# UNDERSTANDING THE EFFECTS OF PRE-OZONATION ON GEOSMIN AND NATURAL ORGANIC MATTER REMOVAL

by

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# ABSTRACT

Taste and odor (T&O) issues continue to cause problems for drinking water utilities because they account for many consumer complaints. However, for consumers, the T&O of drinking water is their way of judging the quality and safety of their tap water (Nerenberg et al., 2000; Srinivasan & Sorial, 2011). This research examined the T&O compound, *geosmin*, found in Pockwock Lake, a water supply in Halifax, Nova Scotia. Geosmin is a microbial metabolite that results from the biodegradation of various types of cyanobacteria found in eutrophic waters and possesses an earthy/musty odor with a human threshold detection limit, of 4 ng/L. There are no health risks associated with geosmin and therefore it is not regulated in the Canadian Drinking Water Quality Guidelines (Health Canada, 2017).

Geosmin is very resistant towards conventional water treatment processes and therefore difficult to achieve non-detect levels (Elhadi et al., 2006). Ozone ($O_3$) oxidation was studied as an alternative treatment approach to combat the T&O compound from raw Pockwock water. $O_3$ is an extremely strong oxidant and disinfectant and has been known to remove T&Os from water. $O_3$ will react with natural organic matter (NOM) via two mechanisms: directly by dissolved molecular $O_3$ and indirectly by hydroxyl radical formation. Understanding the effects of $O_3$ on NOM and how it can be utilized for optimal performance is important for the drinking water industry.

This study examined the ability for pre-ozonation to remove geosmin below 4 ng/L from raw water. The experiment was designed as a $2^3$-factorial experiment using 1 and 10 mg/L $O_3$, 5 and 20 ng/L geosmin, at pH 6 or 8, respectively. The changes in NOM, characterized by parameters such as dissolved organic carbon, $UV_{254}$, fluorescence spectroscopy and zeta potential, due to pre-$O_3$ treatment at 1 and 10 mg/L was also investigated. At an initial geosmin concentration of 5 ng/L, pre-ozonation at both 1 and 10 mg/L at pH 6 and 8 was effective in reducing the T&O to below 4 ng/L. Samples ozonated at pH 8 achieved better results than ozonated at pH 6, suggesting that reaction of hydroxyl radicals with NOM were the main removal mechanism. When initial target geosmin concentration was 20 ng/L, pre-ozonation was less effective at reaching the 4 ng/L target. Following ozonation, all samples were coagulated, flocculated and filtered, simulating full-scale conventional filtration treatment.

NOM removal characterized by various parameters indicated that coagulation preceded by the low $O_3$ dose, improved NOM removal, whereas the high $O_3$ dose resulted in detrimental effects. Although geosmin was removed partially at the high $O_3$ dose, NOM removal was negatively affected. Further research is required to find the optimal operating $O_3$ dose that inadvertently does not disrupt NOM removal while achieving adequate T&O removal.

# LIST OF ABBREVIATIONS USED

| | |
|---|---|
| Alum | aluminum sulfate |
| AOPs | advanced oxidation processes |
| °C | degrees Celsius |
| $CO_2$ | carbon dioxide |
| Da | Daltons |
| DBP | disinfection by-product |
| DI | deionized water |
| DOC | dissolved organic carbon |
| FEEM | fluorescence excitation emission matrix |
| FSP | full scale plant |
| g | gram |
| GAC | granular activated carbon |
| GC-MS | gas chromatography – mass spectrometry |
| HPSEC | high pressure size exclusion chromatography |
| $H_2O_2$ | hydrogen peroxide |
| JDKWSP | John Douglas Kline Water Supply Plant |
| KI | potassium iodide |
| $KMnO_4$ | potassium permanganate |
| L | liter |
| L/min | liters per minute |
| LMW | low-molecular weight |

| | |
|---|---|
| MAC | maximum acceptable concentration |
| m | meter |
| MIB | 2-methylisoborneol |
| µm | micrometer |
| µg/L | micrograms per liter |
| mg/L | milligrams per liter |
| min | minute |
| mm | millimeter |
| MW | molecular weight |
| mV | millivolts |
| ng | nanograms |
| nm | nanometer |
| NaOH | sodium hydroxide |
| NOM | natural organic matter |
| NTU | nephelometric turbidity units |
| $O_3$ | ozone |
| PAC | powdered activated carbon |
| pH | potential hydrogen |
| psi | pounds per square inch |
| RO | reverse osmosis |
| rpm | revolutions per minute |
| SD | standard deviation |
| SEC | size exclusion chromatography |

| | |
|---|---|
| SUVA | specific UV absorbance at 254 nm |
| T&O | tastes and odours |
| TOC | total organic carbon |
| UV | ultra violet |
| $UV_{254}$ | ultra violet absorbance at 254nm |
| WTP | water treatment plant |
| ZP | zeta potential |

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# CHAPTER 1 INTRODUCTION

## 1.1 PROJECT RATIONALE

The presence of tastes and odors (T&O) in drinking water continues to cause problems for water utilities across Canada and the United States. For consumers, the T&O at the tap is their way of judging how clean and safe the water is for consumption. Any off flavor associated with potable water can result in perceived health problems (Elhadi et al., 2006; Nerenberg et al., 2000). A T&O compound found in eutrophic source waters called *trans*-1 10-dimethyl-*trans*-9-decalol (geosmin) is progressively on the rise, resulting in water utilities having to constantly improve treatment processes. Geosmin is often affiliated as having an earthy/musty odor and possessing an extremely low human threshold detection limit of 4 ng/L (Elhadi et al., 2006; Liang et al., 2007). Currently there is no maximum acceptable concentration (MAC) for geosmin in the Canadian Drinking Water Quality Guidelines set by Health Canada (Health Canada, 2017), partly due to it not being a health concern or threat to consumers (Srinivasan & Sorial, 2011).

Geosmin is a complex tertiary alcohol compound derived from the metabolism and biodegradation of various types of cyanobacteria (blue-green algae) or actinomycetes. During warmer temperatures, nutrients accumulate in lakes, rivers, streams etc. which can lead to a proliferation of cyanobacteria blooms (Srinivasan & Sorial, 2011). During these warmer times, geosmin transpires and can remain in surface waters even when temperatures begin to drop. For that reason, geosmin can be detected through the Fall and

Winter months in a water treatment plant (WTP) depending on the treatment processes in place (Jüttner & Watson, 2007).

The J.D. Kline Water Supply Plant (JDKWSP) draws its water from a protected, uninhabited, and pristine lake source known as Pockwock Lake. Water quality in the lake is extremely high, containing low organics, low turbidity, and low color. JDKWSP is a direct dual media filtration plant that has the capacity to treat 220 ML/day. In 2016, the plant produced on average 83 ML/Day ("Water Treatment Plants | Halifax Water," 2017). In late Summer and early Fall of 2012 the local water utility of Halifax experienced a drastic increase in customer complaints because of the T&O experienced at the tap. Geosmin was positively identified in Pockwock Lake and labeled the cause of the T&O outbreak.

Conventional treatment methods (coagulation, flocculation, & filtration) lack the ability to remove geosmin to levels undetectable by humans. Educating the public and finding alternative technologies that can remove this persistent T&O compound is of utmost importance in maintaining customer satisfaction (Elhadi et al., 2006; Ho et al., 2002; Srinivasan & Sorial, 2011). Since the initial outbreak at JDKWSP, the plant converted to passive biofiltration through the removal of pre-chlorination. The objective of removing pre-chlorine from the pre-treatment (rapid mix) was to reduce chlorinated disinfection by-product (DBP) formation. It was hypothesized that by removing prechlorine, the anthracite-sand filters would remove particles as well as operating biologically (Stoddart & Gagnon, 2015). Even with the change in pre-treatment, geosmin continued to persist which led to the inquiry of alternative treatment options at JDKWSP.

The most accessible treatment approach applied to combat seasonal T&O issues is adsorption using powered activated carbon (PAC) or granular activated carbon (GAC) (Zamyadi et al., 2015). Alternatively, other methods include oxidation via chlorine, chloramines, chlorine dioxide, and potassium permanganate ($KMnO_4$) (Lalezary et al.,1986; Nerenberg et al., 2000). Novel treatment methods on the rise are advanced oxidation processes (AOPs). AOPs involve strong oxidants such as ozone ($O_3$), hydrogen peroxide ($H_2O_2$), and/or ultra violet (UV) light or a combination thereof to oxidize or remove target compounds. Because every water matrix is different and complex, there is not one treatment that is guaranteed to remove T&O compounds without the possibility of unintended consequences such as, reduced natural organic matter (NOM) removal, increase in DBPs, reduced filter runtimes etc. For that reason, it is critical for a potential treatment technique to be thoroughly investigated for possible risks and/or benefits to the entire water treatment process.

Based on the current treatment processes at JDKWSP, $O_3$ was considered a viable option to explore as a possible treatment method for removing geosmin. In literature, studies involving pre-ozonation and biofiltration have been investigated and proved suitable in not only T&O removal but also improved effluent quality water. As such, ozone is becoming a more attractive alternative within North America to using chlorine products because of the strict guidelines set on finished water chlorinated disinfection byproducts (DBPs) due to their known carcinogenic attributes (Nerenberg et al., 2000). Ozone is a very strong oxidant and disinfectant and will react with NOM in water to produce low-molecular weight (LMW), oxygenated byproducts that can be removed through biodegradable processes. For that reason, a tandem ozone-biofiltration treatment could remove geosmin below the threshold limit while improving finished water quality through increased NOM removal (Elhadi et al., 2006).

## 1.2 RESEARCH OBJECTIVES

In this study, the ability of $O_3$ to oxidize geosmin from raw water and effectively increase NOM removal during coagulation and flocculation at the bench-scale level was evaluated. A $2^3$-factorial analysis experiment was investigated. The experimental design evaluated raw water with a pH adjusted to 6 or 8, spiked with a known geosmin concentration of 5 or 20 ng/L and then subsequently ozonated at 1 or 10 mg $O_3$/L. The experimental conditions consider the low and high extremity of geosmin concentration experienced by Pockwock Lake, the influence of pH, and a conservative approach when applied $O_3$ is greater than available carbon content (3 mg $O_3$/ mg DOC).

The main objective of this research was to understand and evaluate the potential for pre-$O_3$ to effectively remove geosmin from Pockwock raw water while simultaneously assessing if any additional benefits within the simulated treatment train were achieved. Knowledge and information on pre-$O_3$ in relation to downstream treatment processes (other than taste and odor removal) is very limited and often contradicting in literature (Li et. al., 2009).

The research objectives were as follows:

1. Design a bench-scale procedure for pre-ozone treatment followed by a direct filtration jar test procedure
2. Determine if geosmin can be removed below the human threshold detection limit of 4 ng/L from initial spiked concentrations
3. Determine the downstream impacts or unintended consequences of applied pre-ozone

## 1.3 ORGANIZATION OF THESIS

This thesis is organized as follows:

Chapter 1 provides introduction and background information on the rationale of the research. Chapter 2 outlines the literature review used to understand background content on T&Os, NOM, and $O_3$. Chapter 3 describes all materials and methods used throughout the experiments. Chapter 4 outlines the results and discussion pertaining to geosmin and NOM oxidation and removal post $O_3$. Chapter 4 also examines the role of $O_3$ and how it affects geosmin and NOM throughout chemical coagulation, flocculation and simulated filtration. Chapter 5 provides a conclusion of the results obtained from the bench-scale experiment, as well as recommendations for any further research.

# CHAPTER 2 LITERATURE REVIEW

## 2.1 OVERVIEW OF TASTES AND ODOURS

Tastes and odors associated with potable water tend to receive negative attention and subsequently lower the confidence of the end consumer. It is important for drinking water utilities to continue educating the public on the safety of their water when a T&O issue arises, especially if there is no associated health risk. Common T&Os typically identified throughout the water treatment process are shown in **Figure 1** (Suffet et al., 1999).

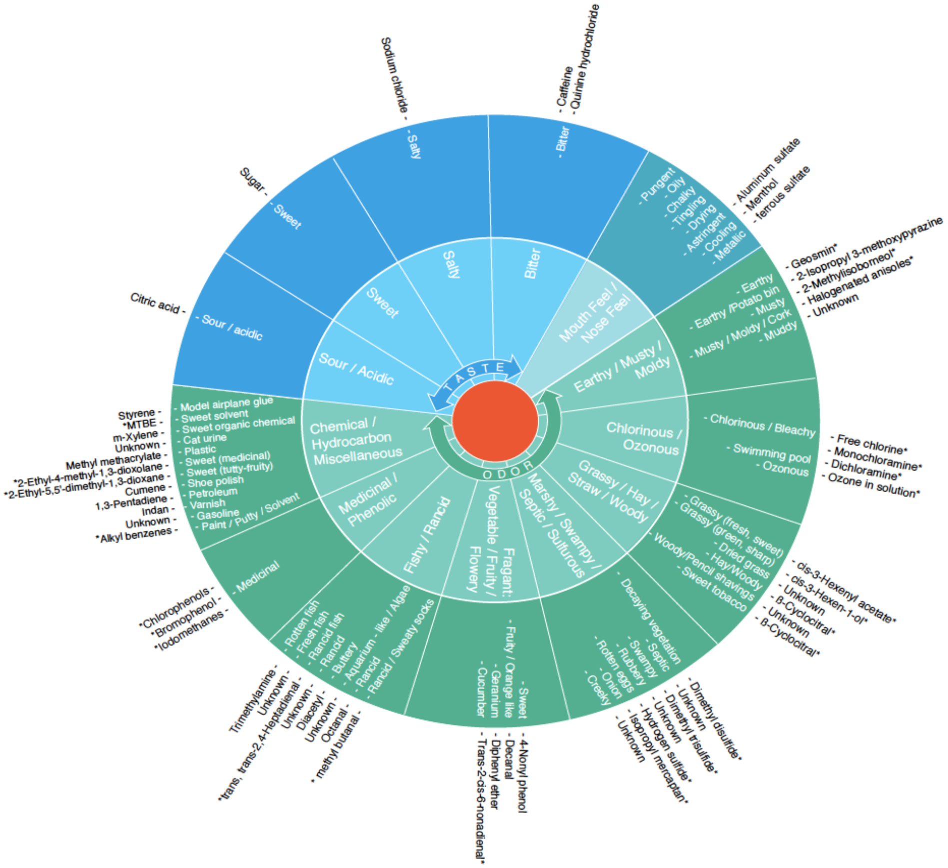

**Figure 1**: Drinking Water Taste and Odor Wheel (Suffet et al., 1999)

A national survey conducted throughout the United Sates (US) in 1985, indicated that more than 15% of consumers used bottled water or in-home treatment devices due to either a taste or odor linked to the tap water (Manwaring et al., 1986). A different survey conducted throughout the US and Canada rated "earthy" as the second highest odor problem based on 244 (of 377) responses. In the survey, water utilities using groundwater only, reported minor and short-term problems than those of surface water only. Additionally, surface water utilities reported T&O issues as a more serious problem whereas ground water only utilities reported their T&O issues as a low concern (Suffet et al., 1996).

The severity of a T&O outbreak is a main concern; however, the duration of the outbreak poses problems, mainly for the end consumer if the T&O is detectable. Approximately 44% of surface water outbreaks lasted longer than one week, compared to 10% of ground water outbreaks reported (Suffet et al., 1996). Utilities relying on surface water sources are prone to more frequent and long lasting T&O problems due to a greater risk of contamination. Unfortunately, surface water utilities can only rely on modifying current processes or adapting seasonally so that T&O problems can be solved.

### 2.1.1 Geosmin

Geosmin (molecular formula: $C_{12}H_{22}O$) is an off flavor and odor compound produced as metabolites by various cyanobacteria and actinomycetes (Zamyadi et al., 2015). The chemical structure of geosmin is provided in **Figure 2**. Geosmin is described as an earthy, musty, or moldy odor compound as shown on the drinking water taste and odor wheel i

Cyanobacteria, also known as blue-green algae, will synthesize geosmin throughout the life cycle and eventually release or store the odorant depending on the phase or surrounding environmental factors. Upon death and biodegradation of the cells, geosmin is released into the environment. Favorable conditions that influence geosmin outbreaks usually consist of excessive nutrients and warmer temperatures, which coincide with cyanobacteria blooms. Therefore, outbreaks tend to occur in late summer to early Fall and effects are subsequently detected during the following months. Humans can acknowledge the presence of geosmin in treated water at concentrations as low as 4 ng/L (Elhadi et al., 2006). Fortunately, geosmin does not pose a health risk for humans and is not regulated under the Canadian Drinking Water Health Guidelines.

Geosmin is present either in intracellular or extracellular form which can vary widely depending on water body type, water composition, as well as cyanobacteria bloom age and producers present (Zamyadi et al., 2015). Most geosmin found in waters is in particulate form (intracellular), bound to proteins or dissolved in the cytosol of the cell and therefore it is important to avoid cell disruption or lysing of cells for that could lead to more problems within the WTP (Jüttner & Watson, 2007). Understanding the complex nature of geosmin and its makeup can make it easier for water utilities to remove from treated water.

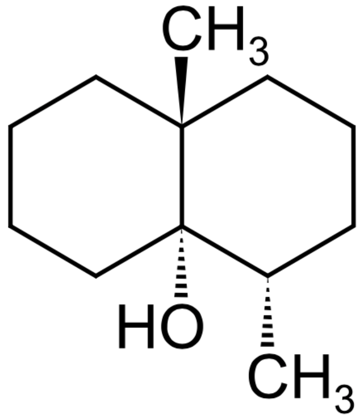

**Figure 2**: Chemical Structure of Geosmin

### 2.1.2 Issues in Drinking Water Treatment Plants Related to Geosmin

For decades, the T&O of finished drinking water acted as the main measure for consumers to judge the safety of their tap water. Having an off flavor/odor gives the perception that the water is unsafe or inadequate for consumption which leads the consumer finding alternative means of drinking water (Parinet et al., 2010; Srinivasan & Sorial, 2011; Zamyadi et al., 2015). Unfortunately, due to the low human threshold concentration, strain is put on water treatment plants to remove T&Os below the detection limit.

Geosmin, along with other compounds that have low odor threshold concentrations, like 2-methylisoborneol (MIB), another earthy/musty T&O are difficult for water treatment plants to remove due to their persistence in conventional processes such as coagulation, sedimentation, filtration and disinfection (Nerenberg et al., 2000). The nature of geosmin and how it exists in the source water is a key factor in the removal efficiency for conventional water treatment plants. When geosmin is present as extracellular, the removal rates of conventional chemical-physical processes are less than 20%. However, if geosmin is cell bound (intracellular), removal of entire cells is more efficient. If cells are damaged via pre-oxidation or throughout treatment by hydraulic stress then cell-bound geosmin may be liberated and released which poses issues downstream (Zamyadi et al., 2015).

Organic material is abundant and normally magnitudes higher in concentration than geosmin in source waters. For that reason, various treatments may not be effective due to the competiveness of organic matter oxidation vs. geosmin oxidation (Srinivasan & Sorial, 2011). Therefore, employing the most effective and efficient treatment method is very important for utilities. However, the cost of treatment year-round can quickly become a financial burden for water treatment plants that may only experience this odor issue seasonally. For example, plants utilizing pre-chlorine year-round as an oxidation step can increase unwanted disinfection byproducts in the finished water. Applying treatment that operates intermittently during outbreaks or during warmer temperatures when cyanobacteria blooms appear could be economical as well as providing operational advantages to the water treatment plant.

## 2.2 TASTE AND ODOUR TREATMENT OPTIONS

### 2.2.1 Adsorption

Activated carbon adsorptions by either granular activated carbon (GAC) or powdered activated carbon (PAC) are common and effective methods used to treat taste and odor issues (Huang et al., 1996). GAC is primarily used in the form of filtration beds and has been effective in removing geosmin below the human threshold limit. However, over time, GAC adsorption capacity can decrease due to the natural competitiveness of organic matter coating the GAC with dissolved organic carbon (DOC) (Srinivasan & Sorial, 2011). Virgin GAC proved useful in removing geosmin but did not maintain effectiveness over long periods of time and changing water quality. Thus, GAC re-generation proved to be a key factor for WTPs and whether the benefits outweighed the drawbacks (Liang et al., 2007; Zamyadi et al., 2015).

Powdered activated carbon is the most widely used and “go-to” method for removing seasonal tastes and odors. Effectiveness is highly dependent on outside factors such as organic matter concentrations, oxidants used, and water chemistry (Bruce et al., 2002; Nerenberg et al., 2000). A study conducted by (Lalezary-Craig et al., 1988) showed that a PAC dose of 10 mg/L was able to reduce geosmin and MIB from 66 ng/L each to 2 and 7 ng/L, respectively. In contrast to GAC, PAC offers a lower capital cost, simpler operating techniques, and fewer personnel, in addition to its seasonal capabilities (Lalezary-Craig et al., 1988). The difficulty with PAC is that it adds solid waste residuals and can cause disposal issues if the plant is not set up to operate as such (Liang et al., 2007).

### 2.2.2 Aeration

Dissolved air flotation (DAF) is a treatment method designed for water that contains low-density particles such as algae or cyanobacteria cells, low turbidity, soft water, and high coloration. The DAF process utilizes air-saturated bubbles that are produced by the release of recycled water. Particles attach to the bubbles and then travel upward towards the surface of the floatation tank and are then sloughed off as floated sludge (Teixeira & Rosa, 2007). Algal cells tend to float and cause great difficulty for conventional treatment plants that employ sedimentation (Zabel, 1985). Because geosmin can exist in nature as cell-bound material, DAF allows removal of entire cells without the risk of damage or lysing to the cells (Teixeira & Rosa, 2007).

### 2.2.3 Biological Filtration

Biological filtration or biofiltration is a widely accepted treatment method for wastewaters, and is gaining interest across North America in the drinking water industry. Because the environment in many drinking water plants is oligotrophic (low levels of growth substrate), the main mechanism of maintaining active bacteria is biofilm attachment on granular media (Nerenberg et al., 2000). Since geosmin is assumed to be biodegradable, biofiltration has been used to remove taste and odor compounds. Factors such as temperature, initial geosmin concentration, and biomass availability are key in removing the unwanted compound (Persson et al., 2007).

### 2.2.4 Oxidation

**Chlorine and Chlorine Products**. Chlorine ($Cl_2$), chloramines ($NH_2Cl$), and chlorine dioxide ($ClO_2$) are oxidants that have been used to target some taste and odors, however they are not capable of removing geosmin to below the odor threshold limit (Nerenberg et al., 2000). Glaze et al., 1990 found that $Cl_2$, $NH_2Cl$, and $ClO_2$ were inefficient at removing geosmin when dosed at 3 mg/L. Chlorination of intracellular geosmin is not effective and may lead to detection in treated water. Formation of DBPs tends to limit the use of chlorine products in surface water treatment as pre-oxidants because of health concerns and guidelines (Glaze et al., 1990; Zamyadi et al., 2015).

**Potassium Permanganate**. Potassium permanganate ($KMnO_4$) is commonly added as a pre-oxidant in many WTPs to oxidize iron (Fe) and manganese (Mn), treat taste and odors, as well as reduce algae growth in pipes and treatment processes (Fan et al., 2013; Nerenberg et al., 2000). One study that looked at different oxidants for removing model taste and odor compounds found that a $KMnO_4$ dose of 3 mg/L achieved only 15% removal of geosmin from a municipal water supply (Glaze et al., 1990). Another study showed that $KMnO_4$ (0.75 mg/L) enhanced removal of blue-green algae when applied as a pre-oxidant to alum coagulation, removing approximately 95% of algae present (Chen et al., 2008).

**Ozone**. Ozone ($O_3$) is typically used in surface water treatment as a disinfectant. Ozone has also been used to remove taste and odors and enhance coagulation processes. As health guidelines continue to become more stringent, $O_3$ is chosen as an alternative disinfectant to chlorine because of its low risk of DBPs (Nerenberg et al., 2000). However, the effectiveness of $O_3$ to oxidize geosmin or other novel taste and odor compounds is highly dependent on dose and water chemistry (Westerhoff et al., 2006). Batch ozone experiments at the bench-scale level found that after a 20-min contact time of 2.5 mg $O_3$ /L, approximately 97% of geosmin was degraded (Bruce et al., 2002). Another study showed that only 35% of geosmin was removed at an ozone dose of 2.0 mg/L, but increased to approximately 90% removal when the ozone dose doubled to 4 mg/L (Glaze et al., 1990).

**Advanced Oxidation Processes**. Advanced oxidation processes (AOPs) typically involve UV light along with a photocatalyst such as hydrogen peroxide ($H_2O_2$) or $O_3$, or by combining chemical oxidants (e.g., $O_3$ with $H_2O_2$). These oxidants can be used to disinfect water from unwanted pathogens or other micro contaminants (Srinivasan & Sorial, 2011). One study found that UV in combination with $O_3$ removed up to 90% of geosmin in solution compared to 50% removal from $O_3$ alone (Collivignarelli & Sorlini, 2004). AOPs require high capital, as well as operating costs, especially for high doses that are required to treat the low concentrations of geosmin (Srinivasan & Sorial, 2011).

### 2.2.5 Integrated Technologies

Various existing technologies that may not completely remove geosmin to achieve below human threshold concentrations have been combined with other treatment options to not only achieve complete removal, but to also enhance treated water effluent (Srinivasan & Sorial, 2011). Because ozone readily degrades organic matter into compounds more amenable to biodegradation, an ozone biofiltration process may remove geosmin while increasing effluent water quality. A prime example is the Lake Bluff WTP (Elhadi et al., 2006; Nerenberg et al., 2000).

The WTP in Lake Bluff, Illinois receives very few customer complaints regarding tastes and odors, compared to the numerous complaints received by other water treatment plants in the surrounding area. All plants draw water from the same source, southwest Lake Michigan, a known earthy/musty water source. The Lake Bluff water treatment plant employs tandem ozone and biofiltration processes. The treatment commences with ozonation, followed by rapid mixing, flocculation, sedimentation, and filtration with biologically active GAC. It was determined via a field campaign as to where in the treatment train tastes and odors were removed. Studies showed that geosmin and MIB were primarily removed due to the ozonation and breakdown of contaminants into more biodegradable compounds that are readily degraded in the biofilters (Elhadi et al., 2006; Nerenberg et al., 2000).

## 2.3 NATURAL ORGANIC MATTER

### 2.3.1 Characteristics of Natural Organic Matter

Natural organic matter (NOM) is a complex heterogeneous mixture of organic compounds, resulting from the decay of plant and animal material in natural waters (Croue et al., 2000; Owen et al., 1995). NOM acts as a contaminant by imposing a yellowish tinge to water and thus, impacts the aesthetic quality of the water. Additionally, NOM impacts other aspects of the water treatment process such as reacting with chlorine to produce carcinogenic DBPs, biological growth within the distribution system, and tastes and odors (Howe et al., 2012; Owen et al., 1995). Various impacts to water quality and processes are outlined in **Table 1**.

**Table 1**: NOM Effects on Water Quality and Treatment Processes (Howe et al., 2012)

| **Parameter** | **Effect of NOM** |
|---|---|
| ***Water Quality Parameters*** | |
| Color | At high concentrations, can yield a yellowish color |
| Disinfection byproducts | Adverse health effects from NOM reactions with different disinfectants |
| Metals/synthetic organics | NOM can bind with metals yielding them more soluble and amenable to environmental transport |
| ***Water Treatment Processes*** | |
| Adsorption | NOM readily adsorbed to activated carbon thereby reducing the adsorption capacity |
| Coagulation | NOM reacts and consumes coagulants thereby requiring higher doses to achieve effective turbidity removal requirements |
| Membranes | NOM readily adsorbs to membranes, increasing fouling and decreasing flux |
| Disinfection | NOM reacts and consumes disinfectants, requiring higher doses |
| Distribution | NOM can lead to corrosion through its biodegradability |

**Quantification of NOM**. Measuring individual NOM compounds is unrealistic, based upon the existence of numerous complex compounds. Therefore, quantification of NOM compounds is typically determined via bulk parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable organic carbon (BOC), biodegradable dissolved organic carbon (BDOC), assimilable organic carbon (AOC), $UV_{254}$ absorbance, and specific UV absorbance (SUVA) (Howe et al., 2012).

**NOM Classification**. NOM can be classified as either humic or non-humic fractions. Most humic fractions are characterized as hydrophobic, comprising of humic and fulvic acids. The non-humic fractions are characterized as hydrophilic, encompassing hydrophilic acids, proteins, amino acids, and carbohydrates (Owen et al., 1995). For water treatment plants, the humic compounds were considered most relevant because they are composed of mostly dissolved organic carbon (DOC), play a major role in contributing to DBP formation, and are considered the target of coagulation in terms of NOM removal (Croue et al., 2000; Thurman, 1985).

NOM can be further classified by the molecular weight (MW) of the compounds. Compounds that have molecular weight of <500 Da are typically considered lower-molecular weight (LMW) compounds, whereas compounds with >1000 Da are deemed higher-molecular (HMW) compounds. Approximately 90 percent of NOM lies within the 500 – 3000 Da range (Howe et al., 2012). NOM humic fractions that contain conjugated double bonds and are aromatic in nature, make-up the majority of natural waters, and are therefore readily removed by chemical coagulation in water treatment. LMW compounds, such as the hydrophilic acids, proteins, amino acids etc. are less amendable to chemical coagulation (Edzwald et al.,1985; Owen et al., 1995).

**Charge of NOM**. Charge of NOM is typically measured in millivolts (mv) using zeta potential (ZP). The majority of NOM in natural waters is composed of humic and hydrophobic compounds that possess a negative charge, due to the associated carboxylic acid groups (R-COOH) and phenolic groups (Matilainen et al., 2010). The use of ZP, in terms of water treatment processes is important because reducing the charge on the particle makes it more amenable to chemical coagulation. Therefore, monitoring the charge can lead to maximum NOM removal. ZP ranges said to achieve maximum NOM removal can range from -10 to +3 mv (Sharp et al., 2006).

### 2.3.2 NOM Removal Processes

**Chemical Coagulation**. Chemical coagulation involves the addition of a chemical reagent such as aluminum or iron salts to water to destabilize colloidal particles. The destabilization of the colloidal particles allows them to form flocs (agglomerate) and is subsequently removed via sedimentation or filtration (Droste, 1997). Coagulation on its own does not remove NOM; additional processes such as sedimentation or filtration are required in combination with a chemical reagent.

The most common coagulants used in water treatment are aluminum sulfate ($Al_2(SO_4)_3$), also known as alum, and ferric chloride ($FeCl_3$). Other derivatives of aluminum and ferric salts are also used for coagulation purposes, but are not as common (Matilainen et al., 2010). The overall reactions of alum and ferric sulfate when added to water are shown in equations 1 and 2, respectively (Droste, 1997).

$$Al_2(SO_4)_3 \cdot 18H_2O + 6H_2O \longrightarrow 2Al(OH)_3(s) + 6H^+ + 3SO_4^{2-} + 18H_2O \qquad [1]$$

$$FeCl_3 \cdot 6H_2O \longrightarrow Fe(OH)_3(s) + 3H^+ + 3Cl^- + 3H_2O \qquad [2]$$

The overall effectiveness of a coagulant to remove NOM is highly dependent on several process and operational parameters. The type of coagulant is important, whether it is an aluminum based or ferric-based salt coagulant will affect the removal efficacy of the NOM, as well as the dose that is being applied. Operational parameters such as mixing settings, pH control, temperature, and water matrix play a role in the adequacy of NOM removal (Matilainen et al., 2010). The critical pH range for alum is 5.5 – 6.3, whereas the range for ferric chloride is between 4.5 – 5.5 (Droste, 1997). Many researchers have developed models and algorithms to help predict or increase NOM removal. One of the most well-known methods is that of (Edwards, 1997), who used a Langmuir-based semi empirical model to predict DOC removal during enhanced coagulation. Enhanced coagulation is defined as removing a specified amount of DBP precursor material (NOM) (Howe et al., 2012).

**Membrane Filtration Processes.** Membrane filtration requires a vacuum or pressure-driven process to remove suspended particulate matter from solution using synthetic porous material. Membrane filters can be divided into various particle size ranges, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis as shown in **Figure 3** (Howe et al., 2012). Microfiltration and ultrafiltration, typically classified as low-pressure membranes, can remove colloidal material, bacteria and viruses, and inorganic particulates, whereas nanofiltration and reverse osmosis are classified as high pressure membranes and are used to remove color, ions, and dissolved organic matter (Zularisam et al.,2006).

Membrane filtration offers many advantages over conventional treatment options. These include small operational footprint, lower energy consumption, limited chemical waste, and ability to treat wide range of feed quality water (Zularisam et al., 2006). However, membranes are prone to fouling which is one of their main disadvantages. Fouling on a membrane is defined as either a decrease in flux or an increase in pressure to maintain equivalent permeate flux. Fouling is characterized by different mechanisms by which it occurs (blockage, constriction, or cake formation), whether it can be removed or not, and by the material causing the fouling (particles, bio fouling, or NOM) (Howe et al., 2012). The humic fraction of NOM is said to be the main foulant on the membrane surface due to its adsorptive capacity (Zularisam et al., 2006). Fouling on a membrane can be reduced with the implementation of a pretreatment process. Occasionally low-pressure membranes will be issued prior to a high-pressure membrane for pretreatment. In addition, physical pretreatment is used to remove larger solids or contaminants before reaching a membrane filter. Chemical pretreatment has been used to alter properties of the foulant and help increase the lifespan and operational performance of the membrane.

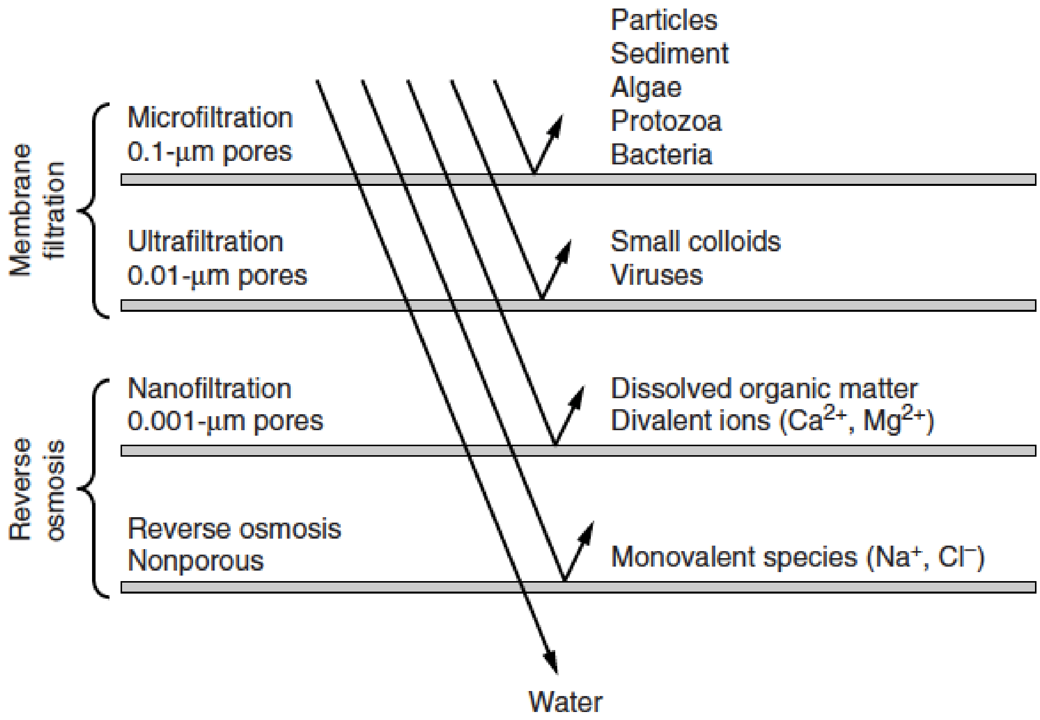

**Figure 3**: Order of Membrane Filtration Processes (Howe et al., 2012).

**Advanced Oxidation Processes.** Advanced oxidation processes (AOPs) are strong techniques for disinfection and for altering NOM characteristics. There are many different combinations of AOPs made available for disinfection, NOM removal, and target compound removal. Working combinations include: UV/$H_2O_2$, UV/$O_3$, $O_3$/$H_2O_2$, UV/$TiO_2$, and $Fe^{2+}$/$H_2O_2$. The attractiveness of AOPs was garnered by the fact that compounds could undergo complete oxidation or partial mineralization, changing the structure or properties to become more amenable to downstream treatment (Matilainen & Sillanpää, 2010).

AOPs have a wide range of versatility and can therefore be placed at different locations throughout the treatment process. AOPs can be used prior to coagulation and flocculation to help improve NOM removal. However, for many of the different combinations, NOM continues to impact the effectiveness of the various techniques (Lin & Wang, 2011).Since AOPs are used for the promotion of •OH and their strong oxidative properties, NOM will react with the •OH and end the reaction, negatively affecting the process (Howe et al., 2012).

## 2.4 OZONE

### 2.4.1 Properties of Ozone

Ozone is an allotrope of oxygen consisting of three atoms and under normal conditions is a gas, light blue in color and possesses a pungent odor (Oyama, 2000). It is a strong oxidant and is used widely in synthetic applications as well as a disinfectant throughout various industries. The boiling, melting, and freezing temperatures of ozone are -119.6°C, -195.2°C, and -195.8°C, respectively (Oyama, 2000). Ozone is an unstable gas and is not stored in vessels; therefore it must be generated at point-of-use (Gray, 2013). The oxidation potential of ozone is 2.07 electron volts (eV), approximately 50% stronger than the 1.36eV that of chlorine (Copeland & Lytle, 2014). The oxidation potential of common disinfectants is shown in **Table 2**. Concerns over the ongoing struggle of managing DBPs within treated water have accelerated the use of ozone as an alternative oxidant and disinfectant to chlorine for many drinking water utilities (Bose & Reckhow, 2007). The only regulated by-product related to ozonation is bromate. Bromate results from ozonating bromidecontaining waters; the current guideline sets a MAC of 0.01 mg/L for treated water (Health Canada, 2015)

**Table 2**: Common Oxidants used in Drinking Water Treatment (Copeland & Lytle, 2014)

| Oxidant | Oxidation Potential (eV) |
|---|---|
| Chlorine | 1.36 |
| Chlorine Dioxide | 1.71 |
| Hypochlorous Acid | 1.49 |
| Hypochlorite | 0.9 |
| Hydrogen Peroxide | 1.77 |
| Hydroxyl Radical | 2.80 |
| Monochloromine (basic) | 0.75 |
| Monochloromine (acidic) | 1.4 |
| Dichloromine (basic) | 0.79 |
| Dichloromine (acidic) | 1.34 |
| Permanganate (basic) | 0.58 |
| Permanganate (acidic) | 1.68 |
| Oxygen (basic) | 1.23 |
| Oxygen (acidic) | 0.4 |
| Ozone | 2.07 |

### 2.4.2 Ozone Generation

**Electrical Discharge (Corona Discharge)**. Corona discharge for $O_3$ generation is one of the most popular means of producing $O_3$ on site. The process involves discharging an oxygen ($O_2$) containing gas (compressed air) through an energy electrical field where a fraction of oxygen is converted into $O_3$. During the discharge of $O_2$ in the electrical field, electrons are accelerated enough to force a split between the double $O_2$ bonds, yielding atomic $O_2$. The atomic $O_2$ atoms then react with diatomic $O_2$ atoms to form $O_3$, as shown in the reaction equation below, equation 3.

$$3O_2 + Energy = 2O_3 \qquad [3]$$

Ozone produced via corona discharge is an exothermic physio-chemical reaction and therefore the energy lost due to the production is in the form of heat. A sound cooling system is essential in generator design. Using air, typically 1 – 2% w/w of $O_3$ is achieved and using $O_2$ about 3 – 8% w/w of $O_3$ is achieved.

**Ultra Violet (UV)**. Ozone generation by UV is a photochemical process that involves air passing over a UV lamp and a limited amount of $O_2$ is converted into $O_3$ by high-energy radiation. This technique for $O_3$ production is less expensive than corona discharge in terms of capital equipment cost; however, the drawback to this method is that only a small amount of $O_3$ is generated, typically 0.1 – 0.3% w/w.

**Unconventional Forms**. Although corona discharge is the most widely used technique for $O_3$ generation within the water and wastewater industry, other methods of generation are continuously being explored and investigated. As such, the electro catalytic generation method explores the use of an anode to oxidize water to $O_3$. Unfortunately, the method is plagued with high costs and short lifetimes. Another technique being studied for $O_3$ generation is radiochemical, the process of using high-energy irradiation of $O_2$ to produce $O_3$. The process is rarely used due to the complicated nature of the application and the risk of radioactive contamination.

### 2.4.3 Stability of Ozone in Water

Organic compounds that contribute to color can be oxidized by $O_3$ and some inorganic compounds can be oxidized as well. Common inorganic compounds oxidized by $O_3$ are shown in **Table 3**. Ozone is unstable in water and undergoes two stages of decay. Initially, $O_3$ will decay fast in natural waters followed by first order kinetics. The half-life of $O_3$ will vary depending on the water chemistry, however it typically ranges from seconds to hours (von Gunten, 2003). Important factors that contribute to the effectiveness of $O_3$ for water treatment include background organics, pH and alkalinity (Ho et al., 2002).

**Table 3**: Inorganic Compounds Oxidized by Ozone and their Reaction Products (Gray, 2013)

| Compound | Reaction Product | Compound | Reaction Product |
|---|---|---|---|
| $Fe^{2+}$ | $Fe(OH)_3$ | $Cl^-$ | HOCl |
| $Mn^{2+}$ | $MnO_2$ | HOCl | $ClO_3^-$ |
| $Mn^{2+}$ | $MnO_4^-$ | $OCl^-$ | $ClO_3^-$ |
| $NH_4^+$ | $NO_3^-$ | $HClO_2$ | $ClO_3^-$ |
| $NH_3$ | $NO_3^-$ | $ClO_2$ | $ClO_3^-$ |
| $NO_2^-$ | $NO_3^-$ | $I^-$ | HOI, $IO_3^-$ |
| $H_2S$ | $SO_4^{2-}$ | $I^-$ | $OI^-$, $IO_3^-$ |
| $S^{2-}$ | $SO_4^{2-}$ | | |
| $CN^-$ | $CO_2$, $NO_3^-$ | | |
| AS-III | AS-V | | |
| $Br^-$ | HOBr | | |
| $Br^-$ | $OBr^-$ | | |
| HOBr | $HBrO_2$ | | |
| $OBr^-$ | $BrO_2$ | | |
| $HBrO_2$ | $BrO_3^-$ | | |
| $BrO_2$ | $BrO_3^-$ | | |

Disinfection occurs predominately through the reaction of molecular $O_3$. Oxidation, however, relies on molecular $O_3$ but also on another feature called the hydroxyl radical (•OH). Due to background organics and water matrix composition, $O_3$ will react with the NOM present and a fraction of the $O_3$ will decompose into •OHs. The •OH is a much stronger oxidant than molecular $O_3$, having an oxidation potential of 2.80eV. Ozone oxidation is selective in terms of oxidizable compounds, whereas •OHs are very strong and react fast with many different types of compounds (Ho et al., 2002). Direct reaction of molecular $O_3$ and NOM typically involves compounds with double bonds, activated aromatic systems, as well as amines and sulfides. However, when a fraction NOM reacts with •OHs, carbon centered radicals are formed and will further react with $O_2$ and produce superoxide radicals. Super oxide radicals will react with $O_3$ and form additional •OHs. The process is referred to propagation and leads to accelerated $O_3$ decrease in waters and is only terminated by inhibitors (von Gunten, 2003). Common inhibitors in natural waters are carbonate and bicarbonate. Carbonate and bicarbonate are also known as scavengers, and by terminating the main •OH production mechanism; increase the life of molecular $O_3$ (Liang et al., 2007). Waters containing low DOC and low alkalinity will consume $O_3$ and •OHs at a faster rate than waters with high NOM (von Gunten, 2003).

Compounds that are $O_3$-resistant and cannot be oxidized by molecular $O_3$ rely on the •OH oxidation mechanism. Ozone decomposition can be accelerated by an increase in pH value (von Gunten, 2003). In a study by (Liang et al., 2007), geosmin and MIB removal efficiencies were evaluated based upon three different pH values of 5, 7, and 9. The authors found that by increasing the pH, $O_3$ auto decomposed at a faster rate yielding higher concentrations of •OH that targeted the T&O compounds.

### 2.4.4 Ozone and Particle Formation

Despite $O_3$ having strong oxidation and disinfection properties, some researches support the theory that pre-ozonation can act as a coagulant aid by reducing the charge on the particles, resulting in charge neutralization and thus lowering the coagulant demand (Eyvaz et al.,2010). However, many researchers remain skeptical as to whether $O_3$ can decrease coagulant dose. A study conducted by (Li et al., 2009) investigated the impact of pre-ozonation on the performance of coagulated flocs and found that as the $O_3$ dose increased, the flocs became more densely packed and a pre-$O_3$ dose of 0.53 mg/mg C was found to be optimal based on floc settling behaviors. In contrast, a study by (Edwards et al., 1994) found that pre-ozonation reduced the particle loading and decreased the headloss buildup at the expense of increased NOM in the finished water.

# CHAPTER 3 MATERIALS AND METHODS

## 3.1 SOURCE WATER AND PLANT DESCRIPTION

J.D Kline Water Supply Plant (JDKWSP) is in Upper Hammonds Plains, Nova Scotia, Canada and is operated under the Halifax Regional Water Commission. JDKWSP provides a daily average of 85 ML/day of potable water to Halifax, Bedford, Sackville, Fall River, Waverly, and Timberlea. The plant draws water from Pockwock Lake, which is protected under the Nova Scotia Environment Act, and therefore is not influenced by anthropogenic sources. An overview of the treatment process at JDKWSP is shown in **Figure 4**.

The lake is characterized as having low pH, low alkalinity, low turbidity and low organics. The data is summarized in **Table 4**. The JDKWSP operates as a direct, dual media filtration plant. Treatment processes begin via a pre-screening at the raw water intake and then subsequently lead to oxidation, coagulation, hydraulic flocculation, direct filtration and disinfection. Lime ($CaCO_3$) is added in the first of three rapid mix tanks to raise the pH up to approximately 10 for complete oxidation of Fe and Mn using $KMnO_4$. The second rapid mix tank provides additional contact time and mixing to allow for the oxidation process. Carbon dioxide ($CO_2$) is added in the third rapid mix tank to decrease the pH (5.5 – 6.0) for optimal coagulation using 8-mg/L alum. During the colder months, a coagulant aid (cationic polymer) is added in the third rapid mix to help increase floc performance. Following the rapid mix are four identical flocculation trains, each having two parallel three stage hydraulic floc tanks. The floc water is then dispersed between seven (eight on site, however one is currently out of commission) anthracite and sand media filters. From bottom to top, each filter contains 12 inches of silica sand and 24 inches of anthracite respectively. Filtered water is then dosed with chlorine for disinfection, sodium hydroxide (NaOH) to bring the final pH to 7.4, zinc/ortho-polyphosphate as a corrosion inhibitor, and hydrofluorosilicic acid to aid in dental health.

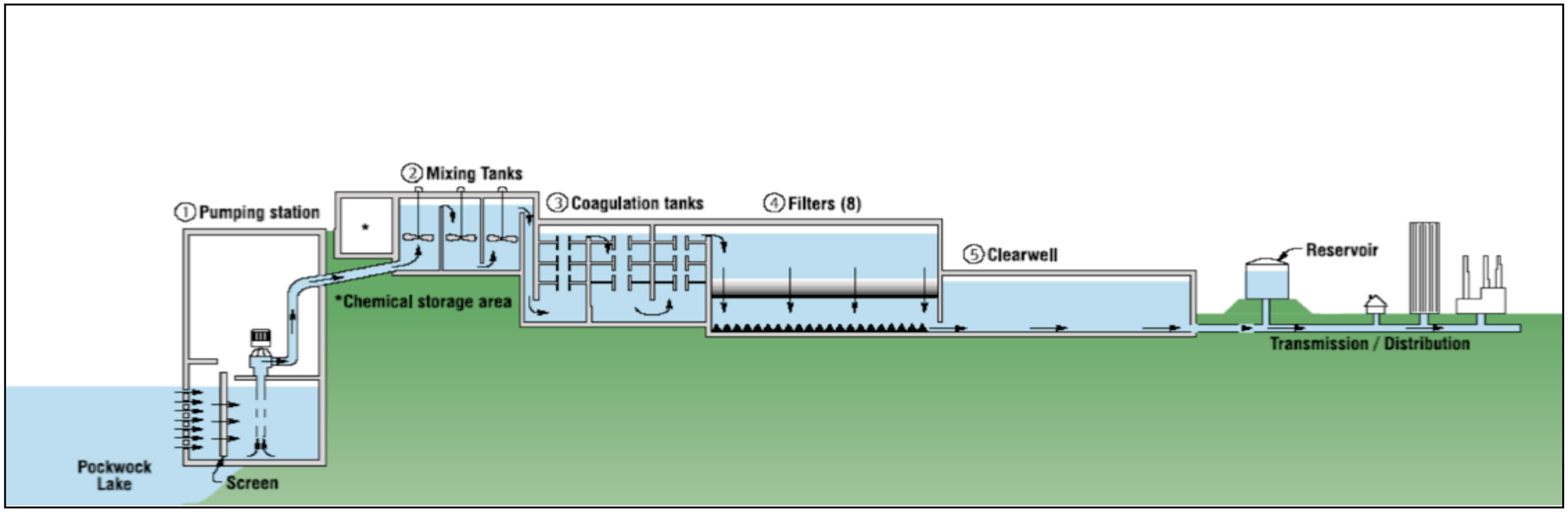

**Figure 4**: Schematic of JDKWSP Treatment Processes (Halifax Water, 2005)

**Table 4**: JD Kline WSP Reported Data from Halifax Water (2014 and 2015)

| **Parameters** | **Raw Water** | | **Treated Water** | |
|---|---|---|---|---|
| | 2014 | 2015 | 2014 | 2015 |
| Alkalinity (as mg/L $CaCO_3$) | < 1.0 | < 1.0 | 20.0 | 22.2 |
| pH | 5.7 | 5.8 | 7.3 | 7.3 |
| Turbidity (NTU) | 0.26 | 0.30 | 0.06 | < 0.09 |
| Total Organic Carbon (mg/L) | 2.5 | 2.6 | 1.5 | 1.5 |

## 3.2 BENCH-SCALE EXPERIMENTAL DESIGN

Three liters of Pockwock Lake raw water was pH adjusted to 6 or 8 using NaOH and nitric acid ($HNO_3$) and then subsequently spiked with a corresponding geosmin dose of 5 or 20 ng/L. Samples were taken immediately following geosmin addition. Remaining sample was then ozonated at 1 or 10 mg/L which resulted in approximately 0.3 and 3 mg $O_3$/mg C. After ozonation, samples were drawn from the contactor and remaining water was used for the bench-scale jar test procedure. Following the jar test, the sample water was filtered and samples were drawn. A process diagram of the bench-scale experimental design is shown in **Figure 5**.

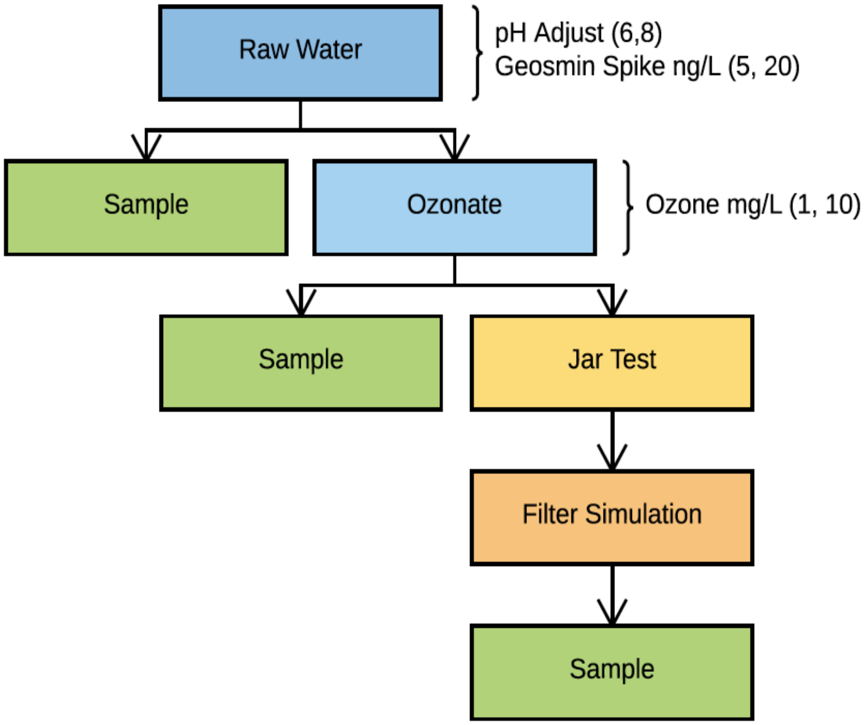

**Figure 5**: Process Diagram for Bench-scale Experiment

### 3.2.1 Bench-scale Ozonation Set-up

The ozonation set-up used in the bench-scale experiment is shown in **Figure 6**. The set-up includes a compressed air cylinder, $O_3$ generator (VMUS-4), a 10 L contactor, and two potassium iodide (KI) off-gas traps. Compressed air at 2 L/min passed through the generator and high voltage corona discharge was used to break off the $O_2$ molecules to form radicals. The radicals then combined with $O_2$ molecules to form the $O_3$. The inlet and outlet tubing to the generator consisted of 4.8 mm diameter MasterFlex® pump tubing (06508-25 PharMed® BPT, Saint-Gobain). Tygon® (R-3603) laboratory tubing was connected to the outlet tubing of the generator by a plastic connector and attached to the contactor. The contactor was fitted with a laboratory stopper (Fisher Scientific #14141R) at the top and included a sample port at the bottom for sample collection. Tygon® tubing was used to attach the contactor to the KI traps. A fine stone bubble diffuser was used to pass the $O_3$ at 2 L/min to the sample solution. Attached to the contactor were the two KI traps, which contained a 2% KI solution (20 g KI in 1 L DI water). The purpose of the traps was to collect any residual $O_3$ gas formed in the reactor. All ozonation experiments were conducted under the laboratory fume hood.

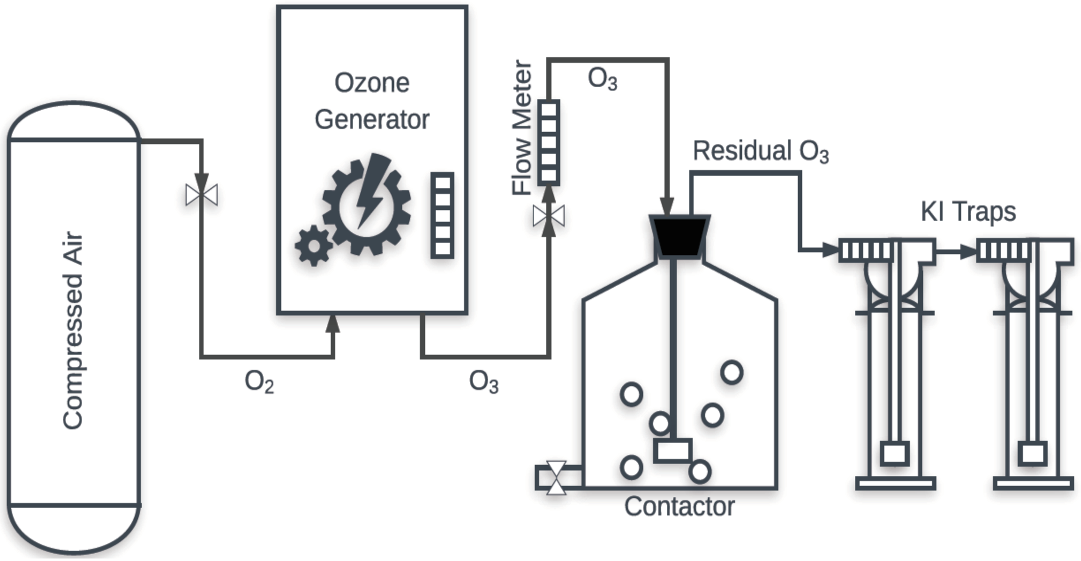

**Figure 6**: Schematic of Ozone Experimental Set-up (Lamsal, 2012).

All ozonation experiments were conducted in semi-batch mode by continuously passing ozone gas for various time intervals. The production of ozone was calculated to be 1.6 ± 0.05 mg $min^{-1}L^{-1}$ following method 2350E (APHA, 1995). The $O_3$ demand of the water sample was calculated by measuring the amount of gaseous $O_3$ collected in the two KI off-gas traps using Equation 4.

$$Ozone\ Demand, mg/\min = ozone\ dose, \frac{mg}{min} - \frac{C*N*24}{T} \qquad [4]$$

C = amount of titrant in mL
N= normality of sodium thiosulfate
T= contact time

### 3.2.2 Jar Test Set-up

Bench-scale jar tests were conducted using a standard Phipps and Bird™ jar tester. All tests were adapted from the typical six-jar test to a one-jar test to better facilitate sampling. Targeting NOM removal and floc formation was the framework for the jar test procedure.

Raw water that was pH adjusted, spiked with geosmin and then subsequently ozonated was used for all bench-scale experiments. All bench scale experiments were conducted immediately following ozonation. pH was adjusted using NaOH and $HNO_3$ to pH 5.8. The coagulant remained constant at 8-mg/L of alum across all treatment combinations. All chemicals were injected using mechanical pipettes. Coagulation and flocculation parameters were chosen based on previous experiments conducted by (Knowles, 2011). Rapid mixing occurred for one minute at 142 rpm, followed by three-tapered flocculation intervals of 12.5 min each at 37, 26, and 18 rpm, respectively.

Immediately following the third flocculation stage was the filtration step. Flocculated water was filtered through a 1.5-µm filter (Whatman, 934-AH) to simulate the direct filtration step at the JDKWSP. Filter paper decreased experimental time for the bench-scale experiment and also proved to provide similar effluent turbidity readings, as cited by (Knowles, 2011).

## 3.3 ANALYTICAL TECHNIQUES

### 3.3.1 General Water Quality Parameters

All pH measurements were conducted using an Accumet XL 50 plastic bodied, gel-filled, accuCap™ combination pH electrode. A three-point pH calibration at 4, 7, and 10 was conducted prior to any measurements using Fisher Scientific standard buffer solutions. Temperature was measured on all raw water using a standard mercury thermometer. Alkalinity was measured following the potentiometric titration to end-point pH method 2320 (APHA, 1995).

### 3.3.2 Natural Organic Matter: DOC, $UV_{254}$, SUVA

TOC and DOC samples were collected and transferred headspace free to 40 mL vials and preserved with concentrated phosphoric acid to pH <2. DOC samples were first filtered through a preconditioned 0.45μm polyethersulfone filter (GVS Life Sciences) that was pre-rinsed with 500 mL of DI water. TOC and DOC samples were analyzed using a TOC-V CHP analyzer (Shimadzu Corporation, Kyoto, Japan). The method detection limit (MDL) for the instrument was 0.5 mg/L. All samples were stored at 4°C prior to analysis. The operating conditions for the TOC analyzer were as follows: TOC standard platinum catalyst, injection volume 50 µL, oven temperature of 680°C, carrier gas flow of 150 mL/min potassium phthalate standards 0 to 10 mg/L, and a correlation of >0.99.

UV absorbance at 254-nm wavelength ($UV_{254}$) was also measured on filtered and non-filtered samples. $UV_{254}$ readings for filtered samples were converted to specific UV absorbance (SUVA) values, which can be used as a surrogate parameter in analyzing the aromatic faction of NOM (Edzwald et al., 1985). The equation used to represent SUVA is shown below. $UV_{254}$ readings were measured on a HACH DR 4000 spectrophotometer (Hach Company, Loveland, CO).

$$SUVA\left(m^{-1} * \frac{L}{mg}\right) = \frac{UV_{254}(cm^{-1})}{DOC\left(\frac{mg}{L}\right)} * 100\ \frac{cm}{m} \qquad [5]$$

### 3.3.3 Molecular Weight Distribution Analysis

A high-pressure liquid chromatograph (Perkin-Elmer Series 200) was used to analyze the molecular size distribution of various organic fractions. All samples were filtered through a 0.45 µm filter that was pre-conditioned with 500 mL DI. Samples were then collected headspace free in pre-cleaned and baked (100°C for 24 hours), 2 mL vials. The method used a TSK G30000SW column (7.5 mm by 300 mm) and a TSKgel SW guard column (7.5 mm by 70 mm) for analysis. The columns were connected to a Perkin Elmer Series 200 Auto sampler and Perkin UV/Vis (254 nm). Samples (100 µL) were injected into the columns at 0.7 mL/min for 30 min. The mobile phase for the SEC-UV/Vis used was 0.02M ammonium acetate. Calibration of the columns consisted of sodium polystyrene sulphonate (PSS) standards at different molecular weights (15000, 7500, 5000, 1500, and 210 Da).

### 3.3.4 Zeta Potential Analysis

Zeta Potential was measured using the Malvern Zetasizer Nano ZS. All measurements were taken at the beginning of each mixing stage during the bench-scale jar test procedures. Measurements were analyzed in triplicate on the instrument.

### 3.3.5 3D Fluorescence Spectroscopy

Samples were filtered (0.45 µm), collected and ran using a benchtop fluorometer (Horiba Aqualog) to yield a fluorescence excitation emission matrix (FEEM). The fluorometer had an excitation range of 230 – 610 nm and an emission range of 250 – 620 nm. The integration interval was 0.1 seconds (s) and the spectral resolution was 3 nm. DI water was used as the blank to perform a validation test for the xenon lamp and to measure the signal-to-noise ratio. The inner filter effect and the 1st and 2nd order Raleigh scattering were removed via normalizing and pre-processing the samples. Samples were then processed following a Fluorescent Regional Integration (FRI) algorithm similar to that of (Chen et al.,2003) which aided in quantifying region-specific changes of fluorescence. Five regions were delineated for all samples. The five regions were defined as aromatic protein I, aromatic protein II, fulvic-like acids, soluble microbial products, and humic-like acids, respectively. The excitation and emission wavelengths for the five regions were as follows, 200 – 250 and 200 – 330, 200 – 250 and 330 – 380, 200 – 250 and 380 – 550, 250 – 340 and 200 – 380, and 250 – 400 and 380 – 550, respectively (Trueman et al., 2016).

## 3.4 TASTE AND ODOUR MEASUREMENT TECHNIQUE

### 3.4.1 Reagent Water

Ultra-pure, deionized (DI) water was obtained using a Milli-Q® purification system and was used to prepare all chemical stock solutions.

### 3.4.2 Solvents

Ethyl Acetate (Fisher HPLC grade) was used to condition the solid phase extraction (SPE) cartridges prior to analysis. Ethyl acetate was also used for the elution factor of the analysis method. Methanol (MeOH, Fisher Optima 0.2μM filtered) was used in combination with various chemicals to prepare working solutions for geosmin analysis. Acetone (Fisher Optima) was used for sterilizing syringes used throughout the procedure for preparing solutions.

### 3.4.3 Chemicals Solutions

**Geosmin and 2-Methylisoborneal Working Calibration Solution.** Geosmin and 2-Methylisoborneal (MIB) mix (100μg/mL in MeOH, SUPELCO 47525-U) was diluted into a 50-mL volumetric flask with MeOH to produce a 150-ng/mL solution.

**Camphor Internal Standard Working Solution.** A 10-mL volumetric flask was used to dilute 20 mg of camphor (Sigma-Aldrich 148075-100G) with MeOH to yield a 2mg/mL stock solution. 50 µL of the stock solution was spiked into a 50-mL volumetric flask yielding a 2µg/mL solution.

**External Quality Control Solution.** A 10-mL volumetric flask was used to dilute 50µL of geosmin (100 µg/mL in MeOH, SUPELCO CRM47522), 250µL of MIB (100µg/mL in MeOH, SUPELCO 47523-U), 80µL of 2,4,6-trichloroanisole (100µg/mL in MeOH, SUPELCO 47526-U), 80µL of 2-isoproply-3-methoxypyrazine (100µg/mL in MeOH, SUPELCO 47527-U), and 80µL of 2-isobutyl-3methoxypyrazine (100µg/mL in MeOH, SUPELCO 47528-U) with MeOH.

### 3.4.4 Geosmin Analysis

Samples were analyzed following the method published by (Wright, Daurie, & Gagnon, 2014) which utilized gas chromatography – tandem mass spectrometry. One internal and one external quality control samples were prepared at 15ng/L of geosmin and MIB working calibration solution and varying concentrations of external quality control solution, respectively. Five standards were prepared using 150ng/L geosmin/MIB stock solution for concentrations of 3, 6, 12, 24, and 48 ng/L, respectively. All samples, quality controls, and standards were spiked with 50µL of camphor internal standard working solution and then subsequently equilibrated to room temperature prior to analysis.

Solid phase extraction (SPE) cartridges were conditioned with 1 mL of ethyl acetate followed by 1 mL of methanol and 3 mL of DI water. A known sample volume is passed through the conditioned SPE cartridge to waste and [any] geosmin present is adsorbed onto the SPE cartridge. Geosmin is then eluted from the SPE cartridge using ethyl acetate solvent. The geosmin-solvent solution is then injected onto the GC-MS where the compounds are chromatographically separated.

Detection of the taste and odor compounds is by MS/MS. The instrument isolates the characteristic “parent” ion of geosmin, which then separates it into “fingerprint” ions, which correspond to positively identify geosmin. The integrated peaks are proportional to the concentration so by using standards, the unknown geosmin concentrations are determined.

The operating parameters of the GC/MS are as follows: Varian CP-3800 GC utilized a CP-8400 Auto sampler, Agilent Ultra Inert 4mm gooseneck liner, injector temperature of 200°C, a 30m x 0.25mm x 0.25µm column using pure helium as the carrier gas, constant flow rate of 0.7mL/min, and a Saturn 2200 ion trap mass spectrometer was used for detection. The parent ion mass of geosmin on the MS has a set parameter of 112 Da, the quantitative ion mass (Da) is set at 97 (Da).

## 3.5 STATISTICAL AND DATA ANALYSIS

Data was analyzed by determining the mean and standard deviation values for the data sets. The error bars presented in each figure are described below each figure as either 95% confidence intervals or one standard deviation. Minitab software was used and factorial analysis by ANOVA was performed to determine which effects were statistically significant. Factors were tested at 95% confidence levels.

# CHAPTER 4 RESULTS AND DISCUSSION

## 4.1 ANALYSIS OF WATER QUALITY PARAMETERS

### 4.1.1 Temperature and Alkalinity

Bench-scale testing was conducted as batch experiments and raw water baseline parameters were measured before each test (**Table 5**). Raw water was collected between March to September of 2015 in 20 L containers and stored at 4°C. All bench-scale experiments reached room temperature (20°C) before undergoing treatment conditions.

Ozonation is affected by several parameters such as the water matrix, alkalinity, pH, and temperature (von Gunten, 2003). The rate of $O_3$ degradation decreases as temperature increases and it follows first order kinetics (Elovitz & von Gunten, 1999). Due to experimental time, constraints, and sensitivity, temperature was not tested as a factor.

Alkalinity of the sample water had a negligible increase when NaOH was added for pH adjustment prior to ozonation experiments based on pH measurements taken before and after ozonation. Samples adjusted to pH 6 and 8 needed an average of 55 and 180 μL of NaOH, respectively. JDKWSP increases the pH to 10 (using Lime) in the first rapid mix basin for optimal performance of $KMnO_4$ oxidation of Fe and Mn. Alkalinity addition was omitted from the jar test procedures due to the complex nature of lime mixing and because $KMnO_4$ was not added.

**Table 5**: Water Quality Parameters Baseline Conditions

| Parameter | Value |
|---|---|
| Alkalinity (mg/L as $CaCO_3$) | 0.3 ± 0.13 |
| Turbidity (NTU) | 0.367 ± 0.065 |
| Temp (°C) | 20 ± 1.03 |
| pH | 5.3 ± 0.05 |
| Geosmin (ng/L) | 3 ± 2.01 |
| DOC (mg/L) | 3.38 ± 0.12 |

### 4.1.2 Background Geosmin Levels

From the Fall of 2012 to Fall of 2016, background geosmin concentrations ranged from 0 to approximately 20 ng/L in Pockwock Lake throughout the year based on data published from Halifax Water (Halifax Water, 2016). Geosmin was measured in the lake and in the treated water leaving the WTP (**Figure 7**). The geosmin concentration profile of the treated water follows suit of the raw water, demonstrating its persistence throughout the various treatment processes. The frequency and cumulative distribution of geosmin observed in Pockwock lake is shown in **Figure 8**. The figure shows that around 50% of the measured geosmin tests were above the human detection limit of 4 ng/L and that 5% of the measured values were greater than 14 ng/L. Conventional treatment lacks the ability of removing geosmin from the water to levels that are undetectable by humans. For that reason, additional processes are necessary to decrease levels below the human threshold limit of 4 ng/L (Bruce et al., 2002; Elhadi et al., 2006; Ho & Newcombe, 2010).

When residents in surrounding communities first detected geosmin in the Fall of 2012, JDKWSP was operating with pre-chlorine (added in the 3rd rapid mix basin). In April of 2013, JDKWSP converted to passive biofiltration through the removal of the pre-chlorination step. Biofiltration is a known technique to improve T&O removal for various source waters (Nerenberg et al., 2000). The months following the conversion to biofiltration, geosmin continued to persist throughout treated water confirming that the pre-chlorination to biofiltration switch did not improve geosmin removal. Strategies to mitigate or improve geosmin removal at the JDKWSP were investigated.

A study conducted in 1996 and 1997 investigated the occurrence of geosmin and other T&O compounds such as MIB in Eastern Lake Ontario and the Upper St. Lawrence River. Conventional sedimentation and filtration water treatment plants within the area experienced many complaints because of an off taste and odor in the finished water. Geosmin and MIB concentrations at that time ranged from 5 to 20 ng/L and 2 to 25 ng/L, respectively. Virtually no change in concentration of the T&O compounds were observed throughout the treatments processes, signifying the inability for conventional treatment plants to mitigate taste and odor control (Ridal et al., 1999).

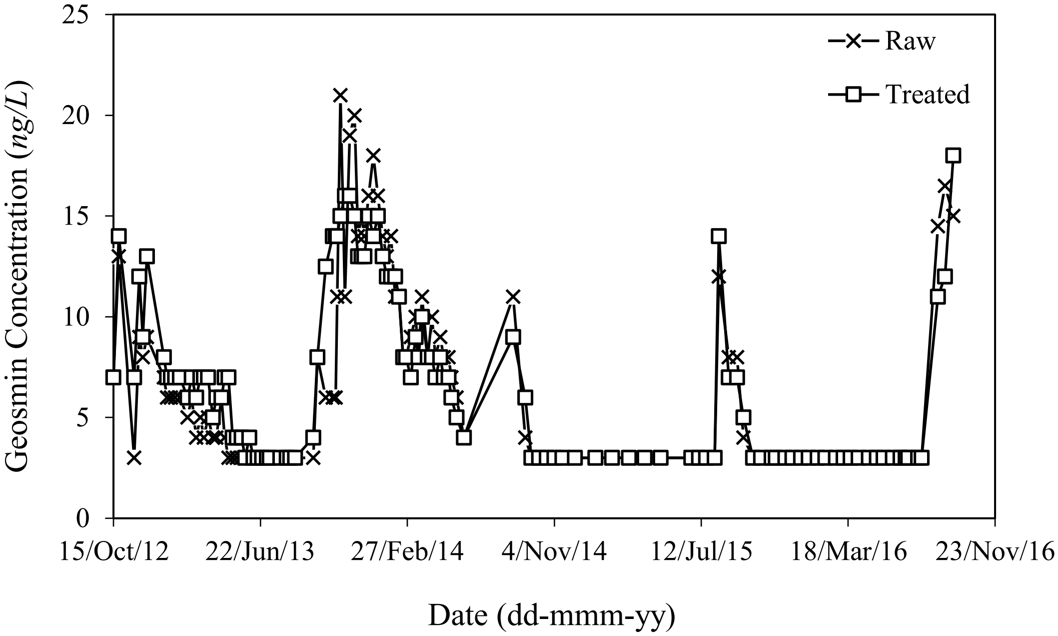

**Figure 7**: Raw and finished water geosmin concentrations at JDKWSP measured from October 2012 to November 2016 (Halifax Water, 2016).

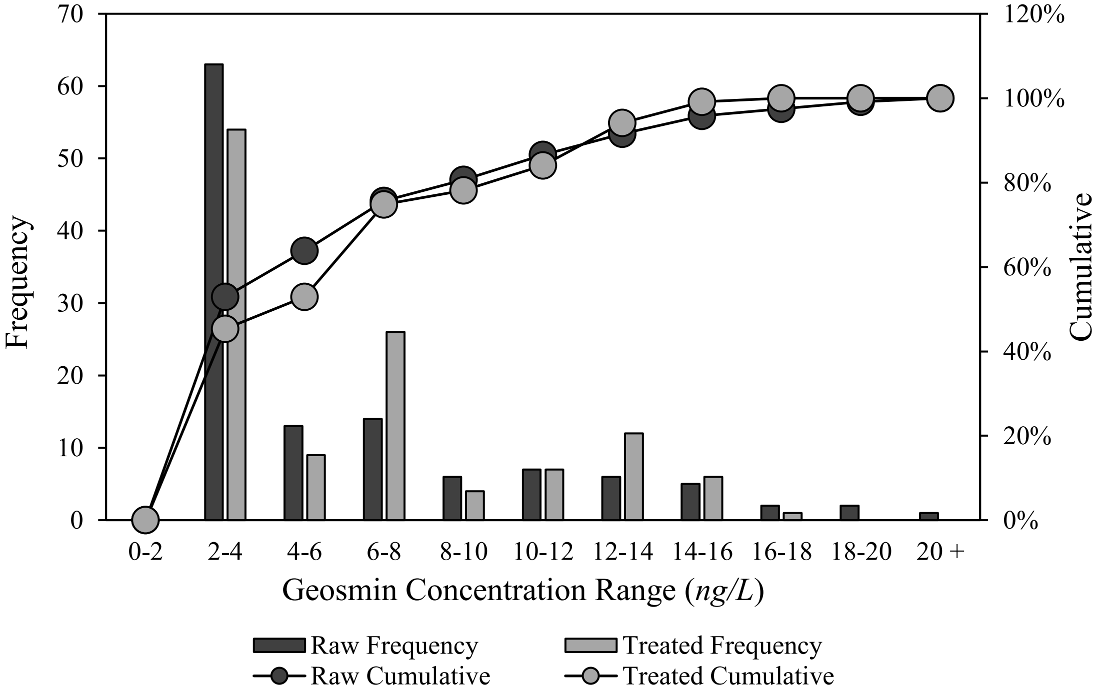

**Figure 8**: Geosmin frequency and cumulative distribution in raw and treated water (Halifax Water, 2016).

## 4.2 PRE-OZONATION ANALYSIS: Demand and •OH Production

### 4.2.1 Ozone Demand

Throughout this study, the theoretical $O_3$ demand of each batch of water was measured using two KI traps in series (**Table 6**). Batches ozonated at 1 mg/L $O_3$ for low and high geosmin concentrations were 91 and 93%, respectively. Batches ozonated at the 10 mg/L $O_3$ for low and high geosmin concentrations were 54 and 59%, respectively. Most $O_3$ was consumed at the low dose, which resulted in very little residual measured in the KI traps. Increased residual $O_3$ was measured in the KI traps at the higher dose, suggesting that some compounds were being oxidized partially or completely. The theoretical stoichiometric amount of $O_3$ needed to oxidize iron and manganese is approximately 0.43 and 0.88 mg/mg, respectively (Langlais et al.,1991). However, determining the amount of $O_3$ required to completely oxidize organic matter is much more difficult to quantify based on the diverse compounds. (Sadrnourmohamadi & Gorczyca, 2015) found that 0.8 mg $O_3$/ mg DOC effectively oxidized organic matter and reduced DOC by 27% while other studies found that $O_3$ had little impact on organic matter removal.

**Table 6:** Ozone Demand of Batch Experiments. Values are in percent

| | **Ozone Dose** | |
|---|---|---|
| **Geosmin Spike** | *Low* | *High* |
| *Low* | 93 | 59 |
| *High* | 91 | 54 |

### 4.2.2 •OH Production

The •OH production from the $O_3$ generator used for the experiments was evaluated using para-chlorobenzoic acid (*p*CBA) as a hydroxyl radical probe compound. The •OH formation was studied on pure DI water and Pockwock Raw water. The same testing conditions for $O_3$ (1 and 10 mg/L) and pH (6 and 8) were evaluated. Water samples were not spiked with geosmin. *p*CBA does not react with $O_3$ or any secondary by-products, but will react and degrade in the presence of •OHs (Pi et al.,2005). The concentration of *p*CBA remaining in solution is directly related to the concentration of •OH formed via ozonation. Each experiment was spiked with approximately 50μM of *p*CBA. The final concentration of each *p*CBA for each experimental condition is shown in **Table 7**. A decrease in *p*CBA concentration was observed for all experiments, signifying the formation of •OHs. Experiments conducted at pH 8 resulted in a greater decline of *p*CBA concentration compared to pH 6 for both pure and raw water.

**Table 7**: *p*CBA Concentration after Ozonation. Points are in triplicate.

| **Ozone Dose** (*mg/L*) | **Pure Water** (*μM*) | | **Raw Water** (*μM*) | |
|---|---|---|---|---|
| | pH 6 | pH 8 | pH 6 | pH 8 |
| 0 | 50.82 | 50.84 | 50.16 | 50.59 |
| 1 | 50.03 | 49.96 | 50.15 | 49.55 |
| 5 | 48.92 | 47.67 | 49.26 | 48.00 |
| 10 | 46.69 | 43.84 | 48.73 | 47.59 |

The degradations rate of *p*CBA in pure and raw water are shown in **Figure 9** and **Figure 10**, respectively. A linear function was fitted for all experiments. The degradation rates for pH 6 in pure and raw water have $R^2$ values of 0.9862 and 0.97106, respectively. The degradation rates for pH 8 in pure and raw water have $R^2$ values of 0.99371 and 0.93003, respectively. Ozone decomposition can be artificially accelerated by increasing the pH, which in turn accelerates the promotion of •OH formation (von Gunten, 2003). A study by (Pi et al., 2005) found that a pH of 8 caused the $O_3$ to decay more rapidly than pH 7 verifying that pH is a factor in •OH formation. In this study the rate of *p*CBA degradation decreased from pure water to raw water at pH 6 and 8 by 38.3 and 37. 9%, respectively. Since most natural waters are partly composed of DOC (humic material), the number of scavenging compounds is greater than pure water. For that reason, the reaction between •OHs and pCBA is inhibited and the oxidization rate of the probe compound is decreased (Pi et al., 2005).

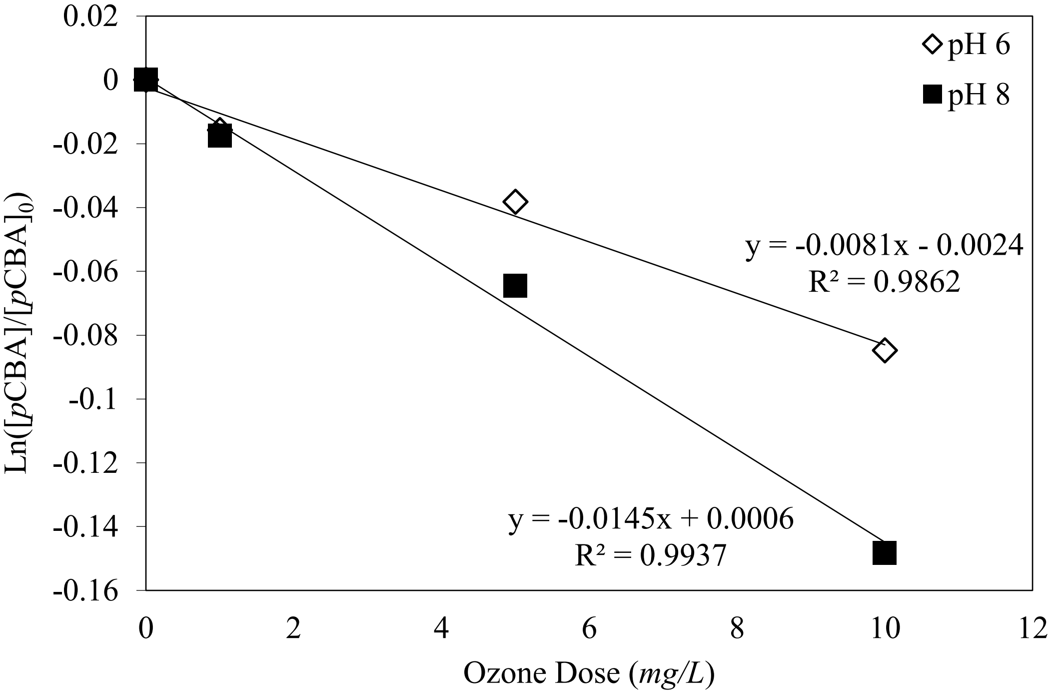

**Figure 9**: *p*CBA degradation in Milli-Q water. Points are in triplicate.

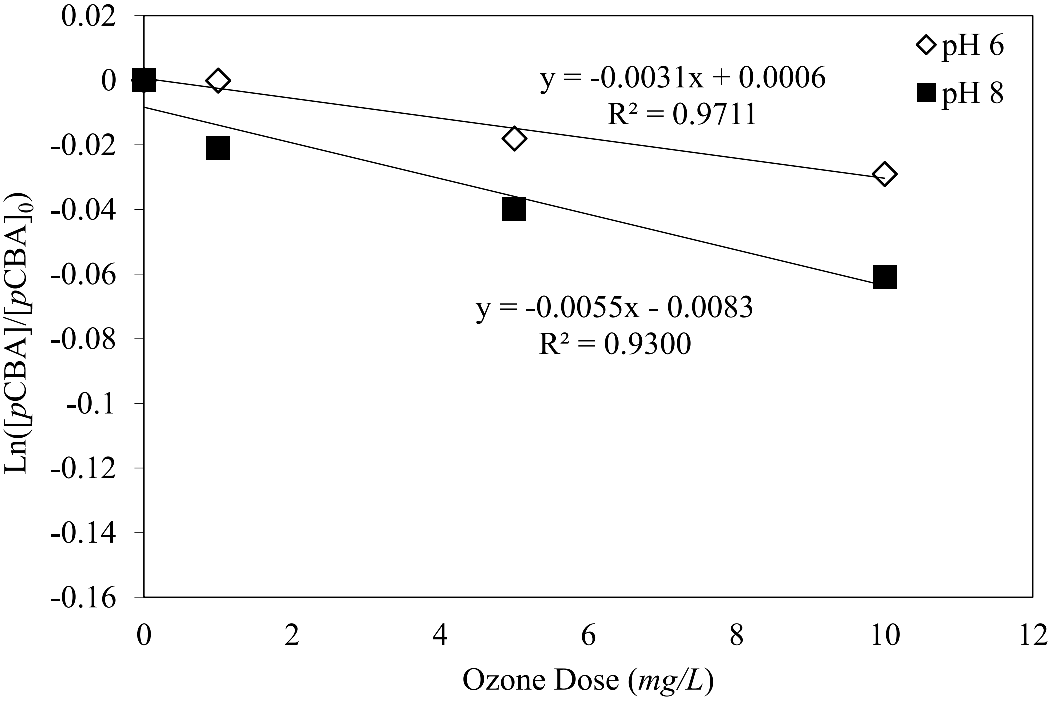

**Figure 10**: *p*CBA degradation in Pockwock lake raw water. Points are in triplicate.

## 4.3 POST-OZONATION ANALYSIS: Geosmin and NOM

### 4.3.1 Effect of Ozone on Geosmin Removal

Geosmin remaining for all treatments post ozonation are shown in **Figure 11** and are as follows. The high-$O_3$/high-GSM/high-pH treatment combination removed the most geosmin post $O_3$ at an average removal efficiency of 79%. Treatment combination, high-$O_3$/high-GSM/low-pH had a removal efficiency of 62%. This corresponds to a 17% increase in removal when the pH was increased from 6 to 8, for the treatment combinations previously mentioned. Alternatively, treatment combinations, high-$O_3$/low-GSM/low-pH and high-$O_3$/low-GSM/high-pH had removal rates of 42% and 62%, respectively. This corresponds to a 20% increase in removal, again by increasing the pH from 6 to 8. Treatment combinations low-$O_3$/high-GSM/low-pH and low-$O_3$/high-GSM/high-pH showed removal efficiencies of 30% and 23%, respectively. Treatment combinations low-$O_3$/low-GSM/low-pH and low-$O_3$/low-GSM/high-pH had removal rates of 20% and 42%, approximately 22% increase from pH 6 to 8.

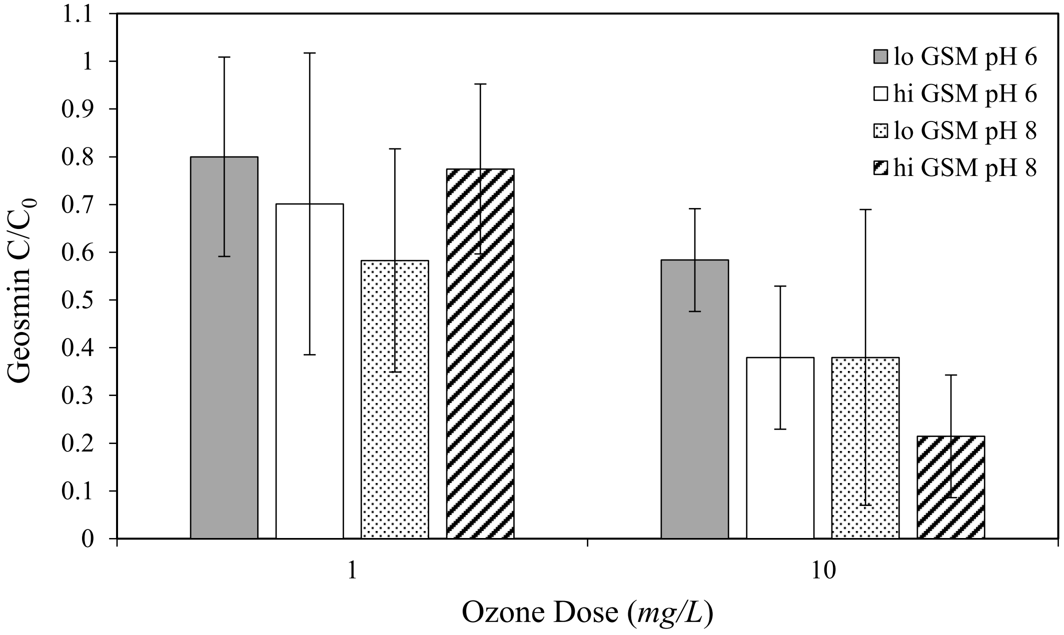

**Figure 11**: Geosmin Removal Post Ozone. Error bars represent a 95% confidence interval.

The additional geosmin removal caused by increasing the pH from 6 to 8 for all treatment combinations (apart from low-$O_3$/high-GSM/High-pH) suggests that •OHs may be a factor. A study by Liang et al., 2007 found that by raising the pH from 5 to 9, geosmin removal increased from 61 to 99% (at an $O_3$ dose of 0.35 mg/L). That study proposed that the additional removal was a direct result of the higher pH causing the auto decomposition rate to increase and promote •OH formation (Liang et al., 2007). The findings from this study support the theory proposed Liang et al., 2007 that a higher pH promotes •OH formation. The *p*CBA data collected in this study (Table 7) also suggests that pH affects $O_3$ decay and plays an important role in •OH formation, thus influencing geosmin removal rates.

The initial geosmin concentration in raw water can influence the type of treatment required for removal and impact the effectiveness of current treatment technologies in a water treatment plant, especially if adsorption is the primary removal technique. In this study, experimental treatment combinations that contained a higher initial geosmin concentration (20 ng/L) achieved slightly greater removal rates than the lower initial geosmin concentration (5 ng/L) except for the low $O_3$ and pH 8 combination. At the low $O_3$ dose and pH 6, there was a 10% removal increase for samples spiked with the 20 ng/L geosmin than at 5 ng/L geosmin. Similarly, samples at the high $O_3$ dose (pH 6 and 8) had approximately 20% and 17% removal increase when initial geosmin concentration was 20 ng/L rather than the low of 5 ng/L, respectively. Contrary to this study, (Yuan et al., 2013) found that the removal rate decreased as initial geosmin concentration increased. However, in their experiments, initial geosmin concentrations ranged from 1 – 2 orders of magnitude greater, making it difficult to draw similarities from the two studies.

A factorial analysis was conducted on the three factors: $O_3$ dose, geosmin concentration, and pH to determine which factors influence the overall removal of geosmin from natural water. Minitab 17 software was used to analyze the three factors as well as the interactions of the three factors. From the analysis, $O_3$ dose was the most significant factor (at 95th confidence interval), having a P-Value of 0.001, in terms of geosmin removal post-$O_3$ (**Table 8**). The normal plot of the standardized effects provides a visual representation of the significant effects (**Figure 12**). Another influential factor was pH, which had a P-Value of 0.088 and therefore was considered insignificant at the 95th confidence interval. The single effect of geosmin concentration (P-Value of 0.526) did not statistically produce a significant effect in terms of geosmin removal from pre-ozonation.

**Table 8**: Analysis of Variance Post-$O_3$

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Model | 7 | 0.92594 | 0.132277 | 3.43 | 0.019 |
| Linear | 3 | 0.71304 | 0.237681 | 6.17 | 0.005 |
| A | 1 | 0.57001 | 0.570011 | 14.80 | 0.001 |
| B | 1 | 0.01621 | 0.016206 | 0.42 | 0.526 |
| C | 1 | 0.12682 | 0.126824 | 3.29 | 0.088 |
| 2-Way Interactions | 3 | 0.17447 | 0.058157 | 1.51 | 0.250 |
| A*B | 1 | 0.10590 | 0.105904 | 2.75 | 0.117 |
| A*C | 1 | 0.00909 | 0.009095 | 0.24 | 0.634 |
| B*C | 1 | 0.05947 | 0.059470 | 1.54 | 0.232 |
| 3-Way Interactions | 1 | 0.03843 | 0.038429 | 1.00 | 0.333 |
| A*B*C | 1 | 0.03843 | 0.038429 | 1.00 | 0.333 |
| Error | 16 | 0.61624 | 0.038515 | | |
| Total | 23 | 1.54218 | | | |

A = Ozone Dose
B = Geosmin Concentration
C = pH

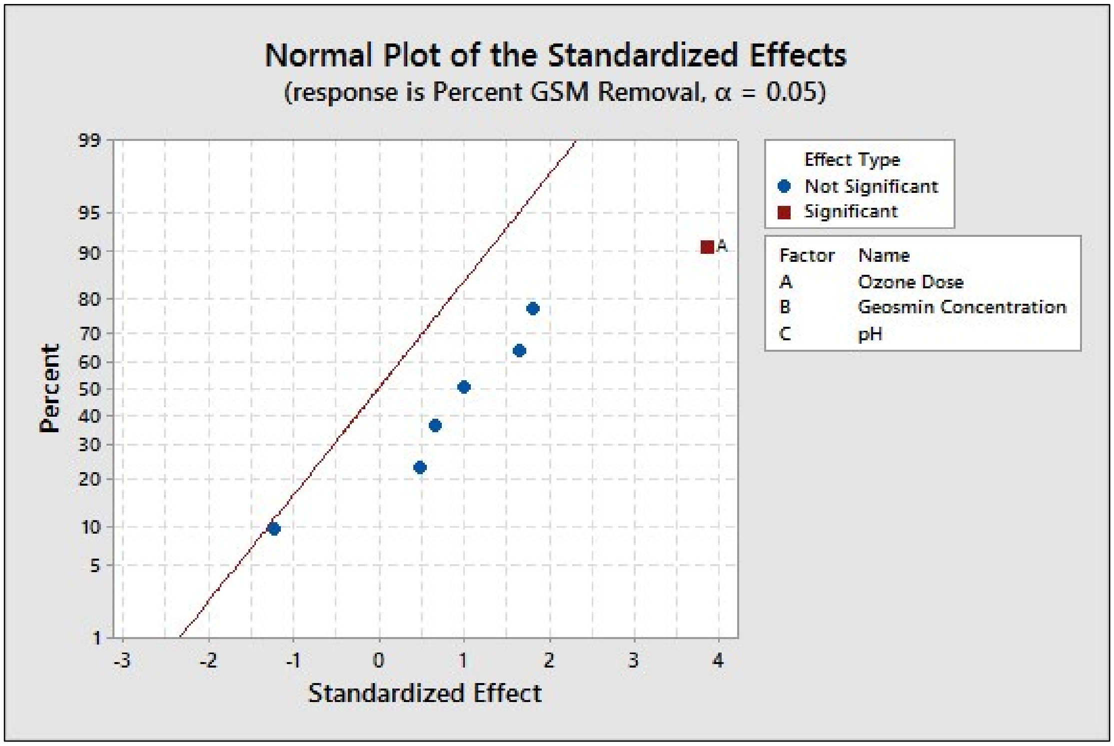

**Figure 12**: Normal Plot of the Standardized Effects (alpha = 0.05)

### 4.3.2 Effect of Ozone on NOM

**Dissolved Organic Carbon**. The effect of $O_3$ on NOM was evaluated by investigating the changes that occur in various NOM parameters. DOC was measured for all treatment conditions following ozonation (**Figure 13**). At the low $O_3$ dose, DOC removal rates ranged from 3 to 10%. At the high $O_3$ dose, DOC removal rates ranged from 2 to 7%. Even though there was no significant removal in DOC from ozonation, the decrease in DOC concentration suggests that several organic compounds experienced partial mineralization. A study by (Sadrnourmohamadi & Gorczyca, 2015) saw similar DOC removal (4% at 0.2 mg $O_3$/mg DOC) but higher DOC removal rates as the $O_3$ dose increased. In this study, the high $O_3$ and DOC ratio was approximately 3 mg $O_3$/mg DOC whereas the high $O_3$ and DOC ratio by (Sadrnourmohamadi & Gorczyca, 2015) was 0.8 mg $O_3$/mg DOC which reduced DOC by 27%. The two $O_3$ doses correspond to concentrations of 10 and 11 mg/L $O_3$, respectively. However, the reason for the difference in DOC removal is presumably the high concentration of DOC available for oxidation by $O_3$ (in the other study).

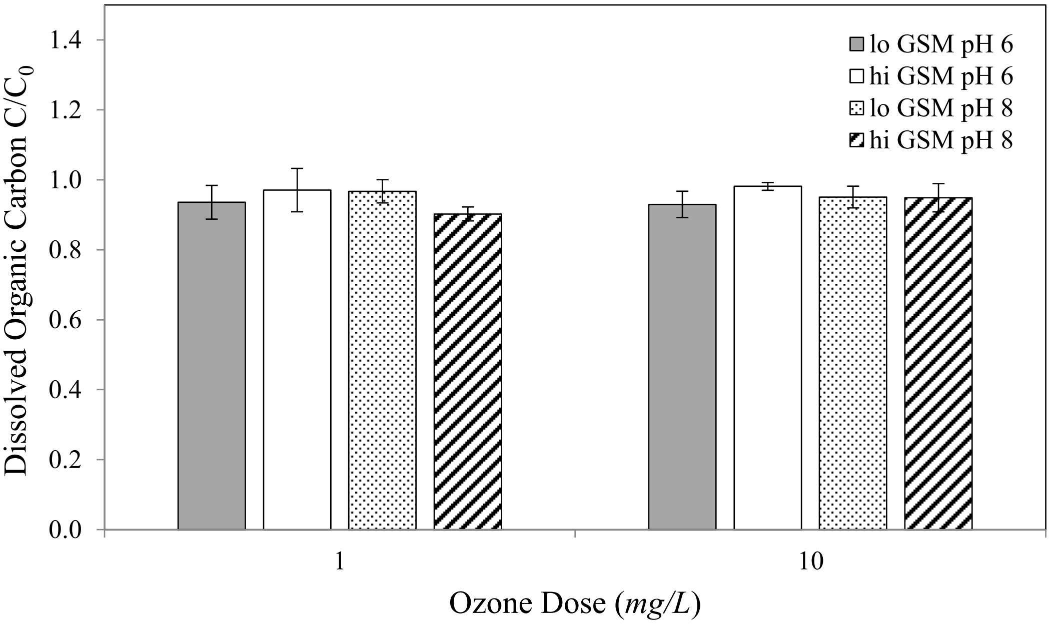

**Figure 13**: DOC removal following ozone. Error bars represent a 95% confidence Interval.

**UV Absorbance at 254 nm**. The UV absorbance at 254 nm ($UV_{254}$) decreased as the $O_3$ dose increased. For all treatment combinations, a reduction in $UV_{254}$ was observed (**Figure 14**) indicating that unsaturated and/or aromatic compounds were oxidized fully and/or partially. At the low $O_3$ dose, $UV_{254}$ was reduced by 3.5% to 6% whereas at the high $O_3$

dose, $UV_{254}$ was reduced by 27% to 31%. The average percent of $UV_{254}$ removal is shown in **Table 9** below. Although $O_3$ is a very selective oxidant, the direct reaction of molecular $O_3$ with double bonded aromatic compounds is said to be the main mechanism rather than •OHs (von Gunten, 2003).

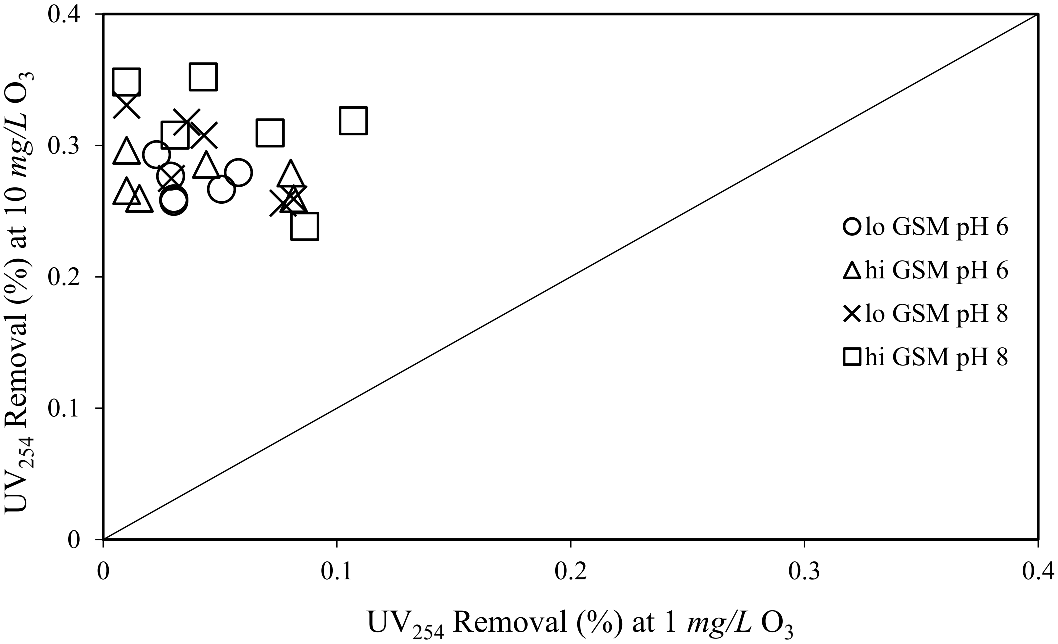

**Figure 14**: Percent $UV_{254}$ Removal Post Ozonation

**Table 9**: Percent $UV_{254}$ Removal Post Ozonation

| | Ozone (1 *mg/L*) | | Ozone (10 *mg/L*) | |
|---|---|---|---|---|
| | pH 6 | pH 8 | pH 6 | pH 8 |
| **Geosmin (5 *ng/L*)** | 3.7 | 4.6 | 27.2 | 29.1 |
| **Geosmin (20 *ng/L*)** | 4.0 | 5.8 | 27.4 | 31.2 |

The substantial decrease in $UV_{254}$ at the high $O_3$ dose and minimal removal in DOC indicated that larger aromatic compounds were mineralized to LMW, oxygenated functional groups such as carboxylic acids, aldehydes, ketones, and alcohols. These smaller MW compounds are resistant to $O_3$ and therefore accumulate within solution. However, due to their high degree of biodegradability, removal can be achieved through biological processes (Camel & Bermond, 1998; von Gunten, 2003) . The increase in $UV_{254}$ removal versus DOC removal is similar to other findings outlined by (Matilainen et al., 2010), confirming that aromatic compounds are removed more efficiently than other NOM fractions.

**Specific UV Absorbance**. A reduction in aromatic compounds and increase in LMW compounds can be problematic for downstream treatment processes. Since the bulk of NOM in natural waters is hydrophobic, humic-like material, and readily removed by chemical coagulation, a change in NOM can complicate the physical/chemical process. Therefore, understanding the quantity and quality of NOM using a parameter such as specific UV absorbance (SUVA) helps to identify optimal treatment techniques. Different SUVA values and their characteristic compositions are shown in **Table 10**. Natural waters with high SUVA values (> 4) typically indicate that organic matter is mostly hydrophobic, HMW, and largely humic-like. Low SUVA values (< 2) indicate that the organic matter is composed of hydrophilic-like material, LMW, and non-humic-like (Edzwald & Tobiason, 2000).

Due to the reduction in $UV_{254}$ at the high $O_3$ dose, a significant decrease in SUVA was observed for all treatments ozonated at 10 mg/L (**Figure 15**). The average SUVA value prior to ozonation was approximately 3.8 $m^{-1}$/mg/L. Very little change in SUVA was observed at an $O_3$ dose of 1 mg/L which corresponds to the limited removal of $UV_{254}$. Treatment combination of high-$O_3$/high-GSM/high-pH resulted in the largest reduction in SUVA value, approximately 29% decrease. This shift in SUVA confirms that $O_3$ changed the composition of NOM, even though very little change in DOC concentration was observed.

In 1998 the United States Environmental Protection Agency (USEPA) issued new guidelines regarding DBPs in drinking water. (Edzwald & Tobiason, 2000) summarized the new regulation and means of controlling DBPs using the treatment strategy of *Enhanced Coagulation* and the requirements that follow. The strategy employs the idea that by removing TOC a decrease in the overall formation of THMs and HAAs in drinking water systems is achieved. TOC removal is based on raw water TOC concertation and alkalinity. The raw water TOC and alkalinity for this study lies within the range of < 2 – 4 mg/L and < 60 mg/L $CaCO_3$, respectively. Therefore, per the USEPA, the required TOC removal is 35%. The expected DOC percent removal at a SUVA value of > 4 and between 2 – 4 is > 50% and 25 – 50%, respectively (for alum coagulation) (Edzwald & Tobiason, 2000). From the results of this study, it is evident that greater DOC removal will be achieved for treatment combinations employing the low $O_3$ dose than treatment with 10 mg/L $O_3$. A study by (Bose & Reckhow, 2007) found that pre-ozonation of raw water mainly reacted with the humic fraction of NOM and caused adverse effects for the coagulation step.

**Table 10**: SUVA and NOM Composition (Adapted from Edzwald and Tobiason 1999)

| **SUVA** (*$m^{-1}$/mg/L*) | **Composition** |
|---|---|
| >4 | High Molecular Weight |
| | High Hydrophobicity |
| | Largely Humic |
| 2 – 4 | Mixture of High and Low Molecular Weight |
| | Mixture of Hydrophobic and Hydrophilic |
| | Mixture of Humic and other NOM Fractions |
| <2 | Low Molecular Weight |
| | Low Hydrophobicity |
| | Mainly Non-Humic |

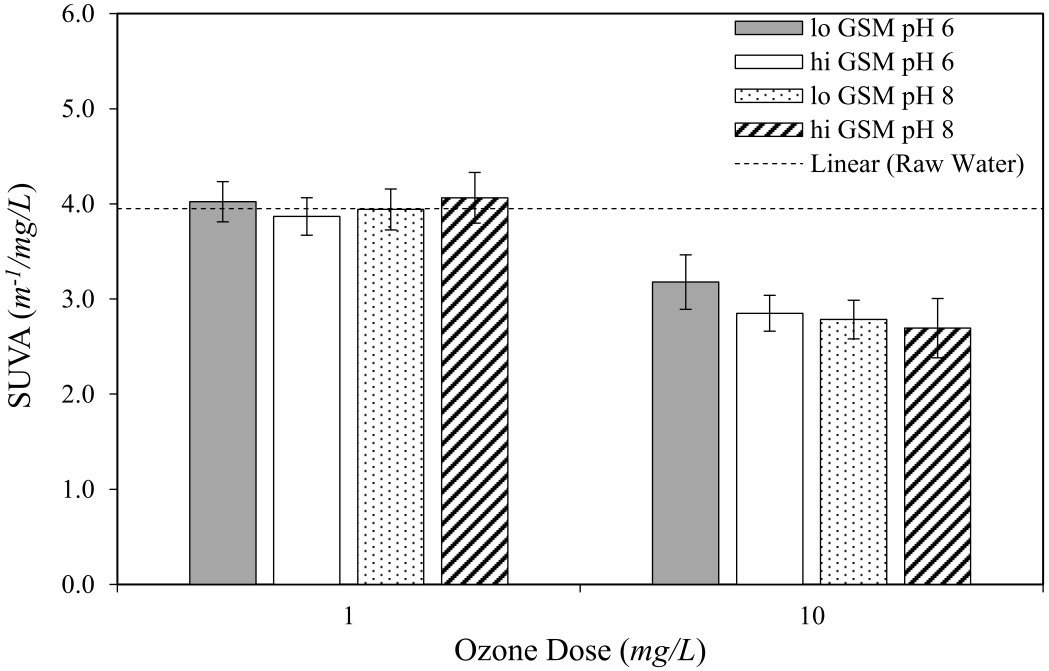

**Figure 15**: SUVA Post Ozonation. Error bars represent a 95% confidence interval

It is expected that by incorporating $O_3$ as a pre-oxidation step, less organic material is present and required to be removed. In this study, organic material post ozonation of 10 mg/L experienced a degree of oxidation which had altered the fractions of organic material that affect other processes. It was shown in Figure 4.9 that $O_3$ played a role in decreasing the SUVA of the natural water and reducing the hydrophobic fraction while increasing the hydrophilic fraction.

**Fluorescence Spectroscopy**. Further characterization of NOM was studied post-ozonation by measuring the intensity of fluorophores within humic and protein-like material. Fluorescent regional integration (FRI) using Matlab Software was used to characterize the change in fluorescence for five distinct regions (**Table 11**), similar to regions delineated by (Trueman et al., 2016). The characteristics of the five regions are as follows, aromatic proteins I, aromatic proteins II, fulvic acid-like, soluble microbial products, and humic acids, respectively. The proportion of total FRI for each region is shown in Table 11 alongside the proportions obtained from (Trueman et al., 2016). FRI for both studies was performed on Pockwock Lake water. Region V is characterized as humic-like organics, representing approximately 79% of the total FRI in this study before any applied treatment. Since humic-like organic matter constitutes most dissolved organic matter in natural waters, effective removal prior to treatment reduces the overall formation potential of DBPs (Bieroza, Bridgeman, & Baker, 2010). All treatment combinations in this study reduced the humic-like region (Region V) by a range of 4 – 45%. An increase in the aromatic protein region I was observed for treatment combinations of high-$O_3$/low-GSM/high-pH and low-$O_3$/high-GSM/high-pH (**Figure 16**).

The fulvic and humic-like regions (III & V) represent over 90% of Pockwock raw water dissolved organic matter. The decrease in $UV_{254}$ absorbance percentage was plotted against the fulvic and humic-like acid region (III & V) removal percentage (**Figure 17**). The coefficient value of $R^2$ for fulvic and humic regions were 0.80 and 0.85, respectively. One study found upwards of 80% removal of fluorescent organic material at the excitation wavelength 290 nm (corresponding to the humic-like region) at $O_3$ dose ranges of 0 – 2 mg $O_3$/mg C (Papageorgious et al., 2017).

**Table 11**: Excitation and Emission Wavelength Ranges for Regions I-V (Adapted from Trueman et al 2016)

| **Region** | **Characteristics** | **Excitation Wavelength** (*nm*) | **Emission Wavelength** (*nm*) | **Pockwock Lake FRI Signal** (*%*) | |
|---|---|---|---|---|---|
| I | Aromatic Protein I | 200 – 250 | 200 – 330 | 1.0[a] | 0.42[b] |
| II | Aromatic Protein II | 200 – 250 | 330 – 380 | 2.1[a] | 1.41[b] |
| III | Fulvic Acids | 200 – 250 | 380 – 550 | 15.2[a] | 12.54[b] |
| IV | Soluble microbial Products | 250 – 340 | 200 – 380 | 9.2[a] | 6.66[b] |
| V | Humic Acids | 250 – 400 | 380 – 550 | 72.6[a] | 78.94[b] |

[a] = Proportions of treated total FRI obtained from Trueman et al. 2016

[b] = Proportions of raw total FRI obtained from this study before simulated treatment

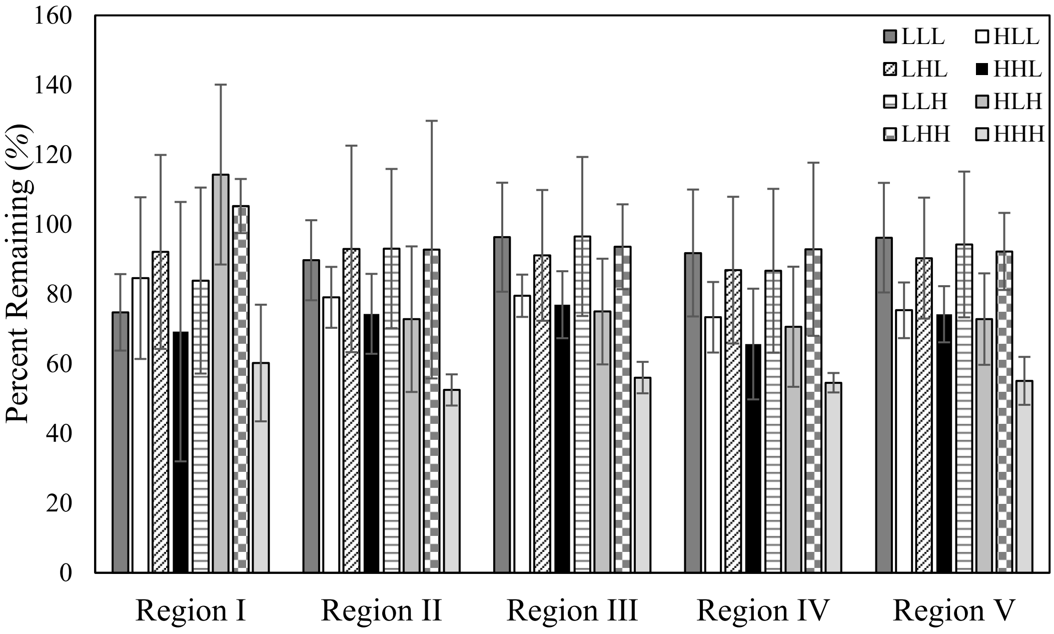

**Figure 16**: Percent remaining for regions I – V post ozone. Error bars represent one standard deviation.

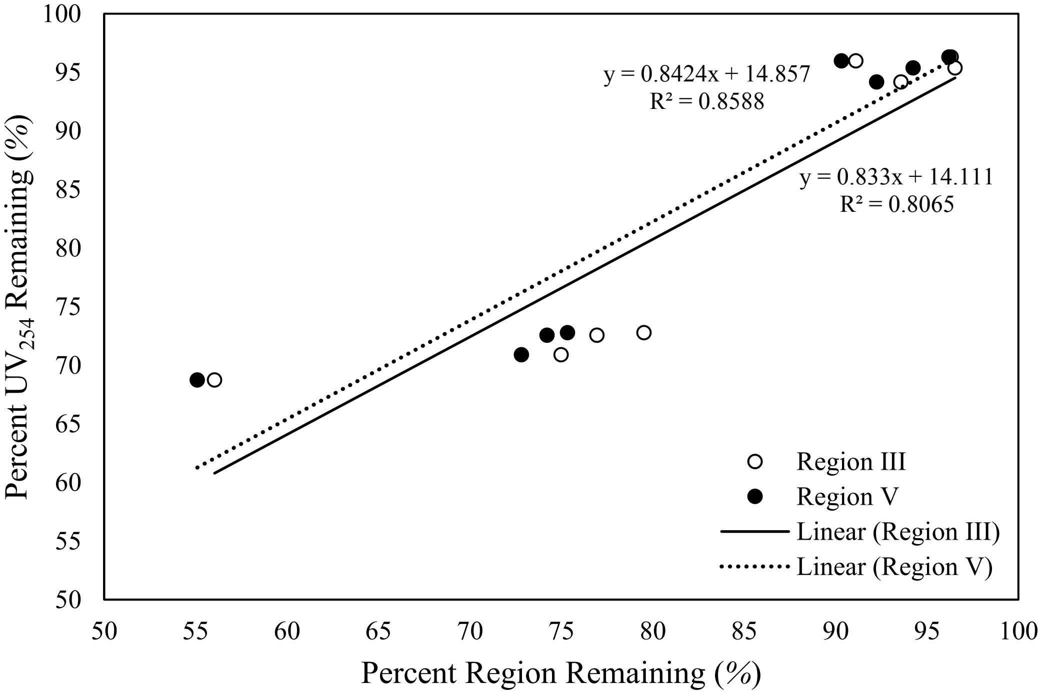

**Figure 17**: Region III & V fluorescence correlated to $UV_{254}$ removal.

## 4.4 TREATMENT SIMULATION ANALYSIS: Geosmin and NOM

### 4.4.1 Effect of Ozone on Coagulation

Zeta potential (ZP) was measured at the start of rapid mix and each subsequent flocculation stage (**Figure 18**). The base control had the ZP hover around -10 mV throughout the duration of the jar test. A ZP of -10 mV lies within the lower end of the desired range for optimal coagulation processes (Sharp et al., 2006). Coagulation of sample water preceded by a low $O_3$ dose experienced ZP values closer in range to the base control. The higher $O_3$ dose caused the ZP to become more negative which resulted in highly charged flocs. Similar observations from other researchers also found that as the $O_3$ dose increased, the ZP decreased (became more negative) (Edwards & Benjamin, 1992; Li et al., 2009).

In a study conducted by (Bose & Reckhow, 2007), detrimental effects on NOM removal during coagulation were observed when pre-oxidized with $O_3$. It was determined that pre-ozonation reacted preferentially with the humic-like substances which resulted in a greater amount of hydrophilic material that was less amenable to coagulation. Floc sized decreased when an $O_3$:DOC ratio of 0.92 was employed, however less than 0.53 mg $O_3$/mg DOC saw no apparent change in floc size (Li et al., 2009). In this study, it was visible that at approximately 3.0 mg $O_3$/mg DOC, floc size was significantly affected. Flocs formed at a slower rate and were smaller in sized compared to samples pre-ozonated at approximately 0.3 mg $O_3$/ mg DOC.

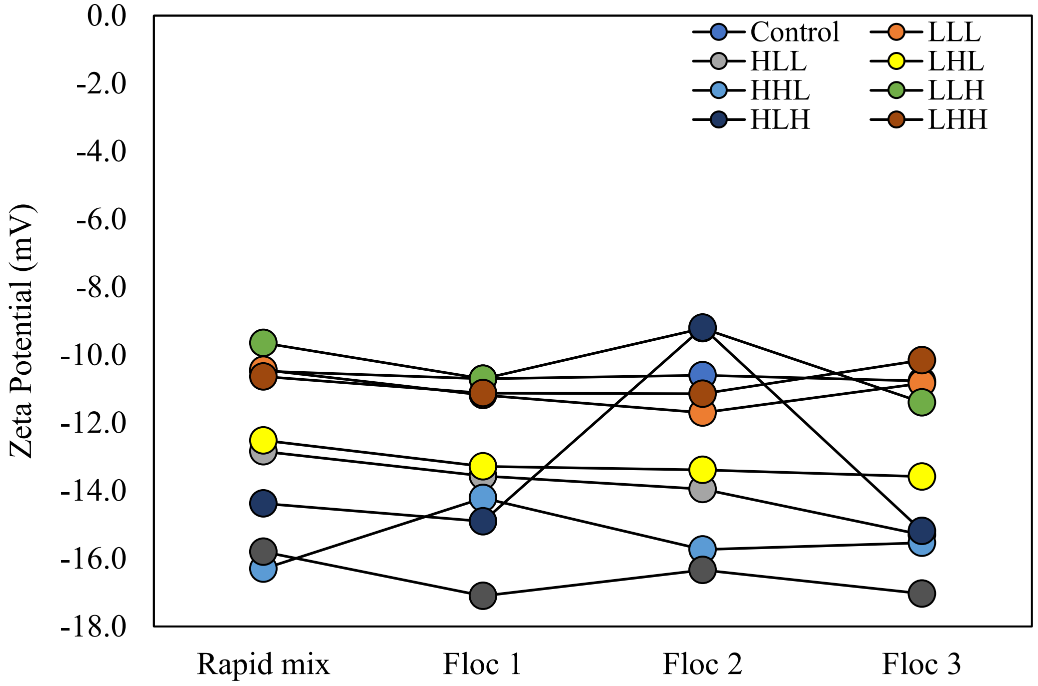

**Figure 18**: Average zeta potential measurement for rapid mix and each corresponding flocculation stage. Legend symbolizes *High or low Ozone Dose/High or Low Geosmin Spike/High or Low pH* (Example, LLL = Low ozone, low geosmin, low pH).

### 4.4.2 Effect of Coagulation, Flocculation, and Filtration on Geosmin Removal

Chemical coagulation was performed using the same alum type (Chemtrade, 48.5% w/w conc.) and dose (8 mg/L) that is applied at JDKWSP. A geosmin spiked (low and high) control test was conducted throughout the duration of the experiment to simulate the treatment removal at JDKWSP. Geosmin concentrations post chemical coagulation, flocculation and simulated filtration were measured after each treatment combination. An increase in geosmin post-filtration was observed for treatment combination lo-$O_3$/high-GSM/low-pH (**Figure 19**). All other treatment combinations experienced some additional geosmin removal. The background control achieved on average 17% removal of geosmin (**Figure 20**). At the high $O_3$ dose, geosmin removal (from treatment) ranged from 10% to 25%. At the low $O_3$ dose, geosmin removal (from treatment) ranged from 3% to 16% (except for the increase of one treatment).

Very little geosmin removal was achieved throughout full-scale treatment (< 5%) based on a yearly average from October 2012 to November 2016. At times, the treated water experienced a slight increase in geosmin compared to raw water. Understanding the ratio of intracellular to extracellular geosmin is important because it tends to influence treatment performance. Removal of extracellular geosmin, in terms of conventional chemical-physical processes is extremely low (less than 20%) whereas removal of cell bound, intracellular geosmin is far more efficient (Zamyadi et al., 2015). Treatment operations and processes such as hydraulic stress or pre-oxidation can lead to lysing of intact cells thereby releasing intracellular geosmin and cause issues downstream (Peterson et al., 1995). The bench-scale filtration step in this study involved a more rigorous filtering mode by vacuuming the sample water through a 1.5 μm filter paper, which had the potential to disrupt intact cells and possibly explain the observed increase of geosmin. Measurement of intracellular versus extracellular geosmin was not within the scope of this research.

Geosmin results post chemical treatment do not follow a similar trend as post-$O_3$, in regards of $O_3$ and pH being a significant influence on removal. At a 95th confidence interval for all factors, $O_3$, geosmin dose, and pH had p-values of 0.133, 0.253, 0.538, respectively (See Appendix for ANOVA results post ozone). Statistical factorial analysis was also conducted using the overall geosmin removal efficiencies (Figure 20). At a 95th confidence interval, $O_3$ was the only significant factor (p-value of 0.001). pH and the interaction of $O_3$ and geosmin concentration, were insignificant factors, having p-values of 0.067 and 0.055, respectively, at the 95th confidence interval (See Appendix for ANOVA results).

Geosmin was removed for all treatments post $O_3$, and post chemical coagulation, flocculation, and filtration. There was one treatment combination that resulted in an increase in geosmin post filtration, however a decrease in geosmin was still observed overall. A summary of geosmin removal is shown in Table 12 below. In general, pre-ozonation and treatment simulation for low geosmin spiked samples achieved adequate removal below the human threshold detection limit of 4 ng/L. In contrast, the samples spiked with the high dose of geosmin did not meet the ideal removal efficiency of below the detection limit except for high-$O_3$/high-GSM/high-pH treatment combination. Final overall geosmin levels for the high dose ranged from 3.6 to 9.2 ng/L.

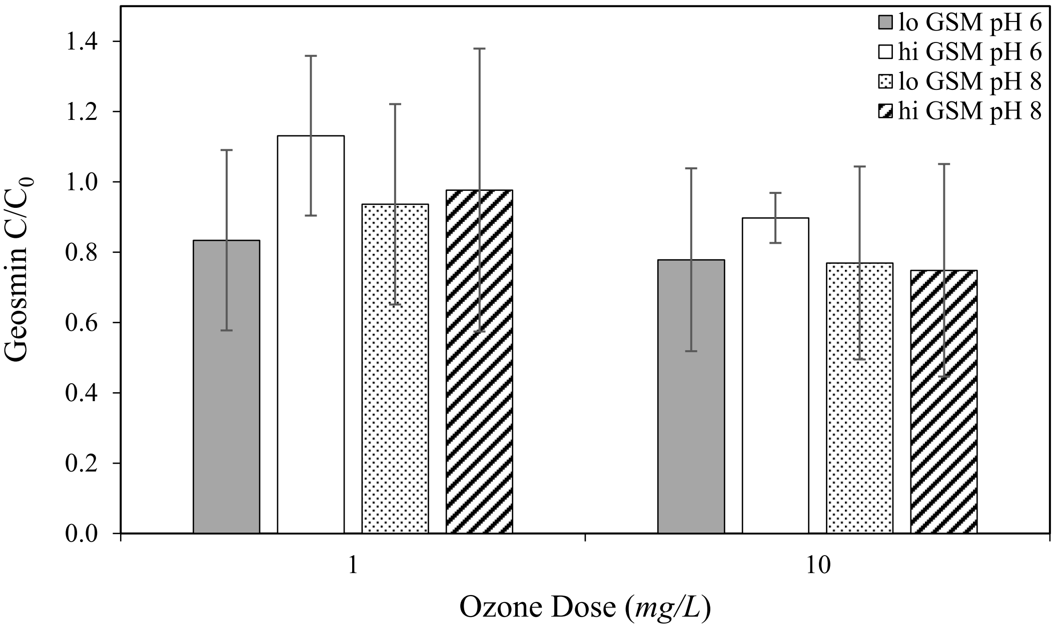

**Figure 19**: Geosmin removal post chemical coagulation, flocculation and filtration. Error bars represent a 95% confidence interval.

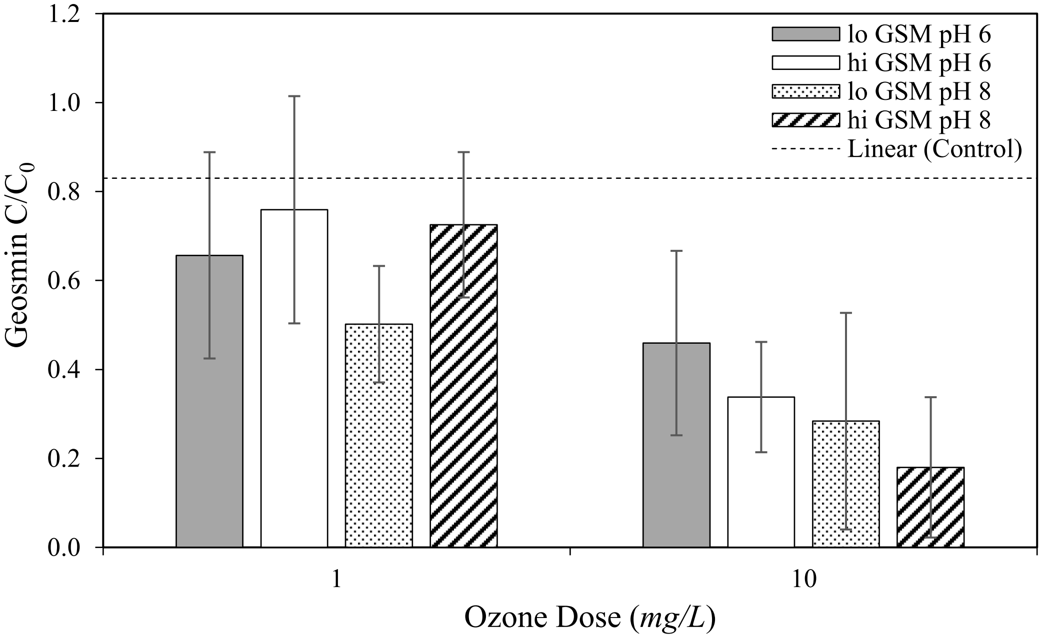

**Figure 20**: Overall geosmin removal post-ozonation and treatment simulation. Errors bars represent a 95% confidence interval.

**Table 12**: Percent average geosmin remaining after each operational process and overall treatment.

| **Ozone Dose (*mg/L*)** | **Geosmin Spike (*ng/L*)** | **pH** | **Post – $O_3$** | **Post – Treatment** | **Overall** |
|---|---|---|---|---|---|
| 1 | 5 | 6 | 80.0 | 83.4 | **65.6** |
| 10 | 5 | 6 | 58.3 | 77.8 | **45.9** |
| 1 | 20 | 6 | 70.1 | 113.0 | **75.8** |
| 10 | 20 | 6 | 37.9 | 89.7 | **33.7** |
| 1 | 5 | 8 | 58.2 | 93.6 | **50.1** |
| 10 | 5 | 8 | 37.9 | 76.9 | **28.3** |
| 1 | 20 | 8 | 77.4 | 97.6 | **72.5** |
| 10 | 20 | 8 | 21.4 | 74.8 | **17.9** |

### 4.4.3 Effect of Coagulation, Flocculation, and Filtration on NOM

**Dissolved Organic Carbon**. Based on the previous DOC results in *section 4.3.2*, little organic matter was completely oxidized by $O_3$ itself. However, the objective of chemical coagulation is to remove colloidal material, infectious agents, and toxic compounds as well as NOM to reduce the DBP formation potential (Howe et al., 2012). Prior to commencing the jar test procedure for NOM removal, it was identified that $O_3$ targeted the humic-like aromatic compounds and partially mineralized larger MW compounds into smaller LMW compounds. Since coagulation targets the HMW, humic-like, and more hydrophobic fractions, detrimental effects were observed for DOC removal post treatment at the high $O_3$ dose (**Figure 21**).

Treatment at the high $O_3$ dose experienced adverse effects in terms of required NOM removal. The control test achieved on average 40% DOC removal whereas the treatment combinations at the high $O_3$ dose achieved between 30 to 35% removal. Treatment combinations involving the low $O_3$ dose ranged from 40 to 45% DOC removal, implying that $O_3$ added an extra 5% removal efficiency compared to the base control.

Results from (Sadrnourmohamadi & Gorczyca, 2015) found that DOC removal via coagulation was enhanced by pre-ozonation. It was observed that at a 0.8 mg $O_3$/mg DOC ratio, greater DOC removal was achieved compared to the lower ratios of 0.2 mg and 0.6 mg $O_3$/mg DOC. It could be hypothesized that by increasing the mg $O_3$/mg DOC ratio in this study, similar results may be overserved since the 0.3 mg $O_3$/mg DOC did provide some added benefit.

In addition, slightly higher DOC removal rates were observed post coagulation for treatments pre-ozonated at the lower pH. As the pH increased from 6 to 8, DOC removal decreased. These results coincide with previous work by others, showing that DOC removal rates on pre-ozonated water decreased as pH increased (Ratpukdi et al., 2010; Sadrnourmohamadi & Gorczyca, 2015).

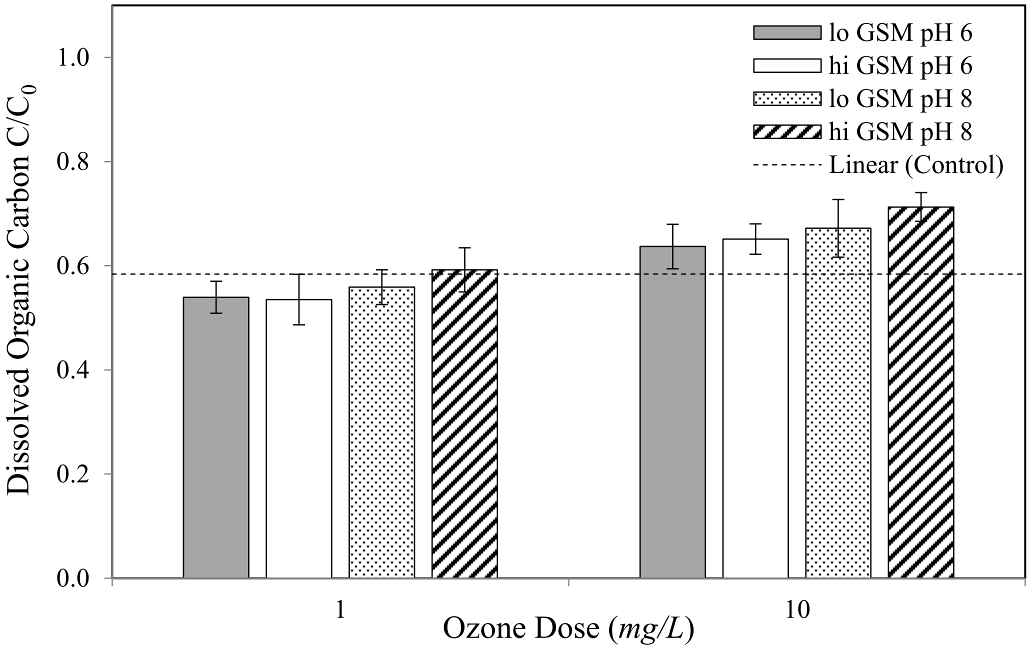

**Figure 21**: Overall dissolved organic carbon removal. Error bars represent 95% confidence intervals.

**UV Absorbance at 254 nm**. The change is $UV_{254}$ throughout the entire treatment process, from pre-ozonation to coagulation and filtration is outlined in **Table 13**. Results obtained post-$O_3$ indicated a substantial decrease in $UV_{254}$ from the high $O_3$ dose. Little reduction was observed at the lower $O_3$ dose. However, after chemical physical treatment, the percent range of $UV_{254}$ remaining for all treatment combinations narrowed, proving that chemical treatment was the main factor for NOM removal.

Post-treatment coagulation results preceded by a low $O_3$ dose resulted in greater overall removal of $UV_{254}$. Samples ozonated at the low and high $O_3$ dose saw removal of $UV_{254}$

range from 69% to 72% and 39% to 63%, respectively, post-treatment. The base control achieved on average 70% reduction in $UV_{254}$. The overall reduction in $UV_{245}$, for both low and high $O_3$ ranged from 70% to 73% and 58% to 73%, respectively. The low $O_3$ dose seemed to provide results that were on par or slightly better than the base control.

**Table 13**: Percent $UV_{254}$ remaining after each operational process and overall treatment.

| Ozone Dose (*mg/L*) | Geosmin Spike (*ng/L*) | pH | Post – $O_3$ | Post – Treatment | Overall |
|---|---|---|---|---|---|
| 1 | 5 | 6 | 96.3 | 30.1 | **28.9** |
| 10 | 5 | 6 | 72.8 | 37.2 | **27.1** |
| 1 | 20 | 6 | 97.2 | 29.8 | **28.8** |
| 10 | 20 | 6 | 72.6 | 41.2 | **30.0** |
| 1 | 5 | 8 | 95.4 | 31.4 | **30.0** |
| 10 | 5 | 8 | 70.9 | 45.9 | **32.4** |
| 1 | 20 | 8 | 94.4 | 28.5 | **26.9** |
| 10 | 20 | 8 | 68.8 | 61.5 | **42.1** |

**Specific UV Absorbance**. Prior to chemical and physical treatment processes, the SUVA values for low and high $O_3$ treatment were substantially different. High $O_3$ treatment decreased the SUVA values between 2 – 4, indicating a decrease in hydrophobic material and increase in hydrophilic material whereas a low $O_3$ dose had little effect on the SUVA value. However, after coagulation, all treatment combinations achieved a SUVA of ± 2, suggesting that most dissolved compounds were LMW, hydrophilic material (**Table 14**). The base control ended with a final SUVA value of approximately 2 after treatment.

The proposed guidelines on the nature of NOM and expected removal outlined by (Edzwald & Tobiason, 2000) recommended a DOC reduction of 25 – 50% for SUVA values ranged 2 – 4. Expected removal was met for all treatment combinations. Although $O_3$ initially reduced SUVA, coagulation and filtration proved to be the main source of removal, based on a similar SUVA observed afterwards for all treatments.

**Table 14**: Average SUVA after each operational process and overall final value

| **Ozone Dose (*mg/L*)** | **Geosmin Spike (*ng/L*)** | **pH** | **Pre – $O_3$** | **Post – $O_3$** | **Treated** |
|---|---|---|---|---|---|
| 1 | 5 | 6 | 3.9 | 4.0 | **2.1** |
| 10 | 5 | 6 | 4.0 | 3.2 | **1.7** |
| 1 | 20 | 6 | 3.9 | 3.9 | **2.1** |
| 10 | 20 | 6 | 3.9 | 2.9 | **1.8** |
| 1 | 5 | 8 | 4.0 | 3.9 | **2.1** |
| 10 | 5 | 8 | 3.7 | 2.8 | **1.8** |
| 1 | 20 | 8 | 3.9 | 4.0 | **1.8** |
| 10 | 20 | 8 | 3.7 | 2.7 | **2.2** |

**Fluorescence Spectroscopy.** The percent fluorescence remaining for all five regions after chemical coagulation and filtration is shown in **Figure 22**. All treatments involving $O_3$ achieved more removal in all five regions than the base control. Regions III and V resulted in the highest removal (for all treatment combinations) due to their higher molecular weight, hydrophobic characteristic nature, and affinity towards coagulation. Therefore, it can be hypothesized that a reduction in THMs would occur, since humic substances are the main contributor to THM formation potential (Sadrnourmohamadi & Gorczyca, 2015).

Regions III and V had an average of 25% to 40% and 28% to 41% remaining, respectively, whereas the base control had approximately 58% remaining for the same regions.

Region I, also known as the aromatic protein I observed the lowest removal rates compared to the other four regions. Treatment combinations high-$O_3$/high-GSM/low-pH and high-$O_3$/low-GSM/high-pH experienced an increase in region I where all other treatment combinations achieved some removal.

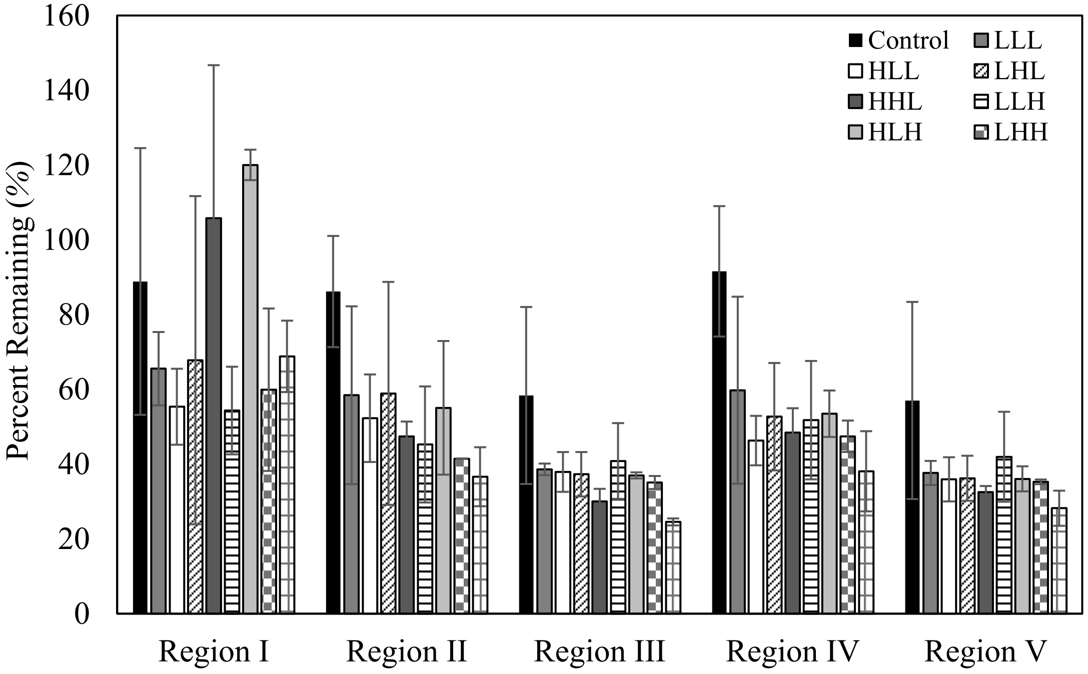

**Figure 22**:Percent Remaining for regions I – V post treatment. (Error bars represent one standard deviation)

## 4.5 PROPOSED GEOSMIN REMOVAL MECHANISM

Geosmin from Pockwock Lake water was partially removed when pre-$O_3$ was applied to the raw water. The formation of •OHs likely had a strong role in oxidizing geosmin, especially when the pH was increased from 6 to 8. A higher pH accelerates the auto decomposition of molecular $O_3$ to •OHs which are far less selective as an oxidant (Liang et al., 2007). Although the initial geosmin concentration was not a statistically significant factor, the removal rates seemed to be more efficient when high concentrations (>20 ng/L) of geosmin were present. Coagulation, flocculation and filtration slightly aided in the overall geosmin removal when preceded by $O_3$. However, for some treatments, an increase in geosmin was observed. It is likely that geosmin was present in both intracellular and extracellular forms and that $O_3$ may have caused some cells to lyse or the filtration step disrupted the cell integrity resulting in an increase in extracellular geosmin.

# CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

## 5.1 CONCLUSION

This study was conducted to determine if applied ozone to Pockwock raw water could oxidize and/or remove geosmin below the human threshold detection limit of 4 ng/L while observing added benefits downstream in terms of improved NOM removal. Pockwock Lake experiences seasonal taste and odor issues related to geosmin occurrences which affects consumers and ultimately poses problems for the local water utility.

This experiment examined the ability of pre-ozonation of geosmin-containing raw water (at various concentrations) at pH 6 and pH 8 to remove the taste and odor compound to undetectable levels by humans. Two applied ozone doses of 1 and 10 mg/L (0.3 and 3 mg $O_3$/ $C^{-1}$) were evaluated. The ozone dose was a statistically significant factor (P-value of 0.001) in terms of geosmin removal at a 95th confidence interval post-ozone, while pH followed (insignificantly) having a P-value of 0.088. The role of hydroxyl radicals was suggested as the main mechanism for geosmin removal post-ozone. Coagulation treatment improved the overall geosmin removal when it was preceded by pre-ozonation. Low levels of geosmin < 5 ng/L in raw water were effectively removed (to below 4 ng/L) at both low and high ozone doses. When geosmin reached levels of >20 ng/L, ozone effectively reduced the taste and odor compound, however non-detect levels were difficult to achieve.

The added benefits of applied ozone to raw water were noticed when characterizing the changes in NOM. Ozone effectively targeted the humic-like substances which was immediately observed in the $UV_{254}$ and SUVA results. At the low ozone dose, coagulation was not negatively impacted and an increase in DOC removal was observed. As the ozone dose increased, detrimental effects were observed during coagulation and flocculation. Increased ozone decreased zeta potential, and in turn, adversely affected floc formation. Thus, DOC removal decreased. Overall, ozone was able to partially oxidize organic compounds and break up larger molecular weight compounds into lower-molecular weight oxygenated products. This improved removal of protein-like material based on the fluorescence removal post treatment.

This bench-scale experiment acts as a preliminary study for those wishing to investigate the relationship of ozone and target taste and odor compounds/coagulant interactions in a more detailed matter. Future research should examine the byproducts formed from pre-ozonation and the potential biodegradation that occurs within a biofilter, specifically if Pockwock Lake raw water is the focus.

## 5.2 RECOMMENDATIONS

Pre-ozonation could be used as an oxidant prior to chemical and physical treatment at JDKWSP to help remove seasonal taste and odor issues. Adding an oxidant such as ozone can alter the characteristics of NOM to become more amenable for biofiltration which can ultimately improve organic matter removal and enhance the finished water quality. The author suggests that future research is needed to evaluate the biological aspect of geosmin degradation and that pilot-scale research would be valuable in determining the optimal operating mg $O_3$/ DOC dose that achieves desired geosmin removal while not adversely affecting NOM removal.

Using ozone versus chlorinated oxidants limits the potential for DBPs downstream which then becomes a more attractive process technique as guidelines on DBPs become more stringent. Introducing other oxidants in combination with $O_3$ to promote hydroxyl radical production could provide better geosmin removal overall. If AOPs are of interest, the author suggests testing at the bench or pilot-scale so that unintended consequences to downstream processes could be studied. Ozone production and maintenance may be cost effective (in comparison to other treatments) but the installation and capital expenditure is costly. Therefore, it is extremely important to determine if the treatment advantages of ozone outweigh customer complaints to a non-health risk, taste and odor issue.

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# APPENDIX

## Factorial Regression: % Remaining Post Treatment versus Ozone, Geosmin, pH

```
Analysis of Variance

Source               DF   Adj SS    Adj MS  F-Value  P-Value
Model                 7  0.34173  0.048819     0.81    0.594
  Linear              3  0.26027  0.086758     1.43    0.270
    Ozone             1  0.15137  0.151368     2.50    0.133
    Geosmin           1  0.08497  0.084966     1.40    0.253
    pH                1  0.02394  0.023940     0.40    0.538
  2-Way Interactions  3  0.07914  0.026379     0.44    0.730
    Ozone*Geosmin     1  0.02954  0.029540     0.49    0.495
    Ozone*pH          1  0.00154  0.001536     0.03    0.875
    Geosmin*pH        1  0.04806  0.048061     0.79    0.386
  3-Way Interactions  1  0.00232  0.002321     0.04    0.847
    Ozone*Geosmin*pH  1  0.00232  0.002321     0.04    0.847
Error                16  0.96805  0.060503
Total                23  1.30978


Model Summary

       S    R-sq  R-sq(adj)  R-sq(pred)
0.245974  26.09%      0.00%       0.00%


Coded Coefficients

Term               Effect     Coef  SE Coef  T-Value  P-Value   VIF
Constant                    0.8775   0.0502    17.48    0.000
Ozone             -0.1588  -0.0794   0.0502    -1.58    0.133  1.00
Geosmin            0.1190   0.0595   0.0502     1.19    0.253  1.00
pH                -0.0632  -0.0316   0.0502    -0.63    0.538  1.00
Ozone*Geosmin     -0.0702  -0.0351   0.0502    -0.70    0.495  1.00
Ozone*pH          -0.0160  -0.0080   0.0502    -0.16    0.875  1.00
Geosmin*pH        -0.0895  -0.0447   0.0502    -0.89    0.386  1.00
Ozone*Geosmin*pH   0.0197   0.0098   0.0502     0.20    0.847  1.00


Regression Equation in Uncoded Units

% Remaining = 0.29 + 0.033 Ozone + 0.0666 Geosmin + 0.073 pH
- 0.0031 Ozone*Geosmin
              - 0.0054 Ozone*pH - 0.0076 Geosmin*pH + 0.00029 Ozone*Geosmin*pH
```

## Factorial Regression: % Overall Remaining versus Ozone Dose, Geosmin Concentration, pH

```
Analysis of Variance

Source                                  DF   Adj SS   Adj MS  F-Value  P-Value
Model                                    7   9553.9  1364.84     4.57    0.006
  Linear                                 3   8050.7  2683.56     8.98    0.001
    Ozone Dose                           1   6831.7  6831.68    22.86    0.000
```

```
    Geosmin Concentration              1     66.1    66.13     0.22    0.644
    pH                                 1   1152.9  1152.87     3.86    0.067
  2-Way Interactions                   3   1434.0   478.01     1.60    0.229
    Ozone Dose*Geosmin Concentration   1   1276.9  1276.92     4.27    0.055
    Ozone Dose*pH                      1     47.7    47.71     0.16    0.695
    Geosmin Concentration*pH           1    109.4   109.40     0.37    0.554
  3-Way Interactions                   1     69.2    69.16     0.23    0.637
    Ozone Dose*Geosmin Concentration*pH  1     69.2    69.16     0.23    0.637
Error                                 16   4781.6   298.85
Total                                 23  14335.5


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
17.2873  66.65%     52.05%      24.95%


Coded Coefficients

Term                                 Effect    Coef  SE Coef  T-Value  P-Value
VIF
Constant                                      48.38     3.53    13.71    0.000
Ozone Dose                           -33.74  -16.87     3.53    -4.78    0.000
1.00
Geosmin Concentration                  3.32    1.66     3.53     0.47    0.644
1.00
pH                                   -13.86   -6.93     3.53    -1.96    0.067
1.00
Ozone Dose*Geosmin Concentration     -14.59   -7.29     3.53    -2.07    0.055
1.00
Ozone Dose*pH                         -2.82   -1.41     3.53    -0.40    0.695
1.00
Geosmin Concentration*pH               4.27    2.14     3.53     0.61    0.554
1.00
Ozone Dose*Geosmin Concentration*pH   -3.40   -1.70     3.53    -0.48    0.637
1.00


Regression Equation in Uncoded Units

% Overall Remaining = 136.9 - 3.3 Ozone Dose - 2.52 Geosmin Concentration
- 12.2 pH
                      + 0.136 Ozone Dose*Geosmin Concentration
+ 0.32 Ozone Dose*pH
                      + 0.561 Geosmin Concentration*pH
                      - 0.050 Ozone Dose*Geosmin Concentration*pH
```