Review of acpd-14-13133-2014

Title: Spatial–temporal variations, sources, and transport of airborne inhalable metals (PM_{10}) in urban and rural areas of northern China

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Overall:

This manuscript reports elemental and Pb isotopic data in PM_{10} samples collected from seven cities in North China. The study further applied factor analysis for identifying the likely sources of selected metals (Al, Fe, Ca, Mg, Zn, Pb, Cu, V, Ni, Cd, and Co) and apportioning the relative contributions by the identified sources. Additionally, this study also analyzed Pb isotope composition for selected samples. However, I have found many fundamental questions particularly in terms of the sample/data representativeness, data quality and the methodologies applied. Results on source identification and apportionment lack verification and cannot be convincing. Moreover, the results are not novel at all essentially because only few common elements (without more specific elements) were analyzed and thus this study can really improve little our understanding of PM pollution sources in China. In addition, I have other concerns than the abovementioned. I give my comments in details as below.

General comments:

1. This first concern is about the application of various factor analyses and verification of relevant results. For the methods used, the authors referred to Thurston et al. (2011). However, there are many differences between this and Thurston's studies: (1) a much larger sample size (n = 46478) used in Thurston et al., compared to only n = 210; (2) over 200 sites, compared to 18 sites; (3) 10 daily samples per month during 5-6 years (2000-2005), compared to poorer time resolution with one 3-d sample per month a year-round; (4) $PM_{2.5}$ collected on PTFE filter, compared to PM_{10} (most of anthropogenic metals preferentially associated with fine mode aerosols) collected on glass fiber with much higher impurities; (5) 48 elements measured and characteristic elements used as tracers of specific sources, compared to 11 elements measured and most of them being too common to serving as suitable tracers (without As and Se, which are the typical tracers of coal combustion; without La which is an important tracer of petrochemical emission that has been postulated as a source by the authors). Thurston et al. concluded that "as the number of observations considered declined, the results became less robust". A variety of validation and verification processes of source identification and apportionment were performed by

Thurston et al., with respect to sensitivity test from region-seasonal aspects, single tracer versus APCA approach, source profiles, comparison, and so on; however this work lacks proper verification. Because of lacking more characteristic elements that can serve as tracers of specific sources, the source identification results are not better than most of published studies. I wonder if there is any limitation in application of the APCS-MLR, such as sample size; if any, please describe. Moreover, I do not see appropriate tracers used for vehicle and petrochemical emissions. Also no typical tracers were used for differentiating the traffic emission and coal combustion in contributing to certain metals such as Cu. I wonder why the source apportionment resolved over 100% (295% of Cu from coal combustion/traffic sources in the WW-YC-TY city group) and negative percentage (-54% of Cd from metallurgical industryin the BJ-DZ city group); the authors may explain.

2. This comment is about the sample representativeness. PM_{10} samples were collected from seven cities in north China, of which five cities had three sites (urban, rural, and rural field), one city (Dalian) had two sites (urban and rural field), and the other city (Beijing) had only one site. A year-round sampling was conducted once per month between April 2010 and March 2011. Only a three-day sample was collected in every month at a given site; therefore, only 36 days (12 samples) were collected at each site during a year. The sample size for each site is virtually very small and poor resolution. The authors claimed that the rural field sites were at least 200 m away from the nearest village. I doubt such so-called rural field (background) site can really reflect the distinct features, if any, from rural sites, as expected, which might thus account for in part their similarities observed. If such result is correct, it might thus implicate traffic emission insignificant in contributing PM and relevant metals. The variability in PM/metal concentrations with spatial and temporal scales (sites/area and months/seasons) observed in the study could be biased because of the insufficient data representativeness.
3. As for data quality, it seems to be of a critical concern. Glass fiber filter was used as collection substrate, but it has very high and not uniform impurities of trace elements. The method detection limits should be given. The acid digestion used only concentrated HNO_3 + $HClO_4$, without HF, which is obviously responsible for the poorer recovery of Al; it might be expected that Fe, Co, Ni, and V are also hard to completely dissolve as they are of crustal origin to a large extent but surprisingly the authors reported good recoveries. Glass fiber filter is not suitable for gravimetric measurement, which would lead to larger error in PM mass and in turn the elemental abundance (ug/g). Accordingly, the relevant discussion in

regards of spatial and temporal distribution of aerosol metal abundance (Section 3.3.1) cannot be convincing and there are no any novel results and ideas.

4. The Pb weight content and isotope composition in the certain potential sources should be given a range (or include one standard deviation), instead of a fix value. More importantly, I highly doubt if the equation used by Kusunoki et al. (2012) for sediment Pb sources could be applied here for deriving the Pb isotope signature of the end component via long-range transport. The variability in Pb abundance in the end component and the sources of PM10 aerosols in the study cities are considerably large, totally different from sediment Pb. In sediment cores, the deeper/older sediments have relatively constant Pb abundance and isotope ratios, thus allowing to be regarded as a background and to estimate the excessive Pb in contemporary sediments; therefore the Pb isotope signature of contemporary Pb in sediments could be quantitatively determined, which is considerably distinct from the conditions of aerosol Pb. Moreover, the concept by Hsu et al. (2006) and Kusunoki et al. adopted in their studies is to regard the upwind source from Asian pollution outflows as a point source. However, I don't think in this study it could be still valid. As shown in Figure 6, the derived source signature of long-range transported Pb is considerably variable, demonstrating my concern and the yielded results useless. If the suggestion that Pb was transported from west to east (Beijing/Taiyuan/Wuwei to Dezhou, and from Taiyuan/Dezhou to Dalian), then the authors could directly use the upwind sites' Pb isotope signature (you measured) as the end component' one to estimate the mixing for the downwind sites.
5. Different sources have been suggested for Cu, such as coal combustion, traffic emission, and industry (mining and smelting) in different sections in the text. I'd like to suggest the authors should make a complete and logical discussion as a whole.
6. Because the recovery of Al is poorer, Fe was thus used a reference element for calculating the EF_{crsut} value. However, Fe has been attributed to anthropogenic (coal combustion and traffic) origins (with 58%) along with natural dust. Therefore, Fe is not suitable in serving as the reference.
7. The authors have used loading (ng/m3) and concentration (mg/kg) in the text. I'd like to suggest changing to concentration (or loading) and weight content (or abundance), respectively, as the unit ng/m3 have commonly been used to refer to "atmospheric concentration" of aerosol species.
8. Because of the abovementioned shortages, I'd like to suggest the authors more concentrating on the chemical characterizations of PM_{10} and extending the chemical data set with inclusion of ionic and carbonaceous constituents (I guess

they have been analyzed). If the sample sizes could be amplified, it would be much better.

Specific comments:
P13135/L11: please split into multiple sentences.
P13137/L1 and L2: please cite references.
P13137/L7 and L14: The authors have overlooked many relevant studies; please cite more references.
P13138/L10: do you mean you have collected gas samples (for which gas species?) and/or measured gaseous phase metals (what metals?)? please clarify.
P13138/L11: how many stages of cascade impactor sampler were used?
P13138/L14: which microbalance? Precision?
P13138/L26: you should compare to the lowest concentration, rather than the mean concentration.
P13140/L25: please change to “of each source to pollutant species”.
P13141/L14: please clarify what average is used here and throughout the text, geometric or arithmetic means or median. Please add the stand deviation.
P13142/L22: Suggest removing the unit from the subhead and changing loadings to concentrations (and thus concentration to weight content).
P13142/L24-25: please add the standard deviations following the means.
P13143/L6: remove with.
P13143/L6-13: I cannot follow the logics. You have introduced the spatial tendency for PM10 but no clear trend for metals; subsequently, you highlighted the remarkable role of PM10 played in levels of aerosol metals. The following sentence is also very unclear (which exceptions? What differences in spatial and temporal variabilities?). You didn’t introduce the spatial distribution of aerosol metals at all.
P13143/L19-20: suggest changing the subhead.
P13143/L21-26: please cite the relevant reference following individual emission sources, and check the quoted metals from that said source.
P13143/L21-P13144/L8: how to link the cited emission sources to your own results? Otherwise, this paragraph should be moved to introduction.
P13144/L19: please specify these metals.
P13145/L11: the interpretation is unconvincing. Moreover, here you attributed to coal combustion for Cu and Pb, and lately to traffic source. Very inconsistent results!
P13145/L24: please first introduce the result of Cu and then give this explanation.
P13146/L4: no typical tracer of petrochemical source was used.
P13146/L10: 100% for Cu?
P13146/L11: no Ni contributed by dust? as the sum of metallurgical and mixed

sources has been over 100%, but the EF of Ni less than 10 should suggest that crustal source could be significant. Same as for V.
P13146/L24: sampling sites? OR samples (or sites)?
P13147/L8: please give the rational.
P13147/L9-10: please introduce the variation.
P13147/L17: please specify the mean values.
P13147/L26-28: I cannot follow your logics! It could be simply due to the similarity of contemporary anthropogenic Pb origins across China.
P13148/L7: The trajectory clustering figure could be moved to the text.
P13148/L14: what PB isotope model analysis? I didn't see until now.
P13149/L5-11: the Pb content in dust/loess (even suspended dust, 14.1-39.3 mg/kg, on P13147/L2) is considerably low, which would lead to dilution, rather than enhancement.
Table 1: please add standard deviations.
Figure 1: Suggest changing to a completely English version.
Figure 6: should indicate the error bars when considering the end component with a Pb isotope signature varying within a range.