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Short Communication

Assessment of PAH loss in passive air samplers by the effect of temperature



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ABSTRACT

Passive air samplers (PAS) have become recurrent methods for environmental monitoring. However, the influence of environmental variables, such as temperature, over these devices has not been fully investigated. Since climate change is likely to induce major environmental changes, the role of the temperature needs to be studied to assure the suitability of PAS for the long-term monitoring of semi-volatile organic compounds (SVOCs) and their utility to compare data from different locations. This study aimed at evaluating the potential loss of polycyclic aromatic hydrocarbons (PAHs) in PAS containing disks of polyurethane foam (PUF) at different temperatures. The gradient of temperature inside and outside the PAS was firstly determined, being noted an internal/external difference of up to 5 °C. Secondly, a lab-controlled experiment was performed by daily analyzing PAHs in PUF-based PAS exposed to 25 °C and 38 °C, for a period of 7 days. A significant loss of PAHs in PUFs was not observed for any of both scenarios, remaining constant through time. Moreover, PAH levels were not significantly different according to the temperature. These findings indicate that the environmental temperature does not affect the stability of PAHs in PAS. Once PAHs have been uptaken, they are not easily volatilized from these devices. Consequently, PAS are good environmental monitors independently on the ambient conditions of temperature, being suitable for the comparability of data, either temporally or spatially, on the airborne concentrations of PAHs.

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1. Introduction

Passive air samplers (PAS) have become a viable alternative to traditional active air samplers (AAS) for the monitoring of semi-volatile organic compounds (SVOCs). PAS are cheaper, smaller, and simpler-to-handle devices than AAS, while they do not require electricity and maintenance (Mari et al., 2008; Vilavert et al., 2013). These characteristics make them very suitable for the surveillance in remote areas of the planet, as well as for the simultaneous collection of samples at different locations and/or scales (Bohlin et al., 2008; Zabiegała et al., 2010; Estellano et al., 2012; Pozo et al., 2012; Vilavert et al., 2014).

PAS are based on the theory of physical advection and diffusion to capture organic compounds through a passive air flow (Wang et al., 2012; Bogdal et al., 2013). Different PAS designs have been developed based on the adsorbent material, being polyurethane foam (PUF) one of the most widely used for air monitoring (Bohlin et al., 2008; Chaemfa et al., 2008). The standard design of PAS is based on a double-dome chamber in which a PUF disk is deployed in order to protect the adsorbent material from rainfall and direct light (Chaemfa et al., 2008; Seethapathy et al., 2008; Choi et al., 2012). However, the influence of environmental variables, such as wind speed and temperature, may significantly affect the accumulation capacity of these devices (Klánová et al., 2008; Seethapathy et al., 2008; Kennedy, 2010).

Temperature plays an important role on the sampling rate of SVOCs by PAS (Kennedy, 2010; Armstrong et al., 2014; Melymuk et al., 2014). High temperatures may cause an increase of molecular diffusivity, resulting in an increased sampling rate of the

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compounds. Furthermore, high temperatures can affect the PAS sorption capacity, shortening the linear uptake phase (Klánová et al., 2008; Seethapathy et al., 2008; Melymuk et al., 2014). These processes lead to a higher variability of PAS sampling rates when comparing different areas or seasons. Although not statistically significant, slight trends of increased sampling rates with increased temperature and relative humidity were reported when measuring airborne organophosphorus pesticides by means of PAS in the US (Armstrong et al., 2014). Temperature also controls the gas-particle partitioning of SVOCs (Klánová et al., 2008; Kennedy, 2010; Chen et al., 2011; Melymuk et al., 2014). Since the environmental temperature is also closely linked to the volatilization of organic compounds and their affinity for the gas phase (Melymuk et al., 2014), potential temperature variations may also critically affect pollutant concentrations in air. The design of the PAS is also a fundamental aspect. The double-dome recovering the PUF is generally made of stainless steel. It may generate a potentially important gradient of the temperature inside/outside the device, caused by the effect of the solar radiation over the metallic housing (Kennedy, 2010). Finally, the internal recirculation of organic compounds close to the PUF may also have a role on the uptake of chemical pollutants (Thomas et al., 2006).

Although temperature may have a critical effect on the sampling rate and the accumulation capacity of SVOCs, their potential loss by volatilization in PUF-based PAS has not been studied yet. The current short-term investigation aimed at evaluating the role of temperature over the loss of polycyclic aromatic hydrocarbons (PAHs), chosen as SVOC representatives, after they were adsorbed in PAS. A field study was firstly conducted to establish temperature differences between inside and outside the device. Subsequently, a lab-controlled study in a climate chamber was carried out to analyze the progressive loss of PAHs from PAS exposed to different temperatures.

2. Experimental procedure

2.1. Materials and reagents

PAS containing PUF disks (diameter: 14 cm; thickness: 1.2 cm; surface area: 360 cm²; density: 0.035 g cm⁻³) were purchased from Newterra (Beamsville, ON, Canada). Prior to use, PUFs were pre-cleaned with dichloromethane (DCM). Certified PAH standard mixtures, supplied by Supelco (Bellefonte, PA, USA), were used to evaluate the loss of PAHs. The mixture contained 13 PAHs (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) at a concentration of 2000 µg/mL in benzene:DCM (1:1 (v:v)). Individual standards of d₈-naphthalene, d₁₀-fluorene, and d₁₂-benzo[a]pyrene were purchased from Supelco (Bellefonte, PA, USA). DCM (purity 99.5%, Scharlab, S.L., Sentmenat, Barcelona, Spain) and hexane (purity 99.5%, Scharlab, S.L.) were used as solvents. Nitrogen for drying, with 99.995% of purity, was obtained from Air Liquid Group (Barcelona, Spain).

2.2. External/internal PAS temperature

The potential temperature gradient inside and outside of PAS was measured in the field. A passive sampler was deployed on the roof of the Campus Sescelades at the “Rovira i Virgili” University (Tarragona, Catalonia, Spain), from June to August 2014. The temperature inside and outside the sampler was monitored by means of a thermometer model Ebro EBI300 (Ebro Electronics, Ingolstadt, Germany). During the sampling period, temperature measurements were recorded every 5 min.

2.3. PAS exposure in a climate chamber

A climate chamber was used to evaluate the influence of the temperature over the PAH loss in the PAS. Two exposure scenarios (base, at 25 °C; and extreme, at 38 °C) were considered, according to the respective mean and maximum temperatures recorded inside the PAS. All the experiments were performed in darkness and at 65% relative humidity. PAHs were determined after 1 h, as well as daily for one week (1, 2, 3, 4, 5, 6 and 7 days after starting). For each exposure time, four PAS with pre-cleaned PUFs were spiked with 50 µL of a TCL PAHs mixture (100 µg/mL in DCM:hexane (1:1)). Subsequently, the four PUF-PAS were deployed inside the climate chamber, and used as replicates. Once they were retrieved from the chamber, PUFs were stored in DCM-cleaned brown glass jars and frozen at -20 °C for subsequent analysis.

2.4. PAH determination

Microwave-assisted extractions were performed with a microwave laboratory system for organic extraction (starT-Basic SK-12, 1200W) (Milestone S.r.l. Sorisole, BG, Italy). A microwave oven was used following an optimized 40 min program that elevates the temperature to 115 °C at a power of 700 W (Method 3546, EPA). Before the extraction, 50 µL of d₁₀-fluorene (100 µg/mL in DCM:hexane (1:1)) were spiked to estimate the process recoveries. Afterwards, PUFs were cut into small pieces and placed in each microwave vessel along with 30 mL of DCM:hexane (1:1). Once the extraction was complete, foams were removed and samples were concentrated in a rotary evaporator to a volume of 1 mL. Subsequently, they were dried under a gentle flow of nitrogen in 1.5-mL amber glass vials. Once the solvent was evaporated, extracts were resuspended in 100 µL of a solution containing d₈-naphthalene and d₁₂-benzo[a]pyrene (50 µg/mL in DCM:hexane (1:1 (v:v))).

The analysis was performed using a gas chromatograph (Hewlett-Packard G1099A) coupled with a mass spectrometer (Agilent MSD5973). A HP-5MS 5% phenyl methyl siloxane capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness) (Agilent 19091S-433) was used for separating the PAHs. Samples (1 µL) were injected in splitless mode. For recovery percentages, four pre-cleaned PUFs were spiked with 50 µL of a PAH standard mixture (100 µg/mL in DCM:hexane (1:1)). Subsequently, these unexposed samples were extracted following the aforementioned procedure. Recovery percentages differed according to individual PAHs, ranging from 65% to 95%. Because of peak overlapping, benzo[b]fluoranthene and benzo[k]fluoranthene were quantified together.

2.5. Data treatment

Data analyses were performed by using the SPSS 19.0 statistical software package. The Levene test was applied to analyze the equality of variances. ANOVA was executed and a probability lower than 0.05 ($p < 0.05$) was considered as statistically significant. The comparison of means was performed using the Tukey's test.

3. Results and discussion

3.1. External/internal PAS temperature

The results from the monitoring of the potential differences of temperature inside and outside PUF-PAS, conducted for a period of 2 months (Summer 2014), are depicted in Fig. 1. Outside the PAS, minimum and maximum temperatures were 12.4 °C and 33.2 °C, respectively. In turn, the temperatures inside the device ranged from 13.1 °C to 38.2 °C (mean: 25 °C). A temperature gradient ranging from 3 °C to 5 °C (when comparing internal and external

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