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Atmospheric Chemistry and Physics Discussions

Interactive comment on "First long-term and near real-time measurement of atmospheric trace elements in Shanghai, China" *by* Yunhua Chang et al.

Anonymous Referee #1

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General comments

The manuscript discusses 1-year continuous measurements of 18 major and trace elements with an online XRF spectrometer in Shanghai, China. The authors argue that some trace elements are affecting human health in various ways, and that knowing the sources and behavior of trace elements will help in reducing these risks. The high time resolution of the measurements (1 hour) enables detection of concentration spikes, with their short-term acute exposure of humans. The dataset is analyzed with various statistical methods to attribute possible sources to the different elements and combinations. This is the first published year-long measurement of PM2.5 metals with

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Discussion paper

hourly time resolution.

The structure of the manuscript, the results and the presentation of the material are good. The topic is relevant and well worth publication in ACP. There are, however, a few changes and additions required before publication.

Specific comments

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

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

Another point is the statistics of the wind data, as shown in Figures 6 and S1. It is unclear how the wind data were processed for statistical analyses. As wind is a vector quantity, averaging and statistics should be done component-wise for u (east-west) and v (north-south) components. Averaging of wind directions may lead to stupid results, e.g. 350 and 10 degs would arithmetically average to 180 degs (a south wind), me-

teorologically however to 0 degs (a north wind). It is not evident from the description, whether the statistics packages used handle wind data correctly. From Figs. 6d and S1 the small variation of wind direction over 1 year appears doubtful, unless strong channeling of the wind had occurred. Furthermore, it is not clear how the wind direction as a circular distribution has been normalized. Here, a short explanation of the normalization procedure used would be helpful, also for interpreting the figures 5, 6, 8, 9, 10, 11.

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

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

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

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

Technical corrections

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

L19 delete 'with', replace 'its' with 'their' L35 'orders of magnitude' (insert 'of') L39 delete 'were' L42 ... was due to the interplay... L51 ... combustion of coal... L64 delete 'John'. The correct reference is Duffus, 2002. L125 write 'distance-based detection in a multi-layered device'. This probably captures the essence of the technique better. L133 Suggest to add the references to Park et al. (2014) and Furger et al. (2017, Atmos. Measurement Techn., doi:10.5194/amt-10-2061-2017) here, as both papers discuss the data quality of the Xact-625. L134 Add (YRD) as an abbreviation for the Yangtze River Delta. L173 ... from Siberia which can cause... L186 ... such as V... L258 ... to do correlation matrix calculations. I am unsure what is missing here. L289 The two methods have been implemented in the ... L295 Replace 'and give the probability of doing so' with 'and with which probability.' L327ff The different limiting values would probably be easier digested when listed in a Table. L338 replace 'with' by 'while' L375 please give a reference. L385 replace 'more' by 'other', and 'shown' by 'showed'. L404 ...in Shanghai has occurred during Sunday (Fig. 6d) (February (Fig. 6c)). – refer to the correct sub-figures. L415 'pads' instead of 'pad'. L416 correct 'less traffic flow in weekends not only lower road suspend dust but also cut metal species emissions' to 'less traffic flow in weekends not only lowers re-suspended road dust but also reduces metal species emissions'. L418 replace 'Ca' by 'Si'. L419 replace 'July' by 'June' and Fig. 10 by Fig. 8. Then replace 'Si' by 'Ca'. Please correct also the remark on the 0100 h Si peak. Do you have an explanation for this huge peak after midnight? L433 'transforming' – do you mean 'transporting'? L488 The text mentions 4 statistically significant factors. Which of the 6 factors in the figure are these? You should indicate the significance for all 6 factors in the Figure. L498 Replace 'were' by 'are'. L514 'plot' instead of 'plots'. Delete 'is'. L545 delete 'that'. L549 delete 'is' L553 write 'combustion of coal is located;' L580 write 'Fig. S4 also evidently reflects that high concentrations of Zn can occur in the northwest of PEMC.' L698 write: 'Duffus, J. H.: ...'

L1066 A land use map (not land uses map) L1115 The grey line indicates one two standard deviations – one or two? Fig. 6 Indicate the wind direction axis (or explain normalization of wind direction, see remark above). L1224 Replace ‘On the bottom’ with ‘Below the diagonal’. L1225 Replace ‘on the top’ with ‘above’. L1247 Write ‘Principal’ instead of ‘Principle’ Fig.15 Explain the circle sizes. Table S1: Caption: different monitoring (x, y) should be indicating the correct, correlated quantities, probably y Xact, x filter.

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