Advanced Water Treatment Strategies for the Removal of Natural and Synthetic Organic Contaminants

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.
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Patrick Halevy

ABSTRACT

Prior to full-scale implementation of process modifications at the Brantford Water Treatment Plant in 2011, a pilot-scale treatability study was conducted to investigate intermediate ozone chemical oxidation, with or without hydrogen peroxide, and to determine the most suitable granular media type (anthracite, GAC, and Filtralite®) for deep-bed biological filtration. The primary objectives of this pilot-scale research were to provide insight into the destruction of natural and synthetic organics that are characteristic of water in Southern Ontario's Grand River, and assess ozonated and halogenated disinfection by-product formation.

Ozone alone was unable to achieve the 1-log removal target for the taste and odour compound geosmin or the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA), unless disinfection-level dosages were applied i.e. ≈ 1 mg O_3/mg DOC. No improvement was observed when adding hydrogen peroxide, a promoter of ozone decomposition reactions due either to the high levels of natural promoters or the scavenging action of radical traps inherently present in Grand River water.

A major obstacle to the implementation of ozonation in bromide-laden source waters such as the Grand River is the formation of bromate, currently the only ozonation by-product regulated by the province of Ontario. It was found that there is a direct correlation between ozone dose and bromate formation and by applying ozone dosages at or above disinfection levels bromate is likely to exceed the 10 μg/L maximum acceptable concentration. However, adding hydrogen peroxide prior to the ozone contactors successfully reduced the amount of bromate formed, and in most cases levels fell below regulatory limits at H_2O_2/O_3 ratios above 0.3:1.0. A linear correlation was established between bromate inhibition and increasing H_2O_2/O_3 ratio (up to 0.5:1.0) at a constant ozone dose.

Amongst the three filtration media investigated, anthracite, Filtralite®, and granular activated carbon, only the latter was capable of meeting the 1-log removal target for

geosmin and MCPA. The superiority of GAC over anthracite and Filtralite® was attributed to its adsorption affinity for these trace organic contaminants but as adsorption sites become saturated by organic foulants, poorer effectiveness is expected over time. Filtralite® and anthracite media were both ineffective for biological MCPA removal due to its non-biodegradable nature under conventional water treatment conditions. If Filtralite® or anthracite media were to be selected for full-scale filter upgrade, then neither could be relied upon to deal with periodic MCPA discharge events leaving intermediate ozonation as the sole effective treatment barrier.

Even at the lowest ozone dosage applied (1 mg/L), ozone-enhanced GAC and Filtralite® biological filters achieved a 1-log geosmin removal. In contrast, to meet the 1-log geosmin removal target, the optimal ozone dose for the anthracite biological filter was 1.44 mg/L (=0.7 mg O_3/mg DOC).

The tandem of ozone followed by biological filtration was proven to be very effective for reducing total trihalomethane formation potential at transferred ozone dosages between 1.0 mg/L and 2.5 mg/L (= 0.33 to 0.95 mg O_3/mg DOC). However, experiments involving the effluent from the anthracite biological filter demonstrated that without prior ozone treatment, TTHM production would more than double with the potential to exceed regulatory standards. As with previous experiments involving the destruction of geosmin and MCPA by the combination of ozone and hydrogen peroxide, TTHM production was unaffected by increasing the hydroxyl radical flux. Extending hydraulic detention times to simulate TTHM levels in the distribution system showed that GAC media outperformed Filtralite® and anthracite with the highest increase after a 24 hour detention time. Nevertheless, the ozonation/biological filtration tandem was very effective for the control of distribution system TTHM production regardless of filter media, with levels well below current and anticipated provincial regulatory limits.
The combination of intermediate ozonation followed by deep-bed biological filtration is well suited for treating Southern Ontario's Grand River water. Scale-up considerations include pairing the proper filter media to the size of the ozone generator in order to secure regulatory compliance with respect to disinfection by-product formation on one hand and

provide effective taste and odour control and meet MCPA removal target on the other. The best two treatment scenarios were: Option 1: select the more expensive GAC media and size the ozone generator to produce a 1 mg/L dose at the design flow rate. In order to maintain peak adsorption capacity, the GAC media would require regeneration every 1 to 2 years. Option 2: select the least expensive anthracite media and size the ozone generator to deliver a 2 mg/L dose at design flow rate. Ultimately, Option 2 was selected for full-scale implementation because all water quality objectives were met in the most cost-effective manner.

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1 Chapter 1: Introduction

1.1 A Brief History of Public Sanitation

Civilization is undoubtedly mankind's greatest accomplishment. Over time, great centers of commerce and education have flourished worldwide, providing the means to develop technology and promote technology transfer. The sustainable growth and health of a community requires sound public sanitation management practices such as the provision and supply of safe, clean drinking water and the proper disposal of waste. Evidence of enlightened and thriving societies can be found in the ancient city of Herculaneum, a suburb of Naples in Italy (Albanes, 2011). Four thousand years ago, the inhabitants were supplied with safe drinking water by a distribution system comprised of lead or clay pipes. Every home disposed of their waste waters by drains connected to closed sewers. Roman engineers recognized the importance of practicing sustainable designs while preserving the environment: Before discharging wastewater to the sea, it was processed in large cisterns connected in series for the purpose of solids settling and anaerobic digestion. Albeit, after a millennia of refinement, the latter treatment principles are still currently applied in secondary wastewater processes (Albanese, 2011).
Paleohydrology is defined as the study of ancient use and handling of water such as urban water supplies and irrigation (Lorenz and Wolfram, 2012). The first aqueducts were built around 312 B.C. by the Romans and the Greeks and designed to convey domestic water from clean sources such as spring water (Walski, 2006). The water was channeled by gravity and discharged into settling tanks for clarification. It was empirically known at the time that the sun's exposure could improve the quality of the water flowing through open channels without being aware of the disinfection properties of UV light. By 200 A.D., Rome was being supplied with almost 500 million liters per day of drinking water (Symons, 2006), an extraordinary engineering achievement taking into account that until the early 19^{th} century, most humans had no other choice than to haul water from source to point-of-use.

Although by today's standards Herculaneum would be deemed a small city with a population of only four thousand, the Industrial Revolution in Europe and America in the 19th Century was the catalyst for the emergence of megacities. The challenges of providing adequate public sanitation, especially in the poorer areas of those modern cities was overwhelming especially when initial planning didn't take into account the influx of workers at a scale never seen before. With this population growth, arose the need for significant quantities of safe, clean drinking water and disposal of ever increasing volumes of wastewaters both residential and industrial. To compound the problem further, modern medicine was in its infancy and ill-equipped to understand the cause of diseases, not to mention administrating effective medical treatments. Living conditions, especially for the poorer classes, were lacking proper hygiene and more often than not, workers were cramped in pest-infested quarters that would favor disease transmission. Means of transportation were largely improving, which further exacerbated disease transmission (Morris, 2007). It was a period of time where modern nations didn't understand the relationship between health and sanitation, a significant departure from the wisdom learned by the Ancient Romans over four millennia ago.

Nineteenth century London, England experienced three major waterborne disease outbreaks in less than a century that, apart from the associated human suffering and death they caused, had a significant impact on the sustainability of the industrial and economic engine. Cholera is the most documented cause of these waterborne disease outbreaks in London and many other European cities. Cholera was endemic in India, and until then, an infected host would die or recover from the disease before ever being able to reach Europe simply because the distances were so enormous and modes of transportation too slow. This was not the case anymore in the 19th century, with the technological advances made in land and maritime transportation. The *Vibrio cholerae* bacterium is an obligate parasite and has an incubation time of 24 to 48 hours, more than enough time to keep the infected hosts alive by the time they reach Russia. Back then, the standard emergency response for a small community stricken by cholera and other serious infectious diseases was quarantine, often enforced by military presence stationed outside of the city's boundaries. However, that practice couldn't be applied to broad areas of a big city. If a city was known to experience a cholera outbreak, ships arriving from those cities would

be quarantined at the destination port as a desperate attempt to control the spread of the disease. In the 19th century, the medical community believed that cholera was an airborne poison, also known as a "miasma" lurking in the foul air of cities especially around their ports and the poor, overpopulated neighborhoods (Goldstein, 2012). Unfortunately, this conclusion wasn't supported by sound scientific observations; rather it was based on intuitive reasoning that seemed to "fit" the facts. Dr. John Snow didn't agree with these widely accepted beliefs and took great interest in unraveling the real cause of the cholera outbreaks in London. Albeit rudimentary by today's standards, he pioneered effective epidemiological tools to demonstrate that the principal mode of transmission of cholera was waterborne in nature and caused by a microorganism. Most waterborne diseases cause diarrhea and vomiting ultimately killing their victims by dehydration. Apart from drinking water, their mode of transmission is via human contact and soiled surfaces (Morris, 2007).

While humans have always recognized the importance and need for access to clean water sources, the definition of what is clean or safe has drastically changed over the ages. In 19th century Europe no one believed that an organism invisible to the naked eye could cause sickness and death, otherwise it would contradict the belief that clear and colorless water is always safe for drinking purposes. This belief was further fuelled by special interest groups such as the private companies supplying drinking water to the City of London. If Snow's theory became widely accepted, they would have no other choice than to treat drinking water instead of merely pumping it out of the Thames River, thus negatively impacting their bottom lines. In 1849, Snow published a monograph entitled "On the Mode of Communication of Cholera", and as expected was received with significant controversy and resistance by the scientific community, public sanitation and lobbying groups. Snow's most compelling evidence was the significant drop in death in the town of Exeter between the first and second cholera outbreaks of 1832 and 1849. During that period, a new water treatment plant was commissioned and the main raw water intake relocated upstream, in a less polluted area. As a result the death toll from cholera dropped from 349 to 20, respectively. In contrast, the town of Hull relocated its raw water intake from a pristine stream in the hills to the river and experienced a 6-fold

increase in the number of deaths by the time the second outbreak took place. These epidemiological findings were published in an article entitled “On the Propagation and Mode of Communication of Cholera” in the London Medical Gazette. The key issue that favored the spread of waterborne diseases was the mismanagement of waste by an ever growing population and the subsequent contamination of drinking water sources. It was common practice to store solid and liquid human wastes in privies, periodically removed by soil rakers and sold as fertilizer to farmers while household waste was carelessly thrown in the streets. Although sewers were intended solely to carry rainwater to the Thames River and its tributaries, a rain event would entrain the aforementioned wastewaters in the same waterways or drain in vulnerable wells. The load of pathogens discharged would then increase significantly, resulting in a greater risk of contaminating drinking water. Other factors that would contribute to the likelihood of waterborne disease outbreaks were the high levels of nutrients and water temperature. As a result most waterborne disease outbreaks were occurring predominantly during the warmer months of the year (Morris, 2007).

London’s General Board of Health was controlled by Edwin Chadwick, an opponent to Snow’s theories and fervent believer that a miasma was cholera’s principal disease transmission pathway. At the core of the problem, decaying human and vegetable waste was accumulating in cesspools under the streets of London releasing “atmospheric substances” or miasma, responsible for the transmission of diseases. As a utilitarian, Chadwick was concerned with the well-being of the working class and based on the accepted belief of the time, determined that the most suited short-term solution to eradicate the cholera-laden miasma was to eliminate cesspools by periodically flushing the sewers. Snow was well aware that if his theory was correct, this solution could only lead to an increase in the contaminant load discharged to the river. Since more than 90% of London’s population had access to untreated water drawn from the Thames, another waterborne disease outbreak was imminent. The third and last major cholera outbreak began in 1853 and peaked in 1854 during an exceptionally warm summer. The scope of Snow’s epidemiological investigation at this point was to accumulate as much evidence as possible to prove beyond a doubt the validity of his theory to the scientific community.

The contamination of the Broad St. Pump was the most notorious and publicized case of cholera outbreak unveiled by Snow (Morris, 2007). The first investigation revolved around Susannah Eley, a resident of Hamstead located four miles away from the Broad St. Pump. Several times a week, she would receive water bottles drawn from the Broad St. Pump. While the reasons for ordering drinking water from that source were unclear since other wells were at closer proximity, it took only two days for her and her niece to die after the onset of the first symptoms of cholera. A few weeks later, in the neighborhood surrounding the Broad St. Pump, 143 residents died within 24 hours. Snow investigated the deaths of 83 residents living in the area and discovered that 73 of them drank the water from the pump. The Board of Guardians of St. James Parish was responsible to oversee the health of the residents located in the north-east districts of London including Broad St. Snow addressed the Board and although his scientific data was received with much resistance, in a desperate effort to curb the elusive disease, the pump's handle was removed as a last recourse. In the final analysis the cholera outbreak killed 623 people and was originally tracked to a child that contracted the disease and living in front of the Broad St. Pump well. The child stricken by severe diarrhea was washed frequently by her mother and the wastewater simply discharged in the street. The wastewater laden with the Cholera bacterium accumulated in cesspools, which eventually was washed away and contaminated the poorly protected well head.

The summer of 1858 was very hot and the water levels in the Thames River were exceptionally low, causing wastewater to stagnate at the points of discharge. The foul smell affectionately referred to as "The Great stink" was so overwhelming that Parliament passed a bill to relocate the sewer discharge pipes 18 miles downstream off the Thames River. Ironically, the stench that shrouded the City of London was the driving force behind eradicating cholera outbreaks, not Snow's link to waterborne diseases (Morris, 2007).

1.2 Water Treatment Milestones

The presence of pathogens in source waters poses the greatest risk to the safety of any drinking water supply. Until 1883, only the symptoms of cholera signaled that the disease was threatening a given population, not the causative agent (Symons, 2006). Robert Koch identified the *Vibrio cholerae* bacterium by microscopy and found that if present in a given water sample, colonies could be grown on plates of solid agar. This innovative tracking method was put in good use during the Hamburg cholera outbreak of 1892 where Koch was instrumental at demonstrating that granular media filters, and more specifically slow sand filters were an effective barrier against the passage of cholera and other pathogens. Until then, slow sand filtration was primarily used to improve the organoleptic and physical quality of drinking water by removing particulate matter but wasn't recognized as an effective barrier against the transmission of waterborne diseases. For the first time a cost-effective treatment tool was readily available to curb the spread of diseases via the drinking water treatment pathway (Morris, 2007).

Louis Pasteur's research on fermentation paved the way to the germ theory published in 1857. He observed that bacteria were responsible for souring wine and beer during the fermentation process and that these microorganisms could be eradicated by boiling the liquid, a technique now known as pasteurization (Morris, 2007, McGuire, 2006). Moreover, he demonstrated that microorganisms can significantly affect the health of larger organisms including humans. It wasn't before Koch and other pioneers in the field of bacteriology confirming the link between microorganisms and diseases, that the germ theory gained industry-acceptance and became the driving force behind the widespread implementation of disinfection practices in public water supplies (Symons, 2006).

Identifying and enumerating the etiologic agents present that have the potential to cause waterborne diseases were a time-consuming task that couldn't be practically implemented to determine the effectiveness and performance of disinfection. The water industry needed an indicator organism that could universally be used as a surrogate for the presence of enteric microorganisms in drinking water. The *Bacillus coli communis*, a

member of the coliform ("colon") group was chosen because its presence signaled the potential for fecal contamination and for its detection simplicity by the multiple-tube procedure. The discovery of this indicator organism had a significant impact on improving disinfection techniques and for routine microbiological monitoring of drinking water. The 1914 Standards of Purity for Drinking Water Supplied to the Public by Common Carriers in Interstate Commerce was the first to release a maximum acceptable limit (≤2.2 coliforms/100 mL) along with a practical analytical method for coliform analysis (McGuire, 2006).

Well-known disinfection chemicals at the turn of the 19th century included ozone and hydrogen peroxide, but none took center stage like chlorine in the water treatment industry. Chlorine disinfection took the water industry by storm because of its high disinfection effectiveness, was relatively cheap and easy to handle (McGuire, 2006). The excitement of this discovery was heralded by the New York Times: "Any municipal water plant, no matter how large, can be made as pure as mountain spring - by the addition of chlorine. Indeed water suppliers all over the country had been looking for such a technology" (Morris, 2007).

It paved the way for water treatment plants to draw from contaminated raw water sources that couldn't until then be considered for the production of safe drinking water. Moreover, utilities had at their disposal a much cheaper alternative compare to the capital and energy costs associated with relocating intakes farther to more pristine source waters, if even feasible. Finally, chlorine had the advantage over many other disinfectants of maintaining a biocide residual for extended periods of time, which was critical to prevent biofouling in plants and regrowth in distribution systems (McGuire, 2006).

By 1914, half of the water suppliers in North America integrated some form of disinfection process, and/or granular media filtration to their treatment (Morris, 2007). Furthermore, Hazen discovered that the sequential combination of filtration and chlorine disinfection processes, improved greatly the effectiveness of pathogen removal because of the recognition that microorganisms can be shielded from the action of a chemical

agent when embedded in particle matter (McGuire, 2006). The consequences of these treatment innovations were immediate and the benefits easily quantifiable: In the early 20th century, the average American had a 5% risk of succumbing to a waterborne disease by the age of 70. The risk decreased to 0.03% by 1940 and 0.00005% by 1990 (Morris, 2007). By the third decade of the 20th century, the water industry entered a golden era known as "the age of safe water" at least for those living in developed countries (Trussell, 2006).

1.3 Those left behind

While industrialized nations have been exceedingly successful at controlling waterborne diseases, the World Health Organization currently estimates that over 2.1 million people die annually from diarrheal diseases, 88% linked directly to waterborne diseases with 90% of the fatalities being children under the age of five. These are not surprising statistics since 1.1 billion people living mainly in developing countries don't have access to safe drinking water supplies. UN secretary Kofi Annan declared that "we shall not finally defeat AIDs, tuberculosis, malaria or any other infectious diseases that plague the developing world until we have also won the battle for safe drinking water, sanitation, and basic health care" (Hrudey and Hrudey, 2004). The significant contrast in death toll rates between industrialized and developing countries are a clear indication that modern water treatment technologies in combination with proper sanitation management practices are effective means of lengthening life expectancy, mainly by decreasing child death rates (Rochelle and Clancy, 2006; Hrudey and Hrudey, 2004).

1.4 Emerging threats

In 1945, Neefe and Stokes established a strong link between the presence of viruses and the incidence of waterborne diseases (Trussell, 2006). These organisms were more difficult to detect because of their small size, impossible to be observed by conventional

microscopy. However, since the 1970's it has been established that viruses such as yellow fever, poliovirus, or Hepatitis A were readily inactivated by free chlorine and others, requiring short contact times combined with dosages commonly applied for the purpose of drinking water disinfection. It confirmed that viruses weren't a threat to drinking water quality by employing the same treatment technologies that were first implemented at the beginning of the 20th century. As long as water systems were well designed, managed, maintained, and operated according to era industry standards, there was an arrogant confidence that the microbial threats to drinking water were minimal no matter the source. This level of belief and comfort was shattered in the mid-1970s with the discovery of a new class of microorganisms, *Giardia lamblia*, a protozoan that can infect warm-blooded hosts including humans and wildlife (also known as "beaver fever"). The consequences were significant because even the most pristine raw water sources had the potential to be vulnerable (Trussell, 2006). Of wider implication, the zoonotic parasite in its cyst form displayed significantly greater resistance to free chlorine disinfection compared to viruses and bacteria. The pathogen concern expanded in the mid 1980s with the emergence of *Cryptosporidium parvum*, another type of protozoan, which in its oocyst form, was virtually resistant to free chlorine and left filtration as the only viable barrier in conventional water treatment systems (Trussell, 2006). Epidemiological studies reviewed for this period revealed that the proportion of waterborne disease outbreaks due to these emerging etiologic agents were significantly more widespread than first estimated: Approximately 10% in European countries such as Sweden, England, and Wales despite the high water quality standards driven by responsible regulatory oversight and around 20% in the United States (Kramer *et al.*, 2001). The 1993 cryptosporidiosis outbreak in Milwaukee, Wisconsin was a high profile case with 400,000 cases of illness and over 100 deaths. The outbreak was sparked by heavy rainfall and runoff followed by the inability of one of the direct filtration plants to control particle removal (McGuire, 2006). This incident was a wakeup call for the water industry and regulatory agencies, spurring in the coming years a plethora of regulatory amendments aimed at protecting public health particularly for those treating vulnerable raw water sources such as surface water and groundwater under the influence (GUDI). These new

regulations also reflected the changing nature of waterborne disease outbreaks throughout the 20th Century (McGuire, 2006).

Research was promptly re-focused on the effectiveness of conventional treatment technologies aimed at the deactivation of *Giardia* cysts, *Cryptosporidium* oocysts and other emerging pathogens. These studies demonstrated that under optimal operating conditions for turbidity removal, conventional treatment barriers could attain from 3 to 5 log-removals of *Cryptosporidium* oocysts while other studies reported *Giardia* cysts log-removal ranging from 1.5 to 3.5 (Xagoraraki *et al.*, 2004). The most important lesson learned in the past twenty years is the critical role of pretreatment to achieve low filter effluent turbidity in order to prevent (Cotruvo, 2010):

- The breakthrough of chlorine-resistant pathogens and
- Particle shielding of microorganisms prior to disinfection

Many researchers have demonstrated that turbidity isn't a sensitive indicator of protozoa breakthrough during filtration (LeChevallier and Norton, 1991). Because of the lack of a more suitable alternative, real-time continuous monitoring of filtered water turbidity has become the industry-standard risk indicator for pathogen breakthrough in treated water.

Since the release of *Silent Spring* in 1962, Rachel Carson ignited international concern by warning that pesticides and other synthetic organic chemicals (SOCs) were damaging the environment as a direct result of human activity (MAS, 1988). Their occurrence, fate and effect in the environment were not well understood due to a lack of accurate analytical methods for trace organic measurements. It wasn't until a decade later that technological innovations in gas chromatography namely the Hall detector, purge-and-trap isolation method and headspace analyzer enabled researchers to make accurate qualitative and quantitative determinations of organic contaminants including SOCs (Trussell, 2006). The discovery in 1974 that chlorination of NOM in drinking water treatment promoted the formation of disinfection byproducts (DBPs) further exacerbated the century old belief that chlorine is a universal disinfectant (Rook, 1974). Its lack of reaction selectivity combined with a high oxidation potential favors the rapid formation of undesirable by-products in the presence of DBP precursors, an inherent fraction of NOM (Gang *et al.*,

2002). Since both surface and ground waters contain NOM to varying degrees, no drinking water supply is exempt from the production of these SOCs after chlorination. DBPs in drinking water have generated controversy and much debate over the conflicting findings regarding their associated health risks (Singer, 2006; White, 1999). Toxicological studies have shown that at high doses, individual or mixtures of DBPs have induced among others, carcinogenicity, mutagenicity, hepatotoxicity, nephrotoxicity, neurologic, reproductive and developmental effects in laboratory animals. However the DBP concentrations administered in these toxicological studies weren't typical of those found in drinking water and didn't account for chronic health effects at low-doses. In addition these experiments didn't examine the effects of other exposure pathways such as inhalation and dermal absorption (Teuschler and Simmons, 2003). Some epidemiological studies have shown an increased risk of bladder, rectal and colon cancers, in addition to reproductive and developmental effects (Singer, 2006). The most recent studies either established a weak association between these conditions and DBP exposure (Wright and Rivera-Nunez, 2011) or determined that they don't pose a substantial health risk at levels commonly detected in drinking water (Drinking Water Editorial, 2012).
Nonetheless, there is wisdom in applying the precautionary principle until more definitive studies are available.

The most prominent classes of DBPs detected were trihalomethanes (THMs) and haloacetic acids (HAAs). However, more recent studies have demonstrated that they only account for a small fraction of the total halogenated organic halides (TOX) derived from chlorination of drinking water. Emerging DBP classes include haloacetonitriles (HANs), haloketones (HKs), cyanogen halides, some of which had more serious genotoxic effects compare to TTHMs and HAAs (Archer and Singer, 2006).
The heightened health risks from chlorine-resistant pathogens and the production of halogenated byproducts during chlorination motivated both government and the water industry to investigate alternative chemical disinfectants such as ozone, chlorine dioxide, and chloramines. In the presence of NOM, halides and other dissolved contaminants, the aforementioned alternative disinfectants generated new DBPs that carry their own toxicities. Richardson *et al.* (2007) reviewed 30 years of research on DBPs generated by

chemical disinfectants and accounted for over 74 emerging DBPs (other than TTHMs and HAAs) that have been detected at moderate levels and which exhibited genotoxic effects.

By the end of the 1970s, novel classes of contaminants in drinking water sources were elucidated, some of which were the result of anthropogenic activities while the remaining were naturally occurring. Some of the most notorious contaminants uncovered were volatile organic chemicals (such as chlorinated organic solvents), heavy metals, numerous pesticides and herbicides, all of which are known for their xenobiotic properties (Trussell, 2006).

Around the same era, health concerns were formulated over the potential for toxic contaminants not present in source water but detected as water undergoes treatment and conveyed to consumers. At the core, water is the most universal solvent and has the ability to dissolve a wide array of organic and inorganic contaminants to varying degrees based on their respective aqueous solubility constants. The opportunity for contaminants to seep into drinking water during treatment and delivery can be broken down into four distinct categories (Trussell, 2006):

1. Impurities ubiquitous in water treatment chemicals most often the result of manufacturing processes.
2. Contaminants leaching from the surfaces of water treatment equipment such as pumps, tanks and flow meters.
3. Intrusion of soil contaminants in distribution pipes.
4. Leaching of contaminants from pipe and plumbing materials (including solder).

Based on standards previously established in the food industry, the National Sanitation Foundation (NSF) was created in 1982 to certify chemicals (NSF 60) and equipment (NSF 61) involved in the treatment and delivery of drinking water (Trussell, 2006). Contaminants limits based on toxicological data were defined in order to receive NSF certification; for example stringent carbon tetrachloride concentration limits present in chlorine were defined based on toxicity with respect to maximum chlorine dosages

applied to drinking water treatment. Similarly, maximum limits on the percentage of lead in solder were set to obtain NSF certification.

The most recent advances in analytical techniques have the ability to detect organic contaminants with method detection limits (MDLs) in the parts per trillion ranges or lower (Cotruvo, 2010; Ongerth and Khan, 2004). Researchers have uncovered new classes of xenobiotic organic contaminants, including personal care products (PPCs), endocrine disrupting chemicals (EDCs) and pharmaceutically active compounds (PhACs) in complex matrices such as raw waters and wastewater effluents. The implications of these contaminants in the environment were the object of intense media scrutiny after estrogen, an EDC was observed to cause adverse reproductive effects in fish (Stanford *et al.*, 2010). The major pathways accounting for their widespread presence in drinking water sources include upstream wastewater treatment discharge, run-off after manure field application, improper biosolids management from livestock operation, hospital wastewater effluents, and leaching of pharmaceutical wastes. Since the majority of these pathways have a more direct route in surface water, it came as no surprise that their levels were generally higher compare to those measured in groundwater. In the last two decades, these emerging trace contaminants have been detected at parts per billion or lower, in source waters and even lower in drinking water supplies with such innovative analytical tools as liquid chromatography coupled with mass spectrometry (LC-MS) (Ternes, 2007); moreover, it was established that they were present in drinking water at concentrations at least two orders of magnitude below their respective therapeutic doses (Ongerth and Khan, 2004). However, long-term exposure from food, air and water and the effect of mixture toxicity on human and the environment remains grossly misunderstood (Williams, 2011; Stanford *et al.*, 2010).

1.5 Multiple Barrier Approach

In all parts of the world, drinking water supplies are increasingly fouled by sources of fecal contamination such as animal and sewage waste. The fecal-oral route is the main

transmission pathway to contract endemic gastrointestinal waterborne diseases, which if left untreated often led to serious illnesses or death targeting mainly children, elders and people afflicted with immune-deficient related diseases. While chemical contaminants are another class of hazards, the associated level of risk is often negligible unless there is a spill or a site-specific contamination of the water source due to industrial or agricultural negligence and infrequently a naturally-occurring source (Hrudey and Hrudey, 2004). The multiple barrier concept applied to water treatment has been advocated by Public Health Engineers since the 19th century and currently remains the best known strategy for managing risk in order to produce safe, clean drinking water. The impetus arises from the recognition that:

- There is no universal treatment process that has the ability to remove all contaminants from a raw water supply (except reverse osmosis filtration under certain conditions but capital cost is often a deterrent to its implementation).
- Human activity will inevitably generate a wide array of contaminants that if left untreated, have the potential to damage the environment and threaten drinking water safety.

In the last century, industrialized countries have seldom suffered from waterborne disease outbreaks and as a result, ironically, there are those that believe that water utilities are chasing diminishing returns by investing in unnecessary redundancies, which leads to the temptation to cut resources (Hrudey and Hrudey, 2004). Reliance on a single treatment process means that in case of failure due to operational or maintenance issues, poorly treated water will reach users and increase the likelihood of contaminant breakthrough into the drinking water supply. The robustness of a drinking water system can be gauged by its ability to produce safe drinking water despite the failure of one or more of its barriers. Furthermore, a water system deemed robust means that in the event that a contaminant breaches a barrier, it is less likely that it will breach the remaining barriers assuming that the system is properly designed, maintained, operated, and managed (Hrudey and Hrudey, 2004). The basic components of a multi-barrier approach are essentially a series of safeguards to ensure drinking water safety, which are summarized below.

1.5.1 Source water protection

The first and most critical barrier remains the protection of raw water supplies especially for those systems that draw from vulnerable sources such as surface water and groundwater under the direct influence (GUDI) of surface water. Few communities have the privilege of owning and maintaining statutory control over their source waters and as such are least impacted by human activities usually resulting in good to exceptional raw water quality characteristics. However, most raw water supplies are located in populated areas and as stated earlier, human activity invariably generates waste that renders water sources vulnerable to contamination. Agricultural runoff, industrial waste, chemical spills, and sewage discharges have the potential to introduce a myriad of pathogenic organisms and chemical contaminants in raw water (Hrudey and Hrudey, 2004).

During the Walkerton Inquiry in Canada, Justice O'Connor stated that "The first barrier to the contamination of drinking water involves protecting the sources of drinking water." The significance of his statement translated into 22 recommendations related to the creation and implementation of source protection plans in Ontario via the Clean Water Act (Stahl *et al.*, 2012). While other provinces in Canada may encourage - on a voluntary-basis, the creation of these plans as a best practice, human death and suffering combined with the economic burden experienced as a result of the Walkerton tragedy was the driving force behind promulgating legislation in the form of an Act in Ontario. Establishing source water protection programs is key to the sustainability of raw water quality and quantity and the health of the ecosystems. In the long run, the economic and environmental benefits of protecting raw water quality far outweigh the resources necessary for restoration activities or to produce safe drinking water from a contaminated water supply (Peckenham *et al*., 2005). Since raw water quality is site-specific, a source protection program should be coordinated and managed at the local level i.e. Conservation Authorities with the participation of a broad range of stakeholders including landowners, farmers, industry, citizens, environmental specialists, public health officials, local government and approved by the MOE (Stahl *et al*, 2012). The first step in developing and implementing an effective source water protection program is to conduct

a risk assessment study. It consists of delineating the source water assessment area, gathering raw water quality data, identify and prioritize the threats posed by contaminants and related site-specific activities that have the potential to impair water quality within the set geographical boundaries. The development of a source protection program should also include a raw water quality monitoring component in order to determine and track the origin of contaminants whether introduced by human activity or naturally occurring (Sham *et al*, 2012). Water quality threats that are the result of the source water's indigenous characteristics should be addressed via treatment-based solutions (Peckenham *et al*, 2005).

Once the major potential sources of contamination have been identified, the next step is to determine the susceptibility of each public supply to the aforementioned threats. The results of the risk assessment study can then be used to empower stakeholders to take the necessary actions that will reduce the sources of contaminants including:

- Enforcing existing land use planning and regulatory requirements or approvals.
- Banning activities that constitute an immediate and significant risk to raw water supplies or forcing polluters to generate and implement risk management plans with emphasis on the measures that will be taken to minimize the specific threats to a water supply (Stahl *et al*, 2012).

The leap from assessment to protection can be challenging especially for private landowners and small businesses. The Ministry of the Environment created the Ontario Drinking Water Stewardship Program in 2007, aimed at providing financial assistance on the basis of need, with the primary objective of reducing threats to public water supplies. Over 28 million dollars in grants have been allocated in a two-tier program to adopt best management practices such as decommissioning or upgrading wells and septic systems, erosion-control measures, storage of fertilizers and pesticides, and investing in public awareness campaigns.

The last step consists of periodically assessing the effectiveness of the mitigation actions especially in the more vulnerable areas of the watershed such as Wellhead Protection Areas and Intake Protection Zones (Volkova, 2012). This can be accomplished by implementing a comprehensive monitoring program to detect changes with respect to raw water quality and by encouraging stakeholders to be vigilant and report incongruous activities in the watershed.

In unprotected source water supplies that have ineffective protection plans, water purveyors must rely more heavily on the other barriers to ensure safe drinking water. Since the level of treatment is primarily based on raw water quality, wherever feasible, a source water protection program should always be implemented to render the drinking water system less vulnerable and lower overall drinking water production costs.

1.5.2 Treatment

The level of treatment to produce safe, clean drinking water from a given raw water supply requires a thorough identification and prioritization of the hazards present, and consideration of the risk each represents to human health. Pristine raw water sources require low levels of treatment because fewer hazards are generally present and their respective severity to cause human illnesses is usually low. On the other hand, polluted sources will require more advanced treatments because of the substantial risk to human health posed by a higher number of hazards and associated likelihood of hazardous events. The greater the risk, the more expensive and complex treatment becomes to produce potable water. Dr. Peter Huck eloquently illustrated the former by stating that "there is no inexpensive way to produce good quality drinking water from a poor quality raw water" (Huck, 1988).

Pristine watersheds are generally protected against the pollution caused by industrial, agricultural, and municipal activities. Although the incidence of chemical contaminants in such source waters might be negligible, there is still a microbial risk posed by wildlife

and recreational activities, which needs to be addressed via a well-designed disinfection barrier. The CT concept provides a level of confidence with respect to curbing microbial risk and with proper monitoring and operational vigilance, continuously ensures a predefined level of disinfection performance (McGuire, 2006).

Improved analytical methods for the detection of *Giardia* cysts and *Cryptosporidium* oocysts have demonstrated that their occurrence in the aquatic environment is more widespread than previously estimated (Rochelle and Clancey, 2006; LeChevalier and Norton, 1991). Because of their resistance to chlorine disinfection at CT values commonly applied in water treatment, additional disinfection barriers should be implemented such as some form of filtration, UV irradiation or alternative chemical disinfectant (McGuire, 2006). The judicious combination of disinfection technologies will usually provide complimentary protection against a wider array of microorganisms.

In more impacted watersheds, the level of treatment will reflect the hazards present along with the cost increase to produce safe drinking water. Complimentary and robust treatment strategies are crucial to effectively treat the contaminants that are present in these source waters. As stated earlier, the leading threat to water quality safety is the breakthrough of pathogens in drinking water. In other words, achieving effective disinfection is the main target. Since particulate matter can shield microorganisms, it is paramount to implement a filtration barrier prior to disinfection. The complexity of the granular or membrane filtration step is governed by the physical and chemical characteristics of source waters. In rapid-rate filtration, the use of a coagulant is critical to achieve low filter effluent turbidity but particle density in raw waters will dictate if inline or conventional filtration should be selected as a pretreatment. Other considerations revolve around the coagulant type, the use of polyelectrolytes to improve floc strength, and whether or not to operate filters in biological mode to enhance DBP precursor removal (Logsdon *et al*, 2006).

Municipal application of membrane filtration first appeared in the early 1970s as an alternative to distillation of sea or brackish waters. Since the commercialization of micro

and ultra filtration membranes in the 1990s, the membrane filtration industry soared in part due to the heighten threat posed by chlorine-resistant protozoa. In waters with a low potential for fouling, these membranes can achieve very low effluent turbidity, lower operating cost compared to conventional filtration, requires significantly less space, and has greater expansion capabilities (Logsdon *et al*, 2006). Advances over the past 30 years have been centered on reducing the susceptibility of membranes to fouling and improved resistance to chlorine. To date, in polluted waters that have an inherent potential for fouling, the use of some form of pretreatment prior to membrane filtration is critical to minimize its negative effects.

Whether granular or membrane filtration is chosen, continuous monitoring of effluent turbidity and achieving low effluent turbidity is crucial for maintaining effective disinfection.

The history of drinking water is one of human tragedy followed by technological advances and regulatory changes. The incrementally-stringent regulatory amendments on turbidity targets promulgated since the 1980s reflect the awareness linking filtered turbidity spikes and the incidence of waterborne disease outbreaks worldwide. The pre-Milwaukee outbreak era promoted treatment practices for turbidity reduction below 1 NTU to specifically control taste and odour and biofilm growth in the distribution system. Since then, turbidity reduction in the US became regulated with targets dropping stepwise from 1.0 NTU to 0.5 NTU and 0.3 NTU in 95% of monthly combined filter effluents with anticipated levels to drop below 0.1 NTU in the future (Logsdon *et al*, 2006). The province of Ontario followed suit soon after the Walkerton tragedy.

Under steady-state conditions, a well-designed, managed, and optimized water treatment plant can generally achieve high water quality standards. However, under rapidly changing conditions, treatment performance is accordingly reduced, which can significantly impact the quality of the finished product. In their review of 548 waterborne disease outbreaks in the US, Curriero *et al* (2001) discovered that over half were preceded by rain events. It shows the need to have properly trained operators who are

knowledgeable in the operation of plant processes, are sufficiently aware to be able to detect the onset of treatment upsets, and are responsive to deteriorating water quality conditions (Christie, 2012). Operators are entrusted with the mandate to safeguard public health and as such provide an essential service that should be valued as much as any other profession in the health industry (Carlisle, 2012).

1.5.3 Distribution

Distribution systems are the last line of defense in the multi-barrier approach and were until recently, grossly underestimated as a major pathway for waterborne disease outbreaks. Craun and Calderon (2001) estimated that out of 619 documented waterborne disease outbreaks in the US, 18% were directly linked to distribution system breakdowns. Similar to the other barriers, distribution systems must be properly designed, operated, maintained, and managed in order to minimize drinking water quality deterioration while in transit to consumer's tap (Kirmeyer *et al*, 2001). The main causes contributing to water quality deteriorations in the distribution system are:

- Low chemical or biological stability of the water entering the distribution system
- Inadequate operation and maintenance practices
- Aging infrastructure and poor network design
- Inadequate response to water quality complaints

The lessons learned to maintain water quality in distribution systems are summarized below as best practices by the water industry.

Reducing detention time in reservoirs and watermains is critical to maintaining high water quality standards. In the past, water age wasn't a design consideration and it was common practice to oversize storage reservoirs and watermains for anticipated future water demand (Kirmeyer *et al*, 2001). Furthermore, drinking water reservoirs were operated full for emergency purposes such as in case of a fire. All these factors contributed to water age leading to water quality degradation, regulatory non-compliance

and the increased likelihood of waterborne disease outbreaks. Water age must be controlled to avoid excessive chlorine residual decay, minimize microorganisms' growth, corrosion-related issues, nitrification in chloraminated systems, aesthetic water quality deterioration and DBP hikes (Spencer, 2012). A proper balance must be struck between hydraulics and preserving high water quality standards in distribution systems (Kirmeyer *et al*, 2001). Considering the complexity of the factors and their interactions that contribute to water quality and structural integrity deteriorations, the use of hydraulic and water quality models have become effective visual tools to identify weaknesses in distribution systems such as area of long detention times, locations prone to breaks or leaks due to pressure transients or corrosion and other water quality vulnerabilities (Spencer, 2012; Lindley and Buchberger, 2002; Besner *et al*., 2001).

Pressure transients in distribution systems are the inevitable consequence of improper pumps, valves, and fire hydrants operations (Collins *et al*, 2012). The pressure gradient profile includes a rapid and significant pressure increase followed by a pressure loss that may lead to negative pressure (Spencer, 2012). They must be swiftly identified and investigated to ensure that contaminants didn't enter the distribution system or affected pipe integrity (Lindley and Buchberger, 2002; Kirmeyer *et al*, 2001).

Establishing a comprehensive flushing program is an important component of distribution system maintenance. The type and frequency of flushing should be selected based on internal water quality goals and objectives (Kirmeyer *et al*, 2001). Although more work-intensive, unidirectional flushing is the most effective practice to maintaining water quality system-wide by removing organic and inorganic deposits and excess biofilm, controlling bacterial regrowth, minimizing nitrification in chloraminated systems, improving chlorine residual, reducing bulk water detention time and maintaining the overall aesthetic quality of drinking water. Conceptually, it consists of directing high-velocity water in a given section of pipe by strategically closing valves and successively opening fire hydrants until flushed water meets predefined water quality targets.
The following operational strategies must be considered for the effective implementation of a unidirectional flushing program: Scouring velocity must reach a minimum of 1.5 m/s

to effectively flush out foreign materials; the section of pipe targeted must be isolated from the rest of the distribution system by closing valves that would otherwise convey water to other area; the general flushing direction should always start from the cleanest locations towards the more problematic areas or dead-ends of the distribution system; flushed out water should be de-chlorinated prior to discharging in the environment; provision for repairing malfunctioning valves and fire hydrants should be performed "on the fly"; water quality and quantity of flushed water should be measured and recorded to ensure adequate cleaning and to prioritize a candidate list for future pipe replacement (Spencer, 2012).

An annual inspection plan should be implemented for drinking water reservoirs (Spencer, 2012). Traditionally, the storage tank was taken offline and drained before being inspected, which significantly interfered with normal operation. Submersible robotic devices are the most recent innovations and have gained popularity because normal operation of the reservoir isn't disrupted with the added benefit of providing visual records of their conditions (Kirmeyer *et al*, 2001). The intent of the inspection is to ensure that excessive sediments haven't accumulated at the bottom, which may generate anaerobic zones accompanied by losses in chlorine residuals, bacterial regrowth and adverse taste and odour issues. The cleaning frequency is site-specific and is in part related to the quality of the water entering the distribution system, the physical and chemical characteristics of the drinking water supply and state of watermains and appurtenances (Spencer, 2012).

To minimize contaminants intrusion due to cross-connections, it is critical to maintain positive pressure (>20 psi) in the distribution network and a backflow prevention program should be put in place especially at high-hazard locations and ideally extended to all metered locations (Spencer, 2012; Lindley and Buchberger, 2002). The added incentives to widespread metering of a distribution system are:

- To assess water losses, an indication of the percentage of water produced but not accounted for once it has reached the distribution system. Although non-specific, water losses provide information about broad-spectrum watermain, service and

appurtenance leakages. Water losses in a healthy distribution system shouldn't exceed 10% of the annual drinking water production. If water losses rise above that threshold, a more aggressive leak detection program should be implemented; this usually underlay the need to enhance the current watermain replacement program (Spencer, 2012).

- To promote water conservation. Consumers become increasingly aware (along with the additional costs) of the monthly volume of water taken, which inevitably results in curbing wasteful behavior (Ferguson, 2012; Norris, 2011).

Monitoring water quality parameters at the point of entry to distribution systems provides confirmation of treatment effectiveness and consistency and sets a baseline for comparison with the analytical results in distribution locations. Many of the most critical parameters can be monitored with continuous analyzers while others should be tested according to a predetermined frequency based on relevancy with regards to process control operation, regulatory requirements and aesthetic objectives. The results should be reviewed in a timely manner not only to ensure regulatory compliance but also to take swift treatment process corrections (Spencer, 2012).

Water quality complaints are an indirect indicator of the transformations water undergoes as it is conveyed through the distribution system. Consumers provide "continuous monitoring" of the overall quality of drinking water in all area of the distribution system. As such their feedback is very helpful to identify deteriorating water quality locations and ultimately assist in the identification of problem areas in the distribution system. A holistic approach to a water quality complaint program should include the following subsets: Initial information gathering; on-site water quality assessment and corrective actions (if needed); follow-up and record keeping (Spencer, 2012).

1.6 Problem Statement

The Corporation of The City of Brantford operates, maintains, and manages a large residential municipal subsystem treating and supplying drinking water to a population of 93,500. The Holmedale Water Treatment Plant draws all of its drinking water from the Grand River, one of the largest watersheds in Southern Ontario with a drainage area of approximately 6,800 km^2 and stretching over 300 km long (Stahl *et al*, 2012). While many other municipalities in the watershed rely on groundwater as the source of their drinking water, virtually all municipalities discharge their wastewaters in the Grand River and tributaries via 26 wastewater treatment plants most of which are located upstream of Brantford. In addition, large areas within the watershed are dedicated for intensive agriculture and livestock activities further impacting raw water quality. The net result is river eutrophication due to an overabundant and steady presence of nutrients despite tentative attempts to limit their widespread release through collaborative programs between the Grand River Conservation Authority (GRCA), private, and public stakeholders (Balpataky, 2012). The scope of these voluntary initiatives targeting the different sources of nutrient discharge in the watershed includes:

- Upgrading or optimizing wastewater treatment plants with a focus on enhanced nutrient reduction.
- Adopting new farming practices to better manage the use of manure and chemical fertilizers and curtail overspreading.
- Planting trees in order to control erosion around river banks to avoid seepage of nutrient-rich soil and other nutrient sources.

The GRCA is currently working in association with the various stakeholders on an action plan, part of the Water Management Plan that will specifically address water quality, quantity, and flooding issues over the next 35 years. The Water Management Plan should be released in 2013 (Balpataki, 2012). Furthermore the MOE has promulgated the Wastewater Treatment Act in a draft form that will set enforceable standards on contaminant discharge in the very near future.

Over the years and despite the constant efforts by City officials and staff to upgrade and optimize water treatment processes, Brantford's drinking water supply has experienced the adverse effects of chemical, physical, and bacteriological contaminants from upstream sources. Although the safety of the drinking water supply was never at risk due to the proper application of the multi-barrier approach, the poor palatability of drinking water justifiably affected public confidence because water consumers often link the safety of a drinking water supply to its aesthetic characteristics (Symons, 2006; Nerenberg *et al*, 2000). The most common contaminants which adversely impacted Brantford's drinking water supply in the past decade are summarized below:

- Nutrient overload promoted the growth of algae and cyanobacteria especially in the summer months with frequent and long-lasting periods of drought and low river flows. Cyanobacterial blooms are common occurrences beginning as early as June and lasting until October culminating with their lyses and the subsequent release of large amounts of odour-causing metabolites in the drinking water supply. Mitigating efforts focused on DOC reduction by overdosing coagulant and powdered activated carbon. These corrective measures were seldom adequate to minimize the resulting earthy and musty odours imparted to drinking water. AWWARF (Nerenberg *et al*, 2000) organized a workshop in 1998 on treatment strategies aimed at mitigating taste and odours issues specifically originating from high levels of geosmin and 2-Methylisoborneol (MIB) and concluded that more often than not, powdered activated carbon isn't an effective treatment.
- Although ammonia and organic nitrogen originating from wastewater plants effluents are quickly degraded in the warmer months of the year, biological activity in the Grand River decreases significantly as water temperature drops to near the freezing point with the subsequent formation of an ice cover, which limits volatilization. Historically, both contaminants haven't been effectively degraded during winter months and as a result, exerted a high chlorine demand that peaked to up to 39 mg/L in 2003 due to the combination of an exceptionally cold winter and a major wastewater treatment plant upstream experiencing process difficulty. Moreover, the rapid fluctuations in their concentrations can

cause serious operational challenges and impart a nuisance "swimming pool" odour due to the formation of high levels of chlorinated organic nitrogen and trichloramine. Unfortunately, Brantford's treatment processes were ill-equipped to curb the aesthetic impact of these contaminants on the municipal drinking water supply.

- Chemical herbicides such as 2-methyl-4-chlorophenoxyacetic acid (MCPA) and methylchlorophenoxypropionic acid (MCPP) were seasonally detected in raw and finished waters albeit at very low concentrations (ng/L). However, of more pressing concern, their levels before and after treatment were virtually indistinguishable indicating the removal inefficiency by conventional water treatment processes. Furthermore, these SOCs don't impart a characteristic odour or alter appearance of the water that would otherwise alert City staff to a spill nor can they be detected with basic water quality monitoring equipment.
- The high TTHM formation potential of pre-treated water before chlorine disinfection caused the plant to operate near halogenated DBP regulatory limits. The addition of powdered activated carbon (PAC) at the intake was designed primarily for low-level seasonal off-flavor control. As a result neither the PAC applied dosage, contact time, nor was the feeding location suited for the effective removal of TTHM precursors.

It was established earlier that source water protection was critical to preserving raw water quality and sets the tone for the level of treatment required to produce safe and aesthetically pleasing drinking water. Since source water protection programs on the Grand River are at their infancy, the City of Brantford must rely heavily on the treatment barrier for providing high quality drinking water. Additionally, the latest population growth projections estimated that by 2025 the maximum day demand may be as high as 140 MLD. Two major process deficiencies were identified that limited current plant production capacity:

- The rapid-rate dual granular media filters were undersized and couldn't process over 80 MLD, which caused significant operational challenges in periods of high water demand.
- The primary disinfection process was repeatedly challenged under high raw water ammonia conditions due to chlorine contact chamber capacity issues. In order to preserve the safety of the drinking water supply, the largest in-plant reservoir (18.5 ML) was converted from chloramines to free chlorine to provide extra contact time (T_{10}) during the coldest months of the year. The process was reversed in warm conditions to avoid excessive chlorinated DBP formation.

Enlightened City officials and managers were committed not only to secure future plant production needs but also address raw water quality challenges such as seasonal taste and odour events, recurrent chemical and bacteriological spills, and ensure compliance with current and upcoming provincial regulations. It was also agreed that based on the heighten level of risk from known and unknown hazards inherently present in the Grand River, the plant's process upgrades should add robustness, redundancy, and reliability to the overall treatment barrier in order to render the treatment processes less vulnerable to contaminant breakthrough.

A pilot-scale treatability study was initiated in 2007 to identify the best available technologies that would fulfill these objectives. The pilot plant was designed to simulate current post-Actiflo treatment (see Figure 3.1) and evaluate the performance of advanced intermediate oxidation and biological filtration processes.

1.7 Research Objectives

The overall objective of this research was to demonstrate and compare treatment alternatives to the then current post-micro sand ballasted (Actiflo®) coagulation processes, and based on the findings, implement the most suited and cost-effective technologies at the Holmedale Water Treatment Plant.

Specifically, the study was sub-divided into five major objectives:

1. Investigate an intermediate ozonation step followed by biofiltration to potentially enhance DOC removal, lower chlorine demand, and assess the fate of natural and synthetic organic contaminants detected seasonally in the Grand River. Geosmin a cyanobacterial metabolite, and MCPA, a synthetic herbicide were selected in the context of this study.
2. Repeat objective 1 by adding hydrogen peroxide simultaneously with ozone (referred to as peroxone) with the goal of optimizing the hydrogen peroxide-to-ozone ratio to enhance destruction of taste and odour compounds and refractory organic contaminants.
3. Investigate bromate formation with respect to raw water bromide levels, ozone dose, and hydrogen peroxide-to-ozone ratio.
4. Compare the impact of select granular filtration media with respect to the removal of organic contaminants. Specifically, three filter media i.e. anthracite, GAC, and a ceramic-based media (Filtralite®) were investigated in biologically active filters for the removal of geosmin and MCPA.
5. Assess halogenated DBP formation potential following conventional and biological filtration.

2 Chapter 2: Literature Review – Advanced Treatments

2.1 Ozone

2.1.1 History of Ozonation in Drinking Water

Ozone owes its name from the Greek "ozein", or "to smell" because of its pungent odour. This slightly bluish gas is comprised of three oxygen atoms (O_3). It was first detected by Van Marum in 1785 from its characteristic odour generated near electrical equipment. Ozone is created when some form of electrical discharge comes into contact with oxygen molecules (White, 1999). As early as 1886, ozone was recognized as a powerful disinfectant and a demonstration generator was manufactured by Siemens and Halske a few years later, which established its effectiveness in drinking water treatment (Langlais and Reckhow, 1991). The first full-scale water treatment application took place in Oudshoorn, Netherlands in 1893, rapidly spreading throughout Western Europe until the onset of World War I, when a breakthrough in the manufacturing of cheap chlorine gas was developed as a direct consequence of the war efforts (Langlais and Reckhow, 1991). Nonetheless ozone plants were still commissioned albeit at a slower pace, because many European communities favored ozonation over chlorination due to the objectionable chlorinous odour imparted to drinking water. Those pioneering plants soon recognized a marked reduction in color and taste and odour, an unintended consequence of applying ozone to contaminated source waters (Langlais and Reckhow, 1991). While ozonation was traditionally the last stage of treatment, significant benefits were uncovered when fed earlier on during treatment, increasing its popularity and culminating in a rapid expansion phase after 1945 in Western Europe Langlais and Reckhow, 1991).

2.1.1.1 Has Regulation been an Engine for Ozonation of Drinking Water?

Unlike Europe, the high capital cost and in general, better-quality source waters were strong deterrents to ozone's widespread implementation on the North American market (White, 1999). In 1980, only 10 full-scale water treatment plants had incorporated ozone in the USA, however, since the 1990s, over 300 ozone plants have been commissioned (Rakness, 2005). The driving force behind the significant increase in ozone popularity began in the last decade of the 20th Century when Congress directed the EPA to amend the Safe Drinking Water Act in response to existing and recently emerging threats to drinking water safety experienced on American soil. Hence, the USEPA promulgated progressively-stringent regulations that primarily focused on:

- Enhancing disinfection effectiveness from known and emerging microorganism threats and,
- Lowering disinfection by-product formation because of the perceived associated health risks, namely bladder cancer, reproductive and developmental adverse effects.

These two objectives seem contradictory in nature since halogenated DBPs are directly linked to chlorination practices destined to control the microbial risk from drinking water: simply lowering the chlorine dose with the intent to reduce DBPs' formation potential might seriously compromise the microbial safety of drinking water.

The American water industry had to adjust its outlook on the supremacy of chlorination by adopting established European disinfection practices such as ozonation. A summary of enacted regulations that fuelled the implementation of ozonation in US public water systems (PWSs) include:

- June 29th 1989, the Surface Water Treatment Rule (SWTR) provides guidance for PWSs treating surface water and GUDI (also referred as Subpart H systems) for the effective inactivation of protozoa (*Giardia lamblia* cysts) and virus (Hepatitis A) by various disinfectants. CT log removal values for G*iardia lamblia* and Hepatitis A were introduced for various disinfectants including ozone (USEPA, 1990).

- December 16th 1998, the Stage 1 Disinfectants/Disinfection By-Products Rule (Stage 1 D/DBPR) was promulgated to improve control over halogenated DBP formation by lowering TTHMs and HAA_5 limits to 80 μg/L and 60 μg/L, respectively. Utilities with conventional filtration treatments that exhibited high levels of halogenated DBPs were directed to improve TOC removal and thus lower DBP precursors prior to chlorination via enhanced coagulation (and enhanced softening) or granular activated carbon adsorption (Tung, 2006, USEPA, 1998b). Ozone generates its own set of DBPs and bromate became the focus of regulation because of its known health risks and an action level of 10 ppb was set.
- Concurrently, the Interim Enhanced Surface Water Treatment Rule (IEWSTR) was ratified as a direct response to the *Cryptosporidium* oocyst outbreaks experienced since the mid-1980s (see Section 1.4) and to balance the pathogen risk from implementing Stage 1 D/DBPR. Since C*ryptosporidium* oocyts are virtually resistant to traditional chlorine-based disinfection practices, emphasis was focused on consistently achieving lower filter effluent turbidity targets in order to obtain 2-log *Cryptosporidium* removal credits in PWSs treating surface water and GUDI and encourage the use of more potent disinfectant technologies such as ozone (USEPA, 1998a).
- The Long-Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) became effective on January 4th, 2006 to strengthen public health protection specifically against the C*ryptosporidium* threat for PWSs that exhibited an elevated risk of contamination. Each PWS had to conduct a site-specific C*ryptosporidium* vulnerability assessment via source water supply monitoring. Based on site-specific risk levels results, the PWSs were classified and a bin allocated (1-4), indicative of the disinfection treatment level required to comply with the amendments; for those filtered systems that fall into bins 2, 3 and 4, between 1.0 and 2.5 extra *Cryptosporidium* log removal credits must be met, above and beyond the minimum requirement for conventional treatment. In unfiltered PWSs, if endemic *Cryptosporidium* levels exceed an average 0.01

oocysts/L, at least 3-log removal must be achieved via a minimum of 2 different disinfectants (USEPA, 2003a).

- Along with the LT2ESWTR, the Stage 2 Disinfectants/Disinfection By-Products Rule (Stage 2 D/DBPR) was promulgated and builds on the requirements of Stage 1 D/DBPR. This new volley of regulations reflected the most current epidemiological and toxicological studies linking halogenated DBP exposure with certain types of cancers as well as developmental and reproductive health effects. It was also recognized that, although a distribution system might comply with Stage 1 D/DBPR, all consumers weren't equally protected against high DBP exposure. Locational running annual averages (LRAA) replaced the traditional RAA to specifically target areas in the distribution system that experience elevated or peak DBPs levels (USEPA, 2003b). Ultimately, these new rules put further pressure on PWSs to lower DBP precursor concentrations prior to chlorination.

The 1993 Milwaukee *Cryptosporidium* high-profile outbreak was the wake-up call for politicians and regulators to implement increasingly stringent drinking water regulations to protect public health from waterborne disease. In Ontario, the impetus arose from the 2000 Walkerton's *E. coli* outbreak and the resulting step-wise incremental approach towards more rigorous regulations. The provincial legislature felt the pressure of the Walkerton tragedy and hard-pressed regulators to amend the Safe Drinking Water Act beginning with the promulgation of Ontario Regulation 459/00 followed three years later by Ontario Regulation 170/03. Many regulatory compliance features that favored the use of ozone in American regulations were mirrored by the province of Ontario. As such, it is more than likely that some of the remaining rules implemented in the US will eventually be part of the next round of Ontario regulatory updates further driving the water industry to encourage the use of alternative disinfectants such as ozone.

Whether or not ozone is incorporated as a consequence of regulatory compliance, it is rarely for one purpose alone. Lofty capital costs combined with extensive operation and maintenance activities and advanced operator skills make ozone an attractive solution

solely if multiple water quality issues can be resolved simultaneously (Rakness, 2005). Although ozonation of drinking water has grown in popularity in the North American market primarily to comply with current or impending regulations, utilities will usually enjoy many other benefits especially for those treating impacted source water supplies.

2.1.2 Ozone Chemistry

The majority of drinking water treatments incorporate ozonation into their process primarily for disinfection purposes. Regardless, oxidative reactions will occur simultaneously and are discussed herein.

There are two distinct reaction pathways by which ozone can oxidize organic matter:

- Direct reaction by molecular ozone (Section 2.1.2.1)
- Indirect reaction via ozone decomposition products such as hydroxyl radicals (Section 2.1.2.2)

2.1.2.1 Molecular Ozone Reaction Mechanisms

Ozone is one of the most powerful oxidants used in drinking water treatment, second only to hydroxyl radicals. Comparative thermodynamic oxidation potential values (E^o) for oxidants commonly used in the water industry are summarized in Table 2.1 (White, 1999).

Table 2.1: Oxidation Potential of Oxidants in Drinking Water

Oxidant	**E^o (eV)**
$OH^{\cdot}$ radical	2.8
O_3	2.1
H_2O_2	1.8
Cl_2	1.4
O_2	1.2
ClO_2	1.0

Because molecular ozone has resonance structures, it can act either as a dipole, an electrophile, or nucleophile. It is a very selective oxidant because it primarily targets unsaturated bonds in aliphatic and aromatic molecules (Langlais and Reckhow, 1991). Its dipolar structure will attack unsaturated bonds via a cyclo-addition reaction also known as the Crigee Mechanism, to form an ozonide ($O_3^{\cdot -}$) intermediate, which in water, will readily decompose to lower molecular weight carbonyl structures such as aldehydes and ketones (Von Gunten, 2007; Langlais and Reckhow, 1991).

In molecules of high electron density such as aromatic compounds, ozone's selective attack will depend on the nature of the functional groups (Langlais and Reckhow, 1991);

- If the ring is substituted with electron donor groups such as -OH, $-CH_3$, $-OCH_3$, the most reactive carbons are the ones bearing the highest electron densities, on the ortho- and para- positions (with respect to the electron donor position).
- On the other hand, the most reactive carbons are at the meta-positions if the ring is substituted with an electron withdrawing group ($-NO_2$, $-CO_2H$, -CHO, -Cl).

In both instances, the electrophilic attack of ozone on the most reactive carbons will lead to the formation of quinoid structures and with ring opening, result in the formation of lower molecular weight aliphatic compounds bearing carbonyl and carboxylic functionalities (Langlais and Reckhow, 1991). From the low TOC removal achieved via ozonation, complete mineralization to carbon dioxide and water isn't a usual outcome in complex media such as natural waters due to the wide variety of competing reactions (Glaze and Weinberg, 1993).

The rate law characterizing the decomposition of a substrate S by ozone is (Langlais and Reckhow, 1991):

$$\text{Rate } (M^{-1}s^{-1}) = -dS/dt = k[O_3]^1[S]^1 \qquad (2.1)$$

The rate law is first order in both substrate and ozone and the bimolecular reaction is second order overall with k as its rate constant (s^{-1}) (Langlais and Reckhow, 1991).

Typically, molecular ozone isn't very reactive towards alicyclic or saturated organics with reaction rates in the order of 1 to 10^3 $M^{-1}s^{-1}$ (Lalelzary *et al*, 1986). However, aromatic and unsaturated compounds are readily oxidized with reaction rates varying between 10^3 and 10^4 $M^{-1}s^{-1}$ when the pH range is maintained between 2 and 6 in order to hinder ozone decomposition reactions (Lalelzary *et al*, 1986).

2.1.2.2 Ozone Decomposition Reaction Mechanisms

Factors affecting the stability or half-life of molecular ozone include pH, temperature, ultraviolet light, ozone dosage, and the concentration of radical initiators, promoters, and scavengers in water (Langlais and Reckhow, 1991). Ozone decomposition rate increases with higher ozone dosages and pH (excess of hydroxide ions) and follows a pseudo-first order reaction. Molecular ozone undergoes a complex series of chain reactions initiated by the attack of hydroxide ions as the rate-limiting step and ultimately resulting in the formation hydroxyl radials ($OH^{\cdot}$). Since the pH and ozone dosage are key factors in ozone decomposition reactions, advanced oxidation reactions involving low-level hydroxyl radical generation will invariably take place during ozonation of natural waters (Langlais and Reckhow, 1991).

The decomposition of molecular ozone, hence the quantity of hydroxyl radicals generated is influenced by a wide array of constituents in water that have the ability to initiate, promote or inhibit the chain reaction process (Von Gunten, 2007; Langlais and Reckhow, 1991):

- Initiators that act like hydroxide ions have the ability to jump-start the ozone decomposition chain reaction. Other initiators include hydrogen peroxide, ferrous ions (+2), humic substances, and ultraviolet light in the 254 nm range.
- Promoters of ozone decomposition are organic and inorganic substances that don't initiate the chain reaction but which react with the products of decomposition i.e. hydroxyl radicals, and propagate the chain reaction step. Specifically, promoters react with hydroxyl radicals to catalyze superoxide anions (O_2^-), which in turn, react quickly with ozone molecules further

generating hydroxyl radicals. Examples of promoters regenerating the superoxide anion include formic acid, primary alcohols, humic acids, and phosphates.

- Inhibitors scavenge hydroxyl radicals without catalyzing the superoxide anion thus effectively terminating the chain reaction and thereby stabilizing molecular ozone from further decomposition reactions. Typical radical scavengers include tertiary alcohols, humic substances, and carbonaceous alkalinity (carbonate and bicarbonate ions).

From a drinking water treatment perspective, if either disinfection or oxidation of unsaturated compounds is the main goal of implementing ozonation, than molecular ozone reactions should be favored while minimizing ozone decomposition reactions. Water treatment strategies to capitalize on molecular ozone reactions include (Rakness, 2005):

- Lowering the pH to decrease the hydroxide ion concentration that would otherwise initiate the free-radical chain reaction.
- Increasing the carbonaceous alkalinity prior to ozonation, a process also known as remineralization. Injecting higher concentrations of the radical traps carbonate and bicarbonate ions will lower the ozone decomposition rate.
- Increasing the applied ozone dosage. Although higher ozone concentrations will increase its decomposition rate and subsequently the formation of hydroxyl radicals, there will still be more molecular ozone available for direct attack.

Interestingly the latter is the preferred treatment option by water purveyors, unless enhanced coagulation (lowering the pH) is also practiced. If no treatment strategies to promote molecular ozone reactions are implemented, the utility will usually benefit from ozone decomposition reactions that will generate sufficient amounts of hydroxyl radicals to oxidize low-levels of recalcitrant organic micro-contaminants (Rakness, 2005). These non-selective secondary reactions are discussed in the following sections.

2.1.3 Ozone Applications in Water Treatment

In recent years, while chemical disinfection has been the most common treatment objective sought after when applying ozone to drinking water in North America, utilities will usually benefit from other attributes making ozonation an attractive alternative to conventional disinfectants including:

Enhanced Particulate and Turbidity Control

The application of ozone prior to pretreatment (coagulation, flocculation, and sedimentation) in conventional treatment process is known as pre-ozonation. Applying ozone ahead of pretreatment can enhance coagulation therefore improving particulate removal, reducing turbidity levels, and lowering coagulant dosage. Chang and Singer (1991) determined that particle destabilization of source waters was dependent on the hardness-to-TOC ratio. An optimal ozone dosage of between 0.4 to 0.8 mg O_3/mg C was most effective to induce coagulation when the raw water hardness-to-TOC ratio was above 25 mg $CaCO_3$/mg C. There are many mechanisms that have been proposed to explain this phenomenon, namely (Singer and Chang, 1989; Reckhow *et al*, 1986):

- Ozone reacts with organic matter and promotes the formation of carboxylic, carbonyl, and phenolic functional groups. The greater bonding affinity of these oxygenated functional groups with aluminum oxides (from aluminum-based coagulants) results in higher NOM removal. Also, the higher number of carboxylic functional groups promotes calcium complexation, which in turn improves surface adsorption of ozonated organics onto metallic coagulants.
- Ozonides $O_3^{\cdot -}$, (resulting from 1-3 dipolar cyclo-addition of ozone on a carbon-carbon double bond, Langlais and Reckhow, 1991) and organic peroxides are generated during ozonation of NOM and in the presence of hydroxylated radicals will form polymerized chains. These biopolymers enhance coagulation by their greater affinity to complex aluminum oxides and improve floc strength.
- Ozone lyses algae in surface waters and the subsequent release of biopolymers enhances coagulation by the same mechanisms described above.

- Ozone ruptures metal-humic complexes resulting in the release of oxidized metals such as Fe (+3) or Mn (+4). These oxidized metals will undergo hydrolysis and act as secondary coagulants, thus promoting the formation of additional microflocs and improving NOM removal.

Enhanced Filterability

The application of ozone following coagulation, flocculation, and/or sedimentation but prior to filtration is also referred to as intermediate ozonation. Intermediate ozonation can improve the performance of granular media filters for turbidity and particulate removal. Lower filter effluent turbidities and longer filter run times (due to slower filter headloss buildup) are routinely observed regardless of media type (Rakness, 2005; Langlais and Reckhow, 1991). Where government regulators have set very low turbidity limits in filtered water, the use of intermediate ozonation has proven to be particularly advantageous for compliance purposes. Moreover, a recent study at the Windsor, Ontario water treatment plant demonstrated that intermediate ozonation enhanced particulate removal of filtered water in the 2 to 5 μm and 5 to 10 μm range (Mazloum *et al*, 2004). Since *Cryptosporidium* oocysts and *Giardia* cysts are within these size ranges, ozone-enhanced filtration performance improves the removal of these chlorine-resistant pathogens and overall disinfection effectiveness.

Oxidation of Inorganic Contaminants

Ozone will oxidize dissolved iron and manganese to their highest oxidation states, resulting in the formation of insoluble metallic ions. These oxidized metals will undergo hydrolysis and act as filter aids thus promoting the formation of microflocs, which are readily removed by a subsequent filtration step. Hydrogen sulfide imparts an objectionable odour to water (rotten-egg smell) and is rapidly oxidized to non-odourous sulfate ions (Rakness, 2005; Langlais and Reckhow, 1991).

Biological Stabilization

Ozone oxidizes organic matter into low molecular weight, biodegradable substrates, which are measured as assimilable organic carbon (AOC). Specifically, ozone converts a

fraction of the non-biodegradable organic matter into biodegradable organic matter. Escobar and Randall (2001) observed a substantial increase in the formation of ozonation byproducts at ozone dosages equivalent to 0.2-0.5 mg O_3/mg DOC and AOC production peaked between 0.5 and 1 mg O_3/mg DOC. The latter is also representative of common ozone dosages applied to achieve effective disinfection. In other words, reaching optimal TOC removal and disinfection compliance goals share the same ozone dosage range. If left unchecked, the higher AOC levels promote biological instability and encourage the proliferation of microorganisms in the distribution system. Hence, a biofiltration step following ozonation is essential in order to minimize biological regrowth (Escobar and Randall, 2001).

The biomass that colonizes the filter media will, under the right conditions, readily consume the biodegradable fraction of NOM, thus lowering DOC, DBP precursors, chlorine demand (with post-filtration chlorine addition), and overall nutrient levels. Biological stabilization was first coined in Germany when applying intermediate ozonation prior to granular activated carbon (GAC) filtration (Langlais and Reckhow, 1991). In tandem, the process is especially beneficial in source waters with elevated levels of natural organic matter (Huck *et al*, 2000). A more thorough description and performance of intermediate ozonation in combination with granular media filtration is presented later.

Without biological filtration, biological stability after ozonation has been accomplished by applying substantially higher chlorine dosages prior to the distribution system (Nerenberg *et al*, 2000). It was found that the growth of bacteria, despite elevated nutrient levels was delayed as long as a free chlorine residual was maintained (Escobar and Randall, 2001).

Color Removal

In natural waters, color is generally associated with natural organic matter predominantly humic and fulvic acids. They are composed of heterocyclic structures that absorb light in the visible region between 400 and 800 nm (Langlais and Reckhow, 1991).

Public perception often links the safety of a drinking water supply to its aesthetic properties (Symons, 2006) and colored water is a major source of water quality complaints. NOM is also responsible for elevated chlorine demand and the formation of halogenated DBPs (Chaiket *et al*, 2002). It is therefore imperative to remove or alter these humic substances before chlorination. Since molecular ozone and chlorine are both electrophilic agents, they share similar modes of attack with respect to humic substances (Chaiket *et al*, 2002). Conventional and direct filtration treatments have the ability to remove upwards of 70% of colored substances in low to moderately colored waters. Other treatment alternatives that have been successful for color removal include chlorine dioxide, GAC adsorption, and membrane filtration. The major disadvantage of the last two physical separation processes is they merely transfer the contaminants from one phase to another and proper waste management activities can be costly (Langlais and Reckhow, 1991).

Ozone is particularly reactive with aromatic compounds and at low doses (1 to 3 mg O_3/mg C) has been reported to achieve color reductions in excess of 95%. In highly colored waters, ozone alone (even at high doses 8 to 13 mg/L) will only achieve color removals between 20% and 60% (Langlais and Reckhow, 1991). Hence, a combination of treatments is necessary to achieve stringent color abatement goals (>90% removal). Ozone-assisted biofiltration processes can considerably enhance color removal by the bleaching action of ozone on the chromophores functionalities of humic substances. Ozone will also augment the biodegradable fraction of NOM thus improving DOC removals via a subsequent biological filtration stage (Langlais and Reckhow, 1991).

Halogenated Disinfection By-Product Formation

Numerous research studies have shown that under conditions that minimize the free-radical ozone decomposition pathway i.e. neutral or acidic pH and in the presence of radical scavengers, molecular ozone reactions prevail resulting in the oxidation of halogenated DBP precursors and a substantial reduction of their reactivity towards free chlorine (Sohn *et al*, 2007; Fonseca and Summers, 2003; Chang and Singer, 1991). Conversely, there isn't a consensus amongst researchers over the impact of hydroxyl radicals on halogenated DBP formation. Some researchers have observed that hydroxyl

radicals enhanced halogenated DBP formation potential along with an increase in the overall chlorine demand (Frimmel *et al*, 2000; Kleiser and Frimmel, 2000) while others have concluded that hydroxyl radicals are very effective at oxidizing halogenated DBP precursors (Yang *et al*, 2012; Ferguson *et al*, 1990).

Taste and Odour Control

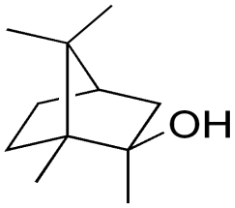
There are many biological and chemical substances which are responsible for imparting objectionable taste and odour to drinking water (Langlais and Reckhow, 1991). The same argument can be made for colored water, undesirable taste and odours in drinking water are a major cause of consumer complaints. In a past survey, it was estimated that 16% of utilities experienced significant T&O problems allocating almost 5% of their annual budgets on mitigation measures (Nerenberg *et al*, 2000). The sources of taste and odour-causing substances include decaying NOM products, anthropogenic contaminants, inorganic compounds, and organic metabolites secreted by living organisms. In an effort to stay concise and in the context of the current research, discussion will be limited to cyanobacteria, the most notorious culprit imparting objectionable tastes and odours in surface waters (Yoo *et al*, 1995).

Cyanobacteria have received worldwide attention over the last three decades because they are ubiquitous in most surface waters (Karner *et al*, 2001) and at least 19 of the 50 known genera produce toxins that pose acute and chronic health risks to human and wildlife alike. The four types of emerging toxins identified include neurotoxins, cytotoxins, endotoxins, and hepatotoxins. A 1989 study conducted by the National Rivers Authority found that between 60% and 70% of all blooms in the UK were toxic (NRA, 1990). Environmental factors promoting their growth include moderate to high levels of nutrients, low nitrogen to phosphorous ratios, warm water temperature, and neutral to alkaline pH.

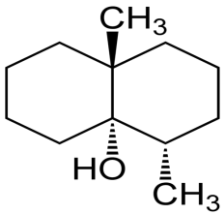
Cyanobacteria are an important contributor to source TOC levels and are a significant producer of chlorinated byproduct precursors (Nguyen *et al*, 2005). They also release secondary metabolites such as *trans*-1,10-dimethyl-*trans*-9-decalol (geosmin) and 2-methylisoborneol (MIB) that are responsible for imparting earthy-musty odours to drinking water at threshold levels as low as in the 5 to 9 ng/L-range (Elhadi *et al*, 2006;

Nerenberg *et al*, 2000; Yoo *et al*, 1995). As illustrated in Figure 2.1, MIB and geosmin are alicyclic alcohols and as such aren't particularly susceptible to direct ozone attack. Therefore, oxidation of these micro-pollutants during conventional ozonation will mainly proceed via hydroxyl radical reactions.

Figure 2.1: Chemical Structures of 2-methylisoborneol and Geosmin



2-methylisoborneol



Geosmin

Numerous studies have shown that ozone typically applied at disinfection dosages (i.e. 1.0 mg O_3/mg DOC) and under raw water conditions that favor ozone decomposition reactions, can oxidize these undesirable contaminants at low to moderate levels (Huck *et al*, 1995; Yoo *et al*, 1995). Alternatively, in high-TOC surface water, Lundgren *et al* (1988) showed that natural organic substances effectively compete with MIB and geosmin thus exerting a marked increase in the ozone demand and requiring higher ozone dosages to oxidize these odourous contaminants to below their threshold odour numbers: Achieving geosmin and MIB removals above 95% required an ozone dose of 7 mg/L with a contact time of 10 minutes while decreasing the ozone dose to common disinfection levels i.e. 1.5 mg/L reduced their removals efficiency to 75% and 45%, respectively. Similar results were reported by Glaze *et al* (1990) when ozonating Colorado River water at typical disinfection dosages. A 2 mg/L-ozone dose resulted in partial destruction of geosmin and MIB with percent removal yields of 40% and 38%, respectively. Doubling the ozone dose was necessary to oxidize these odourous compounds at near their threshold odour numbers.

It should be cautioned that conventional ozone treatment for the purpose of chemical oxidation including the destruction of micro-contaminants received widely diverging

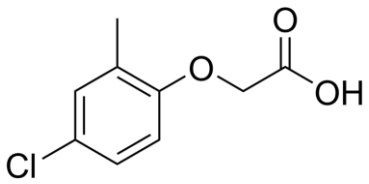
results primarily due to significant source water quality variability (Chang and Singer, 1991).

Oxidation of Organic Micro-Pollutants

Molecules containing high electron density bonds are particularly reactive to molecular ozone's electrophilic attack such as phenolic derivatives and some SOCs (Ikehata and Gamal El-Din, 2005). Furthermore, ozone can effectively degrade saturated natural and synthetic organic micro-contaminants, via the free radical decomposition pathway. Ozonation at dosages routinely applied in water treatment will generate hydroxyl radicals whose effectiveness will depend on trace organic concentration, pH, radical scavenger levels, and NOM in source waters (Rakness, 2005, Langlais and Reckhow, 1991).

In the context of this research, the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) should, in theory be degraded by direct ozone attack because of its high electron density centers (Xiong and Graham, 1992).

Figure 2.2: Chemical Structure of MCPA



In bench-scale experiments using ultra-pure water, Benitez *et al* (1991) determined that under direct ozone attack mode, two moles of ozone fast-reacted with one mole of MCPA. A reaction mechanism was proposed involving ozone's electrophilic attack on nucleophilic activated positions on the aromatic ring resulting in the formation of an ozonide intermediate and subsequent cleavage leading to oxidation products. These decomposition products included short-chain aliphatic acids (2 to 4 carbons chains), carbon dioxide, and chloride ions (Reynolds *et al*, 1989).

Alternatively, Meijers *et al* (1995) conducting bench-scale experiments with pre-treated River Meuse water showed that at an ozone-to-DOC ratio of 0.55:1, 68% of MCPA was oxidized at ambient temperature. Increasing the ozone dose to an equivalent O_3/DOC ratio of 0.95:1 resulted in an 89% degradation of MCPA. At common disinfection dosages, ozonation is an effective technology for the destruction of MCPA (Meijers *et al*, 1995).

In raw water sources that are significantly impacted by saturated organic micro-pollutants such as geosmin and MIB, ozone alone has shown limited success primarily because of its high selectivity and relative low reaction rates (Ikehata *et al*, 2008). On the other hand, hydroxyl radicals are the most powerful oxidants (Table 2.1), are non-selective, and have very high reaction rates with respect to the oxidation of saturated aliphatic and alicyclic organic micro-pollutants (Ikehata *et al*, 2008, Ferguson *et al*, 1990). Purposely enhancing hydroxyl radical formation is commonly referred to as an advanced oxidation process (AOP) (Ferguson *et al*, 1990). There are many treatment options to augment hydroxyl radical yield via free-radical chain reaction pathways including increasing initiator levels such as hydroxide ion concentration, adding promoters, and decreasing carbonaceous alkalinity in order to lower radical scavenger levels. However, there are only two ozone-based treatment strategies that are commonly employed in the water industry, both involve increasing ozone decomposition initiator levels: either applying ultraviolet light or adding hydrogen peroxide (Langlais and Reckhow, 1991).

2.1.4 Ozone-Based Advanced Oxidation Processes

2.1.4.1 AOP: Ozone-UV Tandem

Ozone absorbs in the ultraviolet region with a peak absorption wavelength of 253.6 nm. Ozone will undergo photolysis with the production of oxygen plus an oxygen atom that subsequently reacts very rapidly with water to form hydroxyl radicals.

A secondary reaction in this process worth mentioning involves the secondary attack of hydroxyl radicals in water which generates hydrogen peroxide (Glaze *et al*, 1987). Hydrogen peroxide can then either react with ozone (Peroxone) or undergo photolysis. The latter constitutes the basis for another type of advanced oxidation system that doesn't involve the use of a strong oxidant such as ozone, the UV-hydrogen peroxide process. The photolysis of one mole of hydrogen peroxide should in theory, generate two moles of hydroxyl radicals (Glaze *et al*, 1987). Unfortunately hydroxyl radical formation is significantly impacted by the "cage effect" of water, which lowers the quantum yield by 50% (Oppenlander, 2003). Photolysis effectiveness is also hampered by the low molar extinction coefficient of hydrogen peroxide $\varepsilon = 19.6\ M^{-1}s^{-1}$ at 254 nm compare to $\varepsilon = 3300\ M^{-1}s^{-1}$ for ozone (Glaze *et al*, 1987). Moreover, hydrogen peroxide must compete with other UV-absorbing substance in water further hindering hydroxyl radical formation yields (Andrews *et al*, 1995). Photolysis of hydrogen peroxide is a very inefficient process and in order to generate an acceptable level of hydroxyl radicals, the process must be enhanced by either:

- increasing the concentration of hydrogen peroxide (Glaze *et al*, 1987) and/or
- using high-intensity UV bulbs, at least one order of magnitude higher than those required for UV disinfection (Tuhkanen, 2004).

Andrews *et al* (1995) demonstrated the effectiveness of UV irradiation in combination of hydrogen peroxide for the destruction of geosmin and MIB in river water. Settled water was spiked with 100 ng/L of odourous compounds and irradiated with a 1 KW medium-pressure UV lamp operated at half power. The research showed that at a 5-mg/L hydrogen peroxide dosage, geosmin and MIB were oxidized to below their method detection limits despite the high level of radical scavengers naturally present in the water treated. At an ozone dose of 1 mg/L, the ozone-UV treatment improved their destruction over UV irradiation alone but wasn't as effective as the combination hydrogen peroxide-UV, a surprising result taking into account the higher extinction coefficient of ozone over hydrogen peroxide. In either case the reaction time required was very short - in the order of a few minutes (Andrews *et al*, 1995).

2.1.4.2 AOP: Ozone-Hydrogen Peroxide Tandem: The Peroxone Process

In theory, the O_3/H_2O_2 AOP should be rechristened the ozone-hydroperoxide process or for the purists, the Hydroperoxone Process. In actual fact, hydrogen peroxide has a very low reactivity towards ozone and thus isn't an effective initiator of the free-radical chain reaction (Acero and Von Gunten, 2001). Conversely, in his ionized form, the hydroperoxide ion (HO_2^-) reacts very quickly with ozone ($kO_3,HO_2^- = 5.5 \times 10^3\ M^{-1}\ s^{-1}$) but because of hydrogen peroxide's high pKa (11.6), is only partially dissociated at pH commonly found in drinking water treatment (Von Gunten and Hoigne, 1994; Langlais and Reckhow, 1991). Elevating the pH increases the hydroperoxide fraction, which in turn accelerates ozone decomposition reaction rates and overall hydroxyl radical yield.

The decomposition of ozone fits a second-order reaction rate with respect to ozone and hydroperoxide concentrations. Fortunately, the second-order rate constant is over 6 orders of magnitude faster than that between ozone and hydroxide ions, implying that hydroperoxide are very effective initiators of the free-radical chain reaction even at near neutral pH (Langlais and Reckhow, 1991).

The stoichiometry of the reaction between ozone and hydrogen peroxide is (Rakness, 2005):

$$H_2O_2 + 2O_3 \longrightarrow 2OH^{\cdot} + 3O_2 \qquad (2.2)$$

From equation 2.2, the stoichiometric ratio of H_2O_2 to O_3 is equal to 0.35 (w/w). Below this ratio, the system is reaction-limited because ozone is in excess allowing molecular ozone reactions to proceed and the decomposition of ozone to hydroxyl radicals limited by the concentration of hydrogen peroxide. In contrast, the system is mass-transfer limited at or above H_2O_2/O_3 ratio of 0.35 (w/w), because hydrogen peroxide is in excess and ozone is completely consumed generating the highest yield of hydroxyl radicals (Rakness, 2005; Koch, 1992; Langlais and Reckhow, 1991).

Most studies comparing ozone alone and the combination of ozone and hydrogen peroxide are conclusive on the effectiveness of inducing the free-radical pathway for the enhanced destruction of recalcitrant organic micro-pollutants in natural waters: Overall, hydroxyl radicals effectively oxidize a wide spectrum of organic substances with reaction rates in the 10^7-10^{10} M^{-1} s^{-1} range (Acero and Von Gunten, 2001; Langlais and Reckhow, 1991; Buxton *et al*, 1988). Kinetics experiments in natural waters showed that the rate constants of molecular ozone with MIB and geosmin were 4 to 9 M^{-1} s^{-1} and 5 to 11 M^{-1} s^{-1} respectively whereas their rate constants significantly increased from 10^9 to 6 10^9 M^{-1} s^{-1} and 10^9 to 4 10^9 M^{-1} s^{-1} respectively with hydroxyl radicals (Westerhoff *et al*, 2005). Direct ozone reaction with MCPA yielded a rate constant of 47.7 M^{-1} s^{-1} against 6.6 10^9 M^{-1} s^{-1} in the presence of hydroxyl radicals (Benitez *et al*, 2004).

The high reaction rates over a broad range of organic compounds underscore the lack of selectivity of hydroxyl radicals compare to molecular ozone reactions (Meijers *et al*, 1995; Haag and Yao, 1992).

Groundwater is often characterized by lower DOC and higher alkalinity whereas surface water has generally higher DOC and lower alkalinity. Ozonation of groundwater has a stabilizing effect from ozone decomposition reactions because low levels of DOC don't exert a high ozone demand and the elevated alkalinity hinders the free radical pathway due to the scavenging action of carbonate and bicarbonate ions. Thus, the addition of hydrogen peroxide will substantially accelerate ozone decomposition reactions due to the considerable increase in initiator (HO_2^-) levels (Acero and Von Gunten, 2001).

In surface waters, ozone is rapidly destabilized by the combination of high concentrations of natural promoters in NOM (high DOC) and the lack of radical scavengers (low alkalinity), hastening ozone decomposition reactions, and the production of hydroxyl radicals. An influx of radical-chain initiators such as hydrogen peroxide will not profoundly accelerate ozone decay rate in this type of water and hydroxyl radical yield doesn't substantially increase because the primary ozone decomposition mechanism is mediated by natural promoters (Acero and Von Gunten, 2001).

The oxidation of ozone-resistant micropollutants in low-DOC source waters is best achieved by peroxone over ozone alone, and destruction yields is sensitive to varying hydrogen peroxide to ozone ratio. In contrast, the hydroxyl radical capacity is not as affected by the addition of hydrogen peroxide in high-DOC waters and is thus insensitive to varying hydrogen peroxide to ozone ratio (Acero and Von Gunten, 2001).

Koch (1992) and Ferguson *et al* (1990) reported an optimal H_2O_2/O_3 ratio for the destruction of recalcitrant micro-organic contaminants in one type of source water. They observed that the optimal peroxone ratio for the destruction of geosmin and MIB was between 0.1 and 0.2 (w/w) and since the system is reaction-limited, hypothesized that natural promoters accelerated ozone decomposition reactions. In another type of source water, there was no optimal ratio in the range studied (between 0.1 and 0.3) because of the scavenging effect of carbonaceous alkalinity, consuming a significant fraction of hydroxyl radicals. The ozone dose required to achieve a 90% + MIB removal target was 4 mg/L and was halved at an H_2O_2/O_3 ratio of 0.2. The lower ozone dosages necessary to satisfy organics removal targets in peroxone systems have the potential to reduce operating and energy costs of an existing ozone generator. For engineering design purposes, if the driving force of implementing ozonation is for chemical oxidation applications such as taste and odour control or destruction of recalcitrant trace organics, then substantial cost savings can be expected because lower ozone dosage needs translate into smaller ozone generators.

2.1.5 Ozonation By-Products, a Possible Deterrent to Ozone Treatment?

2.1.5.1 Organic Byproducts

Ozone is a strong oxidant and as such will inevitably generate oxidation by-products (Glaze and Weinberg, 1993). Ozonation of NOM will result in profound physico-chemical changes to its structure and properties. NOM undergoes a marked increase in hydrophilicity, polarity, and biodegradability with high-molecular weight, long-chain

fractions oxidized into lower molecular weight short chain moieties bearing carbonyl, hydroxyl, and carboxylic functionalities. Although ozonation has a negligible impact on TOC removal, there is a significant decrease in UV_{254} because of the loss of aromaticity, and breakage of unsaturated bonds in NOM, both of which absorb strongly at 254 nm. These organic by-products have been shown to either cause regrowth in distribution systems or increase chlorinated DBPs formation potential. Fortunately they are readily removed by a downstream filtration step which supports a biota given that chlorination is delayed at a later stage of treatment (Glaze and Weinberg, 1993).

2.1.5.2 Inorganic byproducts

Inorganic by-products are also formed during ozonation particularly in moderate to high-bromide-containing natural waters (>50 μg/L; Von Gunten, 2007). As such, ozone reacts with bromide to form bromate, a known human carcinogen (Galey *et al*, 2001) and to-date, the only regulated ozone by-product. A maximum acceptable concentration (MAC) was set at 10 μg/L by the Province of Ontario, mirroring the USEPA's action limit based on a 10^{-5} excess cancer risk level of 0.5 μg/L (USEPA, 1998).

Bromate formation is an important factor with respect to the feasibility of implementing ozonation in water treatment particularly if disinfection is a major treatment objective (due to the higher ozone dosages applied). Providing adequate disinfection (especially for *Cryptosporidium* inactivation) and oxidizing micro-contaminants while controlling bromate and other ozonation by-products of potential health concern is more often than not a balancing act from a regulatory perspective (Acero and Von Gunten, 2001; Galey *et al*, 2001).

Understanding the mechanisms leading to the formation of bromate is key to devising mitigation treatment strategies that can be applied to water treatment. pH, alkalinity, NOM, bromide concentration, and temperature are the most important raw water quality factors affecting bromate formation (Galey *et al*, 2001). Figure 2.3 is a simplified version of the ozone reaction pathways in the presence of bromide leading to bromate formation.

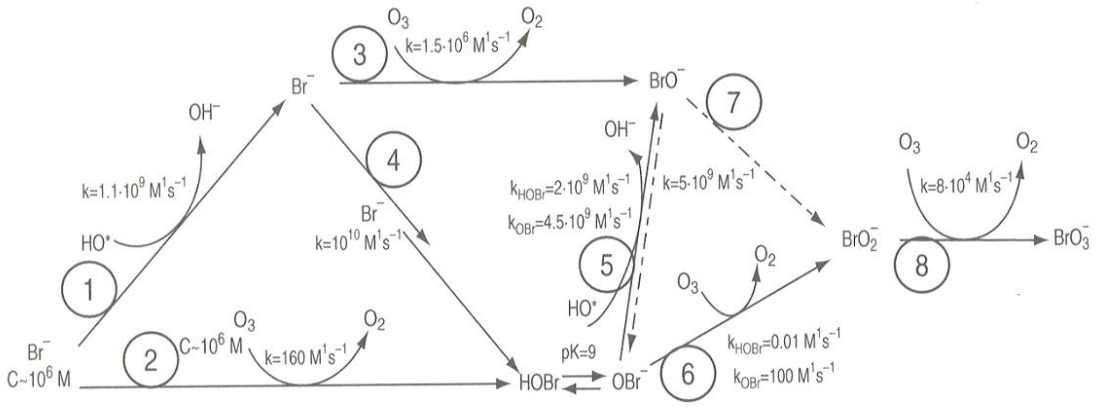


Figure 2.3: Bromate Formation Pathways during Ozonation (Buffle *et al*, 2004)

Reactions 1 and 2 show that bromate formation can be initiated by either molecular ozone or hydroxyl radicals. The oxidation of bromide by molecular ozone is a very slow process ($k = 160\ M^{-1}\ s^{-1}$) thus requiring longer contact time, higher ozone dosages, or elevated bromide concentrations. In contrast, the initial hydroxyl radical attack is significantly faster with a reaction rate equal to $1.1\ 10^9\ M^{-1}\ s^{-1}$. The high reaction rate of the latter makes up for low hydroxyl radical yield commonly generated during conventional ozonation of natural waters. The formation of hypobromous acid and its ionized counterpart, hypobromite ion, is a critical step towards bromate formation with the water's pH influencing strongly subsequent reactions. In an acidic environment, hypobromous acid will be preferentially formed and its subsequent reaction with ozone (reaction 6) is very slow ($k = 0.01\ M^{-1}\ s^{-1}$). However, at higher pH, hypobromite ions become dominant and the reaction with ozone (reaction 6) proceeds at a rate one hundred-fold faster. The oxidation of bromite to bromate is strictly mediated by molecular ozone as depicted by reaction 8.

2.1.5.3 Bromate mitigation strategies

1. Although not practically feasible using conventional water treatment technologies, reducing natural bromide levels would limit bromate formation

proportionally (Song *et al*, 1997; Glaze and Weinberg, 1993). A recent pilot study (Kimbrough *et al*, 2013) investigated electrolysis treatment prior to ozonation in natural waters with high bromide levels ranging between 260 and 280 μg/L. The results showed a dependence of the applied current with respect to bromate formation after ozonation, indicating that electrolysis can effectively convert bromide to bromine. With an applied current of 33 amps, bromate formation decreased by approximately 50% while at 98 amps levels dropped by 92%.

2. On the other hand, applying lower ozone dosages effectively limits bromate formation but can significantly impede disinfection or chemical oxidation performance goals (Galey *et al*, 2001).

3. pH depression will slow ozone decomposition reactions and reduce the hydroxyl radical flux thus minimizing reactions 1, 5, and 7. Bonacquisti (2006) reported a significant reduction in bromate formation when the pH was lowered to 6.0. At low pH, only in the most favorable bromate formation conditions (300 μg/L bromide combined with an ozone dose of 6.4 mg/L) did bromate levels slightly exceeded provincial standards at a value of 11 μg/L. Moreover, decreasing the pH shifts the equilibrium from hypobromite ions to hypobromous acid, further reducing bromate formation rates (Rakness, 2005; Galey *et al*, 2001; Song *et al*, 1997).

4. Pre-ammonia addition converts the bromine formed to monobromamine. In theory, this process should curtail reactions 5 and 6 (Song *et al*, 1997). However, researchers have experienced mixed success in the application of this strategy because, albeit at a slow rate, monobromamine can be oxidized by ozone effectively liberating bromide (Rakness, 2005). The other drawback is due to the excess ammonia residual that exerts a high chlorine demand if breakpoint chlorination is practiced at a later stage of treatment (Glaze and Weinberg, 1993).

5. The chlorine-ammonia process exhibit a higher success rate compare to ammonia alone. Prior to the ozone contactors, chlorine is pre-dosed to completely react with naturally-occurring bromide and form bromine, which in turn reacts with an excess amount of ammonia to form monobromamine. Since ozone reacts slowly with monobromamine ($k = 40\ M^{-1}\ s^{-1}$), very little bromide is liberated and available for bromate formation via the ozone oxidation pathways discussed earlier. The major drawback is to ensure that the pre-chlorination step is well optimized in order to minimize chlorinated byproduct formation (Rakness, 2005).

2.1.6 Biological Filtration

In the absence of disinfectant application prior to, or during backwashing, granular filtration media whether it be sand, anthracite, or GAC will be colonized by a biomass containing indigenous microorganisms capable of metabolizing a wide array of organic and inorganic contaminants including NOM, trace organics, ammonia, nitrate, perchlorate, sulfate, iron and manganese, all at a competitive cost (Zhu *et al*, 2010; Rakness, 2005).

However, consumer acceptance remains a major obstacle to its implementation in drinking water treatment. An AWWARF survey showed that only 25% of respondents were favorable to biological filtration treatment because of the perceived pathogenic threat from bacterial breakthrough and the potential for contamination of drinking water supplies (Evans *et al*, 2008). Several studies have demonstrated that coliforms were seldom detected in biological filtration effluents because microorganisms must compete for low-levels nutrients ubiquitous in drinking water sources (Shirey *et al*, 2012; Zhu *et al*, 2010). The types of bacteria detected at the effluent of the biological process are predominantly non-pathogenic, which are readily killed at low disinfectant dosages (Escobar and Randall, 2001; Huck, 1988). In addition, the biomass doesn't interfere with filter performance engineered for particle removal with reported filter effluent turbidities consistently below 0.1 NTU (Emelko *et al*, 2006).

The biodegradable fraction of NOM or biodegradable organic matter (BOM) is consumed by the biota effectively reducing TOC and corrosion potential while improving the organoleptic properties and biological stability of treated water in downstream processes and in the distribution system (Nerenberg *et al*, 2000). Exploiting this effect, Peldszus *et al* (2012) demonstrated that a chemical-free biofiltration pre-treatment step significantly curbed reversible and irreversible fouling of UF membranes.

Lastly, because of its high susceptibility to chlorine attack, decreasing BOM levels prior to chlorination results in a marked reduction of the chlorine demand and related halogenated DBP levels (Emelko *et al*, 2006; Nerenberg *et al*, 2000; Huck *et al*, 1998).

Several factors strongly influence biofiltration performance with respect to BOM removal including:

- The nature and characteristics of BOM - Not all biodegradable organic fractions are consumed by the biomass at the same rate, with low molecular weight monomers being more rapidly "assimilated" by the bacterial community than their higher molecular weight counterparts. A key factor for maximum BOM consumption and hence DOC removal is the optimal empty bed contact time (EBCT) especially in cold water conditions. Deeper filtration beds providing higher EBCT or operating biofilters at lower hydraulic loading rate (HLR) regimes might be required to meet organics removal objectives in cold water conditions (Emelko *et al*, 2006). Nevertheless, adequate BOM removals are usually achieved within the confine of existing filtration designs optimized for particulate removal (Langlais and Reckhow, 1991).

- Water temperature - As expected, biochemical activity decreases significantly when the temperature drops below 10^{o}C (Huck *et al*, 2000, Prevost, 1989a). Another study (Fonseca and Summers, 2003) showed that when water temperature drops below 3^{o}C, the loss of biomass activity resulted in a 10%

reduction in BOM and DOC removals but with an EBCT of 10 minutes, TTHMs and HAA_6 were still compliance with the USEPA Stage 1 D/DBPR rule.

- Disinfectant residual - In general, the presence of a small free chlorine residual in backwash water had a negligible impact on the viability of the biomass regardless of granular support media except for anthracite in cold water temperature (Liu *et al*, 2001). On the other hand, chloramines are much weaker disinfectants and don't affect BOM removals in warm or cold water conditions (Liu *et al*, 2001). Combining the negative effects of cold temperature and a low free chlorine residual reduced significantly anthracite's BOM removal ability while GAC was only slightly affected except for the less biodegradable fractions of BOM (such as glyoxal). Other studies (Urfer, 1998; Miltner *et al*, 1992) observed significant biomass activity impairment when free chlorine residuals were at or above 1 mg/L regardless of granular media type or water temperature.
- Granular filtration media type - BOM removal efficiency is greatly affected by the selection of filter media. Amongst the filter media commonly used in water treatment, GAC exhibits the highest porosity followed by anthracite and finally sand. Higher porosity implies a greater surface area per unit volume and thus a larger number of attachment sites for bacteria. Researchers have shown that BOM removal increases with biomass density up to a pseudo steady-state threshold value (Rakness, 2005).

GAC has been shown to be consistently more tolerant to harsher biomass conditions when compared to anthracite but because of GAC-catalyzed decomposition reactions with chlorine or chloramines, the presence of these disinfectants in backwash water should be avoided in order to maintain longer GAC lifespan (Rakness, 2005).

GAC has adsorption capabilities that enhance BOM and recalcitrant micro-organics removals compared to anthracite or sand. Once the adsorption sites are occupied, the GAC is exhausted and will either need to be regenerated to recover its adsorption capacity or can be utilized strictly for biological filtration purposes. BOM removal

performance differences between spent GAC and anthracite were reported to be marginal in warm water conditions, with a higher removal yield of the former in cold temperatures (Emelko *et al*, 2006; Langlais and Reckhow, 1991). It was speculated that when exhausted, GAC's improved BOM removal is due to its carbon matrix providing greater protection of the attachment sites against fluid abrasion during backwashing (Emelko *et al*, 2006). It was also theorized that new adsorption sites were biologically-mediated, also referred to as biological regeneration (Zhu *et al*, 2010).

Not all GACs are created equal, lignite-based GAC has been more successful for promoting bacterial attachment compared to bituminous-based GAC (Arora *et al*, 1997). PICABIOL® is a lignite-based carbon with a pore size distribution between 10 and 100 μm and is specifically engineered to maximize biomass density, which in turn reduces the EBCT needed (and the depth of media) to meet BOM removal objectives (Glaze and Weinberg, 1993). As a corollary, good BOM removal yields have been reported with GAC at higher loading rates, thus delaying costly filter capacity upgrades (Langlais and Reckhow, 1991).

Conventional biofiltration is a passive process primarily designed and operated for particle removal and to minimize headloss development. In contrast, engineered biofiltration takes into consideration meeting specific water quality targets as well as maintaining conventional biofiltration design principles. Nutrient loading is an important but often overlooked factor that influences microbial growth and activity. The optimal stoichiometric ratio of assimilable organic carbon to nitrogen to phosphorous (or C:N:P molar ratio) was reported to be approximately 100:10:1 (LeChevallier *et al*, 1991). In a pilot-plant study, Lauderdale *et al* (2012) demonstrated that supplementing a phosphorous-poor influent to a design C:N:P ratio of 100:10:2, resulted in a 75% improvement in DOC removals and a 15% reduction in headloss development relative to the control biofilter. Higher microbially-mediated organic carbon removals were correlated to an increase in adenosine triphosphate (ATP) activity, suggesting that optimal C:N:P ratio plays a key role either in cell synthesis or substrate metabolism.

Several studies have shown that geosmin and MIB are biodegradable and can be consumed as secondary substrates by autochthonous bacteria that were consistently fed with BOM inherent in natural waters (Ho *et al*, 2007; Westerhoff *et al*, 2005; Nerenberg *et al*, 2000). Rittmann *et al* (1995) suggested that the biodegradation mechanisms for geosmin may involve dehydrogenase and monooxygenase reactions resulting in the formation of oxidation intermediates and mineralization. MIB biodegradation may follow similar oxidation pathways via monooxygenase oxidative reactions leading to ring cleavage and mineralization.

Furthermore, Ho *et al* (2007) determined that the biodegradation of geosmin and MIB in acclimated sand filters followed pseudo-first order reactions with rate constants that seem to be a function of bacterial density rather than feed water odourant concentrations.

Hoefel *et al* (2006) identified in biologically-active sand filters three Gram-negative bacterial strains responsible for metabolizing geosmin as *Sphingopyxis sp*., *Novosphingobium sp*., and *pseudomonas sp*. In order to validate these findings, a cocktail of the aforementioned bacteria strains were then inoculated in a bench-scale sand filter, which resulted in a 75% geosmin reduction compare to only 25% in the control biofilter (McDowall *et al*, 2009).

Ozone and ozone-based AOP treatments can significantly enhance NOM's biodegradable fraction and at least partially oxidize natural and xenobiotic trace organic contaminants (Freese *et al*, 1999). Escobar and Randall (2001) observed a substantial increase of ozonation byproducts formed at ozone dosages equivalent to 0.2-0.5 mg O_3/mg DOC and AOC production peaked between 0.5 and 1 mg O_3/mg DOC. The latter is also representative of common ozone dosages applied to achieve effective disinfection. In other words, reaching optimal TOC removal and disinfection compliance objectives share the same ozone dosage range. Increasing ozone dosages beyond the optimal disinfection target of 1 mg O_3/mg DOC, had a negligible influence on NOM's biodegradable fraction and didn't improve BOM removals during biological filtration (Carlson and Amy, 2001, Freese *et al*, 1999).

2.1.7 Enhanced Organics Removal via Ozone and Ozone-Based AOP Treatments in Tandem with Biological Filtration

Ozone or peroxone followed by biological filtration has shown improved removals of DOC and trace organics. That is, the combination of ozone or an ozone-based oxidation stage in combination with biological filtration achieves higher removal yields compare to singular treatments (Nerenberg *et al*, 2000). Ozonation and peroxone increases the BOM fraction of NOM, stimulating biomass growth in downstream biological filters and resulting in higher overall DOC removals. Fonseca and Summers (2003) observed a 37% reduction in filter effluent DOC when the upstream applied ozone dose was 1.3 mg/mg DOC compared to 14% in the non-ozonated control filter. Furthermore, the improved biological activity from filters receiving higher influent BOM concentrations was found to enhance geosmin and MIB removal yields (Nerenberg *et al*, 2000; Egashira *et al*, 1992).

MIB has been identified as a major culprit responsible for seasonal musty/earthy water quality complaints from communities located in the southwestern basin of Lake Michigan (Nerenberg *et al*, 2000). Unlike most utilities in the area, the Lake Bluff Water Treatment Plant hasn't been subjected to these types of complaints primarily due to the implementation of advanced water treatment processes consisting of pre-ozonation, and biological filtration. A full-scale research investigation was conducted to elucidate the contribution of each treatment with respect to odourant removals. At ozone dosages equivalent to 0.66 and 0.88 mg O_3/mg DOC (1.3 mg/L and 1.6 mg/L, respectively), MIB levels were reduced by 36 to 65% while non-detect levels were subsequently measured in downstream biological filters. The filtration media consisted of exhausted GAC and in the opinion of the author had minimal if any remaining active adsorptive sites. It was concluded that the combination ozone/biological filtration was well-suited for the removal of low-to-moderate levels (up to 43 ng/L) of the cyanobacterial metabolite (Nerenberg *et al*, 2000).

While the performance of ozone-assisted biological filtration for NOM removal has been the subject of extensive research, few studies are available on odourant removals focused on optimizing the ozone dose prior to biological filtration (Westerhoff *et al*, 2005). A utility survey conducted by AWWARF in 2005 indicated that the majority of full-scale ozonated water treatment plants were dosing less than 1 mg O_3/mg DOC if taste and odour control was the primary treatment objective (Westerhoff *et al*, 2005). A breakdown of the contribution of these advanced processes showed that percent influent geosmin and MIB removals varied between 10 and 90% for ozonation and 50% for biological filtration. Overall geosmin and MIB removals achieved by the combination of both treatments were between 60 and 100%. As stated earlier, the effect of ozonating water prior to biological filtration will increase the BDOC fraction of NOM and stimulate biomass growth. Since geosmin and MIB are usually present at trace levels (ng/L range), they can solely be consumed by well acclimated biological filters as secondary substrates. Higher applied ozone dosages will improve biomass density and subsequently enhance geosmin and MIB removals (Westerhoff *et al*, 2005).

Elhadi *et al* (2004) studied the behavior of biological filters affected by parameters such as temperature, primary substrates i.e. a cocktail of biodegradable organic model compounds serving as surrogate for ozonation by-products (BOM), and granular media type with respect to the removal of geosmin and MIB. It was demonstrated that all independent variables (BOM, temperature, and media type) significantly affected geosmin and MIB removal yields. As expected, regardless of experimental conditions, exhausted GAC was superior to anthracite while the improved performance of the exhausted GAC over anthracite was most prevalent in worst-case conditions (i.e. cold temperature and low influent BOM concentration). Exhausted GAC and anthracite media performed more similarly in conditions favoring biomass growth such as high temperature and elevated influent BOM levels (Elhadi *et al*, 2004).

Since chlorinated DBP precursors are integral components of NOM, their oxidation by ozone to more biodegradable products and subsequent removal by biological filtration should achieve a marked reduction in TTHM, and HAA formation potentials.

Additionally, molecular ozone and chlorine share similar modes of attack (see Section 2.1.3), which decreases the number of halogenated DBP precursors' reactive sites available in NOM if ozonation precedes chlorination (Sohn *et al*, 2007; Fonseca and Summers, 2003; Chang and Singer, 1991). Chen and Wang (2012) studied the contribution of ozonation and subsequent biofiltration on the removal of halogenated DBPs in river water characterized by a high formation potential. Individually these treatments exhibited relatively poor chlorinated DBP removal performance. Biofiltration alone abstracted 44% and 31% of TTHMs and HAA_6 precursors, respectively, while ozonation alone at dosages between 1.25 mg/L and 10 mg/L (equivalent to 0.15-1.2 mg O_3/mg DOC) oxidized THMFP and HAAFP by 20% and 50%, respectively. However, when combining intermediate ozonation with biological filtration, TTHMs and HAA_6 percent removals steadily increased up to 88% and 93% at maximum ozone dose, insuring full halogenated DBP regulatory compliance.

NOM can be somewhat divided into hydrophobic and hydrophilic fractions. Chen *et al* (2011) fractionated NOM with XAD-8 resin and demonstrated that a higher chlorinated disinfection by-product formation potential was associated with the hydrophobic fraction of NOM rather than its hydrophilic counterpart. As such, greater emphasis should be spent on the removal of the former prior to chlorination in order to lower DBP formation potential. Intermediate ozonation and to a larger extent pre-ozonation were reported to convert part of NOM's hydrophobic fraction into hydrophilic fragments containing alcohol and carboxylic functional groups. The combination of ozonation followed by BAC was found to be very effective to remove either NOM constituents even at low ozone dosages (i.e. 1 mg/L). The filter's removal mechanism of ozonated water for the remaining hydrophobic fraction was via GAC's adsorption capacity while the hydrophilic fraction was more easily biodegraded by the biomass. Conventional treatment followed by ozone-BAC resulted in lowering THMFP and HAAFP by 61% and 72%, respectively.

Miltner *et al* (1992) conducted batch experiments with Ohio River water to determine the relative contributions of ozonation followed by biological filtration on the elimination of halogenated DBP precursors when applying ozone dosages up to 4.5 mg/L (equivalent to

1.7 mg O_3/mg DOC). Individually, ozone reduced TTHMFP and HAAFP by up to 30% and 50%, respectively, while biodegradation eliminated TTHMFP and HAAFP by 40% and 75%, respectively. Combining ozonation and biofiltration didn't significantly enhanced TTHMFP and HAAFP removals relative to biofiltration alone. Increasing the ozone dose from 0.4 to 1.7 mg O_3/mg DOC seldom improved TTHMFP and HAAFP destruction and optimal halogenated DBP removals was reached at the lowest ozone dose studied (i.e. 0.4 mg O_3/mg DOC). However, biotreatment of ozonated water significantly affected THM and HAA species depending on the ozone dosage. At low ozone doses, the proportions of chlorodibromomethane and bromoform increased by 40% and 70%, respectively, while chloroform and bromodichloromethane were reduced by 30% and 20%, respectively. At elevated ozone doses (above 0.7 mg O_3/mg DOC), production of the more brominated DBP species were reduced. Other researchers (Chaiket *et al*, 2002; Speitel *et al*, 1993) reported similar results and hypothesized that at elevated ozone dosages, bromide was oxidized to its highest oxidation state bromate, thus decreasing the concentration of bromide available for bromination reactions with halogenated DBP precursors. At lower ozone dosages, ozone oxidized bromide to bromine, shifting halogenated DBP specie distribution to the more bromine-substituted type. Similar trends were observed for the dependence of haloacetic acid species with respect to the ozone dose.

In a study involving two surface waters of different water quality characteristics, Spietel *et al* (1993) provided insight on the impact of a wide spectrum of ozone dosages in batch ozonation followed by biofiltration experiments. Biotreatment of unozonated water had very little impact on TTHMFP destruction whereas HAAFP was reduced by up to 30%, indicating that HAA precursors are more biodegradable than their THM counterparts. Biotreatment of ozonated water resulted in maximum TTHMFP and HAAFP removals of 50% and 70%. At low to intermediate ozone dosages (between 0.5 to 2.0 mg O_3/mg TOC), the action of ozone was generally limited to rendering DBP precursors more amenable to biodegradation. At the higher ozone dosages (between 3 and 5 mg O_3/mg TOC), DBPFP removal response was mixed depending on the type of surface water studied. HAAFP removal was greatly enhanced in Lake Austin River water while

significant TTHMFP removal was observed with Lake Houston River water. Furthermore, ozonating bromide-containing waters at ozone dosages above 1 mg O_3/mg TOC resulted in regulatory bromate exceedances (>10 μg/L). It was concluded that from a regulatory and economic perspective, ozonation followed by biological filtration at ozone dosages above disinfection practices was found to be undesirable especially above 3 mg O_3/mg TOC.

In river water characterized by its resistance to TOC removal by conventional treatment, Chaiket *et al* (2002) investigated the contribution of ozonation and biological filtration to enhance TOC removal and reduce DBPFP. The pilot-scale study revealed that the point of ozonation whether before coagulation or prior to biofiltration had little impact on halogenated DBP removal yields. The combination of ozonation, coagulation, and biological filtration resulted in a reduction of the TTHMFP between 51% and 66% with best results achieved at higher pH and ozone dose. HAA_9 precursors were slightly more biodegradable compare to their TTHM counterparts with removal yields ranging from 48% to 76% and maximum precursor destruction attained at high pH and low ozone dose. The impact of spiking bromide shifted halogenated DBP species from chlorine-substituted to the more bromate-substituted types.

3 Materials and Methods

3.1 Pilot Plant Description

Figure 3.1 represents a flow diagram integrating the current full-scale and pilot-plant treatment processes.

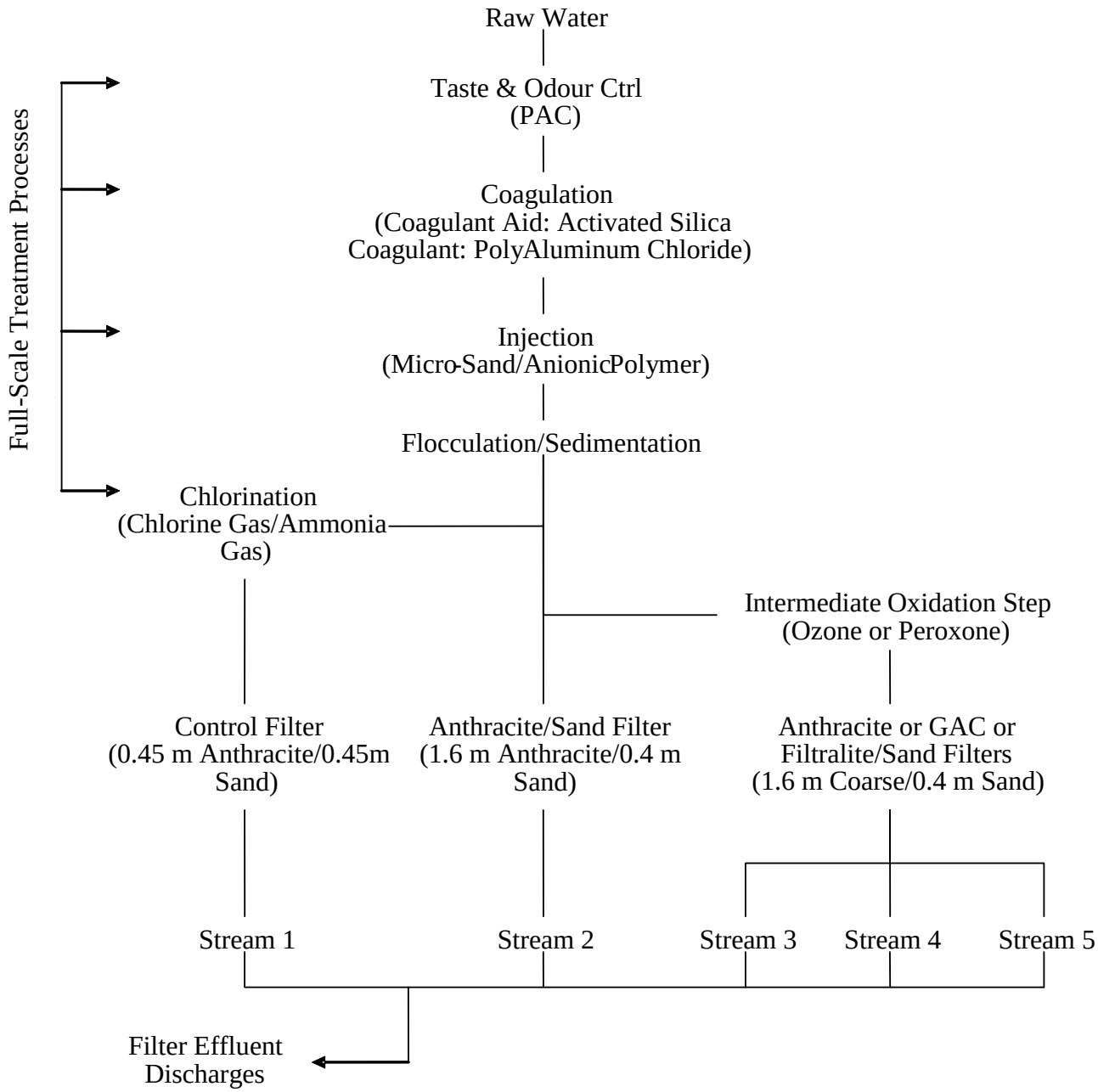


Figure 3.1: Pilot Plant Flow Schematic

The pilot plant was fed with full-scale post-Actiflo® effluent water, which incorporates powdered activated carbon (PAC) for taste and odour control, followed by coagulation, sand-ballasted flocculation and high-rate sedimentation, mainly for particulate and organics removal (Figure 3.1). Two distinct treated waters supplied the pilot plant units: the control filter mirrored full-scale filters and as such, was fed with post-Actiflo® effluent water that was subjected to primary (free chlorination) and secondary (chloramination) disinfection. The other four filters were operated in biological mode and were supplied exclusively with non-chlorinated post-Actiflo® effluent water. Intuitech Inc. (Salt Lake City, Utah) constructed the pilot plant to design specifications. An illustration of the pilot plant layout is shown in Figure 3.2

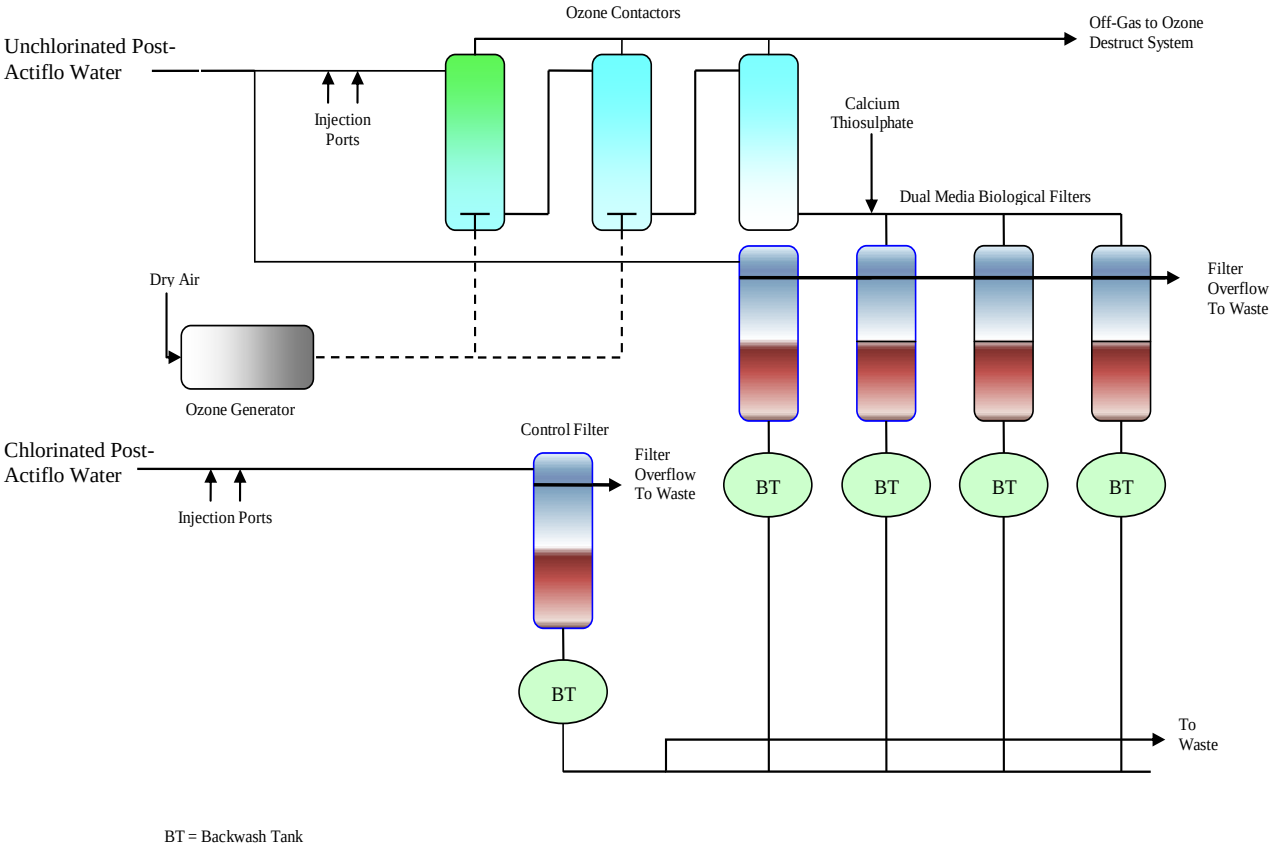


Figure 3.2: Pilot Plant Layout

3.1.1 Ozone Delivery System

The pilot-plant treatment units were designed to simulate full-scale post-Actiflo® processes at the design flow rate of 110 MLD. In the event that ozonation was retained for full-scale implementation, the then current chlorine contact chambers located between the Actiflo® and the filters would be retrofitted for ozone generation. As a result, three pilot-scale ozone contactors/dissipation units connected in series were designed to mimic the hydraulic retention time (T_{50}) of the full-scale chlorine contact chambers (post-Actiflo®) and provided a total contact time of 30.1 min, which corresponds to a flow rate of 7.89 L/min (Figure 3.2).

Each contactor is composed of clear PVC cylinders with an inside diameter of 20.3 cm (8 in.) and a height of 2.44 m. The ozone gas and non-chlorinated Actiflo-treated water flowed in counter-current mode through either the first or second contactor. Ozone was bubbled through horizontal tubular ceramic static diffusers with a 15 micron pore size to generate fine bubbles. For the purpose of this research study, ozone was injected solely in the first contactor thus, the second and third contactors acted as ozone dissipation chambers. A solution of calcium thiosulfate was injected between the last contactor and the filters to quench the ozone residual if necessary.

Injection ports and a static mixer were installed upstream of the ozone contactors to inject hydrogen peroxide and selected chemicals (geosmin or MCPA). The influent and effluent lines of individual contactors were equipped with sampling ports.

The ozone generator was manufactured by Pacific Ozone Technology (Model SGA11-22) and produced up to 12 g/h with dried air as the feed gas. The ozone concentrations in both generator output and contactor off-gas were monitored by continuous ozone monitors (Model HC-12, PCI Ozone Corp.). The ozone transfer efficiency was monitored daily to assess the state of the ceramic bubble diffuser. Typically, experiments were performed at transfer efficiencies above 90% and the diffuser was replaced once the transfer efficiency dropped below 80%. Three on-line ozone residual analyzers (Model Q45H, ATI Inc.) were installed at the effluent of each contactor. Two ambient ozone

analyzers (Model B12, ATI Inc.) were installed near the ozone generator and the filters. Off-gas from the contactors was disposed of in an environmentally-friendly manner by flowing through a thermocatalytic ozone destruction unit (Model D212, Pacific Ozone Technology) with MnO_2/CuO as the catalyst.

3.1.2 Filters

The filters have an inside diameter of 15.2 cm (6 in.) and were made of clear PVC to allow a visual interpretation of operating processes (Figure 3.2). They were operated in a constant rate, constant head (down flow) mode by regulating the height of water above the media with overflow weirs and the flow through individual filters was maintained constant by adjusting an actuated ball valve connected to a flow meter after the filters. As the outlet flow rate decreased due to gradual clogging of the media during filter operation, the flow meter sent a signal to the controller which then adjusted the effluent valve accordingly.

The high rate/deep-bed biological filters were engineered to simulate full-scale post-Actiflo® processes at the design filtration flow rate of 110 MLD, equivalent to a filtration loading rate of 8.0 m/h. The area available for filtration was 0.018 m^2 and the total height of water in the filter was 5.0 m with the overflow weir being 3.0 m above the media resulting in a filtration flow rate of 2.43 L/min, an EBCT of 15 minutes and a hydraulic retention time (HRT) of 37.8 min. However, during the pilot-plant startup operation it was discovered that the height of water in the three ozonated biological filters was decreasing because the filter overflow pipes was directing excess water from the ozone contactors. On one hand, the three ozonated biological filters required a minimum flow rate of 7.29 L/min (2.43 L/min × 3) and on the other, the ozone contactor flow rate was set at 7.89 L/minute to mimic the HRT of the existing chlorine contact chambers. Empirically, decreasing the filter effluent flow rate by approximately 10% (i.e. from 2.43 L/min to 2.20 L/min) stabilized the height of water above the filter media during filter operation. For consistency purposes, the non-ozonated biological filter flow rate was also reduced to 2.20 L/min. At the filtration flow rate of 2.20 L/min, the EBCT and HRT

increased to 16.6 min and 41.7 min, respectively, corresponding to a filtration loading rate of 7.24 m/h and an equivalent design filtration flow rate of 99.6 MLD.

The biological filters had dual-media configurations with 1600 mm of coarse media over 400 mm of silica sand (Figure 3.2). Two different treated water streams supplied the four biological filters as follow:

1. Non-chlorinated Actiflo®-treated water was fed to a biological filter composed of anthracite over sand.
2. Non-chlorinated Actiflo®-treated water that was first subjected to an intermediate oxidation step was channeled to three biological filters containing either anthracite, GAC or Filtralite® media over sand.

Initially, all four biological filters were continuously fed with non-ozonated post-Actiflo water over a period of four months to allow a biofilm to form on the media. Once the ozone generator was switched on, the biofilm community was expected to change in the filters fed with ozonated water because of the enhanced production of a biodegradable organic carbon fraction.

Anthracite was supplied by Anthrafilter Media and Coal Ltd®. The GAC media was derived from bituminous coal and manufactured by Calgon Carbon Corporation under the trade name Filtrasorb® 400 (Pittsburg, PA.). Filtralite® is an expanded clay media characterized by a high porosity and large surface area, which according to the Maxit Group (Oslo, Norway) is well-suited for the water and wastewater industry. The manufacturer claims that the highly porous structure of Filtralite® enhances solids retention capacity, which in turn limits headloss development during filtration thus increasing filter run times and filter productivity compare to other filtration media. The impact of biomass in biological filters on headloss development and turbidity removal performance impairments was raised during discussions with the consultant and media selection became an important consideration for full-scale implementation.

The media in the control filter contained 450 mm of anthracite over 450 mm of silica sand, core-sampled from full-scale plant Filter #3 (Figure 3.1). The total height of water in the filter column was 2.1 m with the overflow weir situated 1.2 m above the media. The control filter's operating flow rate was adjusted to match full-scale filters loading rate (typically with a flow range of 1.4 to 2.0 L/min).

Sand and coarse media effective sizes (d_{10}) for the biological filters were selected based on achieving similar filtration performance compare to the control filter with respect to headloss development, and filter effluent turbidity. Two filtration performance parameters were chosen to achieve these goals: uniformity coefficient (UC) and L/d ratio. The UC is defined by AWWA, B100 Standard for Filtering Materials as a measure of particle size distribution. Lower UCs will result in a narrower distribution range of media particles sizes, which according to Yohe *et al* (2006) considerably improves the length of filter run times and particulate removal especially in the 2-5 micron range. The L/d index is defined as the ratio of the bed depth (L) over the effective size of the filter media (d_{10}) in mono and dual filter media configurations. Two filters with similar L/d ratio fed with the same influent water at equivalent filtration rates should yield comparable filtrate quality (Nix and Taylor, 2002). As shown in Table 3.1, the selection of silica sand and coarse media for biological filtration was based on approximating the L/d ratio and uniformity coefficient of the control filter based on the commercial availability of product.

Table 3.1: Pilot filter Media Configuration

Pilot Filter	Coarse Media Effective Size (mm)	Sand Effective Size (mm)	Uniformity Coefficient (d_{60}/d_{10})	L/d Ratio
Control filter (anthracite/sand)	0.90	0.45-0.55	≤1.4	1333
Biological filter (anthracite/sand)[1]	1.65-1.75	0.55-0.65	≤1.5	1636
Biological filter (GAC/sand)	1.30-1.50	0.55-0.65	≤1.5	1881
Biological filter (Filtralite®/sand)	1.30-2.00	0.55-0.65	≤1.5	1727

[1]Ozonated and non-ozonated anthracite/sand biological filters have the same configuration

Headloss development across the filter media was continuously monitored by pressure gages located below the filter media. Individual filter effluent was monitored continuously by Hach® low range turbidimeter (Model 1720 E with SC 100 Controller). The influent pipe, effluent pipe, and filter columns were equipped with sampling ports.

The base of every filter column contained a Leopold® Universal Type S underdrain with an IMS Cap made of sintered high-density polyethylene beads. Filtrate water was collected in individual 640 L backwash tanks equipped with an overflow pipe which directed the excess to waste (Figure 3.2). When the filter reached either terminal headloss (<1 m) or turbidity breakthrough (>0.30 NTU), backwashing was manually initiated. In most instances, the limiting factor was terminal headloss and backwashing was triggered when there was between 0.9 and 1.1 m of head remaining in the filter. Experiments were conducted at least 24 h after the start of a filter cycle when filter effluent turbidity stabilized below 0.1 NTU.

Huck *et al* (2000) observed that AOC removal remained relatively unchanged when applying air scouring and concluded that biomass detachment wasn't a significant concern during backwashing of biological filters. Hence, biological and non-biological filters share a common backwash sequence approach, including air alone followed by air combined with subfluidization wash water flow to achieve collapse-pulsing conditions and wash water flow adjusted to a set percent bed expansion. The control filter backwash sequence reflected full-scale backwash operating conditions (Table 3.2).

Table 3.2: Backwash Sequence of Biological and Control Filters

Backwash sequence	Control Filter	Biological Filters
Air alone	1 min	2 min
Collapse-pulsing condition	1 min	1-2 min
Bed expansion	45-50%	25-30%

For backwash operation, air was provided by a ¾ HP compressor and wash water was pumped by a submersible pump (0.33 HP, 1 phase) that generated a maximum flow rate of 37.8 L/min at 33 feet of height (14.3 psi).

3.1.3 Primary and Secondary Disinfection

The control filter feed water consisted of post-Actiflo® effluent water that was chlorinated and chloraminated whereas primary and secondary disinfections of the biological filter effluents were performed in bench-scale experiments that mimicked full-scale plant design at the equivalent flow rate of 99.6 MLD. Filtrate samples were simultaneously collected from individual biological filters in chlorine demand-free amber bottles to which sodium hypochlorite was added and allowed to react for 67 min, representing the hydraulic retention time of the new chlorine contact chamber design. Typically, it was shown that reproducible and consistent results were obtained when the applied free chlorine dose was set at 1 mg/L below the current full-scale plant chlorine dose. Ammonium sulfate was then added to achieve a chlorine-to-ammonia ratio between 3-to-1 and 4-to-1 for optimum conversion of free chlorine to monochloramine. Secondary disinfection mirrored the existing 18.5 ML on-site drinking water reservoir with a hydraulic retention time of 291 min at the design flow rate. As per the new water treatment plant design, the treated water would then be considered potable and enter the distribution system.

For simulated distribution system (SDS) experiments, all filtrate samples after chlorination and chloramination were stored in the dark for up to an additional 48 h. At each stage of the disinfection process, chlorine species and total ammonia were measured to determine the chlorine demand and ensure that the chlorine-to-ammonia ratio was generating a large excess of monochloramine relative to free chlorine and dichloramine residuals.

3.1.4 Automated Monitoring System

An automated data acquisition system has been installed at the pilot plant. The PLC module is manufactured by Allen Bradley® and the software used is Histx®. The data from the analog sensors were collected and stored in the hard drive of a computer. The following analog signals were monitored during the course of the study: flow rates, ozone feed gas and off-gas concentrations, ozone residual at the effluent of each contactor,

ambient ozone, filter outlet turbidity, temperature, and pressure differential (headloss profile).

3.2 Analytical Methods

3.2.1 Dissolved Chlorine Species

Free chlorine, monochloramine, dichloramine and total chlorine residuals were determined as per Standard Method 4500-Cl D using a Wallace and Tiernan® bench-top amperometric titrator. Combined chlorine was calculated as the difference between total and free chlorine residuals.

3.2.2 Total Ammonia Residual

Total ammonia was analyzed by Hach's Nessler Method 8038 using a Hach spectrophotometer (either DR 2000 or DR 5000®). This analytical method was derived from Standard Methods 4500-NH_3-N (APHA, AWWA, WEF, 1999).

3.2.3 Total Trihalomethanes (TTHMs)

Water sample preparation and analysis followed USEPA; SW-846, Method 5030B and Method 8260C, respectively. SGS Environmental Services Limited (Lakefield, Ontario) reported a deviation to Method 5030B: "A purge time of 11 minutes and desorb time of 4 minutes are recommended by the reference method. These times have been altered in order to optimize the chromatography of the early eluting components while maintaining sufficient purging efficiency. Reducing the purge time and desorb time reduces the amount of water and methanol that is transferred to the trap and to the GC column".

3.2.4 Geosmin

Geosmin was separated from the water sample by liquid/liquid extraction using hexane. The extract was then concentrated and then injected into a GC/MS. This method was developed by the Analytical Division of SGS Environmental Services Limited (Peterborough, Ontario), accredited by CALA and licensed by the MOE.

3.2.5 Bromide and Bromate

The method was based on USEPA Method 317.0; Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water using Ion Chromatography (IC) with the addition of a Post-Column Reagent for Trace Bromate Analysis. The method was used to analyze samples which are regulated by the Ontario Safe Drinking Water Act (OSDWA). SGS Environmental Services Limited reported a deviation to USEPA Method 317.0: "The additional post-column reagent for bromate analysis as in USEPA Method 317.0 is not used. Hydroxide-selective column was used to improve the selectivity for low level bromate."

3.2.6 Transferred Ozone Dose

The transferred ozone dose is equal to the difference between applied ozone dose (gas) and off-gas ozone levels (gas). The applied and off-gas ozone concentrations were measured by dedicated on-line ozone gas analyzers. The calculations involved in the determination of the transferred ozone dose (in mg/L) are detailed in Rakness (2005).

3.2.7 Ozone Residual

The ozone residual was determined using the indigo trisulfonate method according to Yates and Stenstrom, (2000). The spectrophotometer used was a Hach DR5000®.

3.2.8 Hydrogen Peroxide Residual

The method developed by Klassen *et al* (1994) was employed to quantify hydrogen peroxide in water. The spectrophotometer used was a Spectronic 601.

3.2.9 MCPA

MCPA determinations were performed by the MOE Laboratory Branch based on USEPA Method 515.2.

3.3 QA/QC

3.3.1 Bromate and Bromide Ions

For a given batch consisting of up to 14 samples, a calibration and blank solutions are analyzed at the beginning of the analyses. In addition, one replicate sample, a reference check sample and a spiked sample are analyzed.

3.3.2 Geosmin

For a given batch consisting of up to 20 samples, a calibration and blank solutions are analyzed at the beginning of the analyses. In addition, one replicate sample, a reference check sample and a spiked sample are analyzed.

3.3.3 TTHMs

For a given batch consisting of up to 20 samples, a calibration and blank solutions are analyzed at the beginning of the analyses. In addition, one replicate sample, a reference check sample and a spiked sample are analyzed.

3.3.4 Total Ammonia Residual

Prepare a 0.50 mg/L as NH_3-N dilute solution by pipetting 2.5 mL of a 10 mg/L as NH_3-N standard solution (Hach® Canada) into a 50-mL volumetric flask. Fill the volumetric flask to the mark with Type 2 RO water. Invert the flask twenty times to achieve proper mixing.

3.4 Tracer Studies

Step input tracer studies were conducted on the pilot ozone contactors and biological filter to assess their respective water residence times. The tracer chemical selected was fluoride, which was injected at the inlet of each process and measured over time at the process outlets. The fluoride concentration was normalized over time by dividing the actual fluoride concentration in water (minus background fluoride levels) by the initial fluoride dose injected (AWWARF, 1996). Fluoride in water was measured using an Accumet® XL 600 meter manufactured by Fisher Scientific.

The actual tracer curves for the pilot ozone contactors and biological filters are compiled in Figure 3.3.

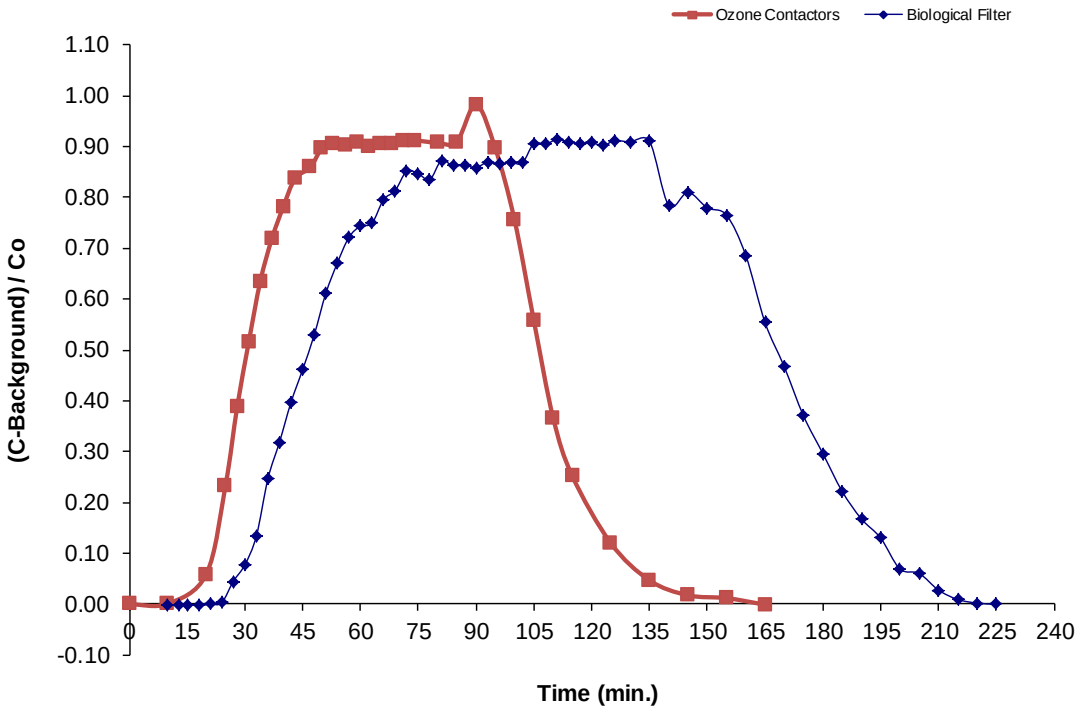


Figure 3.3: Ozone Contactors and Biological Filter Tracer Study Curves

From Figure 3.3, the dimensionless concentration of 0.5 corresponds to the hydraulic retention time (T_{50}) for the ozone contactors and biological filter. Furthermore, a minimum of two HRTs was provided when transitioning between experimental runs. Table 3.3 summarizes the results of the tracer studies.

Table 3.3: Tracer Study Results Summary for the Pilot Ozone Contactors and the Biological Filter

Parameter	Ozone Contactors	Biological Filter
HRT Calculated (min.)	29.7	41.7
HRT Experimental (min.)	31.0	45.2
HRT Accuracy (%)	4.2	7.7

The differences between calculated HRT values and experimental for both the ozone contactors and biological filter are well within tolerance levels (below 10%) and were mainly caused by fluctuations in pump flow rates and analytical uncertainties.

4 Results and Discussion

4.1 Validation of Pilot-Scale Filtration Design by Comparing Control and Full-Scale Filters Performance

When embarking in a pilot plant study, it is paramount to verify that at equivalent process loading rates, water quality control data generated at the pilot-scale level adequately matches that obtained at full-scale (Ford *et al*, 2001). This is an important consideration to determine if the pilot-scale results may be validated for scale-up purposes. A comparative study between the performance of the pilot-scale control filter and an existing full-scale filter was conducted at a loading rate of 12 m/h. The investigation was performed over a 2-week period (Table 4.1 and Appendix 1).

Table 4.1: Performance of Pilot-scale Control versus Full-Scale filter on Select Water Quality Parameters

Parameter	% Error
Temperature	2
Dissolved oxygen	-4
pH	0
Conductivity	0
Turbidity	7
UV_{254}	-1
Apparent color	-6
True color	0
Aluminum	2

The percent error on select water quality parameters between control and full-scale filter effluents remained on average well below the 10%-mark, which provides a high level of confidence that the current pilot-plant will generate data that can be validated for full-scale design.

4.2 Impact of Ozone on the Destruction of Selected Organic Contaminants

4.2.1 Geosmin

4.2.1.1 System Losses

Elhadi *et al* (2004) reported that trace organic contaminants such as geosmin inherently adsorb onto surfaces made of glass and particularly rubber-based materials. Huck *et al* (1995) specified that system losses were minimized by using glass, stainless steel, and Teflon®. This is an important equipment design consideration especially when conducting experiments involving micro-organic contaminants in the ng/L-range. Furthermore, quantifying system losses is paramount before conclusions are made on the effectiveness of a physico-chemical or biologically-mediated process and disregard for these phenomena might explain ozone performance inconsistencies encountered between previous research studies (Elhadi *et al*, 2004). In an attempt to control system losses, geosmin was continuously spiked at 100 ng/L with the ozone generator switched off for an equivalent 5-day period in order to saturate the adsorption sites of all wetted surfaces (such as ozone contactor's columns, chemical feed systems, etc.). All laboratory glassware involved in the preparation of geosmin stock solutions was segregated from those used for routine wet-chemistry analyses. Table 4.2 illustrates the system losses in replicate samples at the end of the 5-day pre-conditioning period.

Table 4.2: Geosmin System Losses in the Ozone Contactors and Appurtenances

Trial	Ozone Influent (ng/L)	Ozone Effluent (ng/L)	% Difference
1	104	101	3
2	110	103	6
3	97	97	0

On average, there was a 3% geosmin loss in the ozone contactors, which demonstrated that the precautionary measures taken were well-suited to control system losses in this

system design. Geosmin system losses were considered negligible and as such, weren't taken into account in the calculations of subsequent experiments.

4.2.1.2 Ozonation of Geosmin

Actiflo effluent water was spiked with geosmin and removal yields were investigated as a function of transferred ozone dosage. The target geosmin spike level was 100 ng/L in order to simulate the higher range of a cyanobacterial bloom in the Grand River. A treatment goal of at least 90% removal of geosmin was set in order to achieve a reduction to below threshold odour number (see Section 2.1.3). Geosmin oxidation at a given ozone dose was evaluated by calculating the difference in geosmin concentrations between the inlet and the outlet of the ozone contactors. Contact time in the ozone contactor was held constant at 30 minutes. For the purpose of this experiment, each test was performed either in duplicate or in triplicate.

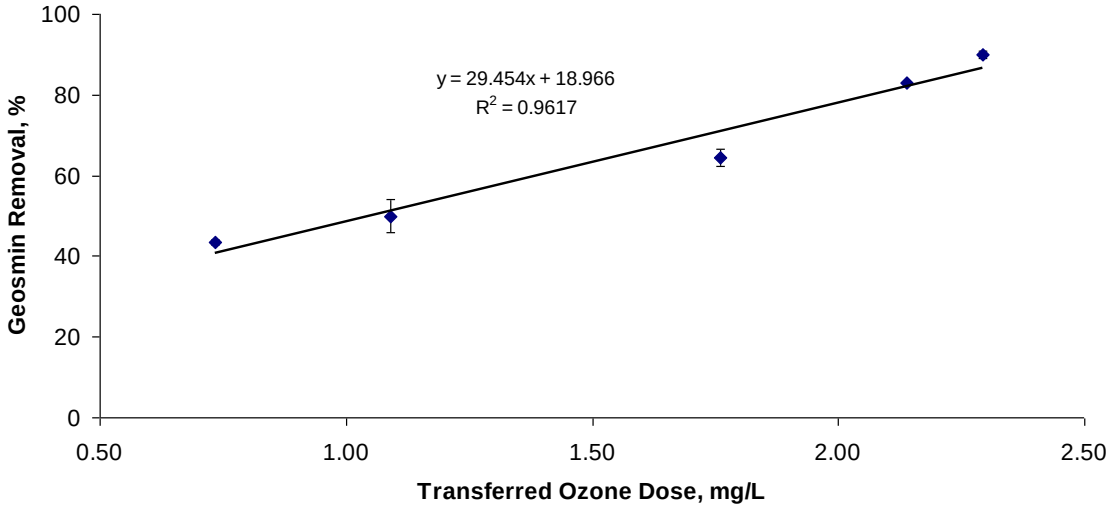


Figure 4.1: Geosmin Reduction as a Function of Transferred Ozone Dose

The experimental data in Figure 4.1 and Appendix 2 shows that geosmin concentration decreased as the transferred ozone dose increased. The dose-response relationship is linear ($R^2 = 0.96$) indicating that the regression model can provide a direct correlation between transferred ozone dose and anticipated geosmin reduction yields. It is well

established in the literature that molecular ozone is a very selective oxidant and as such, isn't the most reactive towards alicyclic alcohols such as geosmin with reaction rate constants up to 11 M^{-1} s^{-1}. Rather, geosmin destruction is attributed to ozone decomposition products such as hydroxyl radicals yielding reaction rate constants of up to 6.6 10^9 M^{-1} s^{-1} (Westerhoff *et al*, 2005). High levels of natural initiators and/or promoters in Grand River water might be responsible for the effective conversion of molecular ozone to active radical species. Therefore, by increasing the ozone dose, higher amounts of hydroxyl radicals were generated, thus improving geosmin oxidation yields. Alternatively, radical traps such as alkalinity might have scavenged excess hydroxyl radicals generated during ozonation.

Only the upper range of the transferred ozone dosages studied, i.e. 2.3 mg/L (equivalent to 0.74 mg O_3/mg DOC) achieved the one-log geosmin removal target. Based on the linear regression equation displayed in Figure 4.1 and DOC levels, in order to improve geosmin removal efficiency to below odour threshold number *i.e.* 4 ng/L or 96% removal yields, the transferred ozone dose would have to be raised to near optimal disinfection dosages i.e. 1 mg O_3/mg DOC. Numerous studies (Huck *et al*, 1995; Yoo *et al*, 1995) agree that effective geosmin removals in waters containing low to moderate odourant levels were attained at ozone dosages adjusted to meet disinfection requirements.

Interestingly, it was observed in this study that earthy-musty odours weren't detectable during odour profiling tests (data not presented) at transferred ozone doses as low as 1.76 mg/L or 0.56 mg O_3/mg DOC. However, during algae bloom events in natural waters, earthy-musty odours may be more complex due to the presence of a variety of algal metabolites and odour profiling test results might differ from those with only geosmin at similar ozone dose.

4.2.2 MCPA

4.2.2.1 System Losses

Prior to measuring system losses, the ozone contactors and appurtenances were pre-conditioned by injecting a low MCPA dose for three consecutive days with the ozone generator switched off. As with the geosmin experiments, the same precautionary measures with respect to laboratory glassware were followed in an attempt to limit surface adsorption issues. System losses were measured in four experimental runs over a 48 hours period. Table 4.3 illustrates the system losses at the end of the pre-conditioning period.

Table 4.3: MCPA System Losses in the Ozone Contactors and Appurtenances

Trial	Ozone Influent (ug/L)	Ozone Effluent (ug/L)	% Difference
1	5.04	5.16	-2
2	5.19	5.58	-8
3	5.30	5.08	4
4	5.91	4.99	16

Although the target MCPA ozone contactor influent dose was set at 10 µg/L, only about 50% of the initial MCPA concentration was measured at the inlet of the ozone contactors. Despite the high affinity of MCPA for the laboratory glassware and chemical feed system, as long as the system losses were low in the ozone contactors, the experiments were conducted without further pre-conditioning.

As shown in Table 4.3, the overall mean system losses in the ozone contactors were approximately 8%. If the result of the fourth trial was considered an outlier, then the system losses in the ozone contactors would become negligible with an average of 4%. The higher percent difference recorded for trial #4 may have been caused by instrument error and as a result MCPA system losses in the ozone contactors were considered inconsequential and weren't taken into account in subsequent experiments.

4.2.2.2 Ozonation of MCPA – Exploratory Phase

The literature is rather limited on ozone effectiveness in water treatment despite the widespread use of MCPA as a herbicide applied for the control of broad-leaf weeds (Benitez *et al*, 2004, Harrison *et al*, 1998). To gain insight on the ability of ozone to oxidize MCPA, Actiflo® effluent water was spiked with the herbicide and removal yields between the inlet and the outlet of the ozone contactors were investigated as a function of transferred ozone dose. Historically, MCPA has been detected in Brantford's drinking water supply at levels up to 100 ng/L. However, as a result of the partnership established between the City of Brantford and the Ontario Ministry of the Environment (MOE), there was a strong interest to investigate ozonation of MCPA in the vicinity of the anticipated MAC value of 10 µg/L (from discussions with the MOE's Approvals Branch) and to simulate a transient discharge condition either caused by runoff after land application or an accidental spill.

Hydraulic detention time in the ozone contactors was 30 minutes. In order to limit the number of samples submitted to the MOE and because at this stage of the study, dose-response relationships were investigated to provide an approximate range of ozone doses suited for the statistical design experiments (section 4.3.2), no replicate samples were collected. Figure 4.2 (Appendix 3) demonstrates the efficacy of ozone for the oxidation of MCPA.

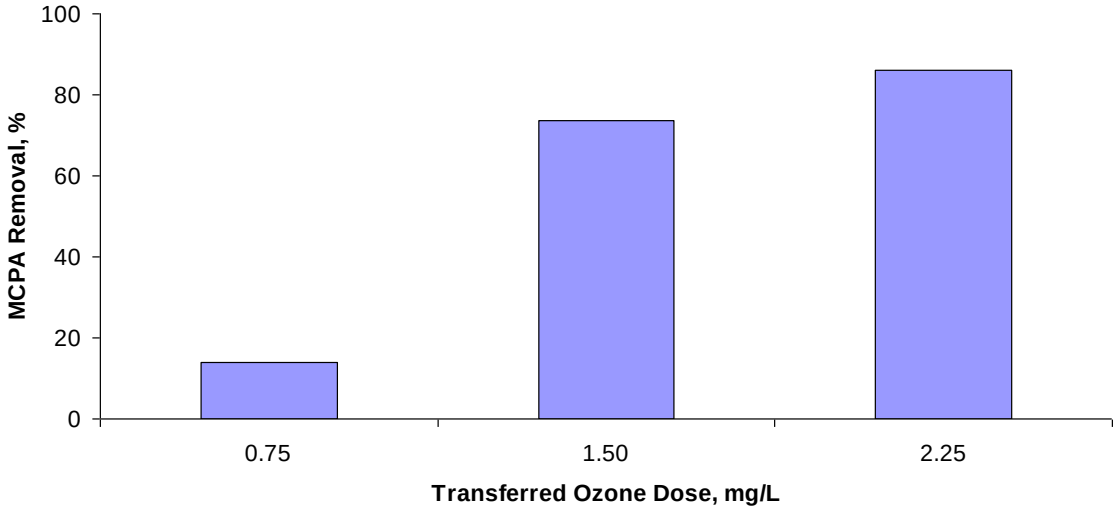


Figure 4.2: MCPA Destruction as a Function of Ozone Dose

As shown in Figure 4.2, MCPA oxidation improved with higher ozone dosages. At transferred ozone doses of 1.50 and 2.25 mg/L, MCPA removals yields equated to 74% and 86%, respectively. Meijers *et al* (1995) observed similar results when MCPA was spiked in River Meuse water with destruction yields of 68% and 89% at ozone dosages of 1.21 and 2.09 mg/L, respectively.

This range of ozone dosages was well suited to carry out the next phase of experiments since:

- at the upper transferred ozone dose (2.25 mg/L), MCPA residuals were above MCPA's MDL (0.05 μg/L) and,
- at the lower transferred ozone dose (0.75 mg/L), percent MCPA removal yield was non-negligible.

4.3 Evaluating the Treatability of Ozone Combined with Hydrogen Peroxide for the Destruction of Select Organic Contaminants

4.3.1 Geosmin

The objective of these experiments was to evaluate the performance of ozone with and without the addition of an accelerant of ozone decomposition reactions, hydrogen peroxide, on the oxidation of geosmin. Ozone contactor flow rate was adjusted to an HRT of 30 minutes in order to mirror the design capacity of the full-scale chlorine contact chambers. Geosmin was spiked at a 100 ng/L dose to simulate a worst-case scenario cyanobacterial bloom event in the Grand River. Transferred ozone dosages ranged from 0.75 mg/L to 3.0 mg/L, which corresponded approximately to ozone-to-DOC ratios ranging from 0.3 to 1.1 mg O_3/mg DOC, respectively.

For a given ozone dosage, three experiments were conducted daily at target peroxide to ozone ratios of approximately 0.00, 0.25 and 0.50 (w/w). Water samples were collected at the contactor influent and effluent of each contactor to determine the concentrations of geosmin, hydrogen peroxide, and bromide. Transferred ozone dose combined with ozone residuals at the effluent of each contactor were measured to assess the ozone demand as a function of time. The percent reduction of geosmin at a given ozone dose was evaluated by calculating the difference in geosmin concentration between the inlet and the outlet of the contactors. Each set of three experiments was performed within an 8-h period to maintain constant background bromide levels and as a result, no replicate samples were collected. Table 4.4 summarizes the background bromide levels measured at the influent of the ozone contactors.

Table 4.4 Background Bromide Levels (µg/L) Measured at the Ozone Contactors' Inlet

H_2O_2-O_3 Ratio	Transferred Ozone Dose (mg/L O_3)		
	1.4	2.1	3.1
0.0	67	67	144
0.3	66	66	140
0.6	65	67	143

As shown in Table 4.4, there were negligible fluctuations in natural bromide levels for a given set of experiments. However, due to raw water quality variability especially in summer months, natural bromide levels more than doubled during the last experimental run compare to the first two, despite the entire experimental study being completed in a 4-day time span.

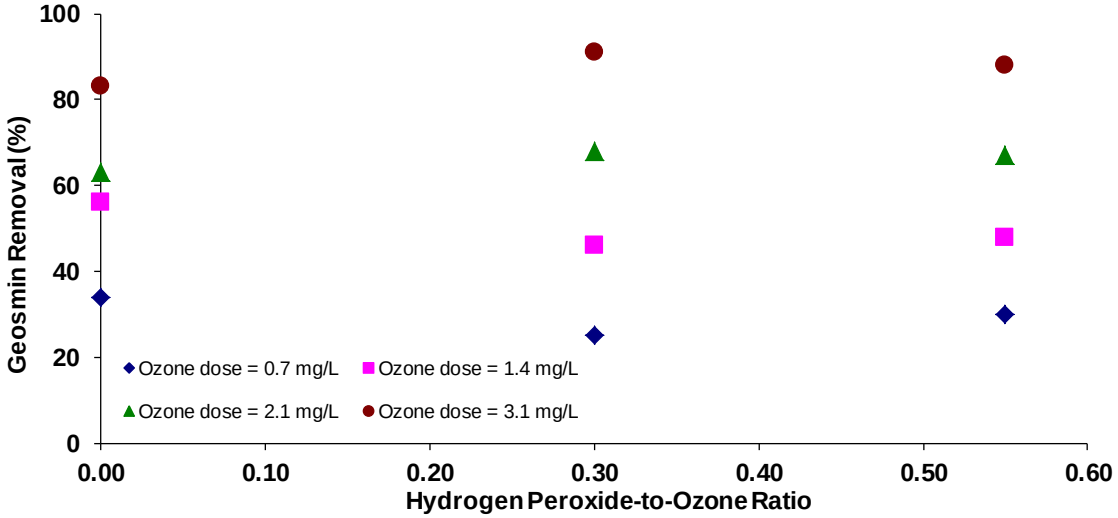


Figure 4.3: Geosmin Oxidation as a Function of Ozone Dose and Hydrogen Peroxide to Ozone Ratio

The data in Figure 4.3 and Appendix 4 demonstrate that increasing the ozone dosage, improves geosmin removal yields, while the addition of H_2O_2 did not. Under these experimental conditions, a 0.7 mg/L-ozone dose resulted in a 34% reduction of geosmin while increasing the ozone dose to approximately 1.4, 2.1, and 3.1 mg/L improved the percent geosmin reductions by 56%, 63% and 83%, respectively.

As discussed earlier, geosmin oxidation can be attributed predominantly to its reaction with hydroxyl radicals (and other radical intermediates). The purpose of feeding

hydrogen peroxide to the contactors was to enhance the conversion of molecular ozone to hydroxyl radicals with the objective of improving geosmin degradation yield compared to ozone alone.

Based on equation 2.2 (Section 2.1.4.2), two moles of ozone react with one mole of hydrogen peroxide to generate two moles of hydroxyl radicals (AWWARF, 1991), resulting in a stoichiometric ratio of 0.35 (w/w). Below the stoichiometric ratio, the system is deemed reaction-limited and molecular ozone is only partially converted to hydroxyl radicals. Above the stoichiometric ratio, hydrogen peroxide is in excess and molecular ozone is effectively converted to hydroxyl radicals. Figure 4.3 demonstrates that at a given ozone dosage, the addition of hydrogen peroxide up to a peroxide to ozone ratio of 0.55 didn't improve the degradation of geosmin compared to ozone alone.

The lack of geosmin removal enhancement with increasing peroxide to ozone ratio needed confirmation since it contradicts the findings of numerous research studies performed with different source waters (Edzwald, 1992; Ferguson *et al*, 1990; Glaze *et al*, 1990). A two-level factorial design was selected to explore and quantify the significance of each independent parameter and their interaction. The independent variables included transferred ozone dose, H_2O_2/O_3 ratio, and the dependent parameter was percent geosmin removal.

Based on the exploratory results displayed in Figures 4.1 and 4.3, low and high values for the independent parameters were selected as shown in Table 4.5.

Table 4.5: Investigated Set Points for the Independent Parameters with Respect to Geosmin Oxidation

Main Effects	Low (-)	High (+)	Center Points (0)
Ozone dose (mg/L)	0.75	2.25	1.50
H_2O_2/O_3 ratio	0.0	0.4	0.2

Each set of experiments was replicated along with four center points (four degrees of freedom from pooled variance) to improve the sensitivity of the statistical analysis. The

order of experiments was randomized to ensure that geosmin removal yield variations were solely credited to changes in the experimental conditions.

Table 4.6: Statistical Design with True and Coded Variables and Actual Geosmin Removal

Ozone Dose (mg/L)	H_2O_2/O_3 Ratio	Ozone Dose (Coded)	H_2O_2/O_3 Ratio (Coded)	Ozone Dose × H_2O_2/O_3 Ratio	%Geosmin Removal Expt#1	%Geosmin Removal Expt#2	Average % Geosmin Removal
0.74	0.00	-	-	+	43.0	44.0	43.5
0.75	0.46	-	+	-	46.0	50.0	48.0
2.18	0.00	+	-	-	83.0	90.0	86.5
2.20	0.52	+	+	+	86.0	87.0	86.5
1.47	0.26	0	0	0	75.0	71.0	73.0
1.47	0.27	0	0	0	79.0	69.0	74.0
1.50	0.25	0	0	0	68.0	72.0	70.0

The data compiled in Table 4.6 was used to build an ANOVA table.

Table 4.7: ANOVA Results of Ozone Alone and Combined with Hydrogen Peroxide for Geosmin Removal

Source	Effect	Sum of Squares (SS)	Degrees of Freedom (df)	Mean Square (MS)	$F_{observed}$	Fobs>Fcrit?
Ozone Dose	40.75	3321	1	3321	$99.6^{(1)}$	Yes
H_2O_2/O_3 Ratio	2.25	10.13	1	10.13	0.3	No
Interaction	-2.25	10.13	1	10.13	0.3	No
Error			4	33.34*		

*Pooled variance estimate

$F_{critical} = F_{1, 4, 0.05} = 7.71$ at a 5% significance level (Referred to standard F-tables). Since the ozone dose is the only independent parameter with a $^{(1)}F_{observed}$ higher than $F_{critical}$, the ozone dose is statistically ($\alpha = 0.05$) the only main parameter responsible for oxidizing geosmin. Generating additional hydroxyl radicals by increasing the H_2O_2/O_3 ratio up to approximately 0.5 didn't improve geosmin removals compared to ozone alone.

These results conclusively demonstrated that augmenting the hydroxyl radical yield by increasing initiator levels (HO_2^-) didn't offer the expected benefits that stem from the significantly higher reactivity between ozone decomposition radical products and geosmin. Huck et *al* (1995) made similar observations when Detroit River water was ozonated at a constant dose of 1.2 mg/L and by varying the hydrogen peroxide to ozone ratio from 0.20 to 0.35.

The two most plausible causes that could explain these results are:

1. background radical promoters in the water's NOM catalyzed molecular ozone decomposition into hydroxyl radicals, or
2. excess hydroxyl radicals generated by the reaction of hydrogen peroxide and molecular ozone were scavenged by radical traps such as alkalinity.

The answer probably lies within a combination of these two mechanistic pathways. The water's high DOC content harbors elevated levels of radical chain promoters and is *de facto* the primary ozone decomposition pathway. As shown in Appendix 5, by applying an H_2O_2/O_3 ratio, the resulting initiator influx consumes the remaining molecular ozone residual but since promoter radical chain reactions constitutes the primary ozone decay mechanism the overall hydroxyl radical oxidation capacity remains relatively constant compared to ozone alone. Furthermore, at the time of the experiments, alkalinity ranged from 179 to 187 mg/L as $CaCO_3$, which implied that elevated concentrations of the radical scavengers were present to neutralize a fraction of hydroxyl radicals generated either by natural promoters or by the addition of hydrogen peroxide.
Acero and Von Gunten (2001) reported similar results when comparing hydroxyl radical production with ozone alone and combined with hydrogen peroxide in a surface water with a high DOC content.

4.3.2 MCPA

The goal of this experiment was to assess the significance of ozone dose and H_2O_2/O_3 ratio with respect to MCPA oxidation. A 2^2 factorial experiment was selected to explore and quantify the significance of each independent parameters and their interaction. The independent variables included transferred ozone dose, H_2O_2/O_3 ratio, and the response factor was percent MCPA removal.

Based on Figure 4.2, an ozone dose of 2.25 mg/L was used as the upper dose limit since the MCPA residual was well above the MCL (= 0.05 ug/L) while a lower ozone dose limit value of 0.75 mg/L was selected because of the measurable MCPA removal response to ozone oxidation. Table 4.8 summarizes the operational parameter values selected to perform the two-level factorial statistical analysis.

Table 4.8: Tentative Set Points for the Independent Parameters with Respect to MCPA Oxidation

Main Effects	Low (-)	High (+)	Center Points (0)
Ozone Dose (mg/L)	0.75	2.25	1.50
H_2O_2/O_3 Ratio	0.0	0.4	0.2

Each set of experiments was replicated with three center points (equivalent to two degrees of freedom) being done in the second experiment. The order of experiments was randomized to ensure that MCPA removal yield variations were solely caused by changes in the experimental conditions.

Table 4.9: Statistical Design with True and Coded Variables for MCPA Removal

Ozone Dose (mg/L)	H_2O_2/O_3 Ratio	Ozone Dose (Coded)	H_2O_2/O_3 Ratio (Coded)	Ozone Dose × H_2O_2/O_3 Ratio	%MCPA Removal Expt#1	%MCPA Removal Expt#2	Average % MCPA Removal
0.75	0.00	-	-	+	50	43	47
0.75	0.44	-	+	-	47	37	42
2.27	0.00	+	-	-	90	94	92
2.29	0.47	+	+	+	97	82	90
1.52	0.15	0	0	0		77	
1.52	0.15	0	0	0		76	
1.52	0.15	0	0	0		70	

The data compiled in Table 4.9 was used to build an ANOVA table:

Table 4.10: ANOVA Results of Ozone Alone and Combined with Hydrogen Peroxide for MCPA Removal

Source	Effect	Sum of Squares (SS)	Degrees of Freedom (df)	Mean Square (MS)	$F_{observed}$	Fobs>Fcrit?
Ozone Dose	46.5	4324.5	1	4324.5	$301.8^{(1)}$	Yes
H_2O_2/O_3 Ratio	-3.5	24.5	1	24.5	1.7	No
Interaction	1.5	4.5	1	4.5	0.1	No
Error			2	14.3*		

*Determined from the variance of the three center points

$F_{critical} = F_{1, 2, 0.05} = 18.5$ at the 5% significance level (Refer to standard F-tables). Statistical analysis by means of ANOVA in Table 4.10 indicated that since the ozone dose is the only independent parameter with a $^{(1)}F_{observed}$ higher than $F_{critical}$, the ozone dose is statistically ($\alpha = 0.05$) the only main factor responsible for oxidizing MCPA. Generating additional hydroxyl radicals by increasing the H_2O_2/O_3 ratio up to approximately 0.5 didn't improve MCPA removal compare to ozone alone. This conclusion is supported by Antoniou and Andersen (2012), who observed that the ozone dosage necessary to achieve 90% removal of atrazine remained unchanged via conventional ozonation or in an O_3/H_2O_2 AOP system with hydrogen peroxide dosed in excess.

These results conclusively showed that enhancing the hydroxyl radical yield by increasing the hydrogen peroxide to ozone ratio didn't offer the potential benefits that stem from the significantly higher reaction rates between the radical products of ozone decomposition and MCPA. As with the geosmin study above, the same arguments could be formulated as to the most probable ozone mechanistic reaction pathways specific to the water matrix and treatment conditions herein. The data in Appendix 6 established that as long as the ozone demand was satisfied and upon addition of hydrogen peroxide, there was complete conversion of molecular ozone to hydroxyl radicals at the first contactor's effluent. Despite favoring hydroxyl radical production by artificially increasing initiator levels, the $^{\cdot}OH/O_3$ yield remained relatively unchanged because the indirect ozone decomposition reaction pathway might govern conventional ozonation reactions. Alternatively, excess hydroxyl radicals generated either by natural promoters or by adding hydrogen peroxide might also have been neutralized by the water's natural alkalinity which at the time of the experiment ranged from 232 to 252 mg/L as $CaCO_3$.

Practical Considerations

This research demonstrated that conventional ozonation and the AOP O_3/H_2O_2 process are equally effective treatments for the control of the trace organic contaminants studied. However, raw data contained in Appendices 5 and 6 also indicate that higher ozone residuals after the first contactor resulted from increasing ozone dosages (once the ozone demand of the water has been satisfied), which have the potential to carry-over into downstream biological filters and adversely impact biomass activity. This was especially true in cold water conditions since the ozone residual is substantially more persistent compared to that observed in warm water conditions (data not shown). If higher ozone dosages are desirable to achieve a specific water treatment performance target, the ozone residual can be effectively controlled without impacting micro- contaminant removal performance while safeguarding filter biological activity by:

- adjusting the H_2O_2/O_3 ratio up to approximately 0.5 ahead of the ozone contactors or
- adding hydrogen peroxide towards the end of the ozone contactors to consume any remaining ozone residuals. Previous research has established that a 1 mg/L

hydrogen peroxide residual will not affect biomass activity in downstream biological filters (Urfer and Huck, 1997).

4.4 Control Strategies to Mitigate Bromate Formation

The overall objective of this component of research was to investigate the impact of raw water bromide level, ozone dose, and hydrogen peroxide to ozone ratio with respect to the production of bromate. This phase of the pilot study was critical to:

1. establish the maximum ozone dose as a function of background bromide levels that would ensure compliance with provincial regulations. The Ministry of the Environment has set the maximum contaminant level (MAC) for bromate at 10 µg/L (Ontario Regulation 169).
2. assist with data for the purpose of full-scale ozone generator sizing in the eventuality that ozone was retained for full-scale implementation.

4.4.1 Bromate Formation

The entire study was completed within a 12- hour period in order to minimize variations in background levels of bromide, NOM, pH, alkalinity, and temperature, all of which significantly affect bromate formation (Galey *et al*, 2001). By controlling these sources of variation, the ozone dose was the sole independent parameter impacting bromate formation.

As with previous experiments, the ozone contactor flow rate was adjusted to an HRT of 30 minutes in order to mirror the design capacity of the then current full-scale chlorine contact chambers. No replicate samples were collected in order to limit natural bromide level variability. Figure 4.4 (Appendix 7) illustrates the relationship between transferred ozone dose and bromate formation.

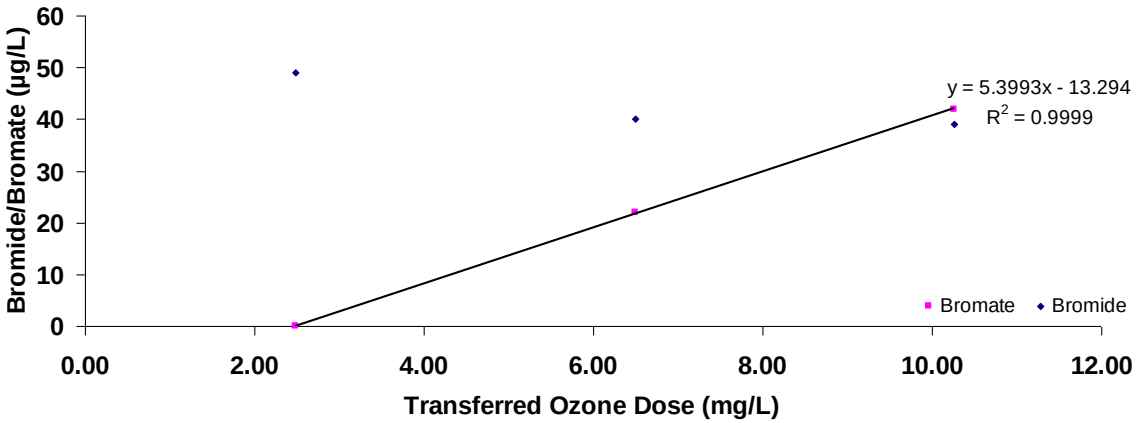


Figure 4.4: Bromate Formation as a Function of Ozone Dose

There is a linear correlation between bromate formation and ozone dose when bromide levels remained relatively constant. The small variations in background bromide levels measured over the course of the study reflect Grand River water quality fluctuations over a 12-hour period. However, these variations appear to have been inconsequential with the linear dose-response relationship involving ozone dose and bromate formation (R^2 = 0.99). Proportionally higher levels of bromate were generated by increasing ozone dosages between 2.5 mg/L and 10.3 mg/L. These results are in agreement with previous studies showing a substantial increase in bromate formation at high ozone dosages (Galey *et al*, 2001; Von Gunten *et al*, 1996).

Song *et al* (1997) developed an empirical model quantifying the effects of water quality parameters and treatment conditions on the production of bromate. With the exception of pH, ozone dose was the most significant factor governing bromate formation.

Figure 4.5 (Appendix 8) illustrates bromate levels formed as a function of ozone dose over a twelve-month period. Bromide levels in the Grand River are considered moderate to high (Rakness, 2005; Jasim *et al*, 1999) with levels fluctuating between 36 and 192 µg/L.

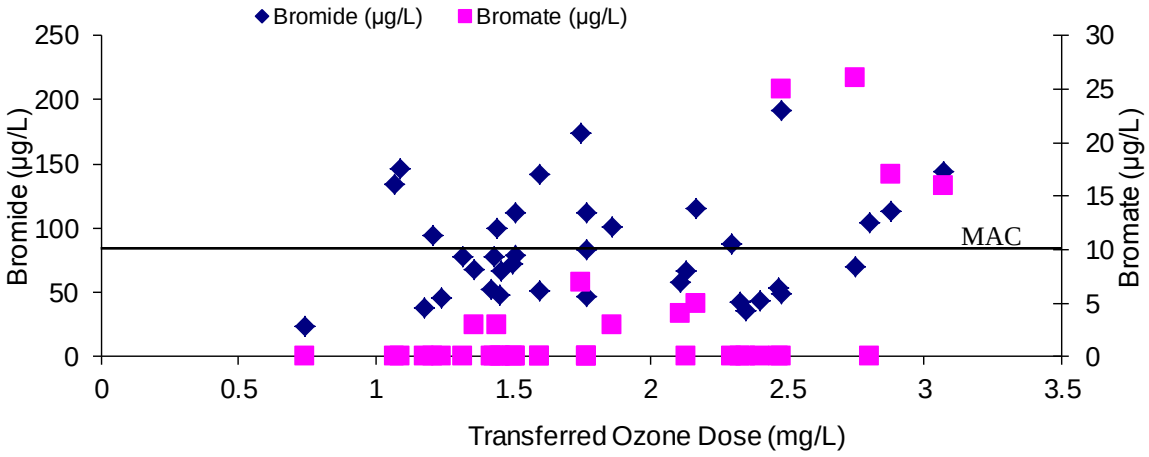


Figure 4.5: Bromate Formation as a Function of Ozone Dose

Bromate was formed at levels above its MAC when the ozone dose reached 2.5 mg/L, irrespective of naturally-occurring bromide levels. Below this ozone dose threshold, even when bromide levels were high, bromate levels remained below regulatory limits (10 µg/L). With this specific raw water source, the ozone dose is the predominant factor in the formation of bromate with bromide levels playing a secondary role. As a result, if intermediate ozonation is retained for full-scale implementation, the dose should be kept at or below 2.0 mg/L to ensure compliance with provincial regulations.

A similar plot is displayed in Figure 4.6 (Appendix 9), representing bromate formation as a function of ozone dose in the presence of hydrogen peroxide at H_2O_2/O_3 ratios ranging from approximately 0.1 to 0.4.

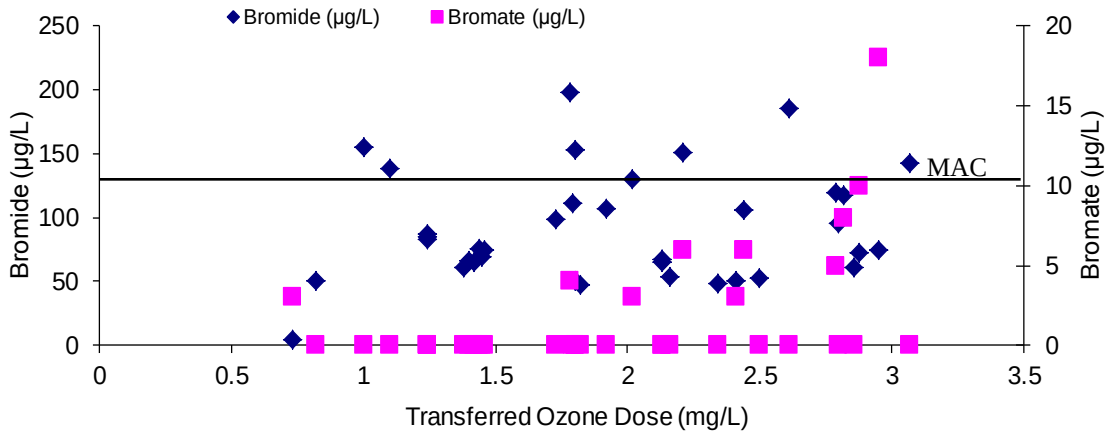


Figure 4.6: Bromate Formation as a Function of Ozone Dose with Hydrogen Peroxide

Background bromide levels were similar to those measured when ozone alone was studied, with levels ranging from 50 to 198 µg/L.

Bromate has the potential to be formed above its MAC when the ozone dose reaches 3.0 mg/L irrespective of bromide levels or hydrogen peroxide to ozone ratio. The data collected herein demonstrated that higher ozone doses were required for bromate formation in the presence of hydrogen peroxide compared to ozone alone.

In order to elucidate the relationship between bromate formation as a function of ozone alone and combined with hydrogen peroxide, a series of experiments was performed at constant ozone dose and varying hydrogen peroxide to ozone ratio between 0.25 and 0.50 approximately. An ozone dose of approximately 3 mg/L was selected because of the higher potential for bromate formation in both systems and to investigate bromate formation at ozone levels commonly applied in the water industry. Each set of experiments was performed within an 8-h period to maintain background bromide levels as constant as possible. The experiments were replicated three times under similar river water quality conditions and are displayed in Figure 4.7 (Appendix 10).

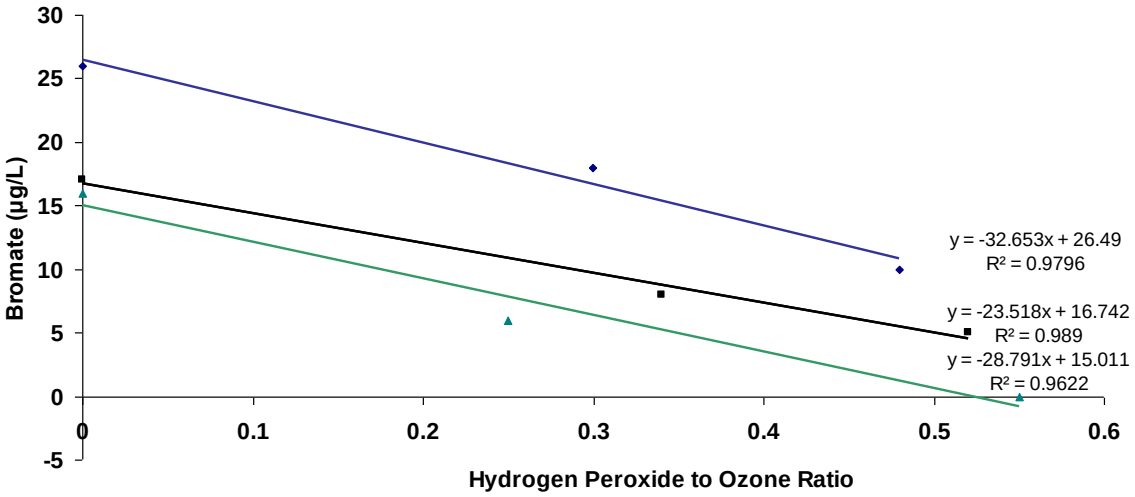


Figure 4.7: Impact of a 3-mg/L Ozone Dose with Varying H_2O_2/O_3 Ratios on Bromate Formation

The three replicates exhibited very different slopes mainly due to differences in water quality conditions between experiments affecting ozone demand and ratio of molecular ozone to ozone decomposition products. As shown in Appendix 10, the highest bromate levels were recorded at the lowest bromide levels amongst all three experiments, which confirm that bromide ions play a secondary role in the formation of bromate.
All three plots display a linear correlation between bromate formation and hydrogen peroxide to ozone ratio ($0.96<R^2<0.99$). To the best knowledge of the author, this is the first time that a direct dose-response relationship has been established between bromate reduction and varying H_2O_2/O_3 ratio at a fixed ozone dose. The highest concentrations of bromate were generated when ozone alone was applied. Incremental increases in hydrogen peroxide doses (up to a $H_2O_2/O_3 \approx 0.5$) resulted in progressively lower levels of bromate produced, indicating that the conversion of molecular ozone to hydroxyl radicals has a suppressing effect on bromate formation.

The most probable mechanisms by which H_2O_2 inhibits bromate formation include:

1. blocking the conversion of bromite to bromate by molecular ozone and/or
2. the rapid oxidation of hypobromous acid/hypobromite ion by hydrogen peroxide

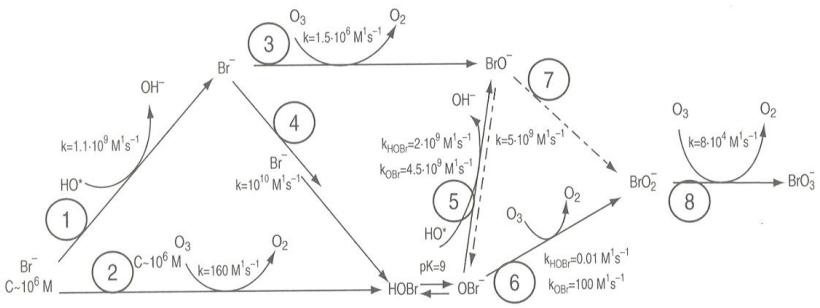


Figure 4.8: Bromate Reaction Pathways (Buffle *et al*, 2004)

1. Conversion of bromite to bromate by molecular ozone is inhibited

Figure 4.8 illustrates the two main pathways leading to the formation of bromate with bromide as the starting point. Both hydroxyl radicals and molecular ozone are key initiators of bromate formation reactions (reactions 1 and 2, respectively), however; the final step (reaction pathway 8) relies solely on molecular ozone to convert bromite (BrO_2^-) to bromate. Increasing the hydrogen peroxide to ozone ratio enhances the hydroxyl radical yield thus lowering the amount of molecular ozone available to react with bromite to form bromate and effectively suppressing equation 8.

Von Gunten and Hoigne (1994) reported a similar trend albeit at hydrogen peroxide to ozone ratios above 0.35. Below the stoichiometric ratio, higher bromate levels were formed compared to ozone alone. The discrepancy between the two studies might be explained by the higher operating pH of 8.0 in Von Gunten and Hoigne work versus 7.4 in the current research. As shown in Figure 4.8, reaction pathway 6, which involves the reaction of hypobromite ion with ozone is favored at higher pH (pKa = 9) and its reaction rate is two orders of magnitude higher compared to that between hypobromous acid and ozone. At a pH of 7.4 (versus 8.0), the hypobromite ion/hypbromous acid ratio decreases, hindering bromite formation and thus decreasing bromate production.

2. Rapid oxidation of hypobromous acid/hypobromite ion by hydrogen peroxide

Alternatively, equation 6 is hindered by the direct reaction of hydrogen peroxide with hypobromite ion (Antoniou, 2012):

$$2OBr^- + H_2O_2 \longrightarrow 2Br^- + O_2 + 2OH^- \qquad 4.1$$

For each mole of hydrogen peroxide, two moles of hypobromite ions are reduced to bromide ions (equation 4.1), preventing subsequent oxidation reactions to bromate (equations 6 and 8, Figure 4.8). Furthermore, Von Gunten and Oliveras (1997) determined that the hypobromite ion/hypobromous acid is the "critical reaction intermediate" that can either be oxidized to bromate or be reduced to bromide by hydrogen peroxide. In the pH range between 6 and 8, the latter was validated by the fast reactions between OBr^- and H_2O_2 and between HOBr and HO_2^- with second-order rate constants equal to $(1.2 \pm 0.2)\times10^6$ M^{-1} s^{-1} and $(7.6 \pm 1.3)\times10^8$ M^{-1} s^{-1}, respectively.

Von Gunten and Oliveras (1998) and Antoniou and Andersen (2012) concluded that hydrogen peroxide addition should be considered as a treatment strategy to control bromate formation in bromide-containing water (to comply with the 10 μg/L-limit).

According to the bromate formation pathways depicted in Figure 4.8 and the most plausible inhibitory mechanisms described herein, increasing the hydrogen peroxide to ozone ratio above 0.35 should in theory, virtually negate the formation of bromate by blocking either equations 6 or 8. In practice, out of the three replicated experiments, only one confirmed that hypothesis (Figure 4.7). This suggests that in the presence of initiators of ozone decomposition products, there are other radical chain reaction pathways leading to the production of bromate, which do not involve the oxidation of bromite to bromate by molecular ozone (see Figure 4.8). Von Gunten and Oliveras (1998) conducted a series of experiments involving hydroxyl radical generation via γ-irradiation of hydrogen peroxide in ultrapure water spiked with bromide. In the pH range commonly found in water treatment processes (pH = 6 to 8), there was strong evidence of bromate formation

and a direct hydroxyl radical pathway leading to the formation of bromate in bromide-containing waters was proposed.

Practical Considerations

- Where the potential for high bromate exists, and whether taste and odour control or oxidation of micropollutants is the primary treatment objective, bromate production can be mitigated by the addition of hydrogen peroxide upstream of the ozone contactors. Furthermore, converting from conventional ozonation systems to the AOP O_3/H_2O_2 process is a relatively low-cost/low maintenance upgrade (Acero and Von Gunten, 2001). However, if the main driving force of ozone treatment is for disinfection purposes, then converting to a hydrogen peroxide-based AOP treatment isn't a suitable option due to the lack of an ozone residual necessary to calculate CT_{10} and hence, quantify primary disinfection. In addition, since hydrogen peroxide is a weak oxidant, a residual may carry-over in downstream treatment processes. It will either be consumed by downstream granular media-based biological filters (Urfer and Huck, 1997) or exert a chlorine demand in post-filtration chlorination processes.

- If post-Actiflo ozonation is selected for full-scale implementation in Brantford, the ozone generator should be sized to deliver up to 2.0 mg/L to secure compliance with bromate standards with a comfortable safety margin. Since DOC levels in settled water hover around the 2.5 mg/L-mark, the maximum transferred ozone dose will be equivalent to an ozone/DOC ratio of approximately 0.8 mg O_3/mg DOC, which is in agreement with industry guidelines for taste and odour control.

4.5 Investigating the Impact of Various Filter Media on the Degradation of Selected Trace Organic Contaminants

In the context of selecting the most suited granular filter media for full-scale implementation, three media i.e. anthracite, GAC, and a ceramic media (Filtralite®) over

sand were studied in biologically active filters for the removal of geosmin and MCPA. The three dual media pilot filters ran for over one year under aerobic conditions to develop a viable media-attached biofilm. This pre-conditioning period was more than adequate to reach pseudo-steady conditions for BOM removal in the three biologically active filters. Although the acclimation period is site-specific, other researchers (Liu *et al*, 2001) have drawn similar conclusions.

No ozone was generated during the experiments.

In order to assess GAC's adsorption capacity over the course of this study, a surrogate DOC parameter, UV_{254} was used to compare organics removal between GAC and anthracite filter effluents. It was assumed that biomass population between the two filter media was similar at any given time and therefore, by measuring the difference in UV_{254} between the two filters, the adsorption capacity of GAC was assessed. Figure 4.9 illustrates the percent UV_{254} difference between GAC and anthracite filter effluents.

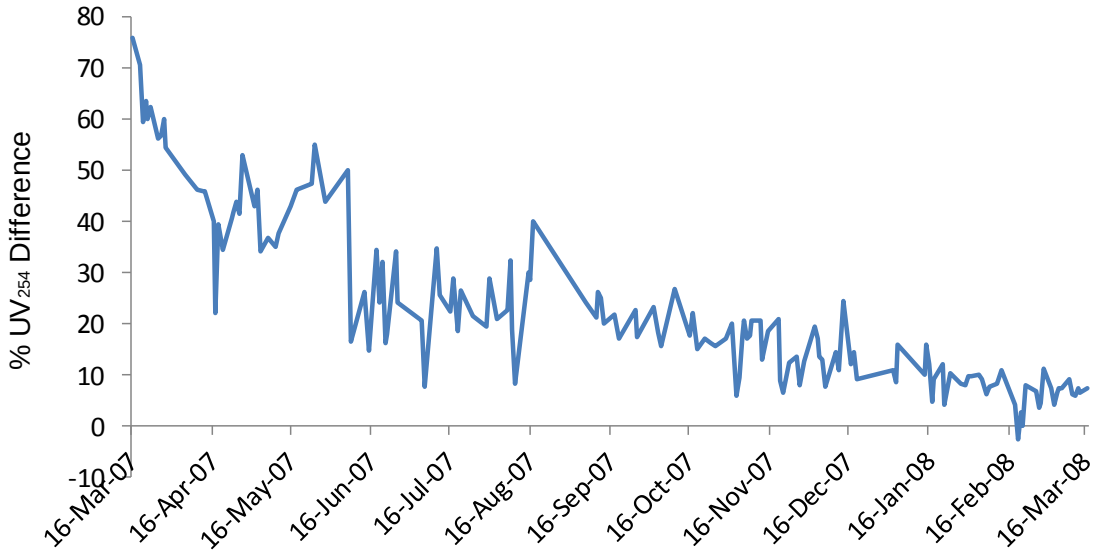


Figure 4.9: Percent UV_{254} Difference between GAC and Anthracite Filters

As shown in Figure 4.9, after one year of operation, the GAC was essentially exhausted with an adsorption capacity residual of approximately 10%.

The percent reduction of geosmin was evaluated by calculating the difference in geosmin concentrations between the inlet and the outlet of individual filters.

4.5.1 Geosmin

4.5.1.1 System Losses

Pre-conditioning of the ozone contactors, filters, and appurtenances with geosmin was simultaneously carried out with the objective of eliminating the contribution of surface adsorption when measuring geosmin removal yields. In an attempt to minimize system losses, geosmin was continuously fed into the ozone contactor inlet at a 100 ng/L dose without ozone generation for an equivalent 5-day period in order to saturate the adsorption sites of wetted process surfaces.

It was assumed that successful pre-conditioning of the ozone contactors also equated to proper acclimation of the filter columns.

4.5.1.2 Geosmin Degradation by Biologically Active Filtration (without Ozone)

The ability of the three filter media to remove geosmin was assessed in two ways (Box *et al*, 1978):

- by comparing geosmin removal mean concentrations to determine if there is significant performance variability between granular media filters.
- by assessing how different the results between the three coarse media are by performing a *Multiple Comparisons Least Significant Difference* (LSD) test using the Bonferroni inequality principle.

The experiments were replicated three times (n =3) to improve the sensitivity of the statistical analysis. Each experimental run involved all three filters running under identical operating conditions to ensure that geosmin removal yield differences were solely attributable to filter media type. Geosmin was fed at the inlet of the filters at a target concentration of 100 ng/L in an attempt to simulate worst case scenario of a cyanobacterial bloom in the Grand River. The filters were backwashed concurrently every 90 hours with non-chlorinated filtered water and the experiments were carried out at least 24 hours after the beginning of the filter runs. Contact time in the filters was held constant with an HRT of 41 minutes representing a design flow rate of 2.20 L/min.

Geosmin destruction yields were measured by subtracting odorant levels between the inlet and outlet of individual biological filters with three replicate sets collected per filter. Percent geosmin removals are displayed in Table 4.11.

Table 4.11: Mean Geosmin Removals as a Function of Granular Filtration Media Type

% Geosmin Removal		
Filtralite®/Sand	GAC/Sand	Anthracite/Sand
86	97	63
85	97	68
87	97	63
Mean = 86%	Mean = 97%	Mean = 65%

Effective and consistent filter removal yields demonstrate geosmin biodegradability by all three granular media. It confirms that, based on influent water quality conditions and within one year of continuous filters operation, their respective biofilms have become acclimated for the biodegradation of geosmin. The data compiled in Table 4.11 was used to build an ANOVA table.

Table 4.12: ANOVA Table

Source	SS	DOF	MS	E(MS)
Between	1621	2	810.8	$\sigma^2 + 3\sigma^2_a$
Within	18.7	6	3.1	σ^2
Total	1640.2	8		

Combining the ANOVA table and the null hypothesis test, the results of the statistical analysis establishes that there are significant performance differences between granular filter media type at a 5% significance level (calculation details in Appendix 11).

A Multiple Comparisons Least Significant Difference (LSD) analysis was used to quantify the performance differences between filter media with respect to mean percent geosmin removals. The results demonstrate that all mean differences are higher than the LSD value, which indicates that geosmin removal performance between filter media differ significantly (Appendix 11). Microbial-mediated geosmin degradation was poorest in the anthracite filter with a 65% average yield followed by Filtralite® and GAC filters

at 86% and 97%, respectively (Table 4.11). The enhanced geosmin removal ability of Filtralite® (assuming no adsorption capability as per manufacturer specifications) over anthracite might be attributed to its high surface area, thus supporting a denser active biomass. These experimental results are supported by the work of Ho *et al* (2007) who studied the effect of administering a microbial inoculum of varying concentrations to laboratory sand filters and assessing their subsequent abilities to degrade geosmin. They observed that enhanced removal yields were achieved in filters that have received a higher initial inoculum concentration suggesting that the active microbial population density (defined as active biomass per unit volume) might have played a key role.

The GAC filter exhibited the best removal performance and consistently met the 1-log removal target due to a combination of biomass activity and residual adsorption capacity. These results are supported by other experimental studies on cyanobacterial metabolites (Elhadi *et al*, 2006; Westerhoff *et al*, 2005; Wang *et al*, 1995), which concluded that biologically active filters using GAC media outperformed anthracite media.
According to Westerhoff *et al* (2005), the pre-acclimation duration to reach microbially-mediated steady-state conditions for geosmin removals in biological active filters is in the order of weeks to months. However, in the current study, the microbial population in the biological filters was exposed to high levels of geosmin (i.e. 100 ng/L) over a 5-day acclimation period primarily for the purpose of controlling system losses (see Section 4.5.1.1). As a result, there wasn't sufficient time allocated to establish steady-state conditions in the biological filters and geosmin was consumed as a secondary substrate by the bacterial community in the filters. Previous research studies (Ho *et al*, 2007; Rittmann *et al*, 1995) have shown that geosmin and other trace odourant contaminants were being used as secondary substrates in biologically active filters due to the presence of NOM in the mg/L-range. Specifically, Ho *et al* (2007) reported that the biodegradation mechanism by which geosmin is decomposed in biological filters not specifically acclimated for its decomposition, might be attributed to microorganisms consuming primary substrates with similar chemical structures such as easily biodegradable alicyclic alcohols and ketones.

4.5.1.3 Tandem Intermediate Ozonation-AOP/Biologically Active Filtration

This set of experiments was designed to compare overall geosmin removal performance when investigating the combined effects of intermediate ozonation and biological filtration. Independent parameters included transferred ozone dose, H_2O_2/O_3 ratio and granular filter media type (anthracite, GAC, and Filtralite®). A low ozone dose (1.00 mg/L equivalent to an ozone/DOC ratio of 0.3 mg O_3/mg DOC) was selected to determine if in tandem, these treatments would lead to enhanced geosmin removals. Because of the long contact times required to conduct these experiments, no replicate samples were taken.

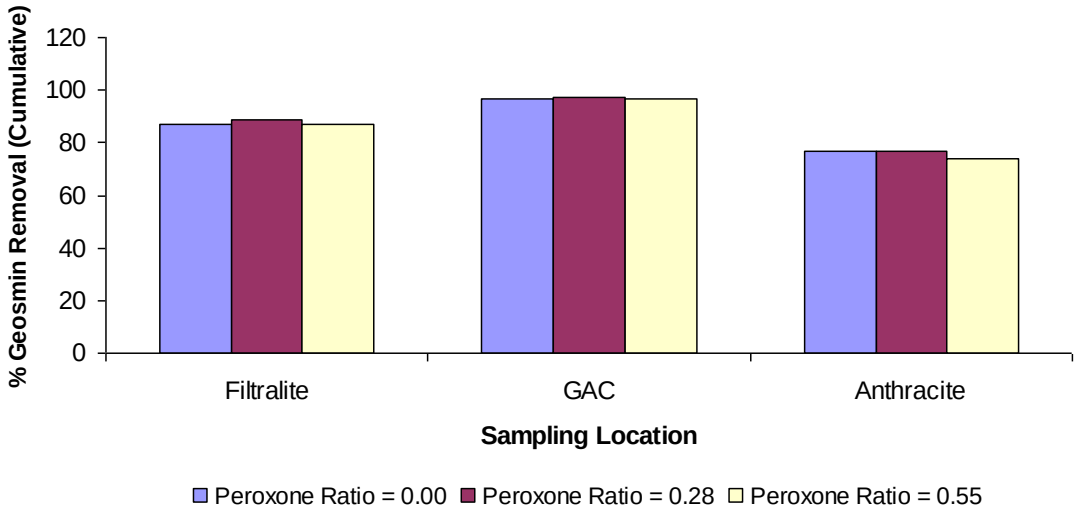


Figure 4.10: Geosmin Removals with a 1.00 mg/L Transferred Ozone Dose as a Function of H_2O_2/O_3 Ratio and Filter Media Type

Figure 4.10 (Appendix 12) shows that the percent geosmin removal yields were independent of H_2O_2/O_3 ratio (in the range of 0.00 to 0.55). This result was expected based on the conclusions drawn from Section 4.2.1.2: It was established that the most probable ozone mechanistic reaction pathways specific to the water matrix and treatment conditions herein implicated the rapid conversion of molecular ozone to hydroxyl radicals, and by artificially increasing initiator levels (H_2O_2/O_3 ratio > 0.00) didn't enhance the $^{\cdot}OH/O_3$ capacity because the indirect ozone decomposition reaction pathway

governed conventional ozonation reactions. Alternatively, hydroxyl radicals generated during ozonation with and without the addition of hydrogen peroxide might have been scavenged by radical traps such as alkalinity. Furthermore, as with Section 4.5.1.2, the null hypothesis test demonstrated that the type of granular filter media had a significant impact at a 5% significance level on geosmin removal yields. The highest removal yields were found to be with GAC followed by Filtralite® and anthracite.

Interestingly, GAC and Filtralite® performed equally well in the presence or absence of an intermediate ozone step: Table 4.11 and Figure 4.10 shows that the percent geosmin removals remained unchanged at 97% and 86% respectively upon addition of a 1-mg/L ozone dose prior to biological filtration compare to those obtained without pre-ozonation. In contrast, the anthracite filter benefited from pre-ozonation with geosmin removal yields improving from an average of 65% without ozonation (Table 4.11) to 77% with a 1-mg/L transferred ozone dose (Figure 4.10).

In order to determine the optimal ozone dose with respect to the three granular filter media, a series of experiments were conducted by varying the ozone dose between 0.7 and 2.1 mg/L (equivalent to an ozone/DOC ratio range of 0.3 to 0.8 mg O_3/mg DOC) and assessing the dose-response relationship based on geosmin removal yields at the filter effluents. Each experiment was conducted daily with the ozone dose adjusted 16 hours prior to the beginning of the run. These experiments were performed in warm water conditions since geosmin is mainly present in source water during the summer months with temperatures ranging from 15 to 23^0C. The order of experiments was randomized. Figure 4.11 shows overall geosmin removal yields as a function of ozone dose and treatment process.

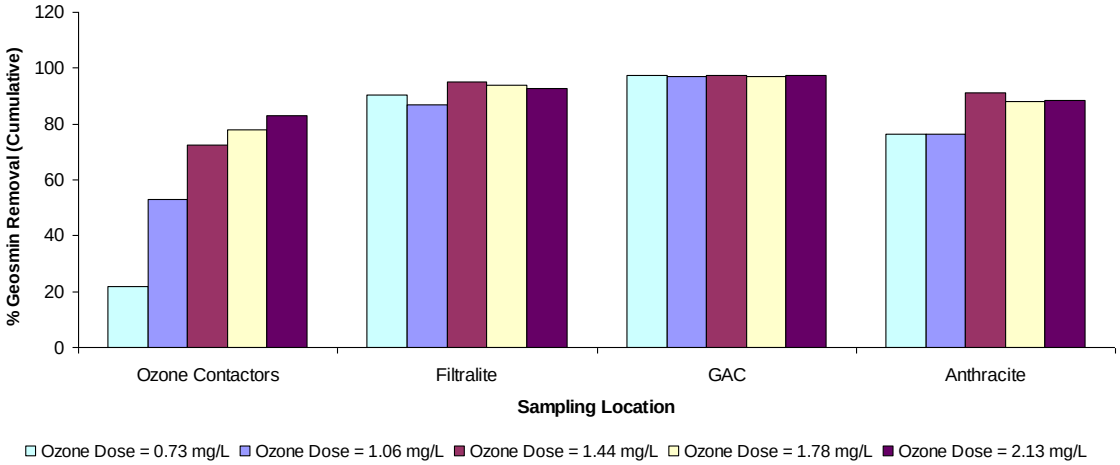


Figure 4.11: Geosmin Removals as a Function of Transferred Ozone Dose and Filter Media Type

Increasing the transferred ozone dose in the ozone contactors from 0.73 mg/L to 2.13 mg/L progressively improved geosmin removal yields prior to biological filtration (Figure 4.11 and Appendix 13). This observation is supported by the experimental data covered in Section 4.3.1.

In tandem with intermediate ozonation, the GAC filter exhibited the highest geosmin removal yields closely followed by Filtralite® and anthracite filters. Transferred ozone dose had a negligible impact on the performance of the GAC and Filtralite® filters with geosmin removals upwards of 97% and 87%, respectively. Nearly complete geosmin removal occurred in the GAC filter due to an effective adsorption affinity towards geosmin combined to an elevated biomass activity. Improved geosmin biodegradation in the Filtralite® filter over the anthracite filter, assuming that Filtralite® media doesn't have adsorption properties (as per manufacturer specifications) may be attributed to higher surface area harboring a denser biomass.

The 16-hour acclimation time allocated for a given ozone dose might account for the small differences in geosmin removal yields within each filter media. Higher ozone dosages will typically increase AOC levels prior to filtration and with the proper conditioning period, enhances biomass density, which in turn improves organics removal.

Anthracite performance was enhanced by pre-ozonation and at an ozone dose of 1.44 mg/L (=0.7 mg O_3/mg DOC), the tandem ozone/anthracite filter eliminated 91% of influent geosmin, thus meeting the geosmin removal target. In contrast, a 2.3 mg/L transferred ozone dose was required (Figure 4.1) to satisfy the 1-log geosmin removal target if solely relying on intermediate ozonation for taste and odour control. At the optimal ozone dose, the tandem ozone and anthracite filter reduced the required ozone dose by 37% and in the process, significantly lowered the risk of exceeding regulatory limits on bromate formation. Nerenberg *et al* (2000) also observed that individually, ozonation and biofiltration will only partially remove geosmin and MIB, but when combined the resulting treatment system can be very effective for taste and odour control. Moreover, geosmin removal improvements can be expected when combining intermediate ozonation and the biological anthracite filter even at non-optimal ozone dosages. Figure 4.12 depicts geosmin removal yields with ozone alone and in combination with the anthracite filter.

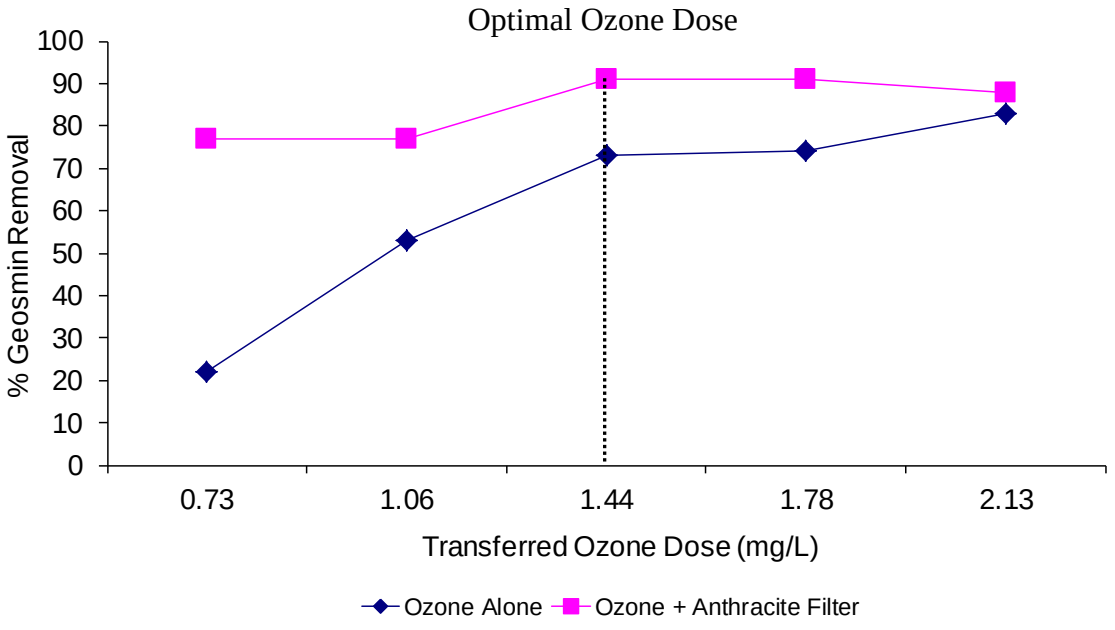


Figure 4.12: Geosmin Removal Enhancement Mediated by the Combination of Ozone Followed by a Biological Anthracite Filter

Within the ozone dose range studied, geosmin removal yields were enhanced when ozonation precedes the anthracite filter whether or not the transferred ozone dose is at the optimal level (1.44 mg/L). As illustrated in Figure 4.12, the benefits of combining treatments are more prevalent at ozone dosages up to the optimal ozone dose. For example, when applying a 0.73 mg/L transferred ozone dose, geosmin degradation yields are 22% and 77% for ozone alone and ozone combined to the anthracite biological filter, respectively. At ozone dosages above the optimal level, geosmin removal improvements via subsequent biological treatment progressively subsided compared to ozone alone since higher ozone dosages promote oxidation rather than biodegradability-enhancement reactions.

Practical Considerations

- Within the range of ozone dosages studied, when ozone precedes the anthracite filter, there is an optimal transferred ozone dose over which little additional geosmin removal benefits can be attained. With a 1.44 mg/L transferred ozone dose (=0.7 mg O_3/mg DOC), the ozone-enhanced biologically-active anthracite filter meets the 90%-geosmin reduction target while ensuring compliance with bromate formation.
- Geosmin removal improvements can be expected when combining intermediate ozonation and the biological anthracite filter even at non-optimal ozone dosages. The highest geosmin removal enhancements are particularly substantial at sub-optimal ozone dosages.
- Increasing the ozone dosage beyond optimal levels promotes direct oxidation reactions over a biodegradation-enhanced mechanism, which from an economic perspective is undesirable.
- The highest geosmin removal yields amongst all three filters were achieved with the GAC media. As adsorption sites on the GAC media becomes saturated, larger differences in geosmin removal yields with and without intermediate ozonation are expected.

- Based on geosmin removal results and overall taste and odour control strategy, GAC is the best granular filtration media candidate and should be considered for full-scale implementation. However, as its adsorption capacity diminishes, and since reactivation wouldn't be cost-effective, geosmin removal yields will progressively decrease and over the long term, behave similarly to anthracite. From a cost-taste and odour benefit perspective, ultimately anthracite is a better candidate since:
    - it is by far the least expensive among the three filter media studied,
    - at optimal ozone dosage, when combined with intermediate ozonation the 90% geosmin removal target is met and,
    - bromate formation complies with provincial regulation without the need for hydrogen peroxide addition (see Figure 4.7).
- During a cyanobacterial bloom, taste and odour events will be best controlled by increasing the transferred ozone dose and not by adding hydrogen peroxide to generate excess hydroxyl radicals. However, if ozone dosages over 2 mg/L are desired, hydrogen peroxide should be injected ahead of the ozone contactors up to a H_2O_2/O_3 ratio of 0.6 to avoid out-of-compliance bromate violations.

4.5.2 MCPA

4.5.2.1 System Losses

Pre-conditioning of the ozone contactors, filters and appurtenances with MCPA were simultaneously carried out with the objective of eliminating the contribution of surface adsorption when measuring MCPA removal yields. In an attempt to minimize system losses, MCPA was continuously fed at the ozone contactor's inlet with a 10 μg/L dose with the ozone generator switched off for three consecutive days in order to saturate the adsorption sites of wetted process surfaces.

It was assumed that successful pre-conditioning of the ozone contactors also equated to proper acclimation of the filter columns.

Table 4.13: System Losses in the Filters

% MCPA Removal		
Filtralite®/Sand	GAC/Sand	Anthracite/Sand
8.8	7.9	-3.2
-6.0	-2.5	2.0
-3.2	-3.3	2.3
Mean = 3.5	Mean = 0.7	Mean = 0.4

Table 4.13 demonstrates that system losses in the filter columns were low indicating that MCPA removal yields will be mainly attributed to filter media removal processes.

During this stage of experiments, the MCPA stock solution was analyzed and the concentrations measured and calculated differed significantly. The analysis revealed that the true concentration was 11.4 mg/L compared to the expected concentration of 16.5 mg/L (corresponding to a 10 µg/L-MCPA dose at the set chemical pump flow rate). The discrepancy between true and calculated MCPA concentrations in the stock solution was most likely caused by glassware adsorption, thus explaining the significant concentration differences observed in the exploratory phase (Sections 4.2.2.1 and 4.2.2.2). This confirms the importance of proper system acclimation prior to proceeding with trace organic removal experiments in order to obtain accurate data (as per Elhadi *et al*, 2004).

4.5.2.2 MCPA Degradation by Biologically Active Filtration (without Ozone)

The ability of the three filter media to remove MCPA was assessed in two ways (Box *et al*, 1978):

- by comparing MCPA removal means to determine if there is significant performance variability between granular media filters.

- by assessing how different are the results between the three coarse media by performing a *Multiple Comparisons Least Significant Difference* (LSD) test using the Bonferroni inequality principle.

The experimental conditions in Section 4.5.1.2 were duplicated to conduct the MCPA biofiltration study. Each experimental run was replicated three times (n =3) involving all three filters running simultaneously under identical operating conditions to ensure that differences in MCPA removal yield were solely attributable to filter media type. MCPA was fed at the inlet of the filters with a target concentration of 10 μg/L. The filters were backwashed concurrently every 90 hours and the experiments were carried out at least 24 hours after the beginning of the filter run. Contact time in the filters was held constant with an HRT of 41 minutes representing a design flow rate of 2.2 L/min.

MCPA levels were measured at the inlet and outlets of the three biological filters and percent removals are displayed in Table 4.14:

Table 4.14: MCPA Removal as a Function of Media Type

% MCPA Removal		
Filtralite®/Sand	GAC/Sand	Anthracite/Sand
6	87	-4
7	90	8
6	88	-30
$\bar{a} = 6.3$	$\bar{a} = 88.3$	$\bar{a} = -8.7$

The GAC filter exhibited the best performance with an 88% mean MCPA removal yield. In contrast, Filtralite® and anthracite filters recorded negligible mean percent removal yields with 6% and -8.7%, respectively.

The data compiled in Table 4.14 was used to build an ANOVA table. Although the last anthracite/sand result was considered an outlier, it was taken into account for the statistical analysis.

Table 4.15: ANOVA Table

Source	SS	df	MS	E(MS)
Between	16158	2	8079	$\sigma^2 + 3\sigma^2 a$
Within	960	6	160	σ^2
Total	17118	8		

Combining the ANOVA table and the null hypothesis test, the results of the statistical analysis establishes that there were significant performance differences between granular filter media type within a 95% confidence interval (calculation details in Appendix 14).

A Multiple Comparisons Least Significant Difference (LSD) analysis was used to quantify the performance differences between filter media with respect to mean percent MCPA removals. Since the mean difference between anthracite and Filtralite® filters is below the LSD value, there is no statistical difference between their ability to remove MCPA. Furthermore, their negligible % MCPA removal means demonstrate that at the experimental conditions investigated, MCPA isn't biodegradable under the conditions tested (Table 4.14, Appendix 14).

It is well documented in the literature that MCPA can be biodegraded in soil and water given that the proper lag time is allocated for microorganism adaptation (Harrison *et al*, 1998). Under aerobic conditions, borehole microcosms were spiked with chlorophenoxy acid herbicides and immersed in a limestone aquifer to promote indigenous biological activity and acclimation on the solid granular supports. The results revealed that a four-day lag time period was necessary for bacterial adaptation and an additional 10 days were required to decrease MCPA levels from 2 mg/L to below MDL (Harrison *et al*, 1998). In contrast, González *et al* (2006) piloted a biological fixed bed reactor to study the biodegradability of MCPA from a WWTP effluent. Within a 24 hour period, the microbial community readily degraded MCPA by 88%. In another microcosm study, *Sphingomonas* species were identified to be effective MCPA-degrader and over 99% of the initial MCPA concentration was eliminated over a three-day period (Önneby *et al*, 2010). Since the primary objective of this research study was to investigate treatment response caused by a transient MCPA discharge event, there would be no lag time for

bacterial acclimation on the various solid supports. The lack of biodegradation in the pilot anthracite and Filtralite® filters highlights GAC's unique properties to effectively eliminate this xenobiotic contaminant. The most likely mechanism by which MCPA can be eliminated under the filtration conditions studied is via GAC's surface adsorption properties. In the early 1990s, the Lincolnshire Limestone, which supplies drinking water to a nearby community, recorded increasing levels of MCPP up to 8 μg/L, thus consistently exceeding the 0.1 μg/L-limit set by the EEC. Since the source of MCPP was traced back to two nearby landfill sites, the long-term solution was to install full-scale GAC contactors. After treatment, levels decreased well below the EEC limit (*i.e.* 0.01 μg/L), which demonstrated the adsorption affinity of GAC towards MCPP (Anon, 1994c). Since the chemical structures of MCPA and MCPP are similar (Harrison *et al*, 1998), it came to no surprise that MCPA was readily eliminated by non-exhausted GAC in the current study.

Practical Considerations

- MCPA removal in the ozone contactors is driven by the transferred ozone dose. Increasing hydroxyl radical yield up to an H_2O_2/O_3 ratio of approximately 0.5 did not improve MCPA removal.
- Conventional biological filters with anthracite and Filtralite® media aren't suited to remove MCPA because of its non-biodegradable nature in conventional water treatment processes. GAC is the only effective filtration barrier against MCPA with a near-90% removal rate, most likely attributed to its residual adsorption capacity.
- If Filtralite® or anthracite were to be selected for the full-scale filter upgrade at the Brantford Water Treatment Plant, then neither filter media can be relied upon to handle periodic MCPA discharge events. However, at transferred ozone dosages of 2 mg/L, MCPA removal yields are upwards of 90%.

4.6 Impact of Ozonation and Ozone-Based AOP Followed by Biological Filtration on TTHM Formation

Currently, trihalomethanes (TTHMs) are the only chlorinated disinfection by-products regulated by the Ministry of the Environment in Ontario. The limit is set at 100 μg/L based on a running annual average of sampling locations in the distribution system characterized by elevated hydraulic detention times. Historically, the Brantford Water Treatment Plant has been operating near the TTHM regulatory limit, especially in the warmer months of the year. Elevated TTHM formation potential can be sourced to a combination of high DOC, elevated water temperature, and treatment defficiencies. Based on current American regulations and trends, it is possible that the TTHM limit in the province of Ontario might be reduced to 80 μg/L in the future. Therefore, studying TTHM formation potential in warm water conditions is a crucial component of this pilot study.

4.6.1 Investigating TTHM Formation as a Function of Ozone Dose and Filter Media Type

The objective of this experiment was to estimate TTHM formation over a duration corresponding to the hydraulic detention time of the new water treatment plant profile as described in Section 3.1.3. Other independent variables studied included transferred ozone dose and filter media type. No replicate samples were taken in order to minimize source water quality variations.

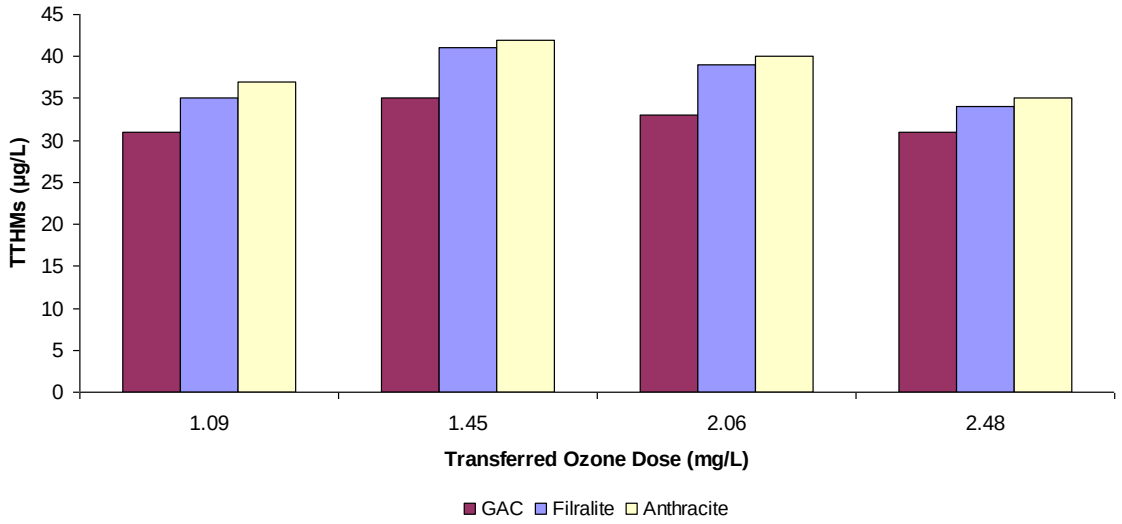


Figure 4.13: TTHM Formation Potential as a Function of Ozone Dose and Filter Media Type

Figure 4.13 (Appendix 15) shows that increasing the transferred ozone dose between 1.0 mg/L and 2.5 mg/L (equivalent to an ozone to DOC ratio between 0.33 to 0.95 mg O_3/mg DOC, respectively), had a relatively minor impact on TTHM formation potential for individual filters:

- The GAC filter performed best yielding TTHM levels between 31 and 35 µg/L,
- The Filtralite® filter was second with levels between 34 and 41 µg/L, and
- The anthracite filter was last with levels between 35 and 42 µg/L

These results are consistent with the work of Miltner *et al* (1992) who observed under steady-state conditions that the tandem ozonation and biofiltration didn't enhance TTHM precursor removals with increasing ozone dosages in the range from 0.3 to 1.7 mg O_3/mg DOC. It was suggested that above a threshold ozone dosage, a fraction of organic matter resistant to ozone attack remains.

The slight improvement in TTHM precursor removal between the Filtralite® filter and the anthracite filter might be attributed to a higher surface area harboring a denser biomass. The GAC filter was most effective due to a combination of adsorption capacity and elevated biomass activity. Nonetheless, even at low ozone dose, all three filters

generated TTHM levels that met current and anticipated regulatory limits. The experimental results show that there is no benefit in increasing the ozone dose to lower the amount of TTHMs formed. At a 1.0 mg/L ozone dose, the tandem intermediate ozonation/biofiltration is very effective at degrading TTHM precursors and controlling TTHM formation.

4.6.2 Investigating TTHM Formation as a Function of Ozone-AOP and Filter Media Type

The goal of this experiment was to assess the contribution of hydroxyl radicals in oxidizing TTHM precursors. A 1 mg/L ozone dose was maintained throughout these trials while varying the hydrogen peroxide to ozone ratio. The hydrogen peroxide to ozone ratio was set at 0.00, 0.25, and 0.50 in order to estimate the effect of increasing the hydroxyl radical flux. No replicate samples were taken in order to minimize source water quality variations.

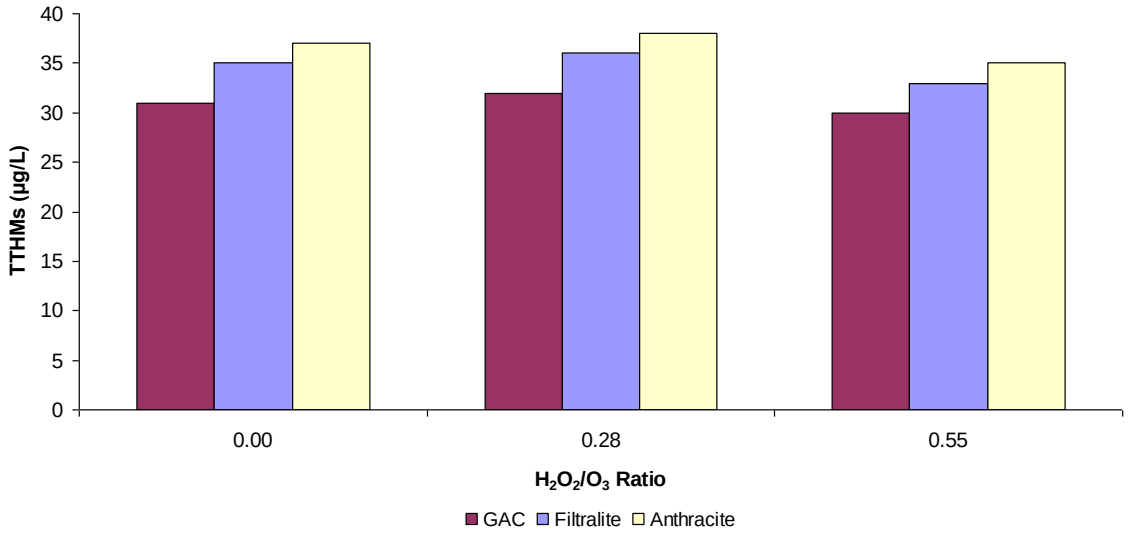


Figure 4.14: Impact of Hydrogen Peroxide to Ozone Ratio and Filter Media Type on TTHM Formation

As per Section 4.6.1, a similar trend is displayed in Figure 4.14 (Appendix 16). GAC outperforms Filtralite® and anthracite filters. Furthermore, TTHM formation yields are unaffected by increasing the hydroxyl radical flux. This result was expected based on the conclusions drawn from Sections 4.2.1.2 and 4.5.1.3. The most probable ozone mechanistic reaction pathways specific to the water matrix and treatment conditions herein implicated the rapid conversion of molecular ozone to hydroxyl radicals, and artificially increasing initiator levels (H_2O_2/O_3 ratio > 0.00) didn't enhance the $^{\cdot}OH/O_3$ capacity because the indirect ozone decomposition reaction pathway governs conventional ozonation reactions. Hence, hydroxyl radicals are responsible for oxidizing TTHM precursors whether hydrogen peroxide is added or not. Similar findings were reported by Ferguson *et al* (1990) when treating two surface waters with pre-oxidation followed by conventional treatment. At an ozone dose of 2 mg/L with a hydrogen peroxide to ozone ratio of 0.0 (no hydrogen peroxide added) and 0.4 yielded after 12 minute contact time, equally low levels of TTHM and HAA formation potentials after filtration. Alternatively, hydroxyl radicals generated during ozonation with and without the addition of hydrogen peroxide might have been scavenged by radical traps such as alkalinity.

4.6.3 Effect of Extended Hydraulic Detention Times and Filter Media Type on TTHM Formation

The primary objective of this phase was to study the impact of filter media on TTHM development subjected to hydraulic detention times typical of those in Brantford's distribution system. The transferred ozone dose was 1.82 mg/L and filtrate samples were chlorinated and chloraminated as per current full-scale disinfection protocol. Point-of-entry (POE) samples to the distribution system were stored in the dark for either a 24 or 48 hours period to simulate distribution system hydraulic detention times (Section 3.1.3). No replicate samples were taken in order to minimize source water quality variations.

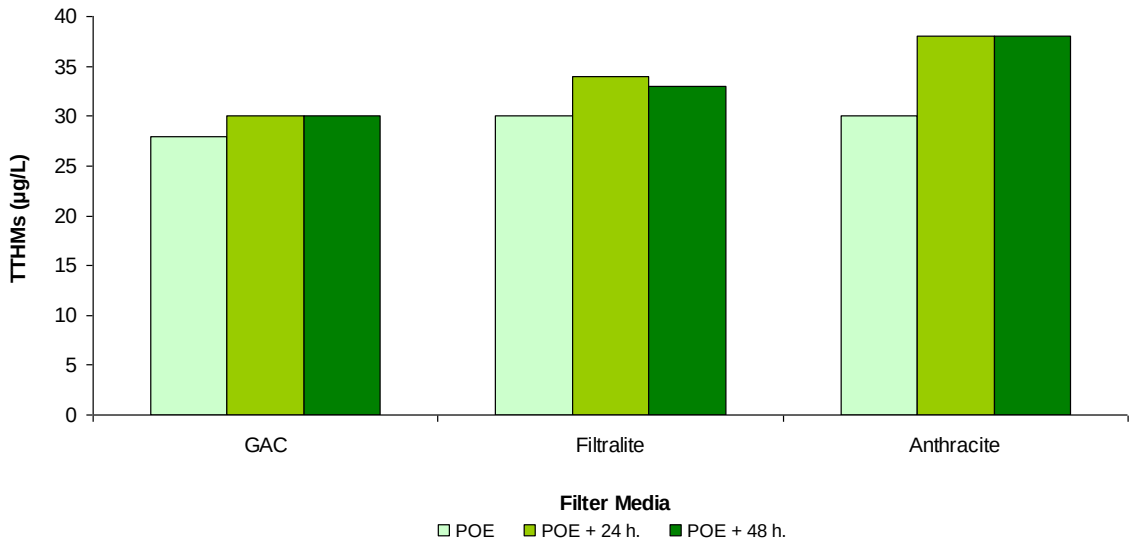


Figure 4.15: Impact of Filter Media Type and Extended Hydraulic Detention Times on TTHM Formation

The highest TTHM formation increase for all three filters occurred over the first 24 hour period. TTHM levels remained unchanged when doubling the hydraulic retention time to 48 hours (Figure 4.15 and Appendix 17). The GAC filter had the highest stabilizing effect on TTHM development with an increase of only 7% followed by Filtralite® and anthracite with 13% and 27% respectively. The experimental results illustrate the effectiveness of the tandem ozonation/biological filtration to control TTHM formation potential in the distribution system regardless of filter media, with levels well below current and anticipated provincial regulatory limits.

4.6.4 Impact of Ozone Dose on TTHM Formation in Anthracite Filter

The goal of this experiment was to confirm the significance of ozonation when combined with the anthracite biological filter on TTHM formation potential in warm water conditions. No replicate samples were taken in order to minimize source water quality variations.

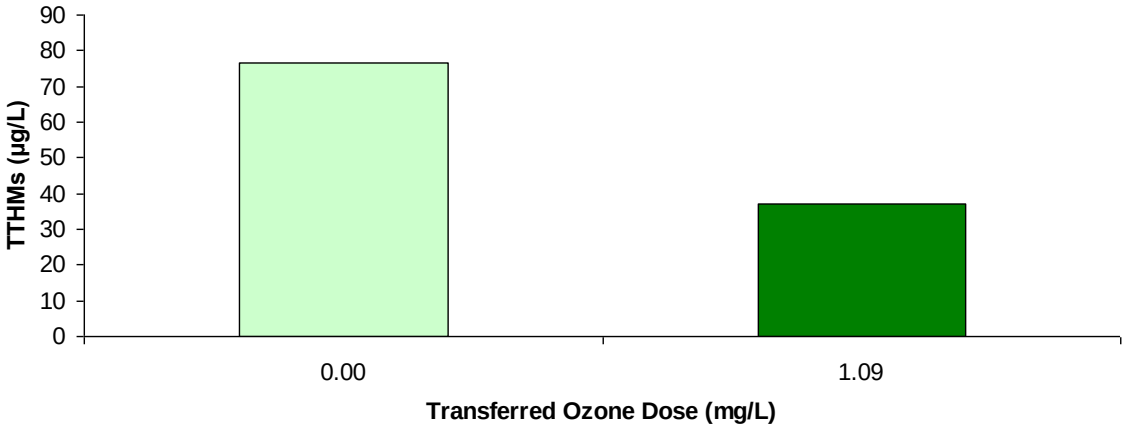


Figure 4.16: Biological Anthracite Filter alone or in Combination with Intermediate Ozonation on TTHM Formation

As shown in Figure 4.16, TTHM formation decreased from 77 to 37 µg/L when a 1 mg/L ozone dose preceded the anthracite biological filter. The data proves that ozone is critical in order to oxidize TTHM precursors prior to biological filtration. Other researchers (Sohn *et al*, 2007; Fonseca and Summers, 2003; Chang and Singer, 1991) have shown that molecular ozone and chlorine share similar modes of attack. As such, ozonation substantially decreases the number of halogenated DBP precursor reactive sites available for subsequent chlorination treatment. Furthermore, without intermediate ozonation, the anthracite biological filter would generate TTHM levels in the distribution system exceeding an anticipated TTHMs regulatory limit of 80 µg/L.

Practical Considerations

1. At a given ozone dose, the GAC filter outperformed the Filtralite® and anthracite filters for TTHM precursors' removal. However, even at a low ozone dose, all three filters generated TTHM levels meeting current and anticipated regulatory limits.
2. Although ozonation is a critical step prior to biofiltration, there are no additional benefits by increasing the ozone dose above 1 mg/L or adding hydrogen peroxide to lower the amount of TTHMs formed.

3. The intermediate ozonation/biofiltration tandem constitutes a very effective sequence of treatments for degrading TTHM precursors and to control TTHM formation potential. Even when subjected to long hydraulic detention times, intermediate ozonation followed by biofiltration effectively controls TTHM development in the distribution system to below anticipated regulatory limits.

4.6.5 TTHM Formation Comparison Between Full and Pilot Scale Plants

Pilot-scale TTHM results were correlated to those obtained once the treatment upgrades were integrated into the full-scale plant. The plant upgrades included intermediate ozonation with the option of switching to ozone-based AOP by feeding hydrogen peroxide ahead of the ozone contactors, deep-bed biological sand over anthracite filters followed by UV and chlorine disinfection. The biomass in the biological filters was allowed to mature over a one year period before collecting TTHM data for the purpose of this comparative study. The Point-of Entry (POE) sampling location in the new plant was simulated at the pilot-scale level by allowing the water samples after chlorination to react for a period of 291 minutes while drinking water samples collected in the distribution system were simulated by extending the contact time by an additional 24 hour contact time. The results of the comparative study are presented in Table 4.16.

Table 4.16: Full vs. Pilot Scale Plant TTHM Results

TTHMs (µg/L)						
Totals	Pilot-Scale Plant			Full-Scale Plant		
	T=291 min.	T=24 h.	Ozone Dose (mg/L)	POE	Distribution Locations	Ozone Dose (mg/L)
Minimum	17	21	0.73	15	19	0.92
Average	30	34	1.50	31	37	1.23
Maximum	48	48	2.48	42	53	1.70
# Observations	23	16	23	14	14	14

As shown in Table 4.16, TTHM levels between pilot and full scale plants are very similar. For the POE, the TTHM range was between 15 and 42 µg/L with an average of 31 µg/L (n=14), while the simulated POE (T=291 minutes) generated levels between 17 and 48 µg/L with an average of 30 µg/L (n = 23). In the distribution system, the TTHM range was between 19 and 53 µg/L with an average of 37 µg/L (n=14), while at the pilot scale, the levels were between 21 and 48 µg/L with an average of 34 µg/L (n = 16). The TTHM results simulated at the pilot scale level provided an accurate estimation of the levels measured at the full scale plant and in the distribution system.

5 Conclusions

The main objectives of this pilot-scale research study were to provide insight into the destruction of natural and synthetic organics that are characteristic of water in Southern Ontario's Grand River when ozonated, with or without hydrogen peroxide, and to determine the most appropriate granular media type for deep-bed biological filtration (anthracite, GAC, and Filtralite®, a ceramic media).

Ozone alone was unable to achieve the 1-log removal target for geosmin, a taste and odour compound or the herbicide MCPA, unless disinfection-level dosages were applied i.e. ≈ 1 mg O_3/1 mg DOC. No improvement was observed when hydrogen peroxide was added at H_2O_2:O_3 ratios of up to 0.5:1.0 either due to the high levels of natural promoters inherently present in Grand River water or the alkalinity acting as radical traps.

A major obstacle to the implementation of ozonation in bromide-laden source waters such as the Grand River is the formation of bromate, currently the only ozonation by-product regulated by the province of Ontario. A direct correlation was established between ozone dosage and bromate formation. It was demonstrated that applying ozone dosages at or above disinfection levels, bromate was likely to exceed the 10 μg/L maximum acceptable concentration. However, adding hydrogen peroxide prior to the ozone contactors successfully reduced the amount of bromate formed and in most cases levels fell below regulatory limits at H_2O_2/O_3 ratios above 0.3:1.0. A linear correlation was established between bromate inhibition and increasing H_2O_2/O_3 ratio (up to 0.5:1.0) at a constant ozone dose. The most likely mechanistic pathways by which hydrogen peroxide inhibited bromate formation included blocking the conversion of bromite to bromate by molecular ozone and promoting the oxidation of hypobromous acid/hypobromite ion back to bromide ions.

Amongst the three filtration media investigated, anthracite, Filtralite®, and GAC, only the latter was capable of meeting the 1-log removal target for geosmin and MCPA. The superiority of GAC over anthracite and Filtralite® was attributed to its adsorption affinity

for these trace organic contaminants (prior to fouling with background organics). While Filtralite® outperformed anthracite media for biological geosmin removal with average removals of 86% and 65%, respectively, they were both ineffective for MCPA removal due to its non-biodegradable nature under conventional water treatment conditions. Unlike GAC and Filtralite®, geosmin removal was enhanced by the tandem ozone/anthracite filter (with and without hydrogen peroxide). Applying a 1.44 mg/L (= 0.7 mg O_3/mg DOC) ozone dose prior to the anthracite filter resulted in a 1-log geosmin removal. In contrast, a 2.3 mg/L transferred ozone dose was required to meet the 1-log geosmin removal target if solely relying on intermediate ozonation for taste and odour control.

At transferred ozone dosages between 1.0 mg/L and 2.5 mg/L (= 0.33 to 0.95 mg O_3/mg DOC), ozone followed by biological filtration marginally affected TTHM formation potential. However, experiments involving the effluent from the anthracite biological filter demonstrated that without prior ozone treatment, TTHM production would more than double with the potential to exceed regulatory standards. As with previous experiments involving the destruction of trace organics by the combination of ozone and hydrogen peroxide, TTHM production was unaffected by increasing the hydroxyl radical flux. At a given ozone dose, the GAC filter slightly outperformed Filtralite® and anthracite filters for TTHM precursors' removal. Extending hydraulic detention times to simulate TTHM levels in the distribution system showed that the GAC filter yielded the lowest TTHM formation after 24 hours with an increase of only 7% followed by Filtralite® and anthracite with 13% and 27%, respectively. In all instances, TTHM levels stabilized when doubling the detention time to 48 hours in distribution system simulations. The experimental results show that even at the lowest of the ozone dosages tested, the ozonation/biological filtration tandem was very effective for the control of distribution system TTHM production regardless of filter media, with levels well below current and anticipated provincial regulatory limits.

The tandem intermediate ozonation followed by deep-bed biological filtration is well suited for treating Southern Ontario's Grand River water. Scale-up considerations include

pairing the proper filter media to the size of the ozone generator in order to secure regulatory compliance with respect to disinfection by-product formation on one hand and provide effective taste and odour control and meet MCPA removal target on the other. The best two treatment scenarios were: Option 1: Select the more expensive GAC media and engineer the ozone generator to produce a 1 mg/L dose at design flow rate. In order to maintain peak adsorption capacity, the GAC media would require regeneration every 1 to 2 years. Option 2: Select the least expensive anthracite media and engineer the ozone generator to deliver a 2 mg/L dose at design flow rate. Option 2 was ultimately selected for full-scale implementation.

6 Recommendations for Future Research

I. The consultant responsible for the design of the treatment upgrades at the Brantford Water Treatment Plant has requested that the following studies be undertaken prior to ordering granular media for the new filters:

- Investigate different combinations of sand and anthracite effective sizes (Es) with the goals of balancing headloss development with particle removal efficiency. Sand Es under consideration are: 0.35-0.45 mm, and 0.45-0.55 mm. Anthracite ES: 1.0-1.2 mm, 1.2-1.4 mm, 1.4 mm-1.6 mm, and 1.6-1.8 mm.
- Optimize filter media depth that will meet DOC, TTHM precursor and micro organic contaminant removal targets.
- Develop optimal backwash sequence that will minimize filter ripening time, maintain particle and biologically-mediated organics removal. Hence, the optimal backwash sequence will provide insight into backwash water quantity needs for the purpose of sizing the full-scale backwash tanks. The operating parameters that will be optimized during this phase of the study include a combination of air scouring duration, bed expansion/wash water flow rate and duration. Bed expansion values will be varied between 20% and 50% and wash water durations will range from 3 to 15 minutes.

II. Other research interests not directly related to the design of the plant upgrades warranting further investigation include:

- Quantify the relative contributions of molecular ozone and hydroxyl radicals during ozone and ozone-based AOP treatment in order to gain a better understanding of the oxidation mechanisms involved in the destruction of geosmin and MCPA. The Rct concept was first developed by Elovitz and Von Gunten (1999) and is defined as the ratio of the exposure of hydroxyl radicals versus the exposure of molecular ozone. Methodology for the determination of Rct values is described in detail in their work.
- Investigate the performance of the tandem ozone and biological filtration towards the removal of other natural and synthetic organic contaminants seasonally

detected in source water such as: MIB, atrazine, 2, 4-dichlorophenoxy acetic acid (2,4-D), carbaryl, chlordane, methoxychlor and metholachlor.

- Investigate alternative chemical disinfectants other than chlorine and chloramines such as chlorine dioxide and hydrogen peroxide.

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Appendices

Appendix 1: Comparison of Water Quality Parameters between Pilot and Full-Scale Filter Effluents – Results from Section 4.1

A. Temperature

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	16.0	16.0	0
24-Apr-07	16.0	16.0	0
25-Apr-07	16.0	16.0	0
26-Apr-07	15.0	14.0	7
27-Apr-07	13.0	13.0	0
2-May-07	14.0	13.0	7
3-May-07	14.0	13.5	4
4-May-07	15.0	14.0	7
7-May-07	15.0	15.0	0
9-May-07	19.0	19.0	0
10-May-07	19.0	19.0	0
Average			**2**

[1]CFE = Pilot Control Filter Effluent, [2]FSFE = Full-Scale Filter Effluent

B. Dissolved Oxygen

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	10.4	10.4	0
24-Apr-07	9.0	9.9	-10
25-Apr-07	9.3	10.3	-11
26-Apr-07	10.3	10.1	2
27-Apr-07	9.5	10.3	-8
2-May-07	9.3	9.9	-7
3-May-07	11.2	11.1	1
4-May-07	10.7	11.2	-5
7-May-07	10.4	10.6	-2
9-May-07	9.4	9.3	2
10-May-07	9.2	10.2	-11
Average			**-4**

C. pH

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	7.63	7.65	0
24-Apr-07	7.43	7.44	0
25-Apr-07	7.45	7.44	0
26-Apr-07	7.34	7.32	0
27-Apr-07	7.34	7.37	0
2-May-07	7.52	7.51	0
3-May-07	7.49	7.50	0
4-May-07	7.45	7.50	-1
7-May-07	7.56	7.54	0
9-May-07	7.39	7.35	1
10-May-07	7.40	7.45	-1
Average			**0**

D. Conductivity

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	720	736	-2
24-Apr-07	677	669	1
25-Apr-07	685	670	2
26-Apr-07	690	664	4
27-Apr-07	670	675	-1
2-May-07	667	687	-3
3-May-07	755	784	-4
4-May-07	698	674	3
7-May-07	796	771	3
9-May-07	825	836	-1
10-May-07	832	828	0
Average			**0**

E. Turbidity

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	0.14	0.11	21
24-Apr-07	0.13	0.12	8
25-Apr-07	0.13	0.12	8
26-Apr-07	0.15	0.14	7
27-Apr-07	0.15	0.15	0
2-May-07	na	na	na
3-May-07	0.15	0.14	7
4-May-07	0.10	0.11	-10
7-May-07	0.12	0.11	8
9-May-07	0.12	0.10	17
10-May-07	0.11	0.10	9
Average			**7**

F. UV_{254}

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	0.060	0.063	-5
24-Apr-07	0.062	0.063	-2
25-Apr-07	0.067	0.069	-3
26-Apr-07	0.065	0.064	2
27-Apr-07	0.066	0.068	-3
2-May-07	0.071	0.072	-1
3-May-07	0.074	0.075	-1
4-May-07	0.069	0.070	-1
7-May-07	0.061	0.060	2
9-May-07	0.061	0.063	-3
10-May-07	0.056	0.057	-2
Average			**-2**

G. Apparent Color

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	2	3	-50
24-Apr-07	0	0	0
25-Apr-07	2	1	50
26-Apr-07	2	2	0
27-Apr-07	2	2	0
2-May-07	1	2	-100
3-May-07	0	0	0
4-May-07	2	3	-50
7-May-07	1	1	0
9-May-07	3	2	33
10-May-07	2	1	50
Average			**-6**

H. True Color

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	1	1	0
24-Apr-07	0	0	0
25-Apr-07	0	0	0
26-Apr-07	0	0	0
27-Apr-07	1	1	0
2-May-07	1	1	0
3-May-07	0	0	0
4-May-07	1	1	0
7-May-07	0	0	0
9-May-07	1	1	0
10-May-07	0	0	0
Average			**0**

I. Aluminum (non-filtered)

Date	CFE[1]	FSFE[2]	%E
23-Apr-07	0.122	0.133	-9
24-Apr-07	0.100	0.103	-3
25-Apr-07	0.105	0.104	1
26-Apr-07	0.065	0.054	17
27-Apr-07	0.047	0.047	0
2-May-07	0.056	0.053	5
3-May-07	0.060	0.056	7
4-May-07	0.071	0.069	3
7-May-07	0.054	0.053	2
9-May-07	0.065	0.069	-6
10-May-07	0.067	0.070	-4
Average			**1**

Appendix 2: Summary Data, Percent Geosmin Removal as a Function of Transferred Ozone Dose – Results from Section 4.2.1.2

O_3 Dose (mg/L)	Mean O_3 Dose (mg/L)	O_3/DOC	%Geosmin Removal	Mean %Geosmin Removal	Stddev.	Temp. (Deg. C)
0.72	0.74	na	43	44	0.7	23.0
0.75		na	44			21.5
1.09	1.09	0.42	47	50	4.2	22.0
1.09		0.33	53			19.0
1.75	1.76	0.56	63	65	2.1	3.0
1.77		na	66			16.0
2.11	2.14	na	83	83	0.0	23.0
2.17		0.80	83			10.5
2.25	2.29	na	90	90	1.0	21.5
2.30		0.74	91			25.0
2.33		na	89			23.0

Appendix 3: Summary Data, Percent MCPA Removal as a Function of Transferred Ozone Dose – Results from Section 4.2.2.2

O_3 Dose (mg/L)	%MCPA Removal	Temp. (Deg. C)
0.75	14	14.0
1.50	74	13.5
2.25	86	14.0

Appendix 4: Summary Data, Percent Geosmin Removal as a Function of Ozone with Varying H_2O_2/O_3 Ratio – Results from Section 4.3.1

Peroxone Ratio	Transferred Ozone Dose (mg/L)			
	0.7	1.4	2.1	3.1
0.00	34	56	63	83
0.30	25	46	68	91
0.55	30	48	67	83

Appendix 5: Ozone Residuals after the First Ozone Contactor as a Function of Transferred Ozone Dose and H_2O_2/O_3 Ratio - Results from Section 4.3.1

Transferred Ozone Dose (mg/L)	H_2O_2/O_3 Ratio	Ozone Residual (mg/L)	Ozone Demand (mg/L)
0.72	0.00	0.00	0.72
0.73	0.55	0.00	0.73
0.75	0.00	0.00	0.75
0.78	0.37	0.00	0.78
2.11	0.00	0.33	1.78
2.16	0.61	0.00	2.16
2.25	0.43	0.01	2.24
2.30	0.00	0.54	1.76

Average Ozone Demand = 1.77 mg/L

Appendix 6: Ozone Residuals after the First Ozone Contactor as a Function of Transferred Ozone Dose and H_2O_2/O_3 Ratio - Results from Section 4.3.2

Transferred Ozone Dose (mg/L)	H_2O_2/O_3 Ratio	Ozone Residual (mg/L)	Ozone Demand (mg/L)
0.74	0.00	0.00	0.74
0.74	0.46	0.00	0.74
0.75	0.00	0.00	0.75
0.76	0.41	0.00	0.76
2.25	0.00	0.55	1.70
2.25	0.47	0.00	2.25
2.28	0.46	0.02	2.26
2.32	0.00	0.69	1.63

Average Ozone Demand = 1.67 mg/L

Appendix 7: Summary Data, Bromate Formation as a Function of Transferred Ozone Dose – Results from Section 4.4.1

Ozone Dose (mg/L)	Bromide (µg/L)	Bromate (µg/L)
2.48	49	0
6.5	40	22
10.26	39	42

Appendix 8: Summary Data, Bromate Formation as a Function of Transferred Ozone Dose and Background Bromide Concentrations – Results from Section 4.4.1

Transferred Ozone Dosage (mg/L)	Bromide (µg/L)	Bromate (µg/L)
0.74	24	0
1.07	134	0
1.09	146	0
1.18	38	0
1.21	94	0
1.24	46	0
1.32	78	0
1.36	68	3
1.42	52	0
1.43	78	0
1.44	100	3
1.45	48	0
1.46	67	0
1.50	72	0
1.51	79	0
1.51	112	0
1.60	142	0
1.60	51	0
1.75	174	7
1.77	83	0
1.77	47	0
1.77	112	0
1.86	101	3
2.11	58	4
2.13	67	0
2.17	115	5
2.30	88	0
2.33	43	0
2.35	36	0
2.40	44	0
2.47	54	0
2.48	192	25
2.48	49	0
2.75	70	26
2.80	104	0
2.88	113	17
3.07	144	16

Appendix 9: Summary Data, Bromate Formation as a Function of Transferred Ozone Dose, H_2O_2/O_3 Ratio and Background Bromide Concentrations – Results from Section 4.4.1

Transferred Ozone Dosage (mg/L)	H_2O_2/O_3 Ratio	Bromide (µg/L)	Bromate (µg/L)
0.73	0.55	40	3
0.82	0.37	50	0
1.00	0.28	155	0
1.10	0.55	138	0
1.24	0.28	83	0
1.24	0.14	87	0
1.24	0.30	85	0
1.38	0.63	61	0
1.40	0.55	66	0
1.42	0.28	65	0
1.44	0.47	76	0
1.45	0.72	69	0
1.46	0.36	75	0
1.73	0.25	99	0
1.78	0.32	198	4
1.79	0.46	111	0
1.80	0.66	153	0
1.80	0.31	50	0
1.82	0.56	47	0
1.92	0.27	107	0
2.02	0.25	130	3
2.13	0.26	65	0
2.13	0.58	67	0
2.16	0.61	54	0
2.21	0.58	151	6
2.34	0.43	48	0
2.41	0.28	50	3
2.44	0.30	106	6
2.50	0.64	53	0
2.61	0.49	186	0
2.79	0.52	120	5
2.80	0.15	96	0
2.82	0.34	118	8
2.86	0.34	61	0
2.88	0.48	72	10
2.95	0.30	75	18
3.07	0.55	143	0

Appendix 10: Summary Data, Impact of a 3 mg/L- Ozone Dose and Varying H_2O_2/O_3 Ratio on Bromate Formation – Results from Section 4.4.1

Replicate#1

Mean Transferred Ozone Dose = 2.86 mg/L		
H_2O_2/O_3 Ratio	Bromide (µg/L)	Bromate (µg/L)
0.00	70	26
0.30	72	18
0.48	75	10

Replicate#2

Mean Transferred Ozone Dose = 2.83 mg/L		
H_2O_2/O_3 Ratio	Bromide (µg/L)	Bromate (µg/L)
0.00	113	17
0.34	118	8
0.52	120	5

Replicate#3

Mean Transferred Ozone Dose = 3.11 mg/L		
H_2O_2/O_3 Ratio	Bromide (µg/L)	Bromate (µg/L)
0.00	144	16
0.25	140	6
0.55	143	0

Appendix 11: Statistical significance of Biological Filter Media towards Geosmin Removals – Results of Section 4.5.1.2

- Are there significant differences between the performances of granular filter media *i*.e. Filtralite®, GAC and anthracite, with respect to geosmin removal?

Using the *null hypothesis* test:

H_0: $\sigma^2 a = 0$ H_1: $\sigma^2 a > 0$

$F_{observed} = MS_B/MS_W = 810.8/3.1 = 262$ and $F_{critical} = F_{2,6,0.05} = 5.14$
Since $F_{observed}$ is significantly higher than $F_{critical}$, we can reject the null hypothesis and conclude that there are significant performance differences between granular filter media type (within a 95% confidence interval).

- Is the source of variability statistically more significant between or within biological filter results?

$\sigma^2 a = (MS_B - MS_W)/3 = 269.2$ and $\sigma^2 = 3.1$
Since $\sigma^2 + 3\sigma^2 a >> \sigma^2$ (Table 4.12), we conclude that there is significantly more variability between filter media type than within individual filter results.

- How different are the performance of the biological filters with respect to geosmin removal?

A *Multiple Comparisons Least Significant Difference* (LSD) analysis was performed in order to simultaneously distinguish between the differences in mean percent geosmin removals with respect to filter media composition.

Bonferroni t-Test: If k = number of means geosmin removals (k = 3) then
C = 3 (number of tests required).
By selecting a small target upper bound "b" = 0.05, the tests will be conducted at a significance level $\alpha = b/C \cong 0.02$ (with $\alpha/2 = 0.01$).

The standard error of the difference between two means is S.E. = $(2\ \sigma^2/n)^{0.5}$=1.43 with n = number of observations/filter (=3) and $t_{6,\ 0.01}$ = 3.14 (Referred to standard t-Student tables).

As a results, the LSD = 1.43 × 3.14 = 4.49 which implies that a difference between a specific pair of means will be significant at the 5% level if it exceeds the LSD value (= 4.49).
Using the percent geosmin removal means with respect to granular filter media type in Table 4.11:

- The mean difference between GAC and anthracite filters is equal to 32 (>LSD)
- The mean difference between Filtralite® and GAC filters is equal to 11 (>LSD)
- The mean difference between Filtralite® and anthracite filters is equal to 21 (>LSD)

Appendix 12: Summary Data, Tandem Intermediate Ozonation (1 mg/L) – AOP/Biologically Active Filtration – Results from Section 4.5.1.3

Filter Effluent	H_2O_2/O_3 Ratio		
	0.00	0.28	0.55
Filtralite®	87	89	87
GAC	97	97	97
Anthracite	77	77	74

Appendix 13: Summary Data, Cumulative Percent Geosmin Removal as a Function of Transferred Ozone Dose and Granular Filter media Type – Results from Section 4.5.1.3

Sampling Location	Transferred Ozone Dose (mg/L)				
	0.73	1.06	1.44	1.78	2.13
Ozone Contactors	22	53	73	74	83
Filtralite®	90	87	95	87	93
GAC	97	97	98	97	97
Anthracite	77	77	91	91	88

Appendix 14: Statistical significance of Biological Filter Media towards MCPA Removals – Results from Section 4.5.2.2

- Are there significant differences between the performances of coarse media *i*.e. Filtralite®, GAC and anthracite, with respect to MCPA removal?

Using the *null hypothesis* test:

H_0: $\sigma^2 a = 0$ H_1: $\sigma^2 a > 0$

$F_{observed} = MS_B/MS_W = 8078.9/160.05 = 50.3$ and $F_{critical} = F_{2,6,0.05} = 5.14$
Since $F_{observed}$ is significantly higher than $F_{critical}$, we can reject the null hypothesis and conclude that there are significant MCPA removals differences between granular filter media type (within a 95% confidence interval).

- Is the source of variability statistically more significant between or within biological filter results?

$\sigma^2 a = (MS_B - MS_W)/3 = 2639.6$ and $\sigma^2 = 160.1$ (Table 4.15)
Since $\sigma^2 a >> \sigma^2$, we conclude that there is significantly more variability between filter media type than within individual filter results.

- How different are the performance of the biological filters with respect to MCPA removal?

A *Multiple Comparisons Least Significant Difference* (LSD) analysis was performed in order to simultaneously distinguish between the differences in mean MCPA removals with respect to filter media composition:

Bonferroni t-Test: If k = number of means MCPA removals (=3) then the number of tests required is C = 3.

By selecting a small target upper bound "b" = 0.05, the tests will be conducted at a significant level $\alpha = b/C \cong 0.02$ (with $\alpha/2 = 0.01$).

The standard error of the difference between two means is S.E. = $(2\ \sigma^2/n)^{0.5}$= 10.3 with n = number of observations/filter (=3) and $t_{6,\ 0.01} = 3.14$ (Referred to standard T-test tables).

As a result the LSD = $10.3 \times 3.14 = 32.4$ which implies that a difference between a specific pair of means will be significant at the 5% level if it exceeds the LSD value (= 32.4).

Using the percent MCPA removal means with respect to granular filter media type in Table 4.14:

- the mean difference between GAC and anthracite filters = 97 (>LSD)
- the mean difference between GAC and Filtralite® filters = 82 (>LSD)
- the mean difference between Filtralite® and anthracite filters = 15 (<LSD)

Appendix 15: Summary Data, TTHM Formation Potential as a Function of Ozone Dose and Filter Media – Results from Section 4.6.1

Transferred Ozone Dose (mg/L)	O_3/DOC Ratio	TTHMs (µg/L)		
		GAC Filter	Filtralite® Filter	Anthracite Filter
1.09	0.33	31	35	37
1.45	na	35	41	42
2.06	Na	33	39	40
2.48	0.95	31	34	35

Appendix 16: Summary Data, Impact of Hydrogen Peroxide to Ozone Ratio and Filter Media on TTHM Formation– Results from Section 4.6.2

Transferred Ozone Dose (mg/L)	H_2O_2/O_3 Ratio	TTHMs (µg/L)		
		GAC Filter	Filtralite®Filter	Anthracite Filter
1.09	0.00	31	35	37
1.00	0.28	32	36	38
1.10	0.55	30	33	35

Appendix 17: Summary Data, Impact of Filter Media and Extended Hydraulic Detention Times on TTHM Formation – Results from Section 4.6.3

Filter	TTHMs (µg/L)			% TTHM Increase
	POE	POE + 24 Hrs.	POE + 48 Hrs.	
GAC	28	30	30	7
Filtralite®	30	34	33	13
Anthracite	30	38	38	27

Appendix 18: Summary Data, Biological Anthracite Filter Alone or in combination With Intermediate Ozonation on TTHM Formation – Results from Section 4.6.4

Transferred Ozone Dose (mg/L)	TTHMs (μg/L)
0.00	76.5
1.09	37.0