Effects of chlorine and chloramines on earthy and musty odors in drinking water

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Abstract Water treatment plants in the US may operate under the assumption that chlorine masks earthy and musty odors from geosmin and 2-methylisoborneol (MIB) in drinking water. To test this hypothesis, we evaluated the effects of chlorine and chloramines on geosmin and MIB by two sensory analysis approaches – a statistical Pairwise Comparison Test, and Flavor Profile Analysis (FPA). All Pairwise Ranking test statistics were significant (p<0.05); we conclude that panelists can differentiate minor differences in geosmin and MIB concentrations in a Pairwise Comparison Test even in the presence of chlorine. FPA appeared to be more challenging in discerning subtle differences in concentrations of geosmin or MIB than did the Pairwise Comparison Test, and the presence of chlorine (0.5–20 mg/L) and chloramines (3–24 mg/L) confused the panelists (i.e showed a larger error in the intensity of response reported by the panel), but did not necessarily mask geosmin or MIB.

Keywords Antagonism; chlorine; earthy; flavor profile analysis; geosmin; MIB; musty

Introduction

Adverse tastes and odors are a source of concern for the water supply industry because consumers associate off-tastes and odors with poor drinking water quality. Some of these off-tastes and odors are caused by naturally occurring compounds in the water; two such compounds, geosmin and 2-methylisoborneol (MIB), produce earthy and musty odors, respectively. These terpenoid-like compounds are produced by cyanobacteria and actinomycetes present in the raw water and released by cell lysis (Rosen *et al.*, 1992) and are detectable at very low concentrations. The odor threshold of geosmin has been reported to be 6–10 ng/L (Persson, 1980; Krasner *et al.*, 1983a; Rashash *et al.*, 1997) and for MIB, 2–20 ng/L (Burlingame *et al.*, 1991; Rashash *et al.*, 1997; Krasner *et al.*, 1983a,b).

An American Water Works Association survey indicated that the major odor complaints reported by water utilities were described as chlorinous, followed by earthy and fishy (Suffet *et al.*, 1995). Although chlorine is one of the most widely used water treatment process for taste and odor control, it is also a major complaint of customers (Suffet *et al.*, 1995). In addition, chlorination can actually cause a greater release of geosmin and MIB from algae and actinomycetes as they are lysed. Therefore, extra chlorination may not be an appropriate strategy to treat these two odor complaints. The practice of using chlorine or chloramines for odor control of geosmin and MIB stems from observations of some water utilities that chlorine can mask the odors of geosmin and MIB (Dougherty and Morris, 1967; Burlingame *et al.*, 1986; Zhang *et al.*, 1992; Suffet *et al.*, 1995). Zhang *et al.* (1992) found that the musty taste of MIB at concentrations of 10 ng/L and 20 ng/L decreased as the free chlorine concentration increased, and that the musty taste of MIB in sand-filtered water increased during decay of the chlorine residual. In the Philadelphia water supply with 2 mg/L monochloramine residual, MIB was detected at its odor threshold, suggesting that no masking occurs of MIB by monochloramine (Burlingame, 2002). Worley *et al.* (2003) determined by FPA that chlorine had a masking effect on both geosmin and MIB, according

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to their taste-and-odor panelists. The panelists in the Worley (2003) study gave higher intensities for geosmin and MIB in the absence of chlorine (in samples both pre-chlorination and post-dechlorination) than with chlorine present.

Flavor Profile Analysis (FPA) is a sensory technique that has been successfully adapted by water utilities for taste and odor evaluation from the food industry and can be used to quantitatively and qualitatively evaluate odors in drinking water (APHA *et al.*, 1994–2000, Method 2170). FPA is a method that allows a trained panel to identify a specific odor or taste in water and indicate the intensity on a 7-point scale (all odd numbers except 1 are not used). Most taste-and-odor events in water will produce intensities in the middle to lower half of the scale. The success of the FPA method, or any sensory technique, is based on a well trained panel in which variations are minimized, thereby obtaining reliable results (Stone and Sidel, 1985). Some chemicals, such as chlorine and geosmin, have been shown to cause panelist fatigue, therefore panel rest periods between samples need to be used (Krasner *et al.*, 1983b; Burlingame *et al.*, 1989).

The relationship between odor intensity and chemical concentration is generally described by the Weber–Fechner Law of 1859 (Suffet *et al.*, 1995). When a mixture of chemicals produces a similar flavor, the relationship between flavor intensity and chemical concentrations can be expressed by an extension of the Weber–Fechner Model in Eq. (1) below (Mallevialle and Suffet, 1987).

$$I_\mathrm{i} = \sum_{i=1}^{p} a_{ij} * \mathrm{Log}\, C_j \qquad (1)$$

where p = the total number of chemicals; I_i = the intensity of odor I; C_j = concentration of chemical j; and a_{ij} = the response constant to odor i of chemical j.

When a mixture of odor-producing compounds is present in aqueous solution, one of the three following results may be found by an odor analysis: additivity, synergism or antagonism (Baker, 1961). Additive means that the total intensity should be the sum of the individual odors, and that one agent does not alter the intensity of another. Synergism is the same as enhancement, and antagonism means a masking effect. In addition, the types of interactions that occur between chemicals may be concentration-dependent. The aim of this study was to investigate the effect of chlorine and chloramines on the intensities of geosmin and MIB odors at concentrations similar to those actually found in drinking water distribution systems.

Methods

Sample comparison by flavor profile analysis

Two different panels (designated Panel 1 and Panel 2, respectively) consisting of at least 5 people were convened to test the hypothesis that chlorine and chloramines mask the taste-and-odor of geosmin and MIB. The panelists were trained in the method of Flavor Profile Analysis APHA, 1994; 2000, respectively.). Panel 1 evaluated concentrations of geosmin and MIB ranging from 5 to 1,200 ng/L. Chloramines were prepared by treating chlorine with ammonia at pH 7; mono- and di- chloramines were not differentiated. Panel 1 evaluated concentrations of 3, 6, and 24 mg/L chloramines, and 0.5, 2.0, and 20 mg/L chlorine. Panel 2 evaluated concentrations of MIB and geosmin at 30, 60, and 120 ng/L (ppt) with 0, 2, and 5 mg/L chlorine. The samples were presented blindly and randomly to the panelists. Descriptors and their intensities were plotted as Weber–Fechner curves for the analysis.

Paired comparison of samples

The Pairwise Ranking Test (Meilgaard *et al.*, 1999) is a sensory technique in which statistics can be used to evaluate several samples compared for a single attribute. Samples are

Table 1 Matrix of testing for pairwise ranking test – derived from Meilgaard *et al.* (1999)

Columns rows	0 ng/L	30 ng/L	60 ng/L	120 ng/L
0 ng/L	–	No. saying 0>30	No. saying 0>60	No. saying 0>120
30 ng/L	No. saying 30>0	–	No. saying 30>60	No. saying 30>120
60 ng/L	No. saying 60>0	No. saying 60>30	–	No. saying 60>120
120 ng/L	No. saying 120>0	No. saying120>30	No. saying120>60	–

arranged on a scale of intensity of the chosen attribute, and assigned a value indicating the differences between samples and the significance of these differences. Geosmin and MIB were tested separately as the attribute under study.

Samples of different concentrations of either geosmin or MIB (note that geosmin and MIB were never paired; the pair contained either geosmin or MIB) with or without chlorine were paired (A versus B) and presented to Panel 2 who were asked to select which sample, A or B, had the highest intensity of the earthy or musty odor. The paired samples contained the same amount of chlorine at levels of 0, 2, or 5 mg/L of free chlorine. The concentrations of geosmin and MIB were 5, 15, 30, 60, and 120 ng/L. Panelists were not given more than five pairs of samples on a given day. For each level of chlorine, samples were prepared according to the matrix in Table 1; panelists respond whether the row sample or the column sample had the greater intensity of "earthy" or "musty" odor. All possible pairs represented in this matrix were compared.

As one moves through this matrix at a diagonal from the upper right hand corner towards the lower left-hand side, the assumption is that the number of respondents would increase if the results were not random. For example, the number of respondents saying that the 120 ppt geosmin sample had a greater intensity than the 0 ppt geosmin sample would approach 100%. The study was conducted in three sessions, on separate days. A total of 15 responses for any pair in the matrix represent five panelists' responses for three sessions.

The Friedman analysis was used to compute the rank sum for each sample. The rank of one is assigned to the sample (A or B) with the higher concentration of geosmin or MIB. The rank of two is assigned to the sample (A or B) that had the lower concentration of geosmin or MIB. Then, the rank sums are obtained by adding the sum of the row frequencies to twice the sum of the column frequencies. The test statistic for the Friedman analysis is computed as follows in Eq. (2):

$$T = (4/pt)\sum_{i=1}^{t} R^2 - (9p\,[t-1]^2), \qquad (2)$$

where p = the number of times the basic design is repeated (i.e. 12 in each matrix), t = the number of treatments, R is the rank sum. T is the test statistic. For example, for critical values of T tabulated for $t = 4$ in Meilgaard *et al.* (1999) for a level of significance of $\alpha = 0.05$, the critical T is 7.81.

Results and discussion

Flavor profile analysis

The results of Panel 1, where geosmin and MIB concentrations ranging from 5 to 1,200 ng/L were evaluated in the presence of chlorine or chloramines, are presented in Figures 1 and 2, below.

The results of Panel 1 do not demonstrate a masking effect of chloramines on geosmin (Figure 1, bottom row). At very high concentrations, the olfactory system can become overloaded (fatigued), resulting in saturation. The results for geosmin did not show a clear trend of either synergism or antagonism, but more likely confusion in the presence of chlorine

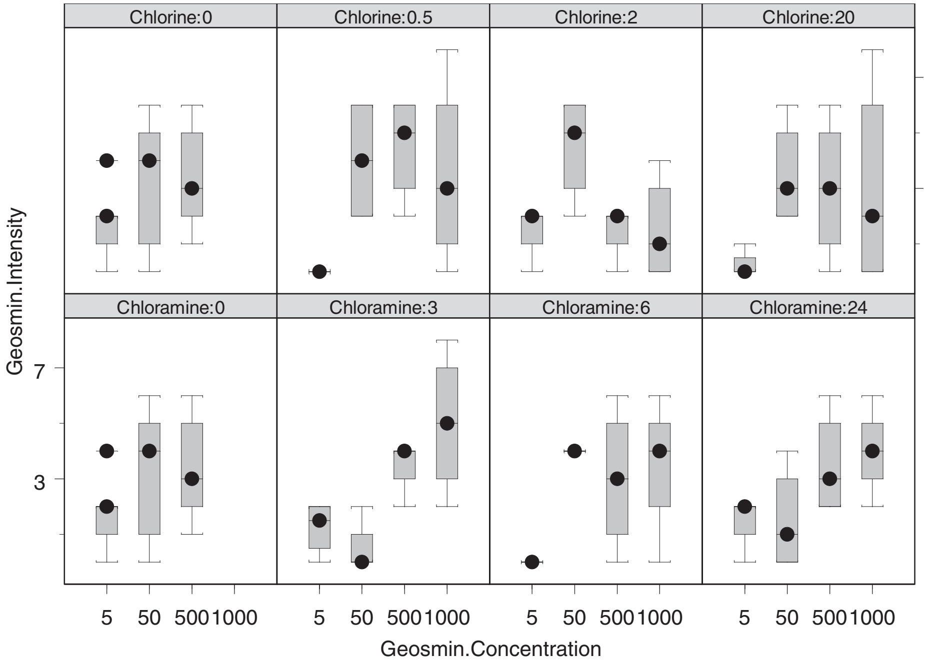

Figure 1 Box and Whisker plots depicting the median (dot), 25th, 75th percentiles (box edges) and extreme values (whiskers) of the Geosmin odor intensity observed by a FPA panel. The top row reflects the effect of different concentrations of chlorine (in mg/L), whereas the bottom row reflects the effect of different concentrations of chloramine (in mg/L). All geosmin concentrations are in ng/L. The extra dot above the box and whisker plots for the 5 ng/L geosmin at 0 chlorine and 0 chloramine indicates an outlier

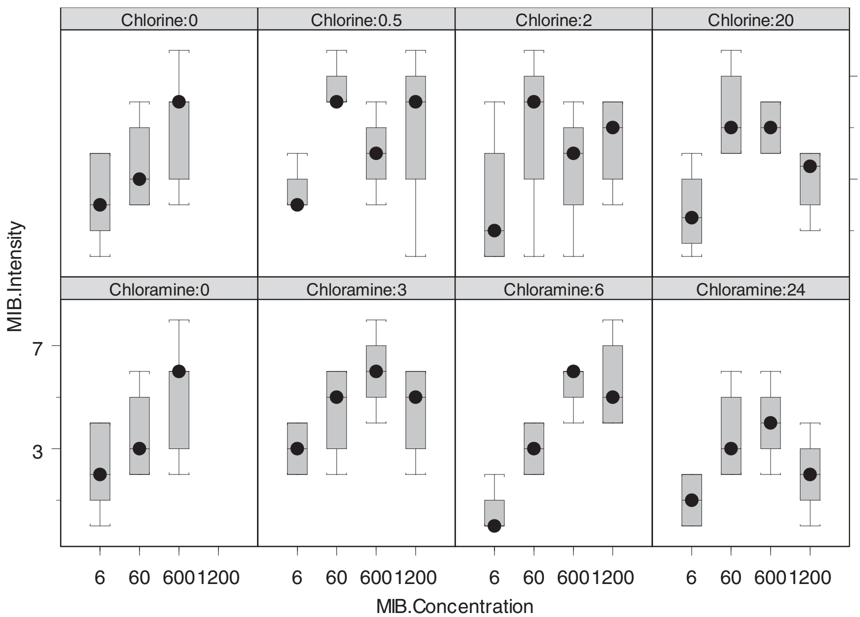

Figure 2 Box and Whisker plots depicting the values of MIB odor intensity observed by a FPA panel. The top row reflects the effect of different concentration of chloramines (in mg/L), whereas the bottom row reflects the effect of different concentrations of chlorine (in mg/L). All MIB concentrations presented are in ng/L

(Figure 1, top row) since the data were more scattered (i.e. had a larger panel intensity error) at the highest concentration of chlorine.

The results of the FPA of Panel 1 for MIB are somewhat ambiguous. There is not a strong indication of antagonism from chlorine or chloramines. A slight indication of antagonism on MIB is suggested at the highest concentrations of chloramines (24 mg/L) and chlorine (20 mg/L).

The FPA results of Panel 2 are presented in Figures 3 and 4. Instead of using the traditional Weber–Fechner curve of a semi-log scale, results are on a linear scale because the concentrations selected spanned only two orders of magnitude to reflect concentrations found in distribution systems. The results show no clear trend of synergistic or antagonistic effects of chlorine on geosmin.

Figure 4 indicates synergistic effects between chlorine and MIB at the highest chlorine (5 mg/L) and MIB (100 ng/L) concentrations, which contradicts the results of Panel 1. A synergistic effect of chlorine on MIB would suggest that strong MIB odor events should not be treated with the addition of extra chlorine. At low concentrations of MIB (0–60 ng/L), chlorine had no clear masking effect, indicating again that chlorine may not be an effective strategy for reducing consumer complaints of MIB. We agree with Worley *et al*. (2003) that dechlorination can be effective in improving sensory odor testing, since chlorine tends to confuse panelists. For water utilities, the question of whether chlorine can effectively mask odors tantamount to fewer consumer complaints may need to be determined empirically. Our data serve as a warning that one cannot automatically expect chlorine and chloramines to be effective in masking odors.

Pairwise ranking test – Friedman analysis

The test statistic for the Friedman analysis on the effect of chlorine was significant at all concentrations of chlorine, demonstrating that Panel 2 was able to determine which samples had higher concentrations of geosmin or MIB, regardless of the presence of chlorine, at chlorine concentrations representative of distribution systems in the United States (Figures 5–10). The percentage of panelists giving the correct answer (i.e. which of two samples has the highest intensity of either geosmin or MIB) for each comparison test can be seen in the figures. Note that for the entire matrix to be statistically significant for any chlorine concentration, most, but not all individual pairs must have >50% of respondents saying that the higher concentration had a higher intensity than the lower concentration.

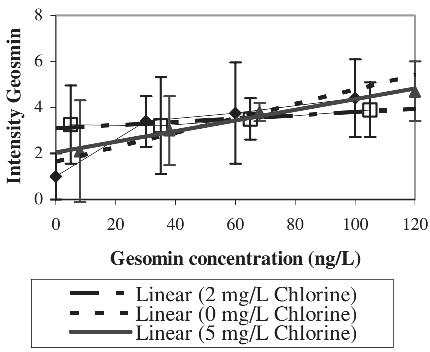

Figure 3 Average intensity vs concentration of Geosmin for different chlorine concentrations

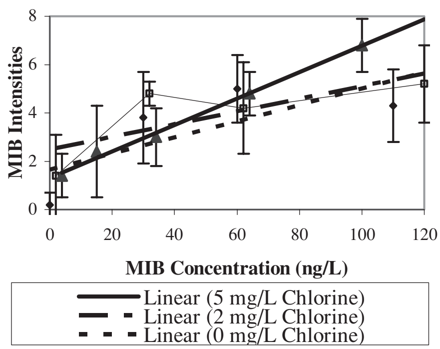

Figure 4 Average intensity vs concentration of MIB for different chlorine concentrations

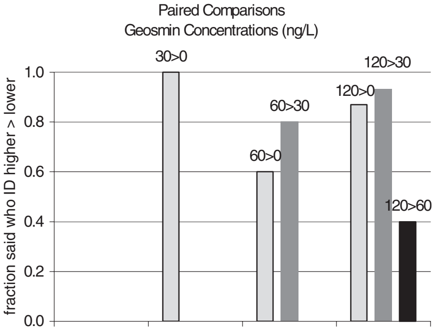

Figure 5 Friedman analysis of geosmin without chlorine (panel 2)

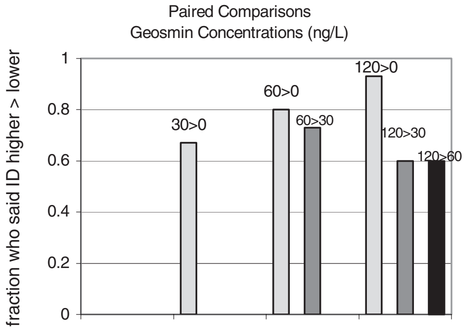

Figure 6 Friedman analysis of geosmin with 2 mg/L chlorine (panel 2)

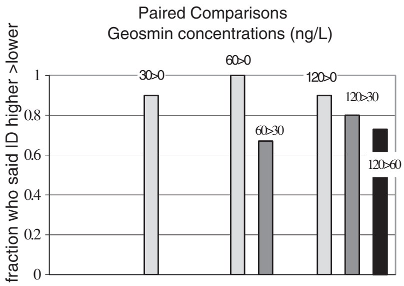

Figure 7 Friedman analysis of geosmin with 5 mg/L (panel 2)

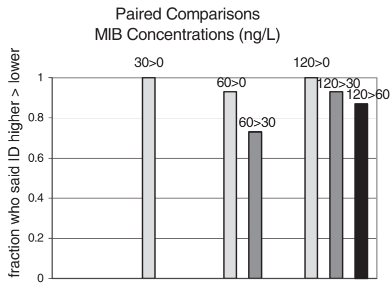

Figure 8 Friedman analysis of MIB without chlorine (panel 2)

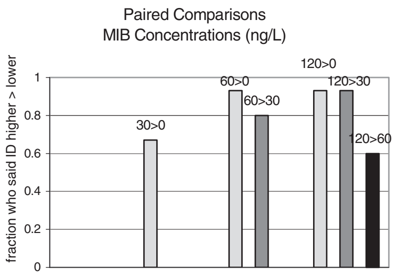

Figure 9 Friedman analysis of MIB with 2 mg/L chlorine (panel 2)

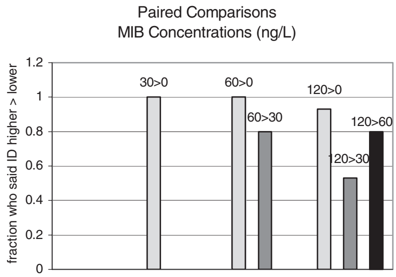

Figure 10 Friedman analysis of MIB with 5 mg/L chlorine (panel 2)

Conclusions

The test statistic for the Friedman analysis of the Paired Comparison Test showed that the panelists were able to determine which samples had higher concentrations of geosmin or MIB (p<0.05) (regardless of the presence of chlorine) at concentrations of chlorine representative of that found in distribution systems in the US. It is also apparent that a statistical (Paired Comparison) approach yields more consistent results than FPA, however, the two tests are generally used for different purposes. FPA is used to gain descriptive information about the taste-and-odor of the drinking water, whereas the paired comparison test is a statistical evaluation of a characteristic known a priori. The statistical method in this study was employed for evaluating the effect of chorine on the intensities of geosmin and MIB. We did not do a statistical evaluation of chloramines, but overall, chloramines appeared to show little masking effect of geosmin and MIB. By FPA, chlorine did not strongly mask either geosmin or MIB, according to our panelists. Therefore, chlorine may not be an effective strategy for reducing or masking other odors in drinking water. Chlorine was shown at times to confuse panelists' ability to ascertain subtle differences in geosmin and MIB concentrations (i.e. develop a larger error of intensity of response). Since chlorine itself can be an offending odor, adding excess chlorine does not necessarily enhance the total organoleptic quality of drinking water.

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