Can we predict the removal of MIB and geosmin with PAC by using water quality parameters?

D. Cook and G. Newcombe
Australian Water Quality Centre, a partner in the CRC for Water Quality and Treatment, PMB 3 Salisbury, SA 5108, Australia
University of South Australia, School of Pharmaceutical, Molecular and Biomedical Sciences, Mawson Lakes SA 5095, Australia (E-mail: david.cook@sawater.com.au)

Abstract Cyanobacterial blooms in source waters are of concern as they can produce some compounds that are aesthetically unpleasant in potable water. Musty–earthy taste and odour compounds 2-methylisoborneol (MIB) and geosmin are produced by some species of cyanobacteria and actinomycetes. These compounds are low molecular weight volatile tertiary alcohols whose presence in treated water even at low ng L⁻¹ levels can result in consumer complaints. Adsorption onto powdered activated carbon (PAC) is often used to remove these compounds during the treatment process. PAC is very efficient at removing these compounds but the presence of natural organic matter (NOM) reduces the efficiency of the PAC. For effective application of PAC the impact of NOM must be taken into account when determining the required dose. In this study the adsorption of MIB and geosmin from several waters was related to water quality parameters of dissolved organic carbon (DOC), UV absorbance at 254 nm and colour to determine if these could be used to predict adsorption. Results obtained showed that the water quality parameters of DOC and UV absorbance at 254 nm could be useful indicators for MIB and geosmin adsorption, although the relationship appears to be specific to the water source in question.

Keywords Adsorption; geosmin; MIB; natural organic matter; powdered activated carbon; water treatment

Introduction
A challenge facing many water authorities that rely on surface waters as a drinking water supply is the tastes and odours that can occur in these water bodies. The removal of musty–earthy tastes and odours often provides the greatest test in drinking water treatment. These can be present as a result of cyanobacterial blooms or from actinomycetes with the two most important being 2-methylisoborneol (MIB) and geosmin. The presence of these compounds in the distribution system even at a few ng L⁻¹, or parts per trillion, is enough to generate customer dissatisfaction.

Conventional treatment processes that employ coagulants to remove turbidity and natural organic matter (NOM), can be effective for the removal of cyanobacterial cells containing tastes and odours but are ineffective for the removal of dissolved MIB and geosmin. Powdered activated carbon (PAC) can effectively remove these compounds; however, the success of PAC depends on the application of a sufficient dose, which in turn depends on water treatment plant (WTP) conditions (flow rate and hence contact time), concentration of target compound(s) and the inlet water quality, particularly the NOM concentration and character. NOM competes with the target compounds for adsorption sites on the activated carbon, reducing its effectiveness.

For MIB, geosmin and the microcystin analogues microcystin-LR (mLR) and microcystin-LA (mLA), it has been established that the amount of compound remaining after PAC addition, expressed as a fraction or percentage, is independent of its initial concentration and is a function of the PAC dose and contact time (Huang et al., 1996; Gillogly et al., 1998; Cook et al., 2001 and Cook and Newcombe, 2002). This relationship can be
used to determine the PAC dose if the influent concentration of the target compound and the
PAC contact time in the water treatment process is known. However, a change in the NOM
character or concentration can result in a change in the PAC dose requirement. If the effect
of NOM on adsorption can be determined from the properties of the competing NOM the
ability to predict the PAC dose requirements would be further improved.

The aim of this work was to determine if the adsorption of MIB and geosmin could be
related to concentration and character of the NOM in the water. This was completed by
determining the amount of these compounds adsorbed from a range of water samples and
relating this to dissolved organic carbon (DOC) concentration, UV absorbance at 254 nm
and colour. These parameters were chosen as they are inexpensive and simple to complete
with UV absorbance at 254 nm and colour routinely analysed at most WTPs.

Materials and methods
Materials

Water samples. Water samples were filtered through a 0.45 µm filter and stored at 4°C until
required.

Powdered activated carbon. Picatif 1100 was supplied by PICA Carbon Australia. It is a
coconut-based steam activated carbon with an average particle diameter of 10 µm. Prior to
use the PAC was dried at 105°C for 24 hours then cooled and stored in a desiccator.

MIB. 14C-labelled 2-methylisoborneol (14C-MIB) was supplied from American Radio
Labelled Chemicals. The solution was found to be > 99% pure by gas chromatography/
mass spectrometry (GC/MS) analysis.

Geosmin. Geosmin was received as a colourless liquid (Ultrafine Chemicals, UK). A stock
solution of geosmin was prepared by dissolving 0.01 g of geosmin into Milli-Q water
(Millipore Pty Ltd, France). This was added to a 100 mL volumetric flask and topped up
with Milli-Q water to minimise headspace. The volumetric flask was sealed with Parafilm
“M” (American National Can, USA) then agitated on a bench top shaker for a period of 7
days and stored at 4°C prior to use.

Analytical methods

Geosmin. Geosmin was analysed using solid-phase microextraction gas chromatogra-
phy/mass spectrometry (SPME-GC/MS).

MIB. MIB was analysed using a Beckman LS2800 liquid scintillation counter. 2.5 mL of
0.45 µm filtered sample was mixed with 17.5 mL of scintillation cocktail (Canberra
Packard) in a 20 mL polyethylene scintillation vial. The concentration of MIB in ng L⁻¹ was
converted from disintegrations per minute using equation 1 below with activity of 14C-MIB
being 55 mCi mmol⁻¹.

\[
\text{MIB concentration (ng L}^{-1}\text{)} = (\text{actual count} - \text{background count}) \times 0.55792
\]  

NOM analysis and characterisation

Samples were filtered through 0.45 µm membrane. Dissolved organic carbon was meas-
ured using a Sievers 820 total organic carbon analyser (Ionics, USA). True colour was
determined by comparing the absorbance of the sample at 456 nm (50 mm path length),
with a platinum/cobalt standard (50 Hazen Units (HU)). Specific colour was determined by
dividing true colour by DOC concentration. UV absorbance was obtained using a GBC UV/Vis 918 spectrophotometer. The specific UV absorbance (SUVA) was calculated using the equation: \( \text{SUVA} = 100 \times \frac{\text{UV absorbance at 254 nm}}{\text{DOC}} \). The molecular weight distributions were determined using high-performance size-exclusion chromatography (HPSEC) analysis based on the method used by Chin et al. (1994). The column (Shodex Protein KW-802.5, apparent molecular weight range 0.1 k-50 k, Showa Denko, Japan) was calibrated using polystyrene sulphonates of molecular weight 35 k, 18 k, 8 k and 4.6 k (Polysciences, USA). These compounds are considered to best represent the structure and conformation of NOM in solution. UV absorbance at 260 nm was used for HPSEC detection.

**Experimental procedures**

**Kinetics.** MIB or geosmin was added to a water sample and after thorough mixing a sample was taken to determine the initial concentration. PAC (pre-wetted overnight) was added to the water sample, with stirring, and samples were then taken at predetermined time intervals. Prior to analysis each sample was pressure filtered with a syringe through a 0.45 µm disposable filter to remove the PAC.

**Results and discussion**

The adsorption of MIB from a series of dilutions of Myponga Reservoir water (sampled in 2001) was investigated to determine the effect of the concentration of NOM on adsorption. The reservoir water was diluted with 0.01 mol L\(^{-1}\) NaCl to maintain a comparable ionic strength between the original sample and the dilutions. This is not strictly representative of a natural system as seasonal factors would not only affect NOM concentration but also character. Table 1 shows the amount of NOM in each dilution and that the character of each water is the same as described by SUVA, specific colour and molecular weight distribution of UV absorbing NOM. The adsorption of MIB from these waters is shown in Figure 1a with the amount of MIB remaining in solution decreasing with increasing dilution (decreasing DOC). Figure 1b shows that the fraction remaining at 30 minutes is directly related to the DOC of the water. The same trends were also noticed for UV absorbance at 254 nm and colour (not shown) and was also evident at other contact times examined. This is because the fraction of NOM that actively competes with MIB for adsorption onto the PAC decreases with increasing dilution along with DOC, UV absorbance at 254 nm and colour.

In Figure 2 the data is presented in terms of minimum PAC dose required to reduce MIB to a level at which there would be little or no customer dissatisfaction. Results obtained for a sample taken from Myponga Reservoir in 1998 are also shown. The PAC doses were determined using the homogeneous surface diffusion model (HSDM), as outlined by Cook et al. (2001). These results show that the minimum PAC dose was directly related to DOC, UV absorbance at 254 nm and colour. The PAC doses calculated on the Myponga 1998

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC (mg L(^{-1}))</th>
<th>UV Abs @ 254 nm (L m(^{-1}) mg(^{-1}))</th>
<th>SUVA (LU mg(^{-1}))</th>
<th>Colour (HU)</th>
<th>Specific colour (LU mg(^{-1}) L)</th>
<th>Molecular weight M(_r)/M(_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myponga</td>
<td>12.6</td>
<td>0.489</td>
<td>3.9</td>
<td>74</td>
<td>5.9</td>
<td>1,470</td>
</tr>
<tr>
<td>Dilution A</td>
<td>6.8</td>
<td>0.269</td>
<td>4.0</td>
<td>42</td>
<td>6.2</td>
<td>1,460</td>
</tr>
<tr>
<td>Dilution B</td>
<td>4.9</td>
<td>0.172</td>
<td>3.5</td>
<td>24</td>
<td>4.9</td>
<td>1,472</td>
</tr>
<tr>
<td>Dilution C</td>
<td>2.6</td>
<td>0.100</td>
<td>3.8</td>
<td>14</td>
<td>5.4</td>
<td>1,466</td>
</tr>
<tr>
<td>Myponga 1998</td>
<td>9.8</td>
<td>0.386</td>
<td>3.9</td>
<td>55</td>
<td>5.6</td>
<td>Not determined</td>
</tr>
</tbody>
</table>
sample also fitted the trend. Myponga Reservoir is situated in a closed catchment and it is possible that this results in a consistency of water quality, in particular NOM character, that makes it possible to predict the adsorption of MIB onto PAC.

The adsorption of MIB was also examined in Happy Valley Reservoir water samples. Water quality data (Table 2) shows that there was quite a variation in DOC and UV absorbance at 254 nm, while the SUVA values of the samples were similar. This consistency in water quality data is quite similar to that of the Myponga Reservoir water samples (Table 1).

For Happy Valley Reservoir water the results obtained (Figure 3) indicate that DOC and

Table 2: Water quality of Happy Valley Reservoir samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>DOC (mg L⁻¹)</th>
<th>UV Abs @ 254 nm (cm⁻¹)</th>
<th>SUVA (Lm⁻¹mg⁻¹)</th>
<th>Colour (HU)</th>
<th>Specific colour (HUmg⁻¹L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/8/99</td>
<td>8.6</td>
<td>0.266</td>
<td>3.1</td>
<td>37</td>
<td>4.3</td>
</tr>
<tr>
<td>6/8/99 diluted</td>
<td>4.5</td>
<td>0.136</td>
<td>3.0</td>
<td>19</td>
<td>4.2</td>
</tr>
<tr>
<td>10/02/98</td>
<td>4.6</td>
<td>0.143</td>
<td>3.1</td>
<td>16</td>
<td>3.5</td>
</tr>
<tr>
<td>29/07/98</td>
<td>6.1</td>
<td>0.198</td>
<td>3.2</td>
<td>26</td>
<td>4.3</td>
</tr>
<tr>
<td>19/07/99</td>
<td>8.0</td>
<td>0.238</td>
<td>3.0</td>
<td>29</td>
<td>3.6</td>
</tr>
</tbody>
</table>
UV absorbance at 254 nm are reasonable indicators to predict MIB adsorption, while colour is not suitable.

When results for MIB and geosmin are plotted for a wide range of waters no significant relationship between required PAC dose and the water quality parameters is seen (Figure 4).

These results indicate that commonly used water quality parameters such as DOC, UV absorbance and colour do not provide sufficient information to allow the prediction of PAC doses in a range of water samples from numerous locations. This suggests that they are not specific indicators of the proportion of NOM competing for the adsorption sites with MIB and geosmin. The DOC concentration is a measure of the amount of NOM in the water while UV absorbance at 254 nm and colour are dependent on the structure of the compounds present. An increase in UV absorbance at 254 nm indicates that the NOM is increasing in aromaticity and unsaturated carbon bonds (–C=–C–) while an increase in colour indicates a greater proportion of compounds with conjugated carbon double bonds (–C=C–C=C–).

For MIB it has been found that compounds of similar size compete most strongly for adsorption sites (Newcombe et al., 1997; Hepplewhite, 2000). The concentration of these low molecular weight compounds may change considerably with little resultant effect on the water quality parameters measured. The concentration of these low molecular weight compounds will depend on a range of factors including catchment land use, rainfall, soil types, climate and reservoir detention time. The development of HPSEC with DOC detection offers the best opportunity to evaluate the presence of these compounds in water samples.
Conclusion
Water quality parameters such as DOC and UV absorbance at 254 nm have proved to be useful indicators for MIB and geosmin adsorption, although the relationship is specific to the water source. It is recommended that at least UV absorbance at 254 nm and if possible DOC be measured during PAC dosing events or during laboratory trials. This information can be used to generate a database to assist in establishing a semi-quantitative relationship between PAC performance and bulk NOM parameters, in an effort to improve PAC dosing in future taste and odour episodes.

References