Estimating the Remaining GAC Removal Capacity for Geosmin and MIB

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
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Degree of Masters of Applied Science
Convocation 2015

ABSTRACT

Granular activated carbon (GAC) is commonly used in drinking water treatment for the control of seasonal taste and odour events. A challenge involving this application is the difficulty in accurately estimating the remaining service life of an existing GAC bed. This study evaluates a documented method that is intended to measure the removal capacity of a GAC contactor.

The method involves collecting core samples of GAC from active beds and creating “mini columns” (10 cm lab-scale GAC columns) that are challenged with geosmin and 2-methylisoborneol (MIB). For this study, the results of the mini column tests were compared to those from parallel tests using pilot-scale GAC columns that were filled with core samples from two water treatment plants. Refinements to the mini column method reported by Gillogly et al. (1999) were examined. Overall, it was determined that mini column testing is in good agreement with corresponding pilot-scale studies.
ACKNOWLEDGMENTS

Foremost, I would like to acknowledge my supervisor, Dr. Ron Hofmann, for his inspiration and advice on this research project, as well as on my study and life at University of Toronto. I’d also like to thank Dr. Bob Andrews and Dr. Susan Andrews for introducing me to the Drinking Water Research Group. It has been a great experience working with the excellent students and professors in this research group.

My appreciation is also extended to Dr. Sarah Jane Payne, for her assistance at the initial stage of this study; Dr. Anwar Sadmani, for his immense help in setting up the experiments; and Dr. Gwen C. Woods, for her generous support on the GC-MS technical issues and on my thesis writing. Thanks to Jim Wang and all my other colleagues in the DWRG for their help in the lab and for all the technical and administrative support.

Thanks to Peel Region and Barrie city for funding this project and providing us the opportunity to set up pilot-scale tests on site. Thanks to Dean Baker, Leo Liao, Jane Bonsteel and everyone else at Lorne Park Water Treatment Plant and Barrie South Surface Water Treatment Plant for their support on this research project.

My deepest gratitude is extended to my family. Thanks for their understanding, support and encouragement while I have been studying abroad.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
</tr>
<tr>
<td>AOP</td>
<td>advanced oxidation process</td>
</tr>
<tr>
<td>CD</td>
<td>constant diffusivity</td>
</tr>
<tr>
<td>Cl₂</td>
<td>chloride</td>
</tr>
<tr>
<td>ClO₂</td>
<td>chlorine dioxide</td>
</tr>
<tr>
<td>DFPSDM</td>
<td>dispersed flow pore surface diffusion model</td>
</tr>
<tr>
<td>EBCT</td>
<td>empty bed contact time</td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>ID</td>
<td>Inner/internal diameter</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>potassium permanganate</td>
</tr>
<tr>
<td>MIB</td>
<td>2-methylisoborneol</td>
</tr>
<tr>
<td>MLD</td>
<td>millions of liter per day</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>NOM</td>
<td>natural organic matter</td>
</tr>
<tr>
<td>OTC</td>
<td>odour threshold concentration</td>
</tr>
<tr>
<td>PAC</td>
<td>powdered activated carbon</td>
</tr>
<tr>
<td>PD</td>
<td>proportion diffusivity</td>
</tr>
<tr>
<td>RSSCT</td>
<td>rapid small scale column test</td>
</tr>
<tr>
<td>SPME</td>
<td>solid phase micro extraction</td>
</tr>
<tr>
<td>SSWTP</td>
<td>south surface water treatment plant</td>
</tr>
<tr>
<td>T&amp;O</td>
<td>taste and odour</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>UF</td>
<td>ultrafiltration</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>ultraviolet with hydrogen peroxide</td>
</tr>
<tr>
<td>WTP</td>
<td>water treatment plant</td>
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1 INTRODUCTION AND RESEARCH OBJECTIVES

Taste and odour (T&O) in drinking water is a common seasonal issue for many water treatment facilities around the world. Though the presence of taste and odour-causing compounds is often not associated with health effects, it can decrease consumer trust and generate issues for water utilities’ public relations. Two frequently identified compounds are geosmin (trans-1,10-dimethyl-trans-9 decalol: C_{12}H_{22}O) and MIB (2-methyl isoborneol: C_{11}H_{20}O). The lowest detected concentration of these two compounds by human senses ranges from about 4 to 20 ng/L (Young et al. 1996). Since it is difficult to eliminate these compounds by conventional treatment, more advanced technologies are frequently applied for T&O removal including powdered activated carbon (PAC), granular activated carbon (GAC), biofiltration, and advanced oxidation processes (AOPs). In Ontario, GAC filters are commonly used in drinking water treatment plants.

One difficulty facing water utilities with GAC contactors is the ability to accurately estimate the remaining removal capacity of an existing GAC bed for geosmin and MIB. Pilot-scale column tests are considered a useful proxy for simulating full-scale contactors, and have been conducted in several previous studies (Gillooly et al. 1999, Ndiongue et al. 2006, Ho and Newcombe 2010). The pilot-scale studies, however, are often costly and labor intensive. Laboratory-scale tests including iodine number tests, adsorption isotherm tests and rapid small scale column tests (RSSCT) are commonly employed to characterize GAC particles, yet they are not designed for nor appropriate for predicting the removal efficiency for taste and odour compounds with used GAC. Thus, there is a need to explore or verify other bench-scale approaches for the purpose of predicting GAC performance for T&O removal.

Gillooly et al. (1999) previously developed a mini column test that was intended to predict the remaining service life of a GAC contactor for taste and odour compounds. A later study by Ho et al. (2010), however, reported that there were inherent limitations with this mini column method, and it was argued that larger laboratory columns were able to more accurately simulate the pilot-scale filters. This current study was designed to validate Gillooly and Ho’s work, and to further explore the impacts of column diameter and sieving method on the experimental results. The effectiveness of mini column tests for predicting the removal of taste and odour compounds from aged GAC was assessed by comparing the results to pilot-scale experiments.
1.1 RESEARCH OBJECTIVES

The primary objective of this study was to develop a protocol for applying mini column tests on a routine basis to track granular activated carbon (GAC) performance. The detailed objectives were as follows:

1. To estimate the remaining taste and odour removal efficiencies with different types of GACs using pilot column tests
2. To optimize the design of mini column experiments, specifically column diameter and the sieving method used
3. To investigate the feasibility of using mini column tests to simulate pilot-scale filters
4. To develop a protocol for applying mini column tests on a routine basis to track GAC performance and to predict the remaining service life

1.2 DESCRIPTION OF CHAPTERS

Chapter 2 provides information about previous research related to this study, including a background of taste and odour issues and the application of GAC for water treatment, and available methods applicable for estimating the remaining removal capacity of partially spent GAC for taste and odour compounds.

Chapter 3 evaluates different types of GAC with varied ages from two water treatment plants using pilot-scale column tests for taste and odour compound removal, and further examines the mini column tests as a potential option to simulate pilot filters for taste and odour compound removal.

Chapter 4 summarizes significant findings from this study and provides recommendations for future research.
1.3 References


2 LITERATURE REVIEW

2.1 FUNDAMENTALS OF GEOSMIN AND MIB

2.1.1 Taste and odour issues in drinking water
Taste and odour compounds that occur in drinking water can distort consumers’ perceptions about the safety of their tap water. Two earthy-, muddy-smelling trace organic compounds, geosmin and 2-methylisoborneol (MIB), are among the most prevalent taste and odour–causing compounds in drinking water. Taste and odour episodes are widely spread throughout the Great Lakes region, as was demonstrated by a survey of ~59 Great Lakes drinking water treatment facilities that found that ~20% of utilities reported annual T&O outbreaks and 27% experienced erratic episodes (Watson et al. 2008). Studies have shown that the majority of T&O outbreaks occur during summertime or fall when biological activity is more prevalent (Rao et al. 2003). Geosmin and MIB are synthesized by a select number of cyanobacteria, actinomycetes, myxobacteria, fungi and other soil microbiota. Most of the MIB and geosmin are produced during algal growth and retained within algal cells which subsequently release the odorants at varying growth phases such as senescence, death or with changes in environmental factors (Srinivasan and Sorial 2011, Watson et al. 2008).

Geosmin and MIB have relatively low odour threshold concentrations (OTCs), ranging from ~4-20 ng/L (Young et al. 1996), and can cause customer complaints. Currently, no uniform standard or guideline defines the acceptable taste and odour levels for water treatment facilities, presumably since studies have shown that the presence of geosmin and MIB is not associated with known health effects. In Canada, only subjective guidelines have been established for taste and odour by various provinces. Ontario, for example, has set an aesthetic guideline which indicates that taste and odour compounds should not be high enough to make drinking water offensive. Such guidelines are vague, non-quantitative, and tend to rely on customer complaints as an indication for action (Watson et al. 2008). Accordingly, utilities would greatly benefit by better understanding the removal capacity of their GAC contactors and subsequently avoiding significant taste and odour events (Srinivasan and Sorial 2011).
2.1.2 Treatment technologies

Geosmin and MIB are semi-volatile compounds, are highly stable and are resistant to conventional water treatment processes, such as coagulation, sedimentation and filtration (Watson et al. 2008). Additionally, research has demonstrated that oxidants including Cl₂, ClO₂ and KMnO₄ are not effective for the removal of these compounds. Currently, the main available technologies for geosmin and MIB removal include GAC/PAC adsorption, biological treatment and advanced oxidation processes (AOPs) (Srinivasan and Sorial 2011). Advanced oxidation processes that have been examined include ozone, UV and H₂O₂. One study reported that 90% geosmin and 60% MIB were removed at the UV dose of 1200 mJ/cm² with 6 mg/L H₂O₂ (Jo et al. 2011). Both compounds were found to decrease primarily due to reaction with hydroxyl radicals, with direct photolysis only as a minor contributor. Ozone combined with UV exposure has also demonstrated a high removal (~90%) for MIB (Collivignarelli and Sorlini 2004). Though AOPs have proven effective for taste and odour compound removal, there are significantly high energy and capital costs associated with these technologies, especially for large-scale applications (Srinivasan and Sorial 2011). Geosmin/MIB removal has also been observed in a biologically active sand filter, and four strains of bacteria were thought to be responsible for this biodegradation (Ho et al. 2007). Research by Elhadi et al. (2006) reported that higher removals of geosmin and MIB were observed when GAC was used as the support media in the biofilter. Meanwhile, various studies have been conducted regarding the application of activated carbon for MIB/geosmin adsorption. More detailed information will be summarized in the subsequent sections.

2.2 APPLICATION OF GAC CONTACTOR FOR TASTE AND ODOUR CONTROL

2.2.1 Adsorption of geosmin and MIB by activated carbon

The physical and chemical properties of MIB and geosmin are important for understanding their potential removal by activated carbon. The basic properties for MIB and geosmin are summarized in Table 2.1. Previous studies have often found that geosmin is absorbed more readily than MIB (Huang et al. 1996), and further research has illustrated that competitive adsorption does not exist between MIB and geosmin (as demonstrated by dual-solute isotherms) (Graham et al. 2000). Similar to other trace organic compounds, the removal of MIB and
geosmin in natural water is independent of their initial concentrations in the range of 50-200 ng/L (Graham et al. 2000, Summers et al. 2013).

Ridal et al. (2001) monitored the performance of a GAC-capped filter for taste and odour control in a full-scale water treatment plant over a 2 year period (1998-1999). It was reported that an average of 60% of MIB and 80% of geosmin was removed from the source water after 2 and 12 months of filter operation, and that reduced efficiencies were observed for both MIB (15%) and geosmin (54%) after 24 months of operation. The authors suggested that longer contact time and higher chlorine residuals are important factors necessary to maximize the removal efficiency for a GAC-capped filter. In contrast, other studies have indicated that low chlorine residual is preferable to improve the efficiency of GAC/PAC removal of MIB (Gilogly et al. 1999, Nerenberg et al. 2000). The varying conclusions from these studies demonstrate that other factors are likely to have an impact on GAC performance.

Table 2.1: Chemical/physical characteristics of MIB and geosmin (Pirbazari et al. 1992)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MIB</th>
<th>Geosmin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C\textsubscript{11}H\textsubscript{20}O</td>
<td>C\textsubscript{12}H\textsubscript{22}O</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>168</td>
<td>182</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>197</td>
<td>165</td>
</tr>
<tr>
<td>Aqueous solubility (mg/L)</td>
<td>195</td>
<td>150</td>
</tr>
<tr>
<td>K\textsubscript{ow}</td>
<td>3.13</td>
<td>3.70</td>
</tr>
<tr>
<td>Henry’s Law constant (atm m\textsuperscript{3}/mol)</td>
<td>5.76 ×10\textsuperscript{-5}</td>
<td>6.66×10\textsuperscript{-5}</td>
</tr>
</tbody>
</table>
2.2.2 Effect of NOM in source water

A major challenge associated with the removal of taste and odour compounds is the presence of natural organic matter (NOM), which is a complex mixture of organic compounds and invariably present in all water sources at much higher concentrations than MIB and geosmin (Srinivasan and Sorial 2011). Various studies have examined the effect of NOM in source waters, and have provided evidence that NOM significantly reduces the adsorption capacity for geosmin/MIB (Newcombe et al. 2002, Cook et al. 2001, Summers et al. 2013). Newcombe et al. (2002) investigated the removal of MIB on six different types of activated carbon in the presence of six well-characterized NOM solutions. The authors concluded that low-molecular-weight NOM effectively competes with MIB for adsorption sites, while larger NOM constituents reduce the equilibrium adsorption capacity by pore blockage and/or restriction. The pore size-to-volume ratio of GAC particles was thought to be the main characteristic impacting the simultaneous adsorption of NOM and MIB.

2.2.3 Reaction between H$_2$O$_2$ and GAC

Water treatment facilities have been combining various technologies to enhance taste and odour control in drinking water (Srinivasan and Sorial 2011). Different water treatment processes combined with GAC can significantly affect the filter performance. The two water treatment utilities studied in this research have treatment trains that include GAC to quench H$_2$O$_2$, and GAC with very high biological activity, respectively. These two factors presumably have an impact on the GAC performance, and as such findings from previous studies were investigated.

There are few papers evaluating the effect of H$_2$O$_2$ on GAC for T&O removal, yet the reaction between H$_2$O$_2$ and GAC was examined in several studies (Li 2013). Li (2013) summarized that reactions between H$_2$O$_2$ on GAC occur either by generating •OH radicals and •OOH radicals as intermediates, or by transferring functional groups between GAC and H$_2$O$_2$ on the GAC surface in a basic medium. •OH radicals can destroy taste and odour compounds, thus changing the GAC performance for MIB/geosmin removal. The alteration of functional groups on GAC surface also potentially affects the adsorption of taste and odour compounds. This current study discusses the observed impact of H$_2$O$_2$ on GAC performance at the Lorne Park Water Treatment Plant.
2.2.4 GAC contactors with biological activity

Biologically active GAC filters are becoming more common in water treatment utilities in Ontario. Yagi et al. (1988) found that approximately 60% of MIB and 70% of geosmin were removed biologically with a contact time of 2.4 min and a loading rate of 8.3 cm/min from a biologically active carbon filter. A comparable range of 26-64% MIB removal was reported by Nerenberg et al. (2000) from a study investigating a 6-year biologically active GAC filter with preozonation. In contrast, only 8% additional geosmin removal and 40% MIB removal was found associated with biological activities from bench-scale studies with sterilized and non-sterilized GAC (Zamyadi et al. 2015). In the current study, GAC contactor performance in the Barrie South Surface Water Treatment Plant was evaluated with consideration of both adsorption and biodegradation.

2.3 AVAILABLE METHODS FOR ESTIMATING REMAINING GAC REMOVAL CAPACITY

2.3.1 Pilot-scale evaluation

Pilot-scale evaluations have commonly been utilized in previous studies for the removal of taste and odour compounds. A major assumption associated with these studies is that researchers assume that the pilot filters have an identical performance to that of a full-scale filter. Various types of pilot-scale experiments have been conducted to simulate the full-scale filters. One type of pilot-scale test has included running pilot filters for a length of time beginning with the same fresh GAC that is installed in the full-scale filter. While running pilot columns in parallel to full-scale treatment, target compounds are spiked into the pilot-scale influent waters and removal efficiencies can be estimated for the full-scale filters. One such pilot-scale GAC study was undertaken with MIB spikes over a 9-month period (Ho and Newcombe 2010). The removal of MIB was observed to remain over 90% throughout the trials over 9-months. Shcarf et al. (2010) likewise constructed pilot-scale filters and operated them for over 700 days with geosmin spiked into influent waters. Approximately 70% geosmin removal was observed by the end of the study. For an existing GAC bed, another experimental design for a pilot-filter includes collecting core samples from the full-scale bed. Such pilot tests were conducted by Ndiongue et al. (2006) to investigate the removal of geosmin and MIB by used GAC extracted from full-scale GAC-capped filters, and 24%–47% geosmin removal was observed with 3-year old GAC. For the
current study, similar pilot-scale breakthrough tests were conducted using the GAC core samples collected from the full-scale filters.

2.3.2 Bench-scale evaluation

2.3.2.1 Isotherm test
In water treatment applications, the amount of adsorbate adsorbed on to a carbon is usually a function of its concentration in the aqueous-phase, and this relationship is known as an “isotherm”. The bottle point technique (Randtke and Snoeyink 1983) was used by previous studies to determine the adsorption capacity of activated carbon for certain contaminant removal. Prewighed oven dried GAC samples were added into Schott bottles with water samples spiked with MIB/geosmin at a target concentration. Headspace-free bottles were agitated on a shaker until equilibrium was reached (Ho and Newcombe 2010). Virgin GAC was usually crushed into smaller particle sizes to achieve equilibrium within a short period of time. For partially spent GAC, however, crushing could result in opening of previously blocked pores, overestimating the adsorption capacity (Ho and Newcombe 2010). As reported by Gillogly et al. (1999) and Ho and Newcombe (2010), preloaded GAC needs to take approximately 120 days to reach equilibrium. Freundlich and linear isotherm models were the common adsorption models applied for evaluating geosmin and MIB removal. Adsorption isotherm parameters were used to predict the bed life for a GAC filter (Scharf et al. 2010), but the authors concluded that this approach was not able to accurately predict expected performance with confidence.

2.3.2.2 Rapid small scale column test
The rapid small scale column test (RSSCT) is a commonly used bench-scale method for the assessment of GAC performance (Summers et al., 2013). The GAC particles are crushed into small sizes with a scaling factor to accelerate the GAC aging process. A dispersed flow pore surface diffusion model (DFPSDM) is used to derive the design equations (Knappe et al. 1997). Two design approaches with proportion diffusivity (PD) or constant diffusivity (CD) need to be selected prior to the test. Dissolved organic matter has been shown to be appropriately described by the PD design, in which the internal diffusion coefficient decreases linearly with GAC particle size (Summers et al. 2013). In contrary, CD design was shown to better describe the removal of trace organic compounds including geosmin, MIB and atrazine (Corwin et al. 2010, Knappe et al. 1997). A study by Knappe et al. (1997) demonstrated that RSSCTs successfully
simulated atrazine removal over large-scale operating time of 3.5-7 months with virgin GAC, while the atrazine removal by preloaded GAC was significantly overestimated. The authors suggested that RSSCTs could be most useful for predicting the initial performance of adsorbers containing fresh GAC. However, this method is not able to evaluate the performance of the partially spent GAC (Gillogly et al., 1999).

2.3.2.3 Mini column test
Since neither isotherm test nor RSSCT was able to evaluate the GAC performance from an existing GAC bed, another bench-scale approach called a mini column test has been developed by Knappe et al. (1999) and Gillogly et al. (1999), aiming at determining the kinetic parameters to describe the rate of adsorption of atrazine and MIB, respectively. This method involved collecting core samples of GAC from active full-scale contactors and creating “mini columns” (1 cm lab-scale GAC columns) that are challenged with the target contaminant. Gillogly et al. (1999) further reported that the mini column test was able to yield identical MIB breakthrough as that from a pilot-scale filter, and presumably as a full-scale contactor. However, a later study by Ho and Newcombe (2010) reported that the mini column test could not predict MIB breakthrough in the pilot-scale trials. In particular, the small volume of GAC used and high filtration rates employed were identified as shortcomings, since 90% breakthrough of MIB after 6-month operation was predicted by the mini column test, while only 30% breakthrough was observed in pilot-study. A modified mini column test was conducted by Ho and Newcombe (2010) using larger laboratory columns with higher GAC bed depth (15 cm GAC in columns with an internal diameter of 25 mm), and it was reported that larger GAC columns were able to more accurately simulate the pilot-scale filters.
2.4 References


3 COMPARISON OF BENCH-SCALE AND PILOT-SCALE TESTS FOR ESTIMATING TASTE AND ODOUR REMOVAL

ABSTRACT

Granular activated carbon (GAC) is commonly used for the control of seasonal taste and odour events. A challenge involving this application is the difficulty in accurately estimating the remaining service life of an existing GAC bed. This study evaluated a method reported by previous studies that was intended to measure the removal capacity of taste and odour compounds in existing GAC contactors by collecting a core sample of the existing bed and subjecting it to a mini column test. In this research, pilot- and laboratory-scale column experiments were conducted to examine the extent of 2-methylisoborneol (MIB) and geosmin removal from two water treatment facilities. Results indicated that mini column tests were able to simulate the pilot-scale filters to within an accuracy of typically ±10% for both geosmin and MIB removal. The impact of specific mini column parameters was further studied: the effect of mini column diameter (11 mm vs. 25 mm) on the removal of geosmin and MIB was minimal, while the particle size and sieving method (wet vs. dry) had an impact on the GAC performance, with the wet sieving method being most accurate. The dry sieving methods required baking the GAC which significantly increased the removal capacity, presumably due to the baking process removing and/or altering NOM constituents that were adsorbed onto GAC. The study was performed with aged GAC from different facilities and provided evidence that GAC performance can be greatly impacted by factors including the type of GAC, the water treatment train at a given facility, and source water characteristics. Overall, the mini column test appears to be an effective method at estimating the remaining removal capacity of taste and odour compounds.
3.1 INTRODUCTION

Taste and odour (T&O) in drinking water is often due to the presence of trace organic compounds produced by cyanobacteria and actinomycetes (Ho and Newbombe 2010). Among these trace organics, geosmin (1,10-trans-dimethyl-trans-9-decalol: C_{12}H_{22}O) and MIB (2-methylisoborneol: C_{11}H_{20}O) are the most frequently identified (Srinivasan and Sorial 2011). The reported concentration of geosmin and MIB that is detectable by humans ranges from as low as 4 to 20 ng/L (Srinivasan and Sorial 2011, Scharf et al. 2010).

Granular activated carbon (GAC) contactors are commonly used in Ontario to control geosmin and MIB. A challenge with this application is the inability to accurately estimate the remaining removal capacity of an existing GAC bed. Pilot-scale GAC columns have been used to simulate the full-scale GAC contactors in many studies, and it is commonly accepted, based on experience, that a pilot GAC column can successfully represent the full-scale contactor (Gillogly et al. 1999, Ho and Newcombe 2010, Scharf et al. 2010). Pilot-scale studies, however, are often costly and labor intensive, and thus the primary objective of this research was to explore a laboratory-scale approach.

Isotherm tests, involving equilibrium theory, are often conducted to measure GAC adsorption capacity as a screening tool when selecting a preferred GAC product since carbon with higher adsorption capacity might be expected to have a longer service life. Adsorption kinetics, however, have a significant impact on bed life and can result in earlier breakthrough than that expected from equilibrium theory (Gillogly et al. 1999). Another method to evaluate GAC performance is the rapid small-scale column test (RSSCT). The RSSCT requires grinding the GAC to a smaller particle size so it is only applicable to virgin GAC and cannot be used to measure the remaining adsorptive capacity of GAC from an existing contactor since grinding partially saturated GAC may lead to the formation of new adsorption sites that were previously blocked by adsorbed compounds.

Gillogly et al. (1999) previously developed a mini column method that was intended to predict the remaining service life of a GAC contactor for taste and odour compounds. Without grinding the GAC, Gillogly et al. (1999) reported that the mini column test could determine whether the GAC was currently effective and how effluent concentrations of taste and odour compounds
would change with varying influent concentrations. Core samples were collected from active GAC beds and a “representative” fraction of GAC was packed into mini columns (1 cm GAC in columns with inner diameter (ID) =10 mm) that were challenged using MIB. The “representative” GAC fraction was the sieve size that accounted for the largest fraction of the external surface area in the filters, which was assumed to be the largest size fraction by weight. The results of the mini column tests were compared to parallel pilot-scale tests and a good agreement between removal capacities was observed. A homogeneous surface diffusion model (HSDM) was then developed using the parameters derived from mini column tests to predict the remaining bed life of a GAC contactor. Gillogly concluded that the bench-scale mini column test can be employed to predict findings from pilot-scale studies. A later study by Ho and Newcombe (2010), however, reported that there were inherent limitations with this mini column method. In particular, the small volume of GAC used and high filtration rates employed were identified as shortcomings, since 90% breakthrough of MIB after 6-month operation was predicted by the mini column test, while only 30% breakthrough was observed in pilot-study. It was argued that the modified test with larger laboratory columns and higher GAC bed depth (15 cm GAC in columns with ID = 25mm) was able to more accurately simulate the pilot-scale filters. Furthermore, the work by Gillogly et al. (1999) only explored the removal of one compound (MIB), and only one type of GAC (F300) with one source of water (filtered water from southern Lake Michigan).

To validate the work by Gillogly et al. (1999) and Ho and Newcombe (2010), and to further explore the effects of column diameter and sieving method, mini column tests were explored in the current study. The mini column tests were conducted using a larger column diameter and a higher GAC bed depth than used in the previous studies. The effectiveness of mini column tests for predicting the removal of taste and odour compounds from aged GAC was assessed by comparing the results to pilot-scale experiments.

3.2 OBJECTIVE
The primary objective of this study was to develop a protocol for applying mini column tests on a routine basis to track granular activated carbon (GAC) performance for the removal of geosmin and MIB. The detailed objectives were as follows:
1. To estimate the remaining taste and odour removal efficiencies with different types of GACs using pilot column tests,
2. To optimize the design of mini column experiments, specifically column diameter and the sieving method used,
3. To investigate the feasibility of using mini column tests to simulate pilot-scale filters,
4. To develop a protocol for applying mini column tests on a routine basis to track GAC performance and to predict the remaining service life.

### 3.3 Materials and Methods

#### 3.3.1 Water Source and site description

The pilot-scale studies of GAC contactors were conducted at the Lorne Park Water Treatment Plant and the Barrie South Surface Water Treatment Plant. The Lorne Park WTP features two trains of water treatment processes: conventional processes and advanced processes involving ultrafiltration (UF) membranes, H₂O₂ + UV disinfection and GAC contactors. The GAC contactors were designed to quench the excess H₂O₂ in summertime and to work as a second barrier for taste and odour, should an event occur. The Barrie SSWTP involves coagulation, UF membranes, GAC filters and chlorine disinfection. Information about the GAC contactors at Lorne Park and Barrie is listed in Table 3.1. The TOC of the treated water prior to GAC contactors at both plants was approximately 2 mg/L and 3.6 mg/L, while the TOC of post-GAC water was 1.7 mg/L and 3.4 mg/L, respectively, demonstrating a limited adsorption GAC removal capacity for natural NOM. Prechlorination with free chlorine of 0.3 mg/L is used at Lorne Park from early May to October for zebra mussel control, with the chlorine residual in the pre-GAC water being 0.15 mg/L for free chlorine and 0.25 mg/L for total chlorine. Barrie likewise prechlorinates at their plant intake for purposes of zebra mussel control, but chlorine is not at detectable levels at the point of introduction into the GAC contactors. Barrie does, however, chlorinate the water used to backwash BAC filter beds, and subsequently their contactors have some exposure to chlorine.
Table 3.1: GAC contactor parameters at LPWTP and BSSWTP

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lorne Park</th>
<th>Barrie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plan area (m²)</td>
<td>107</td>
<td>45</td>
</tr>
<tr>
<td>Average flow rate (MLD)</td>
<td>47.5</td>
<td>18.6</td>
</tr>
<tr>
<td>Media volume (m³)</td>
<td>136.01</td>
<td>127</td>
</tr>
<tr>
<td>Media depth (m)</td>
<td>1.27</td>
<td>2.81</td>
</tr>
<tr>
<td>Average EBCT (min)</td>
<td>4.12</td>
<td>6.05</td>
</tr>
<tr>
<td>Approach velocity (m/hr)</td>
<td>18.36</td>
<td>15</td>
</tr>
<tr>
<td>GAC type</td>
<td>Centaur</td>
<td>F300</td>
</tr>
</tbody>
</table>

3.3.2 Chemicals and reagents

All chemicals including MIB, geosmin, geosmin-D3, NaCl and methanol were purchased from Sigma Aldrich. Geosmin-D3 was used as an internal standard for geosmin and MIB analysis. Reagent grade sodium chloride was used for the extraction of the T&O compounds. Ultrapure water from a Milli-Q system was used for stock solution preparation. Methanol was used as the solvent for calibration stock solutions and check standards.

Stock solutions of MIB and geosmin were prepared in Milli-Q water at a concentration of 1 mg/L each. The feed water for the pilot-scale and mini column tests was collected from the full-scale treatment plants and spiked with the stock solutions at a target concentration of 100 ng/L of each compound.

Sodium azide solution was dosed into the water samples from the effluent of the column tests for sample preservation (166 µL sodium azide at a concentration of 25 µg/L into 23 ml samples). The samples were concentrated using a solid phase micro extraction (SPME) fiber and analyzed on an Agilent 3800 gas chromatography system with a 4200 mass spectrometer. More details about this method can be found in Appendix B. The method detection limit for geosmin and MIB were 7 ng/L and 9 ng/L, respectively.

3.3.3 Pilot-scale experiments

The pilot study was aimed at evaluating the performance of the GAC contactors at the Lorne Park Water Treatment Plant and Barrie South Surface Water Treatment Plant. Three types of GAC samples were tested: 3-year and 4-year old Centaur GAC from the Lorne Park WTP, and 4-year F300 GAC from the Barrie SSWTP. Since it is logistically very difficult to do a full-scale test to assess the remaining removal capacity of a contactor for taste and odour compounds (i.e. it
is prohibitively expensive to spike geosmin/MIB at full-scale), it is assumed that the performance of a pilot filter is identical to that of the full-scale contactor, as has been demonstrated in previous studies (Gillogly et al. 1999, Ndiongue et al. 2006, Ho and Newcombe 2010).

To avoid reactions between GAC particles and the internal wall of the column, glass columns were used. The flow through the column filter was proven to be plug flow in a previous study using the same columns conducted by Li (2013). The GAC at Lorne Park was selected for full-scale treatment purposes to quench H₂O₂ after the UV+ H₂O₂ process and also works as a second barrier for adsorption of taste and odour compounds. The GAC samples were collected from Lorne Park’s Contactor #2 and # 8 using a PVC sampler and transferred to the glass columns with the stratification maintained the same as in the full-scale GAC beds. The core sampler was submerged into the GAC bed when the bed was fluidized by backwash. To maintain the stratification and simplify the procedure, the GAC core sample was divided into three parts with the bottom third carefully packed into the bottom of the experimental pilot column and similarly with the middle and top third of the GAC portions transferred into the glass column in sequence. Contactor #2 and # 8 had been in service for approximately 3 years and 4 years, respectively.

A preliminary pilot-scale trial was conducted to determine variability in column performance with continuous vs. intermittent flow over a total flow time of over 25 hours, specifically to determine the need to run flow through the columns overnight. Influent and effluent samples from the pilot filters were collected in 23 mL vials, preserved with sodium azide and transported to the laboratory for further analysis.

| Table 3.2: Conditions of the pilot scale column tests at LPWTP and BSSWTP |
|-----------------|--------|--------|
| Plant location  | Lorne Park | Barrie |
| GAC bed height (m) | 1.28 | 2.56 |
| EBCT (min) | 4.1 | 6.1 |
| Flowrate (ml/min) | 157.4 | 235.4 |
3.3.4 Bench-scale experiments

Mini column tests, an approach documented by Gillogly et al. (1999) and Ho et al. (2010), were conducted to evaluate the remaining adsorption capacity of aged GAC for MIB and geosmin. The results from the bench-scale column test were compared to those from the pilot column test, to examine the effectiveness of the bench-scale method. Prior to this objective, experiments were conducted to determine the effects of GAC particle size distribution and mini column diameter. The GAC samples were collected from GAC contactors at the Lorne Park Water Treatment Plant. A sieve test with dried GAC and wet GAC was conducted separately to determine the particle size distribution. The sieved particles with the highest fraction of the total sample weight were defined as the size representative particles. Results from the sieve test can be found in Appendix A.1.

Size representative GAC samples after both dry sieving and wet sieving were packed into glass columns with internal diameters of 11 mm and 25 mm, and a length of 30 cm (Figure 3.1). The GAC bed depth was 10 cm, and 1 mm glass beads were used to support the GAC in the columns and also to ensure uniform flow. The GAC samples were rinsed with Milli-Q water before being packed into the columns. Each end of the glass column was sealed with a threaded PTFE adaptor and a filter.

Each mini column was filled with the water collected from the plants immediately upstream of their full-scale GAC contactors, and spiked with geosmin and MIB at a concentration of 100 ng/L. Water then was directed through the columns at the same empty bed contact time (EBCT) of the full scale GAC contactors (4.1 minutes). The columns were run in duplicate in a continuous up-flow mode (to prevent possible bubble-entrainment) for over 24 hours. During the experiment, the influent and effluent samples were collected at regular intervals and analyzed for geosmin and MIB concentration.
As different column diameters and sieve methods may result in different effluent MIB and geosmin breakthrough, the optimal diameter and sieving method was selected by comparing the mini column results to that from the pilot column test (conducted two weeks prior to the mini column trial). The mini column test with optimal diameter and sieving method was conducted later to evaluate the performance of GAC with different ages.

Previous studies reported that the adsorption capacity can be influenced by the procedures used to wash, dry and store GAC (Randtke and Snoeyink, 1983). Accordingly, the effect of storage of GAC was also investigated. Mini column tests were conducted using the freshly collected GAC and GAC that had been stored in a refrigerator at 4°C for two weeks. Both of the results were compared to the breakthrough from the parallel pilot-scale studies, and the difference from these two sets of experiments was examined.
3.4 RESULTS AND DISCUSSION

3.4.1 Determining the operating time for pilot- and bench-scale column tests

3.4.1.1 Pilot-scale column test
A pilot-scale trial was conducted at the Lorne Park WTP to determine the operating mode for pilot filters, examining the variability in column performance with continuous vs. intermittent flow over a total flow time of 25 hours. Three modes were tested: continuous flow with spiked influent for 25 hours (Column 1), intermittent flow with spiked influent in daytime and with the flow stopped overnight (Column 2), and continuous flow with spiked influent during daytime and with non-spiked flow overnight (Column 3). Due to the limited feed tank volume available, each mode was tested with only one pilot filter (i.e. no duplicates). The percent breakthrough of MIB and geosmin from each pilot column was plotted against operating time in Figure 3.2. No obvious difference was observed in the MIB data across the three different columns (Figure 3.2 (a)). The breakthrough increased from 30% to approximately 80% within one hour and stabilized at around 70% after 23 hours of operation. According to the results from column 2 and column 3, desorption of MIB would not affect the GAC performance when it is under intermittent flow mode (Figure 3.2 (a)). In contrast, Figure 3.2 (b) demonstrated that desorption of geosmin occurred when the column was fed with non-spiked influent or was stopped overnight. However, comparable geosmin breakthrough was observed among the three columns again after two hours of operation on Day 2. For the continuously running column, the removal of geosmin stabilized after 4 to 5 hours of operation with a breakthrough of approximately 30% (Figure 3.2 (b)). Overall, it was determined that a continuous flow mode for over 24 hours is preferable for determining the stabilized T&O removal across a pilot filter, yet an intermittent flow mode is acceptable when the operation lasts for over 5 hours following any flow interruption and for at least 10 hours in total.
Figure 3.2: Breakthrough of (a) MIB and (b) geosmin from pilot-scale trial at Lorne Park WTP to compare three different operating modes over 25 hours.
3.4.1.2 Bench-scale column test

**a.**

![Graph showing percent breakthrough of MIB and geosmin over 24 hours from mini column tests using different aged GAC from Lorne Park.](image)

**b.**

![Graph showing percent breakthrough of MIB and geosmin over 24 hours from mini column tests using different aged GAC from Lorne Park.](image)

**Figure 3.3:** Percent breakthrough of (a) MIB and (b) geosmin over 24 hours from mini column tests using different aged GAC from Lorne Park (Data points are an average of duplicate columns with error bars representing maximum and minimum values).
Figure 3.4: Percent breakthrough of (a) MIB and (b) geosmin over 24 hours from mini column tests using GAC from Barrie with particle size of 2.36 mm (sieve #8) and 2 mm (sieve #10) (Data points are an average of duplicate columns with error bars representing maximum and minimum values)
Mini column tests were conducted with continuous flow over 24 hours in the lab using different GAC samples. To determine the time needed for stabilization of geosmin and MIB removal, the influent and effluent samples were collected at regular intervals. The time was converted into treated bed volumes of water due to the different EBCTs of the GAC contactors at Lorne Park (EBCT = 4.12 min) and Barrie (EBCT = 6.05 min). As shown in Figure 3.3, both MIB and geosmin breakthrough demonstrated stability after 300 bed volumes of treated water (approximately 20 hours of operation) for GAC samples from Lorne Park. Data using GAC from Barrie presented acceptable stability after 200 bed volumes of treated water (also approximately 20 hours) for both compounds with a difference within ±5% (Figure 3.4).

3.4.2 Pilot-scale study

3.4.2.1 Effect of GAC age
MIB and geosmin breakthrough tests were conducted in pilot filters at the Lorne Park WTP with an influent concentration of 100 ng/L for both compounds in May, 2015 and July, 2015. GAC samples were collected from Contactor #2 (about 3.2 years in operation in July, 2015) and Contactor #8 (about 4.2 years in operation in July, 2015). The results are shown in Figure 3.5, along with data from previous research for the same contactors conducted in May 2013 using similar methods, when the GACs were only 1 and 2 years old, respectively (Zamyadi et al., 2015). In Figure 3.5, it is observed that the breakthrough of MIB increased from about 25% to 85% after three years of operation. Better geosmin removal was observed compared to MIB, with only 30%-45% geosmin breakthrough using 3-year old or older GAC. Obvious breakthrough increases were observed over the first three years of operation (25%-85% for MIB and 15%-45% for geosmin), while there were only slight differences (~5% for both compounds) between the performance of 3.2-year and 4.2-year GAC, suggesting that a removal equilibrium was reached for T&O compounds after 3 years of operation. These results are in accordance with a previous publication (Scharf et al., 2010) that observed more than 80% geosmin removal through 36 inches (approximately 91cm) of a pilot-scale GAC contactor over 700 days of operation. A further study conducted by Rondtke and Snoeyink (1983) also stated that for large GAC particles and slowly diffusing adsorbates, several years may be required to reach equilibrium. According to Peel Region’s reports, the typical geosmin concentration in raw water has been below 5 ng/L in the summertime over the past three years, which means there was no significant taste and
odour event. The increase of T&O breakthrough over operation time demonstrated that the removal capacity of GAC for T&O compounds is greatly influenced by the amount of NOM adsorbed on the GAC surface. This finding is in accordance with previous publications (Graham et al. 2000, Newcombe et al. 2002) documenting that the adsorption of MIB and geosmin can be reduced by an order of magnitude or more due to the presence of background NOM, mainly because of the competitive adsorption between NOM with low molecular weight and T&O compounds.

The data in Figure 3.5 show error bars representing the maximum and minimum values of stabilized compound breakthrough from pilot-scale filters running continuously for over 24 hours. As discussed in the previous section, the removals of geosmin and MIB were stabilized after the first 5 hours of operation. Breakthrough data were averaged and plotted in Figure 3.5 from 3 samples that were collected after 20 hours of operation for each pilot filter. The removal of geosmin and MIB was both considered stable with the difference between samples less than 5%.

![Figure 3.5](image-url)

**Figure 3.5:** Pilot-scale breakthrough results of MIB and geosmin at Lorne Park, using GAC with different ages. (Error bars represent max/min values of 3 replicates collected from one pilot-filter after 20 hours)
3.4.2.2 Effect of exposure to H$_2$O$_2$

Hydrogen peroxide together with UV disinfection is applied at Lorne Park in summer as the first barrier to T&O compounds. The contactors were exposed annually to H$_2$O$_2$ for approximately three month periods from 2013 to 2015. In 2015, the application of H$_2$O$_2$ started on August 18th. Besides the tests conducted in May and July, another set of experiments was conducted in mid-August, 2015, when the GAC was newly exposed to H$_2$O$_2$ at a concentration of approximately 1.0 to 2.5 mg/L. Figure 3.6 presents the breakthrough of MIB and geosmin from pilot column tests conducted in May, July and August. All the GAC samples were collected from similar locations in Contactor #2. The breakthrough of MIB and geosmin increased by about 10% for MIB and 20% for geosmin from May to July, while breakthrough of both dropped by about 40% in August. The removal capacity increased dramatically after the application of H$_2$O$_2$ in the influent, providing evidence that H$_2$O$_2$ has significant impact on the removal capacity of GAC. There are few papers evaluating the effect of H$_2$O$_2$ on GAC for T&O removal, yet hypotheses of reactions between H$_2$O$_2$ and GAC can be found in previous studies: either generating ·OH radicals or changing the functional group on the surface of GAC (Li 2013). A plausible explanation is that the NOM previously adsorbed on GAC was degraded due to the reactions between H$_2$O$_2$ and GAC, thus generating more sorption sites for geosmin and MIB removal. Additionally, MIB and geosmin can be destroyed directly by the ·OH radicals generated on the surface of GAC, resulting in lower breakthrough of both compounds (Collivignarelli and Sorlini 2004).
Figure 3.6: Comparison of pilot-scale breakthrough of MIB and geosmin using aged GAC at Lorne Park in 2015 (Error bars represent max/min values of 3 replicates collected from one pilot-filter after 20 hours)

3.4.3 Bench-scale study

3.4.3.1 Effect of mini column diameter and sieve method

Mini column experiments (column inner diameter (ID) = 1 cm, GAC bed depth = 1 cm) were documented by Gillogly et al. (1999) to give identical MIB breakthrough as the pilot-column test when operated at the same EBCT, regardless of column diameter and GAC bed depth. In this previous research, a representative-size fraction was selected and packed in the laboratory columns, whereas whether the GAC particles were sieved when they were dry or wet was not specified. Ho and Newcombe (2010) also reported that larger laboratory-scale columns (column ID = 2.5 cm, GAC bed depth = 15 cm) were able to remove MIB to the same extent as in a pilot-scale GAC filter at Myponga, Australia after a 6-month operation. Prior to adopting mini column tests or larger laboratory-scale column tests for GAC performance evaluation, experiments were conducted to validate the lack of impact of column diameter, and to determine an appropriate sieving method.
According to preliminary sieve tests, the representative particle size based on the weight fraction for dry GAC from Lorne Park was 1.7 mm (particles retained in sieve #12), while it was 2.0 mm (particles retained in sieve #10) for wet GAC particles. The dry GAC samples consisted of GAC taken from the contactor and baked at 105°C overnight. Particles from both representative sizes were packed into mini columns with different internal diameters (11 mm vs. 25 mm), and were challenged using geosmin and MIB, both at a concentration of 100 ng/L. The breakthrough data for MIB and geosmin from the four tests are presented in Figure 3.7. These bench-scale experiments are further presented together with the results from a pilot column test for comparison (conducted with the water and GAC collected at the same time as the bench-scale analyses).

A two-way ANOVA was applied to statistically evaluate the impact of column ID and sieve method for MIB and geosmin removal. As shown in Table 3.3, the effect of sieve method is significant for both MIB and geosmin adsorption at a 95% significance level as the F values are significantly higher than the F critical value when α = 0.05. The difference in average MIB and geosmin breakthrough is 30% and 20%, respectively, between the dry and wet GAC (Figure 3.7). Presumably, the baking process removed and/or altered the NOM adsorbed on GAC surface and released more adsorption sites, resulting in higher removal capacity for geosmin and MIB.

No impact of column ID on MIB removal was observed, but the null hypothesis regarding column ID for geosmin removal was rejected with an F value equal to 15 compared to the a critical value of 4.75 . Though an impact on geosmin removal using different column IDs was identified statistically, only a slight difference (~5% less breakthrough with ID=11mm) was observed. By comparing the results to the data from the pilot study, it was found that the larger mini column more closely corresponded to geosmin breakthrough. Column ID and sieve method, however, were demonstrated to not have an interactive effect on taste and odour compound removal. Overall, the data demonstrated that the sieving method used (i.e., wet vs. dry) had the greatest impact on geosmin and MIB removal, while column ID had no impact on MIB adsorption, and only slightly more accurate results for geosmin removal with the larger column (25 mm).
Figure 3.7 Breakthrough of MIB and geosmin from pilot filter and mini column filters with different internal diameters and sieve methods (Error bars on mini column filters represent max/min values of stabilized effluent breakthrough of samples collected after 16 hours from duplicate columns)

Since the sieve method has a significant impact on the lab-scale column results, each column was compared to the parallel pilot-scale test conducted in the WTP to determine the optimal conditions for the mini column tests (Table 3.4). Statistical analysis with the student t-test was applied to evaluate the difference between the pilot and mini column results. Results are shown in Table 3.4. Regarding the results of both MIB and geosmin adsorption, the optimal conditions for the mini column tests were determined to be a column with an internal diameter of 25 mm and loaded with wet sieved GAC. This lab-scale column protocol was utilized in subsequent experiments.
Table 3.3: Two-way ANOVA results of (a) MIB and (b) geosmin for the effect of column ID and sieve method

a. MIB

<table>
<thead>
<tr>
<th>source of variance</th>
<th>F value</th>
<th>F critical(0.05)</th>
<th>Reject or accept the null hypothesis (0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID</td>
<td>1.26</td>
<td>4.75</td>
<td>Accept</td>
</tr>
<tr>
<td>Sieve method</td>
<td>304.69</td>
<td>4.75</td>
<td>Reject</td>
</tr>
<tr>
<td>Interaction</td>
<td>4.39</td>
<td>4.75</td>
<td>Accept</td>
</tr>
</tbody>
</table>

Null hypothesis H₀: No difference among the groups tested

b. Geosmin

<table>
<thead>
<tr>
<th>source of variance</th>
<th>F value</th>
<th>F critical(0.05)</th>
<th>Reject or accept the null hypothesis(0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID</td>
<td>15.49</td>
<td>4.75</td>
<td>Reject</td>
</tr>
<tr>
<td>Sieve method</td>
<td>549.78</td>
<td>4.75</td>
<td>Reject</td>
</tr>
<tr>
<td>Interaction</td>
<td>1.07</td>
<td>4.75</td>
<td>Accept</td>
</tr>
</tbody>
</table>

Null hypothesis H₀: No difference among the groups tested.

Table 3.4: Results of two-tailed t-test assuming unequal variance to compare the pilot-scale test to each mini column test

<table>
<thead>
<tr>
<th>Compound breakthrough</th>
<th>Pilot-scale breakthrough</th>
<th>Difference</th>
<th>P-value (0.05)</th>
<th>Different breakthrough (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry GAC, 11mm</td>
<td>37%</td>
<td>-36%</td>
<td>0.00001</td>
<td>Y</td>
</tr>
<tr>
<td>dry GAC, 25mm</td>
<td>42%</td>
<td>-31%</td>
<td>0.00003</td>
<td>Y</td>
</tr>
<tr>
<td>wet GAC, 11mm</td>
<td>71%</td>
<td>-2%</td>
<td>0.24800</td>
<td>N</td>
</tr>
<tr>
<td>wet GAC, 25mm</td>
<td>68%</td>
<td>-5%</td>
<td>0.09499</td>
<td>N</td>
</tr>
<tr>
<td>Geosmin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry GAC, 11mm</td>
<td>6%</td>
<td>-25%</td>
<td>0.00080</td>
<td>Y</td>
</tr>
<tr>
<td>dry GAC, 25mm</td>
<td>9%</td>
<td>-22%</td>
<td>0.00033</td>
<td>Y</td>
</tr>
<tr>
<td>wet GAC, 11mm</td>
<td>25%</td>
<td>-6%</td>
<td>0.04631</td>
<td>Y</td>
</tr>
<tr>
<td>wet GAC, 25mm</td>
<td>27%</td>
<td>-4%</td>
<td>0.38649</td>
<td>N</td>
</tr>
</tbody>
</table>
3.4.3.2 Effect of GAC storage

It was demonstrated in a previous study (Randtke and Snoeyink 1983) that adsorption capacity of GAC can be impacted by the procedures used to store the GAC. For this research, the wet GAC core samples were carefully collected from a contactor and stored in sealed plastic bags at 4°C for two weeks with the water drained to minimize the disturbance to the GAC particles. Two sets of pilot- and bench-scale tests were conducted to investigate the impact of GAC storage. The first set of experiments was conducted with fresh GAC packed in pilot columns at Lorne Park and two-week old (i.e. stored) GAC loaded in mini columns in the lab. The second set of experiments was tested with the freshly collected GAC in both pilot and mini columns at exactly the same time at Lorne Park. All the experiments were run in duplicate columns. The bench-scale breakthrough was compared to the data from the parallel pilot-scale studies, respectively, and the difference from these two sets of experiments was examined (Figure 3.8). The breakthrough of geosmin and MIB through stored GAC in mini columns was approximately 10% lower than the pilot-scale study. However, the data from mini columns with freshly collected GAC showed the opposite difference (i.e. 10% higher). The reversed difference suggests that GAC storage has an impact on its adsorption capacity. Presumably, the higher removal capacity of stored GAC could be explained by desorption of T&O compounds, as well as the loss of volatile NOM constituents on the GAC particle surface during the two weeks of storage. On the other hand, leakage on the top of pilot column was observed during the second set of experiments, which likely resulted in longer EBCT in pilot filters than that in the bench-scale columns. Previous studies by Gillogly et al. (1999) and Ndiongue et al. (2006) reported that an increase of EBCT can significantly increase the removal efficiency of GAC for T&O compounds.

In summary, the storage of GAC has a slight influence on the removal capacity of T&O compounds. Freshly collected GAC would be a preferable option for bench-scale tests. However, GAC samples stored for less than 2 weeks could still be used, if conditions are not suitable for bench-scale tests with freshly collected GAC.
Figure 3.8 Effect of storage on GAC performance for (a) MIB and (b) geosmin removal using stored and freshly collected GAC from Lorne Park in mini column tests with comparison to parallel pilot-scale study (Error bars represent max/min values of stabilized breakthrough after 20 hours)
### 3.4.3.3 Application of mini column tests to evaluate GAC performance

The mini column test was applied to evaluate the performance of different GAC samples from the Lorne Park WTP. Samples collected from GAC Contactor #2 (3.2 yr in operation) and GAC Contactor #8 (4.2 yr in operation) in July, 2015 were stored at 4°C for two weeks prior to the experiments. The wet stored GAC samples retained in sieve #10 was packed into a glass column with an internal diameter of 25 mm. The bench-scale columns were run for over 24 hr. As discussed in the previous section, both MIB and geosmin breakthrough demonstrated stability after 300 bed volumes of treated water. The stabilized breakthrough after 20 hours of both compounds was averaged and is shown in Figure 3.9. The remaining removal capacity for MIB was almost the same for 3.2-year and 4.2-year GAC, while 4.2-year GAC demonstrated approximately 8% higher adsorption capacity for geosmin removal (Figure 3.9).

![Graph showing stabilized breakthrough of MIB and geosmin from mini column tests using 3.2-year and 4.2-year GAC from Lorne Park WTP.](image)

**Figure 3.9:** Average stabilized breakthrough of MIB and geosmin from mini column tests using 3.2-year and 4.2-year GAC from Lorne Park WTP (Error bars represent max/min values of stabilized replicates collected from duplicate mini columns for each GAC age after 20 hours)
3.4.4 Comparison of bench-scale and pilot-scale studies

3.4.4.1 GAC from Lorne Park water treatment plant

Experiments were conducted in July, 2015 and August, 2015, before and after the H$_2$O$_2$ application in August at the Lorne Park WTP, respectively. The first batch of mini column tests was conducted in the lab two weeks after the pilot column test in July. GAC samples from GAC Contactor#2 and GAC Contactor #8 were examined in this set of experiments. Figure 3.10 presents the data of MIB and geosmin breakthrough from both pilot and mini column tests. Comparable degrees of removal were observed for both compounds in both the 3.2 and 4.2 year old GAC, although mini column tests presented approximately 5%-10% lower breakthrough for both compounds than in the pilot column tests (Figure 3.10). The second batch of mini column tests was conducted at the Lorne Park WTP at exactly the same time together with the pilot column test in mid-August. The data from mini column tests were approximately 10% higher than the breakthrough from the pilot column test (Figure 3.11). As has been discussed in previous section, stored and newly collected GAC both provided comparable breakthrough to the pilot column tests, though the stored GAC used in mini column test had a slightly increased removal capacity.

In general, the data from pilot and mini column tests are in reasonable agreement with a ±10% difference. In consideration of the very different conditions in operation of these two tests, this agreement may be considered acceptable. In further regard to the amount of time and resources required to run the bench- vs. pilot-scale tests, the bench-scale test may be a desirable option for running future experiments.
Figure 3.10 Breakthrough of (a) MIB and (b) geosmin from pilot and mini column tests using two differently-aged GACs from the Lorne Park WTP in July, 2015 (Error bars represent max/min values of stabilized replicates collected from over 20 hours)
Figure 3.11: Breakthrough of MIB and geosmin from pilot and mini column tests with 3.2 year-old GAC from the Lorne Park WTP after exposure to H$_2$O$_2$ in August, 2015 (Error bars represent max/min values of stabilized replicates collected from one pilot-filer over 20 hours)

3.4.4.2 GAC from the Barrie water treatment plant

Geosmin and MIB breakthrough tests were conducted in pilot-scale columns at the Barrie SSWTP, using two GAC columns in duplicate, at the end of July, 2015, to evaluate the remaining removal capacity of Barrie’s GAC. Since the GAC beds at Barrie measured 2.81 m deep, and the pilot-scale glass GAC columns were only 1.28 m long, two pilot columns were operated in series for each duplicate to achieve the similar GAC bed depth (2.56 m) as the actual contactors. Bench-scale column tests were conducted in the lab two weeks after the pilot study. Wet sieve test results showed that an equal fraction (44.7%) of GAC particles were retained in sieve #8 (2.36 mm) and sieve #10 (2 mm), so mini column tests were run in duplicate with both particle sizes. The data from lab-scale columns with both particle sizes after 200 bed volumes of treated water were averaged and plotted in Figure 3.13, with a comparison to the pilot-scale breakthrough. The larger particles retained in sieve #8 (2.36 mm) gave an approximately 5% lower removal for MIB and 10% lower removal for geosmin compared to the particles retained in sieve #10 (2 mm) (Figure 3.13). Presumably, the difference is a result of varied surface area of
the different sized GAC particles (Corwin and Summers 2011). As shown in Figure 3.13, GAC particles retained in sieve #10 are more representative of the pilot-scale results. The difference between pilot and mini column tests conducted using representative GAC from Barrie SSWTP is in good agreement with the results from the Lorne Park WTP, providing evidence that the mini column tests are able to determine the remaining removal capacity of an existing GAC bed. In the future, this method would benefit from further verification at more water treatment plants.

![Figure 3.12](image.png)

**Figure 3.12** Average breakthrough of MIB and geosmin from pilot and mini column tests using aged GAC from Barrie SSWTP (Error bars represent max/min values of stabilized replicates collected at over 20 hours)

(Note: the data from the pilot-scale geosmin breakthrough are under the MDL)

### 3.5 SUMMARY AND CONCLUSIONS

The pilot-scale studies at Lorne Park demonstrated that the remaining removal capacity of a GAC bed for T&O compounds decreased with the increase of years in operation, presumably due to the accumulation of NOM adsorbed on the surface of GAC. There was evidence, however, that the presence of H$_2$O$_2$ in the feed water to the GAC increased the removal capacity by approximately 40%, potentially as a result of reactions between H$_2$O$_2$ and the GAC. As part of a parallel project to the current study, it was discovered that Barrie’s GAC contactors have high biological activity. The higher removal efficiencies at Barrie with the comparable-aged GAC at

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*Department of Civil Engineering, University of Toronto* 2015
Lorne Park, could subsequently be the product of biological activity and warrants further research. The variation in performance of similar-aged GAC from Lorne Park and Barrie suggests that there are factors that can significantly impact the remaining GAC service life (e.g., type of GAC, source water characteristics, treatment train variability, and biological activity).

Bench-scale results indicated that a glass column with an ID = 25 mm and loaded with 10 cm of the size representative fraction of wet GAC based on weight fraction can most accurately simulate a pilot-scale filter. The sieve methods with baked or wet GAC had a significant impact on T&O compound breakthrough, with the baking process potentially removing and/or altering NOM constituents that were adsorbed onto GAC, resulting in error. Due to the stickiness of wet GAC, the wet sieving might not give a real “representative” sample as well. In order to increase the accuracy of mini column tests, the GAC samples with the same particle size distribution as in the full scale filter may be recommended to be tested in mini column tests in the future.

Meanwhile, different drying methods could be explored including freeze drying or air drying, in order to minimize the loss or alteration of NOM adsorbed onto the surface of GAC.

The comparison between pilot- and bench-scale column tests at the Lorne Park WTP and the Barrie SSWTP provided evidence that the mini column tests can determine the extent of T&O compound adsorption in a pilot-scale (and therefore, presumably full-scale) filter with an error within ±10%. While promising, this result is based on a study of only two locations, which included only three types of GAC (two Centaur GACs with different ages (3.2 and 4.2 years) and F300). In the future, this method should be verified under a wider range of conditions, including more types of GAC and more water matrices. Other variables, such as the impact of the temperature of the experiment (the GAC and the water) should be carefully explored, as well as chlorine residual, \( \text{H}_2\text{O}_2 \) exposure to GAC and bioactivities in GAC.
3.6 References


4 RECOMMENDATIONS FOR FUTURE WORK

The main objective of this research was to develop a protocol for applying the mini column test on a routine basis to track GAC performance for future studies, and the results demonstrated that, at least under the conditions tested, it was sufficiently accurate to be useful in practice. This method, however, can be further optimized. Additionally, this bench-scale test can be applied to investigate other factors that might affect the GAC performance. Accordingly, several recommendations derived from this study are listed below:

1. In order to simulate the pilot-scale filters more accurately using a short bed mini column adsorber, different types of representative GAC particles accounting for the largest surface area fraction should be tested. This might include utilizing air-dried GAC, freeze-dried GAC and mixed wet GAC with the same particle size distribution as in a full-scale contactor.

2. The results presented here provide evidence that the application of hydrogen peroxide with GAC should be further explored. The data from Lorne Park suggested that relatively exhausted GAC, when newly introduced to H₂O₂, may have a substantial increase in adsorption or destruction of both geosmin and MIB. Such applications might prove useful during taste and odour events. It would further be interesting to explore the mechanisms involved in the reaction between H₂O₂ and aged GAC.

3. In future work, the mini column tests should be conducted using different types of GAC in different water matrices, and with GAC from facilities utilizing very different treatment trains. These variabilities will enable clarification as to the importance of GAC type, water characteristics (e.g., temperature, pH, NOM, inorganics present), and the impact of treatment plant design.

4. The effect of biological activity in a GAC contactor should also be studied using the mini column test with sterilized GAC and non-sterilized GAC.

5. The effect of water and GAC temperature during the mini column test should be determined.
4.1 REFERENCES

A. PRELIMINARY TESTS

A.1 Determining GAC particle size distribution by dry sieve test

A.1.1 Equipment
Sieves (#8 (2.36 mm), 10 (2 mm), 12 (1.7 mm), 14 (1.4 mm), 16 (1.18 mm), 18 (1 mm), 20 (0.841 mm), 25 (0.71 mm) and 30 (0.232 mm)), sieve shaker, balance, plastic bags, drying oven, desiccator, drying crucibles, wire brushes, Wilson GAC core sampler (consisting of a long PVC pipe with a tennis ball on a rope)

Prior to GAC sample collection, the core sampler was disinfected with 12% chlorine solution and rinsed with sample water. A filter backwash was initiated to fluidize the GAC bed in order to more easily submerge the coring device to the bottom of the contactor. With the bed was fluidized, the core sampler was fully submerged and the rope with tennis ball was pulled to plug the far end of the pipe. Excess water was poured off the top of the core sampler, and the GAC sample was carefully poured out across plastic bags to enable the collection of different filter depths (i.e., top, middle, bottom). The samples were taken at several different locations throughout the filter bed to be representative of the entire filter. The GAC samples for mini column experiments were stored in Ziploc bags at 4°C.

A.1.2 Sample Preparation
1. GAC samples were placed in a bucket and gently washed with sample water. Clean samples were put into drying crucibles and baked in a drying oven for 24 hr at 105°C.
2. Sieves were weighed, and arranged on the shaker in order of size (largest mesh size at the top).
3. GAC samples were removed from the drying oven and allowed to cool to room temperature (≤30 min).
4. Five hundred grams of media was placed in the top of sieves and shaken for 3 minutes. (Note: In absence of a shaker, this step can be done by hand).
5. After shaking was complete, each sieve was re-weighed and the weight of GAC was determined for each. The total weight was determined to be 500g±5.0g.
The GAC samples from Lorne Park WTP and Barrie SSWTP were analysed for particle size distribution and are illustrated in Figure A.1 and A.2. The most representative size fraction of dry GAC from both Lorne Park and Barrie was determined to be the particles retained in sieve #12 (1.7mm), weighing 20% and 27%, respectively.

**Figure A. 1:** Particle size distribution of dry GAC samples from Lorne Park WTP

**Figure A. 2:** Particle size distribution of dry GAC samples from Barrie SSWTP
A.2 Determining GAC Particle Size Distribution by Wet Sieve Test

The equipment needed and sample collection for wet sieve testing was the identical to the dry sieve test process with the exception that GAC was drained and sieved while it was still wet. Due to the stickiness of wet GAC, most of the particles were retained in sieve #8 (2.36 mm), #10 (2 mm), and only a small fraction was retained in sieve #12 (1.7 mm). The sieve test results of wet GAC from Lorne Park WTP and Barrie SSWTP are shown in Figure A.3 and A.4.

The most representative size fraction of wet GAC particles from Lorne Park were those retained in sieve #8, accounting for 47% of the total GAC. For the samples from Barrie, the wet particles retained in sieve #8 and #10 had the same weight fraction (44%) out of the total GAC. GAC with both particle sizes were tested in the bench-scale breakthrough experiments.

Figure A.3: Particle size distribution of wet GAC from Lorne Park WTP
Figure A. 4: Particle size distribution of wet GAC from Barrie SSWTP
B. SUPPLEMENTARY DATA FOR CHAPTER 3

B.1 EFFECT OF COLUMN DIAMETER AND SIEVING METHODS

Figure B. 1: Breakthrough of (a) MIB and (b) geosmin over time through mini columns with varying column diameters and sieving methods (error bars represent the max/min value of replicate samples collected from duplicate columns)
B.2 PILOT TESTS WITH DIFFERENT AGED GAC FROM LORNE PARK WTP

Figure B. 2: Breakthrough of (a) MIB and (b) geosmin over time through pilot filters using 3.2-year and 4.2-year aged GAC at Lorne Park WTP
B.3 Pilot and mini column tests conducted on site at Lorne Park WTP

Figure B. 3 Breakthrough of (a) MIB and (b) geosmin over time from pilot and mini column tests conducted at the same time at Lorne Park WTP (error bars represent the max/min value of samples from duplicate mini columns)
B.4 Pilot column test at Barrie SSWTP

Figure B. 4 Breakthrough of MIB over time through the pilot filter at Barrie (Geosmin breakthrough from this pilot filter was under the detection limit) (Error bars represent the max/min value of samples from duplicate pilot filters)

(Note: the data from the pilot-scale geosmin breakthrough are under the MDL)
C. TASTE AND ODOR COMPOUND ANALYTICAL METHODS

C.1 Principle
Geosmin and 2-methylisoborneol (MIB) were extracted and concentrated from aqueous samples by headspace solid phase micro-extraction (HS-SPME) and quantified using gas chromatography-mass spectrometry (GC-MS). Geosmin and MIB were quantified using an internal standard: $d_3$-Geosmin. The internal standard was used to monitor retention time, relative response, and quantify analytes in the sample. The analysis was carried out with a Varian® 3800 gas chromatograph with a Varian® ion-trap mass spectrometer detector, using electron impact (EI) ionization and an autosampler.

Sample preparation involved first adding 10 mL of Milli-Q® water for calibration standards or 10 mL of the sample into a 20 mL clear vial (Supelco, Bellefonte, PA) that contained 3.5 g of reagent grade sodium chloride (NaCl). Internal standards were then added to samples and calibration standards by dispensing 25 μL of a solution of 10 μg/L of $d_3$-Geosmin to achieve a 25 ng/L concentration. The vial was capped with a Teflon®-lined septum magnetic crimp cap (Supelco, Bellefonte, PA), which is manufactured for use with the autosampler. Vials were placed into a sample tray, where the autosampler took the sample vial and delivered it to a spinning box that was preset to 65°C ± 1 °C at a rotation speed of 500 rev/min (rpm). Samples were shaken for 5 minutes to dissolve the salt. The needle (23 gauge) containing a 1 cm long SPME fiber (Supelco, Bellefonte, PA) was then inserted into the vial through the septum, and the fiber was extended into the vial’s headspace for 30 minutes. At the end of contact time, the fiber was retracted back into the needle, the needle injected into the GC/MS injection port, and the GC/MS run was started. After five minutes of desorption, the sample was carried onto the GC column and analyzed for MIB and geosmin content.
**C.2 REAGENTS**

**Table C. 1:** Reagents needed for MIB and geosmin analysis

<table>
<thead>
<tr>
<th>Reagent [CASRN]</th>
<th>Supplier and Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylisoborneol, MIB (47523-U), 100 μg/mL in methanol</td>
<td>Sigma Aldrich (47523-U), 100 μg/mL in methanol</td>
</tr>
<tr>
<td>(±)-Geosmin</td>
<td>Sigma Aldrich (47522-U), 100 μg/mL in methanol</td>
</tr>
<tr>
<td>D3-Geosmin</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>Sigma Aldrich (646377), ≥99.9%, Chromasolv® Plus</td>
</tr>
<tr>
<td>Acetone</td>
<td>Sigma Aldrich (323772-2L), ≥99.5%, Reagent Plus®</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>EMD (DX0838), HPLC grade</td>
</tr>
<tr>
<td>Sodium Azide</td>
<td>Sigma Aldrich (S2002), ≥99.5%, Reagent Plus®</td>
</tr>
</tbody>
</table>

**C.3 METHOD OUTLINE**

**C.3.1 Sampling and Storage**

1. Prepared micro-column sampling glassware by adding 166 μL of 25 g/L Reagent Plus® , ≥99.5% sodium azide solution (Sigma-Aldrich, Oakville, ON). Sodium azide acts as a preservative (Pei, 2003).
2. Collected samples in 23 mL amber vials with Teflon®-lined septa screw caps, ensuring that the sample was headspace free.
3. Stored samples at 4°C for up to two weeks.

**C.3.2 Geosmin and MIB solution preparation for spiking influent water (Micro-Column Tests, Milli-Q® water based, 1mg/L)**

1. 100 mL volumetric flasks were partially filled with Milli-Q® water.
2. A pipette was used to transfer 1 mL of geosmin (100 ppm) stock solution and 1 mL of MIB (100 ppm) stock solution into the volumetric flask.
3. The volumetric flask to was filled to 100 mL with Milli-Q using a pasteur pipette.
4. The flask was stoppered, wrapped in aluminum foil, and mixed on a magnetic stir plate.
C.3.3 Geosmin and MIB solution preparation for GC/MS analysis (methanol based)

**Calibration Standards Preparation**

1. Prepared calibration standards
2. Pipetted 10 mL of Milli-Q® water into a sample extraction vial that contained 3.5 g of NaCl.
3. Injected the appropriate volume of 10 µg/L combined geosmin and MIB stock solution.
4. Spiked 25 µL of 10 µg/L internal standard into the vial to achieve 25 ng/L.
   
   **Note:** The syringe was submerged into the water to avoid evaporation.

5. Repeated the above steps and prepare 5, 10, 30, 50, 100, 200 ng/L standard solutions.
6. Calibration standards were analyzed right away.

**Sample Preparation**

1. Added 10 mL of sample into a sample extraction vial (with 3.5 g NaCl).
2. Spiked 25 µL of 10 µg/L internal standard into the vial to achieve 25 ng/L.
3. Clamped vial cap and analyzed immediately.

**Blank Sample Preparation**

1. Poured 10 mL of Milli-Q® water into a sample extraction vial (with 3.5 g NaCl).
2. Spiked 25 µL of 10 µg/L internal standard into the vial to achieve 25 ng/L.
3. Analyzed a blank and check standard after every 10 samples.

**Running Standards Preparation (100 ng/L of Geosmin and MIB in Milli® Water)**

1. Pipetted 10 mL of Milli-Q® water into a sample extraction vial that contained 3.5 g NaCl.
2. Injected 100 µL of geosmin, MIB combined stock solution (10 µg/L) into the vial.
3. Spiked 25 µL of 10 µg/L internal standard into the vial to achieve 25 ng/L.
   
   **Note:** Analyzed a check standard after every 10 samples.
C.4 GC/MS OPERATION

Table C. 2: GC/MS operation conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Column</td>
<td>VF-5MS capillary column (30m × 0.25 mm, I.D., 0.25 µm film thickness)</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Helium at 1 mL/min @ 25°C</td>
</tr>
<tr>
<td>Injection Method</td>
<td>Temperature: 250°C Desorbing time: 5min</td>
</tr>
<tr>
<td>Mode</td>
<td>Splitless for first 2 minutes, split after 2 minutes with split ratio of 50</td>
</tr>
<tr>
<td>Split Valve</td>
<td>Open after 2 min, Flow @ 50 mL/min</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>1 µL @ normal speed</td>
</tr>
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<td>Auto Sampler method</td>
<td>Syringe: SPME Fiber</td>
</tr>
<tr>
<td></td>
<td>Supelco Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), d₅ 50/30 µm, needle size 24 ga</td>
</tr>
<tr>
<td></td>
<td>Agitator Temperature: 65.0°C</td>
</tr>
<tr>
<td></td>
<td>Pre-incubation time: 5min</td>
</tr>
<tr>
<td></td>
<td>Extraction agitation speed: 400rpm</td>
</tr>
<tr>
<td></td>
<td>Extraction time: 30min</td>
</tr>
<tr>
<td>GC Method</td>
<td>Initial: starts from 40°C, holds for 2min;</td>
</tr>
<tr>
<td></td>
<td>Ramp: 1. increases to 250°C at 15°C/min;</td>
</tr>
<tr>
<td></td>
<td>Equilibration: hold at 250°C for 7min</td>
</tr>
<tr>
<td>MS Conditions</td>
<td>Scan Mode: SIS (Single Ion Selection)</td>
</tr>
<tr>
<td></td>
<td>Ionization Type: EI</td>
</tr>
<tr>
<td></td>
<td>Emission current: 30uAmps</td>
</tr>
<tr>
<td></td>
<td>Scan average: 3microscans (0.89s/scan)</td>
</tr>
<tr>
<td></td>
<td>Multiplier Offset: 150volts</td>
</tr>
<tr>
<td>Total Run Time</td>
<td>23.00 min/run</td>
</tr>
</tbody>
</table>

Table C. 3: Parameters of the MS scan for determining taste and odour compounds

<table>
<thead>
<tr>
<th>Function</th>
<th>T&amp;O Compounds</th>
<th>Quantitative ions (m/z)</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Geosmin</td>
<td>112</td>
<td>11.2</td>
</tr>
<tr>
<td>1</td>
<td>2-MIB</td>
<td>95</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>D₃-Geosmin (internal)</td>
<td>115</td>
<td>11.2</td>
</tr>
</tbody>
</table>
**C.5 Calculations**

The taste and odour compound concentration was determined by correlation of the sample’s response ratio (ratio of sample’s response to that of the internal standard) with a calibration curve run daily. The calibration curve was determined using standards prepared with geosmin and MIB ($d_3$-geosmin as an internal standard) as an internal standard.

**C.6 References**

D. QA/QC

D.1 Calibration curves

A seven-point calibration curve was prepared with each sample analysis. Additional quality control included a blank sample at the beginning of the run, and a check standard after every 10 samples. The instrument performance drifted probably due to changes in the SPME fiber (initially using a 2 cm fiber and switching to a 1 cm fiber), as well as changes to the instrument (the GC column was replaced). Quality control charts were used to track the concentrations of the running standards throughout the different runs as an indication of method performance.

![Graph showing calibration curves for geosmin and MIB](image.png)

**Figure D. 1:** An example of calibration curves for geosmin and MIB
D.2 CHECK STANDARDS

A quality control chart was maintained for the analysis of geosmin and MIB using check standards with a concentration of 100 ng/L for both compounds. Check standards were prepared at the same time and in the same manner as the and analyzed every 5 to 10 samples. As demonstrated in Figure D.2 below, check standards were plotted on quality control charts.
Figure D. 2: Quality control chart for (a) MIB and (b) geosmin

D.3 METHOD DETECTION LIMIT

The method detection limits (MDLs) for the analysis of geosmin and MIB were determined by multiplying the standard deviation of 9 replicate injections by the student-t value. The average concentration of MDL samples for MIB and geosmin was 42 ng/L and 25 ng/L, respectively. The calculated MDL of geosmin and MIB was 8 ng/L and 9 ng/L, respectively. The results of 9 replicates are indicated in the table below.
Table D. 1: Calculation of method detection limit for geosmin and MIB

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Peak Area count</th>
<th>Peak area ratio</th>
<th>Calculated concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIB</td>
<td>Geosmin</td>
<td>D&lt;sub&gt;3&lt;/sub&gt;-geosmin</td>
</tr>
<tr>
<td>1</td>
<td>4.33E+05</td>
<td>4.93E+05</td>
<td>4.80E+06</td>
</tr>
<tr>
<td>2</td>
<td>4.05E+05</td>
<td>4.49E+05</td>
<td>4.36E+06</td>
</tr>
<tr>
<td>3</td>
<td>4.07E+05</td>
<td>4.75E+05</td>
<td>4.61E+06</td>
</tr>
<tr>
<td>4</td>
<td>4.14E+05</td>
<td>4.92E+05</td>
<td>4.89E+06</td>
</tr>
<tr>
<td>5</td>
<td>4.08E+05</td>
<td>4.64E+05</td>
<td>4.76E+06</td>
</tr>
<tr>
<td>6</td>
<td>4.27E+05</td>
<td>4.54E+05</td>
<td>4.08E+06</td>
</tr>
<tr>
<td>7</td>
<td>3.97E+05</td>
<td>3.54E+05</td>
<td>4.43E+06</td>
</tr>
<tr>
<td>8</td>
<td>4.10E+05</td>
<td>4.92E+05</td>
<td>4.86E+06</td>
</tr>
<tr>
<td>9</td>
<td>4.07E+05</td>
<td>4.78E+05</td>
<td>4.44E+06</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>3.09</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>RSD</td>
<td>7%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>MDL (ng/L)</td>
<td>8.94</td>
<td>7.46</td>
<td></td>
</tr>
</tbody>
</table>

D.4BLANK TEST WITH MINI COLUMNS

Blank tests were conducted to prove that taste and odour compounds were not lost from the mini column systems, which could potentially include adsorption onto the surface of glass beads or in the Teflon tubing. The spiked influent was loaded in the mini columns packed with glass beads for more than 8 hours. Blank tests were conducted in glass columns with different internal diameters (i.e., ID=11mm and ID=25mm) in duplicate. The effluent analysis demonstrated that negligible adsorption occurred for both compounds in the blank mini column systems without GAC (Figure D.3).
Figure D. 3: Breakthrough of (a) MIB and (b) geosmin over 8 hours through blank mini column systems packed with glass beads (error bars represent the max/min values of samples from duplicate columns)