Dear Prof. Willy Maenhaut,

We thank you again for handling our paper and for your valuable comments. Addressing the points, you and two reviewers raised, we have prepared a revised manuscript with track-changes model (page 24-66). Please see our point-by-point reply to the comments of you (page 1-15), reviewer 6 (page 16-21), and reviewer 2 (page 22-23) below.

Co-Editor's Comments:

The manuscript has been substantially improved with the PMF results. The aspect of precipitation scavenging is also presented in a better way, but there are still problems with it as indicated in the report of Anonymous Referee #6. The comments and corrections of both Anonymous Referees need to be fully addressed. I also have several comments and corrections, which are listed below, and need to be taken into consideration. Consequently, substantial revision is still needed before this manuscript can be accepted for publication in ACP.

Main comments for the Main text:

1. *The language and grammar of the manuscript are fair, but there is very much room for improvement. Many alterations are suggested under "Further comments" below.*

Reply: Thank you very much for your careful revision. We had asked a native English speaker for the language correction before the submission, sorry for so many language problems still existed. All the problems you raised have been corrected in the revised MS.

2. *Line 41: The ratio of 0.31 is too low for a V/Ni ratio in shipping emissions. Does the 0.31 perhaps indicate the Ni/V ratio? If so, replace it by the V/Ni ratio. See also the comment of Anonymous Referee #6 on this topic.*

Reply: Sorry for our carelessness. The ratio of 0.31 should be "Ni/V" ratio. Given that "V/Ni" ratio is a well-known term as pointed out by Anonymous Referee #6, we revised

the text and figure accordingly. The previous figure was plotted by Openair package in R, and the revised figure was plotted by OriginPro 2017.

3. *Lines 215-216: Since the Micromatter standards were used for calibration, it is unclear to me how one can then derive independent measured and standard masses from them*.

Reply: No need to derive independent measured and standard masses. The Quantitative Aerosol Generator (QAG) creates an aerosol of known concentration by nebulizing a solution. The resulting droplets are carried out of generation area to a drying chamber where they are dried to salt particles. Depending on the application for the salt particles the size can be varied to a number mean between 0.1 and 2 µm in diameter. The aerosol exiting the drying chamber contains a known concentration of analytes that is calculated from the QAG's input parameters. This reference aerosol produced by the QAG is process traceable to the National Institute for Science and Technology standards and can be used to challenge and evaluate the accuracy, precision, and linearity of measurement methods such as the XACT metal monitor during sampling.

4. *Line 248: Abbreviations and acronyms (here "USEPA" and "QA/QC") should be defined (written full-out) when first used. Since the acronyms are only used here, "USEPA" can simply be replaced by "United States Environmental Protection Agency" and "QA/QC" by "Quality Assurance / Quality Control"*.

Reply: Correct. We revised the text accordingly.

5. *Line 249: It is unclear what is meant by "upscale values"*.

Reply: The term "upscale values" is essentially means "quality-assured values". The second phase of the quality-assurance (QA) run of the XACT metal monitor is the upscale sample. Specifically, the linear actuator is used to introduce a known sample into the analysis area containing a large amount of Cr, Cd, and Pb. A 15 minute XRF analysis of this sample is performed, and the metals data is sent over to the sample

controller. As this XRF analysis is taking place, the sample controller is also performing the QA flow check. The QA flow check uses a different flow path and flow meter to measure and confirm that the sample flow is within the allowed limits.

6. Line 269: The phrasing of "with all elements missed" is somewhat unclear. I suggest to replace "with all elements missed" by "with missing data".

Reply: Agree. We revised the text accordingly.

7. *Page 13, within Figure 2 (and on various other occasions in the manuscript, e.g., in Table 1, data for this study; in line 334; within Figure 4; in line 408; in line 426): The concentration data contain too many significant figures. Two significant figures suffice in case the first significant figure is larger or equal than 2, and when the first significant figure equals 1, three significant figures can be used*.

Reply: Agree. We decided to delete Figure 3 in the revised MS because it is redundant. We keep Table 1 because it is necessary to perform data comparison with other relevant studies. For line 408, we need to specify the mass fraction of several trace elements markers, which cannot be directly reflected in Figure 4. Although the specific figures have been shown in Fig. 4, we treated line 426 as a mini conclusion, and we want to convey this important message to readers. Thank you for your understanding.

8. *Page 20, Figure 6: Please, replace this figure by one with V in the ordinate and Ni in the abscissa, and provide thus regression lines with V in the y-axis. See also the comment of Anonymous Referee #6 on this topic*.

Reply: Agree. We revised the figure accordingly.

9. *Lines 492-494: Literature references are needed for the statements in these two sentences*.

Reply: Agreed; two studies that are relevant in this context have been added in the revised MS.

Morawska, L., and Zhang, J.: Combustion sources of particles. 1. Health relevance and source signatures, Chemos., 49, 1045-1058, doi: 10.1016/S0045-6535(02)00241-2, 2002.

Tian, H. Z., Zhu, C. Y., Gao, J. J., Cheng, K., Hao, J. M., Wang, K., Hua, S. B., Wang, Y., and Zhou, J. R.: Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: Historical trend, spatial distribution, uncertainties, and control policies, Atmos. Chem. Phys., 15, 10127-10147, doi: 10.5194/acp-15-10127-2015, 2015.

10. There are several problems with the References.

Reply: Thanks again for your very careful revision. We've corrected all the problems you mentioned.

11. The following references to which is referred within the text are not in the Reference list:

Line 256: Paatero and Tapper, 1994.

Reply:

Pentti, P., and Unto, T.: Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111-126, doi:10.1002/env.3170050203, 1994.

Line 271: Kim et al., 2005; Kim and Hopke, 2007.

Reply:

Kim, E., Hopke, P. K., and Qin, Y.: Estimation of organic carbon blank values and error structures of the speciation trends network data for source apportionment, J. Air Waste Manage. Assoc., 55, 1190-1199, doi: 10.1080/10473289.2005.10464705, 2005.

Kim, E., and Hopke, P. K.: Comparison between sample-species specific uncertainties and estimated uncertainties for the source apportionment of the speciation trends

network data, Atmos. Environ., 41, 567-575, doi: 10.1016/j.atmosenv.2006.08.023, 2007.

Lines 278-279: Norris et al., 2014.

Reply:

Norris, G., Duvall, R., Brown, S., Bai, S.: EPA Positive Matrix Factorization (PMF) 5.0 fundamentals and user guide prepared for the US Environmental Protection Agency Office of Research and Development. *Washington, DC*, 2014.

Line 279: Brown et al., 2015; Paatero et al., 2014; Wang et al., 2017.

Reply:

Brown, S. G., Eberly, S., Paatero, P., and Norris, G. A.: Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results, Sci. Total Environ., 518-519, 626-635, doi: 10.1016/j.scitotenv.2015.01.022, 2015.

Paatero, P., Eberly, S., Brown, S. G., and Norris, G. A.: Methods for estimating uncertainty in factor analytic solutions, Atmos. Meas. Tech., 7, 781-797, doi: 10.5194/amt-7-781-2014, 2014.

Wang, Q., He, X., Huang, X. H. H., Griffith, S. M., Feng, Y., Zhang, T., Zhang, Q., Wu, D., and Yu, J. Z.: Impact of secondary organic aerosol tracers on tracer-based source apportionment of organic carbon and $PM_{2.5}$: A case study in the Pearl River Delta, China, ACS Earth Space Chem., 1, 562-571, doi: 10.1021/acsearthspacechem.7b00088, 2017.

Line 414: Hjortenkrans et al., 2007.

Reply:

Hjortenkrans, D. S. T., Bergbäck, B. G., and Häggerud, A. V.: Metal emissions from brake linings and tires: Case studies of Stockholm, Sweden 1995/1998 and 2005, Environ. Sci. Technol., 41, 5224-5230, doi: 10.1021/es070198o, 2007.

Line 416: Thorpe et al., 2008.

Reply: It should be “Thorpe and Harrison, 2008”.

Thorpe, A., and Harrison, R. M.: Sources and properties of non-exhaust particulate matter from road traffic: A review, Sci. Total Environ., 400, 270-282, doi: 10.1016/j.scitotenv.2008.06.007, 2008.

Line 435: Chang et al., 2016a. Should the "2016a" perhaps be replaced by "2016"?

Reply: Yes, revised accordingly.

Line 520: Wang et al., 2013. There are "Wang et al., 2013a" and "Wang et al., 2013b" in the Reference list.

Reply: The “*Wang et al., 2013*” changed as *"Wang et al., 2013b"* in the text.

Line 555: Karanasiou et al., 2014. There is "Karanasiou, 2014" in the Reference list.

Reply:

“Karanasiou et al., 2012, 2014” in the text should be changed as “Karanasiou et al., 2012; Karanasiou, 2014”.

12. The is no reference made within the text to the following references that are in the Reference list:

Amato et al., 2011.

Khalaf et al., 1982.

Zhao et al., 2015.

Reply: These references were cited in the original MS. We deleted them in the revised MS.

13. The references in the Reference list are not always in the appropriate order: "Carslaw et al., 2006" should come after "Carslaw and Ropkins, 2012".

"Dall'Osto et al., 2016" should come after "Dall'Osto et al., 2013".

"Hueglin et al., 2005" should come after "Huang, W. et al., 2012".

In case "Karanasiou, 2014" is correct, it should come before "Karanasiou et al., 2012".

"Liu, S. et al., 2014" should come before "Liu, Z. et al., 2015".

"Lu et al., 2008" should come after "Lough et al., 2005".

Furthermore:

Line 520: Replace "Suess et al." by "Suess".

Line 791: Replace "R. A., and" by "R. A. and".

Reply: We've corrected accordingly, thanks!

14. Further comments for the Main text:

Line 25: Replace "at Shanghai" by "at the Shanghai".

Line 28: Replace "Elements related" by "Element-related".

Line 30: Replace "atmospheric" by "the atmospheric".

Line 33: Replace "of elements in" by "of the elements in the".

Line 34: Replace "in brackets" by "in parentheses".

Line 35: Replace "melting" by "smelting".

Line 37: Replace "Contributed by exhaust and non-exhaust vehicle emissions," by "The contribution from the exhaust and non-exhaust vehicle emissions, i.e., the".

Line 38: Replace "shows strong" by "shows a strong".

Line 39: Replace "during rush" by "during the rush" and replace "Shipping" by "The shipping".

Line 40: Replace "almost" by "are almost".

Line 41: Replace "transported from East" by "transported from the East" and replace "fallen" by "falls".

Line 42: Replace "V/Ni in" by "V/Ni ratios in".

Line 43: Replace "K were derived" by "the K was derived".

Line 45: Replace "to trace" by "to the trace".

Line 47: Replace "of trace" by "of the trace".

Line 48: Replace "lower" by "lower the concentration of the".

Line 50: Replace "in urban" by "in the urban".

Line 61: Replace "refers" by "referring".

Line 63: Replace "with unique" by "unique".

Line 67: Replace "on aerosol" by "on the aerosol".

Line 69: Replace "elements components" by "elemental components".

Line 70: Replace "exerted a" by "exert a".

Line 77: Replace "elements species" by "elemental species".

Line 87: Replace "of elemental" by "of the elemental".

Line 92: Replace "in ambient" by "in the ambient".

Line 96: Replace "trace elements" by "trace element".

Line 102: Replace "for elements" by "for elemental".

Line 108: Replace "ambient elements" by "ambient elemental".

Line 109: Replace "trace elements" by "trace element".

Line 120: Replace "National" by "the National".

Line 124: Replace "and Xact" by "and the Xact".

Line 126: Replace "ambient elements" by "ambient elemental".

Line 128: Replace "reactive filter tapes" by "a moving filter tape" and replace "by US" by "by the US".

Line 138: Replace "trade, which has" by "trade and has".

Line 141: Replace "trace elements" by "trace element".

Line 147: Replace "elements species" by "elemental species".

Line 159: Replace "of trace elements will be investigated to examine if water spay" by "of the trace elements was investigated to examine if water spray".

Line 160: Replace "trace elements" by "trace element".

Lines 182 and 183: Replace "Pudong" by "the Pudong".

Line 184: Replace "Pudong" by "The Pudong".

Line 185: Replace "For PEMC" by "For the PEMC".

Line 188: Replace "indicted in Fig. 1c, PEMC" by "indicated in Fig. 1c, the PEMC"

and replace "emissions sources" by "emission sources".

Line 193: Replace "PEMC" by "the PEMC".

Lines 212-213: Replace "of Xact" by "of the Xact" and replace "on blank Nuclepore" by "on a blank Nuclepore filter".

Line 228: Replace "elemental analysis" by "the elemental analysis".

Line 233: Replace "using" by "using the".

Line 238: Replace "collected by the" by "for the".

Line 242: Replace "by Shanghai" by "by the Shanghai".

Line 243: Replace "PEMC" by "the PEMC".

Line 260: Use superscript for "th" in "kth".

Line 268: Replace "elements in" by "elements in the".

Line 276: Replace "et al. 1998" by "et al., 1998".

Line 284: Replace "with BS" with "with the BS".

Line 293: Replace "with similar" by "with a similar".

Line 312: Replace "has described" by "has been described".

Line 316: Replace "of hourly" by "of the hourly".

Line 317: Replace "at PEMC" by "at the PEMC".

Line 323: Replace "summaries" by "summary".

Line 325: Replace "are also shown" by "are shown".

Line 331: Replace "ambient average mass concentrations of elemental" by "the ambient average mass concentrations of the elemental".

Line 332: Replace "between detection" by "between the detection".

Line 342: Replace "airborne" by "the airborne".

Line 345: Replace "on total" by "for the total".

Line 350: Replace "concentration as" by "concentration was", replace "which accounting" by "accounting", and replace "of total" by "of the total".

Line 363: Replace "although a huge" by "a huge".

Line 365: Replace "were given" by "was given".

Line 372: Replace "trace elements" by "trace element".

Line 374: Replace "an order or two" by "one or two".

Line 375: Replace "ranged in the same level as industrialized city" by "were of the same level as in industrialized cities".

Lines 376 and 377 and within Table 1: Use the same city name, either Gwangju or Kwangju.

Line 377: Replace "that of" by "those at".

Line 381: Replace "trace elements" by "trace element".

Line 382: Replace "elements species" by "elemental species".

Line 384: Replace "trace elements" by "trace element".

Line 390: Replace "of the constant" by "of a constant".

Line 392: Replace "explained by" by "obtained with".

Line 403: Replace "to factor" by "to the factor" and replace "sources to" by "sources to the".

Line 408: Replace "the variation" by "the concentration".

Line 410: Replace "In urban" by "In the urban".

Line 415: Replace "tracers for" by "tracers for a".

Lines 417-418: Replace "origins typically" by "origin is typically".

Line 425: Replace "assigned to" by "assigned to a".

Line 432: Replace "of trace" by "of the trace".

Line 434: Replace "hours are" by "hours that are".

Line 435: Replace "of traffic" by "of the traffic".

Line 438: Replace "comes almost" by "come almost".

Line 443: Replace "from east" by "from the east".

Line 444: Replace "from costal" by "from the coastal".

Line 447: Replace "Recent" by "A recent".

Line 450: Replace "in urban" by "in the urban" and replace "with slightly" by "with slight".

Line 458: Replace "during four" by "during the four".

Line 459: Replace "of trace elements in Shanghai" by "of the trace elements in the

Shanghai".

Line 460: Replace "its share" by "their share" and replace "in harbor" by "in the harbor".

Line 461: Replace "Shanghai and its" by "Shanghai and the".

Line 463: Replace "in main engines of ships" by "in the main engines of the ships".

Line 464: Replace "on air" by "on the air".

Line 469: Replace "form of" by "forms of".

Line 471: Replace "during roasting" by "during the roasting".

Line 475: Replace "to total" by "to the total".

Line 483: Replace "shows Au" by "shows that Au".

Line 484: Replace "that different from Ag" by "which is different from that for Ag".

Line 487: Replace "Therefore, element" by "Therefore, the element".

Line 491: Replace "the variation" by "the concentration" and replace "and unexpected" by "and an unexpected".

Line 495: Replace "norther China" by "northern China".

Line 502: Replace "from norther China can transport air" by "from northern China transporting air".

Line 503: Replace "to Shanghai" by "to the Shanghai".

Line 505: Replace "of PM2.5" by "of the PM2.5".

Line 507: Replace "elements concentrations" by "elemental concentrations".

Line 509: Replace "was considered to be originated" by "is considered to originate".

Line 511: Replace "of element K in urban Shanghai were" by "of the element K in urban Shanghai was".

Line 512: Replace "maybe that" by "may be that".

Line 514: Replace "has high" by "has a high".

Line 519: Replace "contained relatively" by "contained a relatively".

Lines 520-521: Replace "in which they detected" by "who observed".

Line 522: Replace "i.e." by "i.e.,".

Line 523: Replace "ATOFMS" by "the ATOFMS".

Line 526: Replace "the explained variation" by "the concentration".

Line 530: Replace "of world" by "of the world".

Line 536: Replace "Since element Cr is reported to be transported over distances by air" by "Since the element Cr is reported to be transported over substantial distances by the air".

Line 540: Replace "of PM2.5" by "of the PM2.5".

Line 550: Replace "particles on the road surface" by "particles".

Line 551: Replace "atop tall" by "atop a tall".

Line 555: Replace "influence PM" by "influence the PM".

Line 556: Replace "of precipitation" by "of the precipitation".

Line 557: Replace "elements concentration" by "the elemental concentrations".

Line 560: Replace "of trace" by "of the trace".

Line 561: Replace "The precipitation" by "A precipitation".

Lines 563 and 564: Replace "should less" by "should be less".

Line 567: Replace "treated as" by "treated as a".

Line 568: Replace "with the duration" by "with a duration".

Line 572: Replace "Fig. S13" by "Fig. S14".

Lines 572-573: Replace "scavenge and remove" by "scavenges and removes".

Line 574: Replace "should lower" by "should be lower".

Line 576: Replace "ambient elements mass" by "the ambient elemental mass".

Line 578: Replace "lasted" by "which lasted".

Line 582: Replace "The variation" by "Variation".

Line 585: Replace "decrement rate of Zn" by "decrease of the Zn".

Line 588: Replace "were aggregated" by "was aggregated" and replace "Before" by "Before the".

Lines 589-590: Replace "than that during" by "than those during the".

Line 591: Replace "reduce PM2.5" by "reduce the PM2.5" and replace "After precipitation" by "After the precipitation".

Line 593: Replace "than that during" by "than during the" and replace "potential" by

"a potential".

Line 595: Replace "as the most" by "as a most" and replace "reflect the" by "reflects the".

Line 597: Replace "decrement rate of Zn concentration and" by "decrease of the Zn concentration and the".

Line 599: Replace "lower ambient" by "lower the ambient".

Line 601: Replace "3.3.1" by "3.3.2".

Line 610: Replace "source mainly includes" by "sources mainly include".

Line 611: Replace "road surface" by "road surfaces".

Line 612: Replace "of coal" by "of the coal".

Line 613: Replace "and Hg have" by "and Hg having a".

Line 614: Replace "of coal" by "of the coal".

Line 616: Replace "different from traffic-related source, coal" by "different from the traffic-related source, the coal".

Line 619: Replace "kept quite" by "remained quite".

Line 626: Replace "The variation" by "Variation".

Line 632: Replace "from Eastern" by "from the Eastern".

Line 633: Replace "to urban" by "to the urban".

Line 638: Replace "from Eastern China sea and then accumulated in" by "from the Eastern China sea which then accumulated in the".

Line 641: Replace "China can" by "China which can".

Line 643: Replace "in Shanghai" by "in the Shanghai".

Line 646: Replace "roses plots" by "roses".

Line 648: Replace "bracket" by "parentheses".

Line 652: Replace "multi-metal monitor" by "multi-metals monitor".

Line 661: Replace "of metal related species comprised" by "of the metal related species amounted to".

Line 664: Replace "measurement and" by "and".

Line 667: Replace "melting" by "smelting".

Line 669: Replace "of ambient" by "of the ambient".

Line 672: Replace "in urban" by "in the urban".

Lines 674-675: Replace "sources of emission" by "emission sources".

Reply: Sorry for wasting you so much time. We should avoid most of these mistakes. All the comments you mentioned have been revised one by one. Please refer to our revised MS with track-change model.

Comments for the Supplement:

The Supplement would benefit from numbering the pages.

15. *Page 2: The regression data in Table S1 contain too many significant figures. Two significant figures suffice in case the first significant figure is larger or equal than 2, and when the first significant figure equals 1, three significant figures can be used.*

Reply: In the first round of review, the reviewer suggested "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". Thank you for your understanding.

16. *Page 3, first line: Replace "Text S2" by "Table S2" and replace "precipitation chosen" by "precipitation events chosen".*

Page 4, line 1: Replace "Text 1" by "Text S1".

Page 4, line 13: Replace "Table below" by "Table S3" and replace "95 of BS" by "95 of the BS".

Page 4, line 14: Replace "50 of BS" by "50 of the BS".

Page 4, line 15: Replace "and other" by "and the other" and replace "95 of BS" by "95 of the BS".

Page 4, line 6 from bottom: Replace "perform PMF" by "performs PMF".

Page 4, line 3 from bottom: Replace "Table below" by "Table S4".

Page 5, line 1 below Table S4: Replace "of BS and DISP method" by "of the BS and DISP methods".

Page 5, line 5 below Table S4: Replace "for PMF" by "for the PMF".

Page 5, line 6 below Table S4: Replace "When factor" by "When the factor".

Page 5, line 7 below Table S4: Replace "than from 4- to 5-factor" by "than is the case when going from the 4- to the 5-factor" and replace "However, a" by "The".

Page 5, line 8 below Table S4: Replace "predetermined" by "selected".

Page 6, line 10: Replace "781" by "781-797".

Page 7, line 1 of figure caption: Replace "Figure 2. Seasonal variations" by "Figure S2. Seasonal variation".

Page 15, line 3 of caption of Figure S10: Replace "Below the diagonal of the diagonal" by "Below the diagonal".

Page 18, caption of Figure S13: Replace "The distribution of precipitation" by "Distribution of precipitation events".

Page 19, line 1 of caption of Figure S14: Replace "The variation" by "Variation".

Reply: We corrected accordingly in the revised MS.

17. Page 9: I do not see any wind direction information in Figure S4. Should ", and wind directions" not be deleted in the figure caption?

Reply: Followed the suggestion by the reviewer in the first round of review, we decided to delete the wind direction information. We also think that it is very strange to plot the normalized data of metal concentration and wind direction in one figure.

Anonymous Referee #6

1. *The paper "First long-term and near real-time measurement of trace elements in China's urban atmosphere: temporal variability, source apportionment, and precipitation effect" is based on a huge and interesting data set. Nevertheless, the paper still includes some points that need revision. Briefly, here is a list of the issues that authors should address for the publication of the paper:*

- To the best of my knowledge, Xact can also quantify Al, S, Cl, and Ti: why were these elements not taken into account?

Reply: Yes, Xact can also quantify Al, S, Cl, and Ti. However, firstly, these four elements have the highest detection limits and their data quality are generally not as good as other elements. Secondly, the display interface of Xact (old version) has limited space to show all the measured trace elements, and the Xact multi-metals monitor used in our study was routinely deployed. For the consideration of data quality assurance (and convenience), we (and also most of other Xact users) decided to remove the data of Al, S, Cl, and Ti.

2. *- Still on Xact: what do you mean with "reactive filter tapes" (line 128)? Referees had already asked this question.*

Reply: Sorry for making such confusion to you. The "reactive filter tapes" means "moving filter tapes", and we've corrected it in the revised MS as suggested by the handling editor of our MS.

3. *- There is quite some confusion between V/Ni and Ni/V ratios: please report only V/Ni ratio values, as this is the main way to report these data. Please revise the abstract (line 41) and figure 6.*

Reply: Sorry for our mistake. We've corrected the text and figure in our revised MS.

4. *- Lines 347-352: the issue of oxides versus reconstructed mass is addressed in a quite simplistic way: could the authors explain the formulas they used for the*

calculation of the oxides and, mainly, how was the data for total PM2.5 mass obtained? The cited reference helps under the methodological point of view, but it would be helpful to know some more specific details (how did the authors calculate EC/OC, sulphate, nitrate etc. for the reconstruction of the mass).'

Reply: Our sampling site is responsible for publicly releasing hourly air quality data of PM_{10}, $PM_{2.5}$, and other criteria pollutants (CO, SO_2, NO_x and O_3) in Shanghai. The hourly mass concentrations of $PM_{2.5}$ were measured by a particulate monitor (Thermo, FH62C-14). Therefore, there is no need to perform the calculation of $PM_{2.5}$ mass closure in our study. We've added this information in the section of 2.1.3, i.e., "Auxiliary measurements".

5. *- Line 450: which is the V/Ni value of the PMF factor? The factor is obviously characterized by the same ratio throughout the year; there is an unclear mix among PMF factor data and raw chemical data.*

Reply: In the PMF analysis, we found that V (100%) and Ni (74%) come almost exclusively from factor 2, while factor 2 contributes to less than 10% of any other elemental species. Therefore, the evolution of PMF factor 2, to a large extent, reflects the variation raw chemical data of shipping-related emissions of trace elements.

6. *- Figure 7, CPF and BPP analysis: I suggest the authors to correlate wind data with the factors/sources, while they did it with elements. This would give more powerful information on sources, even though a single element could have contributions from different sources.*

Reply: We agree with the reviewer that the CPF and BPP analysis could give powerful information on sources. However, when we have the PMF-derived **quantitative** results of the sources, then the CPF and BPP analysis should be an auxiliary tool. Also, we agree with the reviewer that a single element could have contributions from different sources. However, the PMF-derived quantitative results of the elemental sources in our study are interpretable and convincing. Therefore, we have no urgent need to perform

the CPF and BPP analysis for every factor/element. Nevertheless, the CPF and BPP analysis have been applied for Au and Hg, and Cr in our study.

7. *- Section 3.3, "Precipitation effect". The topic is interesting, but authors should comment their results somehow more critically: e.g., how do they explain the fact that Au and Cr increase during the rainfall? I find this result quite strange... Further, no comment is given on the ferrous metal smelting pattern (fig. 11 e). Last, comparing the effect of a rainfall to the expected one for street-washing appear quite simplistic, as in the first case the whole "air column" is washed, while with street washing only the street surface is cleaned.*

Reply: (1) "how do they explain the fact that Au and Cr increase during the rainfall". The discussion of precipitation effect in the MS was divided into two parts, i.e., "3.3.1 Change of mass concentration by species" and "3.3.2 Change of mass concentration by sources". It is not always easy to explain the increase of trace elements like Au and Cr during the rainfall in section 3.3.1 alone. However, when we look at the PMF section, the predominant elements found in factor 3 (nonferrous metal smelting sector) were Au (100%), Cd (65%), and Ag (63%) with 37% of Hg. Meanwhile, factor 5 (ferrous metal smelting sector) was distinguished by high levels of Cr, Mn, and Zn, which represent 100%, 56%, and 52% of the explained concentration, respectively. Therefore, Au and Cr were almost exclusively emitted from nonferrous metal smelting sector and ferrous metal smelting sector, respectively. In the section 3.3.2, different from the sectors of traffic, shipping, and coal combustion, we found that the changes of mass concentrations of trace elements from nonferrous metal smelting sector and ferrous metal smelting sector were very limited during rainfall. This is generally in accordance with the section 3.3.1 that "Au and Cr increase during the rainfall".

(2) "comparing the effect of a rainfall to the expected one for street-washing appear quite simplistic, as in the first case the whole "air column" is washed, while with street washing only the street surface is cleaned."

As we described in the MS, water spray (from sprinkler on road or atop a tall building,

i.e., water-fog cannon) in our study including but not limited to street washing. Indeed, in China, some radical measures like "water-fog cannon" (see Yu, S.: Water spray geoengineering to clean air pollution for mitigating haze in China's cities, Environ. Chem. Lett., 12, 109-116, doi: 10.1007/s10311-013-0444-0, 2014) and "smog cleaning tower" (see https://www.nature.com/articles/d41586-018-02704-9#menu) have been proposed to curb air pollution.

We completely agree with the reviewer that during a rainfall event, "the whole "air column" is washed. And we think that the scavenging effect of rainfall on the ambient trace elements should be much stronger than that of water-spray activities. So our logic is this: If there is no scavenging effect of precipitation on a given source or species of trace element, then we can conclude that it is useless to take water spray as measure to lower the ambient trace elements. If there is a strong scavenging effect of precipitation on a given source or species of trace element, then we can conclude that water spray may be a measure to lower the ambient trace elements. Our results show that the precipitation has limited scavenging effect on the sources of shipping, nonferrous metal smelting, and ferrous metal smelting. However, the ambient concentrations of trace elements from traffic and coal combustion (accounting for 67% of the total mass) experienced a dramatic decrease during rainfall. Therefore, in general, we concluded that water spray may be a way to lower the ambient trace elemental concentration.

8. *- Line 555: in the reference list one more paper by Karanasiou et al. is reported (published in 2011).*

Reply: The paper "Karanasiou et al., 2011" was correctly cited.

9. *- Supplementary material, table S1. Actually, Further, with respect to Fe: could the authors check the regression lines? I find strange that the intercept for all glass filters and all cellulose filters are negative but, then, the intercept for all the filters is positive. Last, what do "*" and "**" stand for?*

Reply: (1) "the inter-comparison between ICP-MS and Xact gives not excellent results

for some elements (e.g., As, Cd, Ba, Pb, for which a slope of roughly 2 is observed): this issue should be discussed in more detail."

Our initial thought about the explanation was that the filters we used are not as good as Teflon filter to collect the ambient trace elements. Prof. Mei Zheng from Peking University recently also performed a method comparison between Xact and ICP-MS (using Teflon filters) in northern China (see table below, for reviewing purpose use only). Unfortunately, except for Pb, the average concentrations of elements like Cd, Ba, and As measured by a Xact were also over two times higher than that measured by ICP-MS. The frustrated thing is that we failed to find another explanation at the current stage.

	XACT (N=1158)			ICP-MS (N=62)		
	Mean	STD	Median	Mean	STD	Median
	ng m^{-3}			ng m^{-3}		
K	2052.71	2022.7	1562.5	1183.222	1069.39	887.68
Fe	534.67	263.11	513.1	436.82	235.91	408.12
Ca	481.41	438.24	358.1	642.48	460.71	494.83
Zn	434.25	547.15	281.3	274.532	175.675	238.705
Pb	121.95	96.35	95.37	97.196	57.1	83.189
Mn	31.96	26.16	26.3	25.45	12.558	22.096
Cu	31.12	37.65	20.22	24.34	19.44	19.05
Cd	24.4	9.6	23.93	2.948	1.991	2.58
Ba	23.32	12.37	21.42	11.131	7.068	9.65
As	12.81	16.35	9.43	5.629	8.088	2.365
Ag	10.29	6.91	6.12			
Se	6.13	4.79	5.43	5.376	3.917	4.465
Hg	2.77	1.64	2.5			
Au	2.57	1.94	2.22			
Cr	2.05	2.26	1.47	6.102	5.333	4.385
Ni	1.77	1.68	1.47	1.92	1.921	1.14
V	0.8	1.03	0.41	6.93	10.62	3.63

(2) "with respect to Fe: could the authors check the regression lines? I find strange that the intercept for all glass filters and all cellulose filters are negative but, then, the intercept for all the filters is positive. Last, what do "*" and "**" stand for? "

After double check, our regression lines are correct. The reason of the "strange" positive intercept for all the filters is because that an abnormal value of Fe (675.0 ng m^{-3}) collected by glass filter was excluded, which is indicated as "*". The original formula

of “all glass filters vs. Xact” and “all filters vs. Xact” are “y=0.77x+119.3 R^2 =0.38 n=11” and “y=0.95x+22.28 R^2 =0.70 n=31”, respectively. Similarly, “**” stands for the deletion of two abnormal values of As (63.0 and 77.7 ng m^{-3}) collected by cellulose filters.

10. - Supplementary material, figure S4. Wind directions are not reported: please add the panel or change the caption.

Reply: Followed the suggestion by the reviewer in the first round of review, we decided to delete the wind direction information. We also think that it is very strange to plot the normalized data of trace elemental concentration and wind direction in one figure.

Anonymous Referee #2

General comments

1. *The manuscript has been significantly altered by basically replacing the hierarchical clustering method by Positive Matrix Factorization (PMF), and by adding information on precipitation effects on metals concentrations. PMF yields 5 emission sources for Shanghai which are well explained by the measured elemental data, and the high time resolution allows for a strong argument for a traffic-related factor. Precipitation effects do show a general trend in reducing the elemental concentrations, however the picture is complicated by other effects playing a role, such as wind/air mass changes. There are still a few minor changes required before the paper can be published. Specific comments*

   The comparison between filters and Xact has been extended in Table S1, but the description (lines 234-239) is not consistent with the new data. The background values have been dropped from the table, as well as the comparison between the filter types. The quoted values on line 237 refer to the very first version of the table. This should be updated. I still do not buy the explanation of the Cr and Ba slopes depending on the background values. If the background values in the original version of Table S1 were correct, than all cellulose acetate filter background values were smaller than the glass filter background values, in contradiction to the statement. Perhaps the authors leave out that part of the sentence (lines 238-239). Table S1 needs more information in the caption, e.g. explain the asterisks (, **) and the n values*.

Reply: Sorry for our carefulness, we updated the results in the revised MS. We decided to delete "the slope values of Cr (1.9) and Ba (2.6) were higher than those of other species, this can be explained by higher background values of Cr and Ba collected by the cellulose acetate filters". "*" indicates that an abnormal value of Fe (675.0 ng m^{-3}) collected by glass filter was excluded. "**" stands for the deletion of two abnormal values of As (63.0 and 77.7 ng m^{-3}) collected by cellulose filters.

2. *In Section 2.1.1. only winter is described. I recommend to add the sequence from the first revision (with my additions): "Winters are chilly and damp, with northwesterly winds from Siberia sometimes causing nighttime temperatures to drop below freezing. In summer, airflow carries moist air from the Pacific Ocean to mainland China, which will also bring the main precipitation. The city is also susceptible to typhoons in summer and the beginning of autumn."*

Reply: Thanks, we've added these sentences in the revised MS.

3. *Technical corrections Table 1, L376, L377 make city names consistent L572 Fig. S14 (not S13)*

Reply: Revised accordingly.

4. *In supplement*

Table S1: explain 'n' and the asterisks in the table

Reply: "n" represents the number of paired samples.

5. *Table S2: Replace 'Text' with 'Table', and insert 'events ' after 'precipitation*'

Reply: Revised accordingly.

6. *Caption of Fig. S10: L3 delete 'of the diagonal'*

Reply: Revised accordingly.

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

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

an appreciable fraction of $PM_{2.5}$ during all seasons, accounting for 8.3% on average. As a comparison, the atmospheric elements concentration level in Shanghai was comparable with that in other industrialized cities in East Asia but one or two orders of magnitude higher than at sites in North America and Europe. Positive matrix factorization (PMF) was applied to identify and apportion the sources of the elements in the $PM_{2.5}$ mass. Five different factors were resolved (notable elements and relative contribution in ~~brackets~~parentheses): traffic-related (Ca, Fe, Ba, Si; 46%), shipping (V, Ni; 6%), nonferrous metal smelting (Ag, Cd, Au; 15%), coal combustion (As, Se, Hg, Pb; 18%), and ferrous metal smelting (Cr, Mn, Zn; 15%). The contribution from the exhaust and non-exhaust vehicle emissions, i.e., the~~Contributed by exhaust and non-exhaust vehicle emissions,~~ traffic-related factor shows a strong bimodal diurnal profile with average concentration over two times higher during the rush hour than during nighttime. The ~~S~~shipping factor was firmly identified because V and Ni, two recognized tracers of shipping emissions, are almost exclusively transported from the East China Sea and their ratio (around ~~0.31~~3.2) ~~fallen~~ falls within the variation range of V/Ni ratios in particles emitted from heavy oil combustion. Interestingly, nearly half of the K ~~were~~ was derived from coal combustion with high mineral affinity (elements associated with aluminosilicates, carbonates and other minerals in coal ash). The contributions of (non)ferrous metal smelting to the trace elements are consistent with a newly-developed emission inventory. Although the precipitation scavenging effect on the mass concentration of trace elements varied among different species and sources, precipitation could effectively lower the concentration of the traffic- and coal combustion-related trace elements. Therefore, water spray to simulate natural types of precipitation could be one of the abatement strategies to facilitate the reduction of ambient $PM_{2.5}$ trace elements in the urban atmosphere. Collectively, our findings in this study provide baseline levels and sources of trace elements with high detail, which are needed for developing effective control strategies to reduce the high risk of acute 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 referrings 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 United StatesUS Environmental Protection Agency (USEPA) in terms of posing the greatest potential health threat in urban areas (see www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants). Depending on the aerosol composition, extent and time of exposure, previous studies have confirmed that most elementals 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 elements are provided by the World Health Organization (WHO) (WHO, 2005). In urban atmospheres, ambient trace elements typically represent a small fraction of $PM_{2.5}$ on a mass basis, while elements elemental species like Cd, As, Co, Cr, Ni, Pb and Se are considered as human carcinogens even in trace amounts (Iyengar and Woittiez, 1988; Wang et al., 2006; 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 the elemental species in remote continental aerosols (Usher et al., 2003; Ridley et al., 2016). These species are usually associated with the impacts of aerosols on respiratory diseases and climate (Usher et al., 2003; Tang et al., 2017).

Health effects of airborne ~~elements~~ elemental species are not only seen from chronic exposure, but also from short-term acute concentration spikes in the ambient air (Kloog et al., 2013; Strickland et al., 2016; Huang et al., 2012). In addition, atmospheric emissions, transport, and exposure of trace elements to human receptors may depend upon rapidly evolving meteorological conditions and facility operations (Tchounwou et al., 2012; Holden et al., 2016). Typical ambient trace element~~s~~ sampling devices collect 12 to 24-hr integrated average samples, which are then sent off to be lab analyzed in a time-consuming and labor-intensive way. As a consequence, daily integrated samples inevitably ignore environmental shifts with rapid temporality, and thereby hinder the efforts to obtain accurate source apportionment results such as short-term elements pollution spikes related to local emission sources. In fact, during a short-term trace elements exposure event, 12 or 24-hr averaged sample concentrations for elemental~~s~~ 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 ~~elements~~ elemental species on a real-time scale is essential for studies on trace elements 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 elements collected by these samplers can be analyzed with highly sensitive accelerator-based analytical techniques, in particular particle-induced X-ray emission (PIXE) or synchrotron radiation X-ray fluorescence (SR-XRF) (Richard et al., 2010; Bukowiecki et al., 2005; Maenhaut, 2015; Traversi et al., 2014). More recently, Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS) (Murphy et al., 1998; Gross et al., 2000; DeCarlo et al., 2006), the National Institute for Standards and Technology (NIST)-traceable reference aerosol generating method (QAG) (Yanca et al., 2006), distance-based detection in a multi-layered device (Cate et al., 2015), environmental magnetic properties coupled with support vector machine (Li et al., 2017), and the Xact™ 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 elementals species. The Xact method is based on nondestructive XRF analysis of aerosol deposits on ~~reactive~~ a moving filter tape~~s~~, which has been validated by the 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 and~~, 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 elements emissions (Duan and

Tan, 2013; Tian et al., 2015). Ambient concentrations of trace element~~s~~, especially Pb and Hg, in the Shanghai atmosphere have been sporadically reported during the past two decades (Shu et al., 2001; Lu et al., 2008; Wang et al., 2013a; Zheng et al., 2004; Huang et al., 2013; Wang et al., 2016). Of current interest are V and Ni, which are often indicative of heavy oil combustion from ocean-going vessels (Fan et al., 2016; Liu et al., 2017). However, previous work rarely presented a full spectrum of elemental~~s~~ 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 elements 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 elements 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 levels and sources of atmospheric trace elements in a complex urban environment, which can be used to support future health studies. Meanwhile, the potential effect of precipitation scavenging on the mass concentration of the trace elements was investigated to examine if water spray~~of trace elements will be investigated to examine if water spay~~ could be proposed as an effective approach to curb severe trace element~~s~~ pollution in China's urban atmosphere.

2 Methods

2.1 Field measurements

2.1.1 Site description

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

borders the provinces of Jiangsu and Zhejiang to the north, south and west, and is bounded to the east by the East China Sea (Fig. 1a). Shanghai has a humid subtropical climate and experiences four distinct seasons. Winters are chilly and damp, with northwesterly winds from Siberia sometimes causing nighttime temperatures to drop below freezing. In summer, airflow carries moist air from the Pacific Ocean to mainland China, which will also bring the main precipitation. The city is also susceptible to typhoons in summer and the beginning of autumn. ~~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).

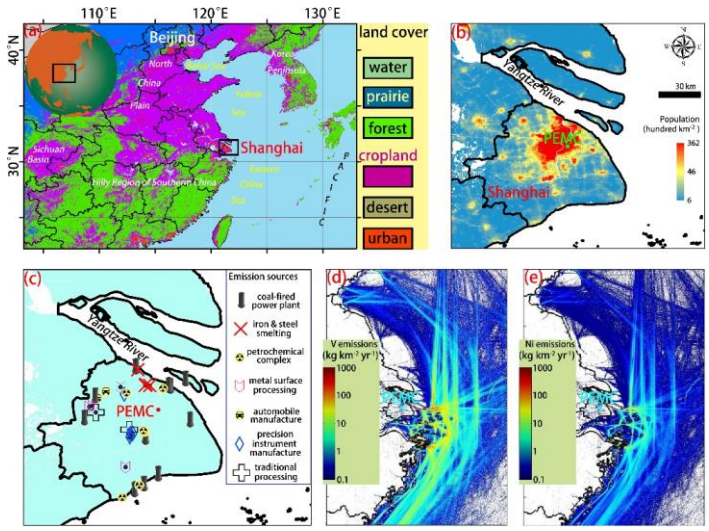

Figure 1. Land use map indicating the location of Shanghai (**a**; black box), as well as the population density (**b**) and the major point sources (**c**) around the sampling site (PEMC). The emissions of V (**d**) and Ni (**e**) from shipping in the YRD and the East China Sea within 400 km of the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

Field measurements were performed at the rooftop (~18 m above ground level) of the

Pudong Environmental Monitoring Center (PEMC; 121.5447°E, 31.2331°N; ~7 m above sea level) in Pudong New Area of southwestern Shanghai, a region with dense population (Fig. 1b). Pudong New Area is described as the "showpiece" of modern China due to its height-obsessed skyline and export-oriented economy. For the PEMC, there were no metal-related sources (except for road traffic) or high-rise buildings nearby to obstruct observations, so the air mass could flow smoothly. More broadly, as indicated in Fig. 1c, the PEMC~~indicted in Fig. 1c, PEMC~~ is surrounded by a multitude of emission~~s~~ sources such as coal-fired power plants (CFPP) in all directions and iron and steel smelting in the northwest. Furthermore, a high level of ship exhaust emissions in 2010 such as V (Fig. 1d) and Ni (Fig. 1e) in the YRD and the East China Sea within 400 km of China's coastline was recently quantified based on an automatic identification system model (Fan et al., 2016). Therefore, the PEMC can be regarded as an ideal urban receptor site of diverse emission sources. More information regarding the sampling site has been given elsewhere (Chang et al., 2017; Chang et al., 2016).

2.1.2 Hourly elemental species measurements

From March 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 elements of interest. These standards were provided by the manufacturer of the Xact, produced by depositing vapor phase elements on a blank Nuclepore filter (Micromatter Co., Arlington, WA, USA). The Nuclepore filter of known area was weighed before and after the vapor deposition process to determine the concentration (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 the PEMC site using a four-channel aerosol sampler (Tianhong, Wuhan, China) on 47 mm cellulose acetate and glass fiber filters at a flow rate of 16.7 L min^{-1}. The sampler was operated once a week with a 24-hr sampling time (starting from 10:00 am). In total 48 filter samples (26 cellulose acetate filter samples and 22 glass fiber filter samples) were collected, in which 8 paired samples were simultaneously collected by cellulose acetate and glass fiber filters. In the laboratory, the elemental analysis procedures strictly followed the latest national standard method "Ambient air and stationary source emission-Determination of metals in ambient particulate matter-Inductively coupled plasma/mass spectrometer (ICP-MS)" (HJ 657-2013) issued by the Chinese Ministry of Environmental Protection. A total of 24 elements (Al, Fe, Mn, Mg, Mo, Ti, Sc, Na, Ba, Sr, Sb, Ca, Co, Ni, Cu, Ge, Pb, P, K, Zn, Cd, V, S, and As) were measured using Inductively coupled plasma-mass spectrometer (ICP-MS; Agilent, CA, USA). The comparisons of different methods (Xact *vs.* ICP-MS) to measure and different filters (glass filter *vs.* cellulose filter) to collect trace elements were reported in Table S2. In general, elements like K, Cr, Mn, Fe, Ni, Cu, and Au were proved to be of high quality, while elements like As, Cd, and Ba have relatively poor data quality.~~results of the 8 paired samples were first compared. Significant correlations~~

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~~were observed for 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 those of 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

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

2.2 Data analysis

2.2.1 Positive Matrix Factorization (PMF) analysis for source apportionment

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

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

where x_{ij} is the j^{th} species concentration measured in the i^{th} sample, g_{ik} is the contribution

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

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

where σ_{ij} are the measurement uncertainties.

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

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

The determination of the geographical origins of trace elements in Shanghai requires the use of diagnostic tools such as the conditional probability function (CPF) and bivariate polar plot (BPP), which are very useful in terms of quickly gaining an idea of source impacts from various wind directions and have already been successfully applied to various atmospheric pollutants and pollution sources (Chang et al., 2017; Carslaw and Ropkins, 2012). In this study, the CPF and BPP were performed on the one-year data set for the major trace elements with a similar source. The two methods have been implemented in the R "openair" package and are freely available at www.openair-project.org (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 element 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 been described in more detail in Carslaw et al. (2006)

and the construction of BPP has been presented in our previous work (Chang et al., 2017).

3 Results and discussion

3.1 Mass concentrations

The temporal patterns and summary statistics of the hourly elemental species concentrations determined by the Xact at the PEMC during March 2016-Feburary 2017 are presented 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 elements.

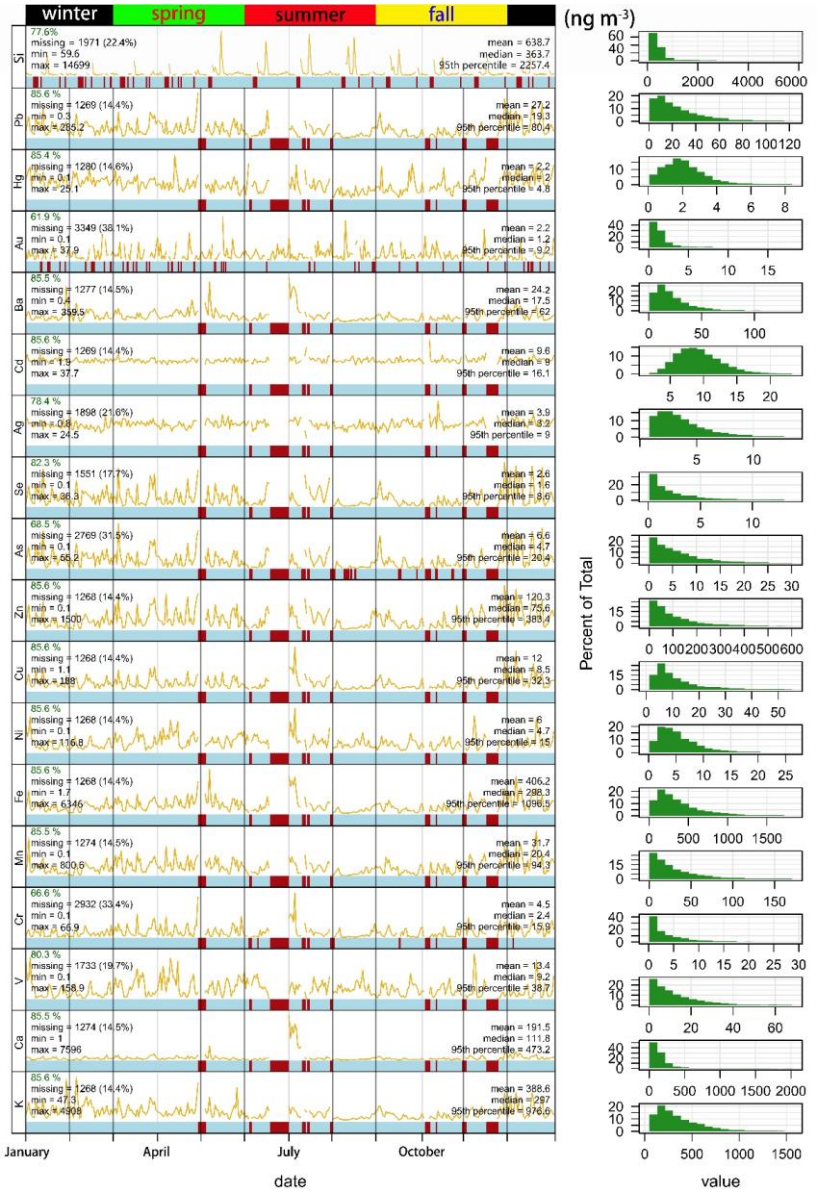
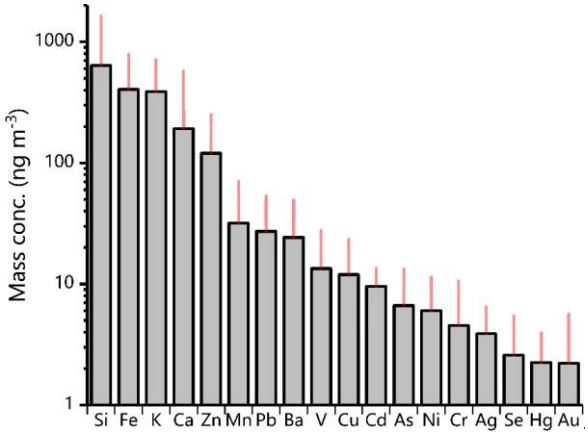


Figure 2. General statistical summary~~ies~~ of 18 trace elements measured in Shanghai. The plots in the left panel show the time series data, where blue shows the presence of data and red shows missing data. The mean daily values are ~~also~~ shown in pale yellow scaled to cover the range in the data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

Taking the study period as a whole, the ambient average mass concentrations of the elemental species varied between the detection limit (ranging from 0.05 to 20 ng m^{-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 ± 385 ng m^{-3}), K (389 ± 326 ng m^{-3}), Ca (192 ± 383) ng m^{-3}, Zn (120 ± 131 ng m^{-3}), Mn (32 ± 39 ng m^{-3}), Pb (27 ± 26 ng m^{-3}), Ba (24 ± 25 ng m^{-3}), V (13 ± 15 ng m^{-3}), Cu (12 ± 11 ng m^{-3}), Cd (10 ± 4 ng m^{-3}), As (7 ± 7 ng m^{-3}), Ni (6 ± 5 ng m^{-3}), Cr (5 ± 6 ng m^{-3}), Ag (4 ± 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, the airborne metal pollution in Shanghai is generally low by the current limit ceilings. Nevertheless, information regarding the specific metal compounds or chemical forms is rarely available given that most analytical techniques only record data ~~on~~ for the total metal content. In the absence of this type of information, it is generally assumed that many of the elements of anthropogenic origin (especially from combustion sources) are present in the atmosphere as oxides. Here we reconstructed the average mass concentrations of metal and crustal oxides as 5.2, 5.0, 2.8, and 3.1 μg m^{-3} in spring, summer, fall, and winter, respectively, while the annual average concentration was 3.9 μg m^{-3}, ~~which~~ accounting for 8.3% of the 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).



~~**Figure 3.** Average 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.~~

Table 1. Overview 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, London (Visser

et al., 2015b); d, $PM_{0.3\text{-}2.5}$, North Kensington, London (Visser et al., 2015b); e, a ~~Road~~ road site in Barcelona (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), but that no detailed information regarding the specific mass concentrations of trace elements ~~were~~ was given.

The toxicological effect of hazardous element~~s~~ species is more evident and well known in soils and aquatic ecosystems, while few (if any) studies on the geochemical cycle of trace metals have considered the fast dynamics of trace elements in the atmosphere. Using a diversity of chemical, physical, and optical techniques, elevated atmospheric concentrations of various element species have been observed globally; however, a tiny minority of them were performed with high time resolution. As a comparison, we compiled previous work related to the near real-time measurements of trace element~~s~~ concentrations in Table 1. The concentrations of most trace elements in Shanghai were commonly ~~an~~ one or two~~order or two~~ orders of magnitude higher than those measured in Europe and North America, and generally were of the same level as in industrialized cities~~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~~ those~~of~~ at Kwangju City. This is expected since Shanghai has the world's busiest container port, and V and Ni were substantially and almost exclusively emitted from heavy oil combustion in ship engines of ocean-going vessels (see more discussion in Section 3.2 and 3.3).

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

3.2 Source analysis

In the PMF analysis, three to ten factor solutions were initially examined, from which possible solutions (i.e., four to six factor solutions) were chosen based on the change of Q/Q_{exp}, the achievement of ~~the~~ a constant and global minimum of Q, the displacement of factor elements, and the interpretation of physically meaningful factors (Text S1; see discussion below). The most reliable solution was ~~explained~~ obtained with~~by~~ five factors. The chemical profiles and average contributions of the five factors are presented in Fig. ~~4~~ 3 with the time-series evolution of these factors included in the Supplement (Fig. S9). On the one hand, we will use various mathematical and physical criteria to constrain different solutions of source apportionment. On the other hand, we will take CPF and BPP as diagnostic tools for quickly gaining the idea of potential source regions, which in turn will contribute to further analysis of source apportionment. Ultimately, the five factors were assigned to different sources, i.e., traffic-related, shipping, nonferrous metal smelting, coal combustion, and ferrous metal smelting.

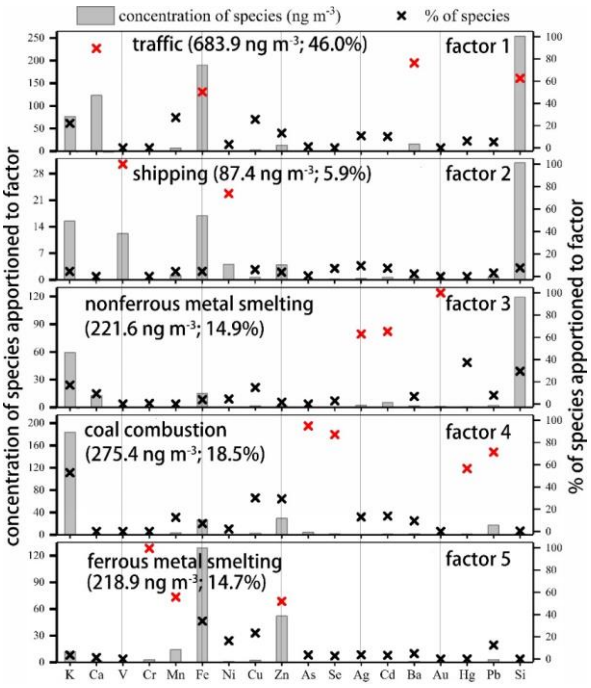


Figure 43. PMF-resolved source profiles (concentration and % of species apportioned to the factor) and average contributions (in the parentheses) of individual sources to the measured total $PM_{2.5}$ elements in Shanghai. The notable species for each factor/source are marked in red.

3.2.1 Traffic-related

Factor 1 was characterized by a large mass fraction of Ca, Fe, Ba, and Si, which explained 89.5%, 50.3%, 76.5%, and 62.6% of the ~~variation~~concentration, respectively. This mixed factor is similar to that reported by Amato et al. (2009, 2013), Bukowiecki et al. (2010), Harrison et al. (2012), and Visser et al. (2015b). In the urban atmosphere, Fe can be released from engine oil or catalyst equipped gasoline vehicles (Chen et al., 2007). Besides, Fe is linked to non-exhaust emissions such as brake wear because it is the support material for brake pads, and the agents present in brake linings typically consist of Ba, Mn and Cu (Lough et al., 2005; Hjortenkrans et al., 2007; Dall'Osto et al., 2016). Therefore, Fe and Ba can be regarded as chemical tracers for a traffic-related source (exhaust and non-exhaust) (Thorpe ~~et al.~~and Harrison, 2008; Lin et al., 2015). Ca and Si are known as two of the most abundant elements in the upper continental crust, and their atmospheric origin~~s~~ is typically attributed to wind-blown dust. Located on the eastern coast of China, Shanghai rarely receives long-range transport of crustal matter from aeolian dust and the Gobi Desert in northwestern China (Huang et al., 2013). Sampling in the urban area of Shanghai, airborne Ca and Si should be dominated by anthropogenic activities like road fugitive dust or urban construction works. In Fig. S10, significant correlations are observed for Ca, Si, Fe, and Ba, suggesting that the measured Ca and Si during our study period were more likely derived from road fugitive dust. Therefore, factor 1 can be assigned to a traffic-related source and it was the largest source in Shanghai, accounting for 46.0% (683.9 ng m^{-3}) of the total measured elemental mass in $PM_{2.5}$.

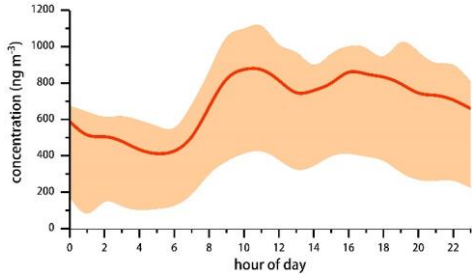


Figure ~~5~~4. Diurnal variation of PMF-derived elemental concentration for factor 1. The red line, bottom boundary, and upper boundary represent the mean, 1st quartile, and 3rd quartile of the concentration value, respectively.

Hourly measurements over one-year periods provide a unique opportunity to examine the diurnal profile of factor 1. As reported in Fig. ~~5~~4, the concentration of the trace elements contributed by factor 1 shows a marked bimodal diurnal cycle, with average values at rush hours that are over two times higher than at nighttime. Such variation pattern agrees well with the diurnal variation of the traffic flow in Shanghai (Chang et al., 2016~~a~~), further confirming that factor 1 can be interpreted as traffic-related emissions.

3.2.2 Shipping

In Fig. ~~4~~3, V (100%) and Ni (74%) come~~s~~ almost exclusively from factor 2, while factor 2 contributes to less than 10% of any other elemental species. V is typically emitted from oil and petrochemical refining and combustion, and natural gas extraction and processing (Duce and Hoffman, 1976; Hope, 1994; Shafer et al., 2012). From CPF and BPP analysis (Fig. S11), higher concentrations of both V and Ni were observed when winds originated from the east, northeast, and southeast directions. The most dominant directions were east and southeast, suggesting the influence from the costal port cluster or petroleum refinery industry located east/southeast of Shanghai (Fig. 1). Gathering evidence revealed that the ratio of V/Ni can serve as a robust indicator of shipping emissions (Tao et al., 2013; Celo et al., 2015; Liu et al., 2017; Viana et al., 2009). A ~~R~~recent study in Shanghai port suggested that the ratio of V/Ni in aerosols emitted from

heavy oil combustion of ocean-going ship engines was 3.4 on average (Zhao et al., 2013). Here measured in the urban area, the average ratio of V/Ni in our study was ~~3.1~~3.2 with slight~~ly~~ seasonal changes (Fig. ~~6~~5), indicating V- and Ni-containing aerosols from shipping emissions subject to minor atmospheric transformation. In short, factor 2 likely corresponds to shipping emissions (instead of petrochemical refining), which is consistent with the results of many previous source apportionment works (e.g., Liu et al., 2017; Zhao et al., 2013; Cesari et al., 20014; Healy et al., 2010).

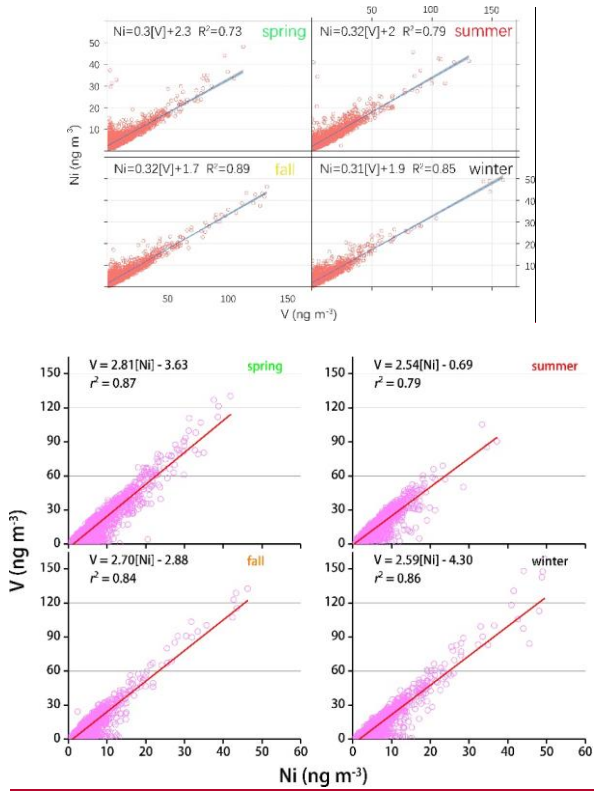


Figure ~~6~~5. Linear correlation analysis between ~~V~~ Ni (x axis) and ~~Ni~~ V (y axis) in Shanghai during the four seasons.

Although shipping emissions only contribute to 5.9% of the trace elements in the Shanghai urban center, their~~its~~ share can be expected to greatly increase in the harbor district (Zhao et al., 2013). The good news is that since 1 January 2016, the sea areas of

Shanghai and ~~its~~ the neighboring ports were designed as shipping emission control area, requiring use of lower sulfur fuels in place of heavy fuel oil in the main engines of the ships (Zhen et al., 2018). Therefore, it is critically important to assess the impacts of fuel changes on the air quality in Shanghai in the future through continuous measurements of trace elements.

3.2.3 Nonferrous metal smelting

The predominant elements found in factor 3 were Au (100%), Cd (65%), and Ag (63%) with 37% of Hg. These four heavy metals are important associated elements in Cu, Pb, and Zn ores. In fact, Cu, Pb, and Zn smelting represent the three most common forms of nonferrous metal smelting in China (Tian et al., 2015). Because of high temperatures during the roasting, sintering and smelting process for the extraction of Cu, Pb, and Zn from ores, metals like Au, Cd, Ag, and Hg in nonferrous metal ores will inevitably be vaporized and released into the flue gas (Pacyna and Pacyna, 2001; Wu et al., 2012). Therefore, factor 3 was interpreted as nonferrous metal smelting emissions and the contribution of this factor was 14.9% (221.6 ng m^{-3}) to the total measured elemental mass in $PM_{2.5}$.

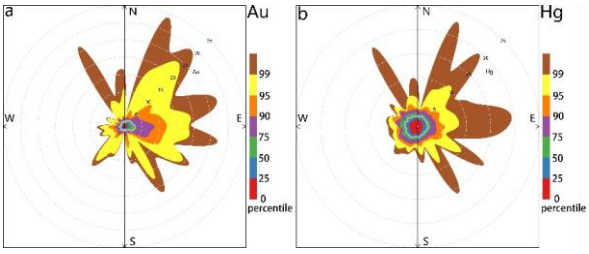


Figure ~~7~~6. Percentile rose plot of Au (**a**) and Hg (**b**) concentrations in Shanghai between March 2016 and February 2017. The percentile intervals are shaded and shown by wind direction.

To further pinpoint the specific subsector of nonferrous metal smelting, here we calculate percentile concentration levels of Au and Hg, and plot them by wind direction in Fig. ~~7~~6 (and Ag, Cd in Fig. S12). It clearly shows that Au and Hg largely share the

same source region which is ~~that~~ different from that for Ag and Cd, indicating that Au and Hg were emitted from a similar subsector of nonferrous metal smelting. In Shanghai, Zn smelting is the most important contributor of Hg emissions from the nonferrous metal smelting sector. Therefore, the element Au resolved in factor 3 during our study period can be expected to be originated from Zn smelting.

3.2.4 Coal combustion

The most abundant elements found in factor 4 were As, Se, Pb, Hg (explaining 56% to 95% of the ~~variation~~concentration) with some contributions of Cu (30%), Zn (29%) and an unexpected large amount of K (53%). As, Se, Pb, Hg, and Cu are typical marker elements for coal combustion (Morawska and Zhang, 2002). In China, 73% of As, 62% of Se, 56% of Pb, and 47% of Hg were found to be emitted from coal combustion (Tian et al., 2015). Coal consumption in southern China (including Shanghai) is mainly driven by industrial boilers and power plant, while in northern China, coal-based heating is also a major sector of coal consumption (Tian et al., 2015). Seasonally, the average mass concentration of coal combustion-related $PM_{2.5}$ trace elements during winter (407 ng m^{-3}) was much higher than that during spring (296 ng m^{-3}), summer (148 ng m^{-3}), and fall (210 ng m^{-3}) (Fig. ~~8~~7). This seasonal pattern was not observed for other sources (not shown). Shanghai has a humid subtropical climate and experiences four distinct seasons. Winters are chilly and damp, with northwesterly winds from northern China ~~can~~ transporting air pollutants (including trace elements) caused by coal-based heating to the Shanghai atmosphere (Huang et al., 2013; Chang et al., 2017). As the largest city-scale coal consumer in China, coal combustion contributed to 275.4 ng m^{-3} or 18.5% of the $PM_{2.5}$ trace elements during our study period.

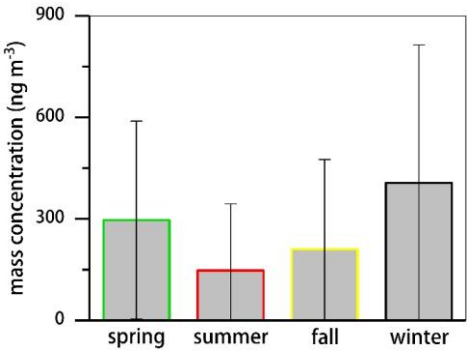


Figure ~~8~~7. Seasonal variation of element~~s~~ concentrations contributed by coal combustion in Shanghai. The error bar indicates one standard derivation.

Traditionally, K in particles ~~was~~ is considered to ~~be~~ originate~~d~~ from biomass burning along with some contribution of fugitive dust (Zhang et al., 2010; Hueglin et al., 2005; Fang et al., 2015). Here we show that over half of the element K in urban Shanghai ~~were~~ was derived from coal combustion. The reason for this discrepancy may be that in most previous studies, K in particles was pretreated using deionized water to extract (Wang et al., 2013b). In fact, K has a high mineral affinity (elements associated with aluminosilicates, carbonates and other minerals in coal ash), and in some extreme cases, only about 1% of K in fly ash from coal combustion can be extracted by water (Querol et al., 1996). For example, particles collected from coal combustion by Wang et al. (2013b) were extracted with deionized water, then atomized and measured by an ATOFMS. The ATOFMS mass spectrum contained a relatively low K peak. The observation by Wang et al. (2013b) was not consistent with that of Suess ~~et al.~~ (2002), ~~in which they~~who ~~detected~~ observed larger K peaks in ATOFMS spectra for coal combustion particles in an in situ measurement (i.e., freshly emitted particles were directly introduced into the ATOFMS and measured).

3.2.5 Ferrous metal smelting

Factor 5 was distinguished by high levels of Cr, Mn, and Zn representing 100%, 56%, and 52% of the ~~explained variation~~concentration, respectively. These elements are

typically emitted from ferrous metal smelting. For example, the steel production industry represents the dominant contributor to Zn emissions, accounting for about 60% in China (Tian et al., 2015). Driven by rapid modernization of its infrastructure and manufacturing industries, China produced more than 49% of the world steel production in 2017 (around 830 million tons), and 6 of 10 of the largest steel producers are in China (data retrieved from https://www.worldsteel.org). Headquartered in Shanghai (20 km northwest of the sampling site), the Baosteel is the fifth-largest steel producer in the world measured by crude steel output, with an annual output of around 35 million tons. Meanwhile, there are several factories of ferrous metal processing located in western Shanghai (Fig. 1). Since the element Cr is reported to be transported over substantial distances by the air ~~flow~~ (Perry et al., 1999), the presence of ferrous metal smelting activities in the west/northwest of the sampling site is inferred to be associated with this factor based on the results of CPF and BBP in Fig. ~~9~~8. Overall, ferrous metal smelting contributed 218.9 ng m^{-3} or 14.7% of the $PM_{2.5}$ trace elements in Shanghai.

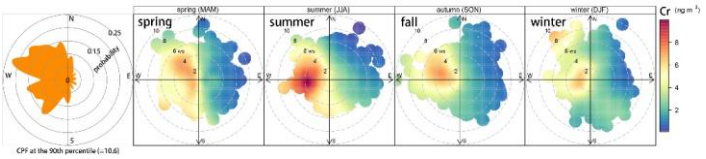


Figure ~~9~~8. Conditional probability function analysis (left) and bivariate polar plots (right) of seasonal concentrations (in ng m^{-3}) of Cr in Shanghai between March 2016 and February 2017. The center of each plot (centered at the sampling site) represents a wind speed of zero, which increases radially outward. The concentration is shown by the color scale.

3.3 Precipitation effect

Theoretically, precipitation could enhance the wet scavenging of airborne pollutants and reduce their ability to suspend because the increased moisture might capture the particles ~~on the road surface~~ (Kuhns et al., 2003; Karanasiou et al., 2011). Water spray (from sprinkler on road or atop a tall building) to simulate natural types of precipitation has been proposed as an important abatement strategy to facilitate the reduction of ambient PM concentrations (including trace elements) in urban China (Liu et al., ~~,~~2014;

Yu, 2014). However, several field measurements revealed that water spray activities did not influence the PM mass levels (e.g., Karanasiou et al., 2012~~,~~; Karanasiou, 2014). Taking advantage of our simultaneous and hourly record of the precipitation amount (up to 36.8 mm) and the ~~elements~~ elemental concentration, here we evaluate the effects of precipitation on the mitigation of $PM_{2.5}$ trace elements. The precipitation (all were in the form of rainfall) distributed during the full year of measurements is shown in Figure S13. The mass concentrations of the trace elements six hours before and after precipitation events were compared from the perspective of individual species and sources. ~~The~~ A precipitation event in this study is defined as (1) there are at least six consecutive hours with hourly rainfall amount higher than 1 mm; (2) the consecutive no-rainy time in a precipitation event should less than six hours; (3) the total no-rainy time should be less than 1/3 of the entire time of a precipitation event; (4) if the rainfall amount of a specific hour is less than 0.1 mm, and there are at least three no-rainy hours before and after the rainy hour, then this hour should be treated as a no-rainy hour. Consequently, 12 precipitation events during our study period were identified with ~~the~~ a duration time and accumulated rainfall ranging from 7 to 55 hours, and 26.4 to 217.5 mm, respectively (Table S2).

3.3.1 Change of mass concentration by species

The average mass concentration of each elemental species before, during, and after every precipitation event is presented in Fig. S14~~3~~. If precipitation effectively scavenges and removes aerosol, then the mass concentrations of trace elements during a precipitation event should be lower than that before and after this precipitation event. However, there is no uniform variation pattern in Fig. S14, indicating that precipitation may not be the predominant factor to influence the ambient elemental~~s~~ mass in some cases. For example, most elemental species had a relatively higher mass concentration during the 12th precipitation event (which lasted from 09:00 25 December to 22:00 26 December; Fig. S14). This can be explained by the much less anthropogenic activities during the periods prior to (3:00 to 8:00) and after (23:00 to 3:00 the next day) the 12th precipitation event.

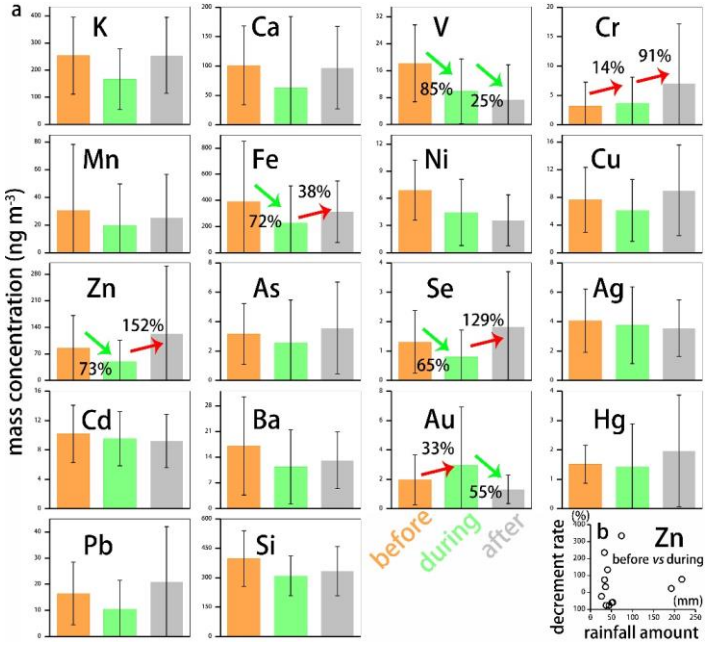


Figure ~~10~~9. (**a**) ~~The v~~Variation of the overall mass concentration of each elemental species before, during, and after the total 12 precipitation events; (**b**) scatter plot of the relationship between the rainfall amount of each precipitation event and the ~~decrement~~ decrease rate of the Zn concentration from the period before precipitation to the period after precipitation.

For each elemental species, the variation of mass concentration before, during, and after every precipitation event ~~were~~ was aggregated and reported in Fig. ~~10a~~9a. Before the precipitation events, the mass concentrations of all species except Cr and Au were higher than ~~that~~ those during the precipitation events (notably V, Zn, Fe), suggesting that water spray could generally help to reduce the $PM_{2.5}$ trace elements load in the atmosphere. After the precipitation events, there were six species (notably V and Au) with their mass concentrations lower than that during the precipitation events, indicating a potential long-lasting aftereffect of precipitation scavenging. Among all elemental species, the mass concentrations of Zn and Se fluctuate as ~~the~~ a most ideal V-shape, which properly reflects the cycle of precipitation. However, as shown in Fig. ~~10b~~9b, a linear relationship cannot be observed between the ~~decrement~~ decrease rate of

the Zn concentration and rainfall amount of each precipitation event. Although we failed to pinpoint the exact value in this study, our results imply that there is a threshold of precipitation amount to lower the ambient $PM_{2.5}$ trace elements mass.

3.3.~~1~~ 2 Change of mass concentration by sources

The variation of the overall mass concentration of trace elements contributed by each source and their relative contributions before, during, and after the total 12 precipitation events is shown in Fig. ~~11a~~ 10a to 10e, and Fig. ~~11f~~10f, respectively. The mass concentration of traffic-related trace elements experienced the sharpest decrease during the transition of no-rainy hours to rainy hours (159%), and a moderate rebound after precipitation (35%). Fang et al. (2015) found that mobile source emissions generated through mechanical processes (re-entrained road dust, tire and break wear) and processing by secondary sulfate were major contributors to water-soluble metals. In our study, traffic-related sources mainly include~~s~~ road dust and brake wear, which can not only be easily removed through precipitation but also can hardly be blown up from wet road surfaces after raining. In comparison, the mass contribution of the coal combustion source was also wet removed rapidly first (139%) due to its tracer elements like As, Se, Pb, and Hg having a~~e~~ larger water-soluble fraction. However, after precipitation, the contribution of the coal combustion source dramatically increased over two times (Fig. ~~11d~~ 10d and ~~11f~~10f). This can be explained that different from the traffic-related source, the coal combustion-related trace elements are generally emitted through elevated chimneys in the sectors of industrial broilers and power plants. The mass concentrations of trace elements contributed by nonferrous and ferrous metal smelting during the three periods ~~kept~~ remained quite flat (Fig. ~~11c~~ 10c and ~~11d~~10d), suggesting that precipitation has little effect on ambient trace elements emitted from metal smelting activities. Nevertheless, given that traffic-related and coal combustion are the dominant contributors to ambient $PM_{2.5}$ trace elements, our results validate that water spray could be an effective approach to help curb the severe atmospheric metal pollution in many Chinese cities.

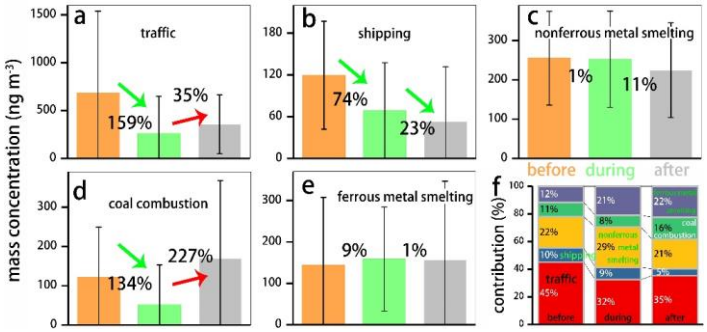


Figure ~~11~~10. ~~The v~~Variation of the overall mass concentration of trace elements contributed by traffic-related (**a**), shipping (**b**), nonferrous metal smelting (**c**), coal combustion (**d**), and ferrous metal smelting (**e**), and their relative contributions (**f**) before, during, and after the total 12 precipitation events.

In Fig. ~~11b~~ 10b and ~~11f~~10f, the contribution of shipping emissions to ambient trace elements (mainly V and Ni) during the three periods reduced continuously. Mostly transported from the Eastern China sea, V and Ni almost exclusively originated from the east of the sampling site. In other words, the contribution of shipping emissions to the urban atmosphere is supposed to be very sensitive to wind speed and wind direction in Shanghai. The wind roses for the three periods are presented in Fig. ~~12~~11. It shows that before precipitation events, the average wind speed (± 1σ) was the lowest (2.3 ± 1.3 m s^{-1}), and easterly winds prevail in most times. These factors are favorable to the transportation of shipping emissions from the Eastern China sea ~~and~~which then accumulated in the Shanghai urban atmosphere. In contrast to the period before precipitation events, the average wind speed after precipitation events was the highest (3.1 ± 2.1 m s^{-1}) with northwesterly and northerly winds from mainland China which can dilute shipping-related trace elements to the lowest levels (Fig. ~~11b~~10b). In brief, the mass concentration of shipping-related trace elements in the Shanghai urban atmosphere is more likely to be influenced by winds instead of precipitation.

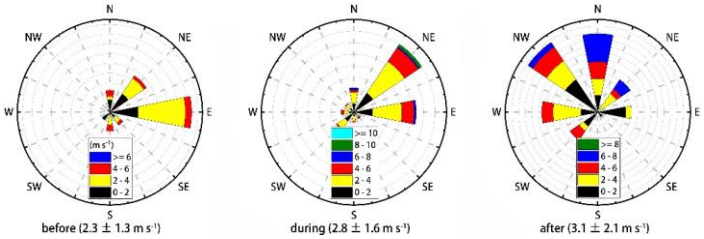


Figure ~~12~~11. Wind roses ~~plots~~ for the periods before, during, and after the twelve precipitation events. The average wind speed (± 1σ) for each period is shown in ~~bracket~~parentheses.

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-metals monitor, conducted at an urban site in Shanghai from March 2016 to February 2017. The scientific significance of this work can be reflected by the general findings as follows:

-The Xact multi-metals monitor was demonstrated as a valuable and practical tool for 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 the metal related species ~~comprised~~ accounted to 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.

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

-The dominant contributors of trace elements (traffic-related and coal combustion) can be effectively removed through precipitation from the atmosphere, suggesting that water spray can be used to curb $PM_{2.5}$ trace elements in the urban atmosphere.

A greater value and more interesting topic to the scientific community would be to fully assess the role of $PM_{2.5}$ chemical constituents (including metal species) and emission 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 for laboratory simulations (see example of Geagea et al. (2007)). Secondly, the Xact multi-metals monitor, Sunset OC/EC analyzer (Chang et al., 2017), and MARGA (Monitoring of AeRosols and Gases) 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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