Natural Organic Matter Characterization of Different Source and Treated Waters; Implications for Membrane Fouling Control

by

Jamie Croft

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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.

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Abstract

The objective of drinking water treatment is to provide water which is free of pathogens, is chemically and biologically stable, and is of good aesthetic quality. Natural organic matter (NOM) is present in all natural waters and can make meeting these goals more challenging. Not only does it undergo adverse reactions with disinfectants such as chlorine, it also impacts the biological stability of water within the distribution system and contributes to undesirable aesthetic qualities such as taste and odour. NOM has also been implicated in membrane fouling, which continues to be a significant operational problem preventing wider implementation of this process. Due to its highly variable heterogeneous nature, NOM can be difficult to characterize in terms of its specific composition, however recent analytical advancements are allowing for a better understanding of its behaviour in water treatment.

Two promising tools for NOM characterization include Liquid Chromatography Organic Carbon Detection (LC-OCD) and Fluorescence Excitation Emission Matrix (FEEM) analyses. In this research both techniques were applied to samples taken from five full scale facilities in Ontario, Canada over all four seasons. The source waters for these treatment locations consisted of both river (Grand River, Ottawa River) and Great Lake waters (Lake Huron, Lake Erie, Lake Ontario), and an additional raw source (Saugeen River) was also monitored. The plants all employed granular media filtration, but had differences including enhanced coagulation, ozonation, biofiltration and sand ballasted flocculation. Other relevant water quality parameters were also monitored (TOC, DOC, UV_{254}, pH, conductivity etc.) as well as plant operating conditions (dosages, flows, filter run times etc.) to investigate their impact on removal of specific NOM fractions. Four of the waters (Grand River, Ottawa River, Lake Erie and Lake Ontario) were selected based on the initial survey due to their NOM composition, for bench scale ultrafiltration (UF) membrane fouling experiments. The experiments were run at constant flux for a period of five days, with an automated

permeation cycle and backwash. The impact of biopolymers on hydraulically reversible and irreversible fouling was of specific interest.

Important seasonal trends were identified for all waters, with biopolymer content increasing at higher temperatures. Useful comparisons could also be made between different treatment processes including conventional and enhanced coagulation. The enhanced process while significantly improving the removal of humic substances, was not beneficial in terms of biopolymer removal, suggesting a different removal mechanism for these two fractions. The removal of low molecular weight ozonation by-products during full scale biofiltration was well demonstrated, and other fractions (building blocks, biopolymers) had varying degrees of removal, which was more dependent on temperature. Principle component analysis (PCA), an advanced multivariate statistical method, was successfully applied to a FEEM data set containing five different waters at varying degrees of treatment. Three principle components related to humic-like, protein-like and particulate/colloidal material were identified, and served as useful complementary information to the LC-OCD results. The humic-like component was found to have relatively good correlation to the humic fraction from LC-OCD analysis, with some deviation in the post-ozonation samples (which underwent greater structural changes not captured by LC-OCD). The biopolymer fraction was shown to have good correlation to hydraulically reversible membrane fouling across all four waters. The same could not be said for hydraulically irreversible fouling for which a combined fouling layer (with particulate and colloidal material) is hypothesized.

This research provides those working in the water treatment sector with greater insight into NOM behaviour during various levels of treatment. As biopolymers were demonstrated to impact hydraulically reversible fouling (relatively independent of water quality), their removal prior to membrane filtration could significantly extend operational cycles by extending time between backwashes, thereby reducing energy requirements. As biopolymers are also suspected in forming a combined fouling layer, their removal can potentially minimize chemical cleaning requirements (and extend the life cycle of the membranes). The

removal of biopolymers through coagulation was well demonstrated. Biofiltration is also expected to perform well as a membrane pre-treatment due its ability to remove biopolymers and particulate/colloidal matter. The ability of biofiltration to control biological re-growth in the distribution system (by removing low molecular weight biodegradable products) was also shown using LC-OCD and FEEM analysis.

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List of Acronyms

AMW: Apparent molecular weight
AOC: Assimilable organic carbon
BDOC: Biodegradable dissolved organic carbon
BOM: Biodegradable organic matter
CA: Cellulose acetate
DBP: Disinfection by-product
DOC: Dissolved organic carbon
EBCT: Empty bed contact time
EDL: Electrical double layer
EfOM: Effluent organic matter
EPS: Extracellular polymeric substances
FA: Fulvic acid
FEEM: Fluorescence excitation emission matrix
FTIR: Fourier transform infrared spectroscopy
GC/MS: Gas chromatography with mass spectra detector
GAC: Granular activated carbon
HA: Humic acid
HMW: High molecular weight
HP-SEC: High pressure size exclusion chromatography
LCOCD: Liquid chromatography organic carbon detection
LMW: Low molecular weight
LPM: Low pressure membrane
MF: Microfiltration
MWCO: Molecular weight cut off
NF: Nanofiltration
NMR: Nuclear magnetic resonance
NOM: Natural organic matter
OND: Organic nitrogen detection
PACL: Polyaluminum chloride

PC: Principal component
PCA: Principal component analysis
PES: Polyethersulfone
POC: Particulate organic carbon
PP: Polypropylene
PS: Polysulfone
PVDF: Polyvinylidene fluoride
RO: Reverse osmosis
SEC: Size exclusion chromatography
SMP: Soluble microbial products
SUVA: Specific ultraviolet absorbance
TOC: Total organic carbon
TMP: Transmembrane pressure
UF: Ultrafiltration
UV: Ultraviolet
UVD: Ultraviolet light detection
UV_{254} : Absorbance of ultraviolet light at a wavelength of 254nm

Chapter 1
Introduction

1.1 Problem Statement

Natural organic matter (NOM) is implicated in some of the major challenges currently facing drinking water treatment. Initially its presence was mostly of aesthetic concern due to its contribution to taste, odour and colour, however as early as the 1970's its role as a precursor to disinfection by-products (DBPs) was recognized, prompting greater interest in its removal. In addition to being a DBP pre-cursor certain NOM fractions act as substrates for biological re-growth in the distribution system, especially after oxidation. Other problems associated with NOM during treatment include higher coagulant demands, transport of metals and hydrophobic chemicals, corrosion during distribution, and the interference in adsorption processes for the removal of other contaminants (Jacangelo et al. 1995). It is recognized that not only the amount of NOM but also its character can have a significant impact on the efficiency of drinking water treatment (Baghoth et al. 2011b) and having a better idea of its composition and associated removal is therefore of interest . Considering that NOM is a complex mixture of thousands of different organic molecules, it is not practical to characterize it in terms of individual constituents and hence it is valuable to group different compounds of similar chemical properties.

Finding appropriate characterizing methods which can describe the behaviour of individual NOM fractions during treatment will ultimately lead to a better understanding of NOM removal and may allow for better selection and optimisation of these processes. Liquid Chromatography Organic- Carbon Detection (LC-OCD) and Fluorescence Excitation Emission Matrix (FEEM) analytical techniques are two relatively new methods that can provide further insight into the nature of NOM. LC-OCD is capable of separating NOM based on apparent molecular weight into fractions of interest including biopolymers (polysaccharides and proteins), humic substances (humic and fulvic acids), building blocks, low molecular weight acids and neutrals (Huber et al.

2011). FEEM spectroscopy acts as an excellent complementary analytical technique, which can identity differences in humic and protein-like composition, while also providing some information relating to the particulate/colloidal material (Peiris et al. 2010).

NOM has also been identified as playing an important role in membrane fouling, which significantly increases operational costs, and remains as a major obstacle for wider implementation (Gao et al. 2011). Different fractions of NOM have been implicated in membrane fouling, but a general consensus on the exact nature of this fouling has still not been reached. In low pressure membrane (LPM) filtration the majority of the material which is deposited on the membrane surface or within the pores (causing fouling), can be removed during backwash (hydraulically reversible). The portion that remains contributes to hydraulically irreversible fouling, and must be removed through chemical cleaning. Although hydraulically irreversible fouling has a significant impact on chemical and maintenance costs, reversible fouling is also a concern due to its impact on operational cycles and backwash frequency (Amy 2008). Using LC-OCD analysis, biopolymers have been shown to act as LPM foulants, contributing to hydraulically reversible fouling during surface water filtration (Hallé et al. 2009). Biopolymer composition (protein content) has also been shown to impact irreversible fouling, in addition to particulate and colloidal content (Peldszus et al. 2011). This work was performed on one water type however, and it remains to be seen whether biopolymer content (and composition) can be used as a predictor for membrane fouling potential across a number of different water types.

1.2 Objectives

To address the above knowledge gaps this research has two major goals;

1. NOM characterizing during full scale drinking water treatment at several different locations
2. Investigating the role of specific NOM fractions in membrane fouling across different waters.

The specific objectives relating to the first major goal are as follows:

- Characterize a range of surface waters with varying raw water characteristics, using LC-OCD and FEEM analysis, to get a better understanding of NOM composition as well as seasonal variability.
- Investigate the removal of specific NOM fractions, through a variety of full scale treatment processes, and determine whether these processes are impacted by seasonal variation in raw water NOM composition. Biofiltration at full scale is of specific interest, as are differences between the filters and the effects of up-stream ozonation.
- Determine how well the results from FEEM analysis relate to the fractions identified using LC-OCD.

The specific objectives of the second major goal are as follows:

- Determine how well hydraulically reversible fouling can be related to the biopolymer content of the different waters with significantly different NOM composition and raw water quality.
- Investigate which NOM fractions are most likely being irreversibly deposited on the membrane surface.
- Determine how well hydraulically irreversible fouling can be related to biopolymer content and evaluate the role of biopolymer composition (protein content using FEEM).

1.3 Thesis Structure

Chapter 2 consists of a literature review to provide an overview of the published material which is relevant to this work. Research needs are identified based on the review, and are presented at the end of the chapter. The remaining chapters were each written as separate articles, and therefore they are intended to stand on their own, providing experimental procedure as well as discussion for the results and conclusions. Chapter 3 is a detailed study of NOM characterization

for six different waters during full scale water treatment over four seasons. Removals through a variety of processes including enhanced coagulation, ozonation, and biofiltration are reported for five full scale facilities. Four of the waters from this investigation were used in the membrane fouling study which is outlined in Chapter 4. Using commercially available bench scale membrane modules, hydraulically reversible and irreversible fouling was assessed in prolonged constant flux experiments which included maintenance cleaning and automated backwash. Chapter 5 presents some of the major implications of the results from Chapters 3 & 4, and offers recommendations for future work.

Chapter 2
Literature Review

2.1 Natural Organic Matter Characterization

Natural organic matter (NOM) is a complex heterogeneous mixture of organic material found in all natural waters. Its presence can be attributed to sources which are both allochthonous (soil derived decaying plant material) and autochthonous (microbial by-products produced in-situ) as well as certain anthropogenic sources (wastewater discharge etc.). NOM composition is highly variable, but is generally expected to consist of six major compound classes including humic substances (humic and fulvic acids), hydrohphilic acids, carboxylic acids, amino acids, carbohydrates and hydrocarbons (Thurman 1985). As it is a variable mixture containing thousands of different chemical constituents, it is not practical to investigate NOM composition on an individual compound basis. It is therefore desirable to group different fractions with similar chemical properties. Many different analytical techniques have been developed to describe NOM composition, each offering certain advantages and disadvantages. Some of the major characterization methods of interest are reviewed in the following sections

2.1.1 Bulk Parameters

Total organic carbon (TOC) is most commonly used as a surrogate parameter to describe the total quantity of NOM. Typically it is measured by oxidizing NOM to carbon dioxide which is quantified using an infrared detector. Dissolved organic carbon (DOC) is operationally defined as the organic carbon which is smaller than 0.45μm, while the content which is larger is referred to as particulate organic carbon (POC). Ultraviolet absorbance at a wavelength of 254nm (UVA_{254}) is also commonly used as a surrogate parameter for NOM, taking advantage of the light absorbing chromophore (often aromatic) structures which will vary depending on composition (Crittenden and MWH, 2005). Other specific wavelengths are also of interest,

including absorbance at 220nm which is associated with carboxylic –like chromophores (Korshin et al. 2009). Specific UV absorbance (SUVA) defined as UVA_{254} divided by DOC in mgC/L is another important parameter which can give some indication of hydrophobicity/hydrophilicity. A water with SUVA>4 is considered to have NOM with greater hydrophobicity (mostly aquatic humics), while a SUVA<2 is indicative of low hydrophobicity (less humic content) (Edzwald and Tobiason, 1999).

2.1.2 Resin Fractionation

Resin fractionation is one of the earlier developed techniques for characterizing NOM, and is still commonly used to distinguish between the hydrophobic and hydrophilic fractions of the DOC. The most widely employed method involves commercially available Amberlite XAD resins which were adopted by the International Humic Substances Society (IHSS) as a standardized way of isolating fulvic (FA) and humic acids (HA) (Matilainen et al. 2011). This approach involves passing organic matter through two specific resins (Amberlite XAD-8 and XAD-4) which are configured in series. The XAD-8 resin adsorbs the hydrophobic material, while the XAD-4 resin adsorbs the weakly hydrophobic fraction (referred to as transphilic), leaving the hydrophilic material (not adsorbing to either) to pass through (Croué 2004; Sharp et al. 2006). Through modification of this method, other researchers have further divided these fractions to include the common classifications outlined in Table 2.1(Source: Swietlik et al. 2004).

Table 2.1: Resin isolated fraction composition (Source: Swietlik et al. 2004)

Fraction	Organic Compound Class	Reference
Humic Acid (HA)	Humic substances fraction which precipitate at pH<1	Peuravuori et al. 1997
Hydrophobic	Soil fulvic acids, C_5-C_9 aliphatic carboxylic acids,	Leenheer 1981; Marhaba

Fraction	Organic Compound Class	Reference
acid (HOA)	1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols	et al. 2000;Aiken et al. 1992
Hydrophobic base (HOB)	Humic substances retained by XAD-8 resin at pH=7 (eluted by HCl); 1- and 2-ring aromatic amines except pyridine, proteinaceous substances	Leenheer 1981; Marhaba et al. 2000
Hydrophobic neutral (HON)	Mix of hydrocarbons; $>C_5$ aliphatic alcohols, amides, esters, ketones, aldehydes; long chain (>C9) aliphatic carboxylic acids and amines; > 3-ring aromatic carboxylic acids and amines	Leenheer 1981; Marhaba et al. 2000
Hydrophilic acid (HIA)	$<C_5$ aliphatic carboxylic acids, polyfunctional carboxylic acids, mixture of various hydroxyl acids	Aiken et al. 1992;Leenheer 1981; Marhaba et al. 2000
Hydrophilic base (HIB)	Amphoteric proteinaceous material containing aliphatic amino acids, amino sugars, peptides and proteins; $<C_9$ aliphatic amines pyridine	Leenheer 1981; Marhaba et al. 2000
Hydrophilic neutral (HIN)	Short chain aliphatic amines, alcohols, aldehydes, esters, ketones; <C5 aliphatic amides; polyfunctional alcohols; carbohydrates; cyclic amides; polysaccharides	Leenheer 1981; Marhaba et al. 2000

Although the composition will vary significantly among sources, humic substances (humic and fulvic acids) are generally recognized as constituting the largest fraction of the DOC (50-75%) and correspond to the hydrophobic material which adsorbs to XAD resin at a pH of 2 (Thurman 1985). The hydrophilic fraction which is not adsorbed generally represents 20 to 30% of the DOC (Croué 2004; Thurman 1985). As many earlier (and some recent) studies characterized NOM using the classifications presented in Table 2.1 it is important to have an understanding of how they relate to other fractions of interest. Leenheer (1981) reported that the hydrophilic neutral (HIN) fraction had similar infrared spectra as polysaccharides, suggesting that a portion of biopolymers (discussed further in section 2.1.4) are part of this classification. This is

consistent with Amy (2008) who stated that if organic colloids (which were found to have a polysaccharide and protein-like identity) were not pre-isolated by dialysis (prior to resin fractionation), they would end up in the hydrophilic fraction. This fraction would also be expected to contain lower molecular weight material, including short chain amines, alcohols, aldehydes, ketones and esters (Leenheer 1981). Croué (2004) used resin fractionation in addition to size exclusion chromatography (SEC) to provide a clearer relationship between the two characterization methods. The authors found that after isolating the large colloids, the remaining hydrophilic material largely consisted of a peak corresponding to low molecular weight acids. They also stated that transphilic material eluted as a shoulder corresponding to low molecular weight aromatic acids. This shoulder appears to be similar to the building block fraction which is defined by LC-OCD analysis (see section 2.1.4). Although resin fractionation has been widely used to characterize NOM, there are important disadvantages which must be considered when using this method. These include physical alterations from pH extremes, irreversible adsorption and contamination from resin bleeding (Matilainen et al. 2011).

2.1.3 Molecular weight distribution (membrane filtration)

Some studies have also characterized NOM by apparent molecular weight (AMW), using progressive filtration through membranes with decreasing pore sizes. Owen et al. (1995) used hydrophilic ultrafiltration membranes (UF) with molecular weight cut offs (MWCO) ranging from 500-30,000Da to describe NOM transformation during treatment. Although the results are useful in describing relative removals of different sized fractions, the limitations of this method have been widely reported (Aiken 1984; Assemi et al. 2004). Amy et al. (1987) found the majority of NOM from a number of natural sources to be in the 500-10,000 and 10,000-20,000 AMW ranges using successive membrane filtration steps. The authors also recognized the inherent problems with this approach, which were associated with adherence of NOM in the membrane pores as well as surface deposition causing non-ideal rejection. Assemi et al. (2004) reported that the results for UF fractionation were not in good agreement with flow field fractionation (chromatography method). The authors suggested that the molecular structure of

organics also impacted rejection, and found significantly smaller fractions being rejected by high MWCO membranes. Although characterization studies using this approach may still be useful, the limitations must be considered when interpreting the results.

2.1.4 High Pressure (Performance) Size Exclusion Chromatography (HP-SEC)

High pressure size exclusion chromatography is a useful and relatively recent tool for separating NOM into different fractions based on apparent molecular weight (AMW) and chemical interaction. This process involves a mobile phase (buffer solution of specific ionic strength containing the dissolved sample) which passes through a stationary phase (polymer or silica based column) where molecules are separated according to their size, shape, and interaction. Large molecules elute first, while smaller molecules elute later (due to greater diffusion into pores of column) and are then measured by means of an online detector (UV-vis, DOC etc.) (Lankes et al. 2009). One specific type of HP-SEC known as liquid chromatography organic carbon detection (LC-OCD) developed by Huber and Frimmel (1991) is increasingly being used due its high degree of sensitivity and minimal sample pre-treatment. Using this instrument, NOM can be characterized in terms of biopolymers, humic substances, building blocks, low molecular weight (LMW) acids and neutrals. The integration boundaries for a typical fresh water chromatogram (organic carbon signal) are illustrated in Figure 2.1 for the various fractions. The LC-OCD instrument also has online ultraviolet detection (UVD) and organic nitrogen detection (OND) which provides additional information which is useful for NOM characterization.

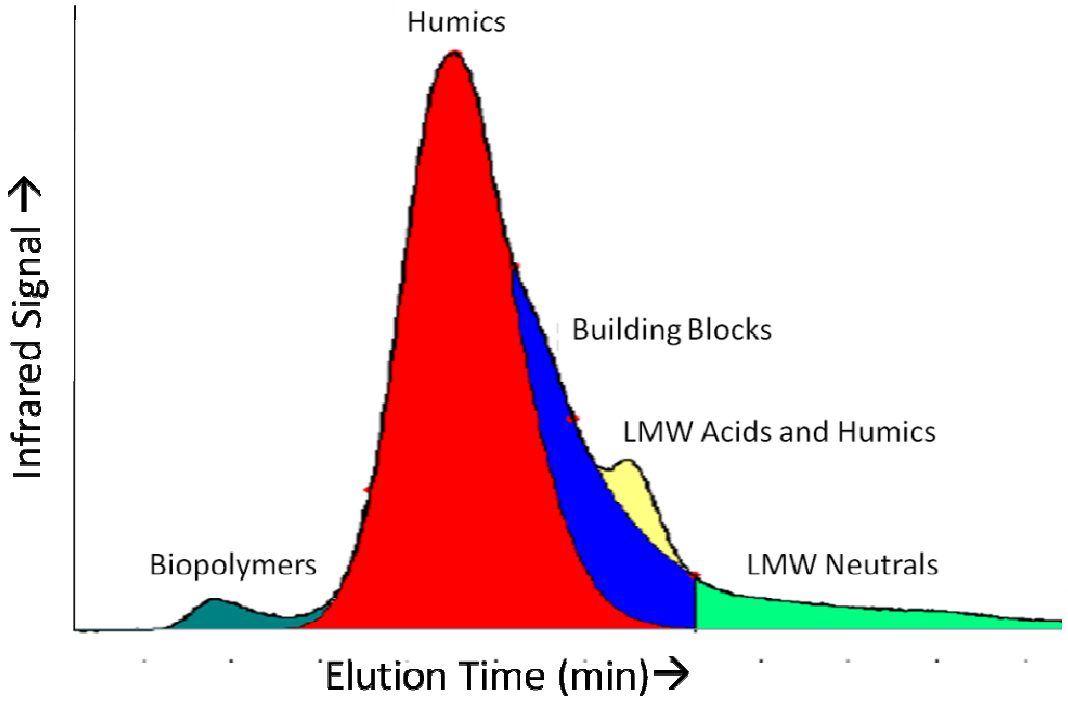


Figure 2.1: LC-OCD chromatogram integration boundaries for different NOM fractions (Source: DOC-Labor Huber; 2010)

Biopolymers are a high molecular weight (>10,000Da) hydrophilic fraction consisting largely of polysaccharide and protein like material (Huber et al. 2011). They are the first fraction to elute from the SEC column, and generally do not respond to UVD due to a lack of unsaturated structures (Huber et al. 2011). Produced through numerous biological processes, biopolymers are the major component of extracellular polymeric substances (EPS), soluble microbial products (SMP) and effluent organic matter (EfOM)(Haberkamp et al. 2011). Polysaccharides make up a large proportion of this material, being used as both a nutrient source (released from living and decaying cells) and structural component for the cell walls of bacteria and algae. Polysaccharides are expected to have greater short term stability, while the protein fraction is known to be more rapidly degraded through biological activity (Flemming and Wingender 2001).

The second fraction to leave the column is the humic substances (humic and fulvic acids) fraction which forms the dominant peak of the LC-OCD chromatogram. The average molecular weight of this group is approximately 1000Da (Velten et al. 2011) however it can be expected to contain molecules up to and greater than 10,000Da (Chadik and Amy, 1988). The humic acids are larger and generally elute first, while fulvic acids are known to be smaller, and contain a higher phenolic and carboxylic content. The humic substances have a significant response in the UV signal, which arises from its aromatic and unsaturated structures (Huber et al. 2011). The building block fraction which elutes as a shoulder to the humic peak consists of the degradation products of the humic substances in the range of 300-450Da and has variable degrees of UV absorbance. The low molecular weight (LMW) acids are an aliphatic fraction which co-elutes with LMW humics as a compressed peak. A correction is made during integration based on UV absorbance (only the LMW humics absorb UV), to differentiate between the two fractions. Finally the LMW neutrals elute last, which are weakly charged hydrophilic or slightly hydrophobic compounds such as alcohols, aldehydes, ketones or amino acids (Huber et al. 2011).

2.1.5 Fluorescence Excitation Emission Matrix (FEEM) and Principal Component Analysis (PCA)

Fluorescence spectroscopy is a superior technique for characterizing NOM when compared to more traditional methods (UV-vis) due to its higher sensitivity and selectivity (Bieroza et al. 2009; Peiris et al. 2010; Matilainen et al. 2011). This method involves the excitation of electrons to higher energy levels by the adsorption of energy (photon of light), and the subsequent fluorescence which occurs as energy loss (emission of light) while the electrons return to their original ground state. The compound structures which absorb light are called chromophores while those that absorb and remit light (fluoresce) are referred to as fluorophores. Three dimensional FEEM data is generated by measuring emitted radiation intensity values at various wavelengths, in response to excitation at different wavelengths. Due to the energy sharing, unpaired electron structure which is characteristic of many aromatic organic compounds, several NOM constituents are readily detected using this process (Hudson et al. 2007). In addition to

humic and fulvic-like material, protein-like (tyrosine and tryptophan-like) substances have also been reported (Baker et al. 2008; Coble 1996; Chen et al. 2003; Liu et al. 2011; Spencer et al. 2007). A summary of intensity peaks which are reported in the literature for different NOM fractions are presented in Table 2.2 (Source: Matilainen et al. 2011).

Table 2.2: Reported excitation-emission ranges for humic and protein-like material (Source: Matilainen et al. 2011)

Excitation Range (nm)	Emission Range (nm)	NOM Component	References
270-280	310-320	Protein (Tyrosine)-like	Coble (1996), Baghoth et al. (2009)
270-285 **(220-235)**	340-360	Protein (Tryptophan)-like	Coble (1996),Spencer et al. (2007), Baker et al. (2008), Hudson et al. (2008), Baghoth et al. (2009)
320-350	400-450	Fulvic-like	Spencer et al. (2007), Baker et al. (2008)
310-320	380-420	Humic-like (Marine)	Coble (1996), Baghoth et al. (2009)
330-390	420-500	Humic-like	Coble (1996),Spencer et al. (2007), Baghoth et al. (2009)

In addition to NOM related intensity peaks FEEM spectra are also known to contain various light scattering regions. Raman scattering which results from the light scattering property of water (vibration of the O-H covalent bond) can be corrected by subtraction using an ultrapure blank (Hudson et al. 2007; Peiris et al. 2010). Colloidal and particulate matter also contribute to light scattering (Stramski and Wozniak 2005), and more specifically Peiris et al. (2010) demonstrated that this relationship is significant in the first and second order Raleigh scattering regions. The typical fluorescence features for the Grand River water reported by Peiris et al. (2010) are outlined in Figure 2.2.

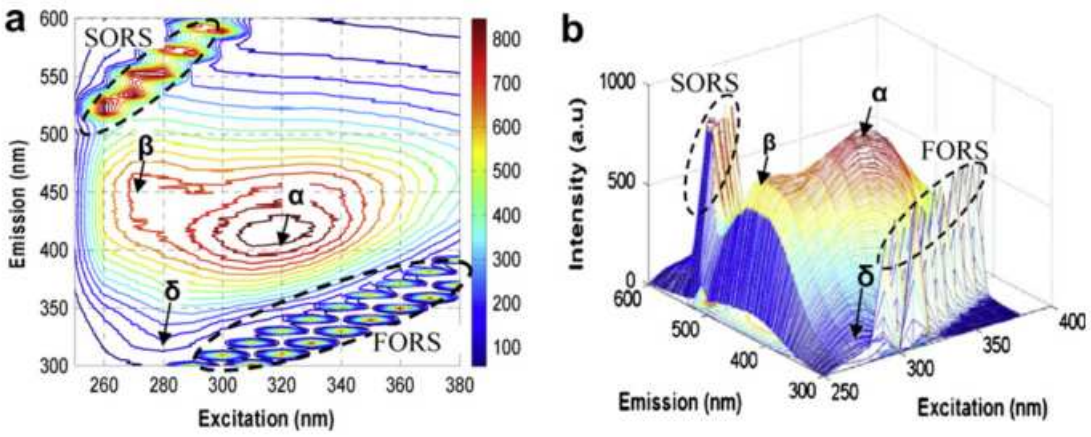


Figure 2.2: Typical FEEM fluorescence features for the Grand River: primary fulvic-like peak (α), secondary humic substances peak (ß), protein-like peak (δ), first and second order Raleigh scattering regions (FORS/SORS) (Peiris et al. 2010)

One of the major challenges in interpreting FEEM spectra is the quantity of data which is generated by scanning such a wide array of wavelength combinations. Traditionally "peak picking" methods have had some success in describing NOM composition differences based on maximum fluorescence intensity values for specific wavelength combinations of interest (Coble 1996, Bieroza et al. 2010; Liu et al. 2011). Due to the heterogeneous nature of NOM however these simplistic methods may not adequately capture the information contained in the full FEEM spectrum which may have more than 10,000 data points. Different investigations have highlighted the importance of analysing the entire spectrum through a variety of advanced data analysis techniques used to decompose multi-dimensional data (Persson and Wedborg 2001; Chen et al. 2003; Stedmon et al. 2003).

Principal component analysis (PCA) is one such technique which is capable of extracting new variables (known as principal components) which are uncorrelated, orthogonal and capture a large portion of variance in the original matrix (Peiris et al. 2010). The model created by PCA

analysis breaks down the original matrix X as the sum of the product of two vectors t_i (scores) and p_i (loadings) with a remaining matrix E(variation not captured by the model) as outlined in Equation 2.1 (Eriksson et al. 2001).

$$X = \sum_{i=1}^{k} t_i \times p_i + E \tag{2.1}$$

The number of linear principal components is selected so that the model describes the physical and chemical differences between the samples while excluding fluctuations due to measurement error. Prior to performing PCA, each three dimensional sample matrix needs to be unfolded into a column matrix (2 dimensions) with each excitation-emission pair being a variable and it's corresponding intensity reading being the dependent variable (Stedmon et al. 2003). The remainder of the analysis is performed within commercially available computer software. The data set is first scaled and mean centered by the program, in order to remove the effects of differences in the magnitude of the numbers and standard deviations. The principal components are then calculated based on the directions of maximum variance, through an iterative approach to minimize the residual error and fit the vector space to the original data set (Persson and Wedborg, 2001). The model can then be cross validated, to determine how well it could be applied to an independent data set. This can be done using a variety of approaches, which normally involve removing a portion of the data and applying a model which is built based on the remaining data set to see how well it can fit the variation.

The physical significance of the loading variables can be assessed after the model results are obtained, by comparing the loading plot (FEEM representation of the loading vector), to see whether it corresponds to regions of interest. Component scores describe how well each new loading variable (i.e. principal component) is reflected in an individual sample, thereby providing a simple comparison basis for differences in FEEM data. Other multivariate data analysis techniques have also been applied to FEEM data including regional integration (Chen et

al. 2003) and PARAFAC analysis (Baghoth et al. 2011a; Stedmon et al. 2003) and have also proved to be useful.

2.1.6 Other NOM characterization methods

Other techniques which have been used to characterize NOM include nuclear magnetic resonance (NMR) spectroscopy, pyrolysis gas chromatography/mass spectrometry (Pyr-GC-MS), and Fourier transform infrared spectroscopy (FTIR) (Croué et al. 2004; Lankes et al. 2008; Frimmel et al. 2004). NMR is capable of detecting certain functional groups of interest (carboxylic structures etc.) by applying a magnetic field and measuring the resonance frequency of different sample nuclei (typically carbon or hydrogen nuclei). FTIR methods are also useful in identifying different functional groups by making use of the absorption spectrum from infrared light (resulting from the vibrational energy of atomic bonds) which acts as specific fingerprint for different compounds (Matilainen et al. 2011). Although these characterization techniques are useful they typically require NOM to be concentrated due to the low concentrations which are normally present in natural waters (Peiris et al. 2008). These methods can also be relatively difficult to interpret due to the similar overlapping spectral features of many different NOM components (Matilainen et al. 2011).

2.2 NOM removal in drinking water treatment

Prior to the 1970's interest in NOM removal was largely driven by the desire to remove colour, as an aesthetic goal for treatment. With the introduction of disinfection by-product regulations however, there has been an increased amount of research to further the understanding of NOM removal (Jacangelo et al. 1995). Typically the processes which are applied to remove NOM include coagulation /flocculation /sedimentation, biofiltration, membrane filtration, activated carbon filtration, advanced oxidation processes and ion exchange resins (MIEX) (Matilainen et al. 2011). A number of these processes are relevant to the current investigation and therefore the related processes for NOM removal are reviewed in the following sections.

2.2.1 Coagulation/Flocculation/Sedimentation

Coagulation has historically been used for de-stabilizing particulate and colloids, but as it is also capable of removing dissolved NOM, it has become important for minimizing DBP formation as well as reducing NOM related aesthetic problems in finished water (taste, odour and colour). It has been demonstrated that for many surface waters, coagulant demand is actually controlled by NOM concentration rather than by turbidity due to its higher charge density (Edzwald 1993; O'Melia et al 1999; Budd et al. 2004). To meet DBP requirements certain water treatment facilities have in fact optimized this process to target NOM removal (through enhanced coagulation). Inorganic salts (usually aluminum or iron based) are typically employed, and when added to water they will dissociate to form trivalent ions (Al3+, Fe3+), which then undergo hydrolysis to form positively charged complexes (Crittenden and MWH, 2005; Matilainen et al. 2010; Edzwald and Tobiason, 1999). Depending on the concentration and pH, these complexes can be either dissolved or precipitate from solution, and are responsible for NOM removal through several mechanisms.

The primary mechanisms for NOM's removal include charge neutralization (or destabilization), entrapment, adsorption and complexation. As NOM composition is highly variable, different mechanisms will apply to different organic fractions (Sharp et al. 2006; Parsons et al. 2004). Due to its predominantly negative charge, positive complexes as well as pre-hydrolyzed positive ions can act to destabilize NOM colloids by reducing the electrical double layer (EDL). The EDL consists of the Helmoltz layer (cations adsorbed to negative surface) and the diffuse layer (excess cations that extend in the bulk solution until electroneutrality is reached). When the EDL is compressed (reduction of charge due to attachment of oppositely charged ions) particles can more easily come together and attach due to Van der Waals forces (Crittenden and MWH, 2005). As this is a particle removal mechanism, it only applies to NOM in particulate or colloidal form, while truly dissolved material is removed by precipitation or co-precipitation (Jacangelo 1995). Adsorption and complexation mechanisms occur when positively charged hydrolysis products form complexes with negatively charged NOM, which can then either precipitate directly or

become adsorbed to precipitated hydroxide solids (O'Melia et al. 1999). Enmeshment (or entrapment) involves the aggregation of these products and is achieved during flocculation. This mechanism occurs more effectively when the hydrolysis products are high molecular weight polymers while the other mechanisms (complexation, adsorption, charge neutralization) have a higher ability to remove NOM when they are of medium polymer or monomer size which occurs when pH is slightly lower than minimum solubility (Yan et al. 2008).

There are several operational factors impacting NOM removal including coagulant type, dose, pH, mixing, temperature, changes in NOM composition and water quality. There has been some indication that ferric based coagulants are superior in terms of NOM removal when compared to aluminum based coagulants (Jacangelo et al. 1995; Matilainen et al. 2010; Budd et al. 2004) although alum is most commonly used in water treatment. Pre-hydrolyzed coagulants (ex. Poly-aluminum chloride (PACL)) are also increasingly being used due to their low temperature dependence and controlled formation of hydrolysis products which are immediately available for coagulation (Edzwald 1993). Organic polyelectrolytes have also been used as coagulant aids, and can be beneficial in terms of organics removal (Matilainen et al. 2010). Generally they are more effective in removing particulate and high molecular weight NOM, while relatively ineffective in removing dissolved NOM, and are not expected to perform as well as a primary coagulant when compared to metal salts (Jacangelo et al. 1995).

The pH has an important impact on NOM removal which arises from its effect on the speciation of certain NOM fractions as well as the hydrolysis products which are formed during coagulation. The carboxyl functional group of the dominant humic fraction for example loses a proton under higher pH conditions causing it to be more negatively charged. The positive charge of the coagulant species is also decreased at higher pH, and therefore coagulation for NOM removal is less effective (Crittenden and MWH, 2005). Therefore the maximum removal occurs under acidic conditions in the range of the iso-electric point of the coagulant and NOM which is pH 4.5-5.5 for iron based coagulants and pH 5-6 for aluminum based coagulants (Sharp et al. 2006). Higher coagulant dosages are required at higher pH, both to overcome the higher NOM

charge density and also to allow for the precipitation of hydroxide products. Enhanced coagulation (optimized for the removal of organics in addition to particles) typically involves pH adjustment as well as higher coagulant dosages, and can provide significantly higher NOM removal (Volk et al. 2000; Bud et al. 2004). Inorganic ions also have an important impact on NOM removal during coagulation. Divalent cations can lower the required coagulant dosage by binding to NOM functional groups, while certain anions (hydroxide, sulfate) compete with anionic NOM for adsorption sites (Jacangelo 1995).

The nature of NOM will also determine how susceptible it is to removal during coagulation. Many studies have reported the effect of hydrophobicity, with the hydrophobic fraction generally identified as having a higher removal (Sharp et al. 2006; Parsons et al. 2004; Edzwald 1993). Hydrophobic acids (humic and fulvic) are known to be more aromatic in nature containing conjugated double bonds which are responsible for light absorption (represented as SUVA). Waters with high SUVA values have been shown to have higher NOM removal during coagulation with SUVA reduction being proportionally higher than overall DOC removal (Volk et al. 2000). The difference in DOC removal for high SUVA (>4) and low SUVA (<2.5) waters is presented in Figure 2.3, which consists of results from a variety of coagulation studies (Parsons et al. 2004).

For high molecular weight organic material, the main mechanism for removal is charge neutralization, while low molecular weight NOM requires adsorption onto hydroxide surfaces and therefore requires higher doses (Matilainen et al. 2010). Generally high molecular weight fractions are more easily removed than low molecular weight NOM (Chadik and Amy 1988; Edzwald 1993) and higher charged fractions are also less amenable to coagulation. Fulvic acids for example which have a higher carboxylic acid and phenolic content (higher charge density) are more difficult to chemically coagulate by charge neutralization than humic acids with their lower charge density (Sharp et al. 2006). Having a good understanding of NOM character will allow for better prediction in its removal during coagulation. The removal of non humic fractions such as biopolymers is not well reported in the literature.

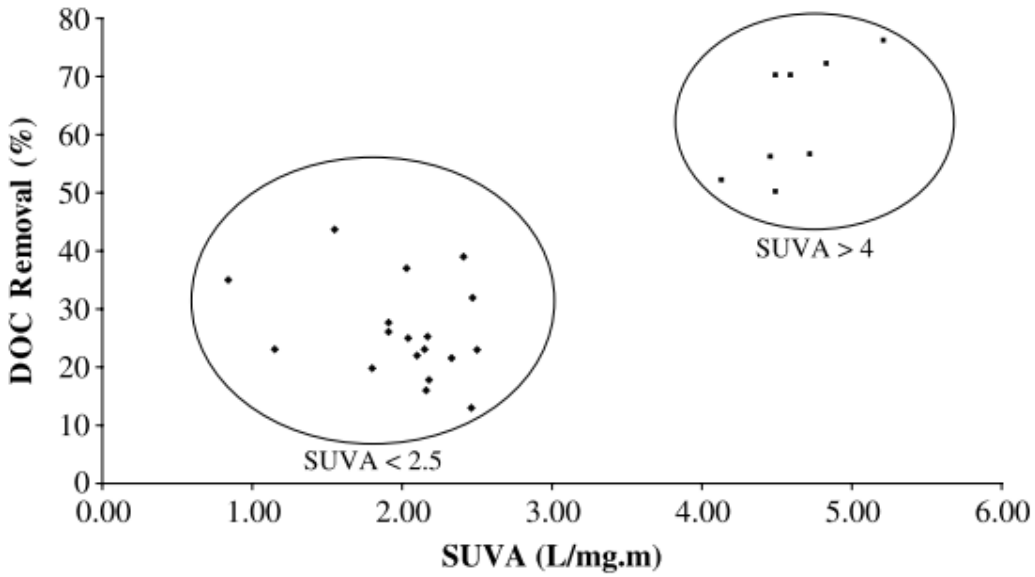


Figure 2.3: SUVA vs. DOC removal (Source: Parsons et al. 2004)

2.2.2 Ozonation

Ozonation is employed in water treatment for a number of purposes including disinfection, taste and odour control, oxidation of iron and manganese, and the removal of colour. Ozone also reacts with NOM to create low molecular weight biodegradable by-products which can cause biological re-growth in distribution systems if left untreated. Additional effects include the loss of double bond and aromatic structure, increase in hydrophilicity and polarity as well as the formation of hydroxyl, carbonyl and carboxyl groups (Urfer et al. 1997). Principal organic ozonation by-products include aldehydes, ketones and carboxylic acids (Westerhoff et al. 1999). When ozone reacts with NOM, hydroxyl radicals are formed and will further react with organic material or other compounds as shown in the following reaction pathway.

$$O_3 + NOM \rightarrow HO\bullet + byproducts$$

$$HO\bullet + NOM \rightarrow byproducts \qquad \text{(Crittenden and MWH, 2005)}$$

The degree of NOM transformation and removal is highly dependent on the ozone dose and specifically its ratio to NOM content. At very high doses (7.5mgO_3/mgC) up to 40% of TOC has been shown to be converted to specific organic acids (oxalic, acetic, fomic etc.), while at lower dosage (<2mgO_3/mgC) these products account for approximately 15% of the TOC (Edwards and Benjamin, 1992). Owen et al. (1995) found little DOC reduction (0-24%) with ozone doses of 1mgO_3/mgC however noted significant reduction in SUVA indicating a change in structural character. The authors also found an increase in assimilable organic carbon (AOC), biodegradable dissolved organic carbon (BDOC) and acidity (6.4 to 12.6 meq/gC) after ozonation, and the degree of by-product formation was thought to be controlled by the original NOM composition. At a similar ozone dose (1mgO_3/mgC) Chandrakanth et al. (1998) reported a significant increase (8 to 43%) in low molecular weight NOM (<500Da) after ozonation, and also found that the production of oxalic acid was correlated to the applied ozone dose. Swietlik et al. (2004) also demonstrated considerable NOM composition change during ozonation, reporting significant reductions in hydrophobic acids (50%) and increases in hydrophilic acids (19%) and bases (7%). In a subsequent study by the same author using both fluorescence spectroscopy and resin fractionation, an increase in small amino acids in the hydrophilic acid and base fractions was also observed following ozonation (Swietlik and Sikorska, 2004). The transformation from hydrophobic material to hydrophilic material was also reported by Marhaba et al. (2000), however this group found the hydrophobic base fraction to have the highest reduction during ozonation. Although ozonation does not normally achieve significant NOM removal, it has important impact on NOM character in water treatment.

2.2.3 Biological Filtration

Biological filtration is an effective treatment process for reducing biodegradable organic matter (BOM), which may otherwise promote biological re-growth in the distribution system. Although

traditionally biological treatment consisted of slow sand or bank filtration, rapid sand filters are also capable of producing biologically stable water while meeting turbidity requirements (Bouwer and Crowe, 1988; Le Chevalier et al. 1992). Additional interest in rapid biological filtration has largely been driven by increased use of ozonation, which results in an increase in NOM biodegradability (Huck et al. 2000; Hozalski et al. 1995). The typical surrogate parameters for BOM include assimilable organic carbon (AOC) and biodegradable organic carbon (BDOC). AOC is a measure of biodegradable material which can be converted to cell mass (reported as a carbon concentration), while BDOC measures the organic carbon which is removed by heterotrophic microorganisms either under batch incubation conditions, or in specialized media columns. Although both measurement techniques are useful in representing BOM, they are both subject to certain limitations (Huck 1990). Having a better understanding of the different fractions which constitute BOM (including humic substances, amino acids, carbohydrates and ozonation by-products) is of interest (Urfer et al. 1997).

A single stage biological filter is essentially a conventional filter which is operated to promote the growth and attachment of heterotrophic bacteria, while still meeting particle removal requirements. Bacteria attach to the filter media in the form of a biofilm, and use BOM as a source of energy and carbon (Huck et al. 2000). Operational parameters can have a significant impact on biological removal including the presence of oxidants (in the influent or backwash), water temperature, empty bed contact time (EBCT), filter media type, filter run time and backwash procedure. Temperature has an impact on microbial kinetics and mass transfer rates and therefore theoretically should have an impact on BOM removal (Urfer et al. 1997). Emelko et al. (2006) demonstrated such a temperature effect, stating that oxalate removals were higher during warmer conditions for both GAC and dual media filters, and also finding GAC media was superior during cold water temperatures. Similarly Krasner et al. (1993) found that glyoxal had higher removals for GAC-sand filtration at higher temperature, and that the time to reach this steady state removal was lower for GAC (compared to anthracite) under lower temperature conditions. Lower biopolymer removal was reported by Hallé et al. (2009) in the winter, and the

operationally defined active phase for the biofilters was found to occur when temperature ranged from 10 to 25°C.

The importance of empty bed contact time (EBCT) has also been highlighted by a number of investigations and is defined as the occupied volume of the filter media divided by the volumetric feed flow rate (Hozalski et al. 1995). Longer EBCTs have been shown to improve the removal of TOC, DOC, AOC and BDOC (Le Chevallier et al. 1992; Huck et al. 2000). Huck et al. (2000) stated that this relationship is less than proportional, and found a diminishing improvement when contact time is increased. The same authors found that easily biodegradable ozonation products require relatively short contact times while the removal of DBP pre-cursors required the longest. The diminishing returns of increased EBCT were also demonstrated theoretically through a kinetic model in a separate study (Zhang and Huck, 1996). The importance of contact time on the removal of biopolymers has also been shown in anthracite-sand pilot scale filters, where EBCT ranged from 5-15min (Peldszus et al. 2012).

The selection of filter media may also impact the performance of biologically active filters. Although the pores of GAC are too small (1-100nm) for the growth of bacteria (>200nm), its irregular surface provides added protection from shear stress (during backwash).Its specific surface area for attachment is lower than that of sand however (Urfer et al. 1997). Huck et al. (2000) concluded that media type (anthracite vs. GAC) did not have a major impact on removals at higher temperatures, however GAC performed better under cold water conditions. GAC was also found to be more resilient to shock due to chlorination and periods when the filters were out of service. Conversely, Le Chevallier et al. (1992) did find that GAC-sand filters had slightly better performance considering AOC removal than anthracite-sand filters, and also found better GAC performance at lower temperatures. The authors of this study recognized however that the GAC media may not have been fully exhausted in terms of adsorption capacity, and attributed some of the AOC removal benefit to this. Krasner et al. (1993) also concluded that the biological population in GAC was more resilient to operational perturbations, and stated that biological activity developed sooner for this media.

Biological filters need to be backwashed properly to remove the build-up of solids, but also to minimize the detachment of biomass which may impair performance. Some studies have found that while conventional performance parameters depend on backwash procedure, BOM removal is not very sensitive to these conditions (Emelko et al. 2006). It has been demonstrated that a significant amount of biomass is not lost during backwash (Servais et al. 1991), which suggests that it has better attachment than non-biological particles (Urfer et al. 1997). Filter run time has been shown to have an impact on BOM removal which might be caused by solids building up and inhibiting bacterial activity (Prévost et al. 1995) and therefore the backwash frequency is also important. The effect of chlorine in backwash water has also been investigated. Miltner et al. (1995) concluded that chlorine in the backwash may only have a small impact on BOM removals, although it does significantly lower the amount of biomass (measured as phospholipids) especially in the top portion of the filters. Similarly Huck et al. (2000) found no measurable impact of chlorine in backwash water for the removal of oxalate, AOC or DOC in a GAC/sand filters, however did observe some effects for anthracite/sand.

2.3 Membrane Filtration

2.3.1 Background

Membrane filtration is increasingly becoming an attractive technology for water treatment. Depending on the application (turbidity reduction, organics removal, softening, desalination etc.), there are generally four types of membranes commonly used in the provision of drinking water; Microfiltration (MF), Ultrafiltration(UF), Nanofiltration (NF) and Reverse Osmosis(RO) (Viessman et al. 2009). Lower pressure membranes (MF and UF) which act as effective barriers against bacteria and parasites have lower energy input requirements, while high pressure membranes are relatively energy intensive. High pressure membranes are more typically used for desalination applications as they are able to remove dissolved organic material and inorganic salts. In addition to removing colloids, bacteria, and parasites, UF membranes are also capable of achieving varying degrees of virus removal (Jacangelo et al. 1995b; AWWA 2005). The

general pore size range and level of rejection for the different membrane types are presented in Figure 2.4. While MF membranes are typically rated in terms of pore size, the lower porosity membranes are more often rated in terms of molecular weight cutoff (MWCO). The retention ratings of UF membranes have been reported between 1000 Da to 500,000 Da (Crittenden and MWH, 2005).

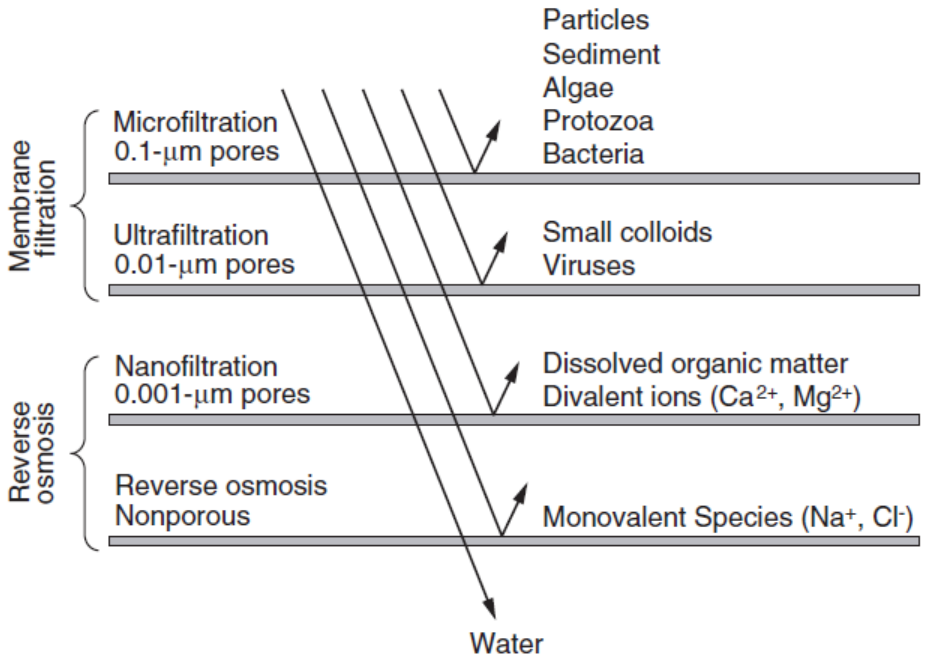


Figure 2.4: Summary of different membrane removals (Source: Crittenden and MWH, 2005).

Low pressure membrane (LPM) filtration consists of pushing water through a porous material by means of a pressure gradient otherwise known as trans-membrane pressure (TMP). Water passing the membrane is referred to as permeate, while the remaining concentrated fraction is known as the retentate. The specific rate of permeation (typically reported in units of L/m^2*hr), is called flux. While many configurations are possible (flat sheet, tubular, spiral wound), hollow fibre membranes are increasingly becoming the most common in water treatment using LPM (AWWA, 2005). Hollow fibre membranes can either be submerged (for vacuum driven

permeation) or configured in pressurized vessels. As deposited material builds up on, and within the membrane, it subsequently causes a loss in productivity (increase in required TMP to maintain constant flux or declining flux at constant pressure) and is referred to as fouling (Zularism et al. 2006). LPM fouling can be controlled by periodic backwashing involving flow reversal and is often accompanied by an air scour (will be discussed further based on membrane fouling in the following section).

Important mechanisms for particle removal during membrane filtration include straining, cake layer formation and adsorption. Straining is the process by which the particles or molecules which are larger than the membrane pores are retained, while smaller constituents pass through. Considering non uniform pore size distribution and tortuosity, electrostatic interactions, as well as the varying orientation and flexibility of many macromolecules, there is evidently no absolute rejection which can be stated for particles/molecules which are in the same size order as the membrane pores. For UF membranes MWCO is normally based on the molecular weight at which 90% rejection is achieved for dextran solutions (Crittenden et al. 2005). NOM can also become adsorbed on the membrane surface or within the membrane pores which can provide rejection of smaller dissolved organic matter (Jucker and Clark 1994). This also causes further constriction of the membrane pores which increases resistance to flux. Finally cake layer formation consists of the deposited solids which were rejected by the membrane, and provides additional filtration (and rejection) on the surface of the membrane. These mechanisms are represented in the modified Darcy's law equation for flux decline, which is dependent on TMP, viscosity and membrane resistance.

$$J = \frac{1}{A}\frac{dV}{dt} = \frac{\Delta P}{\mu(R_m + R_t)} \qquad (2.2)$$

Where J= Flux (L /m^2 *hr)

ΔP=Transmembrane pressure drop (bar) (AWWA 2005)

μ =dynamic viscosity (kg/m*s)

R_m = Clean water membrane resistance (m^{-1})

R_t = Total fouling resistance (due to pore blocking, adsorption and cake layer) (m^{-1})

As flux is related to water viscosity, it also has a strong dependence on temperature. Flux can be corrected to ambient temperature (20^oC) using equation 1.3. Flux can also be further normalized by dividing it by the applied TMP to obtain specific flux (also called permeability).

$$J_{20} = J_{ambient} \times \frac{\mu_{ambient}}{\mu_{20}} \qquad (2.3) \quad \text{(AWWA 2005)}$$

In addition to pore size and MWCO, important membrane properties include material composition, pure water permeability, contact angle, zeta potential (surface charge) and surface roughness (Amy 2008). Contact angle is a measure of the hydrophobicity/ hydrophilicity of the membrane surface which is quantified by the angle between the surface of a water droplet and the membrane. Hydrophobic materials have high contact angles while hydrophilic surfaces have low contact angles (Lee et al. 2004). Due to their non-polar nature, hydrophobic materials "dislike" water and also tend to be more prone to fouling than membranes which are more hydrophilic (Zularism et al. 2006, Laine et al. 1989). LPMs are typically made of synthetic polymers (polymeric) or ceramic material. Some common polymeric materials include polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES), polypropylene (PP) and cellulose acetate (CA) which each offer certain advantages/ disadvantages in terms of hydrophilicity and chemical resistance. CA membranes for example are hydrophilic making them resistant to fouling, however they can only be used in the presence of low oxidant concentrations (AWWA 2005). PVDF which is relatively hydrophobic is increasingly being used due to its high strength, durability and chemical resistance (Kennedy et al. 2008, Huang et al. 2007). Membrane surface charge and roughness also have an impact on fouling. Many membranes are negatively charged and therefore have varying degrees of repulsion with NOM

and particles which are also predominately negatively charged. Rough membranes have also been shown to experience greater fouling than smooth surfaces (Crittenden and MWH, 2005).

2.3.2 Membrane Fouling

Although the use of low pressure membranes for the production of drinking water continues to grow, membrane fouling still remains as a significant operational challenge, as it increases maintenance and energy costs (Gao et al. 2011). LPM fouling can be both hydraulically reversible and irreversible depending on whether permeability can be recovered after backwash. The majority of the hydraulically irreversible fouling can be removed through chemical cleaning (chemically reversible) and a very small portion will remain as truly irreversible fouling as illustrated in Figure 2.5. Although hydraulically irreversible fouling has a significant impact on chemical and maintenance costs, reversible fouling is also a concern due to its impact on operational cycles and backwash frequency (Amy 2008).

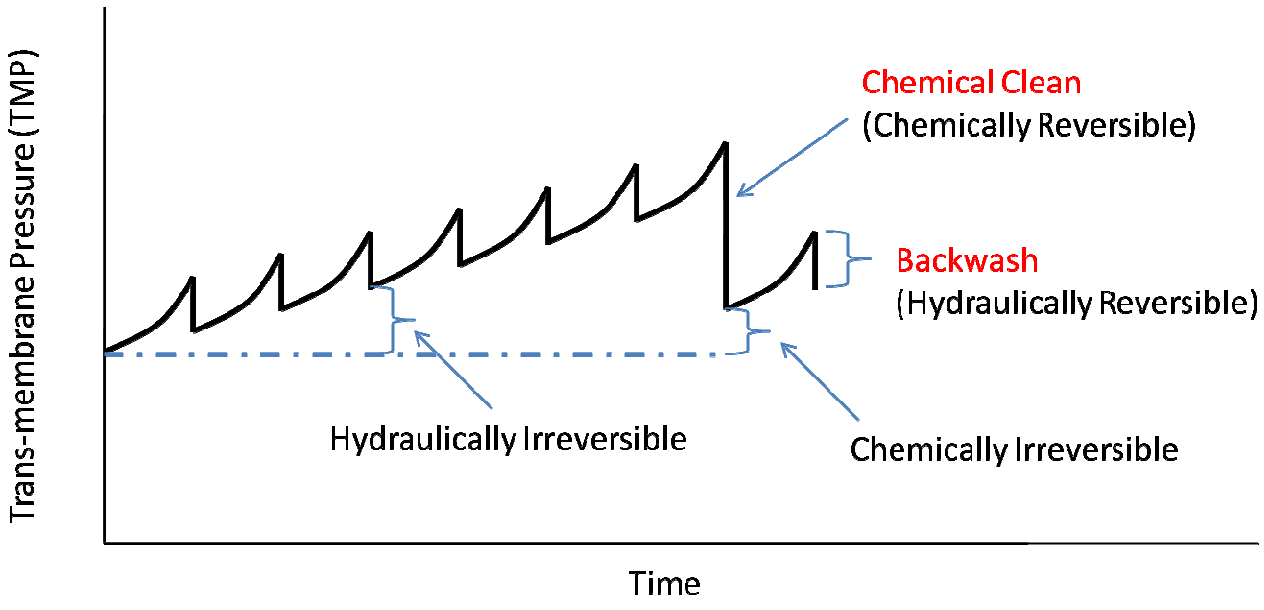


Figure 2.5: Fouling components during constant flux LPM filtration

There are generally four types of fouling classifications including organic fouling, inorganic fouling (scaling), colloidal fouling and bio-fouling (Amy, 2008). Inorganic fouling occurs when the solubility of inorganic salts is exceeded near the surface of the membrane (due to concentration) which can result in precipitation and subsequent scaling. As the pores of low pressure membranes allow easy passage of inorganic ions, significant inorganic fouling is not to be expected. This type of fouling is more often encountered in high pressure membrane filtration, where higher rejection of multivalent ions is achieved (Li and Elimelech, 2006). Bio-fouling is associated with the growth of microorganisms on the membrane surface forming a gel layer known as biofilm. This is achieved by the release of extracellular polymeric substances (EPS) (polysaccharides, glycoproteins, lipoproteins etc.) which adhere to the membrane and act to hold the biofilm together causing significant problems in terms of fouling (Flemming et al. 1997). Bio-fouling is of increased importance in wastewater applications (bioreactors), and is generally controlled through chlorinated backwash in drinking water treatment (Crittenden and MWH, 2005).

Natural organic matter (NOM) which has already been described in detail plays an integral role in fouling of UF membranes during surface water filtration (Amy and Cho, 1999). As humic substances often comprise the largest fraction of NOM, many early investigations for both surface and wastewater focused on its role in irreversible fouling. Jucker and Clark (1994) who used humic substances from the Suwannee River found that there was significant humic adsorption on different UF membrane types with varying hydrophilicity, surface roughness, and zeta potential. They also concluded that higher calcium content and lower pH increased this adsorption. Similarly Combe et al. (1999) demonstrated significant humic adsorptive fouling on UF membranes with surface modification, however concluded that decreased hydrophobicity and increased negative charge did not significantly reduce this adsorption. The importance of the carboxyl functional group of the humic substances was proposed by Lin et al (2001), who found its contribution to flux decline to be greater than that of fractions with more phenolic character and emphasized the importance of ionic strength. Other research groups also highlighted the

significance of solution chemistry (pH, ionic strength) in contributing to the degree of humic adsorptive flux decline (Jones and O'Melia, 2001). While these early investigations were able provide important insight into the behaviour of humic material during membrane filtration, the humic solutions may not accurately reflect the complexity of natural waters which are known to contain higher molecular weight hydrophilic fractions (polysaccharides and proteins) as well as inorganic particulates. More recent studies continue to investigate the role of humic substances in UF fouling (Mousa 2007; Sutzkover et al. 2010) however it is important to note that they often use membranes with lower MWCO (20-150kDa), and that typically looser membranes are employed in practice.

Further investigations using model solutions which included not only humic substances but also surrogates for inorganic particulate (or colloids) and high molecular weight (HMW) hydrophilic material, were able to improve the understanding of the contributions and synergistic effects of these compounds to a certain extent. Such an investigation was performed by Jermann et al. (2008), who used humic acid (2mgC/L), alginate (0.2mgC/L) and kaolinite (100mg/L) as part of a synthetic solution which was subjected to filtration through flat sheet PES filters. The most detrimental flux decline was found to be due to a synergistic effect between NOM and the colloidal particles (kaolinite), while kaolinite alone did not cause significant fouling. They also concluded that polysaccharides (alginate) were responsible for initial pore blocking and subsequent cake layer formation. A similar investigation performed by Zularism et al. (2011) made comparable conclusions concerning synergistic effects, and identified the hydrophilic surrogate material (dextran) as being the most detrimental foulant due to adsorptive fouling mechanisms.

Model solution experiments can be very helpful in elucidating fouling mechanisms due to their controlled nature, however they may not fully capture the complexity of natural waters, which are heterogeneous mixtures of NOM components as well as inorganic particles of varying sizes. Using a number of natural waters (and membrane types) Howe and Clark (2002) demonstrated that the majority of observed UF fouling was caused by small colloids (3-20nm), which were

both inorganic and organic in origin. Similarly, Lee et al. (2004) attributed the majority of flux decline in their investigation using natural waters to large hydrophilic organic colloids and macromolecules. Both of these investigations however were run over short periods of time at constant pressure, and only the second study simulated backwash by "turning over" the flat sheet membranes to investigate permeability recovery. In practice irreversible fouling layers form over prolonged periods of time, and therefore neither investigation was able to significantly differentiate between hydraulically reversible and irreversible fouling. In a study using Chitose river water (Japan) polysaccharides were identified as being responsible for irreversible fouling on UF membrane fibres from a pilot plant that had been in operation for over five months (Kimura et al. 2004). Making use of FTIR analytical methods and a series of cleanings of fouled membrane fibres with various chemical reagents the authors concluded that polysaccharide like material was responsible for irreversibly fouling the membrane.

The importance of biopolymers (polysaccharides and proteins) in surface water was further confirmed by Hallé et al. (2009), who found that the reduction of this fraction through direct biofiltration pre-treatment had a significant impact on the degree of hydraulically reversible and irreversible fouling in commercially available UF membranes. These results were also demonstrated at pilot scale in an investigation which was performed over a two year period (Peldszus et al. 2012).The authors stated that the composition (specifically protein content) rather than the absolute concentration may be more important for hydraulically irreversible fouling. This was later confirmed using FEEM data and PCA to correlate protein content to irreversible fouling under normal operating conditions. The authors also recognized the possible role of colloidal/particulate matter in forming a combined fouling layer, which in addition to protein content contributed to irreversible fouling. Similar conclusions were made in an investigation using wastewater effluent (Haberkamp et al. 2011) where total biopolymer concentration was also well correlated to hydraulically reversible fouling. An earlier study using both wastewater effluent and surface water with two different membrane types(PES and PVDF) also found hydraulically reversible fouling was related to colloidal/HMW NOM (Huang et al. 2007).

2.4 Research Needs

2.4.1 NOM characterization through full scale water treatment

Although many studies have contributed to the current understanding of NOM removal during drinking water treatment, the introduction of more sophisticated analytical techniques has provided greater opportunities for furthering this understanding. LC-OCD is a relatively new analytical tool available for NOM characterization, and has the potential to accurately quantify a number of NOM fractions which were previously poorly defined. Recently a limited number of studies have investigated NOM removal through full scale drinking water treatment using LC-OCD (Baghoth et al. 2011a; Baghoth et al. 2009; Kalibbala et al. 2011) however they typically only focus on one water source and treatment location. To get a better understanding of the impact which NOM character has on its removal, it would be beneficial to compare multiple waters with significantly different NOM compositions. Sampling multiple treatment locations would also provide important information relating to the effectiveness of different treatment processes (enhanced vs. conventional coagulation etc.) on different water types. As LC-OCD analysis has proved to be useful in quantifying the degradation of biopolymers during direct pilot scale biofiltration (Peldszus et al. 2012), it would also be beneficial to relate this to full scale biofiltration (evaluating the effects of upstream processes). The removal of biodegradable LC-OCD fractions for full scale biological filtration is not apparent in the literature, and it would be useful to investigate the effects of ozonation on this process.

Similarly there are a limited number of investigations which have used FEEM analysis to characterize NOM removal during treatment (Bieroza et al. 2010) and which have applied multivariate data analysis techniques (PARAFAC) to this data (Baghoth et al. 2011a; Baghoth et al. 2011b). As FEEM may be capable of serving as an online (or near online) monitoring tool for NOM removal (Bieroza et al. 2010; Peiris et al. 2010), having reliable data analysis techniques is of interest. Peiris et al. (2010) demonstrated that PCA of FEEM spectra could be used to monitor the performance of membrane pre-treatment (biofiltration) as well as UF and NF. PCA

has not been applied to NOM removal during full scale water treatment however, where it may also serve as an important tool for assessing performance. Typically only one water source is included while performing PCA, however having a model which could describe NOM removal for multiple water types would also be beneficial.

2.4.2 Role of NOM in membrane fouling

It is apparent in the current literature that a general consensus on the relative contributions of different organic and inorganic constituents to LPM fouling has not yet been achieved. Many earlier investigations highlighted the importance of humic substances (Combe et al. 1999; Jones and O'Melia, 2001; Jucker and Clark, 1994) in fouling, and some studies continue to report their significance (Mousa 2007; Sutzkover et al. 2010) albeit for tighter UF membranes. More recently, the role of HMW hydrophilics (polysaccharides etc.) has been reported, using model solutions (Jermann et al. 2008; Zularism et al. 2011), and in some small bench scale flat sheet studies using natural surface water (Lee et al. 2004). The role of biopolymers in the fouling of commercially available hollow fibre membranes using Grand River water was demonstrated by Hallé et al. (2009), especially in terms of hydraulically reversible fouling. The impact of biopolymer composition (protein content) on hydraulically irreversible fouling using FEEM analysis was later confirmed (Peldszus et al. 2011). It remains to be seen however if the absolute biopolymer concentration and its composition can be used to predict membrane fouling potential across a number of different natural water types, with different NOM and inorganic compositions. If biopolymer content (and composition) alone (or in combination with other readily available water quality parameters) can be used as a predictor for membrane fouling potential, this may reduce the need for long term pilot studies.

Chapter 3
NOM Characterization in Full Scale Water Treatment

This chapter is based on an article with the title “Using LCOCD and FEEM analyses in parallel to better understand differences in raw water NOM and its removal during treatment” submitted for potential publication in a scientific journal in August 2012. As such, it contains individual sections including introduction, materials and methods, results and conclusions. More detailed background is provided in Chapter 2, while Chapter 5 discusses some implications of this work for the water treatment industry. References are consolidated in the bibliography at the end of the thesis.

3.1 Introduction

Natural organic matter (NOM) has a significant impact on water treatment. Its heterogeneous nature makes it especially difficult to characterize, as it is a complex mixture of organic molecules with varying sizes and functional groups (Thurman 1985). Having a good understanding of its character is important in predicting removal efficiency as well as minimising adverse reactions at different stages of treatment. NOM quantification parameters which are most commonly used in drinking water treatment include total organic carbon (TOC), dissolved organic carbon (DOC) and absorption of UV light (UVA_{254}). These traditional parameters however provide only limited insight into NOM character (Matilainen et al. 2010). Specific UV absorbance (SUVA) (defined as UVA_{254} divided by DOC in mgC/L) can provide some indication of NOM character in terms of aromaticity (Chandrakanth et al. 1998).

More sophisticated characterization techniques such as resin fractionation and high pressure size exclusion chromatography (HP-SEC) have also been used to separate NOM according to hydrophobicity, hydrophilicity and apparent molecular weight (Croué 2004; Swietlik et al. 2004). A specific type of HP-SEC known as Liquid Chromatography Organic Carbon Detection

(LC-OCD) developed by Huber and Frimmel (1991) has recently gained popularity due to its high degree of sensitivity and minimal sample pre-treatment. It is capable of separating NOM into different distinct fractions of the DOC; biopolymers (polysaccharides and protein-like material), humic substances (humic and fulvic acids), building blocks, low molecular weight (LMW) acids and neutrals (Huber et al. 2011).

Fluorescence excitation-emission matrix (FEEM) spectroscopy has also been widely used in NOM characterisation and has been applied to both natural and treated waters (Her et al. 2003; Baghoth et al. 2011a). This technique is capable of identifying both humic and protein-like material as well as providing information on the nature of colloidal and particulate matter (Peiris et al. 2010). Multivariate data analysis such as principal component analysis (PCA) (Peiris et al. 2010), or parallel factor analysis (PARAFAC) (Stedmon et al. 2003) have been used to capture different NOM fractions in complex FEEM spectra.

Although some studies have investigated NOM characteristics in water treatment (Allpike et al. 2005; Baghoth et al. 2011a), there is generally a lack of understanding of the change in NOM character across different stages of treatment (Baghoth et al. 2009). With the complex data sets being generated using FEEM, reliable data analysis techniques which can be applied to multiple water types also need to be further investigated. The concurrent use of LC-OCD and FEEM can exploit their complementary nature and assist in identifying limitations associated with the use of only one technique. The current study does this and, unlike most studies that focus on one water, includes FEEM data for multiple waters at different stages of treatment. The application of PCA (vs. other types of data analysis) to this type of data set is also unique and biofiltration was of specific interest. The waters investigated are representative of many other waters internationally and include several Great Lakes.

3.2 Materials and Methods

3.2.1 Sampling Description

Five full scale drinking water treatment facilities located in Southern Ontario, Canada were monitored over a period of eight to sixteen months (February 2011 to June 2012), depending on the location. The surface water treatment plants had both river (Grand River and Ottawa River) and lake (Lake Ontario, Lake Erie and Lake Huron) water sources. In addition, a raw river (Saugeen River) water source was also monitored during the study. Each location was sampled approximately every six to eight weeks. In addition to LC-OCD and FEEM analysis, TOC, DOC, UVA_{254}, pH, conductivity and turbidity measurements were also taken for each sample. All locations employed granular media filtration with some individual differences as presented in Table 3.1.

Table 3.1: Treatment Facility Description

Location	Ottawa River	Grand River	Lake Ontario	Lake Erie	Lake Huron
Treatment Processes	Enhanced Coagulation, Flocculation, Sedimentation, (Bio) Filtration	Coagulation, Flocculation, Sedimentation, Ozonation, (Bio) Filtration	Pre-chlorination Coagulation, Flocculation, Sedimentation, Filtration	Seasonal PAC addition (taste and odour)Coagulation, Flocculation, Sedimentation, Pre-chlorination Filtration	Coagulation, Sand Ballasted Assisted Flocculation, Sedimentation, Pre-chlorination, Filtration
Treatment Flow (m^3/s)	1.6-2.2	0.40-0.70	2.9-7.4	0.41-0.77	0.032-0.089
Coagulant Description	Alum (Sulfuric pH adjustment), Silicate	PACL, Polymer	Alum	Acidified Alum, Polymer	Acidified Alum, Polymer, Silicate
Average pH	5.8	7.7	7.5	7.1	7.3
Average Dose(mg/L)	31	25	7	37	24

Location	Ottawa River	Grand River	Lake Ontario	Lake Erie	Lake Huron
Filter Media	Filter 2 &3: 560mm (A) 300mm (S)	Filter 1&2: 1070mm (G)	Filter 1,2,7,8: 457mm(A) 305mm(S)	Filter 1,2,3,4: 457mm(A) 305mm(S)	Filter 1,2,3,4: 457mm(A) 305mm(S)
Anthracite (A)	Filter 14&17 610mm (A)	Filter 3: 1280(G)			
Sand (S)	460mm (S)	Filter4: 1280(A)			
GAC (G)		All: 300mm (S)			

3.2.2 LC-OCD

Liquid Chromatography Organic Carbon Detection – Organic Nitrogen Detection (LC-OCD-OND – DOC-Labor Dr. Huber, Karlsruhe/Germany) was performed using a HW-50S SEC column (Tosoh Bioscience Tokyo/ Japan). The mobile phase (purified phosphate buffer) is delivered along with the sample to the column using a HPLC pump, where the sample is fractionated according to molecular size. Non-destructive UV detection (UVD) is performed ahead of OCD and OND, allowing for the analysis of SUVA for specific fractions. NOM is oxidized to CO_2 using UV light within the Gräentzel thin film reactor, and is then measured using an infrared detector. A side stream is diverted after UVD which enters a 4m long helical capillary, where organically bound nitrogen is converted to NO_3 and measured using a UV (220nm) detector (Huber et al. 2011). Integration of the chromatograms generated by this instrument was done using the customized ChromCALC software (DOC-Labor). LC-OCD samples were filtered through 0.45µm PES filters within 24hrs of sampling and stored at a temperature of 4^{o}C before being processed (generally within 48hrs of sampling).

3.2.3 FEEM

FEEM results were obtained for the samples taken between August 8, 2011 and June 14, 2012 using a Varian Cary Eclipse Fluorescence Spectrofluorometer (Palo Alto, CA). 301 Emission Intensities (between 300-600nm) at 10nm increments of Excitation wavelengths (between 250 and 380nm) were measured. The spectra obtained for MQ ultrapure water was subtracted from all sample spectra to account for Raman scattering and all samples were measured at room temperature (22^{o}C) within 48h of sampling. Disposable UV-grade polymethlmethacrylate (PMMA) cuvettes were used for this analysis. Sample pH ranged from 5.5 to 8.4 and no pH adjustment was made prior to analysis. Spencer et al. (2007) concluded that significant intensity changes only occurred at pH extremes, and that differences in moderate pH ranges (6 to 8) were minimal. They also stated that adjusting the pH to common values was not recommended, as NOM from different waters responds differently to these pH changes. Little difference in the FEEM spectrum (and PC scores) was observed in the current investigation when the pH was altered from 6 to 8 (using NaOH) for Ottawa River water. The decision was therefore made to run all samples under natural pH conditions. Inner filtering and fluorescence quenching caused by high DOC concentrations were also thought to be negligible due to much lower concentrations (1.6-7.6mgC/L) in this study than the 25mgC/L limit reported by Hudson et al. (2008).

3.2.4 Treatment of FEEM data

Data pre-treatment was performed using the procedure outlined by Peiris et al. (2010). Each sample FEEM contained 4214 intensity values which were unfolded from the initial sample matrix into a single column form. A total of 188 FEEM samples were taken over the course of the investigation (Fluorescence analysis was initiated only after LC-OCD procedures were established and began on August 8th 2011). Seven samples were removed due to problems with the instrument (missing intensity values), and sixty nine samples needed to be removed due to a peak that arose from contamination in the cuvettes. The original batch of cuvettes(with some

contamination) was used in the Fall of 2011 and early Winter of 2012, and hence many samples from this period needed to be removed. The PCA analysis therefore included a total of 112 samples, each representing a column in the 112×4214 matrix for which PCA was performed. PCA is capable of extracting new variables (known as principal components) which are uncorrelated, orthogonal and capture a large portion of variance in the original matrix. The model created by PCA analysis breaks down the original matrix X as the sum of the product of two vectors t_i (scores) and p_i (loadings) with a remaining matrix E(variation not captured by the model) as outlined in Equation 3.1 (Eriksson et al. 2001).

$$X = \sum_{i=1}^{k} t_i \times p_i + E \qquad (3.1)$$

3.2.5 Additional Parameters

TOC and DOC were measured using an OI-Analytical TOC analyzer (model 1010, College Station,TX) by wet oxidation as described in Standard Methods (2012) 5310D.Conductivity was determined using a conductivity meter (Hach 44600) following Standard Methods (2012)2510.Turbidity was taken from online readings given at the treatment plants and using a turbidity meter (Hach 2100P) following the Standard Method (2012) 2130 when online data was not available. UV was measured using a spectrophotometer (Hewlett Packard 8453) as described in Standard Methods (2012) 5910. A 5cm path cell was used to increase the precision as the majority of the samples had low absorption (<0.15cm^{-1}).

3.3 Results and Discussion

3.3.1 Raw Water Comparison for LC-OCD NOM fractions of six different waters

The three river waters were characterized by higher TOC when compared to the three Great Lakes Waters (Table 3.2). Significant seasonal temperature variations were recorded as sampling

covered both summer and winter months. High turbidity conditions were consistently observed for the Lake Erie water (6.1-240NTU), while the other waters had moderate to low turbidity variation (0.54-16NTU). The Saugeen and Grand River had the highest SUVA variation (2.4-3.5L/mg*m), which was consistent with the higher TOC variability (2.7-6.8mgC/L) for these waters. The lake waters conversely had much lower, stable SUVA (0.57-1.3L/mg*m). The Ottawa River was relatively unique with low pH (6.9-7.1), conductivity (6.7-8.1mS/m) and high SUVA (3.5-3.7L/mg*m).

Table 3.2: Raw water characteristics during sampling

Location	Ottawa River	Grand River	Lake Ontario	Lake Erie	Lake Huron	Saugeen River
Temperature (^{o}C)	0.60 - 21	2.0 - 25	3.0 - 17	2.1 - 17	1.2 - 22	0.50 - 22
TOC/DOC (mg/L)	6.2 - 7.6 /6.1 - 7.6	5.0 - 6.8 /4.8 - 6.7	1.8 - 2.4 /1.8 - 2.3	1.9 - 2.2 /1.9 - 2.2	1.6 - 2.1 /1.6 - 2.0	2.7 - 6.8 /2.7 - 6.7
Turbidity (NTU)	2.2 - 4.2	1.9 - 12	0.13 - 1.1	6.1 - 240	0.54 - 16	3.0 - 6.5
pH	6.9 - 7.3	7.8 - 8.3	7.6 - 8.2	7.6 - 8.0	7.6 - 8.2	8.0 - 8.2
Conductivity (mS/m)	6.7 - 8.1	51 - 74	29 - 34	25 - 30	19 - 23	45-61
SUVA (L/mg*m)	3.5 - 3.7	2.5 - 3.3	1.0 - 1.3	1.0 - 1.2	0.57 - 1.0	2.4 - 3.5

All of the waters surveyed had biopolymer concentrations within a similar order of magnitude (100-710 μgC/L), with the highest concentration being encountered in the Grand River (source significantly impacted by municipal and agricultural activity) (Figure 3.1). The Ottawa River which, was found to have the highest humic content, of the surveyed waters, had one of the lowest biopolymer concentrations. Compared to the river waters, the lake waters contained a proportionally higher content of biopolymers (12-21% of the DOC in the lake waters vs. 3-11% in the river waters). This is important in the context of water treatment, as biopolymers have

been shown to play an important role in fouling of low pressure membranes (Hallé et al. 2009).The relatively high content of biopolymers (105-365µgC/L) in the lake waters was not necessarily expected. Thurman (1985) reported that carbohydrates (mainly in the form of polysaccharides) accounted for 5-10% DOC in river waters and 8-12% DOC in lake waters (however biopolymers are expected to contain both polysaccharides and protein like material). As LC-OCD is a relatively new characterization technique, there is still relatively limited information on the composition of different types of surface waters in terms of these newly-defined fractions.

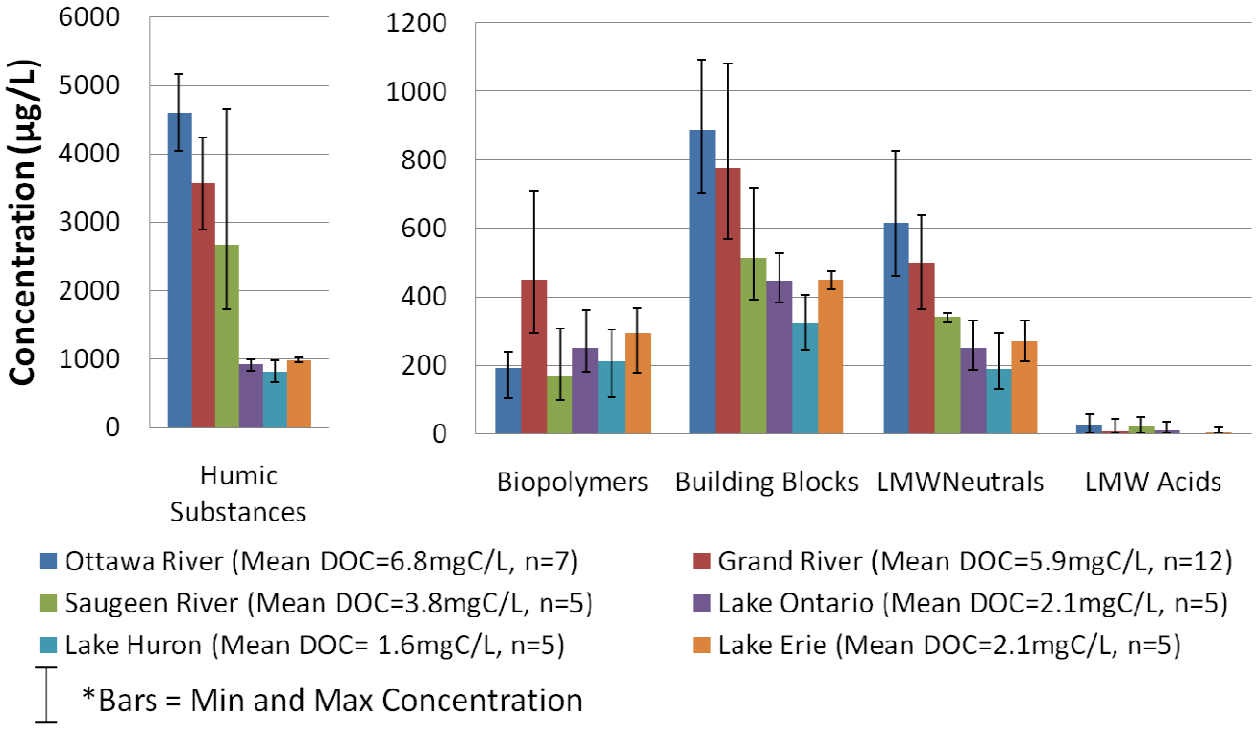


Figure 3.1: LC-OCD fractions for six raw waters over four seasons

Humic material was the dominant fraction in all waters, accounting for 53-77% and 41-56% of the bulk DOC in the river and lake waters respectively. It has been widely reported that the humic fraction typically accounts for 50-75% of the total DOC (Thurman 1985; Marhaba et al. 2000). The higher humic concentrations (1730-5160µgC/L) in the river waters compared to the lake waters (660-1020µgC/L) appear to be largely predicted by higher SUVA for these waters.

Further insight into the character of the humic fraction can be gained by the humic substances diagram developed by Huber et al. (2011) presented in Figure 3.2. All of the river waters surveyed are in the fulvic acid region and are largely allochthonous (soil derived) in origin based on their higher aromaticity and molecular weight. The lake waters consist rather of autochthonous FA material derived in-situ which is characteristic of low aromaticity and a lower molecular weight (Her et al. 2002).

Building blocks and low molecular weight neutrals followed similar trends to the humic substances with higher concentrations in the river waters. Low molecular weight (LMW) acids accounted for less than 0.8% of the total DOC in the raw waters, and were often not detected. Low detection of this fraction using LC-OCD was also reported by Baghoth et al. (2009), who suggested this was likely due to co-elution with LMW humic substances, and lack of distinction between the two during integration (software performs calculation based on UV-absorption of this fraction).

Biopolymer content varied seasonally with temperature as shown in Figure 3.3. Seasonal biopolymer fluctuations ranged from 139μgC/L in the Ottawa River to 417μgC/L in the Grand River with higher concentrations being observed in the warmer summer months. This trend is likely due to greater microbial activity within the waters at the higher temperatures causing a greater primary production of microbiological by-products. Greater concentrations of polysaccharides were reported by Sachse et al. (2001) for Lake Große Fuchskuhle near Berlin in July and August using SEC. In contrast, Haberkamp (2008) noted lower biopolymer concentrations in treated sewage effluent in the summer, and attributed this to greater biodegradation of biopolymers in the wastewater treatment plant at higher temperatures. The greater production of biopolymers in the Grand River is thought to be related to contributions from agricultural activity and municipal wastewater effluents upstream of the sampling location, which would have provided greater nutrients for microorganisms. In some cases an increase in temperature over a period of months did not result in a direct increase in biopolymer

concentration (Lake Huron, Grand River), suggesting there may be a delayed response in terms of biopolymer production in the water body. It also appears that there are annual differences in terms of biopolymer production as biopolymer concentrations in June of 2012 were much higher than the previous year. Humic content was not found to fluctuate significantly with changes in seasonal temperature. This was especially true for the lake water sources which had less than 20% variation in terms of mean concentration.

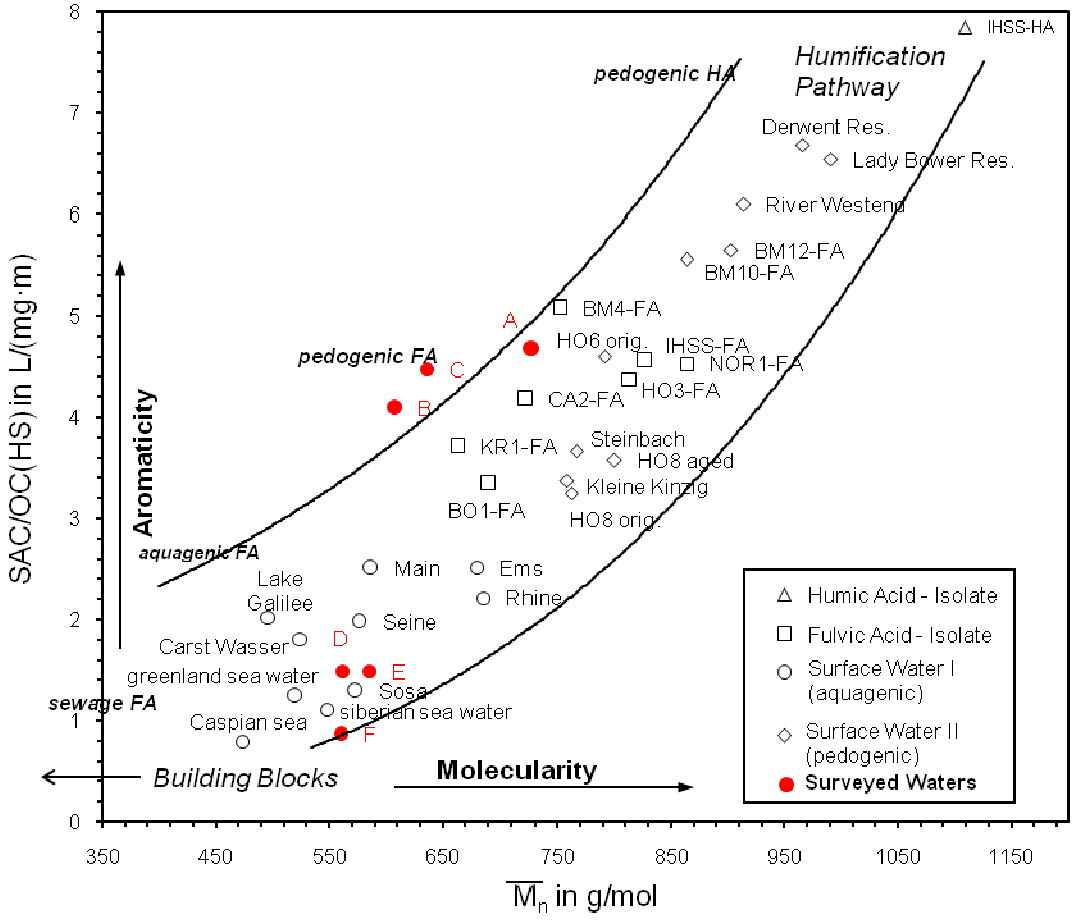


Figure 3.2: Humic Substances Diagram (Huber et al. 2011) for the Ottawa River (A), Grand River (B), Saugeen River (C), Lake Erie (D), Lake Ontario (E), Lake Huron (F) in terms of average molecular weight(M_n) and SUVA of the humic fraction

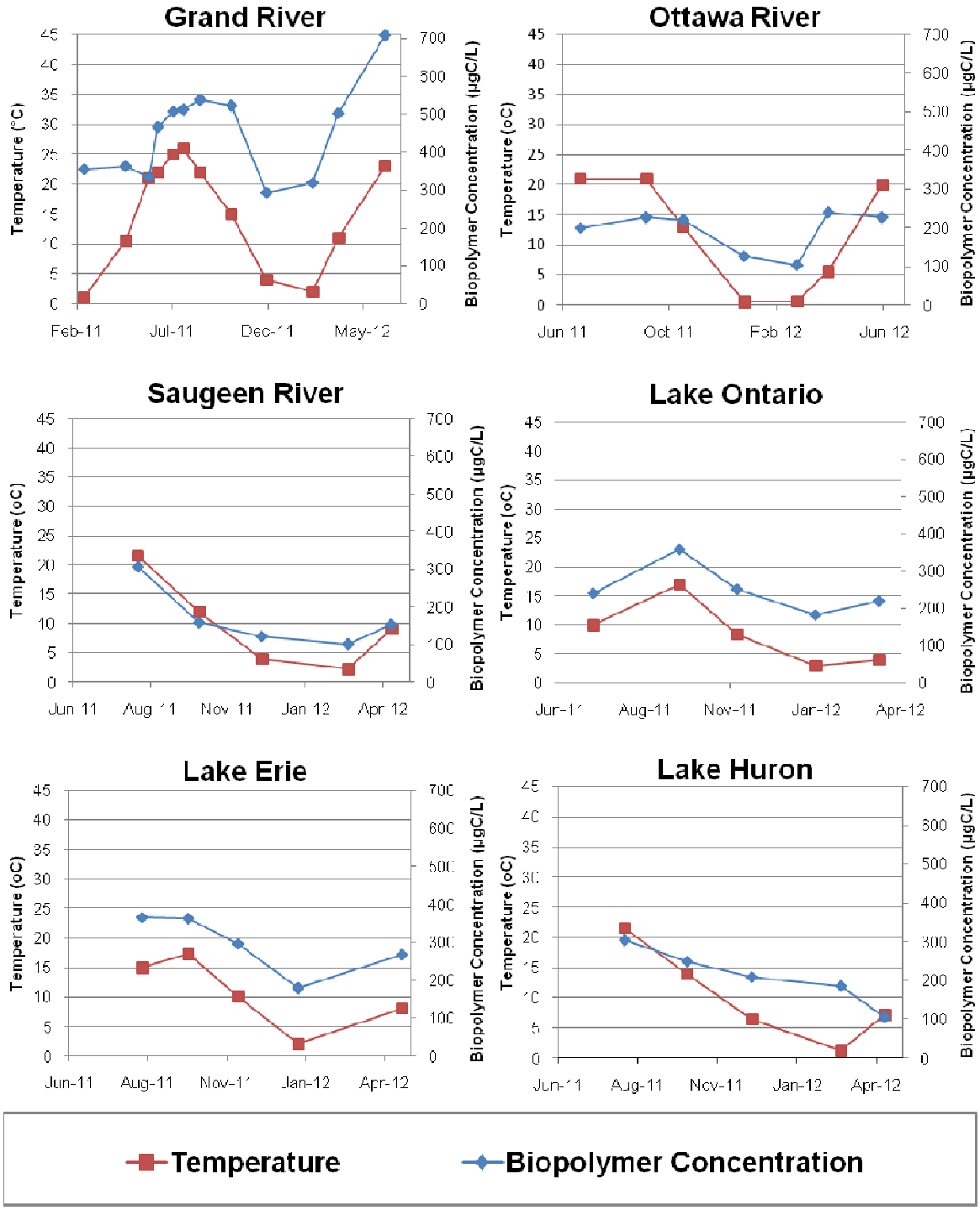


Figure 3.3: Seasonal Biopolymer Changes in Six Water Sources

The variation in humic content was more visible in the river water sources, with the Saugeen River displaying the highest fluctuation (1.5-4.5mgC/L) in the fall season. This may have been caused by the observed increase in runoff during this period, and differences in the contributions of allochthonous material from the catchment area. The importance of rain events in the fall months for the Nanaimo River (British Columbia, Canada) caused by leaf litter has been reported to cause significant increases in transported allochthonous DOC (Thurman, 1985). As the Saugeen River is the smallest river surveyed, it may have been more heavily impacted by similar factors. The limited number of sampling points prevents further elucidation of these results.

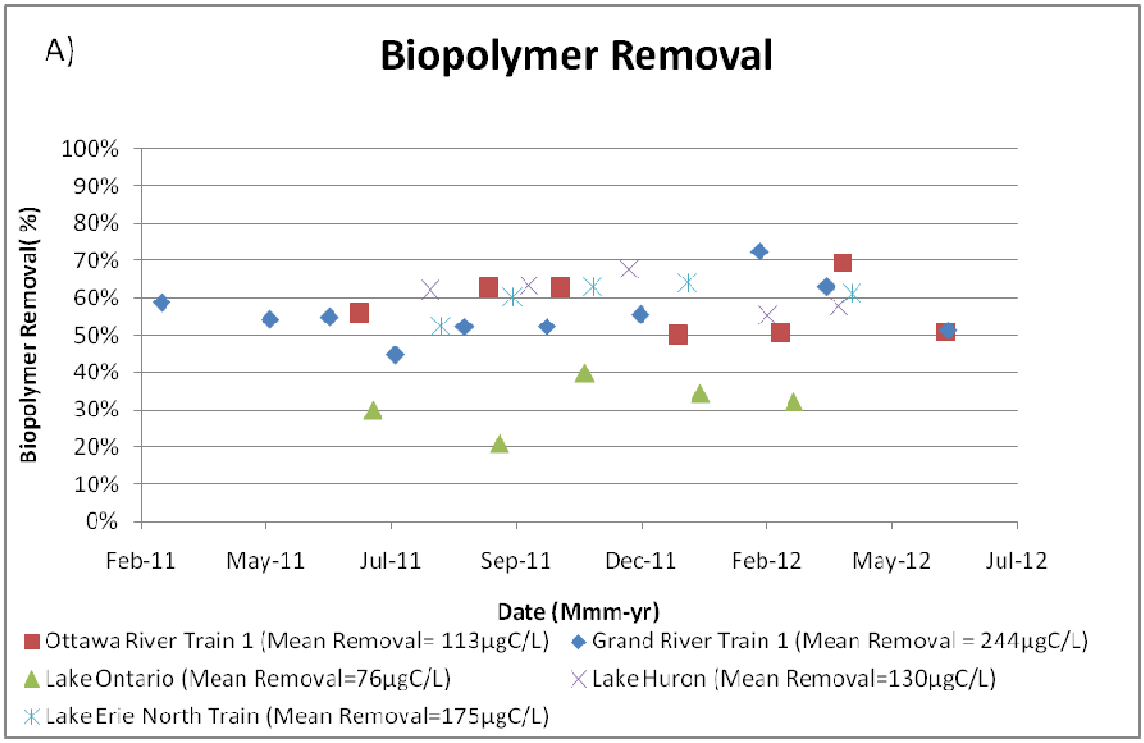
3.3.2 LC-OCD NOM Fraction Removal through Coagulation/Flocculation/ Sedimentation

Biopolymers were generally well removed by coagulation/flocculation/sedimentation. Approximately 45 to 73% was removed in all treatment plants excluding the Lake Ontario location (Figure 3.4) (note: percentage removals were plotted for biopolymer fraction as there was significant seasonal variation). The Lake Ontario plant had a lower removal (21-40%), and was the only plant not to use a coagulant aid or acidified alum. It is important to note that this plant employed lower coagulant dosages (5-9mg/L) and had a higher average pH (7.5) during coagulation.

The use of enhanced coagulation at the Ottawa River location did not appear to improve biopolymer removal although it did significantly improve the removal of the humic fraction (Figure 3.4, 58-78% vs. 8-52% removal). The removal of the humic fraction may be more dependent on pH and coagulant dose. Humic and fulvic acids are known to have a high charge density arising from phenolic and carboxylic functional groups, making them more amenable to charge neutralization (Owen et al. 1995). This mechanism may be more important for the removal of the humic fraction compared to that of the biopolymers. Excluding the enhanced coagulation results, it appears that biopolymers (largest molecular size) are the most preferentially removed fraction through coagulation/flocculation/sedimentation. A contributing

factor may be that, due to their larger size, they may be more easily adsorbed by particles during flocculation. An investigation using treated sewage effluent (Haberkamp et al. 2007) also attributed preferential removal of the biopolymer fraction to co-precipitation, and found the protein content to be especially amenable to this process. The chromatograms for the Grand River treatment plant (Figure 3.5) show that larger humic substances are more easily removed than the smaller humic fractions. This is consistent with the results of Baghoth et al. (2011b), who also used LC OCD. Other studies using different characterization techniques (isolation, SEC with UV detection) have also reached similar conclusions (Jacangelo et al. 1995; Chadik and Amy 1988; Sinsabaugh et al. 1986).

Removal of both biopolymers and humic content is relatively consistent throughout the year. Building block removal was lower than that for the other two larger fractions, and low molecular weight neutrals were essentially not removed through any of the treatment processes investigated.



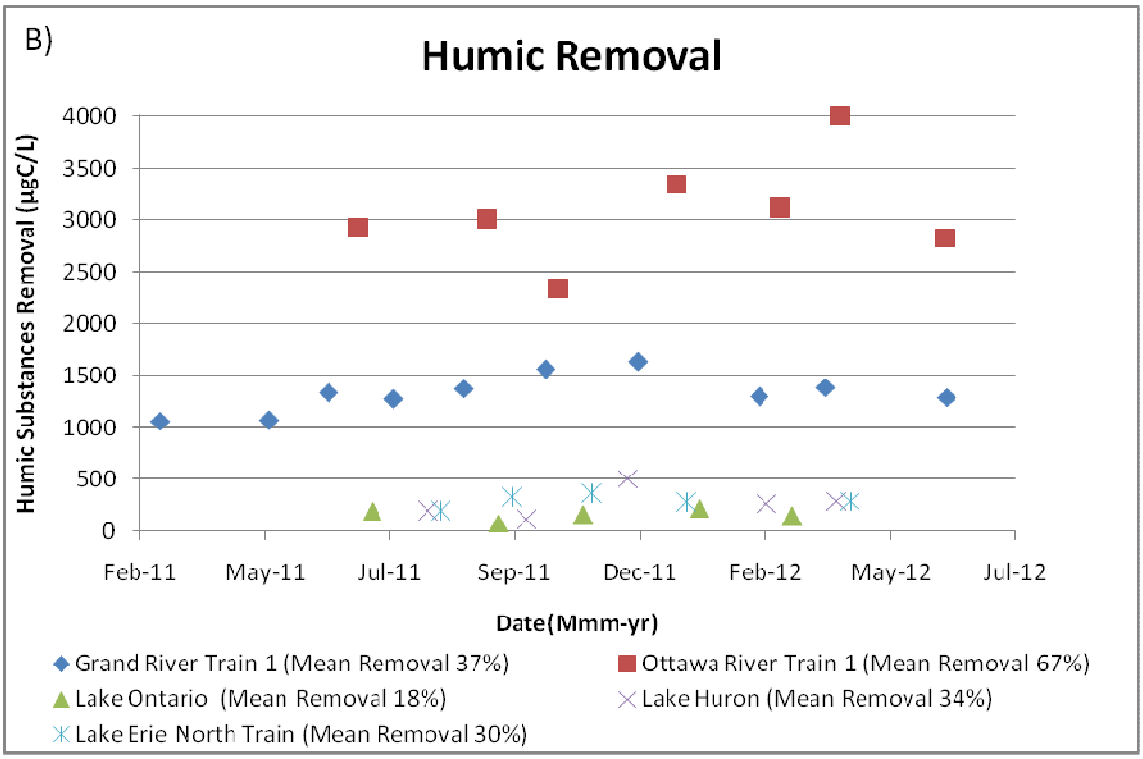


Figure 3.4: Removal of Biopolymer (A) and Humic Fractions (B) through Coagulation, Flocculation and Sedimentation

Similar trends to those which were observed for humic removal through coagulation were seen for SUVA reduction (results not shown). SUVA reduction was not however directly quantitatively correlated to humic removal and was often lower than the humic substances removal results using LC-OCD.

3.3.3 Effect of Ozonation on LC-OCD NOM Fractions

LC-OCD chromatograms for the Grand River treatment process (the only one employing ozonation) are shown in Figure 3.5. Biopolymers and humic substances had an average decrease of 9% and 11% respectively after ozonation, while lower molecular weight (LMW) acids and humic material were consistently generated during ozonation and removed during full scale biofiltration. On average 90µgC/L of LMW acids were produced after ozonation indicating that

the larger molecular weight humic and biopolymer fractions were being oxidized into lower molecular weight hydrophilic material. Other studies looking at the effects of ozonation on NOM have also reported a decomposition of higher molecular weight fractions, in part generating lower molecular weight, hydrophilic by-products such as aldehydes and carboxylic acids (Chandrakanth et al. 1998 using isolation; Swielik et al. 2004 using GC/ECD and HPSEC with UVD).

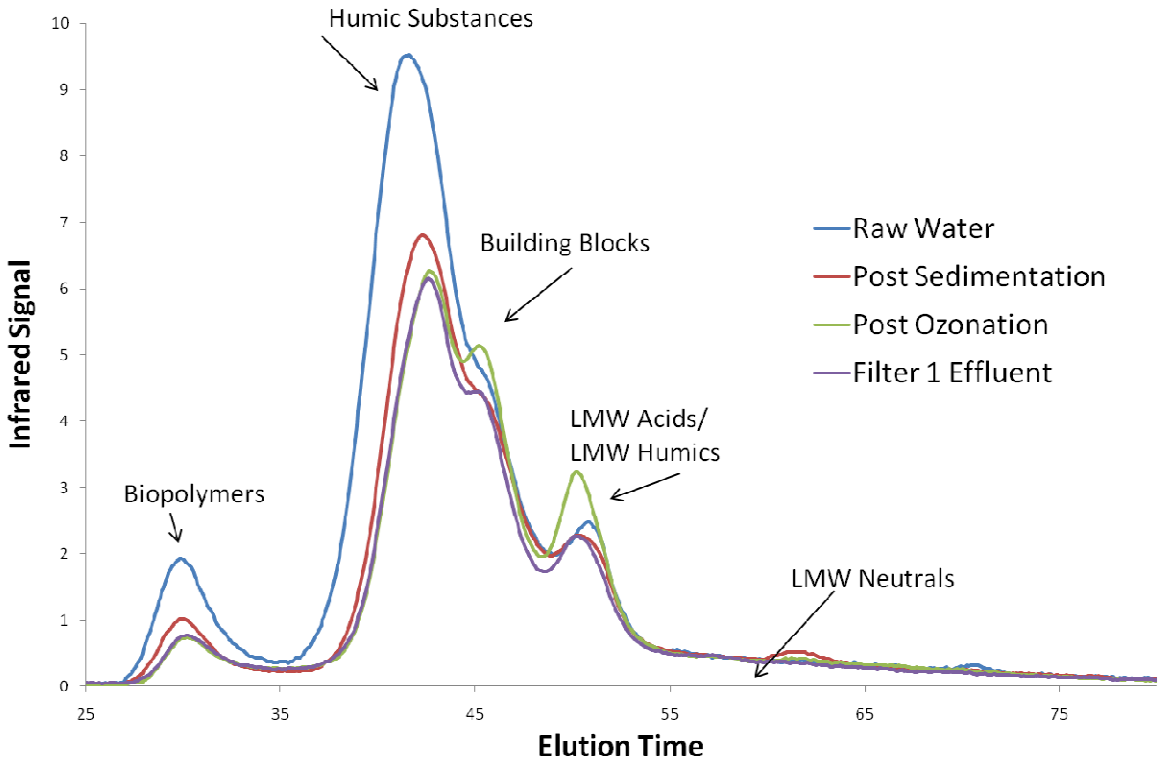


Figure 3.5: LC-OCD Chromatograms for Grand River Treatment Process

3.3.4 Removal of LC-OCD NOM Fractions Through Biofiltration

LMW acids generated during ozonation were largely biodegraded in the filters at the Grand River treatment location (Figure 3.6). The mean removal was 84%, with up to 100% removal being achieved in some instances. The full scale filters differed in both media type (GAC in

Filters 1-3 vs. Anthracite in Filter 4) and to some degree media depth (Filters 1 =1727mm, Filter 2= 1753mm, Filter 3= 1626mm, Filter 4=1575mm). There does not however, appear to be a consistent superior LMW acid removal performance by any one of the filters. As BOM is known to increase after ozonation and be removed during biofiltration (Huck et al. 2000), it is reasonable to conclude that the LMW acid fraction may contribute to traditional BOM measurements (AOC and BDOC). Earlier studies performed on the filters at the Grand River location(media since topped up/changed) found no measurable difference in BDOC removal between anthracite and GAC media, however GAC was found to give better performance in removing specific BOM components (oxalate) at temperatures below 5^0C (Huck et al. 2000). This temperature effect was not observed for LMW acid removal, however it is important to note that only two sampling days had temperatures below 5^0C. The study performed by Huck et al (2000) also found increasing BOM removals with increasing EBCT, however the effects were less than proportional. Since filter depth varied at most by 10% at the Grand River facility, it was likely not substantial enough to observe performance differences.

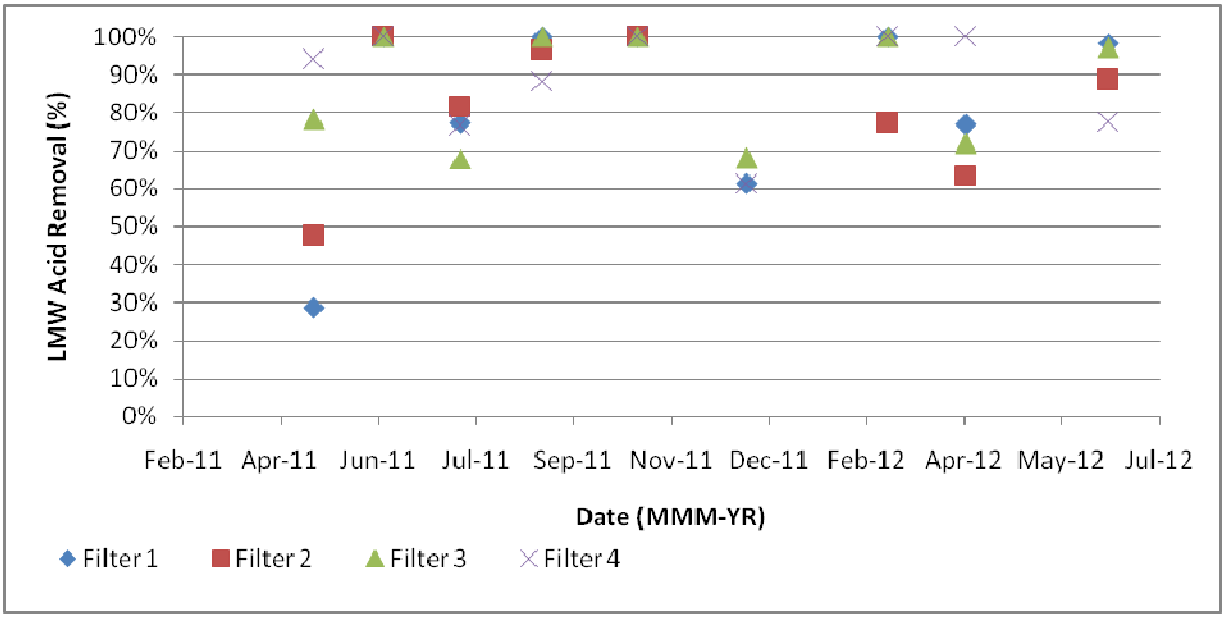


Figure 3.6: LMW Acid Removal through Filtration at the Grand River Treatment Facility

Building block material produced during ozonation was also observed to be partially biodegraded through the filters (Figure 3.7). The mean removal (10%) was much lower however than for LMW acids. Removal efficiency was reduced at lower temperatures. It is possible that this fraction was less easily biodegraded due to structural differences (larger, more aromatic), and had greater temperature dependence. Grünheid et al. (2005) found that under aerobic conditions, aliphatic carbon sources are preferentially used (vs. aromatic structures under anaerobic conditions). It is likely that this fraction was more aliphatic in nature after ozonation at the Grand River location, and therefore had better removal. A similar trend was also noted for the building block fraction at the Ottawa River location (Figure 3.8), however absolute removals were lower (126µgC/L mean removal for Grand River vs. 19µgC/L at Ottawa River). This is likely because the Ottawa River facility did not employ ozonation prior to filtration and therefore the fraction may have been less biodegradable. Similar seasonal trends for building block removals through filtration were observed at the Ottawa River location, with higher removals being observed at higher temperatures (14% mean removal for T> 10^{o}C, and -6% for T<10^{o}C).

Seasonal differences in biopolymer removal were observed during biofiltration at the Ottawa River location (Figure 3.9, 16% mean removal for T> 10^{o}C, -2% for T<10^{o}C). Once again there were differences in media depth (and hence EBCT) for the Ottawa filters (Filters 2&3: 86mm, Filters 14&17: 107mm) however superior performance by the deeper beds was not apparent. A seasonal difference in biopolymer removal through biofiltration was not visible at the Grand River facility. As ozonation is practiced ahead of filtration, it may be possible that the microbial community is acclimated to easily biodegradable fractions (LMW acids, building blocks etc.), and therefore preferentially removes this material over biopolymers. It is also important to note that chlorine residual was present in the backwash water at this location and that EBCTs were lower (9.8-20min) when compared to the Ottawa River location (16-29min). An earlier study performed by Huck et al. (2000) concluded that for GAC/sand filters (at the Grand River

location) the removal of oxalate, AOC and DOC was not impacted by the presence of chlorine in the backwash water. There was some indication of a greater impact on the anthracite/sand filters, but the authors emphasized that the difference was minimal. Filter 4 (anthracite/sand) often had the lowest biopolymer removal compared to the other filters (GAC/sand) in the current investigation as well, suggesting that the difference in media type may have had a small impact on biopolymer removal.

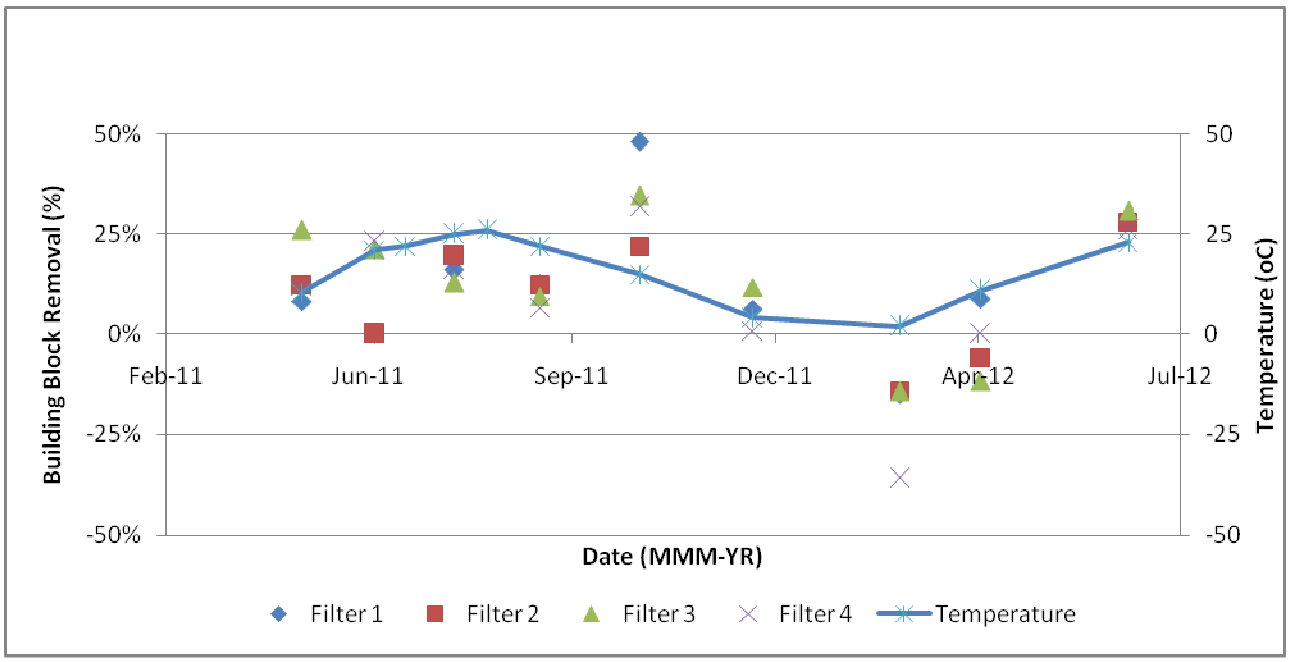


Figure 3.7: Building Block Removal at the Grand River Location

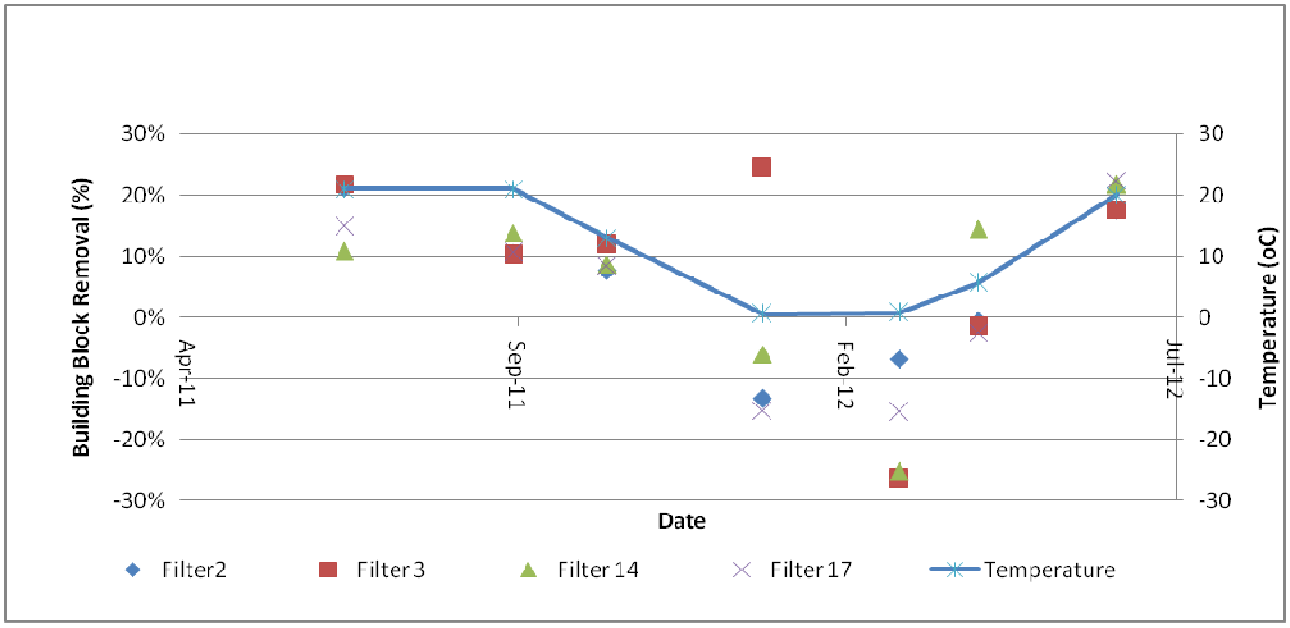


Figure 3.8: Building Block Removal at the Ottawa River Location

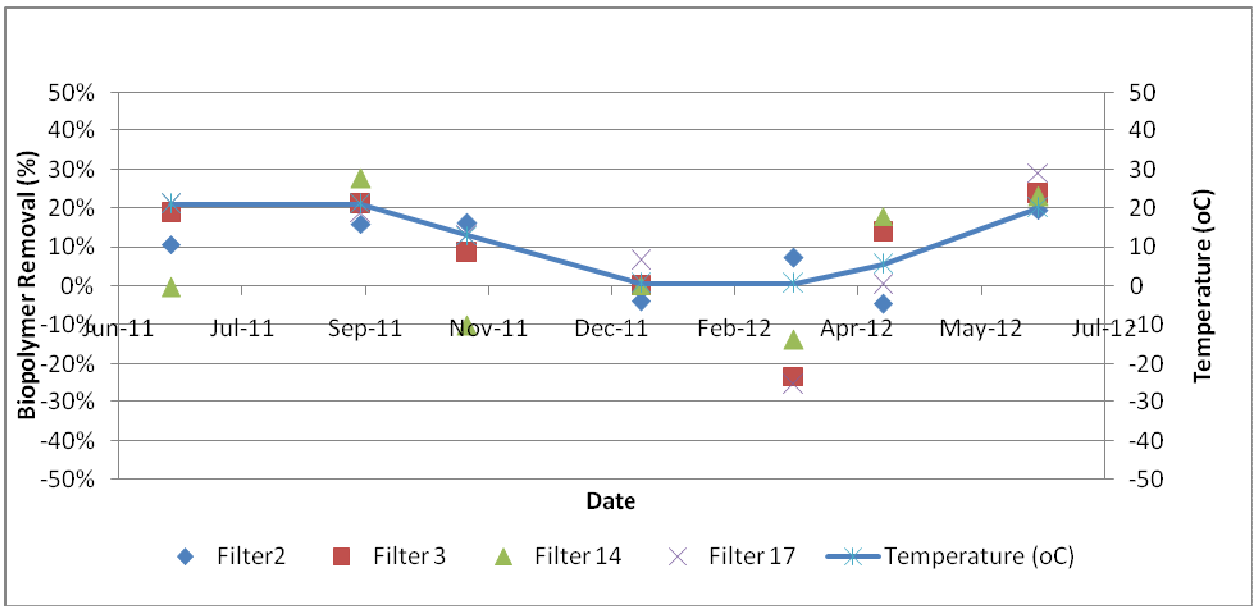


Figure 3.9: Biopolymer Removal at the Ottawa River Location

The reduction of biopolymer content through direct biofiltration (roughing filter pre-treatment only) at pilot scale was much more significant (Figure 3.10) although for operational reasons, the pilot scale biofilters were being operated at a low flow during the period when these measurements were made. An average of 81% removal was achieved through the filter with the longest EBCT (Filter C=70min), which was higher than the average 62% removal observed through the combined coagulation, flocculation, sedimentation, ozonation and filtration processes at full scale. Previous results for the pilot filters with a 15min EBCT showed an approximate 34-62% biopolymer reduction depending on the season (Peldszus et al. 2012). This indicates that direct biofiltration without any pre-treatment may be comparable to conventional processes in terms of biopolymer removal. The significantly lower biopolymer reduction in the full scale filters (following coagulation, flocculation, sedimentation and ozonation) suggests that the up-stream processes either preferentially remove the more biodegradable portion of the biopolymers, or perhaps hinder further biodegradation of the biopolymer fraction.

The three lake water plants all employed pre-chlorination as well as seasonal intake chlorination for zebra mussel control. Biopolymer removal through filtration was not observed at any of these locations, which is not surprising considering the chlorine residual in the filter influent. As this difference between biopolymer removals in the biofilters vs. conventional filters was observed it appears more likely that, when biopolymer removal occurred, biodegradation was responsible rather than physical mechanisms. There does appear to be some removal of the building block fraction through filtration at the lake water plants, especially at the Lake Ontario treatment location (data not shown). It has been reported that AOC removal is not inhibited for GAC/sand filters with the application of pre-chlorination (LeChevallier et al. 1992). The filters at the Lake Ontario location are anthracite/sand however and due to the chlorine residual in the influent, biological activity would not be anticipated.

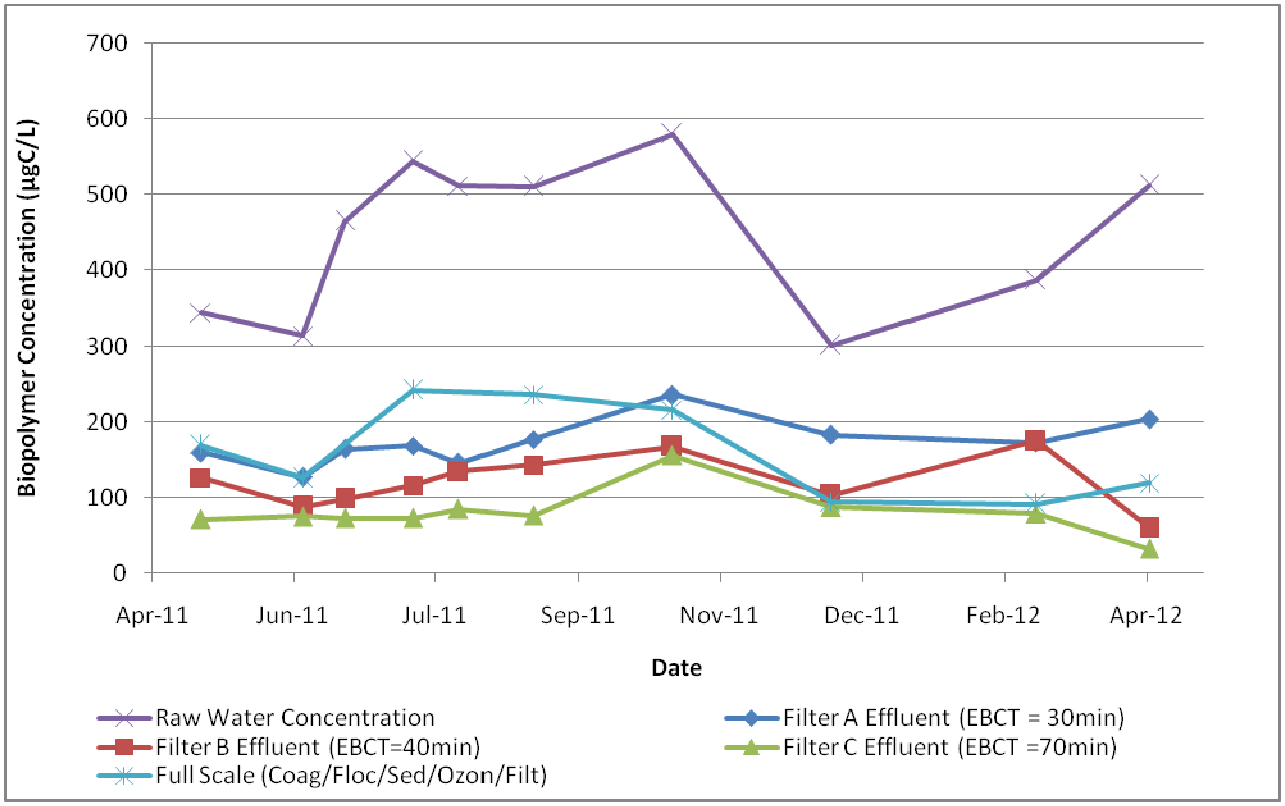


Figure 3.10: Biopolymer Removal Comparison for Direct Pilot Scale Biofiltration to Full Scale Conventional Treatment

3.3.5 Raw Water Comparison for FEEM Results

FEEM plots for the different raw waters were initially qualitatively assessed based on peak location and intensity (Figure 3.11). Primary fulvic peaks (α)(Ex/Em: 320/415) and secondary humic substances shoulder peaks(ß) (Ex/Em:270/460) were observed in the Grand River water in similar ranges to those which have been previously reported (Peiris et al. 2010; Sierra et al. 2005). These peaks are thought to represent mostly humic- and fulvic-like content, and were also present in the Ottawa River and Saugeen River FEEM plots. The Lake Ontario water also had visible peaks in these regions, but at much lower intensities. The Lake Erie and Lake Huron waters did not appear to have visible α peaks, but had different distinct peaks (Ex/Em: 270/430) close to the β region identified for the other waters. Deviations of the FEEM contours in the δ

region (Ex/Em: 280/330) were visible in all waters (excluding Lake Erie) and are thought to be related to protein-like content (Chen et al. 2003; Peiris et al. 2010). As the Lake Erie water often had high turbidity (6.1-240NTU) the raw water FEEMs consequently had irregularities associated with reduced light transmission, and were therefore difficult to interpret. Protein-like peaks for this water were not visible, however it is thought that the problems associated with high turbidity may have prevented distinction between this peak and the scattering regions. First and second order Raleigh scattering regions which are thought to be related to particulate/colloidal like material (Peiris et al. 2010) varied in intensity for all waters, with the higher turbidity waters displaying greater scattering.

The fluorescence measurement technique which relies upon the presence of certain NOM structural properties (fluorophores) is quite different from LC-OCD (and conventional DOC). Further, there was no pre-filtration of the fluorescence samples, which was required for LC-OCD measurement. As peak locations are known to shift according to different compositions and relative concentrations, it is important to analyze the entire spectrum rather than just individual peaks (Chen et al. 2003; Stedmon et al. 2003). It has also been demonstrated that high humic substances concentrations may interfere with the protein-like substances signal (Haberkamp, 2008). This is another reason why relating concentration to individual peak intensities may not be possible, and why the use of further data analysis techniques (such as PCA) are valuable for capturing independent changes within the entire FEEM spectrum. Coupled with PCA, fluorescence may act as a good monitoring tool for water treatment because it can be measured quite readily, with minimal sample preparation.

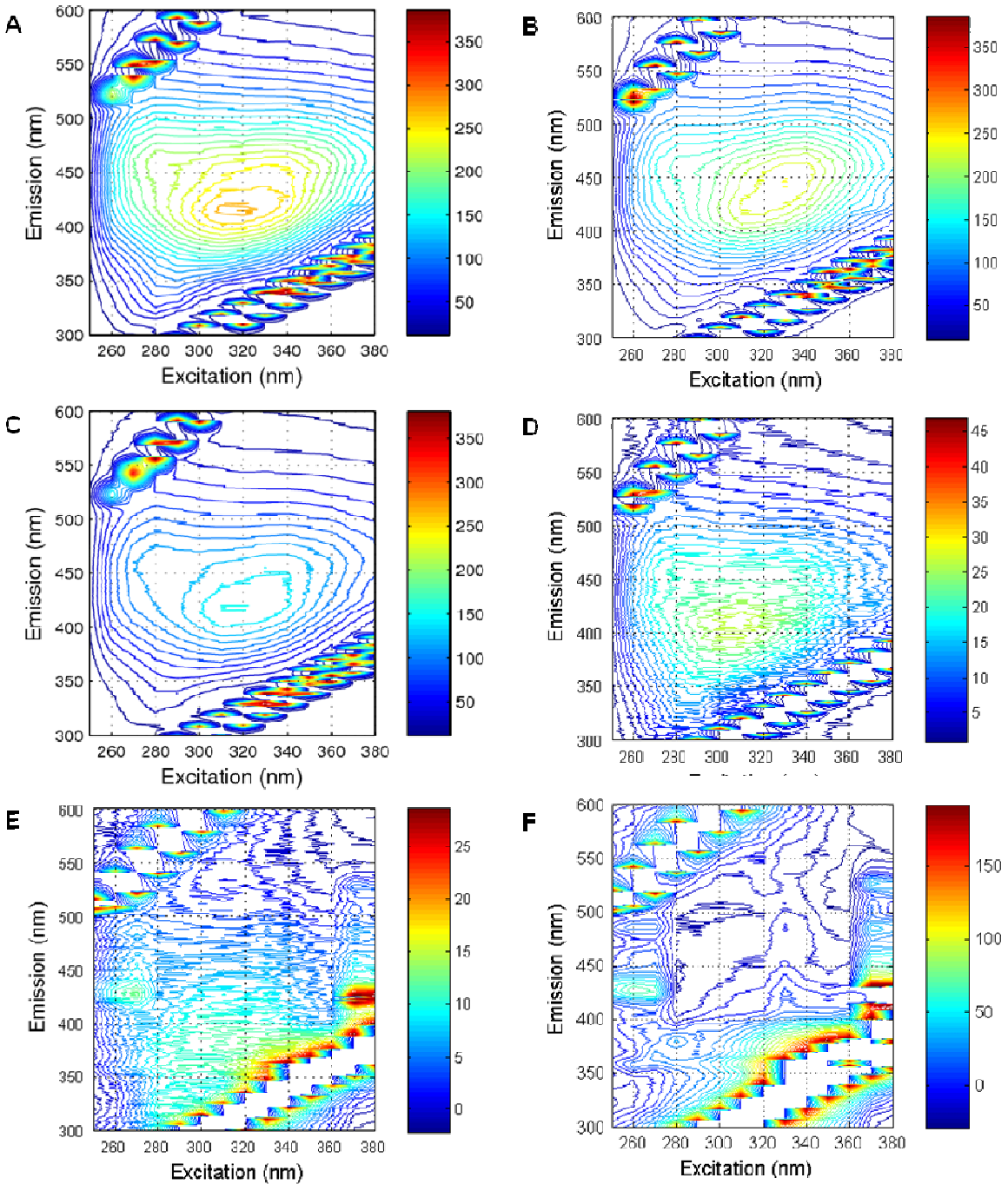


Figure 3.11: Raw water FEEM for a) Grand River b) Ottawa River c) Saugeen River d) Lake Ontario e) Lake Huron f) Lake Erie

In general, the higher DOC waters had much higher fluorescence responses in the humic and fulvic regions. The relative intensity of the humic and fulvic like peaks did not appear to be directly related to concentration, as the Ottawa River (which had the highest humic content using LC-OCD analysis) had lower intensities than the Grand River. Intensities for the low-DOC lake waters were either very low (by approximately 10 times), or sometimes not visible. The LC-OCD humic content results for the lake waters were not as low (3-6 times lower), which indicated that the fluorescence intensities were largely impacted by the presence of certain fluorophores rather than by absolute humic concentration.

3.3.6 PCA loading plot results

PCA was successfully applied to five different waters at different stages of water treatment. In contrast to other NOM treatment studies using FEEM, multiple waters were included in the same model. Loading plots for three PCs generated in the PCA model are presented in

Figure 3.12. The three PCs accounted for 91% of the variation in the model (78%, 8.4% and 4.5% for PC1, 2 & 3 respectively). Additional PCs were not included due to low % variation (<3%) and lack of physical significance in terms of loading plots. The contour plot for PC1 has the highest loading values in the 270-310/420-500 (excitation/emission) region which has been largely associated with humic and fulvic like material (Chen et al. 2003; Sierra et al. 2005). The contours for PC1 are relatively broad, likely due to the number of different waters included in the model (peaks are not identical among waters, or with seasonal changes). PC2 has the highest loading contours in the first and secondary Raleigh light scattering regions, which have been associated with higher particulate/colloidal matter (Peiris et al. 2010). The loading plot for PC3 has a peak in the 260-280/310-350 excitation/emission region. This region has been associated with protein (tyrosine and tryptophan) like substances (Her et al. 2003; Chen et al. 2003). The PC3 loading plot also has some peaks in the Raleigh scattering regions which have been associated with colloidal and particulate matter. As proteins can be in the colloidal size range, it is thought that they may contribute to some of the light scattering regions. Natural colloids are

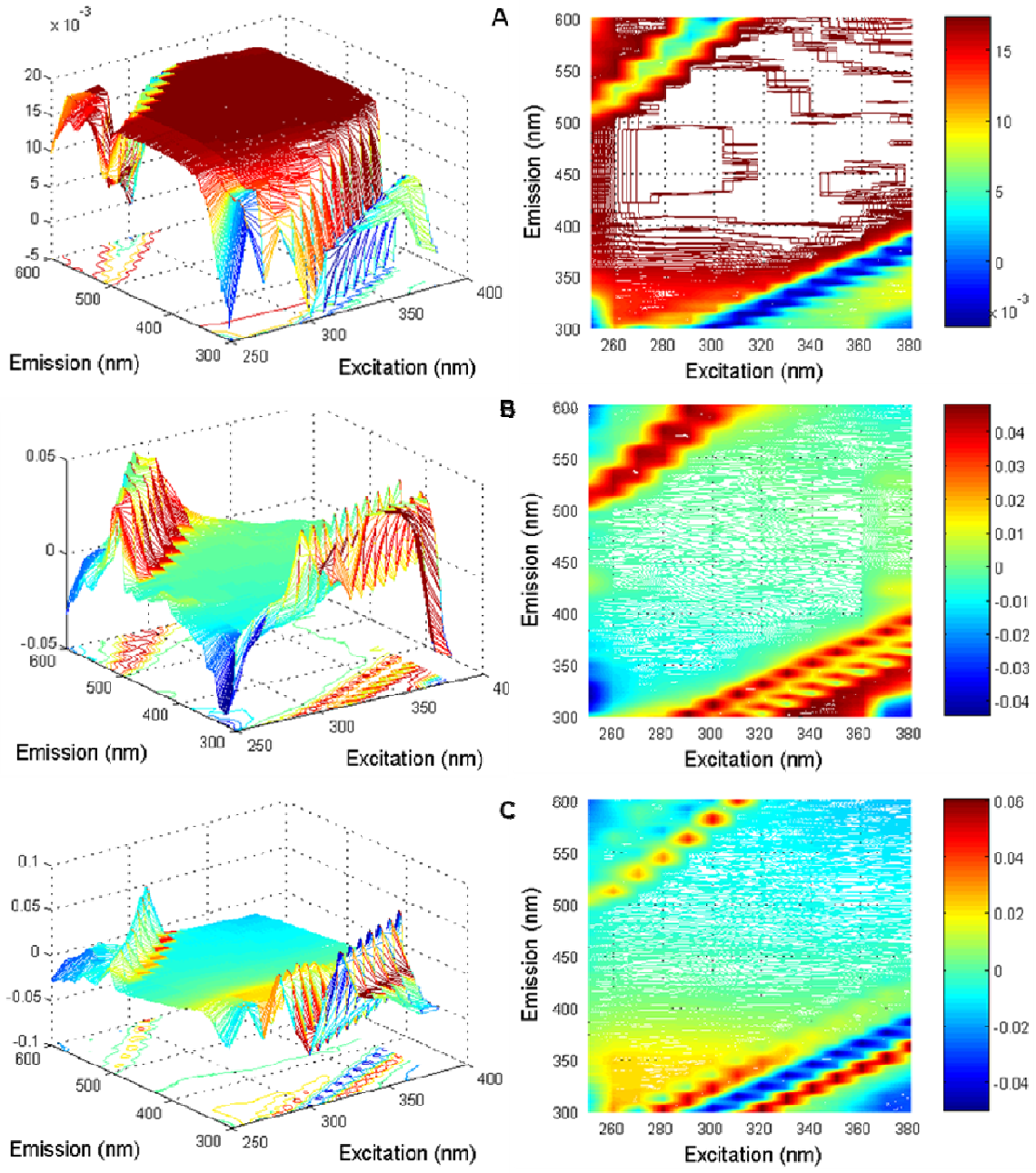


Figure 3.12: PCA loading plots for a)Humic and Fulvic Material (PC1) b) Colloidal and Particulate (PC2) c)Protein like material (PC3)

also not homogeneous, and interactions can occur between inorganic and organic materials, allowing combined aggregates to be formed (Buffle et al. 1999).

The three PCs generated in the current model are largely similar to those presented by Peiris et al.(2010) for Grand River water alone. The general similarity between the two models indicates that this approach can include multiple water types in the same model to identify humic-like and protein-like material.

3.3.7 Raw water PCA score comparison

PC scores were generated for each sample and indicate the extent to which the loading variable is reflected in the FEEM spectrum. These scores can be both positive and negative, and do not indicate an absolute concentration, but rather a relative scale for which the spectral region is represented in the sample. Average PC scores (with min/max bars) for five different raw waters are shown in Figure 3.13. Lake Erie raw water samples were excluded from the model due to high turbidity (6.1-240NTU) which caused erratic results (reduced light transmission). There is relatively good agreement between the LC-OCD humic concentration results and PC1.This was expected as humic material would not be impacted by pre-filtration (much smaller than 0.45um pre-filter) , and presumably a large portion of its chemical structure would fluoresce. PC1 (humic) scores were generally highest in the river waters. The high degree of variability in the Saugeen River PC1 scores does appear to be consistent with the large variation in humic concentration which was observed using LC-OCD. The lake waters had negative PC1 scores indicating a much lower fluorescence response in this region. The structure of the lake water humic substances using LC-OCD results was deemed to be less aromatic, considering the lower SUVA as presented in Figure 3.2 . The lake water LC-OCD humic concentrations were also much lower than those of the river waters. The humic material structural differences between the waters likely impacted the response of the PC1 score in addition to concentration, which may help to explain some of the differences between LC-OCD and PC1 results. The Ottawa River for

example had the highest humic substances concentration based on LC-OCD, but had a lower PC1 response than the Grand River.

The results for PC2 (colloidal and particulate material) only follow turbidity trends observed in the raw waters to a certain extent. The Grand River, which had the highest turbidity variation (2-12 NTU) also had the highest PC2 variation. The average turbidity was lowest in the Lake Ontario water (0.6NTU) and this water also had the lowest PC2 scores. Turbidity could not however act as an exact predictor for PC2. Particle/colloid size distribution as well as number impact turbidity and it would be reasonable to expect that they would also impact the response for PC2, although potentially in a different way. Variability of PC2 for samples with similar turbidity might be explained by differences in particle size distribution.

Similarly, PC3 (protein-like material) did not directly follow the trends observed for biopolymers from the LC-OCD results. It is possible that to some degree pre-filtration could have contributed to the differences between the LC-OCD and fluorescence results, since protein content which may have been adsorbed to particulates larger than 0.45um would be present in the FEEM sample but not in LC-OCD. Also, only a certain portion of the proteins would be expected to fluoresce. The Ottawa and Saugeen Rivers, which were found to have lower biopolymer concentrations, also had lower PC3 (protein-like) scores. The Grand River, which had the highest biopolymer concentration, had a moderate PC3 score (similar range to Lake Ontario), whereas Lake Huron had the highest PC3 score. Biopolymers are comprised of both polysaccharides and protein-like materials for which the exact composition is largely unknown. Dissolved organic nitrogen (DON) content of the biopolymers was also available from LC-OCD analysis, and showed a similar disagreement between the two results. The fluorescence peak for protein-like substances (PC3) would also be expected to include smaller fractions which contain amino acids (Haberkamp et al. 2011), and therefore a good relationship between PC3 and biopolymers would not necessarily be expected.

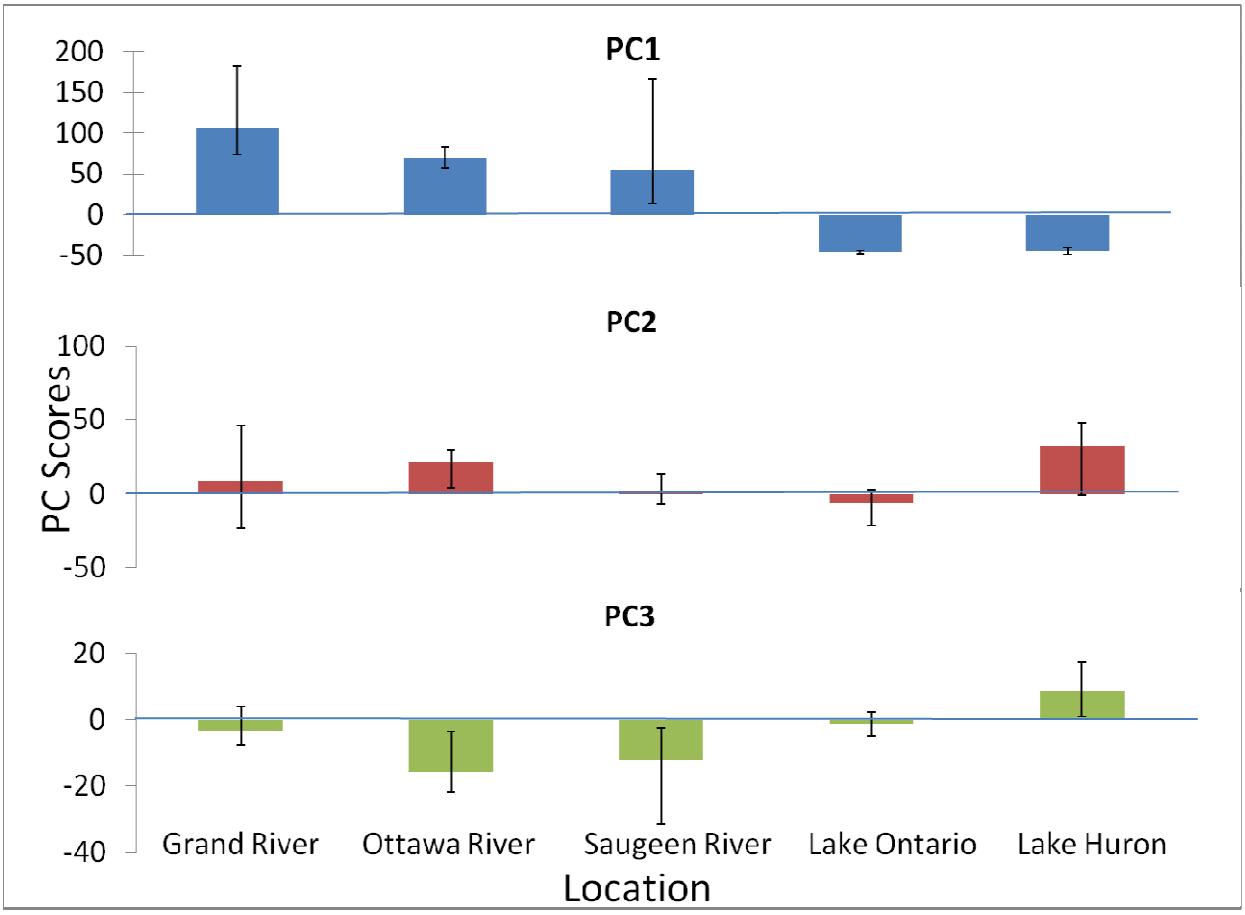


Figure 3.13: Average PC Scores for Five Different Waters (with Min/Max bars for n= 3-4 samples)

3.3.8 NOM and Removal Efficiency using PCA scores

The reductions in PC1 during treatment of the Grand and Ottawa Rivers are presented in Figure 3.14. The effectiveness of enhanced coagulation for the removal of humic substances appears to be captured by the greater reduction in PC1 observed for the Ottawa River location. The average reduction of PC1 through this process was 1.8 times greater than that of conventional coagulation, at the Grand River location. The average removal of humic substances using LC-OCD results was 2.5 times greater for the enhanced coagulation process, suggesting that the fluorescence results may act as a predictor of humic substances removal through coagulation,

flocculation and sedimentation. The PC1 removal results also appear to be relatively consistent throughout the year, similar to the LC-OCD results.

Significant reduction in PC1 scores were observed after ozonation (Figure 3.14). This was not reflected in the LC-OCD results, where ozonation resulted in a reduction of only 11% of the material defined as humic substances, which were partially degraded to lower molecular weight fractions. This suggests that the fluorescence results are capturing a greater structural change in the humic fraction than was apparent in the LC-OCD results. As FEEM is sensitive to the presence of certain fluorophores which could become oxidized during ozonation, this technique is sensitive to these changes in molecular structure. Therefore it appears that the fluorescence results cannot be relied upon to directly predict bulk humic concentration changes during oxidation processes. The minimal reduction of PC1 scores through filtration was consistent with the humic LC-OCD results.

There was little reduction of PC1 during treatment at the Lake Huron and Lake Ontario locations. It may be that the PCA model was not sensitive enough to capture changes in the low intensity FEEM spectrums for these waters, however in terms of absolute concentration removal (using LC-OCD results), the lake water treatment trains had much lower humic substances removal (see Figure 3.4) than the river waters.

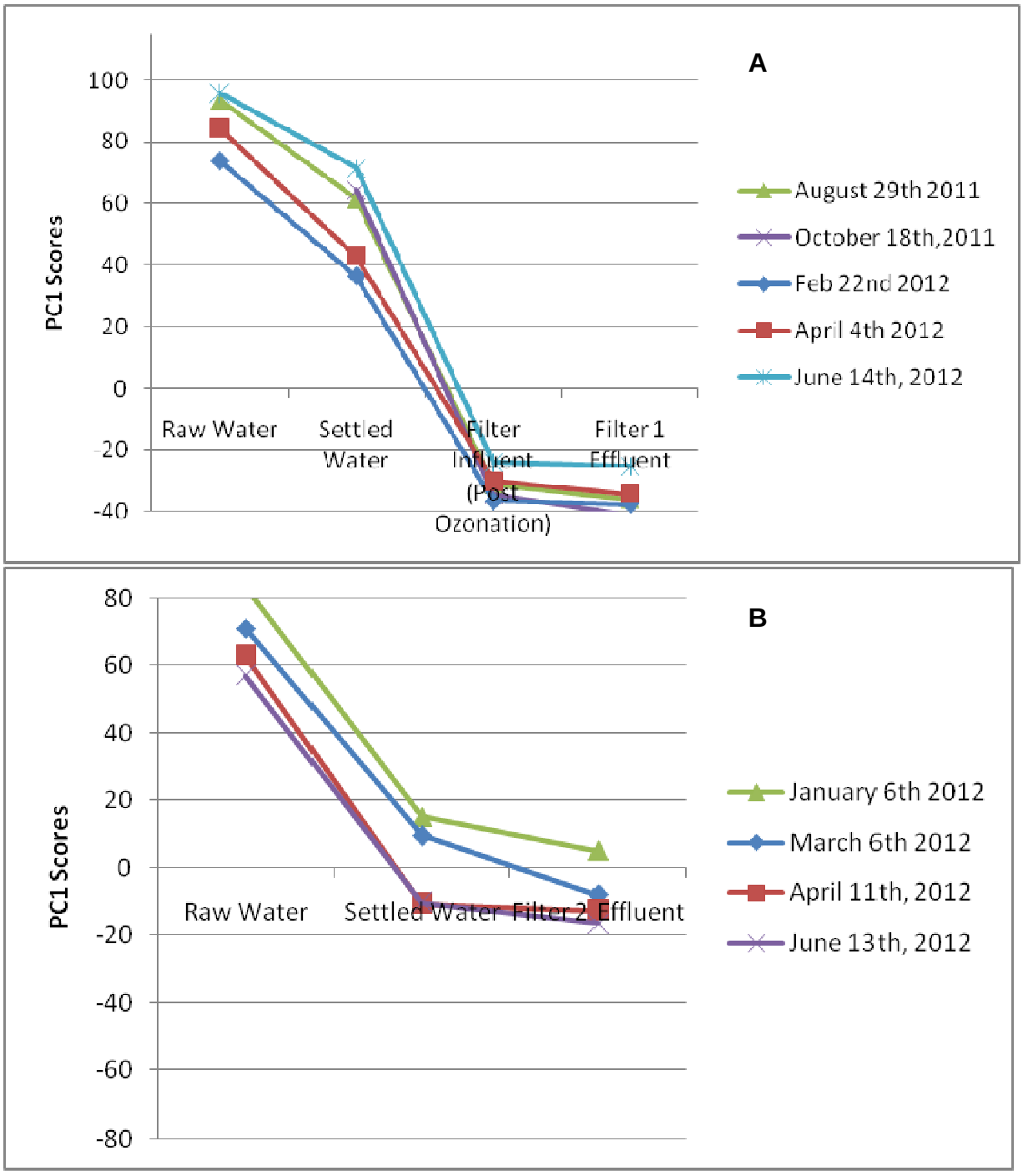


Figure 3.14: Grand River (A) and Ottawa River (B): PC1 (Humic Like Material) as a Function of Treatment Step

The trends for PC2 were less apparent (refer to Appendix D) but in general followed those observed for turbidity. It is reasonable to think that the PC2 response is sensitive not only to the number of particles/colloids in a sample, but also to their size, causing some difficulty in the interpretation of the results. There was generally a decrease in PC2 (scattering regions) after sedimentation, which is intuitive based on particulate settling. When reductions in turbidity after sedimentation were less dramatic, the results were less clear (small decrease, or increase in PC2). However a consistent decrease was also observed after filtration, which was expected. The observed increase in PC2 scores after ozonation was unexpected and a possible explanation may be a slight agglomeration of dissolved content into a more colloidal size range, causing a greater response in the light-scattering regions. Such formations of colloidal particles during ozonation have been noted to increase turbidity after ozonation (Jekel 1994). Turbidity largely remained the same or decreased after ozonation, however there were some instances where it increased.

Trends in PC3 removal were also more difficult to decipher, although generally there was an increase in PC3 after sedimentation(refer to Appendix D). As noted earlier, PC3 loading plots not only had a response in the protein-like region of the FEEM spectrum, but also in the colloidal (scattering) regions as well. It is possible that the response increased after sedimentation due to an agglomeration of dissolved content into larger colloidal like particles. Another possibility is that the structure of the protein-coagulant complexes may have a greater degree of fluorescence than the raw protein structure, and that they were not well removed during sedimentation. PC3 generally decreased during filtration, which would either be due to physical filtration or possibly biodegradation. The observed reduction during ozonation is likely due to structural changes rather than significant removal.

3.3.9 Comparison between LC-OCD Fractions and FEEM PCA scores

PC1 had a relatively good correlation with the humic substances fraction from LC-OCD analysis (Figure 3.15). Samples that were outliers were the raw Ottawa River water samples (region B), and post-ozonation samples at the Grand River location (region A). The structural differences of these samples were likely why they did not correlate directly to concentration. For example it was shown earlier that the fluorescence signal intensities were lower for the Ottawa River than the Grand River, even though the concentration of humic substances was higher. The ozonated samples are also considered to have undergone significant structural changes, causing lower PC1 scores, whereas little concentration change was observed using LC-OCD. Similar observations were made by Bagoth et al. (2011b) who found that ozonation resulted in the quenching of the fluorescence signal.

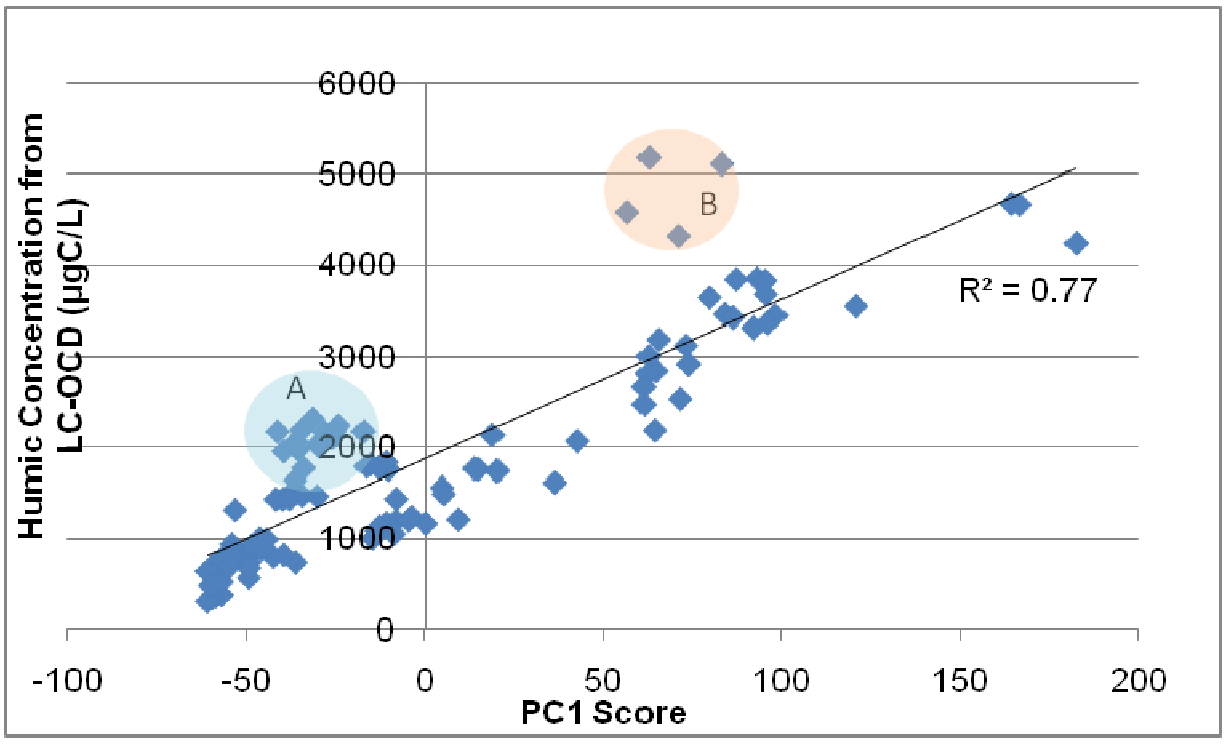


Figure 3.15: Humic Concentration (LC-OCD) vs. PC1

PC3 (protein like material) did not have a good correlation with the biopolymer content (R^2 =0.07) or the dissolved organic nitrogen content of the biopolymer fraction (R^2 =0.01). As only a small portion of proteins are known to fluoresce (only three amino acids), and considering they may be present as smaller polypeptides eluting much later than the biopolymer fraction (Haberkamp et al. 2011), a strong correlation may not necessarily be expected. It is also important to note that the sample pre-treatment for LC-OCD involved filtration (0.45μm) whereas fluorescence samples are measured without any pre-treatment. It may be possible that LC-OCD pre-treatment removes some of the protein content that is captured in fluorescence (i.e. agglomerated colloids etc.).

3.4 Conclusions

Characterization of NOM removal at five full scale water treatment facilities treating substantially different types of water (including several of the Great Lakes) over several seasons using LC-OCD and FEEM PCA analysis provided considerable insight into the behaviour of NOM. The most important conclusions are as follows:

- Full scale biological filtration was found to very effectively remove low molecular weight acids generated during ozonation. In addition, the LMW building block fraction appeared to be partially biodegraded in full scale filtration. Little additional biopolymer removal was observed after coagulation/flocculation/sedimentation at full scale, perhaps because of both lower concentration and removal of the more easily biodegradable biopolymers by the upstream processes.

- Coagulation/flocculation/sedimentation removed 21-73% of the biopolymers and 8-78% of the humic substances depending on the location and little variation was noted in terms of seasonal removals. Enhanced coagulation provided much higher humic removals (58-78%), however did not improve biopolymer removal. It thus appears that biopolymers are potentially removed through coagulation/flocculation/sedimentation by a different mechanism than humic substances.

- Biopolymer content was found to vary seasonally with temperature (higher concentrations in the warmer months). The lake waters contained proportionally higher biopolymer content than the river waters, although the DOC in the former was lower.

- PCA was successfully applied to capture variation in FEEMs from six different water sources. The results could be used as a predictor for the removal of humic substances

throughout full scale treatment (excluding oxidation processes).The PCA results for humic-like material were relatively well correlated to humic substance concentrations from LC-OCD analysis.

- LC-OCD and FEEM provided complementary insight into NOM removal during full scale treatment. NOM structural changes which were not captured by LC-OCD were apparent in the FEEM results. Using either technique on its own may lead to incomplete interpretation of changes in NOM character.

Chapter 4
Impact of Natural Organic Matter (NOM) Composition of Four Surface Waters on Low Pressure Membrane Fouling

This chapter is based on an article of the same title submitted for potential publication in a scientific journal in October 2012. As such, it contains individual sections including introduction, materials and methods, results and conclusions. More detailed background is provided in Chapter 2, while Chapter 5 discusses some implications of this work for the water treatment industry. References are consolidated in the bibliography at the end of the thesis.

4.1 Introduction

Low pressure membranes (LPM) are increasingly being used as a robust treatment option for supplying safe drinking water. Organic fouling however still remains as an operational challenge, as it increases maintenance and energy requirements, which have a significant impact on cost (Gao et al. 2011). Natural Organic Matter (NOM) has been identified as playing an integral role in fouling of ultrafiltration (UF) membranes, however varying conclusions have been made concerning the contributions from different NOM constituents, as well as the role of inorganic particles (Jermann et al. 2008; Zularisam et al. 2011). Although some investigations have highlighted the importance of humic substances (Combe et al. 1999; Jones and O'Melia, 2001; Mousa 2007), the larger molecular weight hydrophilic fractions (polysaccharides, proteins) are now recognized as being significant LPM foulants (Lee et al. 2004; Kimura et al. 2004, Zularism 2011).

Advancements in analytical techniques available for the characterization of NOM have provided important tools for furthering the understanding of this process. Liquid chromatography organic carbon detection (LC-OCD) is one such technique which effectively separates NOM based on apparent molecular size to quantify the fractions of interest (biopolymers(polysaccharides,

proteins), humic substances, building blocks and low molecular weight acids and neutrals)(Huber 2011). The importance of biopolymers in surface water was demonstrated by Hallé et al. (2009), who found that the reduction of this fraction through direct biofiltration pre-treatment had a significant impact on the degree of hydraulically reversible and irreversible ultrafiltration (UF) membrane fouling.

Fluorescence excitation emission matrix (FEEM) methods are also useful and provide information related to the humic, fulvic and protein-like composition of NOM (Sierra et al. 2005; Her et al. 2003) as well as the particulate and colloidal matter (Peiris et al. 2008). The application of multivariate data analysis such as principal component analysis (PCA) to FEEM data has also proven to be useful in relating NOM composition to UF fouling events (Peiris et al. 2010).More recently the composition of the biopolymer fraction and specifically the protein-like content (using FEEM analysis) has been shown to impact hydraulically irreversible fouling (Peldszus et al. 2011; Haberkamp et al. 2011).

One of the major challenges remaining in implementing membrane filtration is predicting the degree of fouling which would be expected for different surface waters (without performing extensive pilot studies). Much of the work which has already been done in the drinking water field has focused on relating fouling to model solutions (Gray et al. 2011; Jermann et al. 2008; Zularisam et al. 2011) or is performed over short filtration periods at constant pressure using natural waters (Howe and Clark 2002; Lee et al. 2004). In practice however, membrane treatment facilities are operated at constant flux (Crittenden 2005), and model solutions may not be able to fully capture the complexity of NOM-colloidal interactions (Buffle et al.,1998).

The intention of this investigation was to apply LC-OCD and FEEM techniques to a range of surface waters undergoing UF treatment to see if the fouling relationship to biopolymer concentration and composition are independent of water type, and whether it can be used to predict the fouling potential of different waters.

4.2 Materials and Methods

4.2.1 Selection of target waters

The selection of the waters for this investigation was done based on an earlier survey within Ontario using LC-OCD and FEEM analysis as outlined in Chapter 3. Target waters were identified based on mean biopolymer and humic concentration as well as differences in mean turbidity conditions. Two high DOC river waters (Grand and Ottawa Rivers) and two low DOC Great Lake waters (Lake Ontario and Erie) were deemed to be of interest. The Grand River had the highest mean biopolymer concentration, while the Ottawa River (with the highest humic content) had the lowest. The two lake waters had moderate biopolymer concentrations with Lake Ontario displaying consistently low turbidity (<1 NTU), and Lake Erie having the highest turbidity (up to 240NTU).

4.2.2 Bench Scale Apparatus Description

Experiments were run for five days at constant flux (50LMH) using a commercially available hollow fibre polyvinylidene fluoride (PVDF) ultrafiltration (UF) membrane as part of a fully automated system outlined in Figure 4.1. The submerged module was contained in a 1.6L vessel and was operated using an "outside-in" dead end filtration mode whereby permeate was drawn under vacuum. Water was collected no more than 48hrs prior to starting the experiment, and stored in a 1300L stainless steel tank which provided enough capacity for five days. The water was allowed to warm to room temperature (approximately 20^{o}C) providing temperature corrected TMP readings (minimizing the impact of viscosity changes with temperature), The storage tank was also mixed to prevent particulate settling. Under normal operation, flow to the system was controlled using a flow meter from an overhead tank (V1 closed), to match the rate of permeation and thereby keep the level in the membrane vessel constant. Actuated solenoid valves were controlled using a program logic controller (PLC) (Allen Bradley model number 75 PICO-1760-L 12AWA-NC) and the reversible peristaltic permeation/ backwash pump (Masterflex L/S drive model number 07550-50; Cole-Parmer Canada) was controlled digitally

using Masterflex Linkable Instrument Control Software (WinLIN). The permeation cycle lasted for thirty minutes at which point a twenty second backwash with air scourge (air valve V2 opened at 60PSI) was performed by reversing the direction of the permeation/backwash pump. After backwash the membrane vessel was fully drained and refilled in less than two minutes from the overhead tank (by opening valves V3 and V1). Transmembrane pressure (TMP) was recorded using a pressure tranducer and data logger (Lakewood Systems, model number: CPXA).

Maintenance cleaning was performed on day three and at the end of the experiment to investigate its effect on recovery by submerging the module in a 100mg/L sodium hypochlorite solution for 15min before resuming normal operation. This was also done to avoid excessive TMP, as the membrane manufacturer specified a maximum recommended TMP of 60kPa. A full chemical clean was performed at the end of the experiment to recover the original permeability by soaking the membrane in a 200ppm sodium hypochlorite solution for 5hr followed by a 5g/L solution of citric acid for another 5hr. Clean water permeability tests using deionised (DI) water were used to confirm the effectiveness of each chemical clean and were done by measuring TMP at four specified values of flux. Membrane integrity tests were also performed regularly to ensure there was no problems with the module used in the experiments (no more than 2kPa pressure drop over 2mins from the initial 70kPa).

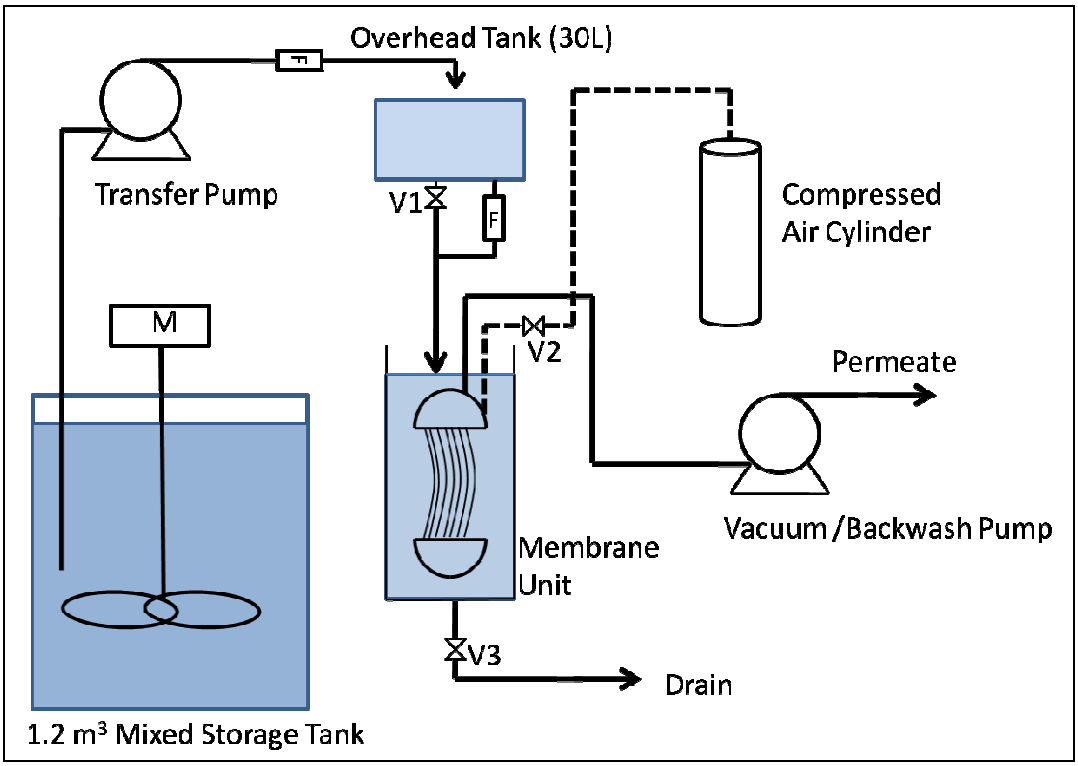


Figure 4.1: Schematic of Experimental Setup

4.2.3 Sampling Procedure

Both LC-OCD and Fluorescence samples were taken throughout the experiment in addition to TOC, DOC, UV_{254}, pH and conductivity. Temperature and turbidity were recorded manually at regular intervals in addition to permeate flow to ensure near constant flux. To further investigate irreversible organic deposition on the membrane surface an approximated "mass balance approach" was taken whereby concentrations from the feed, permeate, concentrate and backwash were taken across one cycle. Using known influent and permeate flows and concentrations, as well as the mass of organics leaving in the backwash, the intention was to quantify the unaccounted fraction which would presumably correspond to the irreversibly deposited material on the membrane. To distinguish between concentrate and fractions leaving during backwash, the membrane vessel was drained prior to backwash (mixed sample taken), at which point it was filled with permeate (known concentration, similar ionic strength to raw water), and then the

normal backwash was performed. The difference between the permeate concentration and the solution from the drained vessel after backwash was deemed to be the fractions being released from the membrane surface during backwash.

4.2.4 Liquid Chromatography Organic Carbon Detection (LC-OCD)

Liquid Chromatography Organic Carbon Detection-Organic Nitrogen Detection (LC-OCD-OND – DOC-Labor Dr. Huber, Karlsruhe/Germany) was performed within 48hrs of sampling after being filtered through 0.45μm PES filters and stored at a temperature of 4^{o}C. Samples were delivered to the HW-50S(Tosoh Bioscience Tokyo/Japan) size exclusion column (SEC) column via mobile phase (purified 28mmol/L phosphate buffer at pH 6.58 and 1ml/min) using a HPLC pump, followed by non-destructive Ultra-violet detection (UVD) at 254 nm. Organic carbon detection was performed after the fractionated sample was oxidized in the Gräentzel thin film reactor to CO_2 which was then measured by an infrared detector. The OND was supplied by a side stream prior to the Gräentzel reactor where organically bound nitrogen was converted to NO_3 and measured using a UV (220nm) detector (Huber et al. 2011).

4.2.5 Fluorescence Excitation Emission Matrices (FEEM)

FEEM measurements were done at room temperature (22^{o}C) within 24hrs of sampling using a Varian Cary Eclipse Fluorescence Spectrofluorometer (Pal Alto, CA). FEEM spectra intensities were measured for 301 emission values (300-600nm) and 14 excitation wavelengths between 250 and 380nm (10nm increments). To account for Raman scattering MQ ultrapure water spectra were subtracted from all samples. Disposable UV-grade polymethlmethacrylate (PMMA) cuvettes were used and no pH adjustment was made prior to analysis (pH ranged from 7.3-8.3). No significant change in the FEEM spectrum was observed for small pH adjustments (pH 6 to 8 using NaOH), which was similar to the results reported by Spencer et al. (2007) who found moderate pH change had little effect on intensity changes. All samples were therefore run under natural pH conditions. As DOC for the waters were relatively low (2.3-7.6mgC/L) compared to

the upper limit of 25mgC/L reported by Hudson et al. (2008) for inner filtering and quenching effects, no dilutions were made.

4.2.6 FEEM Data Analysis

Principal component analysis (PCA) was performed on the FEEM data set using the procedure outlined by Peiris et al. (2010) to extract the important variation in the data. A total of 92 samples were taken from the four experiments. Unfortunately the FEEM data from the first two experiments (Grand River and Lake Ontario waters) could not be used due to an unexpected peak that occurred across the corresponding FEEM spectra. It was later determined that this peak arose from a contamination source in the disposable cuvettes which were used for these two experiments. Therefore only 46 samples from the Ottawa River and Lake Erie experiments were available for further analysis. New variables from the FEEM data set which are uncorrelated and orthogonal can be generated using PCA analysis which is applied to the original matrix X (containing all sample spectra unfolded into single column form). A model which best represents the systematic variation in the data is then created which is the sum of the product of the score (t_i) and loading (p_i) vectors and has the remaining matrix (E) which represents variation not captured by the model (Peiris et al. 2010).

4.2.7 Additional Parameters

Turbidity samples were also taken at regular intervals throughout the experiment for the raw and permeate streams using a Hach 2100P instrument following Standard methods (2012) 2130. Temperature was measured manually using a thermometer and conductivity was determined using a Hach 44600 instrument following Standard Methods (2012) 2510. TOC and DOC was measured for all samples using an OI-Analytical TOC analyzer (model 1010, College Station,TX) by wet oxidation as described in Standard Methods (2012) 5310D. UV absorption was measured using a spectrophotometer (Hewlett Packard 8453) as described in Standard

Methods (2012) 5910 using a 5cm path cell for any samples which had low absorption ($<0.15 cm^{1}$).

4.2.8 Fouling Analysis

The hydraulically reversible fouling was assessed by performing linear regression on the increase in TMP across a 30min permeation cycle. This was done after 24hr of experimental run-time (and subsequently at 48hr, 72hr, 96hr and 120hr). To ensure a representative fouling increase was calculated, the linear regression procedure was repeated for five cycles for which the mean was taken. The cycles that were selected were those which were immediately prior to sampling so that NOM content could be related to the fouling at that time. The mean hydraulically irreversible fouling rate was assessed by partitioning the fouling curve into regions of linear TMP rise. The resulting slope (kPa/hr) corresponds to the fouling rate, and the mean rate was calculated by weight averaging these values (according to the length of time for each partition). This approach was also taken when calculating the hydraulically irreversible fouling rate for each 24hr period, however for the most part the mean fouling rate is discussed (result is less sensitive to individual irregularities in the fouling curve).

4.3 Results and Discussion

4.3.1 Hydraulically Reversible and Irreversible Fouling

Important water quality parameters taken during the experiments are summarized in Table 4.1.The water characteristics were largely as expected with the Grand River having the highest biopolymer concentration and the Ottawa River having the lowest. The Ottawa River also had the highest humic concentration making it important in terms of distinguishing between contributing organic foulants. Lake Erie had the highest turbidity and moderate to high biopolymer concentration. The biopolymer concentration in the Lake Erie water also had relatively high variability during the experiment, which was not observed for the other waters,

and may have been caused by interactions with particulates considering the turbidity was much higher in this water (which may have partially settled despite mixing).

Table 4.1: Summary of Water Quality Parameters

	Grand River		Lake Ontario		Ottawa River		Lake Erie	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Biopolymer Concentration (ug/L)	343	28	208	28	147	8	293	69
Humic Concentration (ug/L)	3864	70	1078	66	5062	357	939	207
Turbidity (NTU)	2.4	1.1	0.90	0.32	3.9	0.27	7.5	1.4
pH	8.2	0.04	7.9	0.16	7.5	0.19	7.9	0.12
Conductivity (mS/m)	63	0.27	35	0.31	9.5	.52	27	0.06

Results for the five day fouling cycle of the four waters are presented in Figure 4.2. Prior to the first maintenance cleaning the Grand River (highest biopolymer content) had the highest degree of hydraulically irreversible fouling, reaching a maximum TMP of 32.5 kPa (post backwash). It also had the highest degree of hydraulically reversible fouling (up to 15kPa/hr). The Ottawa River which had the lowest biopolymer concentration also had a relatively high rate of irreversible fouling, and reached a TMP of nearly 30kPa prior to maintenance cleaning. This water had the lowest degree of hydraulically reversible fouling (maximum 4.3kPa/hr), suggesting the biopolymer concentration is indicative of this type of fouling. This trend continued for the other two waters which had moderate degrees of hydraulically reversible fouling and moderate to high biopolymer content (will be discussed further based on individual days).

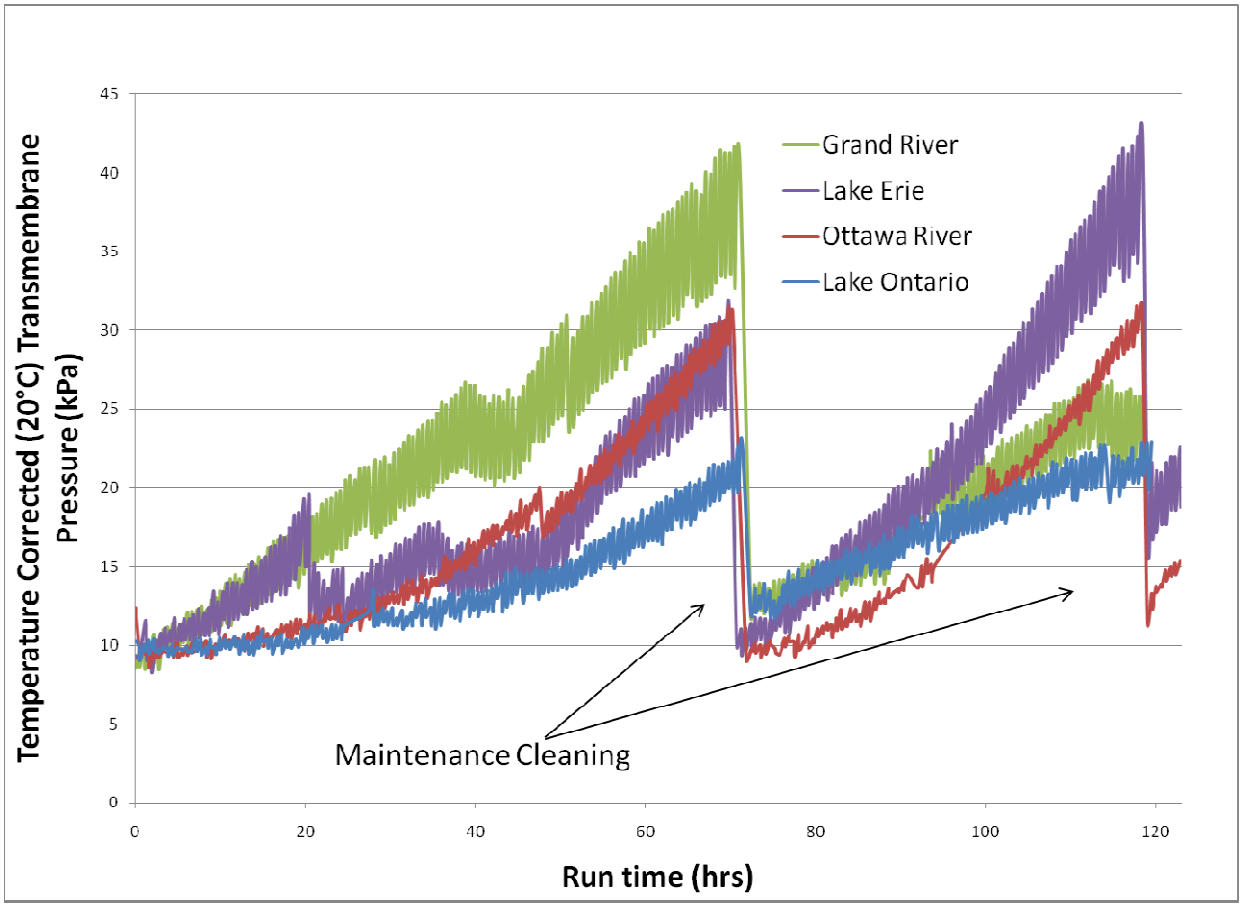


Figure 4.2: Fouling profile of four waters

There are some irregularities on the fouling curves which are attributed to small problems during the five day experiments. An example is when the timing of the air scour became delayed for the Lake Erie water (for the initial 22hrs), causing a less than effective backwash, which explains the initial early rise in irreversible fouling. Once the problem was corrected, the TMP dropped rather drastically, which may suggest the layer causing the initial irreversible fouling was relatively amenable to backwash if working properly (i.e. proper air scour). This may provide some insight into the relationship between hydraulically reversible and irreversible fouling, as the irreversible fouling is dependent on how well the fouling layer is removed during backwash. Lee et al. (2004) found gel/cake layer formation to be an important mechanism in UF fouling, which may be why the air scour was critical for the removal of the fouling layer. Other problems included

power outages for the Ottawa River (95hr) and Grand River (90hr) experiments which caused some loss in recorded TMP data.

As the degree of hydraulically reversible fouling was observed to increase over the length of the experiment (Figure 4.3), it was also investigated based on individual days to capture any additional trends. After each 24hr period, linear regression was performed on individual TMP increase over the 30min permeation cycle to obtain the rate of fouling (kPa/hr), and this was done over five cycles to obtain the mean value for each day (and water). As LC-OCD samples were only taken on days 1-4, the results were only plotted for these days.

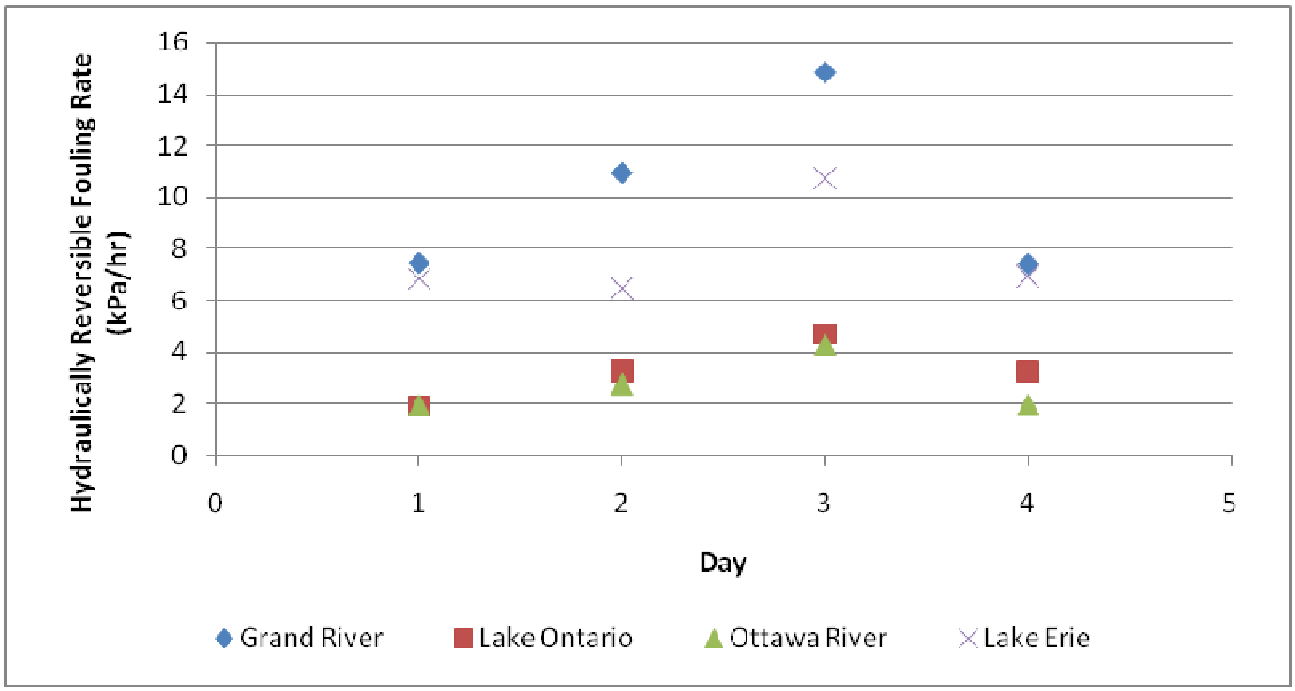


Figure 4.3: Hydraulically reversible fouling rate increase by day (Note: Maintenance cleaning performed prior to day 4).

Hydraulically reversible fouling appears to be impacted by biopolymer concentration despite differences in the four waters as demonstrated in Figure 4.4 to Figure 4.7. This is in good agreement with Hallé et al. (2009), who demonstrated biopolymer concentration can be correlated to hydraulically reversible fouling in the Grand River Water. The results of the current

investigation have further supported this finding in that biopolymer concentration can be used to predict hydraulically reversible fouling across different waters with significantly different characteristics (useful in assessing initial fouling potential).

Similar plots were made for turbidity and humic substances concentration, which were found to have virtually no correlation to hydraulically reversible fouling (see summary table in Appendix E). It is also apparent that the hydraulically reversible fouling rate increases by day, with greater increases for waters with higher biopolymer content (Grand River) as shown in Figure 4.3. This indicates that the waters with higher hydraulically reversible fouling (and higher biopolymer concentration) are more heavily impacted as the experiment proceeded. The slope decreases for day 4 results (after maintenance cleaning which removed the hydraulically irreversible fouling layer). This may imply there is a relationship between hydraulically reversible and irreversible fouling. Peldszus et al. (2011) postulated that the hydraulically reversible fouling layer can transition to a hydraulically irreversible fouling layer, as the combined fouling layer becomes less amenable to backwash. The relationship between hydraulically reversible and irreversible fouling was further investigated by plotting the two fouling rates against each other (Appendix E).There does not appear to be any direct relationship between these two fouling rates in terms of this plot however. Refer to Appendix E for a summary of the reversible and irreversible fouling relationships.

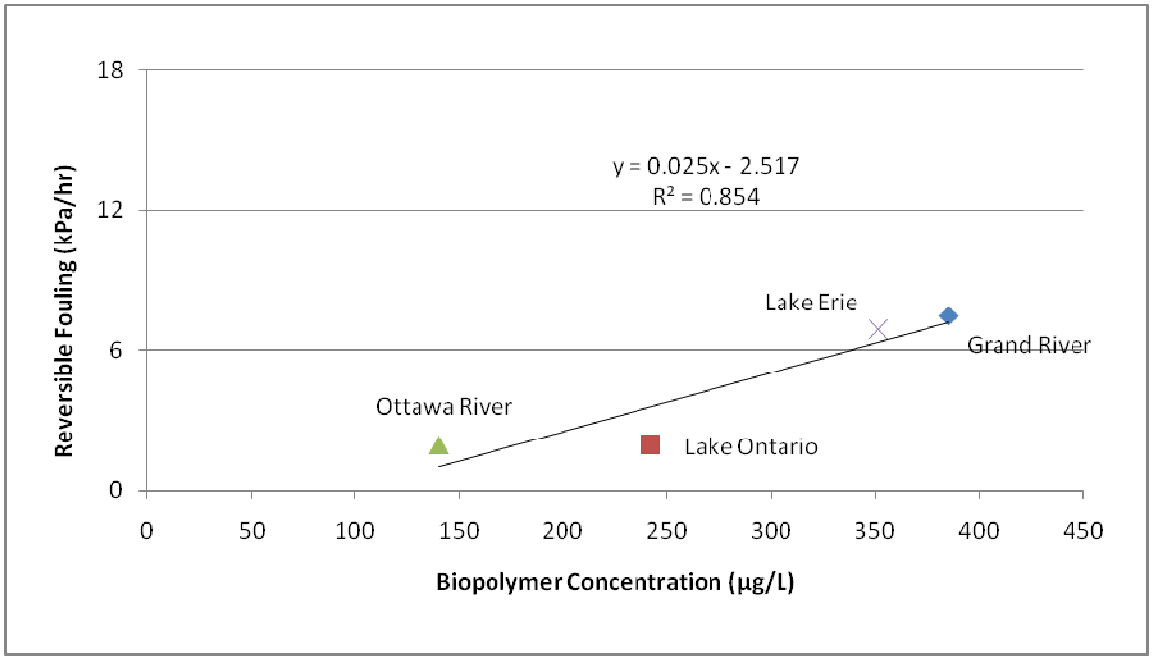


Figure 4.4: Hydraulically reversible fouling vs. Biopolymers (Day 1)

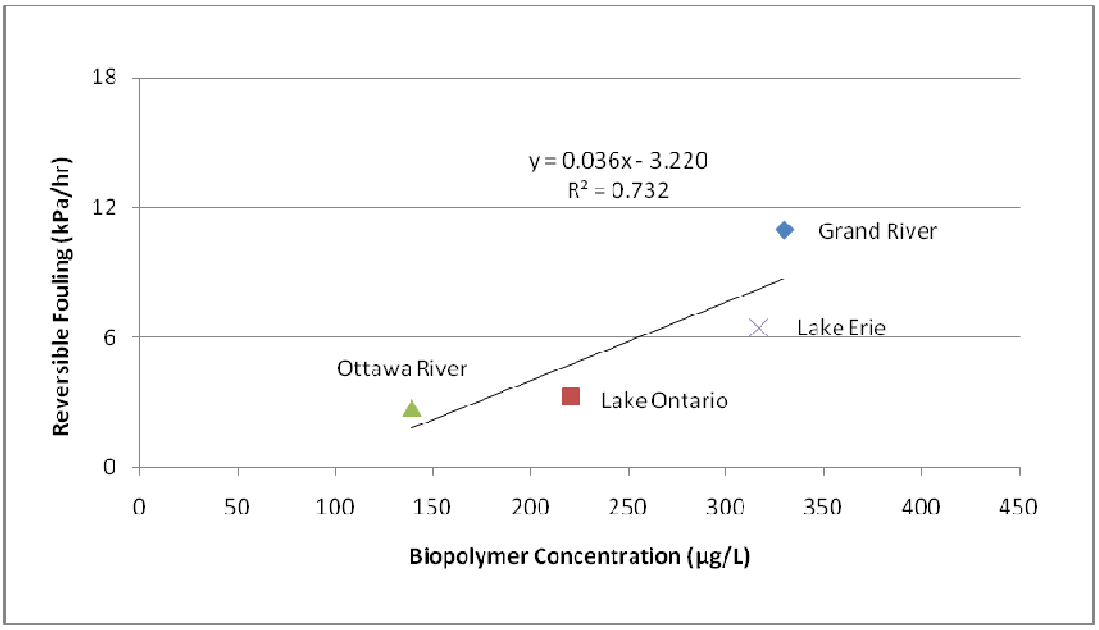


Figure 4.5: Hydraulically reversible fouling vs. Biopolymers (Day 2)

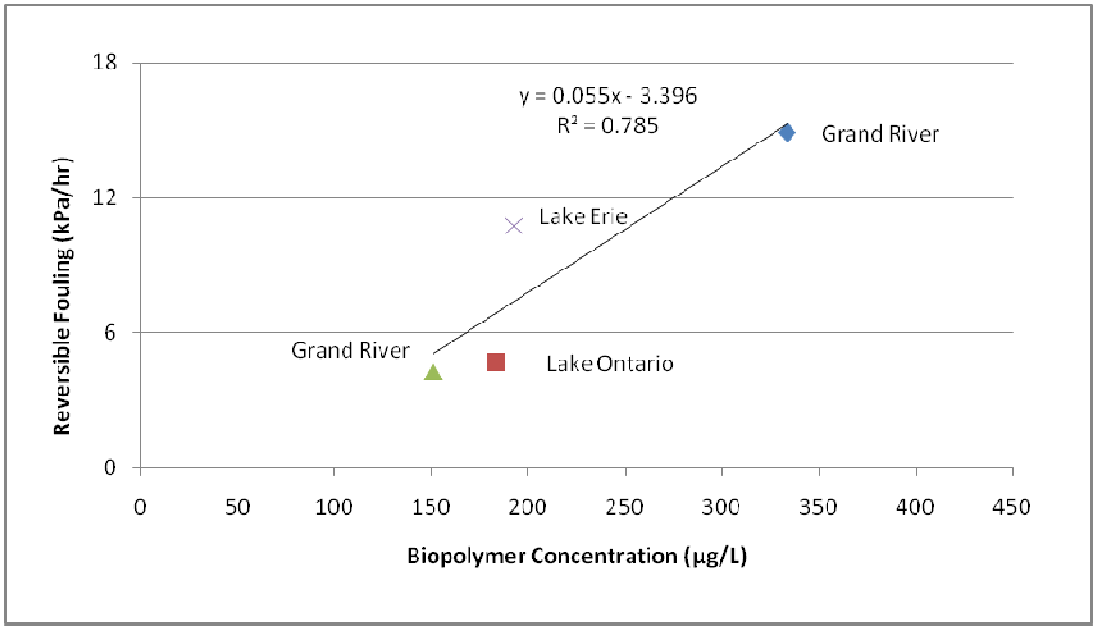


Figure 4.6: Hydraulically reversible fouling vs. Biopolymers (Day 3)

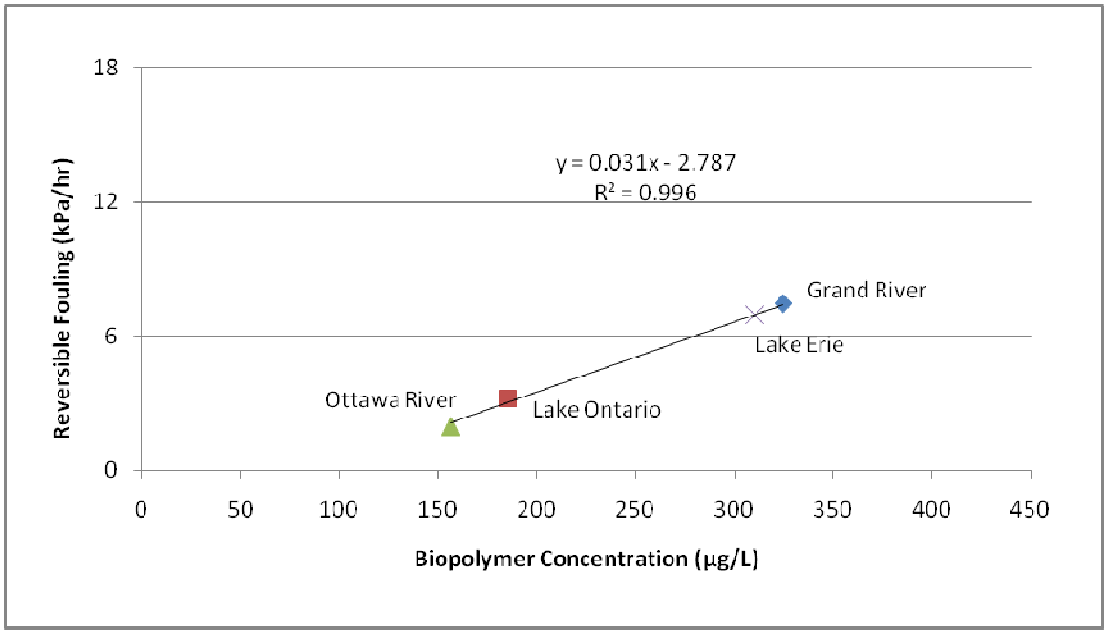


Figure 4.7: Hydraulically reversible fouling vs. Biopolymers (Day 4)

Hydraulically irreversible fouling did not have the same correlation to biopolymer content (Figure 4.8). Irreversible fouling was investigated by partitioning the fouling curve into linear

regions of TMP rise, which were weight averaged according to the length of time for each partition. This approach was also taken for individual 24hr periods to investigate hydraulically irreversible fouling by day. The Ottawa River which had the lowest biopolymer content of the waters had a relatively high mean fouling rate (0.35kPa/hr). This was also true for the Lake Erie water, which had a moderate to high biopolymer content, and the highest mean turbidity (7.5NTU). When hydraulically irreversible fouling was plotted by day, there was also essentially no correlation to biopolymer content (R^2 =0.004 to 0.507), and little progression in the trend with time.

Turbidity of natural waters is largely attributed to inorganic and organic particulate/colloids which reduce light transmission. Turbidity had a marginally better correlation to hydraulically irreversible fouling (Figure 4.9), however it appeared to develop over the fouling experiment. On day one there was no correlation to turbidity (R^2 =0.006) however with greater filtration time, a relationship between turbidity and hydraulically irreversible fouling appears to develop, (R^2= 0.063, 0.444, 0.715 for days 2-4 respectively).This may indicate that the deposited particulate was initially well removed (not irreversibly adsorbed), however it may transition into a combined fouling layer with longer filtration time (due to binding with organic material) causing greater hydraulically irreversible fouling as the experiment progressed. This is best illustrated by comparing the fouling curves of the Ottawa River and Lake Ontario in Figure 4.2. Initially, they appear to have a similar rate of irreversible fouling (first 24hrs), however the fouling becomes much more detrimental for the Ottawa River (higher turbidity) as the experiment progresses. It is likely that the particulate as well as the biopolymer fraction were involved in forming a combined fouling layer. The importance of synergistic effects (cake layer formation and pore blocking) between colloids (organic and inorganic) and dissolved organic fractions has been demonstrated in the literature using mostly model solutions (Jermann et al. 2008; Li and Elimelech, 2006).In this investigation the water with the lowest rate of irreversible fouling was Lake Ontario, which had the lowest turbidity (<1NTU), and a moderate biopolymer concentration. It is postulated that the most severe fouling occurs when there are enough organic

and inorganic particles in a certain size range, in addition to the biopolymer fractions which are largely retained on the membrane surface resulting in a more detrimental fouling condition.

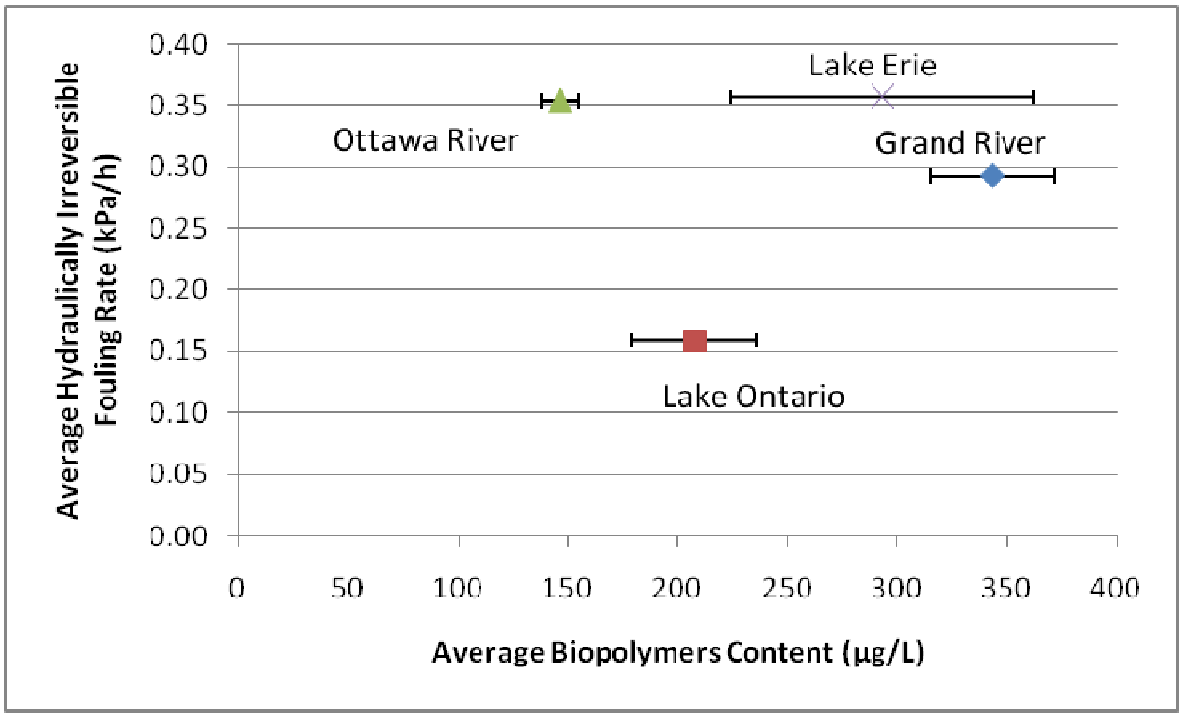


Figure 4.8: Mean hydraulically irreversible fouling rate vs. mean biopolymer content
****Note this was also plotted by day: Day 1 (R^2 =0.441), Day 2 (R^2 =-0.145), Day 3 (R^2 =0.004), Day 4 (R^2 =0.507)**

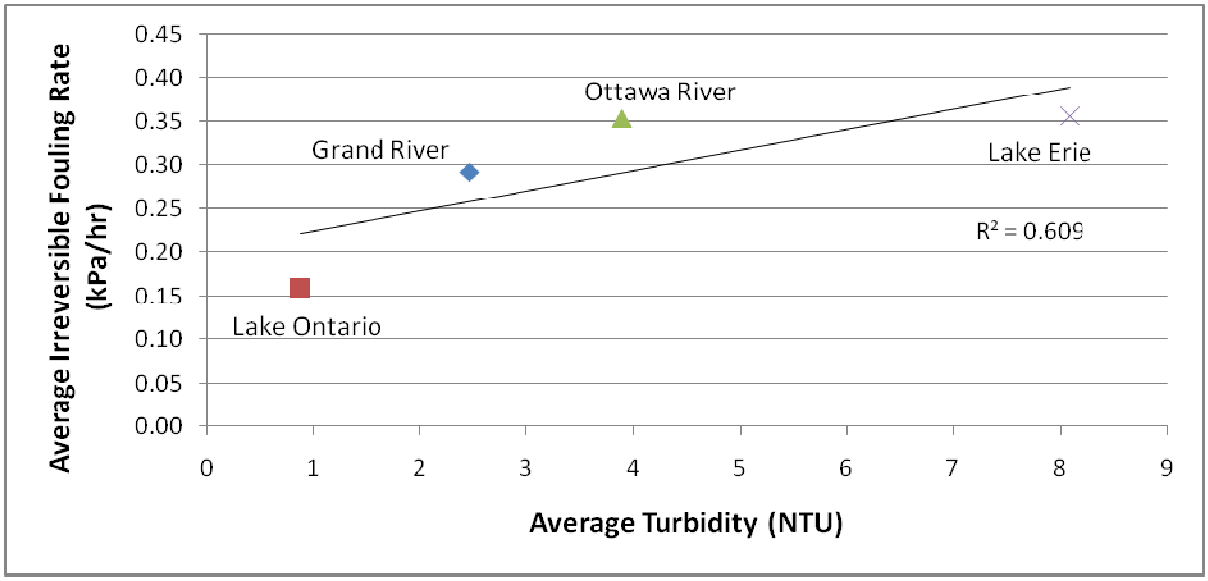


Figure 4.9: Mean hydraulically irreversible fouling rate vs. mean turbidity Note this was also plotted by day: Day 1 (R^2 =0.006), Day 2 (R^2 =0.063), Day 3 (R^2 =0.444), Day 4 (R^2 =0.715)**

The relationship between humic substances and irreversible fouling was also investigated. The mean humic concentration and fouling rate showed little correlation (Figure 4.10). The results were also plotted by day (see summary table in Appendix E) and for the most part there is no visible trend (there was good correlation on day 2). Humic substances have also been shown to irreversibly adsorb to UF membranes (Jucker and Clark, 1994), however usually to those with lower MWCOs. As the membrane in the current study is known to be looser (MWCO approximately 400KDa) and considering the lower observed rejection of humic substances (mean rejection =5%), it is believed that the majority of the humic material was not deposited on or within the membrane. Calcium content has been shown to play a role in terms of irreversible fouling by humic substances in low pressure membranes, due to its effect on the agglomeration of this fraction (Yamamura et al. 2007). Considering the large differences in calcium hardness between the Grand and Ottawa Rivers (265mg/L CaCO3 in Grand River, 24.7mg/L in Ottawa River) differences in humic substances rejection was of interest. Both waters were found to have very low rejection of humic material however with the Ottawa River having a slightly higher

(5%) mean rejection than the Grand River (0%). Once again, due to the relatively high MWCO of the membranes, it is likely that the humic material did not have a significant interaction with the membrane, and therefore little to no impact of calcium content was observed.

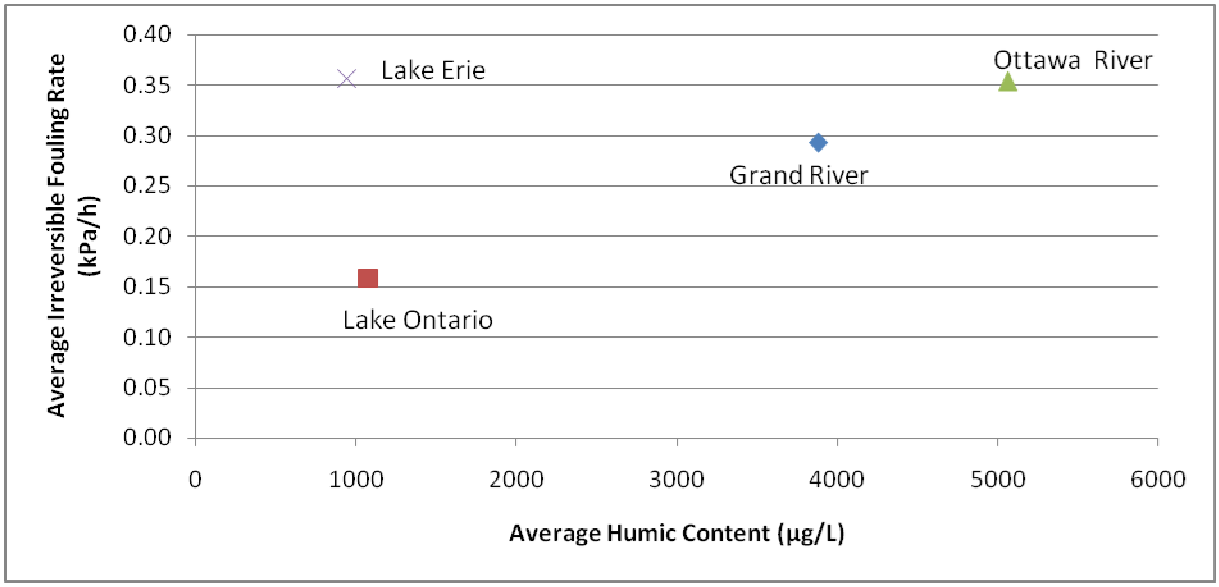


Figure 4.10: Mean hydraulically irreversible fouling rate vs. mean humic content **Note this was also plotted by day: Day 1 (R^2 =0.216), Day 2 (R^2 =0.994), Day 3 (R^2 =0.241), Day 4 (R^2 =0.058)

4.3.2 Mass Balance Results

The mean percent of the influent biopolymer mass leaving through permeate, concentrate and backwash is presented in Figure 4.11 for all four waters. The permeate fraction consists of biopolymers which pass through the membrane and ranged from 35-37% of the total influent for the Ottawa River, Lake Ontario and Lake Erie. The Grand River had a higher rejection of biopolymers (75%) with 25% exiting in the permeate, which may signify that the biopolymers in this water have different properties than the others (e.g. may be larger). The higher degree of fouling for the Grand River (caused by higher biopolymer concentration) could have also improved the rejection biopolymers for this water.

The majority of biopolymers which entered the system were removed during backwash (33-47%), indicating that a large proportion are being deposited (at least marginally) on the membrane surface. The differences between waters for this stream also indicate that the biopolymers have different properties. Lake Ontario for example had a higher portion in the retentate (bulk solution prior to backwash). This might suggest that the biopolymers for this water had less interaction with the membrane surface possibly due to size, charge effects or other differing chemical properties. The "unaccounted fraction" is the percent of mass entering the system which is not leaving through those three measured streams. In the case of positive values, this would be assumed to be mass which is irreversibly deposited on the membrane surface (not removed during backwash). If the value is negative, this can be interpreted as excess mass being released during backwash (which did not enter during the 30min permeation cycle, and may be caused by a more effective backwash for the current cycle.

The results for the "unaccounted fraction" are initially somewhat ambiguous. What is clear is that the quantity of biopolymers being irreversibly deposited on the membrane is very small and relatively difficult to detect (in the range of 0-200 micrograms over 30min permeation cycle). The detection limit of the LC-OCD is in the low ppb range (Huber et al. 2011), which is in the same order as the mass being deposited over the 30min permeation cycle. In some instances negative results were also obtained (consistently for Lake Erie water). The results for this fraction are also a function of what quantity of mass is actually detectable using this technique and how sensitive these results are to experimental and analytical error (i.e. there would be errors associated with measurement, integration of chromatograms etc.). A negative result is also physically possible if a greater quantity of the fouling layer was removed during the backwash for the given cycle for which the measurements were performed.

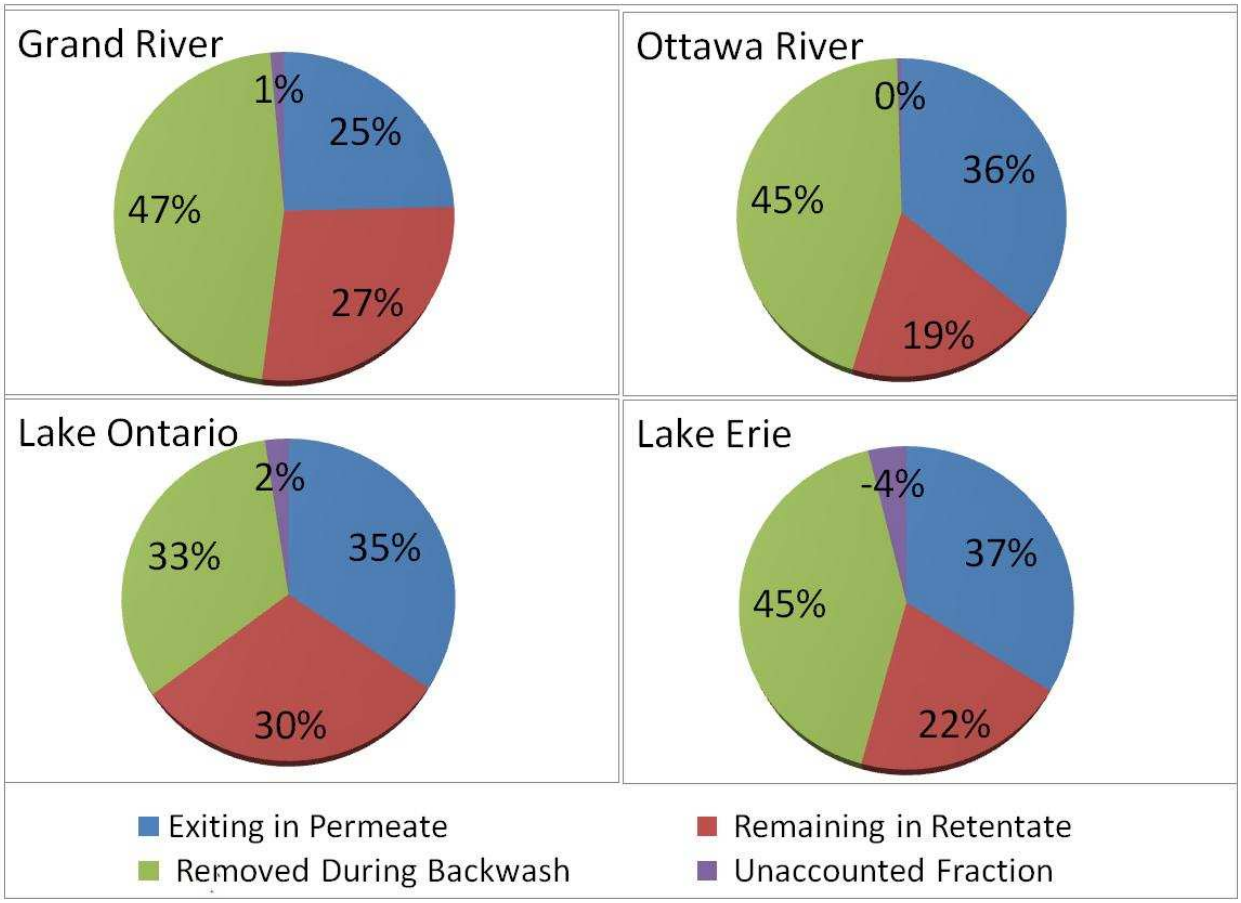


Figure 4.11: Mean Biopolymer Mass (as % of mass entering in influent) Results (n=5 mass balances over 4 days) for membrane fouling experiments on four waters

Another trend which provides further insight in terms of biopolymer adsorption is the biopolymer removal by day (Figure 4.12). From days 1-3 for all of the waters, there was a relatively consistent decrease in biopolymer removal (10-15%). This was then recovered to different degrees after maintenance cleaning (performed on day 3), for each water. This may indicate that there is initially some additional biopolymer removal due to adsorption and once these sites are occupied, removal is lower.

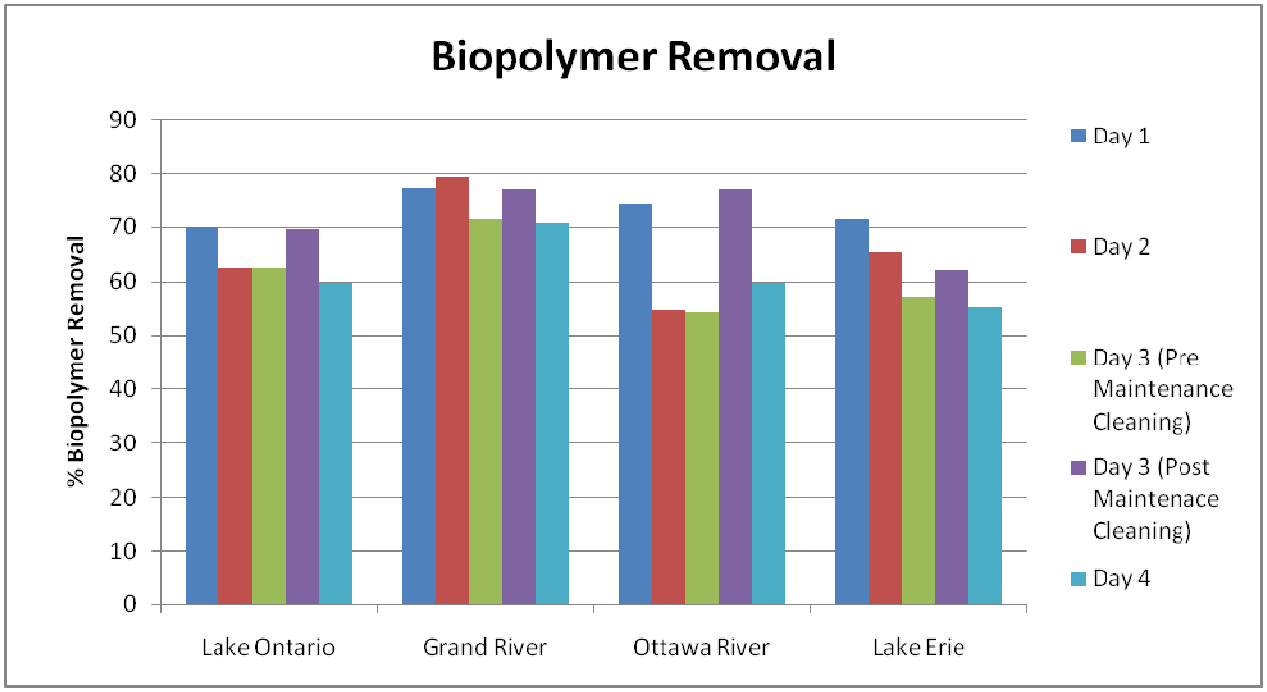


Figure 4.12: Biopolymer Removal by day for four waters

A similar mass balance approach was taken for humic substances to see if any of this material was being deposited on the membrane surface. The majority of the humic substances were found to pass through the membrane however and rejections were only 0-7% depending on the water. The lake waters were on the upper end of humic rejection (7%), which may have been due to the lower influent humic concentration which would increase the time before adsorption sites became occupied.

4.3.3 FEEM results

PCA was run on the combined Lake Erie and Ottawa River data, and loading plots for the three principal components accounting for 95% variation in the model (i.e. 77%, 15% and 3% for PC1, 2& 3 respectively) are presented in Figure 4.13. It should be noted that the percent variation for PC3 (3%) is rather low for a principal component, however due to the physical significance of its loading plot contours, it will be further discussed. The original intention in using the FEEM data

was to determine whether there was a relationship between the composition (protein-like material) of the biopolymer fraction and hydraulically irreversible fouling rate. Unfortunately as only two waters were available for this analysis (for reasons discussed earlier), this objective could not be fully realized. This data can still provide important qualitative information however, and will be therefore discussed further based on the Ottawa River and Lake Erie results.

PC1 has a very broad peak in the 270-380/425-575 excitation/emission region which seems to largely correspond to areas associated with humic and fulvic like content reported in the literature (Chen et al. 2003,Sierra et al. 2005). The broadness of this peak may be related to the substantial differences between the Ottawa River and Lake Erie waters in terms of humic content (5mgC/L vs. 1mgC/L for the Ottawa River and Lake Erie respectively using LC-OCD results). It was also clear in looking at the raw FEEM spectrums that the intensity values in this region were much lower for the Lake Erie water when compared to the Ottawa river(further analysis of differences between the FEEMs of different waters discussed in Chapter 3).

PC2 has the greatest response in the regions associated with Raleigh scattering, which have been attributed to particulate and colloidal like material (Peiris et al. 2010). PC2 also contains a response in the 260-280/310-350 excitation/emission contour region which has been associated with protein like material (Chen et al. 2003, Her et al. 2003). It is possible that particulate and colloids were rejected at the same time as protein, and hence the model cannot differentiate between the two fractions. It has also been hypothesized that the protein-like and the colloidal/particulate matter undergo aggregation, resulting from concentration polarization (Peldszus et al. 2011), and this may be why there is a response for both in this principal component.

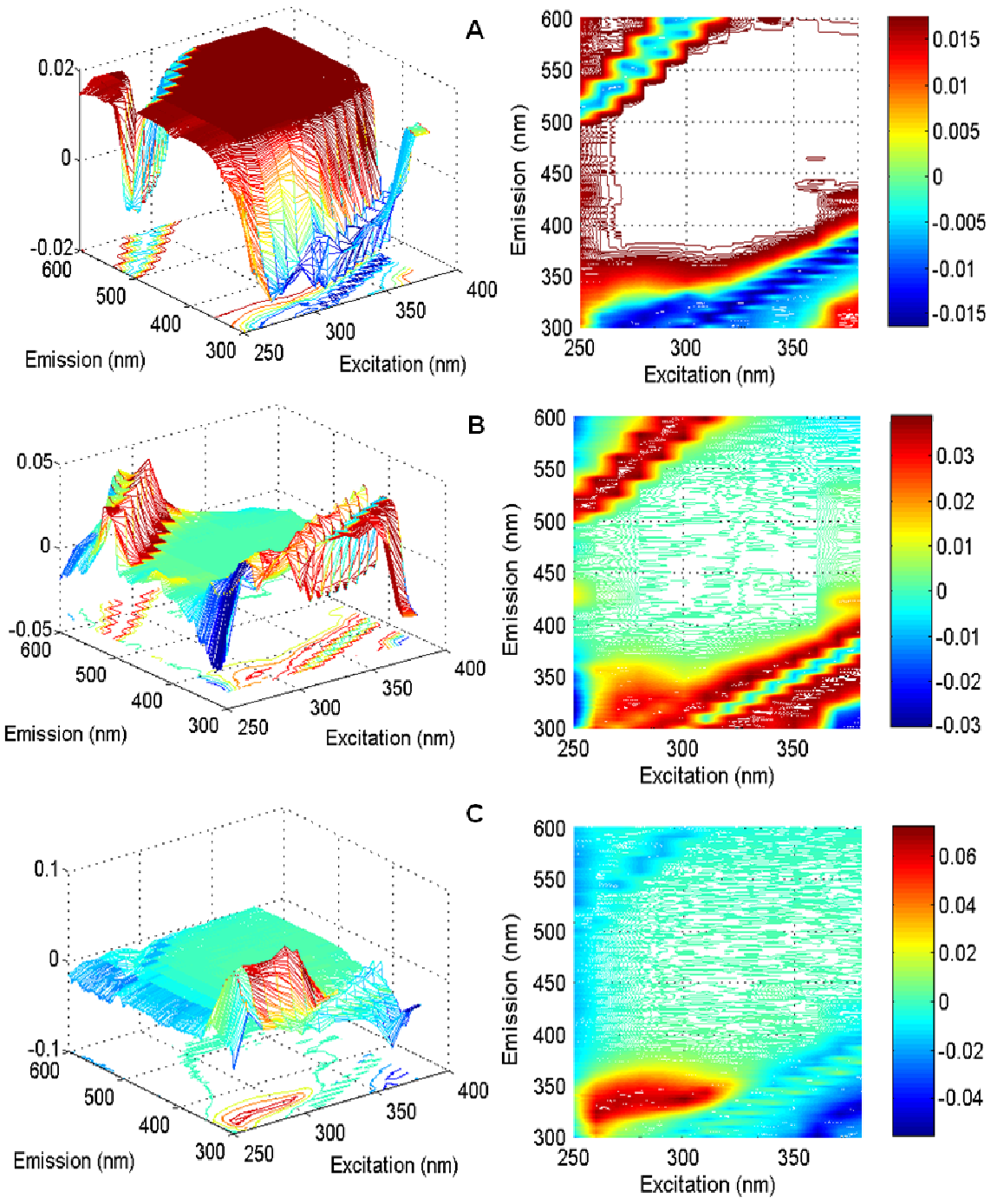


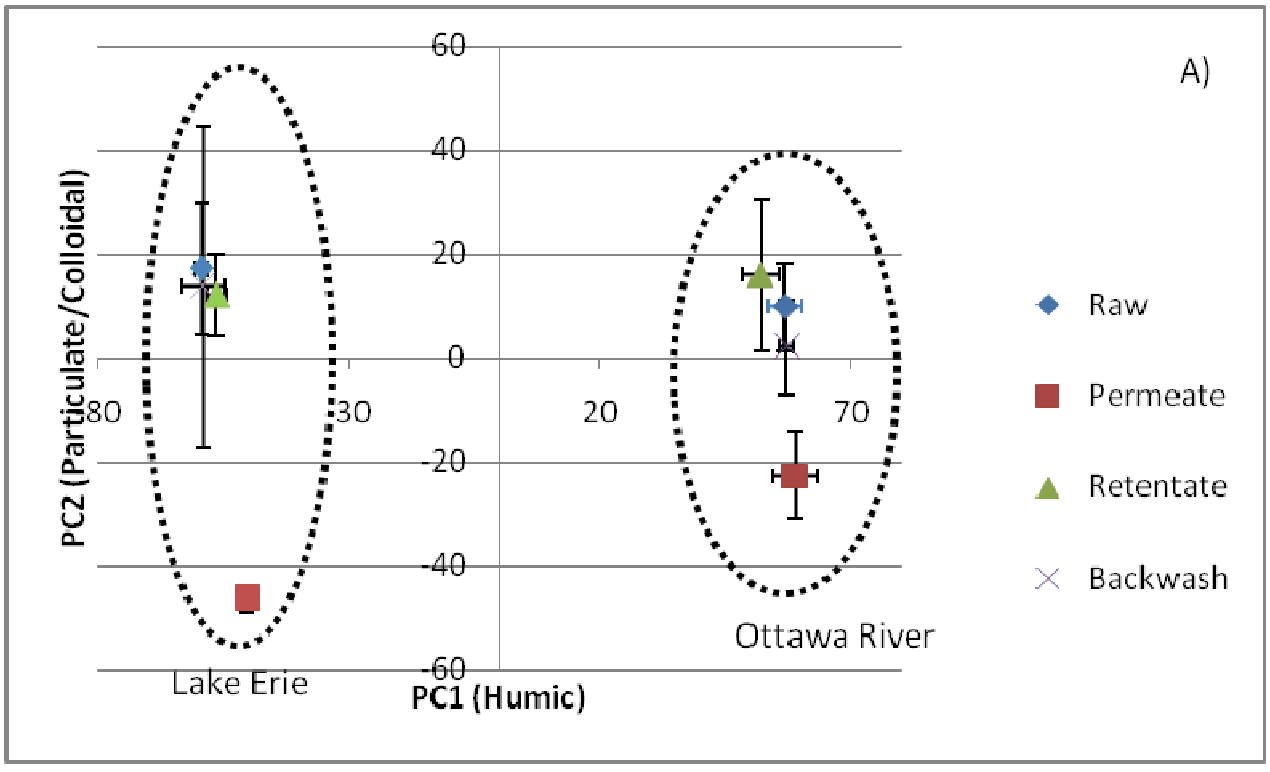
Figure 4.13: PCA loading plots for a) PC1 (77%) b) PC2 (15%) and PC3 (3%)

PC3 has a sole contour peak in this same 260-280/310-350 excitation/emission contour region, suggesting that it may also be related to protein like material. Although it captures relatively little of the variation in the model (3%) it has a very defined peak in this region, with no visible response in other contour areas. This result differs from what has previously been observed by Peiris et al. (2010) as well as an earlier study performed by the authors using these waters, where PC3 was found to have loading contours in the same protein-like region but with some Raleigh scattering interaction as well.

Differences in PC1 (humic-like) scores were attributed to water source rather than level of treatment as seen in Figure 4.14. Lake Erie samples had negative PC1 scores, while the samples from the Ottawa River experiment were all positive. Large differences in PC1 would not be expected within the membrane experiments as little humic rejection was achieved during filtration (mean humic rejection =5% from LC-OCD results). Permeate samples had a consistently lower PC2 (particulate/colloidal) score when compared to the other samples, which was true for both water types. This was expected as particulate and colloidal material would be retained on the membrane surface. There is a visible difference in this trend between the two waters in that the magnitude of PC2 reduction is larger in Lake Erie water. This is logical considering that the Lake Erie water had a higher turbidity and therefore a higher reduction of particulates and colloids. It is also important to note that PC2 had a portion of its response in the protein-like region, and therefore this trend could also be capturing the rejection of proteins during filtration in addition to particulate removal. As the backwash was performed into permeate during the “mass balance” investigation, it is also clear that PC2 increased within the backwash sample capturing removal from the membrane surface during this procedure. There is no visible difference between the raw and retentate PC2 scores, indicating that the permeation cycle was not sufficiently long enough to see a marked increase in retained solids concentration over this period.

The trends for PC3 (Figure 4.14b) are relatively unclear however considering its low percent variation it may not represent a fraction of physical significance. It is important to note that the

error bars (standard deviations) are large especially in the direction of PC3 results, and that no difference between the raw, permeate, retentate or backwash can really be stated with any significance. This may be the result of the low percent variation of this fraction, which is more impacted by experimental and analytical error. The permeate samples appear to have a marginally higher PC3 response, which is counterintuitive if protein-like material is removed during membrane filtration. Another possibility however is that PC3 is capturing smaller protein-like fractions which are not necessarily retained by the membrane. FEEM peaks for protein-like like substances may represent not only macromolecules but also smaller polypeptides (Huber et al. 2011). If PC3 consisted of these smaller fractions only, then it may be possible that there is a greater response in the permeate, where there would be less interference from particulate and colloidal signals during FEEM acquisition.



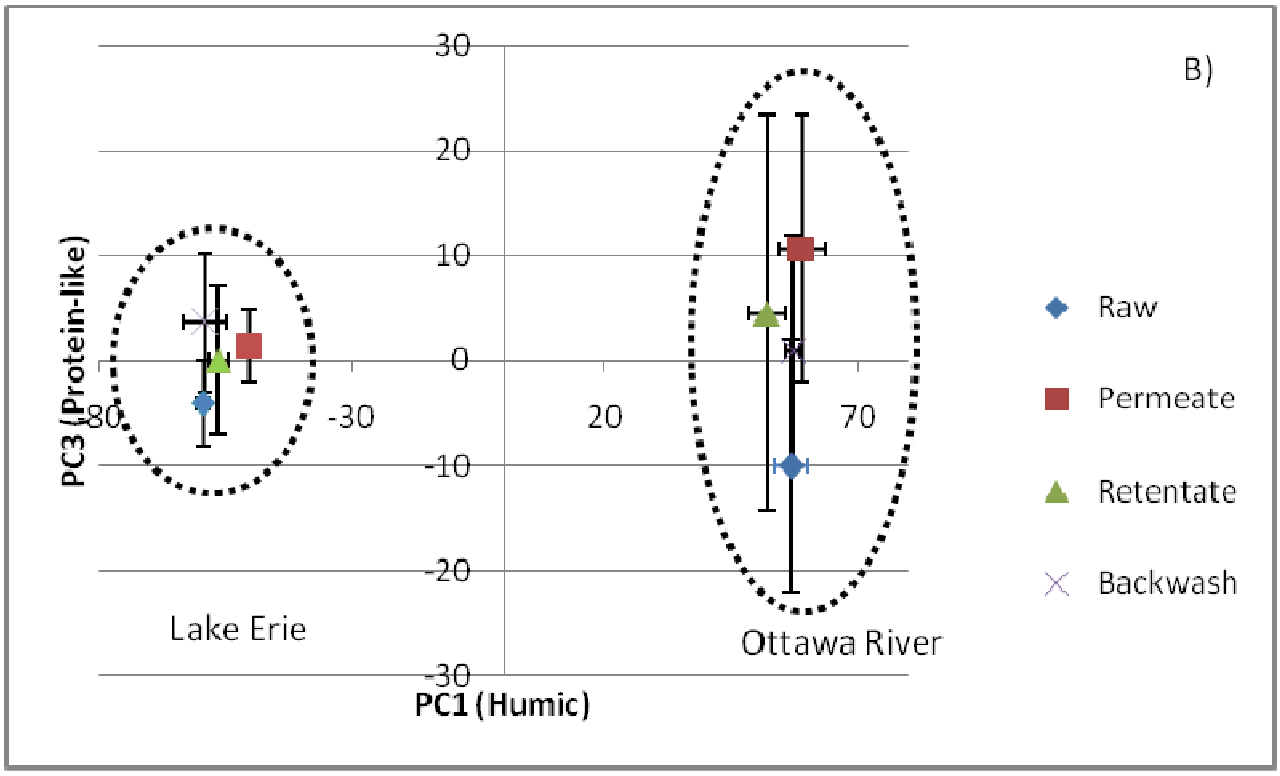


Figure 4.14:PC score plots for a) PC2 vs. PC1 and b) PC3 vs. PC1. Note: bars refer to standard deviation

As only two of the waters could be assessed using FEEM analysis, the PCA results could not be related to the degree of hydraulically reversible and irreversible fouling. This approach however provides an indication of particulate/colloidal (and potentially protein) rejection by the membrane, and therefore is expected to act as a possible technique for measuring foulants which are adsorbed during filtration.

4.4 Conclusions

- Hydraulically reversible fouling was found to have a relatively good correlation with biopolymer content across four different waters.

- Hydraulically irreversible fouling could not be directly related to biopolymer content (or any other fraction of the NOM). As turbidity had a moderate correlation with irreversible fouling, it is likely that particulate/colloids also play an important role in forming an irreversible fouling layer. This would suggest a combined fouling effect.

- The mass balance approach was not sensitive enough to capture the portion of biopolymers being irreversibly adhered to the membrane surface. It did provide some insight into biopolymer removal during backwash, with some indication that there are differences between the biopolymers of the different waters and their interaction with the membrane surface.

- PCA analysis of FEEM data was only able to capture 2 principal components: PC1 (Humic-like) and PC2 (Colloidal/Particulate with some response in protein-like region). PC1 varied the greatest in terms of water type with no visible trend in its removal (which was consistent with LC-OCD results in that humic content was not removed through membrane filtration). PC2 had consistent removal, and also increased after backwash suggesting primarily particulate (and possibly protein-like) properties. PC3 was discussed primarily due to its well defined response in the protein-like region, however due to the fact that it represented very low percent variation for the PCA model (3%), little conclusions could be drawn on this component.

Chapter 5
Conclusions and Recommendations

The major conclusions of this work were presented at the end of Chapters 3 and 4, which are summarized again in this chapter, followed by implications and recommendations for future work.

5.1 Summary of Conclusions

The following conclusions were made based on the NOM characterization study which was done at five different full scale drinking water facilities within Ontario (which was discussed in Chapter 3).

1. Full scale biological filtration was found to very effectively remove low molecular weight acids generated during ozonation. In addition, the LMW building block fraction appeared to be partially biodegraded in full scale filtration. Little additional biopolymer removal was observed after coagulation/flocculation/sedimentation at full scale, perhaps because of both lower concentration and removal of the more easily biodegradable biopolymers by the upstream processes.

2. Coagulation/ flocculation/sedimentation removed 21-73% of the biopolymers and 8-78% of the humic substances depending on the location and little variation was noted in terms of seasonal removals. Enhanced coagulation provided much higher humic removals (58-78%), however did not improve biopolymer removal. It thus appears that biopolymers are potentially removed through coagulation/flocculation/sedimentation by a different mechanism than humic substances.

3. Biopolymer content was found to vary seasonally with temperature (higher concentrations in the warmer months). The lake waters contained proportionally higher biopolymer content than the river waters, although the DOC in the former was lower.

4. PCA was successfully applied to capture variation in FEEMs from six different water sources. The results are considered a good predictor for the removal of humic substances throughout full scale treatment (excluding oxidation processes).The PCA results for humic-like material were relatively well correlated to humic substance concentrations from LC-OCD analysis.

5. LC-OCD and FEEM provided complementary insight into NOM removal during full scale treatment. NOM structural changes which were not captured by LC-OCD were apparent in the FEEM results. Using either technique on its own may lead to incomplete interpretation of changes in NOM character.

The major conclusions from the membrane fouling work which was done using commercially available ultrafiltration membranes are presented below. The work investigated both hydraulically reversible and irreversible fouling of four waters with different NOM composition.

1. Hydraulically reversible fouling was found to have a relatively good correlation with biopolymer content across four different waters.

2. Hydraulically irreversible fouling could not be directly related to biopolymer content (or any other fraction of the NOM). As turbidity had a moderate correlation with irreversible fouling, it is likely that particulate/colloids also play an important role in forming an irreversible fouling layer. This would suggest a combined fouling effect.

3. The mass balance approach was not sensitive enough to capture the portion of biopolymers being irreversibly adhered to the membrane surface. It did provide some insight into biopolymer removal during backwash, with some indication that there are differences between the biopolymers of the different waters and their interaction with the membrane surface.

4. PCA analysis of FEEM data was only able to capture 2 principal components: PC1 (Humic-like) and PC2 (Colloidal/Particulate with some response in protein-like region). PC1 varied the greatest in terms of water type with no visible trend in its removal (which was consistent with LC-OCD results in that humic content was not removed through membrane filtration). PC2 had consistent removal, and also increased after backwash suggesting primarily particulate (and possibly protein-like) properties. PC3 was discussed primarily due to its well defined response in the protein-like region, however due to the fact that it represented very low percent variation for the PCA model (3%), little conclusions could be drawn on this component.

5.2 Implications and Recommendations

Based on the conclusions outlined above, different recommendations and implications for future work related to membrane fouling and NOM characterization during conventional treatment are summarized below.

1. Considering the lake waters had relatively little humic content, and biopolymers accounted for a larger portion of the DOC, direct biofiltration for membrane pre-treatment may be especially applicable to these waters. It was shown that for the direct biofiltration at pilot scale, a significant amount of biopolymers were removed, which was comparable to full scale removal through coagulation/ flocculation. Biopolymers were also found to be directly related to hydraulically reversible fouling (largely independent of water quality) and

are suspected of forming a combined irreversible fouling layer with particulate and colloidal material. As biofiltration is capable of removing a large portion of these constituents (presumably through biological processes and physical mechanisms), membrane pre-treatment using this process may significantly extend the time between backwash and chemical cleaning of the membranes. Biofiltration studies using the lake waters for larger scale implementation would be of specific interest, as no humic removal would be required, whereas river waters would likely still require coagulation/flocculation to reduce colour and disinfection by-product formation. One important consideration for biofiltration pre-treatment using lake waters however would be chlorine quenching, as chlorination for the control of zebra mussels is usually required at raw water intakes.

2. Biopolymers were found to have a significant seasonal trend, with higher concentrations occurring in the summer months. This may have important implications for membrane facilities which are currently operating with minimal pre-treatment. It would be of interest to investigate how both hydraulically reversible and irreversible fouling rates change by season using full scale data at such locations, while also monitoring biopolymer concentrations and other relevant water quality parameters. For membrane plants which operate with coagulation as a pre-treatment, optimizing for biopolymer removal would be beneficial. It was shown that the removal mechanism for biopolymers compared to humic material is likely different (enhanced coagulation significantly improved humic removal while not that of biopolymers), but generally biopolymers are well removed through coagulation. If significant humic reduction is not required (for DBP control), the dose for membrane pre-treatment could largely be determined by biopolymer removal. Coagulation reduces particulate and colloidal matter as well as biopolymer content. This is likely why it has been used effectively as a membrane pre-treatment. Agglomerated particles will still reach the membrane surface however, and may still be irreversibly deposited. It remains to be determined whether biofiltration may be superior to coagulation in some instances. A direct comparison between the two pre-treatment methods would be beneficial.

3. The mass balance approach outlined in Chapter 4 was not sensitive enough to definitively capture organic material being irreversibly deposited to the membrane (although there was some indication that it was a very small portion of the biopolymers). One option to improve this approach would be to choose a longer permeation cycle where presumably a greater mass would be deposited and more easily detected. This would have to be done while still keeping the permeation cycle in a reasonable range however, or else it may not be representative of typical fouling conditions for surface water treatment. Another option would be to perform LC-OCD and FEEM analysis on the chemical cleaning solution. The elevated concentration of the cleaning agent (chlorine) however may change the nature of the original foulants.

4. Low molecular weight fractions were readily removed in full scale biological filtration (especially LMW acids), and it is reasonable to assume that these fractions might correspond to what is currently being measured using AOC methods. As AOC is relatively labour intensive, it would be helpful to find more rapid measurements. LC-OCD may offer an alternative to AOC measurements, especially if AOC could be directly correlated to different NOM fractions (LMW acids, building blocks or even biopolymers).

5. Results from the FEEM analysis coupled with PCA were shown to act as a good predictor of humic removal during treatment, and they corresponded well to LC-OCD analysis (excluding oxidation processes). As FEEM data can be acquired very rapidly, it may serve as a good monitoring tool for treatment performance from an operational standpoint. Specifically the removal of humic substances through coagulation (and enhanced coagulation) was well captured using this data. Although the results for the PCA model containing all waters was useful in describing qualitative differences, it would be

more useful from a treatment monitoring perspective to develop a model specific to each water type (this would require more data than was collected during this investigation).

6. Finally, LC-OCD and FEEM were shown to be good complimentary monitoring tools for assessing NOM removal performance for a variety of processes. LC-OCD alone could not capture some of the structural changes which occurred during oxidation, however it is sensitive enough to quantify lower molecular weight products which were formed. It is therefore advisable to use a combination of NOM characterization techniques when assessing NOM behaviour during treatment, as the results from one method alone may not be sufficient.

Bibliography

AWWA. (2005). *Microfiltration and ultrafiltration membranes for drinking water*. Denver, CO.: American Water Works Association.

Aiken, G. (1984). Evaluation of ultrafiltration for determining molecular weight of fulvic acid. *Environmental science & technology*, *18*(12), 978-981. Retrieved from http://pubs.acs.org/doi/abs/10.1021/es00130a016

Aiken, G., McKnight, D., Thorn, K., & Thurman, E. (1992). Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Organic Geochemistry*, *18*(4), 567-573. Retrieved from http://www.sciencedirect.com/science/article/pii/014663809290119I

Allpike, B. P., Heitz, A., Joll, C. a, Kagi, R. I., Abbt-Braun, G., Frimmel, F. H., Brinkmann, T., et al. (2005). Size exclusion chromatography to characterize DOC removal in drinking water treatment. *Environmental science & technology*, *39*(7), 2334-42. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/15871273

Amy, G. (2008). Fundamental understanding of organic matter fouling of membranes. *Desalination*, *231*(1-3), 44-51. doi:10.1016/j.desal.2007.11.037

Amy, G., & Cho, J. (1999). Interactions between natural organic matter (NOM) and membranes: Rejection and fouling. *Water Science and Technology*, *40*(9), 131-139. Retrieved from http://www.sciencedirect.com/science/article/pii/S0273122399006496

Amy, G. L., Collins, M. R., Kuo, C. J., & King, P. H. (1987). Comparing Gel Permeation Chromatography and Ultrafiltration for the Molecular Weight Characterization of Aquatic Organic Matter. *Journal - American Water Works Association*, *79*(1), 43-49.

Assemi, S., Newcombe, G., Hepplewhite, C., & Beckett, R. (2004). Characterization of natural organic matter fractions separated by ultrafiltration using flow field-flow fractionation. *Water research*, *38*(6), 1467-76. doi:10.1016/j.watres.2003.11.031

Baghoth, S A, Sharma, S. K., & Amy, G. L. (2011). Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation emission matrices and PARAFAC. *Water Research*, *45*(2), 797-809. Elsevier Ltd. doi:10.1016/j.watres.2010.09.005

Baghoth, S. A., Dignum, M., Grefte, A., Kroesbergen, J., & Amy, G. L. (2009). Characterization of NOM in a drinking water treatment process train with no disinfectant residual. *Water Science & Technology: Water Supply*, *9*(4), 379. doi:10.2166/ws.2009.569

Baghoth, S. a., Sharma, S. K., Guitard, M., Heim, V., Croué, J.-P., & Amy, G. L. (2011). Removal of NOM-constituents as characterized by LC-OCD and F-EEM during drinking water treatment. *Journal of Water Supply: Research and Technology—AQUA*, *60*(7), 412. doi:10.2166/aqua.2011.059

Baker, a, Tipping, E., Thacker, S. a, & Gondar, D. (2008). Relating dissolved organic matter fluorescence and functional properties. *Chemosphere*, *73*(11), 1765-72. Elsevier Ltd. doi:10.1016/j.chemosphere.2008.09.018

Bieroza, M., Baker, A., & Bridgeman, J. (2009). Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. *The Science of the total environment*, *407*(5), 1765-74. Elsevier B.V. doi:10.1016/j.scitotenv.2008.11.013

Bieroza, M. Z., Bridgeman, J., & Baker, a. (2010). Fluorescence spectroscopy as a tool for determination of organic matter removal efficiency at water treatment works. *Drinking Water Engineering and Science*, *3*(1), 63-70. doi:10.5194/dwes-3-63-2010

Bouwer, E. J., & Crowe, P. B. (1988). Biological Processes in Drinking Water Treatment. *Journal - American Water Works Association*, *80*(9), 82-93.

Budd, G. C., Hess, A. F., Shorney-darby, H., Neemann, J. J., Spencer, C. M., Bellamy, J. D., & Hargette, P. H. (2004). Coagulation application for new treatment goals. *Journal - American Water Works Association*, *96*(2), 102-113.

Buffle, J., Wilkinson, K. J., Stoll, S., Filella, M., & Zhang, J. (1998). A Generalized Description of Aquatic Colloidal Interactions: The Three-colloidal Component Approach. *Environmental Science & Technology*, *32*(19), 2887-2899. doi:10.1021/es980217h

Chadik, P. ., & Amy, G. L. (1988). Molecular Weight Effects on THM Control by Coagulation and Adsorption. *Journal of Environmental Engineering*, *113*(6), 1234-1248.

Chandrakanth, M. S., Amy, G. L., & Epa, W. S. (1998). Effects of NOM source variations and calcium complexation capacity on ozone-induced particle destabilization. *Water Research*, *32*(1), 115-124.

Chen, W., Westerhoff, P., Leenheer, J. a, & Booksh, K. (2003). Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental science & technology*, *37*(24), 5701-10. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/14717183

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Marine Chemistry*, *51*(4), 325-346. doi:10.1016/0304-4203(95)00062-3

Coble, P. G., Green, S. A., Blough, N. V., & Gagosian, R. B. (1990). Characterization of dissolved organic matter in the Black Sea by fluorescence spectroscopy.pdf. *Nature*, *348*, 432-435.

Combe, C., Molis, E., Lucas, P., Riley, R., & Clark, M. . (1999). The effect of CA membrane properties on adsorptive fouling by humic acid. *Journal of Membrane Science*, *154*(1), 73-87. doi:10.1016/S0376-7388(98)00268-3

Crittenden, J. C., & Montgomery Watson Harza (Firm). (2005). *Water treatment principles and design*. (J. Wiley, Ed.) (2nd ed.). Hoboken, N.J.

Croué, J.-P. (2004). Isolation of humic and non-humic NOM fractions: structural characterization. *Environmental monitoring and assessment*, *92*(1-3), 193-207. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/15038544

Edwards, M., & Benjamin, M. M. (1992). Transformation of NOM by Ozone and its Effect on Iron and Aluminum Solubility. *Journal - American Water Works Association*, *84*(6), 56-66.

Edzwald, J. K. (1993). COAGULATION IN DRINKING WATER TREATMENT : PARTICLES , ORGANICS AND COAGULANTS. *Water Science & Technology*, *27*(11), 21-35.

Edzwald, J., & Tobiason, J. (1999). Enhanced coagulation: US requirements and a broader view. *Water Science and Technology*, *40*(9), 63-70. Retrieved from http://www.sciencedirect.com/science/article/pii/S0273122399006411

Emelko, M. B., Huck, P. M., Coffey, B. M., & Franklyn Smith, E. (2006). Effects of media, backwash : and temperature on full-scale biological filtration. *Journal - American Water Works Association*, *98*(12), 61-73. American Water Works Association. Retrieved from http://cat.inist.fr/?aModele=afficheN&cpsidt=18356723

Eriksson, L., Johansson, E., Kettaneh-Wold, N., & Wold, S. (2001). *Multi- and Megavariate Data Analysis, Principles and Applications* (p. 533). Umea, Sweden: Umetrics Academy.

Flemming, H. C., & Wingender, J. (2001). Relevance of microbial extracellular polymeric substances (EPSs)--Part I: Structural and ecological aspects. *Water science and technology : a journal of the International Association on Water Pollution Research*, *43*(6), 1-8. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11381954

Flemming, H.-C., Schaule, G., Griebe, T., Schmitt, J., & Tamachkiarowa, a. (1997). Biofouling—the Achilles heel of membrane processes. *Desalination*, *113*(2-3), 215-225. doi:10.1016/S0011-9164(97)00132-X

Frimmel, F. H., Saravia, F., & Gorenflo, A. (2004). NOM removal from different raw waters by membrane filtration. *Water Science & Technology: Water Supply*, *4*(4), 165-174.

Gao, W., Liang, H., Ma, J., Han, M., Chen, Z.-lin, Han, Z.-shuang, & Li, G.-bai. (2011). Membrane fouling control in ultrafiltration technology for drinking water production: A review. *Desalination*, *272*(1-3), 1-8. Elsevier B.V. doi:10.1016/j.desal.2011.01.051

Gray, S. R., Dow, N., Orbell, J. D., Tran, T., & Bolto, B. a. (2011). The significance of interactions between organic compounds on low pressure membrane fouling. *Water Science & Technology*, *64*(3), 632. doi:10.2166/wst.2011.488

Grünheid, S., Amy, G., & Jekel, M. (2005). Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. *Water research*, *39*(14), 3219-28. doi:10.1016/j.watres.2005.05.030

Haberkamp, J., Ernst, M., Paar, H., Pallischeck, D., Amy, G., & Jekel, M. (2011). Impact of organic fractions identified by SEC and fluorescence EEM on the hydraulic reversibility of ultrafiltration membrane fouling by secondary effluents. *Desalination and Water Treatment*, *29*, 73-86. doi:10.5004/dwt.2011.1975

Haberkamp, J., Ruhl, A. S., Ernst, M., & Jekel, M. (2007). Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration. *Water research*, *41*(17), 3794-802. doi:10.1016/j.watres.2007.05.029

Hallé, C., Huck, P. M., Peldszus, S., Haberkamp, J., & Jekel, M. (2009). Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water. *Environmental science & technology*, *43*(10), 3878-84. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/19544902

Her, N., Amy, G., Foss, D., & Cho, J. (2002). Variations of molecular weight estimation by HP-size exclusion chromatography with UVA versus online DOC detection. *Environmental science &*, *36*(15), 3393-3399. Retrieved from http://pubs.acs.org/doi/abs/10.1021/es015649y

Her, N., Amy, G., McKnight, D., Sohn, J., & Yoon, Y. (2003). Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water research*, *37*(17), 4295-303. doi:10.1016/S0043-1354(03)00317-8

Howe, K. J., & Clark, M. M. (2002). Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environmental science & technology*, *36*(16), 3571-6. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/12214651

Hozalski, R. M., Goel, S., & Bouwer, E. J. (1995). TOC removal in biological filters. *Journal - American Water Works Association*, *87*(12), 40-54.

Huang, H., Lee, N., Young, T., Gary, A., Lozier, J. C., & Jacangelo, J. G. (2007). Natural organic matter fouling of low-pressure , hollow-fiber membranes : Effects of NOM source and hydrodynamic conditions. *Water research*, *41*, 3823-3832. doi:10.1016/j.watres.2007.05.036

Huber, S. A., & Frimmel, F. H. (1991). Flow injection analysis for organic and inorganic carbon in the low-ppb range. *Analytical Chemistry*, *63*(19), 2122–2130. ACS Publications. Retrieved from http://pubs.acs.org/doi/abs/10.1021/ac00019a011

Huber, S. a, Balz, A., Abert, M., & Pronk, W. (2011). Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography--organic carbon detection--organic nitrogen detection (LC-OCD-OND). *Water research*, *45*(2), 879-85. Elsevier Ltd. doi:10.1016/j.watres.2010.09.023

Huck, P. M. (1990). Measurement of Biodegradable Organic Matter and Bacterial Growth Potential in Drinking Water. *Journal - American Water Works Association*, *82*(7), 78-86.

Huck, P. M., Coffey, B. M., Amirtharajah, A., & Bouwer, E. J. (2000). *Optimizing Filtration in Biological Filters*. AWWA Research Foundation.

Hudson, N., Baker, A., & Reynolds, D. (2007). Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. *River Research and …*, *23*(6), 631-649. doi:10.1002/rra

Hudson, N., Baker, A., Ward, D., Reynolds, D. M., Brunsdon, C., Carliell-Marquet, C., & Browning, S. (2008). Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England. *The Science of the total environment*, *391*(1), 149-58. doi:10.1016/j.scitotenv.2007.10.054

Jacangelo, J. G., Demarco, J., Owen, D. M., & Randtke, S. J. (1995). Selected processes for removing NOM : an overview : Natural organic matter. *Journal - American Water Works Association*, *87*(1), 64-77. American Water Works Association. Retrieved from http://cat.inist.fr/?aModele=afficheN&cpsidt=3383050

Jacangelo, Joseph G, Adham, S. S., & Laine, J.-M. (1995). Mechanism of Cryptosporidium, Giardia, and MS2 Virus Removal by MF and UF. *Journal American Water Works Association*, *87*(9), 107-121.

Jekel, M. R. (1994). Flocculation Effects of Ozone. *Ozone: Science & Engineering*, *16*(1), 55-66.

Jermann, D., Pronk, W., Kägi, R., Halbeisen, M., & Boller, M. (2008). Influence of interactions between NOM and particles on UF fouling mechanisms. *Water research*, *42*(14), 3870-8. doi:10.1016/j.watres.2008.05.013

Jones, K. L., & O'Melia, C. R. (2001). Ultrafiltration of protein and humic substances: effect of solution chemistry on fouling and flux decline. *Journal of Membrane Science*, *193*(2), 163-173. doi:10.1016/S0376-7388(01)00492-6

Jucker, C., & Clark, M. M. (1994). Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. *Journal of Membrane Science*, *97*(94), 37-52. Retrieved from http://www.sciencedirect.com/science/article/pii/037673889400146P

Kalibbala, H. M., Kaggwa, R., Wahlberg, O., & Plaza, E. (2011). Characteristics of natural organic matter and formation of chlorination by-products at Masaka waterworks. *Journal of Water Supply: Research and Technology—AQUA*, *60*(8), 511. doi:10.2166/aqua.2011.076

Kennedy, M. D., Kamanyi, J., Salinas, S. G., Lee, N. H., Schippers, J. C., & Amy, G. (2008). *Advanced membrane technology and applications*. (N. N. Li, Ed.). Hoboken, N.J.: John Wiley & Sons.

Kimura, K., Hane, Y., Watanabe, Y., Amy, G., & Ohkuma, N. (2004). Irreversible membrane fouling during ultrafiltration of surface water. *Water research*, *38*(14-15), 3431-41. doi:10.1016/j.watres.2004.05.007

Korshin, G., Chow, C. W. K., Fabris, R., & Drikas, M. (2009). Absorbance spectroscopy-based examination of effects of coagulation on the reactivity of fractions of natural organic matter with varying apparent molecular weights. *Water research*, *43*(6), 1541-8. Elsevier Ltd. doi:10.1016/j.watres.2008.12.041

Krasner, S. W., Sclimenti, M. J., & Coffey, B. M. (1993). Testing Biologically Active Filters for Removing Aldehydes Formed During Ozonation. *Journal - American Water Works Association*, *85*(5), 62-71.

Laine, J.-M., Hagstrom, J. P., Clark, M. M., & Mallevialle, J. (1989). Effects of Ultrafiltration Membrane Composition. *Journal - American Water Works Association*, *81*(11), 61-67.

Lankes, U., Lüdemann, H.-D., & Frimmel, F. H. (2008). Search for basic relationships between "molecular size" and "chemical structure" of aquatic natural organic matter--answers from 13C and 15N CPMAS NMR spectroscopy. *Water research*, *42*(4-5), 1051-60. doi:10.1016/j.watres.2007.09.028

Lankes, U., Müller, M. B., Weber, M., & Frimmel, F. H. (2009). Reconsidering the quantitative analysis of organic carbon concentrations in size exclusion chromatography. *Water research*, *43*(4), 915-24. doi:10.1016/j.watres.2008.11.025

LeChevallier, M. W., Becker, W. C., Schor, P., & Lee, R. G. (1992). Evaluating the performance of biologically active rapid filters. *Journal - American Water Works Association*, *84*(136-146). Retrieved from http://apps.awwa.org/waterlibrary/scholarabstract.aspx?an=JAW_0031535

Lee, N., Amy, G., Croué, J.-P., & Buisson, H. (2004). Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water research*, *38*(20), 4511-23. doi:10.1016/j.watres.2004.08.013

Leenheer, J. (1981). Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental science & technology*, *15*(5), 578-587. Retrieved from http://pubs.acs.org/doi/abs/10.1021/es00087a010

Li, Q., & Elimelech, M. (2006). Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter. *Journal of Membrane Science*, *278*(1-2), 72-82. doi:10.1016/j.memsci.2005.10.045

Lin, C. F., Liu, S. H., & Hao, O. J. (2001). Effect of functional groups of humic substances on uf performance. *Water research*, *35*(10), 2395-402. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11394773

Liu, T., Chen, Z.-lin, Yu, W.-zheng, & You, S.-jie. (2011). Characterization of organic membrane foulants in a submerged membrane bioreactor with pre-ozonation using three-dimensional excitationeemission matrix fluorescence spectroscopy. *Water Research*, *45*(5), 2111-2121. Elsevier Ltd. doi:10.1016/j.watres.2010.12.023

Marhaba, T. F., Van, D., & Lippincott, R. L. (2000). Changes in NOM Fractionation through Treatment: A Comparison of Ozonation and Chlorination. *Ozone: Science & Engineering*, *22*(3), 249-266. doi:10.1080/01919510008547209

Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A., & Sillanpää, M. (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere*, *83*(11), 1431-42. Elsevier Ltd. doi:10.1016/j.chemosphere.2011.01.018

Matilainen, A., Vepsäläinen, M., & Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment : A review. *Advances in Colloid and Interface Science*, *159*(2), 189-197. Elsevier B.V. doi:10.1016/j.cis.2010.06.007

Miltner, R., Summers, R., & Wang, J. (1995). Biofiltration performance: part 2, effect of backwashing. *Journal of the American Water …*, *87*(12), 64-70. Retrieved from http://bases.bireme.br/cgi-bin/wxislind.exe/iah/online/?IsisScript=iah/iah.xis&src=google&base=REPIDISCA&lang=p&nextAction=lnk&exprSearch=52532&indexSearch=ID

Mousa, H. (2007). Investigation of UF membranes fouling by humic acid. *Desalination*, *217*(1-3), 38-51. doi:10.1016/j.desal.2007.02.006

Owen, D., Amy, G., Chowdhury, Z., Paode, R., McCoy, G., & Viscosil, K. (1995). NOM characterization and treatability. *Journal American Water Works Association*, *87*(1), 46–63. AWWA. Retrieved from http://apps.awwa.org/waterlibrary/scholarabstract.aspx?an=JAW_0037643

O'Melia, C. R., Becker, W. C., & Au, K. K. (1999). Removal of Humic substances by coagulation. *Water Science & Technology*, *40*(9), 47-54.

Parsons, S. A., Jefferson, B., Goslan, E. H., Jarvis, P. R., & Fearing, D. A. (2004). Natural organic matter – the relationship between character and treatability. *Water science and technology : water supply*, *4*(5-6), 43-48.

Peiris, B. R. H., Hallé, C., Haberkamp, J., Legge, R. L., Peldszus, S., Moresoli, C., Budman, H., et al. (2008). Assessing nanofiltration fouling in drinking water treatment using fluorescence fingerprinting and LC-OCD analyses. *Water Science & Technology: Water Supply*, *8*(4), 459. doi:10.2166/ws.2008.095

Peiris, R. H., Hallé, C., Budman, H., Moresoli, C., Peldszus, S., Huck, P. M., & Legge, R. L. (2010). Identifying fouling events in a membrane-based drinking water treatment process using

principal component analysis of fluorescence excitation-emission matrices. *Water research*, *44*(1), 185-94. doi:10.1016/j.watres.2009.09.036

Peldszus, S., Benecke, J., Jekel, M., & Huck, P. M. (2012). Direct biofiltration pretreatment for fouling control of ultrafiltration membranes. *Journal - American Water Works Association*, *104*, E430-E445. doi:10.5942/jawwa.2012.104.0093

Peldszus, S., Hallé, C., Peiris, R. H., Hamouda, M., Jin, X., Legge, R. L., Budman, H., et al. (2011). Reversible and irreversible low-pressure membrane foulants in drinking water treatment: Identification by principal component analysis of fluorescence EEM and mitigation by biofiltration pretreatment. *Water research*, *45*(16), 5161-70. doi:10.1016/j.watres.2011.07.022

Persson, T., & Wedborg, M. (2001). Multivariate evaluation of the fluorescence of aquatic organic matter. *Analytica Chimica Acta*, *434*(2), 179-192. doi:10.1016/S0003-2670(01)00812-1

Peuravuori, J., Pihlaja, K., & Välimäki, N. (1997). Isolation and characterization of natural organic matter from lake water: two different adsorption chromatographic methods. *Environment international*, *23*(4), 453-464. Retrieved from http://www.sciencedirect.com/science/article/pii/S0160412097000500

Prevost, M., Niquette, P., Maclean, R. G., Thibault, D., Lafrance, P., & Desjardins, R. (1995). Removal of Various Biodegradable Organic Compounds by First and Second Stage Filtration. *12th Ozone World Congress*. Zurich, Switzerland: International Ozone Association.

Sachse, A., Babenzien, D., Ginzel, G., Gelbrecht, J., & Steinberg, C. E. . (2001). Characterization of dissolved organic carbon (DOC) in a dystrophic lake and an adjacent fen. *Biogeochemistry*, *54*(3), 279-296. Retrieved from http://www.springerlink.com/index/k2536v3317793685.pdf

Servais, P., Billen, G., Bablon, G. P., & Ven, C. (1991). Microbial Activity in GAC Filters at the Choisy-le-Roi Treatment Plant. *Journal - American Water Works Association*, *83*(2), 62-68.

Sharp, E. L., Parsons, S. A., & Jefferson, B. (2006). Seasonal variations in natural organic matter and its impact on coagulation in water treatment. *Science of the Total Environment*, *363*, 183-194. doi:10.1016/j.scitotenv.2005.05.032

Sierra, M. M. D., Giovanela, M., Parlanti, E., & Soriano-Sierra, E. J. (2005). Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques. *Chemosphere*, *58*(6), 715-33. doi:10.1016/j.chemosphere.2004.09.038

Sinsabaugh, R. L., Hoehn, R. C., Knocke, W. R., & Linkins, A. E. (1986). Precursor size and organic halide formation rates in raw and coagulated surface waters. *Journal of Environmental Engineering*, *112*(1), 139-153.

Spencer, R. G. M., Bolton, L., & Baker, A. (2007). Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations. *Water research*, *41*(13), 2941-50. doi:10.1016/j.watres.2007.04.012

Stedmon, C. a, Markager, S., & Bro, R. (2003). Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry*, *82*(3-4), 239-254. doi:10.1016/S0304-4203(03)00072-0

Stramski, D., & Wozniak, S. B. (2005). On the role of colloidal particles in light scattering in the ocean. *Limnology and Oceanography*, *50*(5), 1581-1591. doi:10.4319/lo.2005.50.5.1581

Sutzkover-Gutman, I., Hasson, D., & Semiat, R. (2010). Humic substances fouling in ultrafiltration processes. *Desalination*, *261*(3), 218-231. Elsevier B.V. doi:10.1016/j.desal.2010.05.008

Swietlik, J, Dabrowska, a, Raczyk-Stanisławiak, U., & Nawrocki, J. (2004). Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water research*, *38*(3), 547-58. doi:10.1016/j.watres.2003.10.034

Swietlik, Joanna, & Sikorska, E. (2004). Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone. *Water research*, *38*(17), 3791-9. doi:10.1016/j.watres.2004.06.010

Thurman, E. M. (1985). *Organic Geochemistry of Natural Waters*. Dordrecht, Netherlands: Martinus Nijhoff/Dr. W. Junk Publishers.

Urfer, D., Huck, P. M., Booth, S. D. J., & Coffey, B. M. (1997). Biological filtration for BOM and particle removal : *Journal - American Water Works Association*, *89*(12), 83-98.

Velten, S., Knappe, D. R. U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M., & Meylan, S. (2011). Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water research*, *45*(13), 3951-9. doi:10.1016/j.watres.2011.04.047

Viessman, W., Hammer, M. J., Perez, E. M., & Chadik, P. A. (2009). *Water Supply & Pollution Control* (8th ed., p. 843). Upper Saddle River, NJ: Pearson Prentice Hall.

Volk, C., Bell, K., Ibrahim, E., Verges, D., & Amy, G. (2000). Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. *Water research*, *34*(12), 3247-3257. Retrieved from http://144.206.159.178/ft/1092/13316/270607.pdf

Westerhoff, P., Debroux, J., Aiken, G., & Amy, G. (1999). Ozone-Induced Changes In Natural Organic Matter (NOM) Structure. *Ozone: Science & Engineering*, *21*(6), 551-570.

Yamamura, H., Okimoto, K., Kimura, K., & Watanabe, Y. (2007). Influence of calcium on the evolution of irreversible fouling in microfiltration/ultrafiltration membranes. *Journal of Water Supply: Research and Technology—AQUA*, *56*(6–7), 425. doi:10.2166/aqua.2007.018

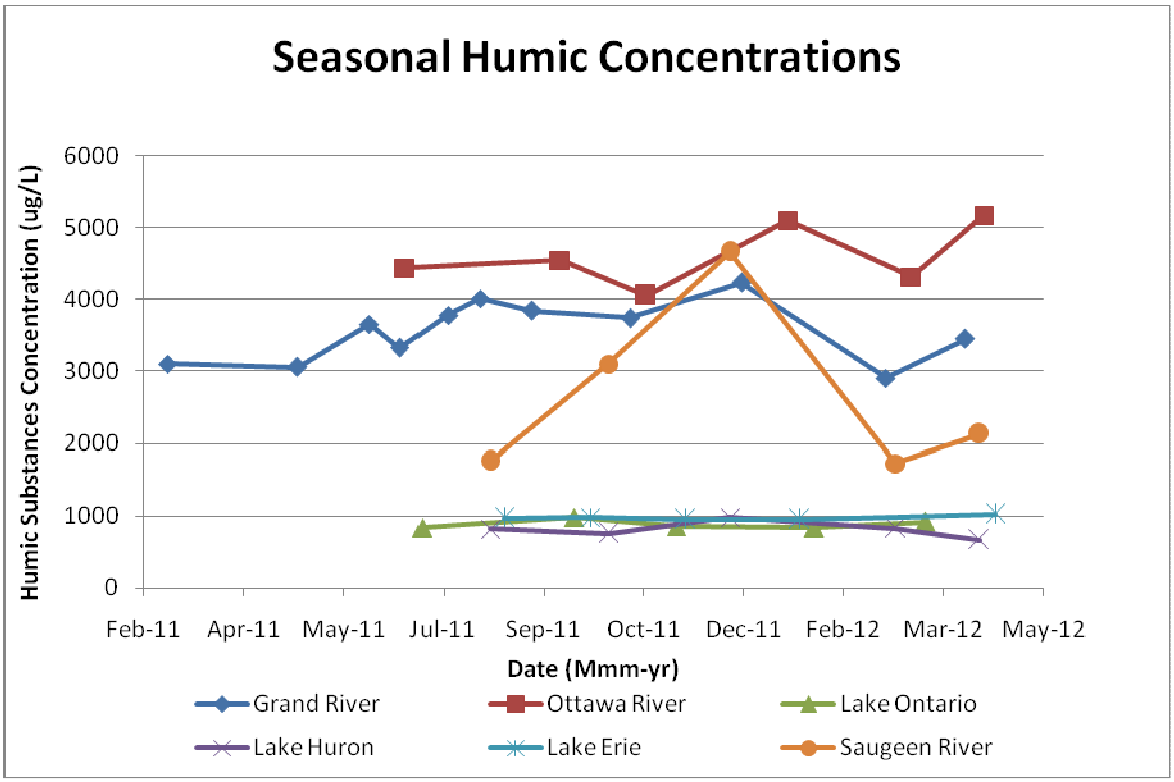
Yan, M., Wang, D., Qu, J., Ni, J., & Chow, C. W. K. (2008). Enhanced coagulation for high alkalinity and micro-polluted water: the third way through coagulant optimization. *Water research*, *42*(8-9), 2278-86. doi:10.1016/j.watres.2007.12.006

Zhang, S., & Huck, P. (1996). Removal of AOC in biological water treatment processes: a kinetic modeling approach. *Water Research*, *1354*(95), 1195-1207. Retrieved from http://www.sciencedirect.com/science/article/pii/004313549500260X

Zularisam, a. W., Ismail, a. F., & Salim, R. (2006). Behaviours of natural organic matter in membrane filtration for surface water treatment — a review. *Desalination*, *194*(1-3), 211-231. doi:10.1016/j.desal.2005.10.030

Zularisam, A. W., Ahmad, A., Sakinah, M., Ismail, A. F., & Matsuura, T. (2011). Role of natural organic matter (NOM), colloidal particles, and solution chemistry on ultrafiltration performance. *Separation and Purification Technology*, *78*(2), 189-200. Elsevier B.V. doi:10.1016/j.seppur.2011.02.001

Appendix A: Additional Full Scale Information and Seasonal Data



Location	Grand River												
Date	May 4th, 2011	Jun 9th, 2011	Jul18th, 2011	Aug 29th, 2011	Oct 17th, 2011	Dec 12th, 2011	Feb 22nd, 2012	Apr 2nd, 2012	Jun 14th, 2012	Avg	Stdev	Max	Min
TOC (mg/L)	5.00	6.24	6.30	6.61	6.47	6.78	5.33	5.63		6.04	0.64	6.78	5.00
DOC (mg/L)	4.85	6.24	6.20	6.53	6.30	6.69	5.21	5.62		5.95	0.66	6.69	4.85
Turbidity (NTU)	3.03	1.92	2.87	2.64	4.60	12.07	2.92	2.10	4.464	4.07	3.14	12.07	1.92
pH	8.25	7.87	7.86	7.94	7.86	8.33	8.04	7.84	7.82	7.98	0.19	8.33	7.82
Conductivity (mS/m)	515.00	591.00	539.00	534.00	540.00	541.00	743.00	565.00	551	568.78	68.71	743.00	515.00
UVA (m^{-1})	15.84	18.66	17.63	17.72	17.19	21.46	13.17	15.78	18.37	17.31	2.29	21.46	13.17
SUVA (L/mg*m)	3.26	2.99	2.84	2.72	2.73	3.21	2.53	2.81		2.89	0.25	3.26	2.53
Temperature (^oC)	10.50	21.00	25.00	22.00	15.00	4.00	2.00	11.00	23	14.83	8.48	25.00	2.00
Plant Flow (m^3/s)	0.60	0.40	0.50	0.50	0.50	0.40	0.40	0.40	0.7	0.49	0.11	0.70	0.40
Coagulant Dose (mg/L)	21.8	23.8	30.0	25.6	25.9	26.7	22.0	21.3	23.0	24.5	2.8	30.0	21.3
Ozone Dose (mg/L)	2.8	3.0	3.6	3.8	4.0	3.2	2.3	2.7	3.5	3.2	0.6	4.0	2.3
Polymer Dose (mg/L)	0.28	0.38	0.27	0.30	0.28	0.26	0.33	0.24		0.29	0.05	0.38	0.24

Location	Ottawa River										
Date	Jun 27th, 2011	Sep 12th, 2011	Oct 25th, 2011	Jan 4th, 2012	Mar 6,2012	Apr 11th, 2012	Jun 13th, 2012	Avg	Stdev	Max	Min
TOC (mg/L)	6.87	6.57	6.24	7.61	7.40	7.44		7.02	0.55	7.61	6.24
DOC (mg/L)	6.85	6.44	6.12	7.77	7.41	7.04		6.94	0.61	7.77	6.12
Turbidity (NTU)	4.19	2.17	3.84	2.27	3.64	3.88	3.83	3.33	0.88	4.19	2.17
pH	7.06	6.92	7.06	6.99	7.12	6.95	7.26	7.02	0.08	7.26	6.92
Conductivity (mS/m)	66.60	67.00	74.70	81.30	80.80	73.80	71.30	74.03	6.38	81.30	66.60
UVA (m^{-1})	25.67	22.97	21.41	27.64	26.10	26.44	24.11	25.04	2.36	27.64	21.41
SUVA (L/mg*m)	3.75	3.57	3.50	3.56	3.52	3.75		3.61	0.11	3.75	3.50
Temperature (^oC)	21.00	21.00	13.00	0.60	0.70	5.60	20.00	10.32	9.43	21.00	0.60
Plant Flow (m^3/s)	2.07	1.79	1.67	2.19	1.98	1.57	1.93	1.88	0.24	2.19	1.57
Coagulant Dose (mg/L)	35.0	31.0	29.0	30.0	30.0	30.0	30.0	30.8	2.1	35.0	29.0

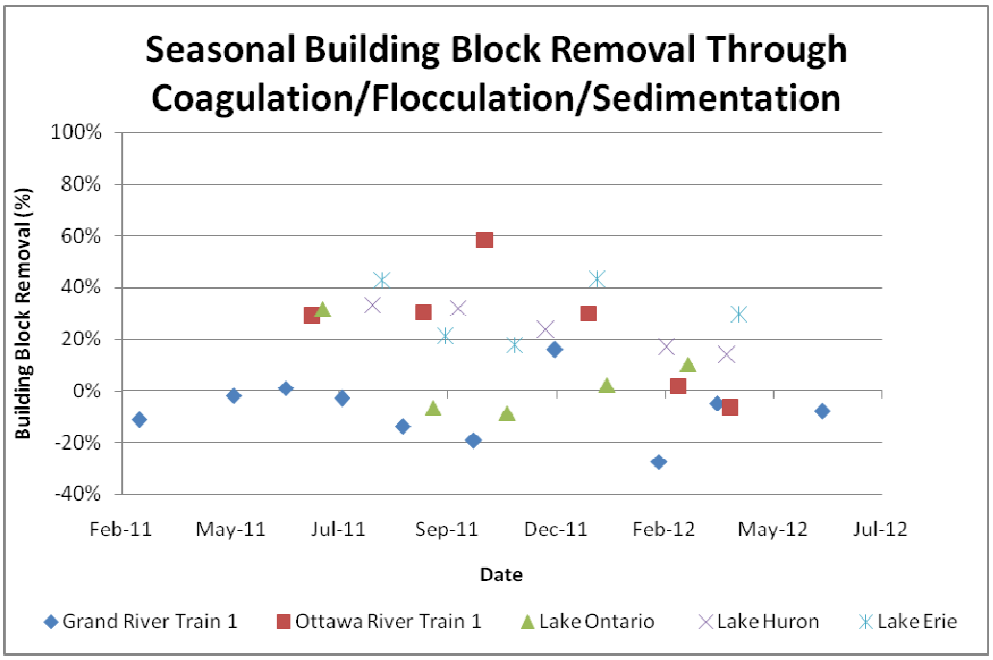
Location	Lake Huron								
	Aug 8th, 2011	Oct 6th, 2011	Dec 6th,2011	Feb 27th, 2011	Apr 9th,2011	Average	Stdev	Max	Min
TOC (mg/L)	1.62	1.62	2.13	1.64	1.54	1.73	0.27	2.13	1.54
DOC (mg/L)	1.71	1.65	1.98	1.68	1.60	1.73	0.17	1.98	1.60
Turbidity (NTU)	0.54	0.78	16.50	6.10	4.36	6.94	6.75	16.50	0.54
pH	8.23	8.12	7.93	7.81	7.61	7.87	0.21	8.23	7.61
Conductivity (mS/m)	191.60	208.00	233.00	235.00	217.00	223.25	12.97	235.00	191.60
UVA (m^{-1})	0.97	1.14	1.85	1.77	1.48	1.56	0.32	1.85	0.97
SUVA (L/mg*m)	0.57	0.69	0.94	1.05	0.93	0.90	0.15	1.05	0.57
Temperature (^oC)	21.60	14.00	6.50	1.22	7.20	7.23	5.24	21.60	1.22
Plant Flow (m^3/s)	0.09	0.09	0.03	0.05	0.05	0.05	0.02	0.09	0.03
Coagulant Dose (mg/L)	20.4	21.5	30.9	20.9	23.0	24.09	4.63	30.90	20.43

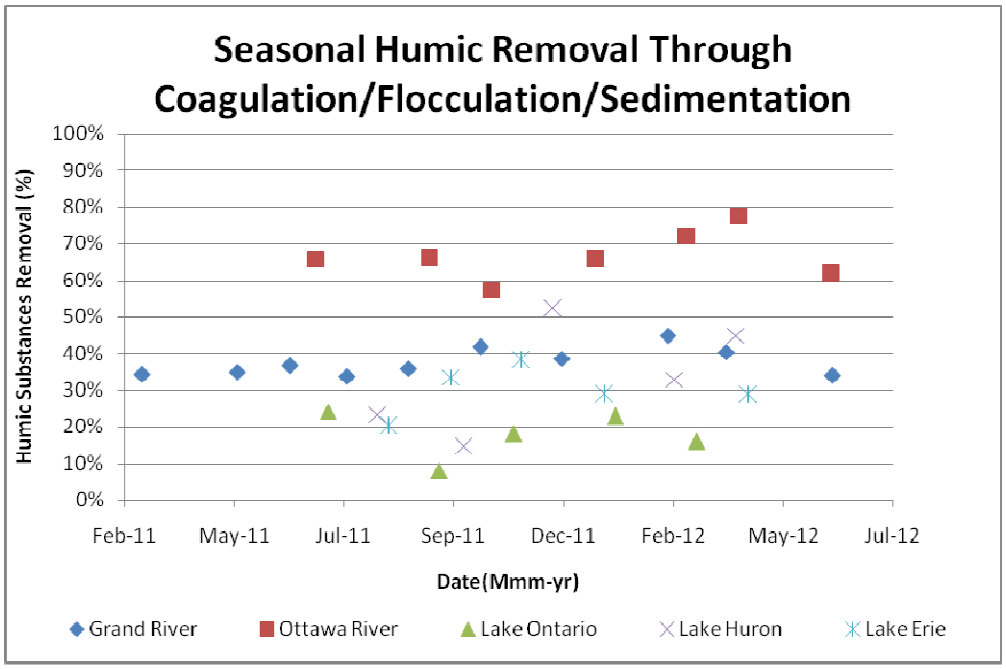
Location	Lake Ontario								
	Jul 5th, 2011	Sep 19th, 2011	Nov 9th, 2011	Jan 17th, 2012	Mar 13th, 2012	Avg	Stdev	Max	Min
TOC (mg/L)	1.82	2.42	2.14	2.10	1.98	2.16	0.18	2.42	1.82
DOC (mg/L)	1.86	2.29	2.06	2.08	1.97	2.10	0.13	2.29	1.86
Turbidity (NTU)	0.13	1.06	0.25	0.40	0.27	0.50	0.38	1.06	0.13
pH	7.63	8.21	7.92	7.85	7.99	7.99	0.16	8.21	7.63
Conductivity (mS/m)	306.00	290.00	340.00	330.00	320.00	320.00	21.60	340.00	290.00
UVA (m^{-1})	2.20	2.41	2.15	2.33	2.53	2.35	0.16	2.53	2.15
SUVA (L/mg*m)	1.18	1.05	1.04	1.12	1.28	1.13	0.11	1.28	1.04
Temperature (^oC)	10.00	17.00	8.40	3.00	4.00	8.10	6.38	17.00	3.00
Plant Flow (m^3/s)	7.35	4.06	4.38	3.37	2.86	3.67	0.68	7.35	2.86
Coagulant Dose (mg/L)	4.0	9.0	7.0	7.0	5.0	7.0	1.6	9.0	4.0

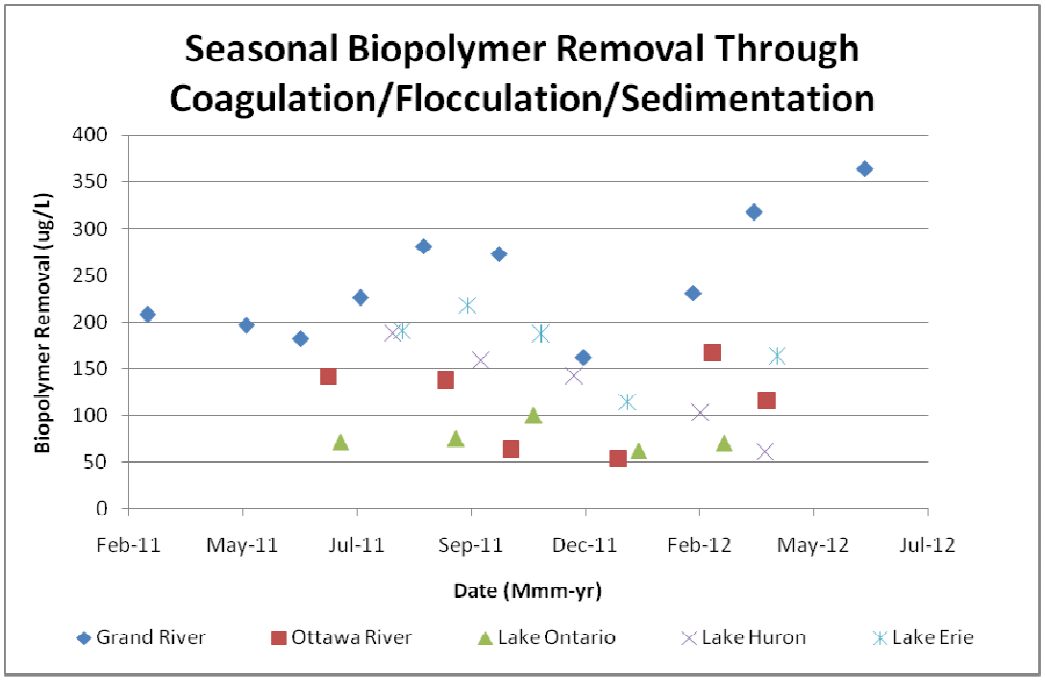
Location	Saugeen River								
	Aug 8th, 2011	Oct 6th,2011	Dec 6th,2011	Feb 27th, 2011	Apr 9th,2011	Average	Stdev	Max	Min
TOC (mg/L)	2.74	4.87	6.86	3.66	3.31	4.68	1.60	6.86	2.74
DOC (mg/L)	2.76	4.88	6.70	3.66	3.32	4.64	1.53	6.70	2.76
Turbidity (NTU)	3.01	6.53	3.45	3.45	4.01	4.36	1.47	6.53	3.01
pH	8.19	8.04	8.13	8.16	8.05	8.10	0.06	8.19	8.04
Conductivity (mS/m)	566.00	606.00	449.00	600.00	566.00	555.25	72.99	606.00	449.00
UVA (m^{-1})	8.60	15.27	23.76	8.90	10.02	14.49	6.78	23.76	8.60
SUVA (L/mg*m)	3.11	3.13	3.55	2.43	3.02	3.03	0.46	3.55	2.43
Temperature (^oC)	21.60	12.00	4.00	0.50	9.00	6.38	5.12	21.60	0.50

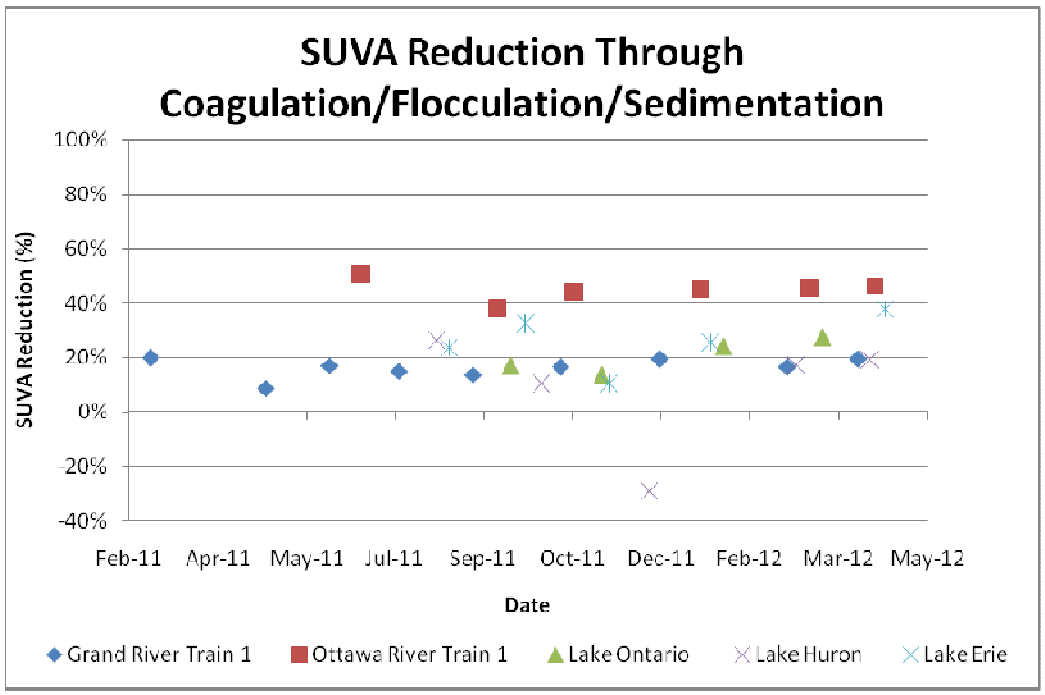
Location	Lake Erie								
	Aug 15th, 2011	Sep 27th, 2011	Nov 14th, 2011	Jan 10th, 2011	Apr 17th, 2011	Average	Stdev	Max	Min
TOC (mg/L)	1.91	2.05	2.17	2.01	2.13	2.09	0.07	2.17	1.91
DOC (mg/L)	2.02	2.14	2.37	2.11	2.25	2.22	0.12	2.37	2.02
Turbidity (NTU)	6.13	17.60	240.30	103.80	86.20	111.98	93.28	240.30	6.13
pH	7.61	7.98	8.00	7.98	7.78	7.94	0.10	8.00	7.61
Conductivity (mS/m)	261.00	275.00	304.00	254.00	268.00	275.25	21.06	304.00	254.00
UVA (m^{-1})	2.34	2.27	2.63	2.64	2.58	2.53	0.18	2.64	2.27
SUVA (L/mg*m)	1.16	1.06	1.11	1.25	1.14	1.14	0.08	1.25	1.06
Temperature (^oC)	15.00	17.30	10.10	2.10	8.09	9.40	6.27	17.30	2.10
Plant Flow (m^3/s)	0.41	0.63	0.77	0.41	0.41	0.55	0.18	0.77	0.41
Coagulant Dose (mg/L)	30.0	30.0	40.0	40.0	40.0	37.5	5.0	40.0	30.0
PAC Dose (mg/L)	4.0	4.0	2.0	0.0	0.0	1.5	1.9	4.0	0.0

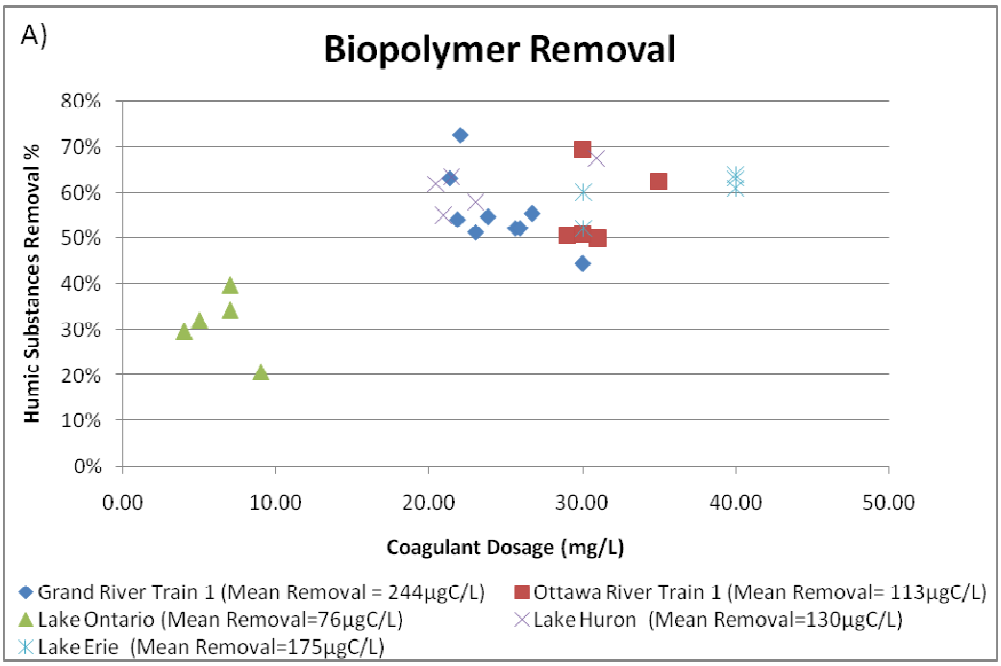
Appendix B: Additional Coagulation Data

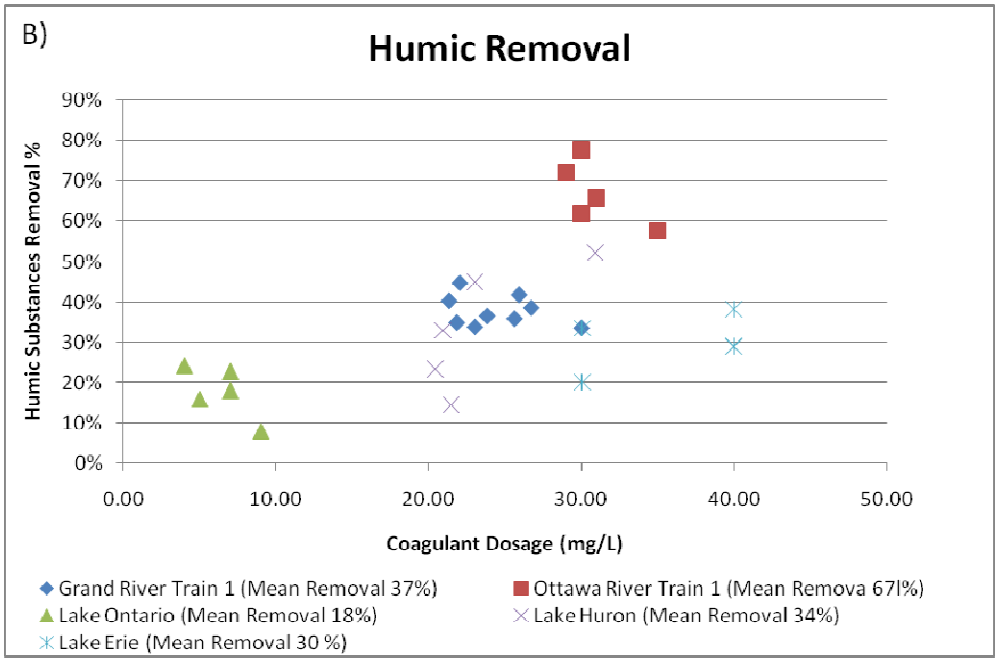





Seasonal Biopolymer Removal Through Coagulation/Flocculation/Sedimentation
Biopolymer Removal (ug/L)
400
350
300
250
200
150
100
50
0
Feb-11
May-11
Jul-11
Sep-11
Dec-11
Feb-12
May-12
Jul-12
Date (Mmm-yr)
Grand River
Ottawa River
Lake Ontario
Lake Huron
Lake Erie

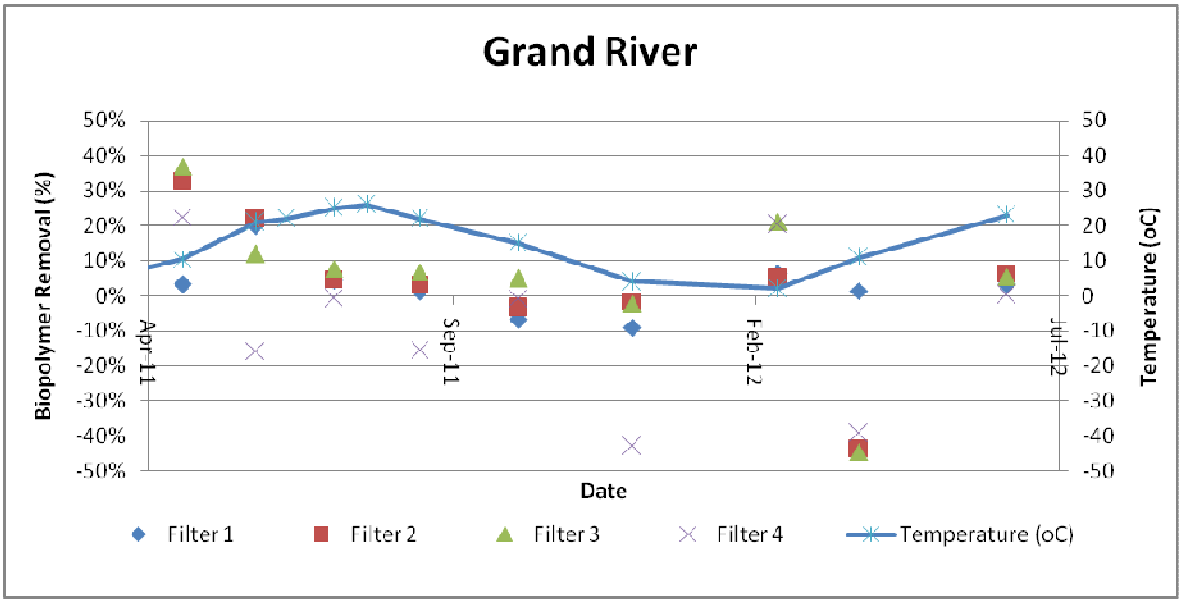

SUVA Reduction Through Coagulation/Flocculation/Sedimentation
SUVA Reduction (%)
100%
80%
60%
40%
20%
0%
-20%
-40%
Feb-11
Apr-11
May-11
Jul-11
Sep-11
Oct-11
Dec-11
Feb-12
Mar-12
May-12
Date
Grand River Train 1
Ottawa River Train 1
Lake Ontario
Lake Huron
Lake Erie

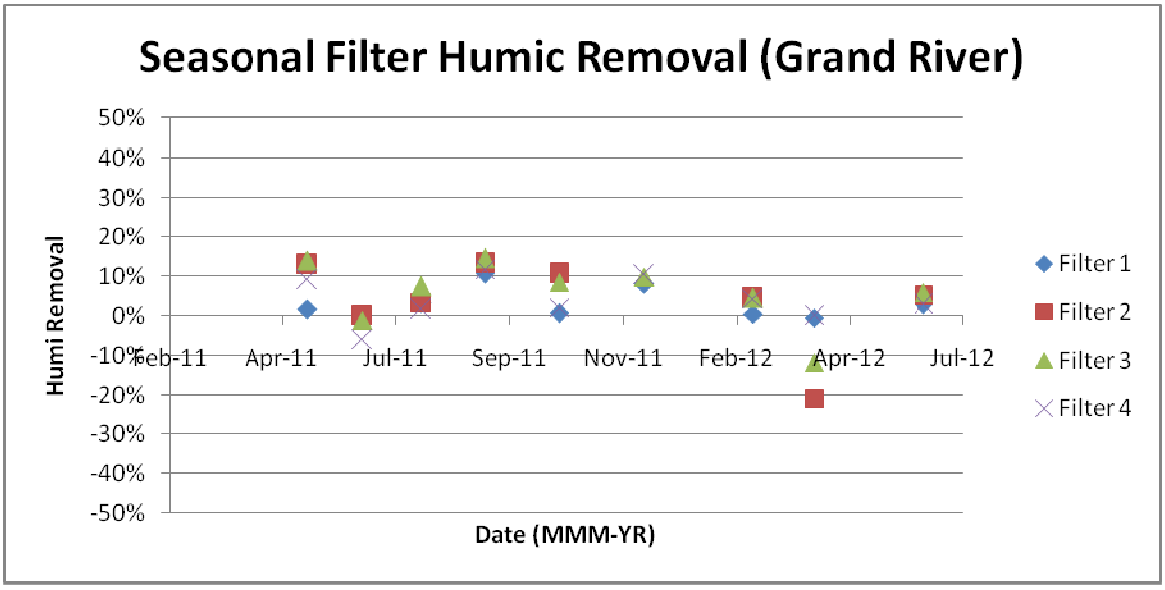

A)
Biopolymer Removal
Humic Substances Removal %
80%
70%
60%
50%
40%
30%
20%
10%
0%
0.00
10.00
20.00
30.00
40.00
50.00
Coagulant Dosage (mg/L)
Grand River Train 1 (Mean Removal = 244µgC/L)
Ottawa River Train 1 (Mean Removal= 113µgC/L)
Lake Ontario (Mean Removal=76µgC/L)
Lake Huron (Mean Removal=130µgC/L)
Lake Erie (Mean Removal=175µgC/L)

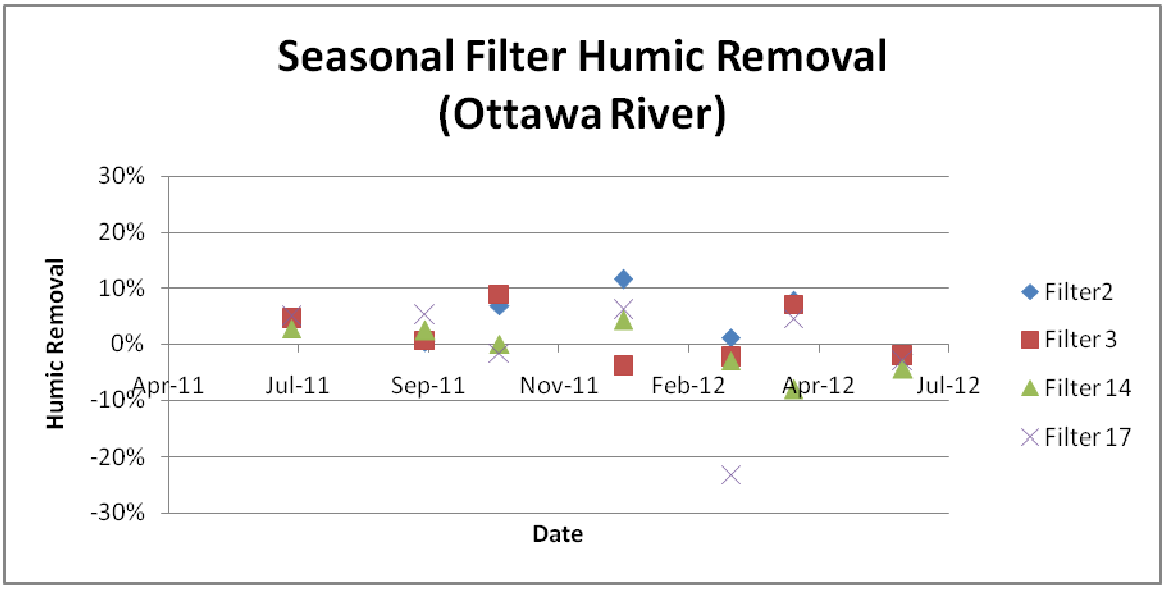

B)
Humic Removal
Humic Substances Removal %
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0.00
10.00
20.00
30.00
40.00
50.00
Coagulant Dosage (mg/L)
Grand River Train 1 (Mean Removal 37%)
Ottawa River Train 1 (Mean Remova 67l%)
Lake Ontario (Mean Removal 18%)
Lake Huron (Mean Removal 34%)
Lake Erie (Mean Removal 30 %)

Appendix C: Additional Biofiltration Data

Average NOM Fraction Removal Through Filtration (ppb)												
	Biopolymers				Humic Substances				Building Blocks			
Location	**Mean**	**Std. Dev.**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Min**	**Max**	**Mean**	**Std. Dev.**	**Min**	**Max**
Mannheim	1	24	-54	57	88	139	-305	338	122	160	-210	454
Brittania	9	12	-13	32	19	91	-268	202	19	98	-196	179
Elgin	-4	9	-15	21	-37	75	-187	103	36	86	-66	199
Kincardine	-9	13	-26	16	23	81	-108	195	8	62	-112	84
R.L. Clark	-3	13	-21	17	-39	69	-163	89	95	54	-1	169

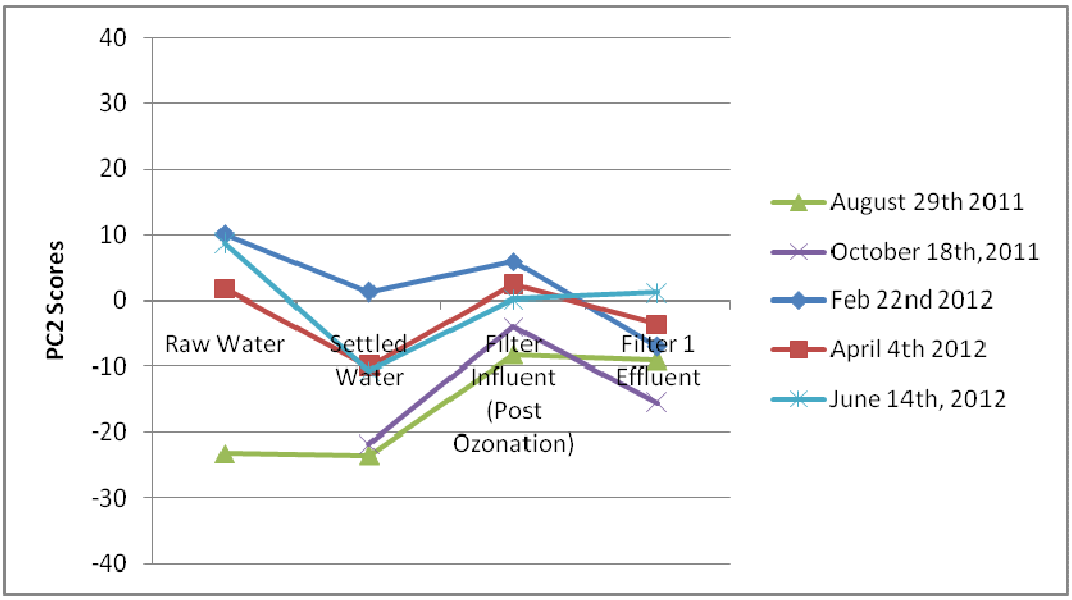


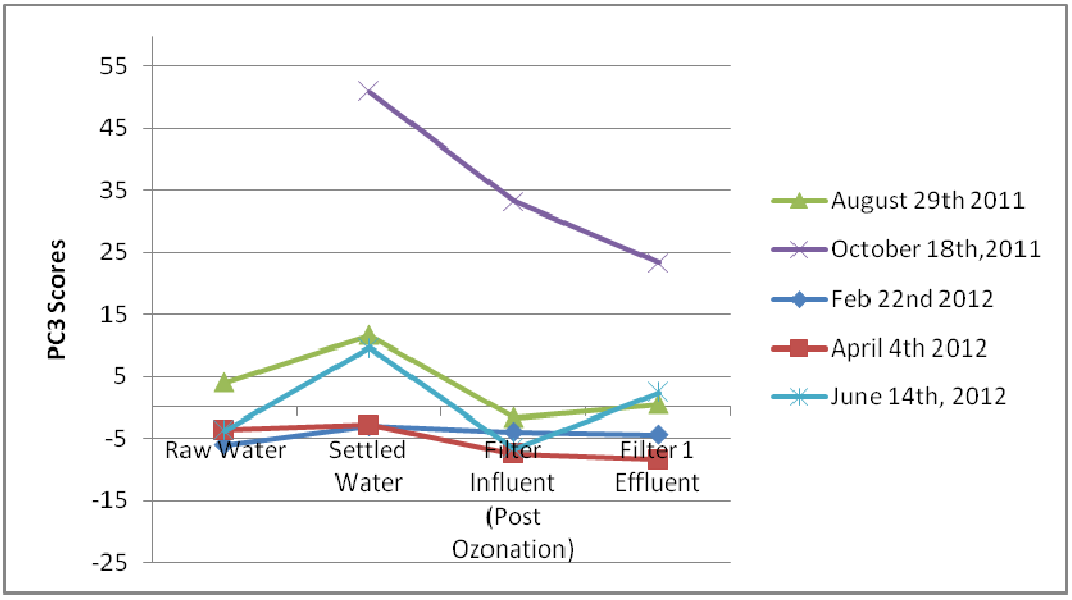

Seasonal Filter Humic Removal (Grand River)
50%
40%
30%
20%
10%
0%
-10%
-20%
-30%
-40%
-50%
Humi Removal
Feb-11
Apr-11
Jul-11
Sep-11
Nov-11
Feb-12
Apr-12
Jul-12
Date (MMM-YR)
Filter 1
Filter 2
Filter 3
Filter 4


Seasonal Filter Humic Removal (Ottawa River)
30%
20%
10%
0%
-10%
-20%
-30%
Humic Removal
Apr-11
Jul-11
Sep-11
Nov-11
Feb-12
Apr-12
Jul-12
Date
Filter2
Filter 3
Filter 14
Filter 17

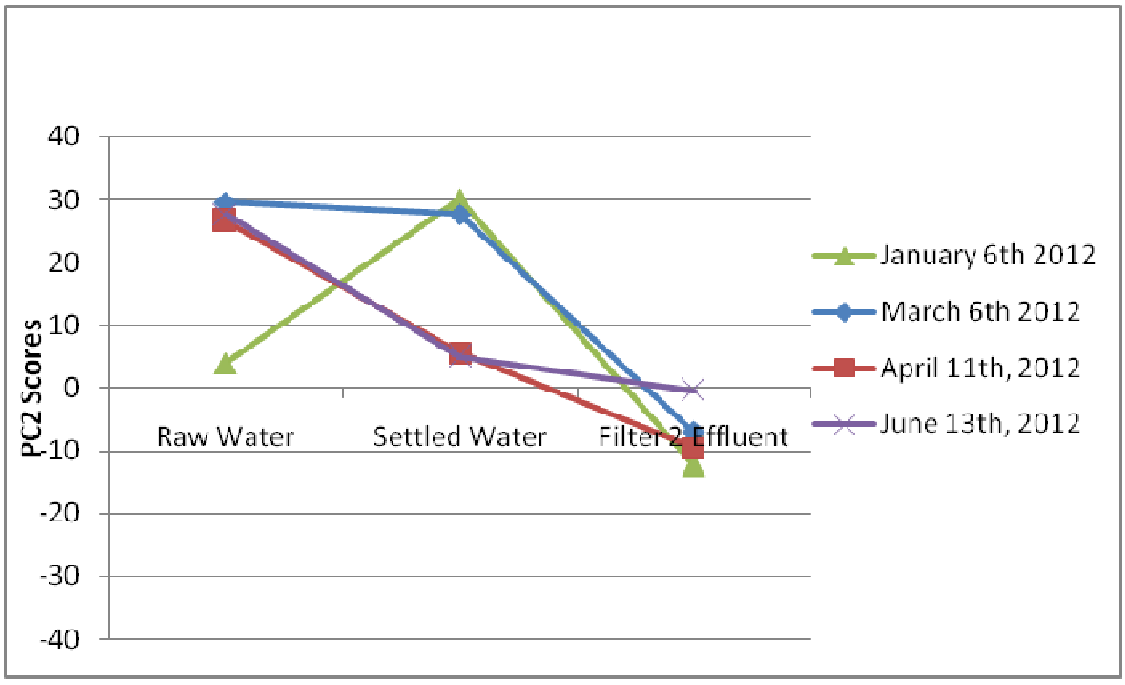
Appendix D: Additional Principal Component Data

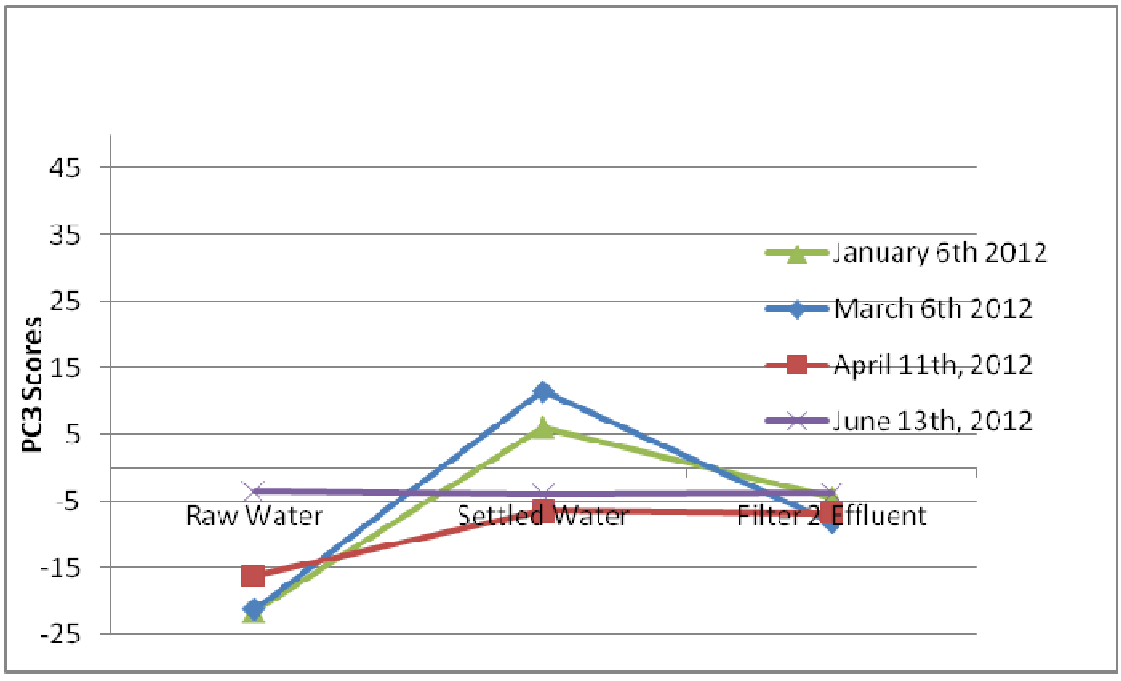
Grand River:



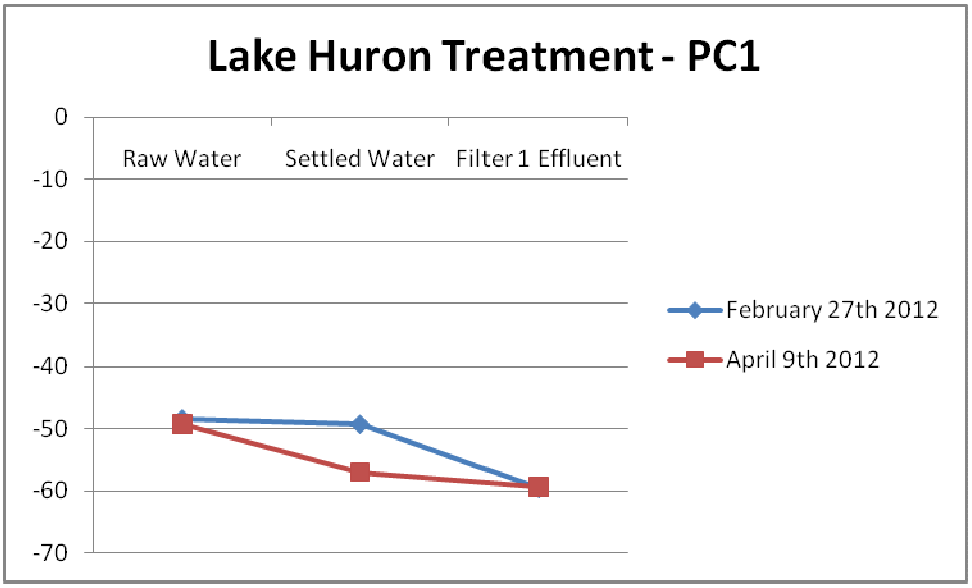


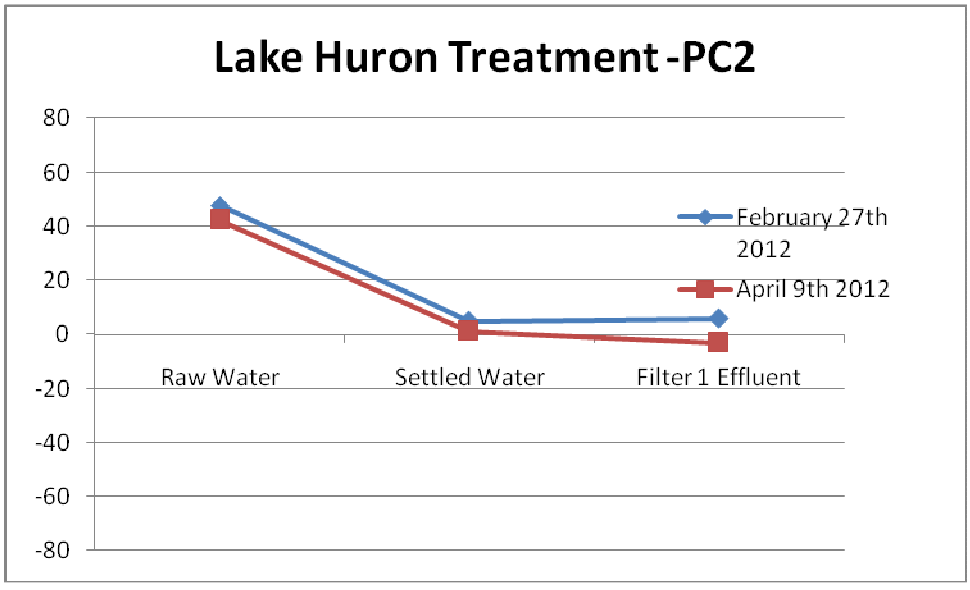
Ottawa River

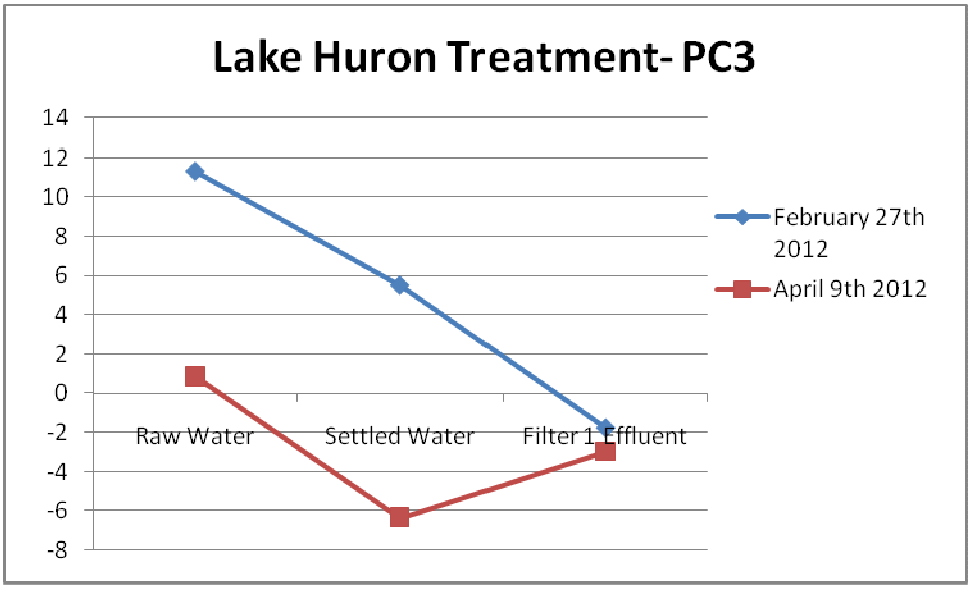




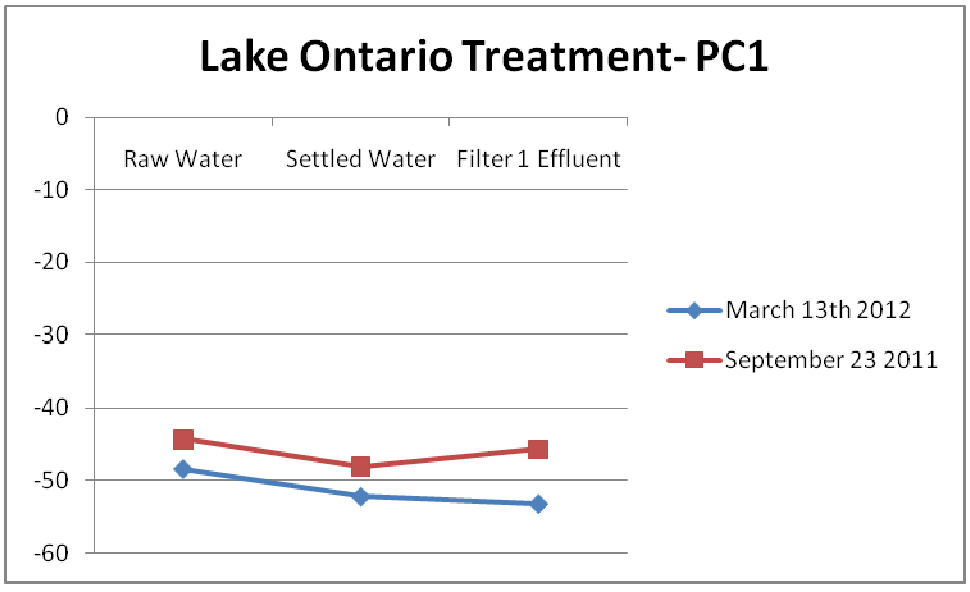
Lake Huron

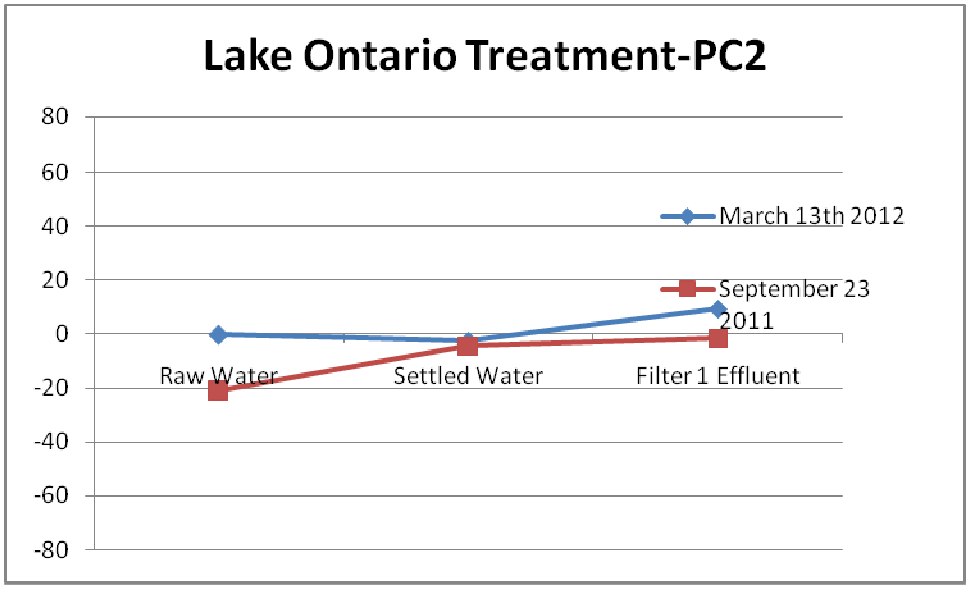

Lake Huron Treatment - PC1
0
-10
-20
-30
-40
-50
-60
-70
Raw Water
Settled Water
Filter 1 Effluent
February 27th 2012
April 9th 2012

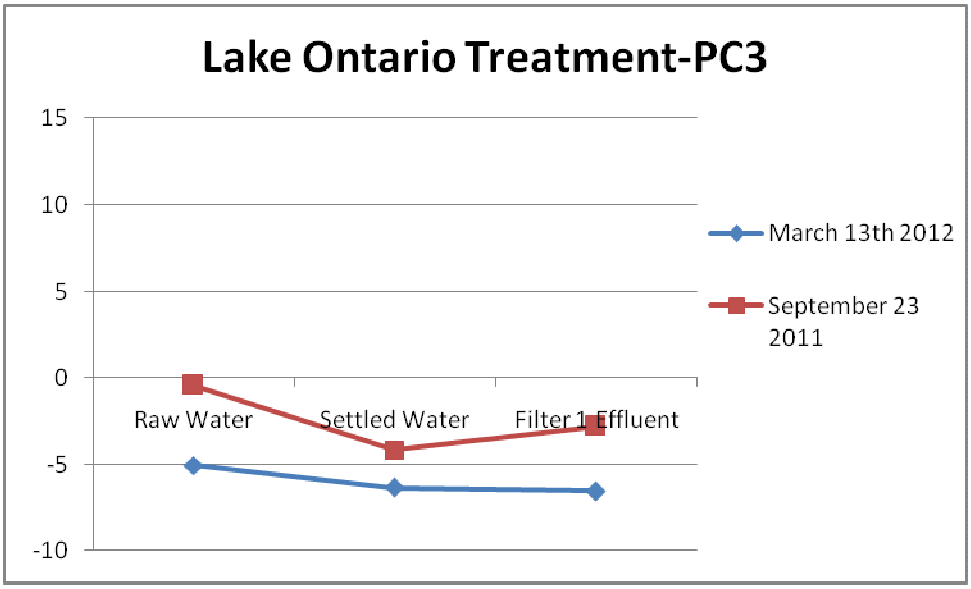

Lake Huron Treatment -PC2
80
60
40
20
0
-20
-40
-60
-80
Raw Water
Settled Water
Filter 1 Effluent
February 27th 2012
April 9th 2012



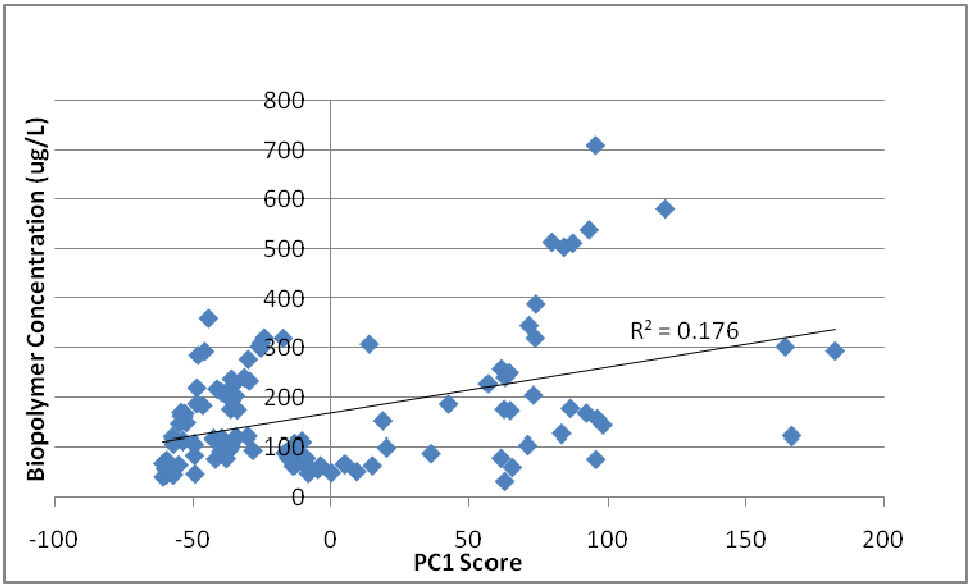
Lake Ontario



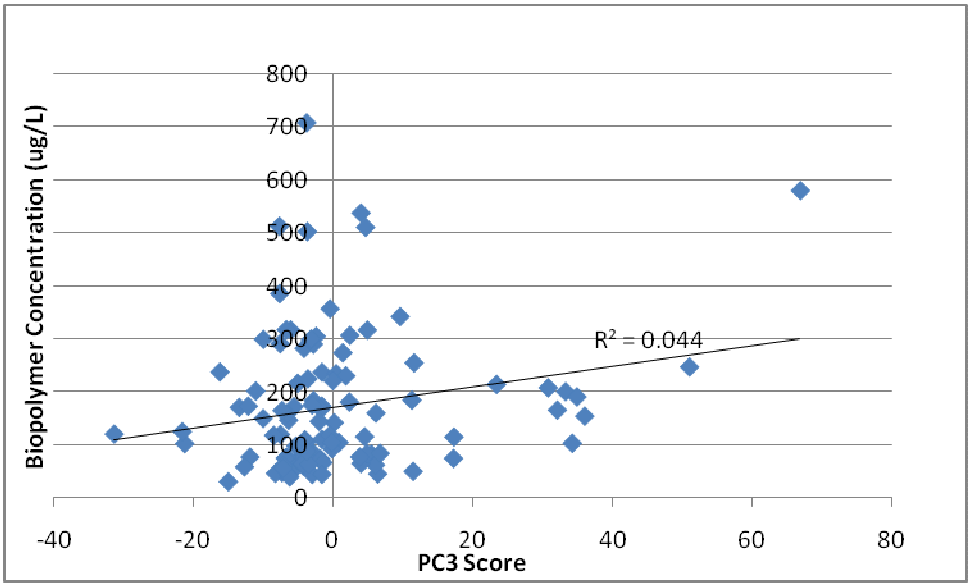

Lake Ontario Treatment-PC2
80
60
40
20
0
-20
-40
-60
-80
Raw Water
Settled Water
Filter 1 Effluent
March 13th 2012
September 23 2011


Lake Ontario Treatment-PC3
15
10
5
0
-5
-10
Raw Water
Settled Water
Filter 1 Effluent
March 13th 2012
September 23 2011

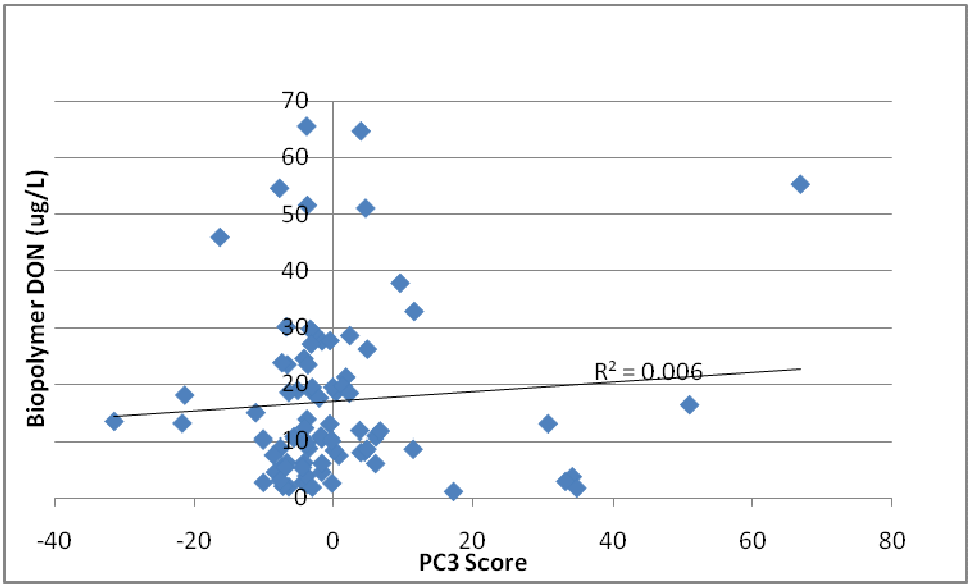
Biopolymer Concentration vs. PC1 Score



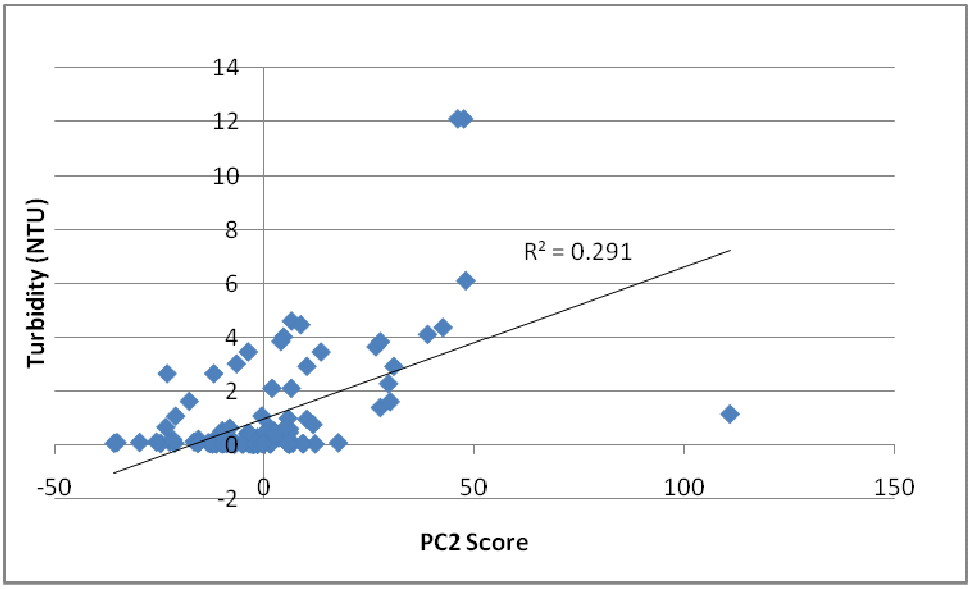
Biopolymer Concentration vs. PC3



Dissolved Organic Nitrogen Content of Biopolymers vs. PC3



Turbidity vs. PC2



Chapter 3 PCA Results

	Sample		Scores on PC1 (77.93%)	Scores on PC2 (8.43%)	Scores on PC3 (4.50%)	Hotelling T^2 (90.66%)	Q Residuals (9.14%)
Grand River (Feb 22nd 2012)	1	Pilot Raw Water	73.98	30.87	-7.66	4.67	1220.90
	2	Pilot Filter A Eff.	64.72	-3.97	-13.45	2.32	241.53
	3	Pilot Filter B Eff.	62.49	-9.86	-12.16	2.28	175.35
	4	Pilot Filter C Eff.	61.41	-15.72	-11.91	2.63	163.90
	5	Raw Water	73.77	10.14	-6.07	2.15	308.55
	6	Settled	36.45	1.28	-2.99	0.46	333.41
	7	Post Ozonation	-36.46	5.94	-3.95	0.59	232.27
	8	Filter 1 Eff.	-37.46	-7.06	-4.41	0.67	177.08
	9	Filter 2 Eff.	-39.75	-13.40	-4.19	1.08	304.57
	10	Filter 3 Eff.	-41.70	-5.03	-6.75	0.85	225.50
	11	Filter 4 Eff.	-37.78	-1.43	-4.70	0.56	186.66
Grand River (April 2nd 2012)	12	Pilot Raw Water	79.83	6.43	-7.69	2.38	515.10
	13	Pilot Filter A Eff.	73.12	-17.92	-11.08	3.21	338.34
	14	Pilot Filter B Eff.	65.44	-22.56	-12.71	3.63	244.25
	15	Pilot Filter C Eff.	62.71	-21.37	-15.02	3.73	213.22
	16	Raw Water	84.18	1.81	-3.68	2.24	818.99
	17	Settled	42.78	-10.02	-2.79	0.88	443.15
	18	Post Ozonation	-29.98	2.33	-7.54	0.60	187.98
	19	Filter 1 Eff.	-34.20	-3.59	-8.51	0.79	180.82
	20	Filter 2 Eff.	-33.83	-2.88	-5.60	0.55	119.56
	21	Filter 3 Eff.	-36.17	-7.60	-1.61	0.57	62.49
	22	Filter 4 Eff.	-33.09	-10.33	-1.38	0.64	66.59

Ottawa River (March 6th, 2012)	23	Raw Water	71.06	29.62	-21.29	6.51	466.06
	24	Settled Side 1	9.53	27.66	11.51	2.91	1151.61
	25	Settled Side 2	0.31	10.14	-7.33	0.59	273.16
	26	Filter 2 Eff.	-8.07	-7.10	-8.27	0.54	237.29
	27	Filter 3 Eff.	-3.65	-11.47	-3.67	0.45	149.80
	28	Filter 14 Eff.	-4.58	-7.21	-5.53	0.32	213.15
	29	Filter 17 Eff.	-8.04	-12.39	-4.28	0.55	221.68
Ottawa River (April 11th,2012)	30	Raw Water	62.88	26.59	-16.24	4.65	397.83
	31	Settled Side 1	-10.83	5.66	-6.52	0.36	256.92
	32	Settled Side 2	-8.75	11.61	-6.60	0.64	295.64
	33	Filter 2 Eff.	-12.87	-9.57	-6.85	0.57	180.76
	34	Filter 3 Eff.	-13.63	-6.90	-7.12	0.47	127.24
	35	Filter 14 Eff.	-12.84	-9.60	-4.15	0.40	66.30
	36	Filter 17 Eff.	-14.72	-12.96	-3.74	0.62	71.02
Lake Erie (April 17th 2012)	37	Settled (North)	-36.09	110.71	34.15	41.32	1353.21
	38	Filter 1 Eff.	-53.51	-7.19	-1.60	1.03	71.72
	39	Filter 3 Eff.	-56.97	-1.50	-3.80	1.07	51.99
Lake Ontario (March 13th 2012)	40	Raw1	-48.47	-0.26	-5.06	0.86	169.92
	41	Raw2	-52.39	-1.66	-5.28	1.00	170.99
	42	Settled	-52.25	-2.52	-6.37	1.07	161.05
	43	Filter 1 Eff.	-53.24	9.31	-6.56	1.34	259.49
	44	Filter 2 Eff.	-52.86	1.38	-7.31	1.15	165.99
	45	Filter 3 Eff.	-54.20	-0.57	-1.74	0.91	55.13
	46	Filter 4 Eff.	-54.05	6.78	6.17	1.23	745.17

Lake Huron/ Saugeen River (Feb 22nd 2012)	47	Raw Huron	-48.45	48.03	11.31	7.91	426.96
	48	Huron Settled	-49.32	4.91	5.51	0.98	172.74
	49	Huron Filter 1 Eff.	-59.62	5.90	-1.77	1.20	172.20
	50	Huron Filter 2 Eff.	-59.40	-2.50	-1.78	1.11	222.81
	51	Huron Filter 3 Eff.	-60.75	-7.26	-1.44	1.28	159.34
	52	Saugeen Raw	20.35	-3.87	-5.33	0.32	156.41
	53	Southampton Raw	-42.37	-0.59	17.35	2.21	992.96
	54	Southampton Perm	-49.13	12.11	6.41	1.37	426.31
Lake Huron/ Saugeen River (Apr 9th 2012)	55	Raw Huron	-49.33	42.57	0.85	5.84	211.55
	56	Huron Settled	-57.04	1.14	-6.35	1.22	95.25
	57	Huron Filter 1 Eff.	-59.39	-2.98	-2.98	1.15	52.93
	58	Huron Filter 2 Eff.	-60.69	-1.67	-6.22	1.34	67.21
	59	Huron Filter 3 Eff.	-59.89	3.38	-7.17	1.41	167.49
	60	Saugeen Raw	18.99	4.56	-10.02	0.72	176.80
	61	Southampton Raw	-39.44	38.94	4.54	4.85	167.15
	62	Southampton Perm	-49.82	-3.70	-5.44	0.96	51.09
Grand River (August 30th, 2012)	63	Pilot Raw Water	87.38	-12.02	4.68	2.85	710.84
	64	Pilot Filter A Eff.	86.52	-16.75	-2.99	3.12	207.17
	65	Pilot Filter B Eff.	98.36	-35.12	0.18	6.42	771.28
	66	Pilot Filter C Eff.	95.75	-35.77	17.29	8.04	1258.71
	67	Raw Water	93.30	-23.16	4.01	4.25	329.19
	68	Settled	61.48	-23.50	11.64	3.45	449.99
	69	Post Ozonation	-31.27	-8.26	-1.58	0.50	154.63
	70	Filter 1 Eff.	-35.91	-8.98	0.45	0.62	196.68
	71	Filter 2 Eff.	-29.42	-24.71	1.85	2.00	411.63

	72	Filter 3 Eff.	-35.42	-11.47	-0.01	0.75	144.53
	73	Filter 4 Eff.	-29.85	-11.55	1.40	0.66	153.00
Grand River (Oct. 18th 2011)	74	Pilot Raw Water	120.90	6.48	66.90	29.28	1561.93
	75	Pilot Filter B Eff.	92.29	-25.75	32.00	10.11	442.52
	76	Pilot Filter C Eff.	96.25	-29.75	35.95	12.44	321.78
	77	Settled	64.36	-21.83	50.98	16.95	246.90
	78	Post Ozonation	-34.46	-3.96	33.20	6.49	1010.55
	79	Filter 1 Eff.	-41.20	-15.51	23.28	4.19	1064.16
	80	Filter 2 Eff.	-39.46	-1.56	30.70	5.68	880.04
	81	Filter 3 Eff.	-35.86	-0.13	34.82	7.08	933.70
Grand River (Dec. 12 2011)	82	Pilot Raw Water	164.42	47.59	-9.98	15.15	1562.06
	83	Raw Water	182.49	46.12	-7.59	16.44	1837.45
	84	Filter 1 Eff.	-28.12	-15.85	-0.14	0.95	249.02
Ottawa River (Jan. 6th, 2011)	85	Raw Water	83.34	3.94	-21.64	4.74	602.17
	86	Settled Side 1	15.17	30.01	6.09	2.81	461.68
	87	Filter 2 Eff.	4.96	-12.25	-4.41	0.54	146.51
	88	Filter 17 Eff.	5.39	1.48	4.00	0.10	379.76
Saugeen River	89	Raw (Aug. 8 2011)	14.08	-6.63	-2.42	0.22	171.14
	90	Raw (Dec. 6 2011)	166.75	13.50	-31.39	14.42	1144.42
Lake Ontario (Sep 23rd 2011)	91	RLRW_230911	-44.28	-21.16	-0.44	1.86	1031.50
	92	RLSED_230911	-48.04	-4.50	-4.16	0.86	950.72

	93	RLFEF1_230911	-45.65	-1.62	-2.81	0.69	888.70
Lake Ontario (Sep 23rd 2011	94	Raw 1	-46.28	2.95	2.36	0.71	238.67
	95	Raw 2	-54.75	-3.46	-1.98	0.97	135.59
	96	Settled	-57.25	-9.99	-0.46	1.28	294.04
Lake Erie	97	ELSEDN_110112	-55.05	6.01	-3.49	1.09	308.35
	98	ELFEF1_110112	-57.01	-5.34	-1.60	1.08	88.60
Grand River (June 14th, 2012)	99	Raw Water	95.60	8.68	-3.78	3.07	577.53
	100	Settled	71.54	-10.69	9.64	2.39	1287.90
	101	Post Ozonation	-24.03	0.23	-6.71	0.42	223.20
	102	Filter 1 Eff.	-25.17	1.22	2.42	0.23	103.05
	103	Filter 2 Eff.	-25.22	-2.20	-3.25	0.27	99.90
	104	Filter 3 Eff.	-25.76	-0.15	-3.14	0.26	241.29
	105	Filter 4 Eff.	-17.17	17.65	4.93	1.10	398.97
Ottawa River (June 13th, 2012)	106	Raw Water	56.88	27.68	-3.61	3.21	482.09
	107	Settled Side 1	-10.31	4.97	-4.05	0.19	272.10
	108	Settled Side 2	-13.01	2.41	-0.21	0.07	141.07
	109	Filter 2 Eff.	-16.45	-0.39	-3.77	0.16	275.42
	110	Filter 3 Eff.	-12.48	9.07	4.87	0.41	453.29
	111	Filter 14 Eff.	-10.80	5.99	6.76	0.39	291.78
	112	Filter 17 Eff.	-15.26	5.51	3.84	0.24	331.13

Appendix E: Additional Membrane Fouling Data

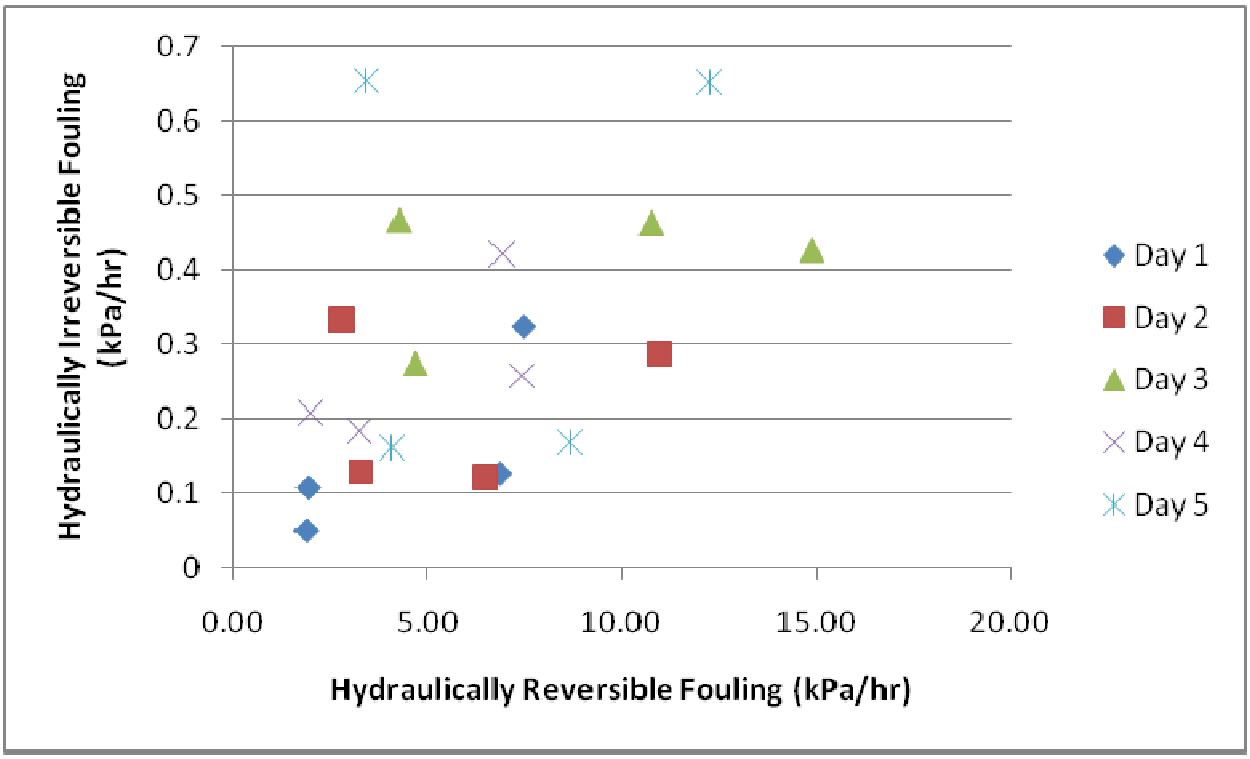
Summary of Fouling Relationship to Biopolymer, Humic substances and Turbidity

Fouling Relationship Summary Table						
			Day 1	Day 2	Day 3	Day 4
Biopolymer	Hydraulically Reversible Fouling	R^2	0.854	0.732	0.785	0.996
		Slope (kPa *L/ hr*µg)	0.025	0.036	0.055	0.031
	Hydraulically Irreversible Fouling	R^2	0.441	0.146	0.004	0.507
		Slope (kPa *L/ hr*µg)	7.15E-04	-4.65E-04	8.00E-05	8.94E-04
Turbidity	Hydraulically Reversible Fouling	R^2	0.202	0	0.004	0.051
		Slope (kPa / hr*NTU)	0.392	0.002	0.119	0.21
	Hydraulically Irreversible Fouling	R^2	0.006	0.063	0.444	0.715
		Slope (kPa / hr*NTU)	0.002	0.008	0.021	0.031
Humics	Hydraulically Reversible Fouling	R^2	0	0.039	0.003	0.079
		Slope (kPa *L/ hr*µg)	-3.00E-05	4.10E-04	-1.28E-04	-3.75E-04
	Hydraulically Irreversible Fouling	R^2	0.216	0.994	0.241	0.138
		Slope (kPa *L/ hr*µg)	3.00E-05	6.00E-05	2.00E-05	-2.00E-05

Qualitative Fouling Summary

	Grand River	Ottawa River	Lake Ontario	Lake Erie
Biopolymer	High	Low	Moderate	Moderate
Tubidity	Moderate	Moderate	Low	High
Humics	High	High	Low	Low
Hydraulically Reversible Fouling	High	Low	Moderate-low	Moderate-high
Hydraulically Irreversible Fouling	High	High	Low	High

Hydraulically Irreversible Fouling vs. Hydraulically reversible fouling on five separate days



Mean (n=4days) Hydraulically Reversible Fouling vs. Biopolymer Concentration (Note: bars represent standard deviation for individual days)