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A novel enhanced diffusion sampler for collecting gaseous pollutants without air agitation

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ABSTRACT

A novel enhanced diffusion sampler for collecting gaseous phase polycyclic aromatic hydrocarbons (PAHs) without air agitation is proposed. The diffusion of target compounds into a sampling chamber is facilitated by continuously purging through a closed-loop flow to create a large concentration difference between the ambient air and the air in the sampling chamber. A glass-fiber filter-based prototype was developed. It was demonstrated that the device could collect gaseous PAHs at a much higher rate (1.6 ± 1.4 L/min) than regular passive samplers, while the ambient air is not agitated. The prototype was also tested in both the laboratory and field for characterizing the concentration gradients over a short distance from the soil surface. The sampler has potential to be applied in other similar situations to characterize the concentration profiles of other chemicals.

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KEYWORDS

Sampler; PAHs; air-to-surface exchange

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants that originate from incomplete combustion and can cause adverse health effects including lung cancer.^[1] After emitted into the environment, PAHs move within and between various environmental media. Among these movements, air-to-soil exchange is one of the most important processes, governing the multimedia fate of PAHs.^[2] This is also true for many other semi-volatile organic pollutants of concern.^[3,4]

Pollutants in the air can be sampled either actively or passively. The former is fast and readily quantified, while the latter requires no power and causes no air agitation. Although both techniques are extensively used, they cannot be directly applied to characterize the air-to-soil exchange process of PAHs. In fact, such exchange is often quantified using multimedia fugacity modeling without direct observation-based validation.^[5]

To quantify the air-to-surface exchange flux of CO₂, CH₄, mercury, and other compounds, there are several well-developed methods including dynamic flux chambers and micrometeorological approaches.^[6,7] Since on-line measurements are required, these methods cannot be applied to quantify PAHs or other similar organic pollutants. For these chemicals, observations of vertical gradients can help to calculate the air-to-surface flux. Among the efforts made to measure the gradients of these chemicals, a disc-shaped sampler was developed to sample pesticides that were re-emitted from the soil.^[8] In another study, three active samplers were deployed at different heights to quantify the concentration differences of pesticides and

identify the direction of air-to-soil exchange.^[9] Since air mass is strongly disturbed by active sampling, the vertical concentration profile, which occurs over only a few centimeters above soil surface,^[10] can easily be disturbed. Another attempt utilized an array of passive samplers to quantify the vertical concentration profiles of PAHs over soil surfaces.^[10] However, the sampling rate was so slow that the process took months.

To sample the air near the soil surface without agitation, a novel enhanced diffusion sampler was proposed. The basic design is a sampling chamber separated from the ambient air by a micropore filter, which allows the diffusion of PAHs into the chamber while preventing air penetration. The chamber is connected to sampling media and a pump in a closed-loop. The PAHs in the chamber are continuously purged and trapped on the sampling media to generate a large concentration difference between the chamber and the ambient air so that the diffusion can be accelerated. In the meantime, equal air pressures inside and outside of the chamber prevent air penetration. The samplers can be deployed close to the soil surface at various heights to characterize the vertical concentration profile associated with the air-to-soil exchange of PAHs and other similar chemicals without agitating the air.

Materials and methods

Prototype

The concept was realized by a prototype using a glass-fiber filter (Fig. 1). The sampling chamber has a dimension of 220 mm ×

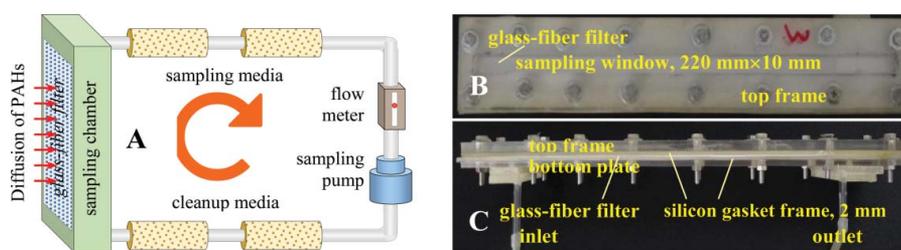


Figure 1. Design of the enhanced diffusion sampler. (A) Setup of the sampling system with the sampling chamber, sampling/cleanup media, pump, and flow meter with the arrow indicating the direction of the loop-flow; (B) Top-view of the sampler; and (C) Side-view of the sampler.

10 mm × 2 mm with a sampling window area of 2,200 mm². The sampling/cleanup media are polyurethane foam cartridges (PUF, 45 mm o.d. × 60 mm high, 0.03 g/cm³). Based on the result of a breakthrough test, two cartridges were used for either sampling or cleanup. The pumping flow rate is controlled by an adjustable pump and a flow meter.

Sample analysis and quality control

The PUFs were extracted to analyze the four representative PAH compounds with different molecular weights, which were acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), and pyrene (PYR). The procedure of extraction, cleanup, analysis, and quality control has been described in detail in the literature.^[11] In brief, Soxhlet extracts were purified using silica-alumina gel columns, and the eluates were analyzed using a gas chromatograph coupled with a mass spectrometer. Duplicate sampling and measurements, procedure and reagent blanks, internal standards, and surrogate monitoring were applied.

Performance test

General performance tests for the blank, breakthrough, sampling rate, and the influence of the sampler dimensions were conducted in the open air in the laboratory using paralleled samplers, which were operated for 60 min at a pumping flow rate of 4.1 L/min. The procedure blank was derived by conducting the sampling operation with the sampling window sealed by a plastic film. The procedure blank results were subtracted from the sampling measurements. The breakthrough of the sampling cartridge was defined as $Q_3/(Q_1+Q_2+Q_3)$, where Q_1 and Q_2 are the quantities of PAHs trapped in the first and the second cartridges (sampling media), respectively, and Q_3 is the quantity of leaked PAHs (two cleanup cartridges). By assuming Q_2/Q_1 equals Q_2/Q_3 and leakage from the third cartridge can be neglected, Q_3 was calculated as $Q_2^2/(Q_1^2 + Q_1Q_2 + Q_2^2)$. The sampling rate was defined as the volume of air containing the quantity of the target PAHs trapped in the sampling media per unit of time (L/min). The possible penetration of an air mass into the sampler chamber was tested by observing the trajectory of a plume from incense smoke over the surface of the filter of a vertically positioned sampler.

Laboratory and field tests

The samplers were tested in both the laboratory and the field to characterize the vertical concentration profiles of PAHs in the

air near the soil surface. For the laboratory test, a thoroughly mixed soil sample from a heavily contaminated site at the former Beijing Coking Company was held in an open box (50 mm × 320 mm × 130 mm). The concentrations of ACY, FLO, PHE, and PYR in the soil were 9.4, 13.9, 32.0, and 17.6 μg/g, respectively. The samplers were deployed 2, 5, 10, 20, 40, and 70 mm above the soil surface. For the field test, the site was located immediately next to a student canteen on the Peking University campus. The concentrations of ACY, FLO, PHE, and PYR of the soil were 0.13, 0.17, 1.6, and 2.5 μg/g, respectively. The samplers were set at 8, 12, 15, 20, 40, and 70 mm above the ground. In both cases, two sets of the samplers were installed side-by-side, and the sampling operation was conducted twice, generating a total of four replicates. Since no significant difference ($p = 0.05$) was found between the two sampling sets, the four values were treated as duplicates. For both laboratory and field tests, the pumping flow rate was 4.1 L/min, and the sampling process lasted for 20 min in the laboratory and 6 hours in the field.

Results and discussion

Influence on air movement

In principle, the resistance of the PUF cartridges to air flow cannot be totally avoided, which causes a drop in the air pressure from the outlet to the inlet. Still, if the resistance is smaller than that caused by the glass-fiber filter, the slight pressure drop will not necessarily lead to the leakage of the air mass across the filter. To test this theory, the trajectories of a plume passing over the surface immediately outside of the sampling window of a vertically positioned sampler were observed. As shown in (Fig. 2), for the original design with both the inlet and outlet orthogonally facing the filter (A), the incense plume moved straight up until it reached a segment facing the outlet, where the smoke was partially sucked towards the chamber. The problem was solved by shortening the length of the sampling window from 280 mm to 220 mm to keep the inlet and the outlet from orthogonally facing the filter. With such a modification, the smoke was no longer sucked towards the chamber (B), indicating no air mass movement towards the filter.

General performance

The effect of the chamber dimension on the sampling process was tested. According to the results, the width of the sampling chamber was reduced from 100 mm to 10 mm since the 100-mm filter trembled, which was likely due to the unsteady flow

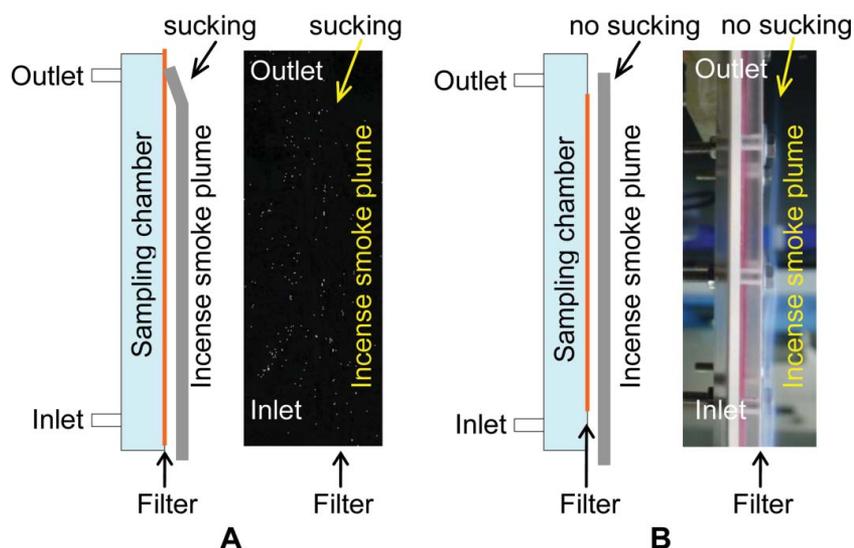


Figure 2. Observed trajectories of a plume passing over the surface of the filter outside the sampling window. (A) The design with the 280 mm window length where the tip of the plume was sucked towards the filter, and (B) the design with the 220 mm window length where the entire plume went straight up.

pattern and softness of the filter. Meanwhile, the thickness was also reduced from 80 mm to 2 mm. By reducing the cross-section area of the chamber, the flow velocity, which depends on the thickness of the stagnant film and consequently the pumping flow rate, increased. The effect of the flow velocity on the sampling rate can be interpreted by the single-film model theory, based on which the higher the flow velocity, the thinner the stagnant film, and the faster the chemicals diffuse through.^[12]

(Fig. 3) shows the result of the breakthrough test with four replicate runs. On average, the breakthrough for the two series-connected cartridges was approximately $2.1 \pm 1.1\%$. This result means that second sampling cartridges are needed, and the breakthrough would be $14 \pm 3.8\%$ without a second cartridge. Moreover, two cleanup cartridges are also needed to remove the PAHs that are leaked from the contamination of the pump, which cannot be cleaned in advance.

Sampling rate

To quantify the sampling rates, two samplers were deployed in the laboratory together with a low-volume active sampler to

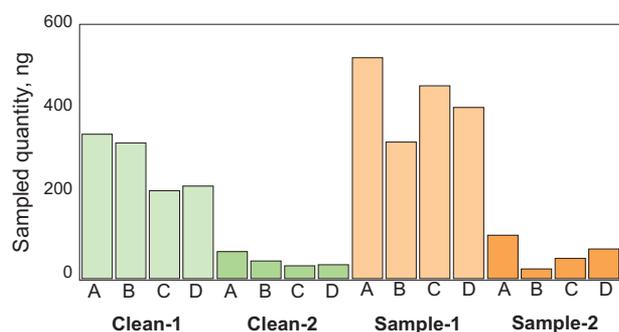


Figure 3. Quantities of PAHs trapped in the individual cleanup and sampling cartridges during the breakthrough test. Clean-1 and Clean-2 are the first and the second cartridges for cleanup, while Sample-1 and Sample-2 are the first and the second cartridges for sampling. There were four replicates for each step (from A to D).

simultaneously collect gaseous PAHs. The test was conducted three times for 60 min each time at pumping flow rates of 4.1 and 2.2 L/min for the diffusion and the active samplers, respectively. The sampling rates of the diffusion samplers were derived based on the quantities sampled by the diffusion sampler and the mean concentrations in the air determined by the active sampler. Based on the total quantities of the four PAHs sampled, the mean sampling rate was 1.6 ± 1.4 L/min, which is several orders of magnitude higher than those of conventional passive samplers using the same media. For example, the sampling rates of a set of conventional passive samplers for characterizing the vertical PAH concentration profiles in the air near the soil surface were from 0.008 ± 0.002 to 0.017 ± 0.006 L/min.^[10]

The sampling rate depends on many factors including flow velocity (a function of the pumping rate and the cross-section area of the chamber), sampling area, and temperature (correlated with molecular diffusion rate). Another important parameter is the molecular weight of target chemical, which affects molecular diffusion across the stagnant film. In fact, the correlation coefficient between the measured sampling rates and the square root of the reciprocal of the molecular weights of the four PAHs is 0.77, which is significant at $p < 0.05$ and is in line with the general relationship between molecular diffusion coefficients and molecular weights.^[12] Theoretically, the sampling rate would not exceed that of an active sampler operated at the same pumping rate. This is because when the concentrations in the chamber (outlet end) are same as the ambient concentrations, the diffusion will reach equilibrium.

Laboratory and field tests

(Fig. 4) shows the vertical profiles of the quantities of ACY, FLO, PHE, and PYR sampled by the diffusion samplers deployed at various heights over the soil surface in both the laboratory (the four panels on top) and the field (the four panels at the bottom) tests. For all cases except PYR in the field test, there are clear increasing trends towards the soil surface. Such

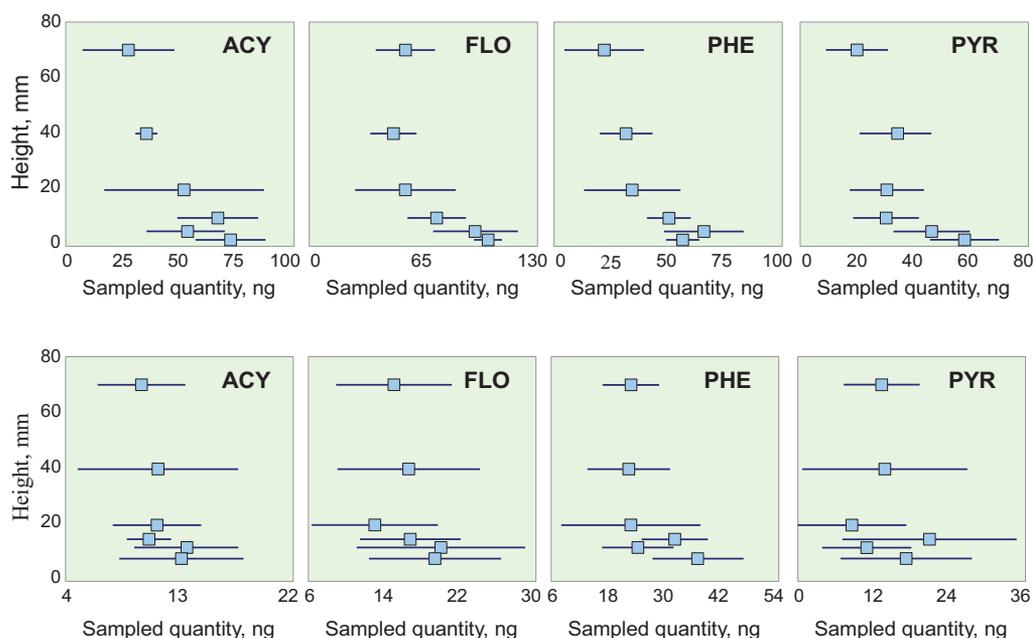


Figure 4. The quantities of ACY, FLO, PHE, and PYR sampled by the samplers at various heights over the surface of a contaminated soil sample in the laboratory (top row) and the surface of a test site in the field (bottom row). The heights were 2, 5, 10, 20, 40, and 70 mm for the laboratory test and 8, 12, 15, 20, 40, and 70 mm for the field test. The means (symbols) and standard deviations (bars) of four replicate tests are presented.

significant differences were confirmed by the results of a one-way analysis of variance ($p < 0.05$). The increasing trends indicate the diffusion of PAHs from the soil to the air. In fact, the soil used in the laboratory test was not the only severely contaminated soil, as the site near the student canteen was also contaminated to a certain extent with soil PAH concentrations much higher than those at a background site on the same campus.¹⁰ The influence of the soil emissions on the air concentrations was limited to only a few centimeters, and this agrees well with the results of a study that used an array of passive samplers at two contaminated sites in the Beijing Coke Company.¹⁰ No significant difference of PYR at the field site was found, which was likely due to the high variation of the individual measurements. The results confirm that the sampler developed in this study can be applied to monitor the vertical concentration profiles above the soil surface, which can provide essential information for calculating air-to-soil exchange fluxes.

Discussion

To the best of our knowledge, this is the first device that can sample gaseous PAHs much more efficiently than the conventional passive samplers without agitating the surrounding air mass. Since the concentration change over the soil surface mainly occurs within a few centimeters,¹⁰ the concentration profile can be easily disturbed or destroyed by an air mass disturbance. In this study, the performance of the enhanced diffusion sampler has been successfully demonstrated for studying the near-surface air concentration profiles of gaseous PAHs without air disturbance. In addition, the developed device has a potential to be used in other cases when air agitation is to be avoided. For example, fugitive emissions of various gaseous phase pollutants from a point (e.g., a stove) or a linear (e.g., a busy street) source can be monitored by deploying an array of samplers along the direction in question from the source. In

principle, other similar trace chemicals such as organochlorine pesticides or polybrominated diphenyl esters in the air can also be sampled as long as they can be effectively trapped on a sampling media and purged from the chamber. Sorbents other than PUF can be chosen given that the resistance to air flow is sufficiently low. Moreover, chemicals in other fluid media such as water can also be sampled in similar way.

The sampler has a number of constraints. Like the conventional active sampling technique, power is required, which reduces the flexibility of field deployment. On the other hand, the sampler shares a disadvantage with passive samplers in that the quantification must be calibrated against an active sampler. In addition, the design of the current prototype is complicated, resulting in the relatively high error and low repeatability of the measurements. Closely deployed samplers may affect the performance of each other by reducing the ambient air concentrations of the targeted chemicals. Still, there is room for further improvement. For example, a rigid filter that would prevent the trembling of the sampling interface could be tested. In addition, a rigid filter will simplify the assembly and deployment of the sampler, as the rigid filter would occupy less space than the glass-fiber filter sampler in the field; this is particularly important when more than one unit needs to be deployed and operated simultaneously. The PUF cartridge can also be redesigned. By increasing the diameter/length ratio of the sampling cartridge, the resistance, and consequently the pressure drop, can be reduced, while the trapping efficiency will remain unchanged.

More tests both in the laboratory and the field are required before the sampler can be fully put into use. The influences of various filter materials and pore sizes on the sampling efficiency and repeatability need to be further tested. Different geometric shapes of the PUF and other potential sampling media for different chemicals can be compared. The operational parameters such as the flow rate and sampling duration can be optimized.

The possible interaction among units that are deployed close to one another should be carefully assessed. The effects of environmental factors, such as wind speed, wind direction, and temperature, need to be addressed. The performance should be compared with other samplers in the field. Last but not least, a method to quantify the relationship between the vertical concentration profile and the air-to-soil exchange flux needs to be developed.

Conclusion

A novel enhanced diffusion sampler was developed to collect gaseous phase PAHs at a relatively fast sampling rate without disturbing air mass. The sampling technique was tested in both the laboratory and the field, and it shows potential for application to other similar purposes.

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