Responses to Anonymous Referee #2

We greatly appreciated the reviewer for the insight comments and suggestions for improving the quality of this manuscript. Below, we have addressed your concerns and provided our point-by-point responses in blue.

This study provides various information on the concentrations and solubilities of many metal ions in the atmosphere around Mt. Lushan, southern China. Since air pollution in China has been an important issue which can affect air quality not only in China, but also in other parts in East Asia due to the long-range transport. Thus, I think that this study is worth publishing to reveal information of the metal ions in fine particulate matters in the atmosphere in East Asia.

2.2. Sample collection: More details of the sampling of the cloud residues must be described.

The sampling system of the cloud residues was initially used at Mt. Tai in 2010 (Li et al., 2011). As shown in Figure R2-1, the moisture of the cloud droplets is removed by a diffusion dryer filled with desiccant (silica gel) to prevent the impact of the water vapor on TEM grids. Then, the individual residues are collected onto TEM grids using a single-stage cascade impactor with a 0.5 mm diameter jet nozzle. The calculated effective size d_{50} for cloud droplet is about 0.7 μm and the collection efficiency is estimated to be 5-10%. In this study, a low sampling flow rate of 0.5 l min^{-1} and an optimum sampling time of about 12 min were employed, neither destroying the TEM grids nor overlapping each individual residues.

We have added the description of the sampling system of cloud residues into the supplement.

2.3.2 Water-soluble fraction: How can avoid precipitation of highly insoluble elements such as Fe3+ and Al3+ by extraction using pure water. If the pH is above 5, the soluble Fe3+ in water is less than 60ppb. Is it possible to keep ferric ion in the water and to avoid formation of iron precipitates in your samples?

Ultrapure water were used to extract water-soluble metal ions in atmospheric particles in many studies, representing the highly soluble/bioavailable fraction. The extraction method was improved based on a chemical speciation scheme of trace elements in fine particles (Fernández-Espinosa et al., 2004), which was interpreted in the responses to the editor comment in detail. Ultra-sonication was implemented to prevent the formation of precipitates by keeping the dissolving constituents of insoluble elements (such as Fe^{3+} and Al^{3+}) in colloidal state at neutral pH as much as possible during the extraction procedure. The filtered solution was immediately transferred into glass bottles and high pure hydrochloric acid was then added to adjust the pH to less than 1, transforming the colloidal metal back to dissolved state and lessening the adsorption by glass walls. Thus, we expect that the dissolved fraction (by water) of highly insoluble elements in aerosols were sufficiently extracted and determined.

Results and discussion: (1) The solubility of metal ions has been investigated in various studies. Thus, it is essential for the authors to compare their results with other published data. In particular, the difference of the protocol to extract metal ions among different studies must be reviewed to compare each result.

Comparison of aerosol element solubility in various studies was displayed in supplement (Figure S5). No significant relationships were observed among these studies except the commonly low solubility for crustal elements such as Fe, Al and Cr. Accordingly, environment type, extraction method and analysis instrument are compared in Table R2-1. The major experimental differences are the type of environment and extraction method for total content of trace elements. The higher solubility for Mn, Cu and Fe at Mt. Lushan should be attributed the frequent cloud events at high altitude. Larger aerosol size (TSP) and stronger acid mixture (HNO_3-HF) were responsible for the various gap of solubility for Ba, Mo, Fe and Al in TSP over East China Sea and in $PM_{2.5}$ at Mt. Lushan. However, the differences of extraction method were not so much remarkable and the overall solubility trend for most elements were similar (decreasing from Zn to Cr) in each study, indicating the

much less significance of extraction method than the type of environment in these studies. The water solubility estimated from this study is still meaningful to assess the bioavailability and mobility of aerosol trace elements. More important influencing factors were investigated in the manuscript.

We have added Table R2-1 and reviewed the differences of protocols and results among various studies in the supplement.

(2) The experiment for the cloud processing is interesting. However, please write more details about the experiment such as (i) how did you collect the cloud water and (ii) how did you prepare the cloud residue.

(i) Bulk cloud water samples were collected by the improved Caltech Active Strand Cloudwater Collector (CASCC2 (Demoz et al., 1996)). The CASCC2 is a single-stage collector with a sampling flow rate of 24.5 m^3 min^{-1}. Air with cloud droplets are inhaled into the instrument and impacted on vertical 508 μm diameter Teflon strands. The droplets are then collected into a Teflon sample trough along the strands and flows into a 500 ml high-density polyethylene bottle. The theoretical sampling efficiency for size cut of 3.5 μm droplet diameter corresponds to 50%. In this study, the sampling interval of cloud water was 2 to 3 hours. Filtered cloud water (~ 30 ml) were immediately stored in brown glass bottles at 4 °C with preservation of 1% v/v high pure hydrochloric acid.

We have added the sampling of cloud water into section 2.2 of the revised manuscript and the supplement.

(ii) The sampling process is described above. Copper TEM grids coated with carbon film were placed in the impactor to collect individual cloud residues. An optical microscopy with magnification from ×500 to ×1200 was immediately used to check whether the carbon film and particle distribution on the TEM grid were suitable for analysis. If suitable, the grid would be placed in a sealed, dry plastic tube and stored in a desiccator at 25 °C and 20 ± 3% RH until the laboratory TEM/EDS analysis. Otherwise, another satisfactory sample shall be collected and preserved.

We have described the more detailed preparation of cloud residues in the revised manuscript.

(3) This study suggests that Ba is of metallurgical smelting origin. What kind of smelting activity can be suggested as a source of Ba.

Ba is a widely distributed alkaline-earth metal that primarily exists in barite ($BaSO_4$) and witherite ($BaCO_3$). In most case, Ba is clustered with Al, Fe and Ca, which indicates a source of crust or soil. However, we found Ba had relatively high EF values (>10) and was clustered with As and Cr at Mt. Lushan. Table S2 also showed an obviously higher concentration of Ba at Mt. Lushan than the other mountains and Shanghai, suggesting the anthropogenic pollution of Ba. Furthermore, Figure 6(k) identified southeastern Hunan and central Jiangxi as the most potential source regions. Since there are abundant mineral resources such as barite and realgar in Hunan province which is the most important production and export base of mineral products in China, the vast opencast mining of barite is considered to be the primary source of fine particle Ba at Mt. Lushan.

P.13010, L1: “contributed the highest” should be “contributed to the highest”.

It has been changed in the revised manuscript.

P.13012, L1: “applied to identify” should be “applied to identification of”.

It has been changed in the revised manuscript.

P.13017, L13: “That” should be “This result”.

It has been changed in the revised manuscript.

P.13017, L22: “contributed the” should be “contributed to the”.

It has been changed in the revised manuscript.

Fig. 2: Unit must be shown for the vertical axis.

The unit of the vertical axis is ng m^{-3}. For concision and good-looking, the unit is added into the figure caption in the revised manuscript.

Table R2-1. Differences of environment type, extraction method and instrument in determining aerosol element solubility in various studies.

Location	Type of environment	Extraction method		Instrument	Ref
		Soluble	Total		
Mt. Lushan ($PM_{2.5}$)	Rural mountain	Ultrapure water	HNO_3-H_2O_2, microwave digestion	ICP-MS	This study
East China Sea (TSP)	Sea surface	Milli-Q water	HNO_3-HF, microwave digestion	ICP-MS	(Hsu et al., 2010)
Edinburgh,UK ($PM_{2.5}$)	Urban background	Ultrapure water	HNO_3-HCl, heating	ICP-MS	(Heal et al., 2005)
Nanjing, China ($PM_{2.5}$)	Urban city	Glycine	HNO_3-H_2O_2, microwave digestion	ICP-OES & ICP-MS	(Hu et al., 2012)

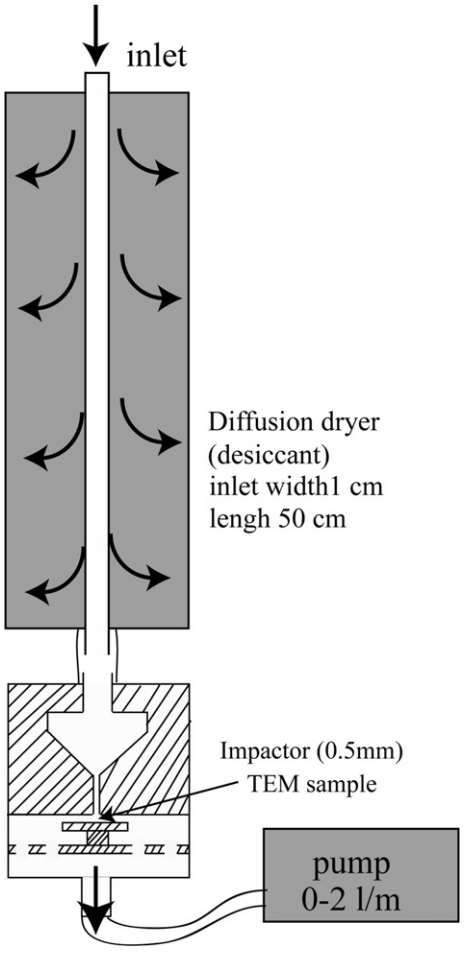

Figure R2-1. Schematic of the cloud droplet sampling system.

References:

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