Impact of UV–H_2O_2 Advanced Oxidation and Aging Processes on GAC Capacity for the Removal of Cyanobacterial Taste and Odor Compounds

Arash Zamyadi[1,2], Emma Sawade[3], Lionel Ho[3], Gayle Newcombe[3] and Ron Hofmann[2]

[1]UNSW Water Research Centre, School of Civil and Environmental Engineering, University of New South Wales (UNSW), Sydney, New South Wales, Australia. [2]Department of Civil Engineering, University of Toronto, Toronto, Canada. [3]Australian Water Quality Centre (AWQC) – South Australian Water Corporation (SA Water), Adelaide, South Australia, Australia.

Supplementary Issue: Current Research in Water Treatment

ABSTRACT: Cyanobacteria and their taste and odor (T&O) compounds are a growing concern in water sources globally. Geosmin and 2-methylisoborneol (MIB) are the most commonly detected T&O compounds associated with cyanobacterial presence in drinking water sources. The use of ultraviolet and hydrogen peroxide (H_2O_2) as an advanced oxidation treatment for T&O control is an emerging technology. However, residual H_2O_2 (>80% of the initial dose) has to be removed from water prior final disinfection. Recently, granular activated carbon (GAC) is used to remove H_2O_2 residual. The objective of this study is to assess the impact of H_2O_2 quenching and aging processes on GAC capacity for the removal of geosmin and MIB. Pilot columns with different types of GAC and presence/absence of H_2O_2 have been used for this study. H_2O_2 removal for the operational period of 6 months has no significant impact on GAC capacity to remove the geosmin and MIB from water.

KEYWORDS: advanced oxidation, UV–H_2O_2, granular activated carbon, GAC, taste and odor, cyanobacteria, water treatment

SUPPLEMENT: Current Research in Water Treatment

CITATION: Zamyadi et al. Impact of UV–H_2O_2 Advanced Oxidation and Aging Processes on GAC Capacity for the Removal of Cyanobacterial Taste and Odor Compounds. *Environmental Health Insights* 2015:9(S3) 1–10 doi: 10.4137/EHI.S29431.

TYPE: Original Research

RECEIVED: June 22, 2015. **RESUBMITTED:** August 18, 2015. **ACCEPTED FOR PUBLICATION:** August 26, 2015.

ACADEMIC EDITOR: Timothy Kelley, Editor in Chief

PEER REVIEW: Four peer reviewers contributed to the peer review report. Reviewers' reports totaled 1,251 words, excluding any confidential comments to the academic editor.

FUNDING: This study was supported by (1) Natural Sciences and Engineering Research Council of Canada (NSERC), (2) NSERC industrial chairs at University of Toronto Drinking Water Research Group, (3) Australian Water Quality Centre (AWQC) and South Australian Water Corporation (SA Water), and (4) Water Research Australia Ltd. (WaterRA) funding scheme (project number 1021). The authors confirm that the funders had no influence over the study design, content of the article, or selection of this journal.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

CORRESPONDENCE: a.zamyadi@unsw.edu.au

COPYRIGHT: © the authors, publisher and licensee Libertas Academica Limited. This is an open-access article distributed under the terms of the Creative Commons CC-BY-NC 3.0 License.

Paper subject to independent expert blind peer review. All editorial decisions made by independent academic editor. Upon submission manuscript was subject to anti-plagiarism scanning. Prior to publication all authors have given signed confirmation of agreement to article publication and compliance with all applicable ethical and legal requirements, including the accuracy of author and contributor information, disclosure of competing interests and funding sources, compliance with ethical requirements relating to human and animal study participants, and compliance with any copyright requirements of third parties. This journal is a member of the Committee on Publication Ethics (COPE).

Published by Libertas Academica. Learn more about this journal.

Introduction

Cyanobacteria, also known as blue-green algae, are prokaryotic photosynthetic microorganisms present in both marine and freshwater sources.[1–3] Cyanobacterial nitrogen-fixing capacity (the ability to convert atmospheric N_2 to NH_3) and their contribution to global soil and water fertility have long been recognized.[1,2,4] They have shown an exceptional capability to adapt to the global changing environment and grow well in water bodies impacted by human activities and climate change.[5–7] Nutrient load from agricultural watersheds[8,9] to water bodies is a major cause of cyanobacterial proliferation.[8,10–12] Additionally, warmer global temperatures, low water level in lakes, low river flows, and reduced water quality associated with drought conditions and climate change favor the growth of cyanobacteria.[6,13] As a result of all of these factors, issues associated with cyanobacteria in water treatment for human consumption are increasing worldwide even in more temperate regions like Canada.[7,14,15]

The major water quality implications of cyanobacterial blooms for the water industry are (a) production of cellular metabolites, which can cause esthetic issues, eg, compounds that impart taste and odor (T&O); (b) release of toxic cellular metabolites (cyanotoxins), which can severely impact aquatic, animals', and human health; and (c) treatment process disturbance because of the breakthrough of cells into plants.[1,14,16–19] Toxic effects of detected cyanotoxins (mainly microcystins, nodularins, anatoxins, cylindrospermopsin, and saxitoxins) include hepatotoxicity, liver cancer, neurotoxicity, cytotoxicity, genotoxicity, dermatotoxicity, and human gastroenteritis.[1,2,10,16–18] In Australia and Canada, many troublesome species of cyanobacteria proliferate in drinking water sources, in particular, species of *Dolichospermum*, *Microcystis*, *Aphanizomenon*, *Anabaena*, *Pseudanabaena*, and *Cylindrospermopsis*.[10,15,20] These cyanobacteria have the potential to produce the T&O compounds and cyanotoxins.[2,10,15,19]

Geosmin and 2-methylisoborneol (MIB) are the most commonly detected T&O compounds associated with cyanobacterial presence in drinking water sources.[19,21–23] Their characteristics and chemical structure are shown in Figure 1. Additionally, production of neurotoxic anatoxins and hepatotoxic microcystins by T&O-producing species has been reported.[22] The presence of geosmin and MIB has been

mainly recorded during the warm summer season and/or early autumn during bloom lysis period.[24] Hence, cyanobacterial T&O issues are perceived as a temporary issue. Consequently, management and treatment adjustment information are focused on temporary options, such as addition of powdered activated carbon only during the bloom season and/or detection of a bloom event.[19] However, full-year monitoring results have documented the presence of these T&O compounds and their producing cells during cold season or pre/postbloom season.[25,26] Furthermore, assessment of existing treatment trains for the removal of harmful cyanobacterial metabolites has demonstrated the vulnerability of these barriers to climate change scenarios.[27]

Cyanobacterial T&O compounds are detectable by humans in very low concentrations, as low as 10 ng/L.[19] Additionally, conventional treatment options including chlorination are inefficient for their removal.[21,28] Preoxidation using strong oxidant agents, such as ozone, advanced oxidation techniques, and/or adsorptive barriers, eg, activated carbon, is required for their efficient removal from water.[21,28,29] The use of ultraviolet light (UV) and hydrogen peroxide (H_2O_2) as an advanced oxidation treatment for T&O control is an emerging technology.[30,31] A major challenge associated with UV–H_2O_2 is that the majority (>80%) of the applied H_2O_2 remains in the water following UV–H_2O_2 treatment.[31] The residual H_2O_2 has to be removed prior to disinfection process as it exerts a strong chlorine demand.[31–33] Unsuccessful removal of H_2O_2 post UV–H_2O_2 advanced oxidation process (AOP) and consequent breakthrough of H_2O_2 residual to chlorination process would (a) compromise the final disinfection of water prior distribution and (b) lead to insufficient (ie, below regulation) chlorine residual within distribution system.

Granular activated carbon (GAC), which is a strong adsorbent and is used for removal of a wide range of contaminants via adsorption,[34] can also serve as a catalyst or catalyst support for H_2O_2 decomposition.[31,35,36] Successful H_2O_2 decomposition using GAC has been reported by previous publications.[36–39] Metz et al.[40] have reported that GAC can quench excess H_2O_2 while removing unexpected degradation products in drinking water treatment. Owing to the recent nature of this practice, prior operational experiences regarding H_2O_2 removal using GAC are limited.[31,36] Furthermore, the H_2O_2 quenching impact on GAC capacity to further remove T&O compounds from water is unknown. This becomes a pertinent question for utilities where H_2O_2 is not dosed continuously throughout the year, and the T&O episodes have been documented in so-called off-season, ie, nonbloom season.

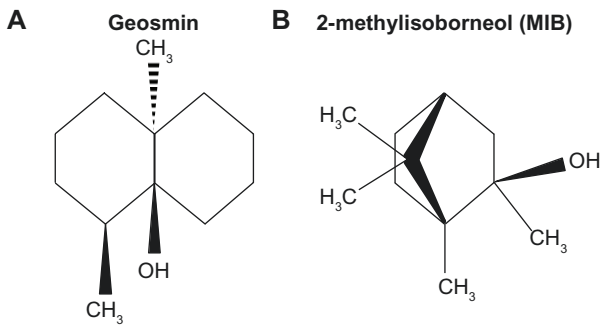

Figure 1. Chemical structure of (**A**) geosmin and (**B**) MIB.[21,22]

Water utilities need to learn about the impact of H_2O_2 on GAC capacity to remove T&O and support biofilm, post quenching period. Hence, the objective of this study is to assess the impact of H_2O_2 removal post UV–H_2O_2 advanced oxidation and aging processes (with and without advanced oxidation prior to GAC) on GAC capacity for the removal of T&O compounds associated with cyanobacterial blooms.

Material and Methods

Pilot-scale GAC column testing in Canada. Multibarrier treatment system in a water treatment plant (WTP) in southern Ontario, Canada, includes the use of UV–H_2O_2 as an advanced oxidation treatment for T&O control (Fig. 2). The studied Canadian WTP is using GAC contactor to quench the residual H_2O_2 (Fig. 2). This pilot study was conducted to verify the performance of virgin and aged GAC (from quenching H_2O_2) at different depths for the removal of geosmin and MIB. Figure 3 demonstrates the schematic representation and the complete installation of the pilot setup that was installed in the studied Canadian WTP. The conditions of the columns are presented in Table 1.

The GACs were selected based on the material (Table 2) used for their preparation and also the current application of a particular type at the studied Canadian WTP. The characteristics of all GAC types are presented in Table 2. Treatment at the Canadian WTP (Fig. 2) comprised prechlorination in water temperatures >12 °C, ultrafiltration (UF), UV disinfection, injection of H_2O_2 during the algal bloom season (September to November), adsorption on GAC, and postchlorination. The plant draws water from the Canadian side of Lake Ontario, with average total organic carbon of 2.5 mg-C/L and 8.0 pH. There was negligible chlorine remaining by the time the water was directed onto the GAC pilot setup. The GAC contactors had been in service for approximately 1 year (130,000 bed volumes) and 2 years (260,000 bed volumes). The contactors had only been exposed to H_2O_2 on one occasion from September 2012 to November 2012 (approximately 32,000 bed volumes) with an average concentration of 4 mg/L H_2O_2 during that period. Therefore, the pilot GAC columns were aged using 4 mg/L of H_2O_2 for 3 and 6 months, 33,000 and 65,000 bed volumes, respectively.

An array of 16 pilot-scale glass columns containing virgin GACs was used for this test (Fig. 3). The 16 columns allowed for the testing of the GAC in duplicate. The columns were each 2.5 cm in diameter and 128 cm in depth to simulate the GAC depth of the full-scale plant. Quality control tests confirmed that such a diameter led to perfect plug flow conditions with no short-circuiting as a result of wall effects.

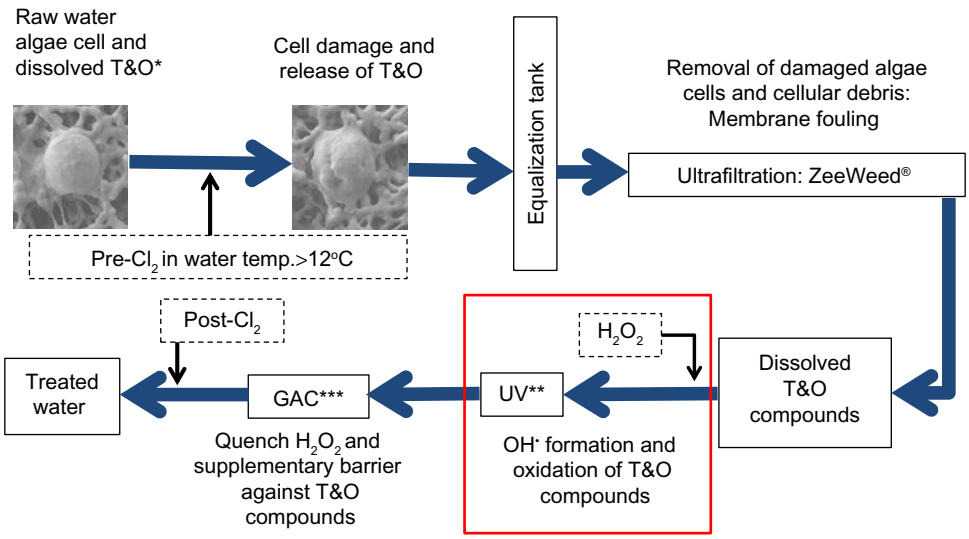

Figure 2. Schematic representation of a UF and advanced oxidation plant in Ontario, Canada, and fate of algal cells and their by-products during the treatment: red square highlights the UV–H_2O_2 process that causes the residual H_2O_2 in the water post-AOP
Notes: *T&O, T&O compounds; **UV, ultraviolet advanced oxidation; and ***GAC, granular activated carbon.

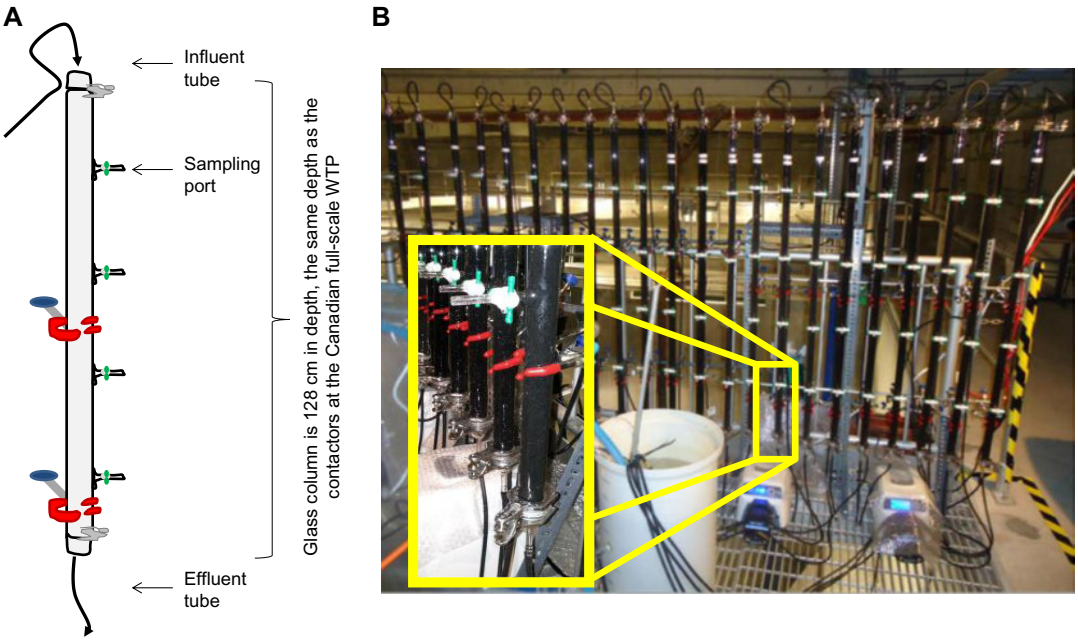

Figure 3. Pilot setup at the Canadian plant: (**A**) schematic representation of the GAC columns and (**B**) general view of the fully built functional pilot and details of the sampling ports.

Table 1. Filter column conditions: pilot-scale (Canada) and laboratory-scale (Australia) parameters.

COLUMN CONDITIONS	PILOT-SCALE (CANADA) PARAMETERS	LABORATORY-SCALE (AUSTRALIA) PARAMETERS
Column internal diameter	2.5 cm	2.5 cm
Filter medium bed height	128 cm	15 cm
Empty bed contact time (EBCT)	4.1 min	15 min

Thus, these control tests confirmed that adsorption kinetics were consistent with the plug flow within the columns. Water obtained post UF membrane and prior to UV disinfection at the WTP was directed through pilot-scale GAC columns (Fig. 3) with empty bed contact time (EBCT) of 4.1 minutes (similar to the full-scale plant operational EBCT). Per each GAC type, two columns were aged using only the membrane permeate, and another two columns were aged using membrane permeate spiked with 4 mg/L of H_2O_2. The columns were run in a continuous downflow operation, with no

Table 2. Detailed characteristics of the GAC used.

TEST (COLUMN) LOCATION	MATERIAL	SUPPLIER, PRODUCT	PARTICLE SIZE (mm)	IODINE NO. (mg/g)	TCN NO.	APPARENT DENSITY (g/L)
Canada	Bituminous coal-based; catalytic	Calgon, Centaur	–	1044	7.8	530
Canada	Lignite coal-based; acid washed	HD3000	–	601	9.6	421
Canada	Coconut-based	TN5	–	861	7.1	599
Canada and Australia	Bituminous coal-based	Calgon, F300	0.8–1.0	847	5.5	501
Australia	GAC	Acticarb, GAC1000N	0.5–0.7	–	–	–

provision for backwash, as the quality of the UF membrane permeate feed led to no observable accumulation of head loss over the period of operation. At times 0 month (virgin), after 3 months, and 6 months of aging, the capacity of GACs to remove 100 ng/L of geosmin and MIB was evaluated (Table 3). At these predetermined time intervals (ie, 0, 3, and 6 months), the aging process was stopped, and membrane permeate was spiked with 100 ng/L of geosmin and MIB, which is the highest detected value in Lake Ontario, Canada. The geosmin and MIB containing membrane permeate were filtered through the columns for equivalent of 1-week bed volume. Geosmin and MIB concentrations were measured along the depth of the column (ie, inlet; 25 cm, 50 cm, 75 cm, and 100 cm; and outlet).

Laboratory-scale GAC column testing in Australia. Figure 4A shows the schematic representation of the column setup for the Australian trials (without advanced oxidation prior to GAC), and Figure 4B is a photograph of the columns in the laboratory at a WTP located in South Australia. Four laboratory-scale columns were set up and run at the Australian WTP, fed with water from the settled water ducts. The performance of two types of GAC for the removal of geosmin and

Table 3. Range (including analytical method bias) of concentrations used for spiking periods, T = 0, 3, and 6 months, for geosmin and MIB.

METABOLITES	SET-UP	TIME 0 MONTHS (HIGH CONCENTRATION)	TIME 3 AND 6 MONTHS
MIB	Pilot (Canada)	100 n/L	100 ng/L (Duration 1 week)
	Laboratory (Australia)	50 ng/L	Week 1 (low concentration): 15 ng/L Week 2 (high concentration): 50 ng/L
Geosmin	Pilot (Canada)	100 ng/L	100 ng/L (Duration 1 week)
	Laboratory (Australia)	50 ng/L	Week 1 (low concentration): 15 ng/L Week 2 (high concentration): 50 ng/L

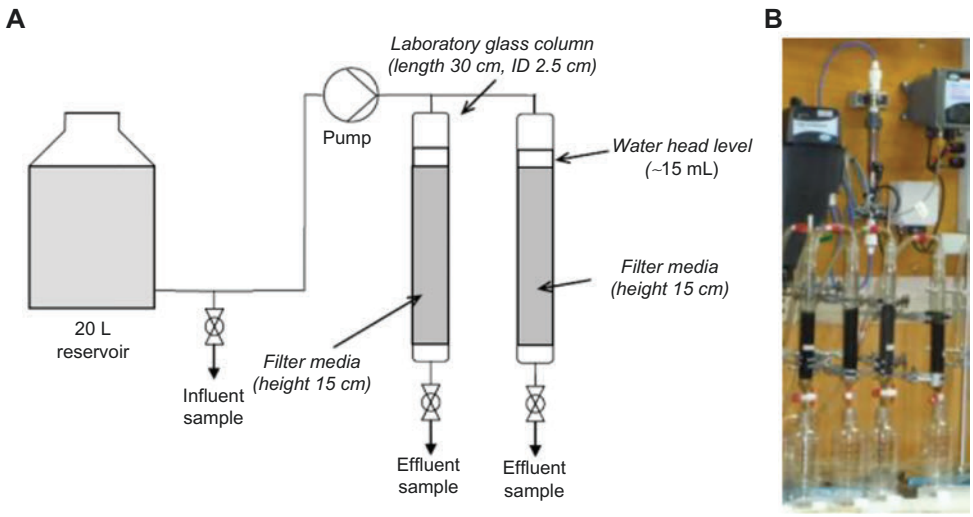

Figure 4. Laboratory setup at the Australian plant: (**A**) schematic representation of the columns and (**B**) general view of the functional columns.

MIB was verified using the laboratory-scale experiment over a period of 6 months. This setup provides the opportunity to conduct the test in duplicate. Column conditions and GAC details are presented in Tables 1 and 2, respectively. Spiking trials were conducted at 0, 3, and 6 months after commissioning to determine the removal of cyanobacterial metabolites. Two inlet concentrations of metabolites were used for the conducted trials. During the spiking trials, for 1–2 weeks, metabolites were dosed in continuously, and samples were collected from the influent and filtrate daily for analysis. The percent removal values and the mean removal values for each inlet concentration (errors associated: standard deviation) were calculated. Table 3 presents the target concentration for the spiking trials.

Cyanobacterial metabolite materials and water quality analysis. Geosmin and MIB were purchased from commercial suppliers (Novachem Pty Ltd. and Ultrafine Chemicals) and dissolved in ultrapure water (Millipore Pty Ltd.) to prepare a stock solution. Aliquots from the stock solution were then dosed into waters at the required target concentrations.

Samples for dissolved organic Carbon (DOC) and UV absorbance were filtered through 0.45 µm prerinsed (ultrapure water) membranes. DOC was measured using a Sievers 900 Total Organic Carbon Analyzer (GE Analytical Instruments). UV absorbance at 254 nm was measured through a 1 cm quartz cell using an Evolution 60 Spectrophotometer (Thermo Scientific).

All analyses were conducted in triplicate for each sample. Bench-scale experiment samples for geosmin and MIB analyses were concentrated using a solid-phase micro extraction syringe fiber (Gerstel) and analyzed on a 7890A Gas Chromatograph System with 5975C VL Series Mass Selective Detector (Agilent Technologies) against quantified labeled internal standards (Ultrafine Chemicals). Full details of this method have been documented by Graham and Hayes.[41] The reporting limits for MIB and geosmin were 4 and 2 ng/L, respectively. Significant difference between the removals of T&O compounds using GAC exposed to different aging processes was statistically assessed.

Two methods were used to monitor the biological activity: (1) adenosine triphosphate (ATP) and (2) scanning electron microscopy (SEM). In Canada, total ATP (in nanogram/gram) is measured using a commercially available *deposit and surface analysis* (DSM™) test kit (Luminultra). In Australia, ATP was measured (in nanogram/gram) using a method outlined by McDowall.[42] Samples of the filter media were taken from the top of each column prior to and immediately after the spiking events.

For SEM analysis, samples of the filter media were taken before and after the 6-month laboratory- and pilot-scale trails. They were fixed for 1 hour using EM fixative (4% paraformaldehyde/1.25% glutaraldehyde in PBS, +4% sucrose, and pH 7.2), washed in buffer (Phosphate-buffered saline (PBS) and +4% sucrose), post-fixed with 2% osmium tetroxide in water for 30 minutes, and then dehydrated with increasing ethanol solutions (70%, 90%, and 100%). Subsequently, the samples underwent critical point drying and were mounted on a stub and coated with carbon ready for analysis on a Field Emission Scanning Electron Microscope (FESEM). Samples of the virgin filter media were also mounted and coated ready for analysis. Photographs were obtained using a Philips XL30 FESEM.

Results and Discussions

Impact of advanced UV–H_2O_2 oxidation and H_2O_2 residual quenching on GAC capacity to remove T&O compounds. AOP used in the studied Canadian WTP (Fig. 2) includes H_2O_2 dosage prior to UV oxidation to generate very strong $OH^{\bullet}$ radical oxidant.[43,44] The elementary reaction in the UV–H_2O_2 advanced oxidation system is as follows (Equation 1):

$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \quad (1)$$

where hv is the UV irradiation.

In this plant, GAC contactors are used to remove the residual H_2O_2 post AOP from water prior to chlorination. Previous publications[31,36] have demonstrated that for all types of GAC (Table 2) used in this study, the H_2O_2 quenching rate decreased significantly up to 25,000 bed volumes and then stabilized to a constant rate (±5 variation) for over 2 years of operation. These results are in accordance with the performance of GAC in 3 full-scale plants in North America and Europe to remove H_2O_2 for over 6 years without media replacement.[31]

During the operation of the Canadian plant, H_2O_2 is only dosed during the bloom season (September to November). Therefore, the AOP is only available during this time period as a strong oxidation barrier against T&O compounds in water. For the rest of the operational time, adsorption on GAC is the only treatment process for the removal of these compounds. The pilot study was used to study the impact of H_2O_2 quenching on GAC capacity to adsorb geosmin and MIB to ensure the efficiency of available treatment barriers at all times. For geosmin treatment, 25–50 cm of virgin GACs were sufficient for the removal of 100 ng/L to below detection limit, which is 2 ng/L (Fig. 5). However, after 3 months of quenching 4 mg/L of H_2O_2 with an EBCT of 4.1 minutes, the entire 128-cm column depth was required to remove >93% of the geosmin. No significant difference was observed between the geosmin removal capacity of columns with (Fig. 5) and without (data not shown) H_2O_2 quenching.

All GAC types and ages, even virgin GAC, were less efficient for the removal of MIB compared to geosmin. Furthermore, after 3 months of pilot operation, MIB centration in column permeates reached >10 ng/L. However, similar to geosmin removal, the GAC capacities for MIB removal were not significantly affected by the H_2O_2 quenching, as similar removal values were observed with (Fig. 6) and without (data not shown) H_2O_2 quenching. Ndiongue et al.[45] demonstrated

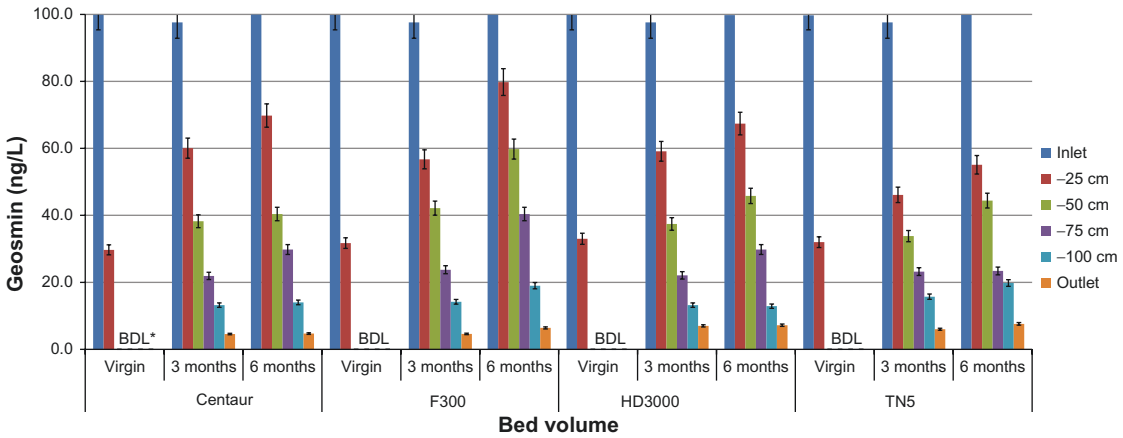

Figure 5. Geosmin removal using virgin carbon, and after 3 and 6 months of H_2O_2 quenching. Similar geosmin concentrations were measured in water samples from columns (at all depths) without H_2O_2 quenching (data not shown).
Note: *BDL, below detection limit.

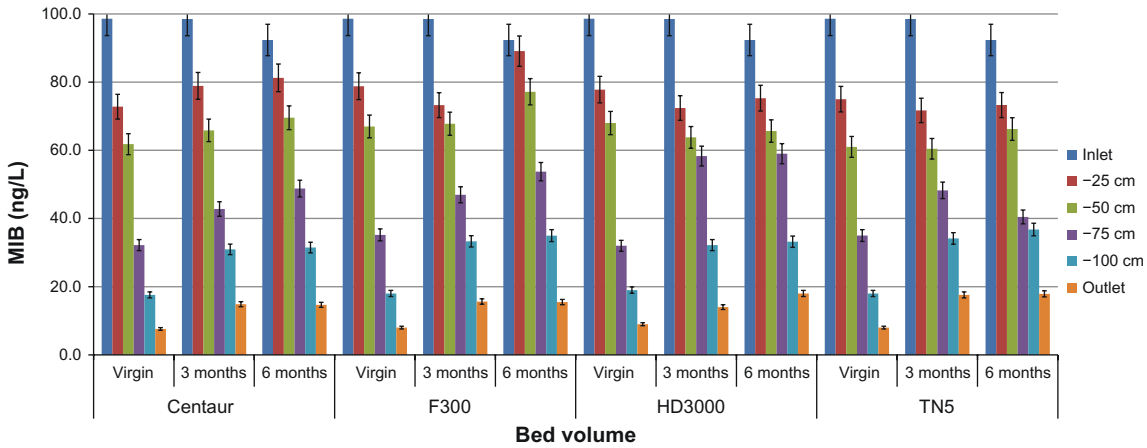

Figure 6. MIB removal using virgin carbon, and after 3 and 6 months of H_2O_2 quenching. Similar MIB concentrations were measured in water samples from columns (at all depths) without H_2O_2 quenching (data not shown).

that an increase in GAC depth or EBCT would significantly improve the removal of geosmin and MIB from water. Furthermore, other studies have also observed better (minimum 13%) geosmin removal compared to MIB removal by GAC.[46,47]

All four types of GAC provided similar performance for the removal of geosmin with and without advanced oxidation (Fig. 5). Centaur and F300 provided the best MIB removal in both the absence and presence of H_2O_2 quenching aging process (Fig. 6). Independent of the GAC type, the top 25 cm of GAC was the most effective for the removal of geosmin (Fig. 5). In the meantime, the top 75 cm of GAC removed the greatest percentage of MIB (Fig. 6).

While biofilm formation covers the adsorbent surface of carbon, the biological activity of microorganisms could lead to biodegradation of T&O compounds.[48–51] SEM is a qualitative method that can be used to investigate the existence and composition of a biofilm on filter media. Although SEM does not allow the identification of individual organisms, it can be used to show the abundance and diversity of organisms within the biofilm. SEM analysis provides the opportunity for visual observation of GAC surface during AOPs and adsorption experiences (Fig. 7). SEM images from the Canadian pilot study for six virgin GACs and six GAC aged with membrane permeate and H_2O_2 after 33,000 bed volumes are shown in Figures 7A–7H. These SEMs demonstrate that a significant biomass has accumulated during the trials. The observation of biofilm formation on GAC surface after aging was also reported in the study by Yu et al.[34]

The biofilms are composed of a variety of organisms, including bacteria, protozoa, fungi, and diatoms, and it is held together by extracellular polymeric material. It is not possible to identify individual microorganisms with analytical methods used in this study, and so no differences can be established between the different GAC types. However, it is clear that abundance and diversity of microorganisms exist within the thriving biofilms. The level of biological activity of

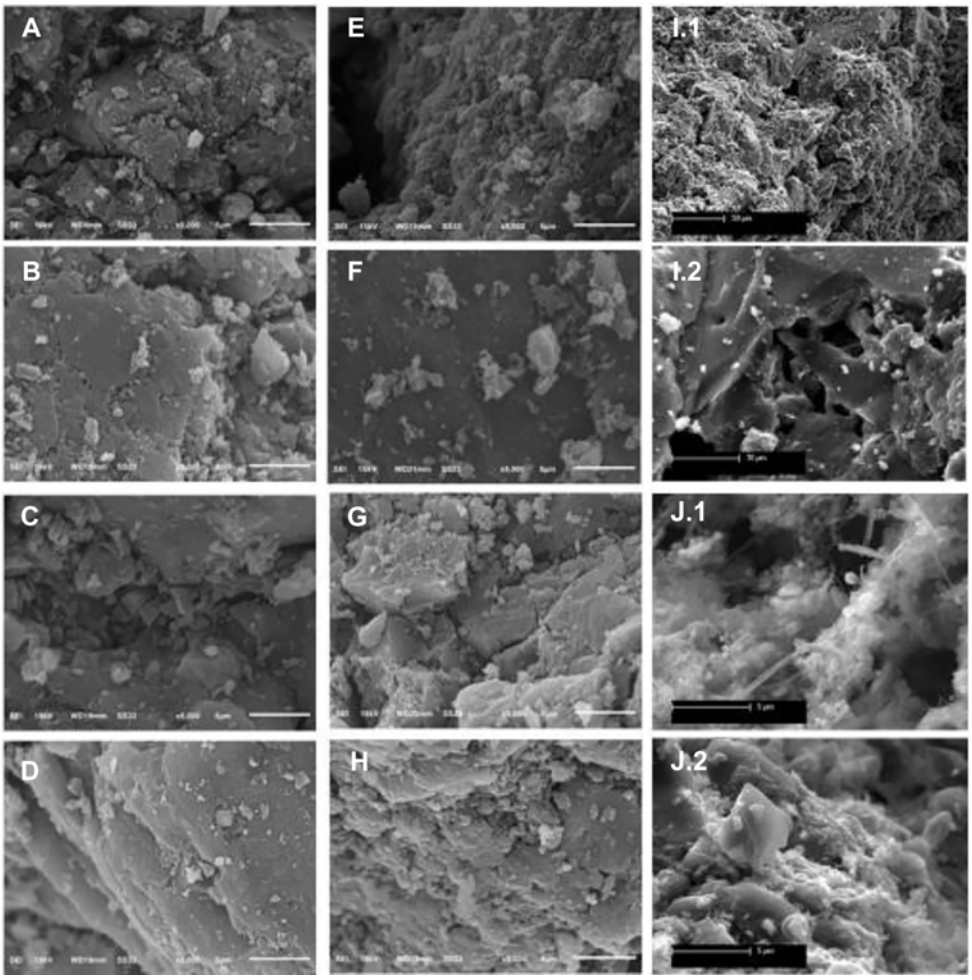

Figure 7. SEM data: Centaur (**A**) virgin, and (**B**) aged with NOM at 45,000 bed volumes; F300 (**C**) virgin, and (**D**) aged with NOM at 33,000 bed volumes; HD3000 (**E**) virgin, and (**F**) aged with NOM at 33,000 bed volumes; TN5 (**G**) virgin, and (**H**) aged with NOM at 33,000 bed volumes (Figs. 7A to 7H scale is 5 μm); AND GA1000N (AWQC) particle size 0.5–0.7 mm diameter (**I**) virgin (Fig. 7.I.1 scale is 50 μm and Fig. 7.I.2 scale is 10 μm), and (**J**) 6 months after commissioning (Figs. 7.j.1 and 7.j.2 are taken from different angels at 5 μm scale).

the established biofilm would determine the potential for the biodegradation of T&O compounds. ATP is present in all active microorganisms; therefore, ATP concentrations can be used as a measure of biological activity and an indicator for the presence of an active biofilm on filter media. Samples of the filter media were taken prior to the spiking trials and directly after collecting the final effluent from the spiking trial to look at the impact of the spiked settled water on the biological activity of the filter media. GAC appeared to have negligible ATP activity before and after the spiking trials.

GAC capacity to remove T&O compounds in the absence of advanced oxidation barriers. To compare the geosmin and MIB removal with GAC depth with and without advanced oxidation, the results from the Canadian study were compared to the laboratory-based column study conducted in Australia. H_2O_2 removal on GAC was not the focus of the study conducted in Australia. In all Australian assays, geosmin was removed to below detection limit (data not shown). Figure 8 demonstrates that for MIB removal, the F300 GAC was performed as well as the GA1000N over the trial period. An application of analysis of variance ($P > 0.1$) to the GAC data showed that there was no significant decrease in the removal by the GAC over the trial period. As for the percent removals for the two inlet concentrations (low and high), similar results were obtained for GAC aged for 3 and 6 months.

The results for the duplicate columns over 6 months demonstrate good (<7% error) reproducibility of the column data over the trial. GAC was very effective for the removal of MIB and geosmin over the trial period with an average of 98% and 100% removal, respectively. This result supports the previous work by Ho,[48] who investigated the removal of MIB and geosmin by GAC at the laboratory and pilot scales. Such high removals had been shown previously to be attributable to physical adsorption only[50,51]; however, as the removal values were high throughout the test period, it was not possible to differentiate between physical adsorption and biological degradation in this study.

Figures 7I and 7J show SEM images of the initial GAC media as new, prior to the column trials and after 6 months in contact with settled water from the Australian WTP.

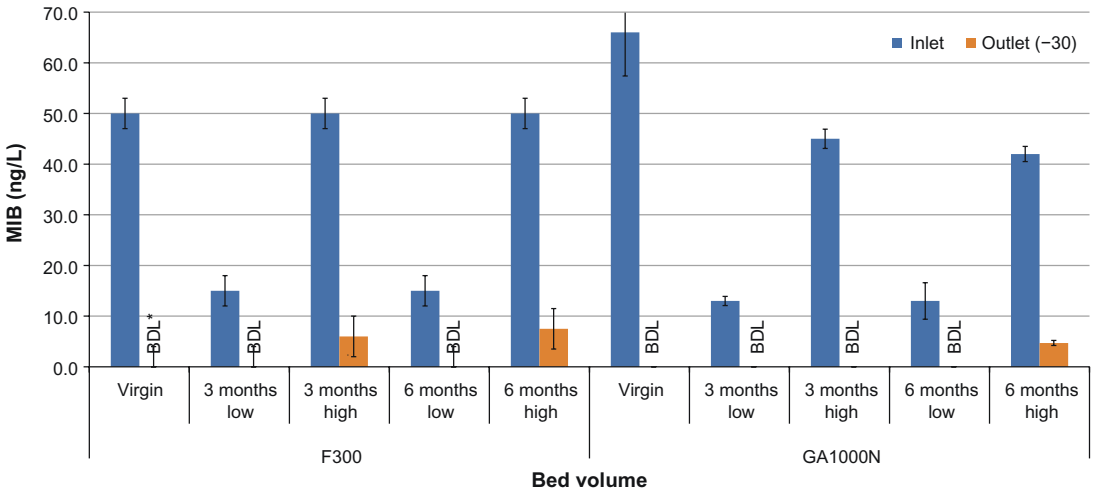

Figure 8. MIB removal by two types of GAC during the Australian experiment.
Note: *BDL, below detection limit.

However, similar to the Canadian pilot study, no significant biological activity was recorded. This result was unexpected, based on previous publications.[52] GAC surface is known to promote significant biofilm growth within 4–6 weeks of filter commissioning.[53] The low value of ATP on the GAC suggested that the adsorbent interfered in some way with the ATP analysis. These results suggest that no biological removal had occurred.

This study has focused on the fate of dissolved geosmin and MIB during advanced oxidation and adsorption and/or biodegradation by GAC. The multibarrier treatment systems that are in use in the studied conditions (Fig. 2) prior to GAC contactors reduce significantly the risk of breakthrough of intact cells and intracellular T&O compounds. However, plants with conventional treatment barriers, which are coagulation–clarification and filtration, are vulnerable to breakthrough of intact cells and intracellular and dissolved compounds.[4,14,28,54–56] The removal of cell-bound compound within intact cells is the preferred situation for conventional treatment plants, while plants equipped with advanced oxidation and/or adsorption barriers would be able to handle the presence of dissolved compounds.

However, recent publications[14,57] have demonstrated that breakthrough of cells and their intracellular compounds, even at plants with low risk of cyanobacterial presence at their source, is a major challenge. Also, lysis of accumulated cells within sludge bed or filter media[20,57,58] and release of geosmin and MIB prior to chlorination in the absence of strong oxidant agents (eg, O_3) would lead to breakthrough of these compounds into the potable water. Hence, the intra/extracellular ratio of geosmin and MIB is a key factor for their successful removal and optimization of treatment processes.[25] Several factors, including bloom age, producers present, water quality conditions and available nutrients, and geographical location, could influence the ratio of intra/extracellular compounds.[19,21–23] Table 4 provides a useful summary of existing knowledge about the removal of cyanobacterial T&O compounds by conventional and advanced treatment barriers. However, this ratio and the factor that would influence its variations and the impact of these variations on conventional and advanced full-scale treatment barriers require further investigation.

Conclusion

The results of this study demonstrate that H_2O_2 quenching for the operational period of 6 months has no significant impact on GAC capacity to remove geosmin and MIB from water. Furthermore, type of T&O compounds, concentration of compounds, ratio of intra/extracellular compound, producer species present and duration of bloom season, GAC type, EBCT, and other operational practices are the factors that influence GAC capacity to remove the studied T&O compounds.

During the trial period, all filtration media developed significant biomass. However, there was no evidence of the onset of biological degradation of the cyanobacterial metabolites for any of the GAC types. Measurement of biofilm activity was a limiting factor within this study. Formation and maintenance of an active biofilm is a challenge during the operation of biologically active water treatment processes. The development of rapid methods to monitor the biofilm formation and level of activity would provide the utilities with the essential operational information. The impact of biofilm formation on GAC and its capacity for the removal of H_2O_2 and T&O compounds require further investigation. These results demonstrate the benefits of multibarrier treatment approaches for the removal of emerging cyanobacterial harmful metabolites. However, further investigation would be required to investigate the efficiency of the studied treatment processes for the removal of these metabolites within the context of climate change

Table 4. Treatment processes for the removal of cyanobacterial cells and cell-bound T&O compounds.[1,4,10,20,21,23,28–31,46–50,56,57,59,60]

TREATMENT PROCESS	TREATMENT EFFICIENCY
Oxidation processes	The efficiency of pre-oxidation depends on cell number, species present, type of T&O compounds, compounds concentration, oxidant type and dose, and contact time. Pre-oxidation induce cell membrane damage and/or lysis and consequent increase in dissolved taste and odor compound levels and disinfection by products formation. If applied under controlled situation it might be efficient; pre-oxidation of cells will prevent process disturbances in drinking water treatment plants due to presence of cyanobacteria cells. The natural organic matters in water influence the dose of oxidant agent.
Ozonation	Ozonation is effective for removal of all cells and both geosmin and MIB.
Chlorination Chloramination Chlorine dioxide Potassium permanganate Hydrogen peroxide	Not effective for oxidation of geosmin and MIB. Direct oxidation of cyanobacterial cells would cause release of cell-bound T&O compounds which needed to be removed.
UV Radiation	Induce cell membrane damage and T&O compounds release. However oxidation occurs at impractically high doses or in the presence of a catalyst.
Advanced oxidation processes (AOP)	UV-H_2O_2 or UV-O_3 advanced oxidation processes which lead to generation of $OH^{\bullet}$ are very effective for removal of these T&O compounds. However, processes by products, for example H_2O_2 residual, have to be removed from water.
Adsorption – Powder Activated Carbon (PAC)	Has no documented impact on cell viability or their removal. Efficient for removal of dissolved T&O compounds. The type of PAC, dose of PAC, water quality (including pH and NOM), type of present compounds, and intra/extra cellular ratio plays an important role in their removal by PAC.
Adsorption – Granular Activated Carbon (GAC)	Physical removal of cyanobacteria cells during filtration and simultaneous removal of cell-bound compounds within intact cells. Very effective for adsorption of dissolved compounds based on the type of GAC. However, GAC adsorption of release compounds displays a limited lifetime depending on the compound and the water quality.
Biological filtration	Once the biofilm is established and the process is functioning at the optimum, it can be very effective for the removal of intact cells and T&O compounds. However, factors affecting the removal such as biofilm mass and composition, acclimation periods, temperature and water quality cannot be easily controlled.

scenarios, significantly higher cell numbers, frequent bloom events, higher metabolites concentrations, and varying intra/extracellular ratio.

Acknowledgments

The authors would like to express their gratitude to (a) Jinghong (Elena) Li and Sarah Jane Payne, (b) Jane Bonsteel, Jeff Hennings, and Andrew Farr from Region of Peel (Canada), (c) Sheldon Belbin and Dean Baker from Ontario Clean Water Agency (Canada), (d) Daniel Hoefel, Benoit Lorain, Melanie Vache, Mike Dixon, Najwa Slyman, Martin Harris, Jennifer Dreyfus, and Tim Tang from SA Water (Australia), and (e) operators of the WTP in South Australia which hosted the pilot setup for their invaluable help with this work.

Author Contributions

Conceived and designed the experiments: AZ, ES, LH, GN, RH. Analyzed the data: AZ, ES, LH, GN, RH. Wrote the first draft of the manuscript: AZ. Contributed to the writing of the manuscript: AZ, ES, LH, GN, RH. Agree with manuscript results and conclusions: AZ, ES, LH, GN, RH. Jointly developed the structure and arguments for the paper: AZ, ES, LH, GN, RH. All authors reviewed and approved of the final manuscript.

REFERENCES

1. Chorus I, Bartram J. *Toxic Cyanobacteria in Water: A Guide to Their Public Health Consequences, Monitoring and Management*. Routledge, London: World Health Organization/E&FN Spon; 1999.
2. Agence Française de Sécurité Sanitaire des Aliments (AFSSA), Agence Française de Sécurité Sanitaire de l'Environnement et du Travail (AFSSET). Avis de relatif à l'évaluation des risques liés à la présence de cyanobactéries dans les cours d'eau destinés à la baignade et/ou à d'autres usages. AFSSA-AFSSET, France; 2006: 32.
3. Boerlage S, Nada N. Algal toxin removal in seawater desalination processes. *Desalin Water Treat*. 2014;54:1–19.
4. Zamyadi A. *The value of in vivo monitoring and chlorination for the control of toxic cyanobacteria in drinking water production* [PhD dissertation]. Department of Civil, Geological and Mining Engineering, École Polytechnique de Montréal, Montreal, Quebec, Canada; 2011.
5. Davis TW, Berry DL, Boyer GL, Gobler CJ. The effects of temperature and nutrients on the growth and dynamics of toxin and non-toxic strains of Microcystis during cyanobacteria blooms. *Harmful Algae*. 2009;8(5):715–25.
6. Paerl HW, Huisman J. Climate: blooms like it hot. *Science*. 2008;320:57–8.
7. Paerl HW, Hall NS, Calandrino ES. Controlling harmful cyanobacterial blooms in a world experiencing anthropogenic and climatic-induced change. *Sci Total Environ*. 2011;409(10):1739–45.
8. Giani A, Bird DF, Prairie YT, Lawrence JF. Empirical study of cyanobacterial toxicity along a trophic gradient of lakes. *Can J Fish Aquat Sci*. 2005;62(9):2100–9.
9. Zamyadi A, Gallichand J, Duchemin M. Comparison of methods for estimating sediment and nitrogen loads from a small agrigultural watershed. *Can Biosystems Eng*. 2007;49:21–7.
10. Cooperative Research Centre for Water Quality and Treatment (Australia). *Cyanobacteria: Management and Implications for Water Quality*: 36. Adelaide, Australia; 2007.

11. Gregor J, Marsalek B, Sipkova H. Detection and estimation of potentially toxic cyanobacteria in raw water at the drinking water treatment plant by in vivo fluorescence method. *Water Res*. 2007;41:228–34.
12. Ndong M, Bird DF, Nguyen-Quang T, et al. Estimating the risk of cyanobacterial occurrence using an index integrating meteorological factors: application to drinking water production. *Water Res*. 2014;56:98–108.
13. Paerl HW, Paul VJ. Climate change: links to global expansion of harmful cyanobacteria. *Water Res*. 2012;46(5):1349–63.
14. Zamyadi A. Emerging toxic cyanobacterial issues in freshwater sources: influence of climate change. In: Botana LM, ed. *Seafood and Freshwater Toxins*: *Pharmacology*, *Physiology*, *and Detection*. 3rd ed. (Chap. 5). Florence: Taylor and Francis; 2014:105.
15. Fortin N, Munoz-Ramos V, Bird D, Levesque B, Whyte LG, Greer CW. Toxic cyanobacterial bloom triggers in Missisquoi Bay, Lake Champlain, as determined by next-generation sequencing and quantitative PCR. *Life*. 2015;5:1346–80.
16. Carmichael WW. Cyanobacteria secondary metabolites – the cyanotoxins. *J Appl Bacteriol*. 1992;72(6):445–59.
17. Carmichael WW. The toxins of cyanobacteria. *Sci Am*. 1994;270(1):78–86.
18. Fleming LE, Rivero C, Burns J, et al. Blue green algal (cyanobacterial) toxins, surface drinking water, and liver cancer in Florida. *Harmful Algae*. 2002;1(2):157–68.
19. Hobson P, Fazekas C, House J, et al. Tastes and odours in reservoirs – Research report 73. Water Quality Research Australia, Adelaide, Australia; 2010:96.
20. Zamyadi A, Dorner S, Sauvé S, et al. Species-dependence of cyanobacteria removal efficiency by different drinking water treatment processes. *Water Res*. 2013;47(8):1080–90.
21. Jüttner F, Watson SB. Biochemical and ecological control of geosmin and 2-methylisoborneol in source waters. *Appl Environ Microbiol*. 2007;73(14):4395–406.
22. Suurnakki S, Gomez-Saez GV, Rantala-Ylinen A, Jokela J, Fewer DP, Sivonen K. Identification of geosmin and 2-methylisoborneol in cyanobacteria and molecular detection methods for the producers of these compounds. *Water Res*. 2015;68:56–66.
23. Su M, Yu J, Zhang J, et al. MIB-producing cyanobacteria (*Planktothrix* sp.) in a drinking water reservoir: distribution and odor producing potential. *Water Res*. 2015;68:444–53.
24. Westerhoff P, Rodriguez-Hernandez M, Baker L, Sommerfeld M. Seasonal occurrence and degradation of 2-methylisoborneol in water supply reservoirs. *Water Res*. 2005;39:4899–912.
25. Durrer M, Zimmermann U, Juttner F. Dissolved and particle-bound geosmin in a mesotrophic lake (lake zuè rich): spatial and seasonal distribution and the effect of grazers. *Water Res*. 1999;33(17):3628–36.
26. Zamyadi A, Henderson R, Stuetz R, Prévost M, Ho L, Newcombe G. Assessment and management of aesthetic and health risks associated with cyanobacteria: case study report. Water Research Australia, Adelaide; 2015:26.
27. Carrière A, Prévost M, Zamyadi A, Chevalier P, Barbeau B. Vulnerability of Quebec drinking water treatment plants to cyanotoxins in a climate change context. *J Water Health*. 2010;8(3):455–65.
28. Newcombe G, House J, Ho L, Baker P, Burch M. Management Strategies for Cyanobacteria (Blue-Green Algae): A Guide for Water Utilities. Research Report No 74. Adelaide, SA, Australia; 2010.
29. Zamyadi A, Ho L, Newcombe G, et al. Release and oxidation of cell-bound saxitoxins during chlorination of *Anabaena circinalis* cells. *Env Sci Technol*. 2010; 44(23):9055–61.
30. Smith KM. Characterization of activated carbon for taste and odour control *[M.A.Sc. Thesis]*. University of Toronto, Canada; 2011: 136.
31. Li J. *Quenching H_2O_2 residuals after UV/H_2O_2 drinking water treatment using granular activated carbon* [Thesis for the degree of Masters of Applied Science]. Department of Civil Engineering, University of Toronto, Canada; 2013.
32. Dotson A, Corwin C, Rowley C, Downs M, Linden K. Dynamic Bench-scale quenching of H_2O_2 by GAC. In: Water Quality Technology Conference (WQTC), American Water Works Association (AWWA), Savannah, GA; 2010.
33. Dotson AD, Keen VS, Metz D, Linden KGUV. /H_2O_2 treatment of drinking water increases post-chlorination DBP formation. *Water Res*. 2010;44:3703–13.
34. Yu ZR, Peldszus S, Huck PM. Adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon. 1. Adsorption capacity and kinetics. *Env Sci Technol*. 2009;43:1467–73.
35. Collins J, Pirnie M, Cotton C, Jousset S, Dotson A, Linden K. *Evaluation of Hydrogen Peroxide Quenching Alternatives for AOP Treatment*. Savannah, GA: AWWA WQTC; 2010.
36. Zamyadi A, Li J, Bonsteel J, Hofmann R. *Quenching H_2O_2 Residuals After UV/H_2O_2 Drinking Water Treatment Using Granular Activated Carbon*. Long Beach: AWWA WQTC; 2013.
37. Huang HH, Lu MC, Chen JN, Lee CT. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. *Chemosphere*. 2003;51:935–43.
38. Huang HH, Lu MC, Chen JN, Lee CT. Influence of surface modification on catalytic activity of activated carbon toward decomposition of hydrogen peroxide and 2-chlorophenol. *J Environ Sci Health A Tox Hazard Subst Environ Eng*. 2003;38(7):1233–46.
39. Rey A, Zazo JA, Casas JA, Bahamonde A, Rodriguez JJ. Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen peroxide. *Appl Catal A Gen*. 2011;402:146–55.
40. Metz DH, Reynolds K, Meyer M, Dionysiou DD. The effect of UV/H_2O_2 treatment on biofilm formation potential. *Water Res*. 2011;45:497–508.
41. Graham D. Hayes KP. Application of solid phase micro extraction for the analysis of off-flavours in water. In: Proceedings of the WaterTECH Conference, Brisbane, Australia; 1998.
42. McDowall B. *Removal of geosmin and 2-methylisoborneol from drinking water through biologically active sand filters* [PhD Dissertation]. Adelaide, Australia, University of Adelaide; 2008.
43. Crittenden JC, Hu S, Hand DW, Green SA. A kinetic model for H_2O_2/UV process in a completely mixed batch reactor. *Water Res*. 1999;33(10):2315.
44. Song W, Ravindran V, Pirbazari M. Process optimization using a kinetic model for the ultraviolet radiation-hydrogen peroxide decomposition of natural and synthetic organic compounds in groundwater. *Chem Eng Sci*. 2008;63:3249–70.
45. Ndiongue S, Anderson WB, Tadwalkar A, Rudnickas J, Lin M, Huck PM. Using pilot-scale investigations to estimate the remaining geosmin and MIB removal capacity of full-scale GAC-capped drinking water filters. *Water Qual Res J Can*. 2006;41(3):296–306.
46. Kim Y, Lee Y, Gee CS, Choi E. Treatment of taste and odour causing substances in drinking water. *Water Sci Technol*. 1997;35(80):29–36.
47. Ridal J, Brownlee B, McKenna G, Levac N. Removal of taste and odour compounds by conventional granular activated carbon filtration. *Water Qual Res J Can*. 2001;36(1):43–54.
48. Ho L. *The removal of cyanobacterial metabolites from drinking water using ozone and granular activated carbon* [PhD Dissertation]. Adelaide, Australia, University of South Australia; 2004.
49. Ho L, Hoefel D, Bock F, Saint CP, Newcombe G. Biodegradation rates of 2-methylisoborneol (MIB) and geosmin through sand filters and in bioreactors. *Chemosphere*. 2007;66(11):2210–8.
50. Ho L, Newcombe G. Granular activated carbon adsorption of 2-methylisoborneol (MIB): pilot- and laboratory-scale evaluations. *J Environ Eng*. 2010;136(9):965–74.
51. Herzing DR, Snoeyink VL, Wood NF. Activated carbon adsorption of the odorous compounds 2-methylisoborneol and geosmin. *J Am Water Works Assoc*. 1977;69(4):223–8.
52. Velten S, Hammes F, Boller M, Egli T. Rapid and direct estimation of active biomass on granular activated carbon through adenosine tri-phosphate (ATP) determination. *Water Res*. 2007;41(9):1973–83.
53. Newcombe G. *Removal of Algal Toxins Using Ozone and GAC*. Denver, CO: American Water Works Association; 2002.
54. Jung SW, Baek KH, Yu MJ. Treatment of taste and odor material by oxidation and adsorption. *Water Sci Technol*. 2004;49(9):289–95.
55. Persson F, Heinicke G, Hedberg T, Hermansson M, Uhl W. Removal of geosmin and MIB by biofiltration – an investigation discriminating between adsorption and biodegradation. *Environ Technol*. 2007;28(1):95–104.
56. Srinivasan R, Sorial GA. Treatment of taste and odor causing compounds 2-methylisoborneol and geosmin in drinking water: a critical review. *J Environ Sci*. 2011;23(1):1–13.
57. Zamyadi A, MacLeod SL, Fan Y, et al. Toxic cyanobacterial breakthrough and accumulation in a drinking water plant: a monitoring and treatment challenge. *Water Res*. 2012;46(5):1511–23.
58. Zamyadi A, Dorner S, Ndong M, et al. Low-risk cyanobacterial bloom sources: cell accumulation within full-scale treatment plants. *J Am Water Works Assoc*. 2013;105(11):E651–63.
59. Zamyadi A, Hennings J, Bonsteel J, Belbin S, Hofmann R. Emerging operational challenges in ultrafiltration treatment plants: algal compounds removal and membrane fouling. In: 7th IWA Specialised Membrane Technology Conference and Exhibition, Toronto, Ontario, Canada; 2013.
60. Ho L, Dreyfus J, Boyer J, et al. Fate of cyanobacteria and their metabolites during water treatment sludge management processes. *Sci Total Environ*. 2012;424:232–8.