

Responses to the Reviewers' Comments and Suggestions

Review of ACPD-14-13133-2014

Title: Spatial-temporal variations, sources, and transport of airborne inhalable metals (PM₁₀) in urban and rural areas of northern China

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We are very grateful to the reviewers for their critical comments and thoughtful suggestions. Based on these comments and suggestions, we have made careful modifications to the original manuscript. The changes are shown in the marked copy (highlighted in yellow). The point-to-point replies and explanations for all of the revisions are listed below for easy reference. We hope that the revised manuscript can be published in the ACP following these significant changes.

Reviewer #1

Overall:

This manuscript reports elemental and Pb isotopic data in PM₁₀ 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.

Reply and revision: *We very much appreciate the reviewer's detailed evaluations and suggestions. We agree with most of them, and the manuscript has been revised thoroughly according to the reviewer's advice. Regarding the novelty of the results on specific elements, we would like to emphasize that the present study focuses on those general airborne trace metals that are significantly related to human health. The present study is the first to report on spatial-temporal variations, source apportionment, and the transport of air metal pollutants in large regions of north China. The source characteristics and transport of pollutants in the study area are of importance on a global scale, especially in the north Pacific region.*

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 PM₁₀ (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 industry in the BJ-DZ city group); the authors may explain.

Reply and revision: We thank the reviewer for the very good comparisons between our study and that of Thurston et al. (2011). We agree with these evaluations, and are aware of the differences between the two studies regarding field sampling and laboratory analysis. Because our present study focuses on those general airborne trace metals that are significantly related to human health, and on their spatial-temporal variations, potential sources, and transport, we do not intend to do the source apportionment of the overall aerosols. In our current study, we did not analyze all elements, including some specific tracers. The sample size of this study can be a limiting factor for the APCS-MLR statistics, and the results may be less robust in comparison with those of Thurston et al. (2011). In the revised manuscript, considering the roles of all sources, we use the ENTER linear regression method to replace the STEPWISE regression that we used before, to more accurately estimate source apportionment results based our sample size and elemental data. It is worth noting that, in the APCS-MLR method, source contribution estimations are not constrained to be non-negative and less than 100% (Harrison et al., 1996; Guo et al., 2004). Finally, this part has been fully revised according to the reviewer’s comments, and the limitations of methods and results are also discussed in the revised manuscript.

With regard to the Cu data, we have examined all of the individual sampling locations and element concentrations. With the exception of Taiyuan (possibly with locally specific sources of industry – Fig. R1 below), the Cu levels in the PM₁₀ of most of the sampled cities were similar to the values of other cities reported in the literature, such as the city of Ordos in Inner Mongolia of northern China (190 ng m⁻³) (Wang et al., 2012), Beijing 10 years earlier (110 ng m⁻³) (Okuda et al., 2004), Wuhan in central China (40 ng m⁻³) (Querol et al., 2006), Hong Kong in south China (63.5 ng m⁻³) (Ho et al., 2003), Taipei in eastern China (14.6 ng m⁻³) (Gugamsetty et al., 2012), Lahore in Pakistan (73 ng m⁻³,

215 mg kg⁻¹) (von Schneidemesser et al., 2010), and Lecce in Italy (13.0 and 12.8 ng m⁻³, 477 and 494 mg kg⁻¹, for the hot and cold seasons, respectively) (Contini et al., 2010).

Considering the outlier of the city of Taiyuan (TY), the overall data on Cu might not fit the model. Therefore, we have deleted Cu from the revised manuscript to provide a better interpretation of the whole dataset. The statistical results re-calculated with and without the element as follows (Table 2, Table S2, and Table 3):

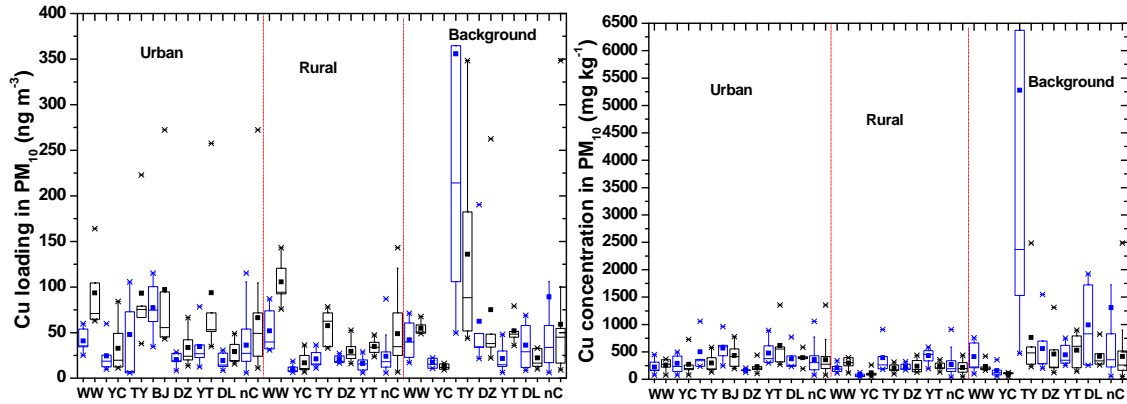


Fig. R1 (in Fig. S1/S2). Concentrations (ng m⁻³) and weight contents (mg kg⁻¹) of Cu in the warm and cold seasonal PM₁₀ of different areas of seven northern Chinese cities (nC, from west to east).

Table 2. PCA rotated component matrix for weight contents (mg kg^{-1}) of trace metals and major elements in the air particulates (PM_{10}) of the warm ($N = 105$) and cold ($N = 105$) seasons of seven northern Chinese cities. Factor loading values ≥ 0.50 are in bold.

Without Cu:

	Warm			Cold	
	PC1	PC2	PC3	PC1	PC2
Al	0.966	-0.047	0.110	0.977	-0.055
Ca	0.788	0.202	0.226	0.912	0.202
Cd	0.120	0.880	0.054	0.111	0.794
Co	0.904	-0.050	0.199	0.968	0.051
Fe	0.830	0.007	0.084	0.951	0.110
Mg	0.945	-0.031	0.174	0.969	0.018
Ni	0.317	0.194	0.823	0.799	0.132
Pb	-0.001	0.853	0.313	0.033	0.934
V	0.155	0.091	0.914	0.877	0.174
Zn	-0.092	0.876	0.003	0.095	0.849
Eigenvalue (>1)	4.60	2.50	1.11	6.15	2.18
% of Variance	46.0	25.0	11.1	61.5	21.8
Cumulative %	46.0	71.0	82.2	61.5	83.3
Main sources	Crustal (Soil/dust)	Coal combustion/Traffic	Oil combustion/Industry	Sandstorm	Coal combustion/Traffic

With Cu (for comparison):

	Warm			Cold	
	PC1	PC2	PC3	PC1	PC2
Al	0.967	-0.038	0.094	0.979	-0.051
Ca	0.791	0.214	0.211	0.909	0.212
Cd	0.094	0.850	0.129	0.101	0.751
Co	0.907	-0.048	0.185	0.967	0.064
Cu	0.068	0.372	-0.181	0.108	0.511
Fe	0.832	0.024	0.062	0.949	0.135
Mg	0.946	-0.029	0.162	0.969	0.024
Ni	0.342	0.186	0.793	0.793	0.183
Pb	-0.010	0.840	0.351	0.017	0.930
V	0.174	0.045	0.916	0.874	0.177
Zn	-0.120	0.842	0.085	0.081	0.840
Eigenvalue (>1)	4.60	2.54	1.13	6.19	2.32
% of Variance	41.8	23.1	10.3	56.2	21.1
Cumulative %	41.8	64.9	75.2	56.2	77.4
Main sources	Crustal (Soil/dust)	Coal combustion/Traffic	Oil combustion/Industry	Sandstorm	Coal combustion/Traffic

Table S2. PCA rotated component matrix for weight contents (mg kg⁻¹) of trace metals and major elements in the air particles (PM₁₀) of different regions (city groups) in northern China.

Without Cu:

	WW-YC-TY (n=105)		BJ-DZ (n=47)			YT-DL (n=58)		
	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3
Al	0.98	-0.01	0.95	-0.07	0.13	0.96	0.10	0.14
Ca	0.82	0.42	0.89	0.30	-0.07	0.89	0.05	0.23
Cd	0.12	0.92	0.14	0.84	-0.04	0.49	0.57	0.15
Co	0.97	0.05	0.92	-0.04	0.19	0.78	0.30	0.22
Fe	0.96	0.04	0.96	-0.03	0.03	0.48	0.63	-0.22
Mg	0.97	0.02	0.96	-0.07	-0.10	0.94	0.09	0.19
Ni	0.62	0.42	0.12	0.07	0.97	0.37	0.11	0.85
Pb	-0.03	0.94	-0.02	0.91	0.03	0.02	0.84	0.25
V	0.97	-0.03	0.64	0.19	0.30	0.15	-0.03	0.94
Zn	0.04	0.77	-0.04	0.89	0.14	0.04	0.89	-0.10
Eigenvalue (>1)	5.98	2.50	4.92	2.46	1.04	4.86	1.94	1.30
% of Variance	59.8	25.0	49.2	24.6	10.4	48.6	19.4	13.0
Cumulative %	59.8	84.8	49.2	73.8	84.2	48.6	68.0	81.0
Main sources	Crustal (soil/dust)	Coal combustion /Traffic	Crustal	Coal combustion /Traffic	Metallurgical/ Petrochemical industry	Crustal	Coal combustion /Traffic	Petrochemical industry, oil combustion

Factor loading values ≥ 0.50 are highlighted and in bold font.

With Cu (for comparison):

	WW-YC-TY (n=105)		BJ-DZ (n=47)			YT-DL (n=58)		
	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3
Al	0.98	-0.03	0.93	-0.09	0.19	0.97	0.04	0.13
Ca	0.83	0.39	0.90	0.28	-0.06	0.89	0.03	0.24
Cd	0.15	0.91	0.18	0.84	-0.15	0.54	0.53	0.09
Co	0.97	0.02	0.88	-0.06	0.39	0.80	0.27	0.19
Cu	-0.02	0.51	0.25	0.03	0.84	-0.03	0.59	0.27
Fe	0.96	0.02	0.93	-0.05	0.25	0.52	0.57	-0.28
Mg	0.97	-0.01	0.95	-0.10	0.08	0.94	0.06	0.19
Ni	0.62	0.42	0.07	0.12	0.73	0.39	0.14	0.83
Pb	0.00	0.94	-0.03	0.90	0.16	0.10	0.81	0.15
V	0.97	-0.05	0.67	0.21	-0.01	0.16	0.02	0.93
Zn	0.07	0.73	-0.05	0.88	0.18	0.10	0.87	-0.18
Eigenvalue (>1)	5.98	2.68	5.10	2.46	1.28	4.94	2.02	1.40
% of Variance	54.4	24.3	46.4	22.4	11.6	44.9	18.4	12.8
Cumulative %	54.4	78.7	46.4	68.8	80.4	44.9	63.3	76.0
Main sources	Crustal (soil/dust)	Coal combustion /Traffic	Crustal	Coal combustion /Traffic	Metallurgical industry	Crustal	Coal combustion /Traffic	Petrochemical industry, oil combustion

Factor loading values ≥ 0.50 are highlighted and in bold font.

Table 3. Contribution (%) of each PC source for each metal in different city groups by ‘enter’ MLR applied to absolute principle component scores after Table S2^a. The bold values stand for the main sources contribute for each metal.

Without Cu:

	WW-YC-TY (n = 105)				BJ-DZ (n = 47)				YT-DL (n = 58)				
	Crustal	Coal combustion /Traffic	UIS ^b	R ²	Crustal	Coal combustion /Traffic	UIS	R ²	Crustal/Long-range	Coal combustion /Traffic	Petrochemical industry, oil combustion	UIS	R ²
Al	107	-3.8		0.99	100	1.0	0.2	0.92	64	21	12	4.3	0.95
Ca	78	31		0.96	80	24		0.98	89	-2.0	20		0.95
Cd	22	85		0.95	-44	174		0.79	41	70	6.4		0.91
Co	90	4.7	6.8	0.95	100	1.7		0.99	36	34	12	22	0.71
Fe	92	4.6	5.5	0.93	106	-2.4		0.99	24	66	-6.8	21	0.64
Mg	98	2.4	2.2	0.94	109	-5.4		0.99	66	21	15		0.99
Ni	63	35	10	0.56	32	24	55	0.11	29	20	50	4.4	0.88
Pb	-3.7	81	31	0.90	3.5	72	27	0.82	-1	97	15		0.95
V	99	-2.2	4.3	0.94	56	19	30	0.49	16	-1.3	73	15	0.93
Zn	-2.9	121		0.78	3	96	3.6	0.81	3	87	-3.2	16	0.81

^a Values are presented as the percentage (%) of the weight content (mg kg⁻¹) attributed to each source, R² is the square of the coefficient of multiple correlation.

^b Unidentified sources.

With Cu (for comparison):

	WW-YC-TY (n = 105)				BJ-DZ (n = 47)				YT-DL (n = 58)					
	Crustal	Coal combustion /Traffic	UIS ^b	R ²	Crustal	Coal combustion /Traffic	Metallurgical industry	UIS	R ²	Crustal/Long-range	Coal combustion /Traffic	Petrochemical industry, oil combustion	UIS	R ²
Al	109	-6.1		0.99	86	-1.9	13	4.0	0.92	75	14	9.1		0.99
Ca	81	27		0.96	77	25	-1.2		0.99	99	-9.0	17		0.95
Cd	30	77		0.94	6.7	173	-55		0.85	49	63	3.3		0.91
Co	91	2.1	7.6	0.95	81	-4.0	24		0.99	45	31	9.3	15	0.71
Cu	-178	368		0.33	35	-18	109		0.89	-16	111	22		0.81
Fe	94	2.6	4.8	0.93	91	-5.1	18		0.99	31	58	-8.6	23	0.64
Mg	99	-0.2	2.6	0.94	98	-4.3	8.4		0.99	75	13	11		0.99
Ni	65	32	11	0.56	12	14	44	36	0.53	35	21	39	4.4	0.86
Pb	1.7	73	38	0.88	2.2	64	12	24	0.83	9.0	93	8.7		0.94
V	99	-3.7	4.6	0.94	49	16	1.8	37	0.50	20	4.6	56	16	0.90
Zn	14	106		0.75	-0.1	85	18	0.5	0.82	7.9	80	-5.8	21	0.79

^a Values are presented as the percentage (%) of the weight content (mg kg⁻¹) attributed to each source, R² is the square of the coefficient of multiple correlation.

^b Unidentified sources.

2. This comment is about the sample representativeness. PM₁₀ 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.

Reply and revision: We appreciate the reviewer's comments on the field sampling programs. Indeed, the sample size of the present study is relatively small considering the extent of the study area. The sampling sites for urban and rural areas are representative in the current research design. With regard to the rural sites, we further distinguish between village and agricultural field sites in the revised manuscript. The rural field sites were selected to be at least 500 m away from the nearest village buildings so that the influence of local village activities could be avoided, and we are aware that these sites cannot be defined as background locations. Such statements and related discussions have been revised accordingly in the manuscript.

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 HNO₃ + HClO₄, 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.

Reply and revision: We thank the reviewer for these comments. Due to the limitation in the field sampling programs, glass-fiber filters (GFF) were used in the present study. We understand that GFF filters are not as pure as quartz or PTFE filters. The digestion method of the sample with HNO₃ + HClO₄ may not be complete for some crustal origin elements. However, the acid digestion method without HF can provide the pseudo-total concentrations of trace elements. The filter blank was acceptable in comparison with the analytical detection limits and field samples. Based on the results of the blanks in all of the batches that were analyzed, the method detection limit (mg L⁻¹) for metals in digests

by ICP-AES (Perkin Elmer Optima 3300DV) is 0.60, 0.44, 0.020, 0.009, 0.056, 0.66, 0.74, 0.013, 0.055, 0.013, and 0.12, for Al, Ca, Cd, Co, Cu, Fe, Mg, Ni, Pb, V, and Zn, respectively. The recovery rate (%) of the standard reference materials (NIST SRM 1648, urban PM) in our study was 58%, 104%, 106%, 111%, 100%, 96%, 87%, 90%, 101%, 95%, and 108%, for Al, Ca, Cd, Co, Cu, Fe, Mg, Ni, Pb, V, and Zn, respectively. As shown by our statistical analysis, it is true that Fe and Co are mostly from crustal sources. The limitations of the GFF filter paper, metal analysis, and PM mass measurement are discussed in the revised manuscript.

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.

Reply and revision: *There is great variability in the abundance of Pb in the end component and in the complexity of PM₁₀ aerosols in the cities under study. We used the mixed model equation the first time to derive the Pb isotope signature of the end component via long-range transport, and the results and possible limitations are discussed in the revised manuscript. In this model, the aerosol Pb isotopic ratio in the warm season of each city was regarded as the characteristic value representing local aerosols of anthropogenic origin (R_{local}); thus, the possible characteristic value for long-range sources to this city in the cold season ($R_{long\ source}$) was estimated. In Fig. 6, the predicted values close to the regional natural soil dust values and/or to the monitored aerosol values of other cities could imply the possible contribution of long-range sources to the city in the cold season. For Pb transport and upwind cities, we only proposed the possible airflow directions, not the exact airflows from one sampling city to another far away, due to other possible sources of Pb in the air flow paths.*

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.

Reply and revision: *As mentioned above, after comparing the elemental patterns with and without Cu, the Cu results have not been included in the modified manuscript.*

6. Because the recovery of Al is poorer, Fe was thus used a reference element for calculating the EF crust 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.

Reply and revision: *The Al recovery is relatively poor with the current digestion method, so we used Fe as the reference element for the EF calculation. Although there was some contribution from anthropogenic inputs for Fe, most of Fe was from natural sources, because of the crustal contributions of 92% and 106% for western and central city groups, with an R^2 of 0.93 and 0.99.*

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.

Reply and revision: *We thank the reviewer for this good suggestion. We now use the concentration (ng m⁻³) and weight content (mg kg⁻¹) in the revised manuscript.*

8. Because of the abovementioned shortages, I'd like to suggest the authors more concentrating on the chemical characterizations of PM₁₀ 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.

Reply and revision: *We are grateful to the reviewer for these kind suggestions. The chemical characterizations of PM₁₀ is a significant issue, but in this study we try to focus on those airborne trace metals that are significantly related to human health, and on the spatial-temporal variations, source apportionment, and transport of metal pollutants on both local and regional scales. For organic pollutants, atmospheric polybrominated diphenyl ethers (PBDEs) in the summer were analyzed by our joint research team (gaseous and particulate phase). Different to trace metals, levels of PBDEs in the sampled regions of northern China were lower than those in southern China, and the concentrations at the urban sites were much higher than those at the rural residential and field sites (Wang et al., 2012).*

Specific comments:

P13135/L11: please split into multiple sentences.

Reply and revision: *Done accordingly in the revised manuscript.*

P13137/L1 and L2: please cite references.

Reply and revision: *Necessary references have been added in the revised manuscript.*

P13137/L7 and L14: The authors have overlooked many relevant studies; please cite more references.

Reply and revision: *The missing references have been added in the revised manuscript.*

P13138/L10: do you mean you have collected gas samples (for which gas species?) and/or measured gaseous phase metals (what metals?)? please clarify.

Reply and revision: *In the overall project, we collected both particle and gas samples using a medium volume cascade impactor. To clarify, we have changed the statements, and only concentrate on PM₁₀ sampling in the revised manuscript.*

P13138/L11: how many stages of cascade impactor sampler were used?

Reply and revision: *A single stage was used in the present study.*

P13138/L14: which microbalance? Precision?

Reply and revision: *We added the information in the revised manuscript (XS-105, Mettler Toledo, Switzerland; Readability 0.01 mg).*

P13138/L26: you should compare to the lowest concentration, rather than the mean concentration.

Reply and revision: *We revised the statements by showing the method detection limits of acid digestion and the ICP-AES determination based on the blanks in all of the analyzed batches.*

P13140/L25: please change to “of each source to pollutant species”.

Reply and revision: *Corrected accordingly.*

P13141/L14: please clarify what average is used here and throughout the text, geometric or arithmetic means or median. Please add the stand deviation.

Reply and revision: *We used the arithmetic means throughout this paper. Necessary information on this has been added in the revised manuscript accordingly.*

P13142/L22: Suggest removing the unit from the subhead and changing loadings to concentrations (and thus concentration to weight content).

Reply and revision: *This is a very good suggestion, which we have adopted in the revised manuscript.*

P13142/L24-25: please add the standard deviations following the means.

Reply and revision: *The required information has been added in the revised manuscript accordingly.*

P13143/L6: remove with.

Reply and revision: *Corrected accordingly.*

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.

Reply and revision: *The results indicate that there are some seasonal patterns for air metal levels (mg/m^3 - concordant with the trend in the PM levels) due to the positive role of PM_{10} mass, but there is no clear spatial pattern for the aerosol metal contents (mg/kg) implying an additional role for particle sources on chemical components. Such a phenomenon was also found in many other studies, which confirms the role of PM loading on metal concentrations. We have clarified this point in the revised manuscript accordingly.*

P13143/L19-20: suggest changing the subhead.

Reply and revision: *Done accordingly.*

P13143/L21-26: please cite the relevant reference following individual emission sources, and check the quoted metals from that said source.

Reply and revision: *The cited references reviewed the sources and relevant metals. We have checked the references again regarding the metals and their different sources.*

P13143/L21-P13144/L8: how to link the cited emission sources to your own results?

Otherwise, this paragraph should be moved to introduction.

Reply and revision: *As a paragraph to facilitate discussion, our intention here is to give some related background information about various emission sources, so that readers will have a better understanding of our results and discussion.*

P13144/L19: please specify these metals.

Reply and revision: *In fact, for northern China as a whole, the average weight contents (mg kg^{-1}) of all of the investigated trace metals in PM_{10} in the cold season were lower than those in the warm season for all types of areas (Figs. 4 and S2), with the exception of the weight contents of Pb and Zn in urban areas, which were still higher in the cold season. We revised this statement accordingly in the manuscript.*

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!

Reply and revision: *We revised the statement accordingly for consistency of the source information. Because the EFs of Pb in urban areas were higher in the cold season than warm season, they should have more intensive anthropogenic input in the cold season, and might be mainly due to the coal combustion.*

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.

Reply and revision: *As discussed above, the Cu results are not included in the PCA and APCS-MLR statistics in the revised manuscript. The source contribution estimated by*

APCS-MLR might be limited due to the small sampling size, especially when the R^2 is relatively low. For Ni and V, the contribution of dust was estimated using the ENTER regression method in the revised manuscript. In western cities, the two elements were mainly from crustal sources (99% for V and 63% for Ni, see Table 3), but for eastern and central cities, the EF increased (Fig. S3). V and Ni were regarded as typical tracers of petrochemical sources (Khan et al., 2010).

P13146/L24: sampling sites? OR samples (or sites)?

Reply and revision: *Thank you for raising this point. We use “samples” in the revised manuscript.*

P13147/L8: please give the rationale.

Reply and revision: *The cited reference suggested that the tendency was influenced by the Th-rich continental crust.*

P13147/L9-10: please introduce the variation.

Reply and revision: *The results of the Pb isotopes in this study varied widely, and it was difficult to link this variation to specific sources.*

P13147/L17: please specify the mean values.

Reply and revision: *Done accordingly. The required information has been added in the revised manuscript.*

P13147/L26-28: I cannot follow your logics! It could be simply due to the similarity of contemporary anthropogenic Pb origins across China.

Reply and revision: *We thank the reviewer for this comment. Besides the similarity of contemporary anthropogenic Pb origins across China, the long-range atmospheric transport of Pb contributing mixed compositions might be another reason for the indistinguishable Pb isotopic ratios in different cities across northern China, and for the seasonal variations in aerosol Pb isotopes.*

P13148/L7: The trajectory clustering figure could be moved to the text.

Reply and revision: *We appreciate the suggestion here. However, considering the length of the manuscript, we have had to put this information under Supplemental Information (SI).*

P13148/L14: what Pb isotope model analysis? I didn't see until now.

Reply and revision: *We have clarified the Pb isotope model in the revised manuscript.*

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.

Reply and revision: *Yes, this is true for metal dilution, but the urban aerosol pollution can be further enhanced by natural dust. We clarified this point in the modified manuscript.*

Table 1: please add standard deviations.

Reply and revision: *Done accordingly.*

Figure 1: Suggest changing to a completely English version.

Reply and revision: *Done accordingly.*

Figure 6: should indicate the error bars when considering the end component with a Pb isotope signature varying within a range.

Reply and revision: *We used the average values to estimate the source values with the model. This should be acceptable for calculating estimates.*

Reviewer #2

This manuscript shows a one year dataset of airborne inhalable metals in PM₁₀ at seven cities in northern China, the source and long-range transport were also investigated. The manuscript presents valuable results and is well interpreted, although there are still some needs to be modified, I therefore recommend this manuscript for acceptance by ACP after modifications.

Reply and revision: *We very much appreciate these comments on our manuscript. The manuscript has been revised thoroughly according to the reviewer's advice.*

1. There is only one sample each month in this study, so the limitation of temporal variation analysis should be mentioned in this manuscript's conclusion.

Reply and revision: *Indeed, in our study, the sample size is one of the limitations for high resolution research with combined local and regional data. This limitation is discussed in the revised manuscript.*

2. Dust storm was emphasized as an important factor impacting the analysis result, but it is not clear to show if any dust event was captured in the dataset and what is detailed difference between dust sample and normal samples.

3. The meteorological condition is quit important for analyzing these results, especially in hazy season of China (winter). Particularly there is only one sample each month, so the meteorological condition of the sampling should be discussed with more details in the manuscript.

Reply and revision: *We appreciate these comments. Because the influence of sandstorm frequency and precipitation on the distribution of PM₁₀ has been discussed in another paper (Li et al., 2014), we have decided not to repeat this discussion in the current manuscript. Several severe dust events were recorded in the spring of 2011, and the sampling programs were affected at most sites by these sandstorms during March, with the exception of those in Dalian). Further information has been added in the revised manuscript.*

4. In Fig 6, why Pb isotopic ratio of Wuwei is so special?

Reply and revision: *We suggest that there might be possible input from the re-suspension of Pb containing tailing materials (Pb ore isotopic ratios are much lower in northern*

than in southern China), such as locally from Wuwei and from nonferrous mining and metallurgy activities in nearby Jinchang.

5. In References section, the second and fourth papers are same.

Reply and revision: *Checked and revised accordingly.*

6. Page 10, line 336, one “from” should be removed.

Reply and revision: *Corrected accordingly.*

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