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Time-Weighted Average Water Sampling in Lake Ontario with Solid-Phase Microextraction Passive Samplers

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In this study, three types of solid-phase microextraction (SPME) passive samplers, including a fiber-retracted device, a polydimethylsiloxane (PDMS)-rod and a PDMS-membrane, were evaluated to determine the time weighted average (TWA) concentrations of polycyclic aromatic hydrocarbons (PAHs) in Hamilton Harbor (the western tip of Lake Ontario, ON, Canada). Field trials demonstrated that these types of SPME samplers are suitable for the long-term monitoring of organic pollutants in water. These samplers possess all of the advantages of SPME: they are solvent-free, sampling, extraction and concentration are combined into one step, and they can be directly injected into a gas chromatograph (GC) for analysis without further treatment. These samplers also address the additional needs of a passive sampling technique: they are economical, easy to deploy, and the TWA concentrations of target analytes can be obtained with one sampler. Moreover, the mass uptake of these samplers is independent of the face velocity, or the effect can be calibrated, which is desirable for long-term field sampling, especially when the convection conditions of the sampling environment are difficult to measure and calibrate. Among the three types of SPME samplers that were tested, the PDMS-membrane possesses the highest surface-to-volume ratio, which results in the highest sensitivity and mass uptake and the lowest detection level.

Introduction

For the long-term monitoring of organic pollutants in water, passive sampling techniques are more attractive, compared to active sampling approaches, since the latter can be time-consuming and very costly (1–4).

Most passive sampling techniques vastly simplify sampling and sample preparation, eliminate power requirements, and significantly reduce the costs of analysis (3). Ideally, passive samplers should be inexpensive and easy to use, both for deployment and analysis (4). The currently available

passive samplers for water sampling are either based on permeation or diffusion (4), such as solvent-filled devices (5–7), semipermeable thin-film devices (SPMDs) (8), passive in-situ concentration/extraction samplers (PISCES) (9), and sorbent-filled devices (10). SPMDs are currently the most widely used type of passive samplers for field water analysis due to their ease of deployment, standardized character, and high sensitivity. However, the main disadvantage of the SPMD technique is the time-consuming sample-treatment the procedure (1, 11).

Solid-phase microextraction (SPME) was developed to address the need for rapid sampling and sample preparation, both in the laboratory and on-site (12). It is a solvent-free sample preparation technique and combines sampling, extraction, and concentration into one step. Since its conception (13), SPME has been widely applied to the sampling and analysis of environmental samples, food, and pharmaceuticals (14–15).

On-site sampling devices based on SPME integrate sampling with sample preparation and sample introduction. The design of these devices was based on different calibration methods, including traditional, equilibrium extraction and several diffusion-based approaches (16).

Several diffusion-based SPME devices have been developed for passive TWA sampling, both in air (17–20) and water (21). These SPME passive samplers are unlike conventional sampling with SPME, in which the fiber is retracted a known distance into its needle housing during the sampling period. Analyte molecules access the fiber coating only by means of diffusion through the static air/water gap between the opening and the fiber coating. Therefore, Fick's first law of diffusion can be used for the calibration. If the sorbent is "zero sink" for the target analytes, the concentrations of analytes in the sample can be calculated with eq 1 (17),

$$C = \frac{nZ}{ADt} \quad (1)$$

where C is the TWA concentration of the target analyte in air or water during the sampling time t , Z is the diffusion path length, A is the cross-sectional area of the needle, D is the diffusion coefficient of the target analyte in air or water, and n is the amount of analyte that is extracted by the fiber during time t .

In 1997, Ai Jiu proposed a dynamic SPME model based on a diffusion-controlled mass transfer process (22, 23). The absorption of an analyte into a SPME liquid coating from the sample matrix can be described by eq 2,

$$\frac{n}{n_e} = 1 - \exp(-at) \quad (2)$$

where n is the amount of the extracted analyte at time t , n_e is the amount of the extracted analyte at equilibrium, and a is a rate constant that is dependent on the volumes of the extraction phase, headspace and sample, mass transfer coefficients, distribution coefficients, and the surface area of the extraction phase. Based on this model, Chen et al. demonstrated the isotropy of absorption and desorption in the SPME liquid coating fiber and a new calibration method, kinetic calibration, was proposed (24, 25). The kinetic calibration method, also referred to as the in-fiber standardization technique (26), uses the desorption of the standards, which are preloaded in the extraction phase, to calibrate the extraction of the analytes. Then, the initial

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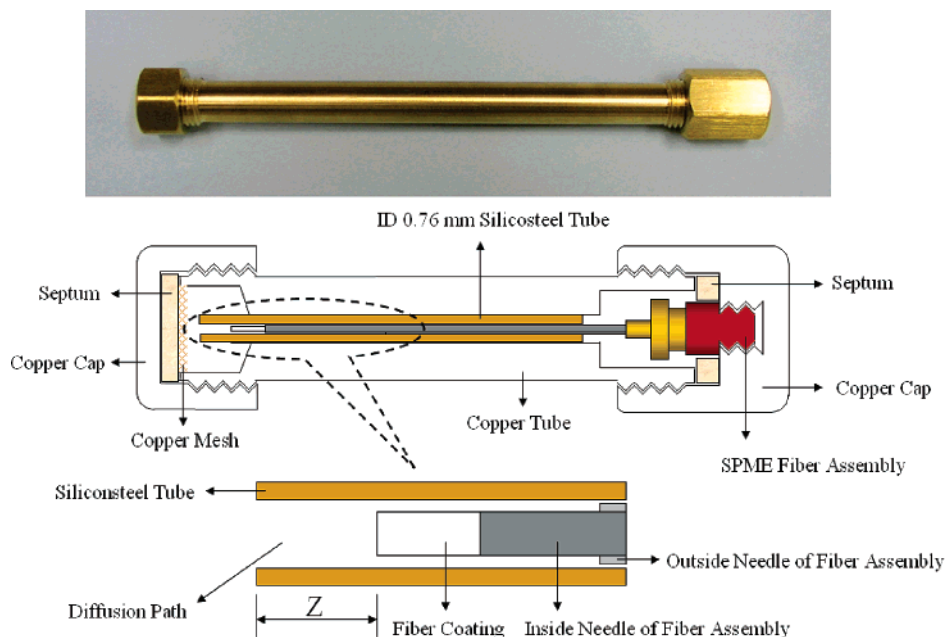


FIGURE 1. Schematic diagram and graphic of the SPME fiber-retracted TWA field water sampler.

concentration of target analyte in the sample, C_0 , can be calculated with eq 3 (27, 28),

$$C_0 = \frac{q_0 n}{K_{es} V_e (q_0 - Q)} \quad (3)$$

where V_e is the volume of the extraction phase, K_{es} is the distribution coefficient of the analyte between the extraction phase and the sample, q_0 is the amount of preloaded standard in the extraction phase, and Q is the amount of the standard remaining in the extraction phase after exposure of the extraction phase to the sample matrix for the sampling time. The distribution coefficients between the fiber coating and air can be estimated with retention indexes from a linear temperature-programmed capillary GC (29, 30). Coating/water distribution coefficients can be determined with a standard flow-through system (31, 32). This technique allows for the use of a simple PDMS-rod or PDMS-membrane as a passive sampler to obtain the time weighted average (TWA) concentrations of the target analytes in the sampling environment (28, 33).

In this study, a modified fiber-retracted SPME field water sampler, which was calibrated with Fick's first law of diffusion, and a SPME PDMS-rod and a PDMS-membrane passive sampler, calibrated with the kinetic calibration approach, were used to determine the TWA concentrations of PAHs in Hamilton Harbor (the western tip of Lake Ontario, ON, Canada). The results demonstrate that these samplers can be used as TWA passive samplers to monitor organic pollutants in water. The distinct features of the three types of samplers are also discussed.

Experimental Section

Chemicals and Supplies. HPLC grade methanol was purchased from BDH (Toronto, ON, Canada). Acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, d_{10} -fluoranthene, pyrene, and d_{10} -pyrene were purchased from Supelco (Oakville, ON, Canada). The SPME holder, the 100 μ m PDMS fibers and the PDMS rods, with a diameter of 1 mm, were also obtained from Supelco. The PDMS membrane, with a thickness of 127 μ m, was purchased from Specialty Silicone Products Inc. (Ballston Spa, NY). Silcosteel-treated tubing (i.d. 0.76 mm) was purchased from Restek (Bellefonte,

PA). Copper wire mesh was purchased from Goodfellow (Devon, PA). Ultrapure water was obtained using a Nanopure filter (Barnstead, Dubuque, IA). All preparations that involved PAHs were carried out in a ventilated fume hood.

Instrument. A Varian 4000 ion trap GC/MS system fit with a SPB-5 column (30 m, 0.25 mm i.d., 0.25 μ m film thickness) (Supelco, Mississauga, ON, Canada) was used for the analyses of the SPME fibers. The GC method has been previously described (21). The PDMS-rod and PDMS-membrane samplers were analyzed using an Agilent 6890 GC and 5873 MSD equipped with an ATAS Optic 3 DTD (direct thermal desorption) LVI (large volume injection) system (veldhoven, The Netherlands). The ATAS system, in combination with the CombiPal autosampler (Leap Technologies, Carrboro, NC), was used for the pneumatic exchange of liners between the cooled autosampler tray to the GC injector. A cryotrap was used to focus the analytes. The Agilent GC was equipped with a varian (Chrompack) CP Sil-8 CB column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). The details of the GC method and the conditions of the instrument have been previously described (33). The instruments were calibrated with six-point calibration curves, which were plotted with six methanolic standard solutions. The concentrations of the solutions ranged from 1 ng/mL to 100 μ g/mL. Peak shape quality, resolution, and retention times were also carefully monitored to ensure that the chromatography was within the required specifications.

Preparation of Field Samplers. Three types of SPME passive samplers (a fiber-retracted device, a PDMS-rod, and a PDMS-membrane) were used to determine the TWA concentration of PAHs in Hamilton Harbor.

SPME Fiber-Retracted Device. In a previous study, a Hamilton 500 μ L gastight syringe was modified as a TWA water sampling device to ensure that all of the air in the SPME needle could be displaced with water. In addition, a removable needle was designed for the device to avoid the effect of the adsorption of the target analytes on the outside wall of the needle (21). The device was validated in the laboratory with a flow-through system of a standard aqueous solution (21, 32).

In this study, the fiber-retracted device was modified for field water sampling. The design of the fiber-retracted SPME TWA field water sampler is illustrated in Figure 1. The sampler was constructed with copper tube and caps and a commercial

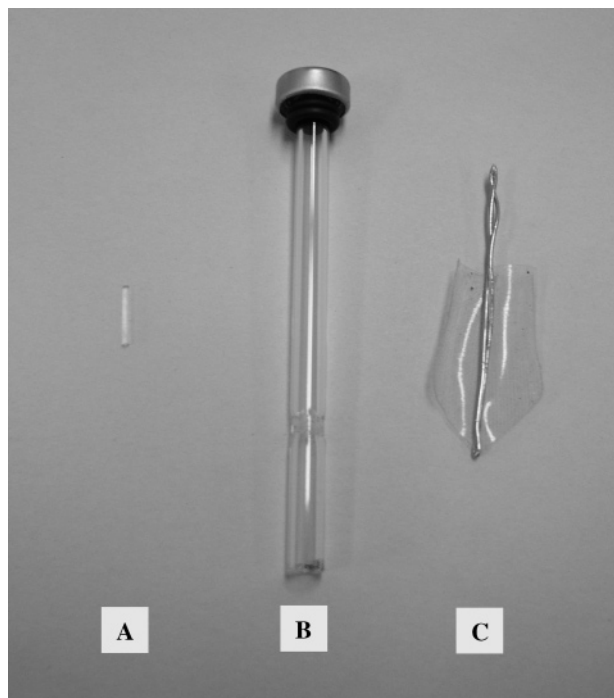


FIGURE 2. PDMS-rod (A) and PDMS-membrane (C) samplers and inlet liner of the GC (B) for automated injection with the ATAS system.

SPME 100 μm PDMS fiber assembly. The copper tube and caps were made in-house in the machine shop at the University of Waterloo. In the previous study, a deactivated Silcosteel-treated tube was used to eliminate the adsorption of analytes to the inside wall of the diffusion path (21). For the modified fiber-retracted SPME TWA field water sampler, a Silcosteel-treated tube with a larger inner diameter (0.76 mm) was used as the diffusion path. The larger diameter ensured that the outside needle of the SPME fiber assembly could be inserted into the diffusion path. Thus, the SPME fiber assembly was maintained in good condition after sampling and could be used for direct injection, since the outside needle of the fiber assembly was not in direct contact with the sample matrix and thus analytes would not be adsorbed onto the needle wall (Figure 1). The Silcosteel-treated tube was placed in the hole of the copper tube. The copper tube was made from a copper rod, and the inner diameter of the drilled hole was the same as the exterior diameter of the Silcosteel-treated tube. Thus, the Silcosteel-treated tube could be placed in position and adjusted with tweezers or pliers. In this trial, the length of the diffusion

path was adjusted to 4 mm for all of the samplers and the response time was less than 10 h for the target analytes. The opening of the device was covered with a copper mesh to avoid biofouling from the sampling environment and PDMS/Teflon septa were used for sealing the device.

When preparing for sampling, the fiber was conditioned at 250 $^{\circ}\text{C}$ for 1 h. The copper tube, the Silcosteel tube, and sampler caps were cleaned and baked at 250 $^{\circ}\text{C}$ for 1 h. After the copper tube and caps were cooled, the SPME fiber was placed into the diffusion tube and the cap (used to fix the fiber assembly) was tightly screwed in place. The diffusion tube was moved with tweezers to adjust the diffusion path length to 4 mm, the fiber assembly was then removed and all parts of the sampler were placed in pure water to displace the air with water. A wire was used with the Silcosteel tube to purge the air because the inner diameter of the tube was too small. After all of the air was eliminated, the fiber was inserted into the diffusion tube and the cap was tightly screwed closed to fix the fiber in place. A copper mesh was placed in the sampling opening, the cap was tightly screwed, and the sampler was then ready for sampling. All of the samplers were constructed in water to eliminate any air in the systems. Prior to deployment, the cap was removed from the sampler opening and the samplers were then deployed at the sampling sites for a set period of time.

SPME PDMS Rod and PDMS Membrane Samplers. The SPME PDMS-rod and PDMS-membrane samplers are illustrated in Figure 2. The pure PDMS-rod, which was used as the TWA passive sampler, was 1 cm long with a diameter of 1 mm and a volume of about 7.85 μL . The SPME-membrane samplers were made with a 127 μm thick PDMS thin-film. The thin-film was cut into a house-like shape using a special cutter, which was manufactured in-house by the University of Waterloo machine shop. The dimension of the SPME PDMS-membrane sampler was 2×2 cm with a 1-cm high triangle on the top of the square. The surface area of one side was 5 cm^2 , and the total volume of each membrane was 63.5 μL . These dimensions were optimized for ease of analysis so that the samplers could be coiled and fit inside a GC liner for injection, with the use of an ATAS high-performance LVI system (33).

The PDMS-rod and PDMS-membrane samplers were conditioned at 250 $^{\circ}\text{C}$ for 1 h prior to use. Two internal standards were chosen for these PDMS-rod and PDMS-membrane samplers: deuterated fluoranthene and deuterated pyrene. The initial loading of the standards onto the PDMS-rod and PDMS-membrane was optimized and subsequently used for field sampling (28, 33, 34). The loading was conducted by placing the rod or membrane directly into the standard aqueous solution with agitation. A standard solution (25 ng/mL) was prepared by spiking 2.5 μL of 100

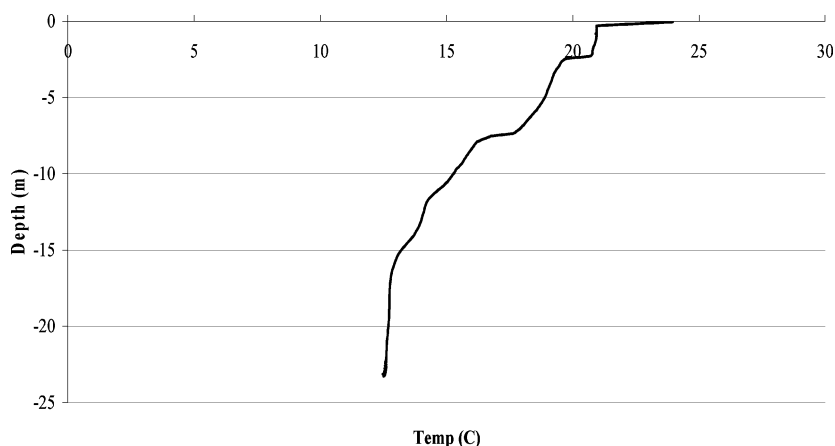


FIGURE 3. Temperature profile of different depths in Hamilton Harbor on June 19th, 2006.

TABLE 1. PAH Concentrations in Hamilton Harbor Obtained by Three Types of SPME Passive Samplers^a

depth	sampler	concentration (ng/L) (<i>n</i> = 3)					
		acenaphthene	fluorene	phenanthrene	anthracene	fluoranthene	pyrene
1 m	fiber-retracted	17.6 ± 2.3	21.7 ± 3.7	28.3 ± 4.0	3.7 ± 0.8	18.9 ± 0.4	22.9 ± 3.4
	PDMS-rod	NQ	NQ	NQ	NQ	17.7 ± 1.7	26.5 ± 3.8
	PDMS-membrane	NQ	NQ	NQ	NQ	14.4 ± 1.6	28.6 ± 2.6
11 m	fiber-retracted	15.2 ± 0.7	ND	ND	ND	7.8 ± 0.8	10.1 ± 0.5
	PDMS-rod	NQ	NQ	NQ	NQ	8.7 ± 2.5	8.4 ± 0.9
	PDMS-membrane	NQ	NQ	NQ	NQ	8.3 ± 1.4	10.1 ± 2.5
21 m	fiber-retracted	15.5 ± 2.9	19.2 ± 2.3	ND	ND	8.6 ± 0.8	9.9 ± 1.2
	PDMS-rod	NQ	NQ	NQ	NQ	6.8 ± 1.4	7.3 ± 1.4
	PDMS-membrane	NQ	NQ	NQ	NQ	5.4 ± 0.5	8.3 ± 1.8

^a ND is not detected; NQ is not quantitated.

μg/mL deuterated standard solution into a 10 mL (for rod) or 20 mL (for membrane) vial containing 10 mL of nanopure water. After mixing, each vial was added to either the PDMS-rod or the PDMS membrane, and the vials were then placed in the agitator of the autosampler for 45 min at 35 °C and 500 rpm. The amount of initial standard loaded onto the samplers was calculated by analyzing these samplers and quantified with the external calibration method.

Field Sampling. The SPME TWA field water samplers were tested in Hamilton Harbor, located on the western tip of Lake Ontario (Ontario, Canada). The sampling site was located in the middle of the harbor, which has been identified as one of the most polluted spots in the harbor, based on data from Environment Canada. Both deuterated fluoranthene and deuterated pyrene were loaded onto the PDMS-rod and PDMS-membrane samplers in the laboratory and maintained at low temperature (0 °C) during storage and transportation. All of the samplers were placed in copper cages to secure the devices and protect them from the sampling environment. The caging did not restrict the flow of analytes from the bulk water sample to the samplers.

The samplers were placed at three different depths at the sample location: 1 m below the surface, considered surface water, 11 m below the surface, considered middle water, and 21 m below the surface, considered bottom water. At each depth, plastic baskets containing the samplers were deployed onto stationed moors that were positioned and maintained by the Technical Operations Services group at Environment Canada. Three replicates of each sampler were deployed at each depth to study the reproducibility of the sampling device and to compare the results obtained by the different approaches.

Six PAH compounds were selected as the target analytes, including acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. The fiber-retracted SPME devices were deployed in June and retrieved in August (2 month sampling period). The minimum sampling time was estimated with eq 1, where *n* was 1 pg, the detection limit of the instrument, and *C* was the approximate concentration of the target analyte in the sample, which is based on the reference data. The SPME PDMS-rod and PDMS-membrane samplers were also deployed in June, but retrieved after 1 month and replaced with new samplers (too long sampling time will cause all of the preloaded standards to be lost). The new samplers were retrieved in August.

After the sampling period was completed, the samplers were removed from the sampling site. The fiber-retracted devices were sealed with the caps. The PDMS-rod and PDMS-membrane samplers were placed in silane-treated glass vials, sealed, and kept cool until analysis. All of the samplers were transported to the laboratory at the University of Waterloo for analysis.

The SPME fibers were gently dried with a lint-free tissue and then the SPME fiber holder was used to introduce the

fibers into the GC injector port for desorption, separation and quantification. The PDMS-rods and PDMS-membranes were gently rinsed with nanopure water to remove the very thin layer of excess silt and then analyzed by GC/MS with the ATAS system.

Results and Discussion

Field Sampling in Hamilton Harbor. For the fiber-retracted devices, the TWA concentrations of the target analytes in the sampling environment were calculated with eq 1. The diffusion coefficients of the target analytes in water, *D*, were calculated with the following empirical equation (35).

$$D_w = \frac{1.326 \times 10^{-4}}{\eta_w^{1.14} \bar{V}^{0.589}} \quad (4)$$

where η_w is the kinematic viscosity of water at the temperature of interest and \bar{V} is the molar volume of the analyte. The average temperatures at the three different depths were used as the approximate temperature for sampling. Figure 3 illustrates the temperature profile of different depths in Hamilton Harbor on June 19. For the SPME PDMS-rod and PDMS-membrane samplers, the TWA concentrations of the target analytes in the sampling environment were calculated with eq 2.

Table 1 presents the TWA concentrations of target analytes at the sampling sites, as determined by the three types of SPME passive samplers. The results illustrate that the concentrations of PAHs were in the low ng/L levels and were a little higher in the surface water compared with the other sampling depths. This may be due to the source of the pollution typically discharged at surface depths.

The data in Table 1 are the average values of PAHs as detected by the three samplers. The RSD values were generally less than 20%. For the PDMS-rod and PDMS-membrane samplers, only fluoranthene and pyrene were quantified since only *d*₁₀-fluoranthene and *d*₁₀-pyrene were loaded as the internal standards. The results in Table 1 illustrate that the concentrations of fluoranthene and pyrene at different depths obtained by three types SPME passive samplers were quite close. The results obtained by the SPME fiber-retracted devices and the PDMS-rod and PDMS-membrane samplers are in the range of the data obtained by spot sampling with traditional liquid–liquid extractions, as reported by C. Marvin of the Water Science and Technology Directorate at Environment Canada. The concentrations of fluoranthene and pyrene in the water from the Hamilton Harbor are in the range of 2–152 ng/L and 1–141 ng/L, respectively (36).

Effect of Turbulence. One problem that is commonly encountered during field sampling is the effect of turbulence on the sampling environment. For field water sampling, the flow rate of surface water sites should be higher than the deeper water sites, since the surface can be easily affected

TABLE 2. Levels of the Extracted Analytes and the Remaining Standards on the PDMS-Rod and PDMS-Membrane Samplers at Three Different Depths in Hamilton Harbor after a Month Sampling Period ($n = 3$)

sampler	depth (m)	mass (ng)			
		fluoranthene	d ₁₀ -fluoranthene ^a	pyrene	d ₁₀ -pyrene ^a
PDMS-rod	1	3.8 ± 0.2	3.1 ± 0.3	4.8 ± 0.3	2.4 ± 0.2
	11	0.6 ± 0.2	37.6 ± 9.6	1.1 ± 0.2	45.5 ± 7.7
	21	0.5 ± 0.1	85.7 ± 3.2	0.6 ± 0.1	77.1 ± 4.3
PDMS-membrane	1	36.7 ± 7.1	3.3 ± 0.3	68.8 ± 8.2	2.9 ± 0.2
	11	5.0 ± 1.5	90.4 ± 12	8.8 ± 0.7	32.9 ± 2.1
	21	3.2 ± 0.2	110.6 ± 1.5	7.3 ± 0.3	52.8 ± 1.6

^a The amounts of preloaded standards are about 168 ng for fluoranthene and 176 ng for pyrene. The RSDs are less than 7%.

by the wind and moving boat traffic. Table 2 presents the amounts of the extracted analytes and the remaining standards on the PDMS-rod and PDMS-membrane samplers at different depths in Hamilton Harbor after a 1-month sampling period. The results indicate that the higher flow rate of the surface water contributed to the higher rate of loss of the preloaded standard. Conversely, the amounts of the target analytes extracted on the PDMS-rod and PDMS-membrane samplers at the surface water were greater than the amounts extracted at other depths. These observations confirm that the kinetic calibration method can effectively compensate for the turbulence factor that can be encountered in field sampling.

For the fiber-retracted SPME device, it has been proven that the mass uptake is independent of the face velocity, due to the extremely small inner diameter of the fiber needle (21). In this field trial, the concentrations of fluoranthene and pyrene at different depths were quite close to the results obtained by the PDMS-rod and PDMS-membrane samplers, which demonstrated that the flow rate of the sampling environment did not affect the mass uptake of the fiber-retracted SPME field water sampler.

For all three types of SPME passive samplers, the effect of the turbulence was avoided or effectively compensated for with a preloaded standard. This feature is desirable for long-term field water sampling, especially where the convection conditions of the sample environment are difficult to measure and calibrate.

Comparison of Three Types of SPME Passive Samplers.

The cost of the field sampler is a very important factor for application. A sampler that is manufactured of PDMS-membrane or PDMS-rod is inexpensive. Conversely, the cost of the fiber-retracted device is higher but the sampler can be reused.

The data in Table 1 illustrate the difference in quantification for the three types of SPME passive samplers. For the fiber-retracted SPME device, all of the analytes were quantified and no internal standard was required. Conversely, the SPME PDMS-rod and PDMS-membrane passive samplers can only quantify analytes with a corresponding internal standard. This is due to the fact that the kinetic calibration method can only calibrate analytes with similar physicochemical properties to the preloaded standard.

With different sampling approaches and different surface-to-volume ratio, the sampling rate of three SPME passive samplers were different. Figure 4 illustrates the sampling rates of three types SPME passive samplers at different sampling depths ($R = n/Ct$, where R is the sampling rate, n is the extracted amount of analyte, C is the TWA concentration of analyte in the sample, and t is the sampling time). The PDMS-membrane sampler exhibited the highest sampling rate, due to the large surface-to-volume ratio. The sampling rate of the fiber-retracted SPME device was much lower than the PDMS-rod and PDMS-membrane samplers, because the extraction phase did not contact the sample matrix directly

and the diffusion of the analyte molecules was very slowly in water. This illustrates that the sensitivity of this type sampler is lower than that of the PDMS-rod and PDMS-membrane samplers. The sampling rates of the PDMS-rod and PDMS-membrane samplers at the surface sampling depth were obviously higher than other depths because the flow rate of the surface water was higher than the deeper waters.

The three types of SPME passive samplers that were used in this field trial possess all of the advantages of SPME: they are solvent-free, combine sampling isolation and enrichment into one step, and can be directly injected into a gas chromatograph (GC) for analysis without further treatment. The three types of SPME passive samplers were easy to deploy and retrieve.

Among these samplers, the PDMS-rod and PDMS-membrane samplers were quite simple, exhibited high sampling rates, and the sensitivity was much higher than that achieved with the fiber-retracted device or other reported samplers since the samplers contact with sample matrix directly. However, the sampling time for these devices is limited because the deployed samplers must be retrieved before all of the preloaded standards are lost. Normally, the sampler should be retrieved in 1 month or less, although the exact time is determined by the flow velocity of the sample matrix.

The structure of the fiber-retracted device is more complex, but the procedures for preparation, deployment, retrieval, and transportation are very simple. It is more suitable for long-term water sampling (months versus weeks) since this type of sampler does not require an internal standard for calibration. The PDMS-membrane possesses the highest surface-to-volume ratio and the largest volume, which results in the highest sensitivity and mass uptake of the devices tested. However, this sampler requires a large volume injector for analysis, while the PDMS-rod and the SPME fiber can be analyzed by a GC/MS with a normal injector.

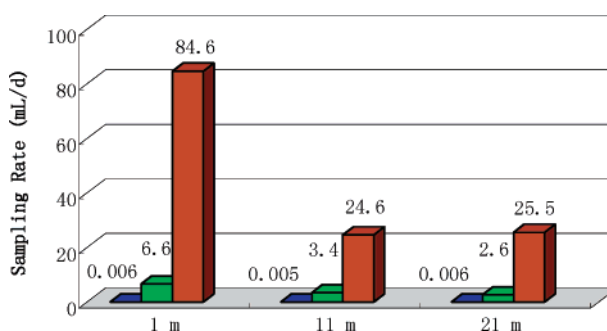


FIGURE 4. Sampling rates of three types of SPME passive samplers at different sampling depths. Blue, fiber-retracted device; green, PDMS-rod; red, PDMS-membrane.

Acknowledgments

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