



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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



Qilu Li ^{a, b}, Kong Yang ^b, Jun Li ^{a, *}, Xiangying Zeng ^a, Zhiqiang Yu ^a, Gan Zhang ^a

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, China

ARTICLE INFO

Article history:

Received 19 September 2017

Received in revised form

11 January 2018

Accepted 16 January 2018

Keywords:

Metals

PUF passive sampling

Seasonal variation

Uptake rate

Source analysis

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.

© 2018 Elsevier Ltd. All rights reserved.

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.

* Corresponding author.

E-mail address: junli@gig.ac.cn (J. Li).

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 cm²; mass, 3.40 g; volume, 207 cm³; density, 0.0213 g cm⁻³) 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 HNO₃ and 3.5 mL HClO₄ 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 HNO₃ 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 m³ day⁻¹, 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⁻³), 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⁻³), followed by HS (1900 ng m⁻³) and CH (1530 ng m⁻³), 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⁻³, 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⁻¹ d⁻¹), consistent with the active samples, followed by CH (8220 ng s⁻¹ d⁻¹) and HS (6490 ng s⁻¹ d⁻¹), which differed significantly from the



Fig. 1. Sampling sites.

active samples. Cu, Al, Fe, and Ni were the dominant components, accounting for an average of 32.0, 22.2, 22.1, and 15.8% of the total concentration, respectively. As shown in Fig. 2, the metal compositions of HS, CH, and GZ differed. GZ and CH had significantly higher proportions of Cu (34.6 and 40.5%, respectively) than HS (21.0%), and CH had a much lower proportion of Fe (13.6%) than HS (25.6%) and GZ (27.3%). Comparing active and passive samples, we found obvious compositional differences at the same site, particularly for Cu and Ni (which were present at significantly higher percentages in the passive samples). This may have been influenced by the different sampling methods. A more detailed discussion is

given in section 3.3.

3.2. Seasonal variation

3.2.1. Active samples

As shown in Fig. 3, the TM concentrations were much higher in winter than in summer (more than double) at all sites, consistent with previous studies (Hao et al., 2007; Kulshrestha et al., 2009; Lee et al., 2007; Wang et al., 2010). The compositions of the metals also exhibited seasonal variation, as shown in Table S2. In general, Cu, Ni, Mn, and Co had relatively higher percentages in summer than in

Table 1
Concentrations of metals in active and passive samples collected in Heshan (HS), Conghua (CH), and Guangzhou (GZ).

| Site | | Cu | Cr | Fe | Zn | Pb | Cd | Ni | Mn | Co | V | Ti | Al | As | Sum |
|-----------------|-----|------|------|-------|------|------|------|------|------|------|------|------|------|------|------|
| HS ^a | AVG | 40.3 | 123 | 800 | 466 | 38.6 | 2.28 | 26.6 | 14.3 | 34.9 | 10.9 | 151 | 641 | 10.8 | 1900 |
| | SD | 30.1 | 89.7 | 986 | 308 | 57.7 | 3.34 | 16.4 | 11.9 | 8.65 | 7.20 | 152 | 569 | 6.90 | 1840 |
| CH ^a | AVG | 55.7 | / | 591 | 319 | 41.3 | 1.73 | 35.4 | 13.5 | 31.3 | 9.63 | 27.8 | 528 | 9.60 | 1530 |
| | SD | 81.4 | / | 440 | 166 | 56.4 | 1.98 | 23.3 | 11.1 | 10.1 | 9.13 | 21.5 | 401 | 9.54 | 1100 |
| GZ ^a | AVG | 85.9 | / | 1490 | 385 | 43.1 | 2.69 | 30.3 | 42.3 | 38.3 | 8.43 | 33.1 | 997 | 11.8 | 3150 |
| | SD | 51.4 | / | 913 | 300 | 48.1 | 3.03 | 11.7 | 44.2 | 11.8 | 6.73 | 10.6 | 608 | 7.89 | 1740 |
| HS ^b | AVG | 138 | 1110 | 1680 | 485 | 14.2 | 0.88 | 1040 | 13.0 | 1.18 | 3.73 | 46.6 | 1770 | 3.17 | 6490 |
| | SD | 788 | 78.0 | 419 | 39.2 | 0.88 | 0.17 | 381 | 9.18 | 1.11 | 0.43 | 40.7 | 356 | 1.96 | 1110 |
| CH ^b | AVG | 3800 | 95.3 | 1280 | 2650 | 12.9 | 0.59 | 1530 | 16.8 | 2.32 | 1.46 | 28.5 | 2390 | 1.02 | 8220 |
| | SD | 4710 | 13.7 | 50.3 | 105 | 10.9 | 0.01 | 1810 | 6.20 | 1.64 | 0.86 | 1.85 | 1690 | 0.10 | 4980 |
| GZ ^b | AVG | 2940 | 116 | 23200 | 481 | 20.1 | 0.91 | 1290 | 37.3 | 9.02 | 4.76 | 63.8 | 120 | 2.10 | 8430 |
| | SD | 2420 | 82.4 | 743 | 346 | 9.22 | 0.43 | 1200 | 31.3 | 9.44 | 2.76 | 37.5 | 943 | 2.30 | 3770 |

^a Indicates active samples (ng m^{-3}).

^b Indicates passive samples ($\text{ng s}^{-1} \text{d}^{-1}$).

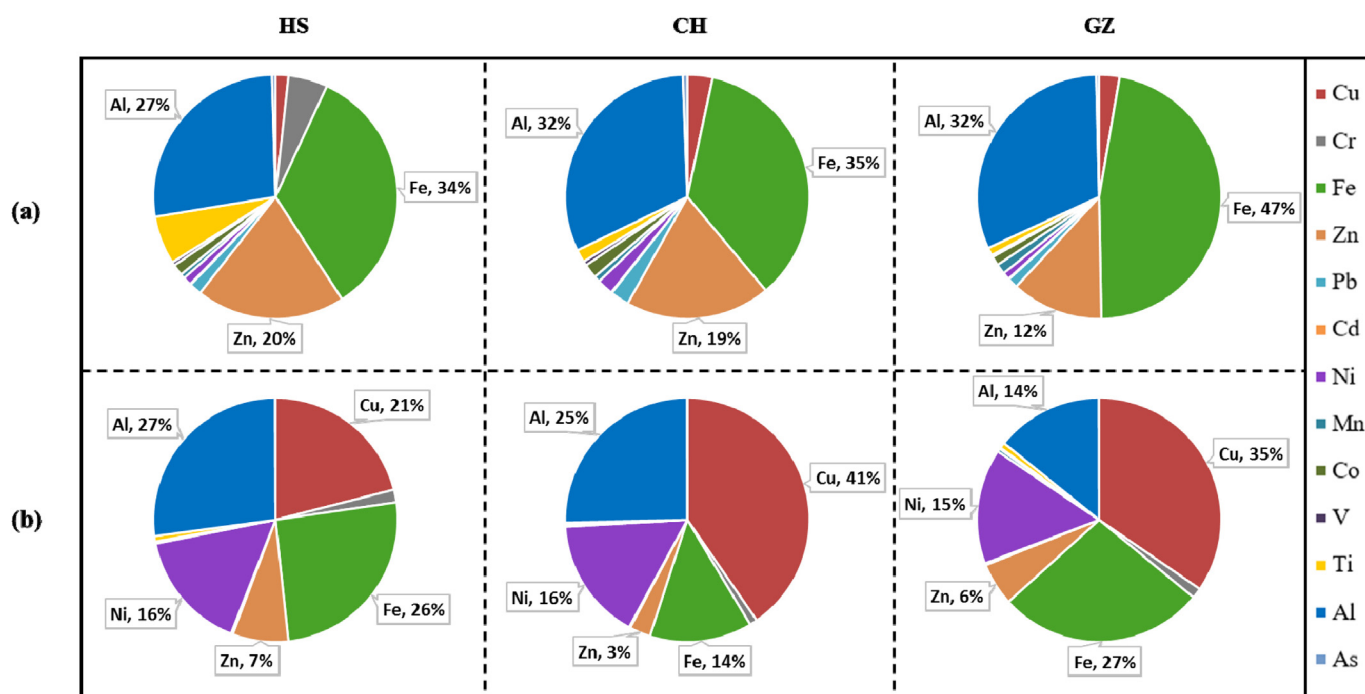


Fig. 2. The metal compositions of active and passive samples collected in Heshan (HS), Conghua (CH), and Guangzhou (GZ). Note: (a) indicates active samples; (b) indicates passive samples.

winter in HS, CH, and GZ, particularly Cu and Mn, whereas Fe, Pb, V, and Al were detected at higher proportions in the winter. Meanwhile, an extremely high Ti percentage was found in HS during the summer (19.9%), which may have resulted from seasonal emissions of relevant industries in HS.

3.2.2. Passive samples

The seasonal variations in mean concentrations in HS, CH, and GZ are shown in Fig. 3. The mean TM concentrations in HS were relatively higher during the winter ($7270 \text{ ng s}^{-1} \text{d}^{-1}$) than in summer ($5710 \text{ ng s}^{-1} \text{d}^{-1}$), whereas CH and GZ had significantly higher TM concentrations in summer ($11,700$ and $11,100 \text{ ng s}^{-1} \text{d}^{-1}$, respectively) than in winter (4700 and $5760 \text{ ng s}^{-1} \text{d}^{-1}$, respectively). This differed greatly from the trend seen with active samples (winter > summer) and may be attributable to the different sampling mechanisms. The variation in metal proportions in HS also differed greatly from those in CH and GZ, as shown in Table S2. Cu and Ni had significantly higher percentages in summer (60.7 and 41.9%,

respectively) than in winter (10.2 and 21.2%, respectively) in CH and GZ, whereas they were present at relatively low percentages in HS during the winter. The proportions of Fe and Al in summer were higher than in winter in CH and GZ (Table S2), whereas HS displayed the opposite pattern. The differences among the three areas may be related to seasonal emissions from local industries, whereas differences in the seasonal variation in composition between active samples and passive samples may have resulted from the differences in passive sampling rates of different metals. In the next section, we discuss potential causes in greater detail.

3.3. Passive uptake rate

We calculated the PUF passive uptake rates for 12 metals in winter and summer at HS, CH, and GZ (Fig. 4). Because of its low detection rate in active samples (8.3%), Cr was eliminated from this study. For the calculation method, see section 2.4. The original purpose of the experiment was to assess the feasibility of passive

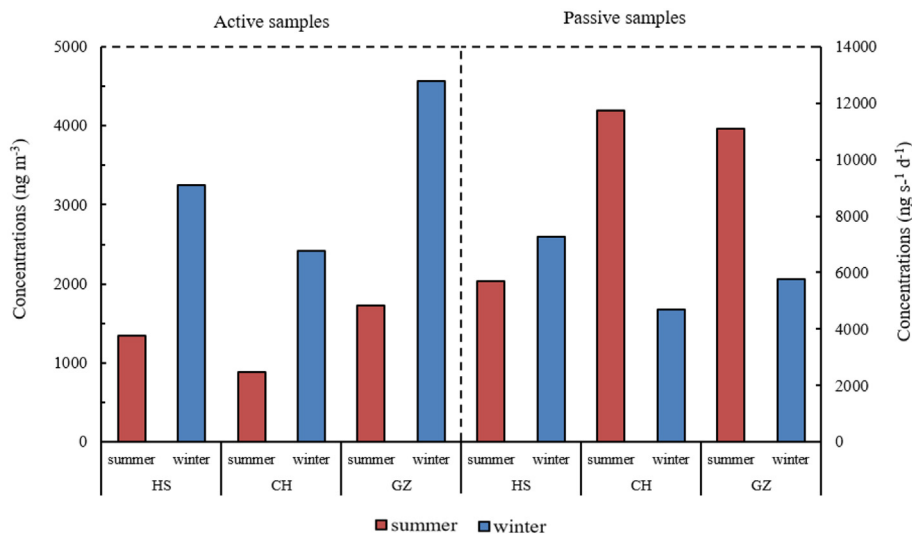


Fig. 3. Seasonal variation in total metal concentrations of active and passive samples collected in HS, CH, and GZ.

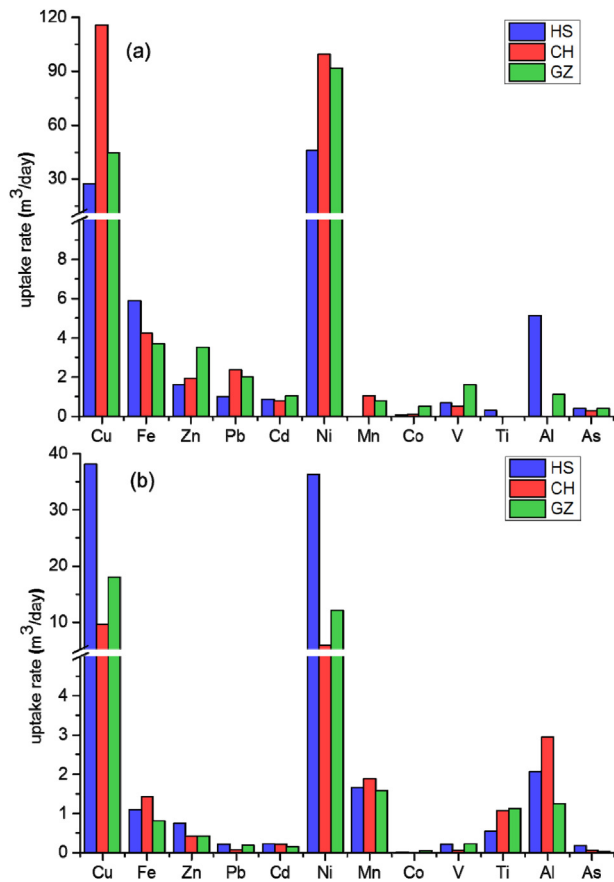


Fig. 4. The passive uptake rates of metals in HS, CH, and GZ. Note: (a) represents summer, (b) represents winter.

sampling of metals, and we collected passive samples for the whole period only rather than in segmented periods. This may have influenced the accuracy of our results, but we were able to discern the general pattern through the results.

The passive uptake rates for metals in HS, CH, and GZ are displayed in Fig. 4. Generally, the uptake rates for most of the metals were consistent among HS, CH, and GZ during the summer and the

winter, indicating that the sampling was relatively stable. For all metals, there were huge differences in uptake rates. Evidently, Cu and Ni had extremely high mean uptake rates (42.2 and $48.5 \text{ m}^3 \text{ day}^{-1}$, respectively), as shown in Table S3, followed by Fe, Al, Zn, and Mn, for which the mean uptake rates were 2.80 , 2.20 , 1.44 , and $1.16 \text{ m}^3 \text{ day}^{-1}$, respectively. Other metals, including Pb, V, Cd, Ti, and As, had relatively low uptake rates (lower than $1 \text{ m}^3 \text{ day}^{-1}$). The differences in uptake rates may be correlated with many factors. Passive sampling collected samples over a longer period and tended to collect relatively finer particles (Chaemfa et al., 2009b), whereas active sampling collected TSP on eight selected days, thus, the mean concentrations were easily influenced by extremes. Additionally, different chemical and physical properties of metals, such as size distribution and chemical speciation, were also probable factors. The metals that tend to exist in fine particles, such as Mn, Cu, Ni, and Zn, may have had relatively higher concentrations in passive samples, leading to higher uptake rates (Tan et al., 2016). Metals of various chemical species in the atmosphere have different occurrence states and stabilities, and the different fractions in various chemical species may have influenced the results. Additionally, we deduced that PUF adsorption capacities to metals may be the most important influence, which will be our focus in future studies. Laboratory simulations and more in-depth studies are required to clarify the causes of the different uptake rates.

The uptake rates of the metals showed obvious seasonal variation, as shown in Fig. 4. Most of the metals, including Cu, Fe, Zn, Pb, Cd, Ni, Co, V, and As, showed significantly higher uptake rates in summer than in winter. By contrast, Mn and Ti had relatively high passive uptake rates in winter (Fig. 4). For Al, the differences in the rates between the two seasons were ambiguous. The relatively high uptake rates in summer were likely influenced by different meteorological conditions, such as temperature (Chaemfa et al., 2009b; Klánová et al., 2008; Seethapathy et al., 2008; Tuduri et al., 2006). According to a previous study on deposition rate, particulates had the highest deposition rate in summer, and the deposition rate was positively correlated with temperature (Norouzi et al., 2017). Klánová et al. reported that target compounds expected to be particle-bound were highly sensitive to temperature (Klánová et al., 2008; Melymuk et al., 2011). The seasonal variations of the metals might be influenced by physical and chemical properties. For example, the size distribution of various metals may be a factor, owing to different particle features between summer and winter.

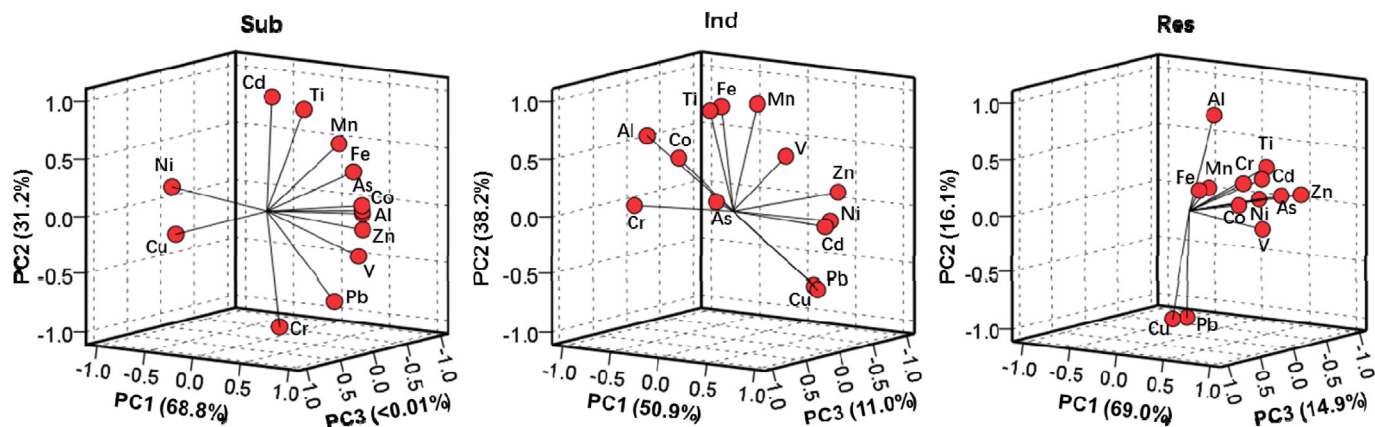


Fig. 5. Principle component analysis of metals in suburban, industrial, and residential areas in the summer.

Interestingly, Cu and Ni presented similar patterns in HS, CH, and GZ (summer, CH > GZ > CH; winter, HS > GZ > CH). This pattern similarity in the same season may have resulted from similarities in migration or adsorption, whereas the differences between summer and winter may have been influenced by differences in regional features or sources.

Based on the above analysis, we surmise that passive sampling is applicable to particular metals, such as Cu, Ni, and Fe. We found several variations among the metals, and between summer and winter. Based on previous studies, we assessed the suitability of passive sampling for particulate metals and the different physical and chemical properties of metals influencing the results, but ascertaining more specific causes, such as the influence of passive sampling, and determining more accurate uptake rates, require further study.

3.4. Source analysis

Metals are a class of chemicals with various sources, mainly crustal and anthropogenic sources (primarily vehicular activity and industrial activity) (Srivastava et al., 2009, 2016). We assessed the probable sources of metals in three functional areas with PCA. Given the low passive uptake rates of most metals in the winter, those results may have been inaccurate. Thus, we focused on the results obtained in summer.

In the suburbs, PC1 and PC2 contributed about 68.6% and 31.2% of the variance, respectively (Fig. 5). Fe and Al mainly originated from crustal sources (Abraham and Parker, 2008; Klos et al., 2011), and had extremely high PC1 scores. Thus, PC1 may represent crustal sources. PC2 had a high loading for Cd, Ti, and Mn, and a positive loading for Ni and Fe. These metals may have come from multiple sources, including special industries (Cd and Cr), long-distance transport (Cd), and vehicular emissions (Mn, Ni, and Pb) (Srivastava et al., 2016). Thus, PC2 may represent a mixed source. In industrial areas, PC1 and PC2 accounted for the predominant percentages (50.9% and 38.2%, respectively) of the total variance (Table S4), whereas PC3 accounted for only 11.0% of the total variance. In the space occupied by PC1, Zn, Ni, Cd, Pb, and Cu had high loading scores (Fig. 5). Some activities, such as automobile exhaust (Ni and Pb), brake wear (Cu), tire wear (Zn), and industrial combustion (Cd and Cu), contribute greatly to the atmospheric deposition of these elements (Basha et al., 2010; Hopke et al., 1980; Srivastava et al., 2016). Thus, PC1 may represent a mixed source of special industrial activity (such as fuel combustion) and vehicular activity. PC2 showed a high loading for Fe, Ti, Mn, and Al, which may represent a crustal source, including the resuspension of road

dust and soil. PC3 represented positive scores for Cr, Co, and As, and industrial activity was found to contribute to their levels (Pacyna et al., 2007; Xiao et al., 2014). Therefore, PC3 may represent industrial sources. For Res, PC1 explained 69.0% of the total variance, with a high loading for most metals, including Cd, Cr, As, V, Zn, Fe, Mn, Ti, and As, which could be contributed by mixed sources related to high levels of vehicular activity (Cd, Zn, and Mn) and uncontrolled emissions (fuel combustion) in Res areas (Fig. 5) (Srivastava et al., 2016). PC2 and PC3 explained 16.1% and 14.9% of the total variance, respectively (Table S4). These two PCs showed obscure fates and may also represent mixtures of various sources, including crustal sources and industrial sources.

4. Conclusion

All 13 selected metals in the atmosphere were collected by high-volume active samplers and PUF samplers in HS, CH, and GZ to assess the passive sampling of metals. Metals in active samples and passive samples differed significantly in terms of composition and seasonal variation. Fe, Al, and Zn were the dominant components in active samples, whereas Cu, Al, Fe, and Ni were dominant in passive samples. Active samples had higher TM concentrations in winter, whereas passive samples had higher TM levels in summer (excluding HS). These contrasting results may be due to the different sampling methods. Accordingly, there were several differences in the passive uptake rates of the metals. Cu and Ni uptake rates were significantly higher than those of the other metals, and Cd, Co, V, and As had extremely low uptake rates, which may have resulted from various factors, particularly the adsorption capacity of PUF to metals. Meanwhile, the uptake rates of most metals showed obvious seasonal variation (summer > winter). These variations may have been influenced by meteorological factors, such as temperature. Furthermore, passive samples were collected at 24 other sites in the PRD to provide a snapshot of the pollution status. The possible sources of the metals were apportioned using PCA. The major potential sources of metals were crustal, traffic, and industrial sources, and the three areas (suburban, industrial, and residential) exhibited different contributions from these three sources. In general, PUF passive samplers are an effective means of detecting atmospheric metals. Future studies should focus on determining accurate uptake rates and crucial impactors.

Acknowledgements

This work was supported by National Key R&D Program of China (2014BAC22B04 and 2017YFC0212000), the National Scientific

Foundation of China (41703126) and the Guangzhou Science and Technology Plan Project (No. 201504010002). This is contribution No. IS-2496 from GIGCAS.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.01.043>.

References

- Abraham, G.M., Parker, R.J., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ. Monit. Assess.* 136 (1–3), 227–238.
- Arnoldsson, K., Magnusson, R., Hägglund, L., Lejon, C., Wingfors, H., 2015. Initial evaluation of an axial passive sampler for PAHs and OPAHs using substrates with and without gas sampling capacity and varying diffusion distances. *Atmos. Pollut. Res.* 6 (4), 673–681.
- Basha, S., Jhala, J., Thorat, R., Goel, S., Trivedi, R., Shah, K., Menon, G., Gaur, P., Mody, K.H., Jha, B., 2010. Assessment of heavy metal content in suspended particulate matter of coastal industrial town, Mithapur, Gujarat, India. *Atmos. Res.* 97 (1–2), 257–265.
- Beamer, P.I., Sugeng, A.J., Kelly, M.D., Lothrop, N., Klimecki, W., Wilkinson, S.T., Loh, M., 2014. Use of dust fall filters as passive samplers for metal concentrations in air for communities near contaminated mine tailings. *Environ. Sci. Process. Impact* 16 (6), 1275–1281.
- Chaemfa, C., Barber, J.L., Gocht, T., Harner, T., Holoubek, I., Klanova, J., Jones, K.C., 2008. Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides. *Environ. Pollut.* 156 (3), 1290–1297.
- Chaemfa, C., Barber, J.L., Kim, K.-S., Harner, T., Jones, K.C., 2009a. Further studies on the uptake of persistent organic pollutants (POPs) by polyurethane foam disk passive air samplers. *Atmos. Environ.* 43 (25), 3843–3849.
- Chaemfa, C., Wild, E., Davison, B., Barber, J.L., Jones, K.C., 2009b. A study of aerosol entrainment and the influence of wind speed, chamber design and foam density on polyurethane foam passive air samplers used for persistent organic pollutants. *J. Environ. Monit.* 11 (6), 1135–1139.
- Dillner, A.M., Shafer, M.M., Schauer, J.J., 2007. A novel method using polyurethane foam (PUF) substrates to determine trace element concentrations in size-segregated atmospheric particulate matter on short time scales. *Aerosol. Sci. Technol.* 41 (1), 75–85.
- Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air pollution and mortality in six U.S. cities. *N. Engl. J. Med.* 329 (24), 1753–1759.
- Estellano, V.H., Pozo, K., Pribylova, P., Klanova, J., Audy, O., Focardi, S., 2017. Assessment of seasonal variations in persistent organic pollutants across the region of Tuscany using passive air samplers. *Environ. Pollut.* 222, 609–616.
- Hao, Y., Guo, Z., Yang, Z., Fang, M., Feng, J., 2007. Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China. *Atmos. Res.* 85 (1), 27–37.
- Hayward, S.J., Gouin, T., Wania, F., 2010. Comparison of four active and passive sampling techniques for Pesticides in Air. *Environ. Sci. Technol.* 44 (9), 3410–3416.
- Holt, E., Bohlin-Nizzetto, P., Boruvkova, J., Harner, T., Kalina, J., Melymuk, L., Klanova, J., 2017. Using long-term air monitoring of semi-volatile organic compounds to evaluate the uncertainty in polyurethane-disk passive sampler-derived air concentrations. *Environ. Pollut.* 220 (Pt B), 1100–1111.
- Hopke, P.K., Lamb, R.E., Natusch, D.F.S., 1980. Multielemental characterization of urban roadway dust. *Environ. Sci. Technol.* 14 (2), 164–172.
- Hu, X., Zhang, Y., Ding, Z., Wang, T., Lian, H., Sun, Y., Wu, J., 2012a. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM_{2.5} in Nanjing, China. *Atmos. Environ.* 57, 146–152.
- Hu, Z., Shi, Y., Niu, H., Cai, Y., 2012b. Synthetic musk fragrances and heavy metals in snow samples of Beijing urban area, China. *Atmos. Res.* 104–105, 302–305.
- Huang, M., Chen, X., Shao, D., Zhao, Y., Wang, W., Wong, M.H., 2014. Risk assessment of arsenic and other metals via atmospheric particles, and effects of atmospheric exposure and other demographic factors on their accumulations in human scalp hair in urban area of Guangzhou, China. *Ecotoxicol. Environ. Saf.* 102, 84–92.
- Klánová, J., ěupr, P., Kohoutek, J., Harner, T., 2008. Assessing the influence of meteorological parameters on the performance of polyurethane foam-based passive air samplers. *Environ. Sci. Technol.* 42 (2), 550–555.
- Klos, A., Rajfur, M., Waclawek, M., 2011. Application of enrichment factor (EF) to the interpretation of results from the biomonitoring studies. *Ecol. Civ. Eng.* 5 (2), 171–183.
- Kulshrestha, A., Satsangi, P.G., Masih, J., Taneja, A., 2009. Metal concentration of PM_{2.5} and PM₁₀ particles and seasonal variations in urban and rural environment of Agra, India. *Sci. Total Environ.* 407 (24), 6196–6204.
- Lee, C.S.L., Li, X.D., Zhang, G., Li, J., Ding, A.J., Wang, T., 2007. Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China—Evidence of the long-range transport of air contaminants. *Atmos. Environ.* 41 (2), 432–447.
- Liu, J., Li, Q., Li, J., Zhang, G., Liu, X., 2012. Theory and concentration calculations of PUF atmospheric passive sampling technique for persistent organic pollutants. *Environ. Monit. Chin.* 28 (3), 107–112.
- Mari, M., Schuhmacher, M., Feliubadaló, J., Domingo, J.L., 2008. Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers. *Chemosphere* 70 (9), 1637–1643.
- Melymuk, L., Robson, M., Helm, P.A., Diamond, M.L., 2011. Evaluation of passive air sampler calibrations: selection of sampling rates and implications for the measurement of persistent organic pollutants in air. *Atmos. Environ.* 45 (10), 1867–1875.
- Mines, L.W.D., Park, J.H., Mudunkotuwa, I.A., Anthony, T.R., Grassian, V.H., Peters, T.M., 2016. Porous polyurethane foam for use as a particle collection substrate in a nanoparticle respiratory deposition sampler. *Aerosol. Sci. Technol.* 50 (5), 497–506.
- Norouzi, S., Khademi, H., Ayoubi, S., Cano, A.F., Acosta, J.A., 2017. Seasonal and spatial variations in dust deposition rate and concentrations of dust-borne heavy metals, a case study from Isfahan, central Iran. *Atmos. Pollut. Res.* 8 (4), 686–699.
- Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., Nitter, S., Pregger, T., Pfeiffer, H., Friedrich, R., 2007. Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmos. Environ.* 41 (38), 8557–8566.
- Pozo, K., Oyola, G., Estellano, V.H., Harner, T., Rudolph, A., Prybilova, P., Kukucka, P., Audi, O., Klanova, J., Metzendorf, A., Focardi, S., 2017. Persistent Organic Pollutants (POPs) in the atmosphere of three Chilean cities using passive air samplers. *Sci. Total Environ.* 586, 107–114.
- Seethapathy, S., Gorecki, T., Li, X., 2008. Passive sampling in environmental analysis. *J. Chromatogr. A* 1184 (1–2), 234–253.
- Shah, M.H., Shaheen, N., 2007. Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan. *Water Air Soil Pollut.* 190 (1–4), 13–25.
- Shoeb, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* 36 (19), 4142–4151.
- Srivastava, A., Gupta, S., Jain, V.K., 2009. Winter-time size distribution and source apportionment of total suspended particulate matter and associated metals in Delhi. *Atmos. Res.* 92 (1), 88–99.
- Srivastava, D., Goel, A., Agrawal, M., 2016. Particle bound metals at major intersections in an urban location and source identification through use of metal markers. *Proc. Natl. Acad. Sci. India Sect. A (Phys. Sci.)* 86 (2), 209–220.
- Strandberg, B., Julander, A., Sjoström, M., Lewné, M., Koca Akdeva, H., Bigert, C., 2018. Evaluation of polyurethane foam passive air sampler (PUF) as a tool for occupational PAH measurements. *Chemosphere* 190, 35–42.
- Tan, J., Duan, J., Zhen, N., He, K., Hao, J., 2016. Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing. *Atmos. Res.* 167, 24–33.
- Tao, S., Cao, J., Wang, W., Zhao, J., Wang, W., Wang, Z., Cao, H., Xing, B., 2009. A passive sampler with improved performance for collecting gaseous and particulate phase polycyclic aromatic hydrocarbons in air. *Environ. Sci. Technol.* 43 (11), 4124–4129.
- Tao, S., Liu, Y., Xu, W., Lang, C., Liu, S., Dou, H., Liu, W., 2007. Calibration of a passive sampler for both gaseous and particulate phase polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 41 (2), 568–573.
- Tuduri, L., Harner, T., Hung, H., 2006. Polyurethane foam (PUF) disks passive air samplers: wind effect on sampling rates. *Environ. Pollut.* 144 (2), 377–383.
- Wang, Q., Ma, Y., Tan, J., Zheng, N., Duan, J., Sun, Y., He, K., Zhang, Y., 2015. Characteristics of size-fractionated atmospheric metals and water-soluble metals in two typical episodes in Beijing. *Atmos. Environ.* 119, 294–303.
- Wang, C.X., Zhu, W., Peng, A., Guichreit, R., 2010. Comparative studies on the concentration of rare earth elements and heavy metals in the atmospheric particulate matter in Beijing, China, and in Delft, the Netherlands. *Environ. Int.* 26, 309–311.
- Xiao, Y.H., Liu, S.R., Tong, F.C., Kuang, Y.W., Chen, B.F., Guo, Y.D., 2014. Characteristics and sources of metals in TSP and PM_{2.5} in an urban forest park at Guangzhou. *Atmosphere* 5 (4), 775–787.
- Xu, W., Yan, W., Zhang, G., Li, J., Miao, L., Huang, W., 2014. Levels and distribution of heavy metals in atmospheric particulate matters over the northern South China Sea. *Environ. Sci. Pollut. Res. Int.* 21 (14), 8774–8781.