

# First long-term and near real-time measurement of trace elements in China's urban atmosphere: temporal variability, source apportionment, and precipitation effect

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**Abstract:** Atmospheric trace elements, especially metal species, are an emerging environmental and health concern with insufficient understanding of their levels and sources in Shanghai, the most important industrial megacity in China. Here we continuously performed a one-year (from March 2016 to February 2017) and hourly-  
25 resolved measurement of eighteen elements in fine particles (PM<sub>2.5</sub>) at the Shanghai urban center with a Xact multi-metals monitor and several collocated instruments. Mass concentrations (mean±1σ; ng m<sup>-3</sup>) determined by Xact ranged from detection limits (nominally 0.1 to 20 ng m<sup>-3</sup>) to 15 μg m<sup>-3</sup>. Element-related oxidized species comprised

an appreciable fraction of  $PM_{2.5}$  during all seasons, accounting for 8.3% on average. As  
30 a comparison, the atmospheric elements concentration level in Shanghai was  
comparable with that in other industrialized cities in East Asia but one or two orders of  
magnitude higher than at sites in North America and Europe. Positive matrix  
factorization (PMF) was applied to identify and apportion the sources of the elements  
in the  $PM_{2.5}$  mass. Five different factors were resolved (notable elements and relative  
35 contribution in parentheses): traffic-related (Ca, Fe, Ba, Si; 46%), shipping (V, Ni; 6%),  
nonferrous metal smelting (Ag, Cd, Au; 15%), coal combustion (As, Se, Hg, Pb; 18%),  
and ferrous metal smelting (Cr, Mn, Zn; 15%). The contribution from the exhaust and  
non-exhaust vehicle emissions, i.e., the traffic-related factor shows a strong bimodal  
diurnal profile with average concentration over two times higher during the rush hour  
40 than during nighttime. The shipping factor was firmly identified because V and Ni, two  
recognized tracers of shipping emissions, are almost exclusively transported from the  
East China Sea and their ratio (around 3.2) falls within the variation range of V/Ni ratios  
in particles emitted from heavy oil combustion. Interestingly, nearly half of the K was  
derived from coal combustion with high mineral affinity (elements associated with  
45 aluminosilicates, carbonates and other minerals in coal ash). The contributions of  
(non)ferrous metal smelting to the trace elements are consistent with a newly-developed  
emission inventory. Although the precipitation scavenging effect on the mass  
concentration of the trace elements varied among different species and sources,  
precipitation could effectively lower the concentration of the traffic- and coal  
50 combustion-related trace elements. Therefore, water spray to simulate natural types of  
precipitation could be one of the abatement strategies to facilitate the reduction of  
ambient  $PM_{2.5}$  trace elements in the urban atmosphere. Collectively, our findings in this  
study provide baseline levels and sources of trace elements with high detail, which are  
needed for developing effective control strategies to reduce the high risk of acute  
55 exposure to atmospheric trace elements in China's megacities.

## 1 Introduction

It is well known that personal exposure to atmospheric aerosols have detrimental consequences and aggravating effects on human health such as respiratory, cardiovascular, and allergic disorders (Pope III et al., 2002, 2009; Shah et al., 2013; 60 West et al., 2016; Burnett et al., 2014). Among the chemical components relevant for aerosol health effects, airborne heavy metals (a very imprecise term without authoritative definition (John, 2002), loosely referring to elements with atomic density greater than  $4.5 \text{ g cm}^{-3}$  (Streit, 1991)) are of particular concern as they typically feature unique properties of bioavailability and bioaccumulation (Morman and Plumlee, 2013; 65 Tchounwou et al., 2012; Fergusson, 1990; Kastury et al., 2017), representing 7 of the 30 hazardous air pollutants identified by the United States Environmental Protection Agency (USEPA) in terms of posing the greatest potential health threat in urban areas (see [www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants](http://www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants)). Depending on the aerosol composition, extent and time of exposure, previous studies have confirmed that 70 most elemental components of fine particles ( $\text{PM}_{2.5}$ ; particulate matter with aerodynamic diameter equal to or less than  $2.5 \mu\text{m}$ ) exert a multitude of significant diseases from pulmonary inflammation, to increased heart rate variability, to decreased immune response (Fergusson, 1990; Morman and Plumlee, 2013; Leung et al., 2008; Hu et al., 2012; Pardo et al., 2015; Kim et al., 2016).

75 Guidelines for atmospheric concentration limits of many trace elements are provided by the World Health Organization (WHO) (WHO, 2005). In urban atmospheres, ambient trace elements typically represent a small fraction of  $\text{PM}_{2.5}$  on a mass basis, while elemental species like Cd, As, Co, Cr, Ni, Pb and Se are considered as human carcinogens even in trace amounts (Iyengar and Woittiez, 1988; Wang et al., 2006; 80 Olujimi et al., 2015). It has been shown that Cu, Cr, Fe and V have several oxidation states that can participate in many atmospheric redox reactions (Litter, 1999; Brandt and van Eldik, 1995; Seigneur and Constantinou, 1995; Rubasinghege et al., 2010a), which can catalyze the generation of reactive oxygenated species (ROS) that have been associated with direct molecular damage and with the induction of biochemical 85 synthesis pathways (Charrier and Anastasio, 2012; Strak et al., 2012; Rubasinghege et

al., 2010b; Saffari et al., 2014; Verma et al., 2010; Jomova and Valko, 2011). Additionally, lighter elements such as Si, Al and Ca are the most abundant crustal elements next to oxygen, which can typically constitute up to 50% of the elemental species in remote continental aerosols (Usher et al., 2003; Ridley et al., 2016). These species are usually associated with the impacts of aerosols on respiratory diseases and climate (Usher et al., 2003; Tang et al., 2017).

Health effects of airborne elemental species are not only seen from chronic exposure, but also from short-term acute concentration spikes in the ambient air (Kloog et al., 2013; Strickland et al., 2016; Huang et al., 2012). In addition, atmospheric emissions, transport, and exposure of trace elements to human receptors may depend upon rapidly evolving meteorological conditions and facility operations (Tchounwou et al., 2012; Holden et al., 2016). Typical ambient trace element sampling devices collect 12 to 24-hr integrated average samples, which are then sent off to be lab analyzed in a time-consuming and labor-intensive way. As a consequence, daily integrated samples inevitably ignore environmental shifts with rapid temporality, and thereby hinder the efforts to obtain accurate source apportionment results such as short-term elements pollution spikes related to local emission sources. In fact, during a short-term trace elements exposure event, 12 or 24-hr averaged sample concentrations for elemental species like Pb and As may be one order of magnitude lower than the 4-hr or 15-min average concentration from the same day (Cooper et al., 2010). Current source apportionment studies are mainly performed by statistical multivariate analysis such as receptor models (e.g., Positive Matrix Factorization, PMF), which could greatly benefit from high inter-sample variability in the source contributions through increasing the sampling time resolution. In this regard, continuous monitoring of ambient elemental species on a real-time scale is essential for studies on trace element sources and their health impacts.

Currently, there are only a few devices available for the field sampling of ambient aerosols with sub-hourly or hourly resolution, i.e., the Streaker sampler, the DRUM

(Davis Rotating-drum Unit for Monitoring) sampler, and the SEAS (Semi-continuous  
115 Elements in Aerosol Sampler) (Visser et al., 2015a, 2015b; Bukowiecki et al., 2005;  
Chen et al., 2016). Mass loadings of trace elements collected by these samplers can be  
analyzed with highly sensitive accelerator-based analytical techniques, in particular  
particle-induced X-ray emission (PIXE) or synchrotron radiation X-ray fluorescence  
(SR-XRF) (Richard et al., 2010; Bukowiecki et al., 2005; Maenhaut, 2015; Traversi et  
120 al., 2014). More recently, Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS)  
(Murphy et al., 1998; Gross et al., 2000; DeCarlo et al., 2006), the National Institute for  
Standards and Technology (NIST)-traceable reference aerosol generating method  
(QAG) (Yanca et al., 2006), distance-based detection in a multi-layered device (Cate et  
al., 2015), environmental magnetic properties coupled with support vector machine (Li  
125 et al., 2017), and the Xact<sup>TM</sup> 625 automated multi-metals analyzer (Fang et al., 2015;  
Jeong et al., 2016; Phillips-Smith et al., 2017; Cooper et al., 2010) have been developed  
for more precise, accurate, and frequent measurement of ambient elemental species.  
The Xact method is based on nondestructive XRF analysis of aerosol deposits on a  
moving filter tape, which has been validated by the US Environmental Technology  
130 Verification testing and several other field campaigns (Fang et al., 2015; Phillips-Smith  
et al., 2017; Jeong et al., 2016; Yanca et al., 2006; Cooper et al., 2010; Park et al., 2014;  
Furger et al., 2017).

Located at the heart of the Yangtze River Delta (YRD), Shanghai is home to nearly 25  
million people as of 2015, making it the largest megacity in China (Chang et al., 2016).  
135 Shanghai city is one of the main industrial centers of China, playing a vital role in the  
nation's heavy industries, including but not limited to, steel making, petrochemical  
engineering, thermal power generation, auto manufacture, aircraft production, and  
modern shipbuilding (Normile, 2008; Chang et al., 2016; Huang et al., 2011). Shanghai  
is China's most important gateway for foreign trade and has the world's busiest port,  
140 handling over 37 million standard containers in 2016 (see  
[www.simic.net.cn/news\\_show.php?lan=en&id=192101](http://www.simic.net.cn/news_show.php?lan=en&id=192101)). As a consequence, Shanghai  
is potentially subject to substantial quantities of trace element emissions (Duan and Tan,

2013; Tian et al., 2015). Ambient concentrations of trace element, especially Pb and Hg, in the Shanghai atmosphere have been sporadically reported during the past two decades (Shu et al., 2001; Lu et al., 2008; Wang et al., 2013a; Zheng et al., 2004; Huang et al., 2013; Wang et al., 2016). Of current interest are V and Ni, which are often indicative of heavy oil combustion from ocean-going vessels (Fan et al., 2016; Liu et al., 2017). However, previous work rarely presented a full spectrum of elemental species in ambient aerosols. Furthermore, recent attribution of hospital emergency-room visits in China to PM<sub>2.5</sub> constituents failed to take short-term variations of trace elements into account (Qiao et al., 2014), which could inevitably underestimate the toxicity of aerosols and potentially mis-estimate the largest influence of aerosol components on human health effects (Honda et al., 2017).

In this study, the first of its kind, we conducted a long-term and near real-time measurement of atmospheric trace elements in PM<sub>2.5</sub> with a Xact multi-metals analyzer in Shanghai, China, from March 2016 to February 2017. The primary target of the present study is to elucidate the levels and sources of atmospheric trace elements in a complex urban environment, which can be used to support future health studies. Meanwhile, the potential effect of precipitation scavenging on the mass concentration of the trace elements was investigated to examine if water spray could be proposed as an effective approach to curb severe trace element pollution in China's urban atmosphere.

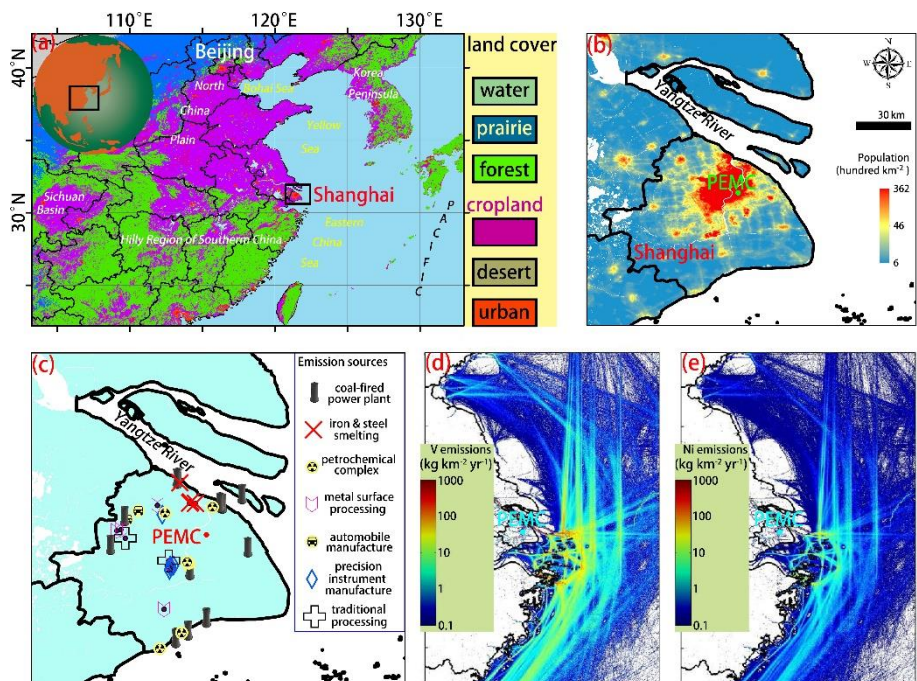
## **2 Methods**

### **2.1 Field measurements**

#### **2.1.1 Site description**

Figure 1a shows the map of eastern China with provincial borders and land cover, in which Shanghai city (provincial level) sits in the middle portion of China's eastern coast and its metropolitan area (indicated as the densely-populated area in Fig. 1b) concentrated on the south edge of the mouth of the Yangtze River. The municipality

170 borders the provinces of Jiangsu and Zhejiang to the north, south and west, and is  
 bounded to the east by the East China Sea (Fig. 1a). Shanghai has a humid subtropical  
 climate and experiences four distinct seasons. Winters are chilly and damp, with  
 northwesterly winds from Siberia sometimes causing nighttime temperatures to drop  
 below freezing. In summer, the airflow carries moist air from the Pacific Ocean to  
 175 mainland China, and it will also bring the main precipitation. The city is also susceptible  
 to typhoons in summer and the beginning of autumn. Air pollution in Shanghai is low  
 compared to other cities in northern China, such as Beijing, but still substantial by world  
 standards, especially in winter (Han et al., 2015; Chang et al., 2017).



180 **Figure 1.** Land use map indicating the location of Shanghai (a; black box), as well as  
 the population density (b) and the major point sources (c) around the sampling site  
 (PEMC). The emissions of V (d) and Ni (e) from shipping in the YRD and the East  
 China Sea within 400 km of the coastline were estimated based on an automatic  
 identification system model (adopted from Fan et al. (2016)).

185 Field measurements were performed at the rooftop (~18 m above ground level) of the  
 Pudong Environmental Monitoring Center (PEMC; 121.5447°E, 31.2331°N; ~7 m  
 above sea level) in the Pudong New Area of southwestern Shanghai, a region with dense

population (Fig. 1b). Pudong New Area is described as the "showpiece" of modern China due to its height-obsessed skyline and export-oriented economy. For the PEMC, there were no metal-related sources (except for road traffic) or high-rise buildings nearby to obstruct observations, so the air mass could flow smoothly. More broadly, as indicated in Fig. 1c, the PEMC is surrounded by a multitude of emission sources such as coal-fired power plants (CFPP) in all directions and iron and steel smelting in the northwest. Furthermore, a high level of ship exhaust emissions in 2010 such as V (Fig. 1d) and Ni (Fig. 1e) in the YRD and the East China Sea within 400 km of China's coastline was recently quantified based on an automatic identification system model (Fan et al., 2016). Therefore, the PEMC can be regarded as an ideal urban receptor site of diverse emission sources. More information regarding the sampling site has been given elsewhere (Chang et al., 2017; Chang et al., 2016).

### 2.1.2 Hourly elemental species measurements

From March 1<sup>st</sup> 2016 to February 28<sup>th</sup> 2017, hourly ambient mass concentrations of eighteen elements (Si, Fe, K, Ca, Zn, Mn, Pb, Ba, V, Cu, Cd, As, Ni, Cr, Ag, Se, Hg, and Au) in PM<sub>2.5</sub> were determined by a Xact multi-metals monitor (Model Xact<sup>TM</sup> 625, Cooper Environmental Services LLT, OR, USA) (Phillips-Smith et al., 2017; Jeong et al., 2016; Fang et al., 2015; Yanca et al., 2006). Specifically, the Xact sampled the air on a reel-to-reel Teflon filter tape through a PM<sub>2.5</sub> cyclone inlet (Model VSCC-A, BGI Inc., MA, USA) at a flow rate of 16.7 L min<sup>-1</sup>. The resulting PM<sub>2.5</sub> deposit on the tape was automatically advanced into the analysis area for nondestructive energy-dispersive X-ray fluorescence analysis to determine the mass of selected elemental species as the next sampling was being initiated on a fresh tape spot. Sampling and analysis were performed continuously and simultaneously, except during advancement of the tape (~20 sec) and during daily automated quality assurance checks. For every event of sample analysis, the Xact included a measurement of pure Pd as an internal standard to automatically adjust the detector energy gain. The XRF response was calibrated using thin film standards for each elements of interest. These standards were provided by the



manufacturer of the Xact, produced by depositing vapor phase elements on a blank Nuclepore filter (Micromatter Co., Arlington, WA, USA). The Nuclepore filter of known area was weighed before and after the vapor deposition process to determine the concentration ( $\mu\text{g cm}^{-2}$ ) of each element. In this study, excellent agreement between the measured and standard masses for each element was observed, indicating a deviation of < 5%. The 1-hr time resolution minimum detection limits (in  $\text{ng m}^{-3}$ ) were: Si (17.80), K (1.17), Ca (0.30), V (0.12), Cr (0.12), Mn (0.14), Fe (0.17), Ni (0.10), Cu (0.27), Zn (0.23), As (0.11), Se (0.14), Ag (1.90), Cd (2.50), Au (0.23), Ba (0.39), Hg (0.12), and Pb (0.13).

As a reference method to validate the Xact on-line measurements, daily  $\text{PM}_{2.5}$  samples were also collected at the PEMC site using a four-channel aerosol sampler (Tianhong, Wuhan, China) on 47 mm cellulose acetate and glass fiber filters at a flow rate of  $16.7 \text{ L min}^{-1}$ . The sampler was operated once a week with a 24-hr sampling time (starting from 10:00 am). In total 48 filter samples (26 cellulose acetate filter samples and 22 glass fiber filter samples) were collected, in which 8 paired samples were simultaneously collected by cellulose acetate and glass fiber filters. In the laboratory, the elemental analysis procedures strictly followed the latest national standard method “Ambient air and stationary source emission-Determination of metals in ambient particulate matter-Inductively coupled plasma/mass spectrometer (ICP-MS)” (HJ 657-2013) issued by the Chinese Ministry of Environmental Protection. A total of 24 elements (Al, Fe, Mn, Mg, Mo, Ti, Sc, Na, Ba, Sr, Sb, Ca, Co, Ni, Cu, Ge, Pb, P, K, Zn, Cd, V, S, and As) were measured using the Inductively coupled plasma-mass spectrometer (ICP-MS; Agilent, CA, USA). The comparisons of different measurement methods (Xact vs. ICP-MS) and different collection substrates (glass filter vs. cellulose filter) are reported in Table S1. In general, the data for elements like K, Cr, Mn, Fe, Ni, Cu, and Au proved to be of high quality, while elements like As, Cd, and Ba have relatively poor data quality.

### 2.1.3 Auxiliary measurements, quality assurance and quality control

Meteorological data, including ambient temperature ( $T$ ), relative humidity (RH), wind  
245 direction (WD) and wind speed (WS), were provided by the Shanghai Meteorological  
Bureau at Century Park station (located approximately 2 km away from the PEMC).  
The hourly mass concentrations of PM<sub>2.5</sub> at the PEMC were measured by a particulate  
monitor (Thermo, FH62C-14). The routine procedures, including the daily  
zero/standard calibration, span and range check, station environmental control, and staff  
250 certification, followed the Technical Guideline of Automatic Stations of Ambient Air  
Quality in Shanghai based on the national specification HJ/T193–2005. This was  
modified from the technical guidance established by the USEPA. Quality Assurance /  
Quality Control (QA/QC) for the Xact measurements was implemented throughout the  
campaign. The internal Pd, Cr, Pb, and Cd upscale values were recorded after the  
255 instrument's daily programmed test, and the PM<sub>10</sub> and PM<sub>2.5</sub> cyclones were cleaned  
weekly.

## 2.2 Data analysis

### 2.2.1 Positive Matrix Factorization (PMF) analysis for source apportionment

The Positive Matrix Factorization or PMF is an effective source apportionment method  
260 to identify and quantify possible emission sources of measurements using the bilinear  
factor model (Paatero and Tapper, 1994)

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}, \quad (1)$$

where  $x_{ij}$  is the  $j^{\text{th}}$  species concentration measured in the  $i^{\text{th}}$  sample,  $g_{ik}$  is the contribution  
of the  $k^{\text{th}}$  source to the  $i^{\text{th}}$  sample (factor time series) and  $f_{kj}$  is the concentration of the  
265  $j^{\text{th}}$  species in the  $k^{\text{th}}$  source (factor profiles). The part of the data remaining unexplained  
by the model is represented by the residual matrix  $e_{ij}$ . The entries of  $g_{ik}$  and  $f_{kj}$  (required  
to be non-negative) are fit using a least-squares algorithm that iteratively minimizes the  
objective function Q:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{e_{ij}}{\sigma_{ij}} \right)^2. \quad (2)$$

270 where  $\sigma_{ij}$  are the measurement uncertainties.

In this work, the US Environmental Protection Agency (EPA) PMF version 5.0 was applied to attribute PM<sub>2.5</sub> trace elements to specific factors/sources. One-year hourly-resolved measurements ( $n = 8784$ ) of eighteen elements in the PM<sub>2.5</sub> fraction were obtained and included for PMF analysis. The measurements ( $n = 1265$ ) with missing data were excluded. An estimated fractional uncertainty of 10% was used to derive the uncertainty data set (Kim et al., 2005; Kim and Hopke, 2007), which did not impact the interpretability of the PMF results. The missing values of individual elements were replaced by their geometric mean of the remaining observations, and their accompanying uncertainties were set to four times the geometric mean. The measurements below detection limit (BDL) were set to half the detection limit, with uncertainties set at five-sixths the detection limit (Polissar et al., 1998). The EPA PMF 5.0 has three uncertainty estimation methods, including bootstrapping (BS), displacement (DISP), and bootstrapping enhanced with DISP (BS-DISP) (Norris et al., 2014; Brown et al., 2015; Paatero et al., 2014; Wang et al., 2017). BS-DISP analysis is time consuming due to the huge data set ( $7519 \times 18$ ), and only BS and DISP analysis were conducted individually. Details of the uncertainty analysis are described in the supporting information (Text S1). In this study, PMF solutions using 3-10 factors were considered, and the final factor number is determined based on the interpretability as well the uncertainty analysis with the BS and DISP methods.

### 290 **2.2.2 Conditional probability function and bivariate polar plot for tracing source regions**

The determination of the geographical origins of trace elements in Shanghai requires the use of diagnostic tools such as the conditional probability function (CPF) and bivariate polar plot (BPP), which are very useful in terms of quickly gaining an idea of

295 source impacts from various wind directions and have already been successfully applied  
to various atmospheric pollutants and pollution sources (Chang et al., 2017; Carslaw  
and Ropkins, 2012). In this study, the CPF and BPP were performed on the one-year  
data set for the major trace elements with a similar source. The two methods have been  
implemented in the R “openair” package and are freely available at [www.openair-  
project.org](http://www.openair-<br/>300 project.org) (Carslaw and Ropkins, 2012).

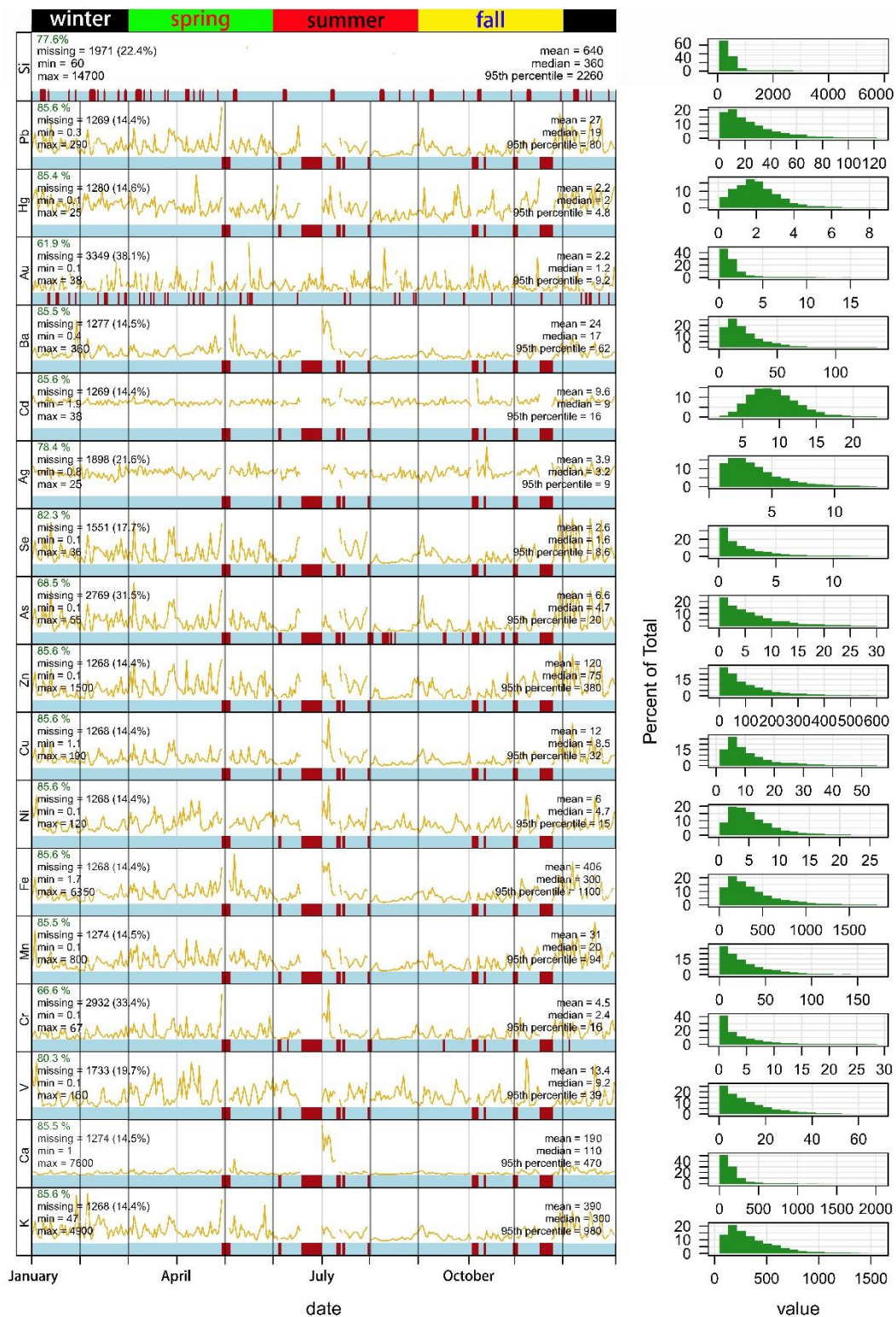
The CPF is defined as  $CPF = m_{\theta}/n_{\theta}$ , where  $m_{\theta}$  is the number of samples in the wind  
sector  $\theta$  with mass concentrations greater than a predetermined threshold criterion, and  
 $n_{\theta}$  is the total number of samples in the same wind sector. CPF analysis is capable of  
showing which wind directions are dominated by high concentrations and with which  
305 probability. In this study, the 90<sup>th</sup> percentile of a given element species was set as  
threshold, and 24 wind sectors were used ( $\Delta\theta = 15^{\circ}$ ). Calm wind ( $< 1 \text{ m s}^{-1}$ ) periods  
were excluded from this analysis due to the isotropic behavior of the wind vane under  
calm winds.

The BPP demonstrates how the concentration of a targeted species varies synergistically  
310 with wind direction and wind speed in polar coordinates, which thus is essentially a  
non-parametric wind regression model to alternatively display pollution roses but  
include some additional enhancements. These enhancements include: plots are shown  
as a continuous surface and surfaces are calculated through modelling using smoothing  
techniques. These plots are not entirely new as others have considered the joint wind  
315 speed-direction dependence of concentrations (see for example Liu et al. (2015)).  
However, plotting the data in polar coordinates and for the purposes of source  
identification is new. The BPP has been described in more detail in Carslaw et al. (2006)  
and the construction of BPP has been presented in our previous work (Chang et al.,  
2017).

## 320 **3 Results and discussion**

### **3.1 Mass concentrations**

The temporal patterns and summary statistics of the hourly elemental species concentrations determined by the Xact at the PEMC during March 2016-February 2017 are presented in Fig. 2. The one-year data set presented in the current study, to the best  
325 of our knowledge, represents the longest on-line continuous measurement series of atmospheric trace elements.



**Figure 2.** General statistical summary of 18 trace elements measured in Shanghai.

The plots in the left panel show the time series data, where blue shows the presence of data and red shows missing data. The mean daily values are shown in pale yellow scaled to cover the range in the data from zero to the maximum daily value. As such, the daily values are indicative of an overall trend rather than conveying quantitative

information. For each elemental species (at hourly resolution), the overall summary statistics are given. The panels on the right show the distribution of each elemental species using a histogram plot.

Taking the study period as a whole, the ambient average mass concentrations of the elemental species varied between the detection limit (ranging from 0.05 to 20 ng m<sup>-3</sup>) and nearly 15 µg m<sup>-3</sup>, with Si as the most abundant element (mean ± 1σ; 640 ± 1010 ng m<sup>-3</sup>), followed by Fe (410 ± 390 ng m<sup>-3</sup>), K (390 ± 330 ng m<sup>-3</sup>), Ca (190 ± 380) ng m<sup>-3</sup>, Zn (120 ± 130 ng m<sup>-3</sup>), Mn (32 ± 39 ng m<sup>-3</sup>), Pb (27 ± 26 ng m<sup>-3</sup>), Ba (24 ± 25 ng m<sup>-3</sup>), V (13 ± 15 ng m<sup>-3</sup>), Cu (12 ± 11 ng m<sup>-3</sup>), Cd (10 ± 4 ng m<sup>-3</sup>), As (7 ± 7 ng m<sup>-3</sup>), Ni (6 ± 5 ng m<sup>-3</sup>), Cr (5 ± 6 ng m<sup>-3</sup>), Ag (4 ± 2.6 ng m<sup>-3</sup>), Se (2.6 ± 2.9 ng m<sup>-3</sup>), Hg (2.2 ± 1.7 ng m<sup>-3</sup>), and Au (2.2 ± 3.4 ng m<sup>-3</sup>). According to the ambient air quality standards of China (GB 3095-2012), EU (DIRECTIVE 2004/107/EC) and WHO, the atmospheric concentration limits for Cd, Hg, As, Cr (VI), Mn, V, and Ni are 5, 50 (1000 for WHO), 6 (6.6 for WHO), 0.025, 150 (WHO), 1000 (WHO), and 20 (25 for WHO) ng m<sup>-3</sup>, respectively. Therefore, the airborne metal pollution in Shanghai is generally low by the current limit ceilings. Nevertheless, information regarding the specific metal compounds or chemical forms is rarely available given that most analytical techniques only record data for the total metal content. In the absence of this type of information, it is generally assumed that many of the elements of anthropogenic origin (especially from combustion sources) are present in the atmosphere as oxides. Here we reconstructed the average mass concentrations of metal and crustal oxides as 5.2, 5.0, 2.8, and 3.1 µg m<sup>-3</sup> in spring, summer, fall, and winter, respectively, while the annual average concentration was 3.9 µg m<sup>-3</sup>, accounting for 8.3% of the total PM<sub>2.5</sub> mass (47 µg m<sup>-3</sup>) in 2016. Detailed calculation of the reconstructed mass has been fully described elsewhere (Dabek-Zlotorzynska et al., 2011).

**Table 1.** Overview of long-term and high-time resolution measurements of ambient trace elements concentrations (ng m<sup>-3</sup>) in fine particles.

Species	Shanghai, CN <sup>a</sup>	Gwangju, KP <sup>b</sup>	London, UK <sup>c</sup>	London, UK <sup>d</sup>	Barcelona, ES <sup>e</sup>	Wood Buffalo, CA <sup>f</sup>	Toronto, CA <sup>g</sup>
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Ag	3.9	/	/	/	/	/	/
As	6.6	9.6	/	/	/	/	/
Au	2.2	/	/	/	/	/	/
Ba	24	52	10	3.7	/	/	1.9
Ca	190	120	79	50	130	54	54
Cd	9.6	/	/	/	/	/	/
Cr	4.5	/	2.3	0.8	8.0	0.04	0.24
Cu	12	15.5	13	4.9	8.0	2.0	3.1
Fe	410	290	350	120	130	60	77
Hg	2.2	/	/	/	/	/	/
K	390	730	27.2	24	82	31	27
Mn	32	24	4.8	2.5	6.0	1.1	1.8
Ni	6.0	3.8	0.5	0.2	3.0	0.08	0.21
Pb	27	49	2.3	1.8	12	/	2.4
Se	2.6	4.3	/	/	/	/	0.3
Si	640	/	/	/	/	140	/
V	13	4.6	1.3	0.6	8.0	0.21	0.11
Zn	120	100	8.9	5.3	25	0.88	11

360 **Note:** a, this study; b, Park et al., 2014; c, PM<sub>0.3-2.5</sub>, Marylebone Road, London (Visser et al., 2015b); d, PM<sub>0.3-2.5</sub>, North Kensington, London (Visser et al., 2015b); e, a road site in Barcelona (Dall'Osto et al., 2013); f, Phillips-Smith et al., 2017; g, Sofowote et al., 2015. We noticed that a huge data set of hourly resolved trace metals had been reported in Jeong et al. (2016) and Visser et al. (2015a), but that no detailed information  
365 regarding the specific mass concentrations of trace elements was given.

The toxicological effect of hazardous elemental species is more evident and well known in soils and aquatic ecosystems, while few (if any) studies on the geochemical cycle of trace metals have considered the fast dynamics of trace elements in the atmosphere. Using a diversity of chemical, physical, and optical techniques, elevated atmospheric  
370 concentrations of various element species have been observed globally; however, a tiny minority of them were performed with high time resolution. As a comparison, we compiled previous work related to the near real-time measurements of trace element concentrations in Table 1. The concentrations of most trace elements in Shanghai were commonly one or two orders of magnitude higher than those measured in Europe and  
375 North America, and generally were of the same level as in industrialized cities like Kwangju in South Korea. Exceptionally, the concentrations of V and Ni in Shanghai

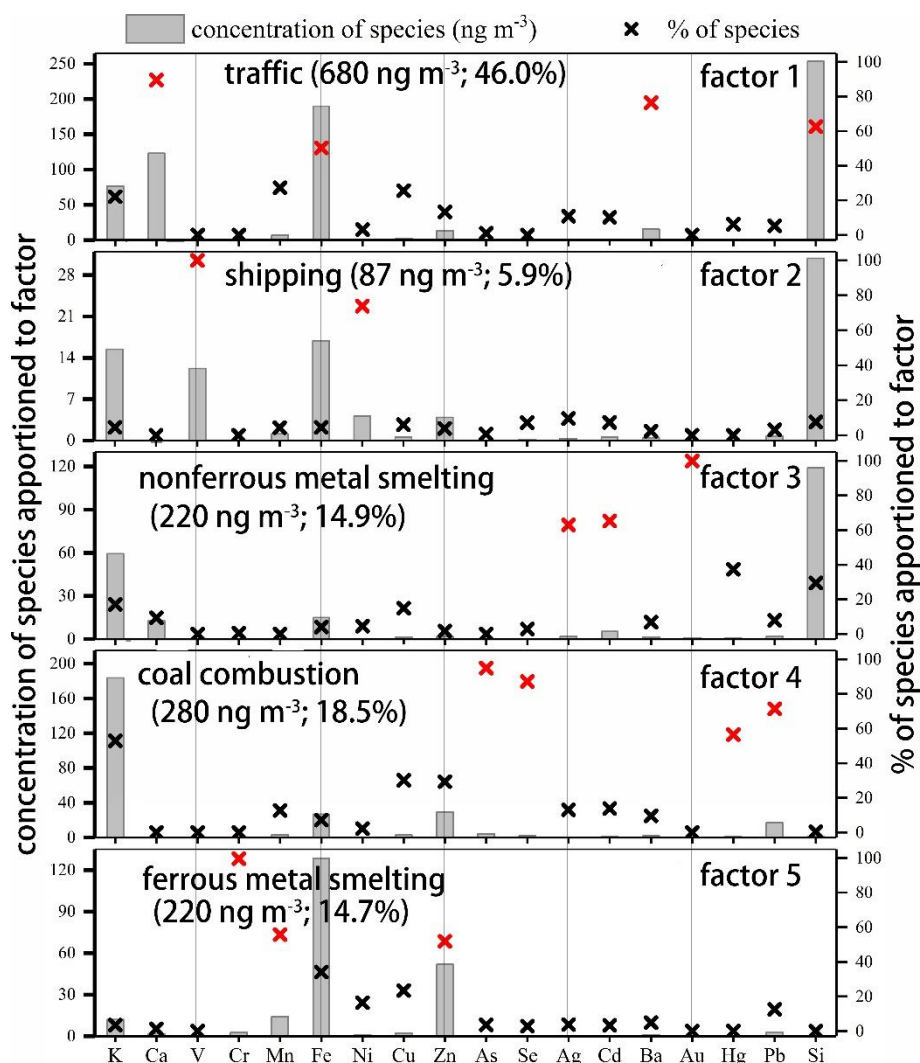


were up to three times higher than those at Kwangju City. This is expected since Shanghai has the world's busiest container port, and V and Ni were substantially and almost exclusively emitted from heavy oil combustion in ship engines of ocean-going vessels (see more discussion in Section 3.2 and 3.3).

In contrast to traditional trace element measurements, the on-line XRF used in the current study enables measurement of elemental species concentrations with 1 hr resolution, which are useful both for source discrimination and in determining the processes contributing to elevated trace element levels through investigation of their seasonal, weekly, weekday-weekend, and diurnal cycles (Fig. S2-S8; see discussion below).

### 3.2 Source analysis

In the PMF analysis, three to ten factor solutions were initially examined, from which possible solutions (i.e., four to six factor solutions) were chosen based on the change of  $Q/Q_{exp}$ , the achievement of a constant and global minimum of  $Q$ , the displacement of factor elements, and the interpretation of physically meaningful factors (Text S1; see discussion below). The most reliable solution was obtained with five factors. The chemical profiles and average contributions of the five factors are presented in Fig. 3 with the time-series evolution of these factors included in the Supplement (Fig. S9). On the one hand, we will use various mathematical and physical criteria to constrain different solutions of source apportionment. On the other hand, we will take CPF and BPP as diagnostic tools for quickly gaining the idea of potential source regions, which in turn will contribute to further analysis of source apportionment. Ultimately, the five factors were assigned to different sources, i.e., traffic-related, shipping, nonferrous metal smelting, coal combustion, and ferrous metal smelting.



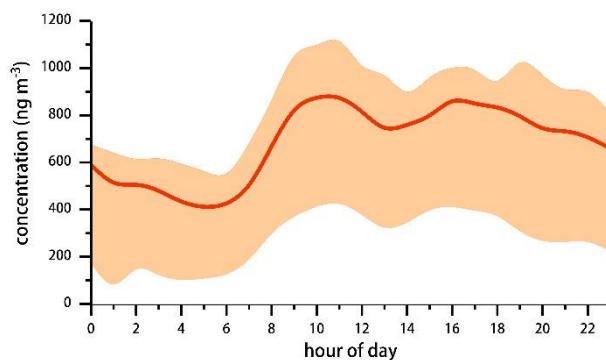
**Figure 3.** PMF-resolved source profiles (concentration and % of species apportioned to the factor) and average contributions (in the parentheses) of individual sources to the measured total PM<sub>2.5</sub> elements in Shanghai. The notable species for each factor/source are marked in red.

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### 3.2.1 Traffic-related

Factor 1 was characterized by a large mass fraction of Ca, Fe, Ba, and Si, which explained 90%, 50%, 77%, and 63% of the concentration, respectively. This mixed factor is similar to that reported by Amato et al. (2009, 2013), Bukowiecki et al. (2010), Harrison et al. (2012), and Visser et al. (2015b). In the urban atmosphere, Fe can be released from engine oil or catalyst equipped gasoline vehicles (Chen et al., 2007). Besides, Fe is linked to non-exhaust emissions such as brake wear because it is the

support material for brake pads, and the agents present in brake linings typically consist of Ba, Mn and Cu (Lough et al., 2005; Hjortenkrans et al., 2007; Dall'Osto et al., 2016).  
 415 Therefore, Fe and Ba can be regarded as chemical tracers for a traffic-related source (exhaust and non-exhaust) (Thorpe and Harrison, 2008; Lin et al., 2015). Ca and Si are known as two of the most abundant elements in the upper continental crust, and their atmospheric origin is typically attributed to wind-blown dust. Located on the eastern coast of China, Shanghai rarely receives long-range transport of crustal matter from  
 420 aeolian dust and the Gobi Desert in northwestern China (Huang et al., 2013). Sampling in the urban area of Shanghai, airborne Ca and Si should be dominated by anthropogenic activities like road fugitive dust or urban construction works. In Fig. S10, significant correlations are observed for Ca, Si, Fe, and Ba, suggesting that the measured Ca and Si during our study period were more likely derived from road fugitive  
 425 dust. Therefore, factor 1 can be assigned to a traffic-related source and it was the largest source in Shanghai, accounting for 46% ( $680 \text{ ng m}^{-3}$ ) of the total measured elemental mass in  $\text{PM}_{2.5}$ .



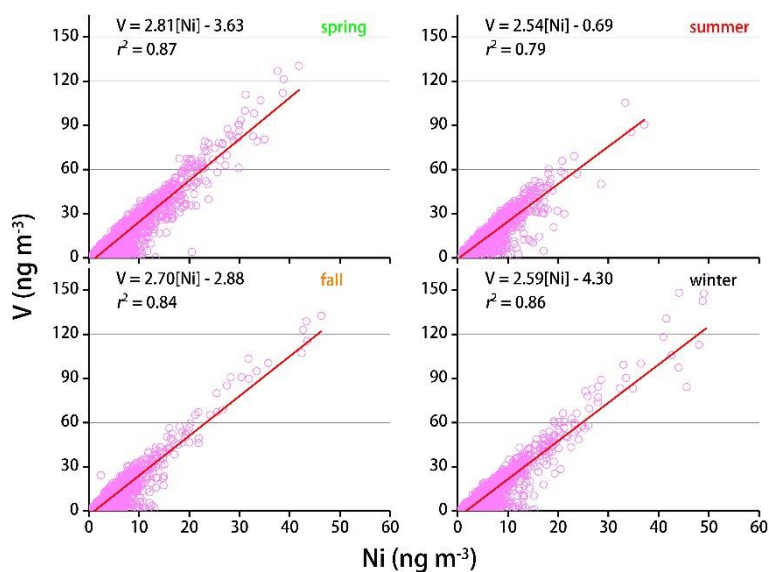
**Figure 4.** Diurnal variation of PMF-derived elemental concentration for factor 1. The  
 430 red line, bottom boundary, and upper boundary represent the mean, 1<sup>st</sup> quartile, and  
 3<sup>rd</sup> quartile of the concentration value, respectively.

Hourly measurements over one-year periods provide a unique opportunity to examine the diurnal profile of factor 1. As reported in Fig. 4, the concentration of the trace elements contributed by factor 1 shows a marked bimodal diurnal cycle, with average  
 435 values at rush hours that are over two times higher than at nighttime. Such variation

pattern agrees well with the diurnal variation of the traffic flow in Shanghai (Chang et al., 2016), further confirming that factor 1 can be interpreted as traffic-related emissions.

### 3.2.2 Shipping

In Fig. 3, V (100%) and Ni (74%) come almost exclusively from factor 2, while factor 2 contributes to less than 10% of any other elemental species. V is typically emitted from oil and petrochemical refining and combustion, and natural gas extraction and processing (Duce and Hoffman, 1976; Hope, 1994; Shafer et al., 2012). From CPF and BPP analysis (Fig. S11), higher concentrations of both V and Ni were observed when winds originated from the east, northeast, and southeast directions. The most dominant directions were east and southeast, suggesting the influence from the coastal port cluster or petroleum refinery industry located east/southeast of Shanghai (Fig. 1). Gathering evidence revealed that the ratio of V/Ni can serve as a robust indicator of shipping emissions (Tao et al., 2013; Celo et al., 2015; Liu et al., 2017; Viana et al., 2009). A recent study in Shanghai port suggested that the ratio of V/Ni in aerosols emitted from heavy oil combustion of ocean-going ship engines was 3.4 on average (Zhao et al., 2013). Here measured in the urban area, the average ratio of V/Ni in our study was 3.2 with slight seasonal changes (Fig. 5), indicating V- and Ni-containing aerosols from shipping emissions subject to minor atmospheric transformation. In short, factor 2 likely corresponds to shipping emissions (instead of petrochemical refining), which is consistent with the results of many previous source apportionment works (e.g., Liu et al., 2017; Zhao et al., 2013; Cesari et al., 2014; Healy et al., 2010).



**Figure 5.** Linear correlation analysis between Ni (x axis) and V (y axis) in Shanghai during the four seasons.

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Although shipping emissions only contribute to 5.9% of the trace elements in the Shanghai urban center, their share can be expected to greatly increase in the harbor district (Zhao et al., 2013). The good news is that since 1 January 2016, the sea areas of Shanghai and the neighboring ports were designed as shipping emission control area, requiring use of lower sulfur fuels in place of heavy fuel oil in the main engines of the ships (Zhen et al., 2018). Therefore, it is critically important to assess the impacts of fuel changes on the air quality in Shanghai in the future through continuous measurements of trace elements.

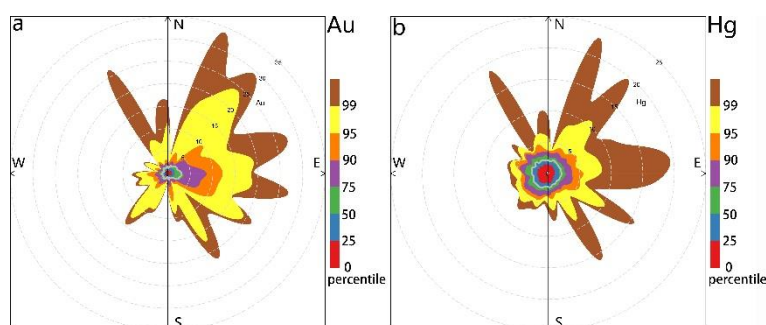
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### 3.2.3 Nonferrous metal smelting

The predominant elements found in factor 3 were Au (100%), Cd (65%), and Ag (63%) with 37% of Hg. These four heavy metals are important associated elements in Cu, Pb, and Zn ores. In fact, Cu, Pb, and Zn smelting represent the three most common forms of nonferrous metal smelting in China (Tian et al., 2015). Because of high temperatures during the roasting, sintering and smelting process for the extraction of Cu, Pb, and Zn from ores, metals like Au, Cd, Ag, and Hg in nonferrous metal ores will inevitably be vaporized and released into the flue gas (Pacyna and Pacyna, 2001; Wu et al., 2012). Therefore, factor 3 was interpreted as nonferrous metal smelting emissions and the

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contribution of this factor was 15% ( $220 \text{ ng m}^{-3}$ ) to the total measured elemental mass in  $\text{PM}_{2.5}$ .



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**Figure 6.** Percentile rose plot of Au (a) and Hg (b) concentrations in Shanghai between March 2016 and February 2017. The percentile intervals are shaded and shown by wind direction.

To further pinpoint the specific subsector of nonferrous metal smelting, here we calculate percentile concentration levels of Au and Hg, and plot them by wind direction in Fig. 6 (and Ag, Cd in Fig. S12). It clearly shows that Au and Hg largely share the same source region which is different from that for Ag and Cd, indicating that Au and Hg were emitted from a similar subsector of nonferrous metal smelting. In Shanghai, Zn smelting is the most important contributor of Hg emissions from the nonferrous metal smelting sector. Therefore, the element Au resolved in factor 3 during our study period can be expected to be originated from Zn smelting.

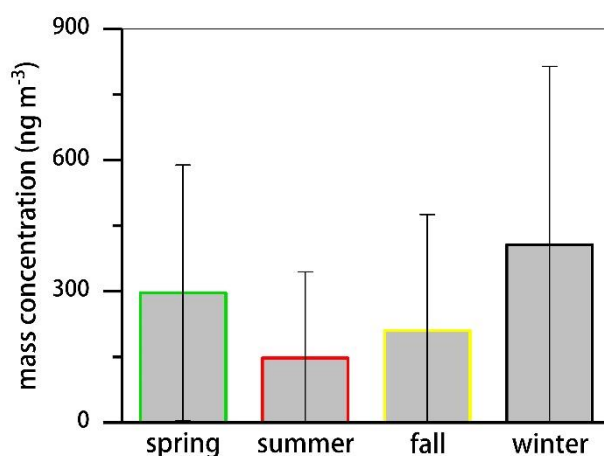
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### 3.2.4 Coal combustion

The most abundant elements found in factor 4 were As, Se, Pb, Hg (explaining 56% to 95% of the concentration) with some contributions of Cu (30%), Zn (29%) and an unexpected large amount of K (53%). As, Se, Pb, Hg, and Cu are typical marker elements for coal combustion (Morawska and Zhang, 2002). In China, 73% of As, 62% of Se, 56% of Pb, and 47% of Hg were found to be emitted from coal combustion (Tian et al., 2015). Coal consumption in southern China (including Shanghai) is mainly driven by industrial boilers and power plant, while in northern China, coal-based heating is also a major sector of coal consumption (Tian et al., 2015). Seasonally, the average

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mass concentration of coal combustion-related PM<sub>2.5</sub> trace elements during winter (410 ng m<sup>-3</sup>) was much higher than that during spring (270 ng m<sup>-3</sup>), summer (150 ng m<sup>-3</sup>), and fall (210 ng m<sup>-3</sup>) (Fig. 7). This seasonal pattern was not observed for other sources (not shown). Shanghai has a humid subtropical climate and experiences four distinct seasons. Winters are chilly and damp, with northwesterly winds from northern China transporting air pollutants (including trace elements) caused by coal-based heating to the Shanghai atmosphere (Huang et al., 2013; Chang et al., 2017). As the largest city-scale coal consumer in China, coal combustion contributed to 280 ng m<sup>-3</sup> or 19% of the PM<sub>2.5</sub> trace elements during our study period.



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**Figure 7.** Seasonal variation of elemental concentrations contributed by coal combustion in Shanghai. The error bar indicates one standard derivation.

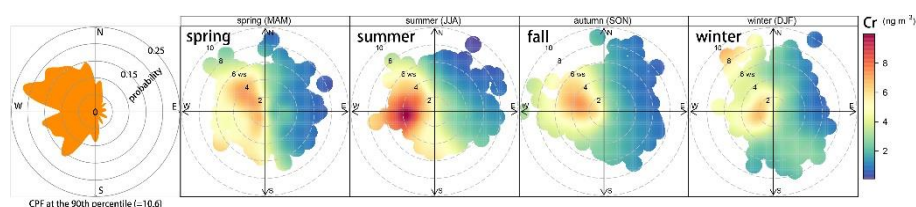
Traditionally, K in particles is considered to originate from biomass burning along with some contribution of fugitive dust (Zhang et al., 2010; Hueglin et al., 2005; Fang et al., 2015). Here we show that over half of the element K in urban Shanghai was derived from coal combustion. The reason for this discrepancy may be that in most previous studies, K in particles was pretreated using deionized water to extract (Wang et al., 2013b). In fact, K has a high mineral affinity (elements associated with aluminosilicates, carbonates and other minerals in coal ash), and in some extreme cases, only about 1% of K in fly ash from coal combustion can be extracted by water (Querol et al., 1996). For example, particles collected from coal combustion by Wang et al. (2013b) were extracted with deionized water, then atomized and measured by an ATOFMS. The

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ATOFMS mass spectrum contained a relatively low K peak. The observation by Wang et al. (2013b) was not consistent with that of Suess (2002), who observed larger K peaks in ATOFMS spectra for coal combustion particles in an in situ measurement (i.e., freshly emitted particles were directly introduced into the ATOFMS and measured).

### 3.2.5 Ferrous metal smelting

Factor 5 was distinguished by high levels of Cr, Mn, and Zn representing 100%, 56%, and 52% of the concentration, respectively. These elements are typically emitted from ferrous metal smelting. For example, the steel production industry represents the dominant contributor to Zn emissions, accounting for about 60% in China (Tian et al., 2015). Driven by rapid modernization of its infrastructure and manufacturing industries, China produced more than 49% of the world steel production in 2017 (around 830 million tons), and 6 of 10 of the largest steel producers are in China (data retrieved from <https://www.worldsteel.org>). Headquartered in Shanghai (20 km northwest of the sampling site), the Baosteel is the fifth-largest steel producer in the world measured by crude steel output, with an annual output of around 35 million tons. Meanwhile, there are several factories of ferrous metal processing located in western Shanghai (Fig. 1). Since the element Cr is reported to be transported over substantial distances by the air (Perry et al., 1999), the presence of ferrous metal smelting activities in the west/northwest of the sampling site is inferred to be associated with this factor based on the results of CPF and BBP in Fig. 8. Overall, ferrous metal smelting contributed 220 ng m<sup>-3</sup> or 15% of the PM<sub>2.5</sub> trace elements in Shanghai.



**Figure 8.** Conditional probability function analysis (left) and bivariate polar plots (right) of seasonal concentrations (in ng m<sup>-3</sup>) of Cr in Shanghai between March 2016 and February 2017. The center of each plot (centered at the sampling site) represents a wind speed of zero, which increases radially outward. The concentration is shown by



the color scale.

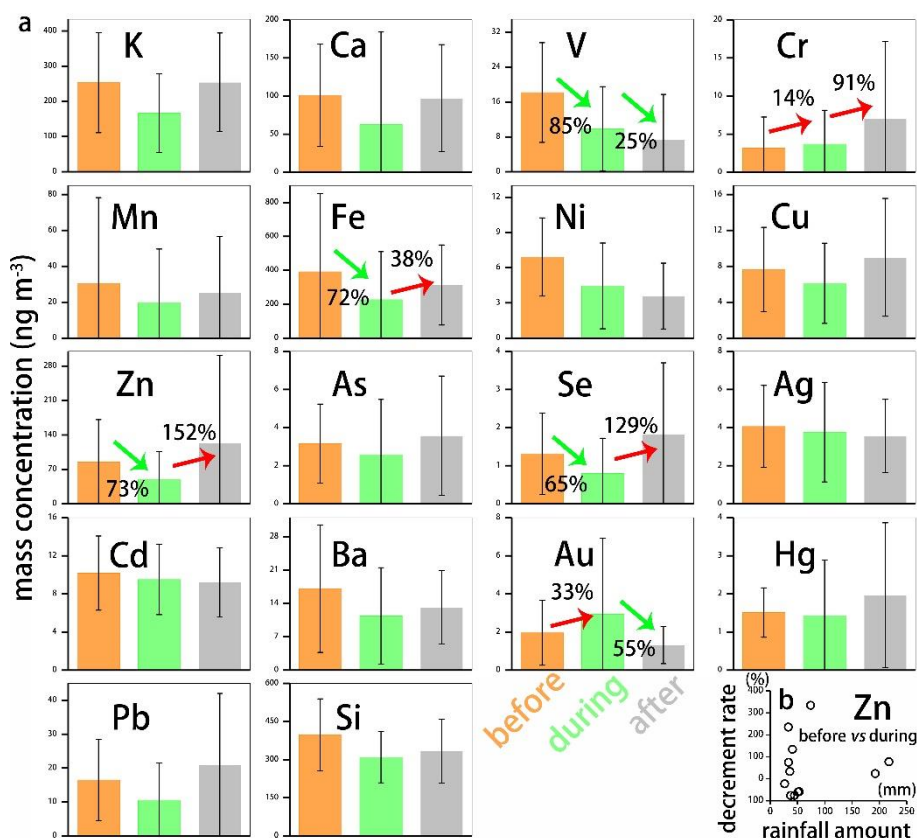
### 550 **3.3 Precipitation effect**

Theoretically, precipitation could enhance the wet scavenging of airborne pollutants and reduce their ability to suspend because the increased moisture might capture the particles (Kuhns et al., 2003; Karanasiou et al., 2011). Water spray (from sprinkler on road or atop a tall building) to simulate natural types of precipitation has been proposed  
555 as an important abatement strategy to facilitate the reduction of ambient PM concentrations (including trace elements) in urban China (Liu et al., 2014; Yu, 2014). However, several field measurements revealed that water spray activities did not influence the PM mass levels (e.g., Karanasiou et al., 2012; Karanasiou, 2014). Taking advantage of our simultaneous and hourly record of the precipitation amount (up to 37  
560 mm) and the elemental concentration, here we evaluate the effects of precipitation on the mitigation of PM<sub>2.5</sub> trace elements. The precipitation (all were in the form of rainfall) distributed during the full year of measurements is shown in Figure S13. The mass concentrations of the trace elements six hours before and after precipitation events were compared from the perspective of individual species and sources. A precipitation event  
565 in this study is defined as (1) there are at least six consecutive hours with hourly rainfall amount higher than 1 mm; (2) the consecutive no-rainy time in a precipitation event should be less than six hours; (3) the total no-rainy time should be less than 1/3 of the entire time of a precipitation event; (4) if the rainfall amount of a specific hour is less than 0.1 mm, and there are at least three no-rainy hours before and after the rainy hour,  
570 then this hour should be treated as a no-rainy hour. Consequently, 12 precipitation events during our study period were identified with a duration time and accumulated rainfall ranging from 7 to 55 hours, and 26 to 220 mm, respectively (Table S2).

#### **3.3.1 Change of mass concentration by species**

The average mass concentration of each elemental species before, during, and after  
575 every precipitation event is presented in Fig. S14. If precipitation effectively scavenges and removes aerosol, then the mass concentrations of trace elements during a precipitation event should be lower than that before and after this precipitation event.

580 However, there is no uniform variation pattern in Fig. S14, indicating that precipitation may not be the predominant factor to influence the ambient elemental mass in some cases. For example, most elemental species had a relatively higher mass concentration during the 12<sup>th</sup> precipitation event (which lasted from 09:00 25 December to 22:00 26 December; Fig. S14). This can be explained by the much less anthropogenic activities during the periods prior to (3:00 to 8:00) and after (23:00 to 3:00 the next day) the 12<sup>th</sup> precipitation event.



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**Figure 9.** (a) Variation of the overall mass concentration of each elemental species before, during, and after the total 12 precipitation events; (b) scatter plot of the relationship between the rainfall amount of each precipitation event and the decrease rate of the Zn concentration from the period before precipitation to the period after precipitation.

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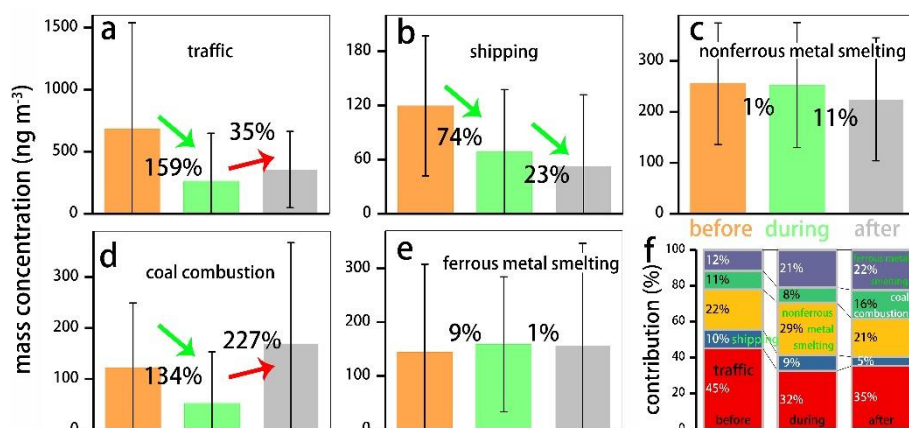
For each elemental species, the variation of mass concentration before, during, and after every precipitation event was aggregated and reported in Fig. 9a. Before the precipitation events, the mass concentrations of all species except Cr and Au were higher than those during the precipitation events (notably V, Zn, Fe), suggesting that

595 water spray could generally help to reduce the PM<sub>2.5</sub> trace elements load in the atmosphere. After the precipitation events, there were six species (notably V and Au) with their mass concentrations lower than during the precipitation events, indicating a potential long-lasting aftereffect of precipitation scavenging. Among all elemental species, the mass concentrations of Zn and Se fluctuate as a most ideal V-shape, which  
600 properly reflects the cycle of precipitation. However, as shown in Fig. 9b, a linear relationship cannot be observed between the decrease rate of the Zn concentration and the rainfall amount of each precipitation event. Although we failed to pinpoint the exact value in this study, our results imply that there is a threshold of precipitation amount to lower the ambient PM<sub>2.5</sub> trace elements mass.

### 605 **3.3.2 Change of mass concentration by sources**

The variation of the overall mass concentration of trace elements contributed by each source and their relative contributions before, during, and after the total 12 precipitation events is shown in Fig. 10a to 10e, and Fig. 10f, respectively. The mass concentration of traffic-related trace elements experienced the sharpest decrease during the transition  
610 of no-rainy hours to rainy hours (159%), and a moderate rebound after precipitation (35%). Fang et al. (2015) found that mobile source emissions generated through mechanical processes (re-entrained road dust, tire and brake wear) and processing by secondary sulfate were major contributors to water-soluble metals. In our study, traffic-related sources mainly include road dust and brake wear, which can not only be easily  
615 removed through precipitation but also can hardly be blown up from wet road surfaces after raining. In comparison, the mass contribution of the coal combustion source was also wet removed rapidly first (139%) due to its tracer elements like As, Se, Pb, and Hg having a larger water-soluble fraction. However, after precipitation, the contribution of the coal combustion source dramatically increased over two times (Fig. 10d and 10f).  
620 This can be explained that different from the traffic-related source, the coal combustion-related trace elements are generally emitted through elevated chimneys in the sectors of industrial boilers and power plants. The mass concentrations of trace elements contributed by nonferrous and ferrous metal smelting during the three periods remained

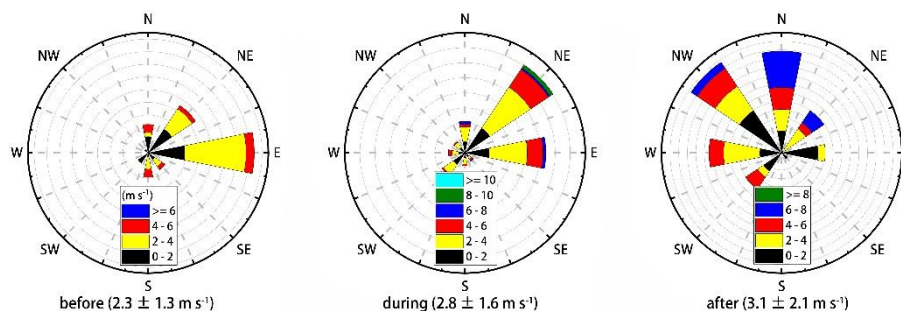
quite flat (Fig. 10c and 10d), suggesting that precipitation has little effect on ambient  
 625 trace elements emitted from metal smelting activities. Nevertheless, given that traffic-  
 related and coal combustion are the dominant contributors to ambient PM<sub>2.5</sub> trace  
 elements, our results validate that water spray could be an effective approach to help  
 curb the severe atmospheric metal pollution in many Chinese cities.



630 **Figure 10.** Variation of the overall mass concentration of trace elements contributed  
 by traffic-related (a), shipping (b), nonferrous metal smelting (c), coal combustion  
 (d), and ferrous metal smelting (e), and their relative contributions (f) before, during,  
 and after the total 12 precipitation events.

In Fig. 10b and 10f, the contribution of shipping emissions to ambient trace elements  
 635 (mainly V and Ni) during the three periods reduced continuously. Mostly transported  
 from the Eastern China sea, V and Ni almost exclusively originated from the east of the  
 sampling site. In other words, the contribution of shipping emissions to the urban  
 atmosphere is supposed to be very sensitive to wind speed and wind direction in  
 Shanghai. The wind roses for the three periods are presented in Fig. 11. It shows that  
 640 before precipitation events, the average wind speed ( $\pm 1\sigma$ ) was the lowest ( $2.3 \pm 1.3$  m  
 $s^{-1}$ ), and easterly winds prevail in most times. These factors are favorable to the  
 transportation of shipping emissions from the Eastern China sea which then  
 accumulated in the Shanghai urban atmosphere. In contrast to the period before  
 precipitation events, the average wind speed after precipitation events was the highest  
 645 ( $3.1 \pm 2.1$  m  $s^{-1}$ ) with northwesterly and northerly winds from mainland China which  
 can dilute shipping-related trace elements to the lowest levels (Fig. 10b). In brief, the

mass concentration of shipping-related trace elements in the Shanghai urban atmosphere is more likely to be influenced by winds instead of precipitation.



650 **Figure 11.** Wind roses for the periods before, during, and after the twelve precipitation events. The average wind speed ( $\pm 1\sigma$ ) for each period is shown in parentheses.

#### 4. Conclusion and outlook

This paper presents the results from a year-long, near real-time measurement study of  
655 18 trace elements (Si, Fe, K, Ca, Zn, Mn, Pb, Ba, V, Cu, Cd, As, Ni, Cr, Ag, Se, Hg, and Au) in  $\text{PM}_{2.5}$  using a Xact multi-metals monitor, conducted at an urban site in Shanghai from March 2016 to February 2017. The scientific significance of this work can be reflected by the general findings as follows:

-The Xact multi-metals monitor was demonstrated as a valuable and practical tool for  
660 ambient monitoring of atmospheric trace elements by comparing online monitoring results with ICP analyses of offline filter samples.

-The metal concentrations in Shanghai are one or two orders of magnitude higher than in north America and Europe, highlighting the need to allocate more scientific, technical, and legal resources on controlling metal emissions in China.

665 -The total of the metal related species amounted to approximately 8.3% of the  $\text{PM}_{2.5}$  mass, which should not be ignored in China's recent epidemiologic study of attributing hospital emergency-room visits to  $\text{PM}_{2.5}$  chemical constituents.

-The full coverage of trace elemental species (18) and the high temporal frequency (hourly) in the work provided unprecedented details regarding the temporal evolution

670 of metal pollution and its potential sources in Shanghai.

-Five sources, i.e., traffic-related, shipping, nonferrous metal smelting, coal combustion, and ferrous metal smelting were identified by PMF analysis, which contributed to 46%, 6%, 15%, 18%, and 15% of the ambient PM<sub>2.5</sub> trace elements, respectively.

-The dominant contributors of trace elements (traffic-related and coal combustion) can  
675 be effectively removed through precipitation from the atmosphere, suggesting that water spray can be used to curb PM<sub>2.5</sub> trace elements in the urban atmosphere.

A greater value and more interesting topic to the scientific community would be to fully assess the role of PM<sub>2.5</sub> chemical constituents (including metal species) and emission sources to human health. Looking towards the future, three major steps will be taken  
680 toward thoroughly addressing these questions. Firstly, characterizing the chemical and isotopic (including metal species) signatures of emission sources will be intensively undertaken through field sampling as well as for laboratory simulations (see example of Geagea et al. (2007)). Secondly, the Xact multi-metals monitor, Sunset OC/EC analyzer (Chang et al., 2017), and MARGA (Monitoring of AeRosols and Gases)  
685 platform will be collocated across a rural-urban-background transect to simultaneously measure hourly metal species, carbonaceous aerosols, and inorganic aerosol components in PM<sub>2.5</sub>. Lastly, integrating all available information regarding PM<sub>2.5</sub> chemical species and isotopes into a receptor model or atmospheric chemical transport model will be carried forward to create more specific and confident source  
690 apportionment results.

### **Competing interests**

The authors declare that they have no competing interests.

### **Data availability**

Data are available from the corresponding authors on request.

### **695 Acknowledgments**

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