Ozone/Peroxide Advanced Oxidation in Combination with Biofiltration for Taste and Odour Control and Organics Removal

by

Divyam Beniwal

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Divyam Beniwal
Master of Applied Science, 2017
Graduate Department of Civil Engineering
University of Toronto

ABSTRACT

Ozone (O_3) prior to biofiltration can be an effective treatment strategy to achieve multiple drinking water quality goals. These goals include primary disinfection, improved removal of biodegradable organic carbon (generated as a result of ozonation), and oxidation of geosmin and MIB. However, O_3 efficiency is dependent on source water characteristics, which impacts performance. This pilot study investigated the effectiveness of advanced oxidation incorporating O_3 and hydrogen peroxide/ozone (H_2O_2/O_3) with biofiltration (containing biologically active carbon (BAC) and anthracite) for geosmin and MIB control and disinfection by-product (DBP) precursor reduction.

Application of 0.2 H_2O_2/O_3 (mg/mg) prior to BAC resulted in optimal MIB and geosmin removal, especially in cold-water conditions ($T = 10^\circ C$). In warmer temperatures ($22^\circ C$), BAC alone was a suitable treatment technology for both geosmin and MIB. In terms of DBP precursor reduction, 0.1 H_2O_2/O_3 (mg/mg) in combination with BAC was found to be the most effective treatment strategy with 37% THM and 10% HAA precursor reductions.

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NOMENCLATURE

%	Percent
±	Plus/minus
°C	Degree(s) Celsius
<	Less than
>	More than
α	Confidence level
~	Approximate
AOP(s)	Advanced Oxidation Process(es)
ATP	Adenosine tri-phosphate
BAC	Biologically active carbon
BAF	Biologically active anthracite
BCAA	Bromochloroacetic acid
BDCM	Bromodichloromethane
BDCAA	Bromodichloroacetic acid
BDL	Below Detection Limit
BDOC	Biodegradable organic carbon
BDOC _r	Rapid biodegradable organic carbon
C	Concentration
CAF	Conventional anthracite filter
Cl	Chlorine
cm	Centimeter(s)
CO ₃ ²⁻	Carbonate

Conventional treatment	Coagulation, flocculation, settling, non-biological filtration
CTS	Calcium thiosulphate
d	diameter
DBAA	Dibromoacetic acid
DBCAA	Dibromochloroacetic acid
DBCM	Dibromochloromethane
DBP	Disinfection by-product
DBP FP	Disinfection by-product formation potential
DCAA	Dichloroacetic acid
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
Fe ²⁺	Ferrous
FP	Formation potential
FSP	Full-scale plant
g	Gram(s)
GAC	Granular activated carbon
GC	Gas chromatography
GC-MS	Gas chromatography – mass spectrometry
GC-ECD	Gas chromatography-electron capture detection
H ₂ O ₂	Hydrogen peroxide
H ₂ O ₂ /O ₃	Hydrogen peroxide/ozone
HO ₂ ⁻	Hydroperoxide anion
HCO ₃ ⁻	Bicarbonate

HAA(s)	Haloacetic acids
L	Litre(s)
LC-OCD	Liquid chromatography-organic carbon detection
LMW	Low molecular weight
m	Meter(s)
m ⁻¹	1/meter(s)
m ²	Squared meter(s)
M	Molar concentration
M ⁻¹	1/molar concentration
MCAA	Monochloroacetic acid
MBAA	Monobromoacetic acid
MDL	Method detection limit
mg/L	Milligram(s) per liter
mg/mg	Milligram per milligram
min	Minute(s)
µg/g	Microgram per grams
MTBE	Methyl-tert -butyl-ether
MW	Molecular weight
NA	Not available
N/A	Not applicable
NaOH	Sodium hydroxide
Na ₂ SO ₄	Sodium sulphate
ng/g	Nanogram(s) per gram

nm	Nanometer(s)
NOM	Natural organic matter
ND	Not detected
NS	Not Sampled
NSERC	Natural Sciences and Engineering Research Council
NTU	Nephelometric Turbidity Unit
O ₃	Ozone
·OH	Hydroxyl radicals
OH ⁻	Hydroxide
ORF	Ontario Research Fund
OTC	Odour threshold concentration
p-value	Probability value
PO ₄ ³⁻	Phosphate
PWTP	Peterborough Water Treatment Plant
PWTPP	Peterborough Water Treatment Pilot Plant
pH	-log (hydrogen ions concentration)
QA/QC	Quality assurance/quality control
R ²	Coefficient of determination
sec	Second(s)
SPME	Solid phase micro-extraction
SUVA	Specific ultraviolet absorbance (at 254 nm)
T	Temperature
t	Student t-test value or student t probability distribution

T&O	Taste and odour
TBM	Tribromomethane
TBAA	Tribromoacetic acid
TCAA	Trichloroacetic acid
TCM	Chloroform
THM(s)	Trihalomethane(s)
THMFP	Trihalomethane formation potential
TOC	Total organic carbon
UC	Uniformity coefficient
USEPA	United States Environmental Protection Agency
UV ₂₅₄	UV absorbance at 254 nm
w/w	Weight per weight

1. Introduction

1.1 Background

O₃ have long been used in drinking water treatment for natural organic matter (NOM) oxidation, taste and odour (T&O) control, color removal, and disinfection in Europe and more recently in North America (Schulz et al., 2014). The amendment of Safe Drinking Water Act by United States Environmental Protection Agency (USEPA) in response to the emerging threats to drinking water safety after 1993 Milwaukee Cryptosporidium outbreak and 2000 Walkerton's E.coli tragedy encouraged the use of incorporation of O₃ as a regulatory compliance (Rice et al., 1998; Hrudey et al., 2003). High initial capital costs combined with extensive operation and maintenance have deterred municipalities in implementing such an attractive solution for extended period of time (Plumlee et al., 2014). However, the benefit of applying an advanced treatment for a purpose of serving a better-quality drinking water (in terms of aesthetics, consumer satisfaction, and regulatory standards), containing lower disinfection by-products (DBPs) have attracted municipalities to implement O₃ as a pre-treatment strategy before filtration.

Although the application of O₃ can achieve multiple treatment benefits, its application in bromine containing waters can produce bromate, an ozonation by-product, which has been classified by USEPA as a probable human carcinogen (USEPA, 2006). pH reduction using chemical addition can reduce bromate formation (von Gunten and Oliveras, 1998). However, such treatment strategies can impact removals of other contaminants, such as T&O compounds with ozonation (Srinivasan and Sorial, 2011). Therefore, site-specific pilot studies should be conducted when considering ozonation.

O₃ has also been used for NOM removal. O₃ breaks down NOM into smaller and more biodegradable organics, which leads to microbial regrowth in distribution systems (Urfer et al., 1997). This has been associated with T&O issues, accelerated corrosion of water mains, and increased chlorine demands. Biofiltration can be used following ozonation to overcome the biological instability and may provide another barrier against organics removal and DBP precursor reduction (Rittmann and McCarty, 2001). However, biofiltration performance using biologically active carbon (BAC) has shown to be impacted by water temperature (Emelko et al., 2006; Moll

et al., 1999), empty bed contact time (EBCT), and accumulation of attached microbial biomass (Elhadi et al., 2006). Because of these factors, BAC performance in terms of geosmin, MIB, as well as DBP precursor removals can vary significantly (de Vera et al., 2016; Elhadi et al., 2004; Guo et al., 2016). In addition, O_3 efficiency is dependent on source water characteristics such as pH, DOC, alkalinity, and temperature (Westerhoff et al., 2006), which warrants site-specific pilot studies for optimization of O_3 and biofiltration treatment.

O_3 efficiency can be improved with the addition of H_2O_2 to produce hydroxyl radicals ($\cdot OH$) with fast reaction rates for geosmin and MIB ($K_{OH} \sim 10^9 M^{-1}s^{-1}$) (Lee and von Gunten, 2016). Previous pilot studies have reported increases of 10-15% in geosmin and MIB removals upon H_2O_2 addition (Park et al., 2015; Wang et al., 2015). However, much of the existing information regarding H_2O_2/O_3 optimization has been based on the bench-scale studies (Chang et al., 2002; Li et al., 2012; Mizuno et al., 2011; Parinet et al., 2010). A pilot-scale study is warranted to substantiate the theoretical optimum ratio of 0.35 $H_2O_2:O_3$ (mg/mg) (Acero and von Gunten, 2001). Below this ratio, O_3 is present in excess, which favors O_3 decomposition over $\cdot OH$ formation. Above this ratio, H_2O_2 is present in excess, and it consumes O_3 , generating $\cdot OH$.

1.2 Objectives

This study investigated the effectiveness of advanced oxidation incorporating ozone (O_3) and hydrogen peroxide/ozone (H_2O_2/O_3) with biofiltration to assess the following objectives:

1. Evaluate biofiltration performance with and without pre-oxidation for geosmin, 2-methylisoborneol (MIB), and DBP precursor removal efficiency.
2. Compare biologically active carbon with biologically active anthracite for T&O control and removal of organics.
3. Assess the impact of advanced oxidation as well as investigate the performance of biofiltration with respect to DBP precursor reduction.

1.3 Description of Chapters

- **Chapter 2:** provides background information about oxidative pre-treatment, and biofiltration.
- **Chapter 3:** describes experimental design, analytical methods, and statistical analysis.
- **Chapter 4:** compares impact of O_3 and H_2O_2/O_3 advanced oxidation alone and in combination with biofiltration for the removal of geosmin, MIB, and DBP precursors.
- **Chapter 5:** provides conclusion and recommendation.
- **Chapter 6:** contains a list of references used
- **Chapter 7:** contains appendices for calibration curves, QA/QC charts, and raw data.

2. Literature Review

2.1 O₃ Oxidation

O₃ reacts by two mechanisms – direct O₃ or with hydroxyl radical (•OH) reaction (von Gunten, 2003). Direct O₃ reaction is selective and occurs with electron-rich moieties mainly double bonds, aromatic phenols and amine functional groups, whereas hydroxyl radical oxidation is non-selective and has fast reaction rates with organics (Acero and von Gunten, 2001). As, advanced oxidation processes (AOPs) are based on enhanced formation of •OH, peroxide (H₂O₂) addition can be cost efficient way for converting an ozone treatment into an AOP based treatment (Park et al., 2015). In this process, •OH are generated by complex radical chain reaction, which consumes two O₃ and one H₂O₂ to produce two •OH (Hoigné and Bader, 1979). The overall reaction is shown in equation 2.1.

At the Peterborough Water Treatment Pilot Plant (PWTPP), O₃ and H₂O₂/O₃ advanced oxidation is applied prior to biofiltration for organics removal and disinfection by-product (DBP) precursor reduction.

2.1.1 O₃ and H₂O₂/O₃ Advanced Oxidation in Water Treatment

Geosmin and 2-methylisoborneol (MIB) have been typically reported as the two common T&O compounds that are seasonally detected in source water supplies (Bruce and William, 2000). As a result of poor removal efficiency of these compounds through conventional treatment (<20%) combined with their low odour threshold concentrations (~10 ng/L), their occurrence in finished water is concern to municipalities (Srinivasan and Sorial, 2011). In recent years, O₃ and H₂O₂/O₃ have been increasingly applied to achieve multiple treatment objectives, including removal of T&O causing compounds. O₃ dose of 1-3 mg/L and a minimum contact time of 10 to 15 min is typically used for the removal of geosmin and MIB for the concentrations present in natural water conditions (Park et al., 2007; Westerhoff et al., 2006). Although O₃ has showed capability of oxidizing geosmin and MIB, presence of O₃ initiators, promoters, and scavengers determine the

availability of O_3 and $\bullet OH$ for reaction. A list of common initiators, promoters and scavengers for O_3 (or $\bullet OH$) decomposition is shown in Table 2-1.

Table 2-1: Typical Initiators, Promoters, Scavengers for O_3 Decomposition (Adapted and Modified from Sonntag and Gunten, (2012))

Initiator	Promoter	Scavenger
OH^-	humic acid	HCO_3^-/CO_3^{2-}
H_2O_2/HO_2^-	primary & secondary alcohols	organics, PO_4^{3-}
Fe^{2+}	aryl-R	tertiary-butyl alcohol

Several studies investigated the impact of different experimental parameters (O_3 dose, pH, temperature) to optimize O_3 and H_2O_2/O_3 advanced oxidation treatment process for geosmin and MIB removal. The O_3 reaction mechanism with NOM was strongly dependent on pH. At acidic water pH (5-7), organics were predominantly oxidized by O_3 , but at alkaline pH (7.5-9), O_3 decomposes into $\bullet OH$, which becomes available for oxidation reactions. The influence of pH on O_3 efficiency for geosmin and MIB removal was evaluated by several authors. Liang et al. (2007) investigated the impact of three pH (5 vs. 7 vs. 9) on O_3 and observed higher geosmin (61% vs. 90% vs. 99%) and MIB (55% vs. 86% vs. 98%) removals with higher pH. Similar removal patterns were observed by others (Yuan et al., 2013; Westerhoff et al., 2006).

Previous studies have also reported impact of water temperature on the O_3 efficiency (Knol et al., 2015). Increasing the temperature increases activation energy, thereby improving O_3 efficiency (Gardoni et al., 2012). Elovitz et al. (2000) observed increased rate of O_3 depletion (initial O_3 dose = 1.0 mg/L) when water temperature was increased from 5 to 35°C. In contrast, rate of $\bullet OH$ depletion was not observed to be impacted with increased temperature.

Another important parameter that can impact the efficiency is applied O_3 dose (Gardoni et al., 2012; Lee et al., 2012). Higher applied O_3 dose result in higher treatment costs that were associated with O_3 generation and chemical addition for quenching the residual. Therefore it is necessary to optimize O_3 dose. Previous studies have reported (40-70%) geosmin and (30-60%) MIB removals when applied with different O_3 dose of 1.5-2 mg/L with a contact time of 8-10 min

(Bruce and William, 2000; Carlson et al., 2007; Park et al., 2007). The impact of pH, temperature, and water matrix from previous studies is shown in Table 2-2.

Table 2-2: Summary of O₃ Studies Characterizing the Impact of Water Matrix on Geosmin and MIB Oxidation

Reference	Study scale, water matrix	Experimental conditions	Observed Removals
Yuan et al. (2013)	Bench-scale Synthetic water	O ₃ = 4.2 mg/L; pH = 5.4, 7.3, 9.1	<ul style="list-style-type: none"> Higher geosmin (>12%) and MIB (>40%) removals observed in alkaline (pH = 9) conditions compared to acidic conditions (pH = 5.4)
Liang et al. (2007)	Bench-scale Surface water	O ₃ = 0.35 mg/L; pH = 5, 7, 9; TOC = 3 mg/L	<ul style="list-style-type: none"> GSM and MIB removals varied from 61% to 99% and 55% to 98% when pH was increased from 5 to 9
Westerhoff et al. (2006)	Bench-scale Pure water and surface water	O ₃ = 3 mg/L; pH = 8.0; H ₂ O ₂ /O ₃ = 0.05 (w/w) TOC = 4.9 mg/L; Alkalinity = 150 mg/L as CaCO ₃	<ul style="list-style-type: none"> Direct oxidation by O₃ resulted in low geosmin/MIB oxidation (<30%) H₂O₂ addition improved MIB removal by 24% (from 74% to 99%)
Acero et al. (2001)	Bench-scale Ground and surface water	O ₃ = 1 mg/L; pH = 7.0; H ₂ O ₂ /O ₃ = 0.0, 0.19, 0.34, 0.70 (w/w) TOC = 3.2 mg/L	<ul style="list-style-type: none"> % pCBA elimination for respective H₂O₂/O₃ ratios = 49%, 72%, 76%, 78% Optimum H₂O₂/O₃ (w/w) = 0.2-0.3 for maximum ·OH formation
Elovitz et al. (2000)	Bench-scale Pure water and Lake water	O ₃ = 1 mg/L; pH = 6-8; T = 5 – 35°C	<ul style="list-style-type: none"> Increase in pH & Temp. resulted in increased rate of O₃ depletion Increase in alkalinity resulted in increased rate of ·OH depletion

Initial geosmin and MIB concentration = 100 ng/L

O₃ efficiency can be improved with the addition of H₂O₂ to produce hydroxyl radicals (·OH) with fast reaction rates for geosmin and MIB ($K_{OH} \sim 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Lee and von Gunten, 2016; Peter and von Gunten, 2007). Previous pilot studies have reported increases of 10-15% in geosmin and MIB removals upon H₂O₂ addition (Glaze et al., 1990; Park et al., 2015; Wang et al., 2015). In addition, few previous studies reported varying H₂O₂/O₃ ratio for optimal geosmin and MIB reduction with changing source waters. Optimal H₂O₂/O₃ ratio ranging 0.1 to 0.2 (mg/mg) and 0.1 to 0.3 were reported by Ferguson et al (1990), while investigating two different source waters.

2.2 O₃ and H₂O₂/O₃ Prior to Biofiltration for Organics Removal

2.2.1 DOC Removal

O₃ and H₂O₂/O₃ can achieve partial removal of dissolved organic carbon (DOC) by transforming larger molecular weight organics into lower molecular weight. Previous studies reported 3-10% DOC removal when applied with O₃ doses of 1-3 mg/L (Volk et al. 1997; Siddiqui et al. 1997). Further, O₃ oxidation increases hydrophilic content present in the NOM, thereby decreasing the DOC content in the hydrophobic fraction (Treguer et al., 2010). The impact of peroxide addition on DOC reduction is ambiguous as few studies have shown no impact, whereas others have showed enhanced DOC reduction (Zha et al., 2016). Lamsal et al. (2010) reported DOC reduction of 6% and 10% when treated with O₃ and H₂O₂/O₃ advanced oxidation. Ozonation has also shown to improve the biodegradability of organics by transforming them into low molecular weight aldehydes and carboxylic acids that result in increased formation of rapid biodegradable organic carbon (BDOC_r) (Carlson et al 2001). These BDOC_r formed can then be preferentially removed by biofiltration (Black and Berube 2014, Hozalski et al. 1999).

2.2.2 DBP Precursor Removal

Ozonation of water can result in reduction of trihalomethane (THM) and haloacetic acid (HAA) formation potentials (Chaiket et al. 2002). Previous studies with low ozone dose (0.5-1.0 mg/mg DOC) did not observe significant (1-5%) reductions in THM FP & HAA FP when compared with conventional treatment (15-30%) (Carlson and Amy 2001; McKie et al. 2015). Whereas, higher O₃ dose (1.5-2.0 mg/mg DOC) reported reductions ranging from 30-60% for both THM FP and HAA FP (Karnik et al. 2005, Vasyukova et al. 2013). This suggest that ozonation when combined with biofiltration may be effective treatment process for overall reductions in DBP precursors, but its applicability may be dependent on O₃ dose optimization. Therefore, further research is needed to elucidate its applicability while optimising for organics removal and DBP formation potential reductions. Previous studies investigating the impact of O₃ and H₂O₂/O₃ oxidation on biofiltration have been summarized in Table 2-3.

Table 2-3: Impact of O₃ and H₂O₂/O₃ Oxidation on Biofiltration

Reference	Scale, Source, Filter media, & EBCT(min)	O ₃ : DOC ratio or H ₂ O ₂ /O ₃ ratio	Observed Removals (%)
Carlson et al. (2001)	Pilot – scale, River water, Anthracite, EBCT (5.4)	0.6:1	DOC (10-15%)
Chaiket et al. (2002)	Pilot-scale, River water, GAC-sand, Anthracite-sand	1:1	DOC (18%) UV ₂₅₄ (16-61%)
Black & Bèrubè (2014)	Bench-scale, Tap water, GAC media, EBCT (20)	1:1 2:1	DOC (~3%) BDOC (13%) SUVA (28%)
Pharand et al. (2015)	Full-scale, River water, Anthracite-sand, EBCT (38)	0.5:1	DOC (15%)
Irabelli et al. (2008)	Pilot-scale Detroit River DOC (3.4 mg/L)	H ₂ O ₂ /O ₃ ratio (0.1, 0.2, 0.35 mg/mg) O ₃ dose (2.0 mg/L)	DOC: H ₂ O ₂ /O ₃ (45%), O ₃ (40%) H ₂ O ₂ /O ₃ observed no impact on THM and HAA FP reduction compared to O ₃
Lamsal et al. (2011)	Bench-scale French River DOC (2.8 mg/L)	H ₂ O ₂ (23 mg/L) O ₃ (4.0 mg/L)	DOC: O ₃ (6%), H ₂ O ₂ /O ₃ (10%) H ₂ O ₂ /O ₃ observed decreased THM and HAA formation potential compared to O ₃

2.3 Research Gaps

Preozonation (O₃ dose = 1-2 mg/L) can be an effective treatment technology in removing geosmin (50-70%) and MIB (50-70%). However, water quality factors such as pH, organic content, alkalinity, and temperature have shown to influence removals. In addition, selection of O₃ dose also play an important role in oxidizing these compounds. Use of H₂O₂/O₃ AOP have shown to improve geosmin and MIB removal efficiencies by 10-15% (Park et al., 2015; Li et al., 2010a; Mizuno et al., 2011). For maximum removals, optimal H₂O₂/O₃ ratio for each water matrix should be tested (Acero et al., 2001). Elevated H₂O₂ concentration can rapidly decompose O₃ into hydroxyl radicals, which react with organics and bicarbonates (Glaze et al. 1990). As a result, the effectiveness on removing geosmin and MIB is impacted. Acero et al. (2011) found that H₂O₂/O₃ ratio of 0.34 resulted in optimum decomposition of a test compound, pCBA. The study observed no significant difference in pCBA decomposition when H₂O₂/O₃ ratios was elevated from 0.34 to

0.70. In 1990, Ferguson et al. observed nearly 10% decrease in geosmin removals when $\text{H}_2\text{O}_2/\text{O}_3$ ratio was increased from 0.2 to 0.3 at an ozone dose of 2.0 mg/L. Further, when $\text{H}_2\text{O}_2/\text{O}_3$ is applied prior to biofiltration, synergistic effects could result in high removals than when used as a stand-alone treatments. Therefore, site-specific pilot-studies need to be conducted to optimize selection of $\text{H}_2\text{O}_2/\text{O}_3$ ratios.

3. Materials and Methods

3.1 Experimental Configuration

3.1.1 Pilot Plant Configuration

The Peterborough Water Treatment Plant (PWTP) is located on the Otonabee River and has a total capacity of 104 MLD. The pilot-plant was located within PWTP and consisted of a biofiltration and an ozone pilot; details of these pilots are provided in section 3.1.2 and 3.1.3, respectively. Pilot-scale studies were conducted using full-scale plant (FSP) settled water from the PWTP post coagulation, flocculation, and settling. The details of the raw and pilot plant influent water quality is provided in the Table 3-1.

Table 3-1: Summary of Raw and Pilot Plant Influent (Settled) Water Quality

Parameter	Raw Water	Settled Water
pH	8.0 - 8.2	7.1 - 7.3
Temperature (°C)	9 - 23	9 - 22
Turbidity (NTU)	0.332 - 0.775	0.127 - 0.185
DOC (mg/L)	5.0 - 5.2	3.0 - 3.3
UV ₂₅₄ (cm ⁻¹)	0.10 - 0.11	0.05 - 0.06
Alkalinity (mg/L as CaCO ₃)	67 - 79	56 - 62
GSM (ng/L)	17 - 24	15 - 24
MIB (ng/L)	13 - 21	11 - 20
THM FP (µg/L)	156 - 184	69 - 85
HAA FP (µg/L)	95 - 157	75 - 108

3.1.2 Biofiltration Pilot

The biofiltration pilot consist of six parallel filter columns. These columns were operated in parallel at an EBCT of 10 min to match full-scale conditions. Three filters contained 50 cm of sand (effective size (d_{10}) = 0.5, uniformity coefficient (UC) = 1.8) and 50 cm of biological

exhausted GAC (Filtrisorb® 300 Calgon Carbon; Pittsburgh, PA) which had been in operation for 12 years and was assumed to be exhausted in terms of adsorptive capacity. The remaining three filters contained 50 cm of sand ($d_{10} = 0.5$, UC = 1.8) and 50 cm of anthracite ($d_{10} = 0.85$, UC = 1.8), which was obtained from the full-scale PWTP. All filters were operated at constant head and declining flow rate, with a water level maintained at 90 cm above the media. In order to maintain conditions conducive to biological filtration, five of the filters were backwashed with their individual (unchlorinated) effluent, while the conventional filter was backwashed with chlorinated water (chlorine residual = 1.5 mg/L) from the FSP.

3.1.3 Ozone and H₂O₂/O₃ Pilot

The O₃ pilot consisted of two parallel trains (4 contactors of 65L each; 2 contactors connected in series), supplied with full-scale settled water, and operated at a flow rate of 11 L/min to achieve an O₃ contact time of 12 minutes. Based on O₃ demand tests conducted using settled water, 2 mg/L O₃ was applied. The selected dose corresponded to a O₃:DOC ratio of 0.625, and within an operational range of O₃ dosages (O₃:DOC = 0.5 to 1) for optimal organics removal (Schulz, 2014; Zimmermann et al., 2011). For geosmin and MIB spiking trials, an influent concentration of 100 ng/L was targeted (Ferguson et al., 1990; Liang et al., 2014). The compounds were spiked continuously for 24 hours to simulate transient T&O events using a Masterflex L/S pump. H₂O₂ was added immediately prior to O₃ to obtain mass H₂O₂:O₃ ratios of 0.1:1, 0.2:1, 0.35:1, and 0.5:1 mg/mg. Residual oxidants were quenched at the exit of the O₃ pilot using calcium thiosulphate (CTS) at a molar ratio of CTS:O₃ = 4:1.

3.1.4 Experimental Design

This study was divided into four experimental conditions as presented in Figure 3-1. In the first condition, geosmin, MIB, and DBP precursor removals were evaluated across the conventional and biological filters with two different media (BAF vs. BAC) without the use of pre-oxidation. In the second condition, the impact of 0.1H₂O₂/O₃ and O₃ were compared as stand-alone treatments and as pre-treatments to BAF and BAC. In the third condition, the impact of 0.2H₂O₂/O₃ was compared to O₃. In the fourth condition, two AOP treatments (0.35 and 0.5 H₂O₂/O₃) were evaluated in parallel.

Condition 1

Condition 2

Condition 3

Condition 4

Figure 3-1: Pilot Plant Schematic for Experimental Condition 1, 2, 3, and 4

3.1.5 Spike and Sampling Procedure

In total, four spike/sampling events were conducted during the months of September, October, and November. Geosmin and MIB samples were collected prior to and immediately after each treatment step to determine removal efficiency. For the condition 1 (when no pre-oxidation was applied), the T&O compounds were spiked into the settled water line immediately prior to each filter. For conditions 2, 3 and 4, T&O compounds were spiked prior to ozonation.

3.2 Analytical Methods

3.2.1 ATP Analysis

Adenosine triphosphate (ATP) analysis was conducted using a Luminultra analysis kit (DSA-100C). Media samples were obtained from the top 5-10 cm of the biofilter and analyzed as per the manufacturer's instructions provided in Appendix Table 7-1.

3.2.2 Dissolved Organic Carbon

DOC was measured based on standard method 5310 D using an O-I Corporation Model 1010 Analytical TOC Analyzer with a Model 1051 Vial Multi-Sampler (APHA, 2005). Samples were filtered into 40 mL amber vials through a 0.45 μm glass fiber filter, and acidified to $\text{pH} \leq 2$ using concentrated sulfuric acid if samples were not analyzed immediately after preparation. The vials were sealed with Teflon®-lined septum screw caps and stored at 4°C. All samples were prepared on the day of collection and tested within 7 days. A summary of the instrument conditions are presented in Table 3-2. DOC concentrations were quantified using anhydrous potassium hydrogen phthalate (KHP) in Milli-Q® water as a calibration solution.

The calibration solutions were prepared at a concentration of 10 mg/L and diluted by the instrument to concentrations of 0, 0.625, 1.25, 2.5 and 5 mg/L for a 6-point calibration curve. A 10 mg/L calibration sample was prepared, diluted and analyzed before each sample set. A sample calibration curve is shown in Appendix Figure 7-1. Check standards ($C = 5 \text{ mg/L}$) were tested after every 10 samples, and at the end of every sample set. Additionally, a minimum of three blank samples were tested after calibration, and before every check standard sample. The reagent list is shown in Table 3-3 and sample analysis procedure is presented in Appendix Table 7-2

Table 3-2: DOC Analyzer Conditions

Parameter	Description
Acid volume	200 µL of 5% phosphoric acid
Oxidant volume	1000 µL of 100 g/L sodium persulphate
Sample volume	15 mL
Rinses per sample	1
Volume per rinse	15 mL
Replicates per sample	3
Reaction time (min:sec)	TIC 2:00; TOC 2:30
Detection time (min:sec)	TIC 2:40; TOC 2:00
Purge gas	Nitrogen
Loop size	5 mL

Table 3-3: DOC Analysis Reagents

Reagent	Supplier and purity
Milli-Q® water	Prepared in the laboratory
Sulphuric acid, H ₂ SO ₄	VWR International, 98%+
Sodium persulphate, Na ₂ (SO ₄)	Sigma Aldrich, 98%+, anhydrous
Potassium hydrogen phthalate (KHP), C ₈ H ₅ KO ₄	Sigma Aldrich, 98%+
Phosphoric acid, H ₃ PO ₄	Caledon, >85%

3.2.3 Geosmin and MIB

Geosmin (CAS# 16423-19-1) and MIB (CAS# 2371-42-8) were purchased from Dalton Pharma Services in Toronto. Samples were extracted using the solid phase micro-extraction (SPME) fiber and analyzed using Gas Chromatography (Varian 3800) with Mass Spectroscopy (Varian 400) operated in electron ionization (EI) mode according to Standard Method 6040D. Details pertaining to the sample extraction, preparation, calibration, and analysis procedure are presented in Appendix Table 7-3. Sample calibration curve for both geosmin and MIB are presented in Appendix Figure 7-2. Check standards ($C = 60$ ng/L) were tested after every 10 samples, and at the end of every sample set. A blank was tested before every check standard.

3.2.4 UV_{254}

UV_{254} is a measure of ultraviolet absorbance at wavelengths of 254 nm, and can be used to approximate the concentration of organic materials in a water sample. Samples were placed in 1 cm quartz cell (Hewlett Packard, Mississauga) and measured using a CE 3055 Single Beam Cecil UV/Visible Spectrophotometer (Cambridge, England). The device was zeroed with Milli-Q® water. The cells were rinsed with Milli-Q® water twice between sampling and rinsed again with the sample water before analysis to minimize contamination.

3.2.5 LC-OCD

Liquid chromatography-organic carbon detection (LC-OCD) characterized the organic compounds found in raw and treated water samples. LC-OCD identifies five different fractions of DOC including: biopolymers, humic substances, building blocks, low molecular weight acids, and low molecular weight neutrals (Huber et al., 2011).

Water samples were filtered using a 0.45 μ m glass fiber filter (Gelman Supor, Gelman Sciences, Ann Arbor, MI) and collected in 40 mL amber glass vials with Teflon® lined silicon septa and screw caps (VWR International, Mississauga, ON). The samples were stored at 4°C until being shipped to the University of Waterloo (Waterloo, ON) for analysis. Based on a method by Huber et al. (2011), the samples are first separated chromatographically using a weak cation exchange column (250 mm x 20 mm, Tosoh, Japan). The mobile phase used was a phosphate buffer exposed to UV irradiation in an annular UV reactor, delivered at a flow rate of 1.1 mL/min

to an autosampler (MLE, Dresden, Germany, 1 mL injection volume). Chromatographic separation was followed by UV₂₅₄ detection (UVD), and organic carbon detection (OCD). The solution was acidified to form carbonic acid from carbonates at the OCD inlet. Total DOC for each sample was measured using a column bypass. Calibration was completed using a potassium hydrogen phthalate (KHP) solution. Data processing and acquisition was completed using a custom ChromCALC software package (Karlsruhe, Germany).

3.2.6 Disinfection By-Product Formation Test

For DBP formation potential, uniform formation condition (UFC) test was employed where samples were chlorinated in duplicate to achieve a free chlorine target residual of 1.5 ± 0.5 mg/L after 24 ± 2 hours at 20° C and pH was not adjusted in order to match the full-scale. If the residual chlorine concentration was correct after 24 hours, the disinfectant in each sample was quenched with 20 mg of L-ascorbic acid. The bottles were then acidified to pH 2 with H₂SO₄ and stored in the dark at 4°C until extraction.

3.2.7 Trihalomethanes (THMs)

Trihalomethane analysis was conducted to quantify the concentration of four compounds: chloroform (trichloromethane; TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (tribromomethane; TBM). A liquid-liquid extraction with gas chromatography was performed based on Standard Method 6232 B (APHA, 2005). The analysis was conducted at the University of Toronto drinking water research laboratory (Toronto, Ontario) using a Hewlett Packard 5890 Series II Plus gas chromatograph (Mississauga, Ontario) equipped with an electron capture detector (GC-ECD) and a DB 5.625 capillary column (Agilent 30 Technologies Canada Inc., Mississauga, Ontario). A THM stock solution (2000 µg/mL) was used to create an intermediate solution (20 mg/L). This intermediate was used to generate calibration standards of 0, 5, 10, 20, 40, 60, 80, 100 µg/L. Sample calibration curve of all the compounds is shown in Appendix Figure 7-3. The instrument conditions and required reagents are presented in Table 3-4 and Table 3-5, respectively.

Table 3-4: THM Instrument Conditions

Parameter	Description
Injector Temperature	200 ⁰ C
Detector Temperature	300 ⁰ C
Temperature Program	40 ⁰ C for 4.0 min 4 ⁰ C/min temperature ramp to 95 ⁰ C 60 ⁰ C/min temperature ramp to 200 ⁰ C
Carrier Gas	Helium
Flow Rate	1.2 mL/min at 35 ⁰ C

Table 3-5: THM Reagent Compounds

Reagent	Source
Milli-Q® water	Prepared in the laboratory
Concentrated trihalomethane stock for calibration	Supelco, 2000 µg/mL in methanol (48140-U)
Sodium sulphate [Na ₂ SO ₄]	Sigma Aldrich, ACS Grade
Methyl-tert-butyl-ether (MTBE)	Fluka, >99.8%

3.2.8 Haloacetic Acids (HAAs)

The analysis of haloacetic acids (HAAs) involved quantifying the following 9 compounds: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). The analysis was completed using a liquid-liquid extraction and a gas chromatograph based on Standard Method 6251 B (APHA, 2005). The analyses were completed at the University of Toronto drinking water research laboratory (Toronto, Ontario) using a Hewlett Packard 5890 Series II Plus gas chromatograph (Mississauga, Ontario) paired with an electron capture detector (GC-ECD) and a DB 5.625 capillary column (Agilent Technologies Canada Inc., Mississauga, Ontario). Details pertaining to the analysis reagents and instrument conditions is presented in Table 3-6 and Table 3-7, respectively.

Table 3-6: HAA Reagent Compounds

Reagent	Source
Diethyl ether [C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ CH ₂ OH]	Sigma Aldrich, 99+%
N-Methyl-N-nitroso-p-toluene sulfonamide (Diazald) [CH ₃ C ₆ H ₄ SO ₂ N(CH ₃)NO]	Sigma Aldrich, 99+%
Potassium Hydroxide (KOH)	BDH, 85.0+%, ACD Grade
Sulphuric acid [H ₂ SO ₄]	E.M. Science, 98+%
Haloacetic acids concentrated stock	EPA 552.2 Acids Calibration Mix in MTBE
Sodium sulphate [Na ₂ SO ₄]	Sigma Aldrich, ACS Grade
Methyl-tert-butyl-ether (MTBE)	Sigma Aldrich, >99.8%

Table 3-7: HAA Instrument Conditions

Parameter	Description
Injector Temperature	200°C
Detector Temperature	300°C
Temperature Program	35°C for 10.0 min 2.5°C/min temperature ramp to 65°C 10°C/min temperature ramp to 85°C 20°C/min temperature ramp to 205°C, hold for 7 minutes
Carrier Gas	Helium
Flow Rate	1.2 mL/min at 35°C

3.3 Statistical Analysis

All comparisons between treatments were conducted using a paired Student t-test (95% significance level). A two-tailed test was used where the objective was to identify whether a difference existed between two treatments (e.g. comparison of two control biofilters), while a single-tailed test was used to determine whether a particular treatment performed better than the other treatment strategy (e.g. comparison of two pre-oxidation strategies O_3 and H_2O_2/O_3) as described by McKie et al. (2015). Reported p-values indicate the level at which difference between two treatments were statistically significant.

4. Ozone/Peroxide Advanced Oxidation in Combination with Biofiltration for Taste and Odour Control and Organics Removal

4.1 Introduction

Geosmin and 2-methylisoborneol (MIB) have typically been reported as the most common taste and odour (T&O) causing compounds and are seasonally detected in drinking water sources as a result of anthropogenic or biogenic factors (Srinivasan and Sorial, 2011). Removal of these compounds by conventional treatment is low (geosmin: <20%; MIB: <15%) and their presence in finished water is a major concern to water treatment utilities (Olsen et al., 2016; Parinet et al., 2010).

Treatment strategies designed to remove geosmin and MIB from source waters have been intensively studied (Antonopoulou et al., 2014; Srinivasan and Sorial, 2011). Adsorption by granular activated carbon (GAC) has proven to be effective for the removal of these compounds, however its efficiency is dependent on media adsorptive capacity (Gilligly et al., 1999; Ho and Newcombe, 2010). Fortunately, when the adsorptive capacity of GAC is exhausted, filters can be operated in a biological mode and continue to remove geosmin (44-87%) and MIB (32-51%), resulting in significant capital cost savings associated with media regeneration or replacement (Elhadi et al., 2004; Zhu et al., 2010). In addition, BAC has been recognized for its ability to reduce biodegradable organic matter (Carlson and Amy, 2001) and disinfection by-product (DBP) precursors (Zha et al., 2016). However, BAC performance is impacted by water temperature (Emelko et al., 2006; Moll et al., 1999), empty bed contact time (EBCT), and accumulation of attached microbial biomass (Elhadi et al., 2006). Because of these factors, BAC performance in terms of geosmin, MIB, as well as DBP precursor removals can vary significantly (de Vera et al., 2016; Elhadi et al., 2004; Guo et al., 2016).

Application of O₃ prior to biofiltration has been shown to be effective for the removal of geosmin, MIB, and DBP precursors (Klausen and Grønborg, 2010; Park et al., 2015; Sánchez-Polo et al., 2006; Yan et al., 2010). An investigation of O₃-biofiltration treatment at full-scale by Nerenberg et al. (2000) reported MIB removals of 36-54% by ozonation (1.3 mg/L O₃) followed by 26-46% removal across biofiltration (17 min EBCT). Chaiket et al. (2002) reported reductions

of 18% dissolved organic carbon (DOC), 61% UV₂₅₄ absorbance, 17% trihalomethane formation potential (THMFP), and 19% haloacetic acid formation potential (HAAFP) when treated with 3 mg/L O₃ followed by BAC (5 min EBCT). It is important to note that O₃ efficiency is dependent on source water characteristics such as pH, DOC, alkalinity, and temperature (Westerhoff et al., 2006), and can be improved with the addition of H₂O₂ to produce hydroxyl radicals ($\cdot$ OH) with fast reaction rates for geosmin and MIB ($K_{OH} \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Lee and von Gunten, 2016; Peter and von Gunten, 2007). Previous pilot studies have reported increases of 10-15% in geosmin and MIB removals upon H₂O₂ addition (Glaze et al., 1990; Park et al., 2015; Wang et al., 2015). However, much of the existing information regarding H₂O₂/O₃ optimization has been based on the bench-scale studies (Li et al., 2012; Mizuno et al., 2011; Parinet et al., 2010; Westerhoff et al., 2006; Yuan et al., 2013; Zhou et al., 2011). A pilot-scale study is warranted to substantiate the theoretical optimum of 0.35 H₂O₂:O₃ (mg/mg) proposed by Acero and von Gunten, (2001). Below this ratio, O₃ is present in excess, which favors O₃ decomposition over $\cdot$ OH formation. Above this ratio, H₂O₂ is present in excess, which it consumes O₃, generating $\cdot$ OH.

H₂O₂/O₃ mass ratios of 0.1:1, 0.2:1, 0.35:1, and 0.5:1 were compared to O₃ alone to better understand the removal of geosmin, MIB, and organics at pilot-scale. The impact of pre-oxidation on subsequent biofiltration performance was also assessed with respect to the same analytes, as well as organic carbon removal (measured as DOC, UV₂₅₄), DBP precursor removal (including precursors to THMs and HAAs), and filter media adenosine triphosphate (ATP). Liquid chromatography–organic carbon detection (LC-OCD) was performed to further characterize the impact of each treatment process and to explore potential relationships between the organic fractions (humics or low molecular weight compounds) and DBP precursor removal.

4.2 Materials and Methods

4.2.1 Source Water

Pilot-scale biofiltration studies were conducted using water from Otonabee River in Peterborough, Ontario. As the PWTP typically observes geosmin (15-22 ng/L) and MIB (10-20 ng/L) during September to November (PWTP, 2015), pilot-scale studies were conducted during

these months using full-scale plant (FSP) settled water obtained post coagulation, flocculation, and settling. Typical pilot influent water quality during the study is shown in Table 4-1.

Table 4-1: Pilot influent (settled) water quality

Parameter	September	October	November
pH	7.3 - 7.4	7.2 - 7.3	7.2 - 7.3
Temperature (°C)	20 - 24	16 - 17	9 - 10
Turbidity (NTU)	0.165 - 0.185	0.127 - 0.143	0.118 - 0.138
DOC (mg/L)	3.2-3.4	3.1-3.3	3.2 - 3.3
UV ₂₅₄ (cm ⁻¹)	0.056 - 0.058	0.052 - 0.054	0.051 - 0.053
Alkalinity (mg/L as CaCO ₃)	60 - 62	59 - 60	57 - 60
Geosmin (ng/L)	15 - 23	17 - 21	11 - 16
MIB (ng/L)	18 - 20	11 - 15	BDL
THM FP (µg/L)	73.4	68.7	85.5
HAA FP (µg/L)	74.6	103.8	108.2

BDL=Below Detection Limit (Geosmin = 5.7 ng/L; MIB = 7.1 ng/L)

4.2.2 Pilot Plant Design and Operation

Six filter columns were operated in parallel at an EBCT of 10 min to mimic full-scale conditions Table 4-2. Three filters contained 50 cm of sand (effective size (d_{10}) = 0.5, uniformity coefficient (UC) = 1.8) and 50 cm of biological exhausted GAC (Filtrisorb® 300 Calgon Carbon; Pittsburgh, PA) which had been in operation for 12 years and was assumed to be exhausted in terms of adsorptive capacity. The remaining three filters contained 50 cm of sand (d_{10} = 0.5, UC = 1.8) and 50 cm of anthracite (d_{10} = 0.85, UC = 1.8), which was obtained from the full-scale PWTP. All filters were operated at constant head and declining flow rate. In order to maintain conditions conducive to biological filtration, five of the filters were backwashed with their individual (unchlorinated) effluent, while the conventional filter was backwashed with chlorinated water (chlorine residual = 1.5 mg/L) from the FSP. All filters were backwashed three times a week,

allowing for 50% filter bed expansion for 8 minutes followed by 4 minutes of slow backwash (20% fluidization) to maintain proper media layer separation (Azzeh et al., 2015).

Table 4-2: Pilot plant configuration depicting operating conditions for each experimental phase

Media	Anthracite/ Sand	Anthracite/ Sand	BAC/ Sand	Anthracite/ Sand	BAC/ Sand	BAC/ Sand
Mode	Conventional	Biological	Biological	Biological	Biological	Biological
Condition 1: No pre-oxidation.						
Influent	Settled water					
Condition 2: O ₃ dose = 2 mg/L; H ₂ O ₂ /O ₃ ratio = 0.1:1.						
Influent	Settled water + O ₃			Settled water + AOP		Settled water
O ₃ dose (mg/L)	2.0	2.0	2.0	2.0	2.0	0
H ₂ O ₂ (mg/L)	0	0	0	0.2	0.2	0
Condition 3: O ₃ dose = 2 mg/L; H ₂ O ₂ /O ₃ ratio = 0.2:1.						
Influent	Settled water + O ₃			Settled water + AOP		Settled water
O ₃ dose (mg/L)	2.0	2.0	2.0	2.0	2.0	0
H ₂ O ₂ (mg/L)	0	0		0.4	0.4	0
Condition 4: O ₃ dose = 2 mg/L; H ₂ O ₂ /O ₃ ratio = 0.35:1 and 0.5:1						
Influent	Settled water + AOP					Settled water
O ₃ dose (mg/L)	2.0	2.0	2.0	2.0	2.0	0
H ₂ O ₂ (mg/L)	0.7	0.7	0.7	1.0	1.0	0

CAF = conventional anthracite filter; BAF = biologically active anthracite filter; BAC = biologically active carbon; AOP = advanced oxidation process

4.2.3 Analytical Methods

Geosmin and MIB samples were extracted using a solid phase micro-extraction (SPME) fiber and analyzed using Gas Chromatography (Varian 3800) with Mass Spectroscopy (Varian

400) operated in electron ionization (EI) mode according to Standard Method 6040D (APHA, 2012). Complete details are presented in Section 3.2.3.

DOC was measured using a persulfate wet oxidation method as described in Section 3.2.2. A CE 3055 Single Beam Cecil UV/Visible Spectrophotometer (Cambridge, England) with 1 cm quartz crystal cuvette (Hewlett Packard, Mississauga) was used for measuring ultraviolet absorbance at 254 nm (UV₂₅₄) and details are presented in Section 3.2.4. Organics were characterized using liquid chromatography – organic carbon detection (LC-OCD), allowing classification into five fractions including: biopolymers (proteins and polysaccharides), humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals. LC-OCD analyses were conducted at the University of Waterloo (Waterloo, ON) according to a method described by Huber et al. (2011) and presented in Section 3.2.5.

Uniform formation condition (UFC) test was employed for DBP analysis, where samples were chlorinated in duplicate to achieve a free chlorine target residual of 1.5 ± 0.5 mg/L following 24 ± 2 hours at 20° C; without pH correction (APHA, 2012). Free chlorine residuals were measured as per Standard Methods 4500-Cl G (APHA, 2012), quenched using L-ascorbic acid. Liquid-liquid extraction and gas chromatography were used to analyze four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and nine HAAs (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid) as per Standard Method 6232 B and 6251, respectively (APHA, 2012). Complete details pertaining to quantification of THMs and HAAs can be found in Section 3.2.7 and Section 3.2.8, respectively.

ATP was measured to quantify the bacterial biomass on the filter media surface (5-10 cm) using a LuminUltra Deposit Surface Analysis Kit (DSA-100C, Fredricton, NB) as per the manufacturer's instructions and is presented in Section 3.2.1.

4.2.4 Statistical Methods

All comparisons between treatments were conducted using a paired Student t-test (95% significance level). A two-tailed test was used where the objective was to identify whether a

difference existed between two treatments (e.g. comparison of two control biofilters), while a single-tailed test was used to determine whether a particular treatment performed better than the other treatment strategy (e.g. comparison of two pre-oxidation strategies O_3 and H_2O_2/O_3) as described by McKie et al. (2015). Reported p-values indicate the level at which difference between two treatments were statistically significant.

4.3 Results and Discussion

4.3.1 Geosmin and MIB Removal by Conventional and Biological Filtration

Geosmin and MIB were spiked at a target concentration of 100 ng/L immediately prior to the pilot filters. Removals across the conventional anthracite filter (CAF), biological anthracite filter (BAF), and biologically active carbon filter (BAC) are shown in Table 4-3. BAC removed 84% geosmin and 80% MIB, whereas BAF removed 82% geosmin and 65% MIB, while the CAF removed 20% geosmin and 8% MIB. This comparison between conventional and biological anthracite filters provides a good indication that biological degradation was responsible for geosmin and MIB removals.

During the study, geosmin and MIB were present in the full-scale plant (FSP) which allowed us to measure their removals across the conventional anthracite filter. It was found that 21 ng/L geosmin and 20 ng/L MIB were present in the FSP filter influent and the FSP CAF removed 28% geosmin and 17% MIB. It should be noted that FSP CAF effluent concentrations were above odour threshold concentration (OTC = 10 ng/L) (Olsen et al., 2016), underscoring the need for an additional treatment barrier to mitigate taste and odour events. Overall, these removals at the FSP are in agreement with published values, where less than 20% geosmin and MIB removals have been reported with conventional treatment (Newcombe et al., 2010; Srinivasan and Sorial, 2011). Consistent with the literature, geosmin was observed to be more readily degraded than MIB (Elhadi et al., 2006; Ho et al., 2007, 2002). Some authors have suggested that the planar structure of geosmin allows for easier biotransformation (Ho et al., 2002; Persson et al., 2006). Since these compounds were not removed below the 10ng/L by biofiltration alone, pre-oxidation strategies were applied to enhance overall removals.

Table 4-3: Geosmin and MIB removals (%) across conventional and biological filters with anthracite and granular activated carbon media for pilot- and full-scale filters

Filters	Geosmin (ng/L)			MIB (ng/L)		
	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
CAF	85 ± 7.3	68 ± 5.5	20 ± 1.4	98 ± 1.1	90 ± 7	8 ± 1.1
BAF	95 ± 2.8	17 ± 6.5	82 ± 1.3	100 ± 1.6	36 ± 8.3	65 ± 1.2
BAC	92 ± 5.7	15 ± 6.3	84 ± 1.4	93 ± 8.1	18 ± 1.2	80 ± 1.2
FSP CAF	21 ± 3.2	15 ± 0.2	28 ± 1.1	20 ± 3.7	17 ± 1.8	17 ± 1.3

±SD = one standard deviation; n=3; CAF = conventional anthracite filter; BAF = biologically active anthracite filter; BAC = biologically active carbon; FSP = Full-scale Plant

4.3.2 Impact of Pre-Oxidation and Temperature on Geosmin and MIB Removal

O₃ was applied at a constant dose of 2 mg/L (0.5 mg/L O₃ residual) and at two water temperatures (16°C and 10°C). O₃ efficiency was observed to change as a function of temperature, resulting in a significant decrease ($p < 0.05$) in geosmin and MIB removal (Table 4-4). Geosmin and MIB removals decreased from 70% to 45% and 55% to 40%, at 16°C and 10°C, respectively (Figure 4-1). The decrease in geosmin (25%) and MIB (15%) removal at 10°C was attributed to temperature, since the source water quality did not change with respect to DOC (3.1-3.3 mg/L) or UV₂₅₄ (0.051-0.058 cm⁻¹). A bench-scale study by Elovitz et al. (2000) also showed a strong dependence between O₃ reaction rates and temperature. The authors reported an 87% decrease in the first-order ozone decay rate from $4.4 \times 10^{-3} \text{ s}^{-1}$ to $6 \times 10^{-4} \text{ s}^{-1}$ for a temperature decrease from 25°C to 5°C. In contrast, the authors reported a negligible effect when considering $\cdot\text{OH}$ exposure, highlighting the benefit of $\cdot\text{OH}$ oxidation in seasonally impacted waters. As $\cdot\text{OH}$ concentration cannot be measured directly, the reduction rate of an O₃-resistant probe compound (para-chloro-benzoic acid, pCBA) was used to calculate the R_{CT} (Acero and von Gunten, 2001; Elovitz et al., 2000) and understand geosmin and MIB kinetics with respect to temperature.

$$R_{CT} = \frac{\int \cdot\text{OH} \, dt}{\int \text{O}_3 \, dt} \approx \frac{[\cdot\text{OH}]}{[\text{O}_3]} \quad (4.1)$$

where R_{CT} is defined as $\cdot\text{OH}$ to O₃ exposure ratios

Table 4-4: Statistical comparison between treatment processes using paired T-tests ($p < 0.05$)

MIB Removal						
	T=16°C	T=10°C	T=16°C	T=10°C		
Treatments	O ₃	O ₃	0.1H ₂ O ₂ /O ₃	0.2H ₂ O ₂ /O ₃	0.35H ₂ O ₂ /O ₃	0.5H ₂ O ₂ /O ₃
O ₃ ^a	1					
O ₃	0.000	1				
0.1H ₂ O ₂ /O ₃ ^a	0.000	NA	1			
0.2H ₂ O ₂ /O ₃	NA	0.000	0.000	1		
0.35H ₂ O ₂ /O ₃	NA	0.000	0.091	0.001	1	
0.5H ₂ O ₂ /O ₃	NA	0.000	0.920	0.000	0.063	1
Geosmin Removal						
O ₃ ^a	1					
O ₃	0.000	1				
0.1H ₂ O ₂ /O ₃ ^a	0.143	NA	1			
0.2H ₂ O ₂ /O ₃	NA	0.000	0.008	1		
0.35H ₂ O ₂ /O ₃	NA	0.076	0.037	0.211	1	
0.5H ₂ O ₂ /O ₃	NA	0.014	0.124	0.937	0.136	1

p-values representing the level of significance of the difference between two treatments ($\alpha = 0.05$)

Bold indicates a significant difference between two sampling points. NA = Not Available. T = Temperature. Note temperature for all trials was 10°C except for two at 16°C as denoted by ^a

Westerhoff et al. (2006) quantified O₃ and •OH reaction rate kinetics for MIB and geosmin for a range of water qualities at bench-scale. The authors also compared the impact of temperature at a fixed O₃ dose and reported R_{CT} to decrease with a decreased temperature when considering surface waters. By lowering the temperature, geosmin and MIB oxidation rates decreased. However, H₂O₂ addition stabilizes the oxidation performance by increasing ozone decay and producing more •OH (Elovitz et al., 2000). As such, H₂O₂ addition improved geosmin and MIB removal efficiencies in cold water condition (10°C) (Figure 4-1).

Figure 4-1: Geosmin, MIB, DOC, UV₂₅₄, THMFP, and HAAFP removals (from settled water) following exposure to 2 mg/L O₃ and a range of H₂O₂/O₃ dose (mg/mg). Vertical bars represent mean absolute deviation of experiments (geosmin, MIB, DOC, and UV₂₅₄: n=3, THMFP and HAAFP: n = 2)

The addition of H₂O₂ at ratios of 0.1, 0.2, 0.35, and 0.5 mg/mg H₂O₂/O₃ statistically improved ($p < 0.05$) MIB removals by 11%, 10%, 23%, and 26%, respectively, compared to O₃ alone (Figure 4-1). These results are consistent with pilot-studies by Ferguson et al. (1990) who reported a 10-20% improvement in geosmin and MIB removal efficiency when a 0.2 H₂O₂/O₃ (O₃ dose = 2mg/L) was applied. A pilot study by Park et al. (2015) reported 7-10% increment in MIB removal with 0.42 H₂O₂/O₃ treatment compared to O₃ alone when tested at four different O₃ doses (0.5, 1, 1.5, 2 mg/L O₃). In the present study, addition of 0.1 H₂O₂ and 0.35 H₂O₂ improved MIB removal by 11% and 23%, respectively, compared to O₃. However, 0.35 and 0.5 H₂O₂/O₃ (mg/mg) were not statistically different ($p = 0.063$) in terms of MIB (~3%) removal; 0.35 H₂O₂/O₃ was identified as an optimal ratio for MIB reduction. Similar results were also observed by others in a bench-scale H₂O₂/O₃ study, where an optimal ratio between 0.19 and 0.34 mg/mg for the •OH model compound, pCBA, was identified (Acero and von Gunten, 2001).

Consistent with the above results, MIB is more susceptible to $\cdot\text{OH}$ oxidation than O_3 . During warmer water temperatures ($T > 16^\circ\text{C}$); effective MIB removals can be achieved with 1.5-2 mg/L O_3 and low $\text{H}_2\text{O}_2/\text{O}_3$ ratios (0.1-0.3 mg/mg). During colder conditions (10°C), effective MIB reduction requires higher $\text{H}_2\text{O}_2/\text{O}_3$ ratios (0.2-0.5 mg/mg).

Addition of H_2O_2 to O_3 also improved geosmin removals by 18%, 10%, and 21%, but did not result in statistically different ($p > 0.05$) reductions at 0.2, 0.35, and 0.5 $\text{H}_2\text{O}_2/\text{O}_3$ ratios, respectively, indicating that at 10°C , an optimal ratio of 0.2 $\text{H}_2\text{O}_2/\text{O}_3$ can provide the most effective geosmin removal (64%). Park et al. (2015) reported an average 10-20% improvement in geosmin removal when O_3 dose was varied from 0.5 to 2 mg/L at a fixed 0.42 $\text{H}_2\text{O}_2/\text{O}_3$ ratio. Wang et al. (2015) reported 91% and 94% geosmin removals at 0.2 and 0.4 $\text{H}_2\text{O}_2/\text{O}_3$ ratios (O_3 dose = 2 mg/L), identifying 0.2 $\text{H}_2\text{O}_2/\text{O}_3$ as an optimal ratio for geosmin removal. Therefore, at warmer temperatures ($T = 16^\circ\text{C}$), effective geosmin removals can be achieved for 1.5-2 mg/L O_3 , however in colder water temperatures (10°C), addition of 0.1-0.2 $\text{H}_2\text{O}_2/\text{O}_3$ is required to match the results of O_3 alone at 16°C .

4.3.3 Impact of Pre-Oxidation and Temperature on MIB and Geosmin Biodegradation

Similar to pre-oxidation, temperature significantly impacted ($p < 0.05$) MIB and geosmin removals across BAC (Table 4-5). For example, the BAC control (no pre-oxidation) removed 85%, 60%, and 46% MIB at 22°C , 16°C , and 10°C , respectively (Figure 4-2 and Figure 4-3, respectively). A decrease in BAC ATP was also observed between 22°C and 10°C from 530 ng ATP/g BAC to 151 ng ATP/g BAC. As such, the decrease in MIB and geosmin removals across BAC may be due to lowered bacterial biomass (Moll et al., 1999). Bench-scale studies by Elhadi et al. (2004) reported a 40% decrease in geosmin and MIB removals ($p < 0.05$) across exhausted GAC/sand filters operated at water temperatures of 20°C vs 8°C . In the present study, at 22°C , BAC alone may serve as a suitable treatment technology for MIB and geosmin treatment however for lower temperatures, an additional treatment process would be required to achieve reductions to $< 10\text{ng/L}$. Application of O_3 (2 mg/L) prior to BAC improved overall MIB removal by 20% and 15% at 16°C and 10°C , respectively.

Table 4-5: Statistical Comparison of Treatment Processes Using Paired T-Tests

Treatments compared		Geosmin Removal	MIB Removal	SUVA	UV ₂₅₄	DOC	THMFP	HAAFP
Control BAC	CAF	0.001	0.000	0.629	0.007	0.000	0.865	0.074
Control BAC	BAF	0.525	0.004	0.987	0.094	0.019	0.237	0.173
Control BAC	BAC	0.674	0.066	0.615	0.158	0.108	0.194	0.260
Control BAC	2mg/L O ₃ -BAF @16°C	0.001	0.006	0.001	0.001	0.007	0.015	0.448
Control BAC	2mg/L O ₃ -BAF @10°C	0.103	0.002	0.000	0.000	0.096	0.030	0.614
Control BAC	2mg/L O ₃ -BAC @16°C	0.001	0.001	0.001	0.000	0.006	0.590	0.022
Control BAC	2mg/L O ₃ -BAC @10°C	0.011	0.000	0.000	0.000	0.101	0.046	0.202
Control BAC	0.1 H ₂ O ₂ /O ₃ -BAC	0.000	0.001	0.002	0.001	0.001	0.011	0.229
Control BAC	0.2 H ₂ O ₂ /O ₃ -BAC	0.001	0.000	0.000	0.000	0.263	0.101	0.559
Control BAC	0.35 H ₂ O ₂ /O ₃ -BAC	0.027	0.143	0.228	0.006	0.022	0.214	0.501
Control BAC	0.5 H ₂ O ₂ /O ₃ -BAC	0.061	0.039	0.211	0.006	0.019	0.778	0.349
0.1 H ₂ O ₂ /O ₃ -BAC	0.2 H ₂ O ₂ /O ₃ -BAC	0.047	0.001	0.273	0.266	0.821	0.061	0.010
0.1 H ₂ O ₂ /O ₃ -BAC	0.35 H ₂ O ₂ /O ₃ -BAC	0.000	0.003	0.727	0.321	0.125	0.015	0.005
0.1 H ₂ O ₂ /O ₃ -BAC	0.5 H ₂ O ₂ /O ₃ -BAC	0.005	0.019	0.609	0.257	0.080	0.008	0.311
0.2 H ₂ O ₂ /O ₃ -BAC	0.35 H ₂ O ₂ /O ₃ -BAC	0.000	0.198	0.352	0.028	0.137	0.913	0.037
0.2 H ₂ O ₂ /O ₃ -BAC	0.5 H ₂ O ₂ /O ₃ -BAC	0.001	0.079	0.275	0.026	0.084	0.097	0.034
0.35 H ₂ O ₂ /O ₃ -BAC	0.5 H ₂ O ₂ /O ₃ -BAC	0.274	0.002	0.927	0.824	0.438	0.056	0.123

p-values representing the level of significance of the difference between two treatments ($\alpha = 0.05$)

Bold indicates a significant difference between two sampling points

Figure 4-2: MIB removal as a result of: no pre-oxidation, ozonation, H₂O₂/O₃ alone and in combination with subsequent biofiltration. Transferred ozone dose = 2 ± 0.1 mg/L; ozone contact time = 12 min; EBCT = 10 min. Vertical bars represent one standard deviation (n=3 for each experiment). OTC = Odour threshold concentration (10 ng/L).

Figure 4-3: Geosmin removal as a result of: no pre-oxidation, ozonation, H₂O₂/O₃ alone and in combination with subsequent biofiltration. Transferred ozone dose = 2 ± 0.1 mg/L; ozone contact time = 12 min; EBCT = 10 min. Vertical bars represent one standard deviation (n=3 for each experiment). OTC = Odour threshold concentration (10 ng/L).

4.3.4 Impact of Pre-Oxidation Organics Removal

Pre-Oxidation and Biofiltration Impacts on DOC and UV₂₅₄ Reduction

O₃ (2 mg/L) and three H₂O₂/O₃ ratios (0.1, 0.2, 0.35) had little impact ($p > 0.05$) on DOC removal ($4 \pm 1\%$), however UV₂₅₄ absorbance significantly reduced by $28 \pm 3\%$ (Figure 4-4), indicating transformation of aromatic organic compounds to low molecular weight aliphatic products (Lautenschlager et al., 2014; Ramseier and von Gunten, 2009).

Pre-oxidation with O₃ and H₂O₂/O₃ improved biofiltration performance in terms of DOC reduction (Figure 4-4). BAC preceded with O₃ (2 mg/L) and 0.1 H₂O₂/O₃ reduced DOC by 11% and 12%, compared to a 6% reduction across the BAC control. BAF operated with the same oxidation conditions showed 10% and 9% DOC reduction, respectively, compared to a 3% decrease for the BAF control. Increasing the H₂O₂/O₃ ratio from 0.1 to 0.5 resulted in a small decrease in DOC (2%-4%) for both BAC and BAF (Figure 4-4). Temperature decreased during this period impacting biofiltration performance. DOC reduction across the BAC control decreased (1-3%) during cold water temperatures (10°C).

Impact of Pre-Oxidation on NOM Characterization

LC-OCD was used to characterize changes in NOM structure following pre-oxidation and biofiltration. Humic substances contributed on average 65% of the total DOC, followed by building blocks (15%), LMW neutrals (12%), and biopolymers (8%) for this source water, which is similar to other water sources in the region (Zheng et al., 2014). Biopolymers represent the largest sized fraction (molecular weight (MW) > 10,000 g/mol) and are composed of polysaccharide- and protein-like molecules. Humic substances represent a mix of polycarboxylic acids and substituted phenols (MW = 500-1200 g/mol). Building blocks represent polycarboxylic acids (MW = 350-500 g/mol); LMW neutrals represent amino acids, aldehydes, and ketones (MW = < 350 g/mol) (Huber et al., 2011).

Figure 4-4: Reduction (%) of (a) dissolved organic carbon (DOC) (b) UV₂₅₄ absorbance, (c) THMFP, (d) HAAFP as a function of O₃ and O₃/H₂O₂ pre-treatment for BAF and BAC filters. Vertical bars for DOC and UV₂₅₄ represent 1 standard deviation (n=3); Vertical bars for THMFP and HAAFP represent mean absolute deviation.

Pre-oxidation with O_3 and $\cdot OH$ decreased biopolymers as a function of H_2O_2/O_3 ratios (Figure 4-5). H_2O_2/O_3 ratio was directly related ($R^2 = 0.89$) with biopolymer removal (increase from -2% to 12%). Biopolymers were observed to preferentially react with $\cdot OH$ rather than O_3 . These results are consistent with those reported by other advanced oxidation studies using UV/ H_2O_2 (Sarathy and Mohseni, 2007; Black and Bérubé, 2014). When considering humic substances, O_3 achieved a 20% reduction, likely resulting in an increase to building blocks (28% increase) (Zietzschmann et al., 2015). No distinct trend was observed with respect to humic substances and H_2O_2/O_3 oxidation. H_2O_2/O_3 oxidation generally achieved higher LMW neutral reductions (range 1% to 15%) when compared to O_3 (6%).

Figure 4-5: % Reduction of LC-OCD fractions from settled water

4.3.5 Pre-Oxidation and Biofiltration for DBP Formation Reduction

Statistically significant ($p < 0.05$) reductions for THMFP and HAAFP from settled water were observed when considering the control BAC, with an average reduction of 13% (range 8% to 16%) and 10% (range -3% to 23%), respectively (Figure 4-4). Further, the observed THM FP and HAA FP across BAC were lower than those for the conventional filter (Appendix Table 7-6), supporting the effectiveness of biodegradation for reduction of THM and HAA precursors.

Although O_3 had little impact on DOC reduction (4%), it reduced THMFP and HAAFP by an average of 10% (range 3% to 18%) and 12% (range 9% to 15%), respectively (Figure 4-1). These reductions can be attributed to oxidation of aromatic constituents into aliphatic products (Swietlik et al., 2004), which contain fewer halogenation sites and therefore result in lower THMFP and HAAFP (Westerhoff et al., 2004). This is also reflected by a large reduction (37%) in specific UV absorbance at 254 nm (SUVA) (from 1.58 L/mg-cm to 0.99 L/mg-cm) after ozonation of settled water. These results are in agreement with the DBP reductions reported by de Vera et al., (2015) and Vasyukova et al. (2013) but in contrast with those by Zha et al. (2016), where authors reported an adverse effect on DBPFP, especially on HAAFP after O_3 (2 mg/L) pre-oxidation. The difference in the latter's HAAFP is attributed to an increased concentration of MCAA from 14 $\mu\text{g/L}$ to 139 $\mu\text{g/L}$ after ozonation, which is most likely due to the generation of newer halogenation sites in relation to the formation of aldehydes, ketones, and alcohols after incomplete ozonation (Kleiser and Frimmel, 2000). A bench-scale study by Karnik et al. (2005) reported slower reaction of HAA precursors with O_3 and suggested a longer contact time for improved reduction.

When considering a low (0.1) H_2O_2/O_3 ratio, significant ($p < 0.05$) THMFP reductions were observed for settled (25%) and ozonated (22%) water, respectively. However, an increase in H_2O_2/O_3 ratio from 0.2 to 0.5 did not have a significant impact on THMFP reductions when compared to both the settled and ozonated waters. This could be explained by LC-OCD fraction reductions. A strong correlation between building blocks and total THMFP concentrations ($R^2 = 0.86$) was observed but only for chlorinated waters following H_2O_2/O_3 treatment. As building blocks have been identified by others as potential THM precursors (Fabris et al., 2008; Vasyukova et al., 2013), an increasing building blocks (28%) due to O_3 were consistent with higher THMFP

compared to 0.1 H₂O₂/O₃. These correlations suggest low molecular weight polycarboxylic acids (represented by building blocks) to be THM precursors. Similar association of building blocks can be inferred with THMFP and other H₂O₂/O₃ ratios (Figure 4-5). Only a 0.5 H₂O₂/O₃ ratio observed 17% lower HAAFP than O₃ (Table S3), likely due to a reduction in biopolymers (Figure 4-5). Biopolymers were moderately correlated with HAAFP ($R^2 = 0.54$ and 0.60) in chlorinated waters after pre-oxidation (O₃ combined with H₂O₂/O₃ and H₂O₂/O₃ alone, respectively), indicating high molecular weight biopolymers to be HAA precursors. Further, we are not aware of any prior studies that have investigated the impact of four H₂O₂/O₃ ratios on LC-OCD fractions for identifying THM and HAA precursors and therefore its impact is worth investigating in different source waters.

O₃ prior to both BAF and BAC reduced THMFP (average reduction of 17% and 32%, respectively) when compared with 13% for the BAC control (Figure 4-4). The slightly improved removal for BAC vs BAF can be attributed to higher biodegradation (Dussert and Tramposch, 1997). H₂O₂/O₃ prior to BAF and BAC also improved THMFP by an average of 25% and 26%, respectively. However, no statistically different ($p > 0.05$) results for either BAF or BAC were observed after pre-oxidation with O₃ and H₂O₂/O₃ (Table 4-5). To some extent, these results corroborate findings by Black and Bérubé (2014), who reported no significant impact on the biodegradation rate of NOM using BAC after pre-oxidation with O₃ and UV AOP.

Application of O₃ and H₂O₂/O₃ prior to both BAF and BAC resulted in no statistical difference ($p > 0.05$) in HAAFP reductions when compared with the BAC control (Table 4-5). In addition, no discernible trend was observed in the performance of BAF, BAC, and the BAC control in reducing HAAFP at colder conditions (10°C) (Figure 4-4). The relatively low reduction of HAAFPs at low temperature can be attributed to poor biodegradability of HAA precursors (Kim, 2009), likely biopolymers. Similar impact on biopolymer biodegradation across biofilters (with O₃ pre-oxidation) was reported by Pharand et al., (2015) when temperature decreased below 10°C. As such, these removals may be enhanced by increasing the biofilter EBCT (de Vera et al., 2016; Seredyńska-Sobecka et al., 2006).

Monitoring NOM fractions using LC-OCD provided deeper insight regarding organic matter behavior over a wide molecular weight range. Treatment-specific correlations were examined between various organic fractions and THMFP as well as HAAFP (Table 4-6). A strong

correlation between building blocks and total THMFP concentrations ($R^2 = 0.86$) was observed but only for chlorinated waters following H_2O_2/O_3 treatment. These results are in agreement with Vasyukova et al. (2013), who reported building blocks to be correlated with THMFP ($R^2 = 0.77$) in chlorinated waters of treatments including pre-ozonation. Similarly, biopolymers were moderately correlated with HAAFP ($R^2 = 0.54$ and 0.60) in chlorinated waters after pre-oxidation (O_3 combined with H_2O_2/O_3 and H_2O_2/O_3 alone, respectively). These correlations suggest low molecular weight polycarboxylic acids (represented by building blocks) and high molecular weight biopolymers to be THM and HAA precursors. Further, we are not aware of any prior studies that have investigated the impact of four H_2O_2/O_3 ratios on LC-OCD fractions for identifying THM and HAA precursors and therefore its impact is worth investigating in different source waters.

Table 4-6: R-squared values for linear correlations between DBP precursors and various organic fractions from LC-OCD analysis

		Biopolymers	Humic substances	Building blocks	LMW neutrals
H_2O_2/O_3 AOP (n=4)	THMFP	0.25	0.11	0.86	0.46
	HAAFP	0.60	0.04	0.19	0.01
Preoxidation (O_3 + H_2O_2/O_3 AOP) (n=6)	THMFP	0.24	0.10	0.19	0.31
	HAAFP	0.54	0.05	0.17	0.07
Biofiltration (with pre-oxidation) (n=16)	THMFP	0.00	0.00	0.50	0.67
	HAAFP	0.09	0.08	0.21	0.66
Pre-oxidation + Biofiltration (n=22)	THMFP	0.00	0.02	0.14	0.19
	HAAFP	0.08	0.11	0.33	0.44

Bold values represent R-squared > 0.5

Correlations between LMW neutrals and THM and HAA formation potentials after biofiltration (with pre-oxidation) ($R^2 = 0.67$ and 0.66 , respectively) were observed, indicating that these fractions play a role in THM and HAA formation potentials. These results suggest that biofiltration (with pre-oxidation) metabolized LMW neutrals thus, reducing the overall THM and HAA formation potentials (Figure 4-6).

Figure 4-6: % Reduction of LC-OCD fractions across biofiltration

4.3.6 Filter Media ATP Analysis

ATP levels on filter media were measured to estimate the active biomass in the top 5-10 cm of the filters (Velten et al., 2011). ATP values of control BAC reached its peak value in early August (765 ng/g) and gradually decreased during September (530 ng/g) to late November (150 ng/g) (Figure 4-7). The decrease in ATP is likely due to variation with respect to assimilable organics in source water that might have impacted biomass formation (Korotta-Gamage and Sathasivan, 2017).

On supplying with ozonated water, BAC resulted in one time two-fold increase of ATP (from 240 ng/g to 475 ng/g) (Figure 6). Further pre-oxidation using O_3 and H_2O_2/O_3 did not result in any improvement in BAC ATP, rather resulted in decreased ATP during October and November similar to those of control BAC. To some extent, these BAC ATP values followed an opposite trend when compared to the literature values, where studies have reported accelerated biomass formation after pre-ozonation (Magic-Knezev and van der Kooij, 2004; Pharand et al., 2014). This could be attributed to decelerated biomass formation in winter compared to summer (van der Wielen and van der Kooij, 2010). Additionally, there was no significant impact of pre-oxidation on BAF ATP. Further, BAF ATP values remained steady from August till November, which is likely due to formation of consistent biomass at the surface. Despite reduced ATP of BAC and control BAC, there was no significant impact on DOC reduction for the conditions tested in this study (Table S1), warranting further research with regard to role of viable biomass in degrading organics.

Figure 4-7: ATP concentrations on the surface of BAF, BAC, and BAC control

4.4 Summary

This pilot study evaluated the effectiveness of O_3 and H_2O_2/O_3 advanced oxidation in combination with biofiltration for geosmin and MIB control, organic carbon removal (DOC, UV_{254} , and LC-OCD), and DBP (THM and HAA) formation potential reduction. This study compared two media types (biologically active carbon (BAC) and biologically active anthracite (BAF)) while investigating the impact of pre-oxidation with O_3 (2 mg/L) and varying H_2O_2/O_3 ratios (0.1, 0.2, 0.35, and 0.5 mg/mg) with respect to geosmin, MIB, and DBP precursor removal efficiency. In addition, performance of biofiltration was compared with conventional treatment while continuously operating the parallel filter trains.

Biofiltration using BAC was effective in achieving geosmin and MIB removal (>80%) in warmer water conditions (22°C). O_3 efficiency and BAC biodegradation rates were significantly impacted in cold water conditions (16°C and 10°C) with respect to geosmin and MIB removal. For instance, at an O_3 dose of 2 mg/L, geosmin and MIB removals decreased from 70% to 45% and 55% to 40% at 16°C and 10°C, respectively. Similarly, MIB removals across BAC without pre-oxidation decreased from 85% to 46% at 22°C and 10°C, respectively. Geosmin removal was sensitive to O_3 oxidation and 0.2 H_2O_2/O_3 (mg/mg) prior to BAC provided an additional barrier at colder water conditions (10°C). At similar water temperatures, pre-oxidation using (0.2-0.5) H_2O_2/O_3 (mg/mg) ratios were required to achieve effective MIB control (>80%).

In terms of DBPFP, the application of O_3 and H_2O_2/O_3 resulted in lower DBPFP compared to conventional treatment. For instance, O_3 decreased THMFP and HAAFP by an average of 10% and 12%, respectively. H_2O_2/O_3 when averaged over four ratios (0.1, 0.2, 0.35, and 0.5 mg/mg) observed THMFP and HAAFP reductions of 13% and 8%, respectively from settled water. Reduction in THMFP was associated with reduction in building blocks which act as THM precursors and correlated well with THMFP concentrations. Except in few instances, H_2O_2/O_3 observed no significant difference on THM/HAAFP reductions when compared to O_3 . These results imply that peroxide addition is beneficial for geosmin and MIB control even in cold water conditions (10°C) but we observed no significant impact on HAAFP reduction compared to O_3 at the conditions that were tested.

5. Conclusions and Recommendations

5.1 Conclusions

- Biofiltration using BAC can be an effective treatment process for geosmin and MIB removal (>80%) at warmer water conditions (22°C) but less effective at lower water temperatures (16°C and 10°C).
- Application of O₃ prior to biofiltration (BAC) can achieve removals to <10 ng/L for geosmin at 16°C and 10°C, but at 10°C the application of 0.2 H₂O₂/O₃ (mg/mg) resulted in optimal removal for both geosmin and MIB.
- Results from this study indicate that geosmin is sensitive to O₃ whereas MIB is sensitive to ·OH oxidation.
- O₃ decreased THMFP and HAAFP by an average of 10% and 12%, respectively whereas, H₂O₂/O₃ values averaged over four ratios (0.1, 0.2, 0.35, and 0.5) observed 13% THMFP and 8% HAAFP reductions, respectively from settled water.
- When compared to O₃, H₂O₂ addition observed no significant difference on THMFP and HAAFP reductions except for 0.1 and 0.5 H₂O₂/O₃ ratios. These results imply that the peroxide addition is beneficial for geosmin and MIB control at cold water conditions but we observed no significant impact on HAAFP reduction.

5.2 Recommendations

- While O₃ (2 mg/L) and 0.2 H₂O₂/O₃ (mg/mg) advanced oxidation observed to achieve multiple treatment objectives including T&O control, organic and DBP (THM and HAA) precursor reduction, future studies are recommended to assess the impact of pre-oxidation in combination with biofiltration on other DBP groups such as haloacetonitriles, trihalonitromethanes, and haloketones.
- O₃ treatment involves quenching of any available residual prior to biofiltration using a reducing agent. This reducing agent can impact chlorine demand during the disinfection process. Future

studies should be designed with respect to maintaining a minimal residual by selecting the O₃ dose based on settled water demand.

- To account for seasonal variability, long term DBP formation studies are suggested using O₃ and H₂O₂/O₃ advanced oxidation prior to biofiltration.
- As ozonation is a highly energy intensive process, energy consumption requirements for micropollutant oxidation is recommended for future studies.
- As O₃ efficiency is dependent on temperature, O₃ efficiency decreases during cold water conditions and leads to incomplete oxidation of DBP precursors, especially HAAs. Therefore, the impact of increasing the O₃ contact time during cold water conditions with respect to HAAFP is recommended for future studies.

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7. Appendices

7.1 Calibration Curves

Figure 7-1: Sample DOC Calibration Curve (May 2016)

Figure 7-2: Sample Geosmin and MIB Calibration Curve (August 2016)

Figure 7-3: Sample THM Calibration Curve (June 2016)

Figure 7-4: Sample HAA Calibration Curve (June 2016)

7.2 Standard Operating Procedure Outline

The following tables outlines the procedure that was used for sample preparation and analysis during the study. Information for the analysis of ATP (Table 7-1), DOC (Table 7-2), geosmin and 2-methylisoborneol (MIB) (Table 7-3), trihalomethanes (THMs) (Table 7-4), haloacetic acids (HAAs) (Table 7-5).

Table 7-1: ATP Analysis Procedure

Calibration	
1.	Add 100 µL of enzyme reagent (Luminase) and 100 µL of ATP standard (Ultracheck 1) in a 12 x 55 mm test tube
2.	Measure the relative light units (RLU) using the luminometer (RLU _{standard})
Sample Analysis	
1.	Weigh 1 g of sample and transfer to a 5 mL (pre-packaged) UltraLyse™7 tube and mix
2.	Wait for 5 minutes
3.	Transfer 1 mL of the UltraLyse™7 solution to a 9 mL (pre-packaged) UltraLute vial
4.	After mixing the UltraLute solution, pipette 100 µL to a new 12 x 55 mm test tube.
5.	Add 100 µL of Luminase and gently swirl 5 times
6.	Place the test tube into the luminometer and measure the RLU (RLU _{sample})
7.	Determine ATP concentration using the following equation:
$ATP \left(\frac{pg \text{ ATP}}{g \text{ media}} \right) = \frac{RLU_{sample}}{RLU_{standard}} \times \frac{50,000(pg \text{ ATP})}{mass_{sample}(g)}$	

Table 7-2: DOC Analysis Procedure

Blanks
Use 40 mL of Milli-Q®
Stock Solution
Mix 2.13 g potassium hydrogen phthalate in 1 L Milli-Q® water. Store at $\text{pH} \leq 2$ by acidifying with H_2SO_4 .
Calibration Solution (10 mg/L)
Add 1 mL of stock solution to 99 mL of Milli-Q® water.
Check Standard (2.5 mg/L)
Add 250 μL of stock solution to 99.75 mL Milli-Q® water.
Samples
Follow SOP for TOC analyzer.

Table 7-3: Geosmin and MIB Extraction and Analysis Procedure

Sample Collection
1. Add 166 μL of 25g/L Reagent Plus®, $\geq 99.5\%$ sodium azide solution in 23 mL sampling amber vials.
2. Collect samples in these amber vials with Teflon®-lined septa screw caps, ensuring that the sample is headspace free.
3. Store samples in the dark at 4°C for up to 14 days before analysis.
4. Remove from refrigerator and bring to room temperature before preparation
Standard preparation
1. Pipette 10mL of Milli-Q® water into a sample extraction vial that contains 3.5g of NaCl.
2. Inject the appropriate volume of 10 $\mu\text{g/L}$ combined geosmin and MIB stock solution.
3. Spike 25 μL of 10 $\mu\text{g/L}$ internal standard (d_3 -geosmin) into the vial to achieve 25ng/L.
4. Repeat the above steps and prepare 0, 10, 30, 50, 80, 100, 150 ng/L standard solutions.
5. Do not store; analyse immediately.

Table 7-3: Geosmin and MIB Extraction and Analysis Procedure (continued)

<p style="text-align: center;">Blank preparation</p> <ol style="list-style-type: none">1. Transfer 10 mL of Milli-Q® water into a sample extraction vial that contains 3.5g NaCl.2. Spike 25µL of 10µg/L internal standard (<i>d</i>₃-geosmin) into the vial to achieve 25ng/L.3. Analyse a blank and running standard after every 10 samples. <p style="text-align: center;">Running standard preparation (60 ng/L of geosmin and MIB)</p> <ol style="list-style-type: none">1. Pipette 10mL of Milli-Q® water into a sample extraction vial that contains 3.5g NaCl.2. Inject 30µL of geosmin, MIB combined stock solution (10µg/L) into the vial.3. Spike 25µL of 10µg/L internal standard (<i>d</i>₃-geosmin) into the vial to achieve 25ng/L. <p style="text-align: center;">Sample analysis</p> <ol style="list-style-type: none">1. Place samples in a sample tray connected to an autosampler. Autosampler delivers the sample to an agitator. Sample is agitated for 5 minutes at 500rpm at 65±1°C.2. Sample extraction and analysis is carried out with the solid phase micro-extraction (SPME) using gas chromatograph (Varian® 3800) with a Varian® ion-trap mass spectrometer operated in electron ionization (EI) mode.3. Follow SOP for GC/MS operation conditions
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Table 7-4: THM Extraction and Analysis Procedure

<p style="text-align: center;">Sample Extraction</p> <ol style="list-style-type: none">1. Collect samples in 20 mL amber vials and quench with 0.020 g of ascorbic acid2. Store samples in the dark at 4°C for up to 7 days before analysis3. Remove from refrigerator and bring to room temperature before preparation4. Blank preparation: Transfer 20 mL of Milli-Q® water into 40 mL vial and prepare with samples.5. Intermediate solution: Prepare 20 mg/L THM solution by adding 10 mL of stock solution (2000 µg/mL) to 990 mL of Milli-Q® water.
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Table 7-4: THM Extraction and Analysis Procedure (continued)

Calibration solutions:

1. Prepare by adding the corresponding amount of intermediate solution to Milli-Q® water to achieve concentrations of 0, 5, 10, 20, 40, 60, 100, 150, and 200 µg/L

****Wipe the syringe tip with a Kimwipe before measuring out of the THM stock or intermediate solutions, and before adding to intermediate and calibration solutions.**

Standard preparation

1. Add 40 µL of intermediate solution to 20 mL of Milli-Q® water in a 40 mL vial and process with other samples. Salt and MTBE should be added after adding intermediate solution.
2. Analyze a blank and running standard after every tenth sample.

Extraction

1. Transfer the contents of each sample vial into a clean 40 mL vial.
2. Add 2 scoops of sodium sulphate (Na_2SO_4) to increase extraction efficiency. Add 4 mL of MTBE extraction solvent and cap with a Teflon®-lined silicon septum and cap.
3. Shake vial vigorously for 30 seconds and place vial on its side. Repeat for all samples, blanks and standards. Place samples upright in a rack and shake for 2 minutes. Let stand for 10 minutes.
4. Extract 2 mL from the organic layer using a Pasteur pipette and place in a 1.8 mL GC vial filled with 2 small scoops of Na_2SO_4 (no water should remain in the vial). Use a clean pipette for each sample. Fill the vial to the top and cap immediately, ensuring there is no headspace. To ensure the MTBE phase was the only one taken, freeze the vials for 2 hours and observe that only 1 phase is visible.
5. If not analyzing immediately, freeze samples for up to 21 days.
6. Analyze using a GC-ECD

Table 7-5: HAA Extraction and Analysis Procedure

Sample Preparation

1. Collect samples in 40 mL amber vials. Ensure that samples are free of headspace.
2. Store samples in the dark at 4°C for up to 9 days.
3. To begin sample preparation, remove from refrigerator and bring to room temperature.

Blank Solutions

1. Transfer 40 mL of Milli-Q® water into 40 mL vials and process with other samples

Calibration Solutions

1. Collect 20 mL of Milli-Q® in 40 mL vial
2. Using a 50 µL syringe and the “sandwich” technique, add 0, 5, 10, 20, 40, 60, 100, and 150 µL of HAA stock (2000 µg/mL each)

****Wipe the syringe tip with a Kimwipe before measuring out of the HAA stock and before adding the stock to other solutions.**

Running Standards

3. Add 50 µL of working solution to 20 mL of Milli-Q® water, process alongside samples.
4. Include blanks and running standards after every tenth sample.

Diazomethane Preparation

5. Set up MNNG diazomethane generation apparatus on ice using a beaker filled with crushed ice and water.
6. Add 2.5 mL of MTBE to outer tube of generator, and cover with tin foil before placing in ice bath.
7. Add ~ 1.25 cm of diazald to inner tube of generator using large end of Pasteur pipette. Add ~0.5 mL of methanol to cover diazald by 3 mm and secure cap and septum.

Table 7-5: HAA Extraction and Analysis Procedure (continued)

8. Place O-ring in glass joint. Position inside tube firmly on top and secure clamp. Ensure that the vapour exit hole is located on the opposite side of the tube from the clamp and
9. Place clamp on the spout of the beaker. Ensure the seal is tight to maximize CH_2N_2 generation and recovery.
10. Let cool on the ice bath for 10 min.
11. Add 600 μL of 20% NaOH solution dropwise to inner tube with a gas tight syringe (1 drop/5 sec). Aim drops directly into the diazald in the bottom of the inner tube. Leave the syringe in place after all of the NaOH is added to avoid a hole in the septum from which CH_2N_2 may exit. Allow CH_2N_2 to form for 30 to 45 minutes on the ice bath.

Sample Extraction

1. Transfer 20 mL of sample into a clean 40 mL vial.
2. Add 3 mL of sulphuric acid (H_2SO_4). Add 6 g of sodium sulphate (Na_2SO_4). Add 5 mL of MTBE extraction solvent and cap with a Teflon®-lined silicon septa and screw cap.
3. Shake sample for ~30 seconds and place vial on its side. Repeat for all blanks, calibration solutions and samples.
4. Place samples upright in a rack and shake for 5 minutes. Let samples stand for 15 minutes.
5. Extract 1.5 mL from the organic layer and place into a 1.8 mL GC vial using a clean pipette for each sample. Add 150 μL of diazomethane to the GC vial (submerging the syringe tip before injection) and seal immediately.
6. If not analyzing immediately, store the samples in a freezer (-20°C) for up to 21 days. Analyze using a GC-ECD.

7.3 Sample Quality Assurance/Quality Control Charts

QA/QC charts were generated by analyzing 9 samples prepared at a concentration equivalent to the expected concentrations in the samples being analyzed after each new calibration. Check standards are prepared at the same concentration, and analyzed after every 10 samples. The check standards are compared to the mean and standard deviation calculated from the original 8 samples as per Standard Method 1020 (APHA, 2005). The calibration is considered unacceptable if:

- 2 consecutive measurements fall outside of the control limit (CL) of the mean $\pm$ 3 times the standard deviation;
- 3 out of 4 consecutive measurements were outside the warning limits (WL) of the mean $\pm$ 2 times the standard deviation;
- 5 out of 6 consecutive measurements were outside of the mean $\pm$ the standard deviation;
- 5 out of 6 consecutive measurements exhibited an increasing or decreasing trend; or,
- 7 consecutive samples were greater, or less, than the mean

If any of these conditions were met a new calibration curve was generated and the samples were reanalyzed.

Figure 7-5: Quality Control Chart for MIB

Figure 7-6: Quality Control Chart for Geosmin

Figure 7-7: Quality Control Chart for TCM

Figure 7-8: Quality Control Chart for BDCM

Figure 7-9: Quality Control Chart for CDBM

Figure 7-10: Quality Control Chart for TBM

Figure 7-7: Quality Control Chart for MCAA

Figure 7-11: Quality Control Chart for MBAA

Figure 7-12: Quality Control Chart for DCAA

Figure 7-13: Quality Control Chart for TCAA

Figure 7-14: Quality Control Chart for BCAA

Figure 7-15: Quality Control Chart for DBAA

Figure 7-16: Quality Control Chart for BDCAA

Figure 7-17: Quality Control Chart for CDBAA

7.4 Raw Data

Table 7-6: Raw Data

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
ATP (ng/g media)	Acclimation	11-May-16	N/A	N/A	N/A	N/A	22	336	336	459	266	334
		11-Jun-16	N/A	N/A	N/A	N/A	36	287	257	363	280	281
		04-Jul-16	N/A	N/A	N/A	N/A	31	370	316	699	338	345
		04-Aug-16	N/A	N/A	N/A	N/A	54	392	221	765	252	293
		17-Aug-16	N/A	N/A	N/A	N/A	51	264	307	749	344	345
	1	14-Sep-16	N/A	N/A	N/A	N/A	52	428	249	533	240	250
	2	20-Oct-16	N/A	N/A	N/A	N/A	97	444	384	340	479	405
	3	14-Nov-16	N/A	N/A	N/A	N/A	89	307	347	346	326	204
	4	05-Dec-16	N/A	N/A	N/A	N/A	93	394	328	151	140	153
pH	1	29-Aug-16	8.15	7.18	N/A	N/A	7.7	7.71	7.18	7.16	7.17	7.23
		14-Sep-16	8.1	7.35	N/A	N/A	7.72	7.57	7.23	7.15	7.14	7.24
	2	3-Oct-16	8.18	7.17	7.31	7.28	7.45	7.37	7.2	7.15	7.15	7.23
		7-Oct-16	7.78	7.27	7.15	7.16	7.62	7.34	7.15	7.12	7.09	7.17
		14-Oct-16	8.05	7.31	7.52	7.33	7.63	7.42	7.18	7.19	7.05	7.11
	3	20-Oct-16	7.96	7.33	7.35	7.32	7.52	7.36	7.1	7.15	7.1	7.12
		28-Oct-16	8.1	7.17	7.38	7.2	7.47	7.47	7.09	7.18	7.07	7.14
		15-Nov-16	8.04	7.28	7.36	7.19	7.53	7.38	7.07	7.14	7.08	7.08
		16-Nov-16	8.1	7.23	7.33	7.24	7.45	7.36	7.1	7.15	7.1	7.1

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
Turbidity (NTU)	1	29-Aug-16	0.575	0.166	N/A	N/A	0.088	0.085	0.081	0.082	0.078	0.092
		14-Sep-16	0.774	0.184	N/A	N/A	0.085	0.083	0.081	0.087	0.074	0.09
	2	3-Oct-16	0.586	0.104	0.188	0.178	0.048	0.062	0.075	0.072	0.075	0.082
		7-Oct-16	0.598	0.114	0.185	0.168	0.076	0.084	0.092	0.075	0.078	0.08
		14-Oct-16	0.5	0.127	0.135	0.148	0.076	0.082	0.087	0.076	0.07	0.073
	3	20-Oct-16	0.58	0.14	0.13	0.124	0.041	0.049	0.078	0.075	0.077	0.069
		28-Oct-16	0.405	0.103	0.151	0.17	0.038	0.06	0.071	0.074	0.078	0.078
		15-Nov-16	0.368	0.154	0.123	0.132	0.065	0.047	0.065	0.059	0.079	0.068
	4	16-Nov-16	0.395	0.155	0.134	0.132	0.056	0.055	0.068	0.064	0.078	0.07
UV ₂₅₄ (cm ⁻¹)	1	29-Aug-16	0.121	0.054	N/A	N/A	0.050	0.047	0.047	0.047	0.044	0.044
		14-Sep-16	0.110	0.061	N/A	N/A	0.050	0.048	0.048	0.044	0.044	0.046
	2	3-Oct-16	0.110	0.057	0.054	0.048	0.040	0.035	0.035	0.049	0.034	0.034
		7-Oct-16	0.122	0.061	0.035	0.037	0.036	0.031	0.033	0.051	0.032	0.031
		14-Oct-16	0.114	0.052	0.032	0.043	0.033	0.030	0.027	0.047	0.030	0.027
	3	20-Oct-16	0.124	0.057	0.039	0.036	0.037	0.033	0.033	0.050	0.031	0.035
		26-Oct-16	0.120	0.057	0.040	0.043	0.037	0.033	0.034	0.051	0.034	0.033
		28-Oct-16	0.121	0.055	0.041	0.043	0.040	0.037	0.036	0.048	0.035	0.036
		15-Nov-16	0.119	0.053	0.033	0.035	0.036	0.034	0.032	0.049	0.033	0.030
	4	16-Nov-16	0.108	0.053	0.038	0.036	0.033	0.031	0.023	0.041	0.024	0.023
		3-Dec-16	0.118	0.057	0.041	0.048	0.037	0.031	0.032	0.051	0.031	0.031

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
DOC (mg/L)	1	29-Aug-16	5.29	3.64	N/A	N/A	3.64	3.63	3.50	3.48	3.44	3.44
		14-Sep-16	5.03	3.29	N/A	N/A	3.30	3.19	3.20	3.05	3.11	3.11
	2	3-Oct-16	5.42	3.58	3.41	3.42	3.50	3.22	3.32	3.41	3.15	3.17
		7-Oct-16	5.22	3.45	3.22	3.33	3.27	3.00	3.07	3.21	2.95	2.92
		14-Oct-16	5.29	3.29	3.19	3.17	3.13	3.03	3.03	3.15	3.02	2.94
		20-Oct-16	4.99	3.12	3.17	3.25	3.05	2.90	2.86	3.06	2.87	2.95
	3	26-Oct-16	5.40	3.39	3.15	3.14	3.09	2.95	3.11	3.16	3.00	3.03
		28-Oct-16	5.21	3.37	3.21	3.22	3.09	2.96	3.01	3.13	2.99	3.03
		15-Nov-16	5.23	3.59	3.32	3.27	3.14	3.02	3.07	3.18	3.09	3.11
	4	16-Nov-16	5.23	3.43	3.38	3.54	3.29	3.16	3.16	3.25	3.20	3.19
		3-Dec-16	4.79	2.92	2.79	2.96	2.65	2.70	2.74	2.87	2.67	2.71
SUVA (L/mg-cm)	1	29-Aug-16	2.29	1.48	N/A	N/A	1.37	1.29	1.34	1.35	1.28	1.28
		14-Sep-16	2.19	1.86	N/A	N/A	1.51	1.50	1.50	1.44	1.42	1.48
	2	3-Oct-16	2.03	1.59	1.58	1.41	1.14	1.09	1.05	1.44	1.08	1.07
		7-Oct-16	2.34	1.77	1.09	1.11	1.10	1.03	1.07	1.59	1.09	1.06
		14-Oct-16	2.15	1.58	1.00	1.35	1.05	0.99	0.89	1.49	0.99	0.92
		20-Oct-16	2.48	1.83	1.23	1.11	1.20	1.14	1.15	1.63	1.08	1.19
	3	26-Oct-16	2.22	1.68	1.28	1.36	1.20	1.12	1.09	1.61	1.15	1.10
		28-Oct-16	2.32	1.63	1.28	1.34	1.29	1.26	1.20	1.53	1.17	1.19
		15-Nov-16	2.06	1.48	0.99	1.07	1.15	1.13	1.04	1.54	1.07	0.96
	4	16-Nov-16	2.06	1.55	1.12	1.02	1.00	0.98	0.73	1.26	0.75	0.72
		3-Dec-16	2.46	1.95	1.47	1.62	1.38	1.15	1.16	1.78	1.16	1.13

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
Geosmin Influent (ng/L)	1	14-Sep-16	25.50	24.70	N/A	N/A	97.30	96.8	92.3	100.4	99.2	78.9
		14-Sep-16	19.20	18.20	N/A	N/A	82.60	97.7	84.7	82.4	91.1	88.2
		14-Sep-16	25.70	20.10	N/A	N/A	90.00	91.4	86.0	78.3	85.2	N/S
	2	13-Oct-16	29.8	24.4	130.8	125.8	28.4	32.0	19.0	109.3	32.3	23.2
		13-Oct-16	29.4	26.8	124.9	128.8	29.8	31.2	22.8	105.9	31.4	22.6
		13-Oct-16	29.4	26.8	127.9	127.3	26.7	27.3	18.6	102.4	24.6	19.2
	3	14-Nov-16	17.1	16.4	96.9	105.4	47.1	46.5	24.1	75.4	44.5	39.8
		14-Nov-16	17.1	16.4	103.8	103.1	51.3	53.1	35.0	49.1	43.2	31.4
		14-Nov-16	17.1	16.4	100.3	104.2	49.2	49.8	29.6	62.2	43.9	35.6
	4	16-Nov-16	16.8	16.3	83.9	83.4	43.4	43.8	34.9	100.3	43.8	34.9
		16-Nov-16	16.8	16.3	88.5	93.3	43.4	43.1	34.9	106.0	43.1	34.9
		16-Nov-16	16.8	16.3	120.0	122.2	43.4	43.1	34.9	106.0	43.1	34.9
Geosmin Effluent (ng/L)	1	14-Sep-16	N/A	N/A	N/A	N/A	81.1	8.0	12.4	5.6	5.8	13.8
		14-Sep-16	N/A	N/A	N/A	N/A	70.1	20.0	35.3	13.9	19.4	12.7
		14-Sep-16	N/A	N/A	N/A	N/A	75.6	23.1	27.9	14.2	19.2	12.7
	2	13-Oct-16	N/A	N/A	37.1	37.2	28.1	BDL	BDL	6.5	BDL	BDL
		13-Oct-16	N/A	N/A	40.2	29.3	26.7	5.4	BDL	7.7	BDL	BDL
		13-Oct-16	N/A	N/A	38.6	33.2	14.8	BDL	BDL	8.3	BDL	BDL
	3	14-Nov-16	N/A	N/A	56.7	37.0	43.9	12.7	BDL	10.3	8.8	BDL
		14-Nov-16	N/A	N/A	59.1	39.1	45.9	14.1	BDL	13.7	9.7	BDL
		14-Nov-16	N/A	N/A	48.1	38.0	43.0	15.8	BDL	11.8	8.9	BDL
	4	16-Nov-16	N/A	N/A	46.2	35.6	29.5	16.7	11.0	25.0	14.8	13.9
		16-Nov-16	N/A	N/A	41.4	36.2	29.5	16.0	11.5	24.3	16.0	11.4
		16-Nov-16	N/A	N/A	41.4	32.9	29.5	16.0	11.5	23.7	17.3	11.4

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
MIB Influent (ng/L)	1	14-Sep-16	21.4	22.0	N/A	N/A	97.9	101.1	91.0	85.3	89.4	98.8
		14-Sep-16	27.1	23.2	N/A	N/A	96.2	97.8	101.8	98.1	85.4	98.8
		14-Sep-16	15.2	14.9	N/A	N/A	98.9	101.4	103.8	101.4	104.2	98.8
	2	13-Oct-16	12.1	11.4	102.2	104.3	45.1	36.8	30.4	114.6	41.0	31.3
		13-Oct-16	13.9	10.9	104.3	105.4	44.8	35.8	29.7	121.6	38.8	32.8
		13-Oct-16	13.9	10.9	103.3	104.8	39.5	31.7	29.9	104.1	34.5	19.9
	3	14-Nov-16	N/A	N/A	88.8	90.0	54.3	58.9	48.1	53.8	45.1	18.4
		14-Nov-16	N/A	N/A	89.5	85.8	47.4	49.5	67.6	50.9	50.7	20.4
		14-Nov-16	N/A	N/A	89.1	87.9	50.9	54.2	57.9	47.4	47.9	17.3
	4	16-Nov-16	N/A	N/A	121.3	113.1	43.7	43.7	36.3	N/S	43.7	36.3
		16-Nov-16	N/A	N/A	119.1	106.4	43.7	43.7	36.3	N/S	43.7	36.3
		16-Nov-16	N/A	N/A	116.1	106.4	43.7	43.7	36.3	N/S	43.7	36.3
MIB Effluent (ng/L)	1	14-Sep-16	N/A	N/A	N/A	N/A	80.5	24.1	37.5	7.3	19.7	23.4
		14-Sep-16	N/A	N/A	N/A	N/A	92.9	43.7	52.9	17.0	18.0	23.4
		14-Sep-16	N/A	N/A	N/A	N/A	97.1	38.8	51.7	17.2	16.7	23.4
	2	13-Oct-16	N/A	N/A	45.6	33.9	36.1	23.8	21.4	43.7	16.4	14.1
		13-Oct-16	N/A	N/A	44.3	36.0	36.4	24.5	25.2	38.3	15.4	13.1
		13-Oct-16	N/A	N/A	48.3	34.8	31.9	20.6	22.2	54.0	7.9	8.4
	3	14-Nov-16	N/A	N/A	53.0	43.5	46.1	39.2	34.3	53.8	28.5	18.4
		14-Nov-16	N/A	N/A	53.4	43.5	41.5	37.8	36.5	50.9	32.2	20.4
		14-Nov-16	N/A	N/A	53.2	43.5	46.5	34.0	29.3	47.4	26.8	17.3
	4	16-Nov-16	N/A	N/A	46.4	38.0	N/S	34.4	25.9	N/S	28.6	20.6
		16-Nov-16	N/A	N/A	41.1	37.6	N/S	32.9	29.4	N/S	27.6	19.3
		16-Nov-16	N/A	N/A	41.1	33.3	N/S	32.9	29.4	N/S	27.6	19.3

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
Total THM (µg/L)	1	14-Sep-16	198.0	72.7	N/A	N/A	74.0	83.8	71.2	68.4	63.4	65.0
		14-Sep-16	170.8	74.2	N/A	N/A	59.1	72.0	73.0	67.6	66.5	57.5
	2	13-Oct-16	159.5	70.8	66.9	49.4	64.8	45.6	48.2	59.0	40.2	43.4
		13-Oct-16	152.7	66.5	68.6	55.4	60.1	46.1	48.2	56.2	61.4	42.1
	3	14-Nov-16	174.6	85.5	72.5	90.3	64.1	87.7	67.9	74.0	57.9	64.4
		14-Nov-16	194.2	85.4	67.3	81.1	79.6	83.6	73.2	72.1	49.5	55.5
	4	16-Nov-16	174.6	85.5	87.0	62.0	61.8	63.8	62.1	66.5	62.8	72.4
		16-Nov-16	194.2	85.4	56.6	72.7	79.7	69.1	77.3	79.5	58.6	78.2
TCM (µg/L)	1	14-Sep-16	158.1	59.0	N/A	N/A	70.2	69.0	59.6	57.2	52.5	54.2
		14-Sep-16	141.5	61.0	N/A	N/A	55.0	59.7	62.9	56.5	57.3	49.5
	2	13-Oct-16	131.9	56.1	40.0	36.1	41.4	32.3	34.1	51.1	29.5	30.8
		13-Oct-16	125.4	53.0	41.2	40.1	38.5	33.2	34.1	45.3	43.7	30.2
	3	14-Nov-16	127.9	59.9	39.8	48.7	27.5	55.8	40.1	52.0	34.3	41.2
		14-Nov-16	145.1	58.9	38.1	45.9	37.8	47.0	44.7	51.3	29.3	32.9
	4	16-Nov-16	127.9	59.9	57.4	36.8	36.7	38.9	42.0	46.1	39.9	46.5
		16-Nov-16	145.1	58.9	36.7	45.0	50.6	46.2	48.2	56.6	39.8	54.6
BDCM (µg/L)	1	14-Sep-16	39.9	13.7	N/A	N/A	3.8	14.8	11.6	11.2	10.9	10.8
		14-Sep-16	29.3	13.2	N/A	N/A	4.0	12.3	10.2	11.1	9.2	8.0
	2	13-Oct-16	27.6	14.8	26.5	12.8	23.0	12.9	13.7	7.9	10.3	12.1
		13-Oct-16	27.3	13.5	27.1	14.9	21.2	12.5	17.0	10.9	17.2	11.6
	3	14-Nov-16	46.8	25.6	32.7	37.7	32.7	27.8	23.9	21.9	19.7	19.2
		14-Nov-16	49.2	26.5	29.2	35.3	36.7	32.6	24.5	20.8	16.3	18.8
	4	16-Nov-16	46.8	25.6	25.7	21.3	25.1	20.8	20.1	20.4	19.1	22.0
		16-Nov-16	49.2	26.5	19.9	23.8	29.1	22.9	25.2	22.9	18.7	23.6

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
Total HAA (µg/L)	1	14-Sep-16	79.2	76.6	N/A	N/A	63.9	81.3	57.6	82.9	59.7	64.9
		14-Sep-16	107.8	72.6	N/A	N/A	56.9	51.9	57.6	67.9	53.3	53.4
	2	13-Oct-16	148.7	75.8	83.7	76.5	61.8	77.5	75.1	72.9	64.8	71.2
		13-Oct-16	112.7	97.9	67.0	84.1	67.0	72.8	61.1	70.3	69.1	77.6
	3	14-Nov-16	146.9	107.2	86.8	125.9	129.8	117.3	116.5	83.4	120.3	101.3
		14-Nov-16	166.7	104.4	109.6	110.5	132.0	93.8	103.2	111.3	121.5	106.9
	4	16-Nov-16	146.9	107.2	98.0	77.1	104.3	99.2	120.8	133.3	95.4	89.4
		16-Nov-16	166.7	104.4	103.6	83.1	90.1	99.2	93.2	84.8	95.4	82.1
MCAA (µg/L)	1	14-Sep-16	2.4	19.2	N/A	N/A	16.8	2.8	4.2	16.5	7.3	9.5
		14-Sep-16	6.6	18.7	N/A	N/A	16.8	6.6	4.2	20.3	7.6	6.5
	2	13-Oct-16	37.7	17.3	24.4	27.5	9.7	34.2	21.8	24.8	15.7	32.8
		13-Oct-16	23.8	18.5	19.9	24.5	25.3	31.5	13.4	21.1	23.0	27.2
	3	14-Nov-16	19.7	29.5	22.0	47.4	13.4	59.5	57.7	22.9	61.4	38.2
		14-Nov-16	33.4	25.8	40.8	36.7	62.1	32.5	43.7	43.1	51.6	47.4
	4	16-Nov-16	19.7	29.5	32.4	20.2	39.9	29.1	43.1	61.2	25.6	16.8
		16-Nov-16	33.4	25.8	34.6	21.0	22.6	29.1	30.6	26.2	25.6	15.3
MBAA (µg/L)	1	14-Sep-16	2.2	1.9	N/A	N/A	2.1	2.3	2.1	2.2	1.9	2.0
		14-Sep-16	3.3	2.0	N/A	N/A	2.1	2.3	2.1	2.2	1.9	2.0
	2	13-Oct-16	2.3	2.6	2.6	2.0	2.7	3.4	2.6	2.8	2.6	2.4
		13-Oct-16	2.5	2.6	2.1	2.6	2.5	2.6	2.6	3.1	2.5	2.5
	3	14-Nov-16	2.3	2.6	2.7	2.7	5.3	3.0	2.8	2.8	3.1	2.8
		14-Nov-16	2.5	2.7	2.8	2.7	3.1	3.0	2.9	2.5	2.9	2.9
	4	16-Nov-16	2.3	2.6	2.6	2.3	2.3	3.0	2.6	2.4	2.9	2.5
		16-Nov-16	2.5	2.7	2.6	2.3	2.7	2.6	2.1	2.3	2.6	2.3

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
DCAA (µg/L)	1	14-Sep-16	30.5	21.1	N/A	N/A	18.9	28.0	18.0	26.7	13.9	14.3
		14-Sep-16	43.5	19.5	N/A	N/A	16.0	15.9	18.0	18.1	14.9	15.5
	2	13-Oct-16	46.7	23.3	23.4	24.3	22.5	17.4	16.7	16.9	16.5	14.2
		13-Oct-16	36.7	31.3	22.7	25.6	18.6	16.4	15.9	17.7	13.9	16.5
	3	14-Nov-16	56.3	35.5	33.2	41.5	58.1	26.4	27.4	24.4	26.1	29.7
		14-Nov-16	59.3	33.3	35.7	38.3	32.4	28.5	27.7	26.6	32.2	27.4
	4	16-Nov-16	56.3	35.5	33.1	29.5	30.8	31.1	37.0	30.0	31.0	32.8
		16-Nov-16	59.3	33.3	32.1	32.0	31.4	31.1	28.4	25.3	31.0	29.3
TCAA (µg/L)	1	14-Sep-16	31.4	18.2	N/A	N/A	14.8	23.6	17.2	21.0	15.3	15.1
		14-Sep-16	38.1	16.2	N/A	N/A	12.8	14.6	17.2	14.8	16.0	16.8
	2	13-Oct-16	48.3	22.9	17.2	13.1	13.9	13.0	14.7	18.9	14.0	12.6
		13-Oct-16	40.3	29.3	12.8	15.5	11.2	12.8	13.2	18.8	13.7	15.4
	3	14-Nov-16	56.9	27.8	17.1	20.1	31.9	17.0	17.4	22.2	17.8	19.0
		14-Nov-16	59.7	26.1	18.4	18.7	17.8	18.3	17.4	23.3	17.9	17.6
	4	16-Nov-16	56.9	27.8	18.2	16.3	15.2	<MDL	21.0	23.8	<MDL	20.4
		16-Nov-16	59.7	26.1	18.0	16.9	16.9	19.9	16.1	20.1	19.5	18.7
BCAA (µg/L)	1	14-Sep-16	3.6	3.5	N/A	N/A	3.5	3.9	3.5	3.8	3.6	3.5
		14-Sep-16	3.7	3.5	N/A	N/A	3.5	3.5	<MDL	3.5	3.5	3.4
	2	13-Oct-16	4.0	3.6	3.8	3.6	3.5	3.5	3.6	3.5	3.5	3.6
		13-Oct-16	3.7	3.9	3.7	3.7	3.4	3.5	3.5	3.5	3.6	3.7
	3	14-Nov-16	3.4	3.6	3.5	3.6	5.1	3.2	3.3	3.2	3.3	3.3
		14-Nov-16	3.5	3.4	3.5	3.5	3.4	3.3	3.3	3.2	3.3	3.3
	4	16-Nov-16	3.4	3.6	3.3	3.1	3.0	<MDL	3.1	3.0	<MDL	3.1
		16-Nov-16	3.5	3.4	3.3	3.2	3.2	3.1	2.9	2.9	3.1	3.0

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
DBAA (µg/L)	1	14-Sep-16	3.5	3.4	N/A	N/A	<MDL	3.6	3.5	3.6	<MDL	3.4
		14-Sep-16	3.5	3.5	N/A	N/A	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	2	13-Oct-16	<MDL	<MDL	<MDL	<MDL	3.4	<MDL	3.5	<MDL	<MDL	<MDL
		13-Oct-16	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	3	14-Nov-16	3.4	2.8	2.8	<MDL	4.2	2.8	2.7	2.8	2.7	2.8
		14-Nov-16	3.4	2.7	2.7	<MDL	2.7	2.8	2.8	2.8	2.9	2.8
	4	16-Nov-16	3.4	2.8	2.6	<MDL	2.6	<MDL	2.6	2.6	<MDL	2.6
		16-Nov-16	3.4	2.7	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
BDCAA (µg/L)	1	14-Sep-16	9.2	9.3	N/A	N/A	<MDL	9.2	9.2	9.2	9.7	9.2
		14-Sep-16	9.2	9.2	N/A	N/A	<MDL	9.2	<MDL	9.2	9.4	9.3
	2	13-Oct-16	6.1	6.2	6.3	5.9	6.0	6.0	6.1	5.9	6.4	5.7
		13-Oct-16	6.0	6.2	5.9	6.1	5.9	6.0	6.3	6.0	6.2	6.2
	3	14-Nov-16	<MDL	5.3	5.6	5.6	6.9	5.3	5.2	5.2	5.8	5.5
		14-Nov-16	<MDL	5.4	5.6	5.6	5.6	5.4	5.5	5.0	5.7	5.6
	4	16-Nov-16	<MDL	5.3	5.7	5.7	5.5	<MDL	6.4	5.4	<MDL	6.3
		16-Nov-16	<MDL	5.4	5.6	5.2	5.7	5.9	5.6	5.4	6.0	6.0
Biopolymers (µg/L)	1	14-Sep-16	N/A	324.1	N/A	N/A	210.7	175.0	170.7	159.5	369.3	348.1
	2	13-Oct-16	N/A	177.3	178.1	181.7	517.0	204.9	173.7	162.0	176.4	166.3
	3	14-Nov-16	N/A	190.9	189.1	203.4	210.8	194.4	201.4	202.3	207.7	198.7
	4	16-Nov-16	N/A	190.9	168.6	167.9	170.1	169.0	157.3	164.4	160.9	157.7
Humic substances (µg/L)	1	14-Sep-16	N/A	1754.7	N/A	N/A	1617.2	1629.9	1590.4	1532.5	1516.7	1543.6
	2	13-Oct-16	N/A	1762.4	1414.1	1609.5	1589.5	1245.5	1360.4	1467.7	1581.1	1503.8
	3	14-Nov-16	N/A	1514.3	1496.2	1499.8	1321.2	1356.5	1363.3	1554.5	1421.5	1395.0
	4	16-Nov-16	N/A	1514.3	1285.7	1323.1	1847.5	1191.9	1183.9	1394.0	1291.4	1732.3

Table 7-6: Raw Data (Cont.)

Analyte	Condition	Date	Raw	Settled	O3	AOP	CAF	BAF	BAF	BAC Control	BAC	BAC
Building blocks (µg/L)	1	14-Sep-16	N/A	1056.5	N/A	N/A	1495.1	1380.8	1372.2	1407.6	1376.6	1390.4
	2	13-Oct-16	N/A	1126.3	1451.3	1199.0	1054.6	1435.3	1315.4	1334.5	1073.7	1122.3
	3	14-Nov-16	N/A	763.6	675.7	881.1	1010.9	919.6	900.3	761.7	811.2	786.5
	4	16-Nov-16	N/A	763.6	966.5	950.6	461.7	952.4	933.5	838.1	878.8	417.7
LMW Neutrals (µg/L)	1	14-Sep-16	N/A	953.8	N/A	N/A	748.9	791.0	764.2	739.2	787.9	792.9
	2	13-Oct-16	N/A	883.5	827.9	790.5	926.1	772.3	825.0	915.1	842.9	808.9
	3	14-Nov-16	N/A	420.8	439.7	468.7	395.0	357.0	373.9	391.8	350.7	375.6
	4	16-Nov-16	N/A	420.8	378.8	371.9	366.7	380.4	367.9	409.1	355.9	386.7