Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: A critical review

Rangesh Srinivasan, George A. Sorial

Environmental Engineering Program, School of Energy, Environmental, Biological, and Medical Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA. E-mail: George.Sorial@uc.edu.

Received 26 July 2010; revised 16 October 2010; accepted 17 November 2010

Abstract

Problems due to the taste and odor in drinking water are common in treatment facilities around the world. Taste and odor are perceived by the public as the primary indicators of the safely and acceptability of drinking water and are mainly caused by the presence of two semi-volatile compounds – 2-methyl isoborneol (MIB) and geosmin. A review of these two taste and odor causing compounds in drinking water is presented. The sources for the formation of these compounds in water are discussed along with the health and regulatory implications. The recent developments in the analysis of MIB/geosmin in water which have allowed for rapid measurements in the nanogram per liter concentrations are also discussed. This review focuses on the relevant treatment alternatives, that are described in detail with emphasis on their respective advantages and problems associated with their implementation in a full-scale facility. Conventional treatment processes in water treatment plants, such as coagulation, sedimentation and chlorination have been found to be ineffective for removal of MIB/geosmin. Studies have shown powdered activated carbon, ozonation and biofiltration to be effective in treatment of these two compounds. Although some of these technologies are more effective and show more promise than the others, much work remains to be done to optimize these technologies so that they can be retrofitted or installed with minimal impact on the overall operation and effectiveness of the treatment system.

Key words: adsorption; drinking water; geosmin; 2-methyl isoborneol (MIB); odor; taste

DOI: 10.1016/S1001-0742(10)60367-1


Introduction

Drinking water industries, even in most industrialized and developed nations, are facing the necessity for more innovative and cost-effective technologies for water treatment and purification. Taste and odor have long been associated with the suitability and safety of our drinking water. It is not uncommon for water utilities, especially those supplied by reservoirs, to be flooded with complaints from consumers about taste and odor in their drinking water, especially during warmer weather. For an average consumer, taste and odor is the only way of determining the safety of tap water (McGuire, 1995). Geosmin (trans-1,10-dimethyl-trans-9 decalol-C_{12}H_{22}O) and MIB (2-methyl isoborneol-C_{11}H_{20}O) have been identified to be the major taste and odor-causing compounds in drinking water obtained from surface water (Fig. 1) (Pirbazari et al., 1993). MIB/geosmin in surface water mainly result from the metabolism and biodegradation of certain types of cyanobacteria that normally bloom in the presence of nutrients at warmer temperatures (Watson et al., 2008). There are currently no regulations for these two compounds as they have not been associated with any health effects (Dionigi et al., 1993a). Presence of taste and odor in drinking water may result in decreased consumer trust and subsequently, decreased water consumption and could eventually cause the public to switch to alternate sources of drinking water such as bottled water and in-home treatment systems. The main problem with the presence of MIB/geosmin is associated with their extremely low odor threshold concentrations (OTC) and their persistence to elimination in a conventional water treatment process such as coagulation, sedimentation, filtration and chlorination (Bruce et al., 2002). The OTCs for MIB/geosmin can range from 4 to 20 ng/L (Pirbazari et al., 1993; Lloyd et al., 1998). Another factor that adds to the challenge faced by drinking water facilities in the removal of these contaminants is the presence of natural organic matter (NOM). NOM, a complex mixture of organic compounds derived primarily from the decay of plant and animal materials, is invariably present in all water sources and at much higher concentrations than MIB/geosmin (Pirbazari et al., 1993).
The treatment methods that have been successfully employed by water treatment plants to remove MIB/geosmin are adsorption by activated carbon or oxidation by strong oxidants such as ozone. Ferguson et al. (1990), Glaze et al. (1990), and Bruce et al. (2002) studied and demonstrated MIB/geosmin removal using oxidants such as ozone, hydrogen peroxide and UV. Addition of chemicals however is expensive and can result in formation of disinfection byproducts (DBPs), which are unacceptable due to health and regulatory concerns. Adsorption by activated carbon, either granular activated carbon (GAC) or powdered activated carbon (PAC) is considered as one of the best available technologies for removal of organic contaminants from water. Numerous studies have looked into GAC and PAC adsorption of MIB/geosmin (Pirbazari et al., 1993; Cooke et al., 2001; Ng et al., 2002a; Jung et al., 2004; Ho and Newcombe, 2005). However, NOM levels of 3–10 mg/L competitively reduce activated carbon adsorption capacity for MIB/geosmin (Pirbazarin et al., 1993; Newcombe et al., 2002a, 2002b). In natural waters, the size and concentration of NOM particles is many folds higher than that of MIB/geosmin, and as a result a large volume of the GAC is not utilized for MIB/geosmin adsorption, thereby significantly reducing the GAC adsorption capacity.

There have been some good reviews of aspects related to MIB/geosmin in drinking water looking at scale of the problem, sources and prediction of these two odorants, that are essential for understanding and managing taste and odor in drinking water (Watson, 2004; Watson et al., 2008). Jutner and Watson (2007) identified the various strains of cyanobacteria responsible for the production of MIB/geosmin in water. The study also identified the possible pathways for biosynthesis of these two odorants. They summarized the MIB/geosmin concentrations in waters around the world, along with the habitat supporting the cyanobacteria source.

1 Sources and contamination of MIB/geosmin in water

It is not uncommon for water utilities to be overwhelmed with consumer complaints about taste and odor when the concentrations of MIB/geosmin exceed the odor threshold, especially during summer months. Studies indicate the main source of MIB/geosmin in water are cyanobacteria (blue-green algae) (Watson, 2004; Watson et al., 2008). Studies have also shown that MIB/geosmin in surface water can be attributed to the presence of certain type of filamentous bacteria or actinomycetes (Zaitlin and Watson, 2006). These cyanobacteria synthesize MIB/geosmin during growth and these algal cells release or store these odorants depending on the growth phase and also based on environmental factors. Most of the MIB/geosmin is released during the death and biodegradation of these cells (Fig. 2). The taste and odor outbreaks are more prominent during eutrophic conditions, when there is an overabundance of nutrients and warmer temperatures. These conditions lead to cyanobacterial blooms in the surface water resulting in significant MIB/geosmin production. Jutner and Watson (2007) identified the various strains of cyanobacteria responsible for the production of MIB/geosmin in water. The study also identified the possible pathways for biosynthesis of these two odorants. They summarized the MIB/geosmin concentrations in waters around the world, along with the habitat supporting the cyanobacteria source.
Studies have detected concentrations exceeding OTCs for MIB/geosmin in various sources of drinking water as well as certain types of wastewater. Watson et al. (2003) investigated MIB/geosmin in pulp and paper mill effluent during secondary treatment. They detected both compounds at concentrations 2000–9000 times their OTCs resulting in a significant local odor in the bioreactor. As expected, the concentrations were highest in the summer months during warmer temperatures and cyanobacteria were reported to be the likely source.

Taste and odor in drinking water is not restricted to certain geographies and is a problem faced by water treatment facilities around the world. Lin et al. (2002) studied the correlation between musty odors and MIB concentration in two drinking water plants in Taiwan. The authors employed flavor profile analysis (FPA), where a trained panel was asked to rate the intensity of the odor on a scale. They also measured the MIB concentrations using solid phase micro-extraction (SPME-GC/MS) and found a good correlation between the FPA and the analytical results. Although the conventional treatment process removed up to 50% of the MIB at an influent concentration range of 30–70 ng/L, only about 30% reduction was observed based on the FPA scale suggesting that the concentrations were still higher than the OTC.

Studies have shown MIB/geosmin accumulate in surface water reservoirs as well (Westerhoff et al., 2005). A recent study with a survey of about 59 drinking water treatment plants in the Great Lakes region found that the taste/odor impairments were widespread with a significant number (20%) of utilities reporting annual outbreaks during the summer months with even a higher number (27%) experiencing sporadic episodes when about (Watson et al., 2008). Studies have shown algal growth occurring in canals supplying water to treatment plants and even in water treatment plants in locations such as uncovered sedimentation and coagulation basins that could result in the production of MIB/geosmin (Bruce et al., 2002).

Since, MIB/geosmin occur seasonally, a flexible treatment system that would allow water utilities to administer treatment of these compounds only during outbreaks like in summer months would make more sense economically than a dedicated system that is operated year round. Tools that predict taste and odor events based on certain environmental/water quality factors would be ideal for cost effective treatment. Recent studies have focused on development of such tools (Downing et al., 2001; Smith et al., 2002; Watson et al., 2007; Dzialowski et al., 2009). Results from studies by Smith et al., (2002) and Downing et al., (2001) showed that trophic state of the reservoir; especially chlorophyll a levels were a good indicator of taste and odor causing compounds. They found cyanobacteria and MIB/geosmin concentrations to be directly proportional to the chlorophyll a concentrations in water. Some state regulatory agencies have evaluated establishing a chlorophyll a criterion in order to maintain water quality in reservoirs by preventing formation of taste and odor causing compounds (Oklahoma Water Resources Board, 2005). Watson et al., (2007) found that taste and odor outbreaks can be correlated to a series of by physical, chemical and biological mechanisms over a range of spatial and temporal scales. Other studies have found prediction of MIB/geosmin outbreaks to be more challenging. Dzialowski et al. (2009) developed a series of predictive models to relate reservoir geosmin concentrations to water quality variables. Their results showed that reservoir trophic state alone could not be used to predict taste and odor episodes. They even observed contradicting results where a reservoir with the lowest nutrient and chlorophyll level had the highest geosmin concentration. A similar trend was also observed by Watson et al., (2007) where geosmin peaks in western Lake Ontario increased significantly over an 8-year period without any change in the ambient nutrient or chlorophyll level. Dzialowski et al. (2009) found inorganic phosphorous limitation and local environmental factors to be most critical for effectively predicting reservoir geosmin concentrations. Interestingly, elevated levels of geosmin were observed in some reservoirs even during the winter months. Based on these results, it could be hypothesized that although temperature and eutrophication are the most important factors influencing synthesis and release of MIB/geosmin, they are not the only factors.

2 Development in analysis of MIB/geosmin in water samples

Analysis of MIB/geosmin was performed by conventional analytical techniques in the late eighties and early nineties. Although methods such as purge and trap (P&T), liquid-liquid extraction were effective, they were expensive, time consuming and highly labor intensive (Lloyd et al., 1998). This led to development of membrane based methods for more accurate measurements of these taste and odor compounds. Hollow fiber stripping analysis (HFSA) used microporous hydrophobic hollow fiber membranes for the analysis and could measure parts per trillion (ppt) concentrations in water (Zander and Pingert, 1997). However the apparatus setup was complex and involved a large number of equipment. Although, solid phase extraction (SPE) was also able to measure very low concentrations, it also suffered from similar drawbacks. In 1996, a new method called solid phase micro-extraction (SPME) was used to measure organic micropollutants, especially volatile organic compounds (VOCs) such as benzene and toluene (Eisert and Levesen, 1996). This method employed a fused silica fiber for extraction of the contaminants from the sample headspace followed by injection into the headspace of a gas chromatography-mass spectrophotometry (GC/MS) for analysis. Like SPE, this method did not require solvent extraction and the analytical procedure was simple and quick. Unlike SPE, the fiber could also be used repeatedly. Since that time, a lot of research has been done to optimize SPME for analysis of MIB/geosmin in water and now it has become the standard method (Lloyd et al., 1998; Zimmerman et al., 2002; Chang et al., 2008; Saito et al., 2008).

Lloyd et al. (1998) compared SPME-GC to P&T-GC for
analysis of MIB/geosmin. It was seen that the precisions and limits achieved with SPME were comparable to P&T, with SPME offering faster analysis with smaller sample size. The authors ran a series of analysis to optimize the analytical method for MIB/geosmin analysis using SPME-GC. They varied the sampling temperature, vial size, sample exposure time to the SPME fiber, percentage headspace to arrive at a method that permitted analysis of both MIB and geosmin at concentrations as low as 10 ng/L. In the last few years, there have been significant improvements in the quality of the SPME fiber, with more robust and sensitive fibers being developed. In a more recent study, an SPME-GC-MS based method was presented where method detection limits (MDL) as low as 2 ng/L were demonstrated for both MIB/geosmin (Zimmerman et al., 2002). The study also details a quality-control analysis to support the method performance. Further optimization of this method has resulted in detection limits being lowered to 0.4 ng/L (Chang et al., 2008). Analysis using headspace sampling, known as HS-SPME-GC-MS has been further optimized for measuring MIB/geosmin with detection limits under 1 pg/L in a very recent study (Saito et al., 2008). Because the OTCs for these compounds are in the nano gram per liter range, it is imperative to have analytical methods that can measure very low concentrations with high accuracy and precision. In addition to improved accuracy, these recent developments in analytical techniques have significantly improved the sample load and turnaround time for analysis, thereby allowing quick analysis of a large number of samples to be practical.

3 Health effects/regulation

Numerous studies have shown that the presence of these taste and odor causing compounds in water is mainly an aesthetic concern and has not been associated with any health effects (Dionigi et al., 1993b). MIB/geosmin have also not been correlated to presence of cyanobacterial toxins which are extremely toxic at even low concentrations (Zimmerman et al., 2002). As a result, there is no maximum contaminant level (MCL) or maximum contaminant level goal (MCLG) for either MIB/geosmin. Studies have detected MIB/geosmin in various species of fish but have concluded that they do not result in any toxicity to either the fish or to humans through consumption of the fish (Schulz et al., 2004; Robedson et al., 2006). Although taste and odor in drinking water is rarely associated with toxic contaminants, for consumers, it is a primary measure to perceive safety of the drinking water. Not only can it undermine consumer trust in the water quality but it can also result in the use of alternative supplies of drinking water, such as bottled water (McGuire, 1995; Watson et al., 2000). Watson (2004) summarized the various types of taste and odors encountered by drinking water consumers and their possible sources. Earthy and musty odors, which are the most frequently type of taste/odor in drinking water, are due to the presence of MIB/geosmin in water. Whelton and Dietrich (2004) found that the water treat-regulation strategy for these odor causing compounds should consider perceived OTCs, values for which show considerable variation among consumers, and is also influenced by other factors such as water temperature. The results showed that reducing the water temperature from 45 to 25°C reduced the perceived odor intensity significantly. This would not have much practical significance since it would be extremely difficult for utilities to control water temperature. Based on some of these studies, it can be said that there is not enough evidence to support an OTC based guideline or regulation and it would be more practical for utilities to be proactive and avoid consumer complaints by treating these compounds down to concentrations below their OTCs during seasonal outbreaks.

4 Treatment technologies

Studies have shown that MIB/geosmin are extremely resistant to removal by conventional water treatment processes such as coagulation, sedimentation and filtration. Bruce et al. (2002) investigated coagulation for removal of these taste and odor compounds and found that alum coagulation could not be optimized for MIB/geosmin removal. No removal was observed under a range of pH and coagulation conditions including different alum dosages. It has been seen that common oxidants such as Cl₂, ClO₂, and KMnO₄ are not very effective for removal of these compounds (Lalezary et al., 1986; Glaze et al., 1990). In a pilot plant study comparing MIB/geosmin removal with different oxidants, removal efficiencies with Cl₂ and ClO₂ were very low and only O₃ showed any appreciable removal of MIB/geosmin (85% for 3.8 mg/L dosage at a contact time (CT) of 6.4 min) (Jung et al., 2004). KMnO₄ has been found to have low removal even at higher dosages and chlorine residuals in some cases have been found to enhance and even mask the musty/earthy odors rather than removing them. Currently, PAC is the most commonly used treatment technology for removal of seasonal tastes and odors in water. However, its effectiveness for removal of MIB/geosmin is less when compared to some other contaminants. Presence of NOM reduces its capacity further but studies have also shown that upstream application of oxidants such as chlorines or chloramines has a negative impact on MIB adsorption by PAC (Nerenberg et al., 2000). Use of advanced oxidation technologies such as ozone or UV with H₂O₂ has been found to be effective in destroying MIB/geosmin. A lot of research has also been performed in the area of bioremediation for treatment of MIB/geosmin. The three main technologies, GAC/PAC adsorption, advanced oxidation processes (AOPs) and biological treatment are discussed in further detail in this section with a focus on advantages and challenges faced in implementation of these treatment alternatives.

4.1 GAC/PAC adsorption

Adsorption with GAC/PAC is being widely used in drinking water treatment plants mainly for removal of organic pollutants. It would be sensible to use this already existing technology for removal of taste and odor...
Table 1  Treatment of MIB/geosmin in water by activated carbon adsorption

<table>
<thead>
<tr>
<th>Key references</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newcombe et al., 2002a, 2002b</td>
<td>- Simultaneous adsorption between NOM and MIB on GAC was mainly influenced by pore size/volume distribution</td>
</tr>
<tr>
<td></td>
<td>- NOM with size similar to MIB resulted in the majority of the competition</td>
</tr>
<tr>
<td></td>
<td>- Smaller NOM particles compete by direct and strong adsorption for the available adsorption sites</td>
</tr>
<tr>
<td></td>
<td>- Larger NOM compounds reduce equilibrium adsorption capacity by adsorbing closer to external surfaces and blocking access to pores</td>
</tr>
<tr>
<td></td>
<td>- To be effective in natural water, carbon should have a bimodal pore distribution</td>
</tr>
<tr>
<td>Cook et al., 2001, 2004</td>
<td>- Geosmin showed better adsorption than MIB on PAC for all waters studied</td>
</tr>
<tr>
<td></td>
<td>- This was attributed to the lower molecular weight and solubility of geosmin</td>
</tr>
<tr>
<td></td>
<td>- Presence of NOM significantly reduced adsorption capacity for MIB/geosmin</td>
</tr>
<tr>
<td></td>
<td>- HSDM predicted successfully PAC doses required to reduce MIB/geosmin to the required levels in waters from three different treatment plants</td>
</tr>
<tr>
<td>Pirbazari et al., 1993</td>
<td>- Developed a model to predict the adsorption of MIB/geosmin in a fixed bed GAC adsorber</td>
</tr>
<tr>
<td></td>
<td>- Experimental data, specifically adsorption and kinetic parameters were inputs for the model</td>
</tr>
<tr>
<td></td>
<td>- The model predicted breakthrough behavior well for both MIB/geosmin</td>
</tr>
</tbody>
</table>

compounds as well. Water treatment plants invariably use GAC in the form of filtration beds. Various studies have looked into use of activated carbon for MIB/geosmin remediation, with their results discussed in detail in this section and some of the key studies summarized in Table 1.

Ridal et al. (2001) investigated the long-term performance of GAC filter beds in a water treatment plant in Canada for removal of MIB/geosmin. When monitored after two months in place, MIB/geosmin were removed to at or below the OTCs, thereby performing effectively. They also found that the removal efficiencies were directly related to Cl residual. In fact, the practice at the plant was to increase the Cl residual during taste/odor episodes. It was also observed that increasing the contact time from 3 to 14 min increased the removal efficiencies of MIB from 43% to 66% and 43% to 78% for geosmin. When the performance of the filters was monitored after 1 and 2 year periods, the performance had dropped significantly and the effluent concentrations were higher than the OTCs. The authors suggested reasons for this, including flow channeling, media mixing and coating of the GAC with dissolved organic carbon (DOC). It is likely that competitive adsorption was a bigger factor for the reduced performance than some of the reasons pointed out by the authors of this study.

MacKenzie et al. (2005) compared various commercially available carbons for adsorption of MIB. Through rapid small scale column tests (RSSCTs) on water obtained from two treatment plants, they found that although wood-based GACs had better breakthrough behavior when compared to coal-based GACs, their affinity for MIB after the odor episode was significantly lower. They compared GAC regenerated with steam-curing reactivation under various conditions with conventional reactivation. The results showed that the breakthrough behavior of the steam-curing reactivated GAC was almost comparable to the virgin GAC and significantly better than conventionally reactivated GAC. Not only were the volume and mass loss with this new reactivation comparable to the conventional method, but it also resulted in a higher BET surface area.

Studies have been undertaken to tailor carbon to enhance its MIB/geosmin removal capacity. Rangel-Mendez and Cannon (2005), investigated MIB adsorption with GAC tailored by thermal treatment with steam or steam + methane that resulted in a significant increase in both micropore and mesopore volumes and treated 5 times more BV when compared to virgin GAC. Although steam treatment showed better results, up to 16% of the carbon mass was also lost during the process. Thermal treatment with steam + methane achieved similar results but with less mass loss.

PAC is another way of using activated carbon for water treatment during taste and odor episodes and in normally used prior to filtration. It is currently the most commonly practiced technology for MIB/geosmin removal. This is mainly because taste and odor episodes are seasonal and PAC offers the treatment plants the flexibility to either turn on/off dosages and also to adjust dosages depending upon the severity of the event. Although the exact location of PAC application is determined based on a treatment plant’s design and operation, it is generally added either at the intake or to the flocc/sedimentation basins. Cook et al. (2001) studied PAC adsorption of MIB/geosmin in four raw waters. They conducted adsorption isotherm experiments and found geosmin showed better adsorption than MIB in all four waters. This was attributed to the lower solubility and molecular weight (MW), along with the flatter structure in geosmin making it more amenable for adsorption. Based on the adsorption isotherms and kinetic experiments, they generated parameters to be used as input for the homogenous surface diffusion model (HSDM) that was used to predict the PAC dosages required. The model results showed good prediction for three of the four waters.

Ng et al. (2002b) investigated geosmin adsorption on PAC obtained from activation of various agricultural by-products and studied the effect of activation method and pore characteristics of these carbon on geosmin adsorption. They found that some pecan shells based PAC had properties comparable to that of a commercially available carbon and showed similar adsorption performance even at a low geosmin concentration of 10 µg/L (Ng et al., 2002a). However, it should be noted that the dosages used in most of the adsorption experiments were high, in the range of 50–250 mg of adsorbent for 500 mL of solution.

Bruce et al. (2002) studied MIB/geosmin adsorption using several different types (brands) of PAC in the waters of the Arizona Canal. They compared adsorption in the natural water with that in nanopure water and found that removal was always lower in the natural water, which is obviously expected. This was attributed to the presence of dissolved organic carbon (DOC) which competed with...
MIB/geosmin for adsorption sites. However, no effort was made to quantify the DOC concentrations and compare the adsorption data. They also found that geosmin removal was always higher than MIB and attributed this to the higher octanol-water partition coefficient value (K_{ow}) in geosmin resulting in higher hydrophobicity and improved removal. The study also found that bituminous coal based PAC performed better than lignite or wood-based PAC. In addition to the pore size distribution, various other PAC factors were identified that influenced MIB/geosmin adsorption and were critical to optimizing the dosage – iodine number, oxygen content, pH, point of zero charge (pHzPC). The key finding of the study was to identify the best performing PAC and generating an implementation guide plot for a particular utility using the Arizona Canal water. For a given influent MIB concentration, the plot could be used to identify the exact PAC dose required to achieve a desired effluent concentration.

Several factors including the adsorbent properties such as pore size distribution and surface characteristics, and also water quality parameters such as presence of NOM, influence the effectiveness of carbon adsorption. Yu et al. (2007) investigated adsorption of MIB/geosmin on PAC obtained from five different sources to better understand the effect of various factors. Among the different pore characteristics studied, only the micropore volume showed a significant correlation with adsorption, with the best adsorption capacity exhibited by carbons with the highest micropore volumes. Ho and Newcombe (2005) found that NOM, especially lower MW fractions, reduced MIB adsorption by PAC during alum coagulation due to competitive adsorption. Increase in turbidity and alum dose resulted in larger floc size which in turn reduced MIB adsorption further due to incorporation of the PAC particles into these flocs.

Newcombe et al. (2002a, 2002b) investigated simultaneous adsorption of NOM and MIB on PAC. By studying NOM adsorption on six different types of carbon, they were able to conclude that NOM adsorption was mainly controlled by the MW distribution and the pore size distribution of the carbon. Competitive adsorption on PAC was done by studying MIB adsorption in six different NOM solutions, with different fractionation and properties. The adsorption isotherms showed significant reduction in the adsorption capacity in the presence of NOM. The authors postulated that only the presence of low MW NOM fractions, comparable in size to the MIB molecule, resulted in competition for the available adsorption sites. It was concluded that for the carbon to be effective, it needs to have a bimodal pore distribution that would provide MIB rapid access to the adsorption sites and at the same time minimize pore blockage by the low MW NOM particles.

Pirbazari et al. (1993) investigated the effectiveness of the dispersed flow homogeneous surface diffusion model (DFHSADM) to predict MIB/geosmin adsorption by a fixed-bed GAC adsorber. They conducted adsorption isotherms and kinetic rate studies to determine the parameters required for model generations. They also conducted these experiments in the presence of NOM to study their impact on GAC adsorption. The DFHSADM adsorber model predicted well the column experimental data. The authors also used the model predictions to estimate the system costs for the removal of these odorants in a full-scale GAC adsorber.

Compared with GAC, activated carbon fibers (ACFs) have attracted increasing attention due to their excellent surface properties, high adsorption capacity and are an ideal adsorbent for targeting the impact of pore size (Lu and Sorial, 2004b). Several studies have looked at adsorption of micropollutants on ACFs to better understand the effect of pore size on both single and multicomponent adsorption (Pelekani and Snoeyink, 1999, 2000, 2001; Lu and Sorial, 2004a, 2004b, 2005, 2007). Multicomponent adsorption has been predicted using the ideals adsorption solute theory (IAST) in some of these studies. Srinivasan et al. (2002) looked at single solute and multicomponent adsorption of MIB/geosmin on three ACFs with different pore size distributions and compared the results with adsorption in the presence of NOM and adsorption on GAC (Srinivasan et al., 2008; Srinivasan and Sorial, 2009). The results indicated that the surface pore characteristics and specifically, the micropore distribution was the single most important factor influencing adsorption. It was seen that presence of NOM affected the adsorption capacity of the ACF, and this effect was more pronounced in ACF with the least microporosity. The IAST model predicted the binary adsorption of MIB/geosmin well and the results indicated that adsorption of these compounds on ACFs was purely through physical adsorption with no oligomerization occurring. Although ACFs seem to be effective for adsorption of these two odorants, more research is required for any practical implementation of this technology.

As seen from the above discussion, various factors have to be considered for successful application of GAC/PAC adsorption for MIB/geosmin removal. Bruce et al. (2002) looked at PAC adsorption of MIB/geosmin in a drinking water treatment plant in Arizona and came up with practical recommendations. Prior to selection of a PAC, it is important to understand its adsorption characteristics in the presence of NOM commonly found in particular water. Frequent monitoring of the influent MIB/geosmin levels is necessary, and in cases where both are present at the similar concentration range, dosages could be based on MIB concentrations since it is normally more challenging to remove. Optimizing the PAC dosage is important since overdosing could result in excessive sludge production, reduced filter performance and larger operating costs.

4.2 Advanced oxidation processes (AOP)

A number of studies have looked into using AOPs such as ozone, UV and H_{2}O_{2} for removal of MIB/geosmin. These methods are normally used in disinfection and are known to completely destroy the target contaminants such as waterborne pathogens and other microcontaminants. Studies looking into removal of MIB/geosmin using AOPs are discussed in detail in this section with some of the key references summarized in Table 2. Collivignarelli and Sorlini (2004) investigated MIB/geosmin removal using ozone and UV. They used raw river water from a water
treatment plant in Italy, spiked with MIB (0.2–0.4 µg/L) and geosmin (0.5 µg/L) and a metachlor (pesticide contaminant). Both MIB/geosmin were persistent to reaction with ozone and showed low (ca. 50%) removal rates. However, ozone followed by exposure to UV increased the removal close to 90%. Molecular ozone had limited reaction with these two compounds and UV radiation was required for decomposition of the ozone molecule for generation of hydroxyl radicals (-OH) which subsequently reacted with MIB/geosmin. Also when compared to metachlor, MIB/geosmin required longer contact time with ozone (2–3 min at 2–3 mg/L) and higher UV doses (500–600 mJ/cm²) for the same degree of removal. It is worth noting that this process did not result in complete removal of MIB/geosmin and the resulting effluent concentrations were higher than the OTCs.

Another study determined the reaction rates for ozone oxidation of several taste and odor compounds in drinking water (Peter and Gunten, 2007). Similar to the results from the previous study, the second order reaction rates for oxidation with hydroxyl radical generated from UV/H₂O₂ (MIB: 0.35 (mol/L)⁻¹sec⁻¹; geosmin: 0.1 (mol/L)⁻¹sec⁻¹) were significantly higher than the rates obtained with molecular ozone (MIB: 5.1 × 10⁸ (mol/L)⁻¹sec⁻¹; geosmin: 7.8 × 10⁸ (mol/L)⁻¹sec⁻¹). Removal of MIB/geosmin was studied in water from two different lakes in Switzerland, and the oxidation efficiency for both compounds was observed to be in the 50%–70% range.

Similar to GAC adsorption, presence of NOM in water can influence AOPs as well. Ho et al. (2002) investigated the effect of NOM characterization on the ozonation of MIB/geosmin. Ozonation of fractionated NOM was studied and it was found that the NOM containing higher MW fractions had higher specific UV absorbance (SUVA) and also showed the highest O₃ demand, which in turn translated into a higher hydroxyl radical generation during ozonation for a given contact time. This was confirmed with the highest MIB/geosmin removal (98%) being observed for the lowest CT, which corresponded to the NOM fraction with the highest MW. However, when the same ozonation was performed on two surface waters, MIB removal was higher in the water containing lower MW/SUVA NOM, thereby contradicting the experimental results. This was attributed to higher hydroxyl radical consumption due to the higher concentration of DOC. The MIB removal observed was similar when the same O₃ dose to DOC ratio was compared. Park et al. (2006) also reached similar conclusion when they looked at kinetics of MIB/geosmin oxidation using H₂O₂.

Westerhoff et al. (2006) conducted batch ozonation experiments to study the effect of ozone oxidation parameters such as pH, ozone and H₂O₂ dosage and water quality parameters such as temperature and initial concentrations on the removal of MIB/geosmin. Like the previous studies, hydroxyl radical dominated the oxidation reaction when compared to ozone and also geosmin showed better reaction kinetics when compared to MIB. Introduction of a hydroxyl radical scavenger during the reaction significantly reduced the removal efficiency. The results showed that removal efficiencies for both MIB/geosmin increased with increase in temperature, ozone dosage, pH and H₂O₂ concentration. An empirical model was developed to predict CT requirement, bromate formation and odorant oxidation, which are all interconnected. The CT ratio of hydroxyl radical to ozone was found to be the most critical factor for oxidation of MIB/geosmin. Liang et al. (2007) also found similar results where they found that pH is a significant factor influencing oxidation as it is directly related to the hydroxyl radical concentrations. Contrary to some earlier results, it was seen that presence of background organics did not have a significant effect on ozonation of MIB/geosmin. Rosenfeldt et al. (2005) looked at UV oxidation of MIB/geosmin and found that dosages higher than normally used for disinfection are required for complete removal. They found that UV combined with H₂O₂ significantly increased the oxidation rates. It was also found that water quality parameters such as turbidity from NOM also influence the removal rates, as the destruction in clear well water was much higher than with raw river water. The authors were also able to effectively predict removal by UV/H₂O₂ through a steady state model for the water tested. Kutschera et al. (2009) investigated MIB/geosmin removal using vacuum UV (VUV) irradiation and found that VUV treatment was more effective than UV. Reaction kinetics and effect of NOM on removal of taste and odor causing compounds was also discussed. According to this study, when compared to UV, VUV has lower energy requirement, lower life cycle costs and provides simultaneous disinfection as well.

The results from the previous study also showed that water quality parameters such as turbidity from NOM also influence the removal rates, as the destruction in clear well water was much higher than with raw river water. The authors were also able to effectively predict removal by UV/H₂O₂ through a steady state model for the water tested. Kutschera et al. (2009) investigated MIB/geosmin removal using vacuum UV (VUV) irradiation and found that VUV treatment was more effective than UV. Reaction kinetics and effect of NOM on removal of taste and odor causing compounds was also discussed. According to this study, when compared to UV, VUV has lower energy requirement, lower life cycle costs and provides simultaneous disinfection as well.
formation of byproducts such as nitrite which is regulated and may require further treatment. The authors do not delve into any details regarding practical application of this technology. A study by Qi et al. (2008) found that bauxite catalyzed ozonation resulted in 75% removal of MIB when compared to 28% with only ozonation after a 10 min experiment. However, bauxite had to be thermally treated at very high temperatures to change its crystalline properties for better catalytic activity during ozonation. Without thermal treatment there was only a 13% increase in the removal efficiency. The study does not look into the cost implications of thermal treatment of bauxite and the issue of using bauxite in drinking water treatment. In another study, Qi et al. (2009) focused on ozonation of MIB and identified hydroxyl radicals to be the main oxidation mechanism. The study also went into detail trying to identify some of the byproducts of MIB degradation. Interestingly, they observed some of these aldehyde byproducts to be causing off-flavors in the water. The study went on to conclude that a polishing treatment is necessary to remove some of these by products from imparting off-flavors during ozonation of MIB.

Removal of MIB/geosmin by AOPs is also dependent on various water quality parameters such as pH and NOM concentrations. The capital and energy costs associated with these technologies can be significantly high, especially for large scale applications. There is also the risk of formation of harmful disinfection byproducts through these processes (White, 2010). For instance ozonation could generate DBPs such as aldehydes, ketones and brominated DBPs in water containing bromide. However these technologies are being used more commonly now and could be retrofitted or optimized for effective removal of these odorants.

4.3 Biological treatment

In the last few years there has been an extensive use of biological treatment for removal of certain contaminants in water and wastewater. Unlike wastewater, biological methods have limited application in drinking water and are mainly used with filtration, or biofiltration. Results from various studies dealing with biological removal of MIB/geosmin are discussed with the key results summarized in Table 3. Huck et al. (1995) were one of the first researchers to study biological removal of odor causing compounds in drinking water. They studied microbial geosmin removal in a lab scale bioreactor. The results demonstrated very low geosmin removal and the authors concluded that biodegradation was not the most effective technology for removal of taste and odor compounds in drinking water. However subsequent research has shown results to the contrary.

Ho et al. (2007) demonstrated removal of MIB/geosmin in a biologically active sand filter. They used water from a river in Australia known for episodes of significant odor outbreaks due to MIB/geosmin. However, the produced water in a treatment plant using conventional treatment is surprisingly free of any MIB/geosmin. The results from this study corroborate the removal of these compounds by biological sand filtration. The authors also determined the pseudo first-order reaction kinetics by running batch experiments with the biofilm obtained from one of the sand filters with rates as high as 0.6 day⁻¹. Four different bacteria thought to be responsible for this biodegradation were identified. In a related study, Hoefel et al. (2006) identified three gram-negative bacteria that coordinated the biological degradation of geosmin and interestingly degradation did not occur even if one of the three isolates was absent.

Elhadi et al. (2006) investigated MIB/geosmin removal in a dual media filter in a bench scale study. They conducted a factorial design experiment to study the effects of different factors on removal efficiency including temperature, media type, presence of biodegradable organic matter (BOM) and influent concentrations. Typical ozonation byproducts were used as BOM to simulate filtration following ozonation. The results showed that removal for both compounds was higher at the higher temperature of 20°C when compared to 8°C. Also removal was better when GAC-sand was used as the media when compared to the anthracite-sand media. And the removal was found to be higher at the higher influent concentrations and at higher BOM concentrations. This was mainly due to higher density of biomass at the higher BOM concentrations. In addition they demonstrated removal at very low influent concentrations of 25 ng/L. The optimum levels for each of the factors for maximum MIB/geosmin removal were listed. Although the study demonstrated a maximum removal of around 60% at an influent concentration of 100 ng/L, the resulting effluent concentrations would still be significantly higher than the OTCs for these compounds, requiring further polishing prior to distribution.

4.4 Integrated technologies

Various studies have looked into the possibility of combining different technologies to enhance removal of MIB/geosmin in water. The combination of methods could be used either as a polishing step or for complete removal of contaminants, which may have not been possible.
with just one technology. Elhadi et al. (2004) compared MIB/geosmin in fresh GAC/sand biofilter with an exhausted GAC/sand filter. The results show that as expected, initial removal was higher in the fresh GAC/sand filter when compared to the exhausted GAC/sand filter because of better adsorption. However with time, as a stable biomass developed on both filters, the removal rates were comparable. Removal rates after a two month run were close to 87% for geosmin and 52% for MIB. This phenomenon of higher removal of geosmin when compared to MIB has been observed in other studies as well confirming that geosmin displays better reaction kinetics (Cook et al., 2001; Cook and Newcombe, 2004). The authors also simulated biofilter startup and transient presence of MIB/geosmin by spiking the influent water accordingly and the biofilter was able to perform consistently under these conditions.

Matsui et al. (2007) demonstrated geosmin removal with a combination of super-PAC (S-PAC) and microfiltration (MF) in a small-scale pilot study. S-PAC was obtained by pulverization of PAC to sub-micron particle size. S-PAC with MF showed better efficiency than PAC at a significantly low dosage. The authors claimed that up to 90% savings in dosage and a better removal could be achieved with S-PAC. However, the cost-effectiveness of this process along with the material loss during the sieving process were not discussed in detail.

Nerenberg et al. (2000) demonstrated ozonation followed by biofiltration in a water treatment facility for removal of MIB/geosmin. They found that ozonation and biofiltration show a synergistic effect. Ozonation resulted in partial destruction of the odorant and also transformed some of the nonbiodegradable NOM into smaller compounds that can be used by the bacteria as substrate. This enhances the ability of the biofilter to completely remove the remaining MIB/geosmin in the water. Park et al. (2007) compared oxidation of MIB/geosmin with ferrate (Fe(VI)) to ozone and found that due to low selectivity of the ferrate ion, the removal rates were significantly lower when compared to ozone.

Jung et al. (2004) looked at MIB/geosmin removal in a pilot study that combined oxidation and PAC adsorption. Chlorine, chlorine dioxide and ozone were the oxidants used in the study. The results indicated that only ozone showed significant removal of MIB/geosmin, especially at higher dosage, whereas with the other oxidants, removal was low. Majority of the MIB/geosmin removal occurred across the PAC filter/adsorber unit. Although the study looked at effect of dosages of PAC and oxidants on MIB/geosmin removal efficiencies, no attempt was made to study the effect on NOM present in the water. Since there was not a significant difference in the overall removal efficiencies with and without ozonation, it was inconclusive whether the use of oxidation along with activated carbon adsorption had a synergistic effect on MIB/geosmin removal. The results were not promising as concentration of approximately 100 ng/L of MIB/geosmin in the influent was reduced to only approximately 30 ng/L in the effluent, which is still higher than the OTCs.

Sagehashi et al. (2005a) looked at MIB removal by combining adsorption on a high silica zeolite adsorbent (USY) with ozonation. This study is based on the principle that MIB can be readily adsorbed and concentrated in these porous adsorbents and can then be rapidly degraded with ozone thereby regenerating the adsorption sites. They initially looked at only adsorption and found that although MIB was readily adsorbed on the adsorbent, it desorbed with time in water containing NOM whereas it stayed adsorbed in case of the pure water. This was attributed to competitive adsorption from the NOM with molecular size in the same range as MIB. Since ozone would also need to be adsorbed and decomposed on the USY adsorbent for the adsorptive ozonation process, they optimized the conditions for adsorption of ozone in water including the pH and range of silica to alumina ratio in the adsorbent (Fujita et al. 2004). The authors developed ozone adsorption equilibrium equations and decomposition reaction rates. The authors then conducted the adsorptive ozonation experiment for MIB removal with USYs with different Si/Al ratios to alumina ratios, and also with another commercially available high silica zeolite and two types of activated carbon (Sagehashi et al., 2005b). The results indicated that USY at a Si/Al ratio of 70 showed the highest adsorption for MIB and also the best kinetics during MIB decomposition with ozone. However, it should be noted that the MIB concentrations used in the study were high at 6–7 mg/L. Based on the same principle, they were able to achieve MIB decomposition even with natural water containing NOM. By optimizing the ozone dosage and contact time and by including additional columns, they were able to demonstrate adsorption and decomposition of NOM particles without affecting the removal of MIB in a continuous flow system (Sagehashi et al., 2005a). However, the authors acknowledge the main limitation, which is the long term effect on the zeolite properties due to continuous accumulation of oxidized products and whether the adsorption sites would be able to keep regenerating by ozone oxidation of adsorbed NOM particles.

It is clear that some of the integrated technologies like GAC + biofiltration and ozonation + biofiltration have shown improved removal of MIB/geosmin and have the potential to be further developed for implementation in the field.

4.5 Other novel treatment methods

The above sections discussed technologies that are conventionally used in water treatment facilities. However, MIB/geosmin removal in water has been demonstrated by other novel methods on a bench/laboratory scale. Lawton et al. (2003) investigated MIB/geosmin removal using titanium dioxide photocatalysis. The results showed rapid degradation of both MIB/geosmin with more than 99% removal within 60 minutes. The pseudo first-order reaction rates were determined. The authors acknowledged the challenges involved with field application of this technology and the uncertainty regarding the process efficiency when applied for water containing NOM. Song and O’Shea (2007) investigated MIB/geosmin removal in
water by ultrasonic irradiation. When water is subjected to ultrasonic radiation, it is associated with generation of heat, and the resulting pyrolysis causes degradation of the MIB/geosmin. The study found that with this method, complete removal could be achieved in a matter of minutes. The authors also developed degradation kinetics and suggested possible degradation pathways. Since the method is not based on chemical removal, the presence of hydroxyl radical scavengers in the water did not influence the MIB/geosmin removal efficiency. Although this technology might be applicable for the aquaculture industry, there are several reasons that would prohibit its large-scale application in a drinking water treatment facility.

4.6 Current status

Although some of the conventional technologies discussed in the previous section are effective for removal of MIB/geosmin in water, it is not necessary for treatment plants to install any one technology exclusively for treating taste and odor. The current practice most commonly followed is application of PAC during severe taste and odor outbreaks. There are several factors that affect PAC dosage as well. Westerhoff et al. (2005) looked at the mechanisms affecting MIB/geosmin concentrations in water supply reservoirs and found that thermal stratification significantly influenced the MIB/geosmin concentrations released into the supplied water. The mechanism of water intake from a reservoir could also influence its MIB/geosmin concentration. Based on the thermal destratification, the amount of MIB/geosmin released and the duration of the episode could be estimated. This data could then be used by the water utility to set the PAC dosage. Water utilities could also optimize the technology they are currently using for MIB/geosmin treatment. This could be done by performing jar tests/bench-scale testing to generate some kind of implementation guide similar to that developed by Bruce et al. (2002), that would allow them to adjust the dosages in case of PAC/GAC or AOPs based on the influent MIB/geosmin concentrations and desired effluent levels. Tests could also be performed to identify locations within a water treatment plant that could be used depending on the scale of the taste and odor episode for the most cost-effective treatment.

Another way of controlling these compounds in water treatment plants is periodic chlorination to prevent algal growth. Although chlorination is effective, its use with PAC results in increased chlorine demand from PAC, reduction in the sorption capacity due to oxidation and has also been found to result in desorption of the adsorbed odorant (Bruce et al., 2002).

Based on this discussion, it is clear that it would not be economical or practical for water treatment facilities to install a technology exclusively for treatment of MIB/geosmin. It would be preferable to have a conventional technology that is optimized for MIB/geosmin removal. An even better alternative would be a system that has been installed for treating other contaminants and that would be effective for these odorants also during severe taste or odor episodes.

5 Conclusions

MIB/geosmin have been identified as the main taste and odor causing compounds in drinking water. Although these two compounds have been not been associated with any serious health effects, the resulting taste and odor from their presence is perceived as unsafe by consumers. The main challenge faced by drinking water utilities in their removal is that they can be detected at extremely low concentrations, down to nanograms per liter. This taste and odor problem is acute in summer months when cyanobacterial blooms are common due to the warmer, nutrient rich conditions. Studies have found that it is extremely difficult to remove these two odorants by conventional water treatment methods. Coagulation, sedimentation and chlorination have been found to be ineffective for their treatment. Currently adsorption by powdered activated carbon (PAC) is the most effective and widely used technology and is routinely used in water treatment plants to treat these odorants during severe outbreaks. Another factor that adds to the challenge faced by drinking water facilities in the removal of these contaminants is the presence of natural organic matter (NOM). Although PAC is practical for intermittent use, there is potential for formation of excessive sludge and resulting increased operating costs. GAC filtration is more effective when the carbon is tailored and also its performance is significantly influenced by the presence of NOM. Competitive adsorption reduces the capacity of the carbon to adsorb MIB/geosmin in the presence of other organic contaminants. Studies have shown that AOPs such as ozone and UV/H2O2 are effective for removal of these compounds in water where the hydroxyl radical is the main mechanism of oxidation. However, the capital and operating costs associated with these AOPs can be significantly high, especially at the higher dosages required for MIB/geosmin. Also they could result in the formation of disinfection byproducts which could be of health or regulatory concerns. Another treatment alternative that has received a lot of attention is biological treatment, specifically biofiltration. Sand filtration is invariably used in most water treatment plants and in most cases these filters support biological activity which enhances filtration. Sand biofiltration has been found to be effective for removal of MIB/geosmin. However, complete removal has been observed mainly where biofilter is supported on GAC or is followed by ozonation. Although some bacteria have been identified for removal of MIB/geosmin, it would be difficult to introduce these microorganisms into the treatment system, before knowing if they have any associated health effects. All these major technologies along with their advantages and challenges associated with their application have been discussed in detail in this review. Because taste and odor events due to MIB/geosmin in water are seasonal, their treatment may not be required at all times. Consequently, a treatment system with PAC, where the dosage can be adjusted easily based on the influent odorant concentrations is preferable. A lot of research has been focused into optimizing PAC dosages and trying to resolve some of the challenges faced by
utilities in its application. Future work in this area would enable drinking water treatment facilities to implement these technologies with minimal operational issues and ensure clean wholesome water to the consumers.

References


McGuire M J, 1995. Ozone and ultraviolet light for the destruction of 2-methylisoborneol and geosmin in drinking water biofil-


