The effect of water source and chlorine and chloramine odorants in drinking water on earthy and musty odour intensity

Jane Curren, Zhengping Wang, Jose Matud, Erin D. Mackey and Mel Suffet

ABSTRACT

Water utilities and laboratory studies have indicated that chlorine or chloramines can mask earthy or musty odours. However, there have been conflicting results. Sensory testing was completed on finished waters from five water utilities and a control to determine whether earthy and musty odours, caused by geosmin and 2-methyl isoborneol (MIB), at concentrations found in drinking water, are dependent on the background water matrix or chlorine ($< 1\,mg\,l^{-1}$ as Cl) or chloramines ($2–4\,mg\,l^{-1}$ as Cl) concentrations found in finished drinking waters. Finished and dechlorinated water samples were spiked with geosmin and MIB and analysed by Flavor Profile Analysis to determine odour intensity and solid phase microextraction/GC-MS to determine actual geosmin and MIB concentrations. The participating utilities for this project represent a wide range of background matrices in terms of both total organic carbon and total dissolved solids. Background water quality did not significantly affect the intensity of earthy and musty odours. Dechlorination and dechloramination increased the intensity of the earthy odour of geosmin ($20.1–61.9\,ng\,l^{-1}$). However, dechlorination and dechloramination did not significantly affect the musty odour of MIB ($18.6\,ng\,l^{-1}$). This may be due to the statistical power of the method used at the low MIB concentration.

Key words | chloramines, chlorine, earthy odours, geosmin, masking odours, methyl isoborneol, musty odours

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INTRODUCTION

Geosmin and 2-methyl isoborneol (MIB) are algal by-products that cause earthy and musty odours, respectively, in drinking water at 10 to 100 nanogram per litre concentrations. These compounds are not removed by the conventional water treatment processes of coagulation and chlorination. Activated carbon, ozonation and advanced oxidation processes are needed to remove these compounds from a water supply (Suffet *et al.* 1995). While it was observed by some water utilities and in laboratory studies that a chlorine or chloramine residual can mask earthy or musty odours (Burlingame *et al.* 1986; Bartels *et al.* 1989; Zhang *et al.* 1992; Suffet *et al.* 1995; Worley *et al.* 2003), there are conflicting results.

Zhang *et al.* (1992), using a trained Flavor Profile Analysis (FPA) panel, found that the musty taste of MIB at concentrations of $10\,ng\,l^{-1}$ at 25°C decreased from 5.3 to 4.0 FPA units with the addition of $0.4\,mg\,l^{-1}$ chlorine, and the intensity of the musty taste of MIB at $20\,ng\,l^{-1}$ decreased from 7.1 to 5.0 FPA units with $0.4\,mg\,l^{-1}$ chlorine. Zhang *et al.* (1992) also found that the musty perceived taste of MIB in sand-filtered water increased during decay of the chlorine residual. Worley *et al.* (2003)

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determined by FPA that chlorine at 1 mg l^{-1} as Cl had a masking effect on MIB at 30 ng l^{-1} in one sample. Panellists gave intensities between 8 and 10 FPA units for both geosmin and MIB in the absence of chlorine, and below 1 FPA unit in the presence of chlorine. In a study by Oestman *et al.* (2004) the results showed that chlorine or chloramines did not strongly mask either geosmin or MIB. However the study used a wider range of MIB and geosmin concentrations (5–1,200 ng l^{-1}) and concentrations of chlorination agents (chlorine levels of 0.5–20 mg l^{-1} or chloramines levels of 3–24 mg l^{-1}) than occurs at water treatment plants. This may be a result of adaptation, as odour panellist adaptation was found at over 400 ng l^{-1} of geosmin and 100 ng l^{-1} MIB (Whelton & Dietrich 2004). In the Philadelphia water supply, with 2 mg l^{-1} monochloramine residual, MIB was detected at its odour threshold, suggesting that no masking of MIB occurs by chloramines (Personal communication with G.A. Burlingame, 2002). The reviewed studies showed mixed results for the ability of chlorine and chloramines odours to mask MIB (musty) odours.

Bartels *et al.* (1989) showed the antagonistic effect of dichloramines on geosmin by a trained FPA odour panel, but did not quantify the results. In a field study by Burlingame *et al.* (1986) where a geosmin odour event was occurring in Philadelphia drinking water, antagonism did occur with monochloramines. Table 1 of the paper reported the relatively low FPA intensity values (<1–4) with relatively high geosmin levels (as high as 88 ng l^{-1}). Worley *et al.* (2003) determined by FPA that chlorine at 1 mg l^{-1} as Cl had a masking effect on geosmin at 30 ng l^{-1} in one sample shown. All the studies showed the masking of geosmin (earthy) odours at drinking water concentrations by chlorine.

Furthermore, the impact of the background water quality matrix on geosmin and MIB had not been evaluated during chlorination or chloramination. Achievable finished water taste and odour goals may be related to source water quality. This study evaluates five different water sources and a control. The overall objective of this study was to complete sensory testing on different background waters from five water utilities and a control water to determine whether levels of earthy and musty odours are dependent on the background water matrix as well as on the presence of chlorine or chloramines.

MATERIALS AND METHODS

Studied waters

The participating utilities for this project represented a wide range of water types with varying background matrices in terms of both total organic carbon and total dissolved solids. Each of these utilities has had differing experiences with earthy or musty odours and a range of taste and odour treatment capabilities. Water source, disinfection agent, experiences with taste and odour events, and treatment methods for taste and odour events for each utility are listed in Table 1.

Water quality background tests

Water samples were collected and studied from background water (non-event) or, in one case, a taste and odour event.

Table 1 | Information on source, disinfection process, and taste and odour events in the studied waters

	Source		Disinfection		Taste and odour events	
Company	Surface water	Groundwater	Chlorine	Chloramine	Occurrence	Treatment
Utility 1	X	X		X		PAC*, permanganate, PAC cake on sand filters
Utility 2	X		X		Episodic	PAC, permanganate
Utility 3	X			X	Frequent	PAC
Utility 4	X	X	X		July to September	
Utility 5	X	X	X		Episodic	PAC
Evian Water (reference water)		X				

*PAC = powdered activated carbon.

Water samples were analysed for pH, turbidity, chlorine residual, conductivity and total dissolved solids (TDS) on site, before being sent to UCLA for TOC analysis. Samples were shipped overnight packed in ice. Upon arrival at UCLA samples were refrigerated at 4°C until they could be analysed. FPA analysis was performed within days of receiving samples. Chlorine residual was measured at UCLA to confirm values reported by the water utility, since chlorine residual will decrease over time.

Odour evaluation

Two Flavour Profile Analysis panels composed of UCLA graduate students between the ages of 22 and 35 were organized for the study. Panellists met once a week for 4 months to be trained to identify and distinguish earthy, musty and chlorine odours. They were also trained in the use of the FPA intensity scale. Since the flow rate of air through the nose can affect perceived odour intensity (Schneider *et al.* 1966), panellists were trained to use a consistent 'bunny sniff' method when smelling samples. During the training process, panellists who were anosmic to earthy or musty odours were eliminated. In the end, two panels were assembled. There were nine panellists altogether. Each panel met once a week in an odour-free room. Panellists were instructed not to eat 30 min before each session and not to wear lotions or perfumes. Panellists recorded their initial impressions of odour character and strength. Panellists were then asked to discuss each sample and then had the opportunity to re-evaluate their response. Panellists were given Evian water as an odour blank during each session.

Each sample was analysed by the two panels and the odour intensities of each panellist were statistically treated in the evaluation of the odour threshold concentration for the FPA panel test temperature of 45°C (*Standard Methods* 2000, Method 2170). Weber-Fechner curves, the relationship between odour intensity and the log of concentration, were completed to determine the odour thresholds of geosmin and MIB.

Waters were dechlorinated with three times the stoichiometric amount of sodium thiosulfate. While Worley *et al.* (2003) reported a 'rotten-egg' odour when excess sodium thiosulfate was used, our panel did not report these 'rotten-egg' odours in dechlorinated waters. Waters were analysed by FPA before and after dechlorination. These results were compared with Evian water as the control.

Since only one water sample source had significant geosmin background, drinking water samples were spiked with geosmin and MIB to simulate an event. Dechlorinated and neat samples were spiked with either geosmin, MIB or both geosmin and MIB. The geosmin and MIB standards were diluted to a target concentration of $15\,\mathrm{ng\,l^{-1}}$. This concentration was chosen because it gives an odour intensity between 4 and 6 for both geosmin and MIB according to the Weber-Fechner curves developed in this study. The true values as measured by chemical analysis were $20.1\,\mathrm{ng\,l^{-1}}$ for geosmin and $18.6\,\mathrm{ng\,l^{-1}}$ for MIB.

Chemical analysis

Water samples were analysed for MIB and geosmin using solid phase microextraction (SPME)/GC-MS analyses following Standard Methods (2000) with maintenance of strict QA/QC procedures. The analytical detection limit (DL) was determined to be $2.7\,\mathrm{ng\,l^{-1}}$ and the limit of quantification was set at three times the detection limit, $8.1\,\mathrm{ng\,l^{-1}}$. Both the blank water and the utility samples were chemically analysed before and after spiking with MIB and geosmin. GC-sensory analysis was done to scan for other earthy or musty compounds (Khiari *et al.* 1992). No other earthy or musty compounds were observed.

Statistical evaluation

A series of linear mixed models (Pinheiro & Bates 2000) were chosen to fit each odour type (chlorine, earthy, musty and earthy/musty) determined by the FPA method. The linear mixed modelling approach has the advantages of correcting estimates from repeated measures, providing unbiased estimates from unbalanced data, accounting for 'panellist effects' and autocorrelation of samples from the same water source. Sixteen water samples were evaluated by FPA from six different water sources using eight different protocols for each source or $16 \times 8 = 128$ FPA analyses. The data were analysed by the statistical analysis package R (R Foundation for Statistical Computing, R Development Core Team 2006).

Each odour type was modelled separately. However, the symbols in all four models are equivalent. The response y represents FPA odour intensity for either chlorine (or chloramine), earthy, musty, or earthy/musty odours as it was detected on treatment combination i by panellist j on water sample k.

$$y_{ijk} = \mu + \beta_t + \beta_m + \beta_g + \beta_{mg} + \beta_{tm} + \beta_{tg} + \beta_{tmg} + b_i + b_j + \varepsilon_{ijk}$$

The different treatment combinations identified by i determines whether the sample had been dechlorinated, any MIB added, or any geosmin added to the sample. The identifier k determined the source of the water. Repeated samples from each water source were used in the experiment. The fixed effects are parameter μ, which represents the estimated average odour intensity of the baseline water sample (i.e. those samples that had not been dechlorinated and to which neither MIB or geosmin had been added). Parameters β_t, β_m and β_g represent the 'main effects', which estimate the additional change in odour intensity observed when the samples were dechlorinated (i.e. the samples were 'treated'), the effect of adding MIB to the samples, and the effect of adding geosmin to the samples. First order interactions are represented by β_{mg}, β_{tm} and β_{tg}, which estimate any additional effect observed after adding both MIB and geosmin to untreated samples, adding MIB to treated samples, and the effect of adding geosmin to treated samples. The second order interaction β_{tmg} estimates any further change in odour intensity that was observed when both MIB and gesomin were added to the treated samples. These interactions were not statistically significant in the earthy and earthy-must models and were removed from the model in order to reduce the variability of the estimates.

Random effects are represented by the parameters b_j and b_{jk}, which account for the effect, or bias, of panellist j detecting odour intensities and any additional bias that the panellist could have when estimating the odour intensities of sample k. Both of these types of bias were assumed to be normally distributed with a mean of zero and a different variance for each random effect. Finally, each of the estimates made in the experiment was expected to include a random error ϵ, which was assumed to be normally distributed with a mean zero and variance σ^2.

The origin of the water sample was treated as a fixed effect, and then separate models were used for each of the four odour types, which also included changes due to dechlorination and addition of earthy and musty odorants and their interactions as 'fixed effects'. The response was measured in FPA units.

The fixed effects were coded as indicator variables. The baseline level was assigned as follows: No geosmin or MIB were added to the water that was originally a chlorinated or chloraminated drinking water sample. The treatment level for dechlorination or dechloramination indicates removing chlorine or chloramines from the water sample. Treatment levels for geosmin and MIB indicate that these contaminants have been added to the sample, either alone or together. Estimates of the FPA values of the combinations of fixed effects were extracted from the models, along with their corresponding standard errors, which were used to construct the figures included in the statistical results. The level of statistical significance has been adjusted downward from the standard $p < 0.05$, in order to account for the multiple comparisons that have taken place. Bonferroni adjustment for the four odours being considered resulted in a level of significance of $p < 0.013$ for pair wise comparisons. The statistical power of the method is limited by the concentrations of the chemicals utilized.

RESULTS

Water quality data

Utility 1 and Utility 3 used final chloramination, producing monochloramine. The other utilities used chlorination. Evian uses ozone, which dissipates before testing and serves as a control without any chlorination or chloramination. Table 2 presents the water quality data for six source waters studied and the control. Turbidity and pH for each of the utilities were similar. Total dissolved solids (TDS) and total organic carbon (TOC) ranged from 34 to 389 ppm and 1.2 to 8.6 mg C l^{-1}, respectively. This variation was enough to allow for a comparison of matrix effects on odour intensity. Notably, the variability in TOC for one utility, Utility 2, was from 3.5 to 8.6, also a significant change in the sample matrix.

Table 2 | FPA results and water quality data of water samples

			Water quality data					
Company	**Sample name**	**Sampling date**	**pH**	**Turbidity (NTU)**	**Chlorine residual (mg l^{-1})**	**Conductivity ($\mu S\ cm^{-1}$)**	**TDS (ppm)**	**TOC (mg l^{-1})**
Utility 1 (Chloramines)	C	22 March 2006	7	0.07	1.9	560	375	2.8
	F	5 April 2006	7	0.08	1.9	580	389	3
	H	10 April 2006	7	0.09	1.69	510	342	3.2
	N	1 May 2006	6.9	0.08	1.95	470	315	2
Utility 2 (Chlorine)	A	28 March 2006	8	0.03	0.93	450	302	8.6
	B	20 March 2006	7.5	0.03	1.04	470	315	3.5
	E	3 April 2006	7.9	0.03	0.92	450	302	4.9
	G	10 April 2006	7.6	0.02	1.02	440	295	4.5
Utility 3 (Chloramines)	D	3 April 2006	8.2	0.02	4	550	369	4.7
	I	10 April 2006	8.1	0.02	4	570	382	3.7
Utility 4 (Chlorine)	L	19 April 2006	7.6	0.99	0.98	70	47	1.2
	M	25 April 2006	7.5	0.9	1	50	34	1.2
Utility 5 (Chlorine)	J	12 April 2006	8	0.05	0.94	140	94	2.4
	K	5 April 2006	7.7	0.04	1.03	130	87	2.1
Evian	Evian	18 May 2006	7.2	0.09	1.01	580	389	3.3

Taste and odour data

Odour threshold concentration of MIB and geosmin

Figures 1 and 2 present the Weber-Fechner curves for geosmin and MIB. The R^2 indicates a straight line relationship with the expected high standard deviation with an error range of 1–3 intensity units. FPA as a panel method has an error associated with it that is larger than the usual chemical analysis error, as human subjects are used as the detector and the log of the concentration is proportional to odour intensity. Although there was a large error, the R^2 are 0.98 for MIB and 0.91 for geosmin. Large error in human perception is expected. Lawless & Heymann (1998) showed that odour threshold concentrations (OTCs) between subjects may vary by a factor of 10. The odour threshold concentration was estimated by extending the line to an odour intensity of 1, the odour threshold limit of the FPA test. The odour threshold concentration for MIB was 2.1 ng l^{-1} and 3.5 ng l^{-1} for geosmin at the experimental temperature of 45°C. Increasing the temperature would be expected to lower the OTC. At room temperature of about 20°C, the OTC of these chemicals was determined to be between 5 and 10 ng l^{-1} as reviewed by Mallevialle & Suffet (1987).

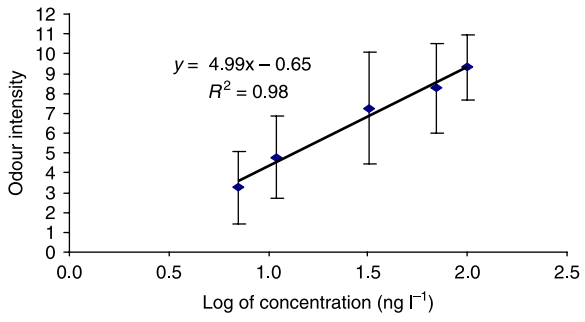

Figure 1 | Weber-Fechner curves developed in this study for MIB at 45°C.

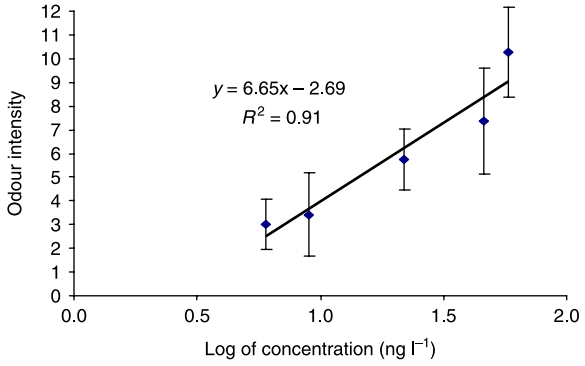

Figure 2 | Weber-Fechner curves developed in this study for geosmin at 45°C.

Reporting earthy and musty odours as earthy, musty and earthy/musty

There were panellists who, even after extensive training, had trouble differentiating the earthy and musty odour. To maintain a large panel for better statistical evaluation, a three category system was established where, if the panellist says earthy or musty, the data are presented as stated. Additionally an earthy-musty category was devised to be the worst case scenario: the higher of the two categories was used so that data would not be ignored due to misclassification. This three category system is also useful because misclassification would also be expected from untrained consumers. Table 3 reports the FPA intensity data in three categories: musty, earthy and earthy-musty.

Comparing earthy and musty FPA data and the analysis of geosmin and MIB

Table 3 presents the background taste and odour data for the waters tested. The FPA panel was aware that they were evaluating earthy/musty odours as they were trained to evaluate these odours. This study shows, as previous studies have shown, that panellists over-identify odours because they have the expectation that earthy and musty odours will be present (Worley *et al.* 2003). This is indicated by the identification of Evian with an earthy/musty odour of 2.3 to 3.0 even though geosmin and MIB concentrations were below the OTC.

Table 3 presents all the FPA and chemical analysis data developed for the water samples themselves before and after dechlorination. For Evian water, there was no difference observed between chlorinated and dechlorinated samples within the average earthy/musty intensity values of 2.3–3.0. The Evian levels of geosmin and MIB of $<2.7\,\mathrm{ng\,l^{-1}}$, the DL, were similar to the FPA results for other drinking waters that have $<2.7\,\mathrm{ng\,l^{-1}}$ geosmin or MIB with a background of total dissolved solids. Utilities 4 and 5 follow the Evian trend of average intensity values of earthy/musty of 1.0–2.8 with $<2.7\,\mathrm{ng\,l^{-1}}$ geosmin or MIB, the DL, reported chemically.

Table 3 shows that all SPME-GC/MS chemical analyses for geosmin and MIB were above the quantifiable limit of $8.1\,\mathrm{ng\,l^{-1}}$ for samples from Utility 1 except one sample that was above the DL but not quantifiable. Table 3 shows geosmin levels of over $40\,\mathrm{ng\,l^{-1}}$ were found in the water at Utility 1. All the geosmin and MIB levels were analysed to be above $8.1\,\mathrm{ng\,l^{-1}}$ when geosmin and MIB were added to the samples. All Utility 3 samples and one Utility 2 sample were above the DL of $2.7\,\mathrm{ng\,l^{-1}}$ but below the quantifiable limit of $8.1\,\mathrm{ng\,l^{-1}}$.

Statistical evaluation of the effect of the origin of the water sample on odour intensity

A fixed effect was used to determine whether the origin of the water sample had any significant effect on the odours' intensity. Figure 3(a) shows the results of the statistical evaluation for 'chlorine odour' as a representative example, since the remaining odour types showed a lesser effect for the water source factor.

Figure 3(a) shows there is no statistically significant difference among the water sources studied in this data set for the chlorine odour. The differences are not statistically significant at the required p-level of <0.013 even though Evian and Utility 2, as well as Utility 3 and Utility 2 do not overlap error bars for the normal water samples. Figure 3(b) shows there is no statistically significant difference among the water sources studied in this data set for the earthy odour. A similar evaluation done for musty and earthy/musty odours shows that source water did not have a significant affect on odour intensity. There were only six types of waters and the result is considered to be only an indication that the effect of the water types used is not significant. A study with a greater number of water sources should be tested to verify these results.

The source waters were treated as a random effect in order to account for possible differences among them. Preliminary models were used to select random effects for not only water source but also for panellist. Figure 4 shows the deviation from the population mean of each panellist for earthy odours. A similar evaluation was done for chlorine, musty and earthy/musty odours. Evaluation of trends in each panellist response allowed for the correction of the 'panellist effect'. No violations of the models' assumptions were found after scrutinizing the residuals of each model fitting.

Table 3 | FPA and SPME-GC/MS results for odour intensity of water samples

			FPA results (average odour intensity ± SD)						SPME-GC/MS results			
			Musty		Earthy		Earthy/musty		MIB (ng l^{-1})		Geosmin (ng l^{-1})	
Company	Sample name	Sampling date	Normal*	Dechlor†	Normal	Dechlor	Normal	Dechlor	Normal	Dechlor	Normal	Dechlor
Utility 1 (Chloramines)	C	22 March 2006	Note‡	Note	2.2 ± 2.0	2.1 ± 1.9	3.2 ± 1.6	2.6 ± 1.8	ND**	ND	d§	d
	F	5 April 2006	1.3 ± 1.5	3.0 ± 2.6	3.8 ± 2.1	1.0 ± 1.4	4.3 ± 1.3	3.3 ± 2.5	ND	ND	16.9	17
	H	10 April 2006	Note	1.5 ± 1.9	Note	2.0 ± 2.3	1.0 ± 1.2	3.5 ± 1.0	ND	ND	41.8	40.7
	N	1 May 2006	3.0 ± 2.6	Note	Note	3.0 ± 3.8	3.5 ± 1.9	3.0 ± 3.8	ND	ND	13	13.6
Utility 2 (Chlorine)	A	28 March 2006	1.8 ± 1.3	3.0 ± 2.6	1.3 ± 1.5	0.8 ± 1.0	1.8 ± 1.3	3.0 ± 2.6	ND	ND	ND	ND
	B	20 March 2006	Note	2.2 ± 2.9	Note	2.6 ± 2.4	Note	4.2 ± 2.3	ND	ND	d	d
	E	3 April 2006	Note	Note	Note	2.4 ± 2.6	Note	2.8 ± 3.3	ND	ND	ND	ND
	G	10 April 2006	Note	3.2 ± 4.1	Note	Note	Note	3.6 ± 4.3	ND	ND	ND	ND
Utility 3 (Chloramines)	D	3 April 2006	3.5 ± 3.0	3.0 ± 3.5	1.0 ± 1.2	1.5 ± 1.9	4.0 ± 2.3	4.5 ± 1.9	ND	ND	d	d
	I	10 April 2006	Note	Note	2.3 ± 2.6	4.0 ± 1.6	2.3 ± 2.6	4.0 ± 1.6	ND	ND	d	d
Utility 4 (Chlorine)	L	19 April 2006	Note	Note	Note	2.0 ± 2.3	Note	2.0 ± 2.3	ND	ND	ND	ND
	M	25 April 2006	Note	Note	Note	Note	Note	Note	ND	ND	ND	ND
Utility 5 (Chlorine)	J	12 April 2006	1.0 ± 1.2	1.5 ± 1.9	Note	Note	1.0 ± 1.2	1.5 ± 1.9	ND	ND	ND	ND
	K	5 April 2006	Note	2.0 ± 2.0	1.2 ± 1.1	Note	2.4 ± 3.3	2.8 ± 1.1	ND	ND	ND	ND
Evian	Evian	18 May 2006	0.8 ± 1.0	1.5 ± 1.9	Note	1.5 ± 1.9	2.3 ± 2.6	3.0 ± 1.2	ND	ND	ND	ND
	DI Water	13 May 2006 18 May 2006	Blank		Blank		Blank		ND	ND	ND	ND
	MIB	18 May 2006	6						18.6			
	GEO	18 May 2006			6						20.1	

*Normal: normal sample = actual sample.

†Dechlor: dechlorinated sample = sample after dechlorination.

‡Note: means that less than half of the panel could not smell the odor. The FPA Method indicates this by the word Note, short for Odor Note. No value is given in this case.

§d = geosmin and MIB values between 2.7 and 8.1 ng l^{-1} are called detectable (d) but not quantifiable.

**ND: Not detected.

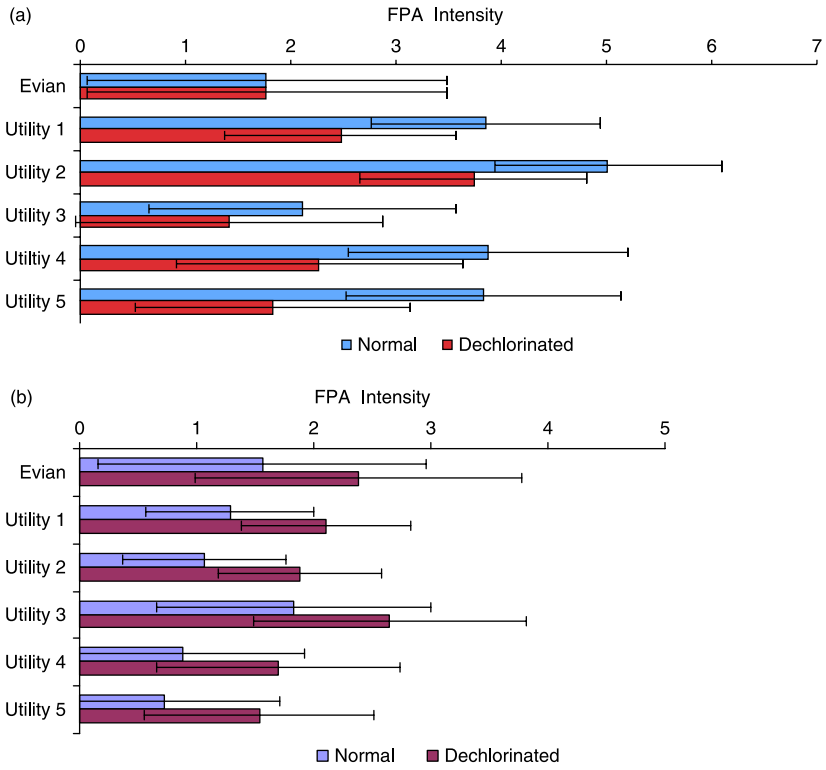

Figure 3 | (a) Chlorine odour intensity; and (b) earthy odour intensity for different water sources; the error bars represent ±2 standard errors.

Statistical evaluation of the chlorine or chloramine odour

The model for chlorine odour treats chlorine and chloramines as the single parameter chlorine. Figure 5 provides a graphical summary of these results.

1. The average intensity of the chlorine or chloramine odour detected on the baseline sample was 7.0 FPA units. Dechlorination or dechloramination caused a decrease in odour intensity of 2.5 units, while adding geosmin and MIB to the sample caused decreases of 3.5 and 3.9 units in chlorine odour intensity, respectively. All were significant at $p = 0.000$.
2. Adding either geosmin or MIB to the dechlorinated or dechloraminated sample decreased the perceived odour of chlorine and chloramine intensity by 1.3 ($p = 0.003$) and 1.6 ($p = 0.000$) units, respectively.

Adding geosmin and MIB (earthy/musty odours) to chlorinated water samples reduced the perceived chlorine odour.

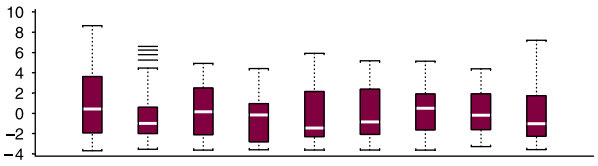

Figure 4 | Deviations from population mean for earthy odours for the nine panellists.

Statistical evaluation of the effect on the earthy odour of geosmin for the water sample by chlorinous odours

The fixed effect results of the model for earthy odour, shown in Figure 6, revealed fewer statistically significant effects than those observed for the chlorinous odour. The results are:

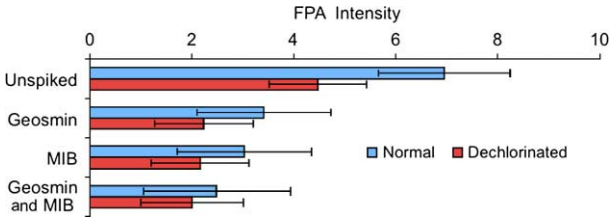

Figure 5 | Chlorine odour intensity; the error bars represent ±2 standard errors; 'Normal' means the water, as received, as chlorinated or chloraminated.

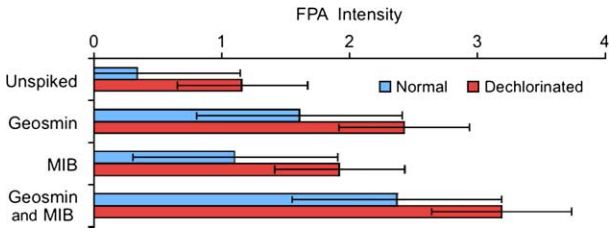

Figure 6 | Earthy odour intensity; the error bars represent ±2 standard errors.

1. The average intensity of earthy odour detected on the baseline sample was 0.3 FPA units, which was not significantly different from zero.
2. Dechlorination caused an increase in odour intensity of 0.8 units ($p = 0.000$) to about threshold. Spiking the sample with geosmin and MIB with or without chlorinous treatment caused increases of 1.3 ($p = 0.000$) and 0.8 ($p = 0.006$) odour units, respectively.

The levels of geosmin are 20.1 ng l^{-1} for all except the Utility 1 samples, which have a naturally occurring level of 41.8 ng l^{-1} and a total of 61.9 ng l^{-1}. It can be concluded that dechlorination of up to 4 mg l^{-1} chloramine as Cl or 1 mg l^{-1} of free chlorine as Cl increased the intensity of the earthy odour of the geosmin ($p = 0.000$). The effect of MIB increasing the earthy odour intensity ($p = 0.001$) in the sample is the mistake by panellists of describing the musty odour of MIB as earthy. This confirms the chlorine odour intensity effect: chlorine does mask the earthy odour of geosmin.

Statistical evaluation of the effect on the musty odour of MIB for the water sample by chlorinous odour

The fixed effect results of the model for musty odour of MIB shown in Figure 7 revealed the following results:

1. The average intensity of the musty odour detected on the baseline sample was 0.4 FPA units, which was not significantly different from zero.

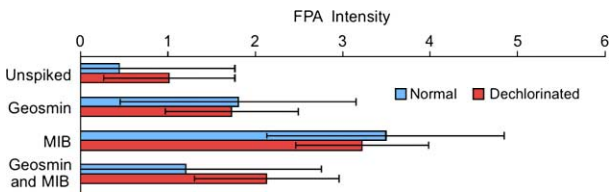

Figure 7 | Musty odour intensity; the error bars represent ±2 standard errors.

2. Dechlorination by itself caused an increase in odour intensity of 0.6 units, which is not significant.
3. Adding geosmin to the sample caused an increase of 1.4 units which was not significant, while adding MIB caused a significant increase of 3.0 units ($p = 0.001$).
4. Adding both geosmin and MIB to the normal water sample significantly decreased the odour intensity of musty odours by 3.6 units ($p = 0.005$), thus neutralizing some of the initial effects of MIB alone. This is most likely due to the misclassification of musty odours as earthy odours.
5. Adding both geosmin and MIB to the dechlorinated sample produced an increase of 1.8 units in the odour intensity which was not significant.

It can be concluded that dechlorination of up to 4 mg l^{-1} chloramine as Cl or 1 mg l^{-1} of free chlorine as Cl does not increase the odour intensity of the musty odour of MIB. Thus at MIB concentrations of 18.6 ng l^{-1} (see Table 3), chlorine does not mask some of the musty odour.

The results may be due to the statistical power of the method used at the low levels of MIB. It was not within the scope of the study to investigate whether this amount of chloramines or chlorine masks higher concentrations of MIB.

Statistical evaluation of the effect on the earthy-musty odours of the water sample by chlorinous odours

The fixed effect results of the model for earthy-musty odours shown in Figure 8 revealed the following results:

1. The average intensity of earthy-musty odour detected on the baseline sample was 1.1 FPA units, which was significantly different from zero ($p = 0.011$).
2. Dechlorination caused an increase in odour intensity of 0.9 units ($p = 0.000$).

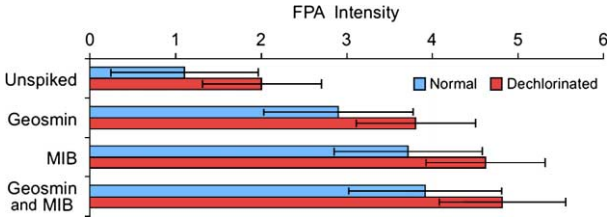

Figure 8 | Earthy-musty odour intensity; the error bars represent ±2 standard errors.

3. Adding geosmin and MIB to the sample caused statistically significant increases in the intensity earthy/musty odour of 1.8 and 2.6 units, respectively ($p = 0.000$).

It can be concluded that dechlorination of up to 4 mg l^{-1} chloramine as Cl or 1 mg l^{-1} of free chlorine as Cl increased the odour intensity of the earthy-musty odour when geosmin (20.1 ng l^{-1}) and MIB (18.6 ng l^{-1}) were added together to the water. This was also the case at Utility 1 where the geosmin concentration of 41.8 ng l^{-1} was natural and the 18.6 ng l^{-1} MIB and 20.1 ng l^{-1} geosmin were added to the water. Thus, chlorine reduced the earthy-musty odour intensity, by reducing the intensity of the earthy odour of geosmin.

DISCUSSION

The background water quality studied did not have a statistically significant effect on the odour perceived by an FPA odour panel for geosmin or MIB (Figure 3(a) and (b)), despite a wide range of water types with varying background matrices in terms of both total organic carbon and total dissolved solids. However, this study had a small sample size ($N = 6$) and only one true taste and odour event. A study with a greater number of source waters would be needed to validate these initial findings.

Dechlorination increased the intensity of earthy odour of geosmin and the earthy odour of the geosmin/MIB combination in the range of 20.1–61.9 ng l^{-1} geosmin, with 1–4 mg l^{-1} of total chlorine as Cl. However dechlorination did not affect the musty odour of MIB or the geosmin/MIB combination. Chlorine or chloramine at levels of 1–4 mg l^{-1} of total chlorine as Cl do not mask the 18.6 ng l^{-1} of MIB (musty) odour.

This study confirms the work of Burlingame *et al.* (1986), Bartels *et al.* (1989) and Worley *et al.* (2003) who determined by FPA that total chlorine had a masking effect on geosmin; trained odour panellists gave higher intensities for geosmin in the absence of chlorine than with chlorine or chloramines present. In a study by Oestman *et al.* (2004) the results showed that chlorine was not able to mask geosmin odours. However, the Oestman *et al.* (2004) study used a wider range (5–1,200 ng l^{-1}) of MIB or geosmin and chlorination agents (chlorine levels of 0.5–20 mg l^{-1} or chloramine levels of 3–24 mg l^{-1}). Panellist adaptation to this odour may have affected the results. The present study evaluated drinking water at low levels of geosmin and MIB (<30 ng l^{-1}, with a few observations between 30 and 60 ng l^{-1}) with chlorine and chloramine also low, at <1 mg l^{-1} and <4 mg l^{-1}, respectively.

This study also confirms that, in the Philadelphia water supply with 2 mg l^{-1} monochloramine residual, MIB was detected at its odour threshold, suggesting that no masking of MIB occurs by monochloramine (personal communication with G.A. Burlingame, 2002). Oestman *et al.* (2004) also showed that chlorine did not have a masking effect on MIB, but used a wider range of concentrations of MIB than normally found in drinking water. However, other studies have shown that increases in chlorine or chloramine concentrations can mask the musty odour of MIB (Zhang *et al.* 1992; Worley *et al.* 2003). This result may be due to the statistical power of the method used or the low levels of MIB (18.6 ng l^{-1}) used in this study. More studies to confirm the results of MIB are needed using a larger range of MIB concentrations from 15 to 60 ng l^{-1}.

CONCLUSIONS

(1) Background water quality of six treated waters did not have a statistically significant effect on the odour perceived by an FPA panel for geosmin (20.1–61.9 ng l^{-1}) or MIB (18.6 ng l^{-1}). The participating utilities for this project represent a wide range of water types with varying background matrices in terms of both total organic carbon (1.2–8.6 mg C l^{-1}) and total dissolved solids (34–389 mg l^{-1}).
(2) Dechlorination or dechloramination significantly increased the intensity of the earthy odour of geosmin and the earthy odour of the geosmin/MIB combination. The odour from chlorine or chloramines, 1–4 mg l^{-1} of total chlorine as Cl, did mask the geosmin (earthy) odour in the concentration range of 20.1–61.9 ng l^{-1}.
(3) Dechlorination does not significantly affect the musty odour of MIB or the geosmin/MIB combination.

Chlorine or chloramines at levels of 1–4 mg l^{-1} of total chlorine as Cl do not mask the musty odour from 18.6 ng l^{-1} MIB. This may be due to the statistical power of the method used at the low levels of MIB.

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