



# An assessment of polyurethane foam passive samplers for atmospheric metals compared with active samplers



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## ABSTRACT

In this study, we conducted an assessment of polyurethane foam (PUF) passive sampling for metals combining active sampling. Remarkably, we found that the metals collected in the passive samples differed greatly from those collected in active samples. By composition, Cu and Ni accounted for significantly higher proportions in passive samples than in active samples, leading to significantly higher uptake rates of Cu and Ni. In assessing seasonal variation, metals in passive samples had higher concentrations in summer (excluding Heshan), which differed greatly from the pattern of active samples (winter > summer), indicating that the uptake rates of most metals were higher in summer than in winter. Overall, due to the stable passive uptake rates, we considered that PUF passive samplers can be applied to collect atmospheric metals. Additionally, we created a snapshot of the metal pollution in the Pearl River Delta using principal component analysis of PUF samples and their source apportionment.

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## 1. Introduction

With rapid industrialisation and urbanisation, air pollution has become a serious environmental problem, particularly in urban areas. Atmospheric total suspended particulates (TSP), an important atmospheric component, have been linked to a number of adverse environmental and human health effects (Dockery et al., 1993; Shah and Shaheen, 2007) because of the complex distribution and composition of contaminants. The presence of metals in atmospheric particles has raised widespread concern (Huang et al., 2014; Wang et al., 2015). Hu et al. reported potential teratogenic effects of As and Cd in humans, and Pb and Hg were toxic to foetuses (Hu et al., 2012a, 2012b).

Generally speaking, metals in atmospheric particulates are collected using active samplers. Active sampling techniques provide reliable quantitative concentration data and high temporal resolution (Hayward et al., 2010). However, these techniques only determine daily pollutant concentrations, which are easily modified by meteorological variations and punctual emissions over a short time course (Mari et al., 2008). Additionally, the relatively high cost, electricity requirements, regular visits by specialised

personnel, calibration, and maintenance of active samplers limit their wide deployment (Beamer et al., 2014). In contrast, passive air samplers collect pollutants over a relatively long-time period, and they are simple, low-cost, and require no energy input. These characteristics make passive samplers better suited to provide data for large-scale monitoring, and they have been developed as supplements to traditional active sampling techniques (Seethapathy et al., 2008).

Polyurethane foam (PUF) passive air samplers are probably the most widely used (Chaemfa et al., 2008), and they have been deployed worldwide because they are inexpensive and easy to use (i.e. prepare and extract). They collect pollutants through spontaneous diffusion of the analyte to the sorbent media, PUF, which has high retention capacity and low sensitivity to sudden episodic fluctuations in pollutant concentrations (Chaemfa et al., 2009a), providing a long-term average pollutant level (Tao et al., 2007). Generally, PUF disks are used to collect semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs) (Tao et al., 2007, 2009), polychlorinated biphenyls (PCBs) (Estellano et al., 2017; Shoeib and Harner, 2002), and polybrominated diphenyl ethers (PBDEs) (Poza et al., 2017). Unlike SVOCs, metals are almost always found in particulates. However, several studies have indicated that PUF disks have the ability to collect particulate pollutants. Holt et al. and Strandberg et al.

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reported that PUF passive samplers collected particulate PAHs, although their sampling efficiency was lower than that of active samplers (Holt et al., 2017; Strandberg et al., 2018). Dillner et al. and Mines et al. found that PUF was a suitable replacement for substrates used to collect atmospheric metals (Dillner et al., 2007; Mines et al., 2016). Therefore, we assessed PUF passive sampling for atmospheric metals. To the best of our knowledge, this is the first study to apply PUF air samplers for metals sampling.

We selected the Pearl River Delta (PRD), a thriving region in southern China, as our study site. We used PUF disks to collect aerosol samples in 10 urban areas, including 8 suburbs, 9 industrial areas, and 10 residential areas, to investigate the pollution status of the region. Simultaneously, we deployed high-volume active samplers in Heshan (HS), Conghua (CH), and Guangzhou (GZ) to collect TSP samples. We compared the levels of 13 selected metals measured in passive samples and active samples. The feasibility of passive sampling for metals was thus assessed by comparing passive samples and active samples, and the passive uptake rate was calculated.

## 2. Sampling and methods

### 2.1. Sampling information

In this study, a sampling campaign was conducted in the PRD of China in summer and winter. Active samples were collected with Teflon filters using high-volume active air samplers in HS, CH, and GZ from July to August 2015 and December 2015 to January 2016 (eight samples per season; each sampling period lasting 24 h). Passive samples were collected using PUF passive samplers (14 cm in diameter  $\times$  1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 3.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>-3</sup>) made by our research team. The PUF samplers were deployed at 27 sites in 10 cities for 60 days, the same time period as the active sampling (Fig. 1; for details on sampling sites, see Table S1). Note that passive sampling sites included HS, CH, and GZ. Based on functional zone features, these sites were classified into three types: industrial areas (Ind), suburbs (Sub), and residential areas (Res). All samplers were deployed in the top floors of buildings with no obvious obstructions around them. All PUF were cleaned using ultrapure water, then pre-treated with absolute methanol for 48 h by Soxhlet extraction. PUFs were wrapped with double layers of polyethylene bags after sampling.

### 2.2. Sample analysis

All 13 selected metals (Cu, Cr, Fe, Zn, Pb, Cd, Ni, Mn, Co, V, Ti, Al, and As) were detected in the collected samples using inductively coupled plasma atomic emission spectrometry (ICP-AES; PerkinElmer Optima 3300 DV, PerkinElmer, Inc., Waltham, MA, USA). Detailed methods were described in a previous study (Xu et al., 2014). Briefly, we divided weighted filters into two pieces using plastic scissors, then cut up the filters and placed the shredded membranes into tubes. Then 14 mL HNO<sub>3</sub> and 3.5 mL HClO<sub>4</sub> were added to fully submerge the filters, and the mixture was shaken using a vortex. The tubes were incubated in a microwave digestive system under a constant temperature of 190 °C for 24 h to completely dissolve the samples. Next 10 mL 5% (v/v) high-purity HNO<sub>3</sub> was added and the tubes were heated at 70 °C for 1 h. The tubes were cooled to room temperature, and the supernatant was decanted into acid-cleaned polyethylene tubes. Finally, the solution was analysed using ICP-AES.

### 2.3. Quality assurance/control

We included procedural and field blanks for each set of eight

samples to test for potential contamination and reproducibility. The results showed that the blanks were <1% of the mean concentration for all metals. The standard reference material (NIST SRM 1648, urban particulate matter) was randomly inserted in the sample analysis. The recovery rates of the reference material were between 82% and 97%. The recovery rate of Al was approximately 57%. This may be due to the influence of aluminosilicate minerals.

### 2.4. Statistical analysis

We assessed the probable sources of metals in 10 urban areas with principal component analysis (PCA) using SPSS software (ver. 22; IBM Corp., Armonk, NY, USA). Prior to the analysis, the data matrix was standardised to eliminate the potential influence of different units and to give each determined variable equal weight.

### 2.5. Calculation of passive uptake rate

PUF passive uptake rates were calculated using the active sampling concentrations (Table 1). The two different types of samplers were deployed at the same site for the same sampling period. According to previous studies (Arnoldsson et al., 2015; Liu et al., 2012), the equation for calculating passive uptake rates can be simplified as

$$R_s = \frac{M_{PAS}}{C_{air}t}$$

where  $R_s$  is the passive uptake rate in m<sup>3</sup> day<sup>-1</sup>,  $M_{PAS}$  is the amount of the target compound (ng),  $C_{air}$  is the concentration of metals in TSP samples as determined by active sampling (ng m<sup>-3</sup>), and  $t$  is the length of the sampling period (days).

## 3. Results and discussion

### 3.1. Pollution characteristics

#### 3.1.1. Active samples

The concentrations of all 13 selected metals in TSP in the active samples in HS, CH, and GZ are shown in Table 1. Evidently, GZ had the highest total metal (TM) concentrations (3150 ng m<sup>-3</sup>), followed by HS (1900 ng m<sup>-3</sup>) and CH (1530 ng m<sup>-3</sup>), which may be attributable to different regional pollution sources. Compared with previous research, the TM concentrations were significantly lower than those in urban and suburban areas (8590 and 6990 ng m<sup>-3</sup>, respectively) from GZ during 2003–2005 (Lee et al., 2007), indicating a reduction in atmospheric metal pollution. Fe, Al, and Zn were the major components in HS, CH, and GZ, on average, accounting for 39.3, 30.5, and 17.3% of the TM concentrations, respectively (Fig. 2), whereas Mn, As, V, and Cd accounted for extremely low percentages (mean values were below 1%). Additionally, there were several differences among the metal compositions in HS, CH, and GZ. As shown in Fig. 2, Fe made up a significantly higher mean proportion in GZ (47.2%) than in HS (34.8%) and CH (35.9%), and Cr and Ti had higher mean proportions in HS (5.36% and 6.57%, respectively) than in CH (not detected and 1.69%, respectively) and GZ (not detected and 1.05%, respectively). These results may have been influenced by different types of pollution or point sources.

#### 3.1.2. Passive samples

The metal concentrations in the passive samples are listed in Table 1. GZ had the highest TM concentration (8430 ng s<sup>-1</sup> d<sup>-1</sup>), consistent with the active samples, followed by CH (8220 ng s<sup>-1</sup> d<sup>-1</sup>) and HS (6490 ng s<sup>-1</sup> d<sup>-1</sup>), which differed significantly from the

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