Removal of geosmin and 2-methylisoborneol by biological filtration

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Abstract The quality of drinking water is sometimes diminished by the presence of certain compounds that can impart particular tastes or odours. One of the most common and problematic types of taste and odour is the earthy/musty odour produced by geosmin (trans-1, 10-dimethyl-trans-9-decalol) and MIB (2-methylisoborneol). Taste and odour treatment processes including powdered activated carbon, and oxidation using chlorine, chloramines, potassium permanganate, and sometimes even ozone are largely ineffective for reducing these compounds to below their odour threshold concentration levels. Ozonation followed by biological filtration, however, has the potential to provide effective treatment. Ozone provides partial removal of geosmin and MIB but also creates other compounds more amenable to biodegradation and potentially undesirable biological instability. Subsequent biofiltration can remove residual geosmin and MIB in addition to removing these other biodegradable compounds. Bench scale experiments were conducted using two parallel filter columns containing fresh and exhausted granular activated carbon (GAC) media and sand. Source water consisted of dechlorinated tap water to which geosmin and MIB were added, as well as, a cocktail of easily biodegradable organic matter (i.e. typical ozonation by-products) in order to simulate water that had been subjected to ozonation prior to filtration. Using fresh GAC, total removals of geosmin ranged from 76 to 100% and total MIB removals ranged from 47% to 100%. The exhausted GAC initially removed less geosmin and MIB but removals increased over time. Overall the results of these experiments are encouraging for the use of biofiltration following ozonation as a means of geosmin and MIB removal. These results provide important information with respect to the role biofilters play during their startup phase in the reduction of these particular compounds. In addition, the results demonstrate the potential biofilters have in responding to transient geosmin and MIB episodes.

Keywords Biological filtration; geosmin; granular activated carbon; MIB; odour threshold; ozone

Introduction
The presence of taste and odour in potable water supplies is an increasingly frequent problem that water utilities face. These problems are recognized worldwide and have been identified in countries such as Japan (Ishida and Miyaji, 1992), Australia (Bowmer et al., 1992), and the United States (Vogel et al., 1997). Approximately forty-three per cent of water treatment utilities in North America reported intense earthy/musty tastes and odour events lasting at least one week (Suffet et al., 1996). Utilities, therefore, may spend a significant part of their budget on taste and odour control. The most commonly identified and problematic taste and odour causing compounds are geosmin (trans-1, 10-dimethyl-trans-9-decalol) and MIB (2-methylisoborneol). Geosmin and MIB are linked to blooms of cyanobacteria and a class of bacteria known as actinomycetes and are primarily responsible for the earthy/musty odour of finished water. They are a major concern for the water treatment industry because they are detectable by the human nose at extremely low concentration levels (i.e. as low as 4 and 9 ng/L for geosmin and MIB, respectively). Powdered activated carbon (PAC) and oxidation are common methods used to remove/ degrade target compounds in drinking water. However, PAC and oxidants such as chlorine, chloramines, potassium permanganate, and occasionally ozone have shown limited success in treatment
of waters containing geosmin and MIB (Lalezary et al., 1986; Hrudey et al., 1995). Fortunately, ozonation followed by biofiltration offers the potential to provide a particularly well-suited combination to treat taste and odour problems caused by geosmin and MIB. Ozonation alone can at least partially destroy geosmin and MIB with removals being dependent on transferred ozone dose and water characteristics (e.g. availability of OH radical precursors). Biofiltration following ozonation has the potential to further significantly reduce the concentration of these highly degradable ozonation products. Additionally, higher biological compounds formed by ozonated water will increase biomass in the filter and thereby enhance the biofilter’s ability to degrade the residual geosmin and MIB as well as reducing the biological instability (Dewaters and DiGiano, 1990; LeChevallier et al., 1992; Rittmann, 1995).

This paper reports on initial investigations on the removal efficiencies of geosmin and MIB by biological filtration and compares fresh granular activated carbon (GAC)/sand and exhausted GAC/sand media. The GAC media was exhausted in terms of total organic carbon (TOC) removal. To simulate the effect on a biofilter of upstream ozonation, typical ozonation by-products were fed to the filters along with the target odour compounds.

Methods
Bench-scale experiments were performed using two 2.0 m high glass GAC/sand filters operated in parallel. Fresh GAC and exhausted GAC were used in these experiments and the GAC layer depth was 50 cm. The effective size of the GAC media was 0.8 mm for fresh GAC and 0.72 mm for exhausted GAC. The sand layer in both columns was 25 cm in depth with an effective size of 0.5 mm. The internal diameter of the columns was 50 mm. The GAC column walls were covered with black insulation material in order to prevent the growth of phototrophic organisms, and to minimize water temperature fluctuations in the filters. Four glass prefilter GAC columns were also used for the dechlorination of the source tap water (Kontes Chromaflex™, Vineland, NJ; ID = 4.8 cm, Length = 60 cm). The GAC media (P-830, PICA USA Inc., Columbus, Ohio) in the GAC filters and in the prefilter GAC columns was exhausted in terms of TOC removal because it had been in use in a full-scale filter for over five years. The hydraulic loading rate (HLR) within the filter was measured and controlled using a pre-calibrated flow meter (Gilmore® Instruments, Barrington, IL), with a valve on the effluent line. The HLR was maintained at a constant rate of 7.5 m/hr, corresponding to a total empty bed contact time (EBCT) of 5.6 minutes, excluding the gravel support layer.

The filter influent was dechlorinated tap water to which concentrated solutions of target-ed BOM components, nutrients and odour compounds were added, as described in the following sections.

Tap water
The tap water used as feedwater to the filters was from local surface water and/or ground-water, which is low in organics and high in alkalinity and hardness. Some typical water quality parameters include: pH: 7.4–7.5; alkalinity: 300–325 mg/L as CaCO₃; hardness: 325–350 mg/L as CaCO₃; total organic carbon (TOC): 1.0–1.1 mg/L; conductivity: 625–725 µS; and temperature: 12–16°C. Conductivity and chlorine residual were monitored daily to document changes in the groundwater/surface water contributions to the tap water. In addition, TOC was monitored weekly to document background organic levels in the water and to determine amounts being removed by the GAC filters and the GAC prefilter columns. Very little background TOC was removed by the prefilter GAC columns as the GAC media was exhausted for TOC removal. Therefore, TOC concentrations entering each GAC filter were relatively consistent throughout the study.
The choice of BOM target components was based on ozonation by-products, because ozonation and biofiltration are closely related processes. Four typical ozonation products chosen as the targeted BOM components in previous bench-scale biofiltration experimental programs (Urfer, 1998; Liu, 2001) were used in this research. For the aldehyde component, formaldehyde and glyoxal were chosen, as relatively easily biodegradable and less readily biodegradable aldehydes, respectively (Krasner et al., 1993; Urfer, 1998). For the carboxylic acid component, formate and acetate were chosen, because they appear to be formed in the largest yield upon ozonation (Gagnon et al., 1997), together with oxalate. The same targeted BOM components and concentrations as were used previously in this laboratory were adopted in this research. The targeted concentrations of the BOM components in the filter influent were: formaldehyde 100 µg/L; glyoxal 30 µg/L; formate 400 µg/L and acetate 300 µg/L. Those concentrations are in the high range of what is usually observed following ozonation (Glaze and Weinberg, 1993; Griffini and Iozzelli, 1996; Gagnon et al., 1997).

Nutrients
A typical empirical formula for a bacterial cell, C_{55}H_{77}O_{22}N_{11}P_2 (Metcalf and Eddy, 1991), indicates a C:N:P ratio of 21:5:1 (w/w/w). Urfer (1998) chose a C:N:P ratio of 15:5:1 (w/w/w) to guarantee that the organic carbon was the limiting nutrient. The same C:N:P ratio was used in this study. Sodium nitrate (NaNO₃) and potassium phosphate (K₂HPO₄) were used as the sources of nitrogen and phosphorus, respectively.

Odour compounds
Target concentrations of 100 ng/L for both geosmin and MIB were introduced into each of the filter influents. These concentrations were in the higher range of what is typically seen in nature to investigate a worst case scenario. The filter columns were spiked with the odour compounds on day 1 of the experiment and were fed on a continual basis for 13 days. After such time, a resting period of 3 weeks was conducted in which the geosmin and MIB feed was discontinued and the columns were fed with BOM and nutrients only. The columns were then spiked again with the odour compounds for an additional 11 days. Finally, an additional resting period of 3 days was provided, after which the columns were spiked with geosmin and MIB for 5 days. This experimental design helps to establish the response of the filters to periodic odour events, and the impact of prior exposure to these compounds. Samples for geosmin and MIB were typically drawn every second day during feeding of these compounds. Sampling was conducted at seven sampling ports for each column. Samples were taken at the filter influent, the filter effluent and at five other sampling ports located below the top surface of the media at depths of 10, 25, 40, 55, and 70 cm.

Solid phase microextraction – gas chromatography – mass spectrometry analyses
Gas chromatography-mass spectrometry (GC-MS) was used in combination with solid phase microextraction (SPME) for analysis of geosmin and MIB in water. The method is based on that described by Watson et al. (2000). Headspace SPME was used. An internal standard of deuterated geosmin and deuterated MIB and 6 g of NaCl were added to a 30 mL sample in a 40 mL vial. The sample was stirred using a magnetic stirrer, in a water bath at 65°C ± 2°C. The SPME fibre (polydimethylsiloxane/divinylbenzene) was exposed in the vial headspace for exactly 30 min, and then injected into the gas chromatograph–mass spectrometer (GC-MS) (desorption time 5 min, injection depth 3 cm) using injection in the splitless mode.

The GC-MS analysis was carried out in the selected ion monitoring (SIM) mode on an
Results and discussion

Removal efficiencies of fresh GAC

Although data for geosmin and MIB removals were collected at various depths throughout the filter column, for purposes of this paper only the total removals within the GAC will be presented and discussed (i.e. at a depth of 55 cm which includes 50 cm of GAC and 5 cm of sand). Some reference, however, is made to the data from samples collected in the upper portions of the GAC media (i.e. at depths of 10, 25, and 40 cm). As noted previously, both filter columns were spiked with the odour compounds on day 1 of the experiment and were fed continually for 13 days. Figure 1 demonstrates the efficiency of the fresh GAC in removing geosmin and MIB over the initial 13 day spiking period.

Over the first 7 days, complete removal of both geosmin and MIB took place within the GAC media, as would be expected. Complete removals actually occurred within the top 40 cm with the majority removed in the first 10 cm (i.e. as much as 74% for geosmin and 60% for MIB). Observed changes in filter influent concentrations of both geosmin and MIB over the duration of the experiment could explain possible fluctuations in per cent removals. After approximately 2 weeks it was apparent that the adsorptive capacity of the GAC in the upper portions was being compromised. The removal efficiencies in the upper portion dropped from 63% and 40% for geosmin and MIB, respectively, to as low as 31% and 27% on day 13 (data not shown). This drop in efficiency indicates that measurable biological removals had not yet begun to occur. As was seen in initial experiments which investigated system losses (Elhadi, 2002), MIB appeared to be more difficult to remove than geosmin. This supports the findings of Ridal et al. (2001). The very high removals observed within the 13 day period, while basically expected, served to confirm that experimental and analytical processes were operating properly.

The second spiking period was initiated after a 3 week resting period (i.e. from day 14 to day 35). Figure 2 shows total geosmin and MIB removals for the fresh GAC over the spiking period that lasted for 11 days. The removal efficiencies after the 3 day resting period (i.e. day 47 to 50) are also shown in the figure.

Total removals for geosmin remained relatively high over the 11 day spiking period, ranging from 76% to 96%. Total removals dropped from 96% on day 13 to 83% on day 36 which indicates a resting period of 3 weeks does negatively impact on filter performance in

![Figure 1 Geosmin and MIB removals in fresh GAC (initial 13 day spiking period)](https://iwaponline.com/wst/article-pdf/49/9/273/421134/273.pdf)
removing geosmin when fresh GAC is used, as the adsorptive capacity is continuously compromised. Changes in influent concentration between day 40 and 42 could explain the decrease from 96% to 76% in total removals over that time. However, based on further analysis of experimental data, removals in the upper portion of the media appeared to increase over the same time frame, which indicates possible biomass formation and its ability to contribute to removals.

Total removals (as well as removals in the upper portion) started to increase slightly after day 42 and continued to rise as high as 87% by day 55. This increase in removal efficiency suggests the establishment of a stable biomass. The 3 day resting period (i.e. day 47–50) appeared to have little effect on geosmin removals, as the per cent removals continued to increase between day 51 and 55.

Total removals for MIB were consistently about 30% lower than geosmin removals, which supports observations by others that MIB is more difficult to remove than geosmin. Total removals dropped from 89% on day 13 to as low as 52% by day 36 which indicates that the 3 week resting period decreases filter performance with respect to MIB removals when fresh GAC is used. Again, changes in influent concentration between day 38 and 42 could explain the decrease from 67% to 47% in total removals over that time. However, more removals occurred in the upper portions of the media which again suggests the establishment of a stable biomass. Total removals (as well as removals in the upper portion) started to increase slightly after day 42 and continued to rise as high as 63% by day 55. As was seen with geosmin, the 3 day resting period (i.e. day 47–50) appeared to have little effect on MIB removals, as the percent removals continued to increase between day 51 and 55.

**Removal efficiencies of exhausted GAC**

As with fresh GAC, for the purposes of this paper only the total removals within the GAC will be presented and discussed (i.e. at a depth of 55 cm which includes 50 cm of GAC and 5 cm of sand). As before, however, some reference is made to the data from the intermediate sampling ports. The sampling regime for the filter column containing the exhausted GAC was the same as that for the column containing the fresh GAC. Figure 3 demonstrates the efficiency of the exhausted GAC in removing geosmin and MIB over the initial 13 day spiking period.

As would be expected, removal efficiencies in the exhausted GAC media proved to be much poorer as compared with the fresh GAC media. On day 1 of spiking geosmin and MIB
removals are as high as 93% and 67%, respectively. However, these had measurably decreased by day 2. Total removals through the entire depth of the exhausted GAC decreased over the first week for both geosmin and MIB, dropping from 69% and 59%, to as low as 51% and 49%, respectively by day 7. Very poor removals of both compounds were also evident in the upper portion of the media based on further analysis of experimental data, particularly throughout the top 10 cm over the first 11 days. Total removals continued to decrease substantially for geosmin and MIB between day 7 and day 11 from 51% and 49%, to as low as 16% and 19%, respectively. This more rapid decrease in total removal could be a result of an increase in influent concentration for both compounds over that time. An increase in total per cent removals of geosmin and MIB was experienced between day 11 and 13, from 16% and 19%, reaching as high as 54% and 49%, respectively.

As with the fresh GAC, the second spiking period was initiated after the 3 week resting period (i.e. from day 14 to day 35). Figure 4 shows total geosmin and MIB removals over the spiking period that lasted for 11 days. The removal efficiencies after the 3 day resting period (i.e. day 47 to 50) are also shown in the figure.

Total removals for geosmin over the first few days of spiking (i.e. day 36 to 38) were still relatively high at 44% (as compared to 54% on day 13). However, this does indicate that the 3 week resting period decreases filter performance somewhat with respect to geosmin removals when exhausted GAC is used. Additionally, this indicates that a biomass has developed within the filter media. Total removals dropped between day 38 and 40, for reasons that are not entirely clear. A significant increase in total removals was seen between day 40 and 44 indicating establishment of a biofilm capable of degrading these compounds.
or existing bacteria switching over their metabolism. Total removals increased from 27% on day 40, to 74% on day 44. Removals increased only slightly by day 46, reaching 76%. Total removals (as well as removals in the upper portion of the media) continued to increase between day 51 and 55, indicating again that there is no significant impact on removals as a result of a 3 day resting period.

Total removals for MIB dropped from 49% on day 13 to 32% by day 36 which indicates that the 3 week resting period decreases filter performance somewhat with respect to MIB removals when exhausted GAC is used. Removals continued to increase between day 36 and 46, reaching as high as 47%. The decrease in MIB removals between day 40 and 44 could be a result of an increase in influent concentration over that time or simply sample variability. A measurable increase in total removals occurred between day 44 and 46 as biomass stabilizes. Removals increased from 32% on day 44 to 44% on day 46. Total removals (as well as removals in the upper portion of the media) continued to increase slightly between day 51 and 55, indicating again that there is no significant impact on removals as a result of a 3 day resting period.

**Conclusions**

This study demonstrates the potential of biofiltration for geosmin and MIB removal from drinking water. In practice, biofiltration may often follow ozonation. For operational simplicity in this research, ozone was not used to oxidize these compounds, thus, typical ozonation by-products were used to simulate a prior ozonation step. The results of this study highlight the important role that biofiltration can play in removing geosmin and MIB. Both fresh GAC/sand and exhausted GAC/sand were used as filtration media. This paper describes the results obtained during the startup phase of the biofiltration columns.

As expected, fresh GAC media provided excellent removals of both geosmin and MIB, in particular over the initial 2 week spiking period, primarily as a result of the adsorptive capacity of the GAC. After a subsequent 3 week period during which only the C, N, P compounds were fed, geosmin removals remained quite high around 83% (decreasing by 13 percentage points), while MIB removals dropped to as low as 52% (decreasing by 37 percentage points) when feeding of the odour compounds was resumed. This would indicate that a resting period of 3 weeks did negatively impact filter performance somewhat in removing geosmin, and substantially impacted filter performance in removing MIB. This impact is a result of the loss in adsorptive capacity of the fresh GAC not being fully compensated by the developing biomass. Both geosmin and MIB removals increased over the next 11 day spiking period (i.e. day 35 to day 46), indicating the establishment of a stable biomass. After the next 3 day resting period, geosmin and MIB removals continued to increase somewhat reaching as high as 87% and 63%, respectively by day 55. This would indicate that the short resting period did not negatively impact filter performance. In addition, MIB removals were consistently about 30% lower than geosmin removals over this 11 day period, which agrees with the literature that indicates that MIB is more difficult to remove.

Exhausted GAC media provided relatively poor removals of both geosmin and MIB over the first 11 days of spiking, as expected, as removals dropped to as low as 20% before subsequently increasing. After a subsequent 3 week period during which only the C, N, P compounds were fed, geosmin removals dropped to 44% (decreasing by 10 percentage points) and MIB removals were reduced to 32% (decreasing by 17 percentage points). This would indicate that a resting period of 3 weeks did negatively impact biofilter performance somewhat using the exhausted GAC in removing both geosmin and MIB. Again, both geosmin and MIB removals increased over the next 11 day spiking period (i.e. day 35 to day 46), indicating the establishment of a stable biomass. After a subsequent 3 day resting
period, geosmin and MIB removals continued to increase reaching as high as 87% and 51%, respectively by day 55. This would indicate that the short resting period did not negatively impact biofilter performance. Finally, as was seen with the fresh GAC media, MIB removals were consistently about 30% lower than geosmin removals over this 11 day period.

Overall the results of these experiments are encouraging for the use of biological filtration as a method of geosmin and MIB removal. In addition, these results provide important information with respect to the removal of these compounds during the startup phase of biofilters. Useful insight into the response of the biofilters to the transient presence of geosmin and MIB was also obtained.

References


