# MANGANESE REMOVAL FROM SURFACE WATER USING BENCH-SCALE BIOFILTRATION

by

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**ABSTRACT**

Research has shown biological filtration can be a successful treatment for manganese (Mn) removal from groundwater and surface water. In this study, bench-scale direct biofiltration was used to remove Mn and dissolved organic carbon (DOC) from a pH 6 surface water source in Halifax, Canada. The removal of Mn in pH 6 surface water was significantly ($\alpha = 0.05$) removed with 200-300 µg/L phosphorus (P), and 500 µg/L hydrogen peroxide ($H_2O_2$). DOC removal was significantly ($\alpha = 0.05$) improved with granular activated carbon (GAC) media, P enhancement at 200-300 µg/L, and $H_2O_2$ enhancement at 500 µg/L. Mn was likely removed by biological oxidation and physical adsorption to biogenic Mn and iron (Fe) oxides. These results show direct biofiltration of surface water at pH 6 can remove Mn below the 50 µg/L aesthetic guideline from a Mn loading of over 1 mg/L. Further research is required to verify the microbial mechanism of Mn removal.

## LIST OF ABBREVIATIONS AND SYMBOLS USED

| | |
|---|---|
| µg | micrograms |
| ANOVA | analysis of variance |
| ATP | adenosine triphosphate |
| C:N:P | carbon, nitrogen, phosphorus nutrient ratio |
| CFU | colony forming units |
| DOC | dissolved organic carbon |
| EBCT | empty bed contact time |
| Fe | iron |
| GAC | granular activated carbon |
| GCDWQ | Guidelines for Canadian Drinking Water Quality |
| HAAfp | haloacetic acid formation potential |
| $H_2O_2$ | hydrogen peroxide |
| $H_2PO_3$ | phosphoric acid |
| HPC | heterotrophic plate count |
| ICP-MS | induced couples plasma mass spectroscopy |
| $KMnO_4$ | potassium permanganate |
| L | litres |
| MDL | minimum detection level |
| mg | milligrams |
| mL | millilitres |
| Mn | manganese |
| $MnSO_4$ | manganese (II) sulphate |
| MOB | manganese oxidizing bacteria |
| NB | New Brunswick |
| NE | nutrient enhanced |
| NE+OE | nutrient enhanced plus oxidant enhanced |
| NOM | natural organic matter |
| NS | Nova Scotia |
| OE | oxidant enhanced |
| ORP | oxidation reduction potential |

| | |
|---|---|
| P | phosphorus |
| pg | picograms |
| pH | potential of hydrogen (hydrogen potential) |
| SEC | size exclusion chromatography |
| SEM | scanning electron microscopy |
| T&O | taste and odour |
| THMfp | trihalomethane formation potential |
| TOC | total organic carbon |
| USEPA | United States Environmental Protection Agency |

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# CHAPTER 1: INTRODUCTION

## 1.1 PROJECT RATIONALE

Manganese (Mn) is a naturally occurring metal that creates aesthetic challenges in drinking water treatment because it causes black water and laundry staining if present in concentrations above the treated water aesthetic objective of 50 µg/L (Health Canada, 2010). Research has suggested this aesthetic objective needs to be less than 10 µg/L to eliminate black water episodes (Kohl and Medlar, 2006). As well, Mn is a public health issue as it has recently been identified as a neurotoxin in children in concentrations around 200 µg/L (Bouchard et al., 2011).

Bennery Lake Water Treatment Plant (BLWTP) in Halifax, Nova Scotia, Canada supplies drinking water to the Stanfield International Airport and surrounding area. Seasonal lake stratification from June to September results in low oxygen and reducing conditions in the hypolimnion layer of Bennery Lake, forcing Mn into the dissolved form as Mn (II). The plant intake is located in this layer, resulting in high dissolved Mn loading into the treatment process. BLWTP is a conventional plant and treats high dissolved Mn concentrations by dosing with potassium permanganate ($KMnO_4$), but due to the daily fluctuations in Mn concentrations, adequate dosing is an operational challenge. Consequently, the Canadian Drinking Water Quality Guideline (CDWQG) Mn aesthetic objective of less than 50 µg/L is not always met. The current process at BLWTP is not robust enough to handle seasonal Mn loading without periods of breakthrough in the treated water, therefore alternative treatment needs to be examined.

To remove Mn, dissolved Mn (II) must first be oxidized to particulate Mn (IV). Mn can then be removed by in-situ treatment with lake aeration, chemical oxidation, oxide-coated media, ion exchange or biological treatment (Kohl and Medlar, 2006). Based on research by Burger et al. (2008b), Kohl and Dixon (2012) and Chapnick et al. (1982), direct biofiltration of surface water could be a viable solution for Mn control at this facility. Biological filtration has been used for many years and recently, engineered biofiltration

has shown to optimally target contaminant removal. Engineered biofiltration enhances biological growth by nutrient and oxidant addition (Lauderdale et al., 2011).

There is potential for biofiltration as a pre-treatment at BLWTP to remove Mn before the metal enters the treatment train. This would eliminate the need for an oxidant pre-coagulation, saving on chemical costs and downstream issues.

## 1.2 RESEARCH OBJECTIVES

In this study, the potential for biofiltration as a pre-treatment for Mn removal was evaluated at BLWTP. Two bench-scale direct biofiltration experiments were conducted: one with nutrient enhancement and another with combined nutrient and oxidant enhancement. These techniques were investigated to determine their effect in removing Mn from a surface water source in Halifax, NS, Canada.

This study fills a gap in the research by examining direct biofiltration to remove Mn from untreated surface water with a pH < 7 and Mn loading of > 100 µg/L. Specific experimental objectives included an evaluation of: utilizing nutrient enhancement with P; nutrient enhancement with P plus oxidant enhancement with $H_2O_2$; and investigating microbial activity and subsequently, the presence of manganese oxidizing bacteria (MOB) in the biofilm. As the information relating to Mn (II) oxidation from surface water and its removal in biofiltration is limited (Kohl and Dixon, 2012), this research will contribute to the field of Mn removal by microbial Mn oxidizing mechanisms.

The research objectives were as follows:

1. Design, construct and operate a bench-scale direct biofiltration set-up
2. Characterize the raw water (biofilter influent) at BLWTP in all four seasons
3. Remove Mn to below 50 µg/L with two enhancement strategies:
    - Nutrient enhancement with P
    - Nutrient enhancement with P plus oxidant enhancement with $H_2O_2$
4. Determine the optimal pH and media type for Mn removal

# CHAPTER 2: LITERATURE REVIEW

## 2.1 CONTAMINANTS

### 2.1.1 Manganese

Mn is a naturally occurring element found in the air, soil, and water and is the second most abundant transition metal on earth. Mn constitutes approximately 0.1% of the earth's crust and is essential in the nutrition and metabolism of plants and animals. Mn can exist in seven oxidation states ranging from -2 to +7. Mn is rarely found in its elemental state and is therefore a component of over 100 minerals and exists mainly as oxides, carbonates, and silicates.

Lakes around the world are known to stratify during the summer, affecting the oxygen concentrations and Mn speciation throughout the lake. During this time, Mn changes from the dissolved form to the particulate form based on oxygen levels. In the hypolimnion layer at the lake bottom, there are low oxygen levels and Mn is typically present in dissolved form. In the epilimnion layer at the top of the lake, Mn is in the particulate (oxide) form as plenty of oxygen exists at the air-water interface. This process is shown in equations 1.1-1.3 (MWH, 2005). Lake stratification occurs in nutrient rich lakes during the summer when the organic matter on the bottom consumes all the available oxygen. The lake stays stratified until a change of ambient temperature and/or wind event causes the lake to mix, redistributing the oxygen throughout (MGH, 2005).

$$Mn^{2+} + 0.5O_2 \rightarrow MnO_{2(s)} \quad [1.1]$$

$$Mn^{2+} + MnO_{2(s)} \rightarrow Mn^{2+} * MnO_{2(s)} \quad [1.2]$$

$$Mn^{2+} * MnO_{2(s)} \rightarrow 2MnO_{2(s)} \quad [1.3]$$

Mn in treated drinking water can also have an effect in customers' homes at concentrations as low as 10 µg/L. Mn can cause black water and laundry staining, as well as induce corrosion in distribution systems (Mouchet, 1992; Pacini et al., 2005). This usually occurs from the oxidation of soluble, colourless Mn (II) to dark brown, insoluble

Mn oxides (Kohl and Dixon, 2012). Mn can also cause taste and odour (T&O) issues at concentrations around 0.2 to 0.4 mg/L (MWH, 2005). Recent research has shown that Mn can cause health related effects by acting as a neurotoxin at concentrations greater than 200 µg/L (Bouchard et al., 2011). High concentrations of Mn can also lead to economic losses due to the constant need for distribution cleanings from build-up and restricted flow. Eliminating or decreasing the Mn concentration entering the plant helps prevent issues that Mn causes during treatment, in the distribution system and ultimately in the consumers home (Kohl and Dixon, 2012).

### 2.1.2 Natural Organic Matter

In surface water bodies, natural organic matter (NOM) encompasses a matrix of organic chemicals that come from natural sources like leaves, soil run off, and biological activity due to algae, protozoa, microorganisms and bacterial decay (MWH, 2005). Most surface water and some groundwater utilities have to optimize their process for organics removal. Natural organic matter can be problematic for utilities because it can cause organic or biological fouling within the treatment process, increase oxygen demand, act as a disinfection by-product (DBP) precursor, and contribute to biological growth in the distribution system (LeChevallier et al., 1992; Escobar et al., 2001). Organic matter is commonly removed with enhanced coagulation but biofiltration has also been a successful treatment for removing NOM, with removals varying between 5-75% (LeChevallier et al., 1992; Rittmann et al., 2002; Perrson et al., 2006). These removals are comparable to enhanced coagulation NOM removals. Even though coagulation is successful in removing NOM, if all or some NOM could be removed during pre-treatment with biofiltration, this could decrease the coagulant demand and subsequent chemical costs.

Numerous studies have correlated NOM removal with biofilter activity which can be measured by adenosine tri-phosphate (ATP), phospholipid fatty acids and dissolved oxygen (DO) uptake (Huck et al., 2000; Liu et al., 2001; Wert et al., 2008). NOM also plays a large role in the transport and concentration of organic and inorganic pollutants. NOM is soluble and negatively charged (MWH, 2005), and can potentially attract metals

like Mn (II) to its surface, although little evidence exists supporting this theory. Sunda and Kieber (1994) showed that Mn oxides can act as chemical oxidants and oxidize humic acids, a portion of NOM, while Stone and Morgan (1984) discovered that Mn oxides can also catalyze NOM degradation. These results suggest that there is potential for NOM degradation with biofiltration.

## 2.2 MANGANESE REMOVAL TREATMENT OPTIONS

There are many ways that Mn can be removed during drinking water treatment. Chemical oxidation is usually required for Mn removal as Mn oxidation by oxygen is very slow at pH < 9. Most drinking water sources exist at pH 6-8; therefore Mn cannot be successfully removed by aeration (Stumm and Morgan, 1996). Several Mn removal options include in situ treatment, chemical oxidation, adsorption to oxide coated media, dissolved air flotation (DAF), membrane filtration, and biological treatment. All of these treatments aim to oxidize Mn into an insoluble form to be removed through filtration (MGH, 2005). A summary of Mn removal studies are shown in Table 1. The most popular Mn removal treatments are discussed below.

### 2.2.1 In Situ Treatment

Removing Mn via in situ treatment involves preventing Mn from entering the plant by keeping Mn in the oxidized rather than the dissolved form (Kohl and Medlar, 2006). This can be done through lake aeration as artificial oxygenation in a body of water prevents spikes of dissolved Mn loading in the influent, as long as the intake pipe is above the aeration depth (Chiswell, 1998). Mn oxidation in freshwater is thought to be from a combination of bacterial oxidation and chemical oxidation with oxygen (Kohl and Medlar, 2006). Aeration does not oxidize organically bound Mn, but in situ treatment is considered a good primary treatment for Mn removal (Raveendran et al., 2001).

### 2.2.2 Chemical Oxidation with Physical Separation

Chemical oxidation is used before a coagulant is added to precipitate Mn (II) from solution so it can be removed with physical separation. In conventional WTPs, physical separation involves a sedimentation tank and subsequent filter.

**Table 1.** Mn removal treatment options

| Water Type | Mn Specific Treatment | Removal Mechanism | pH | ORP (mV) | Nutrient/ Oxidant Present | Mn Removal (%) | Reference |
|---|---|---|---|---|---|---|---|
| GW | Aeration, sand upflow biofiltration-pilot scale | Abiotic, biotic mechanisms | 7.5-8.0 | 361-423 | No | 85-95 | Pacini et al., (2005) |
| GW | Sand biofiltration, polystyrene beads biofilter-bench scale | Biological oxidation by heterogeneous bacteria | 7.2 | 340 | No | 90 + | Katsoyiannis and Zouboulis (2004) |
| GW | Aeration, sand biofiltration-pilot scale | Biological oxidation, bioadsorption | >7.5 | 300-400 | No | 100 | Mouchet (1992) |
| GW | Mn sand biofiltration-pilot scale | Biological oxidation | 7.2 | - | No | 60 | Qin et al., (2008) |
| GW | Sand biofiltration-full scale | Biological oxidation | 6.5-7.5 | 295-368 | No | ~ 100 | Burger et al., (2008c) |
| Synthetic GW | Sand biofiltration-bench scale | Mn oxide adsorbtion, biological oxidation | 6.5, 7.5 | 450-500 | No | 90 | Burger et al., (2008a) |
| Synthetic water | Aeration, plastic media upflow biofiltation-bench scale | Biological oxidation | 6.0-7.0 | 350 | No | 35-95 | Hasan et al., (2011) |
| Synthetic water | Gravel trickling filters-pilot scale | Biological oxidation | 7.0-7.3 | 300-500 | No | ~ 90 | Tekerlekopoulou and Vayenas (2007) |
| Synthetic water | Limestone filtration-bench scale | - | 6.8-7.3 | - | No | 64-92 | Aziz and Smith (1995) |
| SW | Mn oxide pyrolusite filtration-pilot scale | Adsorption and oxidation on Mn oxide coated media | 6.3-8.0 | - | 0.8-3.4 mg/L free Cl | 96 | Knocke et al., (2010) |
| SW | GAC/sand biofiltration-pilot scale | Biological oxidation | - | - | 0.02 mg/L P | ≥ 98 | Lauderdale et al., (2011) |
| SW | GAC/sand biofiltration-full scale | Biological oxidation | 6.5 | - | No | -32-69 | Kohl and Dixon (2012) |
| SW | Anthracite/sand biofiltration-full scale | Biological oxidation | 6.5 | - | No | -124-28 | Kohl and Dixon (2012) |
| SW | GAC/sand, anthracite/sand filration-full scale | Anthracite :IOCME GAC: biological | 6.5-7.0 | - | 0.5-1 mg/L free Cl | 74-100 | Kohl and Dixon (2012) |
| SW | Anthracite/sand filtration-full scale | Biological oxidation | 6.2 | - | Pre oxidant ($KMnO_4$) | 0-23 | Kohl and Dixon (2012) |
| SW | Filtration-full scale | IOCME | 7.0-9.0 | - | Ozone | 86 | Kohl and Medlar (2006) |
| SW | Membrane filtration-full scale | - | 7.0-9.0 | - | Pre oxidant ($KMnO_4$) | 99 | Kohl and Medlar (2006) |

This is the most common method for Mn removal in drinking water treatment. Common oxidants used for Mn oxidation include chlorine, potassium permanganate, and ozone (Kohl and Dixon, 2012). For every oxidation/reduction reaction with these oxidants, an electric potential or oxidation reduction potential (ORP) exists. The oxidizing agent accepts electrons and Mn has been oxidized when it has lost one or more electrons, creating a more positive oxidation state (Snoeyink and Jenkins, 1980). The presence of NOM can complicate this oxidation process as organic matter influences Mn oxidation by changing the nature of the oxidant, changing the speciation of the metal, and competing with the metal for the oxidant (Kohl and Medlar, 2006).

#### *2.2.2.1 Chemical Oxidation with Chlorine*

Oxidation with chlorine requires alkaline pH conditions, long contact times and warm temperatures. Knocke et al. (1990a) discovered that even at chlorine dosages 4 times the stoichiometric equivalent required for Mn oxidation, a 3 hour contact time was necessary to achieve a Mn decrease of 1 mg/L to 0.7 mg/L at pH 7. However, when pH 7 was increased to pH 9, Mn was oxidized to below the aesthetic guideline with a 1 hour contact time. As well, when the temperature decreased from 25$^{o}$C to 14$^{o}$C, Mn oxidation was not possible.

#### *2.2.2.2 Chemical Oxidation with Potassium Permanganate*

Potassium permanganate dosing to remove Mn has been researched since the 1960s and has been recognized as an economical solution for Fe and Mn removal (Robinson et al., 1967). Knocke et al. (1990b) evaluated a wide range of pH and temperature conditions. When permanganate was dosed at 105% of the stoichiometric requirement between pH 5.5 to 9, a temperature of 25$^{o}$C and DOC less than1 mg/L, Mn oxidation occurred within 1 minute. As the temperature decreased to 7$^{o}$C, Mn oxidation still occurred within 1 minute, and within 1.5 minutes at 2$^{o}$C. This study also identified that the presence of DOC decreased the rate of Mn oxidation, but Mn removal could still occur with a contact time of 1-2 minutes. Dosing with permanganate can be challenging since excess permanganate can reduce Mn (VII) to Mn (IV) during treatment and allow Mn oxides to form within the distribution system (Kohl and Medlar, 2006).

#### *2.2.2.3 Chemical Oxidation with Ozone*

Chemical oxidation with ozone is not commonly practiced in drinking water treatment as it has a higher capital cost than other oxidants and can result in pink effluent water if the Mn is completely oxidized to permanganate (Kohl and Medlar, 2006). Mn removal with ozone is also inhibited by the presence of humic materials in the source water and requires an ozone dose 2 to 5 times the stoichiometric requirement. This is due to the Mn and humic carbon competing for the oxidant (Knocke et al., 1990). A study by Gregory and Carlson (2001) evaluated Mn and NOM oxidation with ozone. They discovered that in the presence of NOM, Mn reductions from 200 µg/L to less than 10µg/L were not possible with NOM in the source water. NOM complicates Mn treatment with ozone as it increases the dose required for Mn removal.

### 2.2.3 Chemical Oxidation with Oxide-Coated Media

The induced oxide coated media effect (IOCME) is another common Mn removal technique. With the addition of an oxidant pre filtration, soluble Mn is sequestered and adsorbed onto the Mn oxide coated filter media and oxidized from Mn (II) to $MnO_{2(s)}$ (Kohl and Dixon, 2012). These Mn oxides further coat the filter media and allow for increased adsorption.

Studies have shown that Mn adsorption is increased by higher pH, increased sorption sites and the presence of free chlorine (Knocke et al., 1990a). Mn removal with the IOCME has shown to be a dependable treatment technology and can operate under a wide range of influent conditions (Hargette and Knocke, 2001). Two modes of operation exist: intermittent regeneration and continuous regeneration. Intermittent regeneration involves Mn (II) adsorbing to the filter media in the absence of an oxidant. Chlorine or potassium permanganate is periodically added to regenerate adsorption sites. Continuous regeneration involves Mn (II) converstion to manganese oxides in the continual presence of free chlorine (Kohl and Medlar, 2006).

### 2.2.4 Dissolved Air Flotation

Although dissolved air flotation (DAF) is not specifically a Mn removal treatment, it can be used to remove Mn precipitates (Sommerfeld, 1999). In an Australian study by Roscoe (2002), Mn removal with DAF was outlined. Coagulation with PACl and subsequent treatment with DAF resulted in a Mn reduction from 0.08 mg/L to 0.02 mg/L. DAF is not commonly used as a Mn removal treatment as it is a more effective treatment for source waters with low Mn concentrations (Kohl and Medlar, 2006).

### 2.2.5 Membrane Filtration

Membrane processes can also be used to remove particulate Mn during drinking water treatment. Microfiltration for Mn removal was examined in a study by Schneider et al. (2001). The authors found that when Mn was oxidized with ozone or chlorine dioxide before microfiltration, Mn was reduced from 0.3 mg/L to 0.025 mg/L. Other oxidants such as $H_2O_2$ and $KMnO_4$ were tested and did not result in effective Mn removal. Fouling issues could arise with reverse osmosis or nanofiltration systems if Mn did not remain in dissolved form (Kohl and Medlar, 2006).

## 2.3 BIOLOGICAL TREATMENT

### 2.3.1 Summary of Treatment Technology

Biological treatment is another option for Mn and NOM removal. Biofiltration is practiced in Canada and has gained popularity as it is a cost effective treatment option for Mn removal from drinking water sources, minimizing chemical oxidants that could form unwanted by-products (Burger et al., 2008b). Biological treatment offers a greener technology than chemical oxidation and is a relatively simple treatment to operate.

Biofiltration involves encouraging growth of microbial communities that metabolize contaminants through mediating oxidation-reduction (redox) reactions (Droste, 1997). Biological oxidation of Mn is a biofiltration process that has not been fully explored, although it is believed that Mn (II) oxidation causes Mn (IV) oxide accumulation on the

bacterial surface, attached to the filter media. This accumulated Mn is removed together with excess bacteria and biofilm during backwashing (Kohl and Dixon, 2012).

The most popular form of biological treatment for drinking water applications is the fixed-bed biofilm system (Lauderdale et al., 2011). This system includes a media such as sand, anthracite and/or GAC, which will support biological growth. The most common placement of a fixed-bed biofilm system is just before final disinfection where it oxidizes organic and inorganic contaminants, as well as removing particles (Lauderdale et al., 2011). Biologically active filters (BAFs) are used for drinking water treatment to remove NOM, nitrate, sulfate, iron, arsenic, halogenated organics and Mn (Bouwer and Crowe, 1988) and are usually part of a larger treatment train involving processes such as coagulation, sedimentation, clarification and disinfection. Given the increasing role that BAFs are playing in drinking water treatment, understanding the microbial communities is important when considering treatment process control, DBP control, pathogenic effects and the potential to improve treatment efficiencies (Zhu et al., 2010).

### 2.3.2 Challenges and Benefits of Biofiltration

Biofiltration is not a conventional treatment technology and public perception is not largely accepting of biotechnological applications for drinking water treatment purposes; however, biological treatment processes have been operational in Europe for decades (Kohl and Medlar, 2006; Kohl and Dixon, 2012). Biological treatment has been likely limited due to public perception that encouraging microbial growth during treatment is counterproductive (Evans et al., 2009). Biofiltration has gained more attention recently as an alternative filtration technique because water utilities have had to terminate chlorine dosing before filtration to meet the DBP treatment standards. When chlorine is terminated, biological activity can thrive and a biofilm can form, removing contaminants by biological oxidation. New technical developments are also making utilities consider using biological processes to treat their drinking water. These technologies include using ozone to eliminate colour, control T&O, awareness in decreasing biological activity in the distribution system, and the trend of moving forward with environmentally sustainable water treatment processes. Research has also shown that biofiltration reduces

microbial activity in the distribution system (Characklis, 1988). Biofiltration is becoming more popular with positive research outcomes and increased public acceptance.

Biofiltration also has benefits as an affordable treatment option to remove Mn in developing nations. Building and operational costs of conventional water treatment plants in developing countries has led to the demand for alternative treatment technologies for water processing as a biological oxidation WTP is considerably less expensive than chemical oxidation/filtration systems (Yannoni et al., 1999). Regarding Mn removal, the common practice is to modify the existing filters into biologically active filters for the oxidation and removal of Mn (II). However, if modification is not an option, some utilities have chosen biological oxidation as a pre-treatment. This allows for Mn (II) to be removed prior to entering the plant, thus minimizing Mn fluctuations in the raw water influent (Kohl and Dixon, 2012).

### 2.3.3 Microbial Oxidation

It is known that biological treatment for Mn removal occurs when natural Mn oxidizing microbial communities develop a biofilm on filtration media. MOB are heterotrophic bacteria which use pre-formed organic molecules as their carbon source (MGH, 2005). It is also well known that MOB grow equally well heterotrophically in the absence and presence of Mn (II) (Kohl and Dixon, 2012). Previous studies have identified MOB in biofilter biofilms belonging to the genuses *Metallogenium, Sideocystis, Crenothrix, Hyphomicrobium, Leptothrix, Pseudomonas, Siderocapsa* (Mouchet, 1992)*, Pedomicrobium* (Sly et al., 1993)*,* and *Acinetobacter* sp. (Beukes and Schmidt, 2012). Microorganisms exist in biofilms located on media such as sand, anthracite, or GAC in order to adsorb and oxidize Mn. Biofilms develop by trapping free floating microbes which become irreversibly adherent to the surface and initiate growth of the biofilm and production of extracellular polymeric substances (EPS). Biofilms may then accumulate on a surface. Biofilms create a structure which allows nutrients to reach the biomass and therefore creating thriving bacterial communities (MGH, 2005). Once the microbial communities have developed into these biofilms, bacterial processes are generally quicker than physical/chemical treatments.

Microbial Mn (II) oxidation during biofiltration likely occurs by both biotic and abiotic mechanisms. MOB have been studied since the late eighteenth century and are known for depositing Mn oxides in structures outside their cells (Pacini et al., 2005). These biogenic Mn oxides are produced from intercellular enzymatic Mn (II) oxidation using aerobic respiration, a metabolic process where molecules are oxidized with oxygen as the final electron receptor (MGH, 2005). It is likely these oxides are responsible for further abiotic Mn (II) adsorption at the cell membrane and autocatalytic extracellular oxidation, but at a slower rate than the intracellular microbial oxidation (Czekalla et al., 1985; Gounot et al., 1988; Vandenabeele et al., 1992).

According to Mouchet (1992), bacterial Mn oxidation requires dissolved oxygen (DO) concentrations of > 5 mg/L; an ORP of > 300 mV; and a pH > 7.4. It has also been shown that Mn oxidation can occur at DO concentrations of 3 mg/L and pH 4.8-6.2 (Leeper and Swaly, 1940; Sly et al., 1997). Mn and Fe both exist in surface waters, although conditions for biological Mn removal are different than for Fe. Biological Fe removal can be accomplished with 2 mg/L DO, an ORP of 200 mV at a pH ≥ 7.2 (Mouchet, 1992)

The removal of Mn in drinking water treatment plants in both groundwater and surface water by microbial oxidation processes is gaining world-wide attention; however, continuous research, development and studies are still necessary to fully understand the mechanism of microbial Mn oxidation. Furthermore, to successfully treat drinking water with regards to Mn removal, complete understanding of the microorganisms and enzymes that help in oxidizing Mn is essential (Kohl and Dixon, 2012). Most studies have been targeted at Mn removal from groundwater, while research on Mn removal from surface water is limited. Many of these studies examining Mn removal from surface water have focused on river water contamination in the US and overseas, representing conditions much different from naturally occurring Mn in a Canadian lake.

### 2.3.4 Biofiltration for Groundwater

Biological processes to remove Mn have been researched, but mostly for groundwater sources as biofiltration is usually applied as a pre-treatment for well water (Kohl and Medlar, 2006). In a study by Katsoyiannis and Zouboulis (2004), biological Mn oxidation

was examined in upflow filtration with polystyrene beads with the bacterium *Leptothrix ochracea*. Experimental conditions of pH 7.2, DO 3.8 mg/L and ORP of 340 mV were tested and removed DOC by 30% and dissolved Mn by approximately 88%. They concluded that biological Mn oxidation occurred and the Mn oxides were concentrated on the bacterial surface. Below pH 9, in the absense of MOB, biological Mn oxidation did not occur and the filters would require seeding as MOB did not exist in the groundwater source. They also found that the pH and Mn oxidation rate decreased simultaneously.

Burger et al. (2008c) studied Mn removal in groundwater at four full scale biofiltration plants in New Brunswick, Canada. Sand media biofilters were subjected to influent conditions ranging from pH 6.5-7.5 and ORP from 368-343 mV. All treatment plants obtained near 100% Mn removal and 3 out of the 4 plants tested positive for MOB while only 1 plant had *Leptothrix discophora SP-6* in the biofilm. There were high heterotrophic plate counts (HPCs) for all 4 plants, so biological oxidation was likely a significant removal mechanism. As well, the plants had physical/chemical Mn removal with Mn (II) adsorption to Mn oxides in the filter bed. Pilot scale biofiltration with Mn sand and silica sand was researched in a study by Qin et al. (2009). The biofilters were seeded with *Leptothrix sp*. and experimental conditions of 5 mg/L DO and pH 7.2 resulted in 34-45% Mn removal. Removal was increased to 74% when the DO concentration increased to 9 mg/L. Higher removals were achieved with Mn sand due to the Mn coating, therefore it was believed that chemical as well as biological oxidation was occurring.

### 2.3.5 Biofiltration for Surface Water

There has been limited research on Mn removal from surface water with biofiltration but Persson et al. (2006) suggested biofiltration of surface water could be an option to improve water quality under moderately cold conditions as pre-treatment to chemical treatment or membrane filtration.

Lauderdale et al. (2011) examined pilot scale biofiltration with nutrient enhancement with P and oxidant enhancement with $H_2O_2$ with GAC/sand filters. Almost 100% Mn removal was achieved with both the nutrient enhanced (NE) and oxidant enhanced (OE)

filters at temperatures ranging from 17-30 $^{o}$C. The author did not examine if direct oxidation of Mn by peroxide had occurred so the exact method of Mn removal was unknown. DOC removals of about 75% greater than the control were observed for both enhancement strategies. Peroxide was dosed at 1 mg/L and did not decrease ATP concentrations relative to the control, but did improve filter hydraulics in this experiment. This could be due to microbial peroxide oxidation that removed foulants EPS by mineralization or backwashing.

Kohl and Dixon (2012) also examined Mn removal from numerous surface water sources at two full-scale biofiltration WTPs. Fairfax Water operated between a pH of 7.2-7.6, had GAC/sand media and was able to obtain 97% Mn removal. Less effective Mn removal occurred at Manchester Water Works which had a pH of 6.5 and fewer metal oxides on the media surface. This plant had both anthracite/sand and GAC/sand biofilters. The GAC filters provided better Mn removal than the anthracite filters, 40% and less than 10%, respectively, although MOB were found on both media.

## 2.4 ENGINEERED BIOFILTRATION TO REMOVE MANGANESE

Biofiltration is moving towards an engineered approach. This means that filter design is driven by encouraging biological activity, as opposed to conventional filter design parameters like turbidity and headloss (Lauderdale et al., 2011), although these are still important operating parameters. Engineered biofiltration addresses multiple water quality objectives while maintaining hydraulic performance. Two methods of engineered biofiltration are addressed below.

### 2.4.1 Nutrient Enhancement

Nutrient enhancement involves adding nutrients to optimize bacterial health so the filters optimally remove contaminants. It has been shown that microbially available phosphorus (MAP) is the limiting nutrient in microbial growth and that MAP limited waters result in significantly lower biofilm formation (Lehtola et al., 2002; Polanska et al., 2005; Fang et al., 2009). Source waters can also be carbon, nitrogen and/or phosphorus limited. For successful microbial growth, it is important to maintain a well-balanced nutrient ratio of

100:10:1 of bioavailable C:N:P (USEPA, 1991). If the source water is nutrient limited, biofilm microbial growth will not be optimized and contaminant removal may be limited. This stoichiometric ratio of C:N:P is equivalent to a concentration ratio of 1 mg/L bioavailable carbon, 0.117 mg/L ammonia-nitrogen, and 0.026 mg/L orthophosphate-phosphorus (Madigan et al., 2009). Nutrient enhancement also decreases EPS which is a primary biofilter foulant and contributes to headloss. Bacteria produce EPS when they are nutrient limited (Liu et al., 2006). Nutrient enhancement can decrease EPS by > 30% and increase ATP concentrations by > 30%, therefore maintaining this nutrient ratio is crucial to an efficient biofilter (Lauderdale et al., 2011). Ammonia-nitrogen was not measured in this study but the author recognized the importance of its addition in nitrogen-limited waters to ensure full nutrient supplementation.

### 2.4.2 Oxidant Enhancement

Enhancing biological activity to remove contaminants and biofiltration performance is also achieved by oxidant addition, such as $H_2O_2$. Peroxide causes certain microorganisms to express a class of enzymes called oxidoreductases. This metabolic reaction neutralizes peroxide and releases free radicals which oxidize organic and inorganic contaminants, inactive organisms and their extracellular material, thereby improving biofilter hydraulics (Lauderdale et al., 2011). By adding $H_2O_2$, microorganisms are exposed to increased levels of DO as oxygen is produced from $H_2O_2$ degradation by the catalase enzyme secreted by some bacteria to inactivate the hydrogen peroxide. This additional source of DO encourages the microbial communities to exhibit peroxidases which help catalyze the oxidation of organic compounds. Previous studies conducted have proposed that low peroxide doses (< 1 mg/L) may help mediate the oxidation of inactive biomass and EPS while maintaining biological activity (Christensen et al., 1990; Neyens et al., 2002). A study by He et al. (2009) removed Mn below the 50 µg/L guideline from an influent Mn concentration of 400 µg/L. This was done with the addition of 0.5-5 mg/L $H_2O_2$ on a mixed sand media. Peroxide has the potential to increase NOM removal by oxidation with biofiltration.

## 2.5 BIOFILTRATION DESIGN PARAMETERS

Important design parameters to consider during biofiltration include media type, acclimation period, loading rate, EBCT and backwashing as these factors have shown to influence the microbial community structure in biofilter biofilms (Moll and Summers, 1999).

Conventional rapid filtration media such as GAC, anthracite, and sand are used in biofiltration. The media surface acts as a growth medium for the biofilm; this is where contaminant degradation occurs. It has been shown that GAC can occupy more biomass than anthracite due to its increased surface area (LeChevallier et al., 1992; Wang et al., 1995). Biofilters are typically dual media with GAC or anthracite on the top layer and sand on the bottom layer (Najm et al., 2005).

The time frame for a biofilter to reach steady state biological activity is an important design parameter. The acclimation period in sand filters to achieve consistent Mn removal can be up to 2 months (Mouchet, 1992). Kohl and Dixon (2012) and Liu et al. (2001) found a 40 day acclimation period was sufficient for their anthracite-sand biofilters to degrade biodegradable organic matter (BOM).

Empty bed contact time (EBCT) refers to the time required for the influent water to move through the media and is considered a vital component for effective biofiltration. EBCT is based on the loading rate and the volume of the filter media. An EBCT of 10-20 min has been shown to remove 90% of biofilter influent BOM (Provost et al., 1995).

$$EBCT = \frac{Volume\ of\ the\ filtration\ media}{Flow\ rate} \quad [1.4]$$

Backwashing is essential to biofilter performance. Backwash design considerations include time, water type, loading rate and backwash wastewater handling (Lauderdale et al., 2011). Using chlorinated backwash water has been shown to decrease biofilter organics and Mn removal (Liu et al., 2001; Vokes, 2007). Chlorine addition to backwash water solubilizes Mn adsorbed to the filter media, creating a release of soluble Mn in the filter effluent.

## 2.6 ORGANIZATION OF THIS THESIS

This thesis is organized in chapters by different enhancement strategies for biofiltration. An introduction and project objectives precede a background literature review in Chapters 1 and 2. Chapter 3 explains the methods used in all the experiments. Chapter 4 and 5 outline the results and discussion for the nutrient enhancement and nutrient plus oxidant enhancement bench scale biofiltration experiments. Chapter 4 examines the roles of pH, nutrient enhancement with P, and media type on Mn removal and explores the Mn removal mechanism. Chapter 5 analyzes the effect of oxidant enhancement with $H_2O_2$, nutrient enhancement with P, and media type all at the natural lake pH of 6. Chapter 6 concludes the results from both experiments and provides a synthesis and recommendations for future research.

# CHAPTER 3: MATERIALS AND METHODS

## 3.1 SOURCE WATER AND PLANT DESCRIPTION

Bennery Lake water treatment plant is located in Halifax Regional Municipality, Nova Scotia, Canada and operated by Halifax Water. The lake undergoes seasonal stratification during the summer, resulting in minimal mixing and anoxic conditions. This seasonal stratification occurs due to the temperate climate. A warmer epilimnion is created at the top of the lake, a transitionary thermocline in the middle, and a colder hypolimnion at the bottom (Wetzel, 1975). The anoxic conditions are created from oxidation of chemical species, the aerobic decomposition of NOM (Matthews and Effler, 2006) and no oxygen regeneration due to limited mixing. Due to the anoxic conditions, a reducing environment is created and Mn stays in its dissolved form; Mn (II) (Figure 1) (MWH, 2005). At this time Mn and Fe concentrations reach over 1 mg/L, leading to periods of low level Mn breakthrough and episodes of coloured water. As such, the drinking water treatment process at BLWTP is not optimized to remove Mn.

According to utility plant data, Bennery Lake is nitrogen deficient all year round, with an N concentration of less than 0.05 mg/L. This does not meet the 0.12 mg/L of ammonia-nitrogen required by the C:N:P nutrient ratio for bacterial nutrient supplementation. Phosphorus is not limited during the summer and fall, with values of approximately 0.12 mg/L. Some P limitation occurs during the winter with an average of 0.037 mg/L, with some days less than 0.02 mg/L. The nutrient ratio of 0.026 mg/L of orthophosphate-phosphorus was mostly achieved throughout the year in Bennery Lake.

## 3.2 EXPERIMENTAL DESIGN: NUTRIENT ENHANCEMENT

Three operational factors at two levels were examined in this experiment. Every combination of the factors is equal to the conditions in one biofilter (Table 2). GAC and anthracite were chosen as they have successfully removed Mn in other biofiltration experiments (Lauderdale et al., 2011, Kohl and Dixon, 2012). Media was the controlled factor in this experiment with a GAC/sand and anthracite/sand filter operating with influent raw water at the natural lake pH 6. Research has shown MOB to be capable of

biological oxidation at this pH (Bourgine et al., 1994). A pH of 9-11 was chosen as an upper limit pH comparison as Mouchet (1992) suggested that biological Mn oxidation requires a pH of > 7.4. For simplicity this condition will be referred to as pH 9 for the rest of the paper. Phosphorus was added as phosphoric acid ($H_3PO_4$) to ensure P was not limited in the biofilter influent (Lauderdale et al., 2011). The P dose was determined using the molar ratio of 100:10:1 of C:N:P by measuring the biodegradable dissolved organic carbon (BDOC) in the raw water. The biodegradable portion of DOC is the amount of carbon consumed by heterotrophic microorganisms between day 1 and day 30 (Volk and LeChevallier, 2002). Based on bioavailable carbon concentrations of about 16 µg/L in July 2012, a P dose of 20 µg/L and 200 µg/L were chosen to satisfy the C:P ratio of 100:1 and 100:13, respectively. These doses occupied a wider range than other studies for Mn and DOC removal at 100:1 and 100:2, respectively (Lauderdale et al., 2011) but were similar to P doses previously used for optimal biofilm development (Fang et al., 2009). These design parameters have been compared to a pilot scale and full scale biofilter study (Table 3).

**Table 2.** Nutrient enhancement experimental $2^3$ factorial experimental design

| | **Media** | **P** | **pH** |
|---|---|---|---|
| High | GAC/sand | 200 µg/L | 9-11 |
| Low | Anthracite/sand | 20 µg/L | ~6 (raw water) |

**Table 3.** Comparing bench-, pilot-, and full-scale biofilter parameters for Mn removal

| Parameter | Bench-Scale Biofilter Current Study | Pilot-Scale Biofilter Lauderdale et al., (2011) | Full-Scale Biofilter Burger et al., (2008) |
|---|---|---|---|
| Target Phosphorus Concentration (mg/L) | 0.020 and 0.20 | 0.020 | 0 |
| Media Type | Anthracite-Sand/ GAC-Sand | GAC-Sand | Sand |
| Hydraulic Loading (Q/A, m/h) | 0.0059 | 11 | 23 |
| Media Effective Size ($d_{10}$, mm) | Anth.= 0.89 GAC=1.1 | 1.1 | N.R. |
| Sand Effective Size ($d_{10}$, mm) | 0.52 | 0.55 | 0.55 |
| Media Uniformity Coefficient (U) | Anth.=1.67 GAC=1.40 | 1.40 | N.R. |
| Sand Uniformity Coefficient (U) | 1.53 | N.R. | N.R. |
| Media Depth (m) | 0.1 | 1.02 | N/A |
| Sand Depth (m) | 0.05 | 0.20 | 1.8 |
| EBCT (min.) | 15 | N.R. | N.R. |

N.R. = Not reported

## 3.3 EXPERIMENTAL SET-UP: NUTRIENT ENHANCEMENT

### 3.3.1 Filtration Set-Up

The experimental set-up is illustrated in Figure 1. The bench-scale biofiltration unit consisted of 10 chromatography columns (Kimble Chase Flex Column, 2.5 cm ID by 20 cm) packed with 10 cm anthracite or GAC over 5 cm sand. The 200 L raw reservoir was filled with untreated raw water every 2 to 3 days. Tubing (Cole-Parmer PharMed, size L/S 14) was used with peristaltic pumps cartridges and pump controllers (Cole-Parmer Masterflex), to feed the biofilter influent. Raw water from the raw reservoir (Figure 1) was pumped directly to a GAC/sand and an anthracite/sand control filter. The controls operated at pH 6 with no nutrient enhancement. Another pump brought raw water to four, 4 L mixing bottles representing the four experimental conditions: high P/pH 9; high P/pH 6; low P/pH 9; and low P/pH 6. Each mixing bottle pumped to two filter columns

(GAC/sand and anthracite/sand), with the filter effluent going to waste where it was treated with the full-scale plant backwash water.

### 3.3.2 Stock Solutions

To achieve these conditions, $H_3PO_4$ was dosed at 0.22 mg/L and 2.2 mg/L for the low P and high P stock solutions, respectively and a 0.075 mMole sodium hydroxide (NaOH) stock was used to increase the pH to ~ 9.

### 3.3.3 Flow Rates

The biofilters operated at a loading rate of 0.99 mL/cm$^2$/minute to achieve an EBCT of 15 minutes. This time was chosen as it has been shown that 90% of biodegradable organic matter and Mn can be removed with an EBCT of 10-20 minutes (Bourgine et al., 1994; Provost et al., 1995). The stock solutions pumped at a flow rate of 2 mL/min and the raw water to the mixing bottles at 10 mL/min to achieve an overflow of about 4 mL/min for the pH 9 mixing bottles and an overflow of about 2 mL/min for the pH 6 mixing bottles.

### 3.3.4 Biofilter Backwashing

The filters were backwashed when 20% headloss was reached. Backwashing was done for 30 seconds at a loading rate of 83 mL/cm$^2$/min. This rate was not adjustable as the backwash hose was dependent on the pressure from the full scale filter. After backwashing, the filters ripened for at least 15 minutes before any sample was taken.

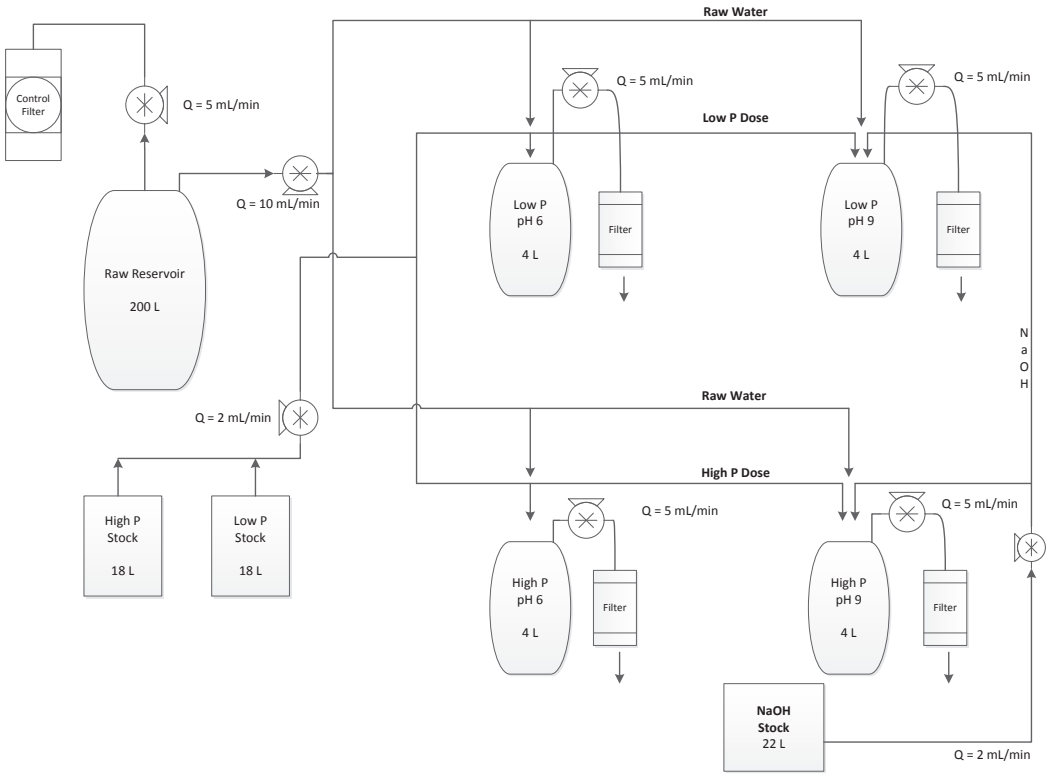



**Figure 1.** Experimental set-up for direct biofiltration with nutrient enhancement
Each filter in the diagram represents two experimental filters, one with anthracite/sand media, and one with GAC/sand media

## 3.4 EXPERIMENTAL DESIGN: NUTRIENT PLUS OXIDANT ENHANCEMENT

Three operational factors at two levels were also examined in this experiment: media type (GAC/sand or anthracite/sand); nutrient enhancement with P (300-500 µg/L); and oxidant enhancement with $H_2O_2$ (0.5 mg/L). Every combination of the factors is equal to the conditions in one biofilter (Table 4). This experiment was run at the natural lake pH of 6. This pH was chosen because the optimal Mn removal occurred at pH 6 during the nutrient enhancement experiment. Phosphorus was added as a nutrient again but was tested at a higher concentration than the previous experiment at a C:N:P ratio of 100:0:19. This dose was chosen to determine if increased nutrient would correspond with increased Mn removal. An oxidant was added in this experiment as $H_2O_2$ to target greater DOC removal than with nutrient enhancement and to reduce headloss. The dose of 0.5 mg/L was chosen as research has shown that organic and inorganic contaminants can be

removed at this low concentration (Christensen et al., 1990; Neyens et al., 2002; He et al., 2009).

**Table 4.** Combined nutrient and oxidant enhancement $2^3$ factorial experimental design

| | **$H_2O_2$** | **P** | **Media** |
|---|---|---|---|
| High | 500 µg/L | 300-500 µg/L | GAC/sand |
| Low | - | - | Anthracite/sand |

## 3.5 EXPERIMENTAL SET-UP: NUTRIENT PLUS OXIDANT ENHANCEMENT

### 3.5.1 Filtration Set-Up

The experimental set-up is illustrated in Figure 2.The bench-scale biofiltration set-up was similar to the nutrient enhancement experiment, and consisted of 8 chromatography columns (Kimble Chase Flex Column, 2.5 cm ID by 20 cm) packed with 10 cm of new anthracite or GAC on top of 5 cm of sand. The 200 L raw reservoir was filled with untreated raw water every 2 to 3 days. Raw water was pumped with tubing (Cole-Parmer PharMed, size L/S 14) and peristaltic pumps, pump controllers, and cartridges (Cole-Parmer Masterflex) to three, 4 L mixing bottles which contained $H_3PO_4$ and $H_2O_2$ solutions for phosphorus addition and oxidant addition, respectively. The three mixing bottles represented the three experimental conditions: P plus $H_2O_2$; only P; and only $H_2O_2$. Each mixing bottles contents were then pumped to two filter columns, one GAC/sand and one anthracite/sand, with the filter effluent going to waste where it was treated with the full-scale plant backwash water. Raw water was pumped directly to two control filters from the raw water tub. A GAC/sand and anthracite/sand control operated at pH 6 with no chemical addition.

### 3.5.2 Stock Solutions

The P stock (2.5 mg/L) and $H_2O_2$ stock (5 mg/L) solutions were prepared with the plant's filtered water and pumped into their requisite mixing bottles, mixing with the raw water.

### 3.5.3 Flow Rates

The 8 biofilters operated at a flow rate of 5 mL/min to achieve an EBCT of 15 min. The stock solutions pumped at a flow rate of 2-3 mL/min and the raw water to the mixing bottles at 10 mL/min. This achieved an overflow of about 2-3 mL/min for the $H_2O_2$ and P mixing bottles, and an overflow of about 5 mL/min for the $H_2O_2$ combined with P mixing bottle.

### 3.5.4 Biofilter Backwashing

The filters were backwashed when the filter effluent decreased to a flow rate of 4 mL/min which was about 80% of the clean bed flow rate. Backwashing was done with un-chlorinated filtered water for 30 seconds at a rate of 420 mL/min. This rate was not adjustable as it was dependent on the full-scale plant filters. After backwashing, the filters ripened for at least 15 minutes before any sample was taken.

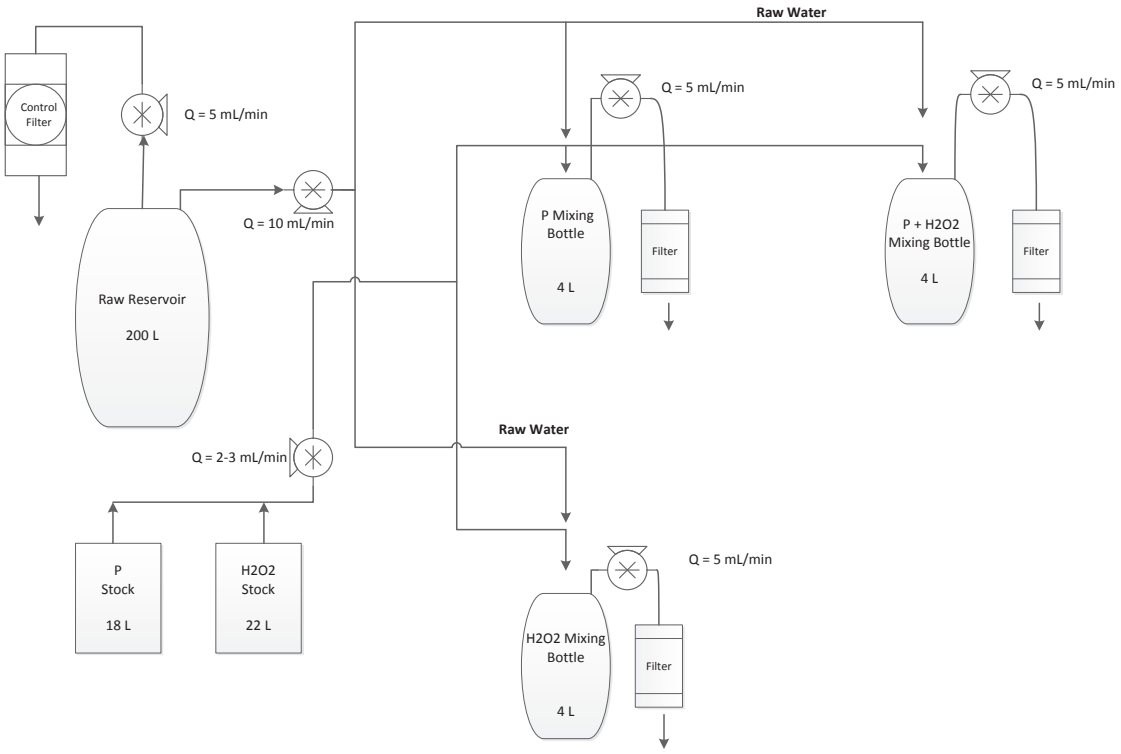



**Figure 2.** Experimental set-up for direct biofiltration with nutrient enhancement plus oxidant enhancement
Each filter in the diagram represents two experimental filters, one with anthracite/sand media, and one with GAC/sand media

## 3.6 ANALYTICAL METHODS

Deionized water (DI) obtained using a Milli-Q purification system was used for cleaning glassware and preparing all the chemical stocks unless otherwise noted. All samples were stored at 4°C pending analysis. All filtration involved 0.45 µm filter membranes that were first conditioned with 500 mL of DI.

### 3.6.1 Manganese and Iron

Biofilter effluent manganese (total and dissolved) was analyzed three times a week using inductively coupled plasma mass spectrometry (Thermo Fisher XSeries 2 ICPMS). For each filter, 5 mL samples were collected in 14 mL test tubes and preserved with nitric acid. Dissolved samples were filtered through 0.45 µm pre-conditioned filter membranes. This filter size was larger than for other studies (Kohl and Dixon, 2012) but as little

difference occurs between 0.22 μm and 0.45 μm filters for Mn (Kohl and Medlar, 2006), the larger ones were used. The minimum detection level (MDL) was 0.8 μg/L.

### 3.6.2 Natural Organic Matter

NOM was measured as total organic carbon (TOC). Filter effluent samples were collected weekly in headspace free 40 mL vials, preserved with three drops of phosphoric acid to pH < 2 and analyzed (Shimadzu TOC-VCSH TOC Analyzer). Samples were filtered through a preconditioned 0.45 μm filter membrane. BDOC was determined using a procedure described by Servais et al. (1989).

### 3.6.3 Phosphorus

Phosphorus was measured using the PhosVer 3 method (#8048) with a HACH DR5000 Spectrophotometer. This method detects P from 0.02 mg/L to 1.60 mg/L. Filter influent P concentration was measured before each sample was taken. Raw water P data was coupled with utility sampling data.

### 3.6.4 Organic Size Distribution

Size exclusion chromatography (SEC) was analyzed with a high pressure chromatograph (Perkin-Elmer Series 200). Duplicate samples were taken bi-weekly to monthly for filter influent and effluent samples to analyze for organic particle size distribution. Samples were filtered through a 0.45 μm pre-conditioned filter membrane and then collected headspace free in pre-cleaned and baked (100°C for 24 hours) 2 mL vials. Samples were stored at 4°C prior to analysis.

### 3.6.5 Disinfection By-Product Formation

Total formation potential for trihalomethanes (THMfp) and haloacetic acids (HAAfp) were analyzed for the raw water and biofilter effluents. The procedure followed Standard Methods (5710).

Samples were adjusted to pH 8 ± 0.2 with borate buffer and 1 N NaOH and 1 N $H_2SO_4$ as necessary. Samples were then dosed with chlorine at 1.2-2.8 mg/L and stored in 130 mL chlorine demand free amber bottles for 24 ± 1 hour at room temperature. Samples were

then transferred from the amber bottles to baked (100°C for 24 h) 20 mL vials and capped headspace free.

THM samples were preserved with 1 drop of 50 g/L ammonium chloride solution (20%), 2 drops of 8 g/L sodium thiosulphate solution (10%) and 3 drops of 0.1 N hydrochloric acid. HAA samples were preserved with 1 drop of 50 g/L ammonium chloride solution (20%). Extracted samples were analyzed using a gas chromatograph (Varian CP-3800, CA).

### 3.6.6 Other Water Quality Parameters

The influent pH was measured before each effluent sample was taken. This was done three times a week with an Accumet XL 50 plastic bodied, gel-filled, combination pH electrode. A three-point calibration at pH 4, 7 and 10 was conducted each day prior to any pH measurements. Temperature was also measured when the calibrated pH probe was placed in each sample. ORP was measured monthly with an Orion® Ag/AgCl electrode. DO was measured monthly with a multi-parameter meter with self-stirring BOD probe.

## 3.7 MICROBIOLOGICAL TECHNIQUES FOR MEDIA ANALYSIS

### 3.7.1 Scanning Electron Microscopy

Media samples from the top 2.5 cm of each biofilter were fixed for SEM using a procedure described by Lauderdale et al. (2011). This procedure involved washing with DI, fixing with gluteraldehyde (2.5%), and paraformaldehyde (4%) in a cacodylate buffer (0.1 M) followed by post-fixing in osmium tetroxide (1%). The media was dried using ethanol at concentrations of 20, 50, 75, 95 and 100%, along with propylene oxide and desiccation. The samples were imaged using a Hitachi S-4700, FE-SEM. This procedure was done immediately after the filters had been taken offline.

### 3.7.2 Manganese Oxidizing Bacteria

The experimental procedure for obtaining MOB isolates was adapted from Burger (2008a). Media samples were taken directly after the 132 day experiment. The media was

homogenized by stirring the top few inches of media. Two grams of media were obtained and suspended in a test tube with 10 mL of phosphate buffered saline (PBS). In order to dislodge the biofilm from the media, the PBS filled tubes were sonicated for 1 minute, put on ice for 1 minute and vortexed for 5 seconds. These steps were done in succession and repeated 5 times. Dilutions to $10^{-6}$ were spread plated with 0.1 mL of sample in duplicate on R2A agar to encourage heterotrophic bacterial growth. Seventeen mg/L of $MnSO_4$ (Fisher Scientific, ON) was added to the R2A agar to allow for the identification of MOB, which appear black due to their oxidation of the Mn(II). After incubating at room temperature for 30 days, the black colonies were counted and heterotrophic plate counts (HPCs) of non-black colonies was conducted.

### 3.7.3 Adenosine Triphosphate (ATP)

Media biofilm ATP samples were collected directly after the filters were taken offline. Media samples (1 g) were collected in sterile containers and biofilm metabolic activity was measured using the Deposit Surface Analysis test (LuminUltra Technologies Ltd., NB). Relative light units were measured using a Kikkoman Lumitester (C-100) and converted to ATP concentrations as per the company's formula.

## 3.8 STATISTICAL AND DATA ANALYSIS

Data was analyzed by determining the minimum, maximum, standard deviation and mean values. The error bars presented in the figures represent the 95% confidence interval of the data set except for Figure 10 and 15, where standard deviation was used. Confidence intervals were used as the standard deviation was large for each biofilter condition. An ANOVA test was done to determine the significance of pH, nutrient enhancement, media, oxidant enhancement and their interactions (Minitab 16). The factors were tested at a 95% significance level.

# CHAPTER 4: RESULTS AND DISCUSSION-NUTRIENT ENHANCEMENT

## 4.1 SOURCE WATER CHEMISTRY AND ACCLIMATION PERIOD

### 4.1.1 Biofilter Acclimation Period

The system took approximately 14 days to acclimate while the P nutrient addition dose was being determined. No samples were taken during this time and no bacterial inoculant was used, therefore the biofilm formed from indigenous Bennery Lake bacteria. This time frame to reach steady-state biological activity was shorter than other biofiltration experiments (Burger et al., 2008b; Peldszus et al., 2012; Kohl and Dixon, 2012). This experiment was done at bench-scale and therefore represented a smaller media surface area for the bacteria to occupy. This could have contributed to the shorter acclimation time than other pilot-scale studies. Mn was consistently removed to concentrations below 50 µg/L for the pH 6 filters since sample day 1 (post 14 day acclimation period); therefore all samples were used for data analysis.

### 4.1.2 Source Water Chemistry

Raw water characteristics were sampled for over 5 months from July 2012 to November 2012 (Table 5). The raw water Mn trend is shown in Figure 3. The raw water Mn concentration reached a high of 1049 µg/L on day 66, decreased to 168 µg/L on day 68 and reached a minimum of 24.8 µg/L on day 130. Fe followed a similar pattern with a high of 2.59 mg/L on day 66, decreased to 0.593 mg/L on day 86, with a low of 0.189 mg/L on day 132. The DOC concentration showed less variation during the experiment. It ranged from 3.5 mg/L to 7.0 mg/L with an average DOC concentration of 5.2 mg/L. DO increased after the lake un-stratified and oxygen was redistributed throughout. The influent raw water averaged 8 mg/L and 277 mV for DO and ORP, respectively. These measurements were made as the raw water (biofilter influent) entered the plant.

### 4.1.3 Summer/Fall and Experiment Temperature

Throughout the experiment, the raw water temperature ranged from 6-16$^{o}$C and increased to an average of 19$^{o}$C once indoors and filtered. Due to the increase in experimental

temperature, the bench-scale results were not directly comparable to the full scale process. As soluble Mn loading is only a summer concern for BLWTP, as long as the MOB were well established in the filter media, they could potentially return to full oxidizing strength after every winter. Research has shown successful MOB Mn removal without biofilter re-inoculation after mild winter conditions (Hoyland, 2013).

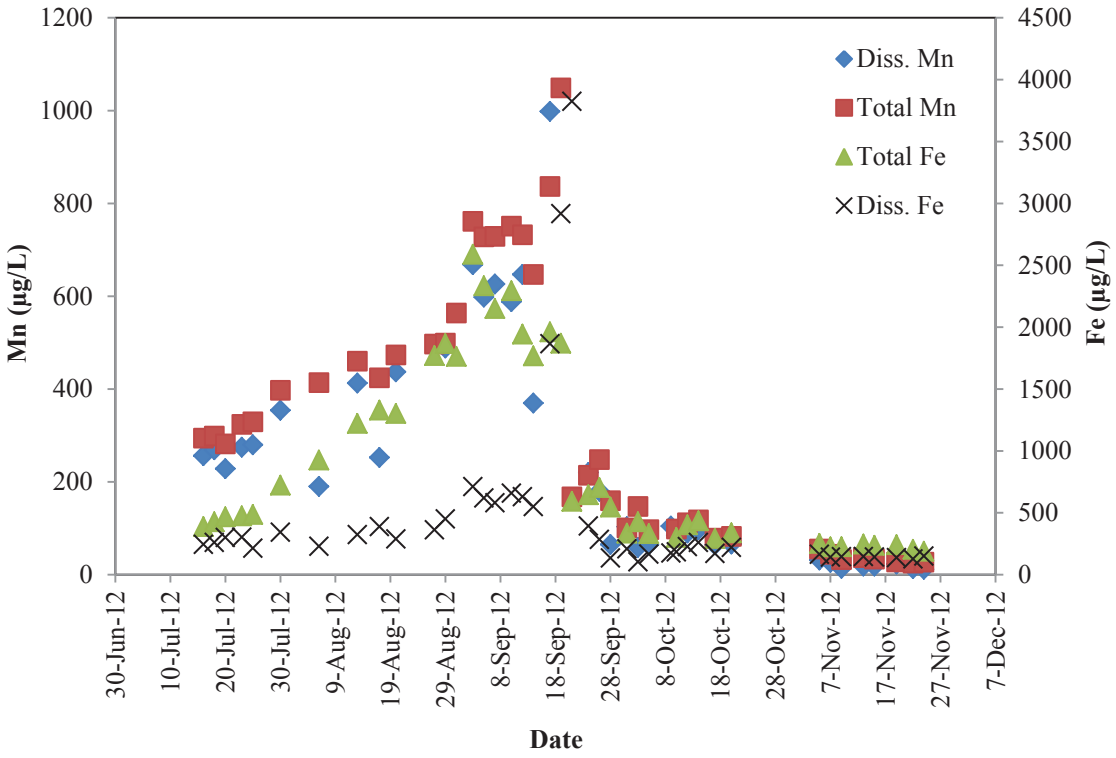



**Figure 3.** Raw water manganese and iron trends from July to November 2012
Metals concentration increased until the lake-turnover in September 2012, followed by lower metals concentrations.

**Table 5.** Raw water quality parameters measured from July 2012 to November 2012

| Parameter | Data Range | Number of Samples | Mean ± Standard Deviation |
|---|---|---|---|
| Total Mn (µg/L) | 24.82-1049 | 41 | 327 ± 277 |
| Total Fe (µg/L) | 189.7-2589 | 42 | 908 ± 751 |
| DOC (mg/L) | 3.47-6.99 | 20 | 5.16 ± 1.27 |
| Turbidity (NTU) | 0.598-5.97 | 27 | 2.56 ± 2.03 |
| pH | 5.84-6.73 | 63 | 6.06 ± 0.22 |
| Raw Lake Water Temp ($^{o}$C) | 6.20-16.5 | 64 | 12.5 ± 2.11 |
| Experiment Temp ($^{o}$C) | 16.4-20.5 | 45 | 19.2 ± 0.768 |
| DO (mg/L) | 4.20-10.3 | 6 | 7.97 ± 2.04 |
| ORP (mV) | 236-329 | 5 | 277 ±35.8 |

## 4.2 ANALYSIS OF FACTORS AFFECTING MANGANESE REMOVAL

The analysis of tested experimental factors that affected Mn removal are as follows. The GAC/low P/pH 6 biofilter removed the most Mn with an average effluent concentration of 18 µg/L, meeting the 50 µg/L aesthetic objective 86% of the time. The NE/pH 6 biofilters for both media obtained an average removal of 91% Mn removal which was 20% greater than the NE/pH 9-11 filters for both media. Figure 4 compares the Mn effluent of the ten biofilters.

### 4.2.1 Effect of Nutrient Enhancement on Mn Removal

Throughout the experiment the raw water P concentration increased from 23 µg/L to an average of 116 µg/L. With this raw water increase and inconsistencies in the peristaltic pump flow rate, the low P target dose of 20 µg/L up increased up to the high P target dose of 200 µg/L and the P dose for all eight filters averaged 230 ± 60 µg/L. The changing influent P concentration meant that P concentration was not found to be a significant factor in Mn removal. The rest of the results will not differentiate between the high P and the low P filter conditions (all filters are enhanced with P). This also meant the controls operated with an average background P concentration of 116 µg/L, satisfying

the C:P nutrient ratio at 100:8. The raw water was P limited (<15 µg/L) at times during July and August 2012.

The anthracite/pH 6 and GAC/pH 6 filters achieved on average 8% and 19% greater Mn removal than the non-nutrient enhanced anthracite and GAC controls, respectively (Figure 4). This trend was not observed for the pH 9 filters. Both the anthracite/pH 9 and GAC/pH 9 filters averaged 8-9% less Mn removal compared to the controls. NE biofilters at pH 6.4-6.7 have shown to remove ≥ 98% Mn with an influent up to 220 µg/L (Lauderdale et al., 2011). Nutrient enhancement encourages optimal microbial growth, increased ATP concentrations and therefore improves the biofilms ability to remove contaminants (Lehtola et al., 2002; Polanska et al., 2005; Fang et al., 2009).

### 4.2.2 Effect of pH on Mn Removal

pH was found to be a significant factor for Mn removal ($\alpha = 0.05$) and pH 6 resulted in more Mn removal than pH 9. The GAC/pH 6 and anthracite/pH 6 biofilters averaged 18-33 µg/L effluent Mn while the GAC/pH 9 and anthracite/pH 9 biofilters averaged effluent Mn of 71-112 µg/L. The pH 6 filters removed 91% Mn and met the aesthetic guideline 88% of the time. The pH 9 filters obtained 70% removal but only met the aesthetic guideline 49% of the time. These findings at pH 6 were within the pH and ORP range suitable for MOB oxidation (Bourgine et al., 1994). Although Mn can theoretically be removed at pH 6 by MOB, only a few studies have actually achieved Mn removal with biofiltration at pH 6 (Bourgine et al., 1994; Hoyland, 2013). Research by Burger et al. (2008b) showed Mn removal from groundwater with biofiltration at pH 6.3 and 6.5. This pH result was not observed by Kohl and Dixon (2012) who found less effective Mn removal at pH 6.5 than between 7.2-7.6. Also, Gage et al. (2001) and Mouchet (1992) stated that the field of activity for biological Mn oxidation cannot occur below pH ~7.4 (Figure 7). As the biofilm was formed from indigenous bacteria which naturally exist at pH 6, it is possible that these bacteria have acclimatized to their environment and oxizide Mn more efficiently at pH 6 than pH 9.

### 4.2.3 Effect of Media on Mn Removal

There was no significant difference in Mn removal between anthracite and GAC. Figure 5 and 6 compare weekly influent and effluent Mn concentrations for the GAC and anthracite biofilters, respectively. In Figure 5, day 64, 68 and 91 were considered statistical outliers for the GAC/low P/pH 6 biofilter. Also, a large spike in effluent Mn was observed in the GAC control on day 128. This was due to filter clogging and necessary increased backwashing. The GAC/pH 9 biofilter experienced Mn breakthrough periodically throughout the experiment and averaged an effluent of 111 µg/L. Limited breakthrough occurred for the GAC/pH 6 biofilter which consistently removed Mn to an average of 18 µg/L. The anthracite/pH 6 biofilter provided more consistent Mn removal than the anthracite/pH 9 biofilter, reducing the average Mn concentration from 327 µg/L to an average of 33 µg/L and 71 µg/L, respectively. After the decrease in influent Mn on day 68 caused by the lake stabilizing and re-distributing the Mn throughout, all the biofilters experienced Mn breakthrough into the filter effluent.

GAC media has been found to remove greater Mn than anthracite media (Kohl and Dixon, 2012), although the above results suggest that Mn can be removed with both GAC and anthracite with an influent DO of 8 mg/L and ORP of 277 mV at pH 6. Hoyland (2013) also found anthracite/gravel to be successful in removing > 98% Mn at pH 6.3.

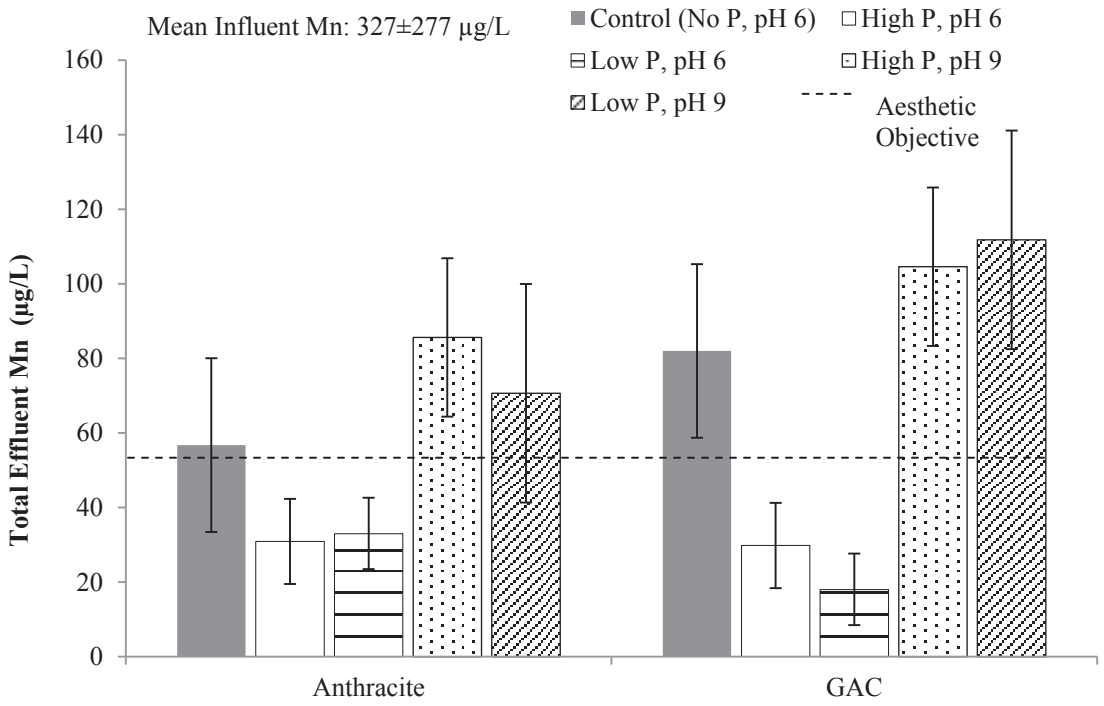



**Figure 4.** Nutrient enhancement biofilter average effluent total manganese concentrations over 132 days
Controls = pH 6 with average background P concentration of 116 µg/L (C:P ratio of 100:8).

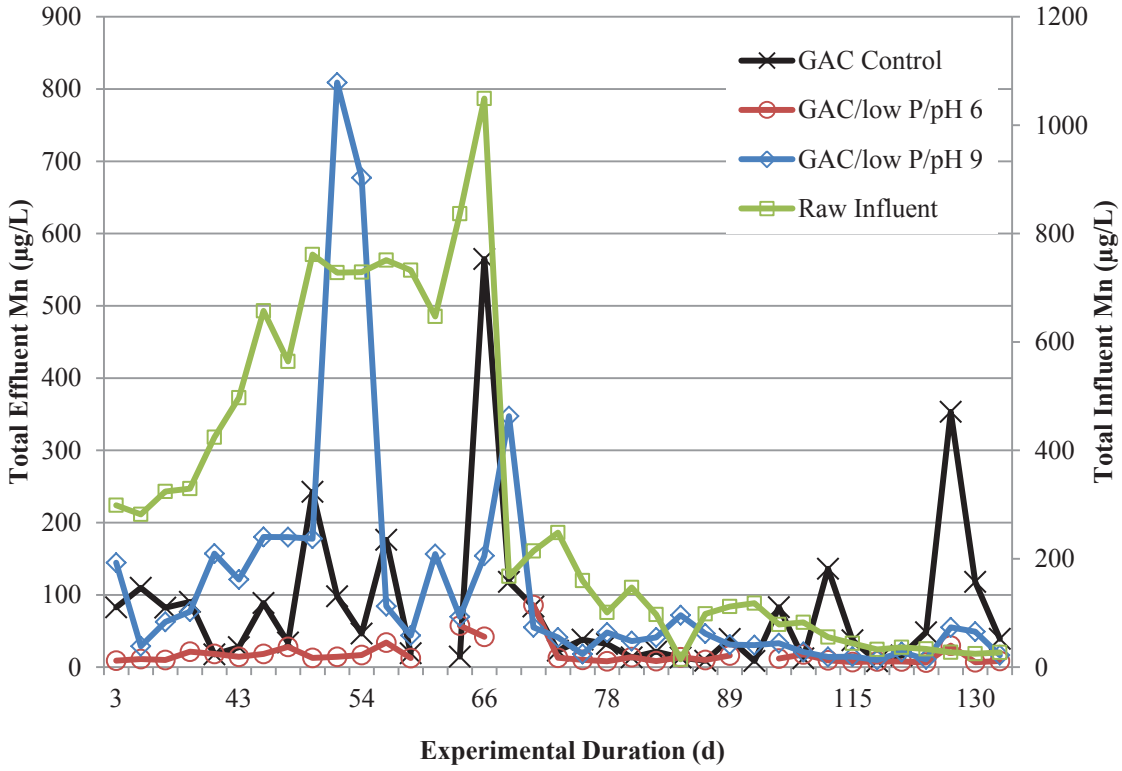



**Figure 5.** Effluent manganese concentrations for a pH 6 and pH 9 GAC biofilter
GAC Control = pH 6 with average background P concentration of 116 µg/L (C:P ratio of 100:8)

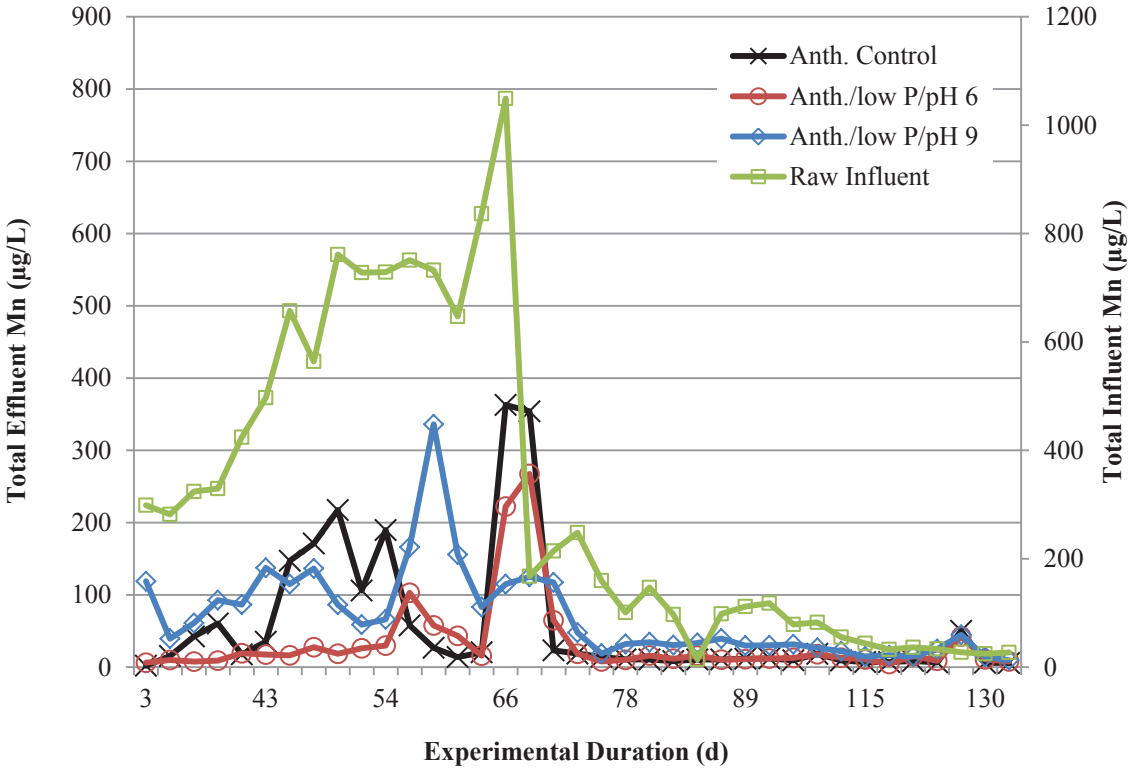



**Figure 6.** Effluent manganese concentrations for a pH 6 and pH 9 anthracite biofilter Anthracite Control = pH 6 with average background P concentration of 116 µg/L (C:P ratio of 100:8)

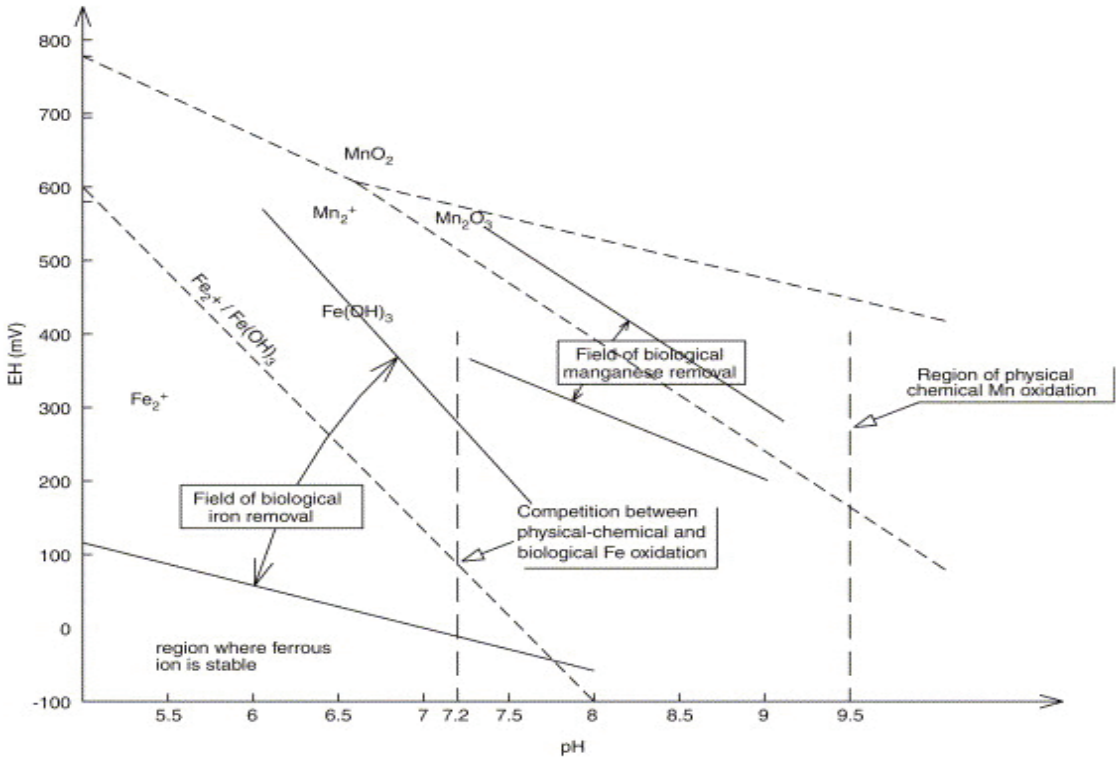



**Figure 7.** Field of activity for biological and physical/chemical manganese removal (Mouchet, 1992)

## 4.3 EFFECT OF P, pH AND MEDIA ON DOC REMOVAL

DOC removal can be seen in Figure 8. Maximum DOC removal was obtained through an anthracite/pH 9 biofilter with a 28% reduction in DOC from an average of 5.16 mg/L to an average effluent of 4.10 mg/L (Figure 8).

Nutrient enhancement, media and pH were not found to be significant factors in DOC removal, although nutrient enhancement was found to increase organics removal. An average of 23% DOC removal was achieved with nutrient enhancement, 11% > the controls. DOC removal was not significantly different between the two media. The GAC/pH 6 and anthracite/pH 6 filters obtained average effluents of 4.2-4.6 mg/L and 4.2-4.7 mg/ and achieved 13% and 9% increased removal over their controls, respectively. The pH 9 filters removed slightly more DOC than the pH 6 filters with average effluents of 4.1-4.4 mg/L and 4.2-4.7 mg/L, respectively.

Other direct biofiltration studies of raw water have shown more limited DOC removal. For example, Peldszus et al. (2012) removed less than 15% DOC. DOC removals have been reported between 5-75% by other authors, but are typically around 10-20% removal (Hozalski et al., 1995; Urfer et al., 1997). To increase DOC removal during biofiltration, a longer EBCT may be needed (Peldszus et al., 2012). The experimental results were within the usual reported removals but were less than Lauderdale et al. (2011) who saw their NE biofilters remove 75% more DOC than the control. As Bennery Lake was nitrogen deficient, nitrogen addition may also increase DOC removal as nutrient limitation can inhibit microbial substrate degradation and organics removal (Nishijima et al., 1997). Organic material was removed with both GAC and anthracite in this experiment at an average temperature of 19$^{o}$C. Other research has shown that TOC removal was similar with GAC and anthracite biofilters at 21-25$^{o}$C (Emelko et al., 2006).

Based on the biofiltration study, it is noted that additional treatment should be considered to improve DOC removal. Biofiltration could potentially act as a pre-treatment to conventional treatment (Zhu et al., 2010) or membrane processes (Peldszus et al., 2012).

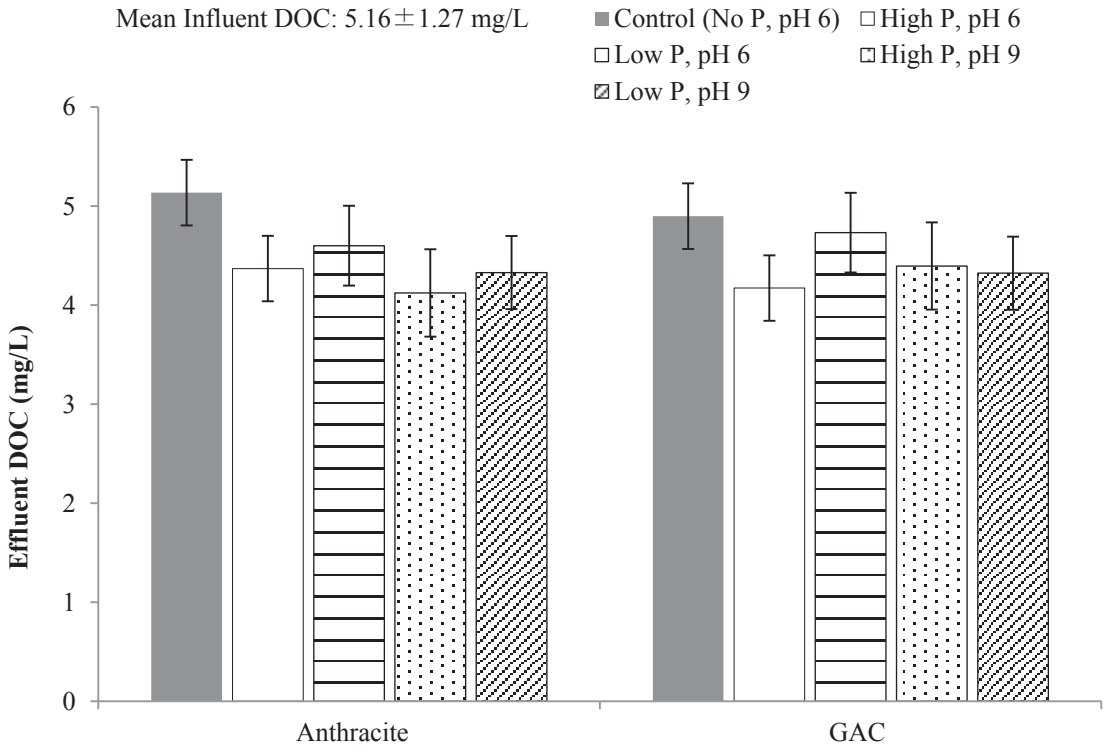



**Figure 8.** Nutrient enhancement average effluent DOC concentrations over 132 days Controls = pH 6 with average background P concentration of 116 μg/L (C:P ratio of 100:8)

4.3.1 Organic Molecule Size Fractions of Raw and Treated Water

Figure 10 represents the effluent molecular weight NOM fractions as per the average peak area based on SEC. Little removal occurred between the influent raw water NOM molecular weight (MW) fractions in the 25880-28800 Da size range and the biofilter effluents. The pH 9 biofilters appeared to remove the most NOM compared to the raw water influent for the 25880-28800 Da NOM fraction. The smaller NOM fractions were not significantly different from the influent raw water. NOM studies have shown that removal of high molecular weight humic material can be achieved through conventional treatment processes. Based on research by Edzwald (1993) and Sharp et al (2006), high MW, hydrophobic fractions are more easily removed during coagulation than other fractions. Studies have also showed correlation between MW and charge density, in that larger compounds have a greater charge density. The larger the negative charge on the

NOM surface, the greater the interaction it will have with the positively charged metal oxidant (Ratnaweera et al., 1999). Overall, biofiltration appeared to target removal of larger MW NOM which are also targeted by coagulation.

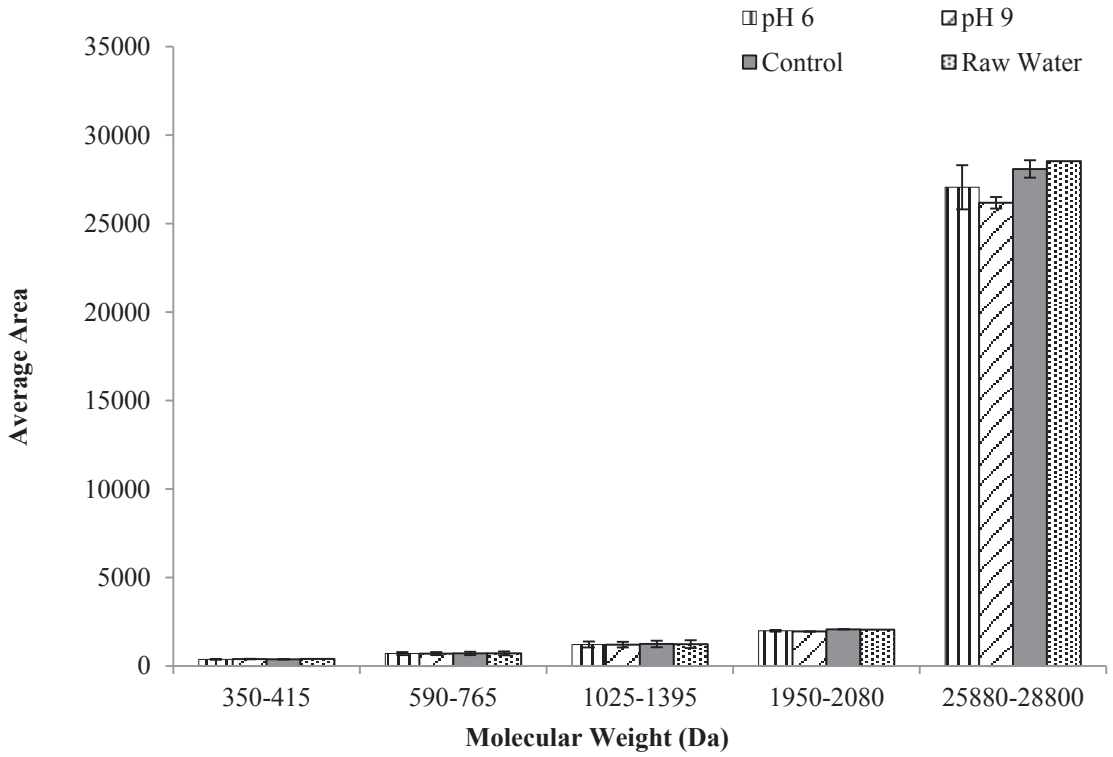



**Figure 9.** Nutrient enhancement biofilter effluent molecular weight NOM fractions as per peak area

4.3.2 DBP Removal

Trihalomethane formation potential (THMfp) and haloacetic acid formation potential (HAAfp) was measured in the raw and treated water. There was not a trend which identified optimal conditions for DBP reduction with biofiltration.

The main THM compound identified in the raw water was chloroform and the average raw water THMfp concentration was 92 µg/L. The pH 9 biofilters ranged from less than 0% to 21% removal with average effluents ranging from 203-73 µg/L . The GAC/pH 9 biofilter that achieved 21% THMfp removal obtained an average effluent of 73 µg/L

which is below the 100 µg/L guideline as set by the NS water treatment standards (NSE, 2012). The pH 6 biofilters did not remove any THMfp compared to the average raw water THMfp. This could have been because DBPs were only measured twice during the experiment duration. More consistent DBP sampling would need to be done to fully examine biofiltrations role in reducing DBPs.

The most abundant HAA compound in the raw water was di- and trichloroacetic acid. The average raw water HAAfp was 155 µg/L. The pH 9 filters ranged from 11% to 25% removal from the raw water HAAfp, obtaining average effluent HAAfp concentrations of 119-104 µg/L. The pH 6 filters ranged from less than 0% removal to 22% HAAfp removal, obtaining effluents of 168-111 µg/L. The biofilters did not remove the HAAfp to below the 80 µg/L guideline as set by the NS water treatment standards (NSE, 2012).

Although some DBP removal was achieved with both the pH 6 and pH 9 biofilters, increased HAAfp removal would be required with biofiltration to meet the current effluent guideline. The experimental THMfp and HAAfp removals were less than what was achieved by the full-scale plants conventional process. This was expected as the conventional coagulation process is capable of removing more DOC and more DBPs than the bench-scale biofiltration set-up. Overall, biofiltration with nutrient enhancement did not play a role in consistently reducing DBP formation potential.

## 4.4 IRON REMOVAL

Fe removal was also observed with biofiltration and NE. Its removal is not a concern at BLWTP as it can be removed with the conventional treatment. The results are reported below. Influent Fe levels varied from 43-2590 µg/L during the experiment. Fe was removed with all the biofilter conditions, but not to below the 0.3 mg/L aesthetic objective (Figure 9). The NE filters obtained similar removals regardless of media. The pH 9 filters removed more Fe than the pH 6 filters with average effluents of 360-474 mg/L (53% removal) and 536-575 mg/L (38% removal), respectively.

These results were expected as Mn and Fe require different treatment conditions for bacterial oxidation (Mouchet, 1992; Kohl and Dixon, 2012). Fe oxides likely helped to

remove both Mn and Fe by adsorption to the oxides within the media. Sahabi et al. (2009) found aged anthracite media with Fe and Mn oxides removed soluble Mn by adsorption and further autocatalytic oxidation. Furthermore, Fe oxides have also been shown to adsorb organics (Korshin et al., 1997), possibly aiding in DOC removal in this experiment.

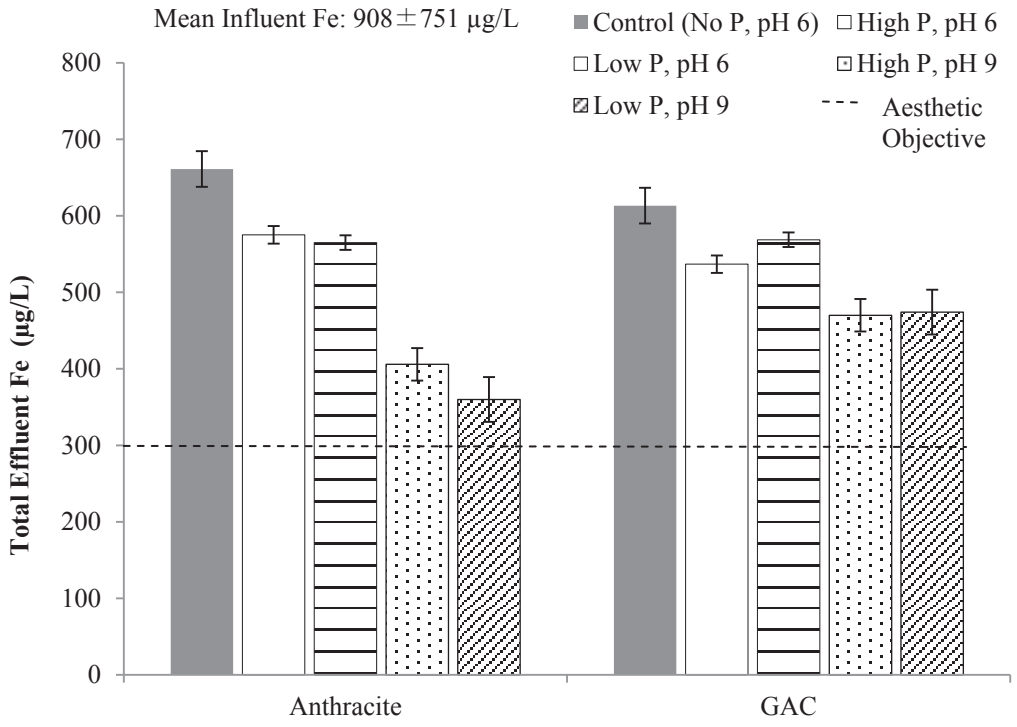



**Figure 10.** Nutrient enhancement average effluent total iron concentrations over 132 days Controls = pH 6 with average background P concentration of 116 µg/L (C:P ratio of 100:8)

## 4.5 MICROBIAL ANALYSIS

### 4.5.1 Biofilm ATP Concentrations

As ATP is the primary energy carrier in all living organisms, it can indicate bacterial metabolic activity and biomass (MGH, 2005). ATP coincided with Mn removal as there

was a significantly higher biofilm ATP concentration for both media in the pH 6 biofilters than the pH 9 biofilters. The GAC/pH 6 filters averaged $1.13\times10^6$ pg/g ATP, 79% > the control. The GAC/pH 9 filters only averaged $3.18\times10^5$ pg/g ATP. The anthracite/pH 6 filters averaged $1.17\times10^6$ pg/g ATP, just 20% > the control. This was due to the anthracite control having a high ATP concentration itself. The anthracite/pH 9 filters only averaged $3.24\times10^5$ pg/g ATP. The 10-fold difference between the pH 6 and pH 9 filters ATP concentrations indicate a lower microbial population and likely a 10-fold lower capacity to biologically oxidize Mn. Other research has shown NE biofilters to have slightly higher media ATP concentrations at the end of a pilot-scale filter run with $1.50\times10^6$ pg/mL. These ATP concentrations led to successful Mn and DOC removal (Lauderdale et al., 2011). These results illustrate the biofilters were biologically active and at pH 6, indigenous bacteria to Bennery Lake can likely remove Mn.

### 4.5.2 Biofilm Manganese Oxidizing Bacteria

To further classify the mechanism of Mn removal, indicative agar plating was conducted to determine MOB presence. Black colonies were identified as MOB and were detected in the biofilm of all the filters except for the anthracite, high P, pH 9 filter (Table 6). On average, the GAC/pH 6 and anthracite/pH 6 filters had $2.67\times10^3$-$3.32\times10^3$ CFU/g, which was greater than both the GAC/pH 9 and anthracite/pH 9 filters ($9.08\times10^2$-$2.20\times10^3$ CFU/g). The heterotrophic bacteria were also measured and ranged from $5.70\times10^6$-$3.60\times10^7$ CFU/g with no significant difference ($\alpha = 0.05$) between the pH 6 and pH 9 filters. MOB represented < 1% of the heterotrophic bacteria. As MOB are slow growing, heterotrophic bacteria may be out competing the MOB on the nutrient agar and producing false-negative results, decreasing the actual MOB concentration.

Similar results were found in a survey of four full-scale biofilters used for Mn removal from groundwater (Burger et al., 2008c). MOB concentrations occurred in the range of non-detect to $10^4$ CFU/g. All plants reportedly achieved 100% Mn removal with an average influent Mn range of 0.86-1.39 mg/L, despite low MOB concentrations, indicating that the mass of MOB did not correlate with higher Mn removal (Burger et al., 2008c). Mature full scale surface water biofilters have shown MOB to occupy 6% of the total HPC (Hoyland, 2013). Kohl and Dixon (2012) also discovered MOB in their

biofilters; however, they did not attempt to correlate MOB concentration with Mn removal within those filters. Several species of MOB include *Pedomicrobium, Leptothrix* and *Bacillus spp.* (Burger et al., 2008c; Cerrato et al., 2010; Kohl and Dixon, 2012). These bacterial species are possibly present in Bennery Lake but further biofilm analysis would be needed to confirm specific MOB responsible for Mn removal.

**Table 6.** Nutrient enhancement biofilm microbial data

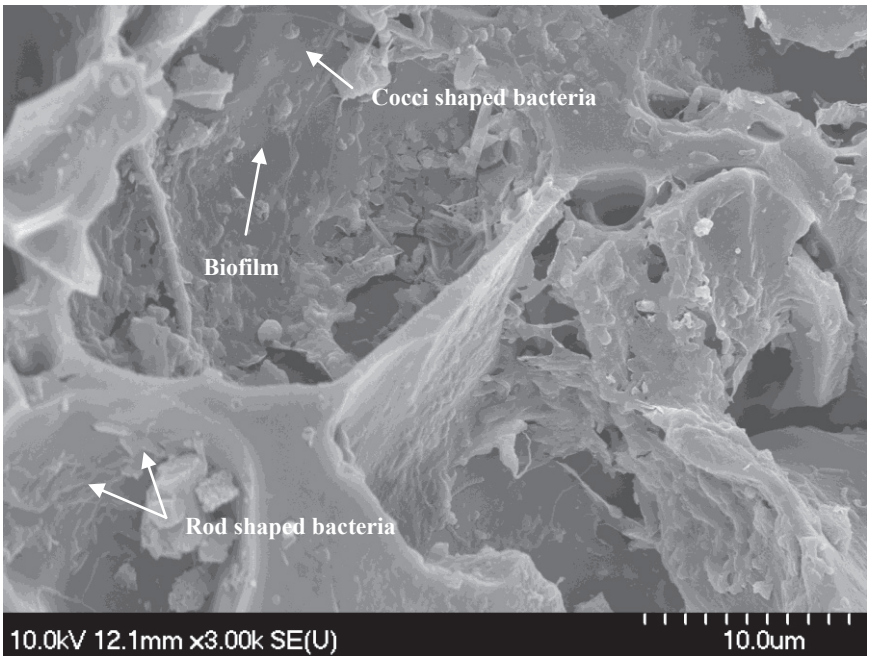
| Media | Condition | ATP (pg/g) | MOB (CFU/g) | Heterotrophic Bacteria (CFU/g) |
|---|---|---|---|---|
| GAC | HP, pH 9 | $3.49\times10^{5}$ | $4.00\times10^{2}$ | $1.84\times10^{7}$ |
| | LP, pH 9 | $2.87\times10^{5}$ | $4.00\times10^{3}$ | $5.28\times10^{7}$ |
| | HP, pH 6 | $1.39\times10^{6}$ | $4.24\times10^{3}$ | $1.08\times10^{7}$ |
| | LP, pH 6 | $8.64\times10^{5}$ | $1.10\times10^{3}$ | $6.28\times10^{6}$ |
| | Control | $2.34\times10^{5}$ | $2.83\times10^{2}$ | $1.42\times10^{6}$ |
| Anthracite | HP, pH 9 | $3.24\times10^{5}$ | < 100 | $9.74\times10^{6}$ |
| | LP, pH 9 | $6.80\times10^{4}$ | $1.82\times10^{3}$ | $1.68\times10^{6}$ |
| | HP, pH 6 | $1.09\times10^{6}$ | $5.59\times10^{3}$ | $1.07\times10^{7}$ |
| | LP, pH 6 | $1.25\times10^{6}$ | $1.05\times10^{3}$ | $4.89\times10^{6}$ |
| | Control | $9.38\times10^{5}$ | $3.00\times10^{0}$ | $4.64\times10^{6}$ |

### 4.5.3 Biofilm SEM Imaging

Figure 11, part A and B compare the SEM images of one NE/pH 6 and one NE/pH 9 filter, respectively. For the pH 6 filter, there was a layer of biofilm with cocci and rod shaped bacteria along with bacterial filaments. In contrast, the pH 9 filter showed no biofilm and very limited bacteria. This likely explains why the pH 6 biofilters supported the highest bacterial populations and consequently, removed the most Mn. There was little to no EPS shown in the SEM photographs. EPS is a common biofilter foulant that bacteria produce when they are nutrient deficient, leading to headloss (Mauclaire et al., 2004). Nutrient limitation did not occur in this experiment and nutrient enhancement has been shown to decrease EPS biofilm concentrations while increasing ATP biofilm

concentrations (Lauderdale et al., 2012). These images represent similar properties of biofilm and bacterial formations as other engineered biofiltration studies (Lauderdale et al., 2011).

A




B

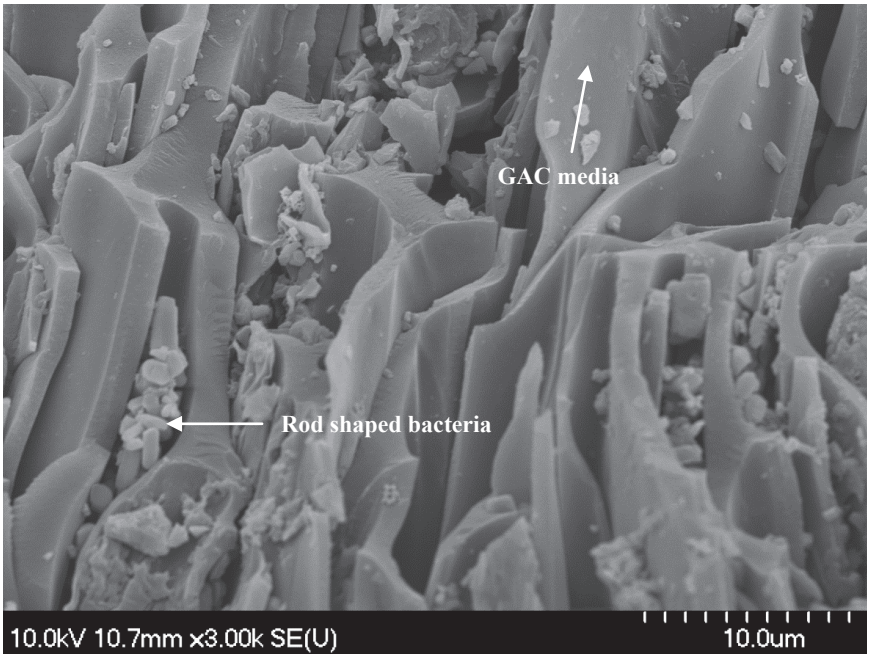



**Figure 11.** SEM micrograph of the biofilm media for the GAC/low P/pH 6 biofilter (A) and the GAC/low P/pH 9 biofilter (B)

## 4.6 PROPOSED MANGANESE REMOVAL MECHANISM

Given that increased ATP and MOB concentrations coincided with increased Mn removal, Mn was likely removed through biological oxidation. Chemical oxidation was not expected as oxygen was the only oxidant, and as Mn was removed at a pH < 9, any Mn (II) removal on the $MnO_{2(s)}$ surface would have only involved adsorption (Morgan and Stumm, 1964). In addition, Mn was likely synergistically removed by physical adsorption to the biogenic Mn oxides as MOB deposit oxidized Mn on their external cell surface (Tebo et al., 2004). Fe oxides on the media likely aided in Mn removal as well. As pH 6 resulted in the greatest Mn removal, further experimentation only considered the raw water pH 6 condition.

# CHAPTER 5: RESULTS AND DISCUSSION-NUTRIENT PLUS OXIDANT ENHANCEMENT

## 5.1 SOURCE WATER CHEMISTRY AND ACCLIMATION PERIOD

### 5.1.1 Biofilter Acclimation Period

The biofilters took about 14 days to acclimatize and consistently remove Mn. The biofilm formed from indigenous raw water bacteria as no inoculant was used. The biofilters with $H_2O_2$ took longer to acclimatize as $H_2O_2$ can be detrimental to developing bacterial communities Thus a finding from this study points to the importance of only adding $H_2O_2$ to the filter after indigenous bacteria have had the opportunity to establish a mature biofilm on the surface of the filter media material. Due to this acclimation period, all analyzed data in this experiment was from after the 2 week acclimation period.

### 5.1.2 Source Water and Filter Influent Chemistry

Raw water characteristics were sampled for 3 months from January 2013 to May 2013. The raw water Mn and Fe trends for those 3 months are shown in Figure 12. Other raw water quality parameters measured are listed in Table 7. The raw water Mn concentration exhibited little variation over the winter and averaged 36 ± 6.2 µg/L with 80% of the Mn in the dissolved form. The lake temperature steadily increased from 2.5$^{o}$C on January 25 to 8.8$^{o}$C on May 1 with an average of 4.2$^{o}$C. This was not the experimental temperature as the water increased to 19$^{o}$C once inside the plant chemical room. This was because the raw water sat in the 200 L reservoir for up to 48 hours before it was filtered. NOM was analyzed as DOC because the majority of organic matter in Bennery Lake is dissolved. The DOC concentration decreased from 6.2 to 3.9 mg/L over the winter with an average of 4.77 ± 0.7 mg/L. The raw water P concentration varied from 0 to 52 µg/L during the experiment with an average of 35 µg/L, satisfying the C:N:P nutrient ratio of 100:0:3 in April 2013. Nutrient (P) limitation occurred throughout the winter. Ammonia-nitrogen was not examined as a nutrient in this experiment, although Bennery Lake is known to have an ammonia-nitrogen concentration of less than 50 µg/L for most of the year.

The influent Mn differed from the raw water Mn concentration after the influent raw water had sat in the holding tub and chemical mixing bottles before being filtered. The influent Mn levels increased to an average of 144 ± 130 µg/L for the NE filters, 213 ± 186 µg/L for the combined nutrient and oxidant enhanced (NE+OE) filters and 187 ± 113 µg/L for the OE filters. It is unclear why the influent Mn loadings were different from the raw water Mn concentration and between each mixing bottle. One theory was $H_2O_2$ oxidized Mn and Fe from NOM in the NE+OE and OE mixing bottles. For the NE biofilter influent it is unknown where the Mn increase came from as no $H_2O_2$ was present, although the phosphoric acid addition could have affected the Mn concentration. The average influent DO and ORP were also measured in the filter influent mixing bottles and ranged from 8.42-8.99 mg/L and 352-372 mV, respectively for all 3 filter conditions. These conditions favor Mn oxidation (Mouchet, 1992; Bourgine et al., 1994). The influent Fe concentrations followed the same trend as the Mn concentrations.

### 5.1.3 Winter/Spring and Experiment Temperature

This experiment ran from January 2013-May 2013. Throughout the experiment, the average raw water temperature was 4.2$^{o}$C ± 1.9$^{o}$C which increased to an average of 19.1$^{o}$C once indoors and filtered. Due to this large temperature and DO increase between the lake temperature to the indoor biofilters, this experiment did not address Mn removal with biofiltration during winter temperatures. Raw water temperatures as low as 2.5$^{o}$C would have to be examined to ensure Mn removal could occur during the winter with biofiltration. Han et al. (2013) have shown Mn can be removed in temperatures ranging from 6-32$^{o}$C. Furthermore, they also found that MOB could survive temperatures of 2-5$^{o}$C and re-establish 70% Mn removal after two days following a one month shutdown.

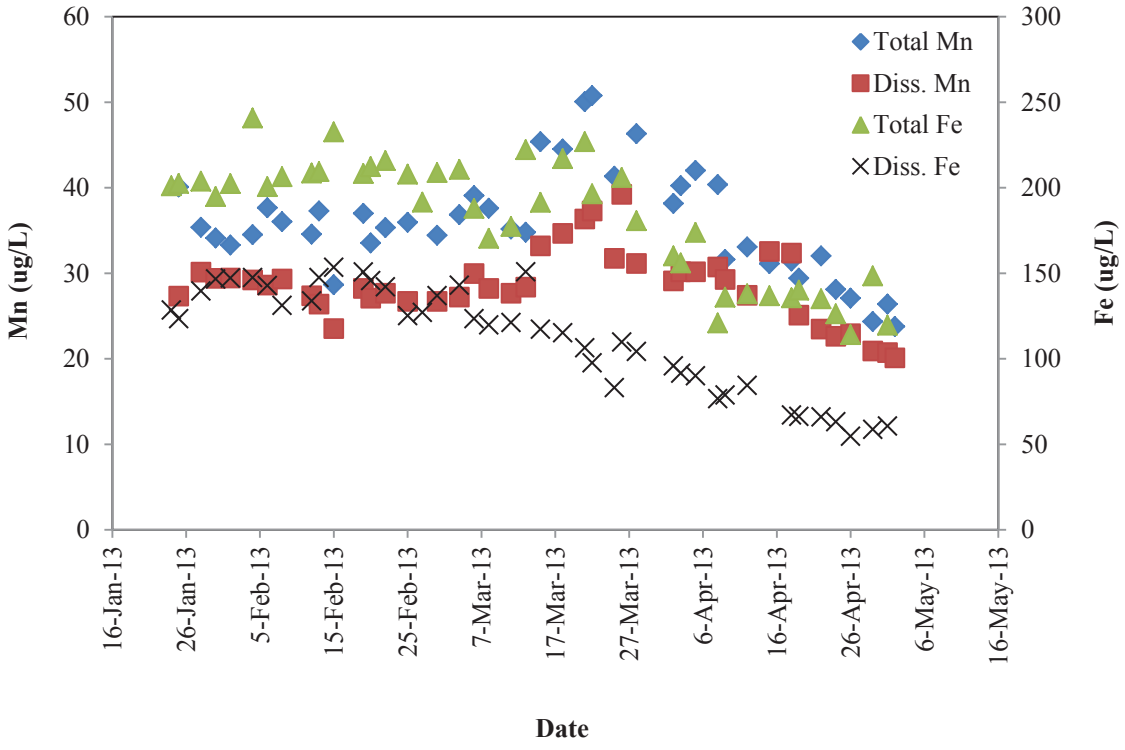



**Figure 12.** Raw water manganese and iron trends from January to May 2013

**Table 7.** Raw water quality parameters measured from January 2013 to May 2013

| Parameter | Data Range | Number of Samples | Mean ± Standard Deviation |
|---|---|---|---|
| Total Mn (µg/L) | 23.8-50.8 | 41 | 35.8 ± 6.23 |
| Total Fe (µg/L) | 114.1-240.8 | 42 | 182.8 ± 35.3 |
| DOC (mg/L) | 3.95-6.21 | 15 | 4.77 ± 0.67 |
| Turbidity (NTU) | 0.39-2.9 | 10 | 1.0 ± 0.8 |
| pH | 5.8-6.9 | 43 | 6.2 ± 0.3 |
| DO (mg/L) | 8.3-10.3 | 9 | 9.4 ± 0.7 |
| ORP (mV) | 189-397 | 11 | 341 ± 61 |

## 5.2 ANALYSIS OF FACTORS AFFECTING MANGANESE REMOVAL

### 5.2.1 Effect of Combined Nutrient and Oxidant Enhancement on Mn Removal

Combined nutrient and oxidant enhancement was a significant factor in removing Mn relative to the unenhanced control ($\alpha = 0.05$). The greatest Mn removal occurred in the GAC/NE+OE biofilter, although all six biofilters achieved Mn removal below the guideline and were not significantly different from each other (Figure 14). The GAC/NE+OE filter received an influent Mn concentration of 187 ± 113 µg/L and reduced Mn by 99% to an average effluent of 2.3 µg/L. This removal was 14% > the GAC control and met the 50 µg/L aesthetic guideline 100% of the time. Figure 13 shows the Mn influent and effluent concentration of the GAC/NE+OE biofilter during the 100 day experiment. The influent Mn concentration in the mixing bottle was greater and varied more than the raw water concentration. To the best of the authors' knowledge, this is the first time Mn has been removed with combined nutrient and oxidant addition. Although the GAC/NE+OE effluent Mn concentration was significantly less than the GAC control, the control met the aesthetic treatment guideline 100% of the time with an average lake P concentration of 35 µg/L.

Mn was measured in the full-scale plants treated water and it was found that the effluent Mn concentration averaged 21.4 µg/L. Bench-scale biofiltration removed 59% greater Mn than the current conventional process. These results are not directly comparable though as these are two different treatment processes at two different scales. Also, biofiltration occurred at approximately 19$^{o}$C and the full-scale process ranged from 4.8-11$^{o}$C.

### 5.2.2 Effect of Nutrient Enhancement on Mn Removal

Nutrient enhancement was a significant factor for Mn removal ($\alpha = 0.05$). From an influent of 144 ± 130 µg/L, NE filters averaged effluents of 2.9 µg/L and 2.7 µg/L (98% removal) for the GAC and anthracite filters, 13% and 14% greater removal than the GAC and anthracite controls, respectively. These results are consistent with other NE biofilters at pH 6.4-6.7 which have shown to remove ≥ 98% Mn with an influent Mn concentration up to 220 µg/L (Lauderdale et al., 2011). Nutrient enhancement encourages optimal

microbial growth, increased ATP concentrations and therefore improves the biofilms ability to remove contaminants (Lehtola et al., 2002; Polanska et al., 2005; Fang et al., 2009). Ensuring the biofilm bacterial communities are sufficiently supplemented facilitates efficient bacterial metabolism and therefore contaminant removal. Nutrient enhancement may also positively affect the ability of the microbes to survive the oxidation stress imposed by the hydrogen peroxide addition.

As stated above, the raw water P concentration averaged 35 µg/L during the experiment. This means the controls were at times nutrient supplemented and operated at an average C:P ratio of 100:2. This likely explains why the controls obtained Mn removal as well as the enhanced filters. However, the NE filters consistently achieved greater Mn removal efficiencies than the unenhanced controls.

### 5.2.3 Effect of Oxidant Enhancement on Mn Removal

The addition of oxidant enhancement also significantly removed Mn ($\alpha = 0.05$). From an influent of 187 µg/L ± 113 µg/L, OE filters averaged effluents of 3.1 µg/L and 2.8 µg/L for the GAC and anthracite filters, 13% and 15% greater removal relative to the GAC and anthracite controls, respectively. Adding an oxidant at concentrations of 0.5 mg/L $H_2O_2$ did not affect the biofilm bacteria's' ability to remove Mn. These results were comparable to those found in other studies. Lauderdale et al. (2011) found complete Mn removal with < 1 mg/L $H_2O_2$ oxidant enhancement, from 180 µg/L to less than the 2.4 µg/L MDL.

### 5.2.4 Effect of Media on Mn Removal

Filter media was not a significant factor in Mn removal in this experiment as both GAC and anthracite removed over 97% of the influent Mn (Figure 14). An additional Mn percent removal graph is shown in the appendix. For the NE+OE filter condition, the anthracite filter removed more average Mn than the GAC filter but they were not significantly different. Both the GAC and anthracite controls effluent Mn concentration was below the aesthetic guideline 100% of the time suggesting that no enhancement strategies would be needed during the winter/spring Mn loading. Anthracite could be an

acceptable growth surface for MOB to establish and remove Mn. Hoyland (2013) found anthracite/gravel to be successful in Mn removal of > 98% at pH 6.3. The GAC/NE and the GAC/OE filter conditions removed more Mn than the anthracite/NE and anthracite/OE filters, respectively. GAC has been found to provide greater Mn removal than anthracite as GAC usually supports greater Mn-oxide coating (Kohl and Dixon, 2012). The Mn-oxide coatings were not measured in this experiment but results suggested that Mn can be removed with both GAC and anthracite between temperatures of 15-20$^{o}$C with an influent DO of approximately 8 mg/L and ORP of approximately 365 mV at pH 6.

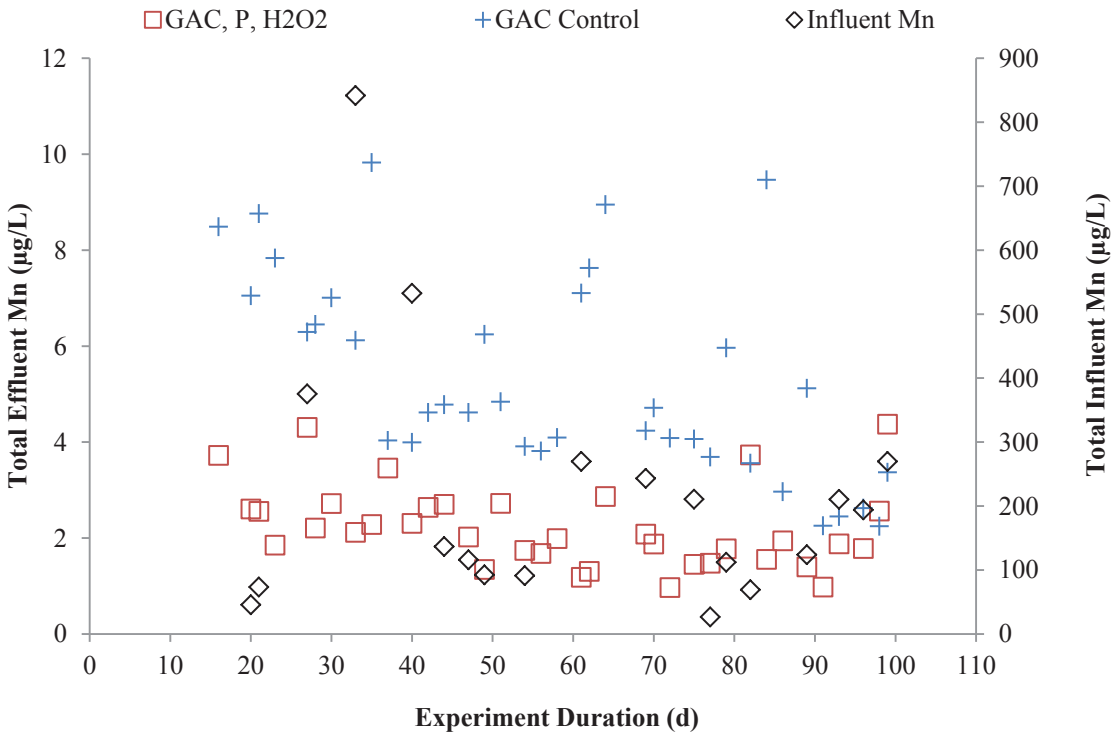



**Figure 13.** Biofilter influent and effluent Mn concentrations for the combined nutrient and oxidant enhanced GAC biofilter

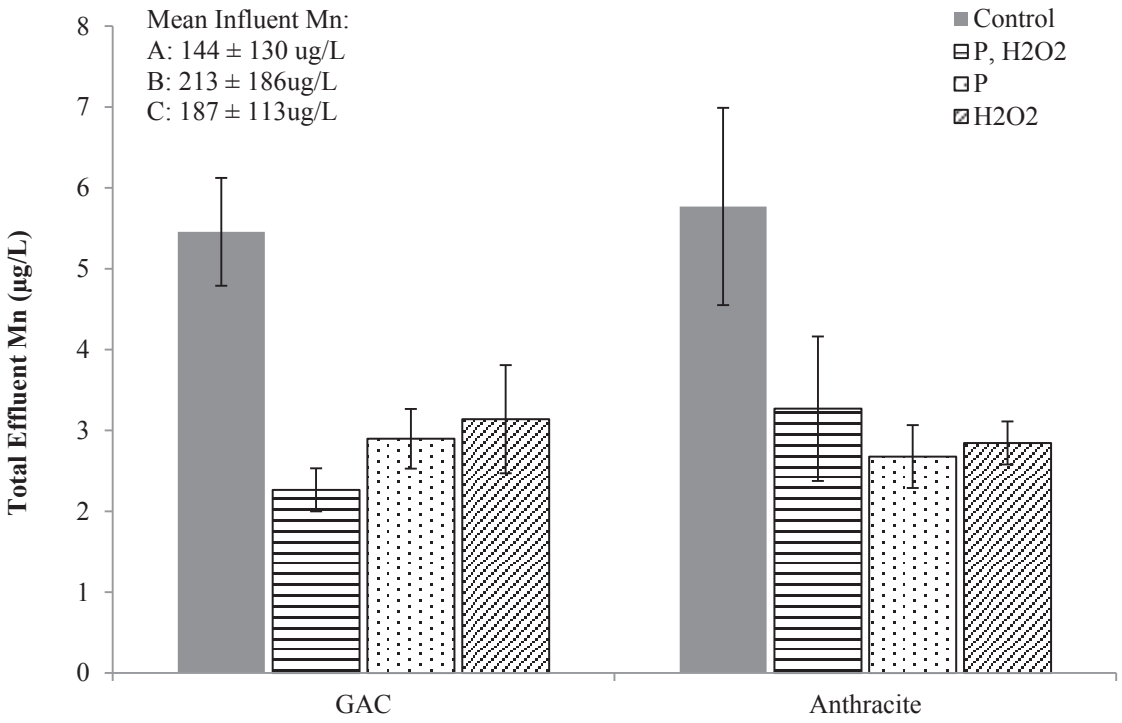



**Figure 14.** Combined nutrient and oxidant enhancement average total effluent Mn concentration over 100 days
A = P influent of 300 µg/L
B = Combined P+$H_2O_2$ influent
C = $H_2O_2$ influent of 0.5 mg/L

## 5.3 EFFECT OF P, $H_2O_2$ AND MEDIA ON DOC REMOVAL

The average influent DOC concentration was 4.77 mg/L and all three factors of media, nutrient enhancement, and oxidant enhancement were significant at the 95% confidence level. As with Mn removal, the GAC/NE+OE biofilter achieved the greatest DOC removal with a 27% reduction to 3.48 mg/L, 16% greater than the GAC control. The anthracite/NE+OE biofilter achieved 18% removal to 3.90 mg/L, almost 15% > the anthracite control (Figure 15). There was a significant difference between the GAC/NE+OE filter and the GAC/NE filter, suggesting oxidant addition was more important than nutrient addition in DOC removal. This was further confirmed as there was not a significant difference between the GAC control and the GAC/NE filter, but there was a significant difference between the GAC control and GAC/OE filter. When

$H_2O_2$ is reduced, free radicals are released which can oxidize organic carbon, reducing DOC and other organic matter in the biofilter influent (Huang et al., 2004). Therefore, dosing an oxidant likely helped to oxidize the NOM before it entered the filter. Furthermore, the addition of a nutrient could have kept the biofilm supplemented which helped to remove further DOC; biodegrading it after it was adsorbed on the media (Carlson and Silverstein, 1998).

Overall, the GAC biofilters resulted in significantly ($\alpha = 0.05$) greater removal than the anthracite. The GAC biofilters averaged effluent DOC concentrations of 3.7 mg/L, achieving over 12% greater removal than the GAC control. The anthracite biofilters averaged effluents of 4.1 mg/L, 11% > the anthracite control. The NE filters had effluent concentrations of 3.95 mg/L and 4.21 mg/L for the GAC and anthracite filters, respectively whereas the OE filters had effluent concentrations of 3.62 mg/L and 4.14 mg/L for the GAC and anthracite filters, respectively.

The GAC biofilters removed an average of over 1 mg/L of DOC since day 1 during the acclimation period and throughout the experiment duration. This was presumably from adsorption to the media and not oxidation by the peroxide. After the adsorption sites were full, NOM was likely being removed by biodegradation in the biofilm. After about a month, the anthracite filters were achieving similar removals. These results show the quickest organics removal occurred with GAC during biofiltration. This removal amount was more than Persson et al. (2006) and Lauderdale et al. (2011) who found about 0.5 mg/L DOC removal in their GAC biofilters. Yapsakli and Cecen (2010) also found GAC to be the most suitable for biodegradation as it has the ability to adsorb and retain organics, increasing the chance of biodegradation. Other research has also shown GAC as better suited for organics removal. LeChevallier et al. (1992) achieved greater TOC removal with GAC (51%) than with anthracite (26%).

Other direct biofiltration of raw surface water has shown less DOC removal than in this experiment. For example, Peldszus et al. (2012) obtained DOC removals of < 15%. Yapsakli and Cecen (2010) found that 47% of DOC was removed from the raw water from an influent of 3.65 mg/L to 1.65 mg/L. An EBCT of about 9 minutes was responsible for the majority of the degradation with the most biomass present in the top

few centimeters of the biofilter (Peldszus et al., 2012). Peldszus et al. (2012) also found that increased EBCTs could potentially remove more DOC. The majority of research with $H_2O_2$ for NOM removal has been coupled in an advanced oxidation process with UV or ozone (Metz et al., 2010; Bazri et al., 2012; Audenaert et al., 2013) so peroxide dosing for DOC removal with direct biofiltration requires further optimization.

The full-scale treated water effluent DOC averaged 1.97 mg/L over the winter. This was lower than the biofilter DOC effluent concentrations. Post biofiltration treatment would have to be considered to increase organics removal at BLWTP if biofiltration was going to be implemented for Mn removal. Also, effluent DBP treatment guidelines were not met. Biofiltration was effective for DOC removal at BLWTP at an ORP of approximately 360 mV and a DO concentration of approximately 8.5 mg/L, but further treatment would be necessary to meet treatment guidelines. Biofiltration could act as a pre-treatment to conventional treatment as biologically active filtration (BAF) is usually applied with other processes like coagulation, sedimentation, clarification and disinfection (Zhu et al., 2010) and these processes are already in place at BLWTP.

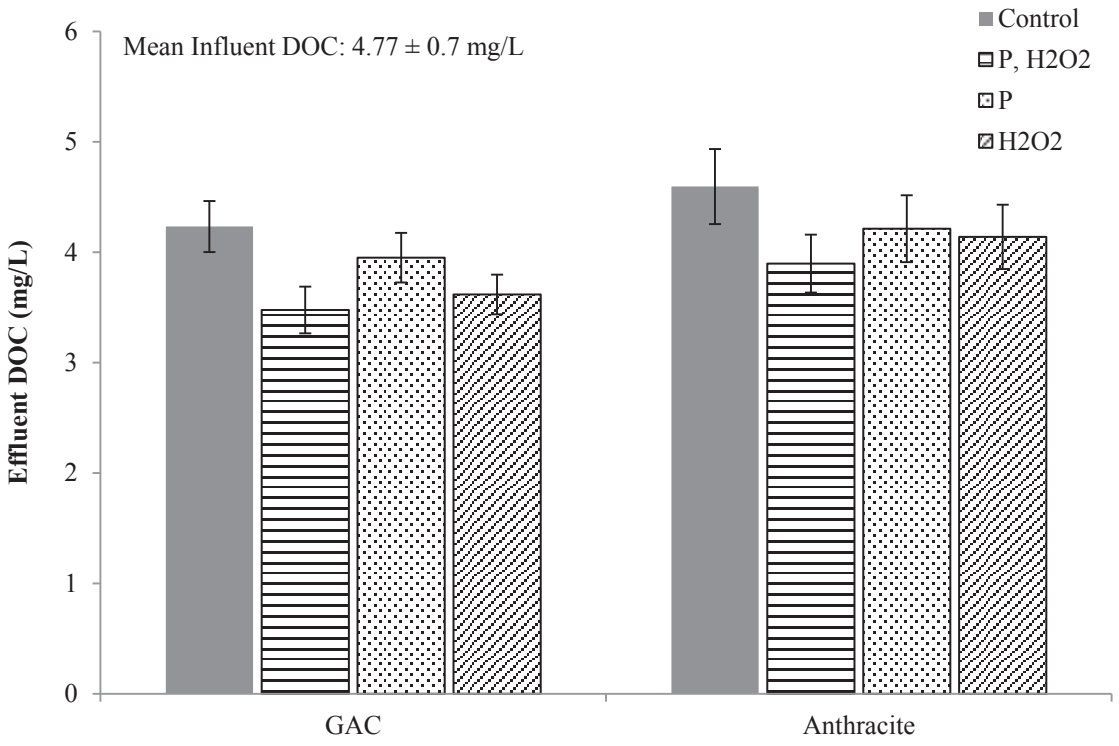



**Figure 15.** Combined nutrient and oxidant enhancement effluent DOC concentrations Controls = pH 6 with average background P concentration = 35 µg/L (C:P ratio of 100:2)

5.3.1 Organic Molecule Size Fractions of Raw and Treated Water

Figure 16 represents the effluent molecular weight NOM fractions as per the average peak area determined by SEC. The GAC and anthracite filter for each biofilter condition was grouped together and the columns without error bars only had one sample. Similar average areas were represented for all three filter conditions as the raw water in the 29760-33043 Da NOM fraction. This result was unexpected as 27% DOC removal was achieved with biofiltration. The small amount of NOM removed in the largest MW fraction could represent part of the 27% DOC removal as only a small portion of NOM is biodegradable (Goel et al., 1995). The DOC removed in this experiment could also be smaller MW NOM particles as these are normally absorbed better at 220nm. The wavelength used by the SEC in this experiment was 254nm. The OE filters also saw some NOM breakthrough as the effluent had a greater area and standard deviation for the 29760-33043 Da size fraction than the influent raw water. The smaller organic MW

fractions saw little, if any removal. The full-scale plant treated water was also measured and the 29760-33043 Da size fraction was fully removed. Also, the smaller MW fractions represented similar areas for the full-scale treated water as the biofilters.

NOM studies have shown that removal of high molecular weight humic material can be achieved through conventional treatment processes. Based on research by Edzwald (1993) and Sharp et al. (2006), high MW, hydrophobic fractions are more easily removed during coagulation than other fractions. Studies have also showed correlation between MW and charge density, in that larger compounds have a greater charge density. The larger the negative surface charge on NOM, the greater the interaction it will have with the positively charged metal oxidant (Ratnaweera et al., 1999). Therefore, the removal of MW fractions of > 29000 Da could be expected with coagulation processes. Further testing with SEC would have to be considered to determine what NOM size fractions are removed with biofiltration as the results do not illustrate what NOM fractions were removed with the 27% DOC removal.

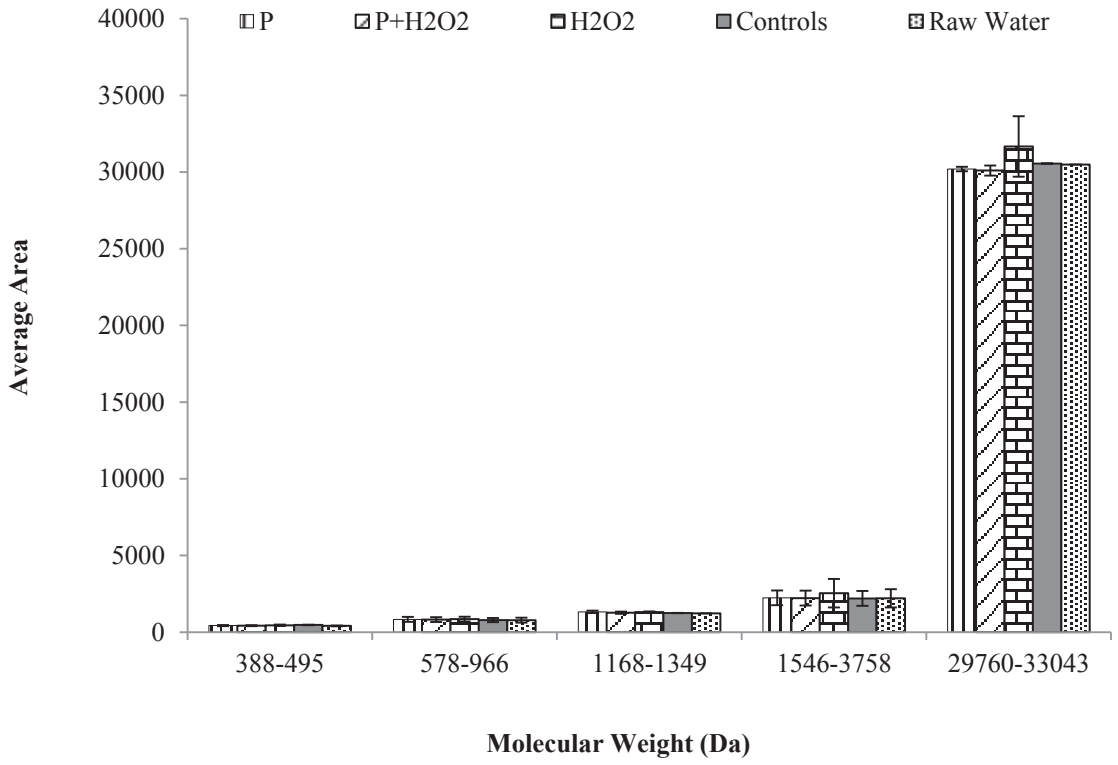



**Figure 16.** Nutrient plus oxidant enhancement biofilter effluent molecular weight NOM fractions as per peak area

5.3.2 DBP Removal

THMfp and HAAfp was measured in the raw and treated water. There was not a trend which identified optimal conditions for DBP reduction with biofiltration.

The main THM compound identified in the raw water was chloroform and the average raw water THMfp concentration was 270 µg/L. The GAC/NE+OE, anthracite/NE+OE and anthracite/OE biofilters all achieved 22% THMfp removal with average effluents of 208-210 µg/L. The other biofilters varied from 2.4-19.3% THMfp removal. Although all the biofilters removed some THMfp, the 100 µg/L guideline as set by the NS water treatment standards was not met (NSE, 2012).

The most abundant HAA compound in the raw water was di- and trichloroacetic acid. The average raw water HAAfp was 173 µg/L. The GAC/OE biofilter achieved 27% HAAfp removal with an average effluent of 127 µg/L. The other biofilters varied from

less than 0 to 25% HAAfp removal. No biofilter condition obtained HAAfp removal to below the 80 µg/L guideline as set by the NS water treatment standards (NSE, 2012).

Although some DBPfp removal was achieved with biofiltration, increased NOM removal would be required to decrease THMfp and HAAfp to meet the treatment guidelines. The experimental THMfp and HAAfp removals were less than what was achieved by the full-scale plant. The full-scale plant also met the effluent treatment guidelines for THMfp and HAAfp. This was expected as the conventional coagulation process is capable of removing more DOC and more DBPs than the bench-scale biofiltration set-up. Overall, biofiltration with combined nutrient and oxidant enhancement did not play a role in consistently reducing DBP formation potential. More consistent DBP sampling would need to be done to fully examine biofiltrations role in reducing DBPs.

## 5.4 IRON REMOVAL

Influent Fe levels varied from 105-889 µg/L for all biofilters. Although the influent concentration was greater than the raw water Fe concentration, Fe was removed to below the 0.3 mg/L aesthetic objective for all biofilter conditions (Figure 17). The NE+OE, GAC biofilter had the greatest removal with an average effluent of 76 µg/L (79% removal), 46% > the GAC control. Removals were similar for both media: the NE GAC and NE anthracite filters both achieved 72% removal and averaged effluents of 96 µg/L and 98 µg/L, respectively. The OE, GAC and OE, anthracite filters averaged effluents of 91 µg/L (76% removal) and 100 µg/L (73% removal), respectively.

Although Mn and Fe require different treatment conditions for bacterial oxidation (Mouchet, 1992; Kohl and Dixon, 2012), the addition of $H_2O_2$ with P increased Fe removal, likely removing Fe by chemical oxidation and/or adsorption to Fe oxides on the media. The removal of Fe in this experiment possibly helped remove Mn by adsorption to Fe oxides within the media. Sahabi et al. (2009) found aged anthracite media with Fe and Mn oxides removed soluble Mn by adsorption and further autocatalytic oxidation.

Furthermore, Fe oxides have also been shown to adsorb organics (Korshin et al., 1997), possibly aiding in DOC removal in this experiment.

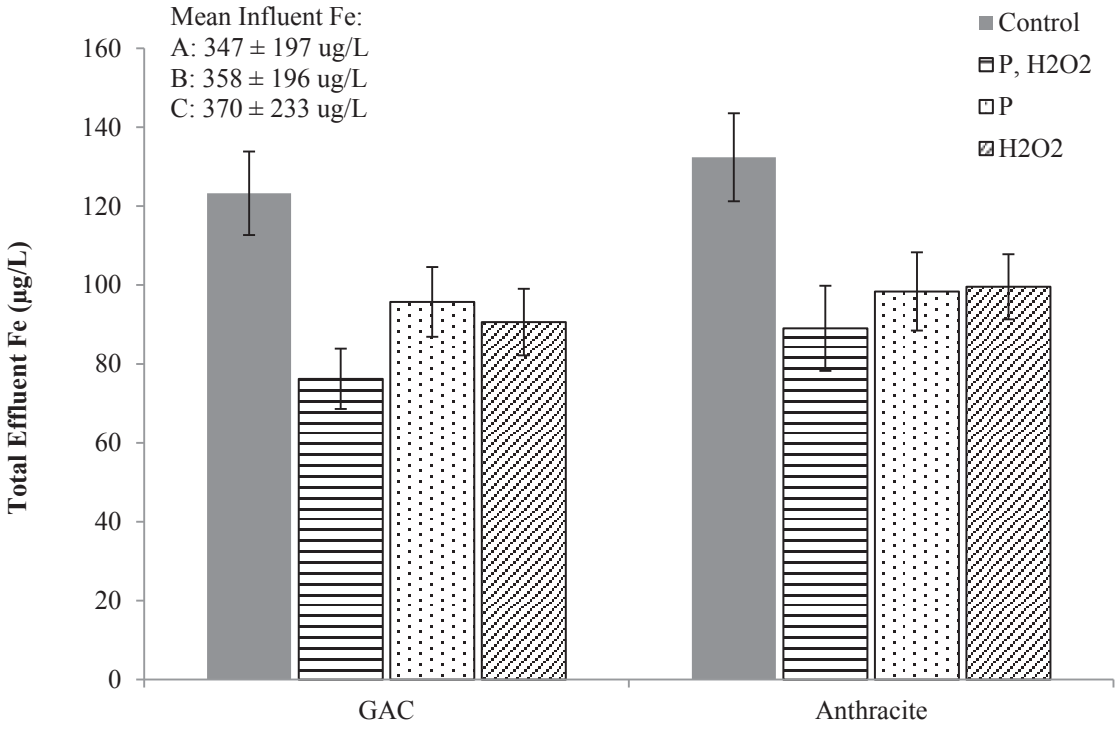



**Figure 17.** Combined nutrient and oxidant enhancement average total effluent Fe concentration over 100 days
A = P influent of 300 µg/L
B = Combined P+$H_2O_2$ influent
C = $H_2O_2$ influent of 0.5 mg/L

## 5.5 MICROBIAL ANALYSIS

### 5.5.1 Biofilm and Aqueous ATP Concentrations

As ATP is the primary energy carrier for all living organisms, it can indicate bacterial metabolic activity and biomass (MGH, 2005). ATP was measured in the top 2 inches of the media, directly after the filters had been taken offline. The highest ATP concentration existed in both the GAC/NE and anthracite/NE filters with $1.23\times10^6$ pg/g and $1.27\times10^6$

pg/g, respectively. The GAC/NE filter had 52% greater ATP than the control, while the anthracite/ NE filter obtained 43% greater ATP than the control. These values and enhancement strategy results were similar to the previous nutrient enhancement experiment results. All the filters had similar orders of magnitude of $10^6$ pg/g, except for the GAC/NE+OE filters which had $9.29\times10^5$ pg/g. This value was still greater than the GAC control. The greatest ATP concentration did not coincide with the greatest DOC or Mn removal, but as the GAC/NE+OE filter had $9.29\times10^5$ pg/g ATP, it was most likely still contributing to biological NOM and Mn removal. These ATP results illustrate that the filters were biological at pH 6 and naturally occurring bacteria can form a biofilm on both conventional media. The addition of peroxide did not decrease bacterial populations relative to the control at the concentration of 0.5 mg/L, suggesting biofilm bacteria were resistant to peroxide supplementation at this concentration. This is consistent with other research who found bacterial populations did not decrease from < 1 mg/L $H_2O_2$ addition (Lauderdale et al., 2011).

Headloss was not directly measured in this experiment but with the relatively low Mn loading, headloss was not an issue. Peroxide did not appear to decrease headloss but there was not a specific headloss issue in this experiment and more research would need to be done to directly examine the effect of peroxide on headloss during biofiltration.

Aqueous ATP was also measured in the biofilter influent and effluent to compare bacterial activity. Influent bacterial concentrations ranged from 197-217 pg/mL with up to $1.27\times10^6$ pg/g within the biofilter. Effluent concentrations ranged from 64-127 pg/mL. These results show encouraging biofilm bacterial activity during biofiltration did not result in large bacterial breakthrough. Research has shown that bacteria involved in Mn removal processes typically involve non-pathogenic bacteria; therefore biofilter effluent pathogen release is not a great concern (Tuovinen et al., 1980; Wilcox et al., 1983).

### 5.5.2 Biofilm Manganese Oxidizing Bacteria

To further classify the mechanism of Mn removal, indicative agar plating was conducted to determine MOB presence. Black and brown colonies were identified as MOB and were detected in all the biofilters (Table 8). All the filters ranged from $1.0\times10^3$-$5.69\times10^3$

CFU/g with the greatest MOB occurring in the NE+OE, GAC filter. This MOB concentration correlated with the greatest Mn removal. Heterotrophic bacteria were also measured and were a similar magnitude to the ATP results. All the filters ranged within $3.11\times10^{6}$-$1.05\times10^{7}$ CFU/g with the greatest HPC count also correlating with the greatest Mn removal. These numbers support the hypothesis that MOB were present in Bennery Lake. These numbers do not likely represent the actual MOB bacterial populations. As MOB are slow growing, heterotrophic bacteria may be out competing the MOB and producing false-negative results, decreasing the MOB concentration.

Similar results were found in a survey of four full-scale biofilters used for Mn removal from groundwater. MOB concentrations occurred in the range of non-detect to $10^{4}$ CFU/g. All plants reportedly achieved 100% Mn removal with an average influent Mn range of 0.86-1.39 mg/L (Burger et al., 2008c). MOB have been shown to achieve 86% soluble Mn removal during biofiltration with an influent Mn loading up to 840 μg/L (Han et al., 2013). Several species of MOB include *Pedomicrobium, Leptothrix* and *Bacillus sp.* (Burger et al., 2008c; Cerrato et al., 2010; Kohl and Dixon, 2012). These bacterial species are possibly present in Bennery Lake but further biofilm analysis would be needed to confirm specific MOB responsible for Mn removal.

**Table 8.** Nutrient enhancement plus oxidant enhancement biofilm microbial data

| Media | Condition | ATP (pg/g) | MOB (CFU/g) | Heterotrophic Bacteria (CFU/g) |
|---|---|---|---|---|
| GAC | P + $H_2O_2$ | $9.29\times10^5$ | $5.69\times10^3$ | $1.05\times10^7$ |
| | P | $1.23\times10^6$ | $3.08\times10^3$ | $4.02\times10^6$ |
| | $H_2O_2$ | $1.09\times10^6$ | $1.05\times10^3$ | $5.74\times10^6$ |
| | Control | $5.94\times10^5$ | $1.00\times10^3$ | $2.54\times10^6$ |
| Anthracite | P + $H_2O_2$ | $1.06\times10^6$ | $1.45\times10^3$ | $3.36\times10^6$ |
| | P | $1.27\times10^6$ | $3.08\times10^3$ | $7.40\times10^6$ |
| | $H_2O_2$ | $1.08\times10^6$ | $4.31\times10^3$ | $3.11\times10^6$ |
| | Control | $7.31\times10^5$ | $7.69\times10^3$ | $2.88\times10^6$ |

### 5.5.3 Biofilm SEM Imaging

Figure 18, 19 and 20 compare SEM images of the three filter conditions media. The NE+OE GAC biofilter represented the greatest Mn, Fe and DOC removal (Figure 18). All filters had similar bacteria diversity consisting of a layer of biofilm with cocci and rod shaped bacteria with bacterial filaments. There was not a large difference in biofilm properties between the three filter conditions, although the anthracite filters appeared to have a less dense biofilm than the GAC filters which could be due to the more flat nature of anthracite media. As all filters were run at the natural lake pH 6, bacteria were likely able to colonize on both media surfaces and remove Mn, Fe and DOC biologically. This was slightly different than what was found by Lauderdale et al. (2011). Their NE biofilters had less biofilm matrix and a higher bacterial diversity than their non-nutrient enhanced biofilters. As Bennery Lake had periods of nutrient supplementation over the winter and spring, the OE filters were likely able to support a diverse bacterial community and remove contaminants. The SEM images illustrated indigenous Bennery Lake bacteria were able to colonize on both GAC and anthracite.

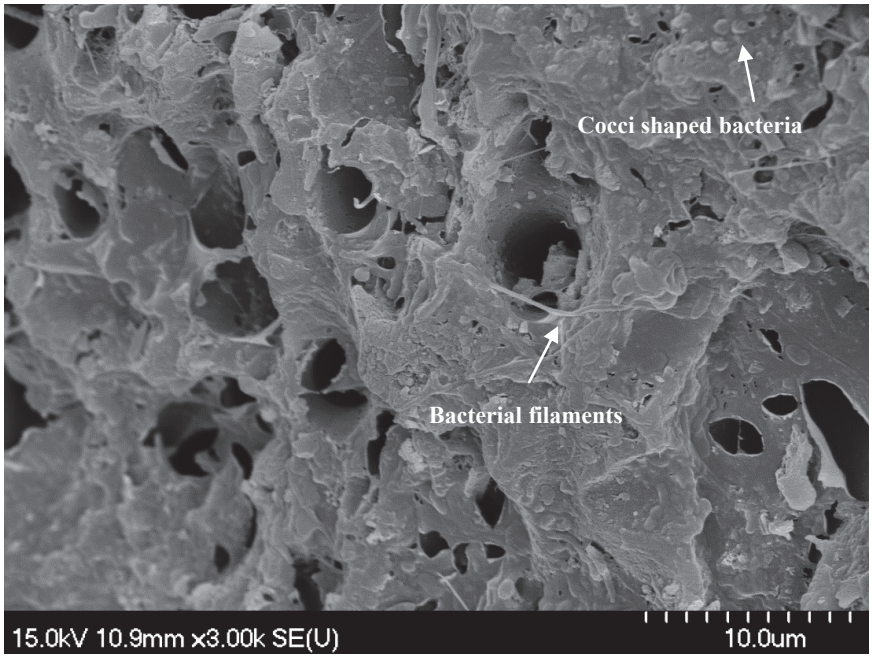



**Figure 18.** SEM micrograph of the biofilm and bacteria in the media from the GAC/NE+OE biofilter

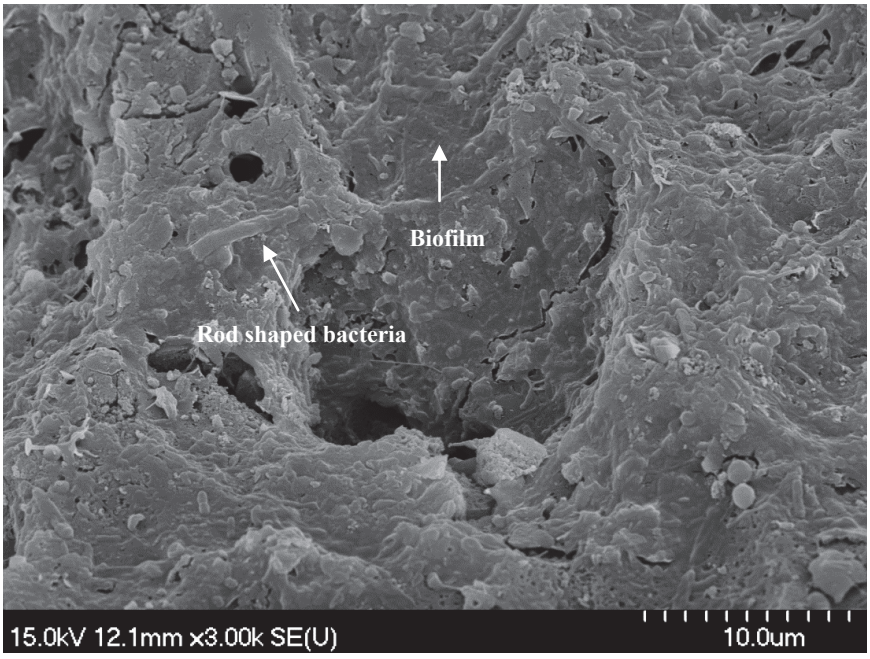



**Figure 19.** SEM micrograph of the biofilm and bacteria in the media from the GAC/NE biofilter

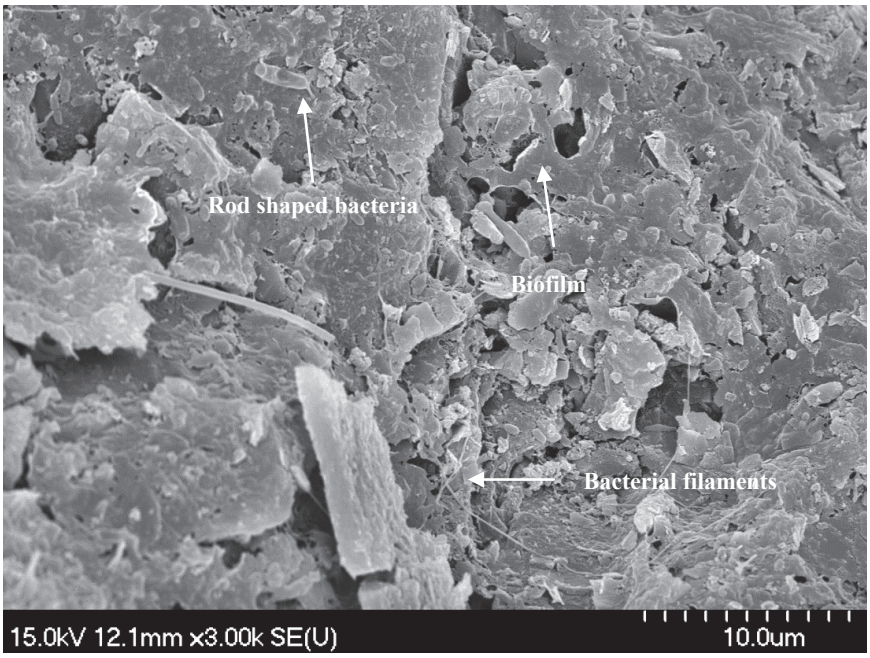



**Figure 20.** SEM micrograph of the biofilm and bacteria on the media from the GAC/OE biofilter

## 5.6 PROPOSED MANGANESE REMOVAL MECHANISM

Peroxide likely had a role in oxidizing Mn and Fe from NOM before the influent water was filtered, so the Mn loading onto the biofilter was possibly partially in particulate form. Given that increased HPC and ATP concentrations coincided with Mn removal and MOB were present in the biofilm, Mn was likely mostly removed through biological oxidation by autotrophic bacteria (Nealson et al., 1992; Sahabi et al., 2009) and MOB. Soluble Mn (II) and $H_2O_2$ at pH 6 do not react (Knocke et al., 1988; Knocke et al., 1990a); therefore chemical oxidation by peroxide was not expected. Mn was removed at a pH < 9, so any Mn (II) removal on the $MnO_{2(s)}$ surface would have only involved adsorption (Morgan and Stumm, 1964). In addition, Mn was likely synergistically removed by physical adsorption to the biogenic Mn oxides as MOB deposit oxidized Mn on their external cell surface (Tebo et al., 2004). Fe oxides could also have played a role in Mn removal by adsorption.

# CHAPTER 6: SYNTHESIS, CONCLUSION AND RECOMMENDATIONS

## 6.1 SYNTHESIS AND CONCLUSION

This study was conducted to determine if biofiltration could remove soluble Mn at BLWTP in Halifax, Nova Scotia, Canada. This facility experiences Mn loading of over 1 mg/L during seasonal summer stratification which presents challenges for the current treatment process and poses a potential public health risk. This experiment examined the ability of direct biofiltration of raw lake water at pH 6 and pH 9-11 to remove Mn below the 50 µg/L aesthetic guideline. Four factors were evaluated with respect to their effect on Mn removal: media, pH, nutrient enhancement with P, and oxidant enhancement with $H_2O_2$. DOC and Fe removal were also examined with biofiltration. All biofilter effluent data for Mn, Fe and DOC can be found in the Appendix.

### 6.1.1 The Role of Media

During all four seasons, both GAC and anthracite media removed Mn to concentrations below the 50 µg/L aesthetic guideline. Media was not a significant factor for Mn removal, therefore either GAC or anthracite would be appropriate for Mn removal with biofiltration. GAC removed significantly more DOC than anthracite.

### 6.1.2 The Role of Nutrient Enhancement

During the high Mn loading, the anthracite/pH 6 and GAC/pH 6 filters averaged 8% and 19% greater removal than the non-nutrient enhanced controls, respectively. An average of 23% of the influent DOC was removed with nutrient enhancement; 11% > the controls. Nutrient enhancement with a P dose of 300 µg/L removed significantly more Mn and DOC than the controls when tested with $H_2O_2$ addition during the winter/spring (low Mn loading). Ninety-eight percent Mn was removed and 17% DOC with GAC, 6% > the non-nutrient enhanced control. Increasing the P dose from 200 µg/L to 300 µg/L during the winter/spring did increase Mn removal over the summer/fall, but this also coincided with a much lower Mn loading. Further testing would be needed to determine if a greater nutrient dose could remove greater Mn during the summer/fall.

### 6.1.3 The Role of pH

pH 6 was a significant factor for Mn removal as was supported by a 10-fold increase in biofilm bacterial activity over the pH 9 filters. During the high Mn loading, the NE/pH 6 biofilters for both media averaged 91% Mn removal, meeting the aesthetic objective 88% of the time. The NE/pH 9 biofilters achieved 70% removal and met the guideline 49% of the time. DOC removal was achieved both at pH 6 and pH 9 while Fe was best removed at pH 9.

### 6.1.4 The Role of Oxidant Enhancement

Oxidant addition at 500 µg/L was a significant factor for Mn and DOC removal and removed significantly more DOC than with nutrient addition. Oxidant addition did not significantly remove more Mn than with nutrient addition as all six experimental biofilters removed significantly more Mn than the unenhanced controls. In examining the impact of an oxidant during the winter/spring (low Mn loading), the NE+OE condition resulted in the greatest Mn, DOC and Fe removal. Ninety-eight percent Mn was removed and 27% DOC coupled with GAC and nutrient enhancement, ~15% and 16% > the controls, respectively.

### 6.1.5 Manganese Removal Mechanism

For both experiments Mn was likely removed by biological oxidation as high ATP and HPCs coincided with increased Mn removal. MOB were also present in the biofilm. Furthermore, Mn oxidation was likely coupled with biogenic oxide adsorption. Although Mn loading was much higher during the summer, removals for the NE biofilters were below the treatment guideline 88% of the time. During winter conditions and much lower Mn loading, biofilter effluents were below the treatment guideline 100% of the time with biofiltration just utilizing the natural lake P concentration. Enhancement strategies were not necessary to achieve effluent Mn concentrations below the aesthetic guideline.

### 6.1.6 Areas for Improvement and Future Research

These bench-scale studies have demonstrated Mn can be removed by direct filtration of pH 6 surface water at 15-20°C. If Mn removal during the winter was eventually wanted

or needed at BLWTP, further experimentation with winter temperatures would need to be examined to determine if Mn can be removed at 2.5$^{o}$C. As Mn removal only presents a problem for BLWTP during the summer, the author does not see this as immediately necessary. Future research should examine the Mn removal mechanism by MOB and autotrophic bacteria and how different enhancement strategies affect their Mn removal ability. Finally, conversion of the full scale filters to biofilters could potentially be a viable option for Mn removal, but additional P would have to be added as any raw water P would be removed with coagulation.

## 6.2 RECOMMENDATIONS

Biofiltration could act as a pre-treatment to the conventional drinking water treatment process to remove Mn from Bennery Lake during the summer/fall high Mn loading, bypassing the treatment in the winter when the Mn loading is below 50 µg/L. This relatively simple treatment to remove Mn could be attractive to small systems as it offers a greener approach because it limits chemical addition and subsequent sludge production. Furthermore, placing biofiltration at the beginning of the treatment train would decrease concerns of bacteria present in the filter effluent as additional treatment steps existing after biofiltration could potential remove any bacterial cells in the effluent. Also, biofiltration coupled with downstream conventional treatment would also remove any remaining NOM in the biofilter effluent. Mn was removed with P doses between 200-300 µg/L. As limited chemical addition is ideal, a P dose of 200 µg/L with either GAC or anthracite would be recommended for Mn removal at Bennery Lake. DOC removal would be recommended using GAC media with a $H_2O_2$ dose of 0.5 mg/L.

As Mn removal to meet the aesthetic guideline is only a concern during the summer/fall, the author would recommend further testing with biofiltration with these high Mn loadings. Pilot-scale biofilters have the surface area to handle the high Mn loadings, perhaps decreasing or eliminating the clogging and Mn breakthrough in the filter effluent. Also, increased raw water DO, ORP, ammonia-nitrogen and orthophosphate-phosphorus measurements should be made during further testing.

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## APPENDIX

Table A1. Nutrient enhancement (summer/fall) biofilter effluent **total manganese** concentrations

| Filter Condition | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| High P dose | | | | Low P dose | | | | No P | No P |
| pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | GAC Control | Anth. Control |
| 127.60 | 108.40 | 5.67 | 5.96 | 144.50 | 118.80 | 9.08 | 6.09 | 82.81 | 1.97 |
| 38.00 | 29.82 | 7.48 | 9.26 | 28.90 | 39.46 | 11.24 | 9.86 | 109.70 | 15.41 |
| 209.50 | 375.60 | 9.16 | 8.55 | 62.61 | 61.11 | 9.97 | 7.73 | 82.26 | 42.44 |
| 121.30 | 110.90 | 23.67 | 12.95 | 76.71 | 92.64 | 21.33 | 9.02 | 90.26 | 60.35 |
| 128.00 | 197.10 | 16.37 | 17.64 | 157.20 | 86.52 | 18.27 | 19.14 | 17.74 | 17.57 |
| 192.60 | 176.10 | 20.44 | 19.79 | 121.20 | 137.40 | 14.28 | 17.53 | 27.72 | 35.07 |
| 280.90 | 112.70 | 27.73 | 32.16 | 180.10 | 114.80 | 18.28 | 16.45 | 88.68 | 147.20 |
| 215.20 | 215.60 | 33.69 | 47.61 | 180.00 | 136.50 | 28.05 | 27.64 | 34.04 | 171.20 |
| 214.10 | 187.20 | 41.92 | 62.74 | 177.80 | 86.21 | 12.72 | 18.51 | 242.70 | 217.30 |
| 503.30 | 95.22 | 92.00 | 107.20 | 809.00 | 58.88 | 14.46 | 26.04 | 97.97 | 106.00 |
| 150.70 | 199.60 | 26.77 | 83.30 | 677.30 | 66.09 | 16.90 | 29.83 | 46.37 | 189.70 |
| 126.60 | 59.62 | 13.12 | 21.57 | 84.36 | 166.10 | 33.96 | 102.90 | 176.30 | 57.70 |
| 181.70 | 148.70 | 12.64 | 17.01 | 43.76 | 336.00 | 12.49 | 57.84 | 19.14 | 26.69 |
| 160.00 | 119.30 | 9.78 | 8.18 | 156.60 | 155.80 | | 43.27 | | 14.02 |
| 114.00 | 99.58 | 9.77 | 10.99 | 69.75 | 83.26 | 57.45 | 15.93 | 14.64 | 20.51 |
| 209.50 | 124.70 | 131.00 | 140.40 | 154.10 | 114.90 | 42.06 | 222.20 | 564.80 | 362.90 |
| 247.40 | 181.30 | 314.00 | 233.00 | 347.30 | 125.00 | | 267.50 | 118.00 | 353.90 |
| 70.53 | 73.53 | 64.69 | 85.04 | 55.15 | 117.20 | 85.89 | 64.92 | 83.91 | 23.24 |
| 42.40 | 37.08 | 15.61 | 14.54 | 41.05 | 47.85 | 13.12 | 18.56 | 22.72 | 18.84 |
| 61.34 | 73.16 | 9.37 | 14.32 | 18.21 | 18.72 | 10.06 | 8.00 | 37.94 | 14.23 |
| 37.80 | 72.16 | 10.00 | 7.98 | 47.93 | 31.99 | 8.10 | 10.10 | 32.11 | 10.80 |
| 26.70 | 26.36 | 13.12 | 11.22 | 36.08 | 34.55 | 13.81 | 16.12 | 13.44 | 10.52 |
| 36.32 | 37.09 | 13.19 | 10.38 | 41.16 | 30.60 | 8.45 | 11.69 | 21.49 | 8.48 |
| 65.96 | 55.32 | 10.89 | 11.36 | 71.99 | 33.41 | 13.80 | 15.93 | 13.19 | 10.60 |
| 50.88 | 35.83 | 8.36 | 8.34 | 46.40 | 39.54 | 9.92 | 10.28 | 8.76 | 10.62 |
| 29.59 | 33.54 | 9.57 | 9.40 | 31.10 | 29.92 | 16.04 | 10.97 | 38.87 | 11.65 |
| 43.32 | 25.08 | 9.26 | 8.03 | 30.47 | 30.20 | | 11.99 | 8.54 | 12.21 |
| 28.39 | 18.76 | 46.08 | 7.51 | 33.21 | 31.73 | 11.87 | 12.78 | 83.01 | 9.59 |
| 16.14 | 16.50 | 23.66 | 7.84 | 20.90 | 26.83 | 17.69 | 17.80 | 12.11 | 18.33 |
| 23.40 | 19.12 | 8.51 | 35.85 | 14.19 | 22.09 | 9.45 | 13.03 | 136.20 | 9.35 |
| 16.35 | 15.21 | 8.54 | 10.88 | 14.66 | 14.75 | 7.08 | 10.66 | 37.24 | 7.04 |
| 10.97 | 10.81 | 7.22 | 6.33 | 10.00 | 16.51 | 7.82 | 4.31 | 8.08 | 6.98 |
| 15.77 | 10.68 | 11.71 | 8.64 | 20.99 | 14.95 | 7.87 | 15.54 | 16.21 | 8.52 |
| 9.71 | 9.11 | 8.40 | 8.93 | 10.81 | 25.02 | 6.37 | 8.90 | 48.29 | 6.61 |
| 40.78 | 37.49 | 21.30 | 28.88 | 55.13 | 44.68 | 29.76 | 42.41 | 353.30 | 50.17 |
| 13.31 | 10.43 | 4.18 | 4.64 | 49.20 | 14.40 | 6.77 | 10.91 | 118.00 | 6.20 |
| 10.14 | 8.73 | 4.69 | 5.44 | 16.57 | 9.79 | 8.61 | 8.04 | 39.19 | 5.82 |

Table A2. Nutrient enhancement (summer/fall) biofilter effluent **total iron** concentrations

| Filter Condition | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| High P dose | | | | Low P dose | | | | No P | No P |
| pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | GAC Control | Anth. Control |
| 215 | 186.4 | 151.6 | 171.7 | 301.9 | 279.4 | 319.7 | 322.7 | 318.1 | 318.2 |
| 101.4 | 78.65 | 298.4 | 308.4 | 83 | 112.8 | 316.9 | 323.4 | 341.2 | 366.6 |
| 821 | 1359 | 268.5 | 295.6 | 225.6 | 270.2 | 312 | 318.2 | 448.8 | 441.8 |
| 302.1 | 265.9 | 342.4 | 355.9 | 213.2 | 233.7 | 318 | 313.3 | 386 | 379.8 |
| 468.3 | 766.7 | 879.3 | 1003 | 802 | 328.3 | 1010 | 1057 | 287.8 | 1119 |
| 933.5 | 804.1 | 1223 | 1444 | 775.7 | 771.7 | 1330 | 1319 | 1604 | 1576 |
| 1207 | 1087 | 1174 | 1265 | 828.8 | 482.9 | 1380 | 1367 | 1801 | 1527 |
| 927.3 | 961.6 | 1242 | 1214 | 815.8 | 640 | 1389 | 1380 | 1733 | 1676 |
| 1040 | | 1268 | 1279 | 1018 | 405.9 | 1172 | 1212 | | 1769 |
| 1373 | 625.2 | 1532 | 1426 | 2920 | 500.1 | 1316 | 1227 | 1546 | 1713 |
| 954.2 | 829.9 | 1384 | 1516 | 1439 | 476.4 | 1297 | 1089 | 1426 | 1488 |
| 877.6 | 535.5 | 1046 | 1187 | 571.7 | 792.1 | 1164 | 1458 | 1262 | 1169 |
| 697.6 | 592.5 | 1018 | 1115 | 315.2 | 1318 | 1079 | 1079 | 1250 | 1241 |
| 856 | 657.3 | 906.7 | 967.7 | 1008 | 699.2 | 937.9 | 1387 | 1181 | 1125 |
| 879.7 | 741.6 | 979.6 | 1175 | 656.9 | 771.1 | 800.5 | 793.9 | 1078 | 824.1 |
| 893.1 | 555.4 | 952.4 | 942.9 | 688.3 | 575.2 | 722.6 | 810.1 | 1262 | 1194 |
| 680.9 | 500 | | 778.4 | 891.2 | 454.7 | 1011 | 832.9 | 860.7 | 1584 |
| 580 | 532.2 | 684.1 | 746.5 | 467 | 837.2 | 842.7 | 687.3 | 537.6 | 487.9 |
| 305.7 | 220.8 | 326.1 | 345.7 | 251 | 350.4 | 329.9 | 341.6 | 409.1 | 381.6 |
| 273.4 | 474.6 | 284 | 528.6 | 164 | 181.9 | 362.7 | 265.3 | 556.6 | 342.5 |
| 242.3 | 311.4 | 246 | 231.6 | 241.8 | 198.3 | 240.5 | 268.2 | 271 | 267.3 |
| 192.1 | 211.9 | 254.6 | 240.8 | 193.2 | 185.1 | 268.7 | 240.4 | 276.6 | 281.6 |
| 220 | 210.5 | 234.3 | 242.6 | 250.1 | 186.1 | 229.3 | 256.4 | 309.9 | 236.9 |
| 286.1 | 224.9 | 262.1 | 274.2 | 285.6 | 183.6 | 272.5 | 240.5 | 272.2 | 285.3 |
| 220.2 | 159.2 | 203.7 | 217.2 | 184.9 | 155.1 | 240.5 | 223.1 | 245 | 269.3 |
| 173.3 | 174 | 205 | 209.9 | 172.4 | 159.5 | 249.6 | 233.3 | 238.6 | 247.8 |
| 209.3 | 157.9 | 213.7 | 192.2 | 176.8 | 183.1 | 178.1 | 243 | 228.9 | 259.4 |
| 184.8 | 120.7 | 334.3 | 194.9 | 172.1 | 173.4 | 212.4 | 200.9 | 233.1 | 244.4 |
| 135.6 | 156.2 | 242.2 | 178 | 145.1 | 168.7 | 216 | 234.7 | 257.8 | 287.1 |
| 184.5 | 184.5 | 180 | 223.2 | 174.7 | 196.2 | 202 | 194.7 | 201.4 | 204.3 |
| 161.1 | 158 | 158.4 | 171.2 | 152.5 | 152.2 | 172.6 | 177.5 | 184.5 | 177.1 |
| 144.3 | 139.6 | 154.3 | 149.3 | 166.1 | 156.4 | 202.2 | 128.6 | 190.1 | 190.4 |
| 153.8 | 139.3 | 157.6 | 158.1 | 165.9 | 163.6 | 181.7 | 189 | 186.9 | 176.2 |
| 110.3 | 112.1 | 169.7 | 143.7 | 148.9 | 177.1 | 140.2 | 162.1 | 161.1 | 156.8 |
| 140.4 | 130 | 124.8 | 136 | 161.2 | 140.2 | 147.7 | 169.3 | 197.8 | 164.7 |
| 121.8 | 127 | 120.3 | 127.8 | 177.4 | 134.7 | 167.6 | 154.5 | 166.4 | 155.7 |
| 122.3 | 120.3 | 103.5 | 125.9 | 139.6 | 120.8 | 171.3 | 143.1 | 168.8 | 136.1 |

Table A3. Nutrient enhancement (summer/fall) biofilter effluent **DOC** concentrations

| Filter Condition | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| High P dose | | | | Low P dose | | | | No P | No P |
| pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | pH 9 GAC | pH 9 Anth | pH 6 GAC | pH 6 Anth | GAC Control | Anth. Control |
| 5.50 | 4.29 | 3.51 | 2.64 | 6.15 | 6.01 | 5.37 | 5.02 | 5.50 | 5.49 |
| 3.80 | 3.69 | 3.78 | 4.21 | 3.34 | 3.53 | 3.57 | 3.94 | 3.57 | 4.51 |
| 2.72 | 2.81 | 3.07 | 3.47 | 3.30 | 2.79 | 3.41 | 3.82 | | 4.06 |
| 3.93 | 3.24 | 3.75 | 4.06 | 3.15 | 3.63 | 4.08 | 4.17 | 4.98 | 5.08 |
| 3.64 | 3.69 | 3.36 | 3.42 | 2.92 | 3.37 | 3.54 | 3.69 | 3.74 | 4.00 |
| 3.87 | 3.04 | 3.48 | 4.04 | 3.22 | 3.09 | 3.40 | 3.58 | 3.73 | 3.76 |
| 3.47 | 2.92 | 3.28 | 3.30 | 2.69 | 3.44 | 3.26 | 3.00 | 3.50 | 3.83 |
| 3.94 | 5.97 | 3.23 | 3.42 | 3.38 | 3.54 | 2.96 | 3.49 | 3.34 | 4.35 |
| 4.73 | 3.82 | 4.05 | 4.86 | 4.38 | 4.77 | 4.21 | 4.47 | 4.71 | 5.30 |
| 5.50 | 6.10 | 5.37 | 5.71 | 4.99 | 5.50 | 6.65 | 7.17 | 6.55 | 6.22 |
| 5.43 | 4.35 | 5.05 | 5.22 | 4.78 | 4.88 | 5.95 | 6.34 | 5.86 | 6.16 |
| 5.38 | 4.50 | 5.30 | 5.21 | 5.20 | 5.10 | 5.13 | 4.33 | 6.05 | 6.43 |
| 4.94 | 4.89 | 5.39 | 5.58 | 5.46 | 5.61 | 5.94 | 6.11 | 5.79 | 6.20 |
| 4.38 | 3.91 | 5.11 | 5.11 | 5.43 | 4.90 | 5.62 | 5.89 | 5.56 | 5.79 |
| 4.70 | 4.63 | 4.87 | 5.30 | 6.46 | 4.77 | 5.92 | 5.97 | 5.72 | 5.88 |

Table A4. Nutrient enhancement plus oxidant enhancement (winter/spring) biofilter effluent **total manganese** concentrations

| Filter Condition | | | | | | | |
|---|---|---|---|---|---|---|---|
| GAC | | | Anthracite | | | No P | No P |
| P, $H_2O_2$ | P | $H_2O_2$ | P, $H_2O_2$ | P | $H_2O_2$ | GAC control | Anth. control |
| 68.82 | 14.9 | 68.01 | | 15.28 | 48.96 | 18.47 | 20.61 |
| 14.74 | 9.894 | 31.39 | 38.72 | 20.54 | 26.76 | 12.76 | 20.93 |
| 12.79 | 10.15 | 26.41 | 33.23 | 16.9 | 17.94 | 17.03 | 19.89 |
| 9.675 | 7.949 | 22.58 | 39.63 | 9.893 | 7.164 | 14.7 | 19.15 |
| 3.519 | 5.178 | 10.01 | 38.24 | 10.27 | 8.984 | 8.219 | 18.43 |
| 3.945 | 7.402 | 10.77 | 15.98 | 7.742 | 6.364 | 10.07 | 18.96 |
| 3.721 | 5.506 | 12.56 | 7.666 | 5.261 | 3.192 | 8.489 | 15.64 |
| 2.604 | 3.753 | 4.475 | 6.983 | 3.181 | 3.627 | 7.049 | 12.5 |
| 2.556 | 3.465 | 3.737 | 8.155 | 3.54 | 3.197 | 8.76 | 14.2 |
| 1.853 | 3.732 | 3.626 | 5.527 | 3.724 | 3.37 | 7.835 | 12.52 |
| 4.306 | 4.087 | 3.975 | 5.798 | 4.724 | 4.358 | 6.295 | 10.6 |
| 2.21 | 3.761 | 3.45 | 4.044 | 2.801 | 2.479 | 6.452 | 7.996 |
| 2.72 | 3.697 | 3.814 | 2.635 | 3.351 | 2.583 | 7.006 | 6.536 |
| 2.118 | 3.175 | 2.676 | 2.229 | 2.543 | 3.416 | 6.121 | 5.65 |
| 2.283 | 4.774 | 3.129 | 2.554 | 3.463 | 4.026 | 9.826 | 9.298 |
| 3.458 | 3.092 | 2.51 | 2.567 | 2.784 | 3.267 | 4.031 | 3.926 |
| 2.304 | 3.414 | 2.357 | 2.839 | 3.189 | 3.356 | 3.991 | 3.986 |
| 2.639 | 3.486 | 2.813 | 3.359 | 3.724 | 3.337 | 4.617 | 4.879 |
| 2.703 | 2.819 | 2.325 | 2.358 | 4.718 | 3.101 | 4.781 | 4.778 |
| 2.02 | 3.47 | 1.819 | 1.823 | 2.049 | 3.139 | 4.616 | 4.381 |
| 1.343 | 2.588 | 3.401 | 2.242 | 2.293 | 2.703 | 6.243 | 6.386 |
| 2.723 | 2.287 | 2.038 | 2.533 | 3.077 | 3.201 | 4.841 | 6.125 |
| 1.741 | 2.867 | 2.064 | 2.058 | 1.861 | 2.639 | 3.909 | 4.538 |
| 1.678 | 2.209 | 2.136 | 1.524 | 1.608 | 2.595 | 3.811 | 4.922 |
| 1.989 | 2.343 | 1.783 | 1.671 | 1.641 | 2.642 | 4.092 | 4.546 |
| 1.18 | 2.015 | 3.924 | 0.969 | 1.565 | 2.423 | 7.105 | 3.115 |
| 1.303 | 1.668 | 2.154 | 1.21 | 1.707 | 2.04 | 7.628 | 3.808 |
| 2.866 | 2.101 | 2.19 | 3.149 | 1.476 | 2.093 | 8.948 | 4.335 |
| 2.08 | 3.028 | 2.076 | 1.7 | 2.049 | 2.478 | 4.236 | 3.49 |
| 1.874 | 2.797 | 3.606 | 1.76 | 2.202 | 2.972 | 4.714 | 3.789 |
| 0.967 | 1.936 | 2.086 | 1.787 | 1.792 | 1.879 | 4.082 | 3.044 |
| 1.451 | 1.68 | 2.06 | 1.446 | 1.915 | 1.785 | 4.061 | 3.062 |
| 1.474 | 2.159 | 1.759 | 1.469 | 2.059 | 1.56 | 3.69 | 2.607 |
| 1.776 | 1.3 | 1.898 | 1.813 | 1.644 | 2.027 | 5.964 | 3.23 |
| 3.734 | 1.496 | 1.969 | 9.106 | 1.575 | 1.789 | 3.559 | 2.72 |
| 1.555 | 1.987 | | 1.639 | 1.932 | 1.783 | 9.465 | 2.784 |
| 1.942 | 1.298 | 2.308 | 1.533 | 1.302 | 3.745 | 2.964 | 2.182 |
| 1.399 | 2.135 | 2.99 | 1.766 | 2.014 | 2.831 | 5.121 | 2.438 |
| 0.979 | 1.162 | 2.198 | 0.954 | 1.456 | 2.623 | 2.254 | 2.777 |
| 1.878 | 2.498 | 2.787 | 1.918 | 2.142 | 2.41 | 2.449 | 2.832 |
| 1.78 | 2.685 | 2.02 | 1.964 | 2.211 | 2.533 | 2.621 | 3.449 |
| 2.562 | 2.284 | 1.573 | 1.828 | 2.106 | 1.711 | 2.245 | 3.341 |
| 4.374 | 3.919 | 3.114 | 3.654 | 3.278 | 2.831 | 3.369 | 3.875 |

Table A5. Nutrient enhancement plus oxidant enhancement (winter/spring) biofilter effluent **total iron** concentrations

| **Filter Condition** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **GAC** | | | **Anthracite** | | | **No P** | **No P** |
| **P, $H_2O_2$** | **P** | **$H_2O_2$** | **P, $H_2O_2$** | **P** | **$H_2O_2$** | **GAC control** | **Anth. control** |
| 103.3 | 115 | 109.1 | 102.5 | 128.4 | 129.6 | 145.6 | 155.4 |
| 118.7 | 113 | 102.6 | 116.3 | 143.3 | 124.5 | 153.9 | 171.9 |
| 93.21 | 111.7 | 118.7 | 152.5 | 125.5 | 122.7 | 160.1 | 179.3 |
| 91.33 | 125.5 | 106.1 | 134.6 | 125.5 | 120.6 | 154.7 | 159.2 |
| 94.94 | 141.9 | 160.1 | 66.5 | 158.2 | 151.4 | 154 | 164.3 |
| 109.8 | 157.2 | 152.9 | 132.8 | 145.1 | 146 | 171.2 | 201 |
| 114.7 | 129 | 111.9 | 110.5 | 133.8 | 113.9 | 145.8 | 156.6 |
| 108.3 | 135.4 | 137.3 | 144.3 | 128.5 | 129.3 | 149.8 | 162.8 |
| 104.3 | 124.1 | 105.5 | 167.4 | 132.3 | 116.9 | 159.7 | 162.1 |
| 70.23 | 101.3 | 99.62 | 169 | 130.7 | 113.7 | 171.9 | 185.1 |
| 141.1 | 127.3 | 142 | 162.1 | 153 | 148.5 | 155.3 | 192 |
| 77.31 | 135.4 | 99.2 | 145.8 | 101.7 | 91.6 | 151.9 | 159.9 |
| 83.81 | 109.5 | 98.49 | 102 | 116.8 | 93.25 | 162 | 157.6 |
| 68.21 | 107.5 | 86.87 | 79.83 | 93.23 | 99.87 | 150.9 | 157.6 |
| 79.85 | 118.4 | 108.4 | 90.56 | 104.6 | 135.5 | 149.1 | 157.6 |
| 106.4 | 114.1 | 88.45 | 96.05 | 169.8 | 116 | 139.6 | 146.3 |
| 76.69 | 122.9 | 87.35 | 103.1 | 113.4 | 120.5 | 137.3 | 151.2 |
| 79 | 130.3 | 92.08 | 93.23 | 109.7 | 115.4 | 134.7 | 153.7 |
| 90.74 | 93.57 | 80.32 | 79.92 | 142 | 107.1 | 130.4 | 143.3 |
| 71.43 | 81.7 | 65.71 | 69.8 | 81.22 | 105.4 | 106.5 | 121.8 |
| 56.74 | 94.13 | 90.47 | 79.62 | 88.3 | 80.59 | 115.2 | 133.1 |
| 48.1 | 94.08 | 74.88 | 85.65 | 105.4 | 107.4 | 111 | 147.1 |
| 77.91 | 100.1 | 86.81 | 94.14 | 89.65 | 101.9 | 111.2 | 135.3 |
| 78.91 | 94.34 | 88.96 | 79.12 | 83.14 | 98.32 | 109.4 | 150.1 |
| 94.22 | 94.6 | 84.76 | 85.48 | 84.33 | 112.3 | 109.2 | 143.8 |
| 61.15 | 86.8 | 135.3 | 58.38 | 78.12 | 115.1 | 156.2 | 134.2 |
| 71.2 | 86.26 | 91.95 | 67.04 | 89.45 | 103 | 154 | 139.9 |
| 85.53 | 95.01 | 94.64 | 82.7 | 79.56 | 100.4 | 161.9 | 141.8 |
| 67.09 | 92.58 | 81.97 | 64.44 | 80.38 | 89.83 | 134.1 | 119.7 |
| 75.89 | 94.46 | 113.7 | 67.37 | 95.33 | 105.5 | 133.3 | 135.1 |
| 23.34 | 80.52 | 78.01 | 75.98 | 77.83 | 75.17 | 114.8 | 110.9 |
| 39.82 | 49.37 | 70.97 | 40.32 | 45.77 | 42.07 | 108.6 | 105.2 |
| 58.96 | 58.92 | 65.82 | 57.05 | 70.72 | 66.28 | 78.04 | 81.9 |
| 48.38 | 59.72 | 67.71 | 63.5 | 70.31 | 67.29 | 93.5 | 89.18 |
| 67.14 | 41.48 | 52.42 | 85.6 | 45.94 | 44.83 | 79.3 | 78.02 |
| 33.29 | 55.49 | 83.57 | 39.76 | 70.27 | 44.91 | 72.88 | 74.32 |
| 44.46 | 35.46 | 43.97 | 37.58 | 36.75 | 83.76 | 67.91 | 70.19 |
| 39.02 | 65.38 | 60.56 | 41.65 | 69.73 | 94.48 | 76.58 | 74.12 |
| 35.8 | 37.36 | 40.71 | 33.22 | 47.85 | 79.11 | 38.86 | 72.61 |
| 63.72 | 77.4 | 61.77 | 65.17 | 68.8 | 64.51 | 72.3 | 74.13 |
| 53.3 | 67.93 | 60.2 | 62.17 | 63.08 | 68.73 | 68.14 | 75.68 |
| 76.59 | 68.87 | 38.06 | 61.98 | 63.88 | 61.7 | 67.13 | 76.39 |
| 93.96 | 90.82 | 76.7 | 81.44 | 88.43 | 71.69 | 81.82 | 91.01 |

Table A6. Nutrient enhancement plus oxidant enhancement (winter/spring) biofilter effluent **DOC** concentrations

| **Filter Condition** | | | | | | | |
|---|---|---|---|---|---|---|---|
| **GAC** | | | **Anthracite** | | | **No P** | **No P** |
| **P, $H_2O_2$** | **P** | **$H_2O_2$** | **P, $H_2O_2$** | **P** | **$H_2O_2$** | **GAC control** | **Anth. control** |
| 3.5965 | 3.536 | 2.965 | 4.3865 | 4.785 | 4.894 | 4.0865 | 5.4935 |
| 3.5575 | 4.217 | 3.7545 | 4.58 | 4.978 | 4.9055 | 4.706 | 5.6595 |
| 4.1335 | 4.5535 | 4.072 | 4.5075 | 5.007 | 4.918 | 4.852 | 5.6805 |
| 3.6935 | 4.7305 | 4.1715 | 5.049 | 5.2995 | 4.962 | 4.9525 | 5.695 |
| | 4.2755 | 4.0095 | 4.2075 | 4.7965 | 4.5965 | 4.8075 | 5.1975 |
| 4.117 | 4.447 | 3.875 | 4.295 | 4.325 | 4.5225 | 4.604 | 5.1405 |
| 3.89 | 4.2095 | 3.9475 | 4.089 | 4.841 | 4.822 | 4.5715 | 5.072 |
| 2.9835 | 3.8915 | 3.5705 | 3.8335 | 4.3875 | 4.347 | 4.131 | 4.454 |
| 3.6015 | 3.7355 | 3.3745 | 3.878 | 3.835 | 3.888 | 3.9125 | 4.138 |
| 3.3375 | 3.4415 | 3.333 | 3.3585 | 3.6765 | 3.5835 | 3.913 | 4.118 |
| 2.815 | 3.649 | 3.3235 | 3.712 | 3.85 | 3.832 | 4.0135 | 4.299 |
| 3.34 | 3.4955 | 3.6565 | 3.594 | 3.5545 | 3.835 | 4.0105 | 4.134 |
| 3.2435 | 3.4105 | 3.2545 | 3.434 | 3.5865 | 3.664 | 3.866 | 4.139 |
| 3.309 | 3.7205 | 3.197 | 3.3965 | 3.803 | 3.3995 | 3.754 | 3.8405 |
| 3.2615 | 3.7935 | 3.243 | 3.3045 | 3.812 | 3.4345 | 3.6425 | 3.829 |

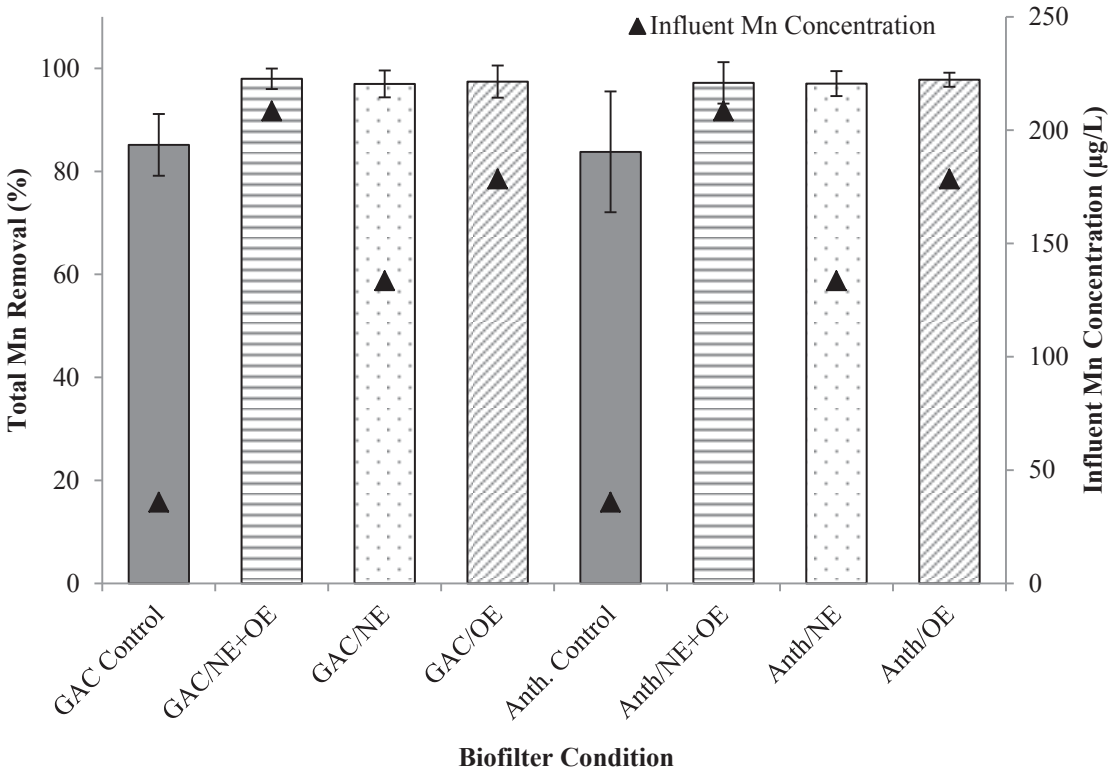


**Figure A1.** Combined nutrient and oxidant enhanced experimental conditions showing average percent Mn removal based on influent Mn concentration over 100 days.

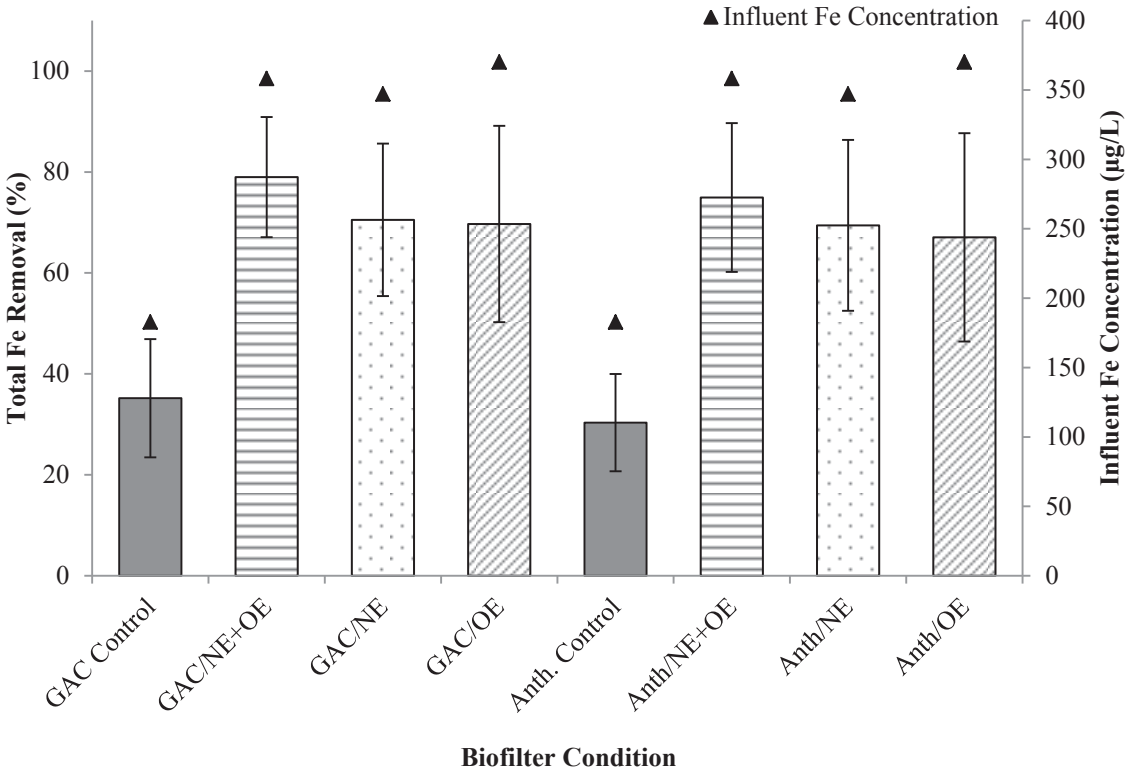


**Figure A2.** Combined nutrient and oxidant enhanced experimental conditions showing average percent Fe removal based on influent Fe concentration over 100 days.

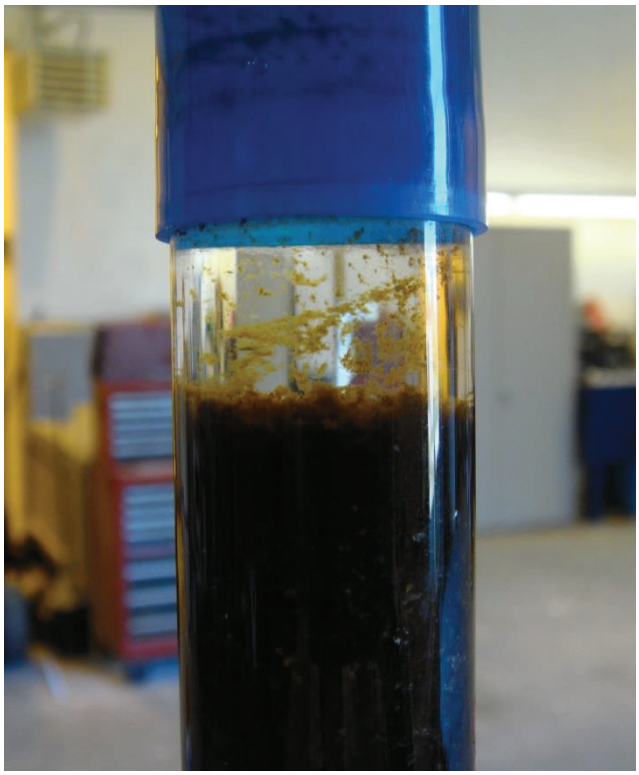

**Figure A3.** Particulate Fe and Mn in a bench-scale biofilter

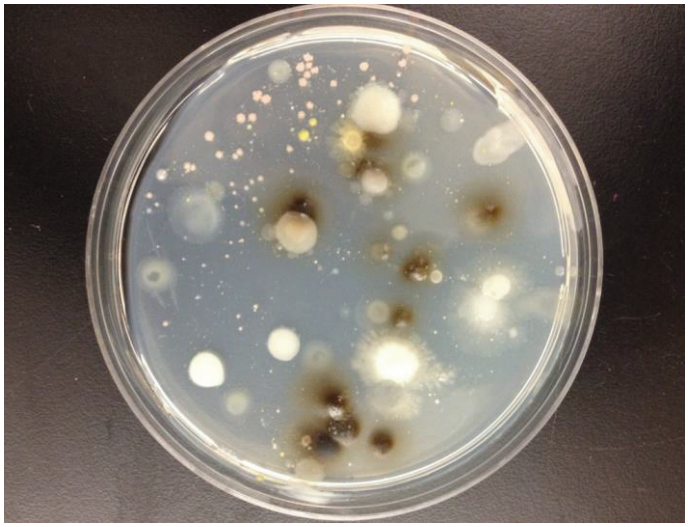

**Figure A4**. Black colonies representing manganese oxidizing bacteria from a biofilter biofilm