We greatly thank the reviewers for their insightful comments, which we've addressed (in bold) point by point in our reply letter below. The revised MS is attached after the reply letter. We are sorry for the delay due to the family affairs of the first author.

Anonymous Referee #1

General comments

The manuscript discusses 1-year continuous measurements of 18 major and trace elements with an online XRF spectrometer in Shanghai, China. The authors argue that some trace elements are affecting human health in various ways, and that knowing the sources and behavior of trace elements will help in reducing these risks. The high time resolution of the measurements (1 hour) enables detection of concentration spikes, with their short-term acute exposure of humans. The dataset is analyzed with various statistical methods to attribute possible sources to the different elements and combinations. This is the first published year-long measurement of $PM_{2.5}$ metals with hourly time resolution. The structure of the manuscript, the results and the presentation of the material are good. The topic is relevant and well worth publication in ACP. There are, however, a few changes and additions required before publication.

Many thanks for the favorable comments and constructive suggestions.

Specific comments

Considering the traditional methods of highly time-resolved trace element sampling and analysis it is stated (L121), '. . .they require a large commitment of analytical time.' This is not fully precise. Analyzing a sample may require only a few seconds (20 s up to a few minutes), which is quite fast. The problem is rather to get access to the accelerator facilities and enough beam time to analyze thousands of samples of one single field campaign. Compared to wet-chemical techniques like ICP-MS, PIXE/SR-XRF is not so bad with respect to analysis time. Maybe some rewording might clarify this point.

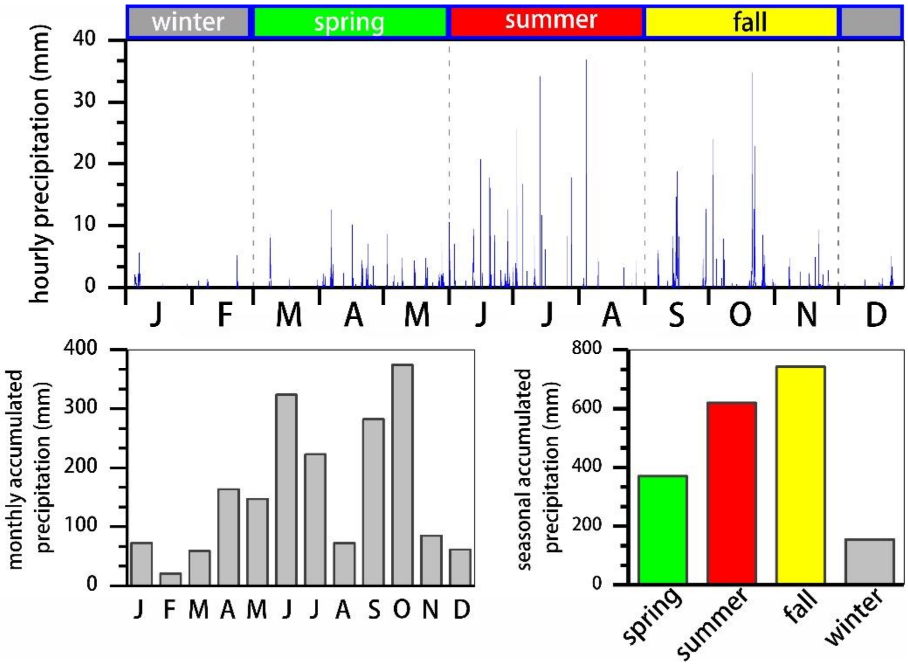
Fully agree. The sentence '. . .they require a large commitment of analytical time' has been deleted in the revised MS.

In Section 2.1.1 the climatological description should be extended to better understand the seasonal variations of the data. Only the winter is characterized so far. To explain seasonal concentration statistics, the meteorological data should also be split seasonally, especially the wind data and precipitation. How is precipitation distributed during the full year of measurements? Does precipitation produce substantial cleansing of the polluted atmosphere? Is there a seasonal wind pattern (e.g. monsoon flow), or is the wind more or less equally distributed over the year? This might be relevant for explaining the origin of the coal combustion emissions in Fig. 17. The discussion of element concentration variations in Section 3.1.2 will also benefit from more climate information.

We appreciate the useful comments, in which the potential effect of wet cleaning on the mass concentrations of trace elements had also been mentioned by referee #2.

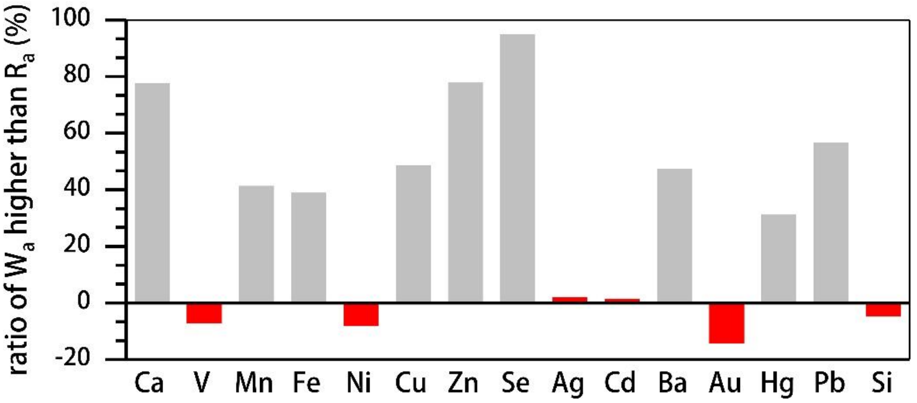
1) How is precipitation distributed during the full year of measurements?

The figure below shows the variations of precipitation at hourly, monthly, and seasonal scales during the full year of measurements. It is clear that the amount of precipitation in winter is much lower than that of other seasons.



2) Does precipitation produce substantial cleansing of the polluted atmosphere?

The short answer is that precipitation produced different cleansing effects on the measured trace elements. In the whole 8760 hours (W in short), there were 1078 hourly rainfall events (R in short) occurred during the full year of our measurements. Here the average mass concentrations of a given species for W and R are defined as W_a and R_a, respectively. The ratio of W_a higher than R_a ($[W_a-R_a]/R_a*100$) for the 15 trace elements is illustrated in the figure below, in which 6 of them (denoted in red) are close or lower than 0, suggesting that they were not influenced by wet scavenging. Note that the R_a for trace elements of K, Cr, and As are not included due to the number of the data points is lower than 719 (two thirds of the 1078 hourly rainfall events).

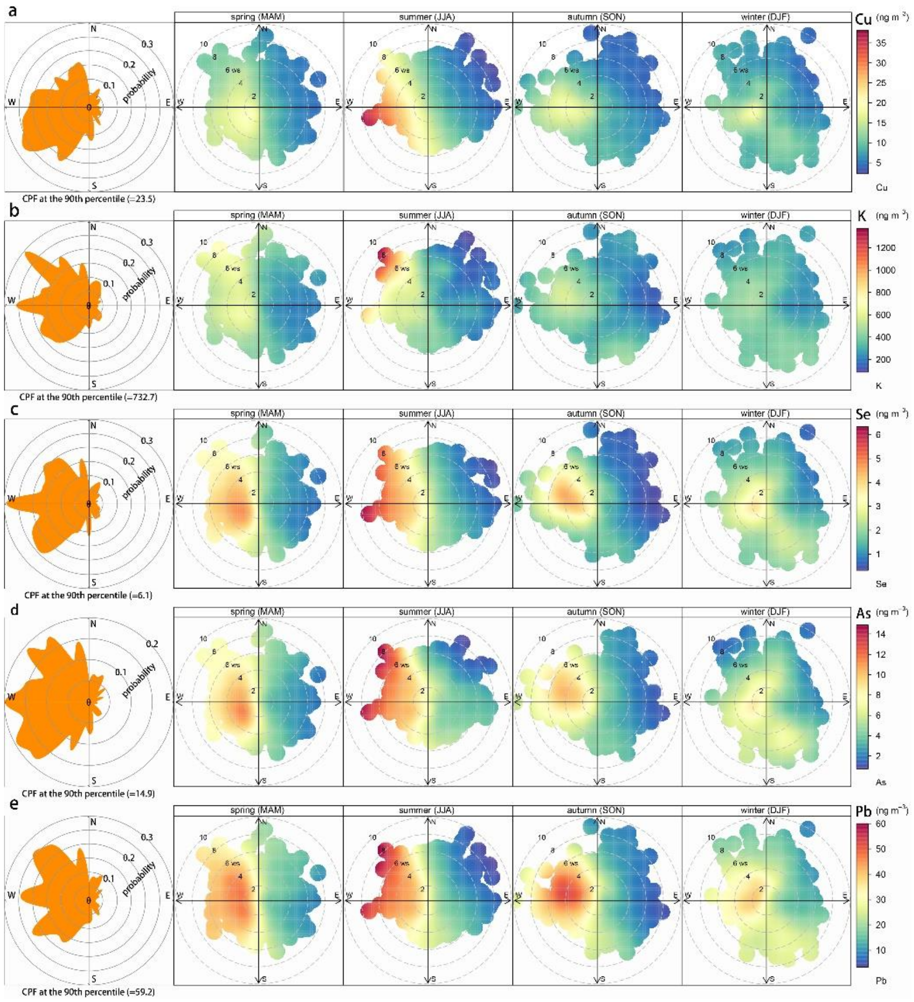


3) **Is there a seasonal wind pattern (e.g. monsoon flow), or is the wind more or less equally distributed over the year? This might be relevant for explaining the origin of the coal combustion emissions in Fig. 17. The discussion of element concentration variations in Section 3.1.2 will also benefit from more climate information.**

As we mentioned in the MS that Shanghai has a humid subtropical climate and experiences four distinct seasons. Winters are chilly and damp, with northwesterly winds from Siberia can cause nighttime temperatures to drop below freezing. In summer, airflow carries moist air from the Pacific Ocean to mainland China. The city is also susceptible to typhoons in summer and the beginning of autumn.

We agree that our discussion related to the explanation of potential sources should be divided into two dimensions: emission sources and winds direction. Specifically, in Fig. 17, the potential source regions of Cu, K, Pb, As, and Se are identified

(shown as below), in which all species are generally transported from far western Shanghai. From the perspective of emission sources, the activities of stationary combustion of coal were concentrated in western Shanghai. Besides, although winds direction in Shanghai varies distinctly in four seasons, western Shanghai was constantly as the most possible source region. Collectively, we concluded that ambient concentrations Cu, K, Pb, As, and Se were mainly originated from coal combustion.



Another point is the statistics of the wind data, as shown in Figures 6 and S1. It is unclear how the wind data were processed for statistical analyses. As wind is a vector quantity, averaging and statistics should be done component-wise for u (east-west) and v (north-south) components. Averaging of wind directions may lead to stupid results, e.g. 350 and 10 degs would arithmetically average to 180 degs (a south wind), meteorologically however to 0 degs (a north wind). It is not evident from the description, whether the statistics packages used handle wind data correctly. From Figs. 6d and S1 the small variation of wind direction over 1 year appears doubtful, unless strong channeling of the wind had occurred. Furthermore, it is not clear how the wind direction as a circular distribution has been normalized. Here, a short explanation of the normalization procedure used would be helpful, also for interpreting the figures 5, 6, 8, 9, 10, 11.

We are sorry for making misunderstanding to the reviewer because of the sentence "all the above online measurement results were averaged to a 1 hr resolution" in the MS. We have to make it clear that we didn't process the meteorological data (including wind speed and wind direction) because they were originally at hourly resolution when we firstly collected from the meteorological station at the Century Park (located approximately 2 km away from the sampling site). However, we agree with the reviewer that "From Figs. 6d and S1 the small variation of wind direction over 1 year appears doubtful, unless strong channeling of the wind had occurred." Therefore, we've decided to delete the normalized data of wind direction in the revised MS.

The text below will explain the normalization procedure in Openair. Sometimes it is necessary or useful to calculate daily means from hourly data. Many particle measurements, for example, are measured as daily means and not hourly means. If we want to analyze such particle data for example, by considering how it varies with meteorological data, it is necessary to express the meteorological (and maybe other data) as daily means. It is of course straightforward to calculate daily means of concentrations and wind speeds. However, as the reviewer point out, this is not the case for wind directions. For example the average of 10° and 350° is 0° (or 360°) and not 180°. The way to deal with this is to average with u and v wind components. A function has been written in the Openair to do this:

```
dailymean <- function(mydata) {

## for wind direction, calculate the components

mydata$u = sin(2 * pi * mydata$wd / 360)
```

```
mydata$v = cos(2 * pi * mydata$wd / 360)

dailymet = aggregate(mydata, list(Date = as.Date(mydata$date)), mean,

na.rm = TRUE)

## mean wd

dailymet = within(dailymet, wd <- atan2(u, v) * 360 / 2 / pi)

## correct for negative wind directions

ids = which(dailymet$wd < 0) # ids where wd < 0

dailymet$wd[ids] = dailymet$wd[ids] + 360

dailymet = subset(dailymet, select = c(-u, -v, -date))

dailymet

}
```

The comparison of the Xact with filter data described in Section 2.1.2 appears not fully plausible. Of the 48 filters, 8 pairs of glass and cellulose filters were sampled concurrently. They are compared in Table S1, which indicates that the glass filters under sample by 10 to 25 % the aerosol relative to the cellulose filters (column 4). In column 5, the (remaining?) 40 filters were analyzed together, relative to the Xact. The variation of the slopes is much larger in this case. Here it would be helpful to distinguish between the glass filters and the cellulose filters to see the effect of the filter type on the regression with the Xact. How are the regressions between Xact and filters for the 8 filters (two groups) individually that were pairwise sampled? I suggest to do the following analyses: Xact vs. glass fiber filters for the 8 filters, Xact vs. cellulose filters for the 8 filters, Xact vs. glass fiber filters for all glass fiber filters, Xact vs. cellulose filters for all cellulose filters, and then perhaps Xact vs. all filters. The argument for the higher slope of the Cr regression is not plausible, as Cr shows a significantly lower background value on cellulose than on glass (ratio 0.19), while Ba shows a ratio of 0.65, which is close to the average ratio cellulose/glass of 0.59. Cd, the third steepest slope, does also not indicate exceptionally high background values. If the background values were relevant, I would expect a shift of the regression line (i.e. a larger intercept), but not a change in slope. Therefore, it is important to know the slopes for both cellulose and glass filters separately to infer something about the influence of background values. I propose to add the respective columns to Table S1, and to consequently distinguish the two filter types in the regression analyses.

Thanks for the useful suggestions.

1) **First of all, we would like to explain that "n = 8" in Table S1 represent the number of collected filter samples rather than the number of data points we compared. We've added the actual number of data points for each elemental species to Table S1 in the revised MS. In some cases, there are only three matched number of data points for some species (i.e., Fe, Cr, As) that we collected concurrently through glass fiber and cellulose acetate filters. This is the biggest reason that some species have high (or low) detection limits but low (or high) intercepts. After double check, the intercept of the inter-comparison of cellulose acetate and glass fiber filters for Cu should be 1.45 instead of 14.52.**
2) **"In column 5, the (remaining?) 40 filters were analyzed together, relative to the Xact."**

Considering a generally better data availability and lower detection for cellulose acetate filters than glass fiber filters, the 8 samples collected through glass fiber filters were excluded in the inter-comparison of Xact and filters (48 samples in total).

3) **"I suggest to do the following analyses: Xact vs. glass fiber filters for the 8 filters, Xact vs. cellulose filters for the 8 filters, Xact vs. glass fiber filters for all glass fiber filters, Xact vs. cellulose filters for all cellulose filters, and then perhaps Xact vs. all filters… I propose to add the respective columns to Table S1, and to consequently distinguish the two filter types in the regression analyses."**

As we mentioned above, we've added the matched number of data points (n) to Table S1 in the revised MS (see below).

Species	8 glass filters vs. Xact	all glass filters vs. Xact	8 cellulose filters vs. Xact	all cellulose filters vs. Xact	all 48 filters vs. Xact
K	$y=1.06x+134.92$ $R^2=0.85$ $n=7$	$y=1.07x+73.51$ $R^2 = 0.87$ $n=21$	$y=1.03x+120.86$ $R^2=0.96$ $n=8$	$y=1.13x+130.50$ $R^2 = 0.91$ $n=25$	$y=1.08x+110.31$ $R^2 = 0.86$ $n=46$
Cr	$y=1.13x+0.51$ $R^2=0.92$ $n=3$	$y=1.77x-16.65$ $R^2=0.75$ $n=8$	$y=1.69x-3.89$ $R^2=0.65$ $n=6$	$y=1.92x-0.54$ $R^2=0.58$ $n=21$	$y=1.83x-0.48$ $R^2=0.49$ $n=29$

Mn	$y=0.87x-5.09$ $R^2=0.92$ $n=4$	$y=0.67x+11.80$ $R^2=0.52$ $n=18$	$y=0.85x-5.89$ $R^2=0.87$ $n=8$	$y=0.89x+9.53$ $R^2=0.66$ $n=25$	$y=0.79x+10.70$ $R^2=0.59$ $n=43$
Fe	$y=2.03x-256.65$ $R^2=0.99$ $n=3$	$y=1.67x-96.97$ $R^2=0.95$ $n=10^{*}$	$y=0.98x-21.43$ $R^2=0.81$ $n=6$	$y=1.01x-21.79$ $R^2=0.82$ $n=20$	$y=1.03x+6.48$ $R^2=0.78$ $n=30^{*}$
Ni	$y=1.62x-6.88$ $R^2=0.32$ $n=6$	$y=2.11x-12.82$ $R^2=0.53$ $n=20$	$y=1.45x-6.08$ $R^2=0.54$ $n=7$	$y=1.09x+3.68$ $R^2=0.55$ $n=23$	$y=1.32x+0.29$ $R^2=0.49$ $n=43$
Cu	$y=1.97x-3.30$ $R^2=0.71$ $n=5$	$y=0.97x+5.63$ $R^2=0.40$ $n=19$	$y=0.89x+5.03$ $R^2=0.71$ $n=8$	$y=1.12+5.06$ $R^2=0.61$ $n=25$	$y=1.10+5.04$ $R^2=0.57$ $n=44$
As	$n=2$	$y=2.05x+0.19$ $R^2=0.48$ $n=5$	$y=2.19x-42.14$ $R^2=0.54$ $n=3$	$y=2.26x-19.19$ $R^2=0.49$ $n=4^{**}$	$y=2.06x-16.28$ $R^2=0.36$ $n=9^{**}$
Cd	$y=2.30x+1.04$ $R^2=0.90$ $n=7$	$y=1.99x+9.01$ $R^2=0.82$ $n=21$	$y=2.07x+4.96$ $R^2=0.80$ $n=8$	$y=1.97x+6.70$ $R^2=0.73$ $n=24$	$y=1.97x+8.06$ $R^2=0.76$ $n=45$
Ba	$y=2.93x-0.12$ $R^2=0.77$ $n=7$	$y=3.09x+0.04$ $R^2=0.78$ $n=21$	$y=2.45x-0.18$ $R^2=0.82$ $n=8$	$y=2.44x+0.29$ $R^2=0.78$ $n=24$	$y=2.65x+0.20$ $R^2=0.81$ $n=45$
Au	$y=0.97x+3.68$ $R^2=0.55$ $n=7$	$y=1.25x+2.03$ $R^2=0.72$ $n=21$	$y=1.18x+1.77$ $R^2=0.82$ $n=8$	$y=1.15x+1.50$ $R^2=0.84$ $n=23$	$y=1.17x+1.81$ $R^2=0.77$ $n=44$
Pb	$y=2.73x-0.12$ $R^2=0.68$ $n=7$	$y=2.06x+0.11$ $R^2=0.54$ $n=19$	$y=2.39x-0.10$ $R^2=0.85$ $n=8$	$y=1.74x+0.04$ $R^2=0.64$ $n=25$	$y=1.80x+0.09$ $R^2=0.59$ $n=44$

Note: *deleted an abnormal value (sample ID: N_glass_12) **deleted two abnormal values (sample ID: N_acetel_14 and N_acetel_24)

The discussion of elements in Fig. 4 might be improved by a quantitative definition of the term 'seasonal variation'. In absolute concentrations, Ca and Si may show the highest degree of variation, but when normalized to their means and standard deviation, other elements might show a stronger relative variation. Si does also not show any variation between spring and summer. Which seasons are compared/considered for the seasonal variation range? Concerning the diurnal variations in Figs. 8 and 9, how would you explain the minimum occurring on Tuesday, i.e. 2 days after the weekend?

We fully agree with the reviewer that the seasonal variation of each metal species can be presented in a more quantitative way. Given that the main purpose of Fig. 4 is to show the seasonal variation of a specific species instead of comparing the levels of variation among different species, we think that the current form of Fig. 4 is suitable.

As to the minimum value occurred on Tuesday in Figs. 8 and 9, we failed to identify the major factor. Alternatively, we think it is more important to check the diurnal variations in Figs. 8a and 9a, in which there is limited difference in terms of variation pattern from Monday to Sunday.

Another aspect is long-range transport, as discussed for V and Ni. The text states that based on Fig. 6 V and Ni are the result of mid- to long-range transport. However, Fig. 13 shows that V and Ni are rather local to mid-range transport from the southeast sector, which indicates that the relevant ship emissions originate both locally from the harbor on the Huangpu River and farther away from the sea east of Shanghai. It would be helpful to clarify what mid- and long-range transport means, i.e. which distances are attributed to this terminology. Does the ship traffic on the Yangtze River not contribute to the V and Ni concentrations observed at PEMC? Why is there not a larger contribution from the northeast? From Fig. 6 it is not clear how the wind direction varies in the course of the day. It appears as if the diurnal development of the atmospheric boundary layer overrides the development of a sea breeze system, if one exists in Shanghai. Fig. 6c also indicates an annual variation of wind direction that would override diurnal wind variations.

1) **"Does the ship traffic on the Yangtze River not contribute to the V and Ni concentrations observed at PEMC?"**

There are several papers concern the emissions and contribution of inland shipping to air pollution (Corbett and Fischbeck, 2000; Fu et al., 2013; Kurtenbach et al., 2016; Keuken et al., 2014); however, none of them have information regarding the mass concentrations of V and Ni. This can be expected because V and Ni are mainly derived from heavy oil (mainly used in marine diesel engines) combustion, which can be inferred through the ratio of V/Ni (Viana et al., 2009). Previous work suggested that the ratio of V/Ni from heavy oil combustion in Shanghai ocean-going ships was around 3.2 (Liu et al., 2017), which is consistent with the value obtained in our study (Fig. 7). This is not the case for inland ships. Therefore, we think inland shipping in the Yangtze River is not an important source for V and Ni emissions.

Reference:

Corbett, J. J.; Fischbeck, P. S., Emissions from waterborne commerce vessels in United States continental and inland waterways. *Environ. Sci. Technol.* 2000, *34*, (15), 3254-3260.

Fu, M.; Ding, Y.; Ge, Y.; Yu, L.; Yin, H.; Ye, W.; Liang, B., Real-world emissions of inland ships on the Grand Canal, China. *Atmos. Environ.* 2013, *81*, (Supplement C), 222-229.

Liu, Z.; Lu, X.; Feng, J.; Fan, Q.; Zhang, Y.; Yang, X., Influence of Ship Emissions on Urban Air Quality: A Comprehensive Study Using Highly Time-Resolved

Online Measurements and Numerical Simulation in Shanghai. *Environ. Sci. Technol.* 2017, *51*, (1), 202-211.

Keuken, M. P.; Moerman, M.; Jonkers, J.; Hulskotte, J.; Denier van der Gon, H. A. C.; Hoek, G.; Sokhi, R. S., Impact of inland shipping emissions on elemental carbon concentrations near waterways in The Netherlands. *Atmos. Environ.* 2014, *95*, (Supplement C), 1-9.

Kurtenbach, R.; Vaupel, K.; Kleffmann, J.; Klenk, U.; Schmidt, E.; Wiesen, P., Emissions of NO, NO_2 and PM from inland shipping. *Atmos. Chem. Phys.* 2016, *16*, (22), 14285-14295.

Viana, M.; Amato, F.; Alastuey, A.; Querol, X.; Moreno, T.; García Dos Santos, S.; Herce, M. D.; Fernández-Patier, R., Chemical Tracers of Particulate Emissions from Commercial Shipping. *Environ. Sci. Technol.* 2009, *43*, (19), 7472-7477.

2) **"Why is there not a larger contribution from the northeast? From Fig. 6 it is not clear how the wind direction varies in the course of the day."**

Firstly, as two of the biggest ports in the world, Shanghai Yangshan port and Ningbo-Zhou port are located in the southeast of Shanghai, not the northeast. Secondly, as we mentioned above that Shanghai has a humid subtropical monsoon climate. Winters are chilly and damp, with northwesterly winds. In summer, southeasterly airflow carries moist air from the Pacific Ocean to mainland China.

The issue with coal combustion is exciting. The authors show that coal-fired power plants are distributed evenly around the receptor site, while non-ferrous metals production is mainly in the west. These observations are illustrated with Hg, Au, and later with Cu, K, Pb, As, Se. What is the reason for such differences in metals emissions between power plants and metals production plants? Are there different cleansing systems in effect?

To our understanding, metal species emitted from coal-fired power plants have more direct relationship with metals content in coal. However, there are many types of metals production plants (including metals processing plants). Different types of metals production plants cold emit different kinds of metals. We are not

sure if we've grasped the meaning of this comment.

Technical corrections

The Lxxx indicate the line number xxx of the manuscript where a correction should be made.

L19 delete 'with', replace 'its' with 'their'

We think that "with" is necessary.

L35 'orders of magnitude' (insert 'of')

L39 delete 'were'

L42 . . . was due to the interplay. . .

L51 . . . combustion of coal. . .

L64 delete 'John'. The correct reference is Duffus, 2002.

L125 write 'distance-based detection in a multi-layered device'. This probably captures the essence of the technique better.

L133 Suggest to add the references to Park et al. (2014) and Furger et al. (2017, Atmos. Measurement Techn., doi:10.5194/amt-10-2061-2017) here, as both papers discuss the data quality of the Xact-625.

L134 Add (YRD) as an abbreviation for the Yangtze River Delta.

L173 . . . from Siberia which can cause. . .

L186 . . . such as V. . .

L258 . . . to do correlation matrix calculations. I am unsure what is missing here.

It also contains specific algorithms to calculate matrices.

L289 The two methods have been implemented in the . . .

L295 Replace 'and give the probability of doing so' with 'and with which probability.'

L327ff The different limiting values would probably be easier digested when listed in a Table.

There are only 5 in 18 metal species have limiting values. Therefore, we decide to list them in the text. Thank you for your understanding.

L338 replace 'with' by 'while'

L375 please give a reference.

Nriagu, J. O.: Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, Nature, 279, 409-411, doi: 10.1038/279409a0, 1979.

Nriagu, J. O.: A history of global metal pollution, Science, 272, 223-223, doi: 10.1126/science.272.5259.223, 1996.

L385 replace ‘more’ by ‘other’, and ‘shown’ by ‘showed’.

L404 . . .in Shanghai has occurred during Sunday (Fig. 6d) (February (Fig. 6c)). – refer to the correct sub-figures.

L415 ‘pads’ instead of ‘pad’.

L416 correct ‘less traffic flow in weekends not only lower road suspend dust but also cut metal species emissions’ to ‘less traffic flow in weekends not only lowers re-suspended road dust but also reduces metal species emissions’.

L418 replace ‘Ca’ by ‘Si’.

L419 replace ‘July’ by ‘June’ and Fig. 10 by Fig. 8. Then replace ‘Si’ by ‘Ca’. Please correct also the remark on the 0100 h Si peak. Do you have an explanation for this huge peak after midnight?

L433 ‘transforming’ – do you mean ‘transporting’?

L488 The text mentions 4 statistically significant factors. Which of the 6 factors in the figure are these? You should indicate the significance for all 6 factors in the Figure.

The “four” in the text should be changed as “six”.

L498 Replace ‘were’ by ‘are’.

L514 ‘plot’ instead of ‘plots’. Delete ‘is’.

L545 delete ‘that’.

L549 delete ‘is’

L553 write ‘combustion of coal is located;’

L580 write ‘Fig. S4 also evidently reflects that high concentrations of Zn can occur in the northwest of PEMC.’

L698 write: ‘Duffus, J. H.: . . ..’. L1066 A land use map (not land uses map)

L1115 The grey line indicates one two standard deviations – one or two? Fig. 6 Indicate the wind direction axis (or explain normalization of wind direction, see remark above).

The wind direction has been deleted.

L1224 Replace ‘On the bottom’ with ‘Below the diagonal’.

L1225 Replace ‘on the top’ with ‘above’.

L1247 Write ‘Principal’ instead of ‘Principle’ Fig.15 Explain the circle sizes. Table S1: Caption: different monitoring (x, y) should be indicating the correct, correlated quantities, probably y Xact, x filter.

All the above-mentioned errors have been revised accordingly. Thanks!

Anonymous Referee #2

Using an on-line x-ray fluorescence system (XACT), this paper describes measurements of trace elements in $PM_{2.5}$ aerosols in Shanghai, the industrial center of China. This pioneer work is informative and valuable in terms of the number of species (18) and the duration of observations (a year cycle with hourly resolution) presented, which permit a thorough analysis of temporal variations and source attribution. Meanwhile, the authors do an extensive validation of the performance of XACT from solution of filter-based metals measurement which they extract a correction factor applied to their data. Overall, this is a nice work and I recommend it for publication.

Comments:

The technical aspects were adequately covered by the referee 1. Particularly, I am also interested in seeing if precipitation produces substantial scavenging of airborne trace metals. Several typical events with strong precipitation can be selected as a better way, in my opinion, to examine the effect of wet removal in the supplement.

Please refer to our reply to the comments raised by reviewer #1 (page 2).

Title: Given that the focus of the MS is trace metals, I suggest the title can be changed as “First long-term and near real-time measurements of atmospheric trace metals in Shanghai, China”.

The title of the MS has been changed as “First long-term and near real-time measurement of atmospheric trace metals in Shanghai, China”.

Table 1: Data of Shanghai should be listed adjacent to that of Gwangju.

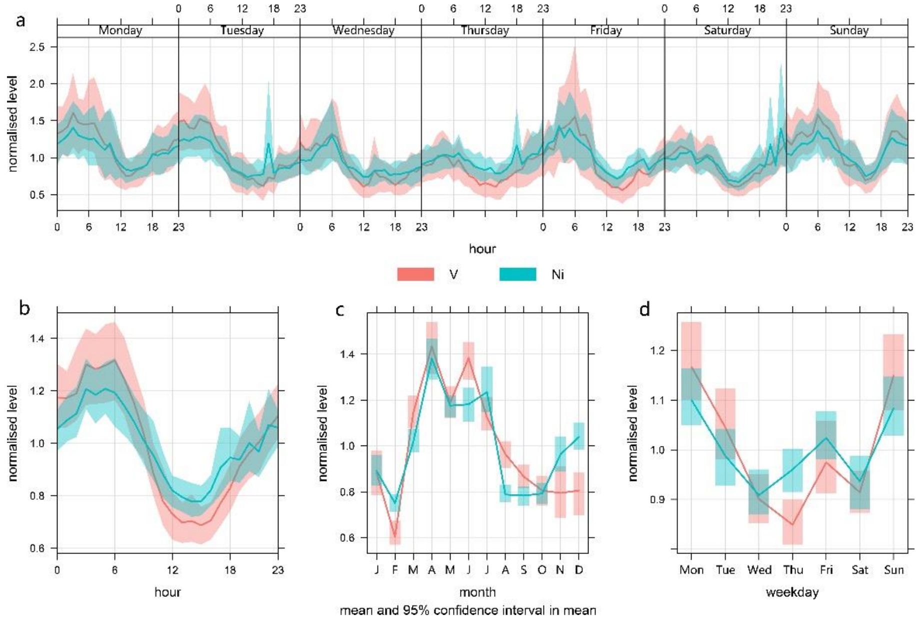
Revised accordingly.

Fig. 1: I didn't saw (a), (b), (c), (d), and (e) in the figure. Moreover, please specify the data sources of population density and major point sources.

Revised accordingly.

Fig. 6: It could be a problem that the variations of wind directions and the mass concentrations of V and Ni are normalized together. I suggest the authors to re-plot Fig. 6 by excluding wind directions.

We've removed the normalized wind in Fig. 6 and replaced as the figure below:



Line 236: Is there necessary to use data like CO, NO_2, and SO_2 in the study?

The statement in the original MS didn't make any sense, thus has been deleted in the revised MS.

Line 457: 3.2.1 Pinpoint the most possible source.

Revised accordingly.

Anonymous Referee #5

This paper presents a full year of temporally highly resolved data (1h resolution) of trace elements in $PM_{2.5}$ as measured in Shanghai (China) using an on-line multi-metal monitor (XRF instrument Xact625, Cooper Environmental). This data is evaluated by applying different statistical methods in order to find correlations between the different elements and evidence of common sources. The article presents probably the longest time series of hourly trace elements in $PM_{2.5}$ so far, and highlights the situation in the largest megacity and a main industrial center in China, where emissions are expected to be high. The article is therefore of high interest, it is reasonably well written (see comments below) and certainly deserves publication in Atmospheric Chemistry and Physics. However, the manuscript needs some re-visions as detailed in the comments below:

1. Abstract: The abstract is much too long and needs to be shortened. Only the most important results should be mentioned in a short and concise way.

Thanks for the suggestion. We decide to delete several sentences that are less important in the revised abstract, e.g., "Here our high time-resolution observations over long-term period also offer a unique opportunity to provide robust diurnal profiles for each species, which are useful in determining the sources and processes contributing to the fluctuation of atmospheric trace elements. Besides, various mathematical methods and physical evidences were served as criteria to constrain various solutions of source identification" (56 word count). Generally, we followed the ACP guidelines to prepare our abstract, i.e., the "abstract should be intelligible to the general reader… After a brief introduction of the topic, the summary recapitulates the key points of the article and mentions possible directions for prospective research". The word count of the abstract in the original MS is 474, which is comparable with many papers published in ACP. The relatively long abstract in ACP is some sort of distinctive in the community of atmospheric journals. Despite the large number of species and the high frequency measurement in our study, the major part of the abstract presents a summative assessment of the results (the most important results) consisting of compact description instead of detailed data. Therefore, there is limited room for us to further shorten the length of the current abstract.

2. Although not a native English speaking person, I find the English is of variable quality. Abstract and introduction are well written, the other sections need careful revisions. Especially the Statistical analysis section has many linguistic and semantic errors. Examples are the lines 256-258, “The “corrplot” package in R is a graphical display of a correlation matrix, confidence interval. It also contains specific algorithms to do matrix.”, and lines 278-279, “The corrplot package can draw rectangles . . .”. Please revise the text carefully.

We are sorry for making many language errors as the reviewer pointed out, which have been corrected accordingly. In the revised MS, the English has been corrected and polished thoroughly by native English speakers with expertise in atmospheric measurement and modeling.

3. The results of the principal component analysis and also the hierarchical clustering do not bring any new insights that go beyond the analysis of pairwise correlations together with CPF and BPP. Section 3.2.2 is not well written and does not give any new information, the discussion about the number of selected clusters appears arbitrary. Moreover, the discussion of the method applied for hierarchical clustering is not sufficient. It remains unclear what exact method has been applied. If it is decided that the results of this data analytical method can remain in the article, then a detailed description of the applied method is required. I suggest to skip section 3.2.2, as it does not provide any new insights and it is also not well written. The paper will certainly benefit from being shortened (the authors could mention in the paper that PCA and hierarchical clustering were applied, but the results did not lead to additional information).

We agree with the reviewer that the discussion of the method applied for hierarchical clustering is not sufficient. In fact, the method of hierarchical clustering we used is not new (maybe still new in investigating the sources of metals). We’ve added the link about the manual and demonstration of hierarchical

clustering the revised MS (2.2.1 Statistical analysis).

Firstly, "the results of the principal component analysis and also the hierarchical clustering does not bring any new insights that go beyond the analysis of pairwise correlations together with CPF and BPP". To identify possible sources of measured trace metals, three methods of statistical analysis, i.e., correlation matrix, principle component analysis (PCA), and hierarchical clustering of reordering correlation matrix, were performed. Although the PCA of the 18 elemental species did not reveal any meaningful factors, it is normally the first (sometimes the most useful) step to examine the major factors contributing to the measured metal species. More importantly, by applying the PCA in the study, we realized that the large influence of nonferrous smelting, coal combustion, and traffic-related emissions on ambient trace metals measured in Shanghai (see discussion in section 3.2.2).

Secondly, "section 3.2.2 is not well written and does not give any new information, the discussion about the number of selected clusters appears arbitrary", "If it is decided that the results of this data analytical method can remain in the article, then a detailed description of the applied method is required". We have to clarify the number of selected clusters was automatically determined by the algorithm of the hierarchical clustering without any artificial adjustment. The method, as we mentioned above, has been elaborated in section 2.2.1 of the revised MS. Therefore, we decide to keep section 3.2.2. In fact, section 3.2.2 is along with section 3.2.1 as the integrated part of section 3.2, i.e., source analysis. In section 3.2.1, we try to pinpoint one source with the highest confidence. In section 3.2.1, many solutions of source apportionment were proposed through a variety of mathematical methods (including CPF and BPP). And the most possible source identified in section 3.2.1 will be used as a diagnostic tool to examine the feasibility of various solutions of source apportionment proposed in section 3.2.2. After all, section 3.2.1 covers only one source and a few species (shipping source; V and Ni in this study) while section 3.2.2 covers many sources with the rest of species. In this sense, section 3.2.2, if not the most important, it must among the most important part of

the MS.

Lastly, "the paper will certainly benefit from being shortened. The authors could mention in the paper that PCA and hierarchical clustering were applied, but the results did not lead to additional information". We are not sure if it is proper to claim that the results did not lead to additional information by simply mentioning the application of the PCA and hierarchical clustering during the preparation of the MS. As to the PCA, even if not important as the reviewer indicated, it is a short part of the MS to say at the least. Different from the PCA, the hierarchical clustering is vitally important to provide the solutions of source apportionment in section 3.2.2.

4. Figure 5 is rather suspicious. The sharp peaks in Cd and Ag at 1am local time are hard to believe. The authors should check again, if there is not another, maybe operational explanation. In Figure 6, normalized wind does not make much sense, should be removed from the graph. Figures 8-11 are of the same type than Figures 5 and 6. They can be shifted to the Supplement.

We've removed the normalized wind in Fig. 6, and Fig. 8-11 have been shifted to the supporting information as suggested by the reviewer. As the sharp peaks in Cd and Ag at 1am, we find that the inter-comparison of Xact and filters for Cd (Ag is not available) shows good correlation (R^2=0.76), and the slope (1.97) and interception (8.06) are relatively high (Table S1). We agree that Figures 8-11 are of the same type as Figures 5 and 6. Given that we need to mention these figures frequently in the MS, we decide to keep them for the convenience of readers. Thank you for your understanding.

Additional comments:

Lines 98-99, Sentence should be changed to e.g. "Typical ambient trace metal sampling devices collect 12 to 24-hr integrated average samples, which . . ."

Revised accordingly.

Line 105, “may be orders of magnitude lower than . . .”. It can easily been estimated that it cannot be orders of magnitude or max 2 orders for 15min samples. Rewrite accordingly.

“may be orders of magnitude lower than . . .” has been changed as “may be one order of magnitude lower than . . .”.

Lines 152-153, ”Meanwhile, most available source evidences were inferred based on filter sampling and off-line analysis, which were not necessarily representative of actual origins.” I don’t understand this sentence, it is probably not correct. Please rewrite.

This sentence has been deleted in the revised MS.

Line 219, please be more precise, should be “glass fiber filters”.

Revised accordingly.

Line 229, should be “spectrometer”.

Revised accordingly.

Lines 242-244: “As data in the current study were collected in near-real time, the importance for quality assurance and quality control (QA/QC) system can be crucial in order to improve data quality throughput.” All measurements independent of time resolution require an appropriate QA/QC. This sentence makes in the present form no sense and should be deleted or revised.

Deleted accordingly.

Lines 294-296, sector. “CPF analysis is capable to 295 show which wind directions are dominated by high concentrations and give the probability of doing so.” Poor English, please rewrite.

Rewritten accordingly. “CPF analysis is capable of showing which wind directions are dominated by high concentrations and with which probability.”

Lines 330-331: The statement that "airborne metals pollution in Shanghai is generally low by the current limit ceilings" is difficult to see from the text, maybe add a table (could also be in the Supplement).

Although there are 18 metal species involved in the current study, only 5 of them (Cd, Hg, As, Mn, V, and Ni) have limit ceilings. We tentatively think there's not much reason to create an additional table in the revised MS. Thank you for your understanding.

Lines 373-375. "Globally, anthropogenic emissions of Ag and Cd exceed the natural rates by well over an order of magnitude*. Please give a reference for this statement.

Two references have been inserted in the MS.

Nriagu, J. O.: Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, Nature, 279, 409-411, doi: 10.1038/279409a0, 1979.

Nriagu, J. O.: A history of global metal pollution, Science, 272, 223-223, doi: 10.1126/science.272.5259.223, 1996.

Line 562, legend of Figure 12, and at elsewhere in the text. The authors mention "significant correlations". It should be explained how significant correlations are defined, how has significance been calculated, what kind of statistical test has been applied.

As "significant correlations", the p value should lower than 0.05. Mann-Whitney test was used.

A.J. Dore (Referee)

Overview

The rapid development and industrialization in China during recent decades has resulted in increased emissions of many pollutants leading to high levels of particulate matter in the atmosphere with severe effects on human health. Amongst the pollutants emitted, heavy metals are of particular concern due to their toxicity at high air concentrations. The problem is of specific regional concern as in other parts of the world (i.e. many European countries) concentrations of heavy metals in the atmosphere have decreased dramatically since their peak values to values which are now well below limit values considered to pose a threat to human health. The study focuses on Shanghai which is a mega-city and a center for heavy industry. The paper suggests that metal concentrations are one or two orders of magnitude higher than in north America and Europe which is a highly significant conclusion as this indicates that a large population is exposed to multiple and serious threats to human health in the region. An extensive data set has been analyzed which includes both a large number of species and high frequency measurement. The chemical analysis covers 18 heavy metal species which allows grouping of metals into different source categories. The hourly measurement of the data is of particular significance as such high temporal resolution of measurements for a full year of monitoring combined with detailed chemical analysis is quite rare and allows analysis using the conditional probability function and bivariate polar plots. The manuscript is well referenced and the text is logically constructed. The experimental set up is clearly described and graphical representation is put to good use to investigate seasonal, weekly and diurnal variation in metal concentrations. Some of the plots (i.e. figures 2 and 12) have details which are in very small print. However, I think this is probably necessary due to the large number of metals to be simultaneously displayed and, as the graphs are of high resolution, the information can be read easily using the zoom function. I have a few queries about interpretation of the results which are raised below. The English is of a reasonable standard. However, the language needs checking as there are various minor grammatical errors in the text (i.e. use of the article a / the) and some inappropriate / unclear expressions for a scientific publication, a few of which (in the early part of the text) are mentioned below. I am pleased to recommend the paper for publication following attention to the comments below.

Examples of minor corrections:

Abstract: - " . . .with poorly constrained on its abundances and sources . . ." Change to: " . . . which have considerable uncertainty associated with the source and magnitude of their atmospheric emissions".

- "collocated" should be "co-located".

- "Besides, various mathematical methods and physical evidences were served as criteria to constrain various solutions of source identification." Change to: "A variety of mathematical techniques were employed with high frequency monitoring data to identify sources for metal emissions."

Main text

- "Among the chemical components relevant . . ." Long sentence. Break into two.
- Line 70 – 80. Health effects of some metals are mentioned here as human carcinogens. However, there are many other individual effects on human health (i.e. brain, lungs, reproduction, kidneys(?) for individual metals which could also be mentioned here. Recent American studies have even linked Pb concentrations to criminal behavior.
- Line 135: ". . . Shanghai is home to nearly 25 million people as of 2015, marked as the largest megacity in China" should be ". . . making it the largest mega-city . . ."
- Line 150: "Meanwhile, most available source evidences were inferred based on filter sampling and off-line analysis, which were not necessarily representative of actual origins." The statement is unclear and needs re-wording
- Line 184: change 'multitudinous' to 'a multitude of'
- Line 199 'resulted' should be 'resulting'
- Line 203 'producing' should be 'produced'
- Line 246: 'were followed' should be 'followed'
- Figure 3 cation: 'A quick glance of the mass concentrations of 18 trace elements measured . . .'. Change to 'Mass concentrations of the 18 trace elements measured . . .'
- Line 338 'which accounting for' should be 'which accounts for'

We are grateful to Dr. Dore for the recommendation for publication. The language errors, including the above-mentioned problems, have been thoroughly corrected in the revised MS.

Specific comments

- To me the title, whilst accurate, is a little awkward. I think 'first' is unnecessary and could be removed as we can argue that all scientific publications are in some way a first. How about "High frequency monitoring of atmospheric trace elements in Shanghai, China"? 'Monitoring' implies long term measurement. A longer version could be:

“High frequency monitoring of atmospheric trace elements in Shanghai, China, and source attribution analysis”

We prefer to keep “first” in the title because online and high-time resolution measurement of trace elements is of critical importance to assess the potential accurate health risks induced by metal species. To the best of our knowledge, all previous studies regarding the analysis of ambient trace elements in China were on a daily basis.

- Mean and variance values of concentrations are quoted to 4 or even 5 significant figures. I think it is unlikely that this degree of accuracy can be attributed to the measuring system. 2 significant figures (or a maximum of 3) would be more realistic.

Revised accordingly.

- Figure 1: Include (a) , (b), (c), (d), (e) next to individual figures

Revised accordingly.

- Line 402: “This can be used to explain that the weekly (monthly) lowest impact of shipping emissions in Shanghai was occurred during Sunday (Fig. 6c) (February (Fig. 6d)).” Check this statement. February doesn’t appear from Figure 6(b) to be the month with the minimum concentrations

Agree and revised accordingly.

- Line 410: “As demonstrated in Fig. 8d and Fig. 9d, there is an evident drop in the concentrations of Si, Ca, Fe, Ba, Mn and Zn after entering weekends.” The minimum concentration in Figures 8(d) and 9(d) appears to be on Tuesday. Can the two day delay between the weekend and peak concentrations be explained? If this is following a weekend dip in activity then perhaps it suggests long range transport? - Wind speed is associated with long range transport in the text. However high wind speeds also cause production of sea salt aerosol and re-suspension of surface dust

Agree and revised accordingly.

First long-term and near real-time measurement of atmospheric trace metals in Shanghai, China

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Abstract: Atmospheric trace elements, especially metal species, are an emerging environmental and health concern with poor controls on their levels of emission 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-resolved measurement of eighteen elements in fine particles ($PM_{2.5}$) at Shanghai urban center with a Xact multi-metals monitor and several collocated instruments. Independent ICP-MS offline analysis of filter samples was used to validate the performance of Xact that was based on energy-dispersive X-ray fluorescence analysis of aerosol deposits on reactive filter tapes. Mass concentrations (mean±1σ; ng m^{-3}) determined by Xact ranged from detection limits (nominally 0.1 to 20 ng m^{-3}) to 14.7 μg m^{-3}, with Si as the most abundant element (638.7±1004.5), followed by Fe (406.2±385.2), K (388.6±326.4), Ca (191.5±383.2), Zn (120.3±131.4), Mn (31.7±38.7), Pb (27.2±26.1), Ba (24.2±25.4), V

(13.4±14.5), Cu (12.0±11.4), Cd (9.6±3.9), As (6.6±6.6), Ni (6.0±5.4), Cr (4.5±6.1), Ag (3.9±2.6), Se (2.6±2.9), Hg (2.2±1.7), and Au (2.2±3.4). Metal related oxidized species comprised an appreciable fraction of $PM_{2.5}$ during all seasons, accounting for 8.3% on average. As a comparison, atmospheric metal pollution level in Shanghai was comparable with other industrialized cities in East Asia but one or two orders of magnitude higher than the sites in North America and Europe. Various mathematical methods and high resolution measurement data provided the criteria to constrain various solutions of source identification. The results showed that atmospheric trace element pollution in Shanghai was due to the interplay of local emissions and regional transport. Different sources of metal species generally have different temporally-evolving patterns associated with different source regions. Specifically, V and Ni were confirmed as the prominent and exclusive tracers of heavy oil combustion from shipping traffic. Fe and Ba were strongly related to brake wear, and exhibited a significant correlation with Si and Ca, suggesting that Si and Ca in Shanghai were primarily sourced from road fugitive dust rather than long-distance dust transport and local building construction sites. Stationary combustion of coal was found to be the major source of As, Se, Pb, Cu and K, and the ratio of As/Se was used to infer that coal consumed in Shanghai likely originated from Henan coal fields in Northern China. Cr, Mn and Zn were the mixed result of emissions from stationary combustion of coal, ferrous metals production, and nonferrous metals processing. Ag and Cd in Shanghai urban atmosphere were also the mixture of miscellaneous sources. Collectively, our findings in this study provide baseline data with high detail, which are needed for developing effective control strategies to reduce the high risk of acute 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; Pope III et al., 2009; Shah et al., 2013; 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 refers to elements with atomic density greater than 4.5 g cm^{-3} (Streit, 1991)) are of particular concern as they typically feature with unique properties of bioavailability and bioaccumulation (Morman and Plumlee, 2013; Tchounwou et al., 2012; Fergusson, 1990; Kastury et al., 2017), representing 7 of the 30 hazardous air pollutants identified by the US Environmental Protection Agency (EPA) in terms of posing the greatest potential health threat in urban areas (see www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants). Depending on aerosol composition, extent and time of exposure, previous studies have confirmed that most metal components of fine particles ($PM_{2.5}$; particulate matter with aerodynamic diameter equal to or less than 2.5 μm) exerted 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).

Guidelines for atmospheric concentration limits of many trace metals are provided by the World Health Organization (WHO) (WHO, 2005). In urban atmospheres, ambient trace metals typically represent a small fraction of $PM_{2.5}$ on a mass basis, while metal 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; 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 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 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 metal species are not only seen from chronic exposure, but also from short-term acute concentration spikes in ambient air (Kloog et al., 2013; Strickland et al., 2016; Huang et al., 2012). In addition, atmospheric emissions, transport, and exposure of trace metals to human receptors may depend upon rapidly evolving meteorological conditions and facility operations (Tchounwou et al., 2012; Holden et al., 2016). Typical ambient trace metal 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 metal pollution spikes related to local emission sources. In fact, during a short-term trace metals exposure event, 12 or 24-hr averaged sample concentrations for metal 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 metal species on a real-time scale is essential for studies on trace metals 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 Elements in Aerosol Sampler) (Visser et al., 2015b; Visser et al., 2015a; Bukowiecki et al., 2005; Chen et al., 2016). Mass loadings of trace metals 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 al., 2014). More recently, aerosol time-of-flight mass spectrometry (Murphy et al., 1998; Gross et al., 2000; DeCarlo et al., 2006), 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 et al., 2017), and Xact^{TM} 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 metal species. The Xact method is based on nondestructive XRF analysis of aerosol deposits on reactive filter tapes, which has been validated by US Environmental Technology 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). 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, which has the world's busiest port, handling over 37 million standard containers in 2016 (see www.simic.net.cn/news_show.php?lan=en&id=192101). As a consequence, Shanghai is potentially subject to substantial quantities of trace metal emissions (Duan and Tan, 2013; Tian et al., 2015). Ambient concentrations of trace metals, 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., 2013; 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 illustrated a full spectrum of metal species in ambient aerosols. Furthermore, recent attribution of hospital emergency-room visits in China to $PM_{2.5}$ constituents failed to take short-term variations of trace metals into account (Qiao et al., 2014), which could inevitably underestimate the toxicity of aerosols and potentially misestimate 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 metals in $PM_{2.5}$ 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 atmospheric abundances, variation patterns and source contributions of trace elements in a complex urban environment, which can be used to support future health studies.

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 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 which can cause nighttime temperatures to drop below freezing. 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).

Field measurements were performed at the rooftop (~18 m above ground level) of Pudong Environmental Monitoring Center (PEMC; 121.5447°E, 31.2331°N; ~7 m above sea level) in 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 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 indicted in Fig. 1c, PEMC is surrounded by a multitude of emissions 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, 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 1st 2016 to February 28th 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 $PM_{2.5}$ were determined by a Xact multi-metals monitor (Model Xact™ 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 $PM_{2.5}$ cyclone inlet (Model VSCC-A, BGI Inc., MA, USA) at a flow rate of 16.7 L min^{-1}. The resulting $PM_{2.5}$ 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 metal element of interest. These standards were provided by the manufacturer of Xact, produced by depositing vapor phase elements on blank Nuclepore (Micromatter Co., Arlington, WA, USA). The Nuclepore filter of known area was weighed before and after the vapor deposition process to determine the concentration (μg 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 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 PM$_{2.5}$ samples were also collected at 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 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, 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 Inductively coupled plasma-mass spectrometer (ICP-MS; Agilent, CA, USA). The results of the 8 paired samples were first compared. Significant correlations were observed for species of K, Cr, Mn, Fe, Ni, Cu, As, Cd, Ba, Zn, and Pb (Table S1), and these species were used to validate the performance of Xact. In Table S1, the slope values of Cr (1.9) and Ba (2.6) were higher than other species, this can be explained by higher background values of Cr and Ba collected by the cellulose acetate filters.

2.1.3 Auxiliary measurements, quality assurance and quality control

Hourly mass concentrations of $PM_{2.5}$ were measured using a Thermo Fisher Scientific TEOM 1405-D. Data on hourly concentrations of CO, NO_2, and SO_2 were provided by PEMC. Meteorological data, including ambient temperature (T), relative humidity (RH), wind direction (WD) and wind speed (WS), were provided by Shanghai Meteorological Bureau at Century Park station (located approximately 2 km away from PEMC).

The routine procedures, including the daily zero/standard calibration, span and range check, station environmental control, and staff 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. QA/QC for the Xact measurements was implemented throughout the campaign. The internal Pd, Cr, Pb, and Cd upscale values were recorded after the instrument's daily programmed test, and the PM_{10} and $PM_{2.5}$ cyclones were cleaned weekly.

2.2 Data analysis

2.2.1 Statistical analysis

To identify possible sources of measured trace metals, three methods of statistical analysis, i.e., correlation matrix, principle component analysis (PCA), and hierarchical clustering of reordering correlation matrix, were performed. The "corrplot" package in R is a graphical display of a correlation matrix, confidence interval. It also contains specific algorithms to calculate matrices. More information regarding corrplot can be found at CRAN.R-project.org/package=corrplot (Wei and Simko, 2016).

Spearman correlations were firstly performed to establish correlations between trace metals, which can be used to investigate the dependence among multiple metal species at the same time. The result is a table containing the correlation coefficients between each variable and the distribution of each metal species on the diagonal. Secondly, principle component analysis (PCA) with a varimax rotation (SPSS Statistics® 24, IBM®, Chicago, IL, USA) was performed on the measured data set, which has been used widely in receptor modelling to identify major source categories. The technique operates on sample-to-sample fluctuations of the normalized concentrations. It does not directly yield concentrations of species from different sources but identifies a minimum number of common factors for which the variance often accounts for most of the variance of species (e.g., Venter et al. (2017) and references therein). The trace metal concentrations determined for the 18 species were subjected to multivariate analysis of Box-Cox transformation and varimax rotation, followed by subsequent PCA. Lastly, we applied an agglomeration strategy for hierarchical clustering, a method of cluster analysis which seeks to build a hierarchy of clusters, to mine the hidden structure and pattern in the correlation matrix (Murdoch and Chow, 1996; Friendly, 2002). In order to decide which clusters should be combined as a source, or where a cluster should be split, a measure of dissimilarity between sets of observations is required. Ward's method is served as a criterion applied in hierarchical cluster analysis. The “corrplot” package can draw rectangles around the chart of the correlation matrix (indicated as a potential source) based on the results of hierarchical clustering. Readers can refer to https://cran.r-project.org/web/packages/corrplot/corrplot.pdf and https://cran.r-project.org/web/packages/corrplot/vignettes/corrplot-intro.html for details regarding the manual and demonstration of hierarchical clustering, respectively.

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

The determination of the geographical origins of trace metals 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 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 metals with similar source. The two methods have been implemented in the R "openair" package and are freely available at www.openair-project.org (Carslaw and Ropkins, 2012).

The CPF is defined as CPF = m_θ/n_θ, where m_θ is the number of samples in the wind sector θ with mass concentrations greater than a predetermined threshold criterion, and n_θ 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 probability. In this study, the 90th percentile of a given metal species was set as threshold, and 24 wind sectors were used ($\Delta\theta = 15^0$). Calm wind (< 1 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 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 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 described in more detail in Carslaw et al. (2006) and the construction of BPP had been presented in our previous work (Chang et al., 2017).

3 Results and discussion

3.1 Mass concentrations

3.1.1 Data overview and comparison

The temporal patterns and summary statistics of hourly elemental species concentrations determined by the Xact at PEMC during March 2016-Feburary 2017 are illustrated in Fig. 2. The mass concentrations of the 18 elements measured in Shanghai were sorted from high to low in Fig. 3. The one-year data set presented in the current study, to the best of our knowledge, represents the longest on-line continuous measurement series of atmospheric trace metals.

Taking the study period as a whole, ambient average mass concentrations of elemental species varied between detection limit (ranging from 0.05 to 20 ng m^{-3}) and nearly 15 μg m^{-3}, with Si as the most abundant element (mean ± 1σ; 638.7 ± 1004.5 ng m^{-3}), followed by Fe (406.2 ± 385.2 ng m^{-3}), K (388.6 ± 326.4 ng m^{-3}), Ca (191.5 ± 383.2) ng m^{-3}, Zn (120.3 ± 131.4 ng m^{-3}), Mn (31.7 ± 38.7 ng m^{-3}), Pb (27.2 ± 26.1 ng m^{-3}), Ba (24.2 ± 25.4 ng m^{-3}), V (13.4 ± 14.5 ng m^{-3}), Cu (12.0 ± 11.4 ng m^{-3}), Cd (9.6 ± 3.9 ng m^{-3}), As (6.6 ± 6.6 ng m^{-3}), Ni (6.0 ± 5.4 ng m^{-3}), Cr (4.5 ± 6.1 ng m^{-3}), Ag (3.9 ± 2.6 ng m^{-3}), Se (2.6 ± 2.9 ng m^{-3}), Hg (2.2 ± 1.7 ng m^{-3}), and Au (2.2 ± 3.4 ng m^{-3}). 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^{-3}, respectively. Therefore, 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 on 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^{-3} in spring, summer, fall, and winter, respectively, while the annual average concentration as 3.9 μg m^{-3}, which accounting for 8.3% of total $PM_{2.5}$ mass (47 μg m^{-3}) in 2016. Detailed calculation of the reconstructed mass has been fully described elsewhere (Dabek-Zlotorzynska et al., 2011).

The toxicological effect of hazardous metal 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 metals in the atmosphere. Using a diversity of chemical, physical, and optical techniques, elevated atmospheric concentrations of various metal 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 metals concentrations in Table 1. The concentrations of most trace metals in Shanghai were commonly an order or two orders of magnitude higher than those measured in Europe and North America, and generally ranged in the same level as industrialized city like Kwangju in South Korea. Exceptionally, the concentrations of V and Ni in Shanghai were up to three times higher than that of 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).

3.1.2 Variations at multiple time scales

In contrast to traditional trace metal measurements, the on-line XRF used in the current study enables measurement of metal species concentrations with 1 hr resolution, which are useful both for source discrimination and in determining the processes contributing to elevated trace metals levels through investigation of their diurnal cycles. We willalso discuss weekly cycles because certain emission sources may make a pause or reduction during weekends. Additionally, Shanghai has a humid subtropical climate and experiences four distinct seasons, which could potentially exert an influence on the mass concentrations of atmospheric metal species. Therefore, monthly and seasonal variations of ambient concentrations for each metal species were demonstrated. The variations in meteorology, including T, RH, wind speed, wind direction, and precipitation, at PEMC during our study period were also illustrated in Fig. S1.

As depicted in Fig. 4, the seasonally-averaged mass concentrations of Ag and Cd stayed exceptionally constant regardless of the season. Moreover, variations of Ag and Cd in Fig. 5 are highly consistent on a weekly and diurnal basis, both exhibiting a sharp increase of (normalized) mass concentrations after midnight and then an outright decline after 1:00 (local time), and keeping quite steady during the rest of the day. Globally, anthropogenic emissions of Ag and Cd exceed the natural rates by well over an order of magnitude (Nriagu, 1996; Nriagu, 1979). Thus, our results strongly signaled that Ag and Cd pollution in highly populous Shanghai had very stable and climate-independent anthropogenic emission sources.

Except for Ag and Cd, other metal species were seasonally variable without a uniform variation pattern (Fig. 4). Specifically, the concentrations of five metal species, i.e., As, Cu, Hg, K, and Pb, were higher in winter and lower in summer, which were consistent with the seasonal variation pattern of aerosol organics, sulphate, nitrate, and ammonium that were fully-explored in China. Generally, severer air pollution in Eastern China during winter were mainly attributed to the accumulation of pollutants emitted from coal-based heating in conjunction with stagnant meteorological conditions (Huang et al., 2013). However, other trace metals like Ba, Cr, Fe, Mn, Ni, V, and Zn showed the highest concentrations in spring, suggesting more complex sources and different physical/chemical formations of atmospheric metal species in Shanghai (see discussion later). A better example is Ca and Si, which exhibited the highest degree of seasonal variations with higher concentration levels in summer.

As with Ag and Cd, another example of covariation is V and Ni (Fig. 6). Diurnally, both V and Ni peaked at around 6:00 and then gradually decreased to the bottom at 14:00, which were generally in agreement with wind speed (Fig. 6c), suggesting that V- and Ni-containing aerosols in Shanghai undergo mid- to long-range atmospheric transport. Co-emitted from heavy oil combustion, previous studies in Shanghai port have concluded that a ratio of 3.4 for V/Ni in ambient aerosols could be a reliable indicator of a ship traffic source. Here performed in urban area, the average ratio of V/Ni in our study was 3.1 with slightly seasonal changes (Fig. 7), which was very close to the ratio of averaged V and Ni content in ship heavy fuel oils, indicating V- and Ni-containing aerosols subject to minor atmospheric transformation and thus can be served as a robust tracer of shipping emissions even in costal urban areas. The office hours for Shanghai customs is Monday through Saturday, and the most important holiday in the Chinese

Calendar-Lunar New Year-is usually celebrated during February. This can be used to explain why the weekly (monthly) lowest impact of shipping emissions in Shanghai occurred during Sunday (Fig. 6d) (February (Fig. 6c)).

Distinctive diurnal variation patterns are observed for Si, Ca, Fe, Ba (Fig. 8) as well as Mn and Zn (Fig. 9), characterized by two marked peaks at noon (10:00-11:00) and evening (17:00-18:00), and agreeing well with the diurnal variation of Shanghai traffic flow. Indeed, as the largest megacity in terms of economy and population in China, the contribution of vehicles, both exhaust and non-exhaust emissions (Thorpe and Harrison, 2008), to ambient trace metals cannot be understated in Shanghai. As demonstrated in Fig. 8d and Fig. 9d, there is an evident drop in the concentrations of Si, Ca, Fe, Ba, Mn and Zn after the start of the weekends. Data collected from Shanghai Traffic Administration Bureau, Fig. S2 shows seasonally average weekly cycles of on-road traffic flow in Shanghai, in which the average traffic flows in weekends were lower than during weekdays. Given that Fe is the support material for brake pads, and the agents present in brake linings typically consist of Zn, Mn and Ba, less traffic flow in weekends not only lowers re-suspended road dust but also reduces metal species emissions (Zhao et al., 2015; Xie et al., 2008). Nevertheless, the monthly variation pattern of Si was different from other metals during April through June (Fig. 8c), and Ca exhibited unusually high levels in July (Fig. 8c) and 16:00 (Fig. 8b). PMF analysis of elemental species has suggested that Fe and Ba in urban atmospheres were primarily caused by vehicular brake wear while high levels of Si and Ca were more likely driven by road resuspended dust (Heo et al., 2009; Harrison et al., 2012; Jeong et al., 2016; Amato et al., 2011; Xie et al., 2008). Besides, construction activities are always thriving in China, which have been confirmed as an important source of Si- and Ca-rich crustal matters (Tian et al., 2015). Building construction activities in Shanghai are concentrated between the end of the spring festival (normally the end of February) and the approach of midsummer heat (August) (Tian et al., 2015). For an annual mean of 16.1 °C, Shanghai averages 28.3 °C in August, and the municipal authority will impose a mandatory moratorium toward outdoor construction once temperature rises to 37 °C

(Chang et al., 2016). Besides, heavy-duty diesel vehicles (mostly for transporting and dumping construction waste) in Shanghai can only be allowed to operate after midnight (Chang et al., 2016), leading to higher emissions from diesel engines and unpaved roads.

In Fig. 10 and Fig. 11, diurnal variations of trace metals like Cu, K, Se, As, Pb, Au, and Hg are seemingly full of clutter. Interestingly however, the monthly and weekly cycles of the above-mentioned metal species are remarkably consistent, suggesting the possibility of sharing similar sources. Apart from anthropogenic activity, the planetary boundary layer height in Shanghai normally reaches its annual maximum during August and September (Chang et al., 2016), which are favorable to the vertical dispersion of air pollutants, leading to the lowest concentration levels in Fig. 10. From a perspective of man-made emissions, coal combustion of industrial boilers and nonferrous metal smelting represent the dominant sources for Se/As/Pb/Cr, and Au/Hg, respectively. China annually emits around 10000 metric tons Cu, which have long been thought to be primarily sourced from automotive braking because copper or brass is a major ingredient in friction material (Tian et al., 2015). However, our results based on field measurements in Shanghai go against the inherent notion of Cu origins. Gathering evidence has shown that topsoil and coal ash are also enriched in K (Schlosser, et al., 2002; Thompson and Argent, 1999; Westberg et al., 2003; Reff et al., 2009). These findings suggest more diverse sources of trace metals in a highly industrialized megacity like Shanghai.

3.2 Source analysis

The goal of source analysis in the current study is twofold. 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.

3.2.1 Pinpoint the best possible source

As the first approach in the source analysis, Spearman correlation matrixes were prepared for all measured elemental species and presented in Fig. 12. From Fig. 12, relatively good correlations are observed between trace metals associated with heavy oil combustion (i.e., V and Ni), brake and tire wear (e.g., Fe, Mn, Ba and Zn), trace crustal matters (i.e., Si and Ca), and coal combustion (e.g., Se, As and Pb), indicating the complex influence of multiple sources in Shanghai. Still, trace crustal matters are also well correlated with metal species related to brake and tire wear. As discussed in Section 3.1, the bimodal variations of Si and Ca are also evident, which jointly suggest that the trace crustal matters we observed in Shanghai urban atmosphere were primarily derived from road fugitive dust. Nevertheless, with approximately 70% of most of the airborne crustal species being present in the coarse size fraction (Huang et al., 2013), here we call for more size-resolved sampling and analysis of PM to provide a more detailed understanding of atmospheric trace metals in the future.

Using multiple lines of evidence above, we have inferred heavy oil combustion from ship engines as the possible source of V and Ni. As shown in Fig. 12, in contrast to all other inter-correlated trace metals, V and Ni are not only highly correlated but also exclusively correlated to each other. For metal species data greater than their 90th percentile, CPF analysis in Fig. 13 shows that over 90% Ni and almost all V observed in our receptor site come from the west (East China Sea). From a perspective of geographical origin, Fig. 13 also clearly shows major air masses containing both V and Ni are sourced from the southwest. Overall, it can be safely concluded that shipping emissions are the most likely source of V and Ni in Shanghai. The successful identification of the most likely source, i.e., shipping emissions, is helpful in terms of examining the feasibility of various source apportionment solutions. In other words, V and Ni should be clustered as a single factor/source in any solution.

3.2.2 Explore and constrain more sources

To determine sources of more trace metals, PCA was applied as an exploratory tool, since much larger datasets are required for definitive source apportionment with PCA.

Therefore, only the most apparent groupings of metal species relating to expected sources in the region were identified. The factor loadings are presented in Fig. 14, indicating six statistically significant factors with eigenvalues equal to or greater than 1. These six factors obtained explained nearly 80% of the variance. Unexpectedly, PCA of the 18 elemental species did not reveal any meaningful factors. This can be preliminarily tested by the large contribution of V and Ni in two different factors, but more importantly, was attributed to the large influence of nonferrous smelting, coal combustion, and traffic-related emissions on ambient trace metals measured at PEMC (see discussion later).

Matrix reorder in conjunction with clustering analysis can be a powerful tool for mining the hidden structure and pattern in the correlation matrix of Fig. 12. Here six solutions of source apportionment, from 3 sources/factors to 8 sources/sources, determined by clustering analysis are presented in Fig. 15. As mentioned above, we can rule out the solution of 3 and 4 sources/factors in Fig. 15a and 15b at first since V and Ni are combined with Au and Hg as a single source.

In Fig. 15c through 15f, Au and Hg are always clustered together as an individual factor, suggesting certain similar source(s) they may share. Globally, anthropogenic sources, including a large number of industrial point sources, annually account for 2320 Mg of Hg released to the atmosphere (Nriagu, 1996). Despite various estimates of emission levels among different studies, Hg emissions from nonferrous metal production, coal consumption by industrial boilers and coal combustion by power plants incontrovertibly represent the top three anthropogenic sources in China, with a share of 33.1, 25.4 and 20.7% for each sector according to Tian et al. (2015). In other words, stationary combustion of coal contributes roughly half of Hg emissions of anthropogenic origins. The distribution of metal-related factories is illustrated in Fig. 1, in which coal-fired power plants encompass our site from all directions while nonferrous metal-related works are concentrated in the west (especially in the northwest) but absent in the east of PEMC. Here we calculate percentile concentration levels of Au and Hg, and plot them by wind direction in Fig. 16a and 16b, respectively. It clearly shows Au and Hg are primarily derived from stationary combustion of coal because the overwhelmingly prevailing air masses are from the west of PEMC. Even though, there are few 99-99.9th percentile data that are originated from the northwest of PEMC (Fig. 16a and 16b), signaling that nonferrous metals production only affect high percentile concentrations of Au and Hg at PEMC.

Statistically, the relatively weak correlation between Ag and Cd (Fig. 12) excludes the possibility that they could equally share the same source. Therefore, the solution of 5 factors/sources illustrated in Fig. 15c is superficially invalid. A knowledge gap remains regarding the emissions of Ag in China, while this is not the case for Cd. In total 456 metric tons in 2010, the major category sources for Cd emissions in China were nonferrous metals smelting (mainly primary Cu smelting industry), coal consumption by industrial boilers and other non-coal sources, which accounted for 44.0, 22.8 and 8.4% of the total emissions, respectively (Tian et al., 2015). Significantly high concentrations of Ag were also observed near the field of nonferrous metals processing works and coal-fired power plants in China, suggesting that nonferrous metal production and industrial coal consumption are also important sources of Ag. As reported in Fig. 16c and 16d, the receptor site, PEMC, evenly receives air masses containing Ag and Cd in all directions, indicating that both Ag and Cd in the Shanghai urban atmosphere are the mixture of miscellaneous sources.

Among the reaming metal species, Cu/K/Pb/As/Se, Cr/Mn/Zn, Fe/Ba, and Ca/Si are grouped together as a population from first to last in Fig. 15. In China, 73% of As, 62% Se, 56% of Pb, and 50% Cu emissions were found to be coal combustion (Tian et al., 2015). Therefore, As and Se are typically treated as the specific tracers of coal-related emissions in China (Tian et al., 2015; Zhang, 2010; Ren, 2006). Different coal fields have significantly different contents of As and Se, which offers an opportunity to infer the possible region of coal production. For example, the average As content of coal in northern China (0.4-10 mg kg^{-1}; mg As per kg coal) and southern China (0.5-25 mg kg^{-1}) are 3 mg kg^{-1} and 10 mg kg^{-1}, respectively (Zhang, 2010; Ren, 2006). With an average value of 2 mg kg^{-1}, the Se content in various Chinese coal fields ranges from 0.1 mg

kg^{-1} to 13 mg kg^{-1} (Zhang, 2010; Ren, 2006). We have no direct information regarding As and Se contents in coal used in Shanghai. As an alternative, here the average ratio of ambient As and Se (As/Se ratio) in Shanghai was calculated as 2.65, which was very close to the As/Se ratio (2.76) in coal (long flame coal of the Jurassic period) of Henan Province in northern China (Zhang, 2010). Note that the As/Se ratios in Shanxi Province, a major coal production region in China, range from 0.24 in Taiyuan (the capital city of Shanxi) to 1.96 in Datong (a prefecture-level city in northern Shanxi) (Zhang, 2010). The emission source regions of Cu, K, Pb, As, and Se are demonstrated in Fig. 17, in which all species are generally transported from far western Shanghai (where stationary combustion of coal is located; Fig. 1) to our sampling site.

It is well known that Ca and Si are two of the five most abundant elements in the Earth's crust, with a reputation of being the most specific tracers of wind-blown dust. Located on the eastern coast of China, Shanghai rarely receives long-range transport of crustal matters from aeolian dust and the Gobi Desert in northwestern China (Huang et al., 2013). Sampling at the east side of Shanghai, a majority of measured Ca and Si must be sourced from road fugitive dust or urban construction sites, which can be further validated by the CPF and BPP analysis of Ca and Si (Fig. S3). As discussed above, ambient Fe and Ba at PEMC are strongly associated with brake wear (Zhao et al., 2015). In Fig. 15, significant correlations are observed for Ca, Si, Fe, and Ba, suggesting that the measured Ca and Si during our study period was most likely derived from road fugitive dust.

As a group of tightly-linked metal species, identifying a principle source for measured Cr, Mn and Zn at PEMC is a challenging task. Cr, Mn and Zn have relatively good correlation with two groups of metal species, i.e., coal combustion-related emissions (i.e., Cu, K, Pb, As, and Se) and brake wear-related emissions (i.e., Fe and Ba). This is basically attributed to the diverse sources of Cr, Mn and Zn themselves in China. For Cr, the national atmospheric emissions from anthropogenic sources in 2010 was 7465.2 metric tons, of which 5317.6 metric tons were emitted from coal consumption by industrial boilers (Tian et al., 2015). Coal combustion is also the dominant source of

Mn at a national scale, while in urban areas with intensive road network, the contribution of brake and tire wear to ambient Mn is appreciable. In contrast to Cr and Mn, the ferrous metals smelting sector (31.3%), especially the pig iron and steel production industry, is the leading contributor to Zn emissions in China, followed by coal combustion (21.7%) and the nonferrous metals smelting sector (19.3%). The Baosteel company in Shanghai, located to the northwest of PEMC (approximately 20 km apart; Fig. 1), is a flagship manufacturer in terms of producing the first-chop iron and steel throughout China. Fig. S4 also evidently reflects that high concentrations of Zn can occur in the northwest of PEMC. In summary, ambient Cr, Mn and Zn in the Shanghai urban atmosphere is highly mixed with coal combustion by industry sectors and power plants, ferrous metal production, and nonferrous metal smelting.

4. Conclusion and outlook

This paper presents the results from a year-long, near real-time measurement study of 18 trace elements (Si, Fe, K, Ca, Zn, Mn, Pb, Ba, V, Cu, Cd, As, Ni, Cr, Ag, Se, Hg, and Au) in $PM_{2.5}$ using a Xact multi-metal 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 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.

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

-The full coverage of trace elemental species (18) measurement and the high temporal frequency (hourly) in the work provided unprecedented details regarding the temporal evolution of metal pollution and its potential sources in Shanghai.

-Various mathematical methods (e.g., correlation matrix, hierarchical clustering, and conditional probability function) and high temporal resolution monitoring data were used to infer the contribution of local emissions (specific sectors) and long-range transport to measured metal species.

A greater value and more interesting topic to the scientific community would be to fully assess the role of $PM_{2.5}$ chemical constituents (including metal species) and sources of emission to human health. Looking towards the future, three major steps will be taken 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 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) platform will be collocated across a rural-urban-background transect to simultaneously measure hourly metal species, carbonaceous aerosols, and inorganic aerosol components in $PM_{2.5}$. Lastly, integrating all available information regarding $PM_{2.5}$ chemical species and isotopes into a receptor model or atmospheric chemical transport model will be carried forward to create more specific and confident source apportionment results.

Competing interests

The authors declare that they have no competing interests.

Data availability

Data are available from the corresponding authors on request.

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Table 1. A collection of long-term and high-time resolution measurements of ambient trace elements concentrations (ng m^{-3}) in fine particles.

Species	**Shanghai, CN**[a]	**Gwangju, KP**[b]	**London, UK**[c]	**London, UK**[d]	**Barcelona, ES**[e]	**Wood Buffalo, CA**[f]	**Toronto, CA**[g]
Ag	3.9	/	/	/	/	/	/
As	6.6	9.6	/	/	/	/	/
Au	2.2	/	/	/	/	/	/
Ba	24.2	52.0	10.3	3.7	/	/	1.9
Ca	191.5	122	78.7	50.1	130.0	54.0	54.0
Cd	9.6	/	/	/	/	/	/
Cr	4.5	/	2.3	0.8	8.0	0.04	0.24
Cu	12.0	15.5	12.8	4.9	8.0	2.04	3.1
Fe	406.2	293.0	350.3	118.9	131.0	60.0	76.8
Hg	2.2	/	/	/	/	/	/
K	388.6	732.0	27.2	23.7	82.0	31.0	27.1
Mn	31.7	24.0	4.8	2.5	6.0	1.12	1.8
Ni	6.0	3.8	0.5	0.2	3.0	0.08	0.21
Pb	27.2	49.0	2.3	1.8	12.0	/	2.4
Se	2.6	4.3	/	/	/	/	0.3
Si	638.7	/	/	/	/	143	/
V	13.4	4.6	1.3	0.6	8.0	0.21	0.11
Zn	120.3	103.0	8.9	5.3	25.0	0.88	11.3

Note: a, this study; b, Park et al., 2014; c, $PM_{0.3\text{-}2.5}$, Marylebone Road (Visser et al., 2015b); d, $PM_{0.3\text{-}2.5}$, North Kensington (Visser et al., 2015b); e, Road site (Dall'Osto et al., 2013); f, Phillips-Smith et al., 2017; g, Sofowote et al., 2015. We noticed that although a huge data set of hourly resolved trace metals had been reported in Jeong et al. (2016) and Visser et al. (2015a), in which no detailed information regarding the specific mass concentrations of trace metals were given.

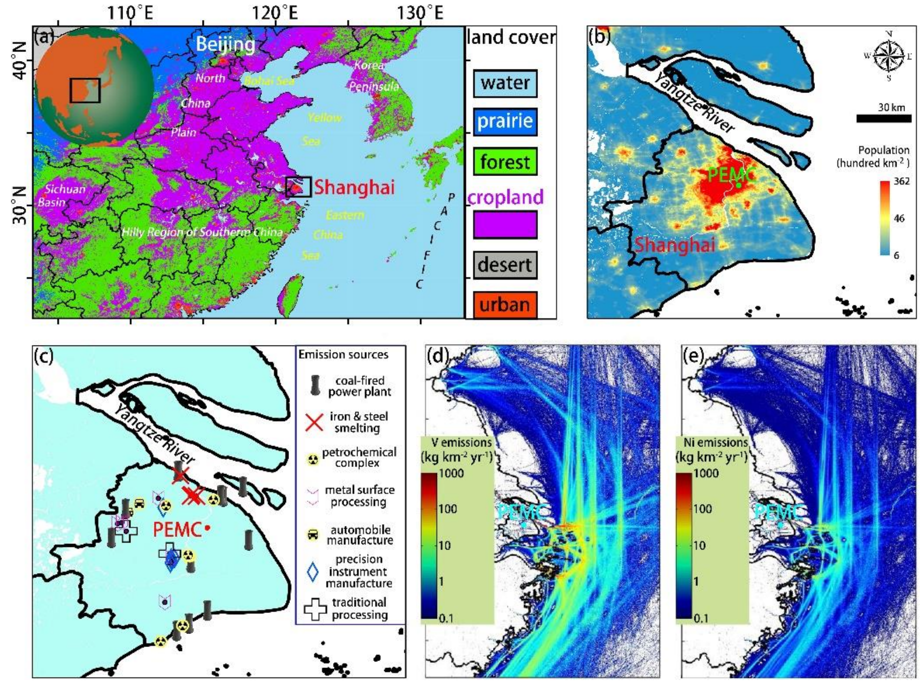

Figure 1. A land use map indicating the location of Shanghai (**a**; black box), as well as the population density (**b**) and the major point sources (**c**) around the sampling site (PEMC). The emissions of V (**d**) and Ni (**e**) from shipping in the YRD and the East China Sea within 400 km of the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

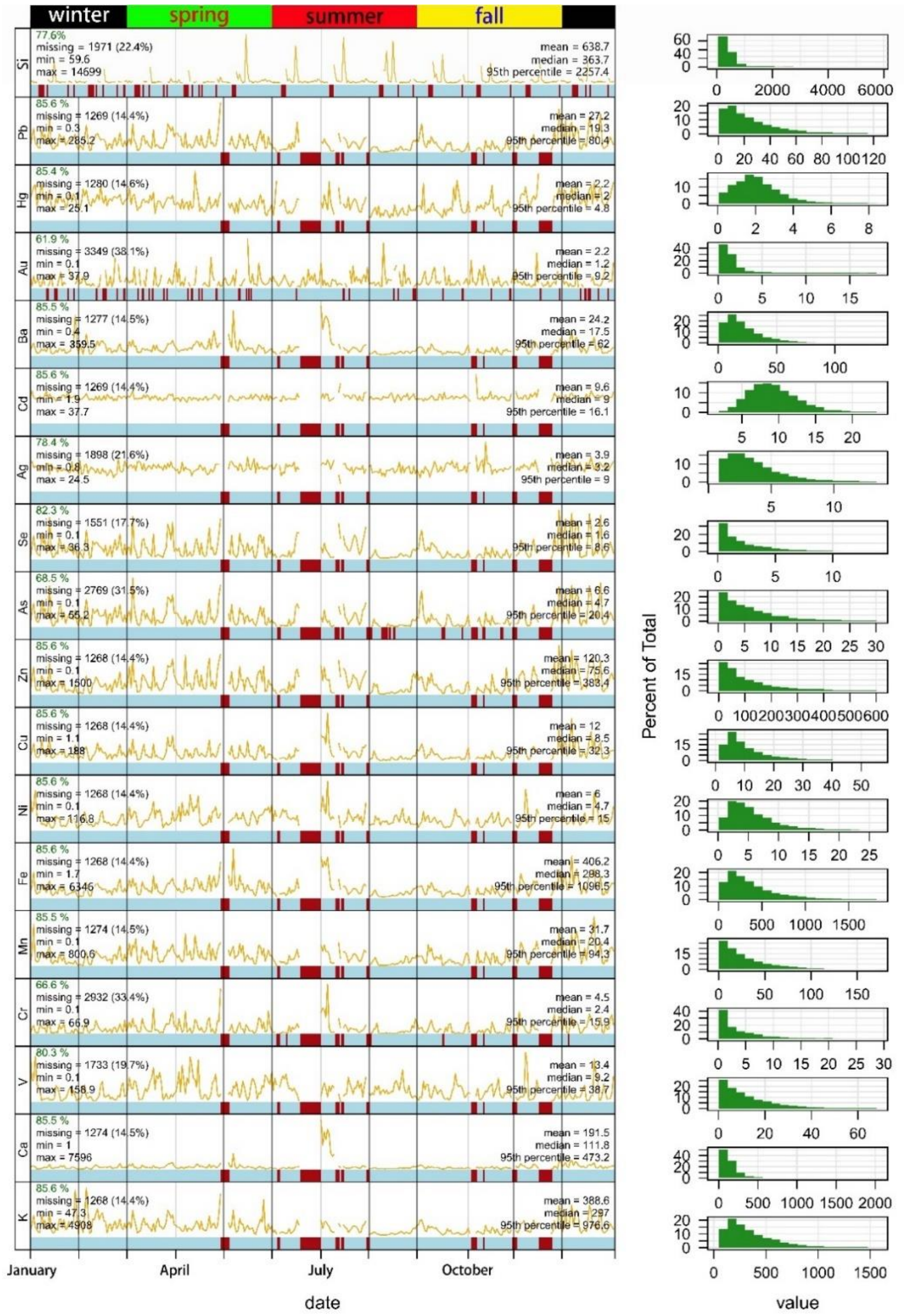

Figure 2. General statistical summaries of 18 trace elements measured in Shanghai. The plots in the left panel show the time series data, where blue shows the presence of data and red shows missing data. The mean daily values are also shown in pale yellow scaled to cover the range in the data from zero 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, the overall summary statistics are given. The panels on the right show the distribution of each elemental species using a histogram plot.

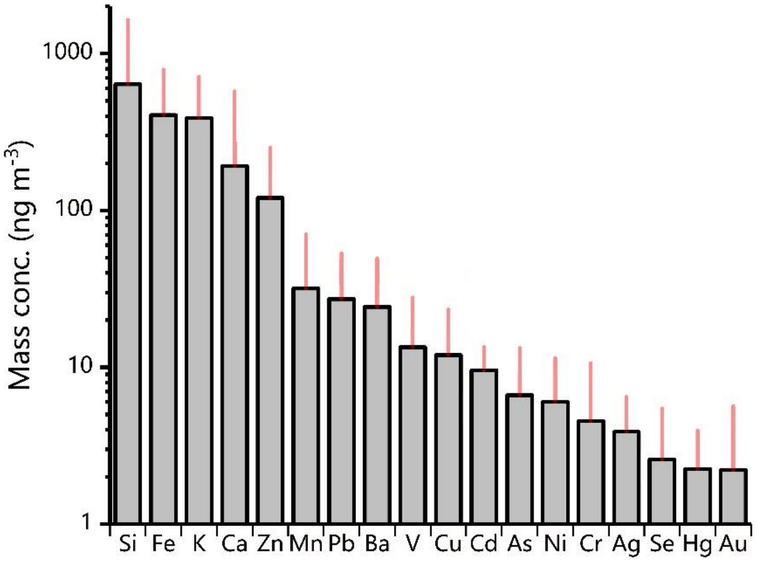

Figure 3. A quick glance of the mass concentrations of 18 trace elements measured in Shanghai as sorted from high to low (log10 scaling). The dark red line indicates one standard deviation.

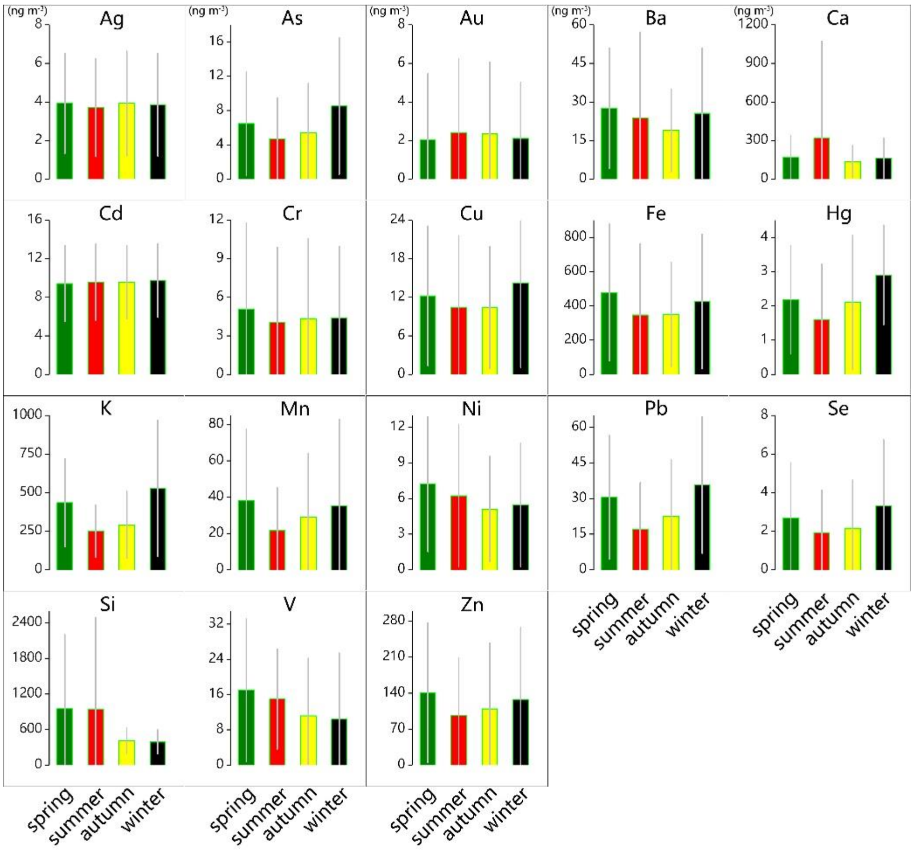

Figure 4. Seasonal variations of mass concentrations for 18 trace elements measured in Shanghai between March 2016 and February 2017. The gray line indicates one standard deviation. Four seasons in Shanghai were defined as follows: March-May as spring, June-August as summer, September- November as fall, and December and January-February as winter.

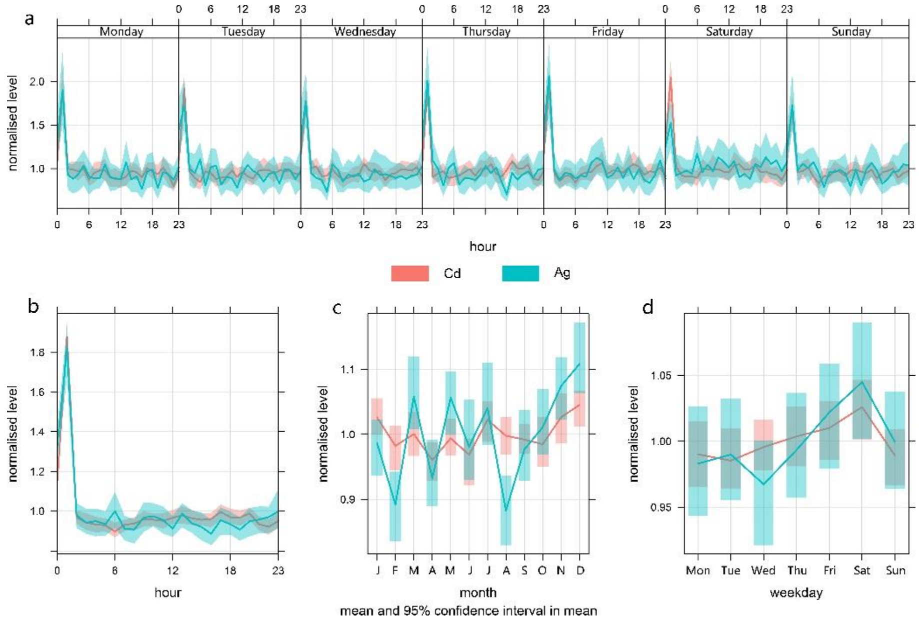

Figure 5. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized Cd and Ag concentrations in Shanghai.

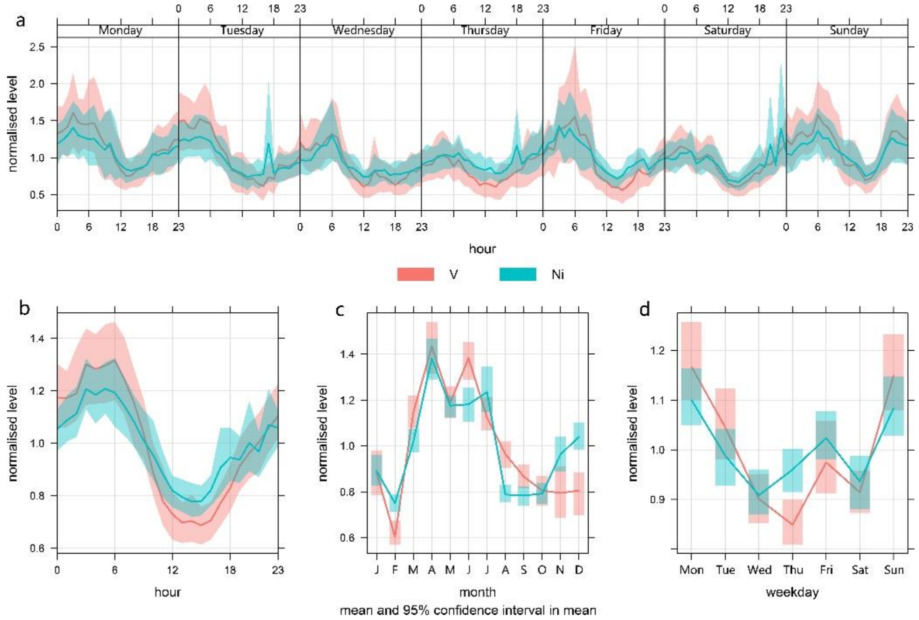

Figure 6. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized V and Ni concentrations, and wind directions in Shanghai.

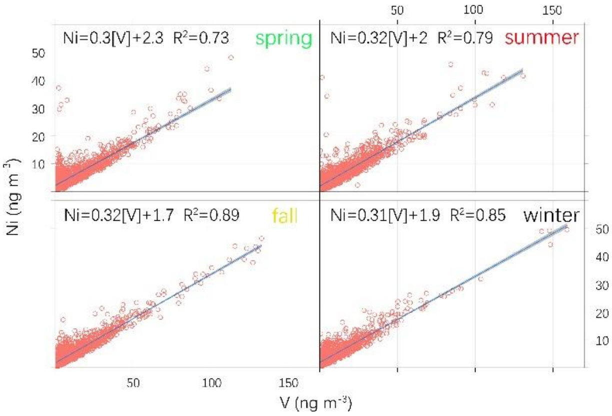

Figure 7. Linear correlation analysis between V (x axis) and Ni (y axis) in Shanghai during four seasons.

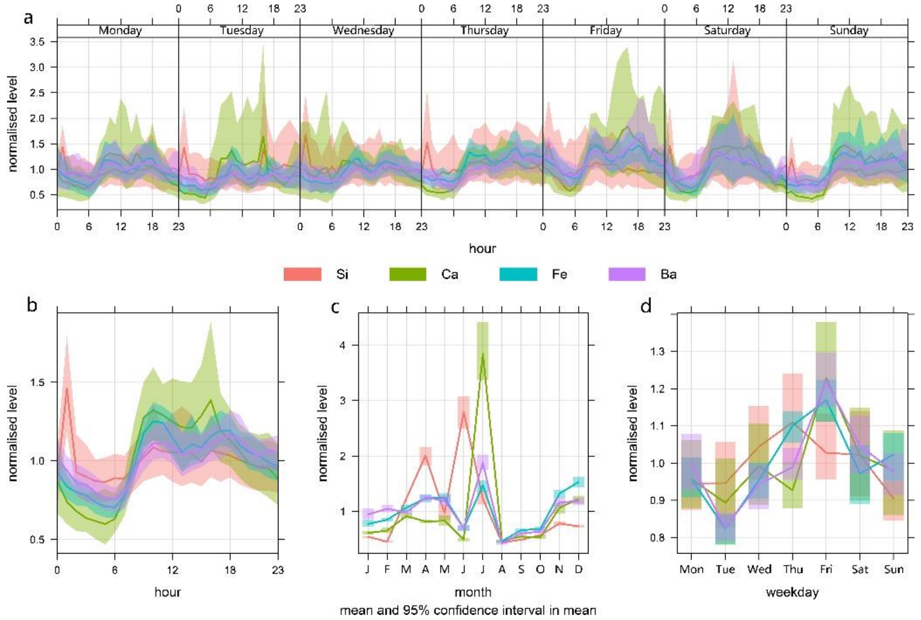

Figure 8. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized Si, Ca, Fe, and Ba concentrations in Shanghai.

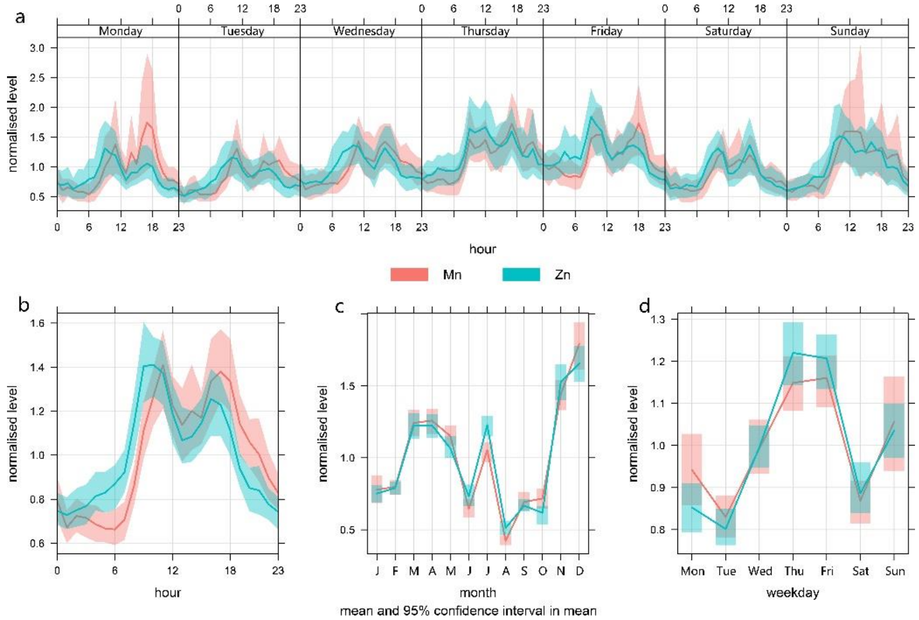

Figure 9. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized Mn and Zn concentrations in Shanghai.

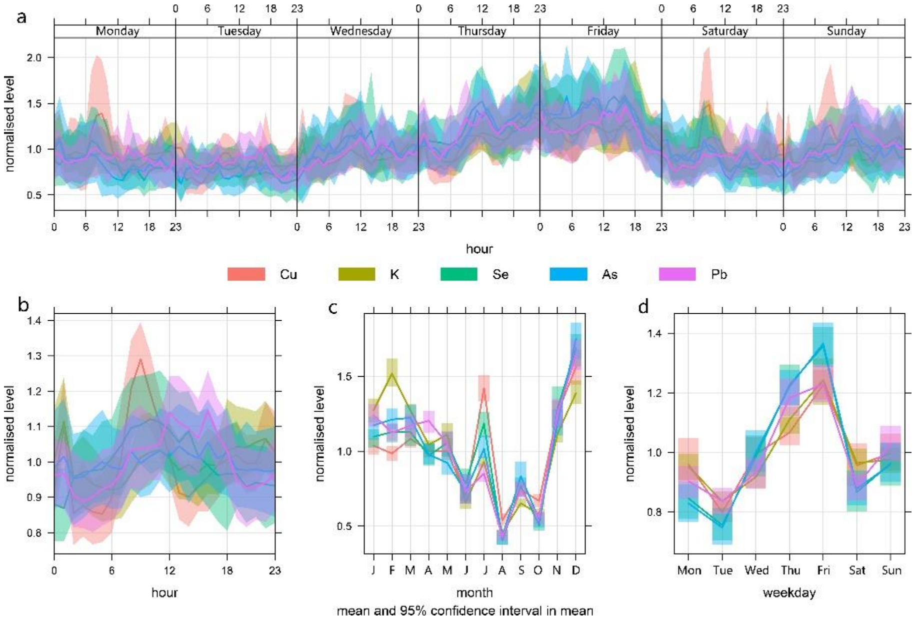

Figure 10. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized Cu, K, Se, As, and Pb concentrations in Shanghai.

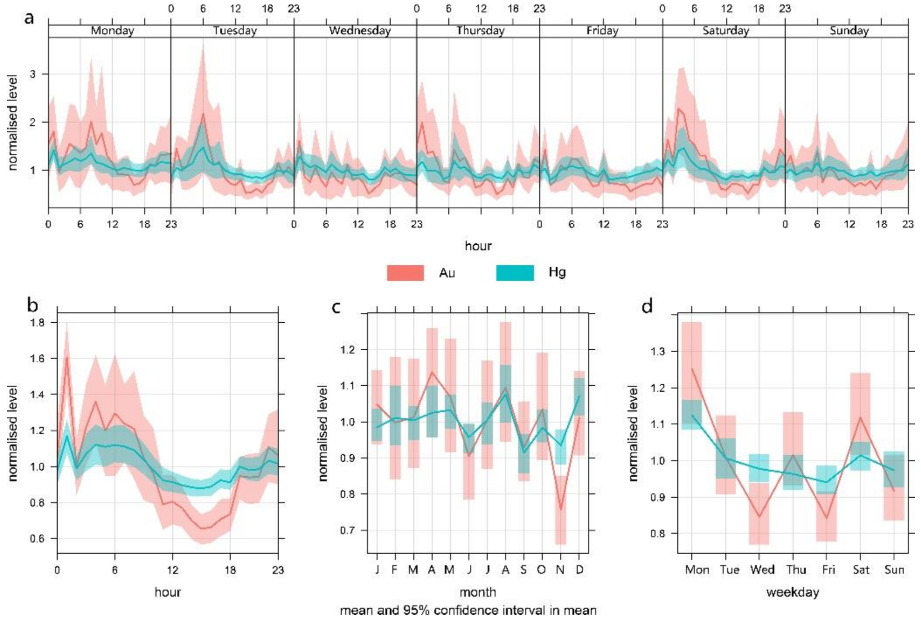

Figure 11. Weekly diurnal (**a**), diurnal (**b**), monthly (**c**), and weekly (**d**) variations of normalized Au and Hg concentrations in Shanghai.

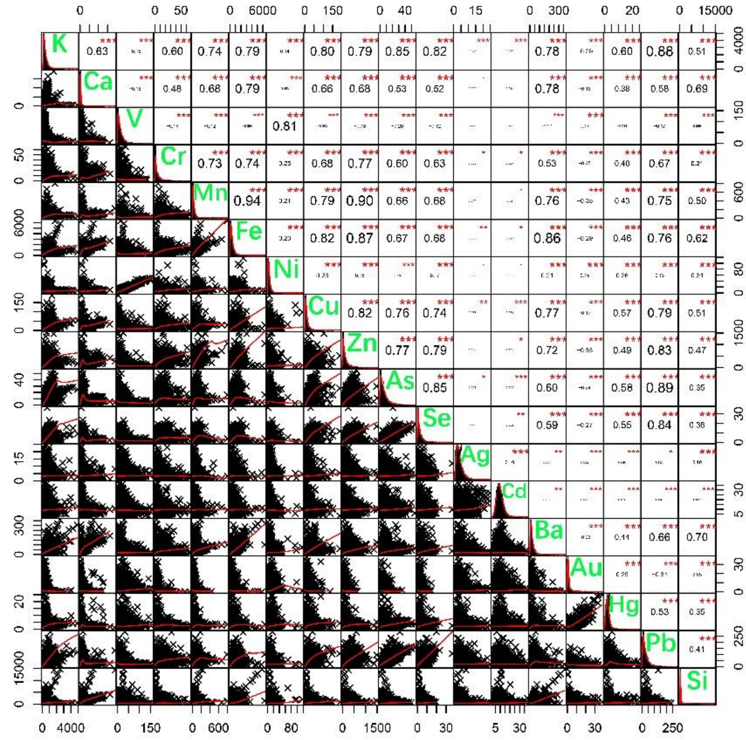

Figure 12. Spearman correlation matrix of 18 atmospheric elemental species in Shanghai between March 2016 and February 2017. The distribution of each species is shown on the diagonal. Below the diagonal of the diagonal, the bivariate scatter plots with a fitted line are displayed; above of the diagonal, the value of the correlation plus the significance level as asterisks. Each significance level is associated to a symbol: *p*-values (0, 0.001, 0.01, 0.05, 0.1, 1) = symbols (“***”, “**”, “*”, “.”, " “).

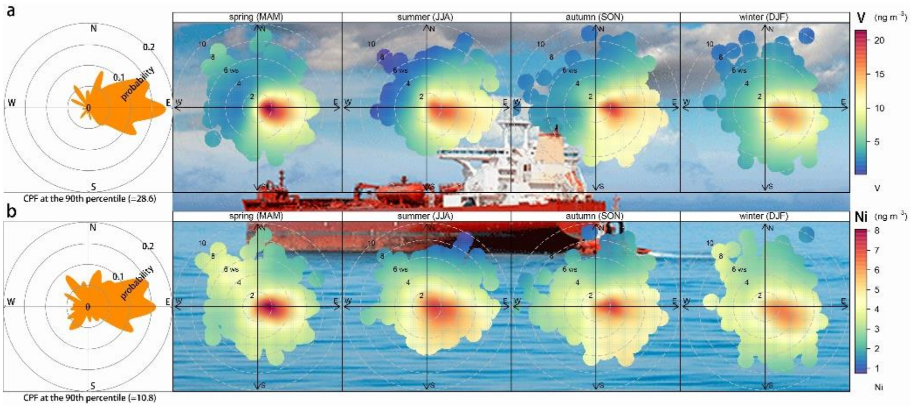

Figure 13. Conditional probability function analysis (left) and bivariate polar plots (right) of seasonal concentrations (ng m^{-3}) of V (**a**) and Ni (**b**) in Shanghai between March 2016 and February 2017. The center of each plot (centered at the sampling site) represents a wind speed of zero, which increases radially outward. The concentrations of V and Ni are shown by the color scale.

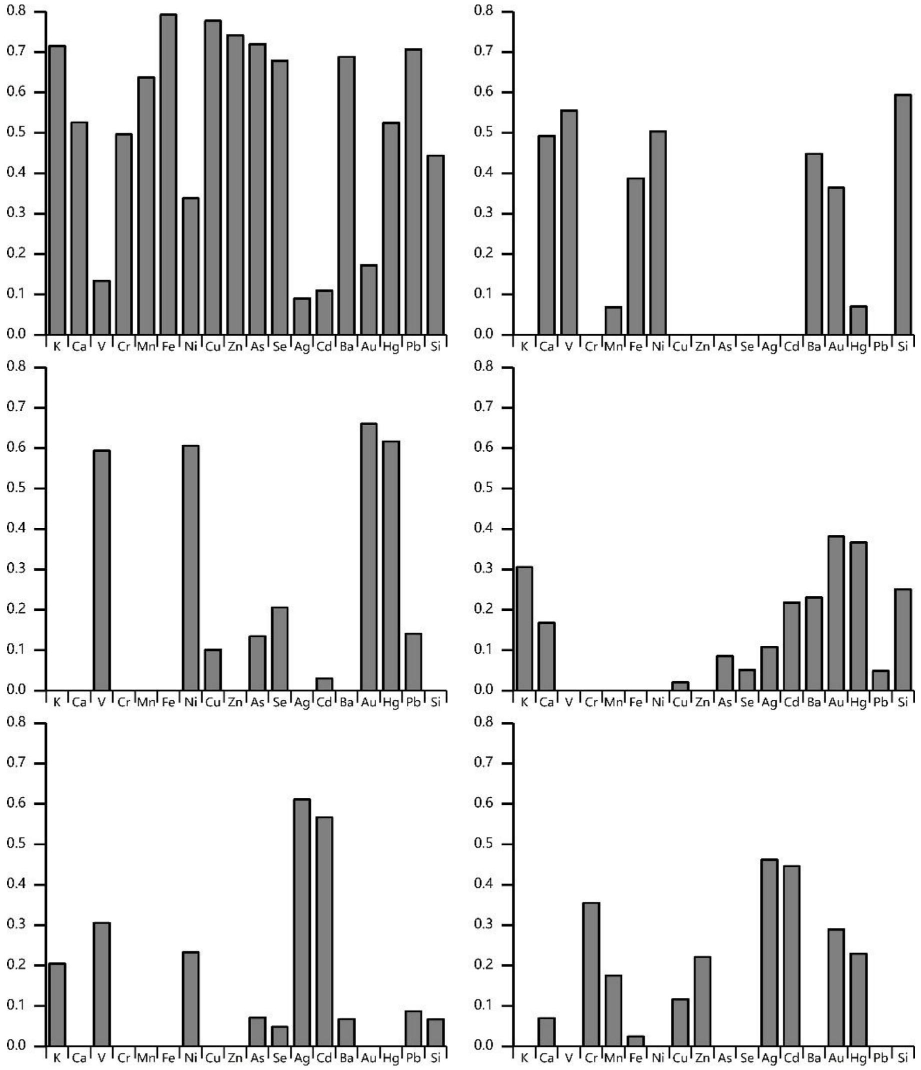

Figure 14. Principle component analysis of the 18 trace metals concentrations measured in Shanghai between March 2016 and February 2017. Six dominant factors are identified.

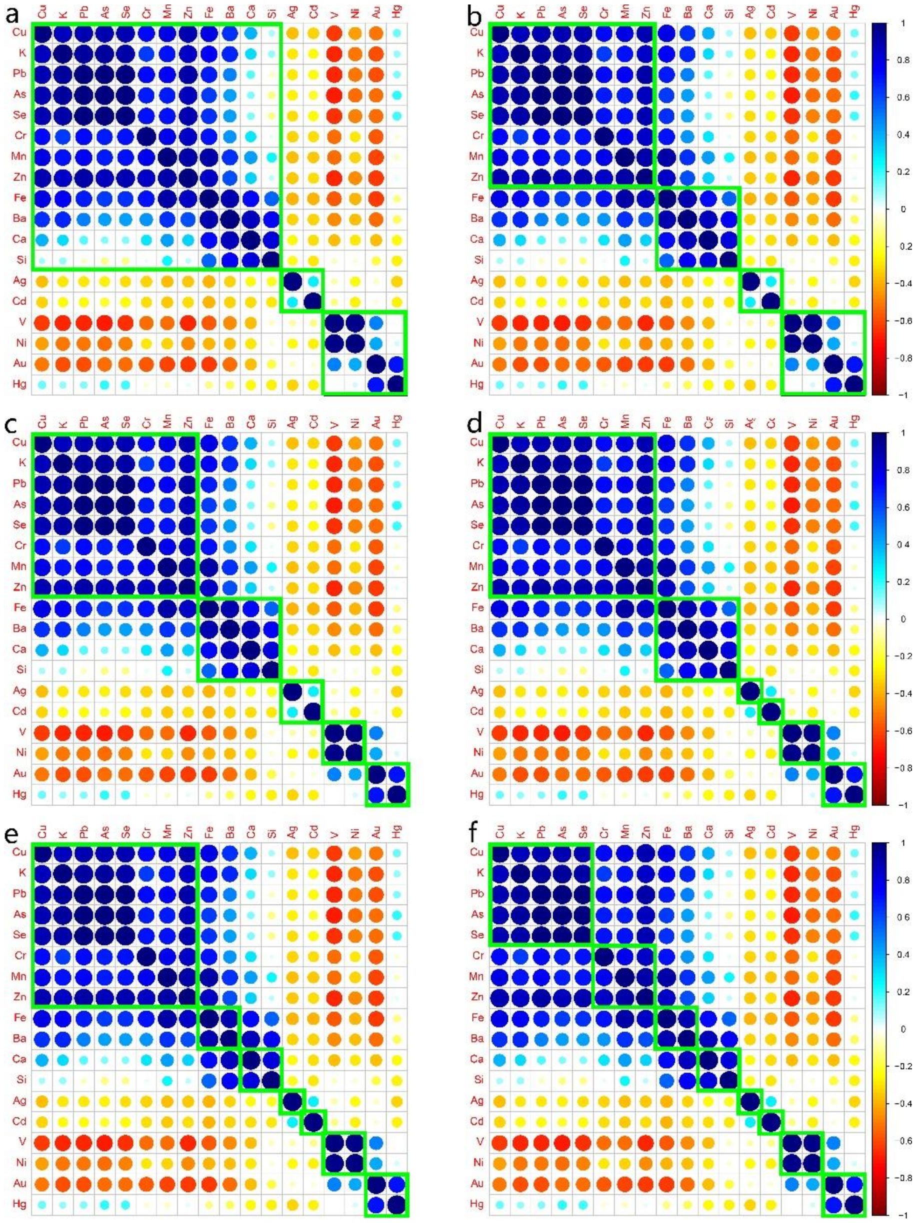

Figure 15. Hierarchical clustering orders of correlation matrix for the 18 trace elements measured in Shanghai between March 2016 and February 2017. Six solutions, from 3 factors to 8 factors, are shown from **a** to **f**.

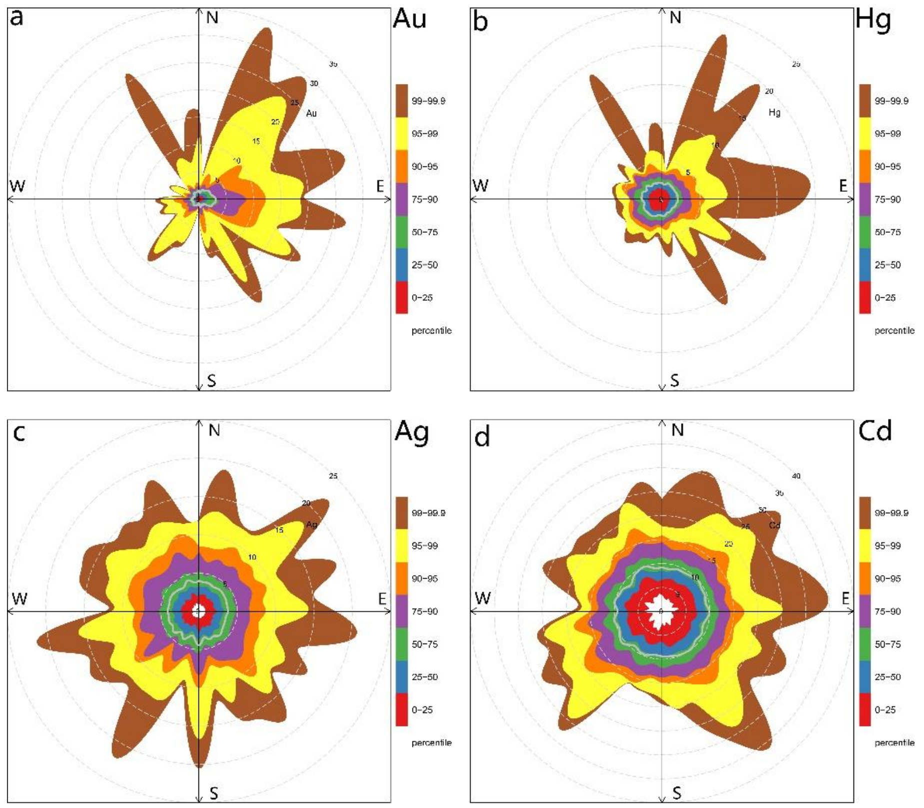

Figure 16. Percentile rose plot of Au (**a**), Hg (**b**), Ag (**c**), and Cd (**d**) concentrations in Shanghai between March 2016 and February 2017. The percentile intervals are shaded and shown by wind direction.

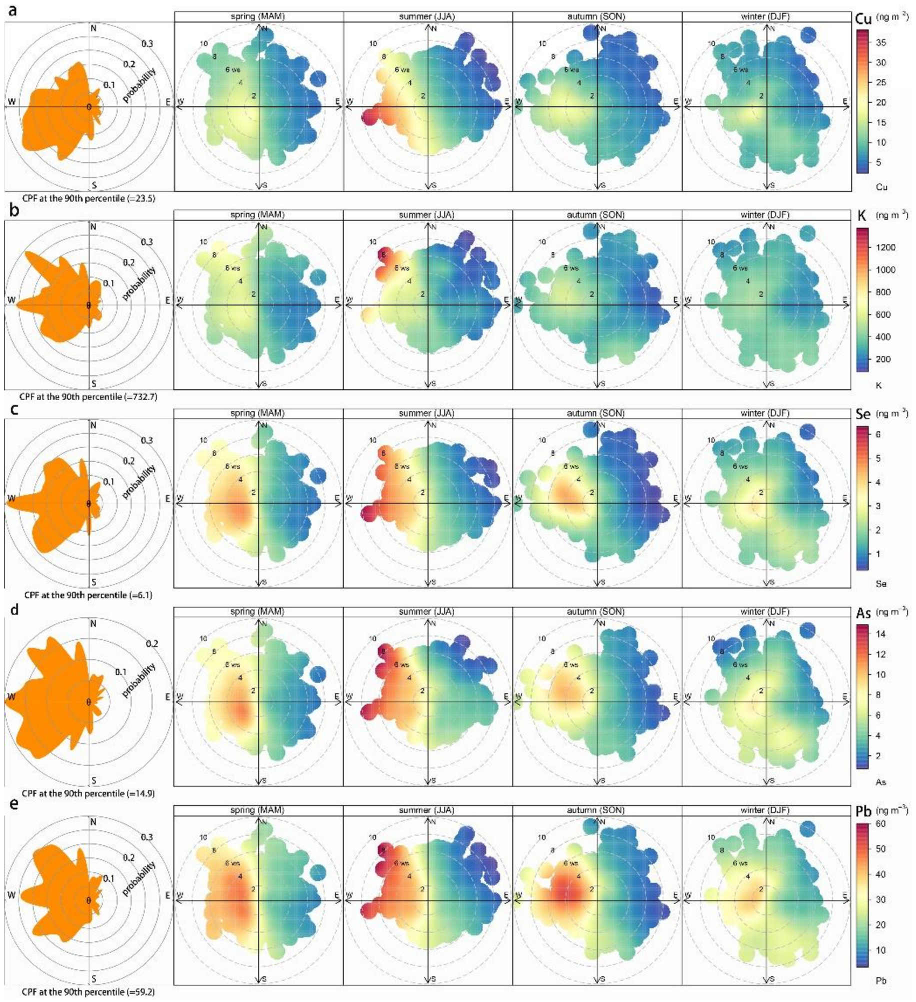

Figure 17. Conditional probability function analysis (left) and bivariate polar plots (right) of seasonal concentrations (ng m^{-3}) of Cu (**a**), K (**b**), Se (**c**), As (**d**), and Pb (**e**) in Shanghai between March 2016 and February 2017. The center of each plot (centered at the sampling site) represents a wind speed of zero, which increases radially outward. The concentrations of each species are shown by the color scale.