

Determination of System Losses of Geosmin and MIB in Bench-Scale Filtration Apparatus

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Geosmin and 2-methylisoborneol (MIB) are two of the causative compounds responsible for the earthy/musty odour problem in drinking water. They are a major concern for the water treatment industry because they are difficult to remove by conventional water treatment practices and are fairly resistant to chemical oxidation. Various studies have been conducted at both bench and full scale to examine the removal of these compounds by adsorption and/or biological filtration. Lack of study at realistic odour compound concentrations and disregard for losses of these compounds by other means (i.e., volatilization or adsorption) represent some of the limitations of such studies. The bench-scale investigation reported herein focussed on system design and minimization of system losses. The results indicated that the preferred system design included the use of Teflon feed bottles, Teflon tubing, and a glass filter column in which the influent feed line descended close to the media surface. Such a design minimized system losses of both geosmin and MIB to 42 and 30%, respectively, based on target influent concentrations of 200 ng/L.

Key words: adsorption, biological filtration, geosmin, MIB, odour compound concentration, system losses

Introduction

The presence of taste and odours in drinking water is an increasingly frequent problem for water utilities. The earthy/musty odours produced by geosmin and 2-methylisoborneol (MIB) are considered one of the most problematic types of taste and odours. Both compounds are resistant to some oxidants and are difficult to remove by conventional water treatment methods. Common odour treatment methods such as powdered activated carbon (PAC), chlorine oxidation, and potassium permanganate are largely ineffective in reducing these compounds (Lalezary et al. 1986; Nerenberg et al. 2000). There are indications that biological filtration processes can be effective in removing or minimizing these odour compounds. Several studies have shown adequate removals of both geosmin and MIB using biological filtration systems (Izaguirre et al. 1988; Ashitani et al. 1988; Namkung and Rittmann 1987). Lack of study at realistic odour compound concentrations and disregard for losses of these compounds by other means such as volatilization or adsorption, include some of the limitations of previous studies. Danglot et al. (1983) reported the physical adsorption of geosmin onto glass vessels or peristaltic pump tubing. The study of these compounds at ng/L levels has magnified the problems created by systemic losses of odour compounds. At these levels, small absolute losses can be substantial on a percentage basis. Therefore, care should

be taken with experimental systems investigating the removal of these compounds at such low concentrations. In addition, losses in control systems must be documented so that the removals attributed to a given treatment process can be reliably assessed. The cost of geosmin and MIB standards also stand to emphasize the importance of designing ideal systems to help minimize system losses.

In reviewing the literature in regard to systemic losses of both geosmin and MIB, it was apparent that pertinent information is limited. One study (Huck et al. 1995) noted substantial losses of geosmin to a bench-scale system. Thus, studies were set up to focus on various system designs for biofiltration investigations at bench scale and subsequent control of system losses.

Materials and Methods

Bench-Scale Apparatus

The initial experiments used five different system designs to determine the relative losses of each odour compound. A general schematic of the bench-scale apparatus used in these experiments is presented in Fig. 1. The various sampling locations used in the study are indicated in the figure as points A to D.

The first trials were performed for 20 days using 4-L amber glass feed bottles, a peristaltic pump, 3 m of Pharmed tubing (1.59-mm internal diameter [ID]) and a custom-made glass filter column 2 m in length (50-mm ID). In these experiments the filter column contained no

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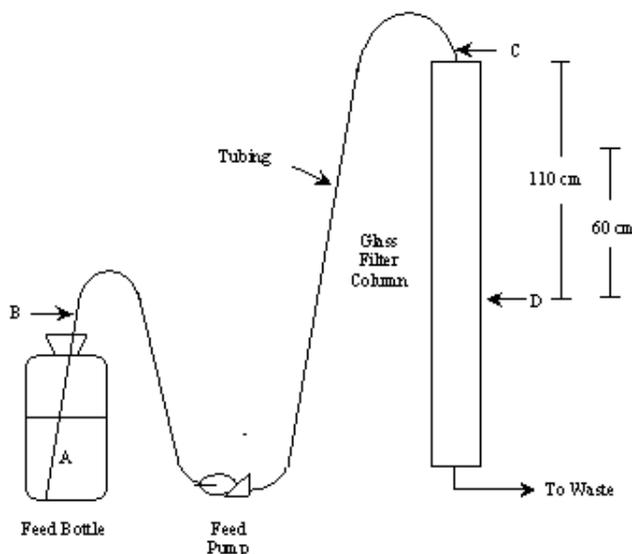


Fig. 1. General schematic of bench-scale apparatus (note: not to scale).

media. Samples were collected at a depth of 110 cm from the top of the filter (Fig. 1D) which is where the top of the media would be in subsequent experiments. Thus, the losses being examined in the filter column refer to the part of the column with which the water above the media would be in contact. The second trials were also run for 20 days and used the same design as in the first, with the exception of no glass filter column. The third, fourth and fifth designs were performed for 20 days and all used 2-L Teflon feed bottles, a valveless piston metering pump, 3 m of Teflon tubing (1.59-mm ID), and either a glass filter column (sampling at a depth of 110 cm, Fig. 1D), no glass filter column, or a glass filter column (sampling at a depth of 60 cm, Fig. 1D), respectively. The depth was reduced to 60 cm by extending a piece of Teflon tubing 50 cm in length into the column in order to minimize the amount of feedwater contact with the glass column. Each of the experiments was conducted with target initial concentrations of 200 ng/L for both geosmin and MIB. In all cases, samples were taken in duplicate during each daily sampling event. Samples were collected directly from the feed bottles (Fig. 1A) as well as from the effluent end of the system. Samples were then stored in the refrigerator overnight at 4°C and subsequently analyzed.

Additional experiments were conducted in order to determine the relative losses of geosmin and MIB to individual system variables including the feed bottles, tubing, and the glass column used in initial experiments. The conditions for these are described below.

Feed Bottles

Experiments were conducted using 4-L glass amber feed bottles, as well as 2-L Teflon feed bottles. The experi-

ments were run for approximately 15 days with target initial feed concentrations of geosmin and MIB of 200 ng/L. Samples were taken daily in duplicate directly from each of the feed bottles (Fig. 1A) and stored overnight before analysis.

Tubing

Experiments were conducted using Pharmed (1.59-mm ID, Cole-Parmer Instrument Company, Vernon Hills, Ill.), Viton (1.59-mm ID), and Teflon PTFE (1.59-mm ID) tubing 3 m in length. Solutions were pumped through the Pharmed and Viton tubing using a peristaltic pump (Model 7553-70, Masterflex L/S, Cole-Parmer, Vernon Hills, Ill.). A valveless piston metering pump head (Model RHOCKO, Fluid Metering, Inc., Syosset, N.Y.) was used to pump solutions through the Teflon tubing. Again the experiments were run for 15 days with target initial feed concentrations of geosmin and MIB of 200 ng/L in the feed bottles. Duplicate samples were drawn daily from the influent (Fig. 1B) and effluent (Fig. 1C) of the tubing and losses of each compound were calculated.

Glass Filter Column

Two custom-made glass filter columns (50-mm ID) were used to conduct these experiments. In these experiments the filter columns contained no media. The target initial feed concentrations of geosmin and MIB were each 200 ng/L in the feed bottles. Duplicate samples were collected daily at the influent of the filter columns (Fig. 1C) as well as at a depth of 110 cm in filter 1 and 60 cm in filter 2 (Fig. 1D) over a 15-day period. As was mentioned earlier, in order to decrease the feedwater contact with glass surfaces a piece of Teflon tubing 50 cm in length was inserted into the top of filter 2, decreasing the filter contact length from 110 to 60 cm. The filter and pre-filter granular activated carbon columns (used for tap water dechlorination) were covered with black insulation materials in order to prevent the growth of phototrophic organisms.

Feed Solutions

Solutions of geosmin and MIB in methanol were purchased from Sigma-Aldrich Canada (Oakville, Ontario). Geosmin solutions were in 1-mL ampoules at a concentration of 2 mg/mL (C\$94.90) and MIB solutions were also in 1-mL ampoules at a concentration of 10 mg/mL (C\$82.00).

Huck et al. (1995) reported very high losses, in the range of 92%, of geosmin during autoclaving, therefore, the stock solution containing geosmin and MIB was not sterilized in these experiments. The feed bottles containing Milli-Q water were autoclaved prior to the prepara-

tion of the solution containing the odour compounds. Geosmin and MIB solutions were transferred as aseptically as possible to the sterile water. The concentrations and the flow rate of the feed solutions were set according to the targeted concentrations (i.e., 200 ng/L of geosmin and MIB) and resulted in a feeding rate of about 3.5 litres per week.

Tap Water in the Filter Influent

The filter influent was dechlorinated tap water to which concentrated solutions of geosmin and MIB were added. Two pre-filter granular activated carbon (GAC) columns in series were used for the dechlorination of the source tap water (Kontes Chromaflex, Vineland, N.J.; ID = 4.8 cm, length = 60 cm). The tap water used as feedwater to the filters was from local surface water and/or groundwater, which is low in organics and high in alkalinity and hardness. Some typical water quality parameters include pH: 7.4 to 7.5; alkalinity: 300 to 325 mg/L as CaCO₃; hardness: 325 to 350 mg/L as CaCO₃; total organic carbon (TOC): 1.0 to 1.1 mg/L; conductivity: 625 to 725 µS; and temperature: 14 to 18°C. Conductivity and chlorine residual were monitored daily to document changes in the groundwater/surface water contributions to the tap water. The hydraulic loading rate (HLR) within the filter was measured and controlled using a pre-calibrated flow meter (Gilmont Instruments, Barrington, Ill.), with a valve on the effluent line. The HLR was maintained at a constant rate of 7.5 m/h.

Analytical Methods

Gas chromatography/mass spectrometry (GC/MS) was used in combination with solid phase microextraction (SPME) for analysis of these compounds in water. The method is based on that described by Watson et al. (2000). Headspace SPME was used. An internal standard of deuterated geosmin (d-5 geosmin, Salford Ultrafine Chemicals, Manchester, UK) and deuterated MIB (2-methyl-d3-isoborneol, Salford Ultrafine Chemicals, Manchester, UK) and 6 g of NaCl were added to a

30-mL sample in a 40-mL vial. The final concentration of the each of the deuterated compounds in the sample was 25 ng/L. The sample was stirred using a magnetic stirrer in a water bath at 65 ± 2°C. The SPME fibre (polydimethylsiloxane/divinylbenzene) was exposed in the vial headspace for exactly 30 min, and then injected into the gas chromatograph/mass spectrometer (GC/MS) (desorption time 5 min, injection depth 3 cm) using injection in the splitless mode.

The GC/MS analysis was carried out in the selected ion monitoring (SIM) mode on an HP 5890 GC with an HP 5970 mass-selective detector and an HP 59940 Chemstation data system (Hewlett Packard, Sunnyvale, Ca.). The GC/MS conditions were injector temp.: 240°C, splitless mode for 2 min; column: DB 1701, 30 m x 0.25 mm ID, 0.25-µm film thickness; temp. program: 60°C for 1 min with 15°C/min to 250°C for 5 min. Mass spectrometer: 180°C, SIM mode detection limit was 2 to 3 ng/L for both compounds. Samples for geosmin and MIB analysis were collected headspace-free in 40-mL EPA vials. The samples were stored for a maximum of 24 hours at 4°C before analysis.

Results and Discussion

Results are presented first for overall system losses and then for individual components.

System Loss Monitoring

Table 1 shows the results of the initial trials investigating geosmin and MIB losses to five different system designs. Each of the trials was run for 20 days in which 15 observations were reported based on daily measurements.

As can be seen from the results of trial 1, there were very high losses of both compounds associated with the use of Pharmed tubing. In trial 2, collection of effluent (Fig. 1C) isolated a substantial portion of both geosmin and MIB losses to the Pharmed tubing and the glass feed bottle. It should be noted that the majority of the losses are likely attributable to the Pharmed tubing. Huck et al. (1995), who reported high losses to the

TABLE 1. System losses

Trial no.	System variables	No. observations	Geosmin average % loss ^a	MIB average % loss ^a
1	Glass bottle/3 m Pharmed tubing/110 cm glass column	15	81 ± 1	73 ± 2
2	Glass bottle/3 m Pharmed tubing/no glass column	15	64 ± 2	58 ± 1
3	Teflon bottle/3 m Teflon tubing/110 cm glass column	15	64 ± 2	43 ± 2
4	Teflon bottle/3 m Teflon tubing/no glass column	15	19 ± 2	13 ± 2
5	Teflon bottle/3 m Teflon tubing/60 cm glass column ^b	15	42 ± 2	30 ± 4

^aAverage losses calculated based on target initial feed concentrations of 200 ng/L for geosmin and MIB.

^b50 cm Teflon tubing inserted into top of glass column to decrease glass column length.

Pharmed tubing, also showed that losses to the glass bottle were insignificant.

After the installation of a pumping system using Teflon tubing and a Teflon feed bottle, losses dropped to 64% for geosmin and 43% for MIB (Trial 3, Fig. 1D). Under this particular system design, effluent samples (Fig. 1C) showed a substantial decline in percent losses of both geosmin and MIB to 19 and 13%, respectively (Trial 4). This indicates that a significant portion of the odour compounds are lost in the glass filter column itself. Finally, after installing a piece of Teflon tubing approximately 50 cm in length into the top of the glass filter column, thereby decreasing the filter contact length to 60 cm, the percent losses dropped to 42% for geosmin and 30% for MIB (Fig. 1D). These results indicate that a preferred system design for bench-scale experiments would involve the system variables used in design number five (Table 1). Thus, Teflon materials are preferable in attempting to reduce system losses of both geosmin and MIB. As well, minimizing solution contact with glass materials is recommended. The system losses identified in these experiments remained at the same level through several years of subsequent experimentation (Elhadi 2004).

Losses to Individual System Components

In an attempt to provide more thorough information with regard to systemic losses of both geosmin and MIB, individual system variables were investigated. Each of the experiments was conducted over a 15-day period in which a total of 10 observations were reported. As discussed previously, the specific components evaluated were the feed bottles, tubing and glass filter columns.

Feed bottles. The average percent loss of each compound to the different feed bottles was calculated. Table 2 shows the results of these experiments after 4 days and after a total of approximately 15 days. The bottles were stored in the dark at room temperature.

There was an apparent increase in percent loss of both compounds over an approximate 4-day period, however, after such time the losses remained relatively consistent (data not shown). Losses of both geosmin and

MIB were significantly higher where glass feed bottles were used. After 15 days the average percent loss for geosmin and MIB was much higher when using the glass feed bottles as compared to using the Teflon feed bottles. Losses were presumably a result of adsorption to the glass and possible degradation in the bottle itself. Losses were not assumed to be due to volatilization as previous studies have demonstrated that cooling samples did not decrease the losses (Huck et al. 1995). In addition, it is indicated in the literature that geosmin and MIB are only semi-volatile (Lloyd et al. 1998; Young and Suffet 1999).

Tubing. Initial experiments were conducted using Pharmed tubing, Viton tubing, and Teflon tubing each 3 m in length. Average losses of geosmin and MIB after 4 days and after 15 days were calculated (Table 3).

The results show a substantial loss of both geosmin and MIB to the Pharmed tubing. More than 50% of both compounds were lost to this type of tubing. Viton tubing was investigated to determine its comparability with the Pharmed tubing. The average losses using the Viton tubing were somewhat lower than those found using the Pharmed tubing. The average losses of both geosmin and MIB dropped to 47% and 41%, respectively. The use of Teflon tubing, on the other hand, decreased the losses of each compound to as low as 19% for geosmin and 14% for MIB. It should be noted that average percent losses of both compounds to the tubing varied only slightly between day 4 and 15. Therefore, it would seem acceptable to run system loss experiments over a shorter period of time.

Losses of geosmin and MIB to all three types of tubing investigated could be attributed to adsorption and degradation within the tubing. In an attempt to minimize these losses experiments were conducted with a piece of Pharmed tubing 3 m in length that had been preconditioned with tap water. Tap water was pumped through the tubing for approximately 18 days in order to examine whether or not certain compounds in the water would occupy some of the adsorptive sites within the tubing itself. Solutions containing geosmin and MIB were then fed through the tubing and the average losses were calculated. Losses of each compound dropped only slightly from those calculated with the unconditioned

TABLE 2. Average percent loss of geosmin and MIB to feed bottles

Feed bottle	Time (days)	No. observations	Average geosmin % loss ^a	Average MIB % loss ^a
Glass (4 L)	4	4	8 ± 5	5 ± 2
	15	10	10 ± 4	8 ± 4
Teflon (2 L)	4	4	0 ± 0	0 ± 0
	15	10	1 ± 0	1 ± 0

^aAverage losses calculated based on target initial feed concentrations of 200 ng/L for geosmin and MIB.

TABLE 3. Average percent loss of geosmin and MIB to Pharmed, Viton and Teflon tubing

Tubing type	Time (days)	No. observations	Average geosmin % loss ^a	Average MIB % loss ^a
Pharmed (3 m)	4	4	56 ± 1	52 ± 1
	15	10	57 ± 1	52 ± 1
Viton (3 m)	4	4	47 ± 1	41 ± 1
	15	10	47 ± 1	41 ± 1
Teflon (3 m)	4	4	19 ± 1	13 ± 1
	15	10	19 ± 1	14 ± 1

^aAverage losses calculated based on target initial feed concentrations of 200 ng/L for geosmin and MIB.

Pharmed tubing (results not shown). The average losses for both geosmin and MIB were still greater than 50%.

As was found previously with the feed bottles, average losses of geosmin were consistently higher than those for MIB when using the Pharmed, Teflon and Viton tubing.

Glass filter column. Experiments were conducted using two custom-made glass filter columns (50-mm ID). Average losses of geosmin and MIB at a sampling depth of 110 cm along the column and at a depth of 60 cm along the column after 4 days and after 15 days were calculated. The results of these experiments are shown in Table 4.

Average losses were very high for both compounds, reaching as much as 54% for geosmin and 37% for MIB. Losses could be attributed to adsorption to the glass or possibly due to volatilization in the head space at the top of the filter columns. In an attempt to minimize the losses associated with the glass, a piece of Teflon tubing, 50 cm in length, was inserted into the top of the filter column. This decreased the feedwater contact with the glass filter column to approximately 60 cm. As a result, the average losses for geosmin dropped to 24% and the average losses for MIB dropped to 16%.

Conclusions

The results of this study highlight the importance of thorough evaluation of experimental systems used to

investigate the removal of trace level compounds, such as geosmin and MIB. For the biological removal of these compounds it is necessary to focus future research at the ng/L level and therefore issues associated with system losses become problematic. These losses must be documented for any experimental system. In practice this means that feed concentrations will have to be increased in order to achieve the desired concentration at the influent of the process under study (in this case, immediately above the filter media).

The following conclusions can be drawn from this study on losses of geosmin and MIB in a bench-scale filtration system.

1. Substantial removals of geosmin and MIB via physical adsorption occurred on glass materials and peristaltic pump tubing (i.e., Pharmed and Viton tubing). Volatilization may have played a role in experiments involving the glass columns.
2. The optimal system for this research consisted of a 2-L Teflon feed bottle, a valveless piston metering pump, 3 m of Teflon tubing, and a glass filter column 60 cm in length (i.e., length of the column with which the water above the media would be in contact). Average losses of geosmin and MIB were 42 and 30%, respectively, based on initial concentrations targeted at 200 ng/L.
3. Average losses to individual system components were also calculated based on initial concentrations

TABLE 4. Average percent loss of geosmin and MIB to glass filter columns

Glass column	Time (days)	No. observations	Average geosmin % loss ^a	Average MIB % loss ^a
110 cm	4	4	51 ± 2	33 ± 1
	15	10	54 ± 3	37 ± 3
60 cm ^b	4	4	25 ± 2	13 ± 1
	15	10	24 ± 1	16 ± 2

^aAverage losses calculated based on target initial feed concentrations of 200 ng/L for geosmin and MIB.

^bIncludes losses in the 50 cm of Teflon tubing.

targeted at 200 ng/L. Losses of geosmin and MIB to the 2-L Teflon feed bottles were 1% each, which were much lower than the losses to the glass feed bottles. Losses to the Teflon tubing were also much lower than those measured using both Pharmed and Viton tubing. The losses using Teflon tubing were 19% for geosmin and 14% for MIB. The length of the glass filter columns had an impact on both geosmin and MIB removals. Decreasing the column contact length from 110 cm to 60 cm, decreased losses of geosmin from 54 to 24%, respectively, and MIB from 37 to 16%, respectively.

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Disclaimer

Mention of commercial products does not constitute endorsement by the authors or the funding agency.

References

- Ashitani K, Hishida Y, Fujiwara K. 1988. Behavior of musty odorous compounds during the process of water treatment. *Water Sci. Technol.* 20(8/9):261–267.
- Danglot C, Amar G, Vilagines R. 1983. Ability of *Bacillus* to degrade geosmin. *Water Sci. Technol.* 15(5/6): 291–299.
- Elhadi SLN. 2004. Removal of earthy/musty odour compounds from drinking water by biological filtration. Ph.D. thesis, Department of Civil Engineering, University of Waterloo, Waterloo, Ont., Canada.
- Huck PM, Kenefick SL, Hruddy SE, Zhang S. 1995. Bench-scale determination of the removal of odour compounds with biological treatment. *Water Sci. Technol.* 31(11):203–209.
- Izaguirre G, Wolfe RL, Means EG. 1988. Bacterial degradation of 2-methylisoborneol. *Water Sci. Technol.* 20(8/9):205–210.
- Lalezary S, Pirbazari M, McGuire MJ. 1986. Oxidation of five earthy-musty taste and odour compounds. *J. Am. Water Works Assoc.* 78(3):62–69.
- Lloyd SW, Lea JM, Zimba PV, Grimm CC. 1998. Rapid analysis of geosmin and 2-methylisoborneol in water using solid phase micro extraction procedures. *Water Res.* 32(7):2140–2146.
- Namkung E, Rittmann BE. 1987. Removal of taste and odour-causing compounds by biofilms grown on humic substances. *J. Am. Water Works Assoc.* 79(7):107–112.
- Nerenberg R, Rittmann BE, Soucie WJ. 2000. Ozone/biofiltration for removing MIB and geosmin. *J. Am. Water Works Assoc.* 92(12):85–95.
- Watson SB, Brownlee B, Satchwill T, Hargesheimer E. 2000. Quantitative analysis of trace levels of geosmin and MIB in source and drinking water using headspace SPME. *Water Res.* 34(10):2818–2828.
- Young CC, Suffet IH. 1999. Development of a standard method-analysis of compounds causing taste and odours in drinking water. *Water Sci. Technol.* 40(6):279–286.

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