The Use of Coagulation as a Pre-treatment to Ultra-filtration Membranes

by

Marek Ratajczak

A thesis
presented to the University of Waterloo
in fulfilment of the
thesis requirement for the degree of
Master of Applied Science
in
Civil Engineering

Waterloo, Ontario, Canada, 2007

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.

M Ratajczak.

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

M Ratajczak.

Marek J. Ratajczak

ABSTRACT

With an increasing population density throughout the world and the current drive to provide fresh water to as many people as possible, innovative methods of providing safe drinking water are in very high demand. In 2002, the United Nations stated in their millennium declaration that one of their priority goals was "to halve, by the year 2015, the proportion of people who are unable to reach or to afford safe drinking water" (UNESCO, 2000). This goal was set with high standards, and will require a great deal of water treatment related research in the short coming years.

Over the past two decades, drinking water treatment via membrane filtration has been widely accepted as a feasible alternative to conventional drinking water treatment. Membrane processes are used in environmental, chemical, food, beverage, pharmaceutical, and various other industries for separation applications. Since the early 1990's, there has been rapid growth in the use of low-pressure hollow fibre membrane processes for the production of drinking water. These membrane systems are increasingly being accepted as feasible technologies for drinking water treatment.

Like with any innovative process, it has limitations; the primary limitation being membrane fouling, which is an accumulation of particles on the surface and inside the pores of the membrane surface. Membrane fouling has the ability to reduce the flux, in doing so, requiring a higher pumping intensity to maintain a consistent volume of water being treated. This project investigated chemical coagulation as a pre-treatment to membrane ultra-filtration, with the goal of mitigating fouling impact in order to maintain a consistent permeate flux, while monitoring several water quality parameters before and after treatment such as turbidity, alkalinity, pH and total organic carbon (TOC).

Two different raw water sources were studied: Grand River water taken from the Hidden Valley intake, located in Kitchener, ON, and Lake Ontario water taken from the Woodward Water Treatment Plant in Hamilton, ON. The evaluated coagulants include alum and ferric chloride, which are widely used hydrolyzing metal salt (HMS) coagulants; and three polyaluminum chloride (PACl) products, which are pre-hydrolyzed coagulants formed by the controlled neutralization of aluminum chloride solution.

Phase 1 of the project involved the coagulation of water using various aluminum and iron-based coagulants. Synthetic water was used at the outset, followed by the use of raw water obtained from two water treatment plants: one on the Grand River and one on Lake Ontario. A series of jar test trials was conducted to determine optimum coagulant dosages for the removal of NOM. These doses were then used as a baseline for subsequent membrane trials in phase 2 of this project.

Phase 2 involved the treatment of raw and coagulated waters with a hollow fibre bench scale UF unit (Zenon Environmental Inc.®, ZeeWeed-1). Membrane trials were performed with the coagulants applied at optimal and sub optimal dosages in order to evaluate the integrated process for mitigation of organic fouling. As all trials were conducted at a constant flowrate, membrane fouling was evaluated by monitoring trans-membrane pressure (TMP) over time.

The raw and treated water were fractionated to obtain quantitative information on the size components of NOM contributing most to fouling. Results will be presented comparing how the different coagulants affected the concentration of each NOM MW fraction in the raw and treated waters.

Collectively, results showed that all four coagulants substantially decreased the rate of TMP increase, particularly with the Grand River water which contained much higher turbidity and TOC concentrations than the Lake Ontario water. During the trials conducted with Grand River, alum performed best, reducing the TMP by 57 % over a 3-day period. The PACl coagulants performed best at reducing the TMP during the Lake Ontario membrane trials; reducing the TMP by 21 % and 19 % for SP 70 and SP respectively. The system's ability to maintain a permeate turbidity level of 0.1 NTU or lower was met, and TOC removals varied a small amount across the four coagulants, ranging from 45-65 % and 15-35 % for the Grand River and Lake Ontario trials, respectively.

ACKNOWLEDGEMENTS

The completion of this thesis would definitely not be possible with the help, support and motivation of several important individuals and institutions.

First and foremost, I would like to thank my supervisors Drs. Peter M. Huck and Kirsten N. Exall for their exceptional expertise, and advice along the way. I feel very grateful for having spent the last 2 years working with these two enlightened individuals.

I would also like to thank Dr. William B. Anderson, my unofficial supervisor, who on countless occasions sat me down to work out a problem, or edited one of my documents over his lunch break. His benevolence and willingness to help out an individual in need is a characteristic that very few people possess, and should never be over looked.

A special thanks to Terry Ridgway, a vital component to the Civil and Environmental Engineering Department at the University of Waterloo. His wealth of knowledge and experience was something that I simply could not have succeeded without.

I would also like to thank Bruce Stickney and Mark Sobon for their assistance in the laboratory, as well as Dr. Sigrid Peldszus for her analytical knowledge of the varied instrumentations that I made use of along the way.

Thanks to Ms. Dana Herriman for her endless patience and assistance. I can't even count how many times I had a last minute request. Dana always had a smile and a helping hand.

Thanks go out to Fraser Kent and Tobias Boadway, employees of GE Zenon Environmental, who provided me with a great deal of knowledge in the design, and the automation of my bench-scale membrane system.

Thanks to Jim Allen from Eaglebrook Coagulants, who provided me with all of the coagulant samples, and for his advice along the way.

I would also like thank all of my friends at the University of Waterloo. In one way or another, they all contributed to the completion of my thesis: Keith Moggach, Scott Gray, Margo Scott, Mason Marchildon, Jeff Randall, Rob Amos, Alex Bardelcik, Caroline Amyot, Michael Makahnouk, Jeff Timko and several others.

I can't forget to give thanks to the Graduate Student Association (GSA) here at the University of Waterloo. I was lucky enough to occupy the position of President for a 1-year term, and during that time, I had the chance to meet many incredible people, and mature as a young professional. To Rose Vogt, the GSA Administrator, but more importantly an Angel at heart. What a beautiful person.

To my sister Ursula, who has always motivated me to be the best that I can be. She has also doubled as second mother throughout the years, love her to pieces.

To my parents, Alice and Andrew Ratajczak, who have supported me in every possible way throughout the duration of my 22 years as a student; If only every person could be so lucky!

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 The Growing Need for Clean Drinking Water

In most countries, water is everywhere. Unfortunately, however, ninety-seven percent of the world's total water is seawater. Of the remaining fresh water, two-thirds of this fresh water is locked in glaciers, ice or snow, leaving only one percent of the world's total water available for direct human consumption. Presently, there is a greater demand than ever before for safe drinking water – not only in North America, but throughout the entire world (MWH, 2005). A generally accepted definition of safe drinking water is water that is free of pathogenic organisms, toxic substances, colour, turbidity, taste and odour, and has an acceptable level of minerals and organic material (WHO, 2004).

The use of low pressure membrane systems has become a widely accepted addition to conventional drinking water treatment. The process has received a great deal of attention, and in many ways, it is a proven, sustainable, and reliable treatment technology used on a variety of scales around the world. In the United States alone, the growing demand for membrane treatment technology such as reverse osmosis (RO), micro-filtration and ultra-filtration, in all water treatment applications rose 6.5 percent annually starting in 1994, reaching $305 million in the year 2001 (Vial and Doussau, 2002), and considerable further growth has been seen since. The process provides water treatment through physico-chemical separation techniques that use differences in permeability and physical blocking of the water constituents as a separation mechanism. Conceptually, it is a reasonably simple technology to understand that has the capacity to achieve high standards of treatment over long periods of time. The use of membranes has been somewhat limited due to high capital costs, although in recent years the cost of membrane systems has decreased substantially. Laîné *et al.* (2000) reported that between 1992 and 2000, a 50 % decrease in cost was observed, with further decreases in cost observed since. This decrease in cost has been mainly attributed to two factors: an increase in membrane surface area per module and an increase in mass production of these membrane modules. As a result of the decreased cost, the use of these systems has seen increased usage over the past 20 years, to become a very attractive and feasible alternative to conventional drinking water treatment. One of the primary limitations to even wider acceptance of membrane systems is the reversible and irreversible fouling that occurs on the membrane. The organic matter that is important for such fouling exists in both suspended and dissolved forms, with the dissolved components causing both organic and biological fouling which are difficult to treat, as compared to the colloidal (suspended particulate) fouling which can be mitigated with the use of cyclic back-wash cycles (AWWA, 2005).

1.2 Research Objectives

The primary goal of this research was to investigate the effectiveness of various chemical coagulation conditions as a pre-treatment to ultra-filtration (UF) hollow fibre membranes for mitigation of fouling caused by particulate matter and natural organic matter (NOM).

The following is a list of specific objectives:

- Optimize coagulation by determining suitable coagulant doses to reduce the concentration of particulate matter (turbidity) and NOM prior to being treated by the UF membrane.
- Develop a laboratory scale setup in which coagulation is incorporated with a hollow-fibre UF membrane process to yield a more consistent flux across the membrane surface.
- Compare the fouling reduction potential of the different coagulation scenarios.

- Fractionate the raw and treated water into a series of molecular weight cut-off (MWCO) fractions, to assist in quantifying what portions of the natural organic matter (NOM) were removed with the settled flocs and/or remained on the surface of the membrane

1.3 Research Approach

After an extensive literature review was completed, the experimental design was divided into two phases:

Phase I: The first part of the work was the coagulation of synthetic water containing a specified amount of NOM in the form of Sigma-Aldrich® humic acid. The project explored two different source waters found in Southern Ontario: Grand River, and Lake Ontario. At the outset, coagulation trials were performed using a variety of synthetic water conditions including those relevant for these waters. These experiments were followed by trials using raw water obtained from the water sources mentioned above.

Phase II: a) The second part of the project involved the treatment of these raw water sources with a ZeeWeed-1® hollow fibre bench test unit. In order to further understand the NOM fouling process, both the raw and coagulated waters were treated with the UF membrane.

Phase II: b) Subsequent to the membrane filtration, both the treated and raw waters were fractionated to analyze what molecular weight fractions of the NOM were removed by the overall process (coagulation/flocculation/settling/membrane). Although not possible in this research because of time constraints, if a fractionation analysis of the flocculated water were included, this approach could determine how the fractions contributed to the permeate flux reduction across the membrane.

1.4 Thesis Layout

This thesis document has been prepared to be read by one with very little knowledge in the area of drinking water treatment, and more specifically membrane treatment technology. It is the hope of the author that after having read the literature review provided in Chapter 2, one would be sufficiently informed to be able to follow the remainder of the dissertation. The literature review presents background information on low pressure treatment systems, coagulation, and the combination of the two.

Chapter 3 of this dissertation contains information on experimental design and analytical methods. The subsequent chapters provide results detailing the coagulation work that was completed, as well the membrane filtration of waters pre-treated with a variety of coagulants.

Chapters 4 and 5 contain summaries of the results and corresponding analysis. The principal conclusions and recommendations are laid out in Chapter 6. The subsequent section contains a complete reference list for all sourced information in the thesis. The last section of this document is the appendix, which contains all of the raw data and plots that were required to obtain the results.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 The Present State of Affairs

The world population has grown tremendously in the last 20 years, to reach a total of over 6.5 billion people, as of the beginning of 2006 (USCB, 2006). Improving access to safe drinking water has just barely kept ahead of population growth during the 1990's, and as a result the percentage of those without access to safe drinking water dropped from 25 % in 1996 to 18 % in 2003. Having said this, more than one billion people still remain without safe drinking water and over two billion lack adequate sources of sanitation. The global need for access to clean drinking water is rising at an alarming rate. The World Health Organization (WHO, 2004) has labelled it as a "silent emergency", as billions of people struggle without clean water or basic sanitation (WHO and UNICEF, 2004).

The need for advanced drinking water treatment technologies is on the rise. Although Canadians have ample water supplies in general, it is important to note that the best way to make sure drinking water supplies are kept clean, safe and reliable is to take a preventive risk management approach, or as it is often referred, a multiple barrier approach (MBA).A MBA is a series of checks and balances from the watershed to the tap of the customer. It is considered, in the water utility profession, to be the most effective way to ensure public health protection. Conventional drinking water treatment in Canada generally consists of several distinct stages: filtration, coagulation, flocculation, sedimentation and disinfection, not necessarily in that order. These practices have been in place for several decades, and these conventional plants are becoming less common due to the stringent water quality regulations that are being passed. The use of low pressure membranes to treat contaminated water has been widely accepted as a feasible alternative, and therefore must be explored even more so in the future to allow for sustainable treatment technologies, both for metropolitan and small communities.

2.2 Background on Membrane Treatment

2.2.1 History and evolution of membrane treatment processes

Micro-porous membranes were first used and patented in the 1920's (Belfort et al., 1994), although they were limited primarily to laboratory use until the 1950's. Initially, they were used for enumerating bacteria, removing microorganisms and particles from liquid and gas streams, and fractioning and sizing macro-molecules such as proteins (MWH, 2005). In the 1950's industries began incorporating membrane filtration, primarily for the sterilization of liquid pharmaceuticals and intravenous solutions. Membrane filtration also slowly began to be used for industrial waste treatment, in order to separate oils, fats, acids and brine.

There are four main categories of membranes used in drinking water applications today: micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO). These membranes are generally classified by pore size, molecular weight cut-off (MWCO) and the applied pressure that they require. Pore size is sometimes expressed as MWCO, which is a measure of the removal characteristics of a membrane in terms of atomic weight or mass, as opposed to pore size; typically measured in daltons (AWWA, 2005). Table 2-1 provides a concise summary of the four membrane types, as well their application, pore size and operating pressure:

Table 2-1: Major membrane filtration processes used in drinking water treatment

Type	Operating pressure (kPa)	Pore size (μm)	Primary applications	Microbes removed
MF	30-50	≥ 0.1	Removal of particles and turbidity	Algae, protozoa and most bacteria
UF	30-50	≥ 0.01	Removal of dissolved nonionic solutes	Algae, protozoa, most bacteria and viruses
NF	500-1000	≥ 0.001	Removal of divalent ions (softening) and dissolved organic matter	Algae, protozoa, most bacteria and viruses
RO	1000-5000	≥ 0.0001	Removal of monovalent ions (desalination)	Algae, protozoa, most bacteria and viruses

Adapted from Taylor and Weisner (1999)

The membrane modules themselves are a part of a larger system which includes all of the operational concepts and conditions that make up a treatment system (Schäfer et al., 2005).

Membrane processes now are used in environmental, chemical, food, beverage, pharmaceutical, and various other industries for separation applications. In water and wastewater treatment, their application as an advanced physical process for clarification and disinfection is established and rapidly gaining popularity (Sethi et al., 2000). Since the early 1990's, there has been rapid growth in the use of low-pressure micro-filtration (MF) and ultra-filtration (UF) membrane processes for the production of drinking water. Specifically, UF membranes are very successful in removing turbidity, which is generally defined as a measure of the cloudiness of water; the cloudier the water, the greater the turbidity. Turbidity in water is caused by suspended matter such as clay, silt, organic matter, plankton and other microscopic organisms that interfere with the passage of light through the water (American Public Health Association, 1998). Turbidity is an indicator of major sources of water impurities in waters (including those in Canada), and therefore is an ongoing parameter of interest for all water treatment processes. The UF membranes can yield permeate streams consistently with turbidity values of less than 0.1 NTU (Nephlometric Turbidity Unit).

The widespread growth of the use of low pressure membrane systems on large scale applications has occurred for several reasons. A major reason is the changes in the regulatory requirements for drinking water in Canada, requiring lower filtered water turbidity and removal of chemical disinfectant-tolerant micro-organisms, such as *Giardia* and especially *Cryptosporidium* (AWWA, 2005). Figure 2-1 shows the tremendous growth in the use of membrane technology in North America in the 15 years prior to 2003.

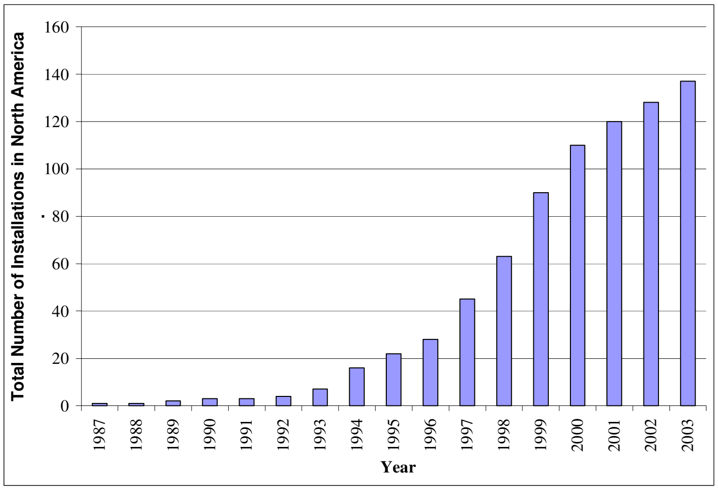


Figure 2-1: The growth in the use of membrane technology (AWWA, 2005)

This trend is continuing at a rapid rate as numerous membrane facilities ranging from 25 to 100 mgd (100 to 380 mLd) in capacity, are either planned, in design or in operation.

Another major cause for the recent expansion in membrane systems utilization is simply the broader applicability that they offer as compared to conventional drinking water treatment. MF and UF systems are particulate filters and unlike nano-filtration (NF) and reverse osmosis (RO) do not remove dissolved constituents. This treatment aspect makes them more suitable for use as a replacement to conventional filters. The cost of low pressure membranes systems is also a major driver for increased membrane application compared with conventional treatment technologies. Every year, the capital cost of MF and UF systems has decreased as economies of scale and a competitive market force innovative developments. Generally, low pressure membrane facilities are one half to one third the cost of an NF or RO facility (Farahbakhsh et al., 2004). In addition, the implementation of innovative backwash or cleaning strategies has reduced operational cost, by reducing the degree of fouling that occurs on the surface and inside the pores of the membranes.

One other key factor that has increased the usage of membrane systems is their operational flexibility. These systems can be used in conjunction with other treatment processes to achieve additional removal. There are several pre-treatment techniques available to use in combination with a MF or UF membrane: pre-filtration, pH adjustment, coagulation, bio-filtration adsorption and pre-oxidation (Kimura et al., 2005).

2.2.2 Description of membrane treatment processes

Process Description

Low pressure membrane processes are generally used for the removal of turbidity in water, and reasonably large pathogens such as *Cryptosporidium* and *Giardia*, and most bacteria (Klijn et al., 2000). The MF process is not very effective at removing NOM (Jacangelo et al., 1997), as these compounds are more efficiently targeted by ultra-filtration (UF) processes and much more efficiently by nano-filtration (NF). The two major issues that utilities have to deal with on a regular basis with UF membrane processes are the quality of the water product, which is related to the rejection of targeted solutes and particulates, and the impact of membrane fouling leading to permeate flux decline and consequent reduction in the efficiency of the membrane filtration process (Linhua et al., 2001).

Membrane processes are modern physicochemical separation techniques that use differences in permeability and size of contaminant as a separation mechanism (MWH, 2005). Effective membrane treatment will remove all or most of the contaminants to produce a water which, with effective disinfection, is of minimum risk to human health, aesthetically acceptable, and economically affordable (Westerhoff et al., 1996). Figure 2-2 shows a simplified form of a membrane process system, represented by the rectangle, which would in practice be a membrane module with a specified surface area. The basic principle of a cross-flow membrane system is as follows: raw water enters the module, where an applied pressure allows water with particles and molecules smaller that the specified pore size to pass through the membrane creating a permeate stream, while the remaining materials travel along the outer surface of the membrane, eventually forming a concentrate, or waste stream.

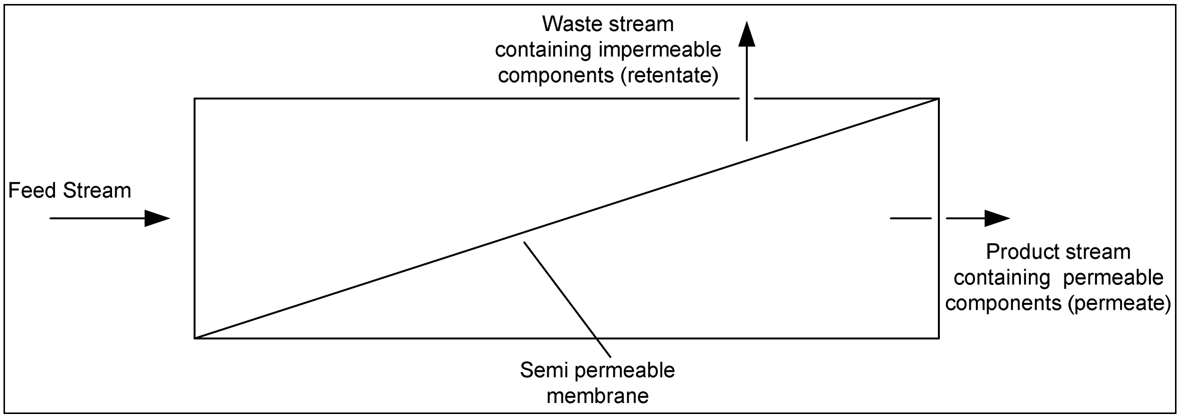


Figure 2-2 Schematic of separation process through semi-permeable membrane

Adapted from MWH (2005)

During the treatment process, the contaminated raw water is fed into the membrane module via a pump, which ensures that water is drawn through by vaccum. This pressurized water is fed into the membrane module, and onto the membrane surface. Generally, the feed stream flows perpendicularly to the membrane surface, although in some cases, the water is top-loaded onto the surface, called dead-end filtration. This set-up is no longer a common practice, as it induces membrane fouling much more than the modern approach of the cross-flow filtration. The membrane is described as semi-permeable, meaning that it is highly permeable to some components (water), and less permeable to other components, usually the contaminants that are found in the waste stream. The volume of water that accumulates in the permeate stream is quantified in terms of membrane flux, which is defined as the amount permeate flow produced per membrane surface area and time. This relationship is shown below:

$$\boxed{J = \frac{Q}{A} = \frac{m^3/day}{m^2} = \frac{m}{day}} \qquad \textbf{(1)}$$

Q represents the volumetric flow rate being fed into the membrane, and A represents the nominal surface area of the given membrane module.

As mentioned previously, UF membranes were the primary focus of this research. These membranes have a tendency to retain colloids and substances with a high molecular weight. Ions such as Mg^{2+} and Ca^{2+} will pass through the membrane pores, while almost all micro-organisms and polysaccharide-sized molecules will be retained. The pressure required to drive a UF membrane varies between 25 – 100 psi, depending on the specific application (Pontius, 1996). This operating pressure often plays a key role in deciding on what specific technological set-up will be implemented, as it represents a substantial cost in the overall scheme, mainly attributed to raising the pressure of large volumes of water.

The pore size and/or the MWCO determine the separation capability of a membrane. Intuitively the smaller the pore size, the greater the capability for rejection that exists. Having said this, a smaller pore size will require a higher trans-membrane pressure, resulting in a larger operating cost. On average, the pore size on any given membrane module can vary up to 35-50 %, depending on the membrane material and age of the module (Takechi et al., 1998). It is important to note that the pore size of membrane modules are not constant throughout, and therefore there exist two distinct methods of classifying membrane pore size: an absolute pore size and a nominal pore size.

An absolute pore size rating specifies the pore size at which a particle of a given size will be retained with 100 % efficiency under strictly defined test conditions. A nominal pore size rating describes the ability of the filter media to retain the majority of particulates (60 – 98 %) at the rated pore size. Process conditions such as operating pressure, concentration of contaminant, etc., have a significant effect on the retention efficiency of the filters (AWWA, 2005).

Figure 2-3 shows the pore size distribution of all the membrane types, and also gives a few examples of microbial particles that fall within the given range:

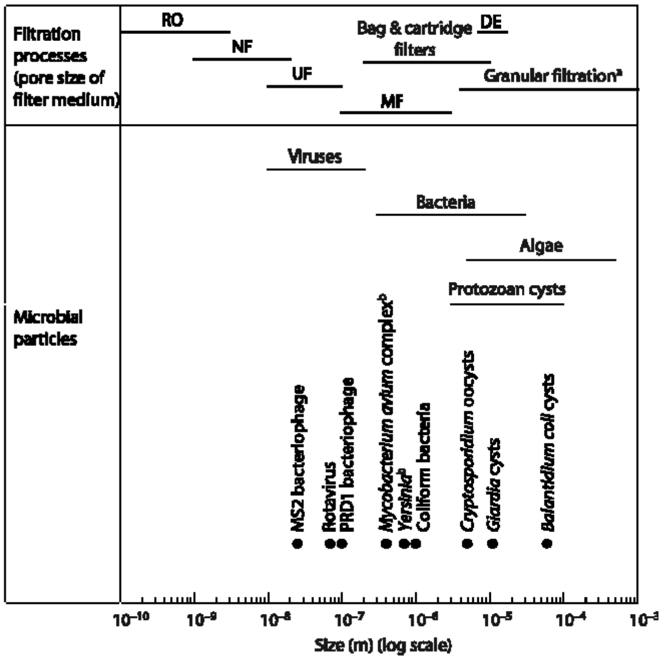


Figure 2-3: Pore size of filter medium and size of microbial particles

Adapted from LeChevallier and Au (2004)

As seen above, UF membranes have a pore size smaller than diatomaceous earth (DE) filtration pores, ranging between 10^{-8} to 10^{-6} meters in diameter. Although size exclusion is the primary mechanism by which contaminants in the feed stream are removed, it is not the only one and therefore pore size cannot be considered the only limiting factor in a UF membrane system. Differences in solubility and/diffusivity, and charge separation also play a role as exclusion mechanisms (MWH, 2005).

Both low pressure membrane systems (MF and UF) remove particulate matter and turbidity as well as larger micro-organisms and viruses. Effluent turbidity values have been consistently reported to be lower than 0.1 NTU (Karimi et al., 1999). Another key feature of UF membranes is their ability to remove particulate metals such as iron and manganese, as MF membranes do not have this consistent capability (Gangloff, 2000). The removal of organic matter and more specifically humic substances by UF membranes is considered to be a challenge due to the associated organic fouling that occurs. Further discussion regarding this topic will be discussed in subsequent sections of this chapter.

Membrane structure and configuration

The structure of a membrane refers to the way it is constructed to optimize surface area, and reduce the degree of fouling by incoming feed water. The most common types of structures are (Schäfer et al., 2005):

- Spiral wound
- Hollow fibre
- Flat sheet
- Tubular/capillary

One of the more common structures for low-pressure membranes is the spiral wound configuration, as it allows for an optimal membrane surface given a very small working space. Figure 2-4 gives provides a summary of what the spiral wound module resembles, and highlights the most important aspects of it:

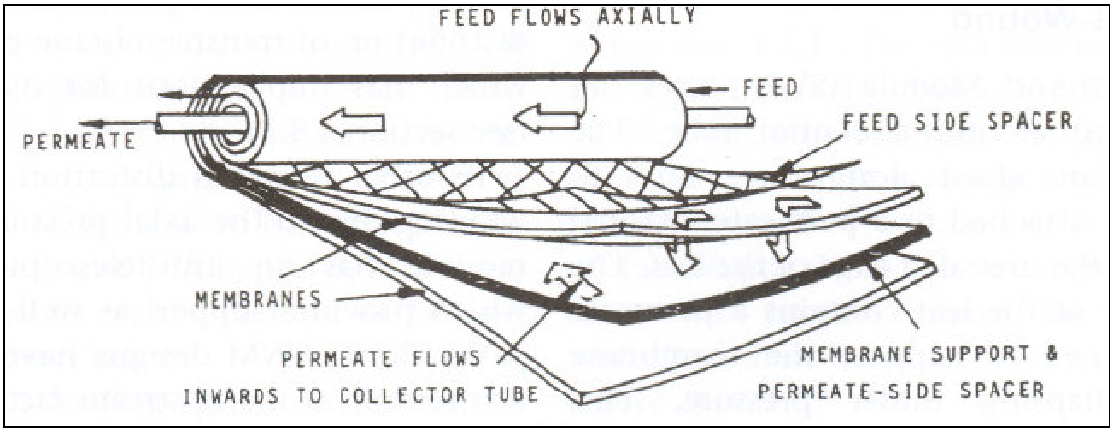


Figure 2-4: Spiral wound membrane module

Schäfer et al., (2005)

The raw feed water is fed axially through the membrane module at one end, and exits in parallel at the other end. As the name depicts, the module is essentially a flat sheet membrane that is wound into a spiral shape, ensuring that there is sufficient space between layers for the water to pass through. On this diagram, one can see that the membrane support is used to ensure sufficient space is provided between sheets. One of the primary reasons why these membrane configurations are being used less frequently on a large scale is because of their tendency to irreversibly foul. Generally, these membranes cannot be back-flushed because of they way they are manufactured. The actual membrane modules are cast onto the interior support material, so any back-wash flow could potentially delaminate the membrane, exposing the inner surface. Because of this, these membranes rely heavily on chemical cleaning to remove any deposits from the membrane surface, representing a higher annual operating cost.

Hollow fibre membranes have gained popularity in the last decade to become the most commonly used configuration in low pressure membrane filtration (MF or UF) for water treatment (MWH, 2005). These membranes usually consist of several hundred fibres encased in a module, whether it is full, pilot or bench scale. They are generally open tubes that are plug resistant and do not accumulate particles between the fibres. The internal fibre diameters are quite small to avoid fibre collapse when exposed to high pressure, range anywhere between 0.4 to 1.5 mm (AWWA, 2005). These membranes can be exposed to frequent backwash cycles, which make them an attractive module type given that fouling is the primary limitation to the technology.

Two types of flow regimes are used in practice, the first being the outside – in configuration, where the membrane is submerged in the feed water, and the untreated water is sucked in through the many porous fibres via a vacuum, and combined to become the permeate stream. The second configuration is the inside-out, where water is pumped into the membrane, and filtered through the fibres exiting into the surrounding water. The advantage of the second flow regime is that the water flows through a narrow channel, and therefore allows for good control over module hydrodynamics. Hollow fibre membranes offer a very high specific surface area to volume ratio, because of the small inner lumens of the fibres, and therefore have the ability to treat a larger volume of water.

One of the major disadvantages to these membrane configurations is the fact that they are very susceptible to fouling, requiring frequent backwash cycles as compared to the spiral wound structures, which cannot be backwashed at all, and therefore are much more susceptible to fouling (Lee et al., 2004). An outside-in membrane will accumulate particles on the outside surface of the membrane, making it not only easier to visually inspect the degree of fouling, but also much easier to backwash such a configuration. The inside-out configuration will accumulate particles on the interior of the membrane module, and represent a more challenging backwash and cleaning procedure. Figure 2-5 presents a schematic of a single cross flow hollow fibre membrane module:

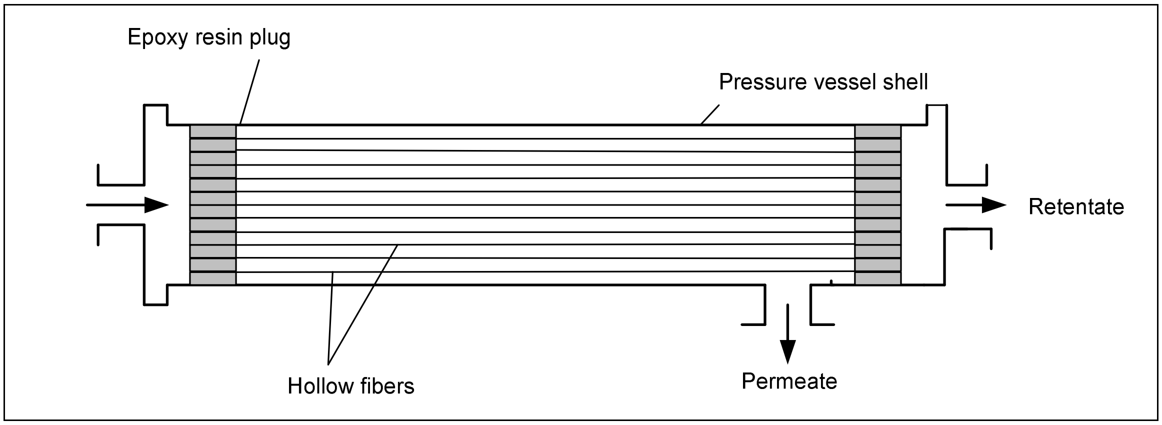


Figure 2-5: Pressure-vessel configuration for hollow fibre membrane filtration

Adapted from MWH (2005)

As clearly seen, water enters at one end of the module, then gets filtered through the numerous fibres, combining to become the permeate stream. The water that does not enter the fibres is also combined to become the retentate or concentrate stream. This brings up one of the few limitations to low pressure membrane systems that has not allowed for even further expansion of this technology. The concentrate stream that is generated must be disposed of accordingly, as it contains a very high concentration of targeted contaminant which is being removed by the membrane. The implementation of a concentrate disposal plan is crucial to an overall sound treatment system.

There are four ways of disposing of these streams in North America: directly to a surface water source, domestic wastewater treatment plants, deep well injections and evaporation ponds. One of the key factor which determines which kind of disposal is implemented is the frequency and concentrations of chemicals used to clean the membrane modules. A concentrate that is relatively free of chemicals can generally be disposed of by discharging into large surface waters, while concentrate streams that have been discharged from membranes exposed to high frequency chemical cleaning may have to be further treated, or simply disposed of in a landfill. Another key item to note is the difference that exists between low pressure membrane concentrate streams, as compared to high pressure systems like NF and RO membranes. High pressure systems often have high concentrations of dissolved solids and metal ions in the concentrate streams, which pose a threat to wildlife and habitats if disposed of directly into surface waters. Low pressure concentrate streams are mainly composed of organic matter and micro-organisms, which originate from surface waters, therefore their disposal is less worrisome (Marcel, 2004).

Membrane material

Membrane performance is influenced strongly by the physical and chemical properties of the material (MWH, 2005). As technology is evolving, membranes are being built with more sophisticated materials and with unique applications for the given source water. The most frequently used membrane materials in both municipal and industrial water treatment are polymer based: Cellulose acetate, acrylic, nylon, polypropylene (PP), polyamide (PA), polyamide-hydrazide (PAH), polyimide (PI) and polyethersulphone (PES). Ceramics and zirconia based materials have also gained popularity, but have not grown to be as popular as the polymer based modules.

The most common polymer based materials are the PA's, PAH's and PI's (Panglisch et al., 2000). It is difficult to identify individual applications for each membrane material, as it can vary tremendously based on factors that are specific to any membrane system. Most consumer systems use cellulose acetate or nylon membrane materials wound in a tubular cartridge. In general, the cellulose acetate membranes are used with municipal water, which has been disinfected with chlorine, while nylon membranes are preferred in systems that use well water. A chlorine based city water supply requires a different membrane than rural "hard" water well based supply. The chemical chlorine will destroy the nylon membrane. (Gangloff, 2000).

The polymeric materials will continue to prosper due to their flexibility, permeability and ability to be formed into a variety of filter components (Gangloff, 2000). However, specialty membrane materials, such as ceramic and composite constructions have the potential to experience rapid growth, although on a much smaller scale, due to their higher unit cost and performance advantages in extreme environmental applications.

Polymers are almost ideal membrane materials, since they can be easily produced with pores of almost any size and are flexible enough to be configured into a wide range of constructions, including flat sheets and hollow fibre cartridge materials (Klijn et al., 2000). However, there are several drawbacks to polymer membranes; the one that stands out most is the tendency toward fouling and clogging. This particularly can be the result of contamination from biological growth. Nevertheless, the advantages of polymers, coupled with the growing use of cross-flow designs, which minimize clogging by directing fluids toward the membrane at an angle, will ensure that for the vast majority of applications, polymers will remain the material of choice for years to come.

Ceramics are another popular membrane material in the treatment of potable water. Ceramic membranes also have drawbacks. Chief among them are brittleness, increased size and higher cost on a square foot basis. These membrane types will remain limited to specific applications that require the performance characteristics offered by ceramics such as the thermal stability, abrasion resistance, durability and bacterial resistance. (Gangloff, 2000). Ceramics can also be placed in dry storage, as compared to polymer based membranes which have to be submerged in water to avoid damaging the material.

However, new applications for ceramic membranes have been observed in the last decade; resulting in a more widely accepted usage, subsequently leading to above average growth (Bottino et al., 2001). Ceramics will also benefit from the growing trend toward composite membranes, which combine ceramic and polymeric membranes into a single system with the advantages of both types. In the end, the advances made to ceramic and composite membranes will prolong the life spans of membranes, slowing growth in replacement sales (Gangloff, 2000).

Membrane cleaning

Membrane modules experience a great deal of wear and tear during the treatment of contaminated water. It is crucial to the life of a membrane that is well maintained and cleaned; otherwise it will have to be replaced, representing a substantial cost to the overall process. There are several ways that a membrane can be maintained in its best working order, mainly by pre-treatment, air-sparging, backwashing and chemical cleaning.

Pre-treatment of membranes has received a great deal of attention in the past decade as it is considered to have a great deal of potential in reducing the degree of fouling on the surface and inside the pores of membranes. This process entails exposing the incoming feed water to a different treatment method prior to the water entering the membrane module. As mentioned previously, research has been conducted using several pre-treatments, such as coagulation, bio-filtration, advanced oxidation, pH adjustment, chlorination, activated carbon and other complexing agents (Kimura et al., 2005). Low pressure membranes have been used as pre-treatment techniques for other technologies such as NF and RO system. Such is the case for the pre-treatment of seawater prior to RO, which has become a more common practice (Vial and Doussau, 2002). When using membranes, surface waters require more pre-treatment as compared to ground waters, as they have elevated TOC and turbidity concentrations.

“The objective of backwashing is to remove the surface cake that develops during the membrane filtration cycle” (MWH, 2005). The term backwashing implies that the flow of water is reversed, and instead of raw water being pushed through the membrane, clean water is pushed in the opposite direction. Most low pressure membrane systems are set up with automatic backwash cycles, with frequency ranging between every 30-90 min (MWH, 2005). Backwashing targets the particles that have caused reversible fouling on the surface, flushing them away to increase permeate flux. Air sparging is another membrane cleaning technique that is generally used in combination with the backwash cycle. This process involves pumping a constant flow of pressurized air through the membrane module, which exits into the surrounding water in the form of gas bubbles. The objective of air sparging is to help scour material off the membrane surface, and in doing so reduce the amount of particles that remain on the membrane surface during the permeate cycle.

The backwashing coupled with the air sparging will be conducted based on a set point, such as time, or a key performance variable such as the rate of TMP increase over time. For example, a system could be set to permeate for 40 min and then conduct a backwash/air sparging cycle before returning to the filtration mode. It could also be set to conduct a backwash every other cycle, and air sparging every cycle. Some systems are set up trigger the backwash cycle once the TMP hits a specified maximum value. The backwash frequency is heavily dependent on the incoming water quality. A raw water with a high total suspended solids (TSS) concentration will required more frequent backwashes, as compared to a raw lake water which has lower TSS concentrations.

Chemical cleaning is used to target the contaminants that cause irreversible fouling to the membrane. The frequency of chemical cleaning is different from that of backwashing, as it ranges from a few days to several months, depending on the membrane characteristics and source water quality. When foulants can no longer be removed from the membrane surface by backwashing, chemical cleaning is required. The procedure typically takes several hours and involves circulating preheated cleaning solutions throughout the membrane modules, draining the system several times and repeating. The large volumes of solution are often heated to temperatures up to 60^{o}C, requiring a tremendous amount of energy, translating into a high cost (MWH, 2005). A variety of agents can be employed for the chemical cleaning of low pressure membranes: detergents, acids, bases, oxidizing agents, sequestering agents and enzymes (AWWA, 2005). Chlorine can also be used in doses ranging from 2 to 2000 mg/L; this in addition to acting as an oxidant capable of disinfection.

It is difficult to accurately quantify the required chemical cleaning frequency of a given membrane system, as it is dependent on a number of factors, such as the concentrations of contaminants, volume of water treated, and required effluent quality. Van Paasen et al. (1998), compared the chemical cleaning frequency of surface water vs. ground water treatment plants, and concluded the membranes that treat groundwater require bi-annual chemical cleaning, while surface water require chemical cleaning 4-5 times a year. The following section provides detail into the membrane fouling phenomenon, which will help tie together the reasoning for backwashing and chemical cleaning of a membrane.

2.3 Membrane Fouling

2.3.1 Introduction

The main limitation to the use of membranes in drinking water treatment is its high energy consumption that can mainly be attributed to membrane fouling, which causes the applied pumping action to work harder to maintain a constant flux (Kimura et al., 2005). Membrane fouling is the process by which the permeate flux through the membrane is reduced as a result of particles accumulating on the surface, forming a cake layer, or the adsorption of particles (both suspended particles and dissolved material) inside the membrane pores (AWWA, 2005). Membrane fouling can be divided into two types: reversible and irreversible fouling. As previously mentioned, reversible fouling can be restored by backwash cycles, while irreversible fouling requires chemical cleaning to be mitigated. There are four major types of fouling mechanisms that affect drinking water membranes:

- Organic fouling
- Bio-fouling
- Scaling
- Colloidal/Particulate fouling

Organic fouling is caused by both dissolved and suspended particles that adsorb inside the pores and on the surface of the membrane. There are several factors already discussed that have the potential to influence organic fouling caused by NOM, although there are three primary ones: MW distribution, the membrane surface and chemical composition of the feed water.

Bio-fouling is the growth of living micro-organisms on the surface or inside the pores of a membrane. The living organisms use the membrane as a support, and in doing so reduce the permeate flux and cause fouling. It has been shown that chlorine dioxide removes bio-film from water systems and prevents biological growth from forming when dosed at a continuous low level. Hypochlorite on the other hand has been proven to have little effect on bio-films (Soffer et al., 2005).

Membrane scaling is a consequence of a given water source's solids concentration exceeding its solubility limit, resulting in precipitation of solids on the membrane. This occurs when the concentration of the given species is too high at the membrane surface, causing it to come out of solution and deposit onto the membrane surface. Precipitated inorganic compounds can act as scalants which can reduce the flux, can damage the membrane surface and cause irreversible pore blocking. When particles block membrane pores, the higher dissolved molecule concentration yields higher osmotic pressure, higher tendency of suspended solids to coagulate and coat the membrane surface, and higher likelihood of pore plugging (scaling) to occur (AWWA, 2005).

Colloidal and particulate fouling is a fouling mechanism in which the particles accumulate on the membrane surface or inside the pores, resulting in reduction of the permeate flux. Colloidal surface charge is related to the zeta potential of given membrane. Zeta potential is the electrical potential that exists at the shear plane of a particle, which is some microscopic distance from the surface (AWWA, 2005). Zeta potential influences the porosity of the cake formation and the hydraulic resistance.

The overall fouling mechanism can be described using the Resistance in Series Model (RSM) (Schäfer et al., 2005). There are four primary components of resistance that contribute to membrane fouling: resistance due to the intrinsic membrane (Rm), resistance due to cake formation (R_c), resistance due to internal pore fouling (R_{pb}) and resistance due to adsorption (R_a). Figure 2.6 shows how the four resistance mechanisms combine together to form an overall resistance to flux (R_{total}).

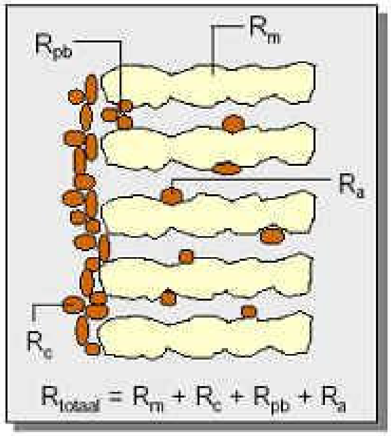


Figure 2.6: Membrane resistance mechanisms

Adapted from Schäfer et al., 2005

Fouling has received a great deal of attention from water treatment research experts, as many situations show that there is no clear distinction as to whether it is the dissolved or suspended particles that contribute to fouling most. Howe and Clark (2002a) concluded that the most significant membrane fouling occurs in the presence of small colloidal matter, ranging from about 3-20 nm in diameter. Their findings demonstrate that the majority of dissolved organic matter (DOM) by itself does not cause membrane fouling, but rather the actual foulant is a relatively small fraction of bulk DOM. Combe et al. (1999) found that NOM adsorbs both inside pores and on the membrane surface, forming a gel layer, which thickens over time reducing the overall flux across the membrane surface.

Fouling is the aspect of low pressure membrane systems that is receiving the most attention in water research today. It represents a very large fraction of the annual cost for a membrane system, as it substantially increases the cost of a process by increasing energy requirements and replacement frequency. One of the least understood aspects of fouling is how NOM affects membrane surfaces. Although a great deal of research has been conducted using NOM, it is only recently that some success has been achieved in understanding what portion of the NOM contributes to fouling most. Because of the importance of NOM for fouling, it is discussed in more detail in the next section.

2.3.2 The Origin of Natural Organic Matter

One of the important group of substances that exist in Canadian surface and ground waters today is NOM, found in concentrations ranging from 1 to 15 mg/L, depending on the season and specific location (AWWA, 2005). Groundwater sources in North America tend to have less than 2 mg/L TOC, while rivers tend to have a slightly more elevated level ranging from 3-6 mg/L.

Natural organic matter (NOM) is primarily made up of humic substances, which are poly-phenolic molecules that give rise to yellow-brown water that is aesthetically undesirable. The NOM also has the potential to combine with disinfection compounds such as chlorine, to form such disinfection by-products (DBP) as organo-chlorines (Maartens et al., 1999). These by-products have been proven to act as carcinogens in bench-scale animal studies (Singer, 1999). The potential for NOM to complex with metals also exists, and as a result, can potentially increase metal solubility, having direct adverse effects on human health (Jones and Bryan, 1998).

Humic substances are a major component of suspended and dissolved NOM in aquatic environments. They are mainly derived from soil and are also produced within natural water and sediments by chemical and biological processes such as the decomposition of vegetation (AWWA, 1999). A major component of NOM found in natural waters are humic substances. Humics are anionic poly-electrolytes of low to moderate molecular weight, ranging between 2000-5000 Da, dominated by phenol groups. The negative charge is caused by the carboxyl and phenolic groups that make up the structure of the compound. They have both aromatic and aliphatic components, allowing them to be surface active, which is the ability of a compound to lower the surface tension of a given medium in which it is dissolved (Kokkola et al., 2006). In addition to humic substances, proteins, polysaccharides, and other classes of biopolymers also contribute to NOM in natural waters. Monomeric species such as simple sugars and amino acids are also present in natural water sources, but they are much less abundant, as they are subject to relatively rapid biodegradation (AWWA, 2000).

This thesis targeted organic carbon in the form of humic acid as a simulator for NOM in true aquatic environments for synthetic water sources, as well NOM found in raw water sources found in Southern Ontario. The name NOM implies that it is of natural origin, but as a practical matter the molecules collected as NOM from any water source can include many organic compounds contributed by human activities (AWWA, 2005).

2.3.3 Fractionation as a fouling prediction aid

Fractionation of a given water sample into a series of molecular weight cut offs serves as a useful method in predicting what fractions were coagulated and potentially which contribute d to the fouling severity of a membrane. Howe and Clark (2002a) performed a series of rigorous experiments to further the understanding of NOM fouling potential. Raw lake water was subjected to a three step sequential filtration process: pre-filtration, fractionation and fouling determination. The raw water was first pre-filtered through a 0.45 μm filter to remove any particulate matter. Aliquots of the filtrate were put through regenerated cellulose (RC) membranes with nominal MWCO's of 3000, 10000, 30000 and 100000 Da, keeping one of the aliquots un-fractionated. By removing any suspended particulates in the pre-filtration stage, the surface cake formation was minimized, and alternate mechanisms of fouling were easier to observe. Each of the fractionated waters was filtered through a 0.2 μm polypropylene membrane and the flux was monitored to determine the fouling caused by each aliquot.

The conclusions that came from these series of experiments were not consistent, as results showed that the mid-sized dissolved particles contributed to 65 % of the fouling, while a second trial with a different source water showed different results. In the first trial, the material that passed through the 100,000 Da membrane contributed to 50 % of the fouling, while in the second trial, over 75 % of the fouling was due to material smaller than 100,000 Da. Colloids that were able to pass through a 100,000 Da membrane corresponded to a colloidal size smaller than approximately 0.02 μm. Having said this, this study supported the notion that fouling is not directly proportional to the TOC level in water, but rather the MW distribution of the NOM and their corresponding concentration that have a larger impact on the severity of fouling.

2.4 Membrane Performance and Fouling by NOM

An understanding of NOM as a membrane foulant and the behavior of NOM components in low-pressure membrane fouling are needed to provide a basis for appropriate selection and operation of membrane technology for drinking water treatment (Lee et al., 2004). Removal of humics by low pressure membrane filtration has in the past been considered challenging because of the strong effect that is induced by organic fouling that occurs on the surface and inside the pores of the membrane surface. In general, the fraction of humic substances removed by membrane filtration depends heavily on the type of membrane used, and the chemistry of the raw water (Ruohomaki, 1999). Several authors (Lin et al., 2000 and Domany et al., 2002) have attempted to quantify the removal of humics by membrane filtration. Lin et al. (2000) observed a removal of 10 % of Aldrich humic acid using a 100 kDa membrane module. This membrane was operated at an initial flow of 330 L/m^{2}h (LMH), reducing to approximately 198 LMH in 25 hours of operation, representing a decrease in flux of 40 %. Domany et al., (2002) performed a similar study, using 100 kDa membrane modules with an initial flux of 200 LMH. Comparatively, there was a 65 % removal of the Aldrich humic acid observed. In both cases, hydrophobic membranes were used, although their material varied slightly. The first study made use of polysulfone membranes, while the second study utilized PES membranes, with a TMP approximately 20 % lower. Although many studies have been performed in an attempt to understand the fouling potential of NOM, still much remains to be learned because of the complexity of its physical state (Maartens et al., 1999).

A hydrophobic component is defined as having a surface that is repelled away from a water surface, while a hydrophilic fraction has the opposite property of having the ability to be attracted to water based surfaces. Many researchers have suggested that the humic fraction of NOM is a major foulant which controls the extent of fouling (Combe et al., 1999; Jones and O'Melia, 2000). On the other hand, other studies have reported that hydrophobic (non humic) fractions might be a more significant foulant (Carroll et al., 2000). Fan et al., (2001) identified potential foulants in order as hydrophilic neutrals > hydrophobic acids > transphilic acids.

Lee et al., (2004) concluded that natural waters with a high content of hydrophilic organic material resulted in more significant flux decline. This was primarily attributed to the fraction containing colloidal and macromolecular organic matter with non-humic properties. He further concluded that distinct differences in flux decline between hydrophobic and hydrophilic membranes were not observed suggesting that other membrane properties may play a larger part in the fouling process. The shape and size of molecules and roughness of the membrane surface were presumably more important factors in affecting flux decline.

2.5 Background on Coagulation

Coagulation and flocculation is defined as the process by which small particles in aqueous solution destabilize because by chemical addition, and aggregate together, forming larger particles known as flocs. With a neutral suspension, the flocculation rate can be enhanced, and the concentration of the given particle distribution in the solution can be reduced (AWWA, 1999). The coagulation process is a complicated one, with many mass transfers and active species that take part in the reaction steps. The process can be broken down into three key steps: Coagulant formation, particle destabilization (coagulation) and inter-particle collisions (flocculation). Enhanced coagulation, often referred as 'low pH coagulation' is often used to increase the removal of TOC and other particles. This is accomplished by reducing the raw water pH to an optimal level: a pH in the range of 4.5-5.5 for iron based coagulants and 5.5-6.5 for aluminum based coagulants (Sharp et al., 2006). In order to understand the mechanism by which coagulants function, one needs to be familiar with the exact type and their form.

This thesis involved the usage of five coagulants: ferric chloride, aluminum sulphate (alum), and three polyaluminum chloride (PACl) coagulants: SternPac, SternPac 70 and SternPac 2300. Ferric chloride and alum are two widely used coagulants both in the drinking and waste water industries. They are known as hydrolyzing metal salt (HMS) coagulants with the active metal being Al^{3+} and Fe^{3+} for alum and ferric chloride respectively (AWWA, 1999). In solution, these small, positively charged ions form a strong bond with oxygen atoms of six surrounding water molecules, e.g., $M(H2O)_6^{3+}$, with the M representing the active metal. The hydrogen-oxygen bond is subsequently weakened, and the hydrogen ions are released into solution. This reaction is known as hydrolysis, and the resulting active metal hydroxide species are known as hydrolysis products. The process is a progressive de-protonation of water molecules in the primary hydration shell (Richens, 1997). Hydrolysis of such ions is generally represented as a sequential replacement of the water molecules by hydroxyl ions (Gregory and Duan, 2001). The simplest representation for Al^{3+} of such a process is the following:

$$\boxed{Al^{3+} \leftrightarrow Al(OH)^{2+} \leftrightarrow Al(OH)_2^{+} \leftrightarrow Al(OH)_3(s) \leftrightarrow Al(OH)_4^{-}} \qquad \textbf{(2)}$$

Each step involves the loss of a proton, with an increase in pH causing the equilibrium to shift to the right. Aluminum hydroxide ($Al(OH)_3$) has a very low solubility in water, with precipitation occurring at intermediate pH values. One must consider the solubility of the metal hydroxide precipitate to maximize performance and minimize residual metals in solution during the coagulation process. At low pH values (below 5.0), the dissolution of the precipitate produces positively charged soluble hydrolysis products and the (aquo) ion. At high pH values, (aluminate) ions are formed (above 7.8). At a pH of 6.5, the precipitated $Al(OH)_3$ is least soluble, therefore optimizing the coagulation process by incorporating the maximum amount of Al in particulate form. This pH of minimum solubility is also a function of temperature, with the pH increasing slightly with decreasing temperature (AWWA, 1999).

As well as the simple monomeric hydrolysis products considered above, the highly charged Al ions can form a variety of polynuclear species: these include $Al_2(OH)_2^{4+}$ and $Al_3(OH)^{4+}$. Various polymeric species, such as $Al_6(OH)_{12}^{6+}$, have been proposed, but their existence has not been convincingly demonstrated. They might be regarded as intermediate forms in the conversion of soluble metal salts to solid precipitates. It is known that hydrolysis precipitation processes at ordinary temperatures are very slow and that true equilibrium can take months or years to achieve. One polynuclear hydrolysis product of aluminium is now well established. This is the so-called "Al_{13}" polymer, $Al_{13}O_4(OH)_{24}^{7+}$, which can be formed by controlled neutralization of aluminum salt solutions (Gregory and Duan, 2001).

The two main ways in which hydrolyzing coagulants act to remove particles are charge neutralization and sweep flocculation. Charge neutralization is a reasonably simple mechanism, which involves the specific adsorption of the cationic hydrolysis products from solution onto the negatively charged particles. NOM and other particles can be destabilized by small amounts of hydrolyzing coagulant. Desirable destabilization corresponds with the neutralization of particle charge, which then leads to aggregation of the neutral particles (Gregory and Duan, 2001). It is important to note that larger amounts of the positively charged coagulants (over dosing) can cause charge reversal, leaving the particles positively charged and thus re-stabilized. When charge neutralization is the dominant mechanism, the coagulant dose is generally considered to be proportional to the concentration of particles in solution, although in some cases, required doses can still be dominated by the type of NOM found in the water, and not simply the concentration.

In some cases it is found that a higher coagulant dose is more effective, due to extensive hydroxide precipitation and the process known as sweep flocculation (Jiang, 2001). Sweep flocculation can overcome two of the primary disadvantages of destabilization by charge neutralization: The first being the fact that very accurate control of the coagulant dose is required to give optimum destabilization, and the second is the fact that the coagulation rate depends on the particle concentration, and can therefore be extremely low for dilute solutions. Sweep flocculation avoids both of these problems by using much higher doses, forming larger quantities of amorphous hydroxide precipitates. The target particles are enmeshed in this growing precipitate, and then can be removed by sedimentation, giving the term “sweep floc”. Sweep floc is the mechanism that takes place when the water pH is above the zero point of charge for the dissolved species formed from the coagulants such as alum.

When HMS’s are added to water, hydrolysis reactions produce hydrogen ions that react with alkalinity species in solution. If the hydrolysis reactions are promoted by addition of a base during manufacturing, the resulting product is a pre-hydrolyzed metal salt coagulant solution. Pre-hydrolyzed coagulants are generally classified in terms of basicity, which is the extent of hydrolysis reactions that were induced during the manufacturing of the coagulant. The following equation shows how the basicity value is calculated:

$$\boxed{Basicity(\%) = \left(\frac{100}{3}\right) * \left(\frac{[OH]}{[M]}\right)} \qquad \textbf{(3)}$$

"Where, [OH] / [M] is a weighted average of the molar ratio of the bound hydroxide to metal ion for all the metal hydrolysis products in the undiluted coagulant solution." (AWWA 1999). Basicity values range between 10-75 %. Values above 75 % make it very difficult to keep the metal hydroxide precipitate from forming in the product solution during storage and shipping. The pre-hydrolyzed coagulants used in this project are formed by the controlled neutralization of aluminum chloride solution, and are generally known as poly-aluminum chloride (PACl). SP 70 and SP 2300 are coagulants produced by Eaglebrook, Inc. (Matteson, IL), with basicity levels of 70 % and 65 % respectively. As compared to the well known alum and ferric chloride, there is much less literature concerning the usage of these coagulants for pre-treatment for membrane filtration. One important point to note is the fact that PACl products already contain some of the polynuclear species of aluminum, which are materials that are very effective at the modification of colloidal charges in water treatment applications. It has also been shown that PACl products give more rapid flocculation and stronger flocs than alum for equivalent dosages. These improved results were found under conditions of elevated TOC (above 6 mg/L) concentrations and pH values between 5.5 and 6.5. (Jiang, 2001).

Gregory and Dupont (2001) found pre-hydrolyzed coagulants to be advantageous over HMS coagulants. Specifically, the authors found benefits of PACl over alum for uses in drinking water treatment applications. These include improved performance at low temperatures, lower aluminum residuals in treated water and significantly reduced sludge volumes. It was also shown that flocs formed with some commercial PACl products are larger, stronger and are more readily separated than those with alum. However, there are several common features, notably the fact that floc volume increases in proportion to coagulant dosage in all cases.

2.6 Coagulation Performance

Although coagulation history goes back three thousand years, the modern use of coagulants for water treatment started approximately 100 years ago, when aluminum sulphate and ferric chloride were used as coagulants in full scale water treatment. Since the 1980's, the optimization of coagulation performance for the removal of NOM has been systematically studied, using various real surface and synthetic waters (Jiang, 2001). In the 1990's, NOM and other precursors of the disinfection by-products were still a primary cause for concern. Prior to that, the focus of coagulation was for particle removal, which has been addressed in the previous section.

2.6.1 NOM removal by coagulation

The removal of organic contaminants by the coagulation process has been studied for decades. Most of the work shows that coagulation substantially reduces the concentration of organic particles; a primary type being components of NOM (Randtke, 1988). It is difficult to predict the percentage removal of NOM from surface waters with coagulation, as it depends on a variety of conditions such as organic matter characteristics and operating conditions. Removal of particulate NOM is achieved primarily through colloidal destabilization, followed by sedimentation and filtration (Randtke, 1988). NOM is traditionally removed by coagulation with the trivalent Al and/or Fe metal ions. The coagulation mechanisms that are thought to dominate with regards to NOM removal are charge neutralization for colloidal material and charge complexation for soluble compounds (Sharp et al., 2006).

In general, the process is maximized under similar conditions that also provide maximum turbidity removal, although maximum turbidity removal can also be achieved over a broader range of conditions. This occurs under acidic conditions with a pH in the range of 4.5-5.5 for iron based coagulants and 5.5-6.5 for aluminum based coagulants (Sharp et al., 2006). Dissolved NOM removals by coagulation ranged between 10 and 90 %, with an average removal of about 30 %. Greater removals were seen when more highly colored waters containing organic matter of higher molecular weight were being treated with a metal coagulant.

In summary, it was concluded that there was not a substantial difference between aluminum and iron based salts.

The coagulant dose plays a very important role in the removal of NOM, generally following one of two patterns. In the one case, the removal increases very quickly within a given range of coagulant dose, and then the concentration stabilizes after that. The second pattern showed that the concentration decreases very gradually, eventually reaching an optimum removal at a much higher concentration than that for the first behavior type (Randtke, 1988).

Several other experimentally based research projects have been undertaken, yielding several conclusions that helped to further the understanding of what effect coagulation has on the removal of NOM in any given source water. The use of specific ultraviolet absorbance (SUVA) as an indicator of the nature of the NOM and the effectiveness of the coagulation process has been explored very thoroughly (Edzwald et al., 1999). SUVA is defined as the normalized UV absorbance of a water sample with respect to the DOC concentration. It is expressed in units of m^{-1} of absorbance per mg/L of DOC (Weishaar et al., 2003).

The humics based portion of the NOM was characterized based on the corresponding SUVA values. Waters with high concentrations of aquatic humics generally have high SUVA values, rising as high as 6-7 L/mg.m). Removal of 50 % or greater is expected for such waters using aluminum based coagulants such as alum or PACl. As the SUVA value of a given water source decreases, so should the removal capacity of the coagulant. Waters that display a SUVA value less than 3.0 generally correspond to removals of less than 30 % (Weishaar et al., 2003).

2.7 Background on the use of Pre-coagulation of NOM to Low Pressure Membrane Systems

When the drinking water industry began to utilize membrane filtration, the water sources being treated with membranes were generally high quality, low turbidity lakes that required minimal treatment (Howe and Clark, 2006). Membranes were able to stand alone, and provide high quality effluent, without the need to integrate other treatment processes. With the high level of success, membrane treatment processes are being implemented for lower quality water sources that required more extensive treatment, and as a result coagulation pre-treatment for membrane filtration is now becoming more common.

The results obtained from research evaluating coagulation as a pre-treatment to low pressure membrane filtration has been inconsistent in quantifying its effects on fouling and flux decline. Several studies have shown improved membrane performance, while others have shown decreased membrane performance. Several studies have shown that the use of coagulation has the potential to either stabilize or improve permeate flux across the membrane surface, while others have shown that the coagulant addition contributes further to the undesirable fouling phenomenon.

Howe and Clark (2006) conducted a study to further understand the effect of pre-coagulation. Their primary objective was to evaluate the effect of coagulant type, its dose, and application conditions on membrane performance. Five different natural surface waters were used, coupled with three different membrane materials. After all of the results were combined, it was concluded that coagulant dose was the most significant factor in determining the severity of fouling, and in turn whether the membrane performance was better or worse. At low doses, the membrane fouling was worse when compared with no coagulant. These doses were generally coupled with minimal floc formation.

Enhanced coagulation has been implemented in pre-treatment research by several authors. As previously mentioned, it is the removal of NOM under conditions of high coagulant dosages, combined with a low pH in the range of 4-6 (AWWA, 2005). It is important to note that elevated coagulant doses will contribute to a reduced pH level. Alum consumes 0.5 mg/L of alkalinity as $CaCO_3$ for each mg/L of alum; each mg/L of ferric chloride consumes 0.93 mg/L of alkalinity as $CaCO_3$. If the dose of alum and/or ferric chloride is increased beyond the available alkalinity it could result in a small concentration of coagulant passing through the treatment process. This occurs because the alkalinity helps to limit the reduction in pH and once it is consumed the lower pH may lead to an increased concentration of dissolved metal than can move downstream to the next treatment stage. When a dose that induces enhanced coagulation was used, the membrane performance was also improved for all coagulants. The third major conclusion that came out of this research was the fact that there exists a linear relationship between the quantity of DOC removed and the increased membrane performance. This conclusion was independent of coagulant type, as whichever one was most effective at removing DOC in a given water source was also most efficient at improving membrane fouling.

Maartens et al. (1999) studied the reduction in fouling of polysulphone UF membranes used for the purification of natural brown water, collected from Suurbraak, in the Southern Cape of South Africa. The raw water was pre-treated by coagulation and by changing the pH of the feed solution. The research showed that the pH of the feed water has a significant influence on the adsorption of NOM onto the membrane surface. The lowest adsorption occurred at a feed water pH of 7. At this pH level, NOM molecules contained equal amounts of COO^- and COOH groups (quantified using a non-aqueous titration method) resulting in a very stable conformation of NOM which lowered the interactive forces between the membrane surface and the foulant molecules. The UF membrane yielded the best performance at this pH value in terms of permeate flux, colour rejection and foulant adsorption. Direct filtration eliminates the use of a flocculation tank, coupled with a reduced coagulant dose. The raw water develops pinpoint flocs while traveling towards the membrane surface, much smaller than the conventional floc formation that occurs in a flocculation tank. Direct filtration treatment of the raw water with the metal ion coagulants decreased overall system performance, by increasing the rate at which the membrane fouled, and increasing the frequency of backwash and chemical cleaning. Therefore it was concluded that no obvious advantages were obtained by this pre-treatment method.

Kabsch-Korbutowicz (2006) studied the pre-coagulation of natural water flowing from the Great Batorow Peatbag River in Poland, followed by membrane filtration using polyethersulphone and regenerated cellulose UF membranes. Pre-coagulation of the feed water with aluminum based coagulants improved the elimination of NOM substances by approximately 15-20 %. The highest removals were observed when PACl products were used, with values ranging between 20-25 % improvement over experiments completed without the pre-coagulation. The highest membrane permeability was observed when alum was used. More importantly, the NOM removal and fouling results were proportional, and therefore the system could be optimized to meet the requirements of both system components. The coagulant dose had a significant impact on the permeate flux of the membranes as well. At low Al doses that would normally not be used if coagulation was the sole treatment process, membrane fouling was higher in comparison to water that was not exposed to any pre-treatment step. Laine et al. (1999) performed similar experiments with regenerated cellulose membranes, discovering elevated concentrations of PACl products yielded a more consistent flux across the membrane surface, and in turn reduced the degree of fouling that occurred.

Kimura et al. (2005) studied the use of pre-coagulation with sedimentation as a pre-treatment to pilot scale polysulfone UF plant at an existing drinking water treatment facility in Ebetsu, Japan. The effect of metal based pre-coagulation on irreversible membrane fouling was studied and compared to a previous study performed (Kimura et al., 2004) where a similar type of membrane effluent was used as a drinking water source.

The study performed in 2004 investigated the water permeability consistency using a chemical cleaning process, and analyzed the composition of the membrane fouling components that desorbed from the membrane after the cleaning cycle. The study concluded that polysaccharide-like organic compounds were primarily responsible for the inducement of irreversible fouling. The results observed using this raw water source, supported the fact that pre-coagulation in some cases would not be effective in mitigating irreversible fouling, as coagulation does not target polysaccharides efficiently. The second study incorporated coagulation, showing very positive results. The pre-treatment significantly mitigated the organic membrane fouling, mainly by reducing the concentration of components that had the potential to cause reversible fouling, which was largely composed of DOM. The study did re-emphasize that irreversible fouling cannot be mitigated with the use of coagulation as pre-treatment to UF membranes (Kimura et al., 2005).

Several other authors have suggested that coagulation, whether it is with sedimentation or direct filtration (i.e. without sedimentation), induced membrane fouling. Shrive et al., (1999) performed a pilot scale membrane trial using water taken from the Ohio River with polypropylene micro-filtration membranes. The purpose of these experiments was to assess the degree of fouling of the membrane when exposed to a water source that was purposely under dosed (1-5mg/L) with alum or PACl. The experiments were performed with sedimentation and in-line coagulation to observe the difference it made on the membrane fouling as well. A large decrease in flux was observed for all coagulants during the in-line coagulation as a pre-treatment, while much less of a decline was observed when coagulation was coupled with sedimentation.

Karimi et al. (1999) observed very similar results when pre-treating feed water to a polypropylene ultra-filtration membrane with 3-5 mg/L of ferric chloride. The treated surface water taken from the Californian interior accelerated the rate of fouling, as observed by increasing trans-membrane pressure. In some cases, the use of a coagulation pre-treatment process not only accelerates the rate of fouling, but also substantially increases the cost of the overall system, in some cases making it prohibitive to implement. Schäfer et al., (2001) concluded in a polypropylene membrane study that pre-treating water containing Suwannee River humic and fulvic acid solutions with ferric chloride significantly increased fouling of micro and ultra-filtration pilot scale membranes. The coagulant dose would also increase the operating cost of the system, emphasizing that the correct dose is crucial to both the efficiency of the system and the overall cost.

In some cases, the results achieved through the study of coagulation pre-treatment were not so much inconclusive, but more so the fact that similar results could have been achieved with a simpler process. Carroll et al. (2000) found that pre-treating water prior to micro-filtration using a polypropylene membrane with 35 mg/L of alum reduced the quantity of reversible fouling by a substantial amount. Moreover, it was discovered that similar results could be achieved by filtering the feed water through a 0.2 μm filter, in doing so removing the particulates that were contained in the water. This comparative worked highlighted the fact that the coagulation in this case was successful at removing particulate foulants, but had no noticeable effect on the dissolved material. Comparing these findings to those of Howe and Clark (2006), several contrasts were observed. The latter work concluded that coagulant dose was the most important factor in quantifying fouling, rather than the state of composition of the TOC in the feed water. Maartens et al. (1999) stated that certain types of fouling cannot be mitigated at all with coagulation pre-treatment, and therefore attention should be focused on other aspects of the experimental design, in hopes of reducing membrane fouling. However, it is worth noting that Howe and Clark (2006) emphasized that an enhanced coagulation process (reduced pH) will yield improved permeate flux, and should be used as a base-lime for future coagulation pre-treatment experiments.

2.8 The Future of Low Pressure Membrane Systems

Membrane technology for drinking water applications has the potential to be the most promising development in water treatment, as it could provide permeate quality that exceeds the present regulatory requirements for drinking water consumption (Farahbakhsh et al., 2004). The technology itself will gain more popularity and research-driven membrane trials will yield more efficient full-scale systems that require less energy input, coupled with membrane modules that have extended life expectancies. (Zularisam et al., 2006).

There are still a variety of problems that limit the expansion of membrane technology: the primary one being the fouling phenomenon. In the 21st century, further understanding is required into what fractions of NOM contribute to fouling most, and one can improve process design and operating conditions to minimize this effect. Just as important are issues such as membrane surface area and robustness, the cost of the operation and maintenance associated with the required high trans-membrane pressure, and the cost of chemicals required to clean the membranes. However, these problems should not be considered a downfall to the further advancement of the technology, but rather as reasons to come up with methods of improvement and optimization. Zularisam et al. (2006) stresses that there is need for further research and development of new membrane materials that are more resistant to both chemical cleaning and mechanical wear and tear. The improvement of cleaning strategies and reduced energy costs will help to increase implementation and improve sustainability of membrane systems.

Experts most familiar with membrane filtration processes predict that future low pressure membrane systems will be larger in capacity with smaller footprints, therefore increasing the available surface area, while reducing the overall space requirement. One way in which membrane treatment technologies will be improved in the future, is by integrating them with other processes such as a coagulation pre-treatment. Government guidelines and regulations governing the use of membrane filtration are expected to expand, and become more standardized, so that researchers, manufacturers and plant operators alike can be on the same page with respect to the implementation of techniques for reducing membrane fouling. The applicability of these systems is also expected to expand, as studies have proved in many cases that membrane systems are the preferred option for pathogen and particulate removal.

2.9 Research Needs

This literature review provided a lot of detail pertaining to the fundamentals of coagulation, and membrane filtration. Although the topic of study is growing every year, there was less detail concerning the combination of the two, and more specifically how the modification of different parameters affect water quality and membrane fouling. There was definitely a gap in literature concerning NOM fractionation, and the effect that each of the size distributions had on membrane performance, and downstream operations.

Another aspect of this research which was not thoroughly discussed in this chapter was how the different membrane properties such as zeta potential, contact angle and surface charge contribute to the fouling phenomenon.

CHAPTER 3

EXPERIMENTAL PLAN AND MATERIALS AND METHODS

3.1 Experimental Plan

The purpose of this research was to quantify the effect of coagulation pre-treatment on the performance of a submerged ultra filtration membrane system. Initially, a series of experiments were conducted with synthetic waters, with known concentrations of humic acid in order to gain an understanding of how the coagulants would behave. The synthetic waters were prepared to cover the range of major characteristics in the two raw waters chosen for study. Subsequently, experiments were carried out with the two different raw waters. The goal of the work was to gain a more fundamental understanding of effects the coagulants have on the fouling potential of a membrane, and their ability to remove TOC and turbidity. All measured standard water quality parameters were regularly assessed to ensure continuity across all membrane trials. Fractionation of both raw and treated water samples into a series of molecular weight cut-offs (MWCO) was conducted. This was an innovative approach, in terms of coagulation pre-treatment experiments, and was done to further understand what portions of the NOM contribute to fouling most.

There were two distinct phases: The coagulation of raw and synthetic waters to determine optimal coagulation dosages, and the treatment of two different raw surface waters with a bench-scale ultra-filtration membrane system preceded by coagulation.

3.2 Source Water Details

This project involved the study of two different Ontario surface waters. The first was water taken from the Grand River, which is the source water for the Mannheim Treatment Plant in Kitchener, ON. The second was water taken from Lake Ontario, which is the source water for the Woodward Water Treatment Plant in Hamilton, ON. Water quality data recorded daily at the plant intakes for the year 2004 were acquired from the Ontario MOE Drinking Water Surveillance Program (DWSP, 2005). Although these two source waters exhibit many different characteristics, the project focused primarily on using only four key parameters to characterize the two different waters: turbidity, total organic carbon (dissolved and suspended), pH and alkalinity.

3.2.1 Grand River Watershed

The Kitchener (Mannheim) Water Treatment Plant, operated by the Regional Municipality of Waterloo, treats water from the Grand River. The Grand River flows 300 km through south-western Ontario from the highlands of Dufferin County to Port Maitland on Lake Erie (GRCA, 2005), draining a predominantly agricultural watershed. Raw water is pumped approximately 10 km from the Grand River to the Mannheim WTP. The process consists of disinfection, coagulation, flocculation, sedimentation, ozone, bio-filtration and UV. In 2002, the filtration stage was either a dual media filter, or granular activated carbon (GAC) filters, depending on seasonal water quality variations. The facility was commissioned in 1992, and presently has a design capacity of 80,000 m^3/day.

All of the raw Grand River water used in this research was obtained from the Mannheim plant's Hidden Valley intake. Water was transported from the intake to the laboratory at the University of Waterloo in 25 L Nalgene containers. The raw water was used within 72 h of collection.

Water quality parameters values in the Grand River are highly variable throughout the year. This variability is likely due to a combination of agricultural, urban and industrial inputs and seasonal impacts such as elevated precipitation and/or drought (GRCA, 2006).

The fluctuations in acidity in the river over a given year are the result of vegetation processes in the river. Limestone bedrock found throughout the Grand River watershed buffers the acidity of the water and tends to cause river water to be more basic, rather than acidic. The average pH level for the month of June, 2005, was approximately 8.4, while in March, 2005 the level dropped to 7.7 (less plant activity). This data was collected by the Drinking Water Surveillance Program (DWSP), a branch of the MOE. The DWSP is a voluntary program operated by the MOE in cooperation with municipalities to gather scientific data on drinking water quality in Ontario. (DWSP, 2005).

The alkalinity of the Grand River also has highly variable values throughout any given year. The alkalinity has an average of approximately 195 mg/L (as $CaCO_3$). The seasonal variations see the alkalinity drop to under 150 mg/L, and well over 240 mg/L, with highest values measured during the months of January and February, and the lowest values in July and August (DWSP, 2005).

Turbidity was a closely monitored parameter in this research, as it plays a key role in the coagulation process of the raw water. The turbidity of the Grand River is influenced generally by human activities such as farming and the construction of dams. It also is a strong of function of weather impacts, such as spring run off and heavy rainfall. In 2005, the average turbidity was found to be approximately 4.4 NTU, with peak values of well over 100 NTU (DWSP, 2005).

The temperature in the Grand River fluctuates over a wide range. In January, the average river temperature entering the treatment plant was recorded as being 0.63 ^{o}C, while in July of the same year the temperature rose to an average of 21.83 ^{o}C (DWSP, 2005).

The TOC concentration found in the Grand River water varied somewhat over the year, ranging from 5.0 – 7.4 mg/L. TOC and DOC analysis (TOC analysis method – Section 3.6.1) was performed in January and February 2006 using water obtained from the Mannheim water treatment plant low lift pumping station showed comparable results, with the TOC ranging from 5.0-6.5, with approximately 90 % of the total concentration in the form of DOC.

3.2.2 Lake Ontario (Hamilton Harbor)

The City of Hamilton treats raw water from Lake Ontario and in its Woodward plant supplies Hamilton, Stoney Creek, Dundas, Ancaster, Waterdown, parts of Flamborough and Glanbrook with treated water. The water treatment process consists of pre-chlorination, screening, clarification by means of coagulation, flocculation by mechanical mixing, followed by sedimentation. The filtration process was upgraded in the year 1998 by the addition of granulated activated carbon (GAC) in the filters to remove taste and odour. This condition is usually present in the water in the late summer, when algae are abundant. Chlorine and ammonia are added to the filtered water to bring the combined chlorine residual to approximately 1.3 mg/L. Hydro-fluosilicic acid (fluoride) is added to the drinking water to promote dental health. The Hamilton Woodward water treatment plant has a rated capacity of 909,000 m^3/day (MOE,2005).

The pH at the Woodward WTP intake was measured and the recorded at the plant intake, and found to be quite similar to that of the Grand River. In 2005, the pH at the intake ranged from 7.8 – 8.2 (DWSP, 2005).

The total alkalinity as $CaCO_3$ was also measured at the plant intake and found to vary between 80 and 100 mg/L (DWSP, 2005).

Turbidity values at this WTP intake stay reasonably constant throughout the year. In 2005, the minimum value was around 0.3 NTU, with a maximum value recorded at 3.0 NTU. Over the duration of the year, the turbidity had an average value of approximately 0.6 NTU (DWSP, 2005).

The water temperature range is similar to that of the Grand River. In January, the average Hamilton intake water temperature was <1.0 ^{o}C, while in July of the same year the temperature rose to an average of 21.5 ^{o}C. The average annual temperature value was 5.0 ^{o}C (DWSP, 2005).

The TOC concentration in 2005 was low relative to the Grand River, ranging from 1.4 to 3.0 mg/L (DWSP, 2005).

The raw pre-chlorinated Lake Ontario water used in this research was obtained from the intake at the Hamilton Woodward WTP. Water was transported from the WTP to the laboratory at the University of Waterloo with the assistance of Environment Canada personnel in two 400L containers. At Waterloo, it was transferred into 25L Nalgene containers, and kept at room temperature for the duration of the membrane trial. The raw water was used within 72 h of collection. The residual chlorine concentration was measured to be approximately 1 mg/L. In order to ensure that no residual chlorine remained in the raw water before beginning experiments, the water was spiked with a 0.2 M sodium thiosulfate (NaS_2O_3) solution to quench the residual chlorine. It was assumed that thiosulfate (NaS_2O_3) and free chlorine (Cl_2) reacted in a 2:1 ($S_2O_3^{2-}$:Cl_2) ratio. Taking this into account, and adding a safety factor of 2 to the mass balance calculations, 7.05 mL of 0.2 M thiosulfate solution was added to every 25 L of raw water to ensure that no residual chlorine remained. The residual chlorine concentrations of all samples were verified to be below 0.02 mg/L before continuing any further experiments.

Table 3-1 shows a summary of the parameters of interest. This data determined the range of values that were studied to try and best simulate each water type for the coagulation trials with the synthetic water (results described in Chapter 4).

Table 3-1: Water quality parameters for the source waters being simulated (DWSP, 2005)

Location	**Parameter**					
Location	**TOC (mg/L)**	**Total alkalinity (mg $CaCO_3$/L)**	**Total hardness (mg $CaCO_3$/L)**	**Temp (^oC)**	**pH**	**Turbidity (NTU)**
Grand River	4.0 – 7.4	150 – 260	170-270	1.0 – 23	7.6 – 8.5	1.0 – 25
Lake Ontario	1.4 – 3.0	80 – 130	110-125	1.0 - 21	7.0 – 8.2	0.5 – 8.5

3.2.3 Synthetic water cocktail

Synthetic water was produced in bench scale quantities using ultra pure water (Milli Q, Millipore Inc., Billerica, MA). Kaolin (VWR International, Mississauga, ON) was used to add turbidity, where each mg of kaolin added to a litre of water yielded approximately 1 NTU. Turbidity levels ranging from 5-25 NTU were used during the synthetic water jar test trials. Alkalinity was added in the form of sodium bicarbonate ($NaHCO_3$) powder (VWR International, Mississauga, ON). Sodium bicarbonate provided a good representation of natural alkalinity, which is typically expressed in terms of mg/L of calcium carbonate ($CaCO_3$) found in solution. 1.68 mg of $NaHCO_3$ provides an alkalinity equivalent to 1 mg of $CaCO_3$. Alkalinity concentrations ranging from 30 – 180 mg/L were used for the trials. Natural organic matter was simulated with Aldrich humic acid (Sigma-Aldrich Inc., St. Louis, MO). For every 1 mg/L of TOC, 2.70 mg/L of the Aldrich humic acid is required. This ratio was determined experimentally by creating 5 standards each with an accurately measured quantity of the Aldrich humic acid solid, ranging from 1 – 10 mg/L, and measuring TOC concentration. No amount of calcium was added to simulate the water hardness.

The synthetic water cocktail was prepared by adding all the necessary compounds into a 1L beaker with approximately 900 mL of ultra-pure water, and mixing for at least 1h, ensuring that the humic acid dissolved. The contents of the 1L beaker were then made up to 20 L with ultra pure water in a plastic container which was manually shaken for 5-10 min before beginning experiments. Figure 3-1 shows a summary of the synthetic water cocktail preparation method:

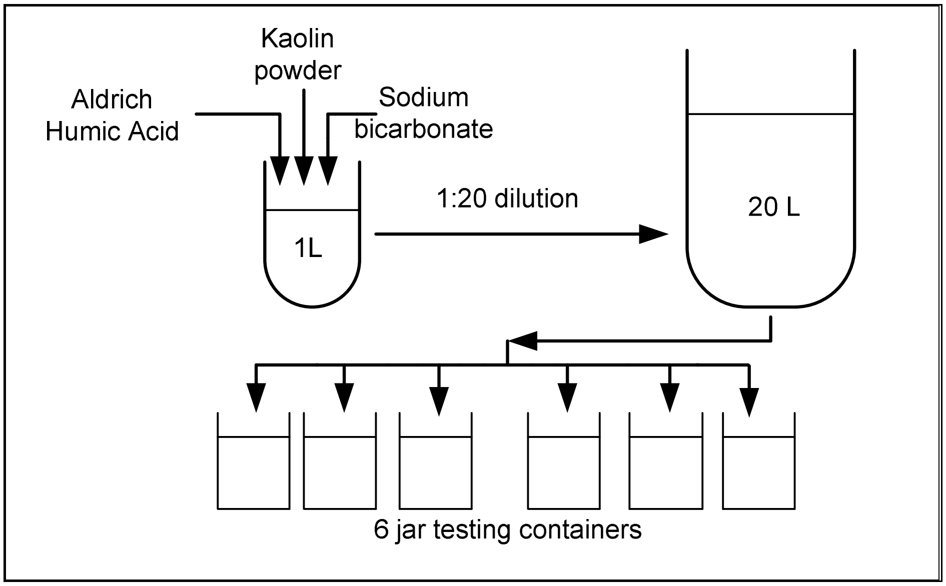


Figure 3-1: Synthetic water cocktail preparation procedure

3.3 Coagulation Method

As described in detail in the literature review section, this thesis involved the use of five coagulants: Ferric chloride, Aluminum sulphate (Alum), and three polyaluminum chloride (PACl) coagulants: SternPac®, SternPac® 70 and SternPac® 2300. Ferric chloride and alum are two widely used coagulants both in the drinking and waste water industries. The three PACl products are not as well known, although the application of PACl has become more popular in the drinking water treatment industry (AWWA, 2005)

Table 3-2 provides a summary of the coagulants used in this study. All coagulants were provided by the Brantford, ON, office of Eaglebrook, Inc. (Matteson, IL).

Table 3-2: Property of coagulants

Coagulant	Concentration as supplied (%)	% Active metal as supplied	Basicity %
Aluminium sulphate	0.48	4.3	N/A
PACl (SP 70)	0.4	5.5	70
PACl (SP 2300)	0.4	5.4	63
PACl (SP)	0.4	5.4	50
Ferric chloride	0.35	11	N/A

PACL = Polyaluminum chloride

The initial step in any coagulation investigation is to conduct jar testing to determine the optimum coagulant dose for a specified water type. As mentioned previously, a synthetic water cocktail was used initially to gain a more fundamental understanding of the behaviour of the coagulants. Numerous combinations of alkalinity, turbidity and TOC were studied to simulate the two Ontario source waters.

Synthetic water jar test trials were conducted with all five coagulants. In order to cover the range of real water conditions shown in Table 3-1 above, a 2-level experimental design was performed, with the turbidity and alkalinity being the varied parameters. The purpose of the 2-level factorial design was to gain an understanding of the impact of the two water quality parameters on the performance of the coagulation process in removing the optimal amount of TOC. Three different TOC values were trialed, the lowest one representing the Great Lakes concentrations in Ontario, the highest concentration representing the Grand River and the mid level concentration representing an intermediate value. Table 3-3 shows a summary of the experimental design

Table 3-3: Jar test trials experimental design

Condition	Turbidity (NTU)	Total alkalinity ($mg\ CaCO_3/L$)	TOC (mg/L)
# 1	20	175	2, 5 and 7
# 2	5	175	2, 5 and 7
# 3	5	30	2, 5 and 7
# 4	20	30	2, 5 and 7

The 2-level factorial design was implemented for all four coagulants, resulting in a total of 48 jar test trials conducted with synthetic water. Figure 3-2 shows a jar testing unit (VWR International, Mississauga, ON); similar to the one used for all of the jar test trials. Each jar was dosed with a different quantity of coagulant, and TOC, pH, alkalinity, turbidity and temperature values were measured and recorded before and after the experiments.

Figure 3-2: Phipps and Bird Jar Testing Unit:

The rapid mixing phase of all of the jar test trials was performed for 2 min at 100 rpm, representing a velocity gradient of 70 s^{-1}. The slow mixing phase of all the trials was performed for 20 min @ 20 rpm, representing a velocity gradient of 10 s^{-1} (Randtke,1988). The settling period lasted 40 min. These time intervals were chosen as a standard jar testing practice, used for both water and waste water related experiments (AWWA, 2005). Once the settling period was over, samples were collected by opening a pinch valve located 2“ (0.051m) above the bottom of the container. Samples were analyzed for TOC and DOC. Residual turbidity and pH values were recorded. The coagulant dose that yielded the lowest TOC concentration in the settled water was deemed the optimal dose, and therefore suitable for subsequent membrane treatment.

3.4 Membrane and Coagulation Bench-Scale Apparatus

The first step of this phase of the research project was to determine the configuration of the bench-scale membrane treatment system. Figure 3-3 shows a process flow diagram (PFD) of the entire membrane pre-treatment system.

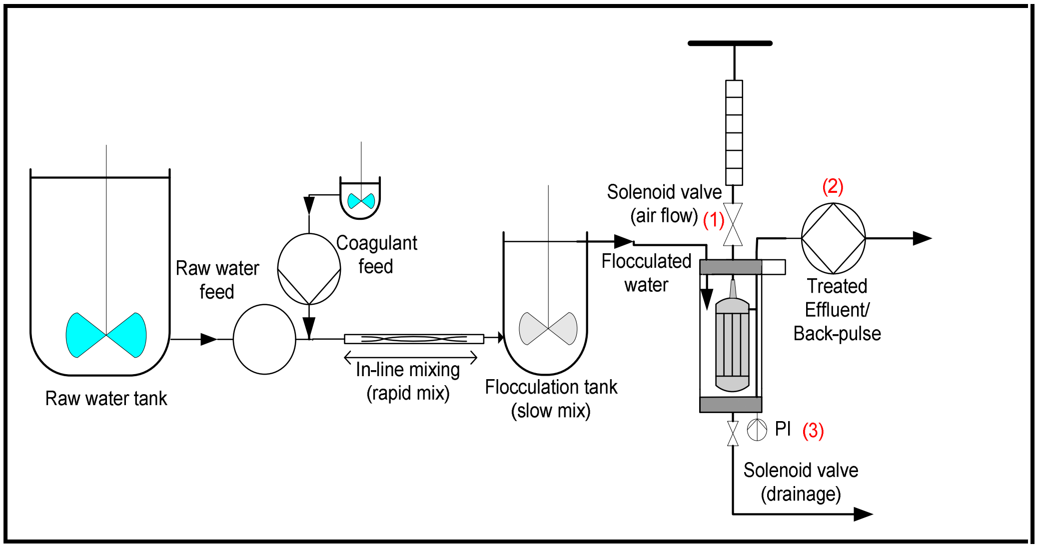


Figure 3-3: Bench scale membrane system process flow diagram

The raw water tank had a capacity of approximately 75 L. The water was set in motion via a positive displacement peristaltic pump (Cole Parmer Inc., Vernon Hills, IL), where it was joined by an injected coagulant stream. The coagulant was injected via a low flow miniature gear pump (Cole Parmer Inc., Vernon Hills, IL).

The coagulant tank had 1 L capacity, and contained a diluted coagulant in a 1:10 ratio. The dilution was necessary to accommodate the fact that the miniature gear pump that fed the coagulant could not pump at flow rates low enough to meet the requirements of an un-diluted coagulant.

The two streams combined and were fed into a 6” (0.152m) long static mixer (Koflo Corp., Cary, IL). The concept behind a static mixer is simple: the two fluids (water and coagulant) flowing through a pipe are channelled through a geometric arrangement of approximately 40 elements. The element geometry within the housing caused the flow to divide, mix, divide again and mix again, until the maximum attainable mixing was complete. The flow then continued on into a glass flocculation tank which had a capacity of 1.5 L.

All trials were conducted with a flocculation tank influent flow of 90 mL/min, therefore yielding a hydraulic retention time (HRT) of 16.1 min. The mixed fluid was fed into the bottom of the flocculation tank, and exited via an overflow port at the top of the tank. The flocculation tank was cleaned every 24 h during trials, as a substantial amount of flocs would accumulate at the bottom of the tank. The coagulated water was fed by gravity into the acrylic membrane tank designed specifically for this application. The membrane tank was a cylinder, with an inner diameter of 3” (0.076m), and a length of 14” (0.356m). At each end, the vessel was threaded, so that industrial strength PVC caps were screwed in creating a water proof seal. The membrane unit fit snugly in the acrylic tank, with no room to move laterally. As seen in the PFD, there were three points of automation that allowed the system to run in a continuous batch mode: the air valve, drainage valve and the permeate pump. The membrane system was designed to run continuously without supervision, automated by a simple programmable logic controller (Rockwell Automation Inc., Milwaukee, WI). All trials were conducted with the following sequence of events:

1. Permeation at 45 mL/min for 35 min
2. Permeation stopped, backwash at 45 mL/min with air pulse at 1 ft^3/min for 20s
3. Tank drainage with air pulse at 1 ft^3/min for 20 sec
4. Membrane tank re-fill (10 min), air and permeate off

5. Repeat steps 1 – 4

The membrane tank had a volume of approximately 1.5 L, with an overflow port installed just above the point where the membrane module is positioned, so as to maintain a constant head. With an incoming flow of 90 mL/min, and a permeate flow of 45 mL/min; 45 mL of water was discarded to waste every minute. This large difference between the feed and permeate flow was attributed to fact that the fill time of the membrane tank after drainage was aimed at being minimized. If the feed flow was similar to the permeate, it would take approximately 20 min to fill the membrane tank, and subsequently the ratio of permeate to fill time would only be 1.5:1. With the increased feed flow, the fill time was reduced to 10 min, increasing the ratio to 3:1. This ratio was deemed reasonable and held constant for the duration of all membrane trials. Figure 4-4 shows a photograph of the complete membrane system.

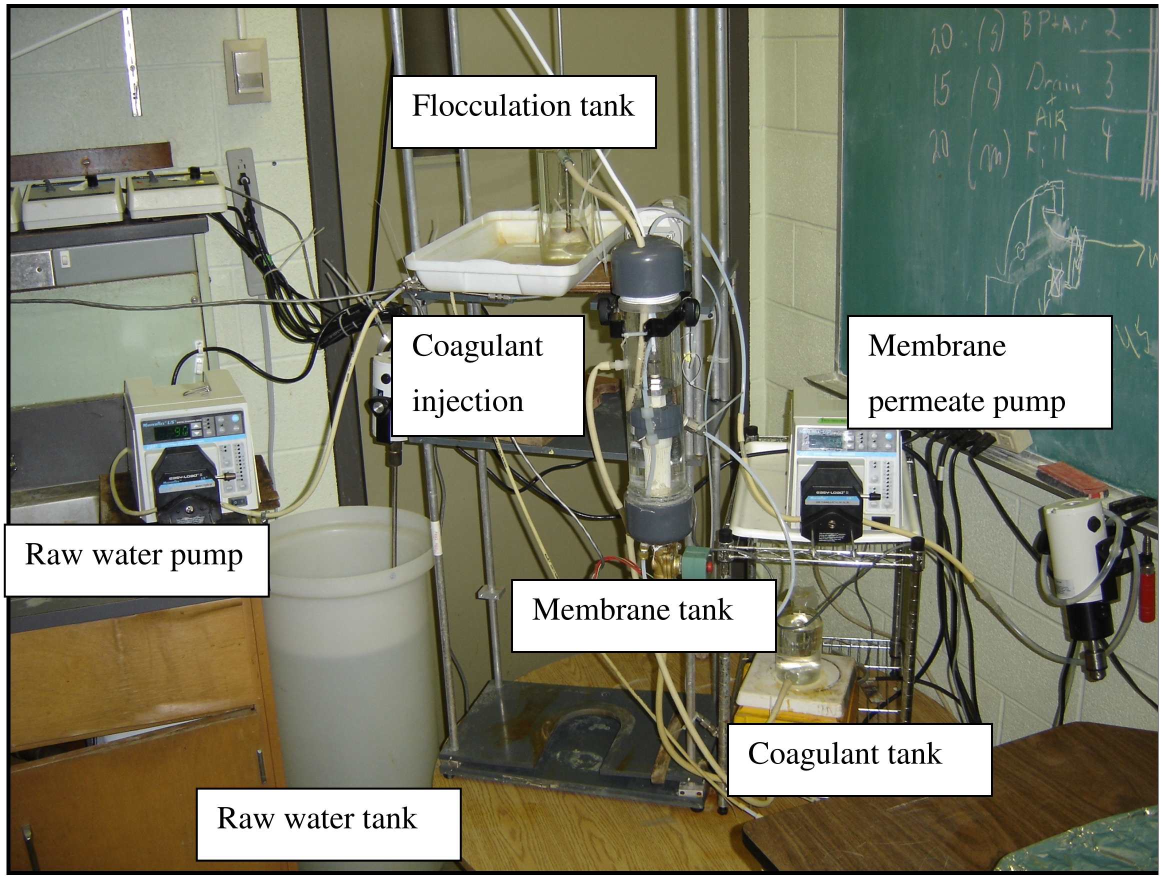


Figure 4-4: Bench scale membrane system

The raw water and coagulant tanks were continuously stirred, ensuring a uniform mixture for both throughout the duration of all membrane trials. The raw water tank was stirred by means of a mechanical mixer, with a 6" (0.152 m) blade, while the coagulant tank was stirred using a 1" (0.025 m) magnetic stir bar. Figure 3-5 shows a close up of the membrane tank with all of its components.

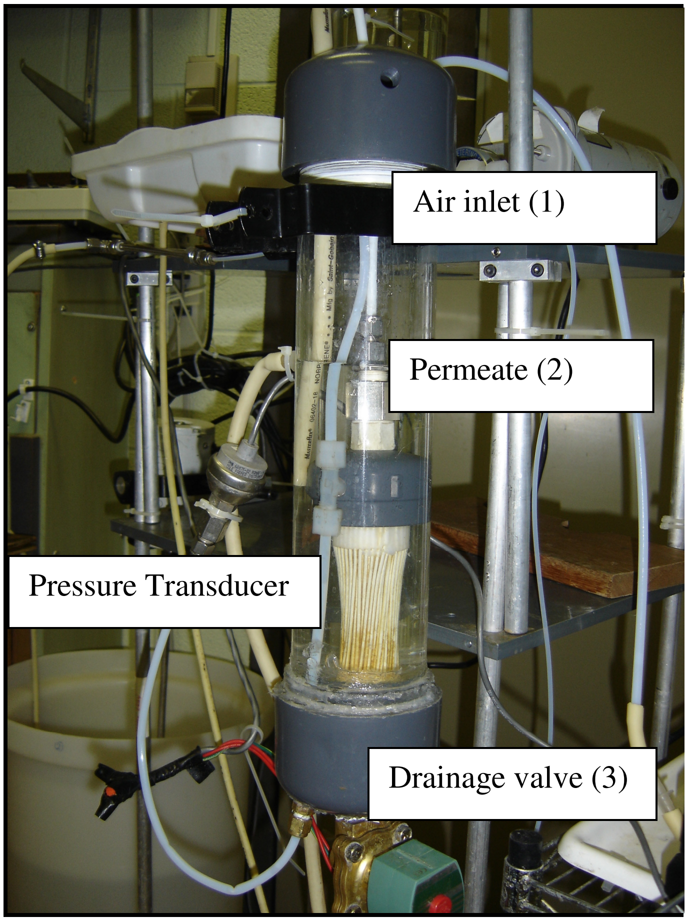


Figure 3-5: Bench scale membrane vessel

As mentioned early, there were three points of automation built into this set up. The air intake (1) was connected to the top of the membrane module, and was activated with the PLC. When running, air bubbles were pushed through the core of the module, and exited between the hollow fibres. The air sparging was conducted in order to remove any loose deposits from the membrane surface, which subsequently were removed from the membrane tank during the drainage cycle. The air sparging was controlled by a standard 120V (normally closed) ¼" orifice solenoid valve (ASCO Valve Inc., Florham Park, NJ). The PLC would send a signal to the valve, and it would open for 20 s, allowing the air to travel through the membrane module. The second point of automation was the membrane permeation (2). When the permeate pump was running, water was sucked in through the pores in each of the fibres, then accumulated at the top of the module and exited via the T-shaped fitting and out of the tank. The third point of automation was the drainage of the membrane tank (3). This was accomplished with the use of a standard 120V (normally closed) ½" orifice solenoid valve (ASCO Valve Inc., Florham Park, NJ). This valve opened when signalled by the PLC, and would return to its normally closed position after 20 s. During the 20 s drainage cycle, the direction of the permeate pump was reversed, and treated water was pumped in the opposite direction, through the hollow fibres and back into the membrane tank. The whole purpose of this sequence of events was to minimize the amount of particulate (both suspended and dissolved) that remained on the surface and in the pores of the hollow fibre membrane strands.

3.4.1 Membrane Modules

A total of 6 membrane units were used for this project. One membrane was designated for each of the four coagulants, and one for each of the two raw water sources. This approach was taken to ensure that there were no cross contaminating effects between the coagulants, and that when raw water was being treated, no residual coagulant was present to effect the results.

Each new membrane as received from the manufacturer was vacuum sealed in a plastic wrapping that contained a thin coating of glycerin on the interior, so as to ensure the membrane fibres remained moist during transportation and storage. Prior to use, membranes were cleaning by running ultra pure water through them for at least 1 hour, to ensure all residual glycerin was removed. All 6 membranes were operated and cleaned in the same manner. After being used, the membranes were cleaned by submerging them in a 200 mg/L sodium hypochlorite (NaOCl) solution for 5-7 h, then rinsed with ultra-pure water. Membranes were cleaned after each trial, and stored in ultra-pure water in the refrigerator for future use. The TMP of each membrane was checked before beginning a 3-day trial. A clean membrane had a TMP of approximately 2.5-3 psi. If the TMP pressure was too high, the cleaning process was repeated until the pressure reached an acceptable level Table 3-4 outlines the details of the membrane properties used for all of the trials.

Table 3-4: Membrane Properties

Properties	Range
Flux	30 - 70 L/m^{2}h
Flowrate	1.4 - 3.3 L/h
Material	PVDF
Membrane surface area	0.047 m^2
Pressure	0 - 70 kPa
Nomimal Pore Size	~ 0.035 μm
MWCO	400,000 Da
Temperature Tolerance	0 - 40 ^{o}C
Chlorine Tolerance	1000 ppm
pH Tolerance	2-11

Throughout this project, the membrane flux held constant at 55 L/m^{2}h, resulting in an average flow rate of 2.7 L/h. The pressure range over which the membrane unit functioned was a function of the type water being treated. For this application, the manufacturer recommended a pressure limit of approximately 18 psi. The nominal pore size, MWCO value and tolerances of the membrane units were also provided by the manufacturer.

3.5 Membrane Trials Experimental Design

The experimental program ran for approximately 6 months. All membrane trials lasted for three days. The membrane trials were separated into six distinct phases, which involved treatment of:

1. Grand River water with optimal coagulant dose for TOC removal
2. Grand River water with equal molar dosing
3. Lake Ontario water with optimal coagulant dose for TOC removal
4. Grand River water with modified mixing rates in flocculation tank
5. Grand River water with modified raw water pH levels
6. Grand River water with half of the optimal coagulant dose

The first round of experiments involved dosing raw water taken from the Grand River with the coagulant dose that resulted in maximum TOC removal in the jar test trials conducted with Grand River water during the first phase of the project. Raw water was tested with no coagulant at the outset, so as to establish a reference point to which to compare all trans-membrane pressure (TMP) trends. Raw water was then spiked with all four coagulants separately. Each trial was executed the same way, with the exception of the coagulant type. The coagulant doses were 1.8×10^{-4} mol Al/L (30 mg alum/L), 2.8×10^{-4} mol Fe/L (45 mg ferric chloride/L), 3.7×10^{-4} mol Al/L (40 mg SP/L), and 4.9×10^{-4} mol Al/L (50 mg SP 70/L) for alum, ferric chloride, PACl (SP) and PACl (SP 70), respectively.

The second round of experiments involved an 'equal molar dosing' approach. This entailed choosing a dose of metal that was used four coagulants, therefore providing results that could be compared on that basis. The equal molar dose of 7.5×10^{-5} mol metal/L was chosen as a reasonable dose. It allowed for all four coagulant doses to be within 15 mg/L of the optimal dose. The corresponding doses were 47.1 mg/L, 38.0 mg/L, 37.5 mg/L, and 36.8 mg/ L for alum, ferric chloride, PACl (SP) and PACl (SP 70), respectively.

The third round of experiments involved dosing raw Lake Ontario water taken from the Hamilton WTP with the coagulant dose that resulted in maximum TOC removal obtained with the jar test trials conducted before the membrane trials. This was done to ensure the required doses were similar to those obtained when the jar test trials were performed during the first phase of the project. The coagulant doses were 4.4×10^{-5} mol Al/L (15 mg alum/L), 1.2×10^{-4} mol Fe/L (20 mg ferric chloride/L), 8.7×10^{-5} mol Al/L (15 mg SP/L), and 1.2×10^{-4} mol Al/L (20 mg SP 70/L) for alum, ferric chloride, PACl (SP) and PACl (SP 70), respectively.

The fourth round of experiments involved the modification of the mixing rate of the mechanical mixer in the flocculation tank. All of the previous experiments were run at 30 rpm. For this set of experiments the mixing rate was raised to 45 rpm. The reasoning behind this parameter modification was two-fold. The first was to quantify the change in TMP as a result of an increased mixing rate. Under these conditions, a larger portion of the flocs were transferred from the flocculation tank to the membrane tank, and subsequently, more flocs had the potential to end up on the membrane surface. Thus this change simulated to some extent direct filtration, whereas the previous trials essentially simulated the inclusion of a sediment step. The second reason for this parameter modification was to determine whether the increased mixing rate would induce a greater TOC removal during the coagulation step. These modified mixing rates were applied to raw Grand River water, applying the optimal coagulant doses that were used in the first round of the experiments.

The fifth round of the experiments involved the modification of the raw water pH to the optimal level for coagulation for TOC removal using the respective metal based coagulants. Optimization of the coagulation process for TOC removal occurs under acidic conditions: at a pH 4.5-5.5 for iron based coagulants and pH 5-6 for aluminum based coagulants (Sharp et al., 2006). Increased TOC removals should reduce the degree of membrane fouling even further than in the first stage of the experiments. The raw water was spiked with reagent grade hydrochloric acid (VWR International, Mississauga, ON) to reduce the pH. These raw water pH modification experiments were performed on Grand River water, applying the optimal coagulant doses that were used in the first round of the real water experiments. During the first round of experiments, the pH of coagulation always remained above 7.

The sixth round of experiments involved two sets of trials, using half the optimal dose of coagulant obtained during the jar test trials conducted during the first phase of the research (i.e. half the dose used in Round 1). Alum and SP were chosen, with doses of 15 mg/L and 20 mg/L for alum and SP respectively. These doses were tested to observe the difference in TOC removal and membrane fouling when the coagulants were severely under-dosed, and were performed because of indications that such lower doses were used at least sometimes in practice.

Table 3-5 shows a complete summary of the experiments performed.

Table 3-5: Membrane trials experimental design summary

Water type	Coagulant type	Dose (mg coagulant/L)	Dose (mol metal/L)	Comments
Tap water (Reference pt)	None	None	N/A	Trial period
Raw Grand River Water	None	None	None	These doses represented the dose for optimum TOC removal for coagulation for this water type
Raw Grand River Water	Alum	30.0	1.8x10^{-4}	
Raw Grand River Water	Ferric chloride	45.0	2.8x10^{-4}	
Raw Grand River Water	PACl (SP)	40.0	3.7x10^{-4}	
Raw Grand River Water	PACl (SP 70)	50.0	4.9x10^{-4}	
Raw Grand River Water	Ferric chloride	38.0	7.5 x 10^{-5}	Equal metal concentration dosing ~ 7.5.0 x 10^{-5}
Raw Grand River Water	Alum	47.1	7.5 x 10^{-5}	
Raw Grand River Water	PACl (SP)	37.5	7.5 x 10^{-5}	
Raw Grand River Water	PACl (SP 70)	36.8	7.5 x 10^{-5}	
Raw Lake Ontario Water	None	None	None	These doses represented the dose for optimum TOC removal for coagulation for this water type
Raw Lake Ontario Water	Alum	15.0	4.4x 10^{-5}	
Raw Lake Ontario Water	Ferric chloride	20.0	1.2x 10^{-4}	
Raw Lake Ontario Water	PACl (SP)	15.0	8.7x 10^{-5}	
Raw Lake Ontario Water	PACl (SP 70)	20.0	1.2x 10^{-4}	
Raw Grand River Water	Alum	30.0	1.8x10^{-4}	Modified raw water pH with optimum coagulant dose
Raw Grand River Water	Ferric chloride	45.0	2.8x10^{-4}	
Raw Grand River Water	PACl (SP)	40.0	3.7x10^{-4}	
Raw Grand River Water	PACl (SP 70)	50.0	4.9x10^{-4}	
Raw Grand River Water	Alum	30.0	1.8x10^{-4}	Modified HRT in flocculation tank with optimum coagulant dose
Raw Grand River Water	Ferric chloride	45.0	2.8x10^{-4}	
Raw Grand River Water	PACl (SP)	40.0	3.7x10^{-4}	
Raw Grand River Water	PACl (SP 70)	50.0	4.9x10^{-4}	
Raw Grand River Water	Alum	15.0	9.0x 10^{-5}	Half optimal dose
Raw Grand River Water	PACL (SP)	20.0	2.8x10^{-4}	

3.6 Chemical Parameters Analysis Method

3.6.1 Total Organic Carbon (TOC)

Total organic carbon (TOC) was measured by wet chemical oxidation using an O/I Analytical 1010 Wet Oxidation TOC Analyser (Graden Instruments, Oakville, ON). The method that was followed is described in Standard Methods: 5310 C Total Organic Carbon Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method (APHA, AWWA, WEF, 2005). All samples were analyzed for TOC and dissolved organic carbon (DOC). DOC samples were obtained by filtering the water through a 0.45µm poly-carbonate membrane filter. The filter was first rinsed with 200 ml of DI and ultra-pure water to ensure no residual organics remained on the surface of the membrane. Following filtration, all samples were acidified to a pH of approximately 2.0 for preservation. Samples were stored in the refrigerator for up to three weeks before analysis.

3.6.2 Alkalinity

Alkalinity was quantified according to Standard Method 2320B (APHA, AWWA, WEF, 2005). All samples were analyzed in duplicate.

3.6.3 pH

pH was measured using the ORION model 420A pH meter (Pollard Water, New Hyde Park, NY). All samples were analyzed in duplicate.

3.6.4 Chlorine

The residual chlorine in the raw water was quantified using the Hach Kit method of measuring chlorine (Hach Co., Loveland, CO), which is based on the Colorimetric Method according to Standard Method 4500-Cl DPD (APHA, AWWA, WEF, 2005). All samples were analyzed in duplicate.

3.6.5 Conductivity

Conductivity in the raw, flocculated, and treated waters was measured using a portable handheld Hach CO150 conductivity meter (Hach Co., Loveland, CO). All samples were analyzed in duplicate.

3.7 Physical Parameters Analysis Method

3.7.1 Turbidity

Turbidity was measured with a portable hand held Hach 2100P turbidimeter (Hach Co., Loveland, CO). Turbidities of the raw, flocculated and treated waters were measured and recorded. All samples were analyzed in duplicate.

3.7.2 Trans-membrane Pressure (TMP)

TMP was recorded with a gauge pressure transducer Model 68075 (Cole Parmer Inc., Vernon Hills, IL) at the point where the treated water exited the membrane unit. This instrument read the current, and outputted a value between 4 and 20 mA. This current was proportional to the TMP according to the following relationship:

$$\text{Pressure (psi)} = -1.875*\text{Current(mA)} + 22.5 \qquad (4)$$

A current reading was taken by the pressure transducer every 20 sec, and stored in a data logger. At the end of all experiments, the data was uploaded onto a computer in the form of a spreadsheet. The TMP value was defined as the following:

$$\text{TMP (psi)} = P_{out} - P_{in} = \Delta P \qquad (5)$$

The pressure transducer read the effluent pressure as a negative value, as the positive displacement peristaltic pump is providing a vacuum, therefore, the harder the pumps needs to pull to maintain a flow of 45 mL/min, the lower the current that was emitted.

3.7.3 Total Suspended Solids (TSS)

TSS was measured for raw, treated and flocculated waters for the last two of three rounds of the experimental design. TSS is reported in terms of mg of suspended solids/L of solution; it is quantified using a filtration method described as the total suspended solids dried at 103-105^{o}C method according to Standard Method 2540D (APHA, AWWA, WEF, 2005). All samples were analyzed in duplicate.

3.7.4 Fractionation Method

The raw and treated waters were fractionated in order to gain a better understanding of what fractions of the NOM contribute to fouling most. The fractionation of any water sample can be based on a number of characteristics, but the most useful method for this research project was to fractionate the NOM in the raw and treated waters in terms of molecular weight.

This method involved the use of a series of UF filtration filters (Millipore Inc., Billerica, MA) with different molecular weight cut offs (MWCO) to sequentially separate the water into a series of molecular weight fractions. The first step of the method was filtering the water through a pre-rinsed 0.45 µm hydrophilic polypropylene filter ((VWR International, Mississauga, ON)) in order to remove any suspended solids that existed in solution. Before starting a filtration, the UF filters were first soaked 3 x 10 minutes in ultra pure water, and then 250 mL of de-ionized water was filtered, ending with 250 mL of ultra pure water before filtering the sample. This thorough cleaning method was conducted to ensure that any residual organics that were on the surface of the UF discs were removed, before beginning the fractionation experiments.

There were a total of five filter UF types used during the fractionation experiments, each having a different MWCO: 30 kDa, 10 kDa, 3 kDa, 1 kDa and 500 Da. The filters were made of regenerated cellulose (30 kDa - 1 kDa) and cellulose acetate (500 Da), all having a 76 mm diameter. The filters were inserted into a pressurized stirred cell apparatus (Millipore Inc., Billerica, MA) and immobilized within a plastic casing. The top of the fractionation cell was connected to a nitrogen tank, which provided pressure to the cell and in doing so, create a permeate stream. Figure 3-6 shows the complete set-up.

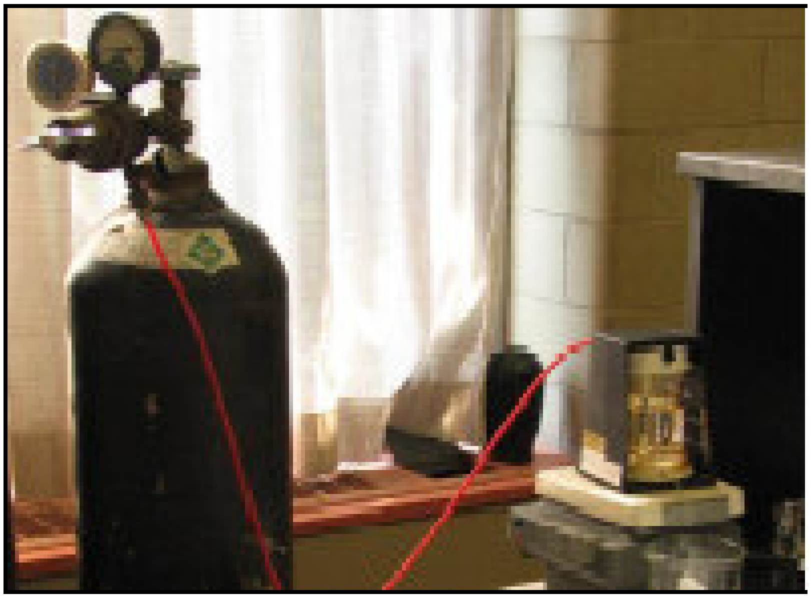


Figure 3-6: Bench-scale fractionation apparatus

Nitrogen gas was provided at variable pressures, as each filter required a different pressure to maintain a consistent flow without damaging the membrane. The method called for a permeate flow to be between 1 mL/min and 10 mL/min. The optimum lay at about 8 mL/min, with a maximum allowed pressure of 60 psig, based on guidelines described by the membrane supplier. The general pressure ranges were as follows:

- 30 kDa = 20 psi (1.38 bar)
- 10 kDa = 20 - 30 psi (1.38 - 2.07 bar)
- 3 kDa = 30 - 50 psi (2.07 - 3.45 bar)
- 1 kDa = 50 - 55 psi (3.45 - 3.79 bar)
- 500 Da = 60 psi (4.14 bar)

A 50 mL sample was taken from each fractionation, as well as a blank to ensure residual organics did not remain on the membrane surface. TOC samples were acidified with phosphoric acid in the same way as all other samples, and stored in the refrigerator until analysis was performed. After each usage, the filters were soaked in a 0.1 M NaOH + 100 mg/L bleach solution for 30 minutes, then rinsed 3 x 10 minutes in ultra pure water before being put in their respective storage solutions.

Each filter was used a maximum of three times, and stored in a 10 % ethanol solution between uses for the regenerated cellulose filters and 0.05 % sodium azide solution for the cellulose acetate filter.

3.8 Standards and Quality Control

One of the most important aspects of any analytical analysis is to ensure consistent results are obtained. This research focused on specific methods that aimed at quantifying a particular substance in water, and comparing these results to those obtained earlier using the same method. Therefore, in order to ensure that the data obtained were statistically sound, a certain set of procedures was followed when sampling and/or analyzing water samples:

- Water quality parameters were always tested in duplicate, or in some cases in triplicate
- During the TOC analysis runs, a calibration curve was utilized, making use of standards and blanks to verify the instruments accuracy
- Sample containers were always thoroughly cleaned and rinsed with sample before collection to avoid any cross contamination, and erroneous results

CHAPTER 4

PRELIMINARY COAGULATION AND WATER QUALITY RESULTS

4.1 Introduction and Objectives

The following section describes the results obtained from the series of jar test trials performed in the early stages of the research project. As previously mentioned, a 2-level factorial design was implemented with the synthetic water cocktail, in order to obtain a better understanding of how alkalinity, turbidity and the level of TOC affect the coagulation process for the waters tested. Results from the jar test trials conducted with raw Grand River and Lake Ontario water will be provided in this section. The objectives for this phase of the research were as follows:

- To gain a better understanding of how the four coagulants behaved when exposed to variations in turbidity, alkalinity and TOC
- To establish an optimum coagulant dose that yields maximum TOC removal for each of the four coagulants, to be used as a reference point for all subsequent membrane trials
- To describe the effect of the coagulant on the two raw water sources

4.2 Jar Test Trials with Synthetic Water Cocktail

All of the synthetic jar test trials were conducted in the same manner. Results were tabulated and a plot of dose vs. TOC and turbidity was generated for each individual jar test. Figure 4-1 is an example of one of the plots, and the remaining ones can be found in Appendix A

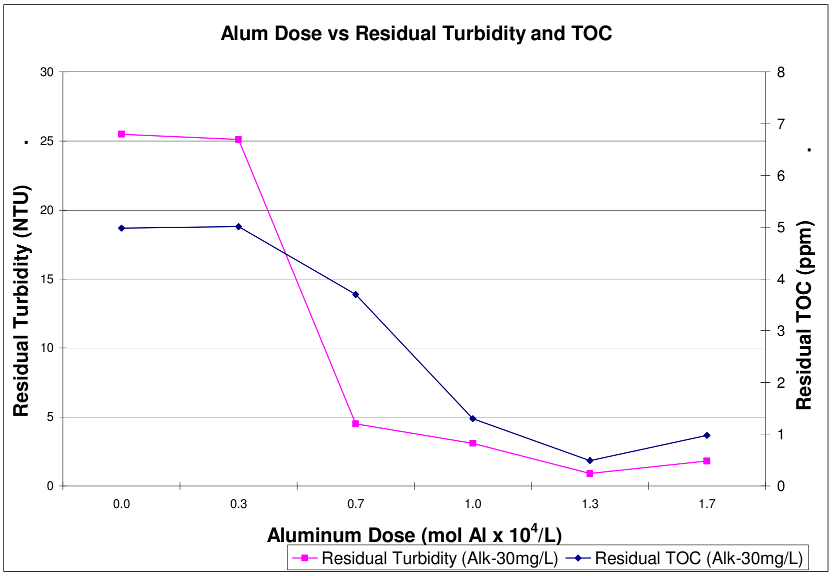


Figure 4-1: Alum dose vs. residual TOC and turbidity (synthetic water) – 30 mg $CaCO_3$/L, 20 NTU, 5 mg/L TOC

This synthetic water cocktail was created with an alkalinity of 30 mg $CaCO_3$/L, a turbidity of approximately 20 NTU and TOC concentration of 5.1 mg/L, as outlined in the jar test trials design in Table 3-3. The optimal coagulant dose was identified as the dose that corresponded to the lowest residual TOC value. In the case shown in Figure 4-1, the optimal dose was $1.3x10^4$ moles of Al/L, which corresponded to a coagulant dose of 35 mg/L of alum. The TOC was reduced to 0.6 mg/L, yielding an 88 % removal, while the turbidity was reduced from 20 NTU, down to 2.1 NTU, yielding a 90 % removal. Table 4-1 provides a summary of the results , based on Figures A.1 to A.9 and A.22 to A.27 found in Appendix A, obtained from the synthetic jar test trials conducted with alum and ferric chloride. As clearly seen, both coagulants performed very well when exposed to the synthetic water cocktails, with ferric chloride having a slightly better ability to remove TOC at an optimal dose. Their effect on pH was also noted, with the ferric chloride lowering the pH slightly more than the alum.

Table 4-1: Summary of Alum and ferric chloride jar test coagulation results

Condition	Alum	Ferric chloride
Floc formation	Fast floc formation (3-5 min) Settled moderately fast (20 min)	Slower floc formation Settled quickly (15 min)
TOC/DOC removal	60-75% removal with high alkalinity (>100 mg/L) 40-45% removal with low alkalinity (<50 mg/L) Higher percentage removal at higher TOC concentrations	65-75% removal with high alkalinity (>100 mg/L) 50-60% removal with low alkalinity (<50 mg/L) Higher percentage removal at higher TOC concentrations
pH	Moderate effect on pH (pH drop ~0.8 units at dose of 50 mg/L)	Large effect on pH (pH drop ~1.0 units at dose of 50 mg/L)
Turbidity removal	Good turbidity removal (1 NTU residual)	Good turbidity removal (1 NTU residual)

Table 4-2 provides the summarized data for the jar test trials conducted with the two pre-hydrolyzed coagulants, PACl (SP 70) and PACl (SP).

Table 4-2: Summary of PACl (SP 70) and PACl (SP) jar test coagulation results

Condition	PACl (SP 70)	PACl (SP)
Floc formation	Large/fast floc formation Settled very quickly (10 min)	Moderate size floc formation Settled quickly (15 min)
TOC/DOC removal	65-75% removal at high alkalinity 40-50% removal with low alkalinity (<50 mg/L) Higher removal at higher TOC concentrations Highest removal with a dose of 40-50 mg/L	75-85% removal at high alkalinity 50-60% removal with low alkalinity (<50 mg/L) Higher removal at higher TOC concentrations Highest removal with a dose of 35-40 mg/L
pH	Small effect on pH (pH drop ~0.4 units at dose of 50 mg/L)	Moderate effect on pH (pH drop ~0.7 units at dose of 40 mg/L)
Turbidity removal	Good turbidity removal (<1 NTU residual)	Good turbidity removal (1 NTU residual)

These coagulants are not as widely used as the two conventional coagulants described above, and their use in drinking water applications is not nearly as widespread. The results obtained were very promising, with both coagulants yielding high TOC removal rates, comparable to the conventional coagulants. One important point to note is that the changes in pH for the two pre-hydrolyzed coagulants were substantially lower, only reducing the pH by 0.4 and 0.7 units at the optimal coagulant dose for SP 70 and SP respectively. This contrast between the two sets of coagulants provides valuable information to assist manufacturers and plant operators with respect to the implementation of techniques to optimize membrane treatment processes for reducing membrane fouling. The fact that the pre-hydrolyzed coagulants do not lower the pH level a great deal implies that less resources and energy may have to be invested in order to bring the water back to a pH level that is acceptable for release into the distribution system.

The high alkalinity synthetic water cocktails (175 mg/L $CaCO_3$) showed better coagulation performance as compared to the low alkalinity waters (30 mg/L $CaCO_3$). This finding is supported by studies performed by O'Melia et al., 1999, which showed that higher alkalinity waters were easier to coagulate because of the higher concentration of positively charged calcium ions that interact with the negatively charged colloids. These results were seen across all four coagulations: the synthetic water trials conducted with the increased alkalinity resulted in a greater TOC removal, on average approximately 15-25 percentage points for all four coagulants.

Coagulating low alkalinity waters can be difficult because the pH may drop too far and because the lower calcium level may lead to less effective co-precipitation of the dissolved organics. A disadvantage of the low alkalinity is that the addition of an excessive amount of coagulant to satisfy demand could reduce the pH below the optimal range. Having said this, a similar problem exists for high alkalinity waters, where the selected dose may yield a pH well above the optimum level for removal of organics (Randtke, 1988). These issues aid in the decision making of a coagulant type, when assessing the water quality and desired removal. The PACl coagulants would be preferred for the low alkalinity waters, since their effect on pH is substantially less as compared to the two conventional coagulants. The removal efficiencies are reduced at low alkalinity levels (Table 4-2), but this would be countered with a minimal effect on the pH. If the raw water had a high alkalinity, similar to that used during those jar test trials with an alkalinity level of 175 mg/L $CaCO_3$, the two conventional coagulants would be better suited for application. Their effect on pH was greater (Table 4-1), and therefore, brought the pH level down closer to the optimal range for both coagulants, which was 5 and 5.5 for ferric chloride and alum respectively.

Raw water turbidity (5 vs. 20 NTU) was less important for determining coagulant dose, as compared to the raw water TOC concentration and alkalinity. This confirms results reported by Edzwald, (1990). There were no distinct observed trends which demonstrated that the optimal coagulant dose and residual TOC concentration were a function of the raw water turbidity. Having said this, NOM removal is generally maximized under the same conditions that provide optimal turbidity removal (Randtke, 1988). This trend was certainly seen throughout the majority of the synthetic water jar test trials, where TOC and turbidity were optimally removed with a similar coagulant dose (Figures A.10 to A.21, Appendix A). The residual TOC and turbidity trend lines generally had a similar shape. The lowest residual TOC concentration corresponded to the lowest turbidity value for the majority of the plots.

4.3 Jar Test Trials with Grand River Water

Triplicate measurements were performed on Grand River raw water in February, 2006 yielding an average of 6.31 mg/L and 6.02 mg/L for TOC and DOC, respectively. The water had a turbidity of approximately 8.1 NTU, alkalinity value of 181 mg/L and pH value of approximately 7.9. These water quality parameters were measured again in August, 2006, prior to beginning the membrane trials. The results obtained in August were 6.81 mg/L and 6.33 mg/L for TOC and DOC respectively. The water turbidity was slightly lower, at 7.2 NTU, the alkalinity level was 185 mg/L, and the pH was 8.1.

The average TOC removals were approximately 53, 39, 56 and 64 % for alum, ferric chloride, SP and SP 70, respectively, based on the results shown in tables B.5-B.8 (Appendix B). All of the tabulated data associated with these plots and the results described above can be found in Appendix B. These values were recorded as an average of the two highest removals for each of the four coagulants. These optimal removals were only 5-15% higher than all of the removals combined for each of the four coagulants. In all cases DOC represented between 85-95 % of the TOC, leaving only 5-15 % of the TOC as suspended organic carbon. The turbidity removals were all reasonably good, with alum and SP 70 having the highest removals, lowering the turbidity down to approximately 0.5 NTU. Ferric chloride and SP removals were not as high, but still these two coagulants lowered the turbidity to approximately 1.0 NTU. The changes in pH were also recorded in duplicate measures, with the two pre-hydrolyzed coagulants having the least effect on pH, and ferric chloride having the largest effect. At a dosage of 50 mg/L, the change in pH was measured as being 0.73, 0.86, 0.46 and 0.32 units for alum, ferric chloride, SP and SP 70 respectively. Figures 4-2 through 4-5 present the jar test results for all four coagulants.

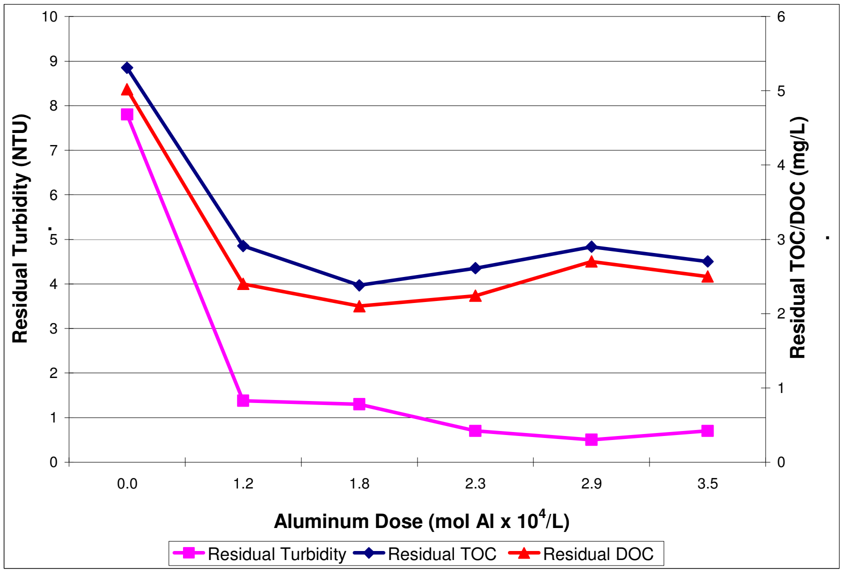


Figure 4-2: Alum dose vs. residual TOC/DOC and turbidity (Grand River)

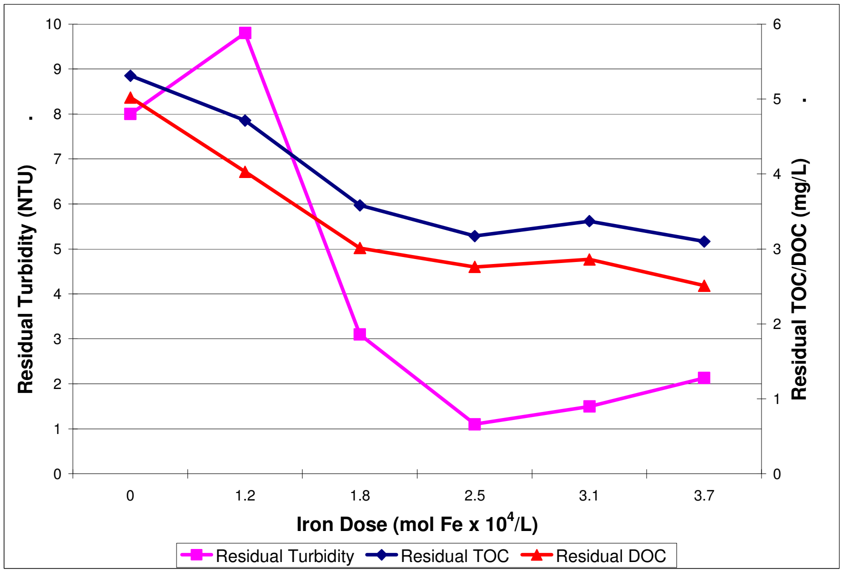


Figure 4-3: Ferric chloride dose vs. residual TOC/DOC and turbidity (Grand River)

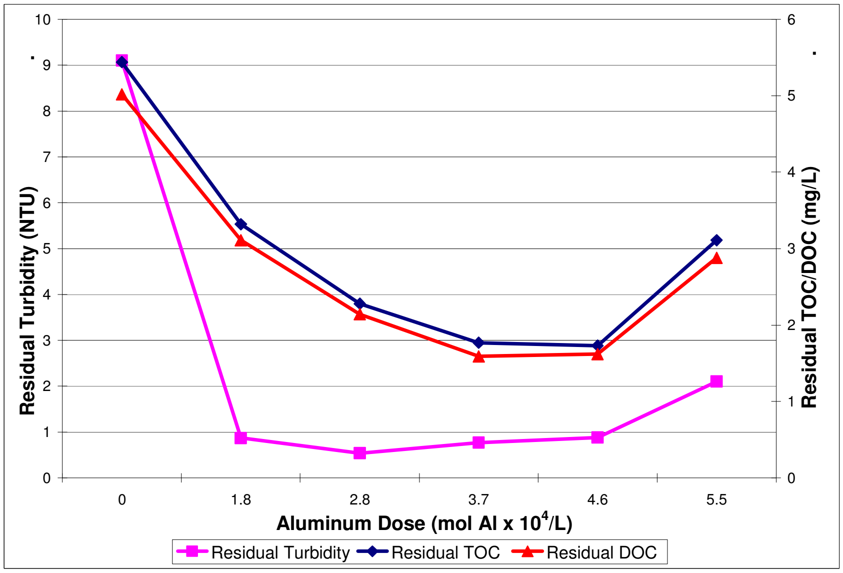


Figure 4-4: PACl (SP) dose vs. residual TOC/DOC and turbidity (Grand River)

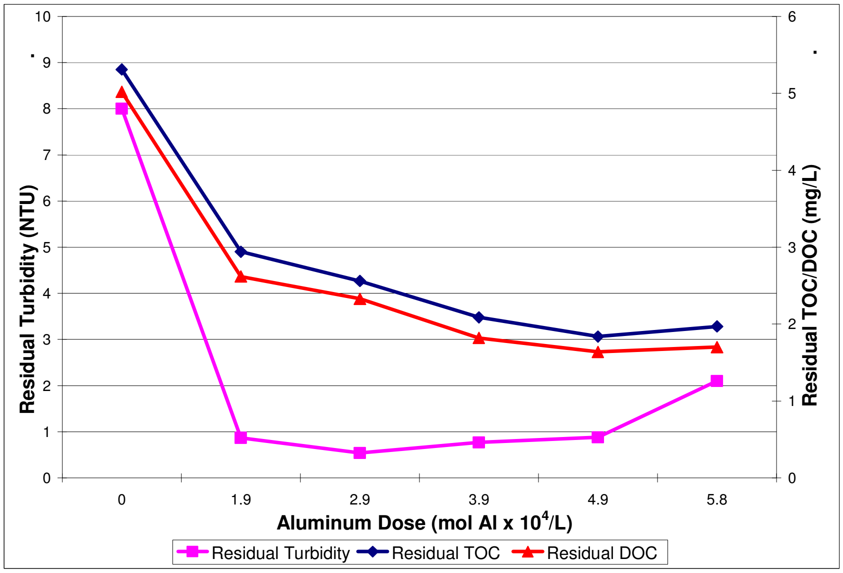


Figure 4-5: (SP 70) dose vs. residual TOC/DOC and turbidity (Grand River)

As clearly seen in Figures 4-2, 4-4 and 4-5, the TOC and DOC concentrations dropped off quickly initially, and then the concentrations decreased gradually until they reached a minimum level. The ferric chloride plot (Figure 4-3) showed a slightly different trend, where the TOC and DOC concentrations decreased slowly, until they leveled off at a concentration of 2.8×10^{-4} mol Fe/L, equivalent to a dose of 45 mg/L. The optimal TOC removal for the aluminum based coagulants was 1.8×10^{-4} mol Al/L (30 mg/L as alum), 4.8×10^{-4} mol Al/L (50 mg/L as PACl) and 3.7×10^{-4} mol Al/L (40 mg/L as PACl) for alum, SP 70 and SP, respectively.

It can also be seen in the figures that with a higher coagulant dose, re-stabilization of the particles occurred; causing a slight increase in the TOC concentration. Table 4-3 shows a summary of the optimal doses, as well the effective dose ranges determined from these trials for the four coagulants.

Table 4-3: Grand River jar test trials coagulant dose summary

Coagulant	Optimal Dose (mol metal/L)	Effective Range
Alum	1.8×10^{-4} (30 mg/L)	20-40 mg/L
Ferric chloride	2.8×10^{-4} (45 mg/L)	30-50 mg/L
PACl (SP)	3.7×10^{-4} (40 mg/L)	40-50 mg/L
PACl (SP 70)	4.8×10^{-4} (50 mg/L)	50-60 mg/L

According to the pH data showin in Appendix B, all four of the coagulants were operating in the sweep floc range (MWH, 2005). Figure 4-4 is the only one clearly showing a TOC increase with an elevated dose. Figures 4-3, 4-4 and 4-5 show a clear rise in turbidity, but no rise in TOC. Figure 4-2 showed no similar trends, as both the turbidity and TOC leveled with an elevated coagulant dose. These trends implied that there existed an optimum dose of coagulant that corresponded to the neutralization of the negatively charged particles. With a higher than optimal dose, the TOC concentration rose as a result of the overall charge in the water being slightly positive. This caused the incomplete coagulation of the colloids, and subsequently re-stabilization occurred. The variation in the results found between the four coagulants could be heavily attributed to experimental variability. More accurate results would have been obtained if these trials were repeated twice, and the results obtained as an average of the two trials.

4.4 Jar Test Trials with Lake Ontario Water

Triplicate measurements were performed on quenched Lake Ontario raw water in October, 2006 yielding an average of 2.67 mg/L and 2.42 mg/L for TOC and DOC, respectively. As a reminder, the quenching process involved spiking the chlorinated water with a 0.2 M sodium thiosulfate (NaS_2O_3) solution to ensure no residual chlorine remained in the water prior to conducting any experiments. The water had a turbidity of approximately 0.6 NTU, an alkalinity level of 104 mg/L, and pH value of approximately 8.0. The water sampled from Lake Ontario was quite different from the Grand River water when comparing the solids concentration. The Grand River had a TOC concentration three times higher, and a turbidity level thirteen times that of Lake Ontario water. Having said this, the pH was quite similar, both very close to 8.0. The alkalinity of the Grand River water was greater, but nevertheless, both were above 100 mg/L.

The detailed data for the jar tests can be found in Appendix B. The average TOC removal was approximately 48, 52, 47 and 42% for alum, ferric chloride, SP and SP 70, respectively. These values were recorded as an average of the two highest removals for each of the four coagulants. Similar to the TOC removal values obtained with the Grand River water, these optimal removals were only 10-15% higher than all of the removals combined for each of the four coagulants. In all cases DOC represented between 80-90 % of the TOC, leaving only 10-20 % of the TOC as suspended organic carbon. The turbidity removals were all reasonably good, with ferric chloride and SP having the highest removals, lowering the turbidity down to approximately 0.15 NTU. Removals observed with alum and SP 70 were not as high, but still these coagulants lowered the turbidity to approximately 0.3 NTU. The changes in pH were also recorded in duplicate measures, with the two pre-hydrolyzed coagulants having the least effect on pH, and ferric chloride having the largest effect. At a dosage of 20 mg/L, the change in pH was measured as being 0.36, 0.39, 0.27 and 0.20 for alum, ferric chloride, SP and SP 70 respectively. Figures 4-6 through 4-9 present the jar test results for all four coagulants.

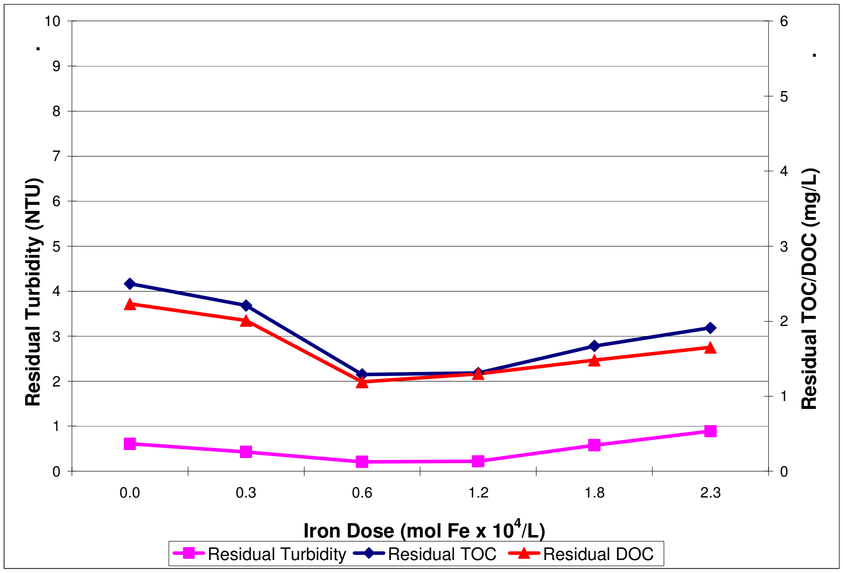


Figure 4-6: Alum dose vs. residual TOC/DOC and turbidity (Lake Ontario)

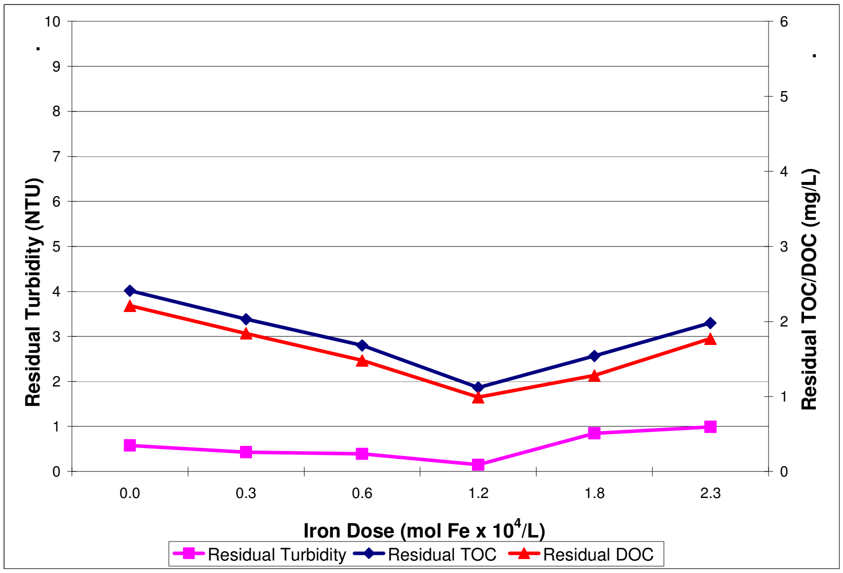


Figure 4-7: Ferric chloride dose vs. residual TOC/DOC and turbidity (Lake Ontario)

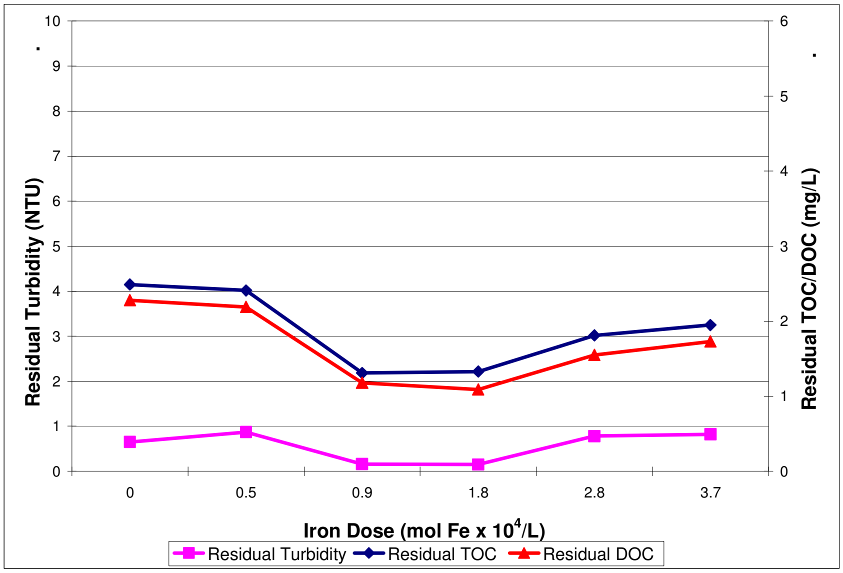


Figure 4-8: PACl (SP) dose vs. residual TOC/DOC and turbidity (Lake Ontario)

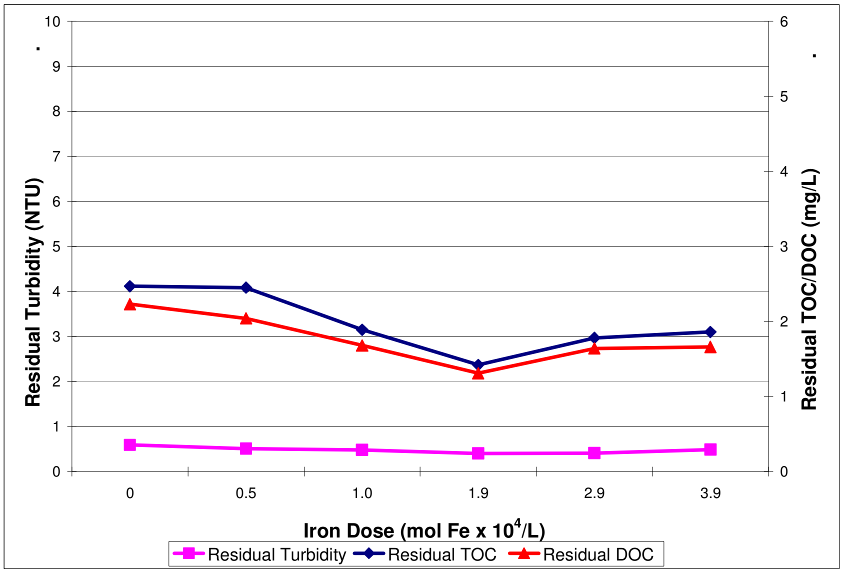


Figure 4-9: PACl (SP 70) dose vs. residual TOC/DOC and turbidity (Lake Ontario)

As clearly seen in the figures, the TOC and DOC concentrations dropped off with coagulant dose at a much slower rate in comparison to trials conducted with Grand River water. The concentrations gradually decreased until they reached a minimum level. The SP plot showed a slightly different trend, where the TOC and DOC concentrations decreased more quickly, until they leveled off at a concentration of 1.4x10^{-4} mol Al/L, equivalent to a dose of 15 mg/L. The dosage at optimal TOC removal for the other coagulants was 9.0×10^{-5} mol Al/L (15 mg/L as alum), 1.2×10^{-4} (20 mg/L as ferric chloride) and 1.9×10^{-4} mol Al/L (20 mg/L as PACl) for alum ferric chloride and SP 70 respectively

Similar to results obtained using Grand River water, it can be seen in the figures that with a higher coagulant dose, re-stabilization of the particles occurred; causing a slight increase in the TOC concentration. Table 4-4 shows a summary of the optimal doses, as well the effective dose ranges for the four coagulants.

Table 4-4: Lake Ontario jar test trials coagulant dose summary

Coagulant	Optimal Dose (mol metal/L)	Effective Range
Alum	9.0×10^{-5} (15 mg/L)	10-20 mg/L
Ferric chloride	1.2×10^{-4} (20 mg/L)	20-25 mg/L
PACl (SP)	1.4×10^{-4} (15 mg/L)	10-20 mg/L
PACl (SP 70)	1.9×10^{-4} (20 mg/L)	15-20 mg/L

Comparing the optimal TOC removals for the two sets of raw water shows that for all the coagulants except ferric chloride, trials conducted with Grand River yielded higher removals. The Grand River trials yielded removals that were higher by 5, 9 and 22 % for alum, SP and SP 70, respectively. The jar test trials conducted with ferric chloride yielded removals that were 13 % lower for the Grand River water, as compared to the Lake Ontario water.

As with the Grand River water the jar test trials conducted with the Lake Ontario water showed trends that lead to the conclusion that sweep flocculation was the dominant particle removal mechanism, primarily attributed to the elevated pH that was seen throughout the trials, This was also due to the fact that the TOC and turbidity concentrations were higher at elevated coagulant doses. NOM is generally considered to be removed through colloidal destabilization and charge neutralization (Randtke, 1988), so therefore the results were a bit unexpected given that sweep flocculation was the dominant mechanism for both the Grand River and Lake Ontario trials

4.5 Summary and Conclusions

The two raw water sources studied during the jar test trials display a variety of contrasting characteristics. Their TOC levels differed greatly, as did their turbidity levels. The TOC levels were three times that of the Lake Ontario water, while the turbidity levels were 10-15 times as high in the Grand River water. Because of this, the required coagulant dose to reduce the concentration of NOM to an optimal level also varies a great deal. Table 4-5 provides a concise summary of the doses that yielded the highest TOC removals for both raw water sources.

Table 4-5: Jar test trials results summary

Coagulant	TOC removal at high alkalinity	TOC removal at low alkalinity	Grand River optimum dose & TOC removal	Lake Ontario optimum dose & TOC removal
Alum	60-70%	35-45%	30 mg/L / 53%	15 mg/L / 48%
Ferric chloride	80-95%	50-60%	45 mg/L / 39%	20 mg/L / 52%
PACl (SP)	70-85%	40-50%	40 mg/L / 56%	15 mg/L / 47%
PACl (SP 70)	60-75%	35-45%	50 mg/L / 64%	20 mg/L / 42%

The first two columns summarize the work conducted with the synthetic water cocktails, reinforcing the fact that the alkalinity level in the water affected the coagulant performance, and subsequently, the degree to which the NOM was removed. As previously mentioned, water with a higher alkalinity is preferred for coagulation since it tends to have more positively charged sodium bicarbonate molecules to interact with the negatively charged colloids (O'Melia et al., 1999). The low level alkalinity water had a much lower concentration of the sodium bicarbonate molecules to react with the NOM particles, and therefore, a small fraction ended up in the floc formation. The hydrolysis reactions that occurred during the multi-stage coagulation process required the presence of these molecules. When the coagulants were added to the raw water, the ensuing hydrolysis reactions produce hydrogen ions that reacted with the alkalinity species in solution (AWWA, 1999). This theory again, explained the fact that the observed TOC removals were much lower for all four coagulants at a lower alkalinity level.

The development and manufacturing of coagulants for the water treatment industry is on ongoing process. The hydrolyzing metal salt (HMS) and PACl coagulants differ most in the manner in which they are produced. The PACl products underwent a pre-hydrolysis step during the manufacturing stage of the coagulant. This step involves the partial reaction of the simple salts (partial hydrolysis) to form the active monomeric hydrolysis species, and possibly some of the polynuclear species: which included $Al_2(OH)_2^{4+}$ and $Al_3(OH)^{4+}$. The variations in the results shown in Table 4-5 were primarily attributed to the wide range of hydrolysis products that were present in the water. The active species that were created during the partial hydrolysis interacted with the colloids and NOM differently, subsequently yielding different removal rates. For both PACl coagulants, the required dose was higher than the HMS coagulants. The SP 70's partial hydrolysis mechanism was carried out to a further extent as compared to the SP coagulant, and therefore its removal capacity was on average 5-10 % lower. The ferric chloride had the highest TOC removal capacity, which was expected given that a larger and heavier floc formation was observed for this coagulant throughout the duration of the jar test trials.

The next section presents the results obtained from membrane treatment trials conducted with the four coagulants, and two raw water sources discussed in this chapter. The results obtained from the jar test trials that were conducted served two major purposes: gain a fundamental understanding of how the four coagulants behaved when exposed to the two different source waters, and establish optimal coagulant doses from which all subsequent membrane trials were based on.

CHAPTER 5

MEMBRANE TREATMENT TRIALS RESULTS

5.1 Introduction and Objectives

The following section describes the results obtained from the series of membrane trials performed during phase II of the research. There were a total of 20 trials performed, each lasting a total of three days. As previously mentioned, all of the trials were performed using the bench-scale UF membrane system described in Chapter 3 of the thesis. During each trial period, Trans-membrane pressure (TMP) values were collected and comparative results can be seen in this chapter highlighting how the different coagulants performed as a pre-treatment to the UF membrane system. Both Grand River and Lake Ontario results are presented, so to be able to make a comparative assessment of the treatment process, when comparing two completely different raw water sources. The objectives for this phase of the research were as follows:

- To quantify the effect of the four coagulants in terms of their ability to reduce organic fouling of the UF membrane
- To examine the TOC/DOC removal capabilities of the four coagulants, alone and in combination with the UF membrane
- To observe the impact of pH and mixing rate on TOC/DOC reduction and fouling control.

All of the membrane trials were conducted between the months of July and December, 2006. Each membrane trial was carried out in the same manner. TMP data was collected, along with all of the water quality data, with all the information presented in this chapter. Each membrane trial yielded approximately 12,900 TMP data points, and all of these raw data plots can be seen in the Appendix C. In order to show the three day trends, 25 TMP values were selected, to yield corresponding summary plots. These plots are presented in this section.

5.2 Membrane Treatment Trials Using Grand River

Figure 5-1 shows an example of one of the raw TMP plots that included the 12,000 data points. This plot represents the results from the Grand River membrane trial conducted with the use of a 45 mg/L ferric chloride pre-treatment.

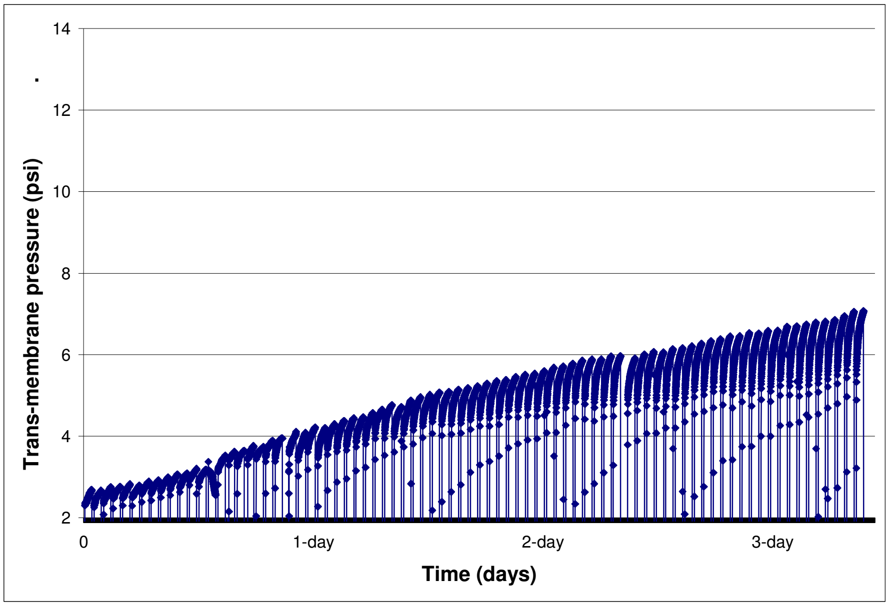


Figure 5-1: Raw Grand River water - 3 day membrane trial (45 mg/L ferric chloride pre-treatment)

As seen in the above figure, the trans-membrane pressure was approximately 2.75 psi (6.9 kPa) at the beginning of the trial. Each of the points on the figure represents a pressure value that was logged by the pressure transducer. The connecting lines are included to show trend that the series of points create. Over a 3-day period, one can see how the points bunch up to create an increasing trend line. As previously mentioned, a clean membrane unit required a pressure between 2.5-3.0 psi to produce a permeate flow of 45 mL/min. This plot and all of the remaining membrane treatment trials will be described in the subsequent sections of this chapter.

5.2.1 Membrane trial using optimal coagulant doses

Figure 5-2 shows a summary of the Grand River membrane trials conducted with the optimal coagulant doses of all four coagulants. Each of the five plots represents a trend line extracted from the raw data plots. These doses were determined during the jar test trials discussed in chapter 4: 30 mg/L, 45 mg/L, 40 mg/L and 50 mg/L for alum, ferric chloride, SP and SP 70 respectively.

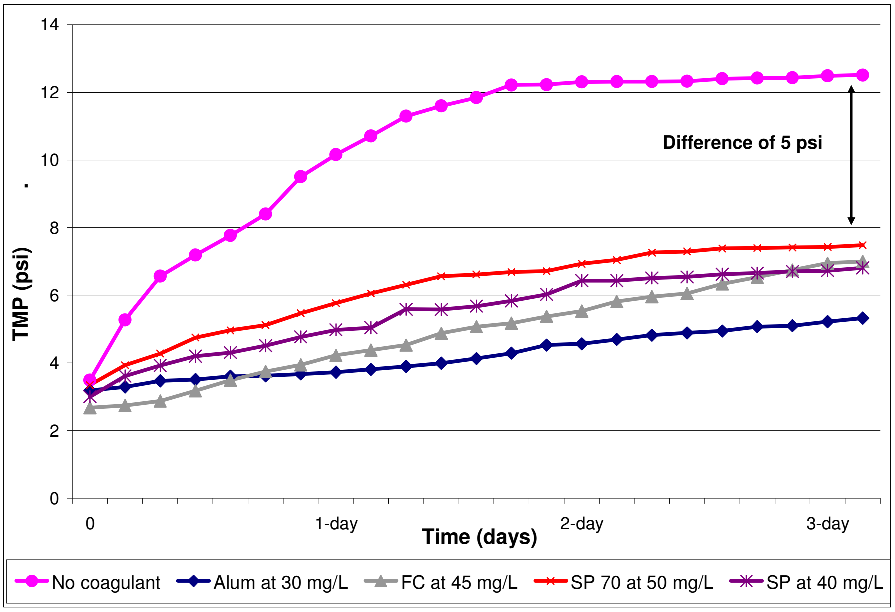


Figure 5-2: Grand River membrane treatment summary (optimal coagulant doses vs. raw water)

Alum performed the best at reducing the membrane fouling, with a final TMP of 5.3 psi, as compared to the raw water membrane trial, which yielded a final TMP of 12.5 psi, representing a 57 % reduction in overall TMP. The three other coagulants yielded TMP reductions of 44 %, 46 % and 40 % for ferric chloride SP and SP 70 respectively. It was surprising to see that the trials conducted with alum outperformed both PACl coagulants, given that better TOC removals were achieved during the jar test trials with SP and SP 70 at optimal does, as compared to alum. At first, this seemed counterintuitive, given that a larger TMP reduction would be expected with an increased TOC removal. Although in this case, it seems that the reason the fouling was reduced for the alum trial is because this coagulant was more efficient at removing the fraction of TOC that causes membrane fouling. So therefore, these results show that although alum was not the best at reducing the overall TOC concentration, but it was in fact the most efficient at removing the fraction of TOC that caused fouling on the UF membrane (How and Clark, 2002b). Looking at the results in terms or relative coagulant dose, there exists a bit of a trend, as alum was the most efficient at reducing fouling, but also had the lowest coagulant dose. SP 70 in this case, performed the worst at reducing fouling, and had the highest coagulant dose, at 50 mg/L. These results support the notion that in many cases, if the coagulant remains in solution, it can contribute to membrane fouling. In the case of the two pre-hydrolyzed coagulants, the increased dose may have resulted in the coagulant ending on the surface or inside the pores of the membrane. Having said this, similar studies have been performed with regenerated cellulose membranes, discovering elevated concentrations of PACl products yielded a more consistent flux across the membrane surface, and in turn reduced the degree of fouling that occurred (Laine et al., 1999).

The four pre-treatment trend lines showed similar shapes. All of them showed a gradual increase in TMP, followed by a small decrease in the slope a small amount towards the end of the trial. However, the raw water (no pre-treatment) trend line showed much different results. In this case, the TMP increased quickly until it reached a value of 12 psi halfway through the three-day trial, and then stabilized, with negligible increases in TMP observed over the remaining time. This trend can be described by the fact that the high concentration of solids in the raw water adsorbed to the majority of the available sites on the surface and/or inside the pores of the membrane during the first day, which contribute to the sharp increase in TMP over the first day. Once the majority of sites were occupied and the cake resistance stabilized, the rate of fouling became more constant, increasing only 1-2 psi over the last two days.

Overall, all four coagulants showed good results as pre-treatments to the UF membrane when an optimal dose for TOC removal was employed. The reduction in TMP ranged from 40-57 %, which would definitely translate into substantial financial savings, if this process were to be extrapolated onto a pilot, or even a full scale system (Judd and Hillis, 2001). Interesting to note, a similar study was conducted, that combined coagulation treatment with membrane filtration using a polypropylene membrane. An alum dose of 35 mg/L reduced the quantity of reversible fouling by a substantial amount. Moreover, it was discovered that similar results could be achieved by filtering the feed water through a 0.2 μm filter, thereby removing the particulates that were contained in the water. This comparative work highlighted the fact that the coagulation in this case was successful at removing particulate foulants, but had no noticeable effect on the dissolved material (Carroll et al., 2000).

Table 5-1 presents a concise summary of the TOC and turbidity removal data for these sets of membrane trials. Samples were taken from the membrane system on a daily basis in duplicate. The first column are results from samples taken after the coagulation and flocculation steps occurred, and the second column represents results obtained after membrane permeate samples were analyzed. The difference in TOC concentration and turbidities between the permeate stream and coagulation/flocculation effluent samples was equivalent to the quantity of TOC removed by the membrane. Therefore, the calculated removals were not cumulative, as the values shown below represent the individual processes, meaning that the basis for the membrane removals was the water being fed into the membrane, and not the raw water being fed into the system.

Table 5-1: Grand River TOC/turbidity summary – trials with optimal coagulant doses

Coagulant	TOC/Turbidity removed by coagulation	TOC/Turbidity removed by UF membrane
Alum	50-55% / 70-75 %	5-10% / 99%
Ferric chloride	55-65% / 60-70%	5-10% / 99%
PACl (SP)	45-50% / 75-80%	5-10% / 99%
PACl (SP 70)	50-55% / 70-75 %	5-10% / 99%

As seen in the above table, all four coagulants performed moderately well at removing the TOC in the form of NOM. When compared to the jar test trials, which represented ideal conditions for coagulation, the removal rates were lower, but only by 10-20 percentage points across all four coagulants. The turbidity removals were also consistent across the four coagulants throughout the coagulation stage. SP showed the highest removals at 75-80 %, and ferric chloride the lowest, but still a good removal at 60-70 %.

It was expected to observe trends showing ferric chloride yielding the highest TOC removal, as ferric coagulants generally achieve greater NOM removals, as compared to aluminum-based coagulants (Fearing et al., 2004). The UF membrane unit did very little at reducing the level of TOC in the treated water. This membrane was designed to primarily target suspended solids, and not dissolved organic matter, which constituted most of the TOC. Having said this, although it was difficult to isolate the exact fouling mechanism, adsorption within membrane pores is dominant for UF membranes, and is less reversible than cake formation. (Carroll et al., 2000). It has also been concluded by several investigators that that the amount of DOC in raw water is not a predictor of the amount of fouling, i.e. lower raw water DOC does not correspond to less fouling (e.g. Best et al., 2000). Moreover, it would be very interesting to observe the fouling rates of the raw Grand River water during a different season, when the TOC composition and TOC levels are different.

As previously mentioned, the nominal MWCO of the membranes was approximately 400,000 Da, whereas the majority of the NOM in the Grand River was smaller than 10,000 Da in size. Therefore, it was expected to observe very little TOC removal through the membrane. The turbidity was very well removed by the membrane, with the permeate stream having a value consistently below 0.15 NTU. These results were also expected, as the UF membrane was designed to target turbidity in the form of particulate matter, which is much larger in size than the NOM. The membrane effluent turbidity showed no signs of being a function of the raw water turbidity, as the influent varied between 5-12 NTU. The lack of a relationship between influent turbidity and permeate turbidity is also expected, since the membrane provides an absolute barrier to particles.

5.2.2 Membrane trial using equal molar dosing

Figure 5-3 shows a summary of the Grand River membrane trials conducted with the equal molar coagulant doses of all four coagulants. Similar to results presented with the optimal doses, the raw water plot is shown in blue, with the four pre-treatment plots shown underneath. These doses were pre-determined while creating the experimental design, when it was decided on $7.5\text{x}10^{-5}$ mol of metal/L as the molar dose. This dose corresponded to 47 mg/L, 36 mg/L, 36 mg/L and 37 mg/L for alum, ferric chloride, SP and SP 70 respectively. The equal molar dose was chosen as an average of all four optimal doses used for the first set of membrane trials.

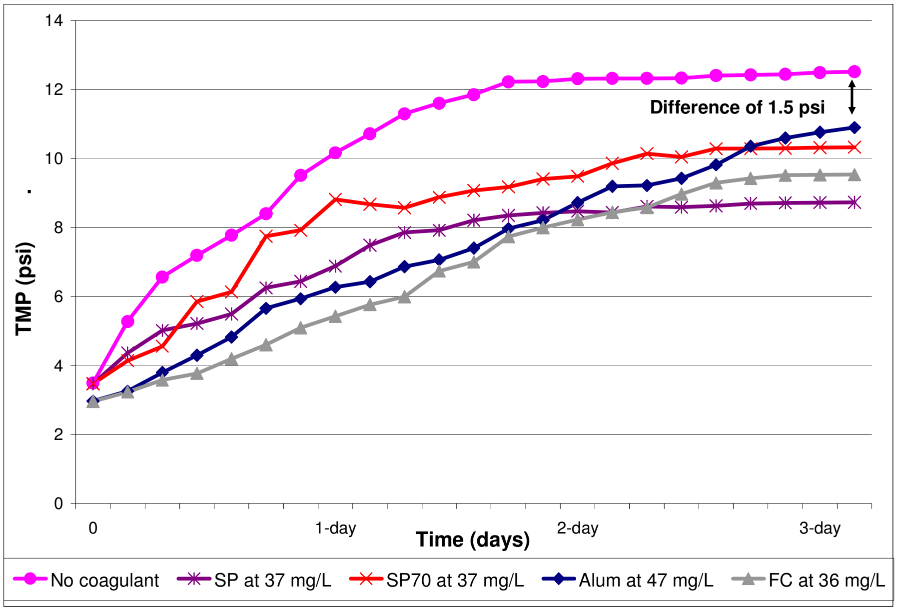


Figure 5-3: Grand River membrane treatment summary (Equal molar metal dose vs. raw water)

SP performed the best at reducing the membrane fouling, with a final TMP of 8.7 psi, representing a 30 % reduction in overall TMP. The three other coagulants yielded TMP reductions of 14 %, 24 % and 18 % for alum ferric chloride and SP 70 respectively. As will be discussed on the next page, the results obtained from this set of membrane trials reinforced the fact that for this specific water the optimal dose for coagulation worked well as a dose for a membrane pre-treatment application. The experimental apparatus was designed to simulated a settled water treatment system, therefore it was desired to remove as many as the flocs as possible. The equal molar doses generated flocculated water that contained more suspended solids, and therefore more fouling occurred.

Figure 5-4 and Figure 5-5 highlight the differences between the trials conducted with the optimal and equal molar doses. In Figure 5-4, the results obtained using the pre-hydrolyzed coagulants are shown.

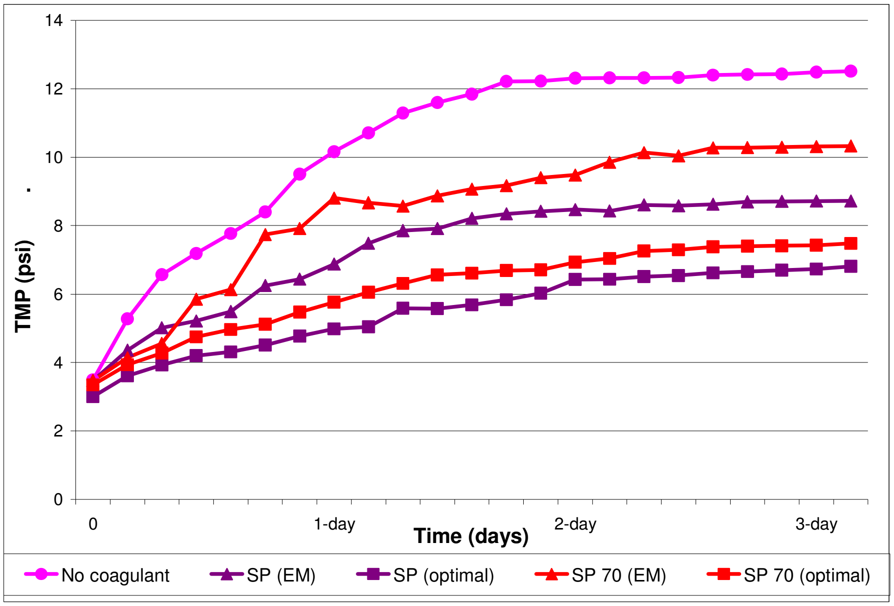


Figure 5-4: Grand River membrane treatment summary (PACl products - equal molar vs. optimal dose)

The equal molar doses for both of these coagulants (36 and 37 mg/L) were below their respective optimal doses (40 and 50 mg/L). This gives reason to believe that the equal molar dose was not sufficient, and under dosing occurred. It can also be seen on above plots that the trend lines for the two sets of coagulants have slightly different shapes. For both trend lines generated form the equal molar dosing experiments, the rate at which the TMP increases was elevated, as the induced membrane fouling occurred sooner. After the first day, the TMPs were approximately 9.0 and 7.0 for SP 70 and SP respectively, compared with 6.0 and 5.0 for the optimal dose plots. Again, this was attributed to the fact that a higher concentration of suspended solids remained un-coagulated during the equal molar trials, and therefore occupied the adsorption sites on the membrane surface and inside the pores, causing a more severe fouling effect. There may also have been less DOM coagulated if the coagulant dose was not sufficient to meet the entire 'coagulant demand' of the organic matter.

Figure 5-5 shows the results obtained using the two conventional coagulants. Similar to the results shown for the pre-hydrolyzed coagulant, the equal molar trend lines for both alum and ferric chloride had elevated rates of TMP change, as well final TMP values, substantially higher than those observed during the optimal dose experiments.

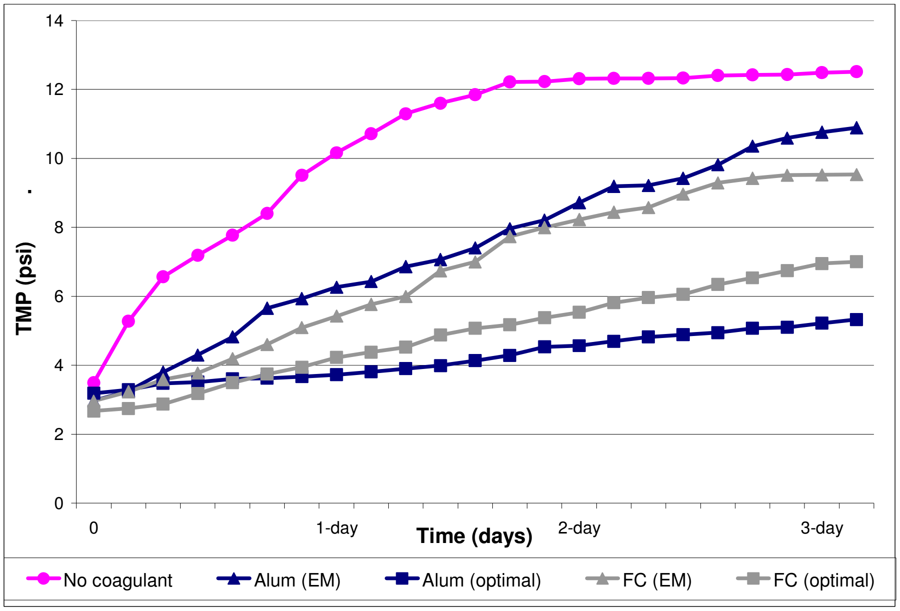


Figure 5-5: Grand River membrane treatment summary (Alum and ferric chloride - equal molar vs. optimal dose)

It was interesting to observe the fact that alum proved to be the most efficient coagulant at reducing membrane fouling at an optimum dose, but when the equal molar dose was employed, alum showed the worst results. These results were most likely attributed to over-dosing, as the equal molar dose was 17 mg/L higher than the optimal dose. Therefore, a re-stabilization of the particles in the raw water most likely occurred. In addition, the production of more floc from the elevated dose would have led to more in suspension. These trends were seen with the jar test trials results (Chapter 4). When a smaller portion of the solids in the raw water are flocculated, more adsorb onto the surface and/or inside the pores of the membrane fibres. Table 5-2 presents a concise summary of the TOC and turbidity removal data for these sets of membrane trials. As with the optimal dose trials, samples were taken from the membrane system on a daily basis in duplicate.

Table 5-2: Grand River TOC summary – trials with equal molar metal dosing

Coagulant	TOC/Turbidity removed by coagulation	TOC/Turbidity removed by UF membrane
Alum	35-45% / 40-50%	5-10% / 99%
Ferric chloride	40-45% / 50-60%	5-10% / 99%
PACl (SP)	35-45% / 55-65%	5-10% / 99%
PACl (SP 70)	25-35% / 50-60%	5-10% / 99%

The UF membrane behaved the same during the equal molar trials as for the optimal dose trials, with 5-10 % and 99 % removals observed for TOC and turbidity respectively. The coagulation/flocculation step removals were lower for all four coagulants. As previously mentioned, this was attributed to the over dosing of alum, and under-dosing of the three other coagulants. The difference for alum was the most extreme, having the worse membrane fouling results; this was coupled with TOC removals that were 15 % lower. As noted previously, lower TOC removals could have also contributed to more fouling, in addition to the effect from higher inorganic turbidity.

5.3 Membrane Trials Using Lake Ontario Water

Figure 5-6 shows a summary of the Lake Ontario membrane trials conducted with the optimal coagulant doses (for that water) of all four coagulants. These doses were determined during the jar test trials (Chapter 4): 15 mg/L, 20 mg/L, 15 mg/L and 20 mg/L for alum, ferric chloride, SP and SP 70, respectively.

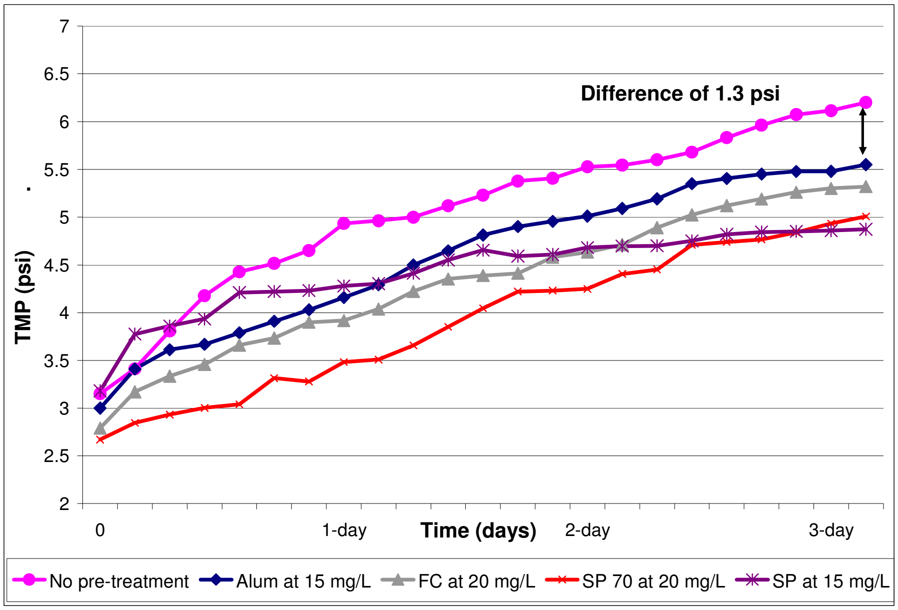


Figure 5-6: Lake Ontario membrane treatment summary (optimal coagulant doses vs. raw water)

The two pre-hydrolyzed coagulants performed the best at reducing the rate at which the TMP increased, with a final TMP of 5 and 4.9 psi for SP and SP 70 respectively, as compared to the raw water membrane trial, which yielded a final TMP of 6.2 psi. These values represented a 20 % and 22 % reduction in final TMP respectively using the two coagulants. The two other coagulants yielded TMP reductions of 12 %, 15 % for alum and ferric chloride respectively.

It is worth noting here, that the rates of TMP increases for these sets of trials cannot be compared to those obtained with the Grand River membrane trials. Lake Ontario's water quality was much better, with an average TOC concentration around 2.5 mg/L, coupled with a raw water turbidity of only 0.5 NTU.

Table 5-3 presents a concise summary of the TOC and turbidity removal data for the Lake Ontario water membrane trials. Sample collection was conducted in the same manner as for all other trials.

Table 5-3: Lake Ontario TOC summary – trials with optimal coagulant doses

Coagulant	TOC/Turbidity removed by coagulation	TOC/Turbidity removed by UF membrane
Alum	30-35% / 30-40%	5-10% / 80-90%
Ferric chloride	25-30% / 5-10%	5-10% / 80-90%
PACl (SP)	20-25% / 50-60%	5-10% / 80-90%
PACl (SP 70)	15-20% / 30-40%	5-10% / 80-90%

The UF membrane behaved slightly worse during the Lake Ontario water trials. The turbidity removal was observed to be between 80-90 %, as compared to the Grand River trials, where 99 % removal was consistently seen. This was attributed to the sizeable difference between the raw water turbidities, which were always consistently a magnitude apart. The membranes permeate quality consistently produced water below 0.1 NTU, but with the Lake Ontario raw water turbidity hovering between 0.5-6 NTU, the percentage removal was lower. As with the Grand River trials, this reinforced the fact that the membrane effluent quality was not a strong function of the raw water turbidity. The TOC percentage removals were similar for the two raw water sources, at 5-10 % efficiency.

The coagulation/flocculation step removals were also observed to be on average lower for trials conduced with Lake Ontario water as compared to Grand River water. Lake Ontario raw water TOC levels were consistently below 2.8 mg/L, coupled with a DOC/TOC ratio well over 90 %. As is often the case with raw water that contains very low TOC concentrations, the fraction of TOC removed was decreased (Shrive et al., 1999). This trend was seen in the jar test trials, for both the raw water and synthetic water cocktail experiments. With these sets of water conditions, a longer hydraulic retention time in the floc tank would have most likely not had a positive effect on the TOC removal. Coagulation reactions occur almost instantaneously, and as long as there is sufficient time for flocculation to occur, which in this case there was, increasing the size of the floc tank would not have made a difference in the TOC removal results. Moreover, the nature of the NOM in the Lake Ontario water was likely different than the Grand River water. Although both included a wide range of humic and non-humic macro-molecular organic compounds, which can have different effects with the coagulant, the Grand River water would be expected to contain a "younger" TOC, with a higher fraction of non-humic material due to wastewater effluents.

5.4 Comparison of Lake Ontario and Grand River Results

The following table shows a concise summary of the TMP reductions that were observed for the two sets of optimal dose trials conducted, with Grand River and Lake Ontario water. It is worth noting here, that the rates of TMP increases for these sets of trials cannot be compared to those obtained with the Grand River membrane trials. Lake Ontario's water quality was much better, with an average TOC concentration around 2.5 mg/L, coupled with a raw water turbidity of only 0.5 NTU, as compared to the Grand River water, which had a TOC concentration over 6 mg/L, and a turbidity of 8.0 NTU.

Table 5-4: Optimal Coagulant Dose Trials TMP reductions

Coagulant	Grand River TOC reduction	Lake Ontario TOC reduction
Alum	57%	12%
Ferric chloride	44%	15%
PACl (SP)	46%	20%
PACl (SP 70)	40%	22%

As it is clearly seen, the TMP reductions were substantially larger during the Grand River trials, for all four coagulants. This was expected given the contrast in TOC and turbidity levels. One interesting point to note was the fact that alum performed best for the Grand River trials, and worse for the trials conducted with Lake Ontario water. This reinforces the fact that the type of NOM that exists in the two source waters is quite different, because if their NOM composition was similar, one would expect to observe similar removal trends.

5.5 Membrane Trials with Modified Parameters

The following section describes the results obtained from the series of membrane trials performed with modified raw water pH and mixing intensities in the flocculation tank. The trials were conducted with Grand River water only, in order to determine the effect of pH and mixing intensity had on membrane fouling and overall water quality. There were a total of 8 trials conducted: the first four trials were performed with the raw water pH reduced to 5.5 for the three aluminum based coagulants, and 5.0 for ferric chloride, while the second half of the trials were conducted with a raised mixing intensity from the 30 rpm (base-line) to 45 rpm. Optimal doses were utilized in both cases, and datum related to TMP and water qualities were recorded in the same manner.

5.5.1 Modified raw water pH

Figure 5-7 shows a summary of the Grand River membrane trials conducted with a reduced raw water pH, coupled with optimal coagulant doses of all four coagulants. As previously mentioned, the raw water was spiked with reagent grade hydrochloric acid (VWR International, Mississauga, ON) to reduce the pH. These doses were pre-determined during the jar test trials (Chapter 4): 30 mg/L, 45 mg/L, 40 mg/L and 50 mg/L for alum, ferric chloride, SP and SP 70, respectively. The reduced pH levels utilized for all four coagulants represented the level that induced optimal coagulation for TOC removal (Sharp et al., 2006, Randtke, 1988). The spiked raw water maintained a reasonably constant pH throughout the 3-day trials, with a pH increase observed of only 0.1-0.2 units.

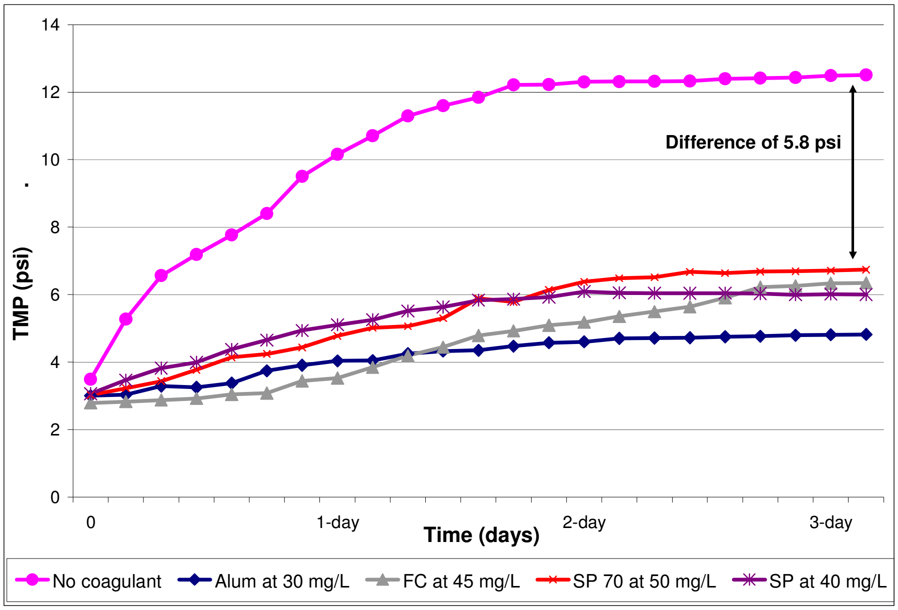


Figure 5-7: Grand River membrane treatment summary (Aluminum based @ pH 5.5, Iron based @ pH 5)

Similar to the trials conducted with optimal coagulant doses without pH adjustment, alum performed the best at reducing the membrane fouling, with a final TMP of 4.8 psi, as compared to the alum trial without pH adjustment (Figure 5-2), which yielded a final TMP of 5.3 psi, representing a 4 % reduction in overall TMP as compared to the optimal dose trials without pH adjustment. The three other coagulants yielded TMP reductions of 44 %, 46 % and 40 %, representing a reduction of 5 %, 6 % and 6 % as compared to the trials without pH adjustment for ferric chloride SP and SP 70 respectively. In the literature, several membrane treatment studies have been conducted with pH reduced raw water, and membrane filtration/performance was always better (e.g. Howe and Clark, 2006).

In all four cases, the reduced pH levels showed a consistent improvement over the base-line trials. A possible reason for the improvement was a stronger floc formation caused by the optimal conditions induced with the reduced pH, and more complete coagulation reaction. A stronger floc formation was less affected by the stirring motion of the mixing propeller, and therefore a larger fraction of the flocculated NOM settled out of solution, resulting in a reduced fouling effect. A comparison of the TOC removal results showed that there was an increase of 5

%, 2 %, 1 % and 2 % for alum, ferric chloride, SP and SP 70 for the trials with pH adjustment as compared to the membrane trials conducted with optimal coagulant doses without pH adjustment

Although not shown in the plots directly, the addition of a coagulant to the Grand River water with a reduced pH enhanced the adsorption and charge neutralization that was displayed in the jar test trials conducted with raw Grand River water. The increased TOC removals observed during these trials were attributed to the enhanced adsorption and charge neutralization. Moreover, this was the primary purpose of reducing the pH, in order to increase the TOC removal during the coagulation step. Under conditions of optimal pH, sweep floc coagulation has less of an effect, as charge neutralization tends to dominate. The specific mechanisms of the coagulant at a reduced pH are much less understood, due to a paucity of knowledge regarding which NOM species were are present in any given raw water source, not just the Grand River and Lake Ontario (Sharp et al., 2006). It is also worth noting here that at elevated pH values (above 7), hydroxyl ions are able to successfully compete with NOM for available metal coagulant ions, reducing the amount of NOM that is coagulated (Randtke, 1988).

The four trend lines showed similar shapes. As compared to the base-line optimal dose trials, these plots did not show signs of an increased slop at the beginning of the trial, but rather the sloped maintained a constant value over the first two days, levelling of a small amount at the end. The difference in the shape of the plots was attributed to the efficiency of the respective coagulants that performed under optimal pH conditions. As with the raw water trials that showed a steep slope (Figure 5-1), followed by the base-line trials that showed a much less extreme slope, an idea pre-treatment system would yield a TMP trend line that has a consistently increasing slope, similar to the ones showed in Figure 5-7 above. Although the fouling and water quality results were improved for the membrane trials with a modified raw water pH, the cost of the overall process is a factor that would have to be heavily considered in the design of any full scale operation. The benefit of operating at a reduced pH may in some cases by outweighed by the cost of chemicals required to first reduce the pH, and then raise the pH back up to potable standards at the end of the process. Depending on the finished water quality requirements, the reduced pH may not be necessary.

5.5.2 Modified mixing intensity in flocculation tank

Figure 5-8 shows a summary of the Grand River membrane trials conducted with a modified mixing intensity in the flocculation tank, coupled with optimal coagulant doses of all four coagulants. These doses were determined during the jar test trials (Chapter 4): 30 mg/L, 45 mg/L, 40 mg/L and 50 mg/L for alum, ferric chloride, SP and SP 70 respectively. The mixing intensities were elevated from 30 to 45 rpm, representing a 50 % increase.

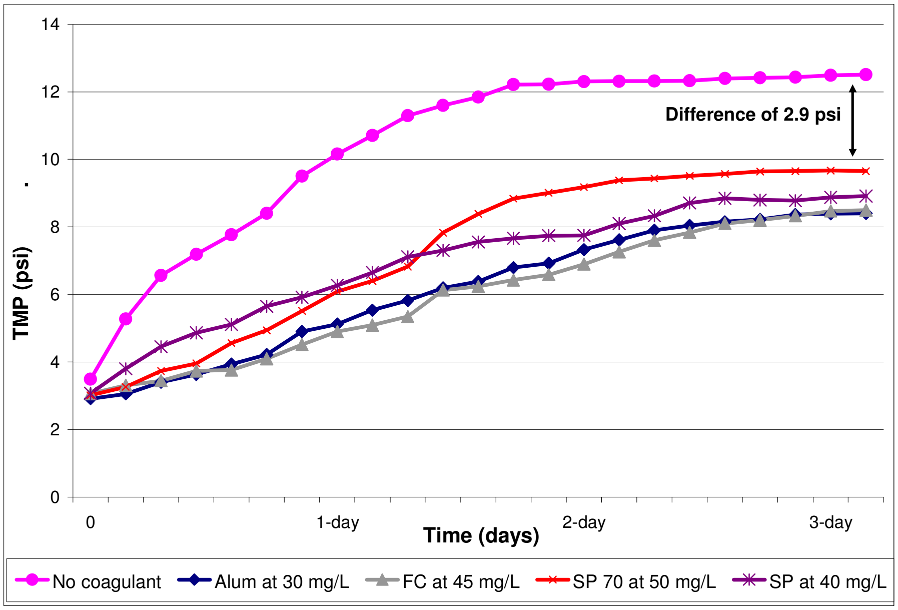


Figure 5-8: Grand River membrane treatment summary (45 rpm mixing intensity in flocculation tank)

All four coagulants showed increased TMP values across the 3-day trial, as compared to the base-line trials conducted with optimal coagulant doses. Table 5-5 provides a concise summary of the results obtained from the membrane trials conducted with modified mixing intensities. The first two columns show the individual TMP reduction results

Table 5-5: Grand River: optimal dose vs. modified mixing intensity

Coagulant	Grand River optimal dose	Grand River optimal dose with pH adjustment	Difference (Δ)
Alum	57%	33%	24%
Ferric chloride	44%	32%	12%
PACl (SP)	46%	28%	18%
PACl (SP 70)	40%	23%	17%

Alum performed the best at reducing the membrane fouling, reducing the final TMP from 12.5 to 8.4 psi, a reduction of 33 %. Having said this, in comparison to the base-line alum trial, an increase of 24 % TMP was observed. Similar results were observed for the other three trials, with reductions of 32 %, 28 % and 23 % for ferric chloride, SP and SP 70 respectively. Once more, these reductions were substantial, but when compared to the base-line trials, elevated TMP results were observed for all three coagulants: 12 %, 18 % and 17 % for ferric chloride, SP and SP 70 respectively. These results were heavily attributed to the design of the bench-scale membrane system.

The flocculation tank had a cylindrical shape, approximately 1.5L in size, and a 4” (0.102m) diameter. The 2.5” (0.064m) diameter mixing blade was located 2” (0.051) above the bottom of the tank. During the base-line optimal dose trials (30 rpm), a particle gradient developed in the flocculation tank. One could visually observe the accumulation of flocs on the bottom of the tank. At the top of the tank, where the effluent spout was located, there were very few flocs, hence the system behaved essentially as a settled water membrane treatment system. The flocculation tank was emptied every 24 h during the 3-day baseline trials, and each time, there was a thick layer of flocs that had accumulated at the bottom of the tank; this trend was observed for all four coagulants.

In contrast, during the trials conducted with the elevated mixing intensities, the solids gradient and the accumulation of particles on the bottom of the tank was not clearly observed, as the faster rotating blade caused the particles to re-suspend, and in doing so, a much larger portion of the flocs transferred over to the membrane tank. These observations, coupled with the increased TMP that occurred under conditions of elevated mixing rates, supported the hypothesis that suspended particles did in fact contribute to the membrane fouling (Lee et al., 2000); although there was definitely a substantial concentration of DOC that existed in solution, the results showed hat the DOC concentration decreased because of the elevated mixing intensity. The DOC concentration was decreased by 6 %, 11 %, 17 % and 12 % for alum, ferric chloride, SP and SP 70 respectively. These conclusions also demonstrate that DOM by itself does not cause membrane fouling, but rather it is a combination of the dissolved and suspended particles that creates the overall effect (Howe and Clark, 2002b).

5.6 Membrane Trials with Half Optimal Coagulant Dose

The final round of experiments involved utilizing coagulant doses that were half the concentration of optimal doses used during the base-line trials. These doses corresponded to 15 mg/L and 20 mg/L for alum and SP respectively. Figure 5-9 shows a plot comparing the two sets of trials (optimal dose and half optimal dose). As a reminder, these doses were tested to observe the difference in TOC removal and membrane fouling when the coagulants were severely under-dosed, and were performed because of indications that such lower doses were used at least sometimes in practice.

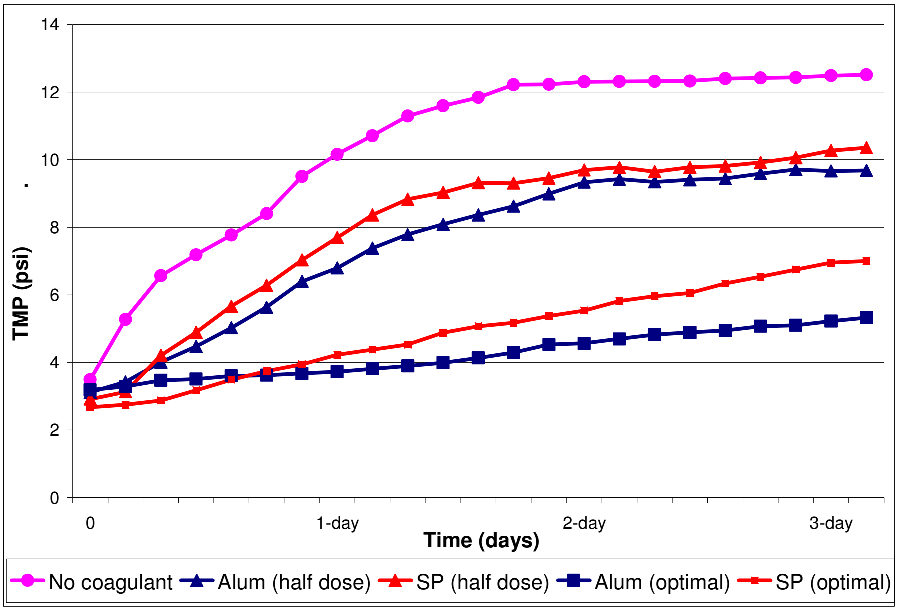


Figure 5-9: Grand River membrane treatment summary (Alum and SP – half optimal dose vs. optimal dose)

The two trials conducted with half the optimal dose trials yielded TMP reductions of 22 % and 17 % for alum and SP respectively. Although these represented substantial reduction, it clearly evident from the plots above, that the trials conducted with optimal coagulants doses provided much better results. Comparing the two sets directly, the trials conducted with half the optimal dose proved to be superior in terms of overall TMP reduction, yielding results that were 34 % and 27 % lower for alum and SP respectively. These results were expected, as these sets of trials simply did not provide a sufficient dose of coagulant, to accommodate the high concentration of solids in the raw water.

Visually, it was clear that that the floc formation was not as strong during these sets of trials; the water flowing into the membrane tank maintained a brownish colour, with an average turbidity of 5.2 and 5.7 NTU for alum and SP respectively, as compared to the base-line trials which had values 2.2 and 2.8 NTU for the same coagulant water combination. The membrane effluent turbidity values were not affected; as previously mentioned, the membrane effluent turbidity was a very weak function of influent turbidity.

Flocculated water samples were not analyzed for TOC during the base-line optimal dose trials. Having said this, the TOC removals for the entire system were quantified for both sets of trials, and these results reinforce the fact that the optimal doses for TOC removal determined during the jar test trials were in fact suitable for bench-scale membrane system design. The TOC removals for the half optimal dose trials were 42 % and 31 % for alum and SP respectively, as compared to 59 % and 52 % for the same coagulants at optimal doses, representing a decrease of 71 % and 60 % for the alum and SP respectively. These results were attributed entirely to the under-dosing of both coagulants. Shrive et al. (1999) discovered similar trends: when a PACl product and alum were under-dosed, there was a sharp decline in flux across the surface of a UF membrane.

These under-dosing trends corresponded very well with the results obtained while conducting the jar test trials. At low aluminium doses, these two coagulants yielded very similar results, with minimal TOC removals observed at doses of 15 mg/L and 20 mg/L for alum and SP respectively. In both cases the jar test trials and the membrane pre-treatment experiments, the provided coagulant doses was simply not large enough accommodate the particle and TOC concentration in the raw water, therefore a large portion of the NOM remained suspended in the water.

5.7 NOM Fractionation Analysis

NOM fractionation was a very innovative part of this research, since by quantifying the different sized fractions of NOM that existed in the Grand River water, the fractionation furthered the understanding of what fractions of the NOM contribute to fouling most. This section presents a series of plots that detail the fractionation of raw and treated Grand River water. The fractionation of any water sample can be based on a number of characteristics, but the most useful method for this research project was to fraction it in terms of its molecular weight cut off (MWCO). Each of figures categorizes the five fraction ranges (x-axis), and presents a TOC concentration corresponding to each of the five ranges (y-axis). As discussed in Chapter 3, this fractionation was accomplished using a series of UF filtration filters (Millipore Inc., Billerica, MA) with different molecular weight cut offs (MWCO) to sequentially separate the water into a series of molecular weight fractions

5.7.1 Raw water

Figure 5-10 shows a histogram that details the results obtained from the Grand River raw water fraction conducted in two separate time periods, one in July, and on in August 2006. Along the x-axis, the first set of bars describe the whole filtered results, which was simply a raw water sample, filtered through a 0.45 μm filter to remove any particulate matter. This was included in the plot to serve as a base-line concentration, from which all subsequent fractions were extracted. It is also worth nothing here that all fractionations were performed with whole filtered water; given that the UF fractionation discs would foul extremely quickly if exposed to a large concentration of suspended solids. The pre-filtration step ensured that the filter discs were only exposed to dissolved organic matter. The DOC concentration in the treated water did not vary a great deal; therefore results using whole filtered water were not affected by the variation in the DOC level in the raw water.

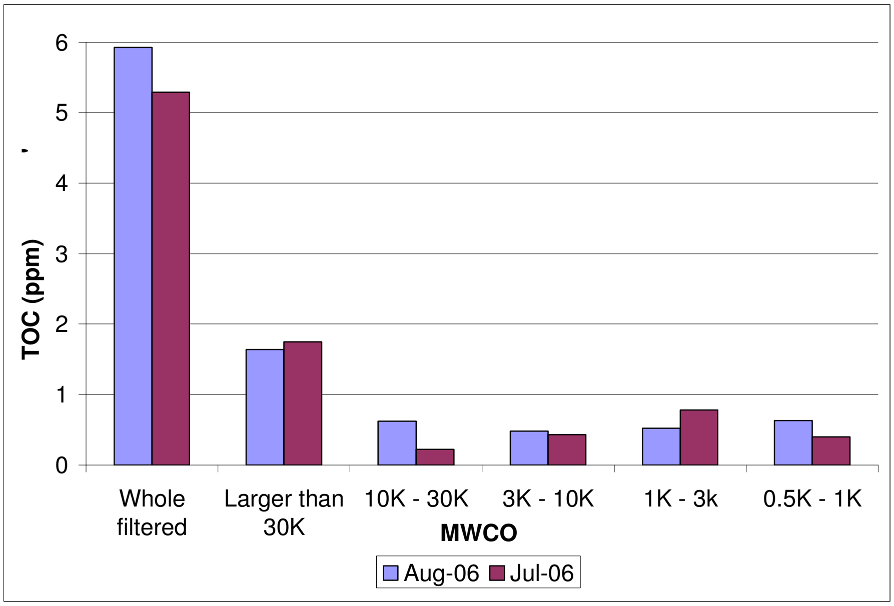


Figure 5-10: Grand River water MWCO distribution (TOC)

As clearly seen in the above figure, the distribution of the NOM across the five MWCO's did not vary a great deal, with the exception of the 'larger than 30K' range, which showed an elevated level of TOC as compared to the other four other distribution categories. Having said this, the 'larger than 30K' distribution differed in the fact that it contained only one limit, therefore including all NOM larger than 30K, as opposed to the true range distributions, which had two fixed boundaries. Scanning across the four other categories, the TOC concentrations ranged from 0.25 to 0.80 mg/L, with no distinct trend as to which of the four contained the most TOC. The fractionation work conducted in August, 2006, had a higher concentration in the '10K-30K' range, but had a lower concentration in the '1K-30K' range. Having said this, it was very difficult to interpret the results obtained from the raw water fractionation, as there were several discrepancies between the two sets of experiments that made it difficult to make accurate conclusions. One major issue that arose during the experiments was the fact that there was construction going on in the vicinity of the lab-bench, which affected the concentration of dust particles in the air, and therefore could have had a direct effect on the fractionation results. Another reason why the two sets of experiments are difficult to compare is because there was no replication performed for these sets of experiments, and without replication one cannot access reproducibility. The two sets of fractionation should be performed on the same day, using the exact same equipment and fractionation discus, to eliminate as many uncontrollable factors as possible.

One conclusion that was clearly evident was the fact that there existed a wide variety of NOM in the raw water, with a large variation in nominal molecular weights. There was a significant TOC concentration in every one of the ranges; therefore proving that the Grand River NOM ranges widely in size, found in all of five of the molecular weight distributions. Even though the nominal pore size of the UF membrane was in the area of 400,000 Da, the larger particles still may have had a tendency of forming a cake layer on the surface of the membrane. The smaller particles would therefore be more inclined to adsorb inside the pores of the membrane, causing the diameter of the pores to be restricted, and subsequently increase the TMP over a time.

5.7.2 Optimal coagulant dose

In order to determine which of the NOM fractions contributed to membrane fouling most, a fractionation study was performed on Grand River water treated with each of the four coagulants during the base-line optimal dose trials. Therefore, four separate membrane effluent water samples were fractionated: these samples had been treated with 30 mg/L, 45 mg/L, 40 mg/L and 50 mg/L for alum, ferric chloride, SP and SP 70 respectively. Figure 5-11 shows a break-down of the results obtained from the fractionation experiments performed with these four samples. The raw water results are shown in the figure as well, so to provide a mode of comparison. The results are plotted as an average of the two fractionations performed with the raw water. The results for each of the other four coagulants are shown individually.

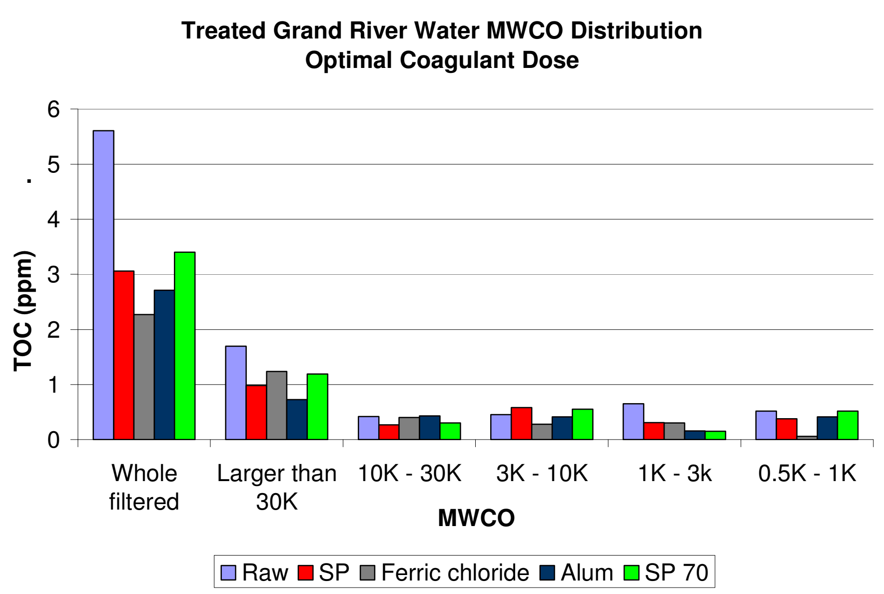


Figure 5-11: Treated Grand River water MWCO distribution (Optimal coagulant dose)

The whole filtered results for the four coagulants were recorded as the DOC contained in the membrane effluent corresponding to the specific coagulant, filtered through a 0.45 μm filter. As it can clearly be seen, the largest difference between the raw water and the four treated water can be seen in the ‘whole filtered’ category. The raw water had a TOC concentration hovering around 5.5 mg/L, while the highest treated water concentration was 3.4 mg/L.

Looking across the four fraction categories, there were two distinct trends observed between the raw and treated waters. A TOC concentration difference of at least 0.5 mg/L and 0.33 mg/L was observed between the raw water and the four coagulants for the 'larger than 30K' and '1K-3K' categories respectively. This indicated that the molecules within these MWCO categories were in fact removed by the membrane pre-treatment system. Coagulation conditions that are effective at removing TOC are also known to be effective at removing the fraction responsible for membrane fouling (Howe and Clark, 2002b). Having said this, it cannot be said with certainty that it was these molecules that contributed to the membrane fouling, as they could have simply been removed by the coagulation pre-treatment process, and never even been exposed to the surface of the membrane. So therefore, the results observed in this case confirm that the system removed a large fraction of molecules that were in the 'larger than 30K' and '1K-3K' range, but further fractionation experiments would have to be performed on both treated and flocculated waters, to isolated the source of both the fouling and NOM removals. Collins et al., (1996) used a UF fractionation method, to determine the apparent MW of humic substances, and one observation that came up was that distortion of the organic molecules under shear in the UF discs allowed passage of larger molecules, than what was expected, based on the nominal pore size of the given fractionation membrane. The fractionation experiments conducted throughout this project could have definitely been affected by this phenomenon, as in several cases, the TOC concentration from one category to the next did not decrease a great deal.

Given the complex nature of interactions involved amongst the wide variety of NOM components, it was not surprising to observe results that were not distinctly conclusive. Several others found little correlation between the apparent molecular weights (AMW) of NOM determined by UF fractionation (Leenheer et al., 1995, Newcombe and Drikas, 2006). This simply reinforces the notion that in order to obtain more concrete results, replication of the experiments with duplicate sampling methods is required. Simply comparing two individual sets of experiments does not offer a great deal of confidence.

5.7.3 Optimal coagulant dose with modified raw water pH

Figure 5-12 shows a summary of the fractionation experiments conducted with treated Grand River water samples, taken from the trials conducted with a reduced raw water pH, coupled with optimal coagulant doses of all four coagulants.

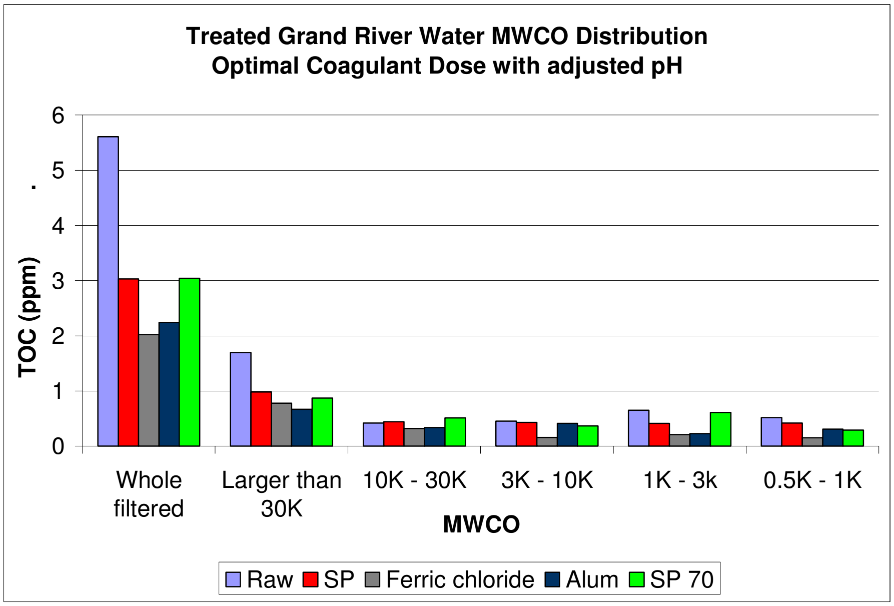


Figure 5-12: Treated Grand River water MWCO distribution (Reduced raw water pH)

The results for these sets of fractionation experiments did not differ a great deal from those conducted with samples taken from the base-line optimal dose trials. As expected, the trials at a reduced pH yielded treated waters that had lower TOC concentrations, which can be seen across all four categories when comparing the two figures. This was attributed to the optimized adsorption and charge neutralization conditions that were induced by the reduced pH. As previously mentioned, the jar test trials also showed trends that gave way to adsorption and charge neutralization as the dominant mechanism, as opposed to sweep flocculation.

One slight difference that was noted was the fact that the ‘larger than 30K’ category showed a decreased TOC concentration for the pH reduced trials, as compared to the base-line optimal dose fractionation results. This trend was seen for all four coagulants, giving rise to the notion the removal of this fraction was altered by the reduced pH, and further investigations would have to be conducted to make more accurate conclusions.

5.7.4 Water fractionation comparison

Figure 5-13 provides a summary of fractionation experiments conducted throughout the duration of this project. The raw water bars were generated from the summary of the two trials conducted with raw water, while the other two plots were created by taking an average of the four coagulants results for both the base-line optimal dose trials and the trials with reduced raw water pH. This plot provides a better visual interpretation of the different effect the coagulant had based on a modified pH. As previously mentioned, one can see a substantial amount of removal in the ‘larger than 30K’ category, as well as the ‘1K-3K’ one.

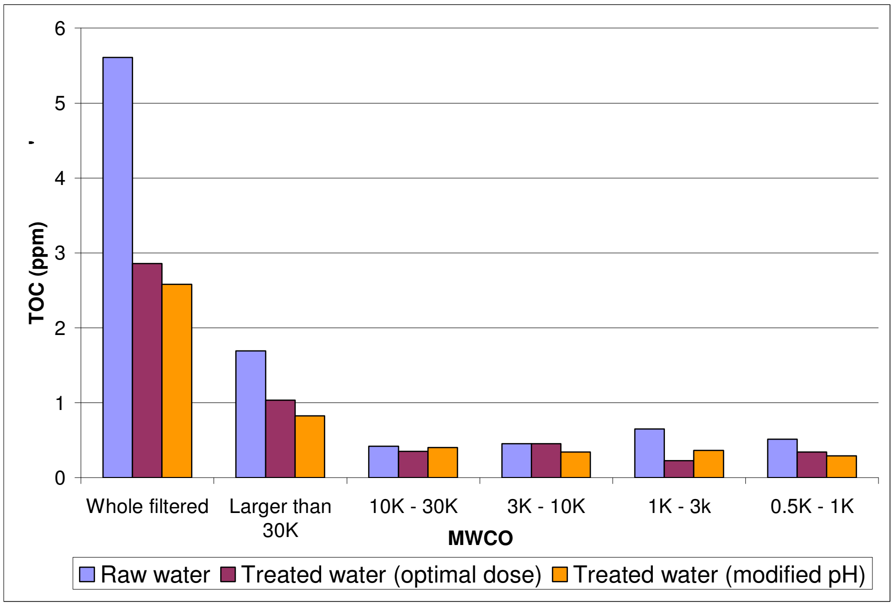


Figure 5-13: Raw vs. Treated Grand River water MWCO distribution (Optimal coagulant dose)

Although this could imply that the majority of NOM removed existed in these two ranges, and that the potential for these two fractions to cause the membrane fouling was increased, this cannot be said with confidence, as these two fractions could have been removed in the coagulation step, and never even reached the membrane surface.

5.8 Residual Metals Analysis Results

Throughout the duration of all the membrane trials, the treated water was sampled on a daily basis, and analyzed for residual aluminum and iron. Figure 5-14 provides a summary of the residual metal analysis data for the trials conducted with alum, SP and SP 70, which were aluminum based coagulants. Ferric chloride was the only iron based coagulant. The ferric chloride results were not included in the figure because iron was not detected in any of the permeate samples. The detection limit for all the iron samples was 0.05 mg/L, and 0.01 mg/L for the aluminum samples. The MOE Drinking Water Standards objectives and Guidelines (MOE, 2003) specified that both these metals were classified as aesthetic objectives, which means that these elements may impair the taste, odour and colour of drinking water, but are not considered to have a significantly harmful effect to humans. Having said this, there still exists room for debate and discussion regarding the possible health effects to humans from exposure to aluminum.

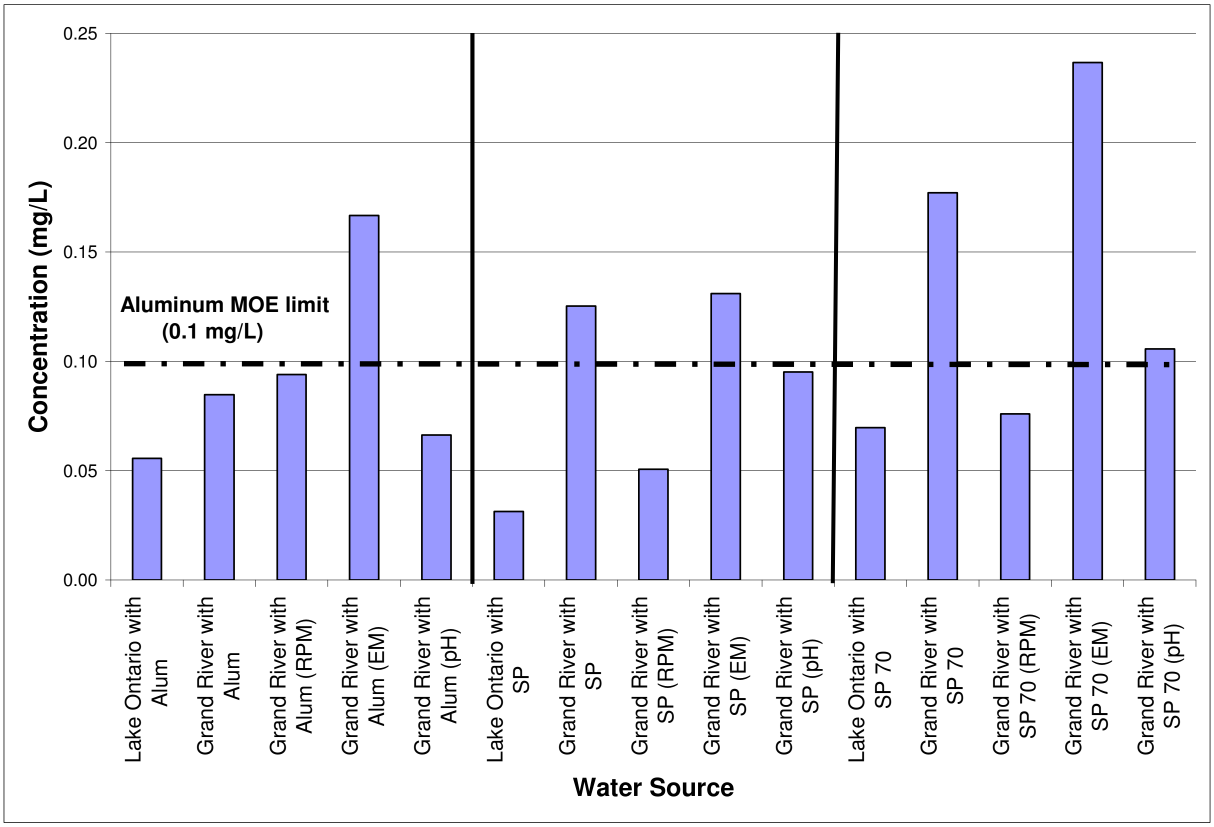


Figure 5-14: Treated water residual aluminum analysis summary

The aesthetic objective for iron, set by appearance effects in drinking water is 0.3 mg/L. Excessive levels of iron in drinking water supplies is seen with a brownish colour. It may produce a bitter, astringent taste in water and beverages; and the precipitation of iron can also promote the growth of iron bacteria in water mains and service pipes. Iron based coagulants such as ferric chloride, the one used in this project, is known to be highly effective in treatment processes at removing particles from water and leaving very little residual iron in the treated water (MOE, 2003). This was proven to be true throughout the duration of this project, as all of the analyses pertaining to trials conducted with ferric chloride yielded 'results that were below the detection limit (0.05 mg/L) established by the laboratory that conducted the work. Cleary, the residual iron concentration coming as a result of the use of ferric chloride as a pre-treatment to membrane bares no concern in the overall process design, as even the equal molar trial yielded results that were below the detection limit.

The results obtained for the residual aluminum analysis were not as convincing as the iron results, as there were several results over the limit legal limit established by the MOE. The aluminum found in the treated water was due to the presence of aluminum left over from use of the coagulant. Ideally, optimization of the treatment should be applied to reduce this residual aluminum to under the aesthetically operational guideline of 0.1 mg/L. High residual aluminum can cause coating of pipes in a distribution system resulting in increased energy requirements for pumping, interferences with certain industrial processes and flocculation in the distribution system (MOE, 2003).

There were a total of six membrane trials that yielded average results that were above the acceptable limit. Trials conducted with the PACl products yielded exceedances for both the base-line optimal dose trials, and the equal molar trials. The SP 70 coagulant also showed an exceedance for the trial conducted with a reduced raw water pH as well. The elevated residual metal concentrations observed with PACl products was not surprising, as they coagulants have a reduced ability of performing the hydrolysis reactions to produce hydrogen ions, as some of this required acid was neutralized with a base during the manufacturing stage. With exception of the analysis performed on the trials conduct with SP and SP 70, the only other result that stood out was the equal molar dosing trial conducted with alum. This was expected; given the fact that the equal molar dose was 17 mg/L higher than the optimal dose of 30 mg/L. The excess coagulant concentration did not participate in the coagulation flocculation step, and therefore remained in solution and passed through the membrane pores, remaining in the permeate stream. This result again, reinforced the fact that the optimal doses determined with the jar test trials were in fact suitable for this membrane filtration experimental design. Figure 5-15 shows the standard solubility diagram for the aluminum (Al^{3+}) ion. As can be seen, the operating range for aluminum hydroxide precipitation is in a pH range of 5.5 to 7.7, with a minimum solubility occurring at a pH of about 6.2 (MWH, 2005). Although temperature was held reasonably constant at room temperature, it is worth noting that the point of minimum solubility for aluminum shifts with temperature, which has a significant impact on full scale plan design where extreme temperature variations occur.

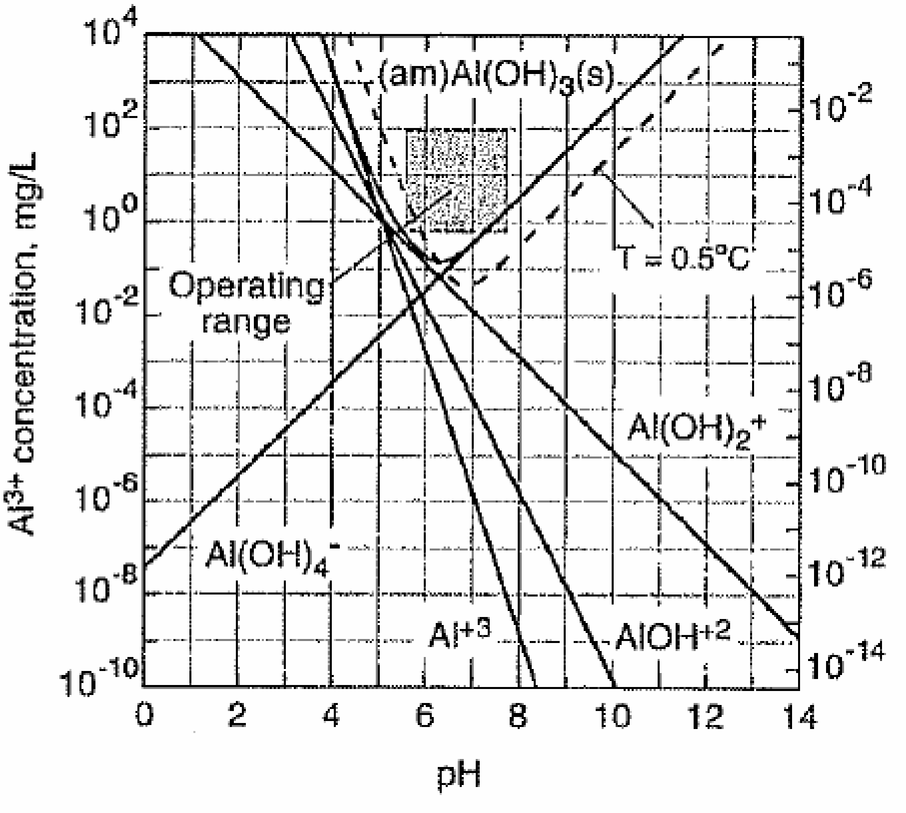


Figure 5-15: Standard solubility diagram for Al(III), (MWH, 2005)

According to the standard solubility diagram, the solubility of the aluminum decreases with an increasing pH level. Therefore as previously as mentioned, the residual metal exceedances observed with the PACl coagulants was not surprising, given that the resultant pH was 0.5 units higher on average for trials as compared to the trials conducted with the two conventional coagulants (alum and ferric chloride).

5.9 Total Suspended Solids Analysis Results

Table 5-6 provides a summary of the TSS analysis results for two sets of trials conducted using Grand River water, with modified raw water pH and mixing intensity in the flocculation tank. As a reminder, both sets of trials were conducted with optimal coagulant doses. The raw water was sampled prior to entering the flocculation tank, the treated water was sampled at the membrane effluent point, and the floc water was sample directly form the flocculation tank.

Table 5-6: Treated water total suspended solids analysis summary

	Total Suspended Solids (TSS) mg/L					
Grand River	Modified pH			Modified mixing rate		
	Raw	Treated	Floc	Raw	Treated	Floc
Alum at 30 mg/L	76.2	0.30	73.1	80.5	0.30	69.8
FC at 45 mg/L	72.8	0.30	73.0	72.5	0.40	81.0
PACl (SP70) at 50 mg/L	78.4	0.30	70.8	69.2	0.30	53.1
PACl (SP) at 40 mg/L	81.1	0.40	75.5	73.5	0.30	86.2

As clearly seen in the above table, there were no substantial differences observed in the results between the two sets of trials. All raw water TSS concentrations ranged between 70-82 mg/L, with the results from the treated waters showing 99 % TSS removal. All of the treated water TSS concentrations were between 0.3-0.4 mg/L, reinforcing the fact that the UF membrane was able to maintain a consistent permeate quality, with a very low turbidity. The flocculated water TSS concentrations varied slightly between coagulants. This was less attributed to the coagulants, and more so to the elevated mixing intensities and sampling method. The water was sampled by collecting the tank effluent (membrane tank influent), and therefore the concentration of solids was not consistent, and a representative sample was not obtained each time. This coupled with the fact that the elevated mixing rates caused the flocs in the tank to re-suspend, and therefore making it difficult to compare solids concentrations under different mixing conditions. Nevertheless, the most important observation was that the membrane was very efficient at removing the TSS, which the results confirmed, across all four coagulants.

5.10 Conductivity Analysis Results

Table 5-7 provides a summary of the conductivity analysis results for two sets of trials conducted using Grand River water, with modified raw water pH and mixing intensity in the flocculation tank.

Table 5-7: Treated water conductivity analysis summary

	Conductivity (μS)					
Grand River	Modified pH			Modified mixing rate		
	Raw	Treated	Floc	Raw	Treated	Floc
Alum at 30 mg/L	514	509	589	515	521	609
FC at 45 mg/L	511	507	599	514	518	610
PACl (SP70) at 50 mg/L	512	510	594	519	519	599
PACl (SP) at 40 mg/L	518	511	594	520	520	603

Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, phosphate anions and also, sodium, magnesium, calcium, iron, and aluminum cations. The organics contained in the Grand River do not conduct electrical current very well and therefore have a very low conductivity, contributing negligibly to the overall conductivity. The variations that do occur in the Grand River are primarily seasonal, because in the winter months much more of the flow is groundwater base flow. Having said this, the results in the above table make sense, as there were no clear trends observed, with the exception of the flocculated water having an elevated conductivity by approximately 18-20 %, induced by the addition of the metal coagulants, which contributed to the conductivity. All four sets of trials showed very similar results; the flocculated water conductivity hovered between 589-610 μS, subsequently reduced down to a level between 507-521 μS. This reduction in conductivity was attributed to the coagulant, which precipitated, and was removed during the filtration process. So the main conclusion that came out of this work was the fact that the elevated water conductivities were not affected by varying the coagulant type, which was expected, as the compounds that contribute to conductivity, are not a function of the varying coagulation conditions. With raw waters with a lower conductivity (below 200 μS), the type of coagulant could make a difference, particularly if different coagulant doses were used.

5.11 Alternative Methods of Interpreting Data

All of the data in this chapter related to the rate of change of TMP has been plotted against time on the x-axis. Every plot was shown as the difference in pressure across the membrane surface over a 3-day period. Figure 5-16 and 5-17 provide an alternative approach to the conventional way of presenting the TMP data. These two plots are essentially linear transformations of Figure 5-2, which was the plot showing results obtained from the membrane trials conducted with the optimal coagulant doses using raw Grand River water. Figure 5-16 shows the TMP data plotted against a cumulative volume of water treated per m^2 of membrane surface area, while Figure 5-17 shows a plot of the pressure data against a cumulative mass of carbon delivered to the membrane surface. It was assumed that the volume of water treated by the membrane was 45 mL/min, which was the flow rate used throughout the duration of this project.

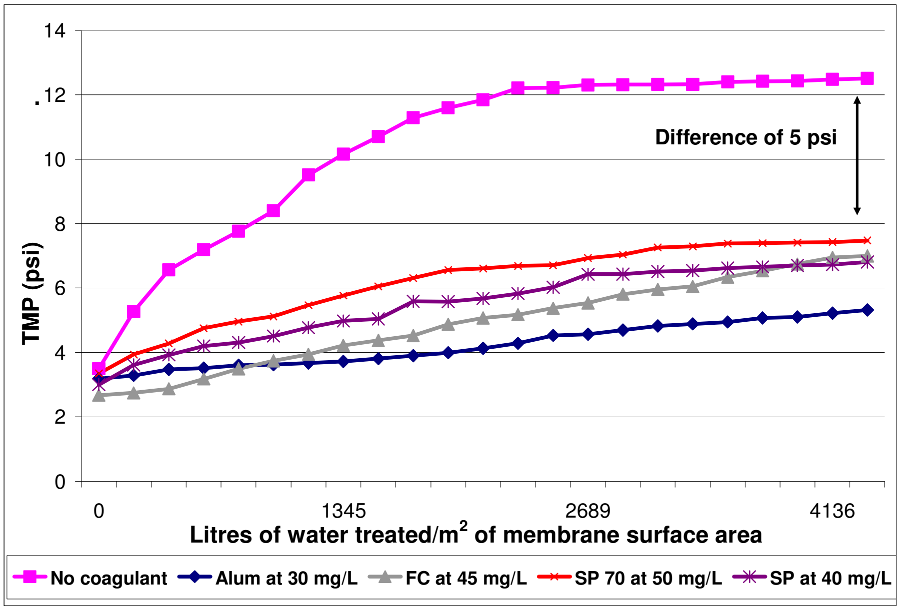


Figure 5-16: Grand River membrane treatment summary (TMP vs. volume of water treated by the membrane)

Using this alternative method of plotting the TMP has the potential to provide very useful results and/or trends to water treatment plant operators and researchers alike. Instead of simply drawing conclusions on how far into the 3-day trial certain trends were observed, one is able to quantify the volume of water cumulatively treated at that time. For example, in Figure 5-16 it was observed that after approximately 2100 L of water was treated/m^2, the TMP stabilized for the remainder of the 3-day trial. This volume of water could now be used as a base-line comparison for other process optimization experiments. One could observe what volume of water it would take for the TMP to stabilize based on different parameter settings, therefore establishing a different approach to assessing membrane fouling. For plant operators, this approach could provide assistance when trying to establish an acceptable limit for the TMP on any full scale system. The need to maximize the amount of water treated before reaching a set TMP point would be very important in the overall process design.

Figure 5-17 provides a slightly different approach to analyzing the TMP data. This plot shows TMP data plotted against a cumulative mass of carbon delivered to the membrane surface. Similarly, this approach could prove very beneficial for plant operators and research; but in a slightly different manner

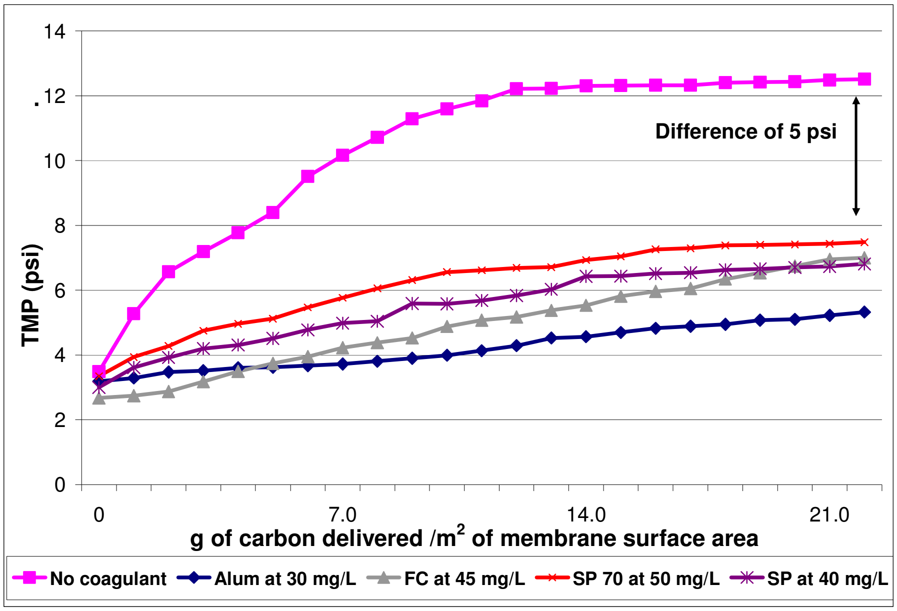


Figure 5-17: Grand River membrane treatment summary (TMP vs. mass of carbon delivered to the membrane)

In this figure, it was assumed that incoming water had an average DOC concentration of 5 mg/L, which corresponded to the raw Grand River water concentration. The raw water did not have any appreciable variations in DOC concentration. Again, looking at the point where the TMP stabilized, there was approximately 12.0 g of carbon treated by the membrane. Plant operators, could utilize this information when establishing thresholds on TMP. If a raw water source with a given water quality takes approximately 12.0 of carbon to reach a TMP pressure of 12 psi, then an increased in TOC concentrations would result in a higher pressure value, corresponding to an increased fouling rate. If it was therefore known that through a given season, the DOC concentration in the raw water drops a known amount, a plant operator would be able to approximate how much more water can be treated until the threshold pressure was reached. Changes in turbidity reaching the membrane would also play a role in a similar manner, as one could determine a threshold on TMP, based on the turbidity level in the in-coming raw water stream. The same method of data presentation is shown in Figure 5-18, for the five membrane trials conducted with Lake Ontario water.

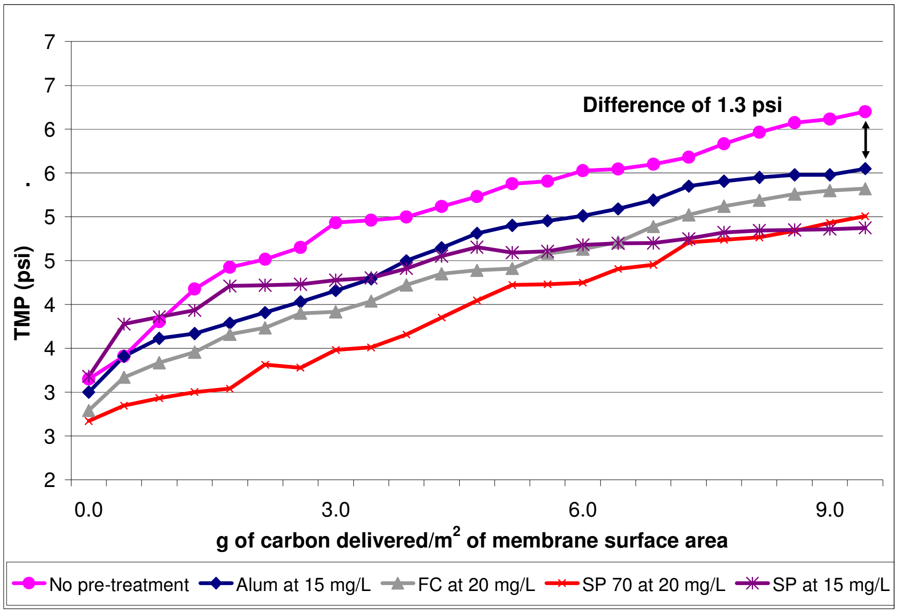


Figure 5-18: Lake Ontario membrane treatment summary (TMP vs. mass of carbon delivered to the membrane)

Similar with the Lake Ontario membrane trials, this form of data presentation would be very useful in a full scale design. It was assumed that the incoming water had an average DOC concentration of 2.1 mg/L, which corresponded to the raw Lake Ontario water concentration. Although Figure 5-17 and 5-18 present results for two different water sources, one can drawn useful comparisons from the plots. In Figure 5-18, the TMP does not really stabilize over the duration of the 3-day trial, as compared to Grand River trials that stabilize at a specific carbon loading value. One conclusion that could be drawn from this comparison is the fact that a raw water source with a lower DOC concentration will be able to stay on-line longer before reaching a threshold TMP value. This compared to water with a higher DOC concentration, which fouls the membrane much quicker, and therefore reaches its TMP threshold (12 psi). Just the same, water treatment researchers can utilize this method of presenting data to optimize bench and pilot scale membrane systems. The DOC concentration is a very crucial parameter in quantifying the fouling rate, membrane life span, and overall finished water quality; and both alternative methods of illustrating the results would contribute towards a sounder process optimization.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions are primarily focused on the reduction of TMP across the surface of a UF membrane. Fouling mitigation was quantified by measuring the TMP over a 3-day period, and plotted against time. The resulting trends were analyzed and several observations were described in this thesis. A lower TMP represented a reduction in membrane fouling, as the highest TMP and fouling effect was observed when raw water was treated without the use of a coagulant pre-treatment. Based on the work presented in this thesis, the following conclusions can be made:

1. Under optimal coagulant dose conditions:
    a. Grand River trials: Alum performed best at reducing the membrane fouling, in doing so, reducing the TMP pressure observed over a 3-day trial period from 12.5 to 5.7 psi, representing a 57 % reduction in overall TMP. The three other coagulants yielded TMP reductions of 44 %, 46 % and 40 % for ferric chloride SP and SP 70 respectively
    b. Lake Ontario trials: The two pre-hydrolyzed coagulants performed the best at reducing the membrane fouling, in doing so, reducing the TMP pressure observed over a 3-day trial from 6.2 to 5.0 and 4.9 psi for SP and SP 70 respectively. This represented a 20 % and 22 % reduction for the two coagulants. The two other coagulants yielded TMP reductions of 12 %, 15 % for alum and ferric chloride respectively.

The subsequent conclusions (2-9) were extracted from trials conducted with raw Grand River water:

2. An equal molar dose was established by taking an average of all four coagulant doses used during the baseline trials, which corresponded to a dose of $1.75x10^{-5}$ mol metal/L. Increased TMP pressures were observed when equal molar metal dosing was utilized. SP performed the best at reducing the membrane fouling, with a final TMP of 8.7 psi, representing a 30 % reduction in overall TMP. The three other coagulants yielded TMP reductions of 14 %, 24 % and 18 % for alum ferric chloride and SP 70 respectively. The results observed with the two PACl products and ferric chloride were attributed to under-dosing, where not enough coagulant was supplied to accommodate the particle concentration in the raw water. Alum was the sole coagulant whose equal molar dose was higher than the optimal dose (17 mg/L higher), therefore, a re-suspension of particles likely occurred, similar to results described with the jar test trials, and subsequently a smaller portion of the solids in the raw water flocculated, and more membrane fouling was observed.

3. Membrane trials conduced with modified mixing intensities, coupled with optimal coagulant doses yielded increased TMP's for all four coagulants in comparison to the base-line line trials. The elevated mixing intensity from 30 to 45 rpm resulted in a larger fraction of the flocs being transferred from the flocculation tank to the membrane tank. This contributed to a faster forming organic cake layer on the surface of the membrane. The increases were 24 %, 12 %, 17 % and 18 % for alum, ferric chloride, SP and SP 70 respectively. These results were heavily attributed to the design of the bench scale membrane treatment system which induced a larger concentration of flocs in the membrane tank.

4. Membrane trials conduced with modified raw water pH, coupled with optimal coagulant doses yielded a reduction in TMP membrane for all four coagulants when compared with trials conducted with no pH adjustment. The three aluminum based coagulants had their respective raw water pH levels lowered to 5.5, while the ferric chloride trial was conducted at a pH level of approximately 5.0. As

compared to the base-line trials, the differences in TMP were 4 %, 5 %, 6 % and 6 % for alum, ferric chloride, SP and SP 70 respectively.

5. Two membrane trials were conducted with half the optimal dose; these trials were carried out at doses of 15 mg/L and 20 mg/L for alum and SP respectively. As expected, these experiments results in severe under dosing of the coagulants, resulting in an elevated rate of TMP increase over the duration of the 3 day trial. The TOC removals for the half optimal dose trials were 42 % and 31 % for alum and SP respectively, as compared to 59 % and 52 % for the same coagulants, representing a decrease of 71 % and 60 % reduction for alum and SP respectively. The TOC removals were substantially lower as compared to the base-line optimal dose trials. These results were attributed entirely to the under-dosing of both coagulants. Shrive et al., (1999). These trends were also observed in the jar test trials, as the lower than optimal doses yielded minimal TOC removals for both coagulants.

6. Overall, the water quality results complemented the TMP trends observed during the membrane trials. High TOC removals were observed during the membrane trials conducted with optimal coagulant doses for both the Grand River and Lake Ontario water. The optimal Grand River trials yielded TOC removals of 59 %, 65 %, 52 % and 47 % for alum, ferric chloride, SP and SP 70 respectively. These results corresponded reasonably well with those observed during the jar test trials; which where 53 %, 39 %, 56 % and 64 % for the same order of coagulants. The TOC removals for the membrane trials conducted with Lake Ontario water yielded TOC removals of 36 %, 31 %, 30 % and 24 % for alum, ferric chloride, SP and SP 70 respectively Unlike the Grand River trials, these results did not correspond very well with the results obtained with the Lake Ontario jar test trials. The jar test TOC removals were substantially higher: 12 %, 19 %, 17 % and 18 % higher for alum, ferric chloride, SP and SP 70 respectively. This was attributed to the experimental conditions that were observed, as the jar test trials represented ideal coagulation conditions.

When the raw Grand River water pH was modified, TOC removals were slightly elevated, as a result of the optimized coagulation conditions. The removals were increased by 2-5 % across all four coagulants. The elevated mixing rates also caused a slight increase in TOC removal, although these results were countered with the fact that an increased rate of fouling was also observed**.** The TOC removals were increased by 2-3 %, except for the alum, which did not show an increased TOC removal.

7. The fractionation work conducted with raw and treated Grand River water was an innovative component of this research. The raw water fractionation experiments demonstrated that the majority of the TOC was distributed into two ranges; components larger than 30,000 Da, and small than 500 Da. The fractionation experiments conducted with treated water showed that the TOC fraction that was best removed by the pre-treatment membrane system was the largest fraction (larger than 30,000 Da). It was concluded that this fraction was responsible for the fouling, as it could have been removed by the coagulation process, and was potentially never exposed to the membrane surface. Further investigations would have to be conducted that included the fractionation of flocculated water, to make a more accurate assessment of what fractions of the NOM contributed to membrane fouling. The fractionation results did not vary a great deal when pH adjusted treated water was used, as compared to the base-line optimal dose treated water.

8. The residual metal analysis yielded very productive results. There were a total of six exceedances observed. Five trials conducted with the PACl products yielded exceedances These results were attributed to the coagulants reduced ability to perform the hydrolysis reactions to produce hydrogen ions. The only other results that stood out were those obtained with the equal molar dosing trial conducted with alum. This was attributed to the fact that the coagulant was over dosed, and the excess coagulant did not participate in the coagulation flocculation step,

subsequently it remained in solution and passed through the membrane pores, ending up in the permeate stream.

9. The TSS and conductivity analysis yielded results that were expected. The TSS of the raw and flocculated waters were similar, and the treated water TSS was consistently between 0.3 – 0.4 mg/L, yielding a 99 % TTS removal efficiency by the membrane. This was anticipated, as the UF membrane used throughout the duration of this project targeted particles that contribute to the TSS and turbidity of the water. The conductivity of the water was not affected by the treatment process, which was predicted given that neither the coagulation nor the membrane targeted the ions that contribute to conductivity. The only trend observed was that with the flocculated water values were elevated by 18-20 %, induced by the addition of the metal coagulants, whose ions contributed to the conductivity.

6.2 Recommendations

The following recommendations should be considered to expand upon the work completed for this thesis:

1. The following is a list of recommendations that should be considered if any future fractionation experiments are to be conducted surrounding this research:
    a. There are several fractionation methods that can be incorporated into drinking water treatment research. This project only utilized variation in the MWCO of the NOM. Future work should incorporate the hydrophobicity of the NOM, as the hydrophobic fraction of the NOM controls the coagulant demand (Sharp et al., 2006). This can be accomplished by performing resin fractionations on the raw and treated water, which separates the hydrophilic and hydrophobic fractions of the NOM. The combination of the methods would have the potential of producing results that would enhance the understanding of what fractions of the NOM contribute to fouling most.
    b. In order to be able to make a more accurate conclusion regarding what fractions of the NOM contribute to fouling most, the flocculated water would have to be fractionated as well. This project involved the fractionation of raw and treated waters, and not the water that exited the flocculation tank (floc water). Future experiments should involve the fraction of all three water types. This would allow the comparison of treated waters vs. floc water, in doing so, isolating the fraction of NOM that remained on surface and inside the pores of the membrane module

2. Another way to expand on this research, while still keeping the experimental design in tact, is to conducted trials with a membrane module position horizontally, as opposed to vertically, which is the way it was set up for the duration of the all the experiments. One of the fundamental flaws of the air sparging method is that there are only four

holes through which the air was able to exit. All four of these holes were located at the bottom of the module, resulting in an uneven distribution of air throughout the fibres. The bottom half of a vertically fixed module does not receive nearly as much air flow, given the vertical set-up and lack of air holes. All the air is propelled upwards, and exits between the fibres at the top of the module. Over the duration of a 3-day trial, the bottom half of the individual fibres were noticeably dark, with a larger amount of particles adsorbed to the surface. If the membrane was positioned horizontally, with more air holes distributed throughout the module, the air sparging would be able to reach nearly the entire length of the module, and subsequently a more consistent re-suspension of particles would occur. Figure 6-1 and Figure 6-2 highlight the differences between the two set-ups discussed.

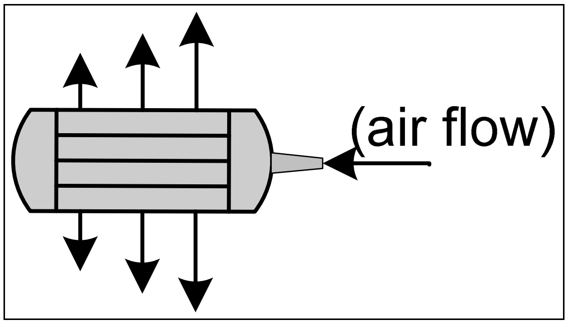


Figure 6-1: Horizontal air sparging

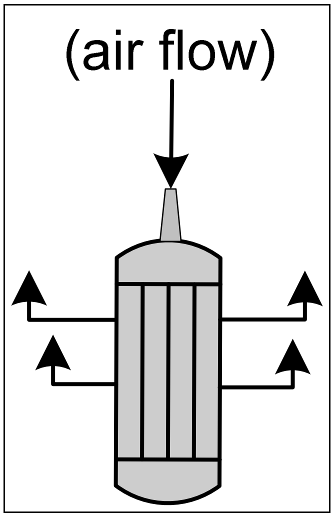


Figure 6-2: Vertical air sparging

The first figure shows the ideal set-up, where the air flows horizontally. Although it would be expected to observe the majority of the air bubbles escape through the first set of holes in the module, still the distribution would be much improved as compared to the later figure, which shows very little air sparging through the bottom half of the membrane.

3. Future experiments should be conducted with a similar experimental design, but with a micro-filtration membrane, as opposed to the ultra-filtration one used for all the experiments in this research. Some experiments suggest that micro-filtration membranes may be more affected by particulate matter than the ultra-filtration membranes used (Howe and Clark, 2006). It would be interesting to compare fouling rates, TOC/turbidity removals, and residual metal concentrations when a micro-filtration membrane is utilized.

4. Future experiments should also be conducted during different times of the year. All of the membrane trials were conducted between August and December 2006, and therefore no results were obtained to represent spring time conditions, where melting snow/run-off has a large effect on the NOM composition in the water. If this research was part of a PhD project, a selected few membrane trials would be

repeated every two months, so to able to assess how the seasonal variations effect fouling and TOC removal.

5. This experimental set-up was designed to simulate a settled water membrane treatment system. The majority of the generated flocs remained in the flocculation tank, but still there was a fraction that was transferred over to the membrane tank. This affected the results, demonstrated with the membrane trials conducted with an elevated mixing rate. The higher mixing rate induced the transfer of more flocs into the membrane tank, and subsequently more fouling occurred. It would be interesting to observe the fouling trends if a secondary tank was introduced, located between the flocculation tank and membrane tank. This would ensure that a very small amount of flocs made it to the membrane tank. This comparison would allow one to assess whether the flocs that were transferred during the trials with a 30 RPM mixing rate induced a more severe fouling effect.

REFERENCES

Aiken, G., Leenheer, J. and Woodside, G. (2004). Removal of Dissolved Organic Matter in a Subsurfaace Recharge System. *Natural Organic Matter Research: Innovations and Applications for Drinking Water.* Adelaide, Australia.

American Public Health Association. (1998). General Information on Turbidity. Washington, D.C.

APHA, AWWA, and WEF (2005). Standard Methods for the Examination of Water and Wastewater, Washington, D. C.

AWWA (1999). Water Quality and Treatment: A Handbook of Community Water Supplies. Fifth Edition. Raymond Letterman (Technical Editor). McGraw-Hill, Inc. Washington, D.C.

AWWA. (2000) Characterization of Natural Organic Matter in Drinking Water. Jean-Phillipe Croue (Technical Editor). American Water Works Association, Denver, Colorado.

AWWA. (2000) Operation Control of Coagulation and Filtration Processes. American Water Works Association, Denver, Colorado.

AWWA. (2005) Microfiltration and Ultrafiltration Membranes for Drinking Water, 1st Edition. American Water Works Association, Denver, Colorado.

Belfort, G., Davis, R. H. and Zydney, A. L. (1994). Behaviour of Suspensions and Macromolecular Solutions in Crossflow Microfiltration. *J. Memb. Sci.*, 96, 1-58.

Best, G. et al (2000). Application of Immersed Ultrafiltration Membranes for Color and TOC Removal. (unpubl).

Bodzek, M., Konieczny, K. (1998). Comparison of Various Membrane Types and Module Configurations in the Treatment of Natural Water by Means of Low-Pressure Membrane methods. *Separation and Purification Technology.* 14, 69-78.

Bottino, A., Capannelli, C., Del Borghi, A., Colombino, M., Conio, O. (2001). Water Treatment for Drinking Purpose: Ceramic Microfiltration Application. *Desal.,* 141(1), 75-79.

Carroll, T., King, S., Gray, S. R. Bolto, B. A. Booker, N. A. (2000). The Fouling of Micro-filtration Membranes by NOM After Coagulation Treatment. *Water Research.,* 34(11), 2861-2868.

Collins, M. R., Amy, G. L. Steelink, C. (1996). The Role of Natural Organic Matter during Formation of Chlorination By-products: A Review. *Environ. Sci. Technol.* 20: 1028-1032.

Combe, C., Molis, E., Lucas, P., Riley, R., Clark, M. (1999). The Effect of CA Membrane Properties on Adsorptive Fouling by Humic Acid. *J. Membr. Sci.* 154, 73-87.

Domany, Z., Galambos, I., Vatai, G. and Bekassy-Molnar E. (2002). Humic Substances Removal from Drinking Water by Membrane Filtration. *Desal.* 145: 333-337.

Droppo, I.G. and Ongley, E. D. (1994). Flocculation of Suspended Sediment in Rivers of Southeastern Canada. Elsever Science Ltd., *Water Research.,* 28(8), 1799-1809.

Edzwald, J.K. and Van Benschoten, J.E. (1990). Aluminium Coagulation of Natural Organic Matter. *Chemical Water and Wastewater Treatment*. © Springer-Verlag Berlin Heidelberg.

Farahbakhsh, K., Svrcek, C., Guest, R.K. and Smith, D.W. (2004). A Review of the Impact of Chemical Pre-treatment on Low-Pressure Water Treatment Membranes. *J. Environ. Eng. Sci*., 3, 237-253.

Fearing, D. A., Goslan, E. H., Banks, J., Wilson, D., Hillis, P., Campbell, A. T. and Parsons, S.A. (2004). Staged Coagulation for the Treatment of Reffractory Organics. *J. Environ. Eng.* 130(9), 975-982.

Gangloff, C. (2000). Membranes are on the Move. *Water Technology Magazine.,* Feb Edition.

GRCA (2006). Recharge and Discharge: Tracking Water as it Moves Through Ground. *Water Shed Report: 2006*.

Gregory, J. and Duan, J. (2001). Hydrolyzing Metal Salts as Coagulants. *Pure Appl. Chem.,* 73(12), 2017-2026.

Gregory, J. and Dupont, V. (2001). Properties of Flocs Produced by Water Treatment Coagulants. *Wat. Sci. & Tech.*, 44(10): 231-236.

Hannah, S.A., Cohen, J.M. and Roebeck, G.G. (1985). Measurement of Floc Strength by Particle Counting. *Jour. AWWA*, 69, 7, 843.

Howe, K.J. and Clark, M.M. (2002a). Coagulation Pretreatment for Membrane Filtration. AWWA Research Foundation Report, Denver, CO. p. 264.

Howe, K.J. and Clark, M.M. (2002b). Fouling of Microfiltration and Ultrafiltration Membranes by Natural Water. *Enviro. Sci. Tech.,* 36: 3576.

Howe, K.J. and Clark, M.M. (2006). Effect of Coagulation Pre-Treatment on Membrane Filtration Performance. *Jour. AWWA,* 98: 4.

Jacangelo, J. G., Trussell, R. R., Watson, M. (1997). Role of Membrane Technology in Drinking Water Treatment in the United States. *Desal.* 113: 119-127.

Jiang, J. (2001). Development of Coagulation Theory and Pre-Polymerized Coagulants for Water Treatment. *Separation and purification method,* 30(1): 127-141.

Jang, N.J., Watanabe, Y. and Minegishi, S. (2005). Performance of Ultrafiltration Membrane Process Combined with Coagulation/Sedimentation. *Wat. Sci. & Tech.,* 51(6-7): 209-219.

Jones, M.N. and Bryan, N.D. (1998). Colloidal Properties of Humic Substances. *Advances in Colloid and Interface Science,* 78: 1-48.

Jones, K. and O'Melia, C. (2000). Protein and Humic Acid Adsorption Onto Hydrophilic Membrane Surface: Effects of pH and Ionic Strength. *J. Membr. Sci.* 165: 31-46

Judd, S.J. and Hillis, P. (2001). Optimization of Combined Coagulation and Microfiltration for Water Treatment. *Water Res.,* 35(12): 2895.

Kabsch-Lorbutowicz, M. (2006). Impact of Pre-Coagulation on Ultrafiltration Process Performance. *Desal.,* 194, 232-238.

Karimi, A. A., Vickers, J.C. and Harasick, R.F. (1999). Microfiltration goes Hollywood: the Los Angelos Experience. Journal AWWA 91(6) June: 90-103.

Kimura, K., Hane, Y., Watanabe, Y. (2005). Effect of Pre-Coagulation on Mitigating Irrervisble Fouling During Microfiltration of a Surface Water. *Wat Sci & Tech.*, 51(6-7): 93-100.

Klijn, R. B., Van der meer, W. G. J., Vriezen, H., van Ekkendonk, F. H. J. (2000). Surface Water Treatment with Zenon Microfiltration Membranes: Minimization of Energy and Chemical use. *Desal.,* 131, 337-343.

Kokkola, H., Sorjamaa, R., Peraniemi, A., Raatikainen, T. and Laaksonen, A. (2006). Cloud Formation of Particles Containing Humic-like Substances. *Geophysical Research Letters.,* 33(10): L10816.

Laîné, J.M, Vial, D. and Moulart, P. (2000). Status after 10 years of Operation – Overview of UF Technology Today. Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Volume 1, Desalination Publications, L'Aquila, Italy. Paris, France: 17-25.

LeChevalier, M. W., Au, K. K. (2004). Water Treatment and Pathogen Control : Process Efficiency in Achieving Safe Drinking Water. World Health Organization, IWA Publishing.

Lee, J.D. et al. (2000). Effect of Coagulation Conditions on Membrane Filtration Characteristics in Coagulation-Micro-filtration Process for Water Treatment. *Envir. Sci.Technol.,* 34(17): 3780.

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(6): 4511-4523.

Leenheer, J.A., McKnight, D.M., Thurman, E.M., and MacCarthy, P. (1989). Structural Components and Proposed Structural Models for Suwannee River Fulvic Acid in Humic Substances in the Suwannee River, Georgia. *Geological Survey Open-File Report*. 87-557

Lin, C., Lin, T. and Hao, O.J. (2000). Effects of Humic Substance Characteristics on UF Performance. *Water Research.,* 34(4): 1097-1106.

Linhua, F., Harris, J. L., Roddick, F. A., Booker, N. A. (2001). Influence of the Characteristics of Natural Organic Matter on the Fouling of Microfiltration Membranes. *Water Research.,* 35(18): 4455-4463.

Maartens, A., Swart, P. and Jacobs, E.P. (1999). Feed-water Pretreatment: Methods to Reduce Membrane Fouling by Natural Organic Matter. *Journal of Membrane Science.,* 163: 51-62.

Mallevialle, J., Anselme, C., Marigny, O. (1989). Effects of Humic Substances on Membrane Processes. *Proceedings of the 193rd meeting of the American Chemical Society, Denver*., 749-767.

Marcel, M. (2004). Basic Principles of Membrane Technology, 2nd Edition. Kluwer Academic Publishers, UK.

Ministry of Environment. (2005). Drinking Water Surveillance Program (DWSP). Queen's printer for Ontario.

MWH. (2005). Water treatment – Principles & Design. 2nd Edition. John Wiley and Sons, Inc, NY.

Newcombe, G., Drikas, M. (2006). Natural Organic Matter: Understanding and Controlling the Impact on Water Quality and Water Treatment Processes. *WaterTECH: AWWA*. Sydney, Australia.

O'Melia, C.R, Becker, W.C., Au, K.K. (1999). Removal of Humic Substances by Coagulation. *Wat. Sci. & Tech.*, 40(9): 47-54.

Nicolaisen, B. (2002). Developments in Membrane Technology for Water Treatment. *Desal.,* 153: 355-360.

Nilson, J. A. and DiGiano, F.A. (1996). Influence of NOM Composition on Nanofiltration. Journal AWWA, 88(5): 53-66.

Panglisch, S., Dautzenberg, W., Kiepke, O., Gimbel, R. (2000). Ultra and Microfiltration in Drinking Water Production From Surface Water. *Water Supply.,* 18(1): 415-418.

Pontius, F. (1996). Regulatory Compliance Using Membrane Processes. Journal AWWA, May 88(5): 12-14

Randtke, S.J. (1988). Organic Contaminant Removal by Coagulation and Related Process Combinations. *Jour. AWWA*, 80(5): 40-56.

Richens, D.T. (1997). The Chemistry of Aqua Ions, Wiley: Chichester.

Ruohomaki, K. (1999). Characterization and Removal of Humic Substances in Ultra and Nanofiltration. *Water Supply.* 17(1): 293-303.

Schäfer, A.I., Fane, A.G., Waite, T.D. (2001). Cost Factors and Chemical Pretratment Effects in the Membrane Filtration of Waters Containing Natural Organic Matter. *Water Research.,* 35: 6: 1509.

Schäfer, A.I., Fane, A.G. and Waite, T.D. (2005). Nanofiltration: Principles and applications. Elsevier Ltd., NY.

Schäfer, A.I., Mauch, R., Fane, A.G. and Waite, T.D. (2002). Charge Effects in the Fractionation of Natural Organics Using Ultrafiltration. *Environ. Sci. Technol.* 36: 2572-2580.

Sharp, E.L., Parson, S.A. and Jefferson, B. (2006). Coagulation of NOM: linking character to treatment. *Wat. Sci. & Tech.*, 53(7): 67-76.

Sethi, S. and Wiesner, M.R. (2000). Simulated Cost Comparisons of Hollow Fiber and Integrated Nanofiltraton Configurations. *Water Research.* 34(9): 2589-2597.

Shrive, C.A. (1999). Assessment of Micro-filtration for Integration Into a Granular Activated Carbon Facility. Proc. 1999 AWWA Membrane Technology Conf., Long Beach, Calif.

Soffer, Y., Aim, R. B., Adin, A. (2005). Membrane Fouling and Selectivity Mechanisms in Effluent Ultrafiltration Coupled with Flocculation. *Wat. Sci. & Tech.*, 51(6-7): 123-134.

Singer, P.C. (1999). Formation and Control of Disinfection By-Products in Drinking Water.American Water Works Association, Denver, CO.

Takechi, T., Minegishi, T., Fukada, S., Ikeda, M., Kageyama, Y. (1998). Drinking Water Treatment Using Micro-Filtration Membrane. *NKK Technical Review.* July 7: 74-79.

Talley. D. et al. (AWWA), (2005). Operational Control of Coagulation and Filtration Processes 2nd Edition.

Taylor, J. S., Wiesner, M. (1999). Membranes, In: Letterman RD, ed. *Water Quality and Treatment.,* New York, McGraw hill, Inc., 11(1): 71.

Thanh, N.C., Hettiaratchi, J.P. (1982). Surface Water Filtration for Rural Areas: Guidelines for Design, Construction and Maintenance. Environmental Sanitation Information Centre, Bangkok, Thailand.

United States Census Bureau (USCB) (2006). World Population Information: International Programs Centre. Washington, D.C. 20233-8800.

Vial, D., Doussau, G. (2002). The use of microfiltration membranes for seawater pre-treatment prior to reverse osmosis membranes. *Desal.,* 153: 141-147.

Weishaar, J.K., Aiken, G.R., Mergamaschi, B.A., Fram, M.S., Fujii, R. and Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.*, 15:37(20): 4702-4708.

Westerhoff, G. P., Thompson, M. A., Vickers, J. C. (1996). Experiences in the Application of Microfiltration and Ultrafiltration Membrane Technology in Drinking-Water Treatment. *Water Supply.,* 14(3/4): 473-486.

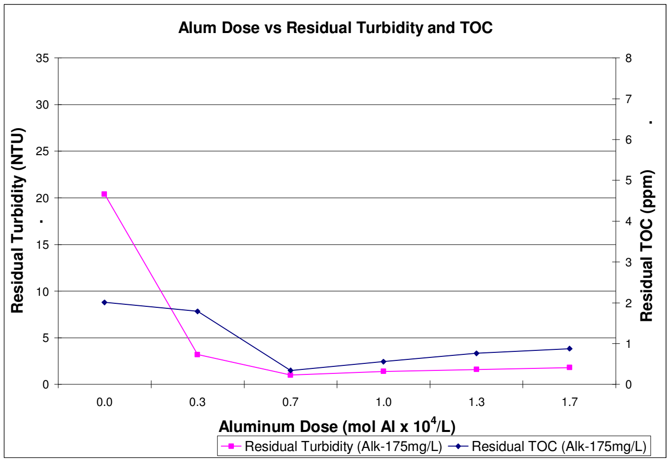
WHO and UNICEF. (2004). Global Water Supply and Sanitation Assessment 2004 Report. World Health Organization and United Nations Children's Fund.

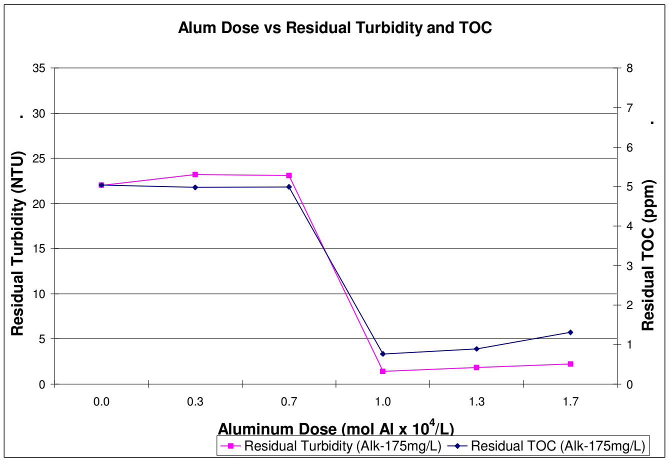
Zulariasm, A.W., Ismail, A.F. and Salim, R. (2006). Behaviours of Natural Organic Matter in Membrane Filtration for Surface Water Treatment – A Review. *Desal.,* 194: 211-231.

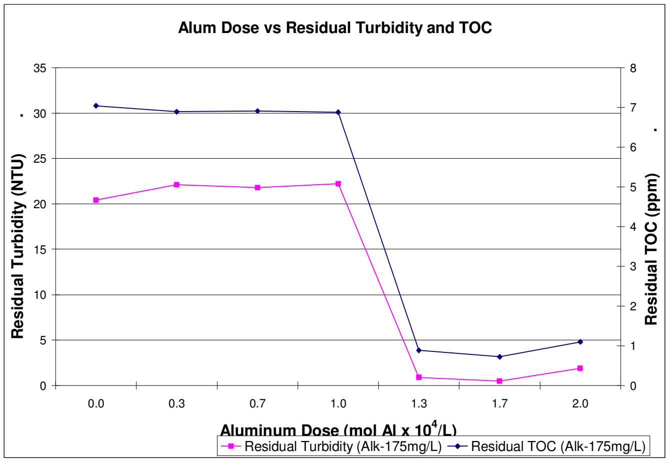
APPENDICES

APPENDIX A: SYNTHETIC WATER JAR TEST TRIALS SUMMARY PLOTS

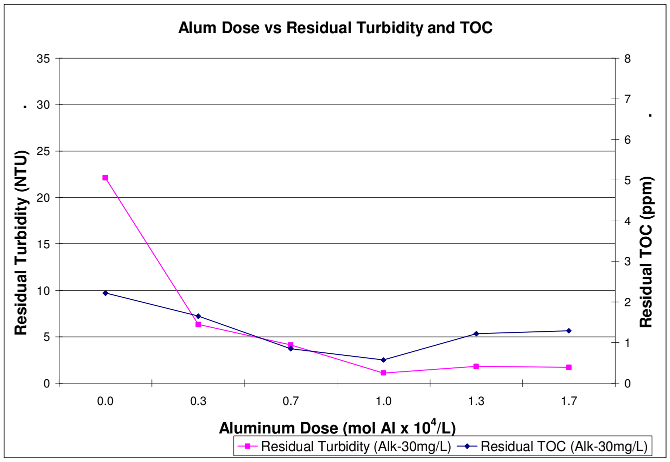
Figures A.1-A.3: Alkalinity – 175 mg $CaCO_3$/L, Turbidity – 20 NTU

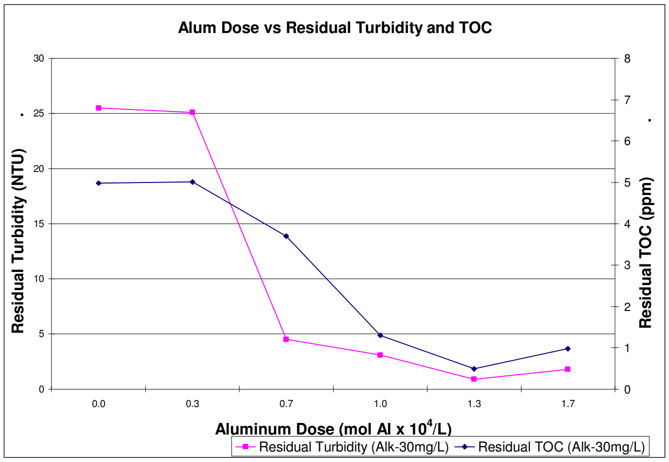


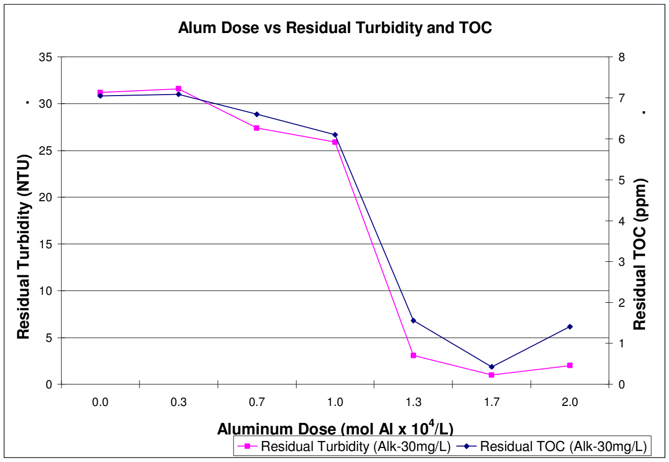




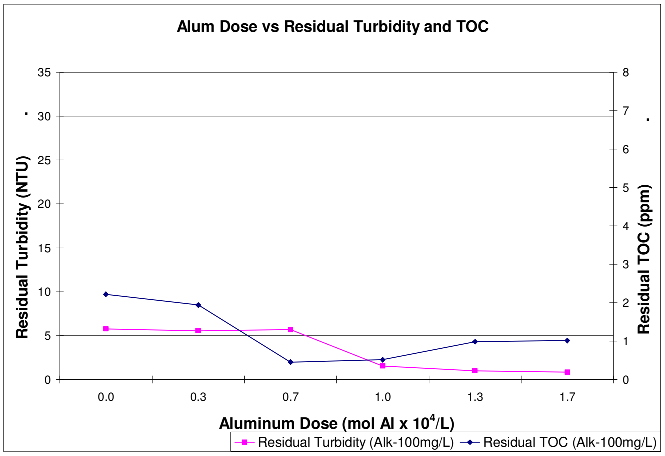
Figures A.4-A.6: Alkalinity – 30 mg CaCO$_3$/L, Turbidity – 20 NTU

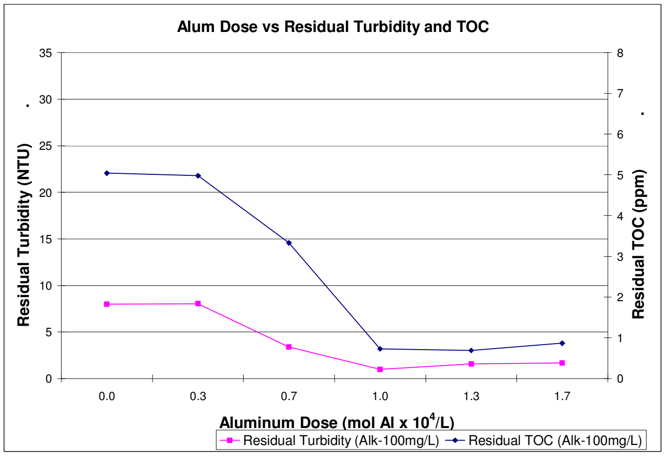


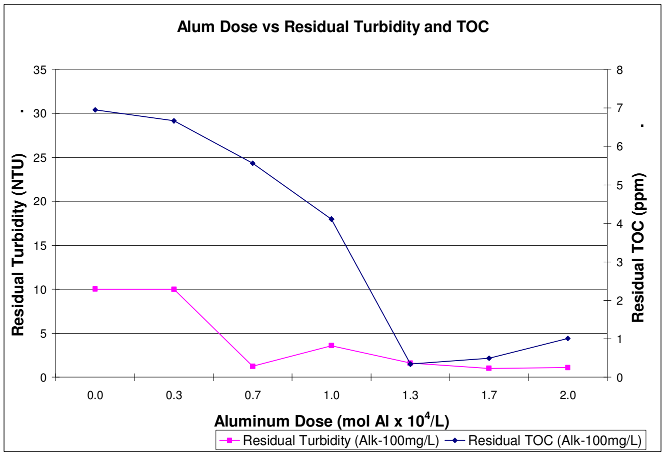




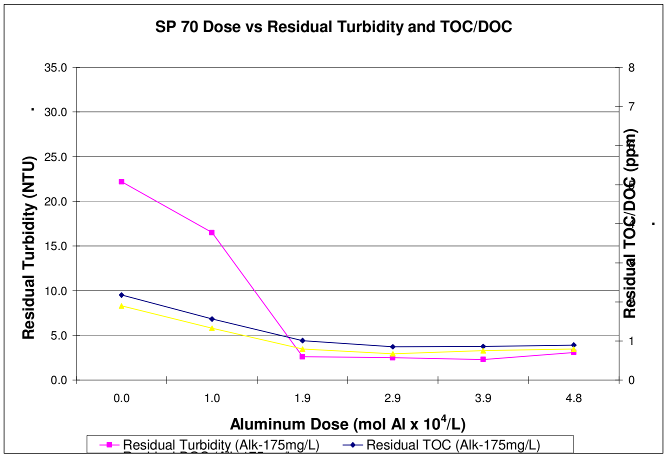
Figures A.7-A.9: Alkalinity – 175 mg CaCO$_3$/L, Turbidity – 5 NTU

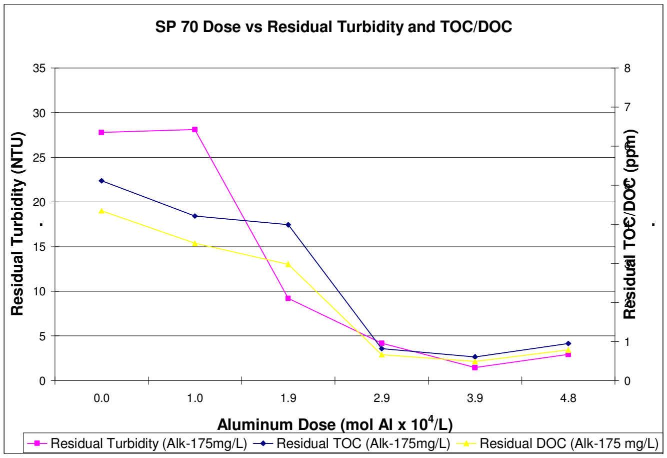


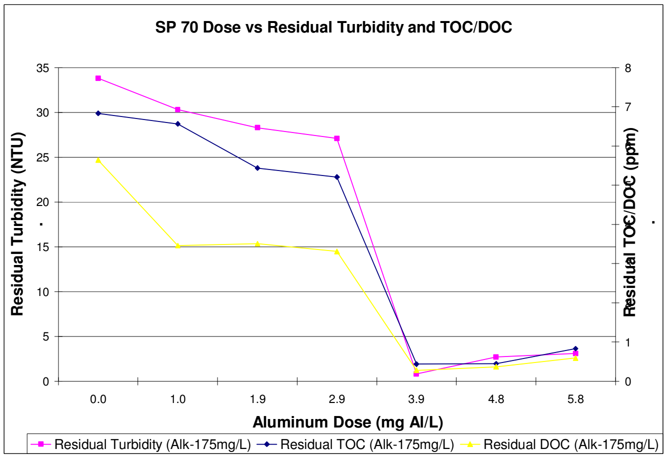




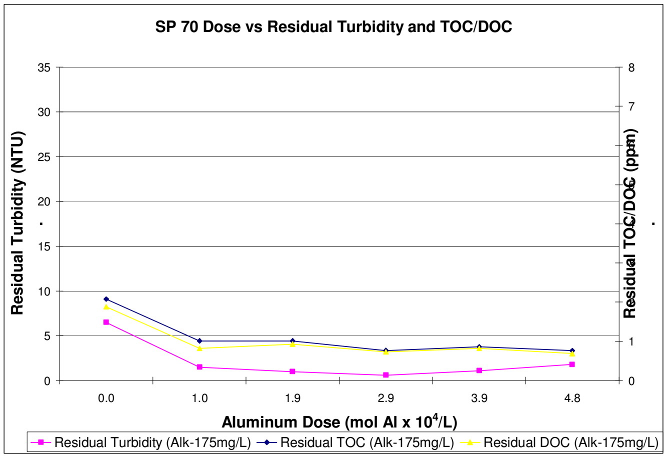
Figures A.10-A.12: Alkalinity – 175 mg $CaCO_3$/L, Turbidity – 20 NTU

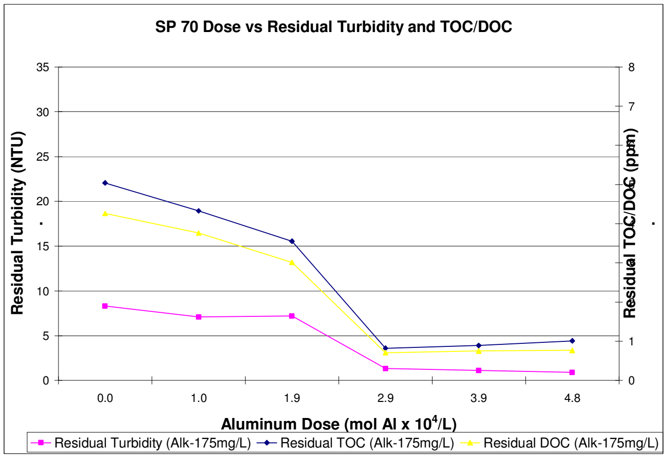


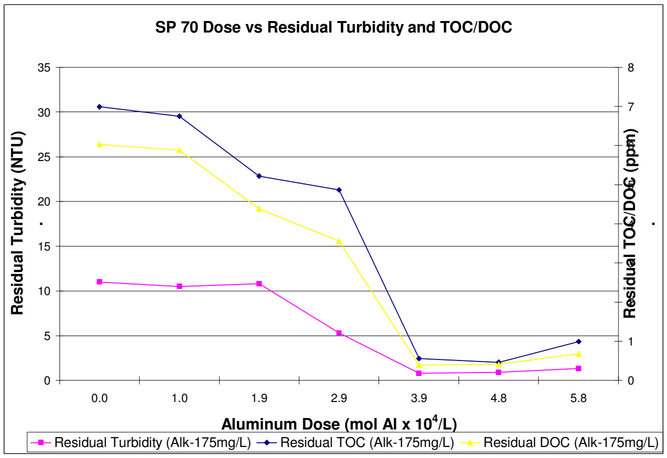




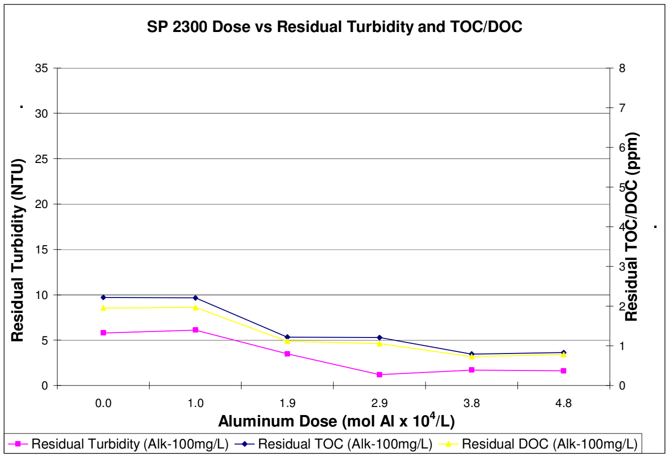
Figures A.13-A.15: Alkalinity – 175 mg CaCO$_3$/L, Turbidity – 5 NTU

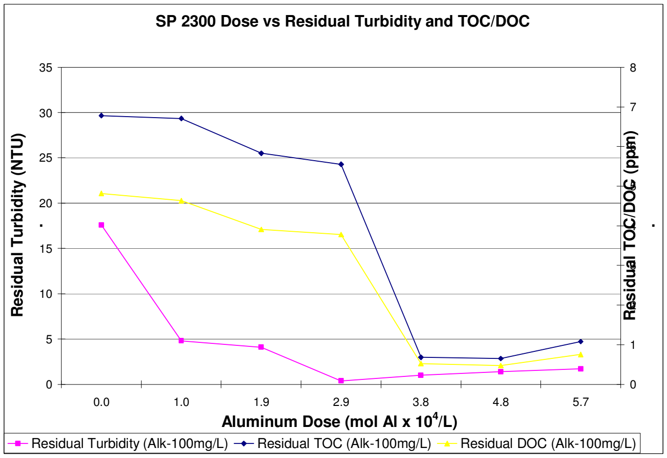


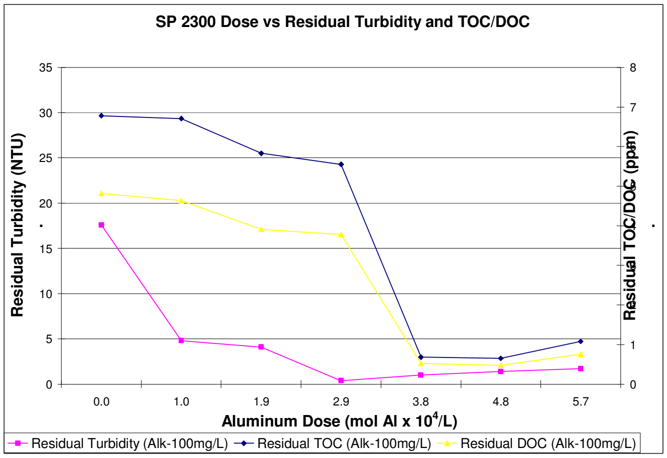




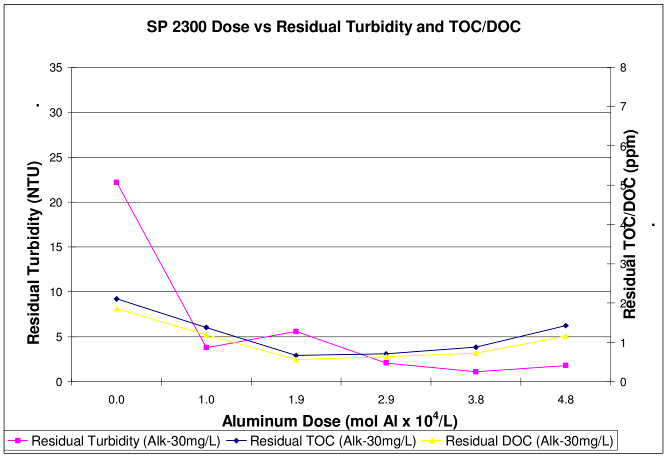
Figures A.16-A.18: Alkalinity – 100 mg $CaCO_3$/L, Turbidity – 5 NTU

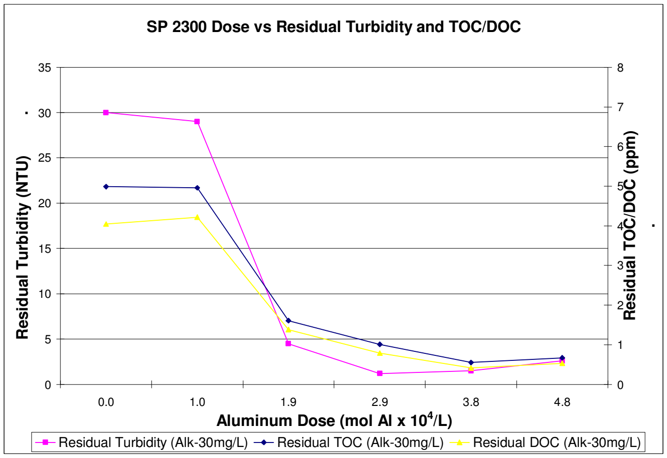


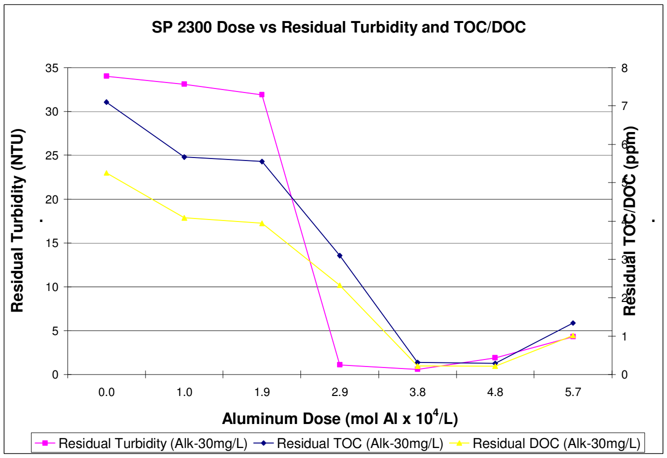




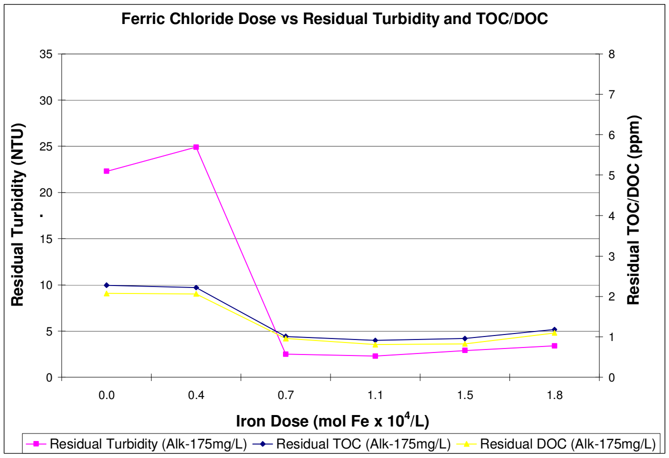
Figures A.19-A.21: Alkalinity – 30 mg $CaCO_3$/L, Turbidity – 20 NTU

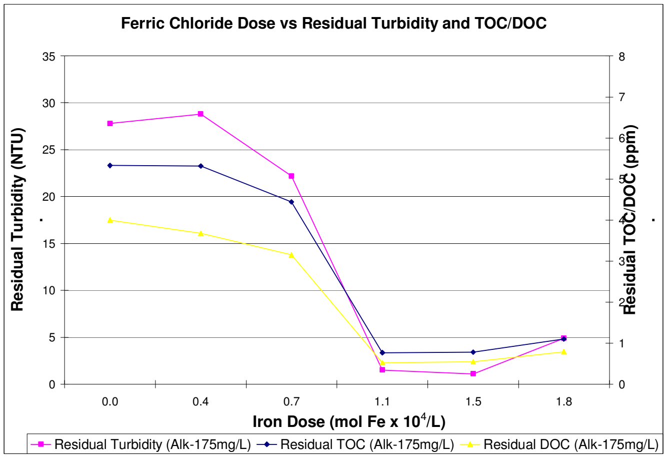


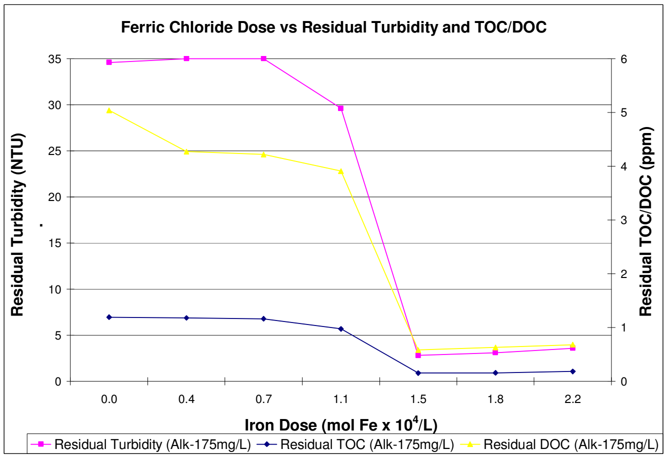




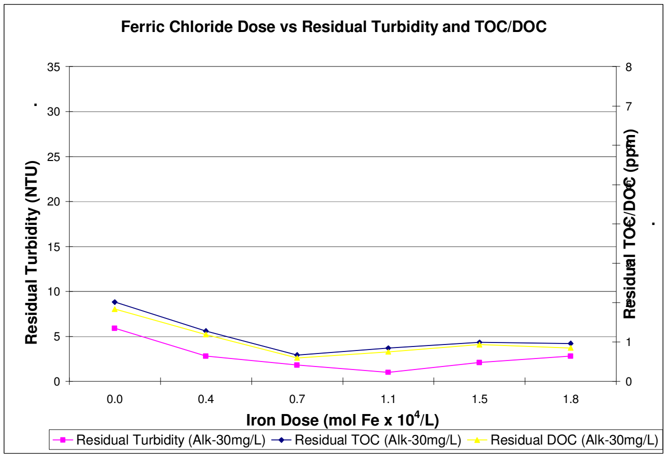
Figures A.22-A.24: Alkalinity – 175 mg $CaCO_3$/L, Turbidity – 20 NTU

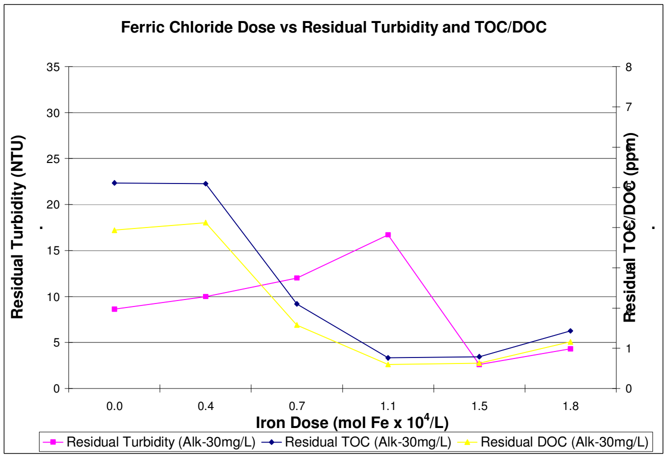


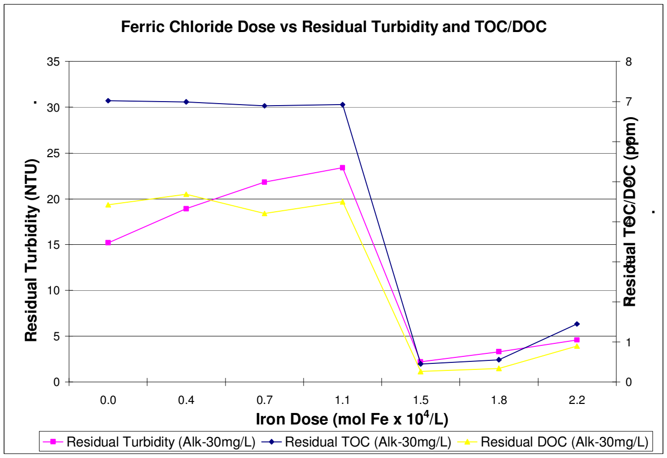




Figures A.25-A.27: Alkalinity – 30 mg CaCO$_3$/L, Turbidity – 20 NTU







APPENDIX B: JAR TEST TRIALS RAW DATA

Tables B.1-B.4: Lake Ontario jar test trials raw data

Date	5-May-06	
Coagulant	Alum	
Lake Ontario	2.51	mg/L TOC
Alkalinity	90-110	mg/L CaCO3
Turbidity	0.5-0.9	NTU

Jar #	**[Alum] mg/L)**	**(mol Al / L)**	**mol Al x 10^4/L**	**Temp (^oC)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0.0	13.1	0.62	0.61	0.01	8.13	8.13	0.00	N	2.5	0.0%	2.23	89.2%
2	5	2.9E-05	0.3	13.2	0.62	0.43	0.19	8.11	8.09	0.02	Y	2.21	11.6%	2.01	91.0%
3	**10**	**5.8E-05**	**0.6**	**13.1**	**0.65**	**0.21**	**0.44**	**8.18**	**7.99**	**0.19**	**Y**	**1.29**	**48.6%**	**1.19**	**92.2%**
4	**20**	**1.2E-04**	**1.2**	**13.0**	**0.69**	**0.2**	**0.47**	**8.17**	**7.81**	**0.36**	**Y**	**1.31**	**47.6%**	**1.3**	**99.2%**
5	30	**1.8E-04**	1.8	13.3	0.67	0.6	0.09	8.20	7.69	0.51	Y	1.67	**33.2%**	1.48	88.6%
6	40	2.3E-04	2.3	13.4	0.62	0.9	-0.27	8.19	7.58	0.61	Y	1.91	23.6%	1.65	86.4%

Date	5-May-06	
Coagulant	Ferric Chloride	
Lake Ontario	2.41	mg/L TOC
Alkalinity	90-110	mg/L CaCO3
Turbidity	0.5-0.9	NTU

Jar #	**[Alum] mg/L)**	**(mol Al / L)**	**mol Al x 10^4/L**	**Temp (^oC)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	13.1	0.61	0.6	0.03	8.22	8.23	-0.01	N	2.41	0.0%	2.21	91.7%
2	5	3.1E-05	0.3	13.2	0.66	0.43	0.23	8.19	8.17	0.02	N	2.03	15.8%	1.84	90.6%
3	10	6.2E-05	0.6	13.1	0.67	0.39	0.28	8.23	8.04	0.19	Y	1.68	30.3%	1.48	88.1%
4	**20**	**1.2E-04**	**1.2**	**13.0**	**0.70**	**0.15**	**0.55**	**8.20**	**7.81**	**0.39**	**Y**	**1.12**	**53.5%**	**0.99**	**88.4%**
5	30	1.8E-04	1.8	13.3	0.68	0.85	-0.17	8.23	7.58	0.65	Y	1.54	36.1%	1.28	83.1%
6	40	2.5E-04	2.5	13.4	0.69	0.99	-0.30	8.19	7.44	0.75	Y	1.98	17.8%	1.77	89.4%

Date	5-May-06	
Coagulant	SP 70	
Lake Ontario	2.47	mg/L TOC
Alkalinity	90-110	mg/L CaCO3
Turbidity	0.5-0.9	NTU

Jar #	**[Alum] mg/L)**	**(mol Al / L)**	**mol Al x 10^4/L**	**Temp (^{o}C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	13.1	0.58	0.59	-0.01	8.18	8.17	0.01	N	2.47	0.0%	2.23	90.3%
2	5	4.9E-05	0.5	13.2	0.62	0.51	0.11	8.19	8.14	0.05	N	2.45	0.8%	2.04	83.3%
3	10	9.7E-05	1.0	13.1	0.61	0.48	0.13	8.20	8.06	0.14	Y	1.89	23.2%	1.68	88.9%
4	20	1.9E-04	1.9	**13.0**	**0.59**	**0.40**	0.19	**8.14**	**7.94**	**0.20**	**Y**	**1.42**	**42.0%**	**1.31**	**92.3%**
5	30	2.9E-04	2.9	13.3	0.58	0.41	0.17	8.14	7.85	0.29	Y	1.78	27.6%	1.64	92.1%
6	40	3.9E-04	3.9	13.4	0.63	0.49	0.14	8.19	7.79	0.40	Y	1.86	24.4%	1.66	89.2%

Date	5-May-06	
Coagulant	SP	
Lake Ontario	2.49	mg/L TOC
Alkalinity	90-110	mg/L CaCO3
Turbidity	0.5-0.9	NTU

Jar #	**[Alum] mg/L)**	**(mol Al / L)**	**mol Al x 10^4/L**	**Temp (^{o}C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	13.1	0.66	0.65	0.01	8.11	8.09	0.02	N	2.49	0.0%	2.28	91.6%
2	5	4.6E-05	0.5	13.2	0.68	0.87	-0.19	8.14	8.03	0.11	N	2.41	3.2%	2.19	90.9%
3	**10**	**9.2E-05**	**0.9**	**13.1**	**0.65**	**0.16**	**0.49**	8.14	**7.99**	**0.15**	**Y**	**1.31**	**47.2%**	**1.18**	**90.1%**
4	20	1.8E-04	1.8	**13.0**	**0.69**	**0.15**	**19.5**	**8.19**	**7.92**	**0.27**	**Y**	**1.33**	**46.4%**	**1.09**	**82.0%**
5	30	2.8E-04	2.8	13.3	0.60	0.78	-0.18	8.14	7.82	0.32	Y	1.81	27.2%	1.55	85.6%
6	40	3.7E-04	3.7	13.4	0.61	0.82	-0.21	8.20	7.79	0.41	Y	1.95	21.6%	1.73	88.7%

Tables B.5-B.8: Grand River jar test trials raw data

Date	10-Feb-06	
Coagulant	Alum	
Grand River	5.31	mg/L TOC
Alkalinity	150-200	mg/L CaCO3
Turbidity	7-8.5	NTU

Jar #	**[Alum] mg/L)**	**(mol Al / L)**	**mol Al x 10^4/L**	**Temp (°C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0.0	23.1	7.9	7.8	0.10	7.91	7.90	0.01	N	5.31	0.0%	5.02	94.5%
2	20	1.2E-04	1.2	23.1	8.1	1.4	6.72	7.88	7.61	0.27	Y	2.91	45.2%	2.4	82.5%
3	30	**1.8E-04**	1.8	23.1	8.2	1.3	6.90	7.83	7.53	0.30	Y	2.38	**55.2%**	2.10	88.2%
4	40	2.3E-04	2.3	23.3	7.9	0.7	7.20	7.91	7.42	0.49	Y	2.61	50.8%	2.24	85.8%
5	50	2.9E-04	2.9	23.2	8.0	0.5	7.50	7.92	7.30	0.62	Y	2.9	45.4%	2.7	93.1%
6	60	3.5E-04	3.5	23.1	8.2	0.7	7.50	7.94	7.21	0.73	Y	2.7	49.2%	2.5	92.6%

Date	10-Feb-06	
Coagulant	Ferric Chloride	
Grand River	5.31	mg/L TOC
Alkalinity	175	mg/L CaCO3
Turbidity	7-8.5	NTU

Jar #	**[FicC] mg/L)**	**(mol Fe / L)**	**mol Fe x 10^4/L**	**Temp (°C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	23.1	7.9	8.0	-0.10	7.91	7.88	0.03	N	5.31	0.0%	5.02	94.5%
2	20	1.2E-04	1.2	23.1	8.1	9.8	-1.70	7.88	7.60	0.28	Y	4.713	11.2%	4.03	85.5%
3	30	1.8E-04	1.8	23.1	8.2	3.1	5.10	7.88	7.55	0.33	Y	3.58	32.6%	3.01	84.1%
4	40	**2.5E-04**	2.5	23.3	7.9	1.1	6.80	7.87	7.48	0.39	Y	3.17	**40.3%**	2.76	87.1%
5	50	**3.1E-04**	3.1	23.2	8.0	1.5	6.50	7.86	7.31	0.55	Y	3.37	36.5%	2.86	84.9%
6	60	3.7E-04	3.7	23.1	8.2	2.1	6.07	7.91	7.05	0.86	Y	3.1	41.6%	2.51	81.0%

Date	10-Feb-06	
Coagulant	SP 70	
Grand River	5.31	mg/L TOC
Alkalinity	175	mg/L CaCO3
Turbidity	7-8.5	NTU

Jar #	**[FicC] mg/L)**	**(mol Fe / L)**	**mol Fe x 10^4/L**	**Temp (^{o}C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	23.1	8.10	8	0.1	7.86	7.86	0.00	N	5.31	0.0%	5.02	94.5%
2	20	1.9E-04	1.9	23.1	8.00	0.87	7.13	7.88	7.74	0.14	Y	2.94	44.6%	2.62	89.1%
3	30	2.9E-04	2.9	23.1	7.90	0.54	7.36	7.88	7.68	0.20	Y	2.56	51.8%	2.33	91.0%
4	40	3.9E-04	3.9	23.3	8.10	0.77	19.5	7.87	7.61	0.26	Y	2.09	60.6%	1.82	87.1%
5	50	4.9E-04	4.9	23.2	8.20	0.88	7.32	7.86	7.54	0.32	Y	1.84	**65.3%**	1.64	89.1%
6	60	5.8E-04	5.8	23.1	8.00	2.1	5.9	7.88	7.42	0.46	Y	1.97	62.9%	1.7	86.3%

Date	22-Aug-06	
Coagulant	SP	
Grand River	5.44	mg/L TOC
Alkalinity	181	mg/L CaCO3
Turbidity	9.2	NTU

Jar #	**[FicC] mg/L)**	**(mol Fe / L)**	**mol Fe x 10^4/L**	**Temp (^{o}C)**	**Turbidity (NTU)**			**pH**			**Floc**	**TOC**	**% removal**	**DOC**	**DOC %**
					before	**after**	**Δ**	**before**	**after**	**Δ**	**(Y/N)**				
1	0	0	0	23.1	9.20	9.1	0.1	7.86	7.86	0.00	N	5.44	0.0%	5.02	92.3%
2	20	1.8E-04	1.8	23.1	9.40	0.87	8.53	7.88	7.78	0.10	Y	3.32	37.5%	3.11	93.7%
3	30	2.8E-04	2.8	23.1	9.50	0.54	8.96	7.88	7.65	0.23	Y	2.28	57.1%	2.14	93.9%
4	40	3.7E-04	3.7	23.3	9.10	0.77	19.5	7.87	7.42	0.45	Y	1.77	**66.7%**	1.59	89.8%
5	50	4.6E-04	4.6	23.2	9.40	0.88	8.52	7.86	7.40	0.46	Y	1.73	**67.4%**	1.62	93.6%
6	60	5.5E-04	5.5	23.1	9.60	2.1	7.5	7.88	7.28	0.60	Y	3.11	41.4%	2.88	92.6%

APPENDIX C: RAW TRANS-MEMBRANE PRESSURE PLOTS

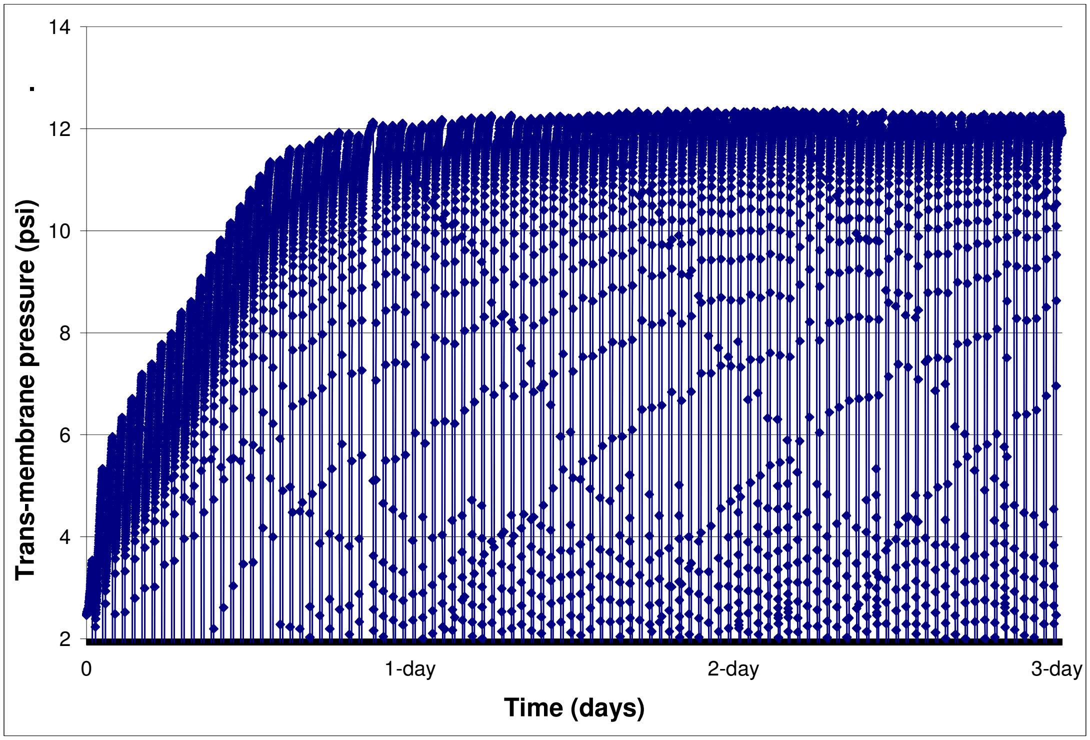


Figure C.1: Grand River water 3 day membrane trial
(No pre-treatment)

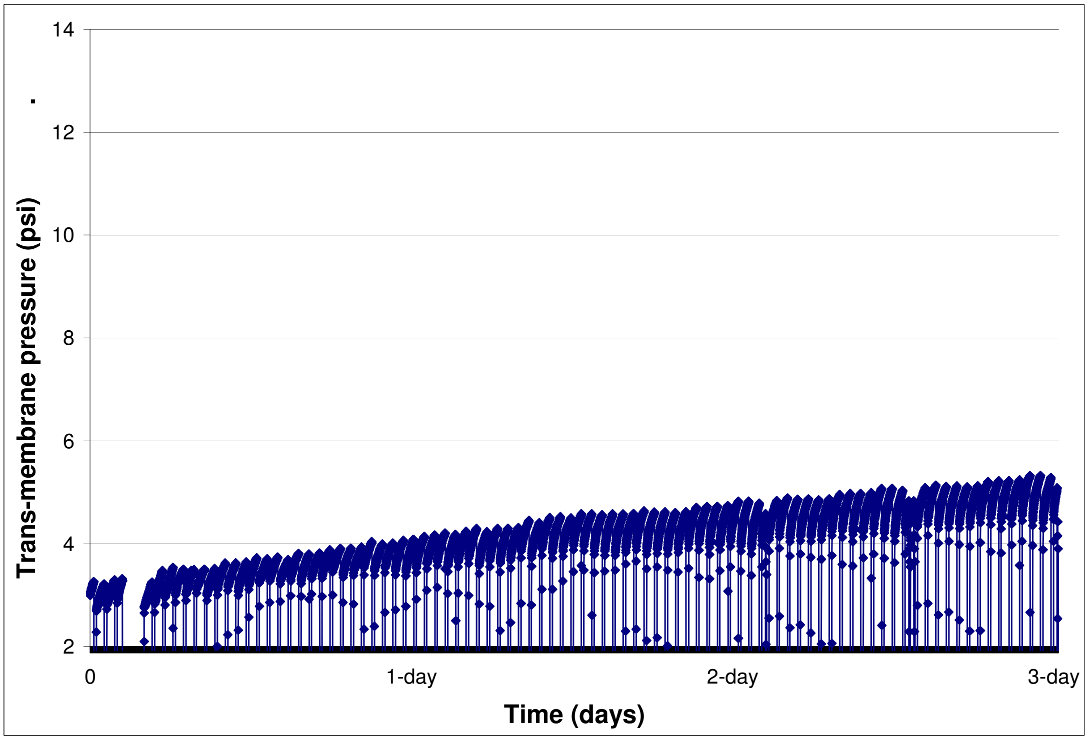


Figure C.2: Raw Grand River water - 3 day membrane trial
(30 mg/L alum pre-treatment)

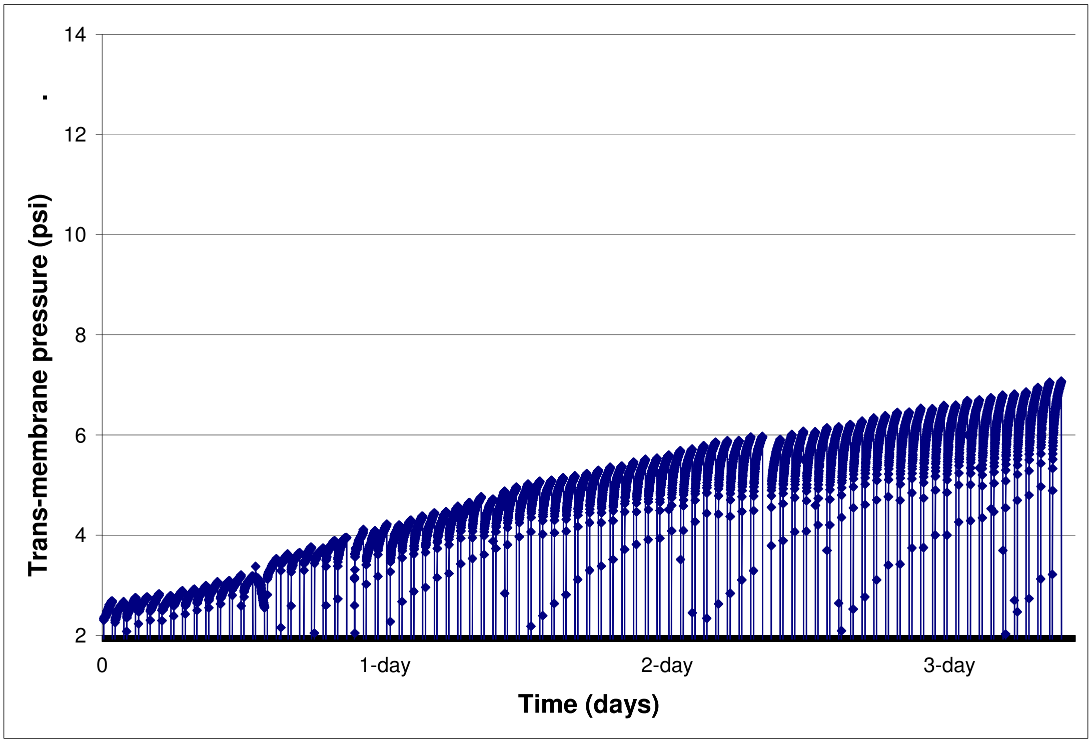


Figure C.3: Raw Grand River water - 3 day membrane trial
(45 mg/L ferric chloride pre-treatment)

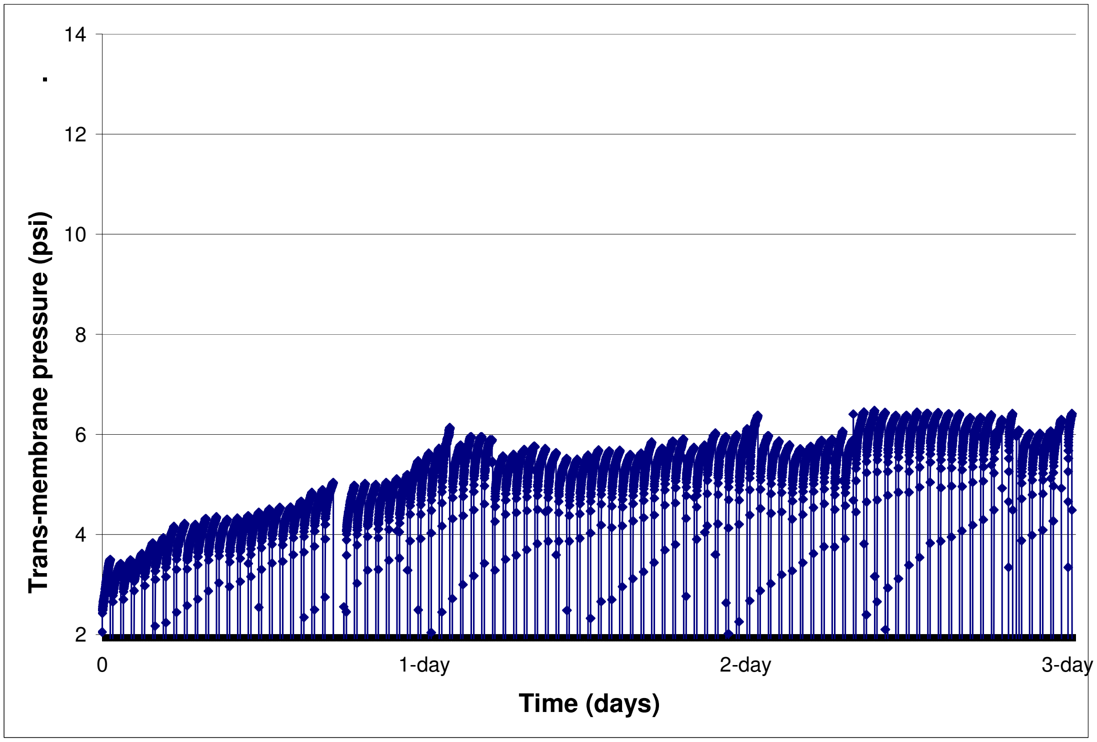


Figure C.4: Raw Grand River water - 3 day membrane trial
(40 mg/L PACl (SP) pre-treatment)

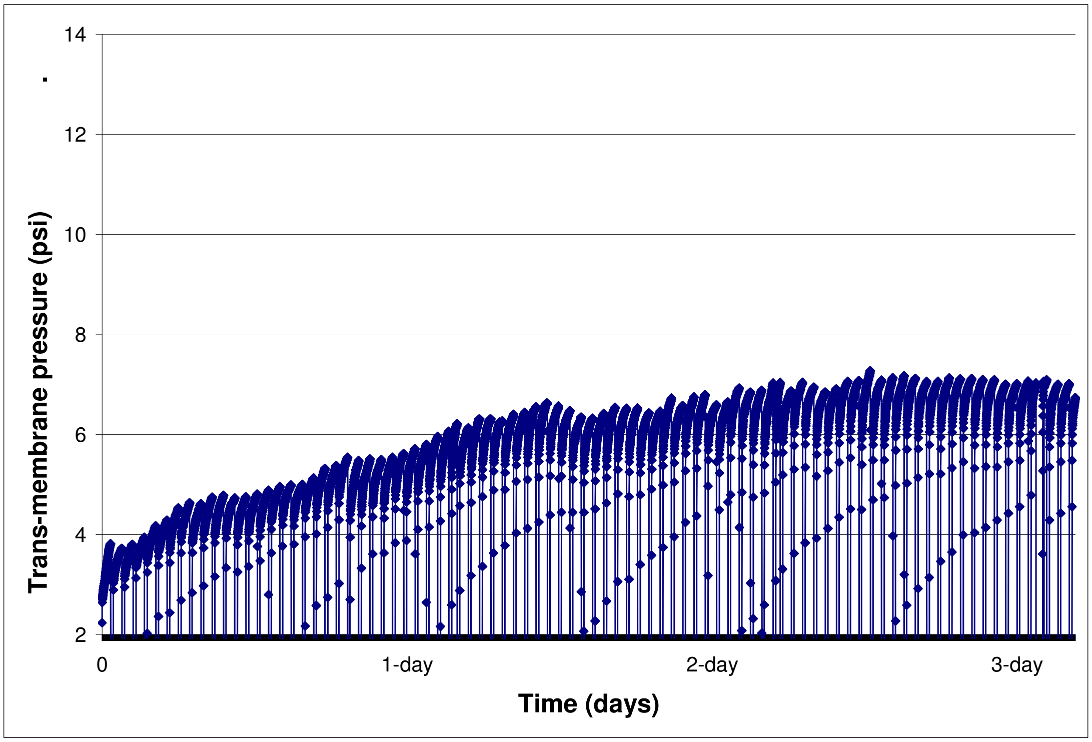


Figure C.5: Raw Grand River water - 3 day membrane trial
(50 mg/L PACl (SP 70) pre-treatment)

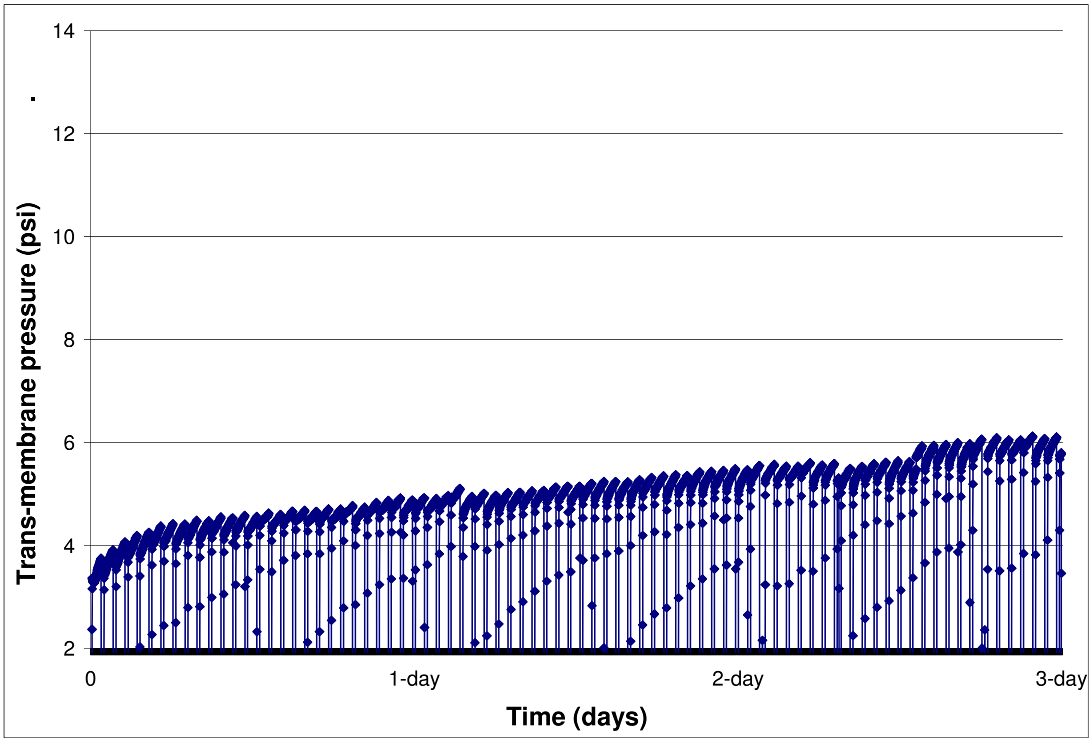


Figure C.6: Raw Lake Ontario water - 3 day membrane trial
(No pre-treatment)

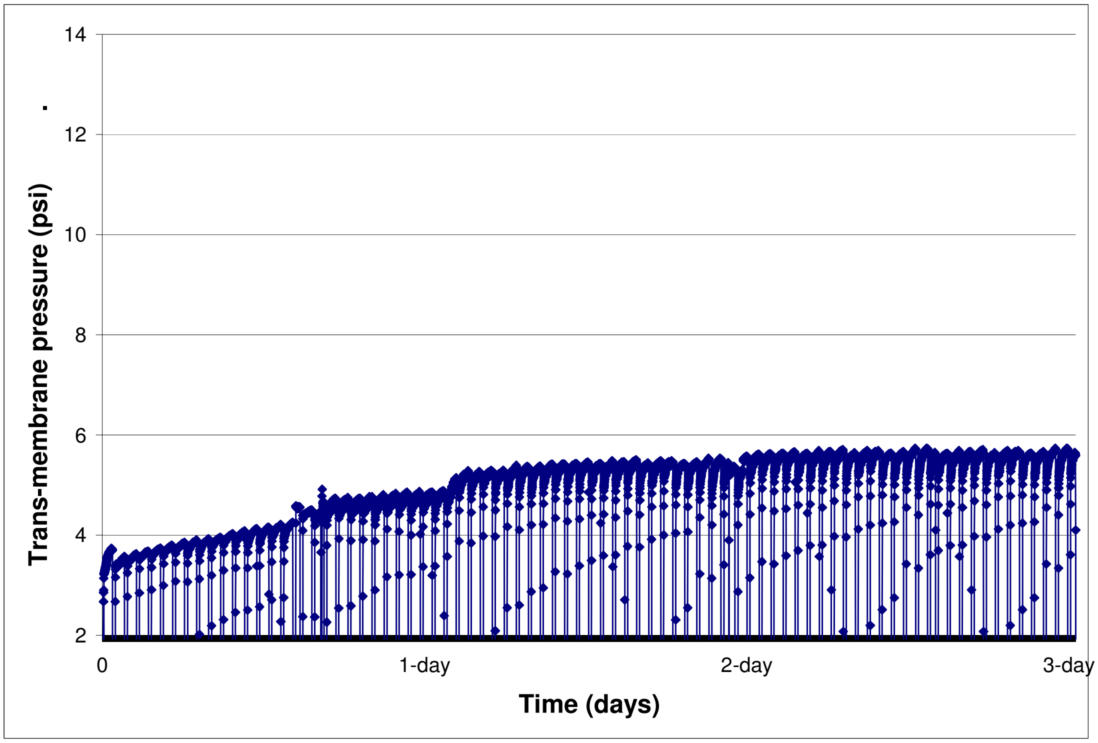


Figure C.7: Raw Lake Ontario water - 3 day membrane trial (15 mg/L alum pre-treatment)

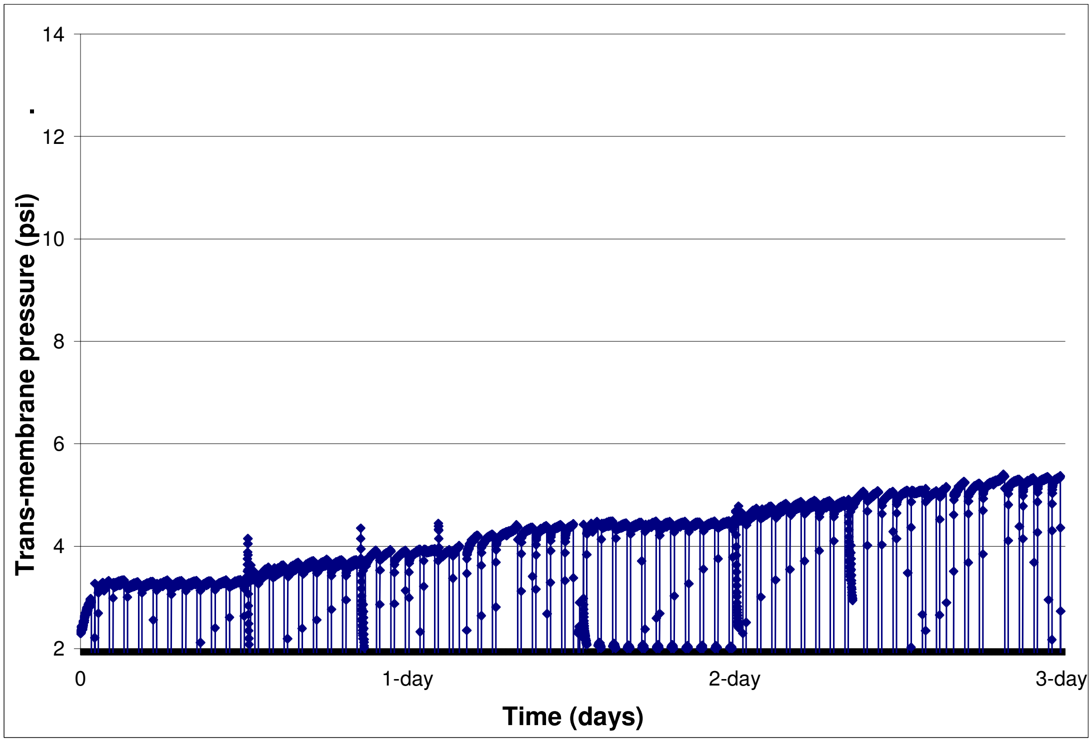


Figure C.8: Raw Lake Ontario water - 3 day membrane trial (20 mg/L ferric chloride pre-treatment)

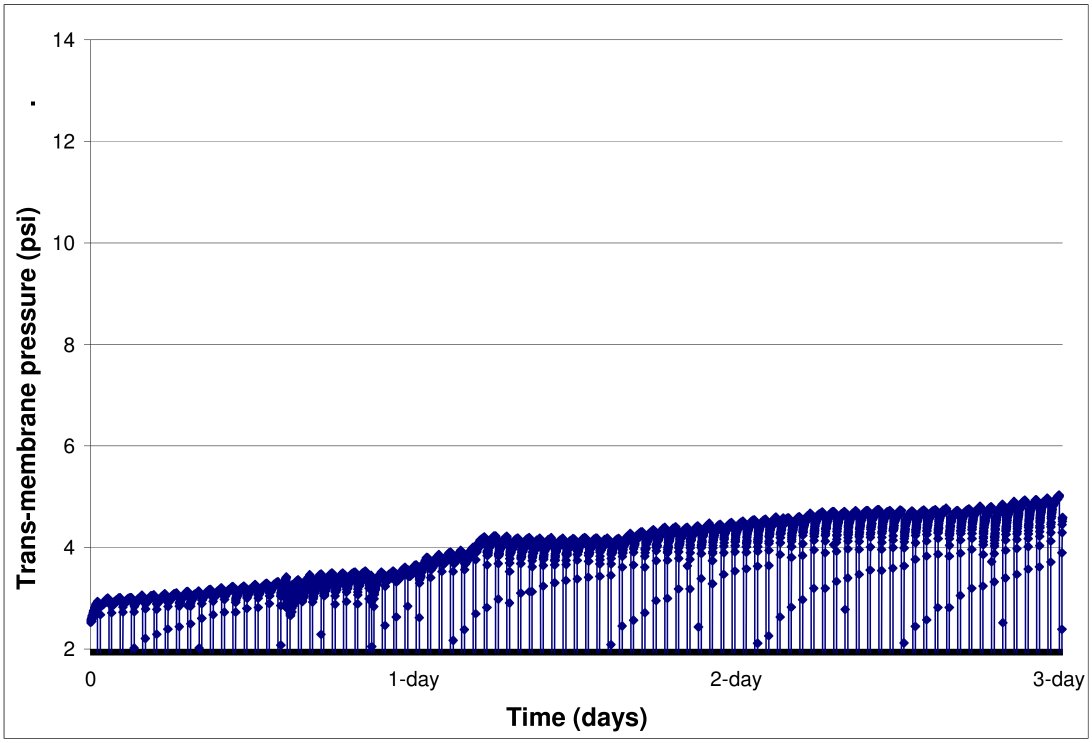


Figure C.9: Raw Lake Ontario water - 3 day membrane trial
(20 mg/L PACl (SP 70) pre-treatment)

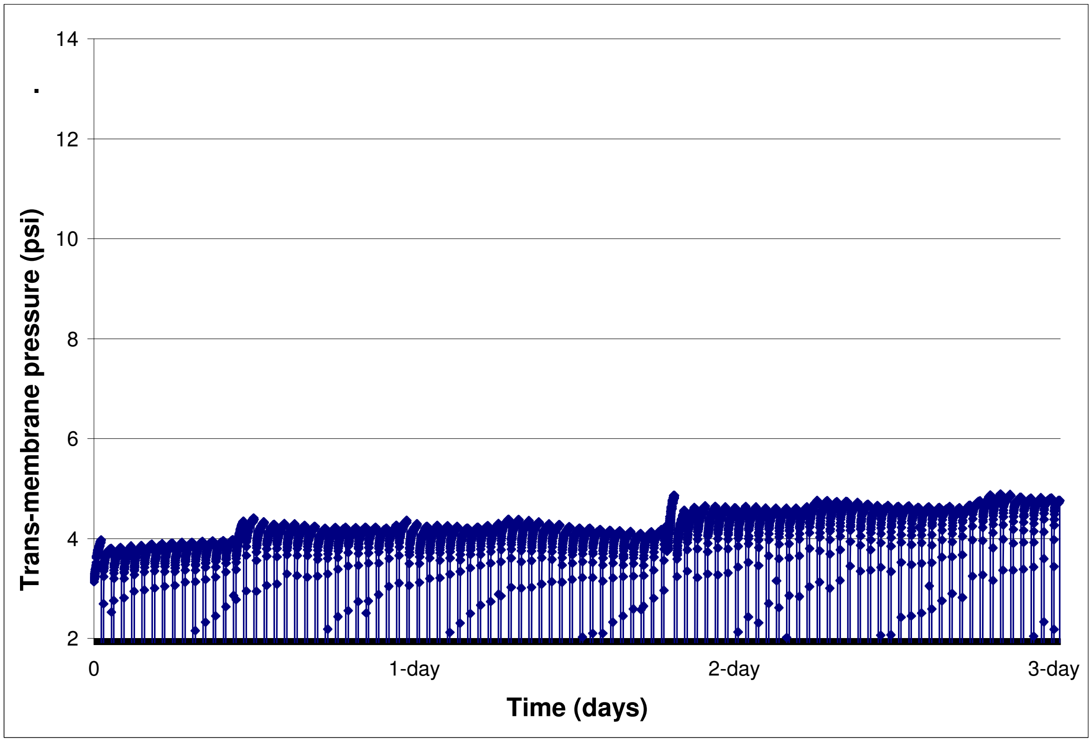


Figure C.10: Raw Grand River water - 3 day membrane trial
(15 mg/L PACl (SP) pre-treatment)

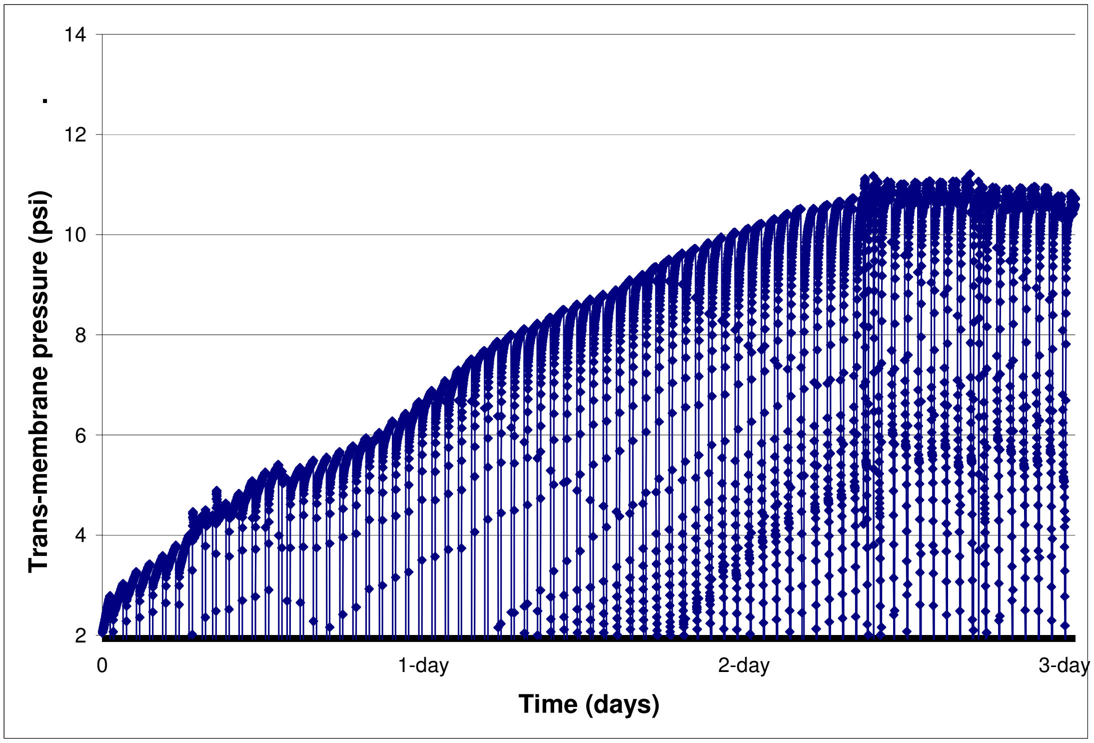


Figure C.11: Raw Grand River water - 3 day membrane trial (equal molar metal dose 7.5 x 10^{-5} mol Al/L, alum pre-treatment)

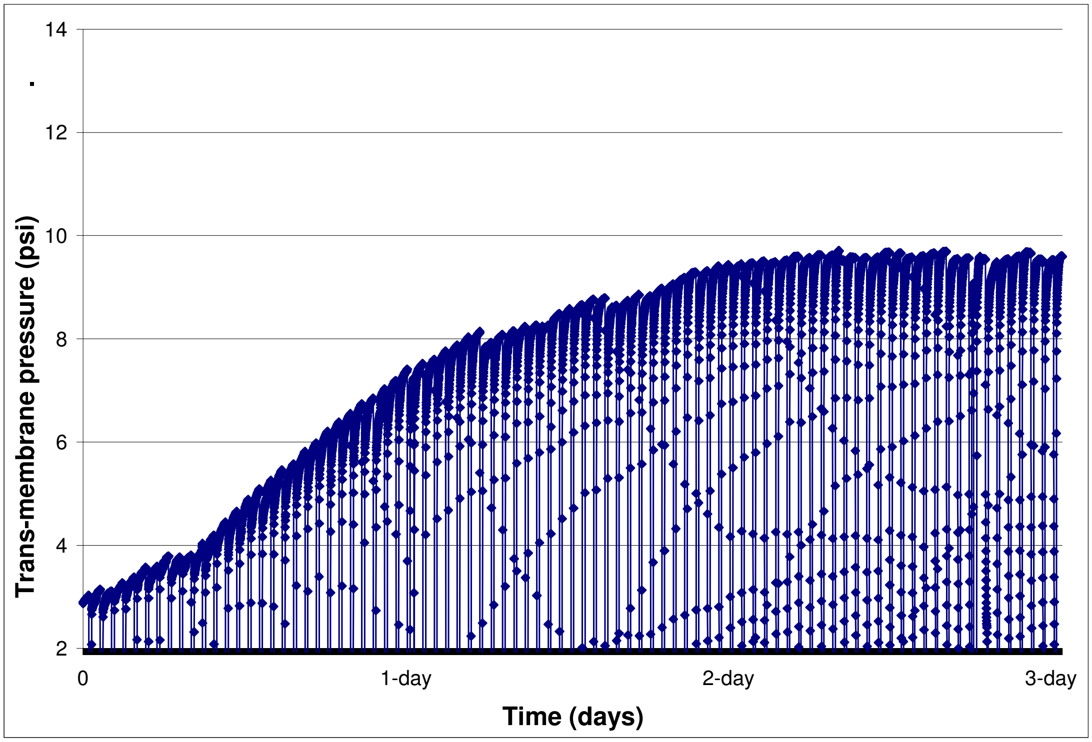


Figure C.12: Raw Grand River water - 3 day membrane trial (equal molar metal dose 7.5 x 10^{-5} mol Fe/L, ferric chloride pre-treatment)

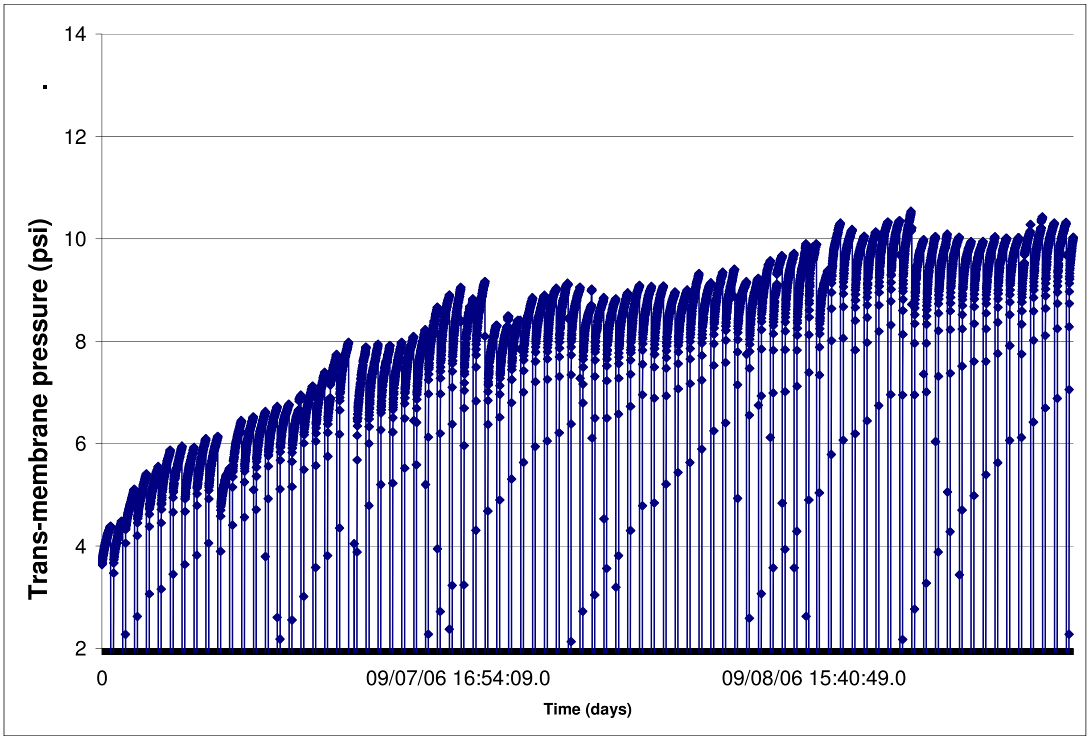


Figure C.13: Raw Grand River water - 3 day membrane trial (equal molar metal dose 7.5 x 10^{-5} mol Al/L, SP 70 pre-treatment)

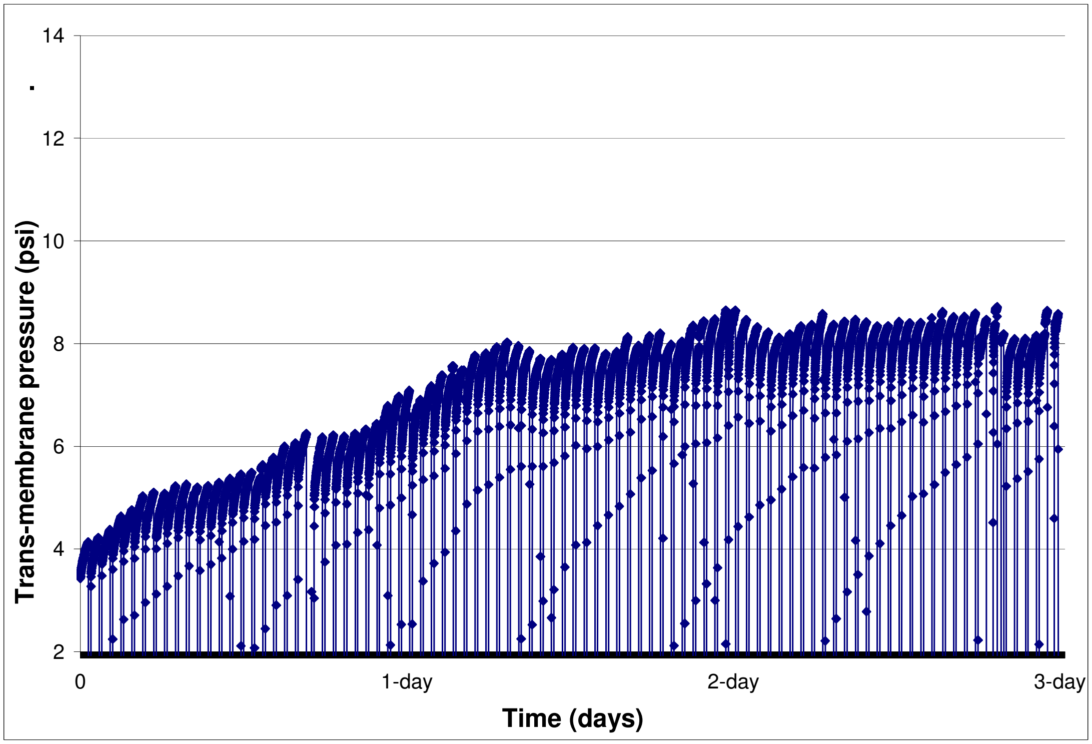


Figure C.14: Raw Grand River water - 3 day membrane trial (equal molar metal dose 7.5 x 10^{-5} mol Al/L, SP pre-treatment)

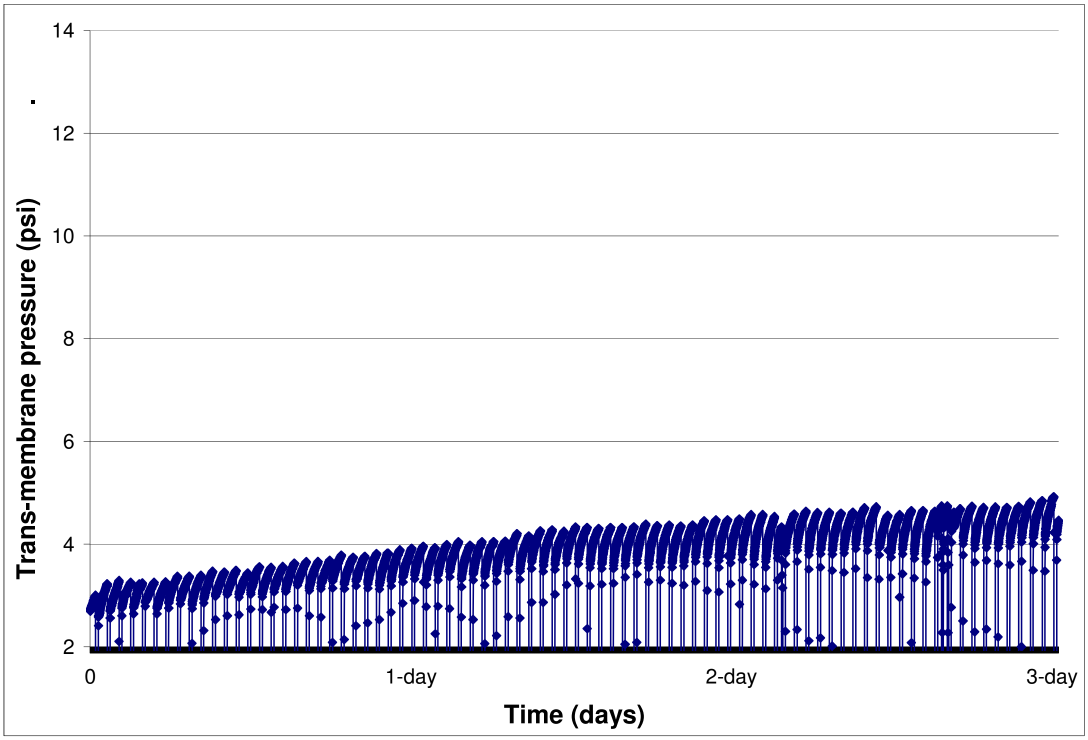


Figure C.15: Raw Grand River water - 3 day membrane trial (modified raw water pH, alum pre-treatment)

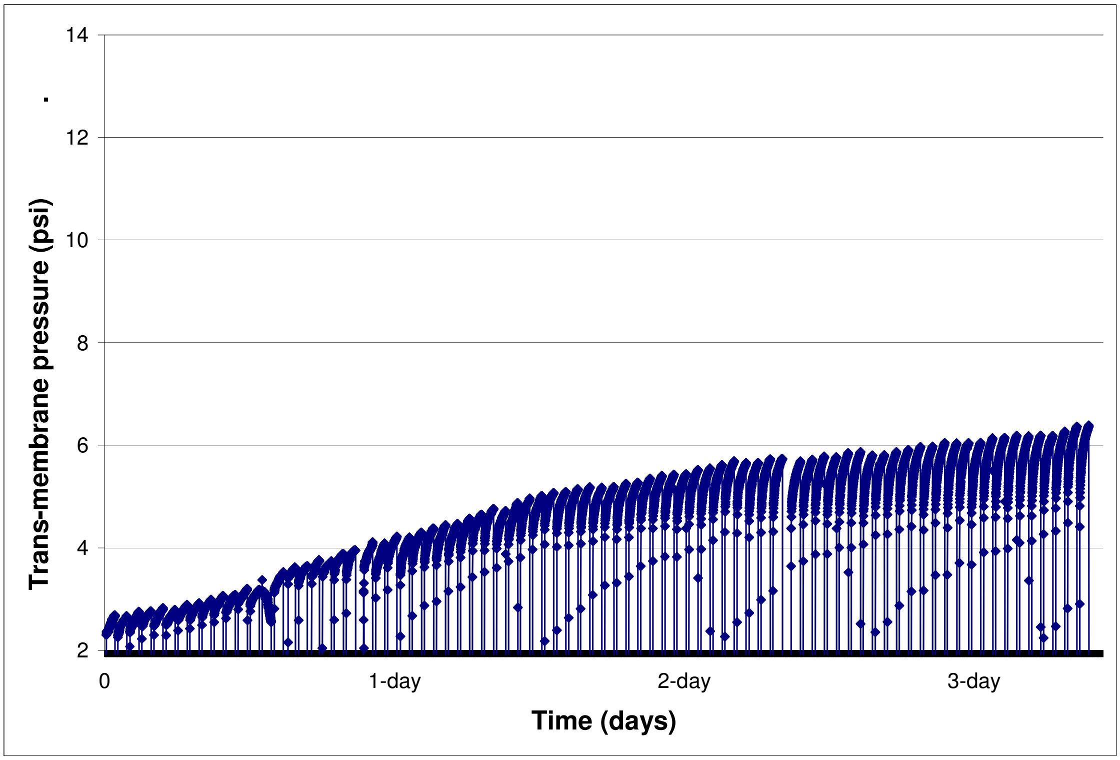


Figure C.16: Raw Grand River water - 3 day membrane trial (modified raw water pH, ferric chloride pre-treatment)

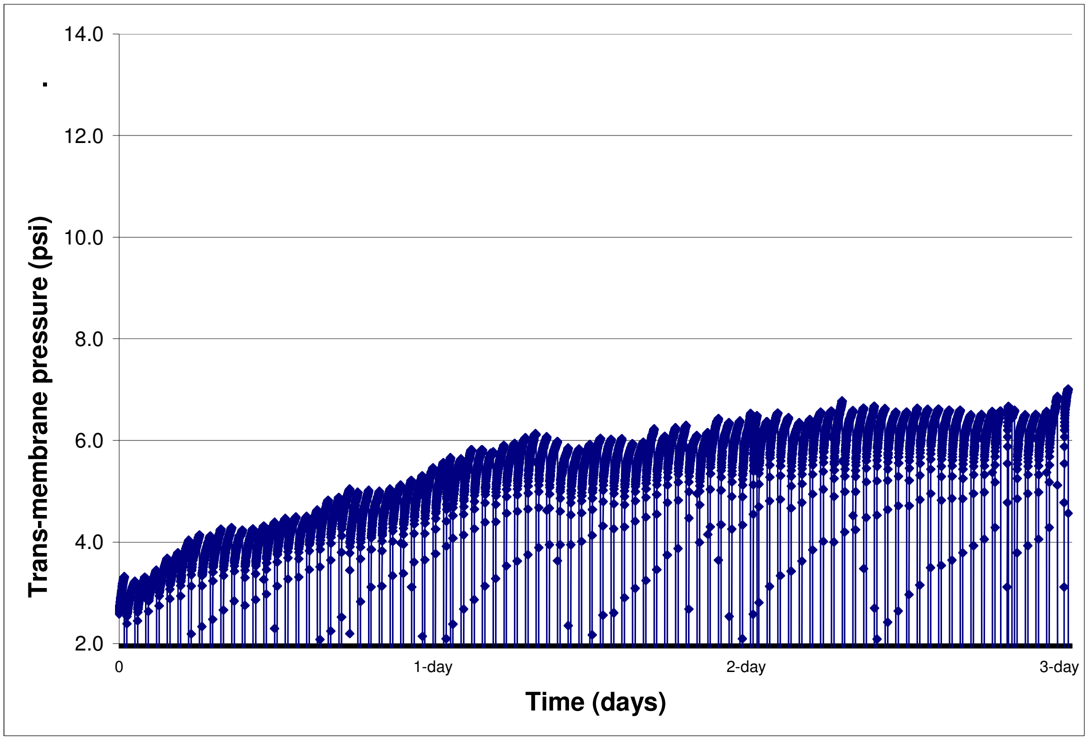


Figure C.17: Raw Grand River water - 3 day membrane trial
(modified raw water pH, SP 70 pre-treatment)

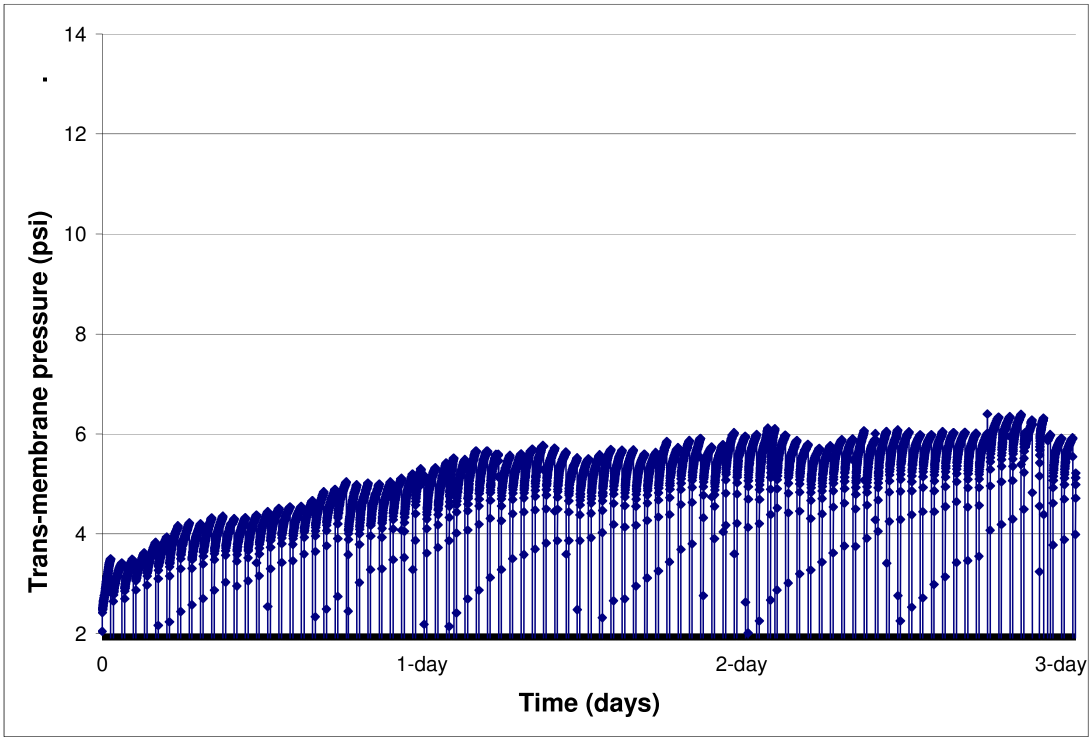


Figure C.18: Raw Grand River water - 3 day membrane trial
(modified raw water pH, SP pre-treatment)

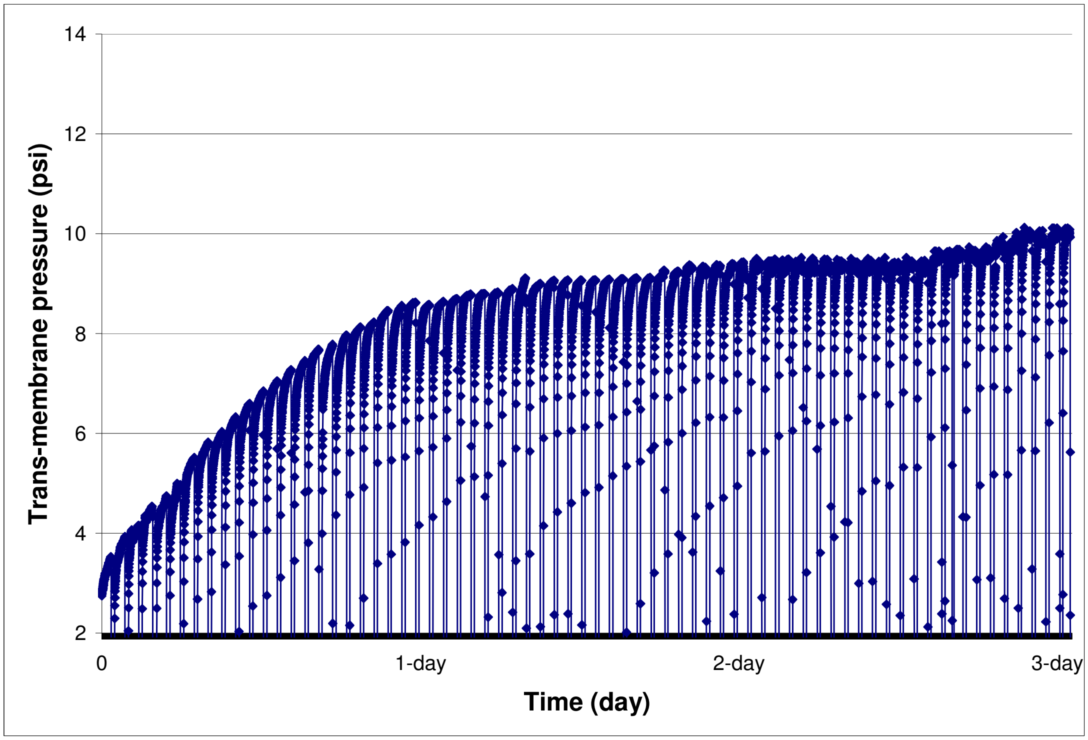


Figure C.19: Raw Grand River water - 3 day membrane trial
(half optimal dose – 20 mg/L, SP pre-treatment)

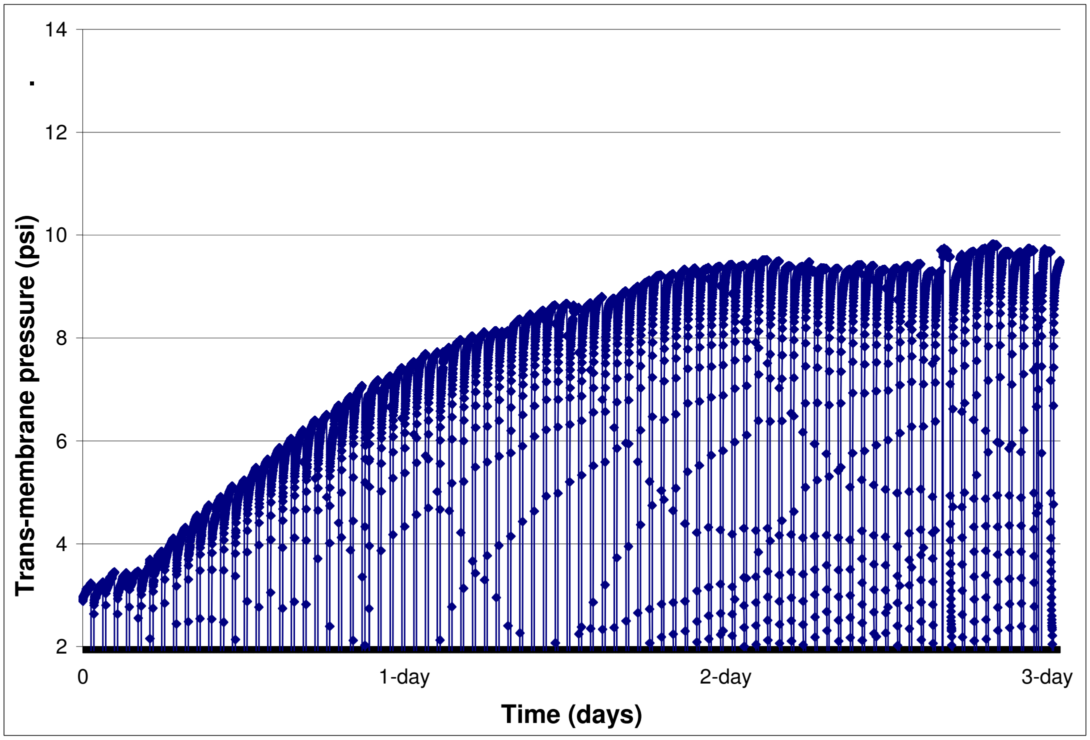


Figure C.20: Raw Grand River water - 3 day membrane trial
(half optimal dose – 15 mg/L, alum pre-treatment)

APPENDIX D: MEMBRANE TRIALS WATER QUALITY DATA

Tables D.1-D.5: Grand River membrane trials data using optimal coagulant doses

Trials #	1
Date	30-Jul-06
Coagulant	None
Dose	None
Source water	Grand River
pH	8.1

Sample time	TOC	DOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.54	6.22	10.12	-	7.81	-
1-day	5.79	5.75	0.11	-	7.68	11.5%
2-day	5.81	5.77	0.10	-	7.77	11.2%
3-day	5.85	5.83	0.08	-	7.59	10.6%

Trials #	2
Date	4-Aug
Coagulant	Alum
Dose	30 mg/L
Source water	Grand River
pH	8.1

Sample time	TOC	DOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.62	6.25	10.12	-	7.81	-
1-day	2.69	2.6	0.11	2.88	7.11	59.4%
2-day	2.7	2.64	0.10	2.79	7.21	59.2%
3-day	2.64	2.58	0.10	2.91	7.09	60.1%

Trials #	3
Date	11-Aug
Coagulant	Ferric chloride
Dose	45 mg/L
Source water	Grand River
pH	7.88

Sample time	TOC	DOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.71	6.29	9.23	-	7.89	-
1-day	2.32	2.28	0.08	2.34	7.29	65.4%
2-day	2.22	2.19	0.06	2.89	7.30	66.9%
3-day	2.27	2.23	0.11	3.11	7.22	66.2%

Trials #	4
Date	25-Aug
Coagulant	SP 70
Dose	50 mg/L
Source water	Grand River
pH	7.88

Sample time	TOC	DOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.36	5.99	8.12	-	7.93	-
1-day	3.4	3.31	0.12	3.1	7.48	46.5%
2-day	3.29	3.28	0.08	3.19	7.61	48.3%
3-day	3.31	3.7	0.09	2.41	7.56	48.0%

Trials #	5
Date	11-Sep
Coagulant	SP
Dose	40 mg/L
Source water	Grand River
pH	7.88

Sample time	TOC	DOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.17	5.61	5.21	-	7.91	-
1-day	3.05	3.38	0.1	2.12	7.41	50.6%
2-day	2.92	3.16	0.06	2.56	7.38	52.7%
3-day	2.9	3.3	0.09	1.99	7.44	53.0%

Tables D.6-D.10: Lake Ontario membrane trials data using optimal coagulant doses

Trials #	6
Date	4-Oct
Coagulant	None
Dose	None
Source water	Lake Ontario
pH	8.04

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	2.72	2.34	N/A	0.61	N/A	8.11	-
1-day	2.363	2.33	N/A	0.06	N/A	8.08	13.1%
2-day	2.247	2.2	N/A	0.04	N/A	8.12	17.4%
3-day	2.248	2.21	N/A	0.07	N/A	8.14	17.4%

Trials #	7
Date	9-Oct
Coagulant	alum
Dose	15 mg/L
Source water	Lake Ontario
pH	8.23

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	2.78	2.22	-	5.21	-	7.91	-
1-day	1.71	1.7	2.09	0.1	0.38	7.51	38.5%
2-day	1.82	1.78	2.13	0.06	0.29	7.48	34.5%
3-day	1.76	1.73	2.31	0.09	0.41	7.44	36.7%

Trials #	8
Date	5-0ct-2006
Coagulant	FC
Dose	20 mg/L
Source water	Lake Ontario
pH	8.32

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	2.633	2.21	-	0.66	-	8.11	-
1-day	1.74	1.71	2.561	0.08	0.61	7.39	33.9%
2-day	1.87	1.78	2.489	0.06	0.53	7.32	29.0%
3-day	1.81	1.77	2.451	0.05	0.52	7.29	31.3%

Trials #	9
Date	17-Sep
Coagulant	SP
Dose	15 mg/L
Source water	Lake Ontario
pH	8.34

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	2.71	1.84	-	0.38	0.38	8.06	-
1-day	1.901	1.758	0.57	0.06	0.25	7.81	29.9%
2-day	1.88	1.691	0.44	0.04	0.21	7.75	30.6%
3-day	1.858	1.722	0.49	0.04	0.29	7.72	31.4%

Trials #	10
Date	17-Sep
Coagulant	SP 70
Dose	20 mg/L
Source water	Lake Ontario
pH	8.32

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	2.524	2.311	-	0.62	-	8.23	-
1-day	1.859	1.811	2.418	0.05	0.31	8.02	26.3%
2-day	2.004	1.923	2.481	0.08	0.34	7.83	20.6%
3-day	1.971	1.854	2.332	0.06	0.56	7.92	21.9%

Tables D.11-D.14: Grand River membrane trials data using equal-molar coagulant doses

Trials #	11
Date	Oct, 2006
Coagulant	alum
Dose	47.1 mg/L
Source water	Grand River
pH	7.88

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.17	5.61	-	5.21	-	7.91	-
1-day	3.57	3.55	4.79	0.1	4.11	7.41	42.1%
2-day	3.62	3.58	5.12	0.06	3.82	7.38	41.3%
3-day	3.68	3.66	4.9	0.09	4.19	7.44	40.4%

Trials #	12
Date	Oct, 2006
Coagulant	FC
Dose	38.0 mg/L
Source water	Grand River
pH	8.14

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.31	5.61	-	4.99	-	8.11	-
1-day	3.21	3.18	4.18	0.1	5.93	7.44	49.1%
2-day	3.33	3.3	4.22	0.12	5.61	7.39	47.2%
3-day	3.08	3.06	3.94	0.14	5.42	7.41	51.2%

Trials #	13
Date	Oct, 2006
Coagulant	SP
Dose	37.5 mg/L
Source water	Grand River
pH	8.14

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.31	6.25	-	4.99	-	8.11	-
1-day	3.66	3.62	4.22	0.1	2.81	7.44	42.0%
2-day	3.58	3.5	4.39	0.12	3.04	7.39	43.3%
3-day	3.59	3.56	4.55	0.14	2.99	7.41	43.1%

Trials #	14
Date	Oct, 2006
Coagulant	SP 70
Dose	36.8 mg/L
Source water	Grand River
pH	7.88

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.17	5.61	-	5.21	-	7.91	-
1-day	4.12	4.04	4.04	0.1	3.41	7.41	33.2%
2-day	3.98	3.94	4.11	0.12	3.21	7.38	35.5%
3-day	3.96	3.91	3.87	0.11	3.17	7.44	35.8%

Tables D.15-D.18: Grand River membrane trials data using optimal coagulant doses with modified raw water pH

Trials #	15
Date	27-Nov
Coagulant	Alum
Dose	30 mg/L
Source water	Grand River
pH	7.99

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.32	6.11	-	6.81	-	8.06	-
1-day	2.23	2.2	3.13	0.06	2.23	5.43	64.7%
2-day	2.18	2.15	2.89	0.09	2.41	5.49	65.5%
3-day	2.31	2.29	3.21	0.10	2.3	5.51	63.4%

Trials #	16
Date	20-Nov
Coagulant	SP 70
Dose	50 mg/L
Source water	Grand River
pH	8.32

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.21	5.99	-	5.55	-	7.99	-
1-day	3.18	3.15	3.15	0.09	2.81	5.67	48.8%
2-day	3.1	3.06	3.22	0.1	2.99	5.7	50.1%
3-day	3.04	3.01	3.51	0.11	3.05	5.72	51.0%

Trials #	17
Date	22-Nov
Coagulant	SP
Dose	40 mg/L
Source water	Grand River
pH	8.11

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.08	5.81	-	5.91	-	8.11	-
1-day	2.91	3.38	2.98	0.09	3.45	5.55	52.1%
2-day	2.84	3.16	2.91	0.09	3.18	5.61	53.3%
3-day	2.77	3.3	2.85	0.1	3.22	5.64	54.4%

Trials #	18
Date	25-Nov
Coagulant	FC
Dose	45 mg/L
Source water	Grand River
pH	8.01

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.31	6.05	-	0.62	-	7.94	-
1-day	2.12	2.05	2.21	0.09	3.87	4.89	66.4%
2-day	2.09	2.02	2.11	0.06	3.56	4.81	66.9%
3-day	2.11	2.04	2.09	0.07	3.77	4.99	66.6%

Tables D.19-D.22: Grand River membrane trials data using optimal coagulant doses with modified mixing intensity in flocculation tank

Trials #	19
Date	Nov, 2006
Coagulant	Alum
Dose	30 mg/L
Source water	Grand River
pH	7.99

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.11	5.81	-	7.12	-	8.06	-
1-day	2.42	2.4	4.67	0.11	2.31	7.11	60.4%
2-day	2.51	2.47	4.41	0.10	2.91	7.21	58.9%
3-day	2.55	2.5	4.41	0.10	3.01	7.09	58.3%

Trials #	20
Date	Dec, 2006
Coagulant	FC
Dose	45 mg/L
Source water	Grand River
pH	8.01

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.34	6.28	-	0.62	-	7.94	-
1-day	1.88	2.04	2.44	0.10	4.18	7.22	70.3%
2-day	1.91	1.89	2.61	0.11	4.22	7.18	69.9%
3-day	1.86	2.02	2.58	0.09	4.11	7.22	70.7%

Trials #	21
Date	Dec, 2006
Coagulant	SP
Dose	40 mg/L
Source water	Grand River
pH	8.32

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.28	5.61	-	0.62	-	8.11	-
1-day	2.81	2.77	3.13	0.06	3.45	7.34	55.3%
2-day	2.76	2.7	3.41	0.05	3.18	7.29	56.1%
3-day	2.79	2.73	3.28	0.8	3.22	7.40	55.6%

Trials #	22
Date	Dec, 2006
Coagulant	SP 70
Dose	50 mg/L
Source water	Grand River
pH	8.32

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	6.34	5.81	-	-	-	7.99	-
1-day	3.11	3.09	3.99	0.09	3.14	7.44	50.9%
2-day	2.99	2.96	3.87	0.11	2.99	7.52	52.8%
3-day	3.08	3.04	3.81	0.07	3.47	7.4	51.4%

Tables D.23-D.24: Grand River membrane trials data using half of the optimal coagulant doses

Trials #	23
Date	5-Dec
Coagulant	Alum
Dose	15 mg/L
Source water	Grand River
pH	8.11

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	5.85	5.49	-	5.98	-	8.01	-
1-day	3.24	3.2	5.21	0.10	5.23	7.66	44.6%
2-day	3.57	3.52	5.11	0.12	5.15	7.59	39.0%
3-day	3.42	3.39	5.17	0.09	5.81	7.61	41.5%

Trials #	24
Date	8-Dec
Coagulant	SP
Dose	20 mg/L
Source water	Grand River
pH	8.04

Sample time	TOC	DOC	Floc TOC	Turbidity	Floc Turb	pH	TOC Removal
0 (RAW)	5.94	5.61	-	6.11	-	8.06	-
1-day	4.11	4.04	4.91	0.07	5.45	7.71	30.8%
2-day	4.01	3.94	4.94	0.09	5.63	7.74	32.5%
3-day	4.23	4.19	5.15	0.10	5.99	7.75	28.8%