting biofilter performance

Brief descriptions of the various factors that affect biofiltration process are provided below. A more detailed description can be found in the review of Urfer *et al.* (1997).

Filter Media – Biofilter media can be non-adsorptive (sand/anthracite) or adsorptive (GAC). Surface area, texture, and cost of the media play an important role in selection. Compared to other common media types (sand/anthracite), GAC surface appear better for bacteria attachment due to its irregularities. GAC has demonstrated better performance in organic removal and biomass development than sand-anthracite filters, especially mesoporous GAC (Pirbazari *et al.*, 1990; Wang *et al.*, 1995).

Contact time – Empty bed contact time can substantially affect biofilter performance if it is too short. Increased EBCT is associated with increased organic removal (Servais 1992). Though EBCT depends on hydraulic loading and depth, these do not regulate BOM removal (Zhang and Huck, 1996; Servais *et al.*, 1994; Wang *et al.*, 1995). EBCT may be different depending on treatment goals and stage of the biofilter, however, EBCT has an optimum value, beyond which increasing contact time will not aid removal (Zhang and Huck, 1996).

Backwashing – There can be different backwash strategies for biofilters such as water only, with air scour, and using chlorinated or non-chlorinated for backwashing. Backwashing has important effects on long term performance (Bouwer and Crowe, 1988) and is recommended when re-starting after a shut-down due to endotoxin build-up (Anderson *et al.*,

2008). Though suspected, Servais *et al.* (1991) did not observe significant biomass loss during backwash. Collapse pulsing was subsequently suggested as a better backwash strategy by Servais *et al.* (1991) and Ahmad *et al.* (1994).

Temperature – Biological activity is temperature dependant and in colder temperature a biofilter requires longer contact time for efficient organics removal (Servais *et al.*, 1992). Temperature also affects media selection. GAC has been shown to perform better than sand-anthracite filters at colder (1 – 3°C) temperatures, while they perform similarly in warmer (21 – 24°C) environments (Emelko *et al.*, 2006).

Other parameters that affect biofilter performance are extreme pH, toxic substances, preceding treatment processes such as ozonation (Rittmann and Huck, 1989), and influent organic concentrations (Zhang and Huck, 1996). However, organic removal is not necessarily proportional to the amount of biomass present (Wang *et al.*, 1995).

2.4.4 Process modeling

Various models are available for the prediction of bioreactor performance using different water quality (feed, available organics, and nutrients) and system environmental parameters (contact time, temperature etc.) as inputs (Brown, 2007). Most consider steady-state conditions (balanced growth and loss) and have some limitations. A non-steady-state condition may arise during changes in operating condition (e.g. backwash) or start-up period (Rittmann and Huck, 1989).

Most drinking water treatment situations deal with much lower raw water BOM concentrations compared to levels dealt with in wastewater treatment situations and BOM is often rate limiting (Rittmann and McCarty, 2001). A model estimates flux of substrate at the biofilm surface as a function of substrate concentration. As microorganisms use organics

they are constantly being diffused into the biofilm and this reduces the concentration of substrate at the biofilm surface more than in bulk liquid, making it difficult to replicate in a model (Rittmann and Huck, 1989).

Some biofiltration process models which have application for drinking water biofilters include the:

- Steady-state biofilm model by Rittmann and McCarty (1980) which uses Monod kinetics and Fick's law and introduced the concept of $S_{\min}$ (below this biofilm cannot be maintained), however, biofilm growth and time are not considered.
- Kinetics of biofilms on activated carbon (BFAC) model by Chang and Rittman (1987) considered biofilm growth, mass transfer, biodegradation and adsorption, filter depth, bed porosity, but does not consider backwash induced non-steady state conditions
- CHARBROL model by Billen et al (1992) is for designing biofiltration processes by estimation of BDOC removal and biomass distribution at select temperatures and EBCTs.
- First order biofilm model (with the concepts of steady-state model by Rittmann and McCarty) by Zhang and Huck (1996), introduced the concept of dimensionless contact time X^* . A related parameter biofiltration factor 'BF' was proposed by Huck and Sozański (2008) which can be used as an important design parameter for biological filters and be defined by percent removal of AOC.
- BIOFILT model developed by Hozalski and Bouwer (2001) includes non-steady state conditions attributed to backwashing.

2.5 Biofiltration as Membrane Pre-treatment

Biofiltration can be employed as a membrane pretreatment directly or following ozonation. Table 2.1 presents some studies where direct biofiltration has been used as membrane pretreatment and significant fouling reduction has been achieved compared to direct polymeric membrane filtration processes. While two earlier studies (Tsujimoto *et al.*, 1998; Park *et al.*, 2002) examined the effect of TOC and metal foulants, more recent studies focus on identifying the fractions of DOC responsible for fouling.

Table 2.1 Observations from biofiltration pretreatment studies for membranes (surface water)

Source water (Ref.)	Membrane type	Biofiltration	Findings
Onga River, Japan DOC: 2.4 mg/L Turbidity: 19 NTU Fe: 0.1-0.97 mg/L Mn: 0.09- 0.17 mg/L (Tsujimoto et al., 1998)	Two hollow fiber UF membranes 1. Cellulose acetate, 150 kDa 2. Polyacrylonitrile, 13 kDa Maximum TMP: 80 kPa (11.6 psi)	Up flow GAC (12 mm) filter Filter depth: 1 m Hydraulic loading: 10 m/h	• CA membrane operated without chemical treatment for 300 days without significant irreversible fouling (stable TMP). • PAN required chemical treatment at 100 day intervals. • TOC, manganese and iron identified as foulants for PAN and CA membranes, respectively. • With GAC pretreatment CA membranes required chemical cleaning after filtering for 530 days. • With citric acid cleaning, membrane's initial performance was recovered.
Tama River, Japan DOC: 2.05 mg/L Turbidity: 2.22 NTU Fe: 0.32 mg/L Mn: 34.2 mg/L Al: 0.28 mg/L (Park et al., 2002)	Hollow fiber polyethylene MF membrane Filtration: dead-end	Down-flow fixed bed coarse polypropylene tube (5X4X3 mm) filter Filter depth: 1.2 m Hydraulic loading: 13.3 m/h EBCT = 6 min	• Biofilter-MF process exhibited less fouling compared to MF only process. • 61.5 % ammonia, 1.5% DOC and 1.1% UV260 removal achieved by biofiltration. • 55.9% turbidity removal by biofilter decrease particle load on MF membrane and decrease TMP rise. • Biofilters show high removal of metal ions and the BF-MF process show 43.1, 47.1 and 57.4% less deposition of Al, Fe and Mn, respectively, on membrane surface compared to MF only process. • Major contribution of metal ions on membrane fouling expected. • Could not draw conclusion regarding organic foulants due to low organic matter removal by the biofilters.

Source water (Ref.)	Membrane type	Biofiltration	Findings
Grand River, ON, Canada DOC: 5-7 mg/L Turbidity: 0.45- 62 NTU Alkalinity: 160- 250 mg/L as CaCO ₃ Hardness: 200- 350 mg/L as CaCO ₃ (Hallé et al., 2009)	Hollow fiber PVDF UF membrane (GE/Zenon, Canada), 400 kDa Filtration: dead- end Maximum TMP: 9 psi Run length- 5 days	Two dual (anthracite/sand) media biofilters in down-flow mode Biofilter preceded by gravel roughing filter (RF) for turbidity removal Total depth- 1.2 m Hydraulic loading: 5 m/h Biofilter 1: depth: 0.4 m, EBCT- 5 min Biofilter 2: depth: 1.17 m, EBCT- 14 min	• Average 11% DOC removal by RF-BF combined system during active period (in winter biofilters considered inactive). • Fractions of DOC more important than total DOC in assessing biofiltration efficiency as membrane pretreatment. • Average % biopolymer removal by BF1 and BF2, 40 ± 26% and 60 ± 22% respectively. • Low removal of humic substance and low molecular weight acids and high (95-98%) removal of turbidity observed from the biofilters. • Increased biopolymer removal by membrane with increased fouling. • With higher EBCT filter, greater removal for biopolymers and lower reversible and irreversible fouling were observed, while other water quality parameters remain unchanged. • Biopolymers found to be more important foulants for this water and membrane type.
Grand River, ON, Canada DOC: 5-7 mg/L Turbidity: 1.38- 24.6 NTU Alkalinity: 160- 250 mg/L as CaCO ₃ Hardness: 200- 350 mg/L as CaCO ₃ (Huck et al., 2011)	Hollow fiber PVDF pilot-UF membrane (GE/ Zenon, Canada) Pore size: 0.04 µm Filtration: Dead- end Run length - >200 h	Three dual (anthracite/sand) media biofilters in down-flow mode following gravel RF Hydraulic loading: 5 m/h Biofilter 1: depth: 0.4 m (Ø-20cm), EBCT- 5 min Biofilter 2: depth: 0.83 m (Ø-20cm), EBCT- 10 min Biofilter 3: depth: 0.55 m (Ø-15cm), EBCT- 15 min	• Lower irreversible fouling observed with higher EBCTs. • TMP recovery data indicated importance of frequent maintenance cleaning. • Biofilters removed turbidity to <1 NTU and turbidity removal efficiency seen to increase with increasing EBCT. • Relating turbidity removal and TMP increase indicated no direct relation between turbidity and irreversible fouling. • Increased biopolymer removal achieved with increased EBCT.

Biofiltration achieved excellent turbidity removal in all cases listed in Table 2.1, although that was not the objective of the process as studied since it was not considered to be a final treatment step. DOC removal is affected by temperature. Peldszus et al (2012) found about 15% DOC removal in warmer temperatures and reported that it dropped to less than 5% during the winter. Figure 2.8 shows substantial removal of biopolymers by the biofilters, as the main fraction seen to be rejected by the UF membrane used (Hallé *et al.*, 2009).

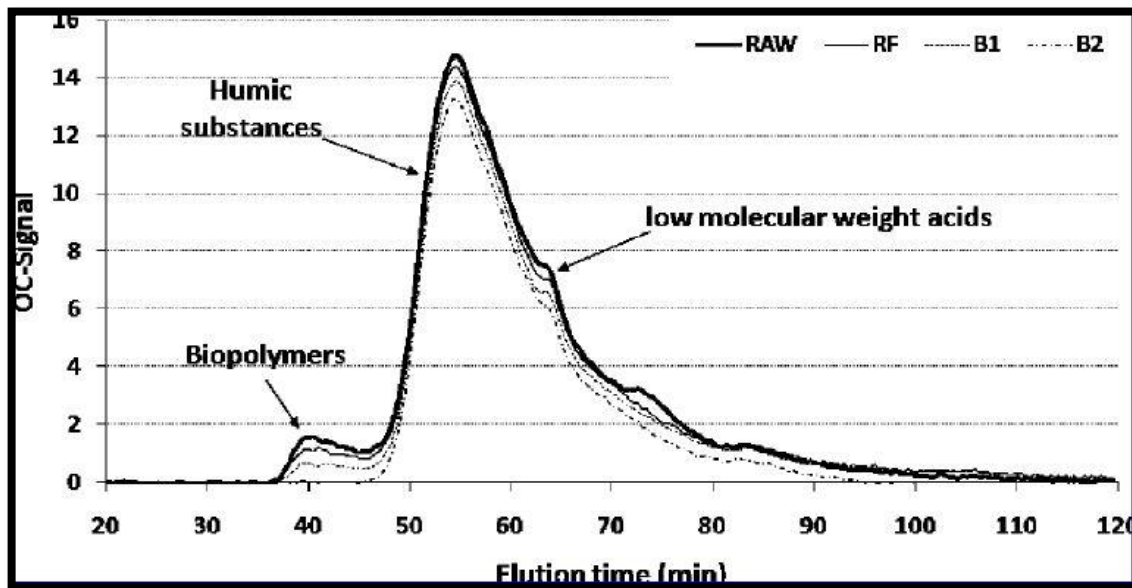


Figure 2.8 LC-OCD chromatogram showing removal of DOC fractions by biofilters combined with roughing filter for Grand River water Ontario, Canada
(Reprinted with permission from Hallé et. al, 2009, © American Chemical Society)

As mentioned previously, EBCT is very important for good performance of biofilters and different studies at bench- and pilot-scale have found benefits in using longer EBCT for fouling reduction (Hallé *et al.*, 2009; Huck *et al.*, 2011; Peldszus *et al.*, 2012). Hallé *et al.* (2009) observed different degrees of fouling with two filters having different EBCTs while the percentage DOC removal was similar which indicates the importance of DOC fractions instead of the total DOC in fouling. They also found a positive correlation between

biopolymer concentrations in water and irreversible fouling with very little effect from turbidity.

Figure 2.9 presents results from Peldszus *et al.* (2012), who found biopolymer removal to be the main factor for membrane fouling reduction by the biofilters though biopolymers constitute only about 10% of the total DOC. They noticed a much higher reduction in hydraulically irreversible fouling by using biofiltration pretreatment for their membranes compared to no pretreatment and better performance was observed with increased EBCT.

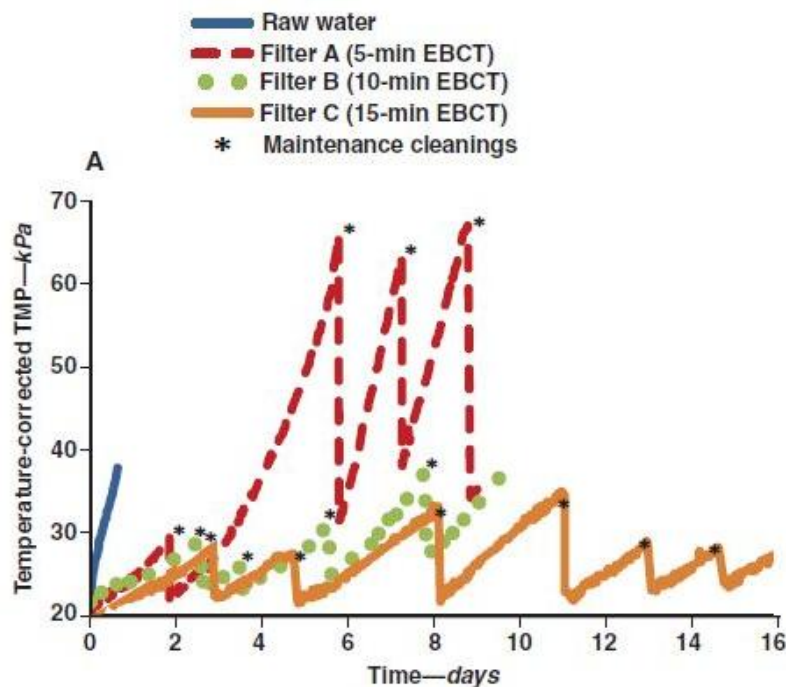


Figure 2.9 Effect of using biofiltration pretreatment and increased biofilter EBCT on membrane TMP (hence, fouling) using a UF membrane with Grand River water, Ontario

(Reprinted from Peldszus et al., 2012, Journal AWWA by permission)

Pre-ozonation can make the DOC in water more biodegradable (Laat *et al.*, 1990; Treguer *et al.*, 2010), and removing this biodegradable fraction by biofiltration can be a solution to problems associated with biological re-growth (Leiknes *et al.*, 2005; von Gunten, 2003a).

Hence, an ozone-biofiltration combined pretreatment can be applied as a robust process that will decrease the NOM-loading on the membranes as well as reducing the threat of DBP formation. This pretreatment technique was shown to be beneficial in reducing membrane fouling (Nishujima and Okada, 1998); however, Geismar *et al.* (2012) found no significant effect of BAC after ozonation on the total fouling index.

2.6 Nutrient Enhancement and Biofilter Performance

Biofiltration processes are highly dependent on the availability of organic carbon as well as key elements (nutrients) as these are essential for the sustenance and growth of biofilm bacteria. Based on biomass chemistry, different ratios of balanced nutrient conditions have been suggested (Rittman and McCarty, 2001, LeChevallier *et al.*, 1991; Sathasivan *et al.*, 1999). The approximate C:N:P ratio of 100:10:1 (Redfield, 1958; USPEA, 1992) is considered important for balanced growth of heterotrophic bacteria and been used to estimate organic or nutrient limitation in biofilters. Lauderdale *et al.* (2012) used this C:N:P ratio to add phosphorus to their biofilters when they found a phosphorus limitation in their biofilters. They also related the phosphorus limitation to increased headloss experienced in their filters. By adding phosphorus in the form of phosphoric acid to one filter they observed a remarkable improvement in the hydraulic performance of the filter (15% decrease in terminal headloss, 75% increase in DOC removal and 30% increase in ATP). Others doing similar nutrient enhancement experiments have also observed positive changes in biofilter performance (Li *et al.*, 2010; Sang *et al.*, 2003). However, this is not the case for all studies. In some cases even with what appeared to be a phosphorus limited condition, phosphorus addition did not result in significant improvement in biofilter performance (Melin *et al.*, 2002; Vahala *et al.*, 1998). Similar experiments for other nutrients such as nitrogen, metal

ions, and peroxide have also been performed (Lauderdale *et al.*, 2012). However, such experiments looking at the effect of enhancement on membrane fouling control were not found in the literature.

2.7 Research Motivation

Although a number of studies have been conducted to-date to find a sustainable membrane fouling reduction mechanism, only a few have investigated direct biofiltration as a pretreatment for membranes. Bench- and pilot-scale studies by Hallé *et al.* (2009) and Huck *et al.* (2011) with Grand River water in Southern Ontario, Canada have demonstrated the potential of this technique. Their research has opened the doors to further exploration and optimization of this technique with different source waters that will have different characteristics and NOM concentrations, and different operating conditions which may pose new challenges. A previous study by Croft (2012) who compared different water sources of Southern Ontario with respect to NOM composition, reported similar highly variable SUVA and TOC in two Ontario rivers (the Grand and Saugeen), but very different biopolymer concentrations (maximum biopolymer concentration 0.7 mg/L and 0.35 mg/L for Grand and Saugeen rivers, respectively). Croft (2012) also found high variation in the humic substance concentration in the Saugeen River. As NOM, especially biopolymers, are important in the context of low-pressure membrane fouling, follow-up biofiltration pretreatment studies for ultrafiltration membranes would provide new information and an opportunity to verify previously reported findings. In addition, more in-depth study of biomass development and organic removal (using LC-OCD) in parallel biofilters would also provide insight to process reproducibility, microbial activity, and biofilter performance and dynamics.

The Saugeen River water historically has low levels of phosphorus. Recent phosphorus enhancement studies for biofilters have not examined its effect on different NOM fractions or how the addition of phosphorus affects the removal of potential membrane foulants. Hence, a phosphorus enhancement study would have the potential to provide new knowledge regarding engineered biofiltration and also membrane fouling mitigation mechanisms.

Chapter 3

Fouling of Low-Pressure Membranes during Drinking Water

Treatment: Effect of NOM Components and Biofiltration

Pretreatment

This chapter is based on a manuscript of the same title submitted to a scientific journal for publication on August 2013. Hence, it contains a separate introduction, methods, results and discussion and conclusions sections. Cited references are in the consolidated list of references at the end of the thesis.

3.1 Introduction

Fouling is a challenge for membrane-based drinking water treatment processes. Fouling decreases the effectiveness of the membrane by accumulation of material (foulant) within membrane pores and on the membrane surface (Crittenden *et al.*, 2005). This reduces the flux through the membrane and increases the transmembrane pressure (TMP) (AWWA, 2005). Two general types of fouling based on backwash recoverability are reversible (or backwashable) fouling and irreversible fouling. Natural organic matter (NOM) plays an important role in membrane fouling (Hong and Elimelech, 1997) and in particular the biopolymer fraction of the NOM has been identified as containing the critical NOM constituents that are responsible for fouling (Peldszus *et al.*, 2011; Filloux *et al.*, 2012).

As fouling results in increased cost for operation and cleaning, as well as a decreased membrane life, various pretreatment options have been studied and practiced to control or reduce fouling. Pretreatment can include both chemical and biological processes, through the addition of coagulants, ozone, adsorbents, or by filtering the water through granular media.

The efficiency of these techniques is highly dependent on the feed water quality and the membrane itself. Of these different pre-treatment methods, biofiltration has emerged as a “green” technique that minimizes chemical usage and wastes generated during water treatment (Brown, 2007; Zhang and Huck, 1996).

Direct biofiltration involves either slow or rapid filtration using sand, anthracite, biologically active carbon or other types of media, without the application of chlorine. The absence of chlorination allows for growth of biofilm on the filter media (Huck *et al.*, 2011) which have the potential to remove biodegradable organic matter (BOM) (Urfer *et al.*, 1997). Temperature, source water quality, media type, surface area for biofilm growth, backwashing, and empty bed contact time (EBCT) are some important factors which affect the overall performance of biofilters (Urfer *et al.*, 1997).

Biofiltration has the potential to remove proteins and polysaccharides (biopolymers) and thus reduce fouling of low pressure polymeric membranes (Hallé *et al.*, 2009). However, the concentration and composition of organic matter in different types of water are not necessarily similar (Her *et al.*, 2003) and this difference may have a considerable impact on fouling behavior (Amy, 2008). Hence, this study evaluated the effectiveness of biofiltration pretreatment for the reduction of membrane fouling using a pilot system and a different river water type than has previously been examined.

3.2 Methods

3.2.1 Feed water

The feed water for this study was collected weekly in two 20000 L batches from the Saugeen River near Walkerton, Ontario, Canada. The river flows northwest to Lake Huron through a watershed that is mostly agricultural land with some forest cover and smaller urban

communities. The water was transported to the test facility and stored in an outdoor 40000 L tank. This storage tank had a heating and circulation system which automatically activated when the atmospheric temperature dropped below 7°C. The circulation system ensured that the water remained mixed.

3.2.2 Experimental set-up

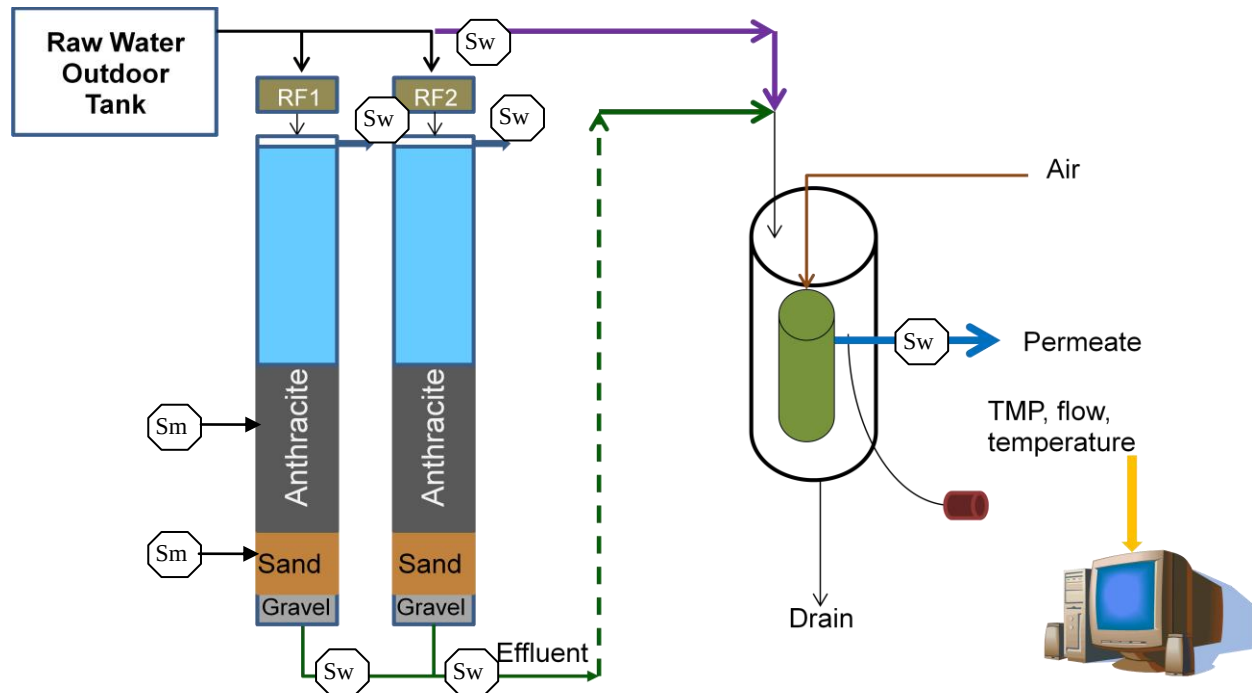


Figure 3.1 Schematic of the experimental set-up and sampling locations

A pilot treatment train was constructed and operated at the Walkerton Clean Water Centre in Ontario, Canada (Appendix A). The set-up (Figure 3.1) included two parallel 5.1 cm diameter $\times$ 2.1 m high glass columns containing dual media biological filters (BF1 and BF2). The media layer consisted of 55 cm of anthracite (uniformity co-efficient = 1.6; effective size = 1 mm) over 25 cm sand (uniformity co-efficient = 1.5; effective size = 0.5 mm) supported by 15 cm of gravel. The biofilters were operated at an empty bed contact time (EBCT) of 10

min corresponding to a hydraulic loading rate of 5 m/h. They were gravity fed and operated in down-flow mode. The biofilters were each preceded by a roughing filter (RF1 and RF2) to minimize the impact of varying turbidity and particle loads on the biofilters. The biofilters were backwashed once per week using biofilter effluent. The backwash process included air scour for 1 min followed by 4 min of air-water collapse pulsing. The water flow was then gradually increased to achieve 25% (1 min) and then 50% (4 min) bed expansion after the air was shut down.

For the membrane fouling experiments, a bench-scale ZeeWeed®-1 (GE Water and Process Technologies, Oakville, Ontario, Canada) polyvinylidene fluoride (PVDF) hollow fiber ultrafiltration membrane was used. The bench-scale membrane module had a nominal surface area of 0.047 m², nominal pore size of 0.04 µm, and was operated at constant flow, outside-in configuration of 57 L/m²h (LMH) flux (temperature corrected to 20°C). The clean membrane surface was non-ionic and hydrophilic (GE, 2013). The clean membrane surface was non-ionic and hydrophilic. The membrane module was maintained in a vertical position in a clear PVC cylindrical tank and was designed to cycle automatically (El-Hadidy *et al.*, 2013). Each cycle included 30 min of permeation followed by a 20 s backwash with air sparging. At the end of each cycle the tank was completely drained and then re-filled with fresh feed water (40 s). Membrane fouling experiments were conducted in batch mode using both untreated and biofiltered river water. The set-up also included a temperature sensor, pressure transducer, and flow monitor connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, Massachusetts, USA) for continuous measurements during the experiments. To measure fouling for both untreated and biofiltered water using the same batch of river water, the run length was selected to be 1.5 days or until it reached our

target maximum TMP (55.2 kPa or 8psi) of the membrane, whichever was reached first. Between each experiment the membrane module was chemically cleaned by placing it in 200 mg/L NaOCl for 5 h, followed by 5 g/L citric acid solution soak at room temperature also for 5 h, and rinsed thoroughly with deionised water between steps. The module was also tested for integrity using a pressure calibrator (Meri-cal DP2001I, Meriam Instruments, Ohio, USA) so that the pressure drop through the membrane was not more than 0.3 psi per 2 min, and each experiment was preceded by a clean water permeability test. Fouling rates were calculated using the transmembrane pressure data from a pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada) and corrected for temperature (20°C) (see supplementary information).

3.2.3 Analyses

Samples were collected from selected points in the treatment train including the roughing filter inlet (raw), roughing filter outlets (RF1 and RF2 effluent), and biofilter outlets (BF1 and BF2 effluent), and were analyzed for different water quality parameters including turbidity, pH, temperature, hardness, alkalinity, conductivity, UV254 absorbance, and SUVA using standard methods. Total and dissolved organic carbon (TOC/ DOC) were measured using a TOC analyzer (OI-Analytical TOC analyzer, model 1010, College Station, TX, USA). Liquid chromatography with organic carbon detection (LC-OCD) analysis was employed to measure the concentrations of the various NOM fractions, especially biopolymer and humic substances in water (Huber *et al.*, 2011). The DOC measured with the LC-OCD was usually a little lower (~10%) than that obtained from the dedicated TOC analyzer instrument.

Media samples, collected from sampling ports located in the middle layers of the sand and anthracite media, were measured with a LuminUltra™ DSA adenosine triphosphate (ATP) test kit (LuminUltra, Fredericton, New Brunswick, Canada).

3.3 Results and Discussion

3.3.1 Water quality and biofilter performance

Biofilter performance and organics removal were monitored for over a year beginning in March 2012. Experiments with the membrane unit to assess the effect of the biofilters on fouling were started only after confirmation that steady-state conditions had been reached. A summary of the raw water quality parameters is presented in Table 3.1 (data Appendix C).

Table 3.1: Biofilter feed water quality (Saugeen River) and biomass measured at biweekly intervals from June 2012 to May 2013 (period of steady-state operation)

Parameter		Range	Average	Number of observations
Raw water	pH	7.8 – 8.4	8.07	26
	Temperature °C	10 – 24	18	25
	Conductivity (µS/cm)	323 – 690	537	25
	Alkalinity (mg/L as CaCO ₃)	156 – 256	226	25
	Hardness (mg/L as CaCO ₃)	200 – 380	327	24
	UV ₂₅₄ (cm ⁻¹)	0.07 – 0.24	0.13	26
	Turbidity (NTU)	0.71 – 17.9	5.74	24
	TOC (mg/L)	2.85 – 7.29	4.45	26
	DOC (mg/L)	2.73 – 7.03	4.32	26
	SUVA (L/mg-m)	2.4 – 3.7	3.1	26
Media	Filter biomass (ng ATP/cm ³ of dry media)			
	BF1 – anthracite	73 – 294	163	22
	BF1 – sand	102 – 269	150	22
	BF2 – anthracite	60 – 241	148	15
	BF2 – sand	24 – 201	134	15

There was substantial variability of TOC, DOC and turbidity values, with higher values occurring during the winter. The high alkalinity, hardness and conductivity values suggested

groundwater infiltration into the river. The specific UV absorbance (SUVA) range confirmed the presence of aquatic humics. Although the river water temperature varied seasonally (0 to 24°C), the pilot feed remained above 10°C due to the feed water collection and storage process employed at the test facility.

The biomass (total ATP) development in both filters was similar (confirmed by a paired t-test, $\alpha = 0.05$). Following 3 months biofilter acclimation the ATP concentrations in the filters remained steady and did not exhibit any seasonal changes.

3.3.2 Biofilter performance in terms of organic removal

The LC-OCD results confirmed the elevated humic content in the Saugeen River (54 to 89% of DOC) with biopolymers accounting for only 2 to 11% of the DOC (data Appendix D). There was no substantial removal of humic substances through the biofilters during the experimental period indicating biofilm organisms could not break down this class of compounds. Although biopolymer concentrations in the feed water were low, average biopolymer removals of 20% and 22% were achieved by BF1 and BF2, respectively (RF combined), with values that ranged between 10 to 35% throughout the year. Biofiltration achieved substantial turbidity removal (27 to 88%) and only relatively low removals of TOC (0 to 12%), DOC (0 to 12%) and SUVA (0 to 17%), while the other chemical properties of water did not change. Low DOC removal by the biofilters was expected as humic substances, which account for most of the DOC, were not removed.

The concentration of biopolymers removed by Biofilters 1 and 2 demonstrated a positive correlation with the concentration of biopolymer present in the feed (Figure 3.2). While it would have been helpful to have additional data above 0.2 mg/L, this relationship was clearly valid in the lower concentration range (0.08 – 0.17 mg/L) and the Y-intercepts were less than

the MDL indicating the extrapolated lines pass very close to the origin. It is also evident from Figure 3.2 that the relationship between amounts removed and initial concentration is linear; which is an indication of first order behavior (Huck et al., 1994). This is evident from Equation 3-1 (Crittenden et al., 2005), which describes first-order kinetics for a batch or plug-flow reactor:

$$C/C_0 = e^{-kt} \quad 3-1$$

Where C is the effluent concentration, C_0 is the influent concentration, k is the rate constant and t is time. If k and t are constant, then the ratio C/C_0 will be constant. This means that the fractional or percentage removal will be constant for a given reactor (e.g. a filter), and is independent of the influent concentration. This is the behavior demonstrated in Figure 3.2.

Zhang and Huck (1996) demonstrated that axial dispersion could be ignored for a biofilter, and that it could therefore be modelled as a plug flow reactor. Since EBCT was not varied in the present study, t remained constant. Although raw water temperature did vary, because of the feeding arrangements the actual temperature of the water fed to the biofilters did not vary by more than a few degrees (Table 3.1), and therefore k remained essentially constant. Thus the conditions required to apply Eq. 3-1 to the data can be considered met.

Figure 3.2 indicates that the removal of biopolymers in the biofilter can be represented by first-order kinetics. This however does not necessarily indicate that the actual biodegradation follows first order kinetics. To make this further inference it would be necessary to assume that other factors (e.g. biomass concentration) are present in excess (which is probably a reasonable assumption), and that mass transfer is not limiting. Zhang and Huck (1996) have demonstrated that first order kinetics can be used for the removal of easily assimilable carbon

(AOC) in biofiltration. In their review article, Huck and Sozański (2008) note that several investigations have shown mass transfer to be not limiting for the removal of easily biodegradable compounds in drinking water biofilters and biofilms. Whether mass transfer would also not be limiting for the generally higher molecular weight biopolymers and whether the actual biodegradation (as opposed to simply the overall removal process) follows first order kinetics remains to be determined.

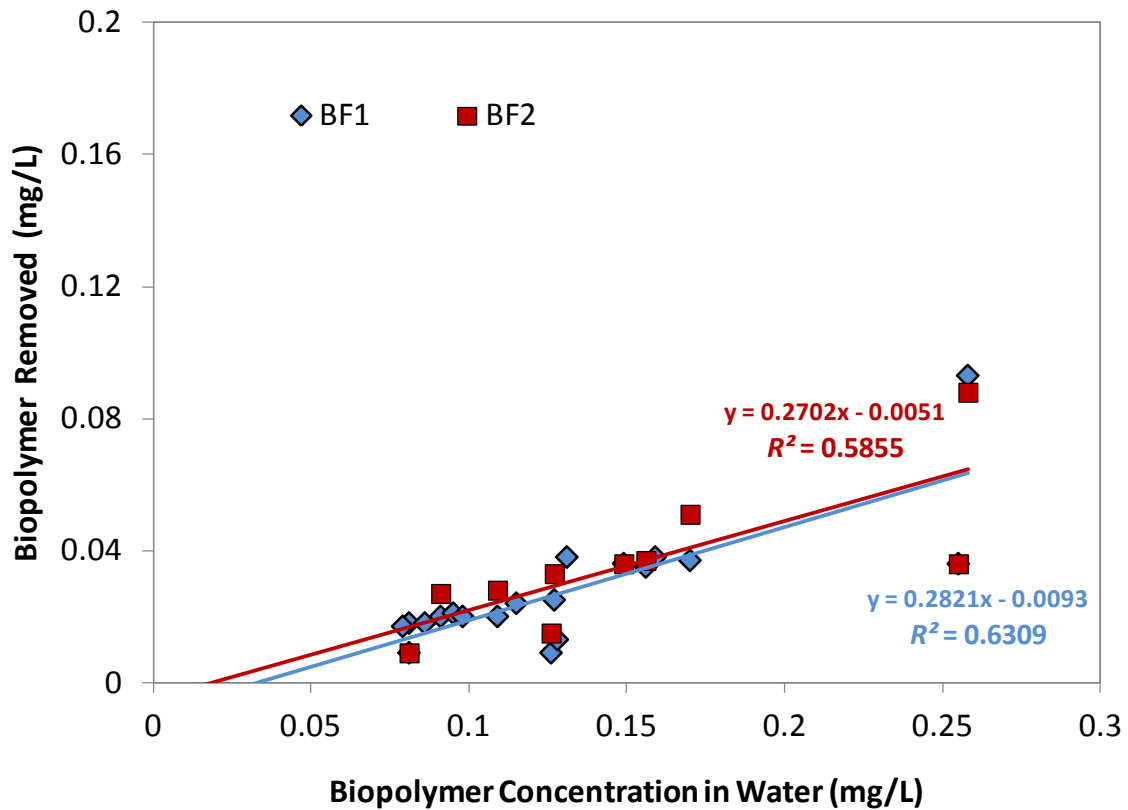


Figure 3.2: Correlation between biopolymer removal by Biofilter 1 (n = 19) and Biofilter 2 (n = 10) and raw water biopolymer concentration (MDL = 0.009 mg/L)

3.3.3 Effect of direct biofiltration in fouling reduction

To determine the effect of direct biofiltration as a pretreatment to reduce membrane fouling, five sets of comparison experiments were conducted between November, 2012 and April,

2013. Each comparison experiment first measured membrane fouling using untreated water, the membrane was then cleaned and fouling was measured using Biofilter 1 effluent. Each comparison experiment was done during the same week using the same batch of river water in order to keep the feed water quality comparable. Afterwards, six individual experiments were conducted with biofiltered water.

An example of the UF membrane fouling experiments (conducted from February 4 to 8, 2013) is presented in Figure 3.3. During the experimental run with untreated water (Figure 3.3A), the TMP increased above the target maximum of 55.2 kPa (8 psi) at about 10 hours with a rapid drop in flux from 58 to 38 LMH (normalized to 20°C). With Biofilter 1 effluent as feed water (Figure 3.3B), the TMP reached only 35.2 kPa (5.2 psi) over the same time and the flux decreased from 57 to 50 LMH. In this experiment, biofiltration pretreatment resulted in a 62% reduction in the irreversible fouling rate and a 43% reduction of average (per cycle) reversible fouling rate (based on TMP). As well the drop in flux due to fouling when using biofilter effluent was 22% less compared to untreated water.

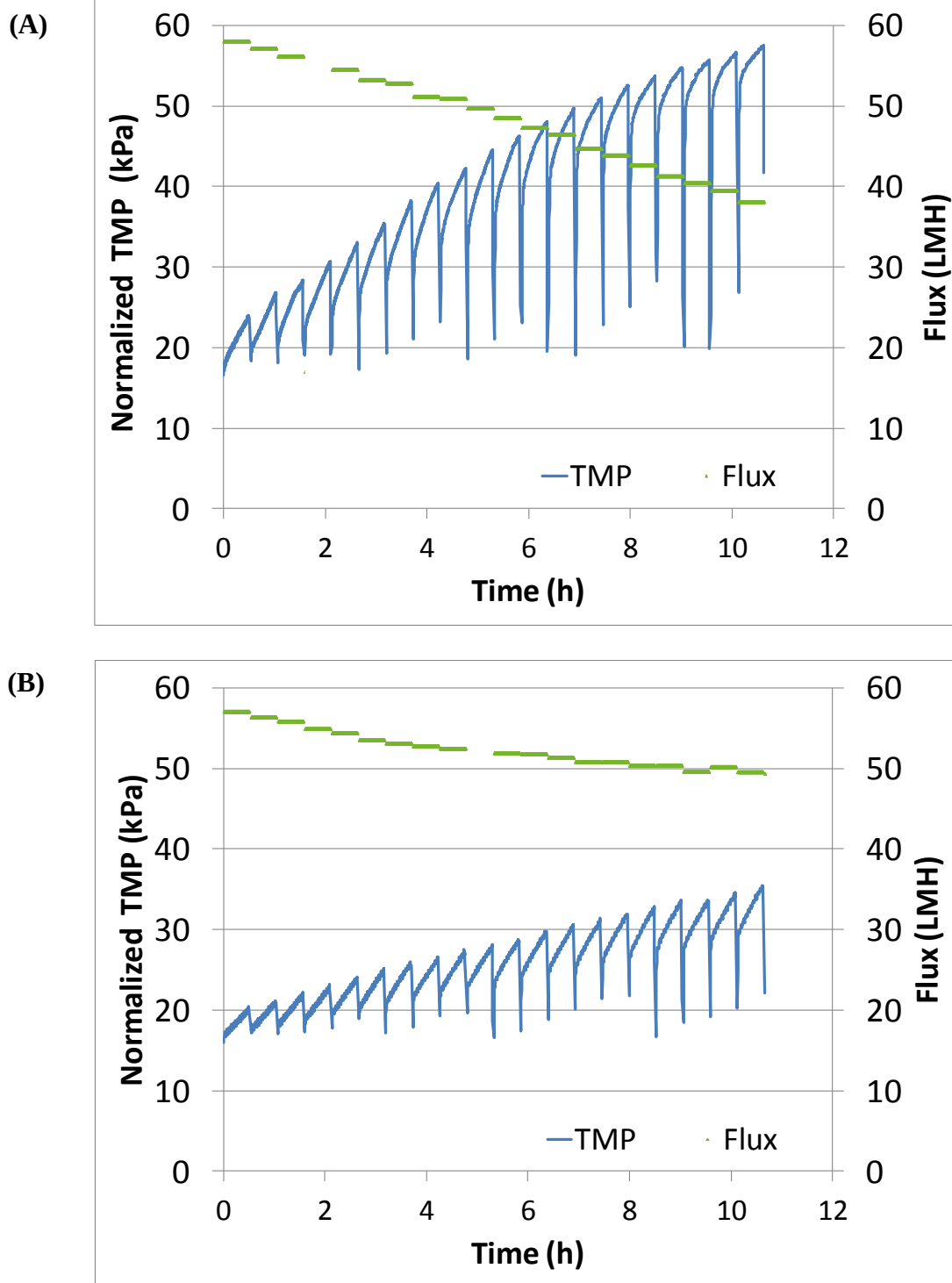


Figure 3.3 Comparison of fouling of a UF membrane measured over 10.5 hours using A) untreated river water and B) biofilter effluent as the membrane feed. The experiment was conducted from February 4 – 8, and the average temperature for A was 13.4°C and for B was 16.6°C

Table 3.2 summarizes NOM (DOC, biopolymers, humics) removal by the biofilters for the five experiments and the corresponding decrease in hydraulically irreversible fouling resulting from biofiltration as pretreatment. The DOC concentrations presented here were obtained from the LC-OCD instrument as a comparison with the biopolymer and humic fractions measured using the same instrument. Results show that direct biofiltration reduced the fouling rates substantially and in 4 out of 5 experiments (exception Feb 11 – 14), and a greater percent biopolymer reduction was found to be related to a greater percent reduction in both irreversible and average reversible fouling rates. Table 3.2 also indicates that the concentration of biopolymers was important and not the presence of humic material in terms of membrane fouling alleviation. It also illustrates the effectiveness of the biofiltration pretreatment in reducing fouling even at low biopolymer concentrations and relatively low biopolymer removals (10 to 30%).

Table 3.2: Effect of direct biofiltration pretreatment on membrane fouling rate (flux was 57 LMH at 20°C)

Experiment date (2012-2013)	Run length a (h)	Biofilter feed (mg/L) b			Removals by biofilter (%)			Fouling reduction c (%)	
		DOC	BP	HS	DOC	BP	HS	Irreversible	Reversible
Nov 26- 30	26.5	4.69	0.138	3.71	0.5	19	0	52	42
Dec 10-14	21.0	6.24	0.128	4.70	8.0	30	6	68	55
Feb 4-8	10.5	5.44	0.238	4.38	1.0	21	0	62	43
Feb 11- 15	27.0	4.55	0.112	3.63	1.0	16	0	14	8
Apr 1-3	21.0	4.15	0.128	3.31	1.5	10	2	49	36

^a length of each membrane experiment (raw/effluent) used for determination of fouling rate,

^b as determined by the LC-OCD instrument; BP = biopolymers, HS = Humic substances,

^c attributable to the biofilter based on TMP

Figure 3.3 (A and B) confirms the observations from Table 3.2. The irreversible fouling rate was highly correlated with the biopolymer concentration in the feed, both in the case of

untreated and biofiltered water (Figure 3.3A). The correlations presented in the figures seem to be biased by one high data-point. Although this particular data-point cannot be ignored, the correlation was recalculated excluding this point and still a considerable correlation ($R^2 = 0.60$) was found with similar slopes for untreated and biofiltered feed. This confirms observations from previous research on the Grand River water, with biopolymer concentrations ranging from 0.09 – 0.53 mg/L (Hallé *et al.*, 2009), regarding the important role of protein-like substances (biopolymer component) in irreversible fouling of low-pressure membranes (Peldszus *et al.*, 2011). Filloux *et al.* (2012) found a similar correlation ($R^2 = 0.88$) between UF membrane fouling resistance and biopolymer concentration (~0.3 – 1.5 mg/L) in wastewater effluent. The results obtained from the experiments with Saugeen River water (biopolymer concentrations 0.06 – 0.26 mg/L) confirm the importance of the biopolymer fraction in fouling.

In the case of humic substances, however, it was found that they did not play a similar role in irreversible fouling (Figure 3.4B), which again confirms the findings of Peldszus *et al.* (2011). A similar comparison of fouling rate and turbidity showed that the raw water turbidity of the water was not related to hydraulically irreversible fouling (results not shown), as reported by Hallé *et al.* (2009) and Peldszus *et al.* (2011).

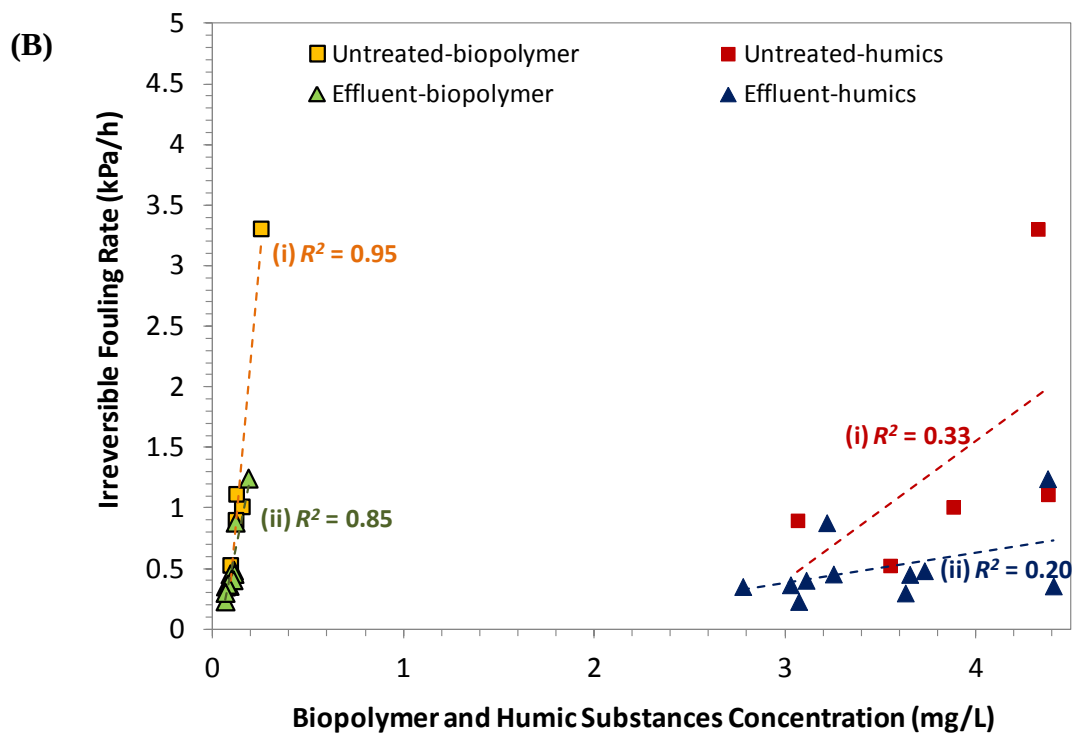
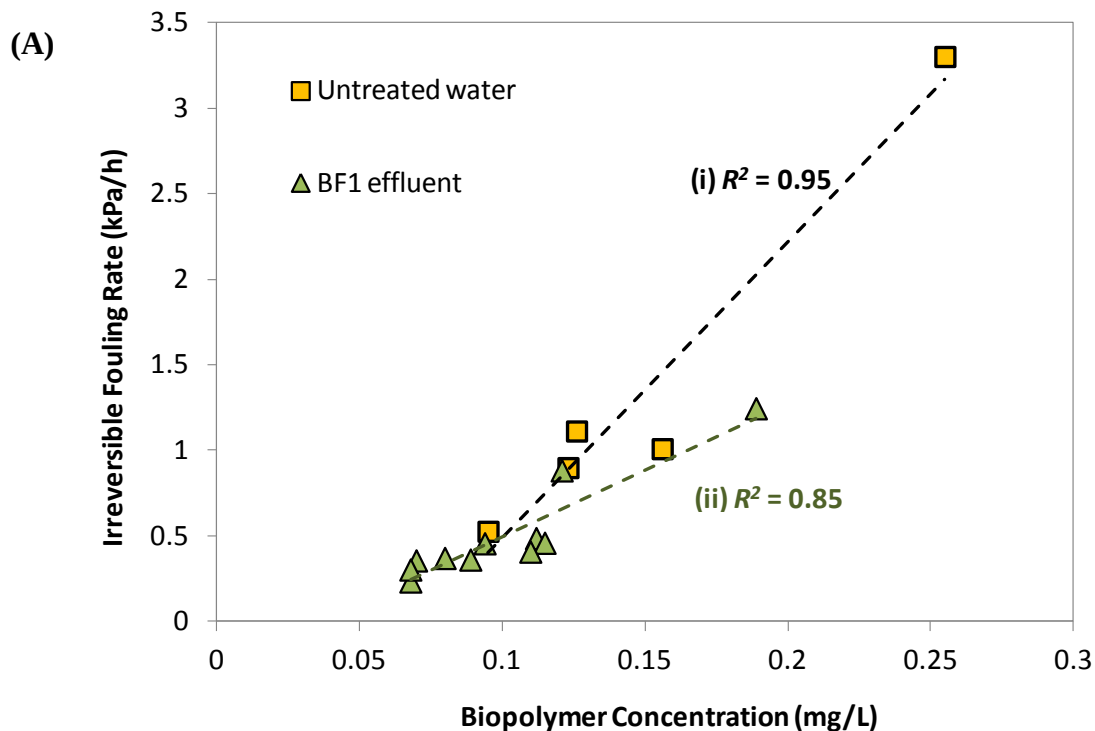


Figure 3.4 Relationship between biopolymer (A) and humic substance (B) concentrations in membrane feed water and membrane hydraulically irreversible fouling rate with (i) untreated water as feed ($n = 5$), and (ii) biofilter effluent as feed ($n = 11$); membrane flux 57 LMH at 20°C

Hydraulically reversible fouling was seen to be lower during the initial cycles and increased to a mostly stable value, indicating a possible change in the fouling layer (Figure 3.5). The average reversible fouling during an experimental run was also found to be related to biopolymer concentration and not with humic substances (Figure 3.6) or feed water turbidity. This observation again confirms that of Hallé *et al.* (2009). Peldszus *et al.* (2011) found a weak correlation between reversible fouling and protein content, but suggested that a combined foulant could result in this fouling effect rather than a single type of foulant.

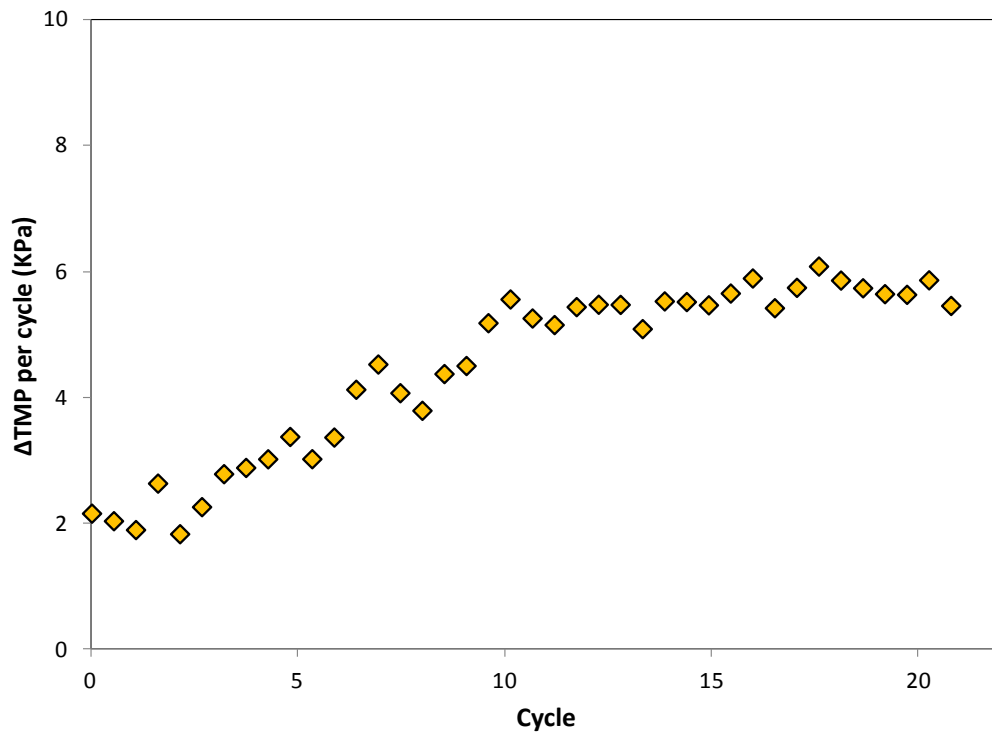


Figure 3.5 An example of increase in membrane TMP during a 21 h experiment with untreated water as feed. Δ TMP per cycle is calculated as the difference between TMP at the start and end (before backwash) of a particular 30 minute cycle (Experiment conducted on December 10, 2012)

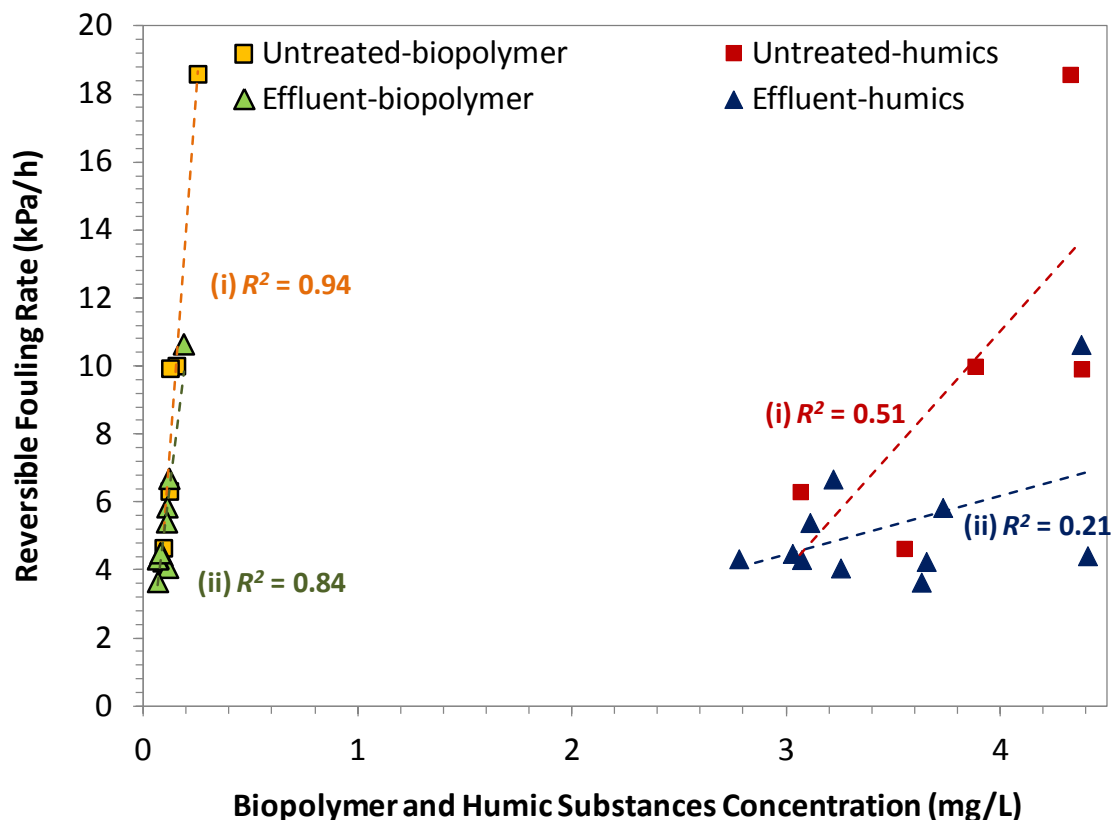


Figure 3.6 Relationship between biopolymer and humic substance concentrations in membrane feed water and membrane average hydraulically reversible fouling rate with (i) untreated water as feed ($n = 5$), and (ii) biofilter effluent as feed ($n = 11$); membrane flux = 57 LMH at 20°C. Reversible fouling was quantified by taking average of Δ TMP from all cycles during the length of the experiment.

3.4 Conclusions

The following conclusions can be drawn from this pilot-scale study using Saugeen River water to evaluate the effect of biofiltration on membrane fouling control:

1. Parallel biofilters performed similarly and achieved on average 21% removal of biopolymers under steady-state conditions. The concentration of biopolymers removed by the biofilters was significantly correlated with the biopolymer concentration present in the feed water.

2. Both irreversible and reversible fouling rates of the membranes were related to the biopolymer concentrations of both untreated and biofiltered water. A similar relationship was not found for the humic substances concentrations in the studied water.

3. Low concentrations of biopolymers can increase the rate of UF membrane fouling (in the range of 0.10 to 0.26 mg/L in untreated water).

4. Direct biofiltration resulted in 14 to 68% and 8 to 55% improvement in the hydraulically irreversible and reversible fouling rates of UF membrane, respectively, compared to water without pretreatment.

3.5 Supplementary Information for Chapter 3

Procedure used to normalize TMP to 20°C (El-Hadidy, 2011)

The transmembrane pressure (TMP) and water temperature during a membrane experiment were recorded every 10 seconds and the TMP was normalized to 20°C using the following equation-

$$\text{TMP corrected at } 20^{\circ}\text{C} = \text{TMP} * 1.025^{(T - 20^{\circ}\text{C})}; \text{ where } T = \text{water temperature in } ^{\circ}\text{C}$$

Procedure used to normalize flux for 20°C (AWWA, 2005)

$$\text{Flux corrected to } 20^{\circ}\text{C}, J_{20} = J \times \mu / \mu_{20}$$

Where, J = flux at ambient temperature

μ = viscosity at ambient temperature

μ_{20} = viscosity of water at 20°C

Relationship between temperature and influent biopolymer concentration and removal

There was no apparent relationship between temperature and the concentration of biopolymers in the influent water (Figure S3-1).

As well, the effect of temperature on the biopolymer removal was not significant (Figure S3-2). It should be noted that the temperature was above 10°C for all experiments (See Chapter 3 section 3.3.1 for explanation).

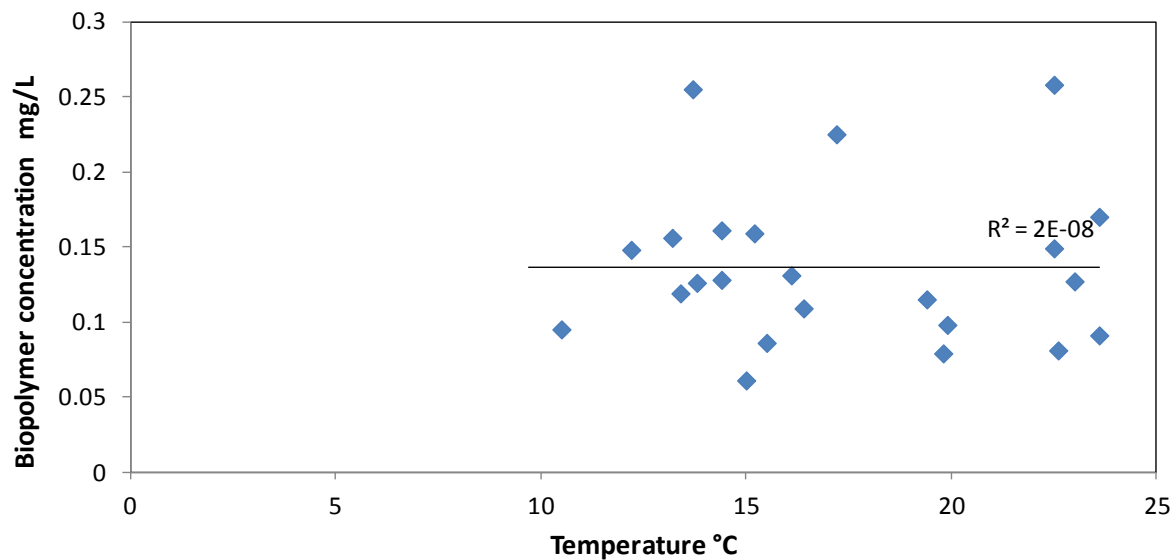


Figure S3-1: Relationship between biopolymer concentration in raw water (from outdoor tank) and raw water temperature on different sampling days (n = 23)

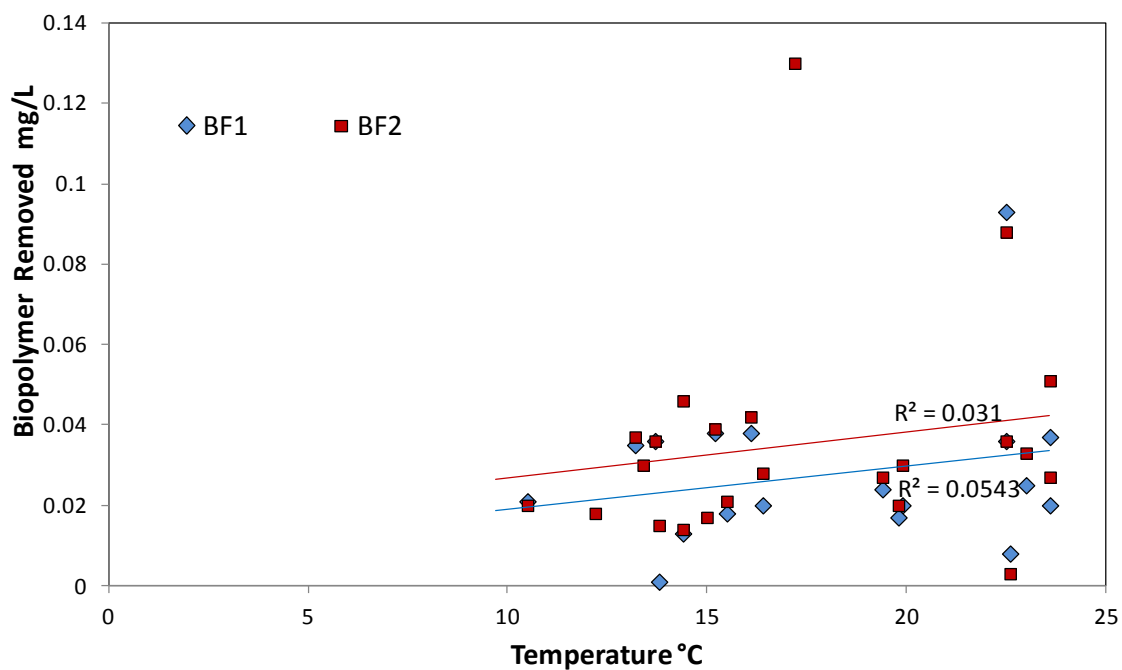


Figure S3-2: Relationship between temperature and biopolymer removal by the biofilters (RF combined); n = 18

Contribution of roughing filters to biopolymer removal

Although the roughing filters were installed to remove larger particles, RF1 and RF2 contributed to an average of 2% removal of biopolymers from the biofilter influent (ranged between 0 to 16%). Figure S3-2 illustrates biopolymer removal by roughing filters prior to BF1 and BF2.

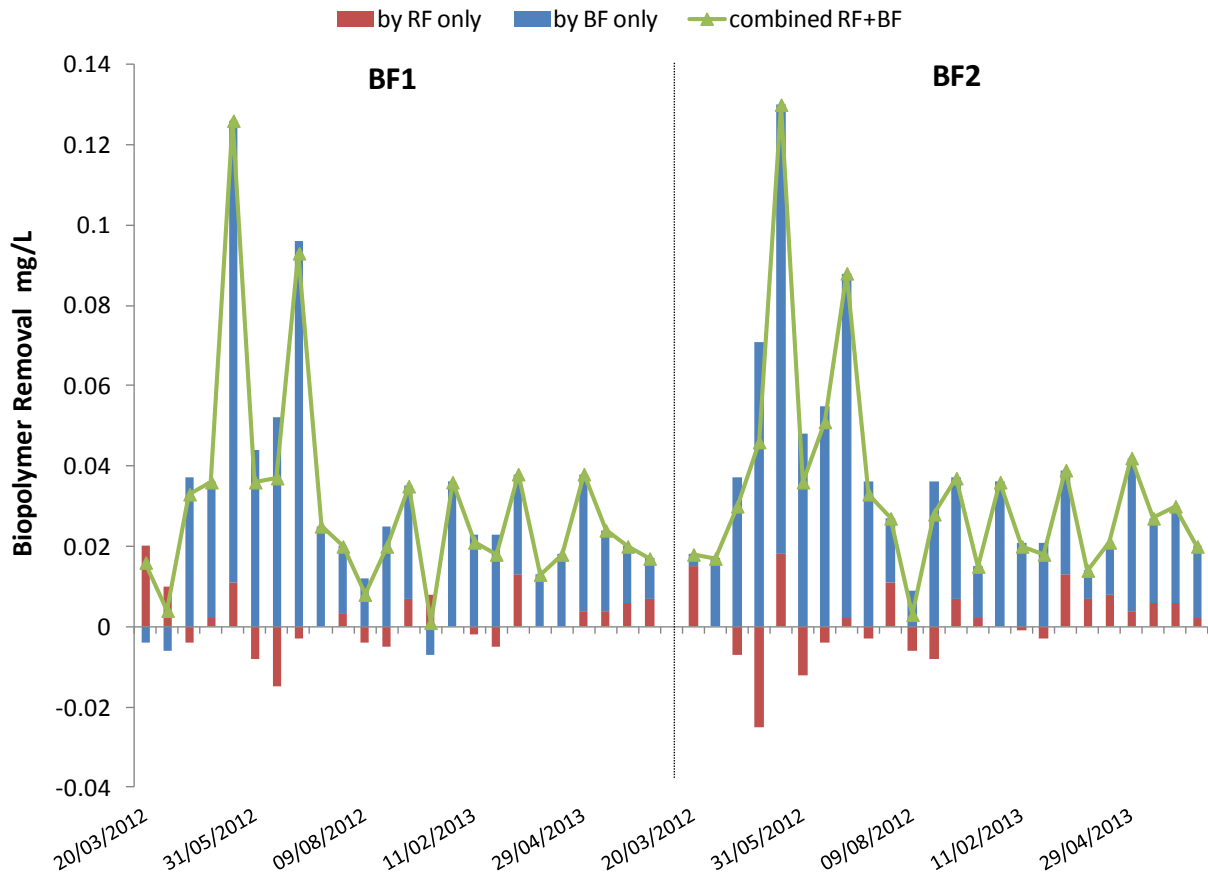


Figure S3-3: Contribution of roughing filters as a part of biofilters in removing biopolymers (average 2%, n = 48)

Chapter 4

Effect of Phosphorus Addition on Biofilter Performance and Membrane Fouling

This chapter is intended to be submitted (with further modifications) to scientific journal for consideration for publication as a paper. Hence, it contains a separate introduction, methods, results and discussion and conclusions sections. Cited references are in the consolidated list of references at the end of the thesis.

4.1 Introduction

Biological filtration has long been used in the field of water treatment in the form of slow sand filtration or river bank filtration, and it is finding newer uses and gaining popularity for its robustness. Now it is used as rapid filtration in drinking water treatment to reduce chlorination by-product pre-cursors (Juhna and Melin, 2006), following ozonation to control bacterial regrowth (Persson *et al.*, 2006), for removing nitrogen compounds (Yu *et al.*, 2007), trace contaminants, odour causing substances (Huck and Sozański, 2008), and biodegradable organic matter (Urfer *et al.*, 1997). Biofiltration process can be applied without prior flocculation or ozonation as “direct biofiltration”. Direct biofiltration, as a pretreatment, also has the potential to reduce polymeric ultrafiltration membrane fouling by removing the fractions of natural organic matter (NOM) responsible for increasing membrane fouling (Hallé *et al.*, 2009). Generally any filter that receives water which does not contain chlorine will act as a biofilter (Huck *et al.*, 2011). Natural water contains organic and particulate matter, dissolved oxygen, inorganic nutrients, and also microorganisms (bacteria, protozoa etc.) which are deposited in and attach to the filter media as water passes through forming a

biological film/layer (Hozalski and Bouwer, 2001) and this biofilm grows on the media in the absence of chlorine (Huck and Sozański, 2008). Limitation of nutrients may also inhibit biofiltration performance as it relates to removal of biodegradable organic carbon, which is usually the main treatment objective for employing biofiltration (Sang *et al.*, 2003, Nishijima *et al.*, 1997).

Drinking water biofiltration for the removal of organic carbon is an aerobic process and most microorganisms involved are heterotrophic in nature requiring organic carbon for food (Rittmann and McCarty, 2001). Heterotrophs use organic carbon for energy generation, which is basically an oxidation - reduction process, and for reproduction (Brown, 2007). Along with carbon, a microbial cell requires nitrogen, phosphorus, sulfur, iron and other nutrients to grow. Based on the general biomass formula ($C_5H_7O_2P_{0.1}N$) it is expected that bacteria require 2 to 8 g of ammonia or nitrate/100 g of carbon. As N has a (-) III oxidation state in this formula, bacteria would prefer (but would not be limited to) ammonia over an oxidized form of nitrogen (nitrite/nitrate) which requires energy to be reduced to a (-) III state, and the inorganic phosphorous requirement for bacterial growth is about 1/5th that of nitrogen (Rittmann and McCarty, 2001). However, a very high percentage of total phosphorus available in water remains in a bound form which has to be broken down by bacteria to a more biodegradable form (e.g. ortho-phosphate) before it can be utilized (Wetzel, 1975; Lehtola *et al.*, 2002). For optimal growth of microorganisms, Redfield (1934) found the ratios of carbon, nitrogen and phosphorus as 100:16:1.8 by weight analyzing planktons in seawater, and later reported the required ratio of to be 106:16:1 analyzing plankton from different sources, and 105:15:1 for seawater (Redfield, 1958). Metcalf and Eddy (1991) stated this ratio to be 100:20:1 (wastewater) and Sathasivan *et al.* (1999)

suggested a C:P ratio of 100:1.7 – 2.0 for (oligotrophic) drinking water environments. A more commonly used adaptation of this C:N:P ratio for drinking water is 100:10:1 according to LeChevallier *et al.* (1991). However, the approximation of 100:10:1 was not based on the experimental results reported in the said literature. Many researchers have investigated the effects of nutrients on biofilm development and biofilter performance, due to the important role of nutrients in microbial growth and structure (Keinanen *et al.*, 2002) and also in regulating the excretion of extracellular polymeric substances. LeChevallier *et al.* (1991) and Van der Kooij (1982) first demonstrated the importance of assimilable organic carbon (AOC) in the growth of heterotrophic bacteria. However, recent studies have shown that, for some water types, phosphorus may be the limiting nutrient. Yu *et al.* (2003) measured a 54% increase in bacterial regrowth potential with the addition of 0.05 mg/L KH_2PO_4 in Huai River basin water in China, and suggested the effect of phosphorous limitation was greater than that of other nutrients, including carbon. Miettinen *et al.* (1997), while studying microbial regrowth in a drinking water distribution network, found that microbial growth could be accelerated by adding as little as 0.01 mg/L of $\text{PO}_4\text{-P}$. Pokanska *et al.* (2005) associated microbially available phosphorus limitation with a lower biofilm formation rate for Belgian water. Lehtola *et al.* (2002) found a good correlation between microbial growth potential and microbially available phosphorus for Flemish drinking waters, and that a variety of treatment processes (e.g. GAC, chemical coagulation, and soil infiltration) can remove phosphorus from water. Thus, upstream processes could cause further phosphorus limitations for a biofilter.

Some studies on the effect of phosphorus enhancement with respect to biofilter performance are presented in Table 4.1. These studies have used a variety of different water

sources (river, lake, and subterranean) in lab, pilot, and full -scale biofilters. Five of the seven studies presented (Lauderdale *et al.*, 2012; Li *et al.*, 2010; Sang *et al.*, 2003; Yu *et al.*, 2003; Nishijima *et al.*, 1997) found positive changes in biofilter performance (increased organics and nutrient removal, and higher biomass quantity and activity) with phosphorus addition, while the remaining two (Melin *et al.*, 2002; Vahala *et al.*, 1998) found no enhancement of growth even though the raw water for all of these studies appeared to be phosphorus-limited according to their C:N:P ratios. However, the effect of phosphorus-enhancement on potential membrane foulant removal has not been reported to-date. As phosphorus-enhancement has been shown to increase the removal of organics, the removal of potential membrane foulants may increase as well, which will result in better performance of biofiltration as membrane pretreatment.

Table 4.1 Literature phosphorus/nutrient dosing

Source Water (Ref.)	Biofilter	Experimental Conditions	Duration of Monitoring with P-dose	Findings
Arlington, Texas 2 Full scale plants DO > 10 mg/L Temperature 11 to 30°C (Lauderdale <i>et al.</i> , 2012)	Pilot scale Media GAC/sand media from full scale plant	Contaminant spiking – 0.05 mg/L Mn, 30 ng/L MIB and shorter period 0.22 mg/L Mn and 160 ng/L MIB Dosing: PO ₄ -P 0.02 PO ₄ -P	6 weeks (2 weeks steady state operation)	Average 15% decrease in headloss in p- dosed filter 75% increase in DOC removal (Removal 0.7 as compared to 0.4 mg/L). statistically significant different by paired t-test 30% higher ATP in nutrient dosed filter, relation between ATP and DOC removal observed No change in turbidity removal with nutrient enhancement
Synthetic groundwater Bench system P conc.: 0.005 – 0.01 mg/L Pilot system P conc. 0.03 – 0.06 mg/L GW TOC : 2mg/L , BDOC 0.3 mg/L (Li <i>et al.</i> , 2010)	Media: GAC (BAC) Bench scale EBCT 20 min Pilot-scale EBCT 18 min	Bench scale P dose: On day 115 of operation as phosphoric acid 0.145 mg/L as P Temperature 18 °C Pilot scale P dose: On day 97 of operation 0.180 mg/L as P Different backwash procedure for bench and pilot	~40 days	Increased removal of nitrate and perchlorate with P dosing, getting them below detection limits in 5 and 15 days for bench and 2 and 16 days for pilot scale P addition resulted in bacteria community change to perchlorate reducing bacteria and reduced the number of gram-positive bacteria (disinfectant resistant) Total biomass increased with P-dosing for bench scale
Reservoir water, Beijing, China TOC: 6.9-8.5 mg/L NH ₄ ⁺ -N: <0.2 mg/L Total-P: 0.002-0.035	Pilot scale Media: Ceramic- porous aggregate (2-5 mm)	Two filters; up-flow with O2 supply for aeration P-dosed into 1 (/2) filter for 60 days continuously at 0.025	2 months	Increase in raw water BRP (50-65%) and BDOC (30-40%) with 0.05 mg/L P-dose P-dosed (0.025 mg/L) biofilter demonstrated increased removals of TOC, BDOC and total-P by 5.7%, 26-30% and a

Source Water (Ref.)	Biofilter	Experimental Conditions	Duration of Monitoring with P-dose	Findings
mg/L Turbidity: 3-10 NTU (Sang <i>et al.</i> , 2003)		mg PO ₄ -P/L rate (as H ₃ PO ₄) Temperature: 10-23 °C		remarkable 109-143% respectively Biomass quantity (phospholipid) and microbial activity (OUR) also increased by 13-22% and 35-45% respectively (higher close to the raw water inlet) More bacteria was found in the effluent of the dosed filter, compared to the control filter
Surface water plant coag/sedimentation effluent, Huai River Basin, China Turbidity: 1.73- 5.94 NTU PO ₄ -P: 0.00883 – 0.032 mg/L NO ₃ -N: 0.11- 0.36 mg/L Ammonia-N: 0.07 – 0.30 mg/L (Yu <i>et al.</i> , 2003)	Pilot scale Media: GAC (0.55 cm)/Sand (0.35 cm) Two biofilters EBCT: 6.4 – 7.2 min	P dose: 0.014 mg/L as K ₂ HPO ₄ -P Temperature: 19.7 – 31.5 °C	1 month	6% increase in COD removal by P-dosed filter compared to control filter, while both filters performed similarly at natural condition (before P-dosing)
Small Full scale (1.5 years) ozonation- biofiltration plant, Mid- Norway Total P: 0.0011 – 0.002 mg/L (Melin <i>et al.</i> , 2002)	Full scale Media: GAC- phonolith-CaCO ₃ EBCT: 26-30 min	Bench test for P (0.1 mg/L) + N (1 mg/L) dosing Ozonated water in 1 L bottle with bacteria inoculums Temperature: 2 – 14 °C	1 month	TOC removal and total p did not have good correlation HPC bacteria ten times higher in P-dosed water bottle test Efficient biofilter performance possible even at P-limiting condition

Source Water (Ref.)	Biofilter	Experimental Conditions	Duration of Monitoring with P-dose	Findings
Lake water Full scale plant, after coag/floc/sand filtration/ozone Finland TOC: 5.7 – 5.8 mg/L N: 0.41 – 0.43 mg/L P: 6 – 8 mg/L (Vahala <i>et al.</i> , 1998)	Full scale Media: BAC Three filters; EBCT – 15 min (8 m/h)	P addition: for 63 days; Phosphoric acid constant 0.027 mg/L P Temperature: 4.2 – 9.6 °C pH 7.4 Alkalinity 0.4 mmol/L TOC: 2.6 mg/L UV 0.026 1/cm	63 days	No effect of P-dosing was found, parallel filters had TOC removal 12 and 14% and UV- absorbing compounds 17 to 19% Increase in HPC ATP did not increase , P-dosed filter had lower ATP than the control Nitrogen (0.135 mg/L N) addition did not change the situation much
River water, pre-treated- coagulation/ sedimentation Spiked-10 mg/L glucose P conc.: 0.002 mg/L (Nishijima <i>et al.</i> , 1997)	Lab scale Media: GAC Two filters; GAC EBCT: 7.5 min, completely mixed reactor	GAC–pre-equilibrated with 10 mg/L Glucose (Calgon Filtrasorb 400) P-dosing: 3.12 mg P/g GAC Experimental temperature 25 ± 2 °C	1 month	Increased DOC removal rate (5X) with 0.01 mg/L P-added condition P-dosed filter reached steady-maximum faster 10 days as opposed to 30 days for control filter Increased bacteria population was also observed Increasing dose to 0.02 mg P/L did not show further improvement in DOC removal performance

This study investigated how phosphorous enhancement would affect a biological filter operating with high organic content feed water from a southern Ontario river that was phosphorus-limited (according to its calculated C:N:P ratio) with a special focus on ultrafiltration (UF) membrane fouling reduction. The objectives of this work were to examine the effect of phosphorus addition with respect to biofilter effluent water quality, biofilter biomass quantity and activity, and to determine if phosphorus-enhanced biofiltration was more effective in controlling ultrafiltration membrane fouling than non-enhanced biofiltration.

4.2 Material and Methods

4.2.1 Feed water

The feed water for this study was collected weekly in two 20,000 L batches from the Saugeen River near Walkerton, Ontario, Canada and stored in an outdoor 40,000 L tank. This storage tank had a heating and circulation system which automatically activated when the atmospheric temperature dropped below 7°C. The circulation system ensured that the water remained mixed. The raw water went directly to the biofilters without any pretreatment steps (and no coagulation) in between.

4.2.2 Experimental set-up

A pilot treatment train was constructed and operated at the technology demonstration facility at the Walkerton Clean Water Centre in Ontario, Canada (Figure 4.1). The set-up included two parallel 5.1 cm diameter × 2.1 m high glass columns containing dual media biological filters (BF1 and BF2). The media layer consisted of 55 cm of anthracite (uniformity co-efficient = 1.6; effective size = 1 mm) over 25 cm sand (uniformity co-efficient = 1.5;

effective size = 0.5 mm) supported by 15 cm of gravel, giving a total depth of 100 (± 4) cm. The biofilters were operated at an empty bed contact time (EBCT) of 10 min corresponding to a hydraulic loading rate of 5 m/h. They were gravity fed and operated in down-flow mode. The biofilters were each preceded by a roughing filter (RF1 and RF2) to minimize the impact of varying turbidity and particle loads on the biofilters. Both biofilters were backwashed once per week using biofilter effluent. The backwash process included air scour for 1 min to break up media plugs, followed by 4 min of air-water collapse pulsing. The water flow was then gradually increased to achieve a 25% bed expansion (1 min) and then to 50% bed expansion for 4 min after the air scour was stopped.

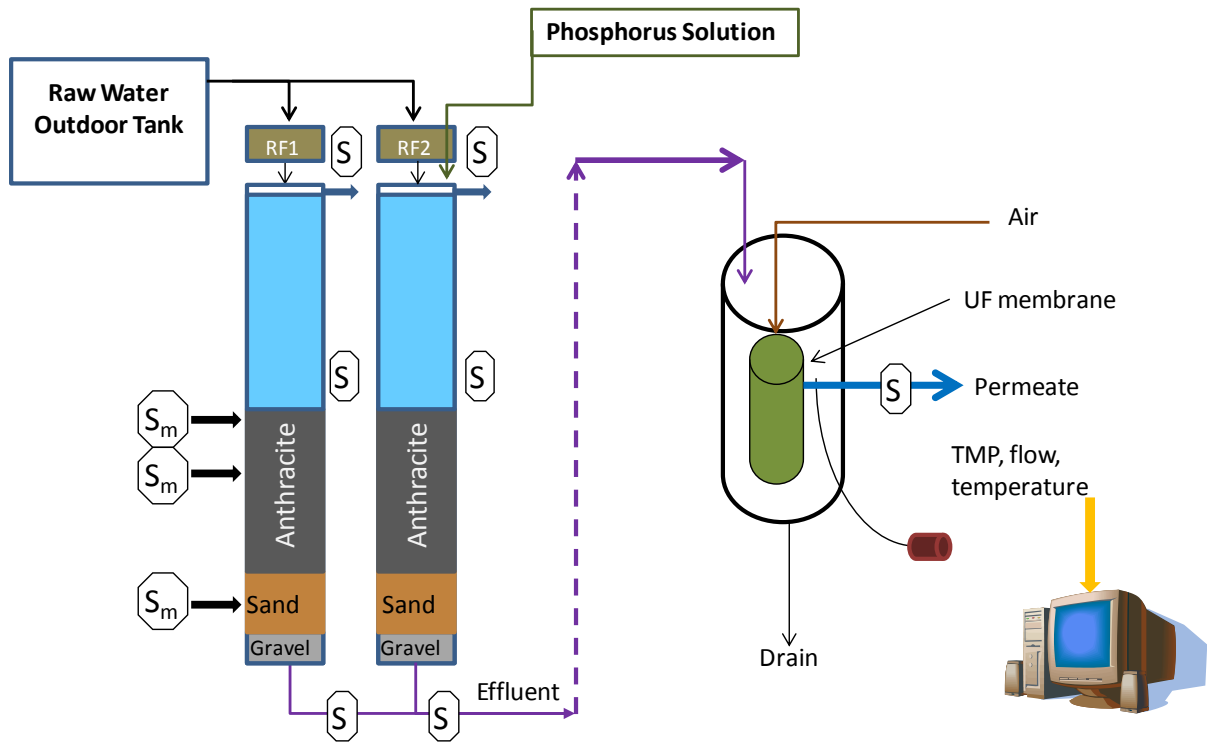


Figure 4.1 Experimental set-up schematic (where, RF = roughing filter, S = Water sample, S_m = media sample)

BF1 and BF2 were operated similarly using Saugeen River water for 11 consecutive months. Phosphorus addition in BF2 began in February 2013, while BF1 was maintained as

a control. Initially a K_2HPO_4 solution was added continuously to the biofilter column inflow for 2 months at a 6.5 mL/min flow rate using a dosing pump (LMI Milton Roy pump, model P021-35251, Acton, MA, USA) to add 0.01 mg/L of phosphorus to the biofilter influent (Appendix G). The dose was then increased to 0.05 mg P/L and continued for an additional 40 days (until the end of May, 2013). The K_2HPO_4 stock solutions were prepared in 1 L ultrapure water, mixed well, and autoclaved for 30 minutes.

For the membrane fouling experiments, a bench-scale ZeeWeed®-1 (GE Water and Process Technologies, Oakville, Ontario, Canada) polymeric (PVDF) ultrafiltration hollow fiber membrane was used. The membrane had an outside-in configuration with a nominal surface area of 0.047 m², nominal pore size of 0.04 µm, and was operated at a constant flux of 57 L/m²h (LMH) (temperature corrected 20°C). The clean membrane surface was non-ionic and hydrophilic. The membrane module was maintained in a vertical position in a clear PVC cylindrical tank and was designed to cycle automatically using a programmable logic controller (Allen-Bradley 1760-L18AWA-EX Pico Controller w/RTC, 18 I/O Expandable, AC, Ser A, Rockwell Automation, 1 Allen Bradley Dr, Cleveland, OH, USA) (El-Hadidy *et al.*, 2013). Each cycle included 30 min of permeation (Masterflex L/S Easy-Load II pump head, model 77202-50, Cole-Parmer, Montreal, Canada) followed by a 20 s backwash with air sparging. At the end of each cycle the tank was completely drained and then re-filled with fresh feed water (40 sec). The set-up also included a temperature sensor (HOBO 12-Bit Temperature Smart Sensor, Onset, Cape Cod, MA, USA), pressure transducer (model 68075-02, Cole-Parmer, Montreal, Canada), and flow monitor connected to a data logger (HOBO Energy Logger, model H22-001, Onset, Cape Cod, MA, USA) for continuous measurements during the fouling experiments. The membrane was chemically cleaned between each fouling

experiment by placing it in 200 mg/L NaOCl for 5 h, followed by a 5 g/L citric acid solution at room temperature for 5 h, and rinsed thoroughly with deionized water between steps. Before each experiment, the module was tested for integrity using a pressure calibrator (Meri-cal DP2001I, Meriam instrument, OH, USA) so that the pressure drop through the membrane was not more than 2 kPa (0.3 psi) over 2 min, which is recommended by the manufacturer. Each experiment was also preceded by a clean water permeability test with deionized water to test for cleaning efficiency at four different fluxes (32, 45, 57, 70 LMH). A detailed description of the methods can be found in El-Hadidy (2011).

4.2.3 Sampling procedure

Water samples were collected from selected points in the treatment train including the roughing filter inlet (raw), biofilter influent approximately 15 cm above the media surface (BF1 and BF2 Influent), and biofilter outlets (BF1 and BF2 effluent). While raw water and biofilter effluent samples could be collected from the lines directly, for the biofilter influent samples, flexible tubing (from the open top of the biofilter column) was lowered into the column to approximately 10 cm above the surface of the media. The influent water sample was pumped out through the tube at a slow rate without disturbing the system. To ensure the collection of representative samples, water was allowed to flow out of the lines before samples were collected. The sampling bottles were rinsed with the samples three times before collecting the water, and were filled to the top without headspace. Samples requiring filtering were filtered with 0.45 μm disk filters (Supor® Membrane Disc Filters, Pall® Life Sciences, Pall Corporation, Port Washington, NY, USA) immediately after arriving at the laboratory and both filtered and unfiltered samples were stored at 4°C until analysis.

Media sampling was conducted after collecting water samples, so that the water samples were not affected by the media disturbance. For media sample collection, the biofilters were first fully drained. Media samples were collected from three sampling ports: i) top-most anthracite port (4 – 12 cm), ii) mid-anthracite layer (24 – 32 cm) and iii) mid sand layer (63 – 71 cm) from the media surface, respectively (Figure 4.1) using sterile glass pipette tips. The samples were transferred into sterile tubes and stored at 4°C until analysis. The biofilters were replenished with sufficient sand and anthracite to replace what was removed, and the columns were backwashed before restarting the inflow.

4.2.4 Water quality analysis

Phosphorus and nitrogen in raw and biofiltered water were analyzed by an Ontario Ministry of Environment accredited laboratory (ALS Global Environmental Laboratory, Waterloo). These samples were collected in containers provided by the laboratory. Total phosphorus and ortho-phosphorus were measured based on American Public Health Association (APHA) method 4500-P B E and both had a detection limit (DL) of 0.003 mg/L. Total nitrogen concentration was calculated by adding the concentrations of nitrate, nitrite (US Environmental Protection Agency (EPA) method 300.0 IC) and total Kjeldahl nitrogen (APHA method 4500-N). Ammonia-N was analyzed colorimetrically both at the commercial laboratory (EPA 350.1; DL = 0.05 mg/L) and with a HACH kit (Method 10023; DL = 0.02 mg/L; Amver™ Low Range Ammonia Reagent Set 26045-45, Hach Company, Loveland, CO, USA) and spectrophotometrically (Odyssey DR/2500 Spectrophotometer, Hach Company, Loveland, CO, USA).

TOC and DOC were measured using OI-Analytical TOC analyzer (model 1010, College Station, TX, USA) by wet-oxidation. LC-OCD (DOC-Labor Dr. Stefan Huber, Karlsruhe,

Germany) analysis was employed to measure the concentrations of the various NOM fractions in water (Huber *et al.*, 2011). TOC, DOC and LC-OCD analyses were all conducted at the University of Waterloo laboratory.

Turbidity (2100P Portable Turbidimeter, Hach Company, Loveland, CO, USA), pH (Orion bench top pH meter, model 420A, Cole-Parmer, Montreal, Canada), and conductivity (Conductivity Portable Meter, Mandel Scientific Company Inc., Guelph, ON, Canada) were analyzed for all water samples. UV254 absorbance was measured with a UV-VIS Spectrophotometer (8453, Hewlett-Packard, CA, USA). SUVA was calculated using UV254 and DOC measured by TOC analyzer (Potter and Wimsatt, 2005; EPA method 415.3). Hardness (method 2340 C) and alkalinity (method 2320 B) in raw water samples were measured according to APHA (2012).

4.2.5 Biomass quantity and activity measurement

Biomass quantity in the media samples was measured using a LuminUltra™ DSA adenosine triphosphate (ATP) test kit (LuminUltra, Fredericton, New Brunswick, Canada). Total ATP was calculated by measuring the extracted media (RLU) with a luminometer (Modulus Luminometer, model 9200-102, Turner BioSystems, Sunnyvale, CA, USA). To assess overall biological activity in the media, a fluorescein diacetate (FDA) hydrolysis assay was used (Green *et al.*, 2006). Briefly, the process involved a 3 h incubation of media samples in a sodium phosphate buffer at 37°C, while the enzymes (proteases, lipases and esterase) that can hydrolyse the FDA cause a release of visible fluorescein. The fluorescein was then measured using a spectrophotometer and compared with a fluorescein standard curve.

4.2.6 Membrane fouling experiments

Membrane fouling experiments were conducted in batch mode using biofiltered Saugeen River water. To assess fouling for biofiltered water from each biofilter column separately, but using the same batch of river water, the run length was selected to be 1.5 days or until our target maximum TMP reached 55.2 kPa (8 psi), whichever was reached first. Fouling rates were calculated using the transmembrane pressure data (corrected to 20°C).

4.3 Results and Discussion

4.3.1 Saugeen River water quality

Carbon, nitrogen and phosphorus monitoring data

The Saugeen River is located in southern Ontario, Canada, and is a part of the lower Saugeen watershed (908 km²) which is mostly agricultural land (76%), with 19% forest cover, and only 1.2% urban area (Saugeen Valley Conservation Authority, 2008). Natural and human activities in the watershed (such as decay of vegetation and animal waste, fertilizers, detergents, treatment plant effluent, landfill leachate, etc.) are responsible for the presence and circulation of nutrients in water (USEPA, 1992). If the nutrients, especially phosphorus and nitrogen, are available in excess they can cause detrimental effects such as eutrophication. However, these two nutrients, along with carbon, are the most important nutrients for the growth and survival of bacteria. If one of the nutrients is limited the biofilm growth and thus the performance of biofilters can be negatively impacted. For this reason, this study first assessed the nutrient levels in the Saugeen River. Biofilter feed water was analyzed for various forms of nitrogen species (total nitrogen, nitrate, nitrite and ammonia),

phosphorus (total and ortho phosphorus), along with carbon (TOC, DOC and molecular weight fractions) measurements.

Historical data (Saugeen Valley Conservation Authority, 2010) indicated that the 4-year average total phosphorus in the lower Saugeen River (Walkerton) has been well below 0.06 mg/L since 1965, and has been gradually decreasing since 1981. The concentration of total phosphorus was reported as 0.04 mg/L (data from 2002 – 06) in the lower main Saugeen River (Saugeen Valley Conservation Authority, 2008) and 0.015 mg/L (median value of data from 2007 – 11) in a report by the Ontario Ministry of the Environment (2012). Overall, the total phosphorus concentrations in the Saugeen River have been reported as below or very close to the Ontario Provincial Water Quality Objective (PWQO) of 0.03 mg/L. However, the historical nitrate concentration has gradually been increasing over the years (Saugeen Valley Conservation Authority, 2011a, b), even though nitrate has been lower than the maximum threshold value (3 mg/L) suggested by the Canadian Water Quality Guidelines (Canadian Council of the Ministers of the Environment, 2012). The Ontario Ministry of the Environment (2012) found, for the rivers in Ontario, also show that there was an increase in nitrogen and phosphorus concentrations during colder periods of the year (December to February) in the general for the rivers in Ontario. A 2003 study on Saugeen River in particular show similar increase in total-P with slight increase in nitrate + nitrite concentration during late Fall (Mohamed, 2009)..

The raw water nutrient data collected from November 2012 to May 2013 are presented in Figure 4.2 (data Appendix E). Figure 4.2 A shows that nitrate in the river water was higher than the other forms of nitrogen (1.35 to 2.94 mg/L) and made up 70 to 90% (average 82%) of the total nitrogen. The nitrate-N concentration was higher during the colder period, which

is in agreement with the Ontario Ministry of the Environment (2012) report. Nitrite-N remained under detection limit (0.10 mg/L) throughout the test period, and ammonia-N (DL 0.05 mg/L) was only detected once (May 23). TKN was fairly consistent and ranged between 0.3 – 0.6 mg/L. Figure 4.2B shows that ortho-phosphorus was low and typically close to the detection limit (0.003 mg/L), and reached a maximum of 0.01 mg/L on March 18. Total phosphorus measurements were initiated on April 3, 2013, and results show that ortho-P ranged from 25 –70% of the total-P (average 38%; std. dev. 17%). Overall data show that there was high total nitrogen (> 1.5 mg/L), and low total phosphorus (< 0.025 mg/L) in the raw water suggested by Dodds *et al.* (1998).

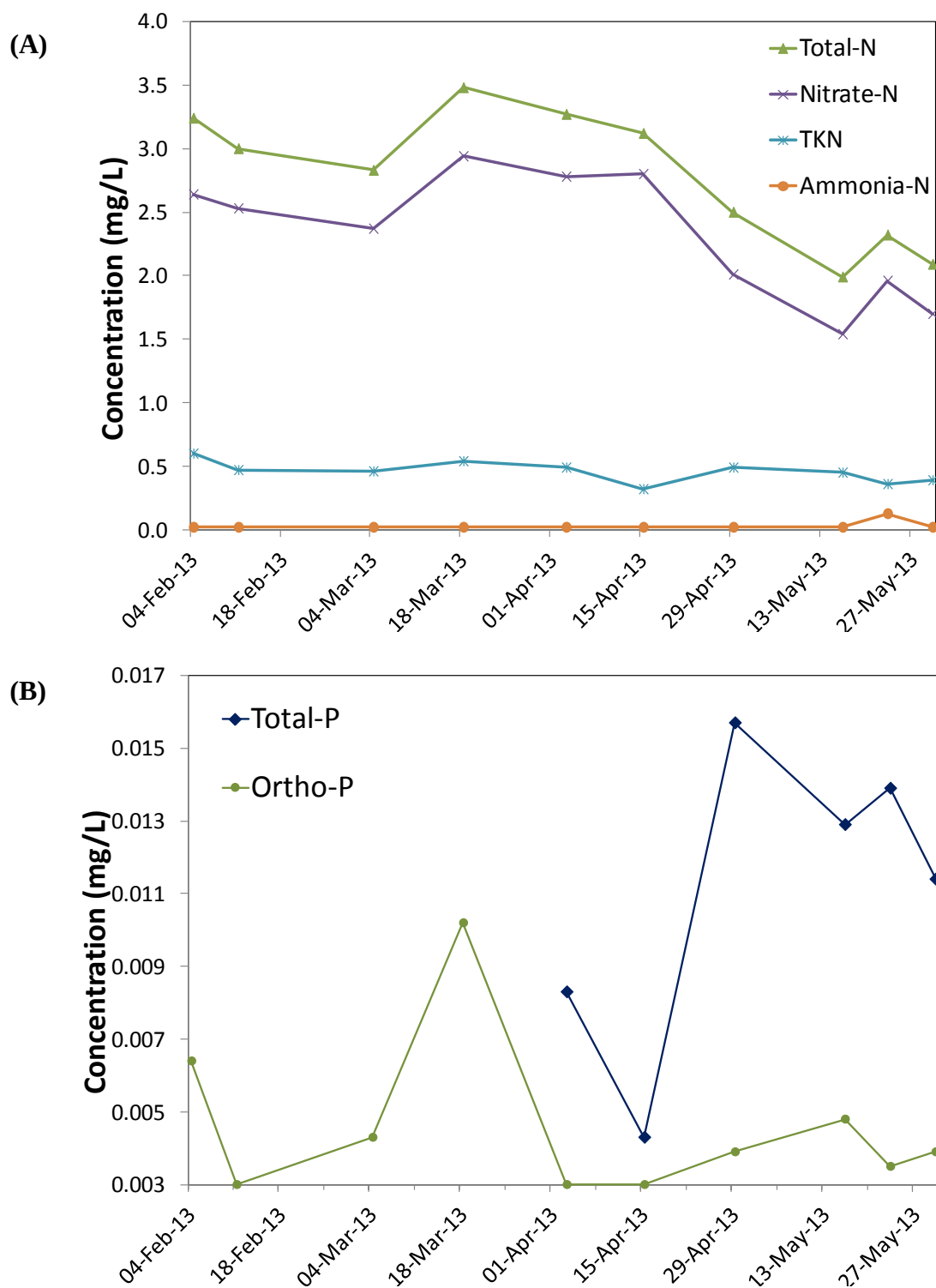


Figure 4.2 A) Concentration of nitrogen compounds in biofilter feed water (Saugeen River), where Total-N = Nitrate-N + TKN; B) Concentration of total and ortho-phosphorus in biofilter feed water; total phosphorus measurements were initiated on April 3, 2013 (Detection limit for both = 0.003 mg/L)

Humic material made up the largest component of the NOM in the raw river water, while the other components, including biopolymers were present in low concentrations (Table 4.2). DOC during this 7 month period ranged between 4.15 to 6.32 mg/L, which is not unusual for river water. However, during the full 14 months of biofilter operation, lower DOC values (as low as 2.66 mg/L) were also observed, and humic substances made up 54 to 89% of the total DOC, while biopolymers were 2 to 11% (Chapter 3). In a separate study, Croft (2012) collected 5 samples directly from Saugeen River between 2011 and 2012, in which the DOC ranged from 2.7 to 6.8 mg/L. This range is similar to those measured in this study. Croft (2012) also found biopolymers to be 3 to 11% of the total DOC, and large variations in humic concentrations were observed which is consistent with measurements made in the current study.

Table 4.2 Concentration of total and dissolved organic carbon and DOC fractions in raw Saugeen River water between November, 2012 and May, 2013

Conc. (mg/L)	TOC	DOC	BP	HS	BB	LMWA	LMWN	TN	TP
Max	6.41	6.32	0.26	4.38	0.55	0.06	0.43	3.48	0.016
Min	4.23	4.15	0.07	2.81	0.33	0.00	0.22	1.92	0.004
Avg	5.00	4.88	0.12	3.54	0.45	0.01	0.29	2.71	0.011
SD	57%	57%	5%	51%	6%	2%	6%	0.4%	56%

(n =13 for C; n = 11 for N; n = 6 for P)

BP = biopolymers, HS = humic substances, BB = building blocks, LMWN = low molecular weight neutrals, LMWA = low molecular weight acids, TN = total nitrogen, TP = total phosphorus

C:N:P ratio

The C:N:P ratio can be calculated in different ways. A common method is to use ammonia-N and ortho-P as key nitrogen and phosphorus sources as these are considered to be biologically available (USEPA, 1992; Lauderdale *et al.*, 2012). However, various forms of these nutrients can also be utilized by bacteria. Phosphorus in water can be present in organic

or inorganic form, as particulate or dissolved phosphorus (ortho-P), or as polyphosphate (largely from detergent), or bound with organic colloids (Wetzel, 1975). The concentration of available inorganic soluble phosphorus (ortho-P) is usually a very low percentage (<5%) of the total phosphorus (Wetzel, 1975). However, bacteria can degrade dissolved organic phosphorus to ortho-P for their requirements (Wetzel, 1975). The data presented in Figure 4.2 (B) indicate the water does not contain much ortho-P; hence, it is postulated that the bacteria could be meeting their phosphorus needs by degrading other forms of available phosphorus (or potentially recycling P in the biofilm), and therefore total-P was used in C:N:P calculations. As well, Figure 4.2 (A) shows the available forms of nitrogen in the raw water and for almost all sampling days there was no detectable ammonia-nitrogen in the water. This is not uncommon in oligotrophic environments or oxygenated water such as sea water or drinking water (Wetzel, 1975). Kirchman and Wheeler (1998) and Allen *et al.* (2002) both found much higher nitrate uptake than ammonia by heterotrophic bacteria in seawater, and Simon *et al.* (2013), following addition of NH_4Cl in nitrogen limited conditions during sea water biofiltration, did not see an improvement in NOM removal capacity. Considering the findings from the above literature and experimental data from this study, nitrate/total-N may have to be considered as N sources, which has precedence in previous literature by Miettinen *et al.* (1997).

Simon *et al.* (2013) also found that biofilter activity related more to biodegradable DOC than to available ammonia. Biodegradable portions of DOC, or biodegradable organic matter (BOM), can be measured using various culture-based techniques including assimilable organic carbon (AOC) which measures an increase in growth of P17 and NOX bacteria strains (van der Kooij, 1992), and biodegradable dissolved organic carbon (BDOC) methods

which measure the removal of DOC in the test water over time (Servais *et al.*, 1989). However, due to the complexity of these methods, for this study only total DOC measurements were performed. Using total DOC for the C:N:P ratio would be an overestimation of the available carbon, as according to the literature biodegradable carbon is a small portion of the total DOC. For instance, AOC can be 0.03 to 27% of the total DOC depending on the nature of water, and was found to be less than 9% for surface waters in a study by van der Kooij, (1982). BDOC was found to be between 27 to 54% of the total DOC for polluted waters, and 28.5% for a less polluted water (Servais *et al.* 1989). Bradford *et al.* (1994) found AOC to be between 0.5 to 31% of the total DOC, but could not find a good correlation between these two forms of organic carbon. Hence, it is hard to predict the biodegradable portion of DOC without direct measurements. However, both of these techniques have their limitations and Huck (1990) in a review article regarding various BOM measurement methods suggested further studies to better understand the application and correlation between these techniques.

As such, C:N:P ratios were computed using total DOC, total nitrogen, and total phosphorus concentrations for April and May, 2013, a period in which data for all variable was available (Table 4.3). Although using DOC as available carbon was an overestimation as total DOC is not readily available to bacteria (also true for total nitrogen and total phosphorus), it was considered that this can still provide an indication of the representative ratio. Results are shown for the computed C:N:P ratio for the raw water (BF1 influent), and suggested potential phosphorus limiting conditions in the water feeding the biofilters (according to the 100:10:1 ratio for balanced conditions).

Table 4.3 Calculated C: N: P ratio for raw water during phosphate dosing phase

P added (mg/L)	DATE	BF1 influent (Raw water)			BF2 (following P-dosing)		
		C	N	P	C	N	P
0.01	03-Apr-13	100	67	0.17	100	65	0.37
	15-Apr-13	100	68	0.09	100	66	0.18
0.05	29-Apr-13	100	46	0.29	100	52	0.64
	16-May-13	100	42	0.28	100	43	1.48
	23-May-13	100	55	0.33	100	52	1.20
	30-May-13	100	41	0.22	100	45	0.71

*C was set as 100

This observation led to an investigation to assess the effect of phosphorus addition on biofilter performance, the results for which are discussed in subsequent sections.

4.3.2 Biofilter activity and performance

Biofilter performance and organics removal were monitored for over 14 months (March 2012 to May 2013), and for the last four months of that period phosphate was added to one of the biofilters (February to May 2013). During the biofilter start-up period, the fresh media was immersed in raw river water in the filters for the first 2 weeks without flow, after which continuous operation started following a backwash (March 20, 2012). Figure 4.3 shows biomass quantity in the anthracite-mid-layer and sand-mid-layer of the filters (BF1 and BF2) showed a rapid increase in total ATP in both anthracite and sand samples until they reached a steady maximum value after about 2 months (data Appendix F). It can also be seen that the rate of increase in ATP was slower for the sand media compared to anthracite, likely due to the sand layer being the lower of the two. Velten *et al.* (2011) made a similar observation in their mono-media GAC filters, which showed a 54% slower rate of biofilm development in the deeper sections (63-71 cm below the media surface), and speculated that it might be an effect of nutrient availability. There was a drop in the ATP values, more prominent in BF2 media samples, on December, 2012 which could be related to a rapid decrease in the water

temperature. However, ATP levels recovered quickly, and overall results show that temperature did not ATP concentrations in the biofilters. Change in ATP concentrations during the P-dosing period is discussed in more detail in section 4.3.3.

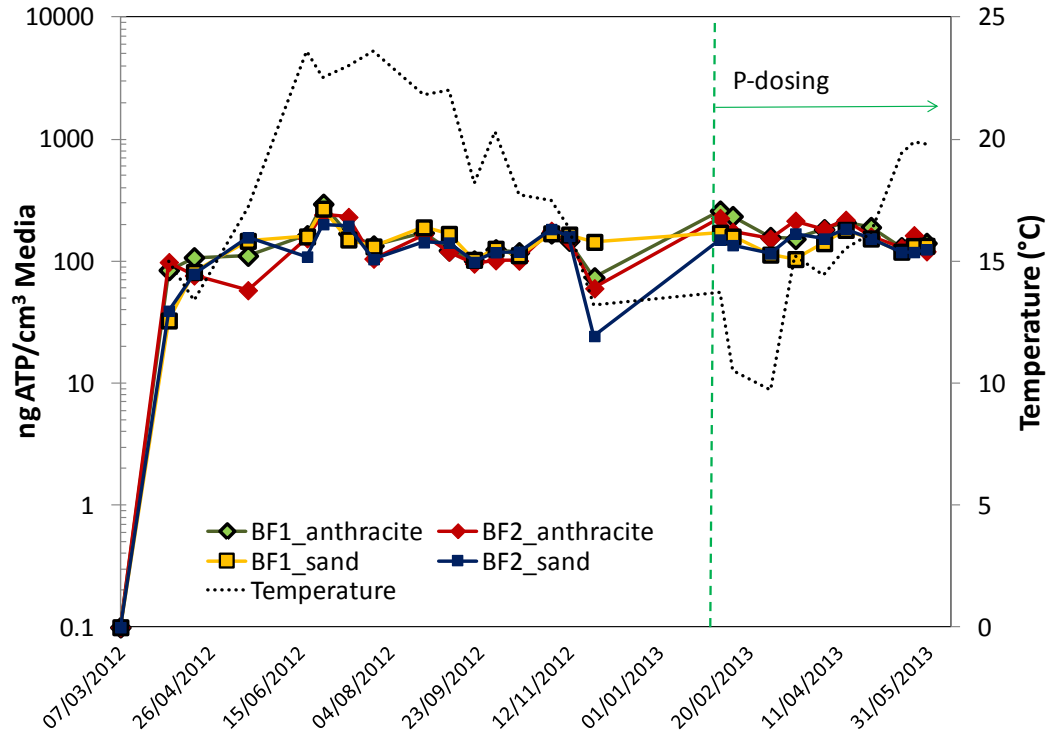


Figure 4.3 Comparison of biomass quantity as measured by ATP in media samples collected from each of the two dual-media biofilters. Samples were collected from the mid-point of each of the anthracite and sand layers (28 and 67 cm from media surface). Start of P-dosing (in BF2) is indicated along with feed water temperature.

Figure 4.4 illustrates the variation of biomass quantity with depth, confirming, as expected, a higher average biomass quantity close to the top surface of the media. In terms of the relationship of depth with biomass, Servais *et al.* (1991) found decreasing biomass and activity with depth during warmer temperature, which was not seen during the colder times of the year. They also found higher BOM removal in the top 40 cm of the filter. Servais *et al.* (1994) later reported similar vertical stratification at a different location.

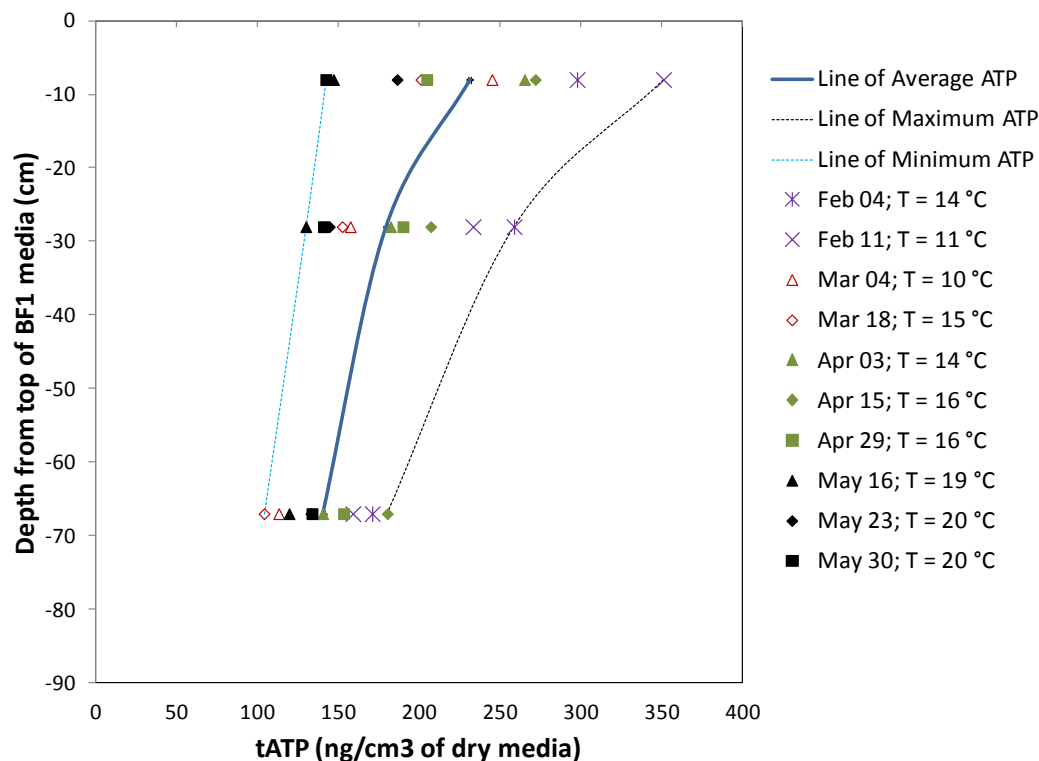


Figure 4.4 Biomass quantity measured in BF1 at the upper-most anthracite port (4 – 12 cm below media surface), mid-anthracite layer (24 – 32 cm) and mid sand layer (30 – 38 cm) with lines showing the average, upper and lower ATP concentrations (n = 10). 0 cm is the top surface of the media.

Microbial activity in the media was measured with FDA hydrolysis on the same samples. The FDA assay is widely used to measure total microbial activity from environmental samples, and provides a measure of overall enzymatic activity, as FDA can be hydrolyzed by a range of non-specific esterases, proteases and lipases which are widespread among microorganisms (Adam and Duncan, 2001). The results in Figure 4.5 show a similar rapid increase in activity as ATP, especially for the anthracite samples, and similarly the increase of activity in the sand samples was slower than in anthracite (data Appendix F). Like ATP, FDA results reached a maximum value by 2 months and then remained essentially constant, and there were no significant temperature effects observed on activity during the steady-state

operation (Figure 4.5). Others have shown that FDA hydrolysis correlates well with ATP and cell density (Stubberfield and Shaw, 1990). However, our correlation was not as good as others ($r = 0 - 0.5$ for different depths and media) and we were unable to identify the reasons behind the difference in findings. Also in this study, activity at the top though was found to be higher on average (Table 4.6). Using different methods to measure activity, others have also shown that, activity, like biomass quantity, was higher at the top surface of biofilters due to the greater availability of substrate (Sang *et al.*, 2003). Also, ATP and FDA did not demonstrate seasonal variations. This finding agrees with those of Persson *et al.* (2006) in the case of attached biomass quantity while working with fairly humic water from Lake Delsjöarna; however, they found respiratory activity (measured as oxygen consumption) to be dependent on temperature.

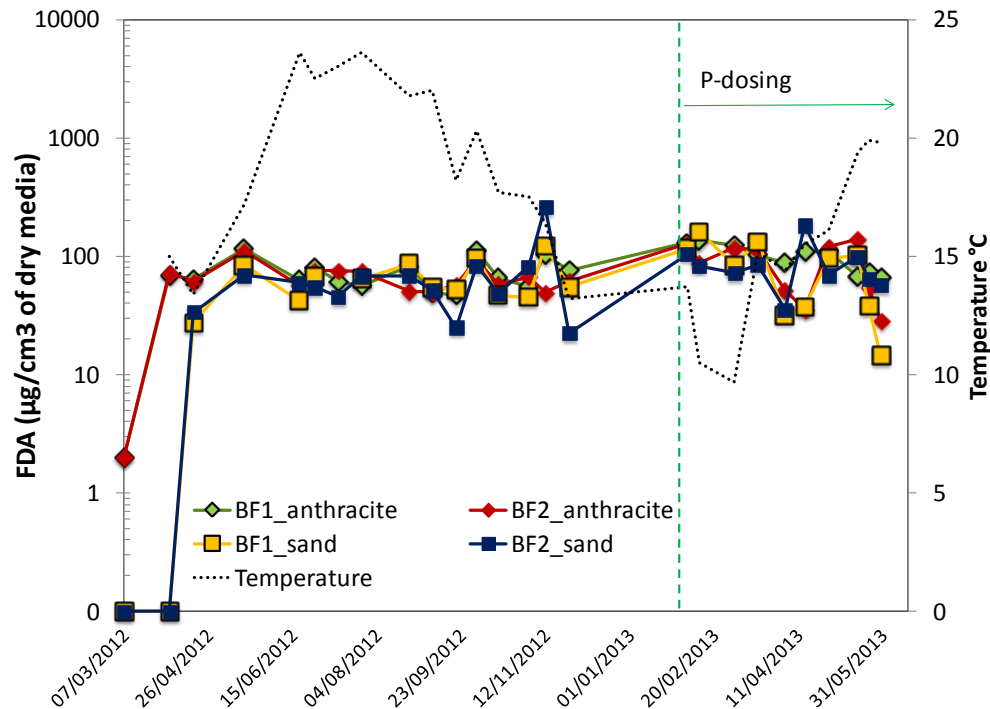


Figure 4.5 Comparison of biomass activity as measured by FDA analysis in media samples collected from each of the two dual-media biofilters. Samples were collected from the mid-point of each of the anthracite and sand layers (28 and 67 cm from media surface). Start of P-dosing (in BF2) is indicated along with feed water temperature.

A t-test ($\alpha = 95\%$) confirmed that there was no significant difference between biomass quantity and activity in the two biofilters during the period of identical operation after the biofilm quantity and activity reached their maximums (i.e. control conditions). From the data, it can be seen that within approximately 3 months of operation the biofilm quantity and activity reached a maximum. The removals of organics, however, were variable over this time period. From the literature, the required time to steady-state operation was found to be 2 weeks for a lab-scale-GAC biofilter (Nishijima *et al.* 1997) and 3 weeks for a full-scale GAC-phonolith (volcanic rock)-CaCO₃ biofilter (Melin *et al.* (2002), respectively, based on TOC removal. Servais *et al.* (1994), who studied GAC biofilters, found steady-state DOC removal may occur well before steady-state biomass development is reached. During their study, 100 days was required for acclimation with respect to biomass development. These results are comparable to the finding of the current research, although the media types were different. The biological availability of substances in the feed is known to be an important factor related to the length of the acclimation period (Xiang *et al.*, 2013), and this may result in different acclimation values between studies.

While some researchers have suggested that the amount of biofilm or activity may not be related to organics removal (Juhna and Melin, 2006, Wang *et al.*, 1995), others, for example, Fonseca *et al.* (2001) found DOC removal to be related to activity. The DOC removals by the two filters (average 0 to 12% for both) as shown in Figure 4.6 were very similar during the steady-state operation period before phosphorus dosing (until February 2013). The removals of biopolymers by the biofilters were also identical (21% and 24% for BF1 and BF2, respectively) (discussed in detail in Chapter 3). However, no relationship was found between either DOC or biopolymer removal and biomass quantity or activity in this study.

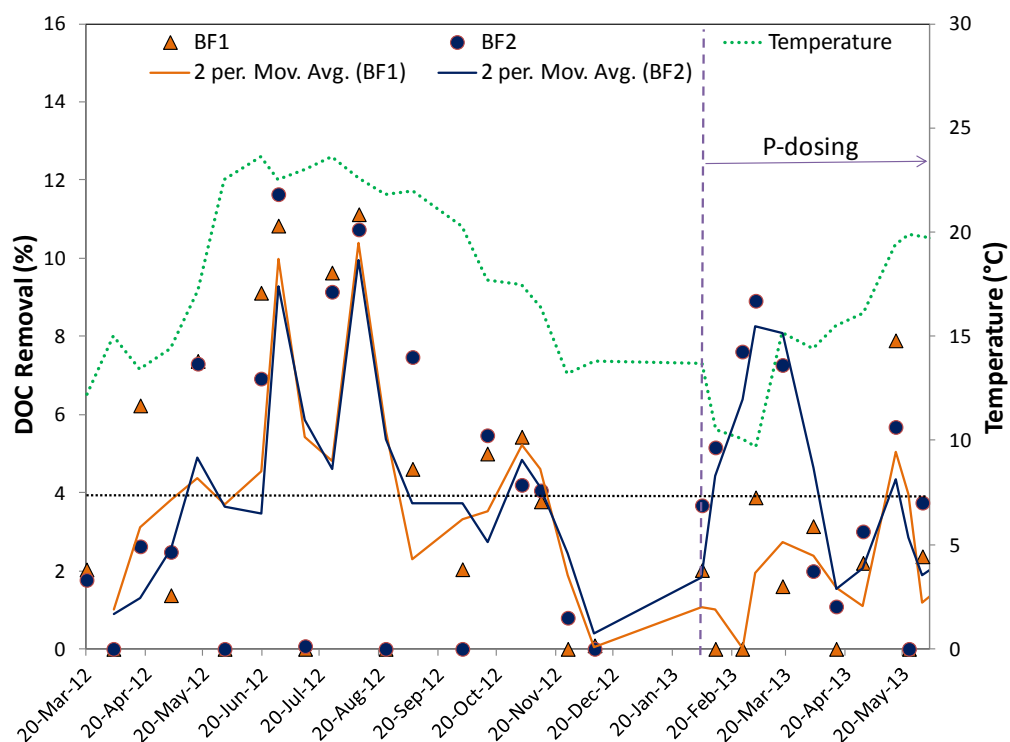


Figure 4.6 Percent DOC removal as shown by plotted values and by moving average lines for Biofilter 1 and 2 throughout the experimental period (n = 20 without P; n =11 with P-added). Average removal by BF1 and BF2 before P-dosing was 4% (indicated by horizontal dotted line).

4.3.3 Effect of phosphorus addition on biofilter performance

Phosphorus addition to BF2 was started on February 4, 2013 at a level of 0.01 mg/L, and was increased to 0.05 mg/L after April 19 which was continued until May 31, 2013. The effect of phosphorus addition to the biofilter was assessed by comparing the performance of BF2 (P-dosed) with BF1 (control filter). The modified C:N:P ratio (as DOC:total-N:total-P) after phosphorus enhancement (BF2) is presented in Table 4.3 along with the existing C:N:P ratio in the raw water, which was used as the BF1 feed. Total P measurements were only started on April 3, 2013, and therefore only reflect data taken after that date.

The table also shows that the initial addition of 0.01 mg P/L although increasing the ratio of phosphorus to C:N, it was still less than 1. When 0.01 mg P/L was added to BF2, there

was no increase in biomass development in terms of quantity (Figure 4.3) or activity (Figure 4.5). An increase in DOC removal was observed when P dosing started, however, DOC removal dropped back to the level of the control filter (BF1) in about a month. The addition of 0.01 mg P/L was continued and biofilter performance was monitored for 2.5 months. When no changes in biofilter performance were observed, the phosphorus addition was increased to 0.05 mg P/L on April 19 and the performance of both biofilters continued to be monitored. The actual phosphorus concentration in the biofilter influent varied from the expected concentration (phosphorus added plus raw water concentration). This was possibly due to loss of added phosphorus through the overflow as the dosing tube was very close to the overflow of the biofilter. Therefore, the measured concentration in the biofilter influent water was used to calculate the C:N:P ratios.

Table 4.4 Removal of carbon, nitrogen and phosphorus through biofilters 1 and 2

P-dose (mg/L P)	Date	Removal by BF1 (no additional P) (mg/L)				Removal by BF2 (P dosed) (mg/L)			
		DOC	Total-N	Total-P	Ortho-P	DOC	Total-N	Total-P	Ortho-P
0.01	04-Mar-13	0.17	0.05	n.m.	0.000	0.38	0.01	n.m.	0.001
	18-Mar-13	0.08	0.11	n.m.	0.001	0.35	0.28	n.m.	0.000
	03-Apr-13	0.15	0.00	0.001	0.000	0.10	0.00	0.017	0.000
	15-Apr-13	0.00	0.00	0.003	0.000	0.05	0.00	0.001	0.000
0.05	29-Apr-13	0.12	0.140	0.003	0.000	0.16	0.00	0.023	0.014
	16-May-13	0.37	0.00	0.003	0.000	0.27	0.150	0.003	0.000
	23-May-13	0.00	0.00	0.005	0.000	0.00	0.090	0.005	0.000
	30-May-13	0.12	0.00	0.004	0.000	0.19	0.00	0.005	0.000

*detection limits: 0.003 mg/L for total-P and ortho-P, 0.15 mg/L for total-N; n.m = not measured

Table 4.4 presents the removal of DOC, total-N, total-P, and ortho-P by the two biofilters. As in Table 4.3, total phosphorus had been measured since April 3, so the table includes data from after that date. The nitrogen and phosphorus consumption were very low. This differs from the findings of Li *et al.* (2010) who reported nearly complete removal of nitrate within

2 days of the start of phosphorus dosing into their pilot-scale BAC filter. Table 4.4 also shows that the removal of total-P within the filters was very low as well, and there was no removal of ortho-P in the filters. One possible explanation for the “0”-removal values of ortho-P and nitrogen could be that the biofilm bacteria re-cycled the nutrients from breaking down dead cells (Melin *et al.*, 2002). Li *et al.* (2010) also reported no significant increase in nitrate uptake with phosphorus addition in BAC biofilters. In Table 4.4 the DOC removal from April 3 on was also somewhat similar in the two biofilters, unlike examples from literature which found a 75% increase (Lauderdale *et al.*, 2012) and a 6 times (Nishijima *et al.*, 1997) increase in DOC removal with P-dose of 0.02 mg/L (P-dosing duration: 6 weeks) and 0.01 mg/L (P-dosing duration: 4 weeks) into their GAC biofilters, respectively. However, as mentioned earlier, better performance in DOC removal was observed for a short period of time (just over a month) during the start of 0.01 mg P/L dosing (Figure 4.6). This is especially important as the DOC removal had been similar (average 3.7% for BF1, 4.1% for BF2) for both biofilters since acclimation (for 8 months). Removal of UV-absorbing components, as measured by UV absorbance at $\lambda = 254$ nm, was also significantly higher ($\alpha = 95\%$, $n = 10$) in BF2 during the initial phosphorus addition period (Figure 4.7). The LC-OCD results confirmed that this increased removal in DOC was in the humics substances fraction (Figure 4.8) and not the biopolymers (Figure 4.9). However, an improvement in DOC and humics removal was not observed at the higher (0.05 mg P/L) phosphorus dose. There was no significant difference between parallel biofilters (Table 4.5) with respect to removing the lower molecular weight NOM fractions (p-value 0.5 and 0.7 for building blocks and LMW neutrals, respectively).

Table 4.5 Difference in performance between BF1 (control) and BF2 (P-enhanced); February 4 to May 30, 2013

Parameter	Raw Water Quality (mg/L)*			% Removal by BF1				% Removal by BF2				n	p-value
	Max	Min	Avg	Max	Min	Avg	SD	Max	Min	Avg	SD		
Turbidity	15.00	4.27	8.07	84	51	69	13	85	52	72	12	9	0.104
UV ₂₅₄	0.18	0.12	0.15	4	0	2	1	6	0	3	2	10	0.020
TOC	5.65	4.34	4.91	9	0	2	3	7	0	4	2	10	0.158
DOC	5.40	4.23	4.78	8	0	2	2	9	0	4	3	10	0.049
Biopolymers	0.159	0.079	0.108	29	10	21	5	32	11	24	6	9	0.037
Humics	3.68	2.81	3.29	5	0	2	2	9	0	4	3	8	0.046

Avg = average; SD = standard deviation

Raw water quality parameters (average): temperature = 15.6°C; pH = 8.1; alkalinity = 231 mg/L as CaCO₃; hardness = 295 mg/L as CaCO₃; conductivity = 449 µS/cm

*except turbidity (NTU) and UV₂₅₄

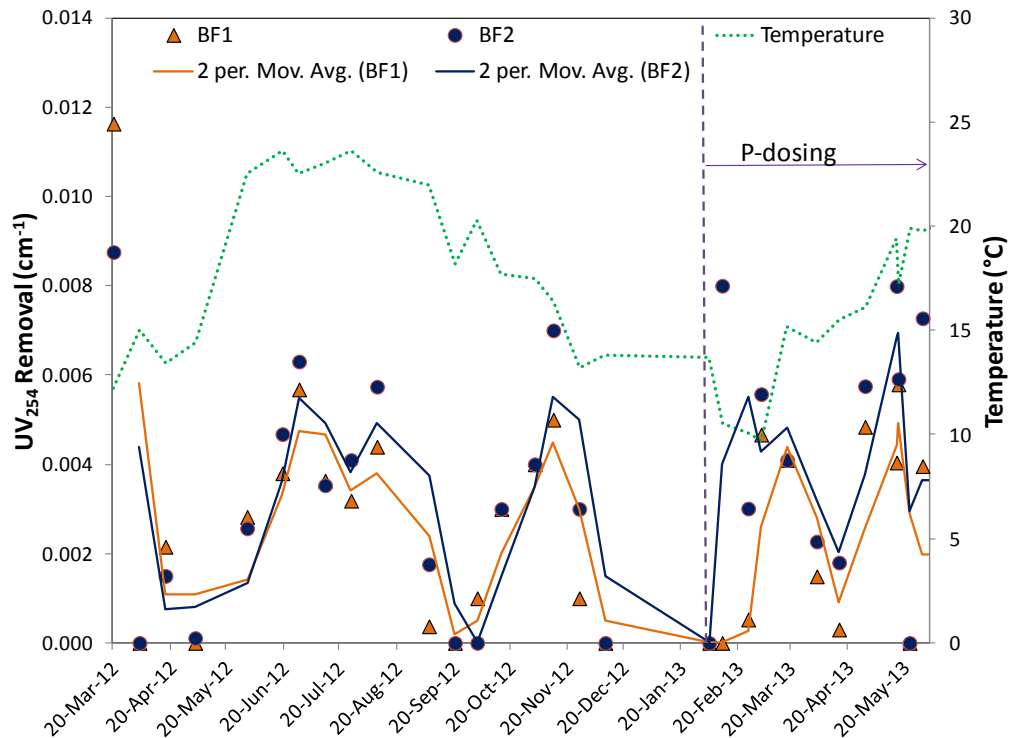


Figure 4.7 Removal of UV absorbance at 254 nm wavelength by Biofilter 1 and 2 (n = 20 without P; n =11 with P-added), which measures mixture of aquatic humics and different hydrophobic and hydrophilic NOM fractions of variable molecular weights in the water.

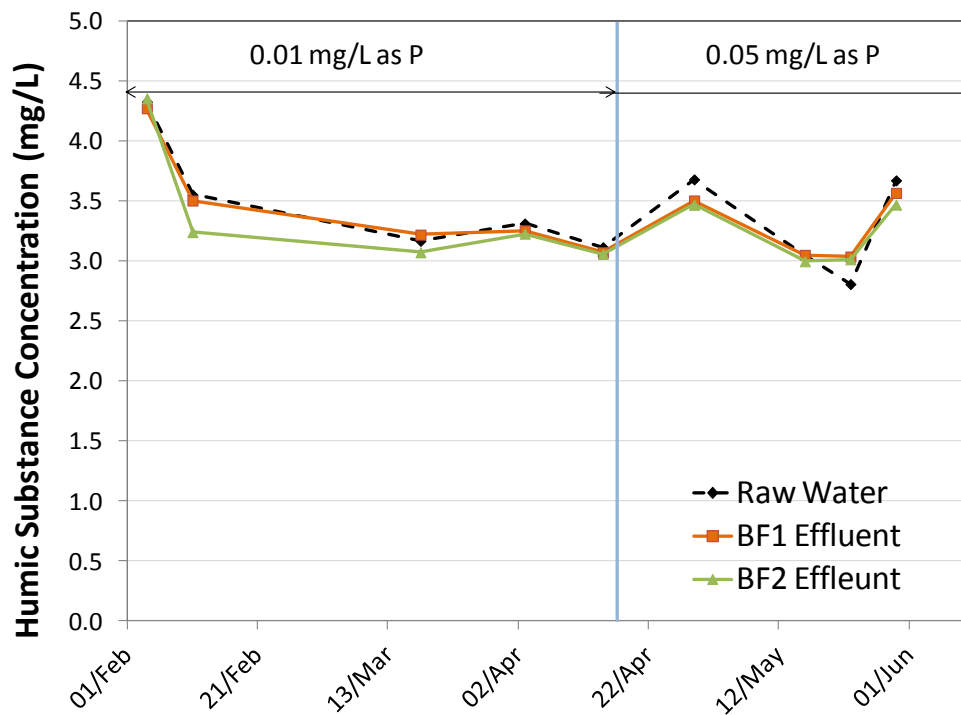


Figure 4.8 Concentrations of humic substances in the untreated water, and the effluents from Biofilter 1 and 2

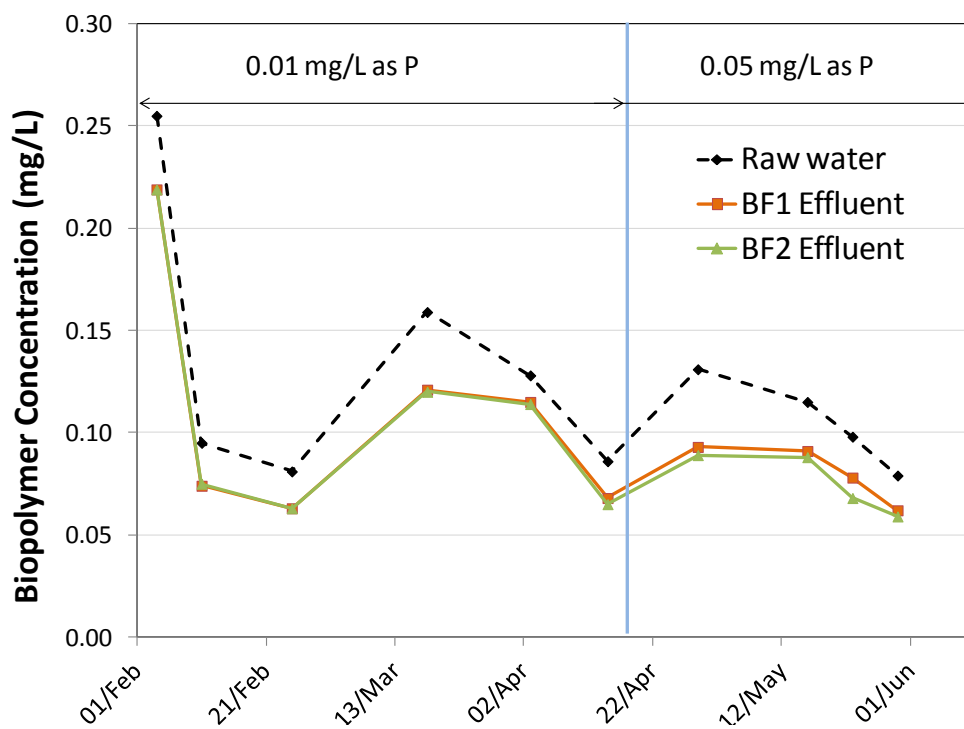


Figure 4.9 Concentrations of biopolymers in the untreated water, and the effluents from Biofilter 1 and 2

Figure 4.10A and B show that total phosphorus consumption within the filters was not different despite biofilter-2 receiving a much higher amount. The only exception was the 1st sampling date (April 29) collected after 0.05 mg P/L addition was started. This day showed high total and ortho phosphorus consumption. This could simply be an outlier or an indication that the filters were going through some changes in microbial structure. Unfortunately in our study there were too few data points collected immediately after P addition to confirm.

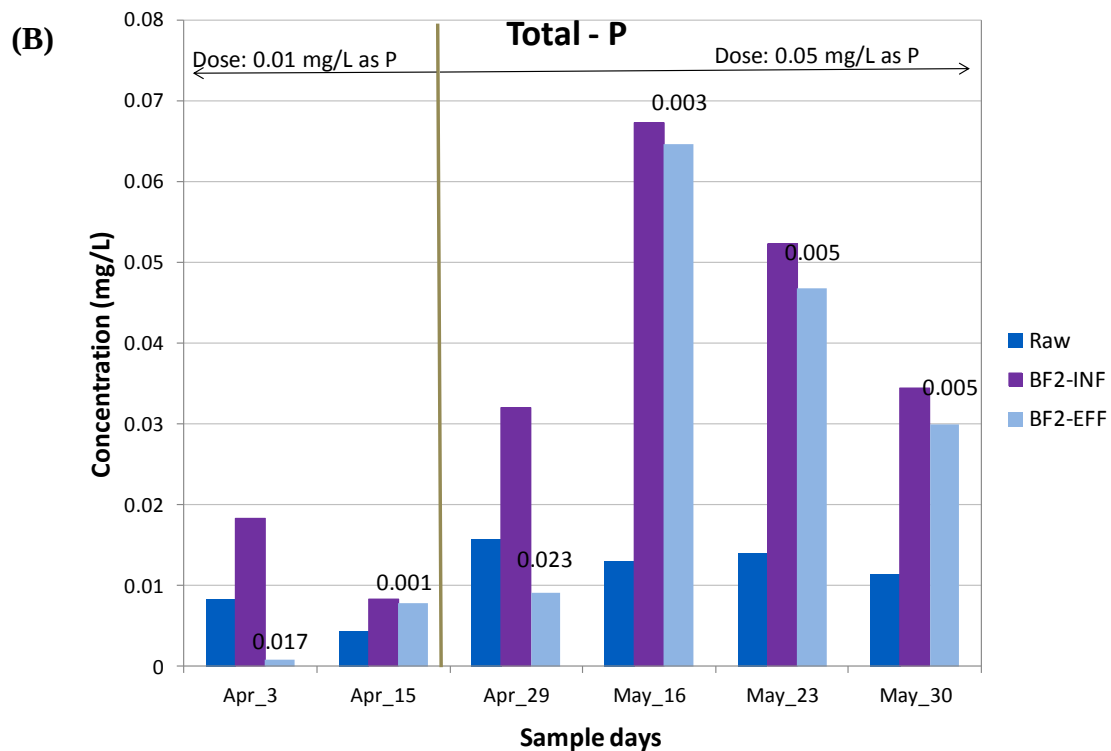
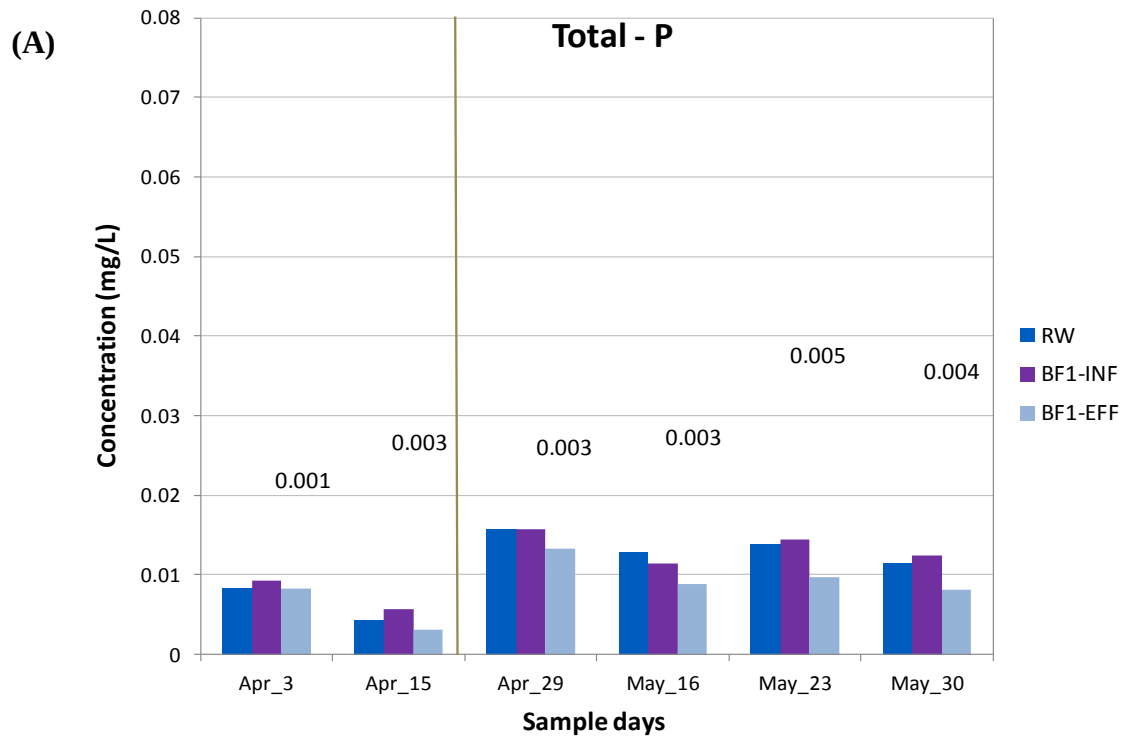


Figure 4.10 Concentration and consumptions of total phosphate in the A) control biofilter (BF1) influent and effluent, and B) BF2 (P-dosed biofilter 2) influent and effluent with concentrations in untreated raw water during April and May, 2013

Microbial biomass quantity or activity did not show an increase after phosphorus dosing. Average ATP and FDA measurements at different depths of the control and P-enhanced filters are presented in Table 4.6 and also in Figure 4.11 (A and B) and Figure 4.12 (A and B), respectively. In fact during the increased phosphorus dosing (0.05 mg P/L), slightly higher biomass and activity is observed in the control filter. Vahala *et al.* (1998) had reported similar observations with full-scale GAC (BAC) biofilters where they found ATP in a P enhanced filter lower than the control filter, despite the fact that there was an increase in heterotrophic plate count (HPC) bacteria in the P-dosed filter. However, Lauderdale *et al.* (2012) found a 30% increase in ATP after nutrient (P) dosing. Interestingly, Chenier *et al.* (2006), though not working with biofilters but river water biofilms, reported different responses of phosphorus dosing in the same river during the same season (fall) but in two different years (1999 and 2001), where in the first year the amount of biofilm increased and during the next year it was not affected.

Table 4.6 ATP and FDA at different depths of parallel biofilters

Biomass in different media depths		0.01 mg P/L dose in BF2				0.05 mg P/L in BF2			
		BF1		BF2		BF1		BF2	
		Avg	SD	Avg	SD	Avg	SD	Avg	SD
ATP (ng/cm ³)	Anthracite –top	267	54.6	239	32.3	170	30.4	159	47.3
	Anthracite-mid	186	34.1	188	27.8	151	26.5	142	21.5
	Sand-mid	139	31.6	151	26.9	135	13.9	129	16.5
FDA (µg/cm ³)	Anthracite –top	99	29.5	170	35.9	137	31.5	108	26.4
	Anthracite –mid	112	18.5	81	36.5	80	21.7	86	53.0
	Sand-mid	90	57.6	92	55.2	63	43.2	73	18.5

Avg = Average; SD = Standard deviation

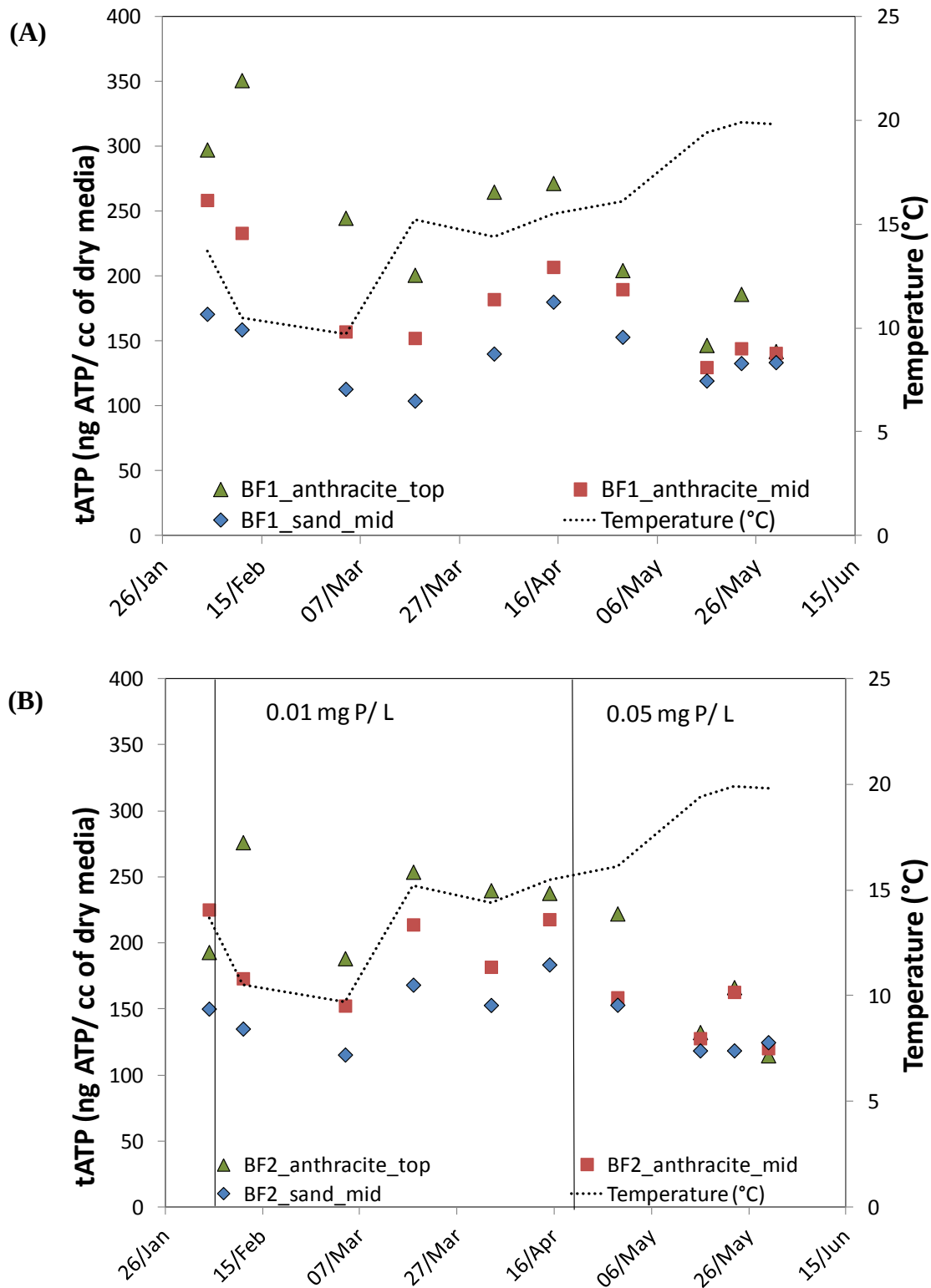


Figure 4.11 Total ATP at different depths of A) BF1 (No P added) and B) BF2 (P-added to BF2 influent) during P-dosing experiment with water temperature.

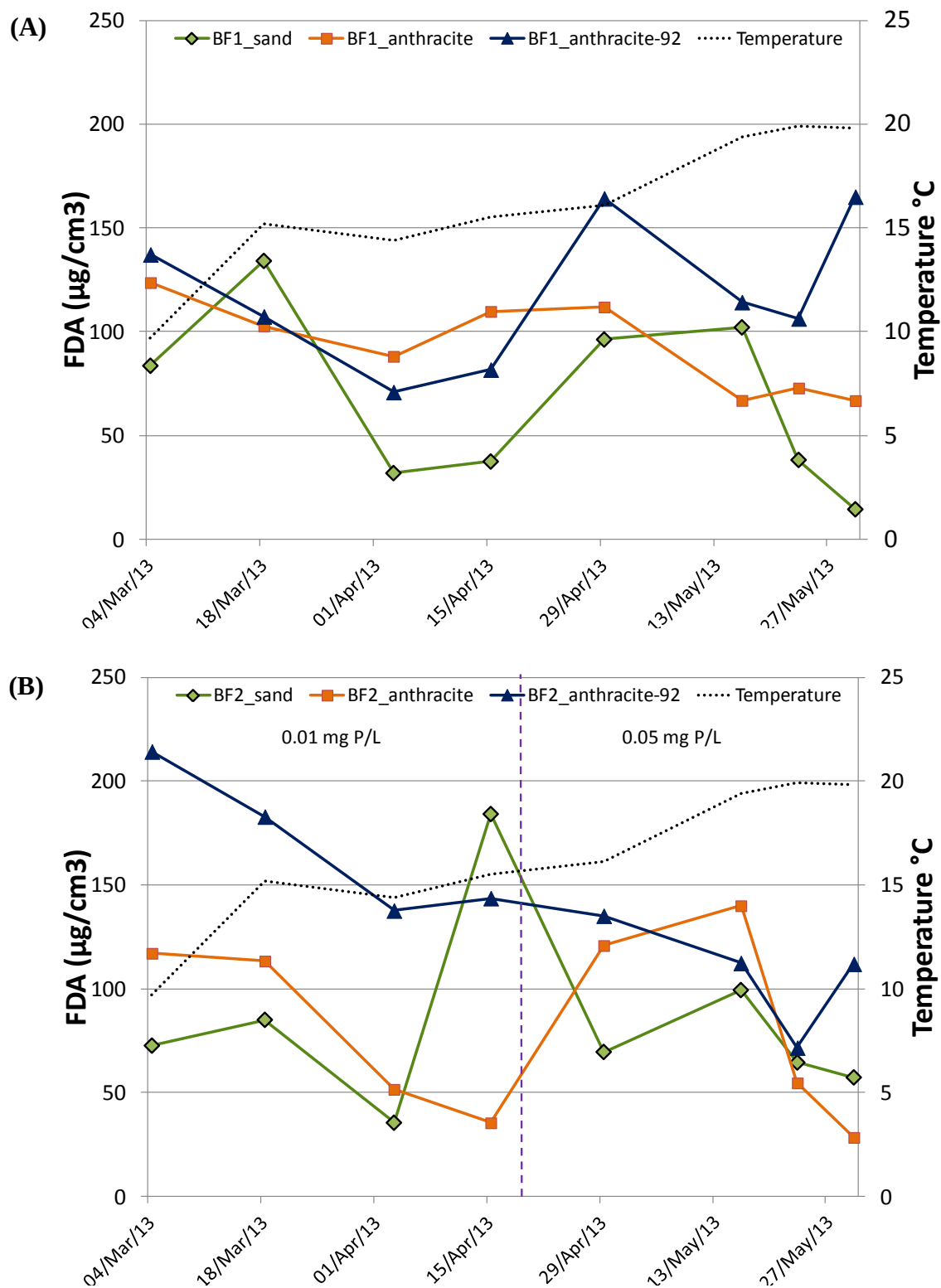


Figure 4.12 FDA at different depths of A) BF1 (No P added) and B) BF2 (P-added to BF2 influent) during P-dosing experiment with water temperature.

An absence of any upward trend in biomass quantity and activity during the four months of phosphorus enhancement indicated many possibilities. A possible explanation why an increase in biofilm activity was not observed is that increased the numbers of bacteria in the biofilters could be removed with the effluent due to lack of adhesion capacity (Sang *et al.*, 2003, Vahala *et al.*, 1998). Also, phosphorus addition may have changed the microbial dynamics or community in the filter (Li *et al.*, 2010), but had not significantly improved its activity or performance. If the experimental feed water was indeed phosphorus-limited, previous literature studies have shown slower but continuous organic removal at phosphorus limited conditions (Melin *et al.*, 2002). Some other factors might have played a role (biodegradable portion of organic carbon, bioavailability of nitrogen) in C:N:P calculations. DOC was used as carbon source in calculating the ratio, which is not fully biodegradable. If microbially available organic carbon was the limiting factor, which is a common scenario in drinking water context (Urfer *et al.*, 1997), it would mean the low ratio of phosphorus had been an underestimation. Hypothetically, assuming the biodegradable portion of the DOC as 20% of the total DOC (based of AOC and BDOC percentages in the literature) the calculated C:P ratios (as in Table 4.3) would be very close of the target ratio of 100:1 (C:P = 100:0.47 to 1.64, calculated setting 20% DOC as 100). The same would be true, if the biofilters were actually nitrogen limited as there was no detectable ammonia present in water, and utilization of nitrate or organic nitrogen is a slower and energy-intensive process. Characteristics of the indigenous bacteria community and microbiologically available portion of phosphorus (Miettinen *et al.*, 1997) are also some important factors here.

4.3.4 Membrane fouling experiments

The role of biopolymers, which include polysaccharides or protein-like substances, in membrane fouling had previously been demonstrated by Hallé *et al.* (2009). Biopolymers were also shown to be important for the membrane fouling experiments conducted for this study (with the control biofilter), where direct biofiltration was found to be effective in biopolymer removal (on average 21%) and UF membrane fouling reduction (Chapter 3). And, during the phosphorus enhancement experimental period (February to May, 2013), biopolymer removal by control and enhanced biofilters were 21% and 24%, respectively, which is similar to the observations from the previous 10 months of operation at natural conditions. For the membrane fouling experiments, effluent from biofilter 1 and later biofilter 2 was used as membrane feed (following a fouling experiment and chemical cleaning). The fouling rates were measured using the transmembrane pressure (TMP) difference. Irreversible fouling here is defined as the rate of increase in the non-backwashable TMP during the full length of the experiment. Reversible fouling was calculated as the rate of average increase in TMP (average of the difference between final and initial TMP for all cycles) during a 30 min cycle. The fouling experiments with control and P-dosed biofilter effluent were done during the same week to keep the water quality as comparable as possible. A total of 5 sets of these experiments were conducted during the P-dosing period. The results from these experiments are presented in Table 4.7. As biopolymer removal in the P-dosed biofilter was not substantially different, a measurable change in the membrane fouling rates was not expected and the data in Table 4.7 confirms this.

Table 4.7 Results from membrane experiments with BF1 (control) and BF2 (P-enhanced) effluent as feed water

Dates of the two membrane experiments (2013)	BF1 Feed				BF2 Feed				Length of experiment (h)
	Biopolymers (mg/L) in feed	Turbidity (NTU) in feed	Reversible (avg.) Fouling Rate (kPa/h)	Irreversible Fouling Rate (kPa/h)	Biopolymers (mg/L) in feed	Turbidity (NTU) in feed	Reversible (avg.) Fouling Rate (kPa/h)	Irreversible Fouling Rate (kPa/h)	
Mar 4 – 8	0.07	2.35	4.33	0.35	0.068	1.09	3.86	0.33	29.8
Mar 18 – 21	0.121	3.23	6.68	0.88	0.085	2.94	5.14	0.66	28.2
May 15 – 17	0.11	0.8	5.33	0.37	0.088	2.82	7.51	1.34	18.7
May 22– 24	0.08	0.8	4.49	0.37	0.068	0.98	4.13	0.45	22.9
May 28– 31	0.068	0.81	3.65	0.30	0.059	0.89	3.09	0.36	24.5

From the table it is clear that phosphorus addition did not make a noticeable change with respect to membrane fouling rates. The difference in the irreversible fouling rate seen during the experiment on the week of May 15 was clearly a biased set of data as the turbidity of the raw water had varied too much (1.4 and 10.4 NTU during BF1 and BF2 experiments, respectively) for an unbiased comparison. The change in turbidity was due to the water level getting low in the storage tank during the experiment with BF2 effluent as feed. As the recirculation system in the storage tank was kept running during the membrane experiments it stirred up settled particles from the tank bottom increasing the turbidity. Other than that experiment, the overall reversible fouling rate was slightly lower for BF2 effluent. Irreversible fouling rates, however, were very close and there was no difference in performance by either filter, although the biopolymer concentration was slightly lower in the effluent of BF2. The reason that biopolymers were slightly lower in the feed was possibly

some degradation of biopolymers over the two days in the raw water tank. Hallé *et al.* (2009) found biopolymers were responsible for reversible fouling of UF membranes, and results in Chapter 3 also showed that during this study there was a strong correlation between influent biopolymer concentration and irreversible fouling rate. Table 4.8 shows the organics (biopolymers, humics) and turbidity removed by the UF membrane (retained on the membrane surface, possible foulants). The concentration of biopolymers removed by the membranes was not very different, and as such the similarity between the fouling rates is not unexpected. There were some differences in humic substances and turbidity removal, however, these were previously found to be less critical for fouling (Chapter 3).

Table 4.8 Removal of NOM and particles by UF membrane (membrane retention) during the fouling experiments

Experiment date (2013)	Removal by BF1 (mg/L; NTU)			Removal by BF2 (mg/L; NTU)		
	Biopolymers	Humics	Turbidity	Biopolymers	Humics	Turbidity
Mar 4 – 8	0.047	0.06	2.10	0.058	0	0.80
Mar 18 – 21	0.088	0.01	2.89	0.065	0	2.53
May 15 – 17	0.071	0.40	0.50	0.064	0	2.64
May 22– 24	0.057	0	0.55	0.050	0	0.78
May 28– 31	0.038	0	0.54	0.037	0.66	0.77

4.4 Conclusions

The raw water used for the study, although originating from a river in a highly agricultural area, appeared to be phosphorus limiting according to the C:N:P ratio typically referred to in the drinking water literature (approximately 100:10:1). Adding phosphorus to the water did not significantly change the biomass quantity or activity in the biofilters and did not substantially affect biofilter performance in terms of organics removal. As the removal of organics did not increase remarkably, the effluent quality from the two biofilters was not

distinct enough to have a discernible effect during the membrane experiments. As such, for this particular water, biofilter phosphorus enhancement did not lead to additional improvement in the reduction of UF membrane fouling.

A number of reasons could be responsible for these outcomes. Although nitrogen was abundant in the raw water, it was primarily available in the form of nitrate or organic nitrogen (as measured by TKN), and may have been poorly or slowly utilized by bacteria in the biofilters (Melin *et al.*, 2002). The biodegradable organic matter (carbon) in the water could have been the limiting factor as well. As only a small portion of the organic carbon is available for microbes, especially for the raw feed water (Saugeen River) which had a high humic concentration (less biodegradable). It could also be the nature of the indigenous microorganisms, which might be adapted for a low phosphorus environment, as the river historically has low levels of phosphorus. Further studies, to improve our understanding of membrane foulant layers along with the nutrient requirements for optimal biofiltration performance are necessary. The overall finding from this phase of research was, even when the concentration of orthophosphate (or even total phosphorus) is low, it does not necessarily mean the biofilters are phosphorus-limited and in such cases phosphorus enhancement by itself may not improve biofilter performance with respect to the removal of organic foulants.

Chapter 5

Conclusions and Recommendations

5.1 Integration of Findings and Conclusions

The first objective of this research was to examine the effectiveness of direct biofiltration for controlling NOM-associated fouling of polymeric UF membranes employed in drinking water treatment applications. Using the Saugeen River in Ontario, Canada, as a raw water source and NOM characterization by LC-OCD analysis, an attempt was made to relate water quality with biofilter performance and irreversible and reversible membrane fouling.

The second objective involved the assessment of phosphorus addition to the biofiltration process. The C:N:P ratio for the Saugeen River suggested that phosphorus may have been a rate-limiting nutrient in terms of growth of the microorganisms in the biofilters. To test this hypothesis, phosphorus was added to the influent of biofilter-2 at concentrations of 0.01 mg P/L and later 0.05 mg P/L for a combined total of 4 months, while biofilter-1 was operated as an un-amended control. During this time the parallel biofilters were compared to quantify changes in biomass quantity, biomass activity, organics removal, and other water quality parameters. UF membrane fouling experiments were conducted separately with biofilter-1 and biofilter-2 effluent waters and membrane fouling rates were monitored. The raw river water trucked in to the centre and stored in an outdoor storage tank with an automatic circulation (heating) system which activated when the air temperature dropped to below 7°C (water temperature range during filter operation was 10 – 24° C). Under the conditions investigated, the following can be concluded from this study:

1. Through 14 months of parallel biofilter operation, about 20% of influent biopolymers were consistently removed, despite their relatively low concentrations (0.08 mg/L to 0.26

mg/L) in raw water. A linear relationship was found between the initial concentration of biopolymers in the raw water and amount removed through the biofilters, indicating that removal could be represented by a first-order process.

2. The parallel biofilters performed similarly in terms of biomass development during start-up, biomass quantity generation and activity during steady-state operation, and for particle and organics removal. Seasonal effects on biofilter performance could not be assessed due to the configuration of the system (which involved automatic heating of an outdoor tank to prevent freezing).

3. The raw water sometimes contained an elevated humic substance concentration (1.36 mg/L to 5.06 mg/L) which made up a substantial portion of the dissolved organic carbon (DOC), ranging from 54 to 89%. However, the biofilters did not substantially remove humic substances during the 14 months experimental period which is consistent with expectations.

4. UF membrane reversible and irreversible fouling rates, which were calculated based on Δ TMP (transmembrane pressure), were found to be highly correlated with the biopolymer concentration in the water, in spite of the low concentration of biopolymers in the membrane feed water, which ranged from 0.10 to 0.26 mg/L for untreated water and 0.07 to 0.19 mg/L in biofiltered water. This was quite remarkable given that the corresponding DOC concentrations were on the order of 5 mg/L. It is also intriguing that the removal of only a small amount of biopolymer material could lead to substantial improvement in UF membrane fouling rates.

5. There was no relationship between fouling (both reversible and irreversible) and the concentration of humic substances present in the membrane feed water (for both untreated and biofiltered waters). Although increased fouling was observed in one elevated turbidity

event (up to 18 NTU), a strong relationship between fouling rate and turbidity was not observed.

6. When UF membrane fouling rates using untreated (raw) and biofiltered water were compared, it was observed that there was 14 to 68% reduction in the hydraulically irreversible fouling rate and an 8 to 55% reduction in the hydraulically reversible fouling rate. This confirmed the effectiveness of biofiltration pretreatment for removing material that can cause fouling of UF membranes.

7. The addition of phosphorus in the influent of biofilter-2 improved the influent C:N:P ratio in general and helped to achieve the target ratio (100:10:1) on some occasions. However, it did not improve biofilter performance substantially in terms of the removal of organics. This was true at both the low and high phosphate doses. Although in the early phase of low P dosing (approximately one month) increased DOC removal was observed in the phosphorus-enhanced biofilter, the portion of DOC which was removed was mostly humic in nature (based on UV removal). There was no change in biopolymer removal performance (21% and 24%) for the two biofilters.

8. The biomass quantity and activity in the biofilters were not affected by phosphorus dose or seasonal changes in the raw water character or temperature (ranging between 10 to 24°C), at least as indicated by the quantification methods used in this study.

9. Membrane fouling experiments did not result in significantly different reversible or irreversible fouling rates using either the P-amended or the control biofilter as feed waters. This makes sense as the biofilter effluents continued to produce similar concentrations of biopolymers, an important membrane foulant, but also indicates that there was no change in biopolymer composition.

10. The data collected suggest that although the concentration of phosphorus was low in the raw water studied, it was not a growth-limiting nutrient for the microorganisms inhabiting the biofilter. Carbon and nitrogen while appearing to be available in higher concentrations, might not have been in a readily available form, thus either could be a growth-limiting factor or a combination of nutrients could be responsible. It is also likely that the indigenous bacteria were accustomed to the low phosphorus levels, which could be the reason for not demonstrating a change in performance/consumption of the surplus phosphorus in the biofilters.

5.2 Implementation of Findings in the Drinking Water Treatment Industry and Recommendations for Future Research

Results of this study confirm previous observations regarding the potential of direct biofiltration as pretreatment for low-pressure polymeric ultrafiltration membranes, but using a different type of water matrix than had previously been examined. Reductions in the membrane fouling rate lead to less frequent backwashes and chemical cleanings; hence, this technology can be used in treatment plants with membrane-based systems to reduce membrane operating costs and reduce the volume of cleaning chemicals required. This will be especially useful in remote communities, as biofiltration operation is simple and commercial ultrafiltration membrane processes are becoming easier to use.

The study also provides further insight into the role of biopolymers in ultrafiltration membrane fouling and biopolymer removal kinetics (first-order) in the biofilters. The information can be useful for decisions regarding source water and treatment process selection. It should be noted that in the case of river water with elevated humic substance concentrations such as the Saugeen River, that humics were not effectively removed by the

biofilters under the conditions investigated. In this case, humic substances were not detrimental to filter or membrane performance, but if a treatment process was designed for other objectives (e.g. DBP precursor reduction), it would be necessary to incorporate other processes to achieve the required humics removal. Also, adjustment in operating conditions in terms of empty bed contact time and backwashing frequency may be necessary if turbidity removal credits are expected from biofiltration alone.

The attempt to engineer the biofilters for better performance with the addition of phosphorus did not provide conclusive data to support theories involving nutrient limitation. Hence, it is recommended that the effect of phosphorus and other nutrients, in particular, nitrogen and carbon be further examined. Other than the nutrient analyses done for this study, quantification of biodegradable organic carbon is recommended. And from analysis point of view, a more refined statistical analysis using the data may provide additional interesting information.

Finally, the membrane fouling reduction potential of biofiltration should be further explored with different membrane types. High-pressure membranes and ceramic membranes are growing in popularity in the field of drinking water treatment. Investigation of the applicability of biofiltration pretreatment for these types of membranes is recommended for future research..

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Appendix A

Schematic and Photos of the Set-up

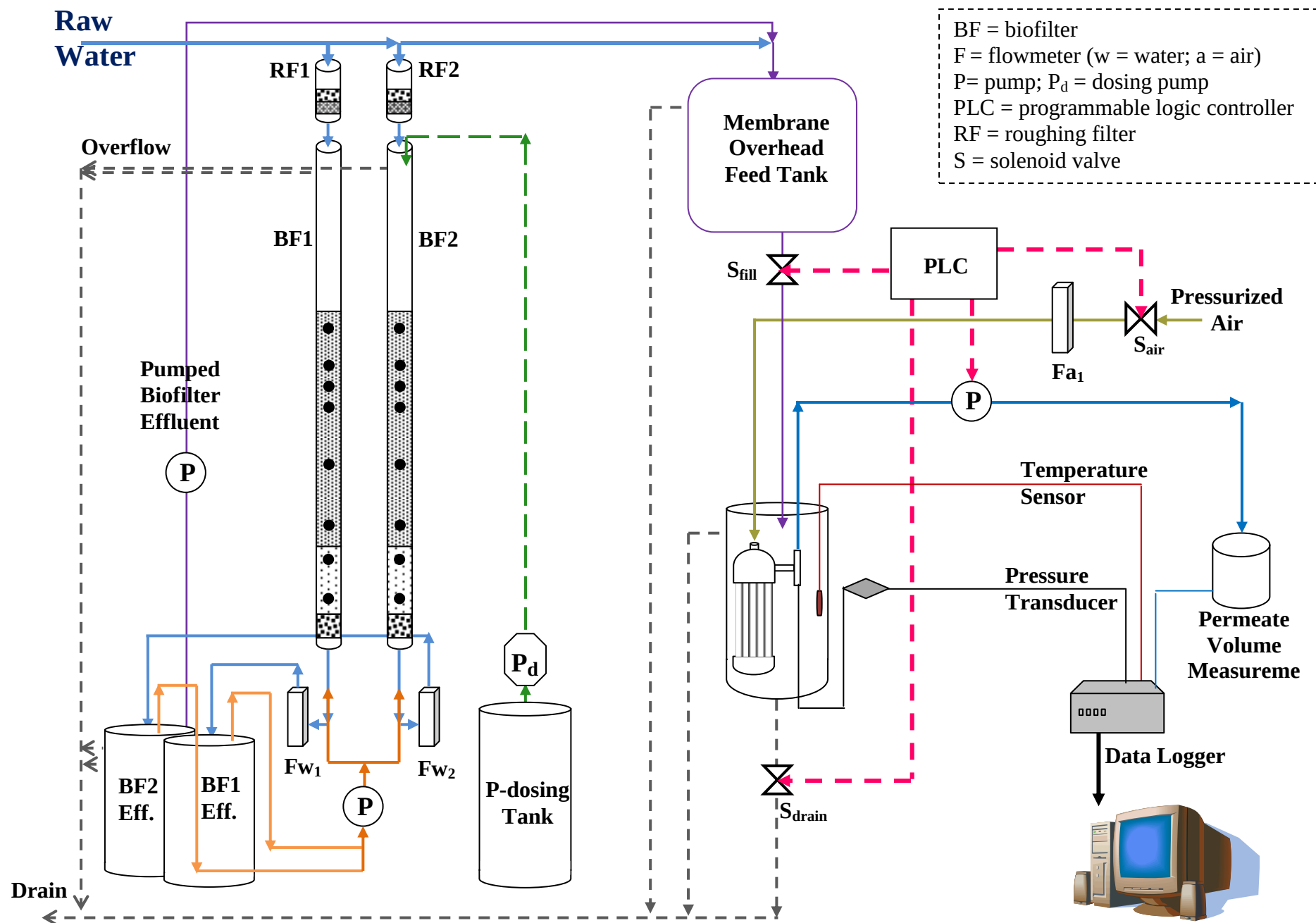


Figure A-1: Schematic drawing of experimental set-up



Figure A-2: Fresh sand and anthracite media in the glass columns



Figure A-3: Roughing filters with gravel as media

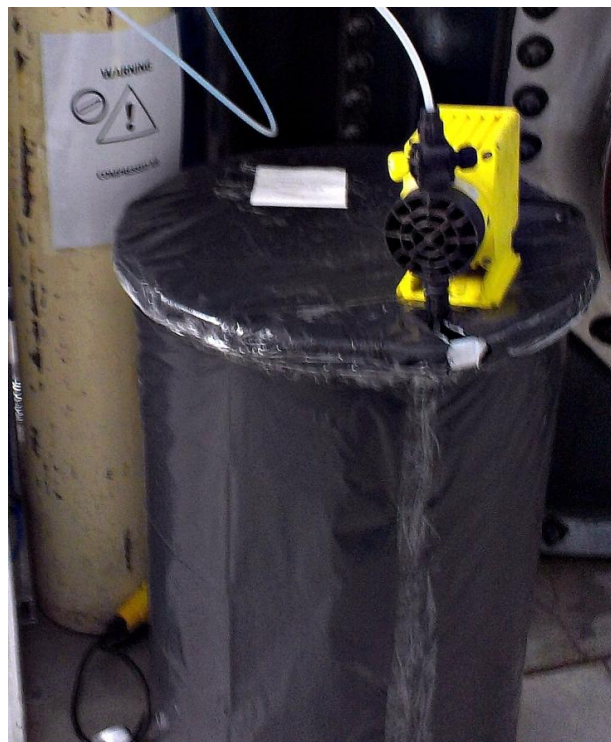


Figure A-4: Phosphorus dosing pump and solution holding tank



Figure A-5: Biofilter set-up with backwash tanks and backwash air compressor



Figure A-6: Collection of media samples from biofilter sampling ports



Figure A-7: Membrane set-up

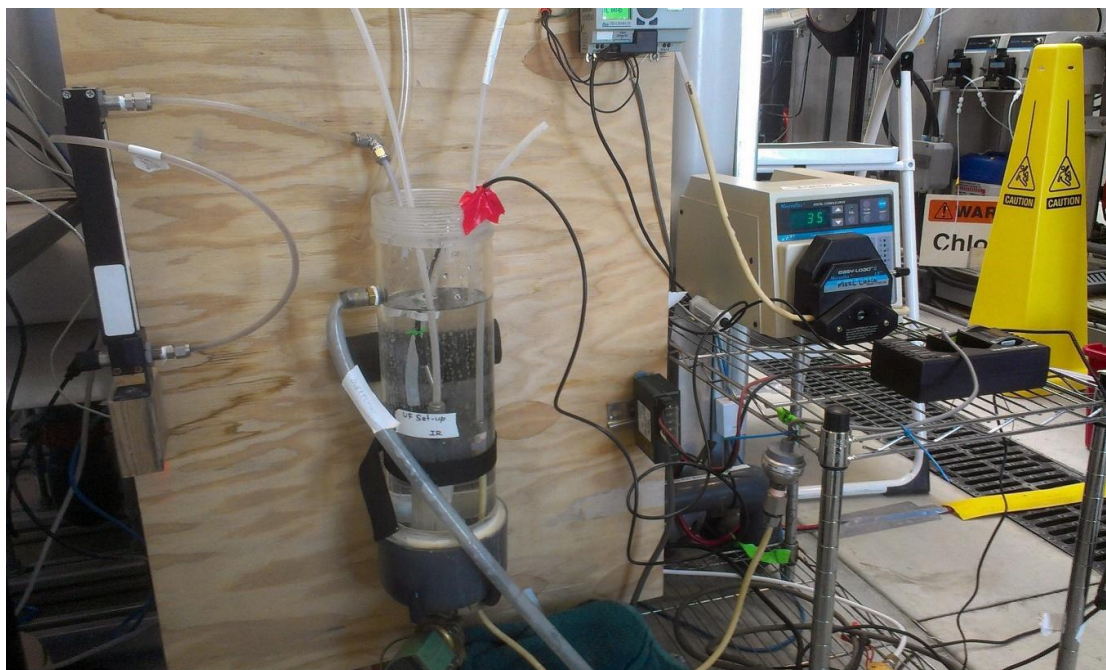


Figure A-8: Membrane set-up parts- membrane holder tank, water flow-meter, permeation pump, temperature sensor, data logger

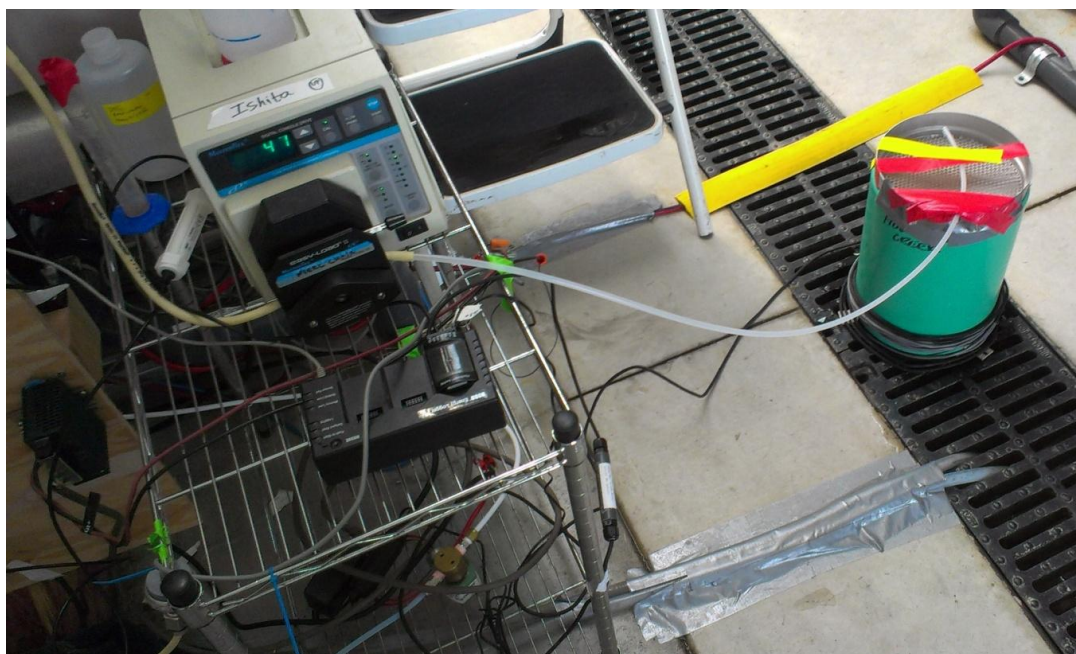
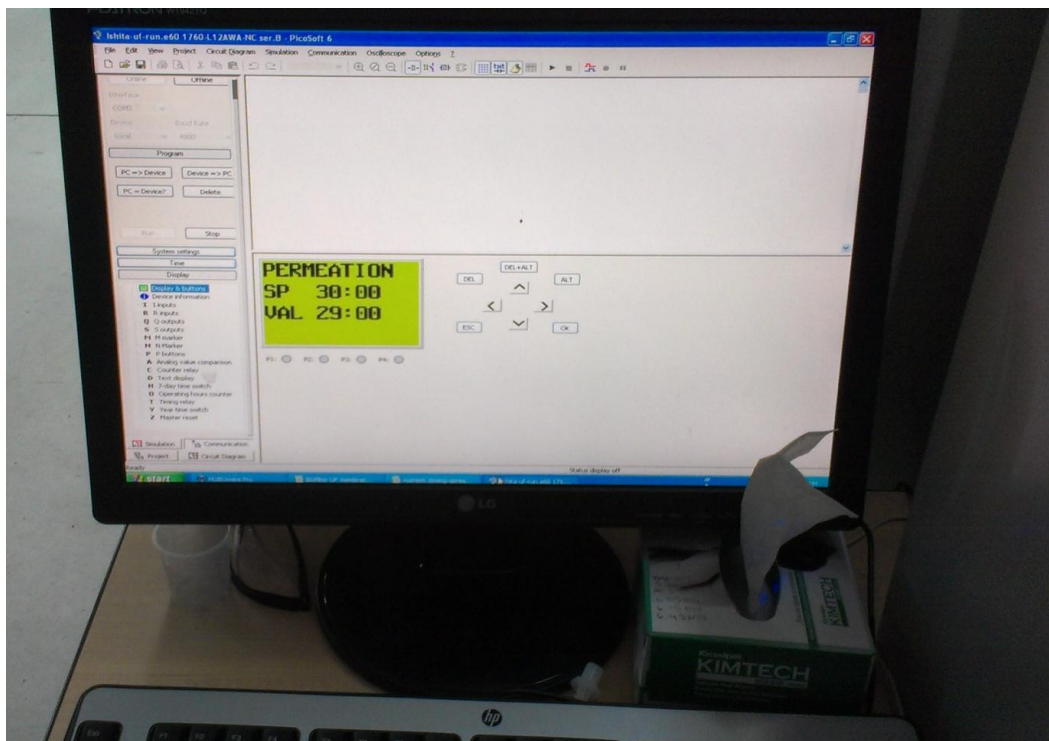


Figure A-9: Membrane set-up flow measurement system



FigureA-10 & 11: Programmable logic controller (PLC) and control screen for automated operation



Figure A-12: ZW-1 bench scale membrane unit



Figure A-13: Fouled membrane unit before chemical cleaning

Appendix B

Media Specifications

Media sieve analysis: Anthracite

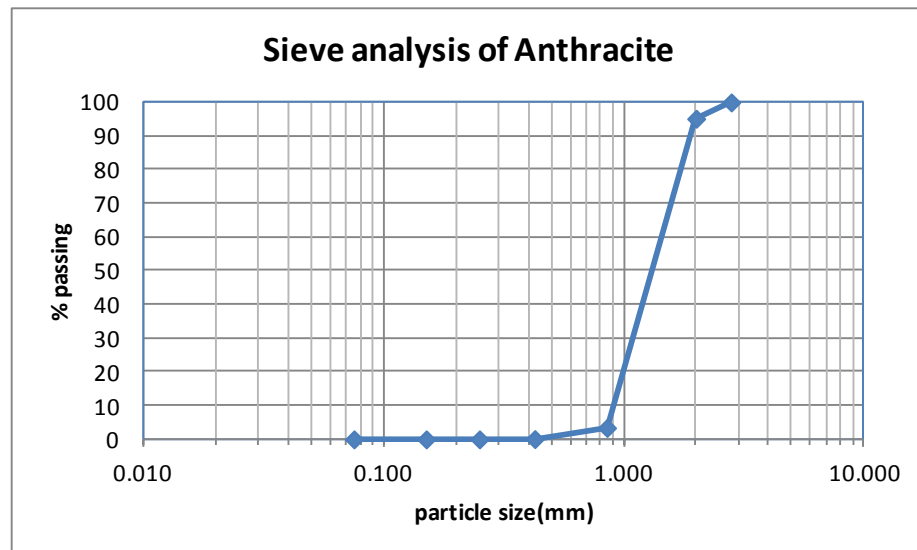
Sieves: 7, 10, 20, 40, 60, 100, 200

Material wt. (initial): 500 g

Gradation Table:

Sieve ID	Opening (mm)	Individual wt. retained (g)	Cumulative wt. retained (g)	Cumulative % retained	% passing
7	2.800	0.1	0.1	0.02	99.98
10	2.000	24.2	24.3	4.86	95.14
20	0.850	458.2	482.5	96.60	3.40
40	0.425	16.6	499.1	99.92	0.08
60	0.250	0.4	499.5	100.00	0.00
100	0.150	0	499.5	100.00	0.00
200	0.075	0	499.5	100.00	0.00
Pan	0.000	0	499.5	100.00	0.00
	Total=	499.5			
	Error %=	0.001			

Gradation Graph:



Effective size: D10 = 0.9 mm

Uniformity coefficient = $D_{60}/D_{10} = 1.5/0.9 = 1.6$

Sand (Anthrafilter, Brantford, Ontario)

Effective size: 0.5 mm

Uniformity coefficient 1.5

Appendix C

Raw Water Quality Data

Date	Temperature (°C)	pH	Turbidity (NTU)	TOC (mg/L)	DOC (mg/L)	UV254 (cm ⁻¹)	SUVA (L/mg-M)	Total Hardness (mg/L as CaCO ₃)	Alkalinity (mg/L as CaCO ₃)	Conductivity (µS/cm)
20-Mar-12	12.2	7.89		4.96	4.88	0.171	3.50		182	384
03-Apr-12	15	8		4.93	4.83	0.143	2.97		241	520
17-Apr-12	13.4	7.92		4.04	3.96	0.097	2.45		258	573
03-May-12	14.4	8.23	5.96	4.51	4.33	0.133	3.07		236	530
17-May-13	17.2	8	3.50	4.85	4.88	0.150	3.08		244	554
31-May-12	22.5	8.03	1.34	3.73	3.38	0.121	3.59		242	572
19-Jun-12	23.6	7.98	1.60	3.76	3.83	0.106	2.78	334	226	580
28-Jun-12	22.5	7.98	3.70	3.41	3.34	0.094	2.80	346	222	609
12-Jul-12	23	7.91	1.50	2.96	2.77	0.077	2.77	358	216	
26-Jul-12	23.6	8.12	0.71	2.85	2.73	0.071	2.59	372	212	676
09-Aug-12	22.6	8.16	1.12	3.11	3.09	0.085	2.76	364	214	657
23-Aug-13	21.8	8.16	3.54	3.69	3.39	0.099	2.93	352	218	636
06-Sep-12	22	7.76	0.74	2.97	2.99	0.079	2.65	370	216	690
20-Sep-12	18.2	8.03		3.50	3.42	0.090	2.62	364	220	656
02-Oct-12	20.3	8.06	6.21	3.04	2.92	0.087	2.98	352	224	560
15-Oct-12	17.7	8.15	1.31	3.14	2.95	0.084	2.85	374	234	580
02-Nov-12	17.5	8.16	4.82	5.59	5.50	0.182	3.31	352	236	542

Date	Temperature (°C)	pH	Turbidity (NTU)	TOC (mg/L)	DOC (mg/L)	UV254 (cm ⁻¹)	SUVA (L/mg-M)	Total Hardness (mg/L as CaCO ₃)	Alkalinity (mg/L as CaCO ₃)	Conductivity (µS/cm)
12-Nov-12	16.4	8.13	9.93	7.29	7.03	0.239	3.40	330	238	650
26-Nov-12	13.2	7.97	6.41	5.19	5.16	0.167	3.24	380	256	602
10-Dec-12	13.8	8.07	4.28	5.60	5.46	0.195	3.57	338	236	611
04-Feb-13	13.7	7.97	17.90	6.61	6.52	0.205	3.14	200	156	323
11-Feb-13	10.5	7.96	8.72	5.38	5.21	0.125	2.40	276	206	419
25-Feb-13		8.27	5.06	4.67	4.61	0.135	2.93	308	238	475
04-Mar-13	9.7	8.14	15.00	4.34	4.31	0.122	2.83	328	246	477
18-Mar-13	15.2	8.02	6.84	5.04	4.85	0.152	3.14	272	212	411
03-Apr-13	14.4	8	4.27	4.99	4.84	0.152	3.14	272	220	400
15-Apr-13	15.5	8.39		4.65	4.58	0.152	3.31			410
29-Apr-13	16.1	7.88	11.60	5.65	5.40	0.166	3.07	250	214	368
16-May-13	19.4	8.05	10.40	4.74	4.68	0.156	3.33	306	240	489
23-May-13	19.9	8.28	4.67	4.59	4.23	0.157	3.72	322	252	521
30-May-13	19.8	8.16	6.06	5.10	5.07	0.184	3.62	318	248	520

Appendix D

Raw Water Biopolymer and Humic Substance Concentration

Samples	Comment	DOC (mg/L)	Biopolymers (mg/L)	Biopolymers (% DOC)	Humic substances (mg/L)	Humic substances (% DOC)
Mar 20, 12	Water-inflow started	4.52	0.18	3.8%	3.47	72%
Apr 03, 12	Outdoor tank	3.24	0.40	10.9%	2.46	89%
Apr 17, 12	Outdoor tank	2.85	0.14	4.3%	2.07	64%
May 03, 12	Outdoor tank	3.78	0.29	6.9%	2.68	63%
May 17, 12	Outdoor tank	4.30	0.26	5.6%	3.05	66%
May 31, 12	Indoor tank	3.55	0.20	5.2%	2.95	76%
June 19, 12	Indoor tank	3.16	0.20	5.8%	2.17	65%
June 28, 12	Indoor tank	2.89	0.29	8.5%	1.97	58%
July 12, 12	Indoor tank	2.33	0.14	5.4%	1.50	60%
July 26, 12	Outdoor tank	2.15	0.10	4.0%	1.36	54%
Aug 09, 12	Outdoor tank	2.59	0.12	4.1%	1.71	60%
Nov 02, 12	Outdoor tank	4.92	0.15	2.7%	3.58	65%
Nov 12, 12	Outdoor tank	7.30	0.23	3.2%	5.06	69%
Nov 26, 12	Outdoor tank	4.87	0.17	3.2%	4.08	75%
Dec 10, 12	Outdoor tank	2.70	0.16	2.6%	2.12	70%
Feb 4, 13	Outdoor tank	5.65	0.36	6.5%	4.26	76%
Feb 11, 13	Outdoor tank	4.52	0.14	3.0%	3.54	79%
Feb 25, 13	Outdoor tank	4.21	0.22	5.8%	3.00	78%
Mar 04, 13	Outdoor tank	3.39	0.08	2.8%	2.78	68%
Mar 18, 13	Outdoor tank	4.02	0.20	4.6%	3.17	73%
Apr 03, 13	Outdoor tank	4.15	0.13	2.8%	3.31	70%
Apr 15, 13	Outdoor tank	4.03	0.11	2.5%	3.11	71%
Apr 29, 13	Outdoor tank	4.53	0.12	3.1%	3.68	73%
May 16, 13	Outdoor tank	4.00	0.22	5.3%	3.04	71%
May 23, 13	Outdoor tank	3.47	0.11	2.7%	2.81	71%
May 30, 13	Outdoor tank	4.91	0.50	9.7%	3.67	71%

Appendix E

Nutrient Concentrations in Water Samples

Data from ALS Global Waterloo laboratory

Total - Phosphorus

DATE	RW	BF1-INF	BF1-EFF	BF2-INF	BF2-EFF
03-Apr-13	0.0083	0.0093	0.0083	0.0183	0.00088
15-Apr-13	0.0043	0.0057	0.0031	0.0084	0.0078
29-Apr-13	0.0157	0.0158	0.0133	0.032	0.0091
16-May-13	0.0129	0.0115	0.0088	0.0672	0.0646
23-May-13	0.0139	0.0144	0.0097	0.0522	0.0468
30-May-13	0.0114	0.0125	0.0082	0.0345	0.03

Ortho – Phosphorus

DATE	RW	BF1-INF	BF1	BF2-INF	BF2
26-Nov-12	0		0		0
04-Feb-13	0.0064		0.0058		0.0064
11-Feb-13	0		0		0.0178
04-Mar-13	0.0043		0.0042	0.0076	0.0066
18-Mar-13	0.0102		0.0055	0.0049	0.0077
03-Apr-13	0	0	0	0	0
15-Apr-13	0	0	0	0.0067	0.008
29-Apr-13	0.0039	0.0037	0.0097	0.0207	0.0065
16-May-13	0.0048	0.0047	0.0046	0.0548	0.0598
23-May-13	0.0035	0.0034	0.0035	0.0333	0.0366
30-May-13	0.0039	0	0.004	0.0214	0.0255

Total – Nitrogen

DATE	RW	BF1-INF	BF1	BF2-INF	BF2
26-Nov-12	1.92				
04-Feb-13	3.24		3.18		3.24
11-Feb-13	3		3.18		2.91
04-Mar-13	2.83		2.78	2.72	2.71
18-Mar-13	3.48		3.37	3.66	3.38
03-Apr-13	3.27	3.16	3.19	3.22	3.26

DATE	RW	BF1-INF	BF1	BF2-INF	BF2
15-Apr-13	3.12	3.12	3.23	3.11	3.11
29-Apr-13	2.5	2.64	2.5	2.49	4.25
16-May-13	1.99	1.96	2.06	2.06	1.91
23-May-13	2.32	2.26	2.45	2.28	2.19
30-May-13	2.09	2.19	2.2	2.04	2.62

Nitrate – N

DATE	RW	BF1-INF	BF1	BF2-INF	BF2
26-Nov-12	1.35				
04-Feb-13	2.64		2.65		2.64
11-Feb-13	2.53		2.58		2.36
04-Mar-13	2.37		2.34	2.32	2.32
18-Mar-13	2.94		2.91	2.91	2.92
03-Apr-13	2.78	2.79	2.79	2.78	2.89
15-Apr-13	2.8	2.8	2.8	2.8	2.78
29-Apr-13	2.01	2.01	2.01	1.99	1.96
16-May-13	1.54	1.53	1.54	1.5	1.47
23-May-13	1.96	1.96	1.97	1.92	1.92
30-May-13	1.7	1.7	1.7	1.67	1.68

TKN

DATE	RW	BF1-INF	BF1	BF2-INF	BF2
26-Nov-12	0.57				
04-Feb-13	0.6		0.53		0.6
11-Feb-13	0.47		0.6		0.55
04-Mar-13	0.46		0.44	0.4	0.39
18-Mar-13	0.54		0.46	0.75	0.46
03-Apr-13	0.49	0.37	0.4	0.44	0.37
15-Apr-13	0.32	0.32	0.43	0.31	0.33
29-Apr-13	0.49	0.63	0.49	0.5	2.29
16-May-13	0.45	0.43	0.52	0.56	0.44
23-May-13	0.36	0.3	0.48	0.36	0.27
30-May-13	0.39	0.49	0.5	0.37	0.94

Appendix F

Biomass Quantity (as ATP) and Activity (as FDA) Data

FDA (ug/cc of media)

Date	BF1_Sand (67 cm)	BF2_Sand (67 cm)	BF1_Anth mid (28 cm)	BF2_Anth mid (28 cm)	BF1_Anth top (8 cm)	BF2_Anth top (8 cm)	Tempera- ture (°C)
7-Mar-12	0	0	2	2			
3-Apr-12	0	0	63	61			15.0
17-Apr-12	27	34	63	61			13.4
17-May-12	84	69	116	111			17.2
19-Jun-12	42	60	63	57			23.6
28-Jun-12	67	55	80	76			22.5
12-Jul-12	0	45	61	75			23.0
26-Jul-12	65	68	57	75			23.6
23-Aug-12	86	68	82	50			21.8
6-Sep-12	55	51	49	50			22.0
20-Sep-12	52	25	47	58			18.2
2-Oct-12	97	84	111	95			20.3
15-Oct-12	47	49	66	58			17.7
2-Nov-12	45	82	56	67			17.5
12-Nov-12	123	263	103	49			16.4
26-Nov-12	55	23	76	62			13.2
4-Feb-13	116	105	131	128			13.7
11-Feb-13	162	83	136	88			10.5
4-Mar-13	84	73	124	117	137	214	9.7
18-Mar-13	134	85	103	113	107	183	15.2
3-Apr-13	32	35	88	51	71	138	14.4
15-Apr-13	37	184	110	35	82	144	15.5
29-Apr-13	96	69	112	121	164	135	16.1
16-May-13	102	99	67	140	114	112	19.4
23-May-13	38	64	73	55	106	72	19.9
30-May-13	14	57	67	28	165	112	19.8

*depth from top of the biofilter media surface in parentheses

ATP (ng ATP/ cc of media)

Date	BF1_Sand (67 cm)	BF2_Sand (67 cm)	BF1_Anth mid (28 cm)	BF2_Anth mid (28 cm)	BF1_Anth top (8 cm)	BF2_Anth top (8 cm)	Tempera- ture (°C)
07-Mar-12	0.1	0.1	0.1	0.1			
03-Apr-12	33	39	85	98			15.0
17-Apr-12	81	79	107	76			13.4
17-May-12	147	156	111	58			17.2
19-Jun-12	159	109	162	154			23.6
28-Jun-12	269	201	294	241			22.5
12-Jul-12	150	195	169	230			23.0
26-Jul-12	132	104	134	105			23.6
23-Aug-12	189	143	171	164			21.8
06-Sep-12	167	142	123	119			22.0
20-Sep-12	102	98	101	95			18.2
02-Oct-12	126	118	125	102			20.3
15-Oct-12	112	119	118	101			17.7
02-Nov-12	169	183	169	177			17.5
12-Nov-12	165	161	147	149			16.4
26-Nov-12	144	24	73	60			13.2
04-Feb-13	171	150	259	225	298	193	13.7
11-Feb-13	159	135	233	173	351	276	10.5
04-Mar-13	113	115	157	152	245	188	9.7
18-Mar-13	104	168	152	214	201	254	15.2
03-Apr-13	140	153	182	182	265	240	14.4
15-Apr-13	180	184	207	218	272	238	15.5
29-Apr-13	153	153	190	159	205	222	16.1
16-May-13	119	119	130	128	147	132	19.4
23-May-13	133	119	144	163	186	166	19.9
30-May-13	134	125	141	120	142	115	19.8

*depth from the top of the biofilter media surface in parentheses

Appendix G

Phosphorus Dosing Calculation Summary

Phosphorous source: Potassium Phosphate Dibasic (K_2HPO_4)

Molar mass = 174.18 g/mol

Pumping rate = 6.48 mL/min = 0.39 L/h

Flow of raw water through the column = 10 L/h

Volume of the dosing tank = 100 mL

Sample calculation for 0.01 mg P/L dosing:

K_2HPO_4 concentration in stock solution = 2.5 g/L

Final expected concentration of P in the influent of biofilter = 0.01 mg/L

Amount K_2HPO_4 solution required to be dosed in BF2 influent to provide 0.01 mg P/L

$$= (0.01 \times 174.18) / 30.1 = 0.056 \text{ mg } \text{K}_2\text{HPO}_4/\text{L}$$

Hence, concentration of K_2HPO_4 required in the feed tank

$$= (0.056 \times 10) / 0.39 = 1.45 \text{ } \text{K}_2\text{HPO}_4/\text{L}$$

Finally, volume of 2.5 g/L stock solution to add to the 100 L feed tank

$$= (1.45 \times 100) / 2.5 = 58 \text{ mL of } \text{K}_2\text{HPO}_4 \text{ stock}$$

Appendix H

List of Publications

Refereed Journal Articles (Submitted)

Rahman, I., S. Ndiongue, X. Jin, M.I. Van Dyke, W.B. Anderson, and P.M. Huck, 2013. Fouling of Low Pressure Membranes during Drinking Water Treatment: Effect of NOM Components and Biofiltration Pretreatment. *Water Science and Technology: Water Supply*. Accepted for publication.

Conference Proceedings/ Presentations (Abstract Reviewed)

Rahman, I., S. Ndiongue, X. Jin, L.F. Moore, M.I. Van Dyke, W.B. Anderson, and P.M. Huck, 2013. Biofiltration as a Pretreatment to Control Low Pressure Membrane Fouling during drinking Water Treatment. Proceedings, the 2013 OWWA/OMWA Joint Annual Conference and Trade Show, Ottawa, Ontario. MON-03 (University Research).

Rahman, I., X. Jin, S. Ndiongue, L.F. Moore, W.B. Anderson, and P.M. Huck, 2013. Biofiltration as a Pretreatment to Control Membrane Fouling during Drinking Water Treatment. Proceedings, AWWA's 2013 Biological Treatment Symposium, Denver, Colorado. THU04-03.

Rahman, I., S. Ndiongue, X. Jin, M.I. Van Dyke, W.B. Anderson, and P.M. Huck, 2013. Low-pressure Membrane Fouling Minimization with Biofiltration Pretreatment during Drinking Water Treatment. Presented at the 7th IWA Membrane Technology Conference, Toronto, ON. August 25-29, 2013.

Invited Presentation

Rahman, I., W.B. Anderson, and P.M. Huck, 2013. Biofiltration Pretreatment for Ultrafiltration Membrane Fouling Control. Invited seminar presented to staff of the Walkerton Clean Water Center, Walkerton, Ontario. August 30, 2013.