Research Article

Geographical and Seasonal Patterns of Geosmin and 2-Methylisoborneol in Environmental Water in Jiangsu Province of China

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This study was conducted to obtain the basic data of two common odorants—geosmin and 2-methylisoborneol (GSM and 2-MIB)—in environmental water. More specifically, the headspace solid-phase microextraction coupled to gas chromatography mass spectrometry (HS-SPME/GC-MS) was applied to determine the levels of GSM and 2-MIB in water samples, and the samples were collected depending on water sources, conventional treatment processes, and seasons. The significant difference was shown for the 2-MIB levels of source water \( (P < 0.05) \), the concentrations of GSM and 2-MIB decreased significantly as treatment process of tap water moved forward \( (P < 0.0001) \), and the significant differences for the levels of GSM and 2-MIB were observed among three sampling periods \( (P < 0.01) \). The levels of GSM and 2-MIB in all water samples were lower than 10 ng L\(^{-1}\), the odor threshold concentration (OTC), and the conventional treatment process plays a significant role in removing odorants in tap water.

1. Introduction

Odorants are troublesome in water samples, because they dramatically influence the esthetic quality and consumers’ acceptability of drinking water [1, 2]. These odorants are often associated with the metabolites that are produced in the degradation of cyanobacteria, actinomycetes, fungi, and blue-green algae [3–5]. The odorants geosmin (GSM) and 2-methylisoborneol (2-MIB) are commonly found in lakes and reservoirs [6, 7], which people can smell their odors in water samples even at the concentration of 10 ng L\(^{-1}\) or less, but it would be difficult to identify and quantify these two trace volatile organic compounds (VOCs) [8–12]. As a result, the low threshold of detection can result in consumer complaints about the odors in recreational waters, aquatic products, and tap water, especially during the outbreak period of algal blooms [13], even if some other quality indicators of water, such as turbidity, number of algal cells, and suspended matter, are acceptable.

In recent years, according to the investigation by Chinese Academy of Sciences [14, 15], the results indicated that freshwater lakes were suffering the odor problems in China, especially in Lake Taihu, Lake Chaohu, and Lake Dianchi. These unpleasant odors occurring in these lakes or the aquatic were caused by the volatile secondary metabolites of the algal overgrowth. Therefore, we had conducted this study in 2012, aiming to obtain the basic data of common odorants (GSM and 2-MIB) in environmental waters in Jiangsu province. To be more specific, the headspace solid-phase microextraction coupled to gas chromatography mass spectrometry (HS-SPME/GC-MS) was applied to determine the levels of GSM and 2-MIB in water samples, and this method can be obtained in our early reports [16, 17]. In addition, the water samples were collected in detail as follows: firstly, for water sources
of tap water, four kinds of water samples were collected respectively from four cities in Jiangsu, including city A (little lakes as the source), city B (the Changjiang River as source), city C (Lake Taihu as source), and city D (underground water as the source); secondly, for conventional treatment process of tap water, including coagulation and sedimentation, filtration, and disinfection, the water samples were collected respectively from above processes; thirdly, for treatment process of tap water, including coagulation and sedimentation, filtration, and disinfection, the watersamples were obtained respectively from each water work in drought period—February to March—by manual sampling, meaning 15 samples in total in one city. Water samples from the water works were analyzed by the proposed method, which were kept in 350 mL sample vials with PTFE-faced silicon septum and stored at 4 °C before analysis. The average length of time between sampling and analysis was 24 hours.

2.4. Water Samples Collection

2.4.1. Water Samples from Different Cities. Based on different sources for tap water, four representative cities were chosen to collect water samples, including city A (little lakes as the source), city B (the Changjiang River as source), city C (Lake Taihu as source), and city D (underground water as the source). Five water works were selected from each city, and raw water, output water, and end water (for consumers) were obtained respectively from each water work in drought period—February to March—by manual sampling, meaning 15 samples in total in one city. Water samples from the water works were analyzed by the proposed method, which were kept in 350 mL sample vials with PTFE-faced silicone septum and stored at 4 °C before analysis. The average length of time between sampling and analysis was 24 hours.

2.4.2. Water Samples from Different Processes of Tap Water Treatment. The conventional treatment of tap water includes four processes, as raw water, coagulation and sedimentation, filtration, and disinfection, and end water was provided for consumers by pipe network as shown in Figure 1. The five water works were selected from city B (shorter distance to laboratory than other three), and one sample was obtained from each process, that is to say, 4 samples in total in one water work.

2.4.3. Water Samples from Different Seasons. For different seasons of water samples, we collected the samples in three periods in Lake Taihu, including the period when a river is at its normal level (November to December), drought period (February to March), and wet season (July to August) when the algae bloom.

2.5. Statistical Methods. The analysis of variance (ANOVA) was applied to the present work, aiming to obtain the significant differences when comparing average values in the two or more groups. More specifically, two-way ANOVA was
applied to compare the GSM and 2-MIB levels in four cities (Tables 1 and 2), while one-way ANOVA was applied in water samples from different processes of tap water treatment and different seasons (Tables 3 and 4).

### 3. Results and Discussion

According to Tables 1 and 2, the significant differences of concentration cannot be observed for both GSM and 2-MIB among the four cities ($P > 0.05$), excepting the 2-MIB levels of raw water ($P < 0.01$). More specifically, the 2-MIB level of raw water in city D was lower than that in three other cities ($P < 0.01$), and the most potential reason could be that the soil or rocks work as natural barrier or filter, keeping the larger particles permeating into raw water. As a result, the level of 2-MIB may be lower in city D. However, there are no significant differences for the levels of GSM among four cities; in other words, the lower 2-MIB levels of raw water in city D never necessarily equal the lower levels of GSM in city D similarly. It can be explained that the levels of two odorants were associated with multiple factors, including the species of algae, acidic condition of environment, rainfalls, and light density [18]. For example, growth and production of 2-MIB was characterized in the cyanobacterium *Phormidium* sp. [19] but was not responsible for GSM. Another example is that the actinomycetes can cause the odorants, but the total colony counts did not necessarily indicate the direct role of actinomycetes in odor problems in environmental water, because their activities would be restricted by other

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**Table 1:** The statistical analysis of GSM levels in four cities ($n = 60$).

| City | Raw water (ngL$^{-1}$) | Output water (ngL$^{-1}$) | End water (ngL$^{-1}$) | Comparative analysis in one city |
|------|------------------------|---------------------------|------------------------|--------------------------------|
|      |                        | F                         | P value                |
| A    | 2.27 ± 1.45            | 0.22 ± 0.1                | 0.09 ± 0.04            | 7.07 0.0143                      |
| B    | 0.72 ± 0.17            | 0.21 ± 0.11               | 0.14 ± 0.09            | 26.08 0.0002                      |
| C    | 3.55 ± 0.66            | 0.56 ± 0.67               | 0.06 ± 0.02            | 44.04 <0.001                      |
| D    | 0.73 ± 0.18            | 0.18 ± 0.17               | 0.08 ± 0.02            | 26.18 0.0001                      |

Comparing among four cities

| F | P value |
|---|---------|
| 0.84 | 0.84 |
| 1.64 | 0.24 |

**Table 2:** The statistical analysis of 2-MIB levels in four cities ($n = 60$).

| City | Raw water (ngL$^{-1}$) | Output water (ngL$^{-1}$) | End water (ngL$^{-1}$) | Comparative analysis in one city |
|------|------------------------|---------------------------|------------------------|--------------------------------|
|      |                        | F                         | P value                |
| A    | 7.56 ± 3.38            | 1.50 ± 0.57               | 0.46 ± 0.33            | 10.24 0.0062                      |
| B    | 7.59 ± 2.85            | 1.64 ± 1.27               | 0.06 ± 0.04            | 11.16 0.0156                      |
| C    | 6.52 ± 2.71            | 1.46 ± 0.70               | 0.04 ± 0.01            | 17.31 0.0004                      |
| D    | 1.30 ± 1.02            | 0.36 ± 0.25               | 0.06 ± 0.04            | 2.43 0.1575                       |

Comparing among four cities

| F | P value |
|---|---------|
| 6.46 | 1.91 |
| 2.56 | 0.17 |

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Table 3: Water samples from different processes of tap water treatment (n = 20).

| Compound | Raw water (ng L\(^{-1}\)) | Coagulation and sediment (ng L\(^{-1}\)) | Filtration (ng L\(^{-1}\)) | Chlorination (ng L\(^{-1}\)) | F  | P      |
|----------|--------------------------|----------------------------------------|----------------------------|----------------------------|----|--------|
| GSM      | 0.72 ± 0.17              | 0.56 ± 0.22                           | 0.12 ± 0.03                | 0.21 ± 0.11                | 15.65 | <0.0001|
| 2-MIB    | 7.58 ± 2.85              | 1.96 ± 0.45                           | 0.75 ± 0.86                | 1.63 ± 1.28                | 16.69 | <0.0001|

Table 4: Water samples from different seasons (n = 45).

| Compound | Water type | Normal level\(^a\) (ng L\(^{-1}\)) | Drought period\(^b\) (ng L\(^{-1}\)) | Wet season\(^c\) (ng L\(^{-1}\)) | F  | P      |
|----------|------------|-----------------------------------|-----------------------------------|-----------------------------------|----|--------|
| GSM      | Raw water  | 4.25 ± 2.56                       | 3.55 ± 0.66                       | 7.61 ± 1.70                      | 7.07 | 0.01   |
|          | Output water | 1.06 ± 0.41                     | 0.56 ± 0.67                       | 1.23 ± 1.03                      | 0.85 | 0.46   |
|          | End water   | 0.18 ± 0.16                       | 0.06 ± 0.02                       | 0.04 ± 0.00                      | 1.71 | 0.25   |
| 2-MIB    | Raw water  | 5.12 ± 2.16                       | 6.52 ± 2.71                       | 10.17 ± 1.96                     | 6.43 | 0.01   |
|          | Output water | 1.02 ± 0.33                     | 1.46 ± 0.70                       | 1.15 ± 0.49                      | 0.89 | 0.43   |
|          | End water   | 0.63 ± 0.63                       | 0.04 ± 0.01                       | 0.21 ± 0.09                      | 1.08 | 0.38   |

Note: \(a\), \(b\), and \(c\) represent algal cell count in their raw waters, and their values were 6.21 m L\(^{-1}\), 3.34, and 11.42, respectively.

evironmental factors [20]. Consequently, the lower 2-MIB occurred in city D, but GSM did not, even though they shared the same water source.

In addition, the decreased levels of GSM or 2-MIB were observed among the raw water, output water, and end water (\(P < 0.05\)), as implied in Table 4. Because both of GSM and 2-MIB were volatile organic chemicals (VOCs), the concentrations would decrease in the water transferred from water works to destination, and similar results are obtained by early reports in China [21]. Meanwhile, the concentration of total residual chlorine in pipe network would necessarily reduce the levels of GSM and 2-MIB [22, 23]. But, however, an experimental error (10–70%) may be observed due to the presence of free residual chlorine, and this error can decline after dechlorination (less than 10%) [22, 24]. Consequently, the average values of two odorants in Table 3 may increase from filtration to chlorination.

Based on Table 3, it is indicated that the concentration of GSM and 2-MIB decreased significantly as treatment process moved forward (\(P < 0.0001\)). The reasons can be as follows: firstly, after the processes of coagulation, sedimentation, and filtration, larger particles had been removed, such as algae, silt, and other plankton, which can produce the musty and earthy odorant in tap water, and the same result was implied in early study [25]. The last process, chlorination, can kill or remove main cyanobacteria and actinomycyes by oxidation [26, 27]. And also some reports indicated that the presence of chlorine would substantially reduce the observed GSM and 2-MIB concentrations, and its impact was larger for lower organic compound concentrations [22]. Consequently, the lower levels of GSM and 2-MIB would appear in output water.

The water samples of different seasons were collected from city C, the Lake Taihu of which was used as source water and blue-green algae blooming in summer in this lake. According to Table 4, the significant differences were observed for the levels of GSM and 2-MIB among the three periods (\(P < 0.01\)); in other words, the GSM and 2-MIB levels of raw water were higher in period of wet water than corresponding levels in other two periods. The most important reason was the algae blooming and reservoir's eutrophication in summer, resulting in higher concentrations of odorants, while the algae or cyanobacteria were dead or inactive in other periods. Moreover, the concentrations were found to correlate with corresponding air and water temperatures, and the average water temperature was 12, 16, and 27°C for normal level, drought, and wet period, respectively. The concentrations of odorants followed a trend of higher levels during the warm seasons [28–30]. Consequently, the levels in wet season (in summer) were higher than those in other two periods. Also, the results implied that levels of odorants were approximately equal between the periods of normal level and drought.

4. Conclusion

The levels of GSM and 2-MIB in water samples were less than 10 ng L\(^{-1}\), the odor threshold concentration (OTC) [12, 31]. And the conventional treatment process of tap water plays a significant role in removing common odorants in running water for these source waters. In particular the largest decrease in concentrations occurs after sedimentation suggesting that removal of GSM and MIB in intact algae cells is important.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors’ Contribution

Zhen Ding and Shifu Peng contributed equally to this paper.
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