Field Sampling with a Polydimethylsiloxane Thin-Film

Leslie Bragg[1], Zhipei Qin[1], Mehran Alaee[2], and **Janusz Pawliszyn[1,*]**

[1]Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 and [2]Water Science and Technology Directorate, Environment Canada, Burlington, Ontario, L7R 4A6, Canada

Abstract

In this research, field samplers are developed using polydimethylsiloxane (PDMS) thin-film as the extraction phase. This technique is based on a similar theory, the solid-phase microextraction (SPME) technique. More specifically, the development of the field sampler involves cutting a section of PDMS thin-film into a specific size and shape, and mounting it onto a stainless steel wire (the handle). The thin-film is then placed into a protective copper cage prior to deployment to prevent biofouling. Kinetic calibration or equilibrium calibration with the standards in the extraction phase is used to introduce an isotopically labeled internal standard for on-site calibration. The initial loading of the standard onto the thin-film and the amount of standard remaining on the thin-film are determined using gas chromatography–mass spectrometry and subsequently used to estimate the concentration of the target analytes. In addition, the field samplers are deployed in the field at two locations (the Meuse River in Eijsden, The Netherlands from April to May, 2005 and Hamilton Harbour located at the western tip of Lake Ontario, ON, Canada from September to December, 2006). Polycyclic aromatic hydrocarbons are identified, and concentrations of fluoranthene and pyrene are estimated in the low ng/L range. The results from both sampling sites are within the expected ranges for environmental samples. This polymeric extraction phase has a high surface-to-volume ratio compared with SPME, which results in higher sensitivity and mass uptake, leading to the detection of lower levels of analytes that many other techniques are unable to achieve.

Introduction

Passive sampling is often used to detect analytes in aqueous environments. This technique utilizes the free flow of analytes from the sample into the receiving phase based on differences in the chemical potential between the two phases. There are two types of passive samplers: equilibrium-passive and kinetic-passive samplers. For equilibrium-passive samplers, the flow of analytes continues until equilibrium, and for kinetic-passive samplers, the samplers are removed from the system prior to equilibrium (1).

For passive samplers, one device can be used over a long time period to determine a time-weighted average (TWA) concentration. There are several types of passive samplers (2,3) currently available for water analyses such semipermeable membrane devices (SPMDs) (4–7), passive in-situ concentration/extraction samplers (8), supported liquid membrane techniques (9), and sorbent-filled devices (10).

There are many advantages to using passive sampling in the field. These devices usually have a relatively simple construction and are easy to use. Because only a few samplers are required in a particular area, the analytical costs are very low, making these devices a cost-effective solution for field monitoring (3). Passive samplers are also less sensitive to extreme variations in the concentration of pollutants in natural water samples (2,3). This type of sampling provides a long-term picture of the environmental conditions, rather than a snapshot at one particular time.

Ideally, passive samplers should be both inexpensive to manufacture and inexpensive to analyze. Often, deployment and removal of samplers is not conducted by scientifically trained personnel, so sampling devices must be designed for easy deployment, and they must also be small enough to be easily transported to the laboratory for further analyses (3).

Calibration for many passive samplers is performed in the laboratory at known exposure concentrations. Extensive calibration studies are used to characterize the uptake of contaminants for different exposure conditions so that a TWA concentration of the chemicals can be determined. The uptake depends upon the physico-chemical properties of the diffusand, sampler design, and environmental variables, such as water turbulence, temperature, and biofouling (1). Passive samplers use information about sampling rates, exposure time, and the amount of analyte trapped in a receiving phase to determine the analyte concentration (1).

SPMDs can use performance reference compounds (PRC) as internal standards to monitor biofouling effects on the sampler (11) or to calculate the sampling rate to estimate the concentration of analyte using the release rate of PRC (12) though the results exhibit poor precision and accuracy probably because of the complexity of SPMD procedures. Also, some work has been done on sampling rates using exposure adjustment factors determined by laboratory studies (6).

A more simplified diffusion-based calibration approach has been used for solid-phase microextraction (SPME) passive sam-

* Author to whom correspondence should be addressed: email janusz@uwaterloo.ca.

plers (13–15). Similar to calibration for passive samplers, the flow of analytes from the sample to the inside of the sampler is completely free and differences in chemical potential are the driving force of the movement of analytes. Determining the concentration of an analyte in a sample is based on an empirical formula rather than extensive laboratory studies on possible environmental conditions. Another method for calibration used involves the use of an internal standard. A kinetic calibration method was developed for SPME to introduce an internal standard for on-site calibration (16–18). The standards are first loaded onto the extraction phase and the amount desorbed from the extraction phase can be used to calibrate the extraction. The extraction phase, loaded with isotopically labeled standards, is placed into a sampling system, removed after a period of time, and the amount of standard remaining is used for calibration. Combining the simplified SPME equation for sampling in a large volume system, $n_e = K_{es}V_eC_0$ (15), with the equations for isotropy of adsorption and desorption, $n/n_e + Q/q_e = 1$ (16), one simplified equation can be used to calculate the concentration (C_0) of the target analyte in the system (16,17):

$$C_0 = \frac{q_0 n}{K_{es}V_e\,(q_0 - Q)} \qquad \text{Eq. 1}$$

where q_0 is the amount of standard loaded onto the thin-film, Q is amount of standard remaining on the extracting phase after sampling, n is the amount of analyte in the extraction phase, K_{es} is the partition coefficient between the extraction phase and the water sample, and V_e is the volume of the extraction phase. This method has been used for the SPME extraction of benzene, toluene, ethylbenzene, and xylenes (BTEX) in wine (16,17) and the headspace (HS)–liquid-phase microextraction (LPME) of BTEX in aqueous samples (19).

The application of SPME fibers as passive samplers can be further extended to include the use of a PDMS membrane or thin-film as the extraction phase. These thin-films have higher extraction capacities, and the large surface area-to-extraction phase volume ratio of the thin-film impacts the extraction rate (20). They can extract a larger amount of analyte within a shorter period of time when compared with PDMS fibers. This results in higher extraction efficiencies and higher sensitivities without sacrificing analysis time (20). Unlike SPMDs or other passive samplers, thin-films do not require a receiving phase to trap or retain the analytes. The analytes are trapped in the PDMS thin-film rather than a solvent or other adsorbent. This significantly reduces the sample cleanup time and solvent usage.

In this study, the principles of kinetic calibration in the extraction phase initially developed for SPME were used for extractions with a PDMS thin-film. The method was partially automated with the use of a total analytical system (ATAS) direct thermal desorption (DTD) large volume injector (LVI) with a pneumatic liner exchange by a CTC CombiPal autosampler (Leap Technologies, Carrboro, NC). PAHs were selected as the target analytes because of their widespread presence in the environment and their known affinity to PDMS. Field analyses from several sites were successfully completed using this type of thin-film extraction.

Experimental

Chemicals and materials

Naphthalene, acenaphthene, fluorene, anthracene, fluoranthene, and pyrene were purchased from Sigma-Aldrich (Mississauga, ON, Canada). Deuterated PAHs, fluoranthene-d_{10} and pyrene-d_{10}, were also purchased from Sigma-Aldrich (Mississauga, ON, Canada). Helium (99.999%), nitrogen (99.999%), liquid nitrogen, and compressed air that were used for the analytical instruments were obtained from Praxair (Waterloo, ON, Canada). Water used in these experiments was Nano-pure water from a Barnstead water system (Dubuque, IA). The PDMS thin-film, with a thickness of 127 µm, was purchased from Specialty Silicone Products Inc (Ballston Spa, NY). Copper wire mesh was purchased from Goodfellow (Devon, PA).

Thin-film samplers

There were several challenges encountered during the development of a field sampler using PDMS thin-films. For example, the intended field application of this device, during which time the device would be placed in a body of water for a long period of time, necessitated the design of a robust sampler that was not prone to clogging by algae or sediment. Thus, the number of parts in the system were kept to a minimum, both for ease of deployment and to minimize the risk of breakage. Copper caging was also used to prevent algal buildup on the device during field sampling (1). PDMS thin-films are used for the extraction of analytes from water samples.

The samplers were made using a 127-µm thick PDMS thin-film for the extraction phase. The thin-film was cut into a spe-

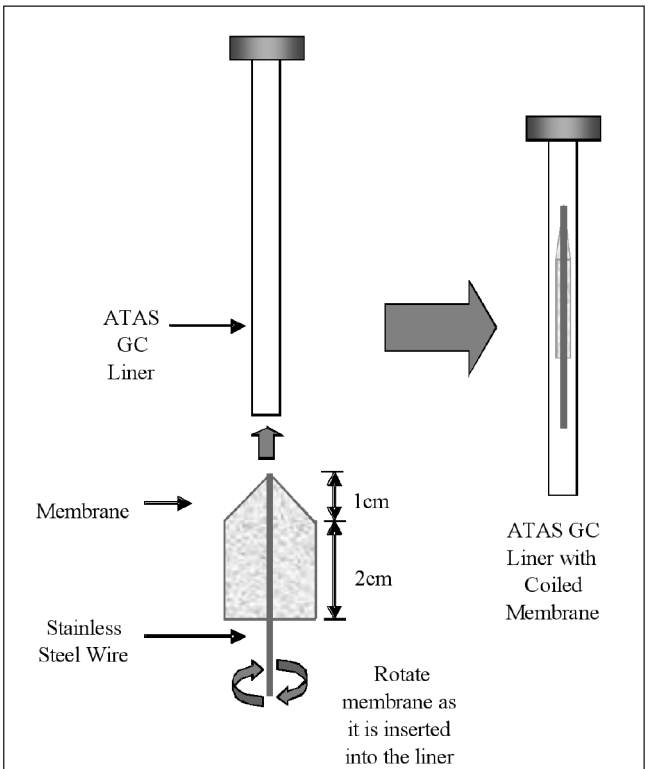

Figure 1. PDMS thin-film design and insertion into the ATAS GC liners for analysis.

cific house-like shape (Figure 1) using a special cutter, which was manufactured in-house by the University of Waterloo Machine Shop (Waterloo, ON, Canada). The dimension of the thin-films was 2 × 2 cm with a 1-cm high triangle on the top of the square. The surface area for one side was 5 cm^2, and the total volume of each thin-film was 0.0635 cm^3. These dimensions were optimized for ease of analysis so that the device could be coiled and fit inside a gas chromatography (GC) liner for injection, with the use of an ATAS high-performance LVI system in the GC–mass spectrometer (MS) (see Figure 1). A piece of stainless steel wire, shaped like the eye of a needle, was used to hold the thin-film for easier movement. The thin-films were conditioned before use with a 2-h bake out period in the GC injector port at 250°C, with a helium flow rate of 1 mL/min.

For deployment in the field, the thin-films were then placed in small copper cages to help secure and protect them. This caging did not restrict the flow of analytes from the bulk water sample into the thin-film. A wire handle was placed on each cage for ease of deployment. Samplers were placed into plastic baskets and the handles of the copper cages were secured onto the top of the baskets. Several replicates of the samplers could be placed inside the same basket.

During storage and transportation, the samplers were kept at low temperatures to minimize the amount of analyte or standard lost. After the samplers were removed from the sampling sites, they were placed in glass vials, sealed, and kept cool until analysis. The losses of analytes from the thin-films throughout this time period were minimal.

Instrumentation

The thin-films were analyzed using an Agilent 6890 GC and 5973 MSD equipped with an ATAS Optic 3 DTD LVI 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 Varian (Chrompack) CP Sil 8 CB column (5% diphenyl–95% PDMS, 30 m × 0.25-mm i.d. × 0.25 µm film thickness) was used with helium as the carrier gas at a flow rate of 1 mL/min. The GC oven temperature started at 40°C, where it was held constant for 13 min. Because the ATAS system was also equipped with a cryotrap to focus the analytes, the temperature of the cryotrap was 0°C for the first 10 min and then increased to 280°C for the duration of the run. Meanwhile, the GC temperature increased at a rate of 15°C/min to 250°C and held constant for 3 min. The total GC run time was 30 min.

For the analysis of the PDMS thin-films, the thin-films were coiled and rotated for insertion into the GC liners (see Figure 1). These liners were purchased specifically from ATAS for this purpose. The top was sealed using a crimped cap, and the bottom was open to the GC column. The liners were held on a cooled DTD tray until analysis. During analysis, the thin-films remained in the GC inlet at 280°C for the entire GC runtime. A splitless flow was held for the first 10 mins of the GC run, then increased to 50 mL/min for the remainder of the GC runtime.

Initial loading of the standard onto the thin-film

There were two internal standards chosen for these experiments: deuterated fluoranthene and deuterated pyrene. It was determined that both of these native PAHs may be present in the field water samples. The initial loading of the standards onto the thin-film was optimized and subsequently used for field sampling. The method was optimized to ensure that the deuterated standards were at equilibrium with the thin-film so that the amount of standard loaded onto the thin-film could be quantitatively measured. Also, the amount of standard loaded onto the thin-film had to be sufficient enough for some to remain after the sampling period was over. The optimized method involved placing 2.5 µL of a 100 mg/L deuterated standard solution into a 20-mL vial containing 10 mL of nano-pure water. After mixing, one thin-film was added to each individual vial. These vials were then placed in the agitator of the autosampler for 45 min at 35°C and 500 rpm. The amount of initial loading was calculated by analyzing these thin-films and using external calibration.

Field sampling

Three replicates of thin-films were cut, conditioned, and prepared for deployment at the sampling sites. The thin-films were placed into sealed copper cages and, for transportation, were placed in sealed glass jars. The samplers were then deployed at the sampling sites for a set period of time (approximately one month).

The only PAHs that were quantitated in the field samplers were fluoranthene and pyrene. These were the only contaminants for which deuterated standards were available. The presence of other PAHs, like naphthalene, fluorene, phenanthrene, and anthracene, was also detected, but their concentrations were not quantitatively determined. For different compounds, there are differences between their physico-chemical properties, but when the differences between the standard and analytes are small (e.g., fluoranthene and pyrene) then the standards can be used to calibrate the analytes directly, but these differences are within the experimental error. When the differences are larger than the ratio between the corresponding diffusion coefficients, a correction factor can be used.

The Meuse River

The Meuse River was heavily polluted with various inorganic and organic substances in the 1960s and 1970s (21). The major contamination sources are agricultural activities and urban pollution (22). Heavy metals and organic pollutants such as PAHs, polychlorinated biphenyls, and chlorinated pesticides have accumulated in high concentrations in the water. Many countries are working together to cleanup this drinking water source (23,24).

The thin-film samplers were first used in the Meuse River in Eijsden, the Netherlands, where the river first enters the country. Samplers were deployed from the side deck of a barge for a time period of 28 days. After the sampling was completed, the samplers were placed in sealed bottles and transported, via airmail, to the laboratory at the University of Waterloo for analysis.

Hamilton Harbour

Sampling in Hamilton Harbour in Lake Ontario, located on

the western tip of Lake Ontario, ON, Canada occurred in one-month intervals over a period of three months. Two sampling sites were chosen in the harbour. Site 1 was in Windermere Arm in the south eastern corner of the harbour. Site 2 was located in the middle of the harbour in a location known as the Deep Hole. Hamilton Harbour has been identified as one of forty-three "Areas of Concern" in the Great Lakes Water Quality Agreement between Canada and the United States (25). There are several steel factories along Hamilton Harbour, which contribute to the high levels of pollutants in the harbour (PAHs, in particular).

At each site, plastic baskets containing the samplers were deployed onto stationed moors that were placed and maintained by the Technical Operations Services group at Environment Canada. The baskets were placed at three different depths: surface water, middle-depth water, and deep water. At site 1, the depths were 1, 11.5, and 21 m (which is approximately 1 m above the bottom of the lake). At site 2, the depths were 2.5 (because of convenience of placing the samplers on existing lines), 11.5, and 22.5 m (approximately 1 m above the bottom of the lake). Three samplers were placed at each depth in both sites.

Sample cleanup and analysis

Once transported to the laboratory (at the University of Waterloo), the thin-films were removed from the copper cages and rinsed with nano-pure water to remove the very thin layer of excess silt, which was attached to the thin-films. The thin-films were then placed into the GC liners, as shown in Figure 1, and analyzed to determine the amount of PAHs in the samples. The thin-films were analyzed a second time to determine the residual PAH remaining on the thin-film after analysis. Blank analyses were also conducted between each sample. Both the carryover analysis and the blanks illustrated much smaller (< 5%) levels of PAHs than the thin-film samples. The carryover was evaluated, and it was found to be negligible.

External calibration curves were completed for six standard PAHs using liquid injection into the large volume injector system, both before and after each set of samplers was analyzed, to determine the amount of PAHs collected on the thin-films. The linearity of the calibration curves was good (R^2 > 0.99), and the RSDs were acceptable (< 5%) for most of the PAHs, excluding naphthalene, which had a higher RSD, possibly because of its higher volatility.

Calibration curves for the standard PAHs and the two deuterated standards were completed in triplicate using liquid injection of 1 µL of each of the concentrations used. There were four concentrations of PAHs analyzed (500 µg/L, 1 mg/L, 5 mg/L, and 10 mg/L), and 1 µL of standard was injected into the GC–MS. The analytes from the field samplers were expected to be in this approximate range. Calibration curves using the standards for the six target PAHs were completed after every group of samplers was analyzed. From the calibration curve data, the initial loading, and the sample analyses (both the deuterated standards and the PAH peaks), the amount of each analyte in the water samples could be determined by Equation 1.

Results and Discussion

Loading and response

The initial loading of the standards onto the extraction phase was completed with a vial that contained the deuterated standard solution. The amount of standard loaded onto the thin-film was determined using a GC–MS with external calibration. It was determined that the standards had reached equilibrium with the thin-film after 45 min so this was the extraction time used for the deuterated standards.

The thin-films were cut precisely with a special cutter, which makes the size reproducibility of the thin-films constant. The advantage of using this type of calibration technique is that the standard that is loaded on the extraction phase will account for size differences between the thin-films because the concentration of the analytes calculated is based on the ratio between the initial loading and the amount remaining on the thin-film after sampling, rather than the initial amount of the standard loaded. Therefore, the initial loading of standards onto the thin-film is similar between the different thin-films. This technique is also particularly useful for field sampling because the standard can also compensate for differences in flow rates or turbulence at the sampling sites.

Thin-film performance in a flow-through system

A standard flow-through system has been developed that employs the use of DispoDialyzers (Spectrum Laboratories, Rancho Dominguez, CA) for the permeation of PAHs into a flowing water system (26). This flow-through system has been described extensively by Ouyang et al. (26) and used with passive TWA SPME-based samplers (27,28). The concentration of PAHs in the system is known to remain constant throughout the sampling period. This same system was used with the PDMS thin-films. Only pyrene was used as a deuterated standard in these experiments. Three thin-films were first loaded with pyrene-d_{10} using an aqueous solution with a concentration of 10 ng/mL and 45 min exposure time of the thin-film to the standard solution. They were then exposed in the flow-through system for periods of 2, 4, 6, and 14 h. After removal and analysis, the amount of PAHs on the thin-films was determined. The concentrations of pyrene-d_{10}, as detected by the thin-film extraction approach for three replicates, were then compared with the concentrations determined by SPME spot sampling, and the results were similar, as shown in Table I.

The SPME method consisted of direct extraction of analytes from a 10-mL vial containing a 10-mL sample of water withdrawn from the flow-though system. It was completed with

Table I. Concentration of Pyrene Determined from the Flow-Through System Using Thin-Film Extraction Over Different Time Periods as Compared with the Results Obtained by Traditional SPME Spot Sampling

	Concentration (ng/L)				
Analyte	2 h	4 h	6 h	14 h	SPME
Pyrene	10.2	11.1	11.1	16.3	15.8

three replicates using a 100-µm PDMS fiber. Equilibrium was reached for these PAHs with SPME within 30 min. The desorption time of the fiber in the GC injector was 10 min, which corresponds to the cryogenic trapping time of the GC method, though it was possible to use a shorter desorption time. RSDs for the thin-film extraction were less than 15%, and the RSDs for the SPME extractions were < 5%. The RSD is slightly higher for the thin-films because three separate thin-films were used for the analyses rather than one single thin-film.

Field sampling results

Two locations were used for field sampling with the PDMS thin-film samplers. Generally, the time period of the sampling was one month. Deuterated standards were loaded onto the thin-films prior to sampling so that the concentration could be calculated using the empirical formula (equation 1). In some cases, the value of n/n_e was greater than 0.95, which shows that the samplers had reached equilibrium by the end of the sampling period. As a result, equation 1 is reduced to the simplified SPME equation for equilibrium conditions:

$$n_e = K_{es}V_eC_o \qquad \text{Eq. 2}$$

However, the results from these two equations are the same. The values obtained were very close to the TWA concentrations because the equilibrium time is almost one month. There were no dramatic shifts in concentration as would be expected if large variations in concentration occur after equilibrium has been reached.

The Meuse River results

The samplers that were placed in the Meuse River were part of a study by the Screening Method for Water Data Information in support of the implementation of the Water Framework Directive (SWIFT-WFD). The SWIFT-WFD objectives include improving, protecting, and preventing further deterioration of water quality across Europe. SWIFT-WFD is a multi-disciplinary project with many different types of spot, continuous, and passive samplers. The results of the larger study illustrated that PAH concentrations are typically within the low to sub ng/L range in the Meuse River, which inhibits detection by most conventional passive samplers (29).

The samplers from the Meuse River were found to be at equilibrium over the time period of the study, thus the equilibrium equations were used to calculate the concentration of analytes collected by all of the samplers at the field site. The three samplers from the Netherlands had slightly different concentrations of target analytes on the thin-films. In the river water samples, the amount of the PAHs was found to be in the sub ng/L range. For fluoranthene, the concentration range was from 0.154–0.346 ng/L, and for pyrene, the concentration range was between 0.165–0.482 ng/L. These results were within the expected concentration range of the study.

Hamilton Harbour results

The concentrations of contaminants in the field samplers in Hamilton were determined over one-month intervals throughout a three-month period at two sampling sites and at three different depths at each site. The results in Table II illustrate that the concentrations of fluoranthene and pyrene were in the low ng/L levels at all of the sampling locations. Generally, the PAH concentrations were higher in the surface water compared with the deeper water depths. This may be because of constant sources of pollution that are fed into the lake water. Also, the thin-film samplers in the surface water were found to have reached equilibrium before the sampling period was completed, but the samplers at the other two depths had not yet reached equilibrium. This may be because of the higher turbulence in the surface water compared with the deeper water, which helps the samplers reach equilibrium faster. The surface water samplers, therefore, used the equilibrium equations rather than the kinetic calibration equations.

The PAH concentrations at the second sampling site were found to be slightly lower than those at the first site at the lower sampling depths, likely because the second sampling site was in the middle of the lake, farther from the steel factory effluents. However, higher concentrations of PAH were detected in the shallow sampling depths at both sampling sites.

The data from both sample sites in the Hamilton Harbour were comparable to the results obtained by traditional liquid–liquid extractions completed by C. Marvin of the Water Science and Technology Directorate at Environment Canada (30). The PAHs were measured in the water and sediment from the harbour and the total concentration of fluoranthene is in the range of 2–152 ng/L and between 1–141 ng/L for pyrene (30). PAH levels are usually higher in the sediment than in the water, so our data was expected to be in the lower range of these concentrations.

The data in Table II are based on the average of three samplers at each sampling site and depth. The RSD values for the samplers were generally less than 20%. There were a few exceptions, such as when the PAH concentration was very low, which resulted in RSDs over 40%. Also, for the samplers at the 2.5 m depth for September site 2, there was only 1 sampler analyzed for that point because the other two had been lost from the sampling basket during sampling because of broken wire in the sampling basket.

Table II. Concentration of PAHs Found in Two Sampling Site in Hamilton Harbour, Burlington, ON, Canada

		Concentration (ng/L)					
		Site 1			Site 2		
Analyte	Date	1 m	11.5 m	21 m	2.5 m	11.5 m	22.5 m
Fluoranthene	Sept	7.2 ± 1.4	8.5 ± 0.4	2.4 ± 1.0	2.5	2.7 ± 1.3	2.4 ± 2.0
	Oct	15.0 ± 2.4	8.7 ± 2.6	2.3 ± 0.4	20.5 ± 3.9	3.2 ± 0.9	2.6 ± 0.2
	Nov	9.6 ± 2.3	2.1 ± 0.2	2.1 ± 0.2	8.4 ± 0.7	7.9 ± 0.1	6.5 ± 0.6
Pyrene	Sept	11.9 ± 8	10.8 ± 1.4	4.9 ± 1.5	1.8	4.4 ± 2.1	6.2 ± 1.9
	Oct	16.6 ± 2.4	10.3 ± 3.1	3.8 ± 0.2	38.4 ± 4.5	3.7 ± 0.3	3.7 ± 1.1
	Nov	10.4 ± 1.5	2.9 ± 0.3	2.6 ± 0.5	22.0 ± 1.4	19.4 ± 0.1	12.7 ± 0.2

Conclusion

There are several advantages to using thin-film samplers for field analysis. The samplers and thin-films are durable and easy to deploy. The thin-films have a large capacity and high surface area for extraction. This enables these samplers to extract analytes in the low to sub ng/L levels in the field. Also, this technique is advantageous because it does not require measuring the uptake of pollutants into the extraction phase like other passive sampling techniques, which makes this simpler and more practical for measuring contaminant levels in water. In this method, Q/q_o is measured rather than uptake rates to determine the concentration of analytes in the sample, so extensive laboratory preparation was not needed. One small disadvantage of this technique is the lack of integration of sample preparation and sample introduction. The thin-films must be manually rolled and placed into the GC liner. However, this approach does not necessitate additional sample cleanup or preparation, as the entire sample is desorbed into the GC injector like SPME devices.

Field sampling has been successfully completed with these thin-films at two different sites that exhibit low PAH concentrations. The initial data are very encouraging. This method is a low-cost application of field sampling, and it produces results similar to traditional techniques that require extensive preparation procedures and often involve higher costs. PDMS thin-films with a thicker coating may be used for TWA sampling because the thicker coating will reach equilibrium at a longer time period compared with the thinner coating. Future work should involve the application of this approach to other sample matrices like sediment.

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