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European reassessment of MIB and geosmin perception in drinking water

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ABSTRACT

Earthy-musty flavors are a prevalent customer complaint for drinking water utilities. Sensory analysis can be used as an inexpensive early warning system to signal a taste and odor (T&O) event and to define the water quality objectives the treatment process has to achieve. T&O threshold concentrations of both 2-methylisoborneol (MIB) and trans-1, 10-dimethyl-trans-9-decalol (geosmin) were reassessed using a French and a Spanish panel, using a flavor-by-mouth protocol. Results of the 2 panels were found consistent and lower than those reported in the literature. Additional sensory testing experiments were performed to investigate the resulting perception when the two compounds (geosmin and MIB) are both present in solution and to clarify the effect of chlorine on both geosmin and MIB (masking or confusion in the perception).

Key words | chlorine, drinking water, earthy musty, taste and odor

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INTRODUCTION

Earthy-musty flavors are a prevalent customer complaint for drinking water utilities. MIB (2-methylisoborneol) and geosmin (trans-1, 10-dimethyl-trans-9-decalol) are the most common odorants with one of the lowest threshold concentrations (in the nanogram per liter range). Reported odor threshold concentrations (OTC) for geosmin and MIB vary significantly but are generally summarized to be in a range of 5–10 ng/L. However, it must be kept in mind that the OTC is the median value of the population tested. Thus, some people will detect MIB or geosmin at concentrations below 5 ng/L (Wang *et al.* 2006).

MIB and geosmin are microbial by-products associated with cyanobacteria and aquatic actinomycetes. Taste and odor (T&O) problems, caused by MIB or geosmin, commonly occur in reservoirs and eutrophic surface waters. Such problems are generally reported as seasonal (summer–fall). The die-off of algae, after blooms, can lead to cell lysis and to a massive release of odorous metabolites in water. The ambient MIB and geosmin concentrations range from 2 to 100 ng/L in influenced water resources. However, values as high 500 or 1,000 ng/L have been reported in the literature (Mallevialle & Suffet 1987).

Common treatment processes for dissolved MIB and geosmin removal include activated carbon sorption (both PAC and GAC), oxidation (mainly ozone) or the combination of ozonation and GAC filtration (Suffet *et al.* 1995).

To assess the removal of geosmin or MIB by the treatment process, sensory analysis is a useful tool for operators and easier to implement than chemical analysis, such as closed loop striping analysis (CLSA) or solid phase micro extraction (SPME) methods combined with gas chromatography-mass spectrometry (GC-MS) for the detection of organic compounds (Wang *et al.* 2006). Results of the sensory analysis will help to define the water quality objectives for treatment plant operators. Treatment process objectives less than 10 ng/L for both geosmin and MIB are commonly reported in the literature (Suffet *et al.* 1995). However, T&O episodes were reported in France for lower concentrations (close to the ng/L).

At a weak odorant concentration, Welthon & Dietrich (2004) demonstrated that the perceived odor intensity was greater when the temperature of the water tested was 45°C instead of 25°C (≈1.5 greater). The importance of the

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temperature when doing the test, but also the sensory analysis method used, can probably explain the large range of threshold concentrations reported in the literature. However, a potential regional effect, associated to different sensitive characteristics of people, might also contribute to this variability but is not documented.

In addition, as reported by several authors (Rashash *et al.* 1997), commercial solutions of geosmin obtained by synthesis are a racemic mixture of both the (−) and (+) enantiomers. As reported by Polak & Provasi (1992), the (−) isomer is naturally present in water, and is reported to have an odor threshold concentration 10 times lower than the (+) isomer. In other words, a greater concentration of the synthetic geosmin would be required before the odor would be detected, leading to overestimation when defining threshold concentrations.

In order to better estimate public perception of these two compounds, the flavor-by-mouth threshold concentrations were assessed at a 25°C water temperature with a group of mainly untrained panelists. The OTC were also characterized for comparison with literature data. According to that methodology, the flavor threshold concentrations of the following compounds were investigated: geosmin(c): commercial product, (−) geosmin isomer, (+) geosmin isomer and MIB. These experiments were performed both in France and Spain.

Additional experiments were also carried out to address the following issues:

(i) The resulting T&O perception when geosmin and MIB are both present in solution.
(ii) The effect of chlorine on both geosmin and MIB perception. Depending on authors, chlorine can act as a masking compound (Zhang 1992; Suffet *et al.* 1995; Worley *et al.* 2003) or can cause confusion in the perception of earthy-musty flavors (Oestman *et al.* 2004).

MATERIALS AND METHODS

T&O threshold concentrations

Preparation of geosmin and MIB solutions

Standards of MIB and geosmin(c) were purchased from Dr Ehrenstorfer, GmbH (geosmin: Ref. LA 14005000ME 10 ng/μL 1 mL, MIB: Ref. LA 15088400ME 10 ng/μL 1 mL).

10 to 15 mg of geosmin enantiomers were generously donated by the laboratoire de recherche organique, Ecole Supérieure de Physique et Chimie Industriel (ESPCI). These pure recrystallized compounds were prepared by synthesis according to a method described by Revial (1989).

From the standards, stock solutions (in the μg/L range) were prepared in ethanol. Solutions of geosmin and MIB, provided to panelists (in the ng/L range), were prepared from the stock solutions by dilution in water (Evian bottled water). It was confirmed that ethanol, used in the stock solutions, was not perceived in the solutions provided to the panelists. In addition, the concentrations of the stock solutions were confirmed, after dilution, by SPME GC-MS analysis.

Sensory testing procedure

Sensory testing experiments were performed according to 3-alternative forced choice procedure (3 AFC), with ascending concentration series, adapted from the ASTM method (E 679-04) (ASTM E 679-04 2004). Each experiment was performed by around 10–15 panelists and more than 2/3 of them were untrained (both in France and in Spain). Some of them were familiar to sensory analysis but not expert.

For each sensory testing session, 5 levels of concentrations were prepared with a constant increase factor of 2. Samples were presented to panelists according to a single staircase of ascending concentrations. For each level of concentration, 3 samples were provided to panelists: 2 references (Evian bottled water) and the solution containing the stimulus (geosmin or MIB at a given concentration). Panelists were asked to identify which sample was different from the others because of an "earthy-musty" flavor.

For the definition of the flavor threshold concentration (FTC), a flavor-by-mouth sensory procedure was used. Water samples (>100 mL) were provided to panelists in plastic cups. The reference water and the 5 concentrated solutions were previously brought to a constant temperature of 25°C.

For the definition of the odor threshold concentration (OTC), a procedure by sniffing was used. Water samples (200 mL) were provided in 500 mL Erlenmeyers with a glass stopper. The reference water and the 5 concentrated solutions were previously brought to a constant temperature of 45°C.

Data processing

By definition, the threshold is the concentration for which the probability of detection of the stimulus is 0.5 (i.e, perceived by 50% of the population).

The threshold concentration of a given compound was estimated by the geometric mean of individual best-estimate threshold (BET), according to the ASTM method (E 679-04). Logarithm (log_{10}) of the individual BET was also calculated to estimate a standard log deviation.

In addition, a graphical approach, by logistic regression (% of "correct answer" versus Ln [Concentration]), was also used to calculate the threshold concentrations (50% of "correct answer") and estimate the 95% confidence interval (C.I.) from the regression calculation. For each concentration, the percent of "correct answer" was calculated according to the following formulation: 100.C/N where N = number of panelists and C = number of "correct answers". The individual "correct answers" were defined according to recommendations provided by the ASTM method (E 679-04).

The threshold concentrations can also be estimated, taking into account 50% percent of "correct answer above chance". The percent of "correct answer above chance" for a 3 AFC procedure was calculated according to the following formula, adapted from the ASTM method (E 1432-04) (ASTM E 1432-04 2004): $100.(3.C - N)/2.N$ where N = number of panelists and C = number of "correct answers".

Results of 2 experiments were compared using the log_{10} of individual BET and according to the t-test statistical procedure (comparison of means). A variance analysis was performed prior to the comparison of means to assess variance homogeneity.

Perception of a mixture of MIB and geosmin

Two sets of "earthy-musty" flavor solutions (3 levels of concentration: 1.25, 2.5 and 5 ng/L MIB), composed respectively with only MIB and a mixture of geosmin(c) and MIB were prepared in bottled water (Evian). Based on the flavor threshold concentrations, previously assessed,

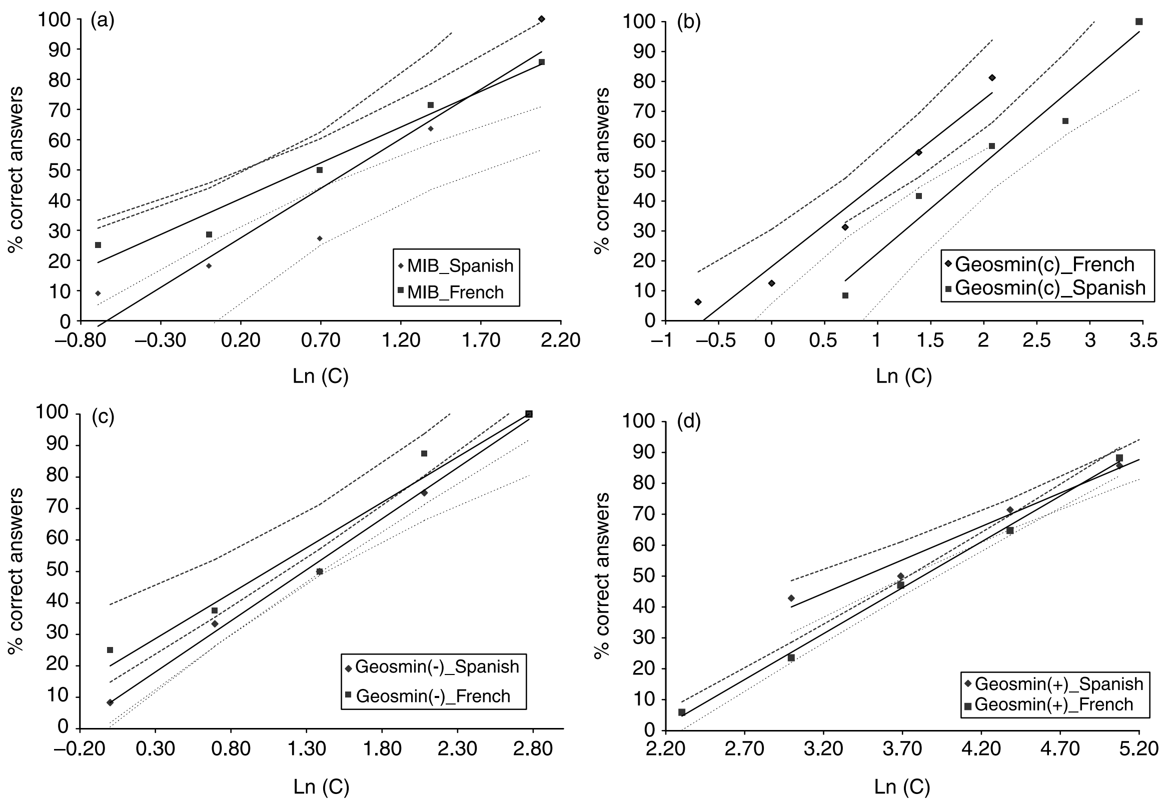

Figure 1 | Results of flavor testing experiments: French & Spanish panel answers for (a), MIB; (b), geosmin(c); (c), (−)geosmin and (d), (+)geosmin.

Table 1 | T&O thresholds for the French and the Spanish panels

		French Panel				Spanish Panel			
	Compounds	Geometric mean (ng/L)	Standard $\log_{10}$ deviation	50% correct answer (ng/L)	No panelists	Geometric mean (ng/L)	Standard $\log_{10}$ deviation	50% correct answer (ng/L)	No panelists
Flavor	MIB	2	0.55	2	14	2.5	0.4	2.5	11
	geosmin (c)	3.2	0.43	3	16	8	0.55	6.7	12
	(+)geosmin	37.5	0.5	44.7	17	40	0.47	30	14
	(−)geosmin	2.8	0.44	2.7	16	3.5	0.41	3.7	12
Odor	MIB	1.2	0.29	1.2	9	1.3	0.27	1.2	7
	geosmin (c)	–	–	–		0.8	0.375	0.8	8
	(+)geosmin	11.2	0.245	9	6	4.6	0.39	4.5	8
	(−)geosmin	0.86	0.14	0.6	7	0.4	0.4	0.4	8

concentrations of geosmin and MIB in the mixture were estimated to provide solutions with a flavor level equivalent to that of a single compound solution.

The 3 levels of concentration were evaluated, for the two sets of solutions, by the same group of panelists, during the same sensory testing session. The percent of "correct answers" was estimated according to the 3 AFC method (flavor-by-mouth procedure) previously described, by providing to panelists 2 references (Evian bottled water) and the solution containing the stimulus (only MIB or mixture of geosmin and MIB at a given concentration). A graphical approach, by logistic regression, was used to compare the panelists' answers for the two sets of solutions. In addition, the threshold concentration was estimated by the geometric means of individual BET (ASTM E 679-04) and calculated for a 50% of "correct answers" (logistic regression).

Chlorine effect

When chlorine is present in solution together with geosmin or MIB, it is possible to have an effect of chlorine on the earthy-musty flavor perception, also called a "*chlorine masking*" effect.

To assess this effect, two sets of "earthy-musty" flavor solutions (3 levels of concentrations: 3, 6 and 9 ng/L of MIB or 6, 9 and 14 ng/L of geosmin(c)), composed respectively of MIB or geosmin and of MIB or geosmin in the presence of 0.5 mg/L Cl_2, were prepared.

The 3 levels of concentrations were evaluated, for the two sets of solutions, by the same group of panelists during the same sensory testing session. Again, a graphical approach, by logistic regression, was used to compare panel answers for the two sets of solutions. In addition, the threshold concentration was estimated by the geometric mean (ASTM E 679-04) and calculated for a 50% of "correct answers" (logistic regression).

Sodium hypochlorite was purchased from VWR International, France (NaOCl 15%, Rectapur).

Chlorine concentration in the different solutions provided to panelists was measured, according to the DPD protocol (APHA 1998), prior and after the flavor testing experiments and the average of these measurements was used for the data processing.

Table 2 | *t*-test *p*-values: comparison of answers of the French and Spanish panels

	Compound	*P*-value
Flavor	MIB	0.63
	geosmin(c)	0.042*
	(+)geosmin	0.875
	(−)geosmin	0.545
Odor	MIB	0.869
	geosmin(c)	–
	(+)geosmin	0.055
	(−)geosmin	0.052

*significant /5% statistical threshold.

Table 3 | T&O thresholds and 95% confidence interval, combining French and Spanish panelists

	Compound	Geometric mean (ng/L)	Standard $\log_{10}$ deviation	50% correct answer (ng/L)	50% above chance (ng/L)	No panelists	Literature values (ng/L)	Reference
Flavor	MIB	2.2	0.48	2.2	3.9	25	18	Young *et al.* (1996)
	geosmin(c)	4.6	0.52	4.2	7.6	28	16	Young *et al.* (1996)
	(+)geosmin	41.8	0.47	43.8	81.2	31		–
	(−)geosmin	3.1	0.42	3.2	5.5	28		–
Odor	MIB	1.2	0.3	1.2	1.8	16	2–20	Rashash *et al.* (1997)
							9	Mallevialle & Suffet (1987)
							15	Young *et al.* (1996)
							4–10	Watson *et al.* (2000)
	geosmin(c)	0.8	0.375	0.85	1.1	8	6–10	Burlingame *et al.* (1991)
							3.8	Young *et al.* (1996)
							4	Mallevialle & Suffet (1987)
							4–10	Watson *et al.* (2000)
	(+)geosmin	6.7	0.38	4.6	9.1	14	78 ± 12	Polak & Provasi (1992)
	(−)geosmin	0.56	0.35	0.4	0.6	15	9.5 ± 1.3	Polak & Provasi (1992)
							1	Sagiura *et al.* (1983)

Table 4 | *t*-test *p*-values: comparison of OTC and FTC (combined data)

Compound	*p* value
MIB	0.000414*
Geosmin(c)	0.047*
(+)geosmin	0.000002*
(−)geosmin	0.000001*

*significant /5% statistical threshold.

RESULTS AND DISCUSSION

T&O threshold concentrations

Figure 1 gives examples of results of the flavor measurement testings and compares the anwers of the French and the Spanish panels for the geosmin(c), (−)geosmin, (+) geosmin and MIB at different concentrations. Table 1 summarizes the results of the sensory testing experiments.

For each compound, the answers of the two panels were compared by comparison of means. The *p*-values of the *t*-test are reported in Table 2. The *p*-values, larger than 5%, except for geosmin(c), indicate that the results of the 2 panels are comparable (no regional effect). The origin of the significant difference, noticed for geosmin(c), remained unclear, since the results for (+)geosmin and (−)geosmin are in agreement.

Table 3 summarizes the sensory testing results by combining the data of 2 panels. In addition, some values from the literature are given for comparison. Most of the OTC were obtained according to a FPA procedure at 45°C.

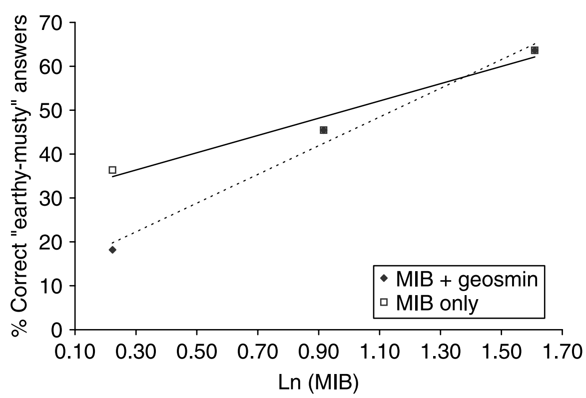

Figure 2 | Comparison of panelist answers for solutions with MIB only or with MIB + geosmin for the same resulting flavor perception scores.

Table 5 | Flavor threshold of the solutions MIB + geosmin & MIB only

	Geometric mean (ng/L)	Standard Log_{10} deviation	50% threshold conc. (ng/L)	No. panelists
MIB + geosmin	2.9	0.36	3.1	11
MIB	2.6	0.41	2.7	11

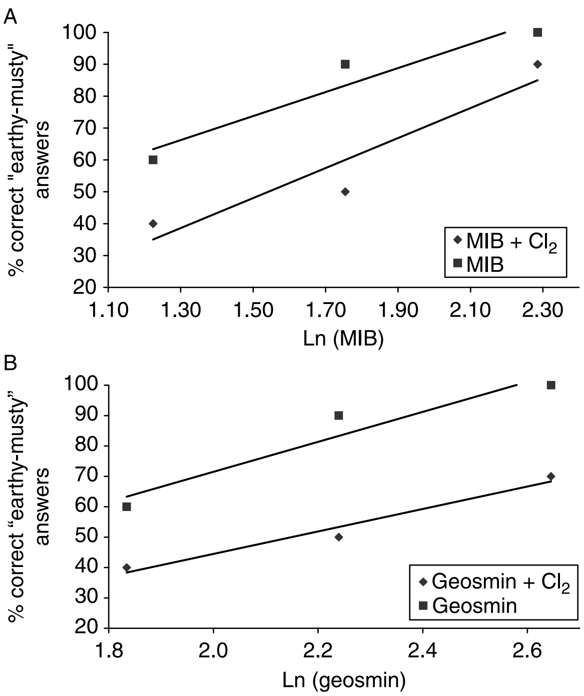

Figure 3 | Effect of chlorine on earthy/musty perception and the effect of earthy/musty flavors on chlorine perception.

From Table 3, the following results can be highlighted:

- The FTC of MIB and geosmin were found to be different (t-test, $p = 0.024$), but in the same range of concentrations. However, the FTC values found were lower (2–5 ng/L) that those reported by Young *et al.* (1996).
- The OTC of MIB and geosmin were found to be close (t-test, $p = 0.22$) and in the ng/L range. These OTC values are consistent with the minimum OTC reported in the literature.
- The FTC and the OTC of different compounds tested were found to be different (Table 4). These results are in agreement with the impact of the experimental temperature, reported by Whelton & Dietrich (2004).
- As reported by Polak & Provasi (1992), the threshold concentrations (FTC and OTC) of the (−) optical isomer of geosmin were found around 10 times lower than those of the (+) isomer. Thus, the main contribution of this (+) isomer, as in the case of a commercial product obtained by synthesis (racemic mixture), is a dilution effect. The (−)geosmin FTC or OTC were found lower than those of the commercial geosmin, even if the difference is not significant. However, our results are significantly lower (10 times) than those reported by the French team of Polak & Provasi (1992). In that case, regional effects cannot explain the discrepancy which can be partly due to differences in the method used to assess the threshold concentrations. In addition, values reported by Polak & Provasi (1992) are close to maximum threshold concentrations reported in the literature for geosmin.

Perception of a mixture of MIB and geosmin

Figure 2 shows the results of the panelists for the 2 sets of solutions (MIB only and MIB + geosmin). The slight difference noticed for the lower concentration is due to a difference of 2 answers among 11.

Table 5 gives the flavor threshold concentrations calculated for the 2 sets of solutions. Similar values were found in both cases. The comparison of the 2 sets of individual BET shows no significant difference (t-test, $p = 0.743$).

Geosmin and MIB both contribute to the "earthy-musty" flavor when present together in the same solution and the resulting flavor level is the sum of the flavor level of each compound. However, additional experiments are needed to confirm this apparent additive effect.

Table 6 | Taste threshold of the solutions MIB or geosmin & MIB or geosmin + 0.5 mg/L Cl_2

	Earthy/musty compound alone			Earthy/musty compound + Cl_2			
	Geometric mean (ng/L)	Standard Log_{10} deviation	50% threshold (ng/L)	Geometric mean (ng/L)	Standard Log_{10} deviation	50% threshold (ng/L)	No. panelists
MIB	3.4	0.16	2.4	4.9	0.26	4.7	10
Geosmin	6.5	0.17	4.8	9	0.23	8.6	10

Chlorine effect

The results, reported in Figure 3, show that the presence of chlorine leads to a shift in the perception of "earthy-musty" flavors, indicating a masking effect of "earthy-musty" flavors by chlorine for both geosmin and MIB.

The presence of 0.5 mg/L Cl_2 was found to double both MIB and geosmin flavor thresholds (Table 6). However, the comparison of the 2 sets of individual BET, for the geosmin and the MIB experiments respectively, shows that differences are not significant (*t*-test, geosmin: $p = 0.144$, MIB: $p = 0.123$). Additional experiments are needed to confirm and quantify this apparent chlorine masking effect.

CONCLUSIONS

The FTC or OTC obtained by the French and the Spanish panels were found similar, indicating no significant regional effect on the perception of geosmin and MIB.

Based on the FTC calculated for a 50% of correct answers above chance, a treatment goal of 5 ng/L can be proposed. These treatment goals are more stringent than those reported in the literature and applied in the United States (10 ng/L).

Use of a commercial racemic solution of geosmin leads to an overestimation of the OTC and FTC of the natural (−)geosmin isomer.

Due to some possible masking effects of chlorine on "earthy-musty" flavors, the dechlorination of drinking water samples is necessary for a relevant estimation of these off-flavor causing compounds.

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