MIB and geosmin removal during adsorption and biodegradation phases of GAC filtration


ABSTRACT

Biologically active carbon (BAC) filtration is a robust process for removal of many contaminants of concern. In this study, the effectiveness of BAC filtration to remove natural organic matter (NOM) and taste and odor (T&O) compounds was investigated by long-term (7 months) bench-scale filtration experiments. Filters contained fresh granular activated carbon (GAC) and a 2-year-old BAC which were fed with ozonated water from a full-scale water treatment plant spiked with 2-methylisoborneol (MIB) and geosmin. The study aims to evaluate T&O removal of GAC transitioning from its adsorptive to biological state, and to determine the effects of changing hydraulic loading during T&O episodes and its effect on dissolved oxygen (DO) consumption. Sequencing of microbial communities in the BAC revealed that 20% of the identified bacteria were of genus *Nitrospira*. Based on nitrate formation and dissolved organic carbon (DOC) removal of the 2-year-old BAC, the fresh GAC turned biological after approximately 32,000 bed volumes. DOC removal of the GAC decreased from the initial 80% to 17%, however, the removal of MIB and geosmin remained >90% throughout the experiment (i.e., from adsorption to biodegradation). The 2-year-old BAC showed 9% lower MIB removals than the transitioned GAC filter indicating a contribution of remaining adsorption sites on MIB removal. When challenging the filters at different hydraulic loadings, higher T&O removal was achieved at higher empty bed contact times, which correlated well with increased DO consumption.

Key words | BAC, dissolved oxygen, geosmin, MIB, nitrate, taste and odor

INTRODUCTION

The occurrence of taste and odor (T&O) in drinking water is a significant challenge for water treatment plants (WTPs) globally. Some species of cyanobacteria and actinomycetes can produce T&O compounds like 2-methylisoborneol (MIB) and geosmin (*Ho et al. 2007*). While neither is toxic, they are aesthetically unpleasant even at low concentrations (ng/L). During the warm summer months, MIB and geosmin are a regular occurrence in the surface waters of reservoirs in South East Queensland (SEQ, Australia). The speciation and concentrations of both T&O compounds is site specific but can range from low (<10 ng/L) to several hundred ng/L. Throughout occurrence events, powdered activated carbon (PAC) is often applied for T&O control as it is cost efficient and can be used only when required (*Cook et al. 2001*). Ozonation in combination with biologically activated carbon (BAC) filtration (*O3/BAC*) has been shown to have the potential to act as an additional barrier for T&O removal (*Elhadi et al. 2004*). Within drinking water treatment, *O3/BAC* finds wide application due to its disinfection and oxidation properties for the inactivation of a wide variety of pathogens. The *O3/BAC* process uses granular activated carbon (GAC) as filter media to physically remove unwanted microorganisms and organic/inorganic matter. As the GAC filter media become exhausted over time, the rough porous surfaces become amenable to bacterial colonisation which develops into an active biofilm capable of removing biodegradable organic matter from the ozonated water (*Scholz & Martin 1997*). In addition, some studies have shown that this
biodegradation process could be an important mechanism for removal of T&O compounds, such as MIB and geosmin (Westerhoff et al. 2005; Brown & Lauderdale 2006).

Often WTPs replace the BAC following the loss of its adsorptive capacity, or have capacity for onsite regeneration. However, this replacement of the media is a large financial investment; therefore, prolonging the filter’s operational life can result in substantial cost savings. Removal of natural organic matter (NOM) in a BAC filter is typically lower than with GAC (Yapsakli & Çeçen 2010) but it can still operate for several years without needing regeneration or replacement. Predictive modelling has shown the potential of BAC to remain effective for T&O removal beyond the exhaustion of adsorptive capacity because of biodegradation and bioregeneration of sorption sites (Scharf et al. 2010). However, it is difficult to estimate the remaining operational life of the GAC/BAC for T&O removal as its performance cannot be monitored on-line. While UV254 is a common surrogate measure for dissolved organic carbon (DOC) which can be measured on site, no surrogate is used in practice for T&O monitoring. MIB and geosmin require special analytical equipment (GC-MS) and skills for their analysis which are not applicable for routine practical applications. T&O removal performance is also impacted by the hydraulic loading of the filter and the empty bed contact time (EBCT) (Yu et al. 2011).

In South East Queensland (SEQ) hydraulic loading and EBCT is determined by varying water demand which could subsequently impact T&O removal. As shown in some studies, dissolved oxygen (DO) can be measured as an indicator of microbial respiration and provide an indirect way of assessing biological activity in the filters (de Vera et al. 2016). Biodegradation of organic matter could also be related to changes in DO consumption in biofilters, including the removal of biodegradable organic matter (Urfer & Huck 2001) and DOC (Ikhlef & Basu 2017). Application of DO measurements in the context of T&O compounds, however, has not yet been explored.

For this study, 2-year-old BAC was sampled from a WTP in SEQ and compared to fresh GAC. The aims were to investigate: (1) if the bench-scale columns used in laboratory testing are a suitable approach for full-scale filter performance assessment; (2) the changes of T&O removal during the transition of GAC to BAC; and (3) if DO is suitable as a simple online monitoring parameter for T&O removal capacity during different hydraulic loadings.

**MATERIALS AND METHODS**

**Experimental**

Experiments were performed using a bench-scale minicolumn biofiltration system in dark conditions (Figure 1), including four glass columns (internal diameter: 1 cm; length: 12 cm) packed with either BAC or GAC (new media effective size =0.7–0.9 mm, apparent density = 435 kg/m$^3$; ACTICARB GA1000N, Activated Carbon Technologies Pty Ltd, Australia), multi-channel peristaltic pumps (Sci-Q 323, Watson Marlow, USA), a DO probe (measuring range specified by manufacturer = 0–20 mg/L; WTW, Germany). Each filtration line was connected to a column using Norprene® tubing (Cole-Palmer, Chicago, IL) drawing pre-ozonated (1–2 mg/L O$_3$) water as filter feed. The pre-ozonated water was sampled as a grab sample in 20 L polyvinyl chloride containers from a drinking water treatment plant in SEQ. Raw surface water was pre-ozonated, followed by coagulation and primary filtration and intermediate ozonation before BAC filtration. Fresh samples were collected after intermediate ozonation every 2 weeks, with samples stored at 4°C until use. DOC and specific ultraviolet absorbance (SUVA) during the 7-month sampling duration did not change significantly: DOC = 1.48 ± 0.09 mg/L, SUVA = 1.1 ± 0.1 L/mg m. Using these bench-scale filters, the experiments carried out were in the following order: (i) monitoring DOC and T&O removal capacity (7

![Figure 1](https://iwaponline.com/ws/article-pdf/18/4/1449/236694/ws018041449.pdf)
months), (ii) comparison of GAC and BAC performance, and (iii) effect of EBCT. The feed water was purged with air to ensure oxygen saturation. BAC media, which were in use for 2 years at the time of sampling, were obtained from the same WTP. Preliminary tests on the BAC collected from the WTP indicated an iodine number of 0, which suggests that adsorption did not play a major role in pollutant removal. New GAC (ACTICARB GA1000N) was purchased from Activated Carbon Technologies Pty Ltd (Australia). Filtration was done upflow with an EBCT maintained at approximately 10 min. In order to cover a wide range of EBCTs the filters (bed volume = 6 mL) were also challenged at EBCTs of 1.5, 3, 8, and 10 min by increasing the flow rate to 3.9 mL/min, 2 mL/min, 0.7 mL/min, and 0.6 mL/min, respectively. Between sampling at different EBCTs, the filtration unit was allowed to stabilise overnight resulting in approximately 60 bed volumes (BV) with a flow rate of 0.6 mL/min.

Stock solutions of MIB and geosmin of concentration of 100 μg/mL in methanol (Sigma Aldrich, Australia) were diluted in the ozonated water to result in a feed water concentration of 40 ng/L. One set of BAC and GAC columns was spiked with T&O compounds and compared with the non-spiked ones, to verify whether methanol (0.00004%) interfered with the results as a carbon substrate during biodegradation. T&O compounds were spiked approximately every 2 weeks in newly sampled ozonated water and the filter was allowed to equilibrate for 5 BV before sample collection. Over the 7-month investigation period, no significant differences (<5%) in DOC removal were observed between the T&O spiked versus the non-spiked BAC and GAC columns.

**Analytical**

Prior to any analysis, all samples were filtered through 0.45 μm PTFE filters (Millipore, Australia). Ammonia, nitrite and nitrate were measured by a Lachat QuikChem8500 Flow Injection Analyzer (Hach Company, USA) using Lachat methods 31-107-06-1-B (NH₄⁺), 31-107-04-1-A (NO₂⁻), and 31-107-05-1-A (NO₃⁻). Method detection limits (MDL) were 1.6 μg/L for NH₄⁺-N, 0.2 μg/L for NO₂⁻-N, and 1.4 μg/L for NO₃⁻-N. The DOC was measured with a Shimadzu TOC-L total organic carbon analyser with a TNM-L total nitrogen analyser unit and ASI-L autosampler (Shimadzu, Japan). The MDL for DOC was 0.1 mg/L. UV-visible absorbance was measured at 254 nm in a quartz cuvette with a Varian Cary 50 Bio UV-Visible spectrophotometer (Varian, Australia). Biodegradable organic carbon (BDOC) was measured following the method using bacteria immobilised on sand (Joret et al. 1993), and 100 g freshly washed bioactive sand was mixed with a 500 g water sample, and cultivated under aeration conditions for 7 days. The difference between the initial and final DOC is defined as BDOC. The bioactive media used in this study was anthracite collected from primary filters in a full-scale plant. Any evaporation losses were determined with a balance and compensated for by the addition of deionised water obtained from a Milli-Q Advantage system prior to analysis.

T&O samples were collected headspace-free in 45 mL acid-washed bottles with caps lined with PTFE septa for subsequent analysis by a gas chromatograph (Agilent 7890B) with a mass spectrometer detector (Agilent 5977A) coupled to a purge and trap (Tekmar) sample induction system using the selective ion monitoring mode. The internal standard used was 3-isobutyl-2-methoxypyrazine (IBMB). MDL was 2.0 ng/L for MIB and geosmin. Recoveries for the spiked geosmin and MIB were 80% and 87%, respectively, due to losses due to volatilisation during experimentation.

The DNA of the surface layer of three BAC filter samples was extracted and amplified by polymerase chain reaction (PCR) using two 16S (27F–519R and 341F–806R) molecular markers to amplify bacterial (16S) communities. Each marker was then sequenced using Illumina next-generation sequencing to produce paired-end reads for each molecular marker. Raw sequences were processed using Quantitative Insights into Molecular Ecology (QIIME 1.8), USEARCH (Ver. 7.1.1090) and UPARSE software. Processed sequences were then clustered and categorised into operational taxonomic units (OTUs) to provide the number of paired reads within each OTU. Sequencing and initial OTU categorisation was performed by the Australian Genome Research Facility Ltd.

**RESULTS AND DISCUSSION**

**Full-scale versus bench-scale minicolumn - BAC filter performance**

The use of minicolumns to assess large-scale filter performance was first evaluated in this study. If applicable, such columns
may be a useful predictive tool for WTP operators to make informed decisions for media replacement. A recent study by Li (2015) showed the feasibility of the minicolumn approach for T&O removal evaluation. In that study, T&O removal efficiency using BAC minicolumns was within 10% of the results obtained from pilot-scale experiments. This, however, was not the case for the study by Ho & Newcombe (2010) where they showed minicolumn results inaccurately predicted MIB removal in pilot-scale plants. In our study, the performance of the minicolumns containing the BAC sampled from a WTP was compared with the performance of the full-scale BAC filter under typical filtration conditions. The comparison was based on the removal of DOC and UV$_{254}$ in both bench-scale columns and a full-scale WTP over a 7-month period. As shown in Figure 2, results of the bench-scale tests agree with those obtained at full-scale.

Of the 1.48 mg/L of DOC in the ozonated BAC filter feed water, 0.27 ± 0.07 mg/L DOC was removed at full-scale (equivalent to 20% ± 6% removal) while 0.21 ± 0.06 mg/L was removed by the bench-scale minicolumns (equivalent to 16% ± 6% removal). Similar to DOC, UV$_{254}$ removal of 25% ± 5% at full-scale was relatively comparable to the removal obtained from the minicolumns (19% ± 4%). This demonstrates that the results of bench-scale minicolumns are in close agreement with the results of full-scale BAC filters. A maximum of 13% absolute difference is considerably good for operational application. In this study, experimental conditions (e.g., EBCT) were carefully matched with the typical full-scale filtration conditions.

**GAC–BAC transition**

Figure 3 shows the removal of T&O and DOC by the GAC and BAC bench-scale minicolumns over 7 months. This is equivalent to 34,000 BV at an EBCT of 10 min. Over the whole period of investigation, the 2-year-old BAC consistently removed on average 0.25 ± 0.08 mg C/L (17% ± 5% of the feed DOC) while consuming 2.3 mg/L of DO. In the ozonated feed water, 27% of the DOC (0.4 ± 0.2 mg/L) was available as BDOC.

The transition from GAC to BAC occurs in a three-stage process. Initially, the majority of DOC removal occurs through physical adsorption to the GAC’s surface with removal efficiencies reported of 40–90% (Simpson 2008). At this stage the media’s associated biofilms are in an acclimation phase. In this study, the DOC removal efficiency started to level off to around 40% after approximately 15,000 BV indicating the physical adsorption phase occurred mainly in
the first 15,000 BV or approximately 3.5 months. Once the GAC adsorption sites become saturated, DOC removal by adsorption gradually decreases while the degree of biodegradation increases. After around 30,000 BV the DOC removal reached a steady state, indicating that biological degradation became the predominant process. At this point the GAC would be considered exhausted as it is saturated with organic matter (Scholz & Martin 1997). The DOC removal efficiency was 17%, which is in accordance with literature reporting between 15% and 45% removal (Simpson 2008).

Figure 4 shows the nitrate concentration in the feed and filtrate of the GAC and BAC filter columns. Over the time period investigated nitrate in the BAC filtrate was measured $24 \pm 8\%$ greater than in the feed. In contrast, nitrate levels in the feed and GAC filtrate are relatively the same due to no or too little biological activity. At 32,000 BV, nitrate levels in the GAC and BAC filtrate converged, suggesting the shift to biodegradation. At this stage, nitrate in the GAC filtrate was $8 \pm 2\%$ greater than in the feed. The nitrate formation after BAC filtration ($24 \pm 8\, \mu g/L$) can only be explained by the loss of ammonia due to its low levels present ($5 \pm 2\, \mu g/L$). Under aerobic conditions organic nitrogen can be converted by bacteria to ammonium which then is converted via nitrite to nitrate. Sequencing results of the BAC revealed the presence of several bacteria related to Nitrospira sp. (20% reads within OTU). Indeed, dissolved organic nitrogen (DON) levels were reduced by $17 \pm 10\, \mu g/L$ after BAC filtration. This is consistent with the NOM removal data during the transition from adsorption to biodegradation after 6 months of operation (Figure 3). Therefore, monitoring nitrate formation across the filter, i.e., feed and filtrate, may give an indication of its biological activity and transition from GAC to BAC.

As previously described, over time the fresh GAC lost its adsorptive capacity for DOC removal while gradually increasing the degree of biodegradation supported by nitrate formation (Figures 3 and 4). MIB and geosmin are both susceptible to biodegradation, which can be attributed to their structures being similar to biodegradable alicyclic alcohols and ketones (Ho et al. 2007). With the onset of biological activity the removal of MIB and geosmin was not observed to decrease (Figure 3). During the 7-month investigation, BAC exhibited an excellent geosmin removal of $97 \pm 1\%$ while GAC was able to remove geosmin by $99 \pm 1\%$ continuously. MIB removal efficiencies of the biologically active GAC (7 months) were as high as new GAC at $97 \pm 1\%$, while the 2-year-old BAC was not able to reach similar levels and remained at $88 \pm 3\%$. The continuous high removal of MIB and geosmin by the biologically active GAC (7 months) may be related to both biodegradation and remaining adsorptive capacity. For example Ho & Newcombe (2010) observed that adsorption still played a major role in the removal of MIB after a 6-month operation with $80\%$ of MIB removal attributed to adsorption and the remaining $20\%$ to biodegradation. The biofilm on the GAC is said to form a relatively porous structure which allows waterborne substances to pass through the biofilm’s water-filled channels towards the GAC surface (Stoodley et al. 1999). While small T&O compounds (<190 g/mol) are able to reach remaining adsorptive sites, the larger NOM molecules may mainly be removed via biodegradation. NOM is highly heterogeneous, as it has various moieties with a wide range of molecular weight and can be categorised into hydrophobic/hydrophilic fractions. In spite of potentially having access to adsorptive sites, the low molecular weight fraction of NOM is less absorbable but easily biodegradable because the majority of these compounds are relatively hydrophilic (Matilainen et al. 2006). The 9% lower MIB removal capacity of the 2-year-old BAC as compared to the GAC (7 months) might be related to a lower remaining adsorptive capacity. This may be because some of the larger NOM molecules are partially or completely

![Figure 4](https://waponline.com/ws/article-pdf/18/4/1449/236694/ww018041449.pdf)
blocking water-filled voids and channels within the biofilm of the BAC (de Beer et al. 1994). This indicates that the GAC (7 months) and BAC were exhausted in terms of DOC removal but not for T&O removal. This is in accordance with the study by Persson et al. (2007) which found that GAC even after four years of operation receiving surface water had the capacity to remove MIB and geosmin by adsorption.

**Dissolved O₂ consumption, EBCT and T&O removal**

Biofiltration targeting the removal of MIB and geosmin is an aerobic process (McDowall 2008). Hence, T&O removal may potentially be directly related to DO consumption, which could be simply tracked at the filter feed and filtrate. In SEQ, hydraulic loading within WTPs depends on the water demand in the region resulting in changing loading rates and EBCTs. Personal communications with WTP operators showed that EBCTs can vary between 3 and 13 min. In order to investigate a potential relation of DO consumption and T&O removal across varying operational conditions, the EBCT was varied between 1.5, 3, 8 and 10 min (Figure 5) using two biologically active filters. As this experiment was done at the end of the testing period, the filters used included both the 7-month-old biologically active GAC and BAC (2.5-years old at the time of this experiment).

As seen in Figure 5, MIB and geosmin removals increase with EBCT. Less than 3% increase in removal was observed when increasing the EBCT between 8 and 10 min. This is consistent with the literature reporting no obvious improvement of MIB and geosmin removal efficiencies with EBCTs greater than 12 min (Yu et al. 2011). Simultaneously, the DO consumption mirrored the MIB and geosmin removal trend with varying EBCTs for both the GAC (7 months) and the BAC filter (Figure 5). This indicates that DO consumption may be a useful monitoring tool for biologically active GAC and BAC performance and subsequently T&O removal. Online monitoring of DO would provide water utilities with a simple tool for assessing BAC performance.

**CONCLUSIONS**

The transition from GAC to BAC and their effectiveness in removing T&O compounds and the usefulness of DO as a monitoring tool were evaluated through long-term (7 months) laboratory study. Experiments were performed using bench-scale minicolumns packed with fresh GAC and a 2-year-old BAC, which were fed with ozonated water sampled from a WTP and spiked with MIB and geosmin. The following conclusions can be drawn from the current results:

- Minicolumn DOC and UV₂₅₄ removal performance was in close agreement with full-scale BAC performance. GAC turned biological after approximately 6 months and 32,000 BV, which was indicated by nitrate formation and a decrease in DOC removal. While DOC removals levelled off at 17%, the GAC (7 months) and BAC (2 years) showed a continued excellent MIB and geosmin removal during the 7-month filtration experiment (34,000 BV).
- In terms of DOC removal the adsorptive capacity of fresh GAC was exhausted after 6–7 months of operation and T&O removal was still high (99% for geosmin, 97% for...
MIB). While T&O biodegradation of geosmin/MIB was occurring, adsorption likely still played a major role in the removal of MIB and geosmin. Based on these results, the BAC filter would not need to be renewed for sufficient T&O control when biodegradation sets in and GAC adsorptive capacity is exhausted in terms of DOC removal.

- T&O removal is reduced at lower EBCTs, which was clearly indicated by lower DOC consumption. T&O analysis can only be done with GC-MS and highly skilled personnel resulting in turnaround times for water utilities of more than 1–2 days. Therefore, DO consumption may be a useful simple online monitoring tool for biologically active GAC and BAC performance and subsequently T&O removal.

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