Development of polypropylene glycol coated hollow fiber membranes as passive sampler for field equilibrium sampling of odorous compounds in environmental waters

Jing-Fu Liu,* Yong Tao, Jia Sun and Gui-Bin Jiang

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A new passive sampling device was developed for field equilibrium sampling of geosmin (GSM) and 2-methylisoborneol (MIB) in surface water. The sampling device was prepared by coating a 50 cm length polypropylene hollow fiber tubing (50 μm wall thickness, 280 μm inner diameter) with polypropylene glycol 4000. The sampler was brought into equilibrium with the sample in the field, and then transferred and immersed into 100 μL of methanol held in a little desorption device for room temperature desorption and preservation of the sampled analytes. After being transported to the laboratory, the analytes were determined by headspace solid-phase microextraction-GC-MS. The large surface area-to-volume ratio of the developed sampler facilitated the reaching of sampling equilibrium in 1 h, while the equilibrium sampling minimized the effects of environmentally relevant sampling conditions. Variation of sample pH (4.0–9.0) and salinity (0–100 mM NaCl) had no significant effects on the distribution coefficients of analytes to the sampler. The desorption device, constructed with a 200 μL glass insert, and a 2 mL brown glass vial with PTFE sealed screw cap, has no loss of analytes during the storage of the sampler. The proposed procedure had detection limits of 4 and 9 ng L^{-1} for GSM and MIB, respectively. This developed sampler was successfully applied to field sampling in Taihu Lake (China), with MIB and GSM detected in the range of 0.11–0.61 $\mu\text{g L}^{-1}$ during a medium out-break of blue-green algae bloom.

1. Introduction

Taste and odor of surface water and drinking water matters as consumers often take offense to off-tastes and odors in drinking water, and natural waters used for recreation.^{1,2} 2-Methylisoborneol (MIB) and *trans*-1,10-dimethyl-*trans*-9-decalol (geosmin, GSM) have been known to be the most common compounds contributing to the undesirable earthy-musty smell of water.¹ Both MIB and GSM are alicyclic alcohols produced by actinomycetes, cyanobacteria and certain blue-green algae.^{3–5} Due to the extremely low odour threshold in drinking water ($\sim 4 \text{ ng L}^{-1}$ GSM, $\sim 9\text{--}15 \text{ ng L}^{-1}$ MIB),^{6,7} very sensitive methods that can sense them at low ng L^{-1} level are required in order to supply high quality drinking water.

The physicochemical properties of the semi-volatile MIB and GSM make gas chromatography (GC) the only choice for their instrumental analysis,^{8,9} and mass spectrometry (MS) is the most commonly used detector.^{9–15} Because of the extremely high sensitivity required for detection of these compounds, it is

essential to have enrichment or extraction steps before GC-MS analysis. A variety of enrichment/extraction techniques including closed-loop stripping analysis,^{12,16} hollow fiber stripping analysis,¹¹ liquid-liquid extraction (LLE),^{14,17,18} solid-phase extraction (SPE),^{10,19,20} purge and trap,^{8,9} headspace liquid-phase microextraction,^{21,22} stir bar sorptive extraction,^{23–25} and solid-phase microextraction (SPME)^{8,13,15,26–31} have been applied to preconcentrate trace amounts of MIB and GSM in water. While most of these sample pretreatment procedures provide detection limits of $\sim 1 \text{ ng L}^{-1}$ for MIB and GSM, lower detection limits were obtained by using closed-loop stripping ($0.01\text{--}0.03 \text{ ng L}^{-1}$),¹² stir bar sorptive extraction ($0.025\text{--}0.041 \text{ ng L}^{-1}$)²⁴ and liquid-phase microextraction (0.05 ng L^{-1}).²² All these sample pretreatment techniques are directed at extracting water samples in the laboratory, except for one report on the LLE of MIB and GSM in sample collection bottles with dichloromethane carried out on board a research vessel.¹⁴

With the global exacerbation in nutrient-rich surface water bodies, the occurrence of earthy-musty off-odor events resulting from MIB and GSM increases subsequently.^{32–36} Thus, more and more surface water samples have to be analyzed to monitor trace amounts of these off-odor compounds to maintain water-quality standards. A traditional method of grabbing 500 mL²⁹ or 1000 mL²⁰ water samples and shipping back to the laboratory for

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing, 100085, China. E-mail: jfliu@rcees.ac.cn; Fax: +86-10-62849192

pretreatment is cost and labour intensive, as these large volume samples have to be stored in a cooler packed with ice or a refrigerator at 4 °C to inhibit the production of MIB and GSM by microorganisms during the shipping time. To overcome this drawback, it is essential to develop *in situ* sampling/field pretreatment methods that can extract and preserve these off-odor compounds from surface water in sampling devices and then bring them back to the laboratory for analysis. Passive sampling, which provides practical advantages such as cost effectiveness, easy operation, and elimination of power requirements, is a very promising approach which can fulfill this purpose.^{37–39} A variety of passive samplers have been developed for different target analytes. As examples, semi-permeable membrane devices (SPMD)⁴⁰ and SPME⁴¹ were developed for sampling hydrophobic organic compounds, while polar organic chemical integrative sampler (POCIS),⁴² Chemcatcher⁴³ and solvent-based cellulose membrane⁴⁴ were developed for sampling polar organic compounds. Nevertheless, to the best of our knowledge, there is no report on field sampling of MIB and GSM with a passive sampler. One possible reason is the relatively high volatility of MIB and GSM requiring the storage and transportation of the sampler with the analytes in liquid nitrogen or a refrigerator, which is difficult to fulfill due to the relatively bulky samplers such as SPMD and POCIS.

Equilibrium sampling, with a small passive sampling device such as SPME⁴⁵ or hollow fiber membrane-based thin liquid film extraction (TLFE),⁴⁶ is a very promising technique for passive sampling MIB and GSM. The large surface area-to-volume ratio of these devices facilitates fast equilibrium sampling in the field.^{45,46} In addition, the working principle of equilibrium sampling, which is based on the partitioning coefficient between the sampling phase and the media, gives the benefit of easy calibration of the analyte concentration. While there is no report on the application of hollow fiber membrane-based sampling devices in real field sampling, SPME has been applied to field sampling volatile analytes.^{47,48} However, the SPME fiber had to be stored in liquid nitrogen⁴⁸ or a refrigerator⁴⁷ to preserve and transport the extracted analytes from the sampling sites to the laboratory. Very recently, stir bar sorptive extraction was adopted for passive enrichment of haloanisole compounds in tap water.⁴⁹

In this present study, a new approach was developed for field sampling MIB and GSM in surface water. A passive sampling device, prepared from hollow fiber membranes coated with polypropylene glycol (PPG), was developed for field equilibrium sampling of MIB and GSM in surface water; while a miniature desorption device was constructed for room temperature preservation and transportation of the sampled MIB and GSM from field to laboratory.

2. Experimental section

2.1 Reagents and materials

Individual standard solutions (100 µg mL⁻¹) of 2-methylisoborneol (MIB) and geosmin (GSM) (99.7% purity, dissolved in methanol), purchased from Supelco (Bellefonte, PA), were diluted in LC-grade methanol to obtain 2 µg mL⁻¹ stock solutions, and working solutions were prepared daily by appropriate

dilution of the stock solutions with water. LC-grade methanol was purchased from J. T. Baker (Phillipsburg, NJ). Polypropylene glycol (PPG, with average molecular weight of 4000) was obtained from Alfa Aesar (Ward Hill, MA). All other chemicals were analytical-reagent grade or higher and were obtained from Sinopharm Chemical Reagent Beijing (Beijing, China). Ultra-purified water (EASY-pure LF, Barnstead International, Dubuque, IA) was used throughout the experiments.

The 50/280 Accurel® PP polypropylene hollow fiber tubing (50 µm wall thickness, 280 µm inner diameter, 0.1 µm pore size) was obtained from Membrana GmbH (Wuppertal, Germany). Polydimethylsiloxane (PDMS) SPME fibers (100 µm) obtained from Supelco (Bellefonte, PA) were used for headspace SPME of the analytes.

2.2 Preparation of the sampling device

The sampling device (Fig. 1) was prepared as follows: the hollow fiber membrane was manually cut into a 52 cm-length and filled with water by using a syringe (BD Micro-Fine Syringe), and then the two ends were sealed with heated tweezers. The fiber was immersed into the mixture of PPG/methanol (2 : 1) to form a uniform organic liquid coating by adsorption. After 30 min, the fiber was collected and the surplus coating liquid on the fiber surface was cleaned with a tissue paper, whereas the lumen was flushed with water after cutting the two sealed ends. After that, into the lumen of the PPG coated hollow fiber membrane (~50 cm length) was inserted a 60 cm length copper wire, and the obtained device was preserved in reagent water for use. This prepared device has a sampling phase (PPG) volume of ~0.46 µL cm⁻¹, calculated based on the difference of the fiber weight after and before coating, and the density of the PPG 4000.

2.3 Equilibrium sampling

Optimization and calibration of the equilibrium sampling procedure was conducted in the laboratory. The PPG coated hollow fiber sampler was completely immersed into 500 mL standard sample solutions held in a capped flask with near zero headspace (Fig. 1). After static sampling or stirring for

Fig. 1 Schematic diagram of the prepared passive sampling device and desorption device, as well as the set-up for passive sampling.

a prescribed time, the sampling device was harvested and transferred into the desorption device. Parameters influencing the sampling, including agitation, sample pH and salinity, as well as sample volume, were optimized with standard solutions containing $0.4 \mu\text{g L}^{-1}$ each of MIB and GSM unless otherwise stated.

2.4 Field sampling

Field sampling was conducted in the northwest part of Taihu Lake in Wuxi (Jiangsu Province, China), with 13 sites in the area of north latitude $31^{\circ} 30' 27'' \sim 31^{\circ} 37' 26''$, and east longitude of $120^{\circ} 07' 06'' \sim 120^{\circ} 15' 26''$ (Fig. 2). During the field sampling, a 500 mL bottle was fully filled with surface water collected at a certain depth (0–0.6 m) and a sampler was deployed, which was completely immersed into the water in the bottle. After 1 h, the sampler was collected and treated as in the laboratory sampling described above (Fig. 1).

2.5 Desorption and transportation

A desorption device (Fig. 1) was developed for desorption, preservation and transportation of the analytes extracted in the PPG coated hollow fiber sampler. The desorption device consists of a 200 μL glass insert and a 2 mL brown glass vial with PTFE sealed screw cap (Agilent, USA). After the passive sampling reached equilibrium, the copper wire was removed and the PPG coated hollow fiber sampler was squeezed and immersed into the 100 μL of methanol held in the 200 μL glass insert. The glass insert was then placed into the 2 mL brown glass vial, and sealed with the PTFE sealed screw cap to prevent losses of MIB and GSM in the glass insert. The extracted analytes in the sampler were desorbed and preserved in the 100 μL methanol during the transportation of the desorption device back to the laboratory. The desorption time was controlled within 72 h.

2.6 Headspace SPME and GC-MS determination

The analytes in the desorption solution were determined by headspace SPME coupled with GC-MS. Headspace SPME of the analytes was performed with a procedure modified from the literature.²⁸ Briefly, the desorption solution was transferred into

a 25 mL conical flask with 10 mL of water, 3.6 g of NaCl and a stir bar. The flask was rapidly sealed with a cap wrapped with aluminium paper and then put on the magnetic stirrer for stirring. The septum piercing needle of the SPME device was introduced into the conical flask and the fiber was exposed in the headspace to allow adsorption of the analytes. After extraction for 60 min, the SPME fiber was retracted, placed into the injector of the gas chromatography-mass spectrometry (GC-MS) instrument and desorbed in splitless mode for 1 min. The GC-MS system was equipped with an Agilent 6890 GC, a 5973 mass selective detector, and a DB-5MS fused silica capillary column (film thickness, 0.25 μm ; 30 m $\times$ 0.25 mm i.d.). The oven temperature program was set as follows: the initial temperature was held at 100 $^{\circ}\text{C}$ for 1 min, increased to 280 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ with a 2 min hold. The injector and detector temperature were set and 280 $^{\circ}\text{C}$, respectively. Quantification was conducted by external calibration with standards to perform the same headspace SPME procedure, and with the mass spectrometer operated in selected ion-monitoring (SIM) mode for detecting the characteristic ion fragments (quantitated ion: $m/z = 95$ for MIB, 112 for GSM; simultaneously monitored ion: $m/z = 125$ for MIB, 135 for GSM).

3. Results and discussion

3.1 Preparation of the sampling device

In this present study, the sampling device was prepared by static coating of the hollow fiber membrane with PPG, *i.e.* the coating was conducted by directly immersing the hollow fiber into PPG. As the high viscosity of PPG retarded the transferring of PPG into the microspores of the hollow fiber membrane, a relatively long coating time (~ 2 h) was required to obtain satisfactory sampling efficiency and reproducibility. In order to reduce the coating time, PPG was diluted with methanol to reduce the viscosity thus enhance the coating efficiency. Experiments showed that the coating time can be shortened to 30 min by using a mixture of $V_{\text{PPG}}:V_{\text{methanol}} = 2:1$.

3.2 Optimization of conditions for equilibrium sampling

The effects of environmentally relevant pH and salinity, as well as agitation and sample volume on the passive sampling of MIB and GSM by the PPG-based sampler were evaluated with standard solutions. Equilibrium passive sampling was adopted in this study as it has the advantage of easy calibration.^{45,46} Primary experiments showed that environmentally relevant sample pH (4–9) and salinity (0–3.5% NaCl) had no significant effects on the equilibration time. Equilibration time was thus evaluated with standards prepared in reagent water at stirring (800 rpm) and static sampling, respectively. Fig. 3 shows the uptake profiles of analytes to the sampler with data fitted to a first-order one-compartment uptake model^{45,46} by using Graphpad Prism (ver. 4.1, GraphPad Software, San Diego, CA):

$$C_{\text{PPG}}/C_{\text{W}} = D_{\text{PPG,W}} \cdot (1 - e^{-k \cdot t}) \quad (1)$$

where C_{PPG} is the analyte concentration in the sampling phase (PPG) of the sampler at time t , C_{W} is the analyte concentration in the sample solution which was regarded as a constant that equals

Fig. 2 Field sampling sites in the northwest part of Taihu Lake in Wuxi (Jiangsu Province, China). The 13 sites (S1–S13) are in the area of north latitude $31^{\circ} 30' 27'' \sim 31^{\circ} 37' 26''$, and east longitude $120^{\circ} 07' 06'' \sim 120^{\circ} 15' 26''$.

Fig. 3 Effect of sampling time on the uptakes of MIB and GSM to the PPG passive sampler. The lines represent the fit of eqn (1) to the data. Sample solution: 500 mL of $0.4 \mu\text{g L}^{-1}$ each of MIB and GSM; Sampling phase: PPG supported on 50 cm of polypropylene hollow fiber. Agitation: stirring at 800 rpm or static. Each point represents the average of three replicates.

its initial concentration as a large sample volume was adopted to avoid sample depletion, k is the rate constant, and $D_{\text{PPG},w}$ is the distribution coefficient of an analyte between the PPG and the aqueous solution.

For both analytes the obtained k values under static conditions (0.060 and 0.107 min^{-1} for MIB and GSM, respectively) were slightly lower than those under stirring (0.100 and 0.134 min^{-1} for MIB and GSM, respectively), suggesting diffusion through the aqueous diffusion layer is the rate limiting process. The calculated 95% equilibration time,⁴⁶ based on $\ln(0.05)/(-k)$, for both analytes were all below 50 min regardless of whether the samples were stirred or not. Since the equilibration time in field sampling will generally be similar or shorter than under static conditions, 60 min can thus be adopted as a conservative estimate of the equilibration time for field sampling.

The $D_{\text{PPG},w}$ values obtained from the fittings under stirring and static sampling were 66.4 and 66.5 for MIB, and 79.8 and 74.2 for GSM, respectively. Although low partition coefficient might cause a limited amount of analytes to be sampled and thus low detection limits, this can be compensated by adoption of samplers with large sampling phase volume, *i.e.* by using a longer sampling device.

Considering the sample pH and salinity might affect the distribution coefficients of analytes between the PPG sampling phase and water ($D_{\text{PPG},w}$), it is necessary to study their effects on the sampling efficiency. Fig. 4 shows the distribution coefficients of samples with pH in the range of 4.0–9.0 normalized to those at pH 7.0 solutions, and samples with salinity of 0–600 mM NaCl normalized to those with zero salinity, respectively. The slight increase of $D_{\text{PPG},w}$ with pH (1.00–1.17 for MIB and 0.85–1.03 for GSM) indicates that sample pH has no significant effects on the sampling efficiency. The slight increase of $D_{\text{PPG},w}$ with sample salinity (Fig. 4b) was attributed to the salting out effect that enhanced the distribution of analytes into the PPG phase. A close look at Fig. 4b found that $D_{\text{PPG},w}$ values in the entire environmentally relevant salinity range (0–600 mM NaCl) and fresh water salinity range (0–100 mM NaCl) were in the range of 1.00–1.22 and 1.00–1.02 for MIB; and 1.00–1.40 and 1.00–1.21 for GSM, respectively. These above results indicated that the

Fig. 4 Effects of pH (a) and salinity (b) on the distribution coefficients of MIB and GSM to the sampling phase (PPG) of the passive sampler. The distribution coefficients were normalized to pH 7.0 and zero salinity, respectively. Sample solution: 500 mL of $0.4 \mu\text{g L}^{-1}$ each of MIB and GSM; Sampling phase: PPG supported on 50 cm of polypropylene hollow fiber; Agitation: stirring at 800 rpm. Each point represents the average of three replicates.

relative standard deviation could be controlled within 21% by adopting standard solutions with zero and 600 mM NaCl (approximately the salinity of sea water) for calibration of fresh water and sea water samples, respectively.

Fig. 5 Effect of sample volume on the uptakes of MIB and GSM to the PPG passive sampler. Sample solution: $0.4 \mu\text{g L}^{-1}$ each of MIB and GSM; Sampling phase: PPG supported on 5 cm of polypropylene hollow fiber. Each point represents the average of three replicates.

The influence of sample volume was studied by exposing 5 cm length samplers to samples with various volumes (Fig. 5) to avoid using too large volume of samples. The $C_{\text{PPG}}/C_{\text{W}}$ value increased with sample volume and then levelled off at sample volumes above 50 mL, suggesting that 500 mL of standard solution was sufficient for avoiding the sample depletion if a 50 cm length sampler was used. This agreed with the calculated sample volume (V_{sample}) for negligible depletion sampling, which had a maximum value of 368 mL for 5% depletion, calculated based on $V_{\text{sample}} = D_{\text{PPG,W}} \cdot V_{\text{PPG}}/(5\%)$ (V_{PPG} is the volume of the PPG on the sampler). In the subsequent study 500 mL of standard solutions were adopted as a conservative sample volume for calibrating field sampling.

3.3 Desorption and transportation conditions

The desorption conditions were optimized to completely desorb the analytes from the sampler and thus obtain high sensitivity and repeatability. Methanol, ethanol and acetone were tested as desorption solvents. Results showed that while acetone gave the lowest extraction efficiencies for both analytes, methanol provided the best desorption efficiency for both MIB and GSM. The GC-MS response decreased with the increased methanol volume in the studied range of 100–200 μL , thus 100 μL methanol was adopted in the following studies.

The desorption profiles of analytes from the sampler are shown in Fig. 6, which shows that both the analytes were almost completely desorbed after static soaking for 10 h. However, the standard deviations at 4 h and 10 h were relatively higher than that at 24 h or above. In cases that fast analysis is required, the desorption can be completed under sonication. Experiments showed that by sonicating the desorption device for 20 min before analysis, similar GC-MS response and precision as that of with 24 h static desorption was obtained.

Fig. 6 also demonstrates that further prolonged static desorption time up to 72 h caused no significant decrease of GC-MS response, indicating that the developed desorption device was able to preserve the analytes in the desorption solution for at least 3 days at room temperature. This benefited the preservation and transportation of the sampled analytes to the

Fig. 6 Effect of desorption time on the desorption of MIB and GSM from the passive sampler. The GC-MS response was normalized to the peak area obtained with a desorption time of 24 h. Sample solution: 500 mL of 0.4 $\mu\text{g L}^{-1}$ each of MIB and GSM; Sampling phase: PPG supported on 50 cm of polypropylene hollow fiber; Desorption solvent: 100 μL methanol. Each point represents the average of three replicates.

laboratory for determination. Instead of grasping 0.5–1.0 L of water sample and transporting in a refrigerator back to laboratory for analysis, the analytes were field passive sampled into a micro-sampling device which was then preserved in a 2 mL vial and brought at room temperature back to the laboratory for direct instrumental analysis. Further experiments showed that by storing the desorption device at 4 $^{\circ}\text{C}$ in the laboratory refrigerator, an additional 2 weeks of preservation caused no loss of analytes. This provided sufficient time for the following determination of MIB and GSM in desorption solutions by HS-SPME coupled with GC-MS.

3.4 Analytical performance

The analytical performance characteristics were evaluated with synthetic standard solutions prepared by spiking various concentrations (0.050–5 $\mu\text{g L}^{-1}$) of analytes spiked in reagent water adjusted to pH 7.0. Results indicated that this proposed method possesses good linearity ($R^2 > 0.996$), good precisions at 0.05 $\mu\text{g L}^{-1}$ level (RSD $< 15\%$, $n = 5$), and low detection limits (0.009 and 0.004 $\mu\text{g L}^{-1}$ for MIB and GSM, respectively). The detection limit was determined with five different sampling devices prepared in different batches, indicating the sampling device can be manufactured reproducibly. The detection limits are satisfactory in monitoring the analytes in environmental surface water, which is the purpose of this study. In cases such as tap water analysis that require lower detection limits, longer hollow fiber sampling device can be adopted.

For evaluation of the proposed procedure for determination of MIB and GSM in real environmental samples, well water, pond water and lake water samples were tested. These samples were collected into a 1000 mL bottle from Wuxi (Jiangsu province, China) in June, 2007 and transported to the laboratory to conduct the entire analysis procedure from passive sampling to GC-MS determination. The results shown in Table 1 indicate that the MIB and GSM contents in the pond and lake waters were between 0.85 and 2.67 $\mu\text{g L}^{-1}$, whereas that in the well water were below the detection limits. The high content of MIB and GSM agreed with the nature of the water samples, *i.e.* samples were collected when a severe blue-green algae bloom broke out, and the pond/lake waters contained large amount of blue-green algae. The recoveries determined by spiking with 0.05 or 1 $\mu\text{g L}^{-1}$ each of MIB and GSM were in the range of 87–110%, which were satisfactory considering that the passive sampling procedure was conducted directly without filtration of the algae.

3.5 Analysis of water samples

To assess its applicability for field sampling, the developed procedure was adopted to survey the MIB and GSM contamination at 13 sites located in the northwest part of Taihu Lake (Fig. 2) in July, 2008, with medium out-break out of blue-green algae bloom. Table 2 shows the MIB and GSM concentration were in the range of 0.11–0.61 $\mu\text{g L}^{-1}$, which were much higher in comparison to that reported in Lake Ontario ($\leq 0.056 \mu\text{g L}^{-1}$)²³ and in a reservoir in Taiwan ($\leq 0.200 \mu\text{g L}^{-1}$)⁵⁰ and were ascribed to the mediate broke out of blue-green algae bloom. However, these detected MIB and GSM contents were much lower than that detected in June 2007 when the blue-green algae bloom broke out severely (Table 1).

Table 1 MIB and GSM concentrations (mean $\pm$ s, $n = 3$) in water samples measured by the proposed procedure in the laboratory

Sample	Spiked/ $\mu\text{g L}^{-1}$	MIB		GSM	
		Detected/ $\mu\text{g L}^{-1}$	Recovery (%)	Detected/ $\mu\text{g L}^{-1}$	Recovery (%)
Well water	0	ND ^a		ND	
	0.05	0.052 ± 0.009	104 ± 18	0.049 ± 0.007	98 ± 14
Pond water	0	1.18 ± 0.19		0.85 ± 0.15	
	1	2.18 ± 0.26	100 ± 12	1.76 ± 0.22	91 ± 12
Lake water 1	0	2.67 ± 0.53		1.95 ± 0.33	
	1	3.61 ± 0.25	94 ± 18	3.05 ± 0.41	110 ± 14
Lake water 2	0	1.40 ± 0.16		1.69 ± 0.13	
	1	2.45 ± 0.22	105 ± 9	2.61 ± 0.16	92 ± 6
Lake water 3	0	1.24 ± 0.21		0.92 ± 0.07	
	1	2.11 ± 0.34	87 ± 15	1.85 ± 0.20	93 ± 10

^a ND, not detected.**Table 2** MIB and GSM concentrations (mean $\pm$ s, $n = 2$) in water samples measured by the proposed procedure with field sampling

Sampling site	MIB/ $\mu\text{g L}^{-1}$	GSM/ $\mu\text{g L}^{-1}$
S1	0.19 ± 0.07	0.50 ± 0.01
S2	0.25 ± 0.09	0.50 ± 0.01
S3	0.15 ± 0.02	0.46 ± 0.08
S4	0.21 ± 0.02	0.28 ± 0.03
S5	0.23 ± 0.06	0.60 ± 0.11
S6	0.17 ± 0.01	0.62 ± 0.16
S7	0.12 ± 0.04	0.45 ± 0.04
S8	0.22 ± 0.02	0.46 ± 0.02
S9	0.22 ± 0.07	0.60 ± 0.07
S10	0.42 ± 0.03	0.37 ± 0.09
S11	0.20 ± 0.05	0.45 ± 0.11
S12	0.26 ± 0.02	0.61 ± 0.05
S13	0.25 ± 0.11	0.57 ± 0.04

4. Conclusions

For the first time, a novel field passive sampling approach was developed for the analysis of GSM and MIB in surface water. The large surface area-to-volume ratio of the PPG coated hollow fiber membrane-based passive sampler facilitates the completion of equilibrium sampling in 1 h, while the sampler can be stored in the desorption device at room temperature for 3 days and at 4 °C in a refrigerator for 2 weeks without loss of analytes. These method merits overcome the drawbacks of the traditional method, *i.e.* storing large volume samples in a cooler packed with ice or a refrigerator at 4 °C to inhibit the production of MIB and GSM by microorganisms during the shipping time. Since the analytes in the desorption solvent were focused and determined by headspace solid-phase microextraction-GC-MS, the proposed procedure has a detection limit of 9 ng L⁻¹ for GSM and 4 ng L⁻¹ for MIB, respectively. This developed sampling device was successfully applied to field sampling in Taihu Lake (China), with MIB and GSM detected in the range of 0.11–0.61 $\mu\text{g L}^{-1}$ during a medium out-break of blue-green algae bloom.

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