Response to Referee #2:

Interactive comment on "Atmospheric wet and dry deposition of trace elements at ten sites in Northern China" by Y. P. Pan and Y. S. Wang

Anonymous Referee #2

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General comments:

The authors measured concurrently the wet and dry deposition fluxes of trace elements at ten sites in Northern China from December 2007 to November 2010. The sites include urban, industrial, suburban, agricultural and rural. Precipitation and dry deposition (particles) were collected every month using an automatic wet and dry deposition sampler. Spatial and seasonal variations in the wet and dry deposition fluxes of trace elements are presented in this paper. I think that those data are valuable, because China is regarded as one of the most significant source regions in the world with regard to anthropogenic emissions to the atmosphere. My comments are given below.

Response: The authors appreciate the Referee #2 for the constructive and insightful comments which are very helpful for the improvement of this manuscript. We have implemented them in the revised paper. Please see below for the responses to the comments point by point.

Page 20649, Lines 13–15: The authors cited a paper of Grantz et al. (2003). Where was this observation conducted?

Response: The observation was conducted in an eastern U.S. deciduous forest by Lindberg and Harriss (1981). The observation found that wet deposition rates for single events were several orders of magnitude higher than dry deposition rates measured for periods between precipitation events. In the revised manuscript this sentence is separated into two parts to make the statements more clear and logic. The original literature by Lindberg and Harriss (1981) was also added in the text.

Page 20652, Lines 9–11: Compared to the case for wet deposition, many uncertainties exist in the methods used to quantify dry deposition. These methods include both direct measurements and modeled estimates. To date, there is no accepted technique that can be used to evaluate the accuracy of these methods. For direct measurements, various surrogate surface, mainly solid surfaces such as Teflon plates, filters, and buckets, have been used in an attempt to quantify dry deposition. It has been shown that both the collector geometry and the surface characteristics have a large impact on the amount of collected material. In this study, the authors used a polyurethane foam (PUF) based glass bucket. What is the reason why the authors used this type of sampler? Uncertainties and problems associated with this dry deposition sampling should be discussed in this paper.

Response: We totally agree with the reviewer that uncertainties exist in the methods used to quantify dry deposition. Although the present approach is far from clearing up all aspects of dry deposition, it adds substantially to the knowledge of atmospheric metal deposition in Northern China. Most important, the direct measurement is essential for model validation in the estimates of dry deposition. After a thorough literature review, however, we did not find any commonly accepted technique for sampling and analyzing dry depositions. Thus, we want to develop a uniform monitoring protocol before we establish the observation network in Northern China. Below are the ideas why we used this type of sampler.

It was suggested by Dasch (1985) that a bucket collected more dry-deposited material than Teflon, foil or coated foil surfaces. In addition to the deposition fluxes of particulate matter, chemical species like polycyclic aromatic hydrocarbons (PAHs) measured by the bucket method were also higher than those by the plate for downward flux methods (Shannigrahi et al., 2005). The difference can be explained by the geometry of a dry deposition collector that affects the amount of material collected (Noll et al., 1988). For example, the bucket has a disturbed flow at the top and the flow around the plate is relatively undisturbed (or laminar) (Shannigrahi et al., 2005). As a result, the bucket collects more deposited material.

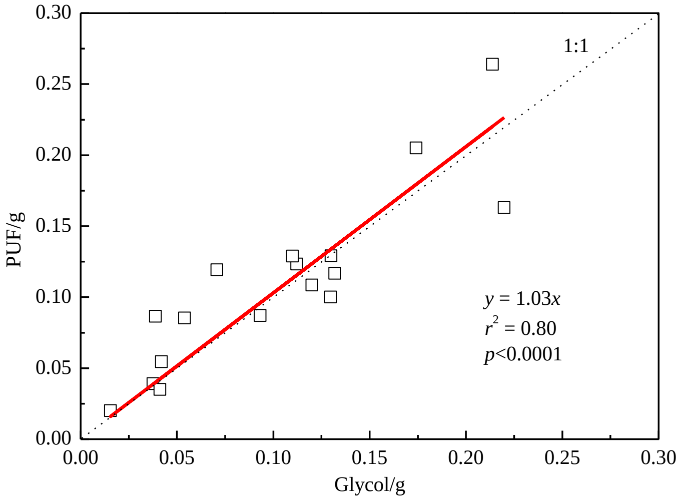
However, resuspension of the dry deposited particles in the buckets is a big problem due to winds in dry season (e.g., the target areas). To address this problem, additional materials such as marbles and glycerol were used to stabilize the deposited dust (McTainsh et al., 1997). However, such treatments make the subsequent sample collection and chemical analysis difficult, especially when the samples were contaminated with bird droppings, dead insects, etc. Although water (Sakata and Marumoto, 2004) or a greased and smooth surrogate surface (Yi et al., 2001) has been successfully used to measure particulate dry deposition fluxes of organic and inorganic air pollutants in recent years, there is still no surface has been established as a standard. Most of important, previously reported surface methods were time consuming and difficult to be used by an untrained operator. Therefore, there is an obvious incentive for developing simple, cost-effective samplers capable of trapping airborne particles.

Besides the collector geometry, as the reviewer noted, the surface characteristics have a large impact on the amount of collected material. It was shown by Dasch (1985) that a bucket collected less dry-deposited material than a nylon filter, quartz-fiber filter, a glass-fiber filter, or a water surface. Deposition appeared to be strongly influenced by the affinity of the surface for gases and the retention characteristics of the surface for particles. Thus, high retention is one of the ideal characteristics of the surface for sampling particles.

Polyurethane foam (PUF) disks are a popular sampling medium because they have a high retention capacity for persistent organic pollutants (POPs) (Chaemfa et al., 2009a; Harner et al., 2004). Meanwhile, particulate POPs can be also trapped by this medium (Shoeib and Harner, 2002). On this line of thinking, it may be desirable to use PUF as the potential surface to collect particles, further considering that the PUF is very easy to make, handle and deploy.

To integrate the advantages of collector geometry and the surface characteristics mentioned above, the PUF-based bucket used as a dry deposition collector was designed in our study. To test our ideas, the PUF-based bucket technique was evaluated and compared to the standard method recommended by the Ministry of

Environmental Protection of China, which uses buckets containing glycol as an alternative surrogate. Then, two types of surface surrogates, i.e., glycol vs. PUF, were placed concurrently in the buckets so that the comparison can be made. After the deposited particles were weighed, results observed for the two types of samplers agreed well with one another (shown in the figure below). The finding indicates a high collection efficiency retention capacity of PUF for trapping dry-deposited particles, compared with that of glycol surface. As an evidence, a more recent study also suggested that particles were trapped on the PUF surface and within the body of the PUF disk, and fine (<1 μm) particles can form clusters of larger size inside the foam matrix (Chaemfa et al., 2009b).



Comparison of atmospheric dry deposited mass collected by different surrogate surface on a monthly basis at the BJ and CZ sites (adopted from our previous report (Pan et al., 2010))

In addition to the important features described above, the PUF surrogate surface can also prevent particle bounce and is relatively inexpensive and simple; it can be used at a variety of locations and over varying time intervals to delineate spatial and temporal information. After collection, it can be divided into several pieces so that replicate can be easily processed. Finally, the PUF was considered to be applicable to the buckets used to measure the deposition fluxes in this study.

Despite the advantages of PUF-based bucket method, uncertainties and problems also exist in this dry deposition sampling. For example, the impaction and interception of fine particles are important for vegetative canopies and their effects are not reproduced in the design of this method and also of any other standardized artificial collection device (Wesely and Hicks, 2000). As discussed by Shannigrahi et al. (2005), the bucket method may be overestimate because it substantially suppresses the upward flux. Due to the gravitational settling, the upward flux of large particles representing mass is negligibly small compared with the downward flux. Thus, the deposition fluxes of particulate matter measured by bucket methods would be close to the net flux (downward minus upward) near urban/industrial areas where particle sizes are large. In regions with fine particles, however, the upward flux should not be neglected. In such a case, dry deposition flux measured by the bucket methods may be higher than the net flux. Even though, other studies have shown that sedimentation is the major mechanism of dry deposition for particles, even for heavy metal species primarily on small particles (Dasch, 1985). Thus, the chemical composition of PUF filters provides a gross understanding of atmospheric deposition.

The bucket method has also been criticized on the basis that the high container walls restrict the entry of all but the largest particles that deposit by gravitational setting. This may result in the underestimation of dry deposition. But Dasch (1985) found that deposition was similar to buckets with 25 cm high walls compared to buckets with only l cm walls, indicating a minor influence of the walls on particle deposition. Additional underestimation of dry deposition flux may be due to the adsorption of particles on the inner wall of the bucket, which is missed by the PUF filter at the bottom. But after the walls were rinsed with water, then dried and weighted, we found this part of particles was insignificant compared with that captured by the PUF filter. Further research is needed to address the degree to which particulate material is trapped on the sides of the bucket, if the factors favor the adsorption such as the presence of dew or the humid weather keeping the bucket wetted for a long time period.

As indicated by Dasch (1985), the collector geometry is less important than the surface characteristics in controlling dry deposition, and the difference in particle collection appeared to be dominated by the retention characteristics of the surface.

Although PUF filter has a high retention for particles with wide sizes (Chaemfa et al., 2009b), part of uncertainties linked to the decomposition of PUF filter itself under high temperature during the long exposure period in summer. The decomposition of PUF filter will result in the underestimation of the mass of dry deposition but it can be corrected with the concurrent sampling (i.e., another glass bucket was sealed during sampling to prevent the PUF filter from dry deposition). Other problems are related to the volatilization of some reactive species during the relatively long sampling period (Pan et al., 2012), but this is not the case for the trace metals, most of which are stable in particles under ambient temperature.

Our measurements are most likely low estimates of dry-deposited particles for the above reasons, but the estimates are not far from the real ones because PUF filter is an efficient collection surface. This simple method has the potential to be a routine procedure for obtaining information on temporal and geographical distribution in dry deposition.

Page 20652, Lines 9–11: Where was the sampler placed at each site (on the rooftop of a building or on the ground)?

Response: We now provide more detailed information on the monitoring site as shown below following the reviewer's suggestion.

The automatic wet-dry collector (height, 1.5 m) was installed on the ground if the underlying surface of the site was grass or lawn. When the underlying surface was bared soil or next to concrete road, the sampler was positioned on the roof of buildings approximately 5-14 m above ground (varied by site), to avoid collecting local emissions such as re-suspended particles.

In the revised version, we added a table to describe the sites' information.

Page 20653, Lines 1–4: The precipitation samples were acidified with HNO3 to dissolve the trace elements associated with suspended particles and to prevent their adsorption on the walls of the bottle. What was the concentration of HNO3 in the samples? How did the authors confirm the dissolution of trace elements associated with suspended particles? I think that crustal elements such as Al and Fe are not dissolved completely in the acidified samples. This makes it difficult to calculate the enrichment factors of trace elements in the precipitation samples relative to the average crust on the basis of Al (Page 20660, Line 21).

Response: We agree with the comments that the calculation of enrichment factors on the basis of Al will be misleading, if crustal elements are not dissolved completely in the acidified precipitation samples.

In this work a 20 mL of the unfiltered sample was acidified to pH~1 with 0.2 ml concentrated nitric acid (65%, Merck). The HNO_3 digestion technique is a powerful tool for studying the acid soluble fraction and minimizing adsorption losses of metals and has therefore been used, in most of studies (Cizmecioglu and Muezzinoglu, 2008; Heal et al., 2005), to determine the concentrations in rain samples. However, so far, the aspect of metal fractions/species in precipitation has not been thoroughly investigated and requires attention, since the majority of literature focus heavily on acid or water-soluble fraction.

In our study, the HNO_3 concentration (1%) in the final samples may be not enough to dissolve the trace elements associated with suspended particles, especially for the crustal elements such as Al and Fe, as the reviewer pointed out. In order to evaluate the presence of elements in their different forms, elemental contents in the soluble and insoluble fractions for precipitation were further investigated by three experiments below. The procedures were applied to a series of 10 sequential rainwater samples collected on Sep. 16, 2010 in Beijing to extract water-soluble (*experiment a*), acid-soluble (*experiment b*) and total metal concentrations (*experiment c*).

1. *Experiment a:* The first set of 10 mL precipitation samples were filtered through a 0.45 μm Sartorius membrane filter to remove the suspended particles, then the filtrate was acidified to pH~1 by 0.1 mL HNO_3. Thus, the determined metal concentrations in this set represent the water-soluble fraction.
2. *Experiment b*: The second set of 10 mL unfiltered precipitation samples were acidified to pH~1 to extract acid-leachable fractions, the concentration of which was considered to represent the environmentally mobile material, termed the acid-soluble fraction.

3. *Experiment c*: The third set of 5 mL unfiltered precipitation samples were acid digested for determination of total metal content, with procedure similar to that of PUF samples described in Sect.2.3. In the digestion of precipitation samples, an optimized sequential acid treatment with a mixture of 2 mL HNO_3, 1 mL H_2O_2 and 0.2 mL HF has been used. Digested samples were diluted to 10 mL volume by Milli-Q water and then transferred into PET bottles until analysis.

The results of the analysis show that the mean concentrations of acid-soluble Na, Mg, K, Ca, Mn, Zn, As, Se, Mo, Cd, Sb, Tl and Th were comparable to that of water soluble fraction. Although acid-soluble concentrations of these TEs were somewhat lower than their total content, their difference was insignificant. The findings indicated that these TEs were well dissolved in the rainwater and the suspended insoluble particles were negligible. There is another indication that the 1% HNO_3 was enough to dissolve the metals completely and to minimize adsorption losses.

In contrast, the concentrations of acid-soluble Be, Al, V, Cr, Fe, Co, Ni, Cu, Ag, Ba, Pb and U were significantly higher than that of water-soluble fraction and lower than that of total metal content. The concentrations of Fe, Ag, Pb, Cr and Al varied more than ten times among experiments a, b and c. Thus, we can conclude that these metals have substantial insoluble suspended particles in the rainwater, which can be not dissolved with 1% HNO_3 method. Consequently, this method will underestimate the total concentrations of crustal TEs, and hence their wet deposition flux.

These new results were added in the revised version to support the ideas pointed by the reviewer. And more discussions on the uncertainties regarding wet deposition flux and enrichment factors were added in the manuscript.

Page 20654, Line 10: What is Mini-Q water? I know Milli-Q water.

Response: We are sorry for this confusion. The typo was corrected in the revised paper.

Page 20661, Lines 6–8: Indicate Fig. S4.

Response: Done.

Page 20664, Lines 27–28: The authors should explain the sampling and elemental analysis of size-resolved particles in the experimental section.

Response: As suggested above, the sampling and elemental analysis of size-resolved particles were added in the experimental section.

Page 20665, Lines 14–15: Did the authors measure the distribution of Cu and Pb between liquid and solid phases in the precipitation samples? This may provide information on the difference in the solubility of both elements.

Response: We did not measure the distribution of Cu and Pb between liquid and solid phases in this study. But we can examine the solubility of metals based on the *experiments a and c* described above for the 10 precipitation samples in Beijing. The results showed that the solubility of Cu (26%) was higher than that of Pb (7%). This finding suggested that the deposition mechanisms of Cu and Pb were not influenced by the solubility, i.e., our original hypothesis proposed in this paragraph was not confirmed.

After carefully checked the size distribution of particles we found that Cu has another peak around 4.7-5.8 μm in addition to that at 0.43-0.65 μm. In contrast, there is only one peak at 0.43-0.65 μm for Pb. Thus, the different deposition mechanisms of Cu and Pb can be explained by the size distribution, and this idea was well clarified in Sect. 3.3.1. Finally, we found that the argument of the first sentence in this paragraph is self-contradictory, and hence the following supporting sentences were meaningless. To avoid misleading the readers we have deleted this paragraph in the revised version.

To confirm the influence of size distribution on the mechanisms of elemental deposition, size distribution of selected TEs was added in the revised version.

Page 20666, Lines 19–21: The authors should explain the sampling and elemental analysis of soils in the experimental section.

Response: Thank you for this suggestion. In the revised paper we added detailed information on the sampling and elemental analysis of soils in the experimental section.

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