**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 #1**

Received and published: 9 September 2014

**General Comments:**

The authors report measurements of atmospheric dry and wet deposition of trace elements in ten sites in the North China Plain area which have experienced serious air quality problems associated with intensive agricultural and industrial activities. The results of this paper are quite interesting.

The authors investigated the relative importance of wet and dry deposition in the removal of airborne trace elements and combined contribution of wet and dry deposition to ecosystems in the region. This will help researchers improve the understanding of the transport of air pollutants from sources to the environment. The findings are important for model validation and are also helpful for policy makers to create legislation to reduce the emissions and protect soil and water from air pollution. Overall, the paper is well presented and straight-forward. I can recommend publication, once the authors address the comments below.

**Response:** The authors appreciate the valuable suggestions given by Referee #1 for improving the overall quality of the manuscript. In the revised version we have made the corresponding corrections according to the reviewer's comments. Below are the responses to every comment one by one.

Page 20648, Line 20-25: Should the author give the full name when he/she first mentions the chemical species? Please carefully check the whole manuscript.

**Response:** We agree with the suggestion above. We have checked through the text to give the full name when a chemical species appeared for the first mention.

Page 20651, Line 19: In the results and discussion part, the author talked about TEs related to local emissions. Could the author add a paragraph in the introduction to briefly introduce the sources of TEs in the atmosphere? What TEs were from human activities and what TEs were from natural sources?

**Response:** We have incorporated the suggestions and briefly added the source information of airborne TEs in the third paragraph in the Introduction.

Page 20651, line 24: It would be better to move figure S1 in the Supplement to the text for the readers' convenience.

**Response:** The suggestion is implemented.

Page 20652, Line 15-20: I noticed this automatic collector was only used in the authors' research group. If this sampler has been used in other studies or in different research groups, please cite one or two of their papers.

**Response:** The automatic collector was produced by a custom company (APS-2B, Xianglan Scientific Instruments Co., Ltd., Changsha, China) and has been used in South China by other research groups (Huang et al., 2010; Wang et al., 2010; Wang et al., 2014; Zhang et al., 2011), but most of them were used to collect wet deposition only. We have cited these papers in the revised version. **[See Lines 145-148]**

Based on the automatic sampler we developed a unique technique sampling dry deposition using a PUF filter combined with a glass bucket. The method was optimized and verified by the national standard method in this study. More details were added in the revised paper. **[See Lines 148-150 and Sect. 2.3.2]**

**Please note the line numbers in our responses refer to the PDF file named "acp-2014-517-manuscript-version4."**

Page 20653, Line 10-15: If the authors used the same sample treatment procedures as others, please cite one or two papers.

Did the author conduct duplicate sampling such as setting up two samplers at one site during the measurements? If the author did this, please include the data in the manuscript. If not, I highly recommend thinking about this in future studies.

**Response:** The sample treatment procedures were established in our previous experiments and reported elsewhere (Pan et al., 2012, 2013b; Pan et al., 2010). We have cited the reports as suggested. **[See Lines 188-189]**

To check the quality of the sampling, different samplers were used to collect precipitation during the site-maintenance visits at the initial stage of the experiment at the BJ and CZ sites. The results showed no significant difference between the samplers for most of TEs. In the revised paper the comparison of two samplers for selected TEs were shown in a figure. **[See Lines 178-185 and Fig. S2]**

Also at the BJ and CZ sites, the PUF-based bucket used as a dry deposition collector was further evaluated and compared to the standard method recommended by the Ministry of Environmental Protection of China, which uses buckets containing glycerol as an alternative technique. The results observed for the two methods agreed well with one another and more discussions were added. **[See Sect. 2.3.2]**

Page 20656, line 21: I suggest the authors move Table S1 (also S2 and S3) in the Supplement to the text for the readers' convenience. Otherwise, please add the 10-site mean values measured in this study in these tables for comparison.

**Response:** Thanks for this comment. We have moved Table S1, S2 and S3 in the Supplement to the revised manuscript.

Page 20659, Line 18: Dust storms are a regional transport episode, but the author only mentioned impacts at the BJ site. Did the author find any evidence indicating impacts of dust storms on the other sites in this region?

**Response:** We are sorry for this confusion. With the exception of BD and TS, most sites in this study suffered from the regional transport of natural dust, especially during spring. To confirm that, we have checked the Sand-Dust Weather Almanac issued by the Chinese Meteorological Administration and found that there were 31 sand-dust weather events recorded in China between 2008 and 2010. Of the total, 16 events reached the target regions during the period (9 events occurred in spring); all of which were blowing or floating dust and no sand-storms were recorded. We thus

conclude that the long-range transport of natural dust from the northern/northwestern deserts and loess deposits results in the relatively high dry deposited elemental flux in spring than in other seasons in this study. In addition, sand-dust weather events decreased eastward due to the effects of distance and particle size. As a result, there were more days with blowing or floating dust at BJ than east coastal site of TG, according to the recorded weather phenomena. Dry deposition of Al at these two sites (2.1 and 1.3 g m$^{-2}$) during spring also supported this phenomenon.

The above discussions were summarized in the revised paper. **[See Lines 555-570]**

Page 20659, Line 23: Beijing is also a coal consumption city during the winter. Did the author find evidence of this at the BJ site? If not, please explain why.

**Response**: We agree with the reviewer that coal is still the primary fuel in Northern China and widely used for industrial processes and daily life, and more coal is combusted for heating in winter. Consequently, dry depositions in the cold seasons were expected to be enhanced in the region where a great deal of coal was combusted. This is supported by the elevated flux of various TEs at the urban and industrial sites of TJ, BD and TS, compared with other sites. In the urban areas of Beijing, however, the energy used for heating and industrial processes was mainly electricity and natural gas except for limited residential coal consumption (Zhao et al., 2013). At present, annual coal consumption in Beijing was about 21 million tons, which is significantly lower than that in Tianjin and Hebei (70 and 300 million tons). As a consequence, the dry deposition of coal combustion related TEs (e.g., Pb and Tl) in BJ was lower than that in TJ, BD and TS, but still higher than that in YC, CZ and XL, indicating the influences of residential coal consumption in the urban areas of Beijing.

In the past ten years, with the gradual replacement of coal by natural gas and electricity in urban Beijing, the sulfate and elemental carbon in winter decreased gradually from 25 and 8.7 μg m$^{-3}$ to 14 and 6.3 μg m$^{-3}$, respectively (Zhao et al., 2013). Further decrease of elemental deposition in Beijing can be expected, if the reduction of coal consumption continues.

We have revised the paper to reflect the above discussions. **[See Lines 574-592]**

Page 20660, Line 19: If the wdfPb was much higher than other places, please explain what are the major sources of wdfPb in this region?

**Response:** Besides natural sources from regional and local soil, possible anthropogenic sources of Pb include coal combustion, vehicle exhaust, cement factories and smelters (Cheng and Hu, 2010). But the relative contribution of the above sources is of spatial and temporal variable. After the phase-out of leaded gasoline in China since 2000, the major emission sources of airborne Pb in eastern and central China were estimated to be coal consumption and non-ferrous metal smelting, instead of vehicle exhaust (Li et al., 2012). However, detailed Pb isotopic signatures of $PM_{10}$ from selected sites in North China indicated its source was mainly anthropogenic, and mostly attributable to coal combustion and vehicle emissions with additional industrial sources (Luo et al., 2014). A case study in Beijing found that airborne Pb predominantly from anthropogenic sources was reduced by approximately 50% during the 2008 Olympic Games due to the mitigation measures implemented by the Chinese Government (Schleicher et al., 2012). Moreover, the temporal variations of Pb concentration correlated to the restrictiveness of relative measures, especially during different traffic restrictions, further demonstrating the significance of traffic sources (Chen et al., 2014). But the vehicular emissions from urban areas (e.g., Beijing) are not likely an important regional source of Pb and thus have insignificant impacts in rural areas (e.g., Xianghe) (Li et al., 2010). We conclude that Pb in wet deposition on the regional scale is mainly emitted from industrial processes and coal burning. These emissions can be widely dispersed throughout the atmosphere and transported to the downwind regions (Zhao et al., 2013), resulting in the high wet depositions at the background site of XL (discussed in Sect. 3.2.3).

The above discussions were added in the revised version. **[See Lines 622-645]**


Page 20662, Line 7: Is there any report of long-range transport effects on wet deposition flux of TEs? The author should add more discussion on this point. The author only mentioned "upwind areas". Is it long-range transport from urban and

industrial areas or rural areas?

**Response:** Yes, the long-range transport effects on wet deposition flux of TEs were well recorded. For example, wet deposition fluxes of TEs measured along the Japan Sea coast have been strongly affected by the long-range transport of air pollutants from the Asian continent during winter and spring (Sakata et al., 2006). A recent study also found that long-range transport of pollutants from south Asia has a significant impact on the trace elements in atmospheric wet deposition in the high altitude remote areas in the southern slope of the Himalayas (Tripathee et al., 2014).

Since the emissions of industrial pollutants and fossil fuel combustion from upwind sources in Tianjin and Hebei are prominent, trace elements in precipitation observed at XL could be from regional emission sources. Imprints of regional transport were indicated by the fact that the metallic episodes experienced at the XL site closely associated with the air mass from southeast that passed TS and TJ, or from southwest that passed BD and SJZ (Pan et al., 2013a).

As suggested we have added more discussion on this issue. **[See Lines 681-704]**

Page 20664, Line 15: Please cite the paper which partially verified this pattern in Northern China.

**Response:** We are sorry for this confusion. In the revised version, "Northern China" was changed to "in this study". That is, this pattern was partially verified in this study.

Page 20667, line 3: I suggest the authors add a figure to show the vertical profile showing the distribution of Mc for each metal vs. soil depth, which will be helpful for the readers to interpret the ideas examined here.

**Response:** We accept this suggestion and have added a figure in the revised paper. **[See Fig. 5]**

Page 20667, line 27: Also, it is better to move Table S4 in the Supplement to the text for the readers' convenience.

**Response:** Done.

Page 20674, Table 1: It would look better if the author can add several black lines in Table 1 to clearly separate the urban, industrial, suburban, agricultural and rural groups.

**Response**: The suggestion is implemented.

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**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**

Received and published: 28 August 2014

**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 paper 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. **[See lines 52-57]**

**Please note the line numbers in our responses refer to the PDF file named "acp-2014-517-manuscript-version4."**

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. There is an obvious incentive for developing a simple, cost-effective sampler 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, or 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. Thus, these two types of surface surrogates, i.e., glycol vs. PUF, were placed concurrently in separate 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 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).
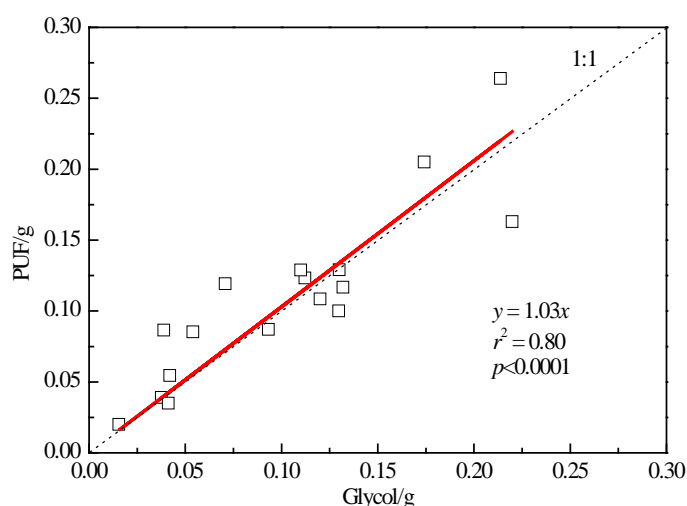


Comparison of atmospheric dry deposited mass collected by different surrogate surface on a monthly basis at the BJ and CZ sites (adopted from our previous report (Pan et al., 2010))

In addition to the important features described above, the PUF surrogate surface can also prevent particle bounce and is relatively inexpensive. 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 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 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, sedimentation is considered to be the major mechanism of dry deposition for particles, even for heavy metal species primarily on small particles (Dasch, 1985). Thus, the PUF-based bucket method provides a gross understanding of atmospheric deposition.

The bucket method has also been criticized that the high container walls restrict the entry of all but the largest particles that deposit by gravitational settling. 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 particles on 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 conditions 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 the 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 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 may underestimate 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 spatial and temporal distributions in dry deposition.

The above discussions were added in the revised paper. **[See Sect. 2.3.2 and 2.3.3]**

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 paper, we added a table to describe the sites' information in detail. **[See lines 155-160 and Table 1]**

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.

In the revised version, these new results were added to support the ideas pointed by the reviewer. And more discussions on the uncertainties regarding wet deposition flux and enrichment factors were also added. **[See Sect. 2.3.1 and lines 619-621]**


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. **[The figure was updated as Fig. S5 in the revised version]**

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. **[See Sect. 2.4.1]**

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 checking 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 sentences were meaningless. To avoid misleading the readers we have re-organized this paragraph. **[See lines 789-806]**

To confirm the influence of size distribution on the mechanisms of elemental deposition, size distribution of selected TEs was added in the revised paper. **[Fig. 4]**

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. **[See Sect. 2.4.2]**

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1 **Atmospheric wet and dry deposition of trace elements**

2 **at ten sites in Northern China**

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**Manuscript revised by using the track changes mode in MS Word. Please note the line numbers in this version may be slightly different from that mentioned in our responses.**

**9   Abstract**

10   Atmospheric deposition is considered to be a major process that removes pollutants

11   from the atmosphere and an important source of nutrients and contaminants for

12   ecosystems. Trace elements (TEs), especially toxic metals deposited on plants and

13   into soil or~~and~~ water, can cause substantial damage to the environment and human

14   health due to their transfer and accumulation in food chains. Despite public concerns,

15   quantitative knowledge of metal deposition from the atmosphere to ecosystems

16   remains scarce. To advance our understanding of the spatio-temporal variations in the

17   magnitudes, pathways, compositions and impacts of atmospherically deposited TEs,

18   precipitation (rain and snow) and dry-deposited particles were collected

19   simultaneously at ten sites in Northern China from December 2007 to November

20   2010.

21   The measurements showed that the wet and dry depositions of TEs in the target

22   areas were orders of magnitude higher than previous observations within and outside

23   China, generating great concern over the potential risks. The spatial distribution of the

24   total (wet plus dry) deposition flux was consistent with that of the dry deposition, with

25   a significant decrease from industrial and urban areas to suburban, agricultural and

26   rural sites~~. In contrast~~, while the wet deposition exhibited less spatial variation. In

27   addition, T~~t~~he seasonal variation of wet deposition was also different from that of dry

28   deposition, although they were both governed by the precipitation and emission

29   patterns.

30   For the majority of TEs that exist as coarse particles, dry deposition dominated the

31   total flux at each site. This was not the case for potassium~~K~~, nickel~~Ni~~, arsenic~~As~~,

32   lead~~Pb~~, zinc~~Zn~~, cadmium~~Cd~~, selenium~~Se~~, silver~~Ag~~ and thallium~~Tl~~, for which the

33   relative importance between wet and dry deposition fluxes varied by site. Whether

34   wet deposition is the major atmospheric cleansing mechanism for the TEs depends on

35   the size distribution ~~and solubility~~ of the particles.

36   We found that atmospheric inputs of ~~Cu~~copper, ~~Pb~~lead, zinc~~Zn~~, cadmium~~Cd~~,

arsenicAs and seleniumSe were of the same magnitude as their increases in the topsoil of agricultural systems. At a background forest site in Northern ChinaIn addition, the total deposition flux of leadPb observed at a forest site in this study (14.1 mg m$^{-2}$ yr$^{-1}$) was twice that of the critical load (7.0 mg m$^{-2}$ yr$^{-1}$) calculated for temperate forest ecosystems in Europe. These findings provide baseline data needed for future targeting policies to protect various ecosystems from long-term heavy metal input via atmospheric deposition.

## 1. Introduction

Air pollution is generally considered an accumulation of substances in the atmosphere of substances that, in sufficient concentrations resulting from excessive anthropogenic emissions and natural sources, endanger human health and the environment. In recent decades, public concern regarding the consequences of worldwide air pollution has motivated considerable political debate regarding emissions control (Chen et al., 2014). In addition to mitigation measures taken by local governments, two primary natural processes have been recognized as participating in the reduction of air pollutants: dry and wet deposition. The removal of pollutants from the atmosphere by wet deposition is often considered an important natural mediating factor in cleansing the atmosphere (Yang et al., 2012). In an eastern U.S. deciduous forest, for example, wet deposition rates for single events were several orders of magnitude greater than dry deposition rates measured for periods between precipitation events (Lindberg and Harriss, 1981). In contrast to the episodic nature of wet deposition, however, Although the rates of dry deposition are orders of magnitude slower than those of wet deposition, the former is also a continuous and dependable process involved in atmospheric cleansing (Grantz et al., 2003). In regions with low precipitation, such as Mediterranean climate area (Muezzinoglu and Cizmecioglu, 2006), dry deposition as a cleansing mechanism is more important than wet deposition on an annual basis. Thus, the relative importance of wet versus dry deposition may depend on the efficiencies of these two mechanisms, but it also varies with the local availability of precipitation (Muezzinoglu and Cizmecioglu, 2006). In the absence of simultaneous measurements of these two processes, however, their relative and combined contributions to the total deposition remain unclear, and debate remains over whether dry deposition is the major cleansing mechanism.

Although natural deposition cleans the atmosphere, its ultimate result is the transfer of nutrients (e.g., reactive nitrogen species) and contaminants (e.g., heavy metals) from the air into the water and soil (Duan et al., 2010; Hovmand et al., 2008).

72    In regions where natural biogeochemical cycles are perturbed by human activities,

73    atmospheric deposition can be important sources of either toxic substances or

74    nutrients for the ecosystems (Hovmand et al., 2009; Meng et al., 2008). Thus, the

75    interest in atmospheric deposition results mostly from concerns regarding the effects

76    of the deposited materials entering the terrestrial and aquatic environments as well as

77    their subsequent health effects (Sakata et al., 2006). When estimating atmospheric

78    deposition flux, it is also important to consider the global biogeochemical cycle. For

79    example, when compared with the riverine input, atmospheric dry deposition is one of

80    the major paths for the transport of chemical species from the continents to coastal

81    and open marine ecosystems (Duce et al., 1991). On the regional scale, the dry

82    deposition process may be particularly important near urban/industrial areas where

83    particle concentrations and sizes are large, such as sites near the Great Lakes (Sweet

84    et al., 1998). Compared with developed regions in the U.S. and Europe, however,

85    relatively little is known about the magnitude and potential impacts of atmospheric

86    deposition in the vast areas of Asia.

87        Northern China is subject to large quantities of emissions. However, measuring

88    the atmospheric deposition flux, particularly the dry deposition of aerosols and their

89    precursors, has thus far received little attention. The components of aerosols in

90    Northern China are characterized by high levels of crustal elements (e.g.,

91    aluminum-Al, , silicon-Si, iron-Fe, potassium-K, sodium-Na, barium-Ba and

92    calcium-Ca) that are mainly generated over upstream arid/semi-arid areas

93    (specifically, episodic dust storms in the springtime); the aerosols also contain

94    abundant acids and heavy metals (e.g., copper-Cu, lead-Pb, zinc-Zn, cadmium-Cd,

95    nickel-Ni, chromium-Cr, selenium-Se, vanadium-V, antimony-Sb and thallium-Tl)

96    that are emitted directly from local anthropogenic sources (e.g., power plants, motor

97    vehicles and industrial facilities) (Chen et al., 2014; Zhao et al., 2013). In addition to

98    the complex emissions, the topography (surrounded by mountains) and climate (lack

99    of rain) are not favorable for the diffusion and wet deposition of pollutants (e.g.,

100   sulfur dioxide$SO_2$, nitrogen dioxide$NO_2$ and ammonia$NH_3$) in Northern China (Yang

101   et al., 2012). Although previous studies have defined the aerosol/precipitation

102 chemistry at a number of sites in the target areas, spatial and temporal information

103 regarding wet and dry deposition derived from local and regional emissions in this

104 complex air shed is limited. To advance our understanding of the transportation and

105 transformation of pollutants from the local to the regional and global scales, our

106 knowledge of the quantitative aspects of atmospheric deposition must be updated with

107 detailed spatio-temporal descriptions. Therefore, a new monitoring network including

108 ten well-distributed sites within the target areas was established in late 2007. The

109 focus of the program was to evaluate the wet and dry deposition of the important trace

110 species, including carbon, nitrogen, sulfur, phosphorus, heavy metals, and polycyclic

111 aromatic hydrocarbons (PAHs). The observations of this monitoring network have

112 recently been presented, with an emphasis on acids and nutrients that most affect

113 natural ecosystems (Pan et al., 2012, 2013b; Pan et al., 2010a; Wang et al., 2012).

114 With the substantial anthropogenic emissions, toxic metals deposited into ecosystems

115 have led to increasing public concerns due to their transfer and accumulation in food

116 chains (Luo et al., 2009).

117     In this paper, we further investigate the atmospheric wet and dry deposition fluxes

118 of 25 trace elements (TEs) to complement the previous studies. The measurements

119 were conducted during a three-year observation campaign at 10 selected sites. This

120 study is the first attempt to conduct long-term direct measurements of the atmospheric

121 deposition flux of crustal and anthropogenic metals in such a vast geographical area

122 of China. The objectives of this research were (i) to clarify the spatial and seasonal

123 variations in the wet and dry deposition fluxes across Northern China, (ii) to examine

124 the relative importance of wet and dry deposition in removing airborne metals, and (iii)

125 to compare the atmospheric deposition flux of TEs to other measurements in the

126 literature and to the anthropogenic metal input to various ecosystems.

127 **2. Materials and methods**

128 **2.1. Site description**

129 Ten sites representing a range of conditions (coast-inland, forest-cropland,

130    source-receptor, urban-rural, etc.) encountered in Northern China were selected for

131    this study (Fig. S1). The observations of atmospheric deposition at all of the

132    monitoring stations were conducted from December 2007 to November 2010. The

133    monitoring network was operated and managed by the Institute of Atmospheric

134    Physics, Chinese Academy of Sciences. The 10 sites are abbreviated using the names

135    of the town/county/city in which they are located, and they are organized according to

136    their urban geographies, energy structures and ecosystem types (Table 1). The types

137    include urban (Beijing-BJ and Tianjin-TJ), industrial (Baoding-BD, Tanggu-TG and

138    Tangshan-TS), suburban (Yangfang-YF and Cangzhou-CZ), agricultural

139    (Yucheng-YC and Luancheng-LC) and rural (Xinglong-XL). The longitudes ranged

140    from 114.69°E to 118.20°E, and latitudes ranged from 36.85°N to 40.38°N. The mean

141    annual precipitation ranged from 400 to 800 mm, and mean annual air temperature

142    was 8–14 °C; more detailed descriptions of the ten selected sites in the study have

143    been reported elsewhere (Pan et al., 2012, 2013b).

144    **2.2. Sampling and analysis**

145    **2.2.1 Wet and dry deposition sampler**

146    In this study, Wwet-only rainwater and dry-deposited particles were collected using a

147    custom wet-dry automatic samplercollector (APS-2B, Changsha Xianglan Scientific

148    Instruments Co., Ltd., China). The sampler has been successfully used to collect wet

149    deposition of various species but scarcely used for dry deposition in most of the

150    previous studies (Huang et al., 2010; Wang et al., 2010; Wang et al., 2014; Zhang et

151    al., 2011). Based on the automatic sampler we developed a unique technique sampling

152    dry deposition using polyurethane foam (PUF)-filter combined with a glass bucket

153    (detailed in Sect. 2.3.2). The wet-dry sampler was equipped with a 707 cm$^2$ aperture

154    and a 177 cm$^2$ polyurethane foam (PUF)-based glass bucket in separate containers to

155    sample daily rainfall and monthly particulate dry deposition, respectively. Because the

156    rainwater sensor allows the collection funnel of the cover device to open/close

157    automatically when rainfall begins/ceases, wet and dry deposition can be collected

7

separately with minor mixing between the two. 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 the site was next to concrete road, the sampler was positioned on the rooftop of a building approximately 5-14 m above ground (varied by site, Table 1), to avoid collecting local emissions such as re-suspended particles. A schematic of the sampler used is shown in Fig. S2S1. In addition, snow samples were collected as soon as possible after the snowfall events using a separate clean plastic bucket with an inner diameter of 22 cm. A detailed description of the sampling equipment and procedures is published elsewhere in a series of data reports (Pan et al., 2012, 2013b).

**2.2.2 Sampling and treatment procedures for precipitation**

The rainwater and melted snow samples were stored in a 50 mLml polyethylene terephthalate (PET) bottle and frozen in a refrigerator at −20 °C immediately after collection at each site. The samples were then delivered in iceboxes to analytical laboratories in the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC, Beijing) by routine monthly site-maintenance visits. In the laboratory, a 20 mL of the precipitation (rainwater and snow) samples were acidified to pH~1 with 0.2 mL concentrated nitric acid ($HNO_3$, 65%, Merck, Germany) to dissolve the TEs associated with suspended particles and to prevent their adsorption on the walls of the bottle. The preserved samples were sealed from the atmosphere and stored in the dark at 4 °C until analysis, which was normally conducted within one month. All delivery and sample-handling processes were conducted using gloves to avoid pollution.

To ensure the quality of the sampling and to check for possible contaminants, two separate clean plastic bags overlapped in a bucket with an inner diameter of 15 cm have been used to collect precipitation at the initial stage of the experiment at the BJ and CZ sites during the site-maintenance visits. After the rainfall ceases the inner plastic bag containing rainwater was collected. Then the rainwater was acidified to

pH~1 and analyzed. The results concurrently collected by the plastic bag and the automatic sampler showed no significant differences (Fig. S2 for selected TEs), indicating that the methodology used in the study was reliable and repeatable.

### 2.2.3 Sampling and treatment procedures for dry deposition

Dry-deposited airborne particles were collected using a PUF-based surrogate surface. Details of the sample preparation have been described previously (Pan et al., 2012, 2013b), but are repeated here for the reader's convenience. Briefly, a PUF filter (15 cm diameter and 1.35 cm thickness with a density of 0.021 g cm$^{-3}$) serving as the surrogate surface was placed in a glass bucket (15 cm inner diameter and 30 cm depth) to collect the dry-deposited particulate matter. At the end of each month, the PUF filter was replaced with a new one. For the first three months of the study, field blanks were handled identically to the samples at each site but were placed in the glass bucket for only 5 minutes. Subsequently, blank filters were taken once per filter change (i.e., monthly) at only the BJ site; the bucket was capped during the sampling period. Filters were handled to minimize contamination. After collection, the PUF filters were sealed in aluminum foil and frozen in a refrigerator at each site until delivery in clean iceboxes to LAPC by routine monthly site-maintenance visits.

To determine the metal content of the dry-deposited particles, the PUF filters were digested using a closed-vessel microwave digestion system (MARS 5, CEM Corporation, Matthews, NC, USA). The microwave oven could accommodate the simultaneous digestion of up to 40 Teflon vessels. Prior to use, the vessels were sonicated for 15 min with 10% HNO$_3$ and soaked in 2% HNO$_3$ overnight to prevent contamination. Finally, these vessels were rinsed with ultrapure water at least three times. Preliminary studies were conducted to determine the recoveries of TEs with various amounts of HNO$_3$ (65%, Merck, Germany), hydrogen peroxide (H$_2$O$_2$, 30%, Beijing Institute of Chemical Reagents, China)HCl and hydrofluoric acid (HF, 40%, Merck, Germany). The results showed that the optimal combination was 5 mLl of

9

214  concentrated $HNO_3$, 2 m~~l~~L $H_2O_2$ and 0.2 ~~ml~~ mL HF (Pan et al., 2010b). The filter was

215  cut into ten to twenty equal portions to obtain a sample mass below 0.5 g, which is the

216  working limit of the microwave vessels. This procedure also allowed for a

217  comparison of the analysis results from multiple strips per filter. To ensure analytic

218  quality, certified soil (GBW07401) and fly ash (GBW08401) materials were

219  employed. Approximately 10 mg of these reference materials was accurately weighed

220  and placed into a Teflon vessel along with the $HNO_3$, $H_2O_2$ and HF. Subsequently, the

221  vessels were capped, fastened on the rack and placed in the microwave oven to

222  undergo the digestion procedure; the temperature-controlled digestion procedure is

223  illustrated in Fig. S3. After cooling to room temperature, the digests were carefully

224  transported to PET vials and diluted with ~~Mini~~Milli-Q water to a final volume of 50

225  m~~l~~L. All samples were stored in the dark at 4 °C prior to analysis. All observed results

226  were blank corrected.


227  **2.2.4 Trace metal analysis for wet and dry deposition**


228  A multi-element analytical program was run at LAPC using an Agilent 7500a

229  inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies,

230  Tokyo, Japan). The instrument was optimized daily in terms of sensitivity (Li

231  (lithium), Y (yttrium), and Tl), level of oxide (Ce-cerium) and doubly charged ion (Ce)

232  using a tuning solution containing 10 μg ~~l~~$L^{-1}$ of Li, Y, Tl, Ce, and cobalt (Co) in 2%

233  $HNO_3$. The standard optimization procedures and criteria specified in the

234  manufacturer's manual were followed. The concentrations of 25 TEs were determined

235  by ICP-MS after calibration using external standards (Agilent Technologies,

236  Environmental Calibration Standard, Part# 5183-4688) and internal standards ($^{45}$Sc

237  (scandium), $^{73}$Gd (gadolinium), $^{115}$In (indium) and $^{209}$Bi (bismuth) at 20 μg $L^{-1}$ in 2%

238  $HNO_3$) added online during TEs analysis. The multi-element standard stock solution

239  containing 10 or 1000 mg $L^{-1}$ of TEs in nitric acid was diluted in 2% $HNO_3$ to obtain

240  five calibration standards (1, 5, 10, 20 and 50 μg $L^{-1}$ for Cu, Pb, Zn, Cd, Arsenic (As),

241  beryllium (Be), Al, Mn, Ba, Co, Ni, Cr, Se, V, molybdenum (Mo), silver (Ag), Sb, Tl,

242 thorium (Th) and uranium (U); 100, 500, 1000, 2000 and 5000 μg $L^{-1}$ for Fe, K, Na,

243 Ca and magnesium (Mg)) plus a blank that covered the expected range for the

244 samples. The analytical reproducibility of the extract concentrations was assessed by

245 replication (the same sample was analyzed three times). The relative percent

246 differences for replicate samples were less than 5%. A check standard was analyzed

247 after the initial calibration and again after every 12 samples. If the relative difference

248 between the measured and actual concentrations was not within 10%, the instrument

249 was recalibrated and the previous 12 samples were re-analyzed.

250      As noted above, two certified materials were prepared in parallel to ensure the

251 quality of the obtained results. The recoveries of the target elements ranged between

252 78% and 115% with the exception of Al (75%). In all experiments, reagent blanks

253 were measured separately. The filter blanks and the final concentrations of metals in

254 the samples are reported after the field blank correction. The detection limits were

255 better than 10 ng $L^{-1}$ for most of the metals determined through analyses of blank

256 samples. The average metal concentrations in the field blanks were well below the

257 detection limits, indicating that no significant contamination occurred during the

258 sampling, handling, delivery or measurement steps.

259

### 2.2.53. Statistics

261 The monthly wet deposition fluxes of TEs ($_{wdf}$TEs) were obtained by multiplying the

262 volume-weighted concentrations of TEs in the precipitation and the volume of

263 precipitation measured by a standard rain gauge at each site during the sampling

264 period. The monthly dry deposition fluxes of TEs ($_{ddf}$TEs) were calculated by dividing

265 the amount of TEs loaded on the PUF-filter by the surrogate surface area during the

266 corresponding period. One-way analysis of variance (ANOVA) and nonparametric

267 tests were conducted to examine the significance of the differences in the annual

268 $_{wdf}$TEs and $_{ddf}$TEs for all ten sites. All analyses were conducted using the software

269 SPSS 11.5 (SPSS Inc., Chicago, IL, USA) and Origin 8.0 (Origin Lab Corporation,

270   Northampton, MA, USA). Statistically significant differences were defined as $P <$

271   0.05 unless otherwise stated.

## 2.3 Methodology evaluation and Uncertainty analysis

### 2.3.1 Acid digestion of precipitation samples

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 the previous 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 thus requires attention. To test if the $HNO_3$ concentration (1%) in the final samples was enough or not to dissolve the trace elements associated with suspended particles, especially for the crustal elements such as Al and Fe, elemental contents in different fractions for precipitation were further investigated by three experiments below. The procedures were applied to a series of 10 sequential rainwater samples collected on September 16, 2010 in Beijing to extract water-soluble (experiment a), acid-soluble (experiment b) and total metal concentrations (experiment c).

*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

*Experiment b*: The second set of 10 mL unfiltered precipitation samples were acidified to pH~1 using 0.1 mL $HNO_3$ to extract acid-leachable fractions, the concentration of which was considered to represent the environmentally mobile material, termed the acid-soluble fraction.

*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 filter samplers described in Sect.3.2. 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 showed 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 the water-soluble fraction (Fig. 2), but somewhat lower than their total content with insignificant difference. The findings indicated that on one hand these TEs were well dissolved in the rainwater and the suspended insoluble particles were negligible, on the other hand the 1% $HNO_3$ was enough to dissolve these metals completely and to minimize adsorption losses. In contrast, the concentrations of acid-soluble Be, V, Co, Ni, Cu, Ba, U, Cr, Fe, Ag, Pb and Al were significantly higher than that of water-soluble fraction and lower than that of total metal content (Fig. 2), in particular for the latter five metals. It suggested that these metals, associated with substantial insoluble suspended particles in the rainwater, cannot be completely dissolved with 1% $HNO_3$ method. Thus, the method used in this study underestimated the total concentrations of crustal TEs, and hence their wet deposition flux.

**2.3.2 Development of a new method estimating dry deposition**

Compared to the case for wet deposition, many uncertainties exist in the methods of direct measurements and modeled estimates used to quantify dry deposition. To date, there is no commonly accepted technique that can be used to evaluate the accuracy of these methods. For direct measurements, various surrogate surfaces, mainly solid surfaces such as Teflon plates, filters and buckets, have been used in an attempt to quantify dry deposition. It was shown that both the collector geometry and the surface characteristics had a large impact on the amount of collected material (Dasch, 1985; Shannigrahi et al., 2005). Thus, we developed a uniform monitoring protocol based on a PUF-based glass bucket, with reasons below.

In general, a bucket can collect more dry-deposited material than Teflon, foil or coated foil surfaces, as suggested by Dasch (1985). In addition to the deposition fluxes of particulate matter, chemical species like 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 attributed to the geometry of the collector that affects the amount of material collected (Noll et al., 1988). Specifically, 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, the dry deposited particles in the buckets could be re-suspended due to winds in dry season. To address this problem, additional materials such as marbles and glycerol can be used to stabilize the deposited dust (McTainsh et al., 1997). However, such treatments would 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., 2001b) has been successfully used to measure particulate dry deposition fluxes of organic and inorganic air pollutants in recent years, there is still no surface being established as a standard. Most of important, previously reported methods were time consuming and difficult to be used by an untrained operator in the field. There is an obvious incentive for developing a simple and cost-effective sampler capable of trapping airborne particles.

Besides the collector geometry, 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 water surface or a filter of nylon, quartz-fiber, or glass-fiber. Deposition appeared to be strongly influenced by the surface affinity for gases, but for particles high retention is one of the ideal characteristics. PUF, a popular sampling medium for gaseous persistent organic pollutants (POPs) (Chaemfa et al., 2009a; Harner et al., 2004), can also trap particulate POPs because of its high retention (Shoeib and Harner, 2002). On this line of thinking, it may be desirable to use PUF as the potential surface to collect particles, which is also very easy to make, handle and deploy.

To integrate the advantages of collector geometry and the surface characteristics mentioned above, the PUF-based bucket was designed in our study to collect dry

deposition. This 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. These two types of surface surrogates, i.e., glycol vs. PUF, were placed concurrently in separate buckets so that the comparison can be made. As shown in Fig. S4, the results observed for the two surfaces agreed well with each other, indicating that the PUF has a high efficiency in trapping dry-deposited particles, which is comparable with that of glycol surface. As an evidence, a more recent study also suggested that particles were trapped on the 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).

In addition to the important features described above, the PUF surrogate surface can also prevent particle bounce and is relatively inexpensive. It can be used at a variety of locations and over various time intervals to delineate spatial and temporal information. After collection, it was divided into several pieces so that replicates would be easily processed. Finally, the PUF was considered to be applicable to the buckets to measure the deposition fluxes in the study, as a uniform monitoring protocol for the observation network in Northern China.

**2.3.3 Uncertainty of dry deposition**

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 any other standardized artificial collection device (Wesely and Hicks, 2000). As discussed by Shannigrahi et al. (2005), the bucket method may 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 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, dry deposition flux measured by the bucket may be higher than the net flux. Even though, sedimentation is considered to be the major mechanism of dry deposition for particles, even for heavy metal species primarily on small particles (Dasch, 1985), so that the PUF-based bucket method provides a gross understanding of atmospheric deposition.

The bucket method has also been criticized that the high container walls may restrict the entry of all but the largest particles deposited by gravitational settling, which would 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 bucket inner wall, which is missed by the PUF filter at the bottom. But after the particles on the walls were rinsed with water, then dried and weighted, this part was found to be insignificant compared with that captured by the PUF filter. But if the conditions favor the adsorption such as the presence of dew or the humid weather keeping the bucket wet for a long time, further investigation is needed to address the degree to which particulate material is trapped on the bucket sides.

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 of the surface. Although PUF filter has a high retention for particles with wide size (Chaemfa et al., 2009b), part of uncertainties link 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 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). In addition, there are problems 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.

Although the present approach is far from clearing up all the aspects of dry

deposition, it adds substantially to the knowledge of atmospheric metal deposition in Northern China. Most importantly, the direct measurement is essential for model validation in the estimates of dry deposition. Our measurements are most likely to underestimate dry-deposited particles for the above reasons, but the estimates are not far from the real ones because the 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 of dry deposition.

## 2.4. Supporting sampling and analysis

### 2.4.1 Size resolved aerosols

Elemental characterization of size-segregated particulate matter was performed synchronously at five sites including urban (BJ and TJ), industrial (BD and TS) and rural (XL) with bi-weekly resolution during the campaign between September 2009 and August 2010. At each site a cascade impactor operating at 28.3 L min$^{-1}$ (Anderson Series 20-800, USA) was installed to collect aerosol samples in nine size ranges (<0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0 and >9 µm). The sampling interval was 24 h at the BJ, TJ, BD and TS sites, but for 48 h at the XL site to collect enough particles permitting a complete chemical analysis. The collected samples were digested with procedures similar to that of PUF filter and then analyzed by ICP/MS (see Sect. 2.2, for detailed analysis methods).

### 2.4.2 Soil profile

There were no soil parameter observations for the ten monitoring sites in this study; the soil profile elemental data presented were obtained from the Chinese Ecosystem Research Network available on the Data Sharing System website (http://www.cerndata.ac.cn/). Soil profile samples at two agricultural sites of LC, YC and one forest site near BJ were collected in September 2005, in compliance with the protocol ISO 11464. In brief, three repeated soil profiles at each site were hand-dug,

and five depths in each of recognizable horizons (0–100 cm) were divided according to the primary aspects except for the forest site where seven layers from 0 to 70 cm depth were collected. The soil samples were air-dried at room temperature and sieved <2 mm to remove plant residues and coarser particles, then thorough mixed and pulverized by an agate mortar to pass through a 100–mesh (149 μm) Nylon screen for elemental analysis.

The soil samples were digested with a mixture of hydrochloric acid (HCl) –$HNO_3$–HF–perchloric acid ($HClO_4$) to measure the total concentrations of elements. After cooling, $HNO_3$ was added to the residue, and then the solutions were diluted to 25 mL with double-distilled deionized water before analysis. Analyses were performed by using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) and Atomic Absorption spectrometry (AAS). Quality control was assured by the analysis of duplicate samples, blanks and National Standard Materials (soil: GBW07403, GSS-3). The analysis results of the reference materials fluctuated within the allowable ranges of the certified values and the relative standard deviation of the duplicate analysis were less than the allowed upper-limits of the National Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004).

## 3. Results and discussion

## 3.1. Dry deposition of TEs

### 3.1.1. Profile of dry-deposited TEs

Fig. 1 3 shows the annual mean $_{ddf}$TEs at the ten sites during the observation period. In general, the magnitude of $_{ddf}$TEs for each element at one station varied substantially, ranging from 0.03 mg m$^{-2}$ yr$^{-1}$ for Ag at the XL site to 10.3 g m$^{-2}$ yr$^{-1}$ for Al at the BD site. When the 25 TEs at each site were roughly identified using enrichment factors (EFs) relative to the average crustal composition with Al as a reference (Duce et al., 1975; Mason and Morre, 1982), only Pb, Zn, Cd, As, Se, Ag and Sb had EFs

467    above 10, suggesting that the fluxes of these TEs were substantially affected by

468    human activities. The primarily crustal elements with EFs lower than 10 (e.g., Al, Ca

469    and Fe) had the highest flux among the 25 TEs. These TEs had fluxes similar to each

470    other; the next highest fluxes were attributed to Na, Mg, K, Mn and Ba. Among

471    dry-deposited particles, Zn was the most abundant anthropogenic metal, followed by

472    Pb, Sb, Cu, Ni, Cr, As, Co, V, Se, Mo, Cd and Tl. Ag had the lowest measured flux

473    among the heavy metals. In general, the average fluxes of the above crustal elements

474    excepting Mn and Ba were 2−4 orders of magnitude higher than those of

475    anthropogenic elements (e.g., Zn, As and Tl). The profile of TEs in dry-deposited

476    particles agrees closely with those described in previous studies (Odabasi et al., 2002;

477    Tasdemir and Kural, 2005). In addition, the dry deposition fluxes of most of the TEs

478    in Northern China, as shown in Fig. ~~1~~3, fell within the range of values reported within

479    and outside China (Table S~~1~~2), with the exception of some crustal elements (e.g., Na,

480    Mg and Al). The relatively high dry deposition fluxes of crustal elements are not

481    surprising because these elements are commonly found in the bare soil of the study

482    area, which constitutes the major proportion of the particulate matter (Chen et al.,

483    2014). Although accounting for only a small fraction of the particles, heavy metals are

484    of great environmental importance due to their toxicity and anthropogenic origins

485    (Almeida et al., 2006). In conclusion, the dry deposition of TEs originating from both

486    regional natural and local anthropogenic sources is closely linked to the dry nature of

487    the soil and the intensive human activities in Northern China.

488    **3.1.2~~.~~ Spatial variation in $_{ddf}$TEs**

489    Generally, the values of $_{ddf}$TEs were significantly higher for urban and industrial sites

490    (e.g., BD, TJ and TS) compared with suburban, agricultural and rural sites (e.g., CZ,

491    YC and XL). For example, the three-y~~ea~~r mean $_{ddf}$Pb was largest at BD (35.6 mg m$^{-2}$

492    yr$^{-1}$), followed by TS, TG and TJ (31.4, 27.3, 23.1 mg m$^{-2}$ yr$^{-1}$, respectively). The

493    $_{ddf}$Pb was similar at YF, LC and BJ, with high values of 17.8, 13.6 and 13.2 mg m$^{-2}$

494    yr$^{-1}$, respectively. At CZ, YC and XL, the $_{ddf}$Pb was relatively low (7.1, 7.1 and 5.7

495    mg m$^{-2}$ yr$^{-1}$, respectively). This spatial pattern was closely linked with local

496    emissions, implying that human activities have affected the dry deposition of TEs and

497    altered their regional budget, particularly for heavy metals. The human impact is more

498    pronounced at the industrial sites of BD and TS. As shown clearly in Fig. ~~1~~3, the dry

499    deposition of some elements was significantly elevated at BD (Al, Be, Pb, Se, Th, Tl,

500    U, V, Cd, Co, As, Mo, Ba, Sb and Cu) or TS (Fe, Mn, Mg, V, K, Ca, Ag and Cr)

501    compared with at other urban or industrial sites. This finding suggests the presence of

502    substantial metal emissions near these two sites. At TS, for example, the highest

503    depositions of Fe, Mn and Cr were observed, which can be attributed primarily to the

504    iron and steel processing industry, particularly the relocation of the Capital Steel

505    Company from Beijing to Tangshan City during the observation period. After this

506    relocation, a substantial decline in airborne steel-related elements has been observed

507    in Beijing (Chen et al., 2014).

508    The two pairs of urban-suburban sites located in the Beijing and Tianjin

509    metropolitan areas allowed us to assess the spatial variation in dry deposition along

510    the environmental gradient. As expected, the dry deposition fluxes of most elements

511    in the megacity, TJ, were higher than those in its suburban counterpart, TG, excepting

512    certain elements such as Mn, Pb, Sb, Cu, Co, Ni and Cr. The relatively high $_{ddf}$TEs

513    observed at TG reflect the industrial activities in the coastal regions near Tianjin

514    Harbor. This pattern is supported by the fact that the pre-2001 Pb level in the coastal

515    waters of Bohai Bay originated primarily from river discharge; after 2001, a

516    declining trend has not been observed due to additional contributions from

517    atmospheric deposition, although the annual runoff levels have declined (Meng et al.,

518    2008). Another recent geochemical study also suggested the contribution of

519    atmospheric inputs of harmful elements to the surface sediments of Bohai Bay (Duan

520    et al., 2010). These findings further indicate the human impact on regional element

521    cycling, particularly on the transport and deposition from inland to coastal areas.

522    Compared with other sites, certain elements were found at the highest or second

523    highest levels at TJ (Zn, Na, As, Cr and Tl) and TG (Ni, Cr, Pb and Mn). Wet

524    deposition of Zn at TJ and Ni at TG was also higher than at other sites (Fig. ~~1~~3).

Relatively high values of certain TEs observed in both wet and dry deposition may indicate special non-ferrous smelters near the site. However, the dry deposition fluxes of some TEs (Mo, As, Tl, Se, Be, Th and U) at TG was relatively low compared with other industrial sites and was comparable to rural sites, suggesting that industry related to these TEs was lacking at TG. Therefore, careful attention must be paid to source apportionment in the future.

The dry deposition fluxes of most elements at another megacity (BJ) were comparable to or lower than those of its suburban counterpart, YF, and also lower than those of other urban and industrial sites. The low values at BJ can be attributed to the restrictions on industrial sources in the fourth rings of Beijing City. In addition, the YF site lies 30 km NW of BJ, where there are some local sources. As a consequence, the $_{ddf}$TEs of Al, K, Pb, Tl, Cd, V, As and Zn were higher at YF than at BJ and were comparable to other industrial sites, highlighting the influence of human activities on dry deposition in suburban areas.

Interestingly, the dry deposition fluxes of some heavy metals (Zn, Cd and Pb) at LC were higher than those at another agricultural site (YC) and comparable to other urban or industrial sites. These elevated heavy metals observed in dry-deposited particles at LC may be due to industrial plumes emitted from Shijiazhuang City (SJZ), the capital of Hebei Province. This conjecture is supported by the fact that the highest values of dry-deposited sulfate were observed at this site (Pan et al., 2013b). Although the $_{ddf}$TEs at the rural XL site were the lowest in the target area, they were still comparable to or higher than the measurements given in Table S12. This finding indicates that the $_{ddf}$TEs in the target region were high and that more attention must be paid to their harmful impacts on ecosystems and human health in Northern China.

**3.1.3. Seasonal variations in $_{ddf}$TEs**

The seasonal mean $_{ddf}$TEs during the three-year period are also shown in Fig. 13. The $_{ddf}$TEs exhibited similar seasonal variations at most sites, with higher values observed in spring/winter than in summer/autumn. In the target areas, the meteorological

conditions during cold seasons are often dry with low precipitation. In addition, strong northwest winds and the lack of vegetation may favor the resuspension of soil particles in the atmosphere, resulting in the increased dry deposition of crustal elements (Chen et al., 2014). With the exception of BD and TS, most sites in this study suffered from the regional transport of natural dust, especially during spring. This effect is more pronounced at the rural and agricultural sites XL, YC, CZ and YF, where natural sources dominated the fluxes.

To confirm the influences of regional dust, we checked the Sand-Dust Weather Almanac issued by the Chinese Meteorological Administration and found that there were 31 sand-dust weather events recorded in China between 2008 and 2010. Of the total, 16 events (9 events occurred in spring) reached the target regions during the period; all of which were blowing or floating dust and no sand-storms were recorded. We thus conclude that the long-range transport of natural dust from the northern/northwestern deserts and loess deposits resulted in the relatively high dry deposited elemental flux in spring than in other seasons in this study. In addition, sand-dust weather events decreased eastward due to the effects of distance and particle size. As a result, there were more days with blowing or floating dust at BJ than at east coastal site of TG, according to the recorded weather phenomena. Dry deposition of Al at these two sites (2.1 and 1.3 g m$^{-2}$) during spring also supported this phenomenon. Moreover,

~~W~~with the exception of Cu, Sb and Ba, the dry deposition elemental fluxes at the BJ site in spring are relatively high compared with the other seasons, coinciding with more days with blowing or floating dust at BJ than at other sites~~episodic dust-storms originating from the northwest (Chen et al., 2014)~~.

At industrial ~~and urban~~ sites ~~such as~~of BD ~~and~~, TS ~~and TJ~~, however, the seasonal distribution of most TEs, except for crustal elements, were relatively high in winter compared with in spring. In addition to the low precipitation, the increased emission strength from coal burning in cold seasons is a major contributor.~~–~~ In Northern China coal is still the primary fuel widely used for industrial processes and daily life, and more coal is combusted for heating in winter. Thus, dry depositions in winter were

expected to be enhanced in the region where a great deal of coal was combusted. This is supported by the elevated flux of various TEs at the urban and industrial sites of TJ, BD and TS, compared with that in other sites. The enhanced fluxes of heavy metals (e.g., Pb and Tl) in winter at TG and LC are also related to coal consumption. In the urban areas of Beijing, however, the energy used for heating and industrial processes was mainly electricity and natural gas in addition to limited residential coal consumption (Zhao et al., 2013). At present, annual coal consumption in Beijing was about 21 million tons, which is significantly lower than that in Tianjin and Hebei (70 and 300 million tons). As a consequence, the dry deposition of coal combustion related TEs (e.g., Pb and Tl) in BJ was lower than that in TJ, BD and TS, but still higher than that in YC, CZ and XL, indicating the influences of residential coal consumption in the urban areas of Beijing. In the past ten years with the gradual replacement of coal by natural gas and electricity in urban Beijing, the sulfate and elemental carbon in the winter decreased gradually from 25 and 8.7 $\mu$g m$^{-3}$ to 14 and 6.3 $\mu$g m$^{-3}$, respectively (Zhao et al., 2013). Further decrease of elemental deposition in Beijing can be expected, if the reduction of coal consumption continues.

In contrast, the minimum fluxes observed in the summer/autumn are attributable to an increase in precipitation. Wet soil conditions and vegetation cover also decrease the amount of re-suspended particles in the atmosphere. The above analysis demonstrates that the $_{ddf}$TEs varied from one season to another due to changes in meteorological conditions and human-induced emissions in addition to the seasonal variation in natural sources.

**3.2. Wet deposition of TEs**

**3.2.1. Profile of TEs in precipitation**

Fig. 1 3 shows the annual mean $_{wdf}$TEs at the ten sites during the observation period. The magnitude of $_{wdf}$TEs for each element at one station varied significantly, from 0.01 mg m$^{-2}$ yr$^{-1}$ for Th at the XL site to 3.1 g m$^{-2}$ yr$^{-1}$ for Ca at the YF site. Of the primarily crustal elements, Ca exhibited the highest flux, followed by Na, Mg and K.

Zn was found to be the most abundant anthropogenic metal in wet deposition, followed by Pb, Sb, Cu, As, Co, Se, Ni, V, Cr, Mo, Cd and Tl. In general, the average fluxes of the above crustal elements were several times higher than those of Mn, Ba, Fe and Al, and 2−4 orders of magnitude greater than those of the anthropogenic elements (e.g., As, Cd and Tl). The profile of TEs in wet deposition determined in this study agrees well with those described in previous reports (Halstead et al., 2000; Hu and Balasubramanian, 2003). In addition, the wet deposition of Cd, Cr, Co, Ni and V in Northern China, as shown in Fig. 13, was comparable to that observed in other sites listed in Table S23. In contrast, the wet deposition of Fe, Al, Mn and Zn was higher in Northern China than in other regions of the world. The $_{wdf}$Pb was also higher in this study than previously reported, with the exception of the North Sea and Singapore (Table S23). The relatively high $_{wdf}$TEs may be attributable to anthropogenic influences in addition to natural emissions, considering that the EFs of the majority of TEs in wet deposition at each site were above 10, with the exceptions of Be, K, Na, Mg, Al, Fe, Ni, Cr, V, Th and U. However, the calculation of EFs on the basis of Al was most probably overestimated because the crustal elements were not dissolved completely in the acidified precipitation samples, as discussed in Sect. 2.3.1.

Since the $_{wdf}$Pb was higher in this study than that in most of the previously reports, one may be interested in the major sources of Pb in the region. Besides natural sources from regional and local soil, possible anthropogenic sources of Pb include coal combustion, vehicle exhaust, cement factories and smelters (Cheng and Hu, 2010). But the relative contribution of the above sources was of spatial and temporal variable. After the phase-out of leaded gasoline in China since 2000, the major emission sources of airborne Pb in eastern and central China were estimated to be coal consumption and non-ferrous metal smelting, instead of vehicle exhaust (Li et al., 2012). However, detailed Pb isotopic signatures of PM$_{10}$ from selected sites in North China indicated its source was mainly anthropogenic, and mostly attributable to coal combustion and vehicle emissions with additional industrial sources (Luo et al., 2014). A case study in Beijing found that airborne Pb predominantly from anthropogenic sources was reduced by approximately 50% during the 2008 Olympic Games due to

the mitigation measures implemented by the Chinese Government (Schleicher et al., 2012). Moreover, the temporal variations of Pb concentration correlated to the restrictiveness of relative measures, especially during different traffic restrictions, further demonstrating the significance of traffic sources (Chen et al., 2014). But the vehicular emissions from urban areas (e.g., Beijing) were not likely an important regional source of Pb and thus had insignificant impacts in rural areas (e.g., Xianghe) (Li et al., 2010). We conclude that Pb in wet deposition on the regional scale was mainly emitted from industrial processes and coal burning. These emissions could be widely dispersed throughout the atmosphere and transported to the downwind regions (Zhao et al., 2013), resulting in the high wet depositions at the background site of XL (discussed in Sect. 3.2.3).

### 3.2.2. Seasonal variations in $_{wdf}$TEs

The seasonal variations in $_{wdf}$TEs showed similar trends at each site (Fig. 13), with a maximum in summer coinciding with the rainy season in Northern China. The minimum values obtained in the winter months were attributable to the low level of precipitation. In general, summer contributed the most to the annual wet deposition flux, followed by spring, autumn and winter. A significant linear correlation between the wet deposition flux and precipitation was observed at each site for heavy metals such as Cu, Pb, Zn, Cd, As and Se. Therefore, precipitation is important in explaining the seasonal pattern of the above TEs collected at a given site. However, this is not the case for most crustal elements (e.g., Al, Mn, Fe, Na and Ba), which exhibit less of a correlation between the $_{wdf}$TEs and precipitation (Fig. S5). This finding suggests that the wet deposition of these metals is more closely related to their concentration in the precipitation than to the precipitation amount.

Although the precipitation in winter was comparable at each site, the spatial variation of $_{wdf}$TEs in the cold season was evident. For example, the wet deposition of Al, Fe, Be, U, Mn, V and Cr showed substantially higher values at TJ, BD, TG, TS and CZ compared with the other sites, indicating different emission strengths among

669     the sites.

670     **3.2.3. Spatial variation in $_{wdf}$TEs**

671     In general, the spatial distribution of $_{wdf}$TEs exhibited less variation. For example, the

672     three-year mean $_{wdf}$Pb was highest at TG (10.1 mg m$^{-2}$ yr$^{-1}$), followed by TS, BD and

673     YC (10.0, 9.9 and 9.2 mg m$^{-2}$ yr$^{-1}$, respectively). The $_{ddf}$Pb was similar at CZ, XL, LC,

674     TJ and BJ, with high results of 8.8, 8.4, 8.2, 8.0 and 6.4 mg m$^{-2}$ yr$^{-1}$, respectively. The

675     lowest value occurred at YF (3.9 mg m$^{-2}$ yr$^{-1}$). This pattern is different from the

676     dry-deposited TEs, for which higher values were found at industrial and urban sites

677     than at suburban, agricultural and rural areas. The wet deposition of certain elements

678     (e.g., Al, Mg, Mn, Se, Th, U, V, Ca, Cd, Ag, Ni, Zn and Cr), however, was somewhat

679     higher at the industrial sites compared with the other sites, indicating that these TEs

680     were affected by local emissions. In Germany, heavy metals were also found to be

681     higher in precipitation in urban–industrial areas than at rural measurement sites

682     (Grömping et al., 1997). Surprisingly, unlike the dry-deposited TEs found in low

683     values at XL, the wet deposition of certain TEs (e.g., Ag, Co, K, Be, Pb, Sb, Th and

684     U) at XL was comparable to or higher than that at other sites, including industrial sites.

685     Since there were no local emission sources near XL, the higher $_{wdf}$TEs most likely

686     resulted from the long-range transport from upwind areas of Northern China (Pan et

687     al., 2013a). The long-range transport effects on wet deposition flux of TEs were

688     recorded elsewhere. For example, wet deposition fluxes of TEs measured along the

689     Japan Sea coast were strongly affected by the long-range transport of air pollutants

690     from the Asian continent during winter and spring (Sakata et al., 2006). A recent study

691     also found that long-range transport of pollutants from south Asia had a significant

692     impact on the trace elements in atmospheric wet deposition in the high altitude remote

693     areas in the southern slope of the Himalayas (Tripathee et al., 2014).

694         Since the emissions of industrial pollutants and fossil fuel combustion from

695     upwind sources in Tianjin and Hebei are prominent, trace elements in precipitation

696     observed at XL could be from regional emission sources. Imprints of regional

transport were indicated by the fact that the metallic episodes experienced at the XL site closely associated with the air mass from SE that passed TS and TJ, or from SW that passed BD and SJZ. It is reasonable because trace elements associated with fine particles can remain in the atmosphere for days or weeks and thus be subject to long-range transboundary transport. They are therefore widely dispersed throughout the atmosphere before they finally deposit through washout by precipitation (below-cloud scavenging) in remote regions (Duce et al., 1975). In addition, aerosols acting as host for the trace elements can enter cloud water mainly through rainout (in-cloud scavenging) and be transported to downwind regions far away from sources (Levkov et al., 1991). Although both rainout and washout pathways contributed to the wet deposition of trace elements, their relative importance during the long-range transport has not been well characterized. Therefore, there is a need for further research to better understand the long-range transport of pollutants from potential source regions with the atmospheric circulation in Northern China.

**3.2.4. Factors influencing the regional distribution of $_{wdf}$TEs**

To investigate the factors controlling the regional distributions of $_{wdf}$TEs, the scavenging ratio ($S_r$) was introduced under the simplified assumption that the concentration of a component in precipitation ($C_p$) is related to the concentration of the respective compound in the air ($C_a$) (Sakata et al., 2006). Thus, $S_r$ can be calculated on a mass basis as follows:

$$S_r = C_p/C_a. \tag{1}$$

When the precipitation volume is expressed as P, the $_{wdf}$TEs depend on $S_r$, $C_a$ and P:

$$_{wdf}TEs = S_rC_aP. \tag{2}$$

Therefore, if $S_r$ and $C_a$ are constant in the region, $_{wdf}$TEs increase in proportion to P. However, for sites with higher values of $C_a$, $_{wdf}$TEs were greater than expected from P based on the above premise (i.e., $S_rC_a$ = constant). Thus, by using the relationship between $_{wdf}$TEs and P, we can evaluate the degree to which $_{wdf}$TEs are governed by anthropogenic emissions at each site.

725    The statistical analysis of data from the three-year period revealed a positive

726    relationship between the annual wet deposition fluxes of 12 trace elements (As, Cd,

727    Co, Cu, Fe, Mn, Pb, Sb, Se, Th, Tl and V) and the corresponding precipitation volume

728    ($0.11 < r^2 < 0.38$; Fig. S4S5). For most of these TEs that exist entirely as fine particles

729    that can act as condensation nuclei, this finding may indicate that wet deposition

730    represents a large contribution of their long-range transport during in-cloud processes.

731    However, only approximately 20% of the variance in the wet deposition fluxes for

732    these TEs is explained by the volume of precipitation. The aforementioned percentage

733    is significantly lower than that estimated in Japan, e.g., 68% and 80% of the variance

734    in $_{wdf}$Sb and $_{wdf}$V is explained using the precipitation volume (Sakata et al., 2006),

735    suggesting marked differences in the $S_r$ and $C_a$ of TEs across Northern China. For

736    example, the $_{wdf}$Pb values at the BD, LC and TS sites in certain years was much

737    higher than expected based on the precipitation amount, indicating a large

738    contribution from anthropogenic emissions. However, the relatively low $_{wdf}$Pb values

739    at the YC, CZ and YF sites compared with those expected from the precipitation

740    amount may be due to the lower number of anthropogenic sources in suburban areas.

741    In contrast, the relationship between the annual wet deposition fluxes and the

742    precipitation amount for the rest of the 13 TEs (Zn, U, Ni, Na, Mo, Mg, K, Cr, Ca, Ba,

743    Be, Al and Ag) is not significant (Fig. S4S5). The results demonstrate that the annual

744    values of these TEs were most likely dominated by the scavenging ratio and

745    atmospheric concentrations across Northern China. Clearly, there is marked difference

746    in the atmospheric concentrations of these TEs throughout the study region (Pan et al.,

747    2013a; Zhao et al., 2013), although the available data are not sufficient. Considering

748    that these TEs exist entirely in coarse particulate form, their wet deposition depends

749    on the below-cloud scavenging of local emissions rather than regional contributions.

750    For TEs in fine particles, however, wet deposition is mainly governed by regional

751    transport (most of which might be from in-cloud scavenging) rather than local

752    emissions.

### 3.3. Total deposition of TEs

### 3.3.1. Wet vs. dry deposition of TEs

A comparison of the $_{wdf}$TEs and $_{ddf}$TEs at each site provided in Fig. 1 3 shows that the dry deposition fluxes of most TEs were significantly higher than their wet deposition values. For example, dry-deposited Cu, Al, Fe, Mn and V dominated the total deposition flux at each site. In contrast, the wet deposition fluxes of K, Ni and As exceeded their dry deposition fluxes at only a single site (XL or YC). For Pb, Zn, Cd, Se, Ag and Tl, however, the relative importance between their wet and dry deposition fluxes varied site by site. The wet deposition of these TEs tended to dominate the total deposition flux at BJ, CZ, YC and XL.

The relative significance of wet vs. dry deposition may change not only based on the efficiencies of the two mechanisms but also with the local availability of precipitation (Muezzinoglu and Cizmecioglu, 2006). In Germany, more than 90% of the total metal amount was reported to exist as wet deposition, and wet deposition is thought to be the predominant mechanism for the removal of ecotoxicologically relevant metals in high latitudes (Grömping et al., 1997). In contrast, dry deposition as a cleansing mechanism is the most important on an annual basis in semi-arid regions with low precipitation (Grantz et al., 2003). This pattern has been verified in a Mediterranean climate area (Muezzinoglu and Cizmecioglu, 2006) and partially verified in this studyNorthern China.

The relative difference between $_{wdf}$TEs and $_{ddf}$TEs is likely due to the difference in the size distributions of TEs in atmospheric particles. Sakata et al. (2008) reported that the wet deposition fluxes of Pb and Se in Japan exceeded their dry deposition fluxes, whereas the reverse was true for Cr, Cu, Mn, Mo, Ni and V. The authors also found that the difference between the wet and dry deposition fluxes of As, Cd and Sb varied by site. Finally, they concluded that the dry deposition of TEs associated with larger particles is expected to be greater than their wet deposition fluxes because coarse particles have much shorter atmospheric lifetimes due to their higher

781    deposition velocities (Sakata and Marumoto, 2004). In contrast, wet deposition may

782    dominate the total flux for TEs exist as fine particles, which act as condensation

783    nuclei for the formation of precipitation.

784        To confirm the above hypothesis, we performed elemental analyses on

785    size-resolved particles collected at five selected sites (BD, BJ, TJ, TS and XL). The

786    results showed that Al, Fe, Th and U were concentrated in coarse particles, whereas

787    Cu, Pb, Zn, Cd, As, Se, Ag and Tl mainly existed as fine particles (Fig. 4). In addition,

788    the size distributions of Be, Na, K, Ca, Ba, Mg, Co, V, Mo, Ni, Sb, Cr and Mn were

789    bimodal at all sites, with two peaks at 0.43–0.65 μm and 4.7–5.8 μm and a valley at

790    1.1–2.1 μm (Fig. 4). The above premise proposed by Sakata et al. (2008) is partially

791    supported by our measurements indicating that the dry deposition fluxes of TEs

792    associated with larger particles (e.g., Al, Mn and Fe) are larger than their wet

793    deposition fluxes. Similarly, the TEs accumulated in fine particles (e.g., As, Pb and Cd)

794    have much larger wet deposition than dry deposition fluxes.

795        Interestingly, however, some metals have a similar size distribution but different

796    deposition mechanisms (e.g., Cu and Pb). This circumstance may be due to the

797    different solubilities of these TEs because the solubility determines the release of

798    metals from particles and their subsequent incorporation into rainwater (Desboeufs et

799    al., 2005). Although the solubility of Cu (43–93%) is comparable to that of Pb

800    (40–93%) in most studies, only 8.4% of Cu was soluble in rainwater sampled at

801    Istanbul (Cizmecioglu and Muezzinoglu, 2008). Thus, the low solubility of Cu may

802    be the cause reason for the low wet deposition fluxes in this study, although the

803    premise must be verified in the future. However, this premise was not verified in the

804    study (e.g., at the BJ site). We did not measure the distribution of Cu and Pb between

805    liquid and solid phases in precipitation, but we can examine the solubility of metals

806    based on the experiments a and c described in Sect. 2.3.1 for the 10 precipitation

807    samples at the BJ site. The results showed that the solubility of Cu (26%) was higher

808    than that of Pb (7%), suggesting that the deposition mechanisms of the two metals

809    were not influenced by the solubility. After carefully checking the size distribution of

810    particles at the BJ site we found that Cu had another peak around 4.7-5.8 μm in

addition to that at 0.43-0.65 μm (Fig. 4). 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 well explained by the size distribution.

**3.3.2. Wet plus dry deposition of TEs**

The annual total (wet plus dry) deposition fluxes of the TEs ($_{tdf}$TEs) at ten sites in Northern China are indicated in Table 4. The 25 measured TEs in Northern China had total deposition fluxes ranging from 101 to 404 kg ha$^{-1}$ yr$^{-1}$, with a ten-site average of $236 \pm 98$ kg ha$^{-1}$ yr$^{-1}$ during the three-year period. The lowest and highest $_{tdf}$TEs were observed for Ag at the CZ site (0.05 mg m$^{-2}$ yr$^{-1}$) and Ca at the TS site (138 kg ka$^{-1}$ yr$^{-1}$), respectively.

The spatial variation in $_{tdf}$TEs was similar to that of dry deposition; the values at LC and YF were higher than those at XL, YC and CZ and lower than those at BJ, TJ, BD, TG and TS. In most cases, the $_{tdf}$TEs for industrial and urban sites were highest, followed by agricultural, suburban and rural sites (e.g., Pb; Fig. S1). Although it is difficult to compare the $_{tdf}$TEs type by type due to the limited available measurement data for the study region, the relatively high $_{tdf}$TEs observed for land use types other than rural areas stem from increased TEs emissions. Most importantly, the $_{tdf}$TEs measured at XL, which can be used as a reference to characterize the background level in Northern China, were still relatively high compared with those of remote regions around the world (Table S5). Thus, the extremely high $_{tdf}$TEs observed in the target areas compared with those reported both within and outside China can be easily understood. Notably, the current deposition fluxes at the XL site (Table 3), which is located in a forest area surrounded by few villages, exceeds the critical load of Pb (7.0 mg m$^{-2}$ yr$^{-1}$) calculated for Dutch forest soils (de Vries et al., 1998). However, this is not the case for the other heavy metals (Cu, Zn and Cd). Although nationwide emissions of TEs from power plants have gradually declined in recent years, Northern China still ranks among the regions that will have the highest emissions in the coming decades (Tian et al., 2014). This result raises important concerns regarding the

839    potential effects of substantial metal deposition on different ecosystems. Therefore, it

840    is important to further reduce the emissions to mitigate the environmental risks posed

841    by TEs in Northern China.

842    **3.3.3. Atmospheric deposition of TEs into ecosystems**

843    To quantify the contribution of atmospheric deposition to the elemental level in

844    receiving ecosystems, it is necessary to know the metal content of a specific surface

845    area for comparison with the atmospheric deposition in the same area. The mass

846    content ($M_c$, mg m$^{-2}$) of TEs in the vertical soil profile is determined according to the

847    following equation:

848    $$M_c = 10D_lB_dC_s \tag{3}$$

849    where 10 is the conversion coefficient and $D_l$, $B_d$ and $C_s$ are depth (cm), bulk density

850    (g cm$^{-3}$) and the metal concentration (mg kg$^{-1}$) in each vertical layer, respectively.

851    In this study, we selected two agricultural sites (LC and YC) and a forest site

852    approximately 100 km to the west of Beijing (BJF), where the elemental content of a

853    typical soil profile (0−100cm) was measured in 2005. Only 11 TEs (Mo, Mn, Zn, Cu,

854    Fe, Se, Cd, Pb, Cr, Ni and As) were selected because the other TEs were not available

855    in the soil profile. The distribution of $M_c$ for each metal vs. soil depth was first

856    examined (data not shownFig. 5). At the YC LC site, the $M_c$ of Mn, Fe and As

857    increased with depth, whereas that of Mo, Zn, Cr and Ni was enriched at 20−40 cm.

858    In addition, Cu, Se and Pb were slightly accumulated in the top soil of 0−10 cm. No

859    systematic pattern was found for Cd, which was rather stable within the profile. At the

860    LC YC site, Zn, Se and Pb contents were found highest in the surface soil and

861    decreased generally with depth. Mo, Mn, Cu, Fe, Cd, Cr, Ni and As were enriched in

862    the plow horizon from 40−60 cm, which is deeper than that for Mo, Zn, Cr and Ni

863    found at YCLC. Note that the $M_c$ of each metal (except for Cr) in the forest soils of

864    Beijing increases with depth (Fig. 5).

865    For TEs whose $M_c$ increase with depth, the trend appears to be largely related to

866    the parent materials of the soils at each site. Alternatively, the enrichment of TEs in

867    the top soil may suggest important sources (e.g., atmospheric deposition) other than

868    the mineralization of indigenous minerals. Presuming that the top soil (0−10 cm) and

869    deep soil (60−100 cm) had the same initial elemental content when riverine alluvial

870    soil was formed at the location, the significant enrichment of TEs in the upper soil

871    layer indicates an anthropogenic origin such as atmospheric deposition, plant litter

872    decomposition, fertilizer application or sewage irrigation.

873    The increase in elemental content (mg m$^{-2}$) in the topsoil (0−10 cm) relative to the

874    deep soil (60−100 cm), which indicates the total anthropogenic input, is calculated

875    and listed in Table S46. The ratio of atmospheric deposition to the total anthropogenic

876    input (R$_{at}$) varied among sites and TEs. Negative values may indicate negligible

877    anthropogenic input compared with the mineralization input. The R$_{at}$ values for Mo,

878    Zn, Cu, Se, Cd and Pb at YC were 0.02, 0.20, 0.01, 0.03, 1.03 and 0.05, respectively,

879    indicating that atmospheric deposition contributed 20% of anthropogenic Zn and

880    almost all of the Cd in the topsoil. The explanation for the R$_{at}$ values lower than 0.05

881    are not clear at present and require further study.

882    At another agricultural site (YC), the R$_{at}$ values of Mn, Zn, Cu, Se, Cd, Pb, Cr and

883    As were 0.01, 0.03, 0.78, 0.11, 0.18, 0.05, 0.01 and 0.10, respectively. Thus,

884    atmospheric deposition accounted for 10−78% of the anthropogenic Cu, Se, Cd and

885    As input. Although the R$_{at}$ of some TEs was lower than 0.05, the contribution of

886    atmospheric input cannot be overlooked when considering a longer accumulation

887    period. A national inventory estimated that the inputs of TEs (As, Cr, Ni and Pb) to

888    agricultural soils via atmospheric deposition were 43–85% (Luo et al., 2009). Thus,

889    long-term parallel measurements of atmospheric deposition and soil profile

890    physico-chemical properties are required to detect the accumulated impacts. In

891    addition, the chemical speciation and bioavailability of atmospheric deposited TEs

892    should be considered given that the mobility of TEs determines their transformation

893    and accumulation from soil and water to plants and humans.

894    As fertilization practices are not applicable in natural ecosystems, forest, for

895    example, may be an ideal upland ecosystems in which to track atmospheric deposition

896    (Hovmand et al., 2008). However, the increasing elemental M$_c$ with depth in the forest

33

897    soils of Beijing makes it difficult to quantify the anthropogenic input using the

898    method described above. Nevertheless, impacts of atmospheric deposition on the

899    urban park and agricultural soils were identified in Beijing (Chen et al., 2005; Lu et

900    al., 2012). Evidence can also be found at the rural forest site of XL, where elevated

901    elemental concentrations were observed in fine particles transported via southern

902    winds from industrial and urban areas in Northern China (Pan et al., 2013a).

903    **4. Conclusions**

904    To our knowledge, this study provides the first long-term direct measurements of

905    atmospheric wet and dry deposition fluxes of crustal and anthropogenic metals on a

906    regional scale across China. The dataset provides a basis for the validation of regional

907    emission inventories and biogeochemical or atmospheric chemistry models. It also

908    facilitates the effective targeting of policies to protect ecosystems (e.g., water and

909    soils) from long-term heavy metal accumulation. Three major findings and

910    conclusions can be drawn:

911    1.  Significantly higher $_{ddf}$TEs were observed at industrial and urban areas than at

912        suburban, agricultural and rural sites, corresponding to the urban-rural land use

913        gradient. The minimum $_{ddf}$TEs that occurred in summer/autumn were attributable

914        to an increase in precipitation, whereas the maximum in winter/spring were due

915        to the additional emissions from coal burning and regional transport of natural

916        dustsandstorms. Elevated $_{ddf}$TEs, most of which originated from coarse particles,

917        are closely linked with the regional dry nature of the soil and the intensive local

918        human activities in Northern China.

919    2.  Due to the precipitation pattern in Northern China, summer contributed the most

920        to annual wet deposition flux, followed by spring, autumn and winter. Although

921        the precipitation in winter was comparable at each site, the spatial variation in the

922        wet deposition fluxes of several TEs in cold season was evident due to the local

923        emissions from house heating. Compared with $_{ddf}$TEs, however, the annual $_{wdf}$TEs

924        had less spatial variation and were influenced by the regional patterns of

925 precipitation and emissions. The wet deposition of TEs that exist as fine particles

926 was mainly governed by regional transport rather than local emissions. However,

927 for coarse particulate TEs, wet deposition was attributed mainly to below-cloud

928 scavenging (most of which might be from local emissions).

929 3. The relative importance between wet and dry deposition flux varied among sites

930 and TEs. Nevertheless, dry deposition flux was significantly higher than the wet

931 deposition flux for most TEs, signifying the dominance of self-cleansing

932 mechanisms in the atmosphere. In addition to the local availability of

933 precipitation,, size distribution and solubility of TEs in particles is also anare

934 important factors determining the relative importance of wet vs. dry deposition.

935 Compared with other measurements around the world, the atmospheric deposition

936 flux in Northern China was very high, indicating that the mitigation of metal

937 emissions is greatly needed in the future.

938 The case study demonstrates that a comparison of atmospheric deposition and vertical

939 soil profile is an appropriate tool with which to characterize the atmospheric input of

940 toxic metals to ecosystems and to differentiate their contributions from other

941 anthropogenic sources. The atmospheric deposition of Cu, Pb, Zn, Cd, As and Se is of

942 the same magnitude as the increase of these TEs in the topsoil; this type of

943 atmospheric deposition may dominate the anthropogenic input to agricultural systems

944 in the future. Our study further highlights the need to focus on the chemical speciation

945 and bioavailability of atmospherically deposited materials and demonstrates the

946 importance of establishing long-term observation studies on the accumulation of

947 heavy metals in food chains as a result of substantial atmospheric deposition.

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1242 **Tables**

1243 Table 1. Descriptions of the ten sampling sites in the wet and dry deposition observation network of Northern China.

| Site | Coordinates | Classification | Location | Population density (persons km$^{-2}$) [a] | Surrounding environment [c] | Underlying surface [a] | Measurements height (m) |
|------|-------------|----------------|----------|------------------------------|-----------------------------|------------------------|--------------------------|
| BJ | 39.96°N, 116.36°E | Urban | North to the Beijing downtown | 5479 | Densely occupied residences and traffic roads | Roof | 8 |
| TJ | 39.08°N, 117.21°E | Urban | South to the Tianjin downtown | 24606 | Densely occupied residences, industry and traffic roads | Lawn | 1.5 |
| BD | 38.85°N, 115.50°E | Industrial | Centre of the Baoding city | 2871 | Densely occupied residences, traffic roads and industry | Roof | 10.5 |
| TG | 39.04°N, 117.72°E | Industrial | 30 km east to the Tianjin city ( Tanggu district) | 865 | Light industry and traffic roads | Lawn | 1.5 |
| TS | 39.60°N, 118.20°E | Industrial | South to the Tangshan city | 2648 | Densely occupied residences, traffic roads and industry | Roof | 13.5 |
| YF | 40.15°N, 116.10°E | Suburban | 40 km northwest to the Beijing city ( Yangfang town) | 470 | Occupied residences and traffic roads | Grass | 1.5 |
| CZ | 38.30°N, 116.87°E | Suburban | 2 km southeast to the Cangzhou city | 2314 | Small villages and high ways | Roof | 5.5 |

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|---|---|---|---|---|---|---|---|
| LC | 37.89°N, 114.69°E | Agricultural | 4 km southeast to the Shijiazhuang city ( Luancheng county) | 958 | Small villages and cropland | Lawn | 1.5 |
| YC | 36.85°N, 116.55°E | Agricultural | 6 km southwest to the Yucheng city | 521 | Small villages and cropland | Lawn | 1.5 |
| XL | 40.38°N, 117.57°E | Rural | Xinglong, on the Mt. Yan with an elevation of 960 m a.s.l. (Hebei Province) | 98 | Forest and few villages | Grass | 1.5 |

1244  [a] The population density was estimated by dividing population by area of the town/district/county in which the monitoring site is located.

1245  Population data were retrieved from the fifth census of China in 2000 and can be accessed online (http://www.stats.gov.cn).

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1248  Table 2. Atmospheric dry deposition fluxes of metals within and outside China (mg m$^{-2}$ yr$^{-1}$, but kg ha$^{-1}$ yr$^{-1}$ for Na, Ca, Mg, Fe, Mn and Al)

| Site | Period | Na | Ca | Mg | Al | Mn | Fe | Cu | Pb | Zn | Cd | Co | Ni | Cr | V | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Xinghua Bay, China | 2004-2005 | 6.69 | / | / | 7.83 | / | 6.83 | 2.71 | 3.83 | 14.39 | 0.08 | 0.28 | 7.82 | 11.63 | / | (Wu et al., 2006) |
| Yellow sea, China | 1995-1996 | 12.42 | 6.32 | 2.89 | 4.49 | 0.08 | 2.55 | 0.23 | 1.92 | 2.91 | 0.04 | 0.2 | 0.63 | 1.11 | 1 | (Liu et al., 1998) |
| East Sea China | 2005-2007 | / | / | / | 0.15 | 0.02 | 0.14 | 4.38 | 0.91 | 6.94 | 0.07 | / | 0.09 | 0.08 | 0.55 | (Hsu et al., 2010) |
| Taiwan China | 2009-2010 | / | / | / | / | 0.08 | 1.52 | 20.8 | 20.03 | 18.03 | / | / | / | 9.20 | / | (Zhang et al., 2012) |
| Hong Kong ,China | 1998-1999 | 6.67 | / | 1.15 | 0.83 | 0.07 | 0.78 | 5.25 | 28.98 | 27.95 | / | / | / | / | 0.19 | (Zheng et al., 2005) |
| Matsuura, Japan | 2004-2006 | / | / | / | 1.32 | 0.09 | / | 3.01 | 1.55 | / | 0.06 | / | 3.72 | 4.28 | 0.54 | (Sakata and Asakura, 2011) |
| Seoul, S. Korea | Spring,1998 | / | 23.0 | / | 19.7 | / | / | / | 73.0 | 73.0 | / | / | 40.2 | / | / | (Yi et al., 2001a) |
| Maagan Michale, Israel | 1994-1997 | / | / | / | 4.97 | 0.11 | 4.32 | 0.23 | 1.54 | 1.98 | 0.07 | / | / | 1.27 | / | (Herut et al., 2001) |
| Chicago, U.S. | 1990s | / | 25.51 | 9.12 | / | 0.4 | / | 69.4 | 46.4 | 266.5 | 4.4 | / | / | 19.3 | / | (Fang, 1992) |
| Chicago, U.S. | 1993-1995 | / | / | 8.29 | 3.80 | 0.21 | / | 23.0 | 13.87 | 43.80 | / | / | / | 2.08 | 1.21 | (Yi et al., 2001b) |
| Sleeping Bear Dunes, U.S. | 1993-1995 | / | / | 0.21 | 0.27 | 0.01 | / | 29.0 | 12.78 | 24.82 | / | / | / | 0.58 | 0.06 | (Yi et al., 2001b) |

| Site | Period | | | | | | | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| South Heaven, U.S. | 1993-1995 | / | / | 1.90 | 1.24 | 0.08 | / | 11.3 | 8.40 | 18.62 | / | / | / | 0.27 | 0.44 | (Yi et al., 2001b) |
| Tor Paterno, Italy | 1999 | / | / | / | / | / | / | 11.03 | 11.41 | 43.64 | 0.36 | / | 12.23 | 17.04 | / | (Morselli et al., 2004) |
| Cap Ferat, France | 1988-1989 | / | / | / | 1.20 | 0.02 | 0.88 | 1.19 | 1.85 | 3.20 | / | 0.02 | 0.33 | 0.38 | / | (Chester et al., 1999) |
| Amman, Jordan | 1995 | / | / | / | / | / | / | 5.55 | 4.20 | 29.69 | 0.15 | / | / | / | / | (Momani et al., 2000) |
| Izmir, Turkey | 2000-2001 | / | 157.32 | 11.32 | / | 0.49 | 44.13 | 45.3 | 80.3 | 697.2 | 8.8 | / | 47.1 | 5.8 | / | (Odabasi et al., 2002) |
| Bursa, Turkey | 2002-2003 | / | 88.44 | 12.88 | / | 0.62 | 29.23 | 71.17 | 55.84 | 366.46 | 1.10 | 2.92 | 46.36 | 22.26 | / | (Tasdemir and Kural, 2005) |

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1252 Table 3. Atmospheric wet deposition fluxes of metals within and outside China (mg m$^{-2}$ yr$^{-1}$, but kg ha$^{-1}$ yr$^{-1}$ for Fe, Mn and Al)

| Site | Period | Fe | Mn | Al | Cu | Pb | Zn | Cd | Cr | Co | Ni | V | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nam Co, central Tibetan Plateau, China | 2007-2008 | 0.05 | 0.003 | 0.055 | 0.23 | 0.06 | 0.27 | 0.002 | / | 0.007 | 0.09 | 0.03 | (Cong et al., 2010) |
| Hong Kong, China | 1998-1999 | 0.78 | 0.04 | 0.62 | 4.67 | 86.94 | 33.15 | / | / | / | / | 2.65 | (Zheng et al., 2005) |
| Yellow Sea, China | 2000-2002 | / | / | / | 1.99 | 0.37 | 0.12 | 37.4 | / | / | / | / | (Liu et al., 2003) |
| Kathmandu, Nepal | 2011-2012 | 2.47 | 0.08 | 2.10 | 1.95 | 1.42 | 24.44 | 0.10 | 1.60 | 1.00 | 0.71 | / | (Tripathee et al., 2014) |
| Dhunche, Nepal | 2011-2012 | 1.00 | 0.04 | 0.98 | 0.02 | 0.02 | 0.18 | 0.00 | 0.00 | 0.01 | 0.02 | / | (Tripathee et al., 2014) |
| Chuncheon, Korea | 2006-2009 | / | 0.03 | 0.10 | 1.21 | 1.06 | 6.93 | 0.05 | / | / | 0.37 | 0.10 | (Kim et al., 2012) |
| Nakanoto, Japan | 2003-2005 | / | 0.07 | / | 1.8 | 10 | 27 | 0.31 | 0.40 | / | 1.40 | 0.78 | (Sakata and Asakura, 2009) |
| Higashi-Hiroshima, Japan | 1995–1997 | / | 0.02 | <0.01 | 0.89 | 1.78 | 6.84 | 0.09 | / | / | 0.42 | 0.33 | (Takeda et al., 2000) |
| Singapore | 2000 | 0.62 | 0.07 | 0.48 | 14.56 | 8.84 | 18.72 | 0.78 | 4.16 | 1.56 | 10.14 | 9.10 | (Hu and Balasubramanian, 2003) |
| Fiordland, New Zealand | 1993–1995 | 3.70 | 0.001 | / | 0.02 | 0.04 | 0.07 | 0.00 | / | / | / | / | (Halstead et al., 2000) |
| New Castle, U.S. | 1996–1997 | 0.14 | / | 0.17 | 0.67 | 0.78 | 8.33 | 0.12 | 0.08 | 0.12 | 0.42 | 0.72 | (Pike and Moran, 2001) |
| Chesapeake and Delaware Bay, U.S. | 1995–1996 | 0.14 | 0.01 | 0.20 | 0.97 | 0.35 | 3.60 | 0.04 | 0.04 | / | 0.82 | / | (Kim et al., 2000) |
| Massachusetts, U.S. | 1992–1993 | 0.36 | 0.01 | 0.29 | 0.70 | 0.86 | 2.70 | 0.21 | 1.50 | 0.01 | 3.00 | / | (Golomb et al., 1997) |

| Site | Year | | | | | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bermuda, U.S. | 1982–1983 | 0.016 | 0.001 | / | 0.07 | 0.31 | 0.66 | 0.02 | / | / | 0.08 | 0.07 | (Church et al., 1984) |
| Ankara, Turkey | 1993–1994 | 0.007 | / | 0.003 | 0.45 | 0.87 | 2.84 | 1.32 | 0.16 | / | 0.20 | 0.21 | (Kaya and Tuncel, 1997) |
| North Sea | 1992–1994 | / | / | / | 10.50 | 11.00 | 31.00 | / | 1.40 | / | / | / | (Injuk et al., 1998) |
| Dutch Delta, The Netherlands. | 1990 | / | / | / | 0.23 | 4.23 | 12.67 | 0.07 | / | / | 0.88 | / | (Nguyen et al., 1990) |

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1256 Table 1 4. Atmospheric total deposition flux of metals in Northern China (mg m$^{-2}$ yr$^{-1}$)

| Type | Urban | | Industrial | | | Suburban | | Agricultural | | Rural | Regional | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | BJ | TJ | BD | TG | TS | YF | CZ | LC | YC | XL | Mean | SD |
| Lat | 39.96° | 39.08° | 38.85° | 39.04° | 39.60° | 40.15° | 38.30° | 37.89° | 36.85° | 40.38° | | |
| Lon | 116.36° | 117.21° | 115.50° | 117.72° | 118.20° | 116.10° | 116.87° | 114.69° | 116.55° | 117.57° | | |
| Ag | 0.10 | 0.17 | 0.38 | 0.09 | 0.32 | 0.10 | 0.05 | 0.09 | 0.06 | 0.06 | 0.14 | 0.11 |
| Be | 0.21 | 0.38 | 0.64 | 0.22 | 0.31 | 0.23 | 0.13 | 0.12 | 0.10 | 0.07 | 0.24 | 0.17 |
| Tl | 0.22 | 0.34 | 0.47 | 0.20 | 0.36 | 0.26 | 0.18 | 0.17 | 0.15 | 0.13 | 0.25 | 0.11 |
| U | 0.28 | 0.48 | 1.27 | 0.30 | 0.46 | 0.31 | 0.19 | 0.19 | 0.17 | 0.11 | 0.38 | 0.34 |
| Cd | 0.46 | 0.56 | 0.98 | 0.50 | 0.61 | 0.49 | 0.43 | 0.64 | 0.39 | 0.29 | 0.54 | 0.19 |
| Mo | 0.69 | 0.94 | 1.82 | 0.68 | 0.80 | 0.56 | 0.50 | 0.46 | 0.63 | 0.26 | 0.73 | 0.42 |
| Th | 1.07 | 1.60 | 3.28 | 1.03 | 1.57 | 1.23 | 0.68 | 0.69 | 0.50 | 0.38 | 1.20 | 0.84 |
| Se | 1.47 | 1.96 | 4.07 | 1.85 | 2.47 | 1.64 | 1.53 | 1.53 | 1.40 | 1.14 | 1.90 | 0.84 |
| Co | 3.47 | 3.54 | 4.88 | 4.10 | 3.55 | 3.64 | 3.06 | 2.88 | 3.07 | 2.38 | 3.45 | 0.69 |
| As | 3.73 | 5.51 | 8.69 | 3.13 | 4.44 | 5.25 | 2.75 | 3.04 | 3.56 | 2.39 | 4.25 | 1.87 |
| V | 4.51 | 6.50 | 11.18 | 5.82 | 11.59 | 5.54 | 2.67 | 2.60 | 1.56 | 1.54 | 5.35 | 3.63 |
| Cr | 6.47 | 9.77 | 8.09 | 12.21 | 15.33 | 6.12 | 3.81 | 4.19 | 3.38 | 3.46 | 7.28 | 4.07 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | 6.63 | 7.39 | 6.66 | 17.45 | 8.54 | 7.30 | 4.83 | 5.00 | 11.19 | 3.69 | 7.87 | 3.97 |
| Cu | 19.8 | 19.4 | 28.5 | 22.3 | 19.1 | 12.1 | 8.4 | 8.4 | 7.9 | 5.3 | 15.1 | 7.7 |
| Pb | 19.6 | 31.1 | 45.8 | 37.3 | 41.4 | 21.7 | 16.4 | 21.8 | 16.2 | 14.1 | 26.5 | 11.5 |
| Sb | 28.1 | 25.6 | 35.7 | 30.3 | 29.2 | 29.1 | 27.2 | 25.9 | 26.3 | 21.6 | 27.9 | 3.7 |
| Mn | 83.0 | 109.7 | 90.0 | 139.1 | 160.8 | 88.8 | 51.3 | 49.7 | 43.0 | 35.1 | 85.1 | 42.1 |
| Ba | 178.3 | 128.7 | 155.0 | 84.9 | 145.8 | 96.4 | 44.9 | 50.8 | 34.1 | 32.5 | 95.1 | 54.2 |
| Zn | 86.5 | 245.8 | 112.1 | 106.4 | 119.9 | 66.0 | 95.7 | 135.0 | 57.0 | 40.7 | 106.5 | 57.1 |
| K | 1841.1 | 2027.1 | 2341.1 | 1598.8 | 2495.3 | 2205.3 | 1173.3 | 1098.2 | 1100.0 | 1716.2 | 1759.6 | 516.4 |
| Mg | 2168.2 | 2999.2 | 2729.8 | 2778.6 | 3684.2 | 2258.8 | 1198.0 | 977.2 | 837.1 | 801.4 | 2043.3 | 1029.0 |
| Na | 2126.5 | 3021.5 | 1761.7 | 2383.4 | 2281.2 | 3145.1 | 2867.9 | 1314.9 | 1162.3 | 966.0 | 2103.1 | 784.6 |
| Fe | 3358.7 | 4604.3 | 4793.6 | 4386.8 | 10440.0 | 3644.1 | 2045.1 | 2453.0 | 2388.8 | 1456.8 | 3957.1 | 2547.7 |
| Al | 5076.8 | 6678.2 | 10337.2 | 4727.5 | 7179.3 | 5982.1 | 3269.0 | 3028.8 | 2297.3 | 1889.2 | 5046.5 | 2602.1 |
| Ca | 8807.5 | 11722.1 | 10493.5 | 10317.0 | 13777.1 | 8236.0 | 5511.8 | 5852.8 | 5516.0 | 3106.2 | 8334.0 | 3322.1 |
| Sum | 238.2 | 316.5 | 329.8 | 266.6 | 404.2 | 258.2 | 163.3 | 150.4 | 135.1 | 101.0 | 236.3 | 97.8 |

Sum denotes a total deposition flux of 25 TEs in Northern China, with the unit of kg ha$^{-1}$ yr$^{-1}$

Table 5. Atmospheric total deposition fluxes of metals within and outside China (mg m$^{-2}$ yr$^{-1}$)

| Site | Period | Cd | Cu | Ni | Pb | Zn | As | Mn | V | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Pearl River Delta, China | 2001–2002 | / | 18.6 | / | 12.7 | 104 | / | / | 2.1 | (Wong et al., 2003) |
| Hong Kong ,China | 1998-1999 | / | 9.92 | / | 115.92 | 61.1 | / | 10.29 | 2.84 | (Zheng et al., 2005) |
| Kushiro, Japan | 2008 | 0.02 | 0.56 | 0.72 | 0.98 | 4.02 | / | 4.74 | / | (Okubo et al., 2013) |
| Tokyo Bay, Japan | 2004-2005 | 0.39 | 16 | 6.8 | 9.9 | | 2.9 | 87 | 6.9 | (Sakata et al., 2008) |
| Virolahti, Finland | 2007 | 0.04 | 1.00 | 0.14 | 1.1 | 3.8 | 0.09 | 2.3 | 0.36 | (Kyllönen et al., 2009) |
| Paris, France | 2001–2002 | 0.24 | 6 | 0.62 | 4.2 | 30 | / | / | / | (Motelay-Massei et al., 2005) |

| Site | Period | | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Massachusetts Bay, US | 1992–1993 | 0.27 | 2.5 | 1.5 | 1.8 | 7.8 | 0.02 | 3.4 | | (Golomb et al., 1997) |
| Chesapeake Bay, US | 1992–1993 | 0.05 | 0.26 | 0.26 | 0.56 | 1.34 | / | / | / | (Motelay-Massei et al., 2005) |
| Lake Superior, US | 1993–1994 | 0.46 | 3.1 | 0.8 | 1.5 | 8.8 | 0.17 | 4.2 | 0.34 | (Sweet et al., 1998) |
| Lake Michigan, US | 1993–1994 | 0.45 | 1.9 | 0.61 | 1.6 | 6 | 0.14 | 2.8 | 0.14 | (Sweet et al., 1998) |
| Lake Erie, US | 1993–1994 | 0.49 | 4.2 | 0.74 | 1.8 | 17 | / | / | / | (Sweet et al., 1998) |
| Fiorland, New Zealand | 1993–1995 | 0.004 | 0.023 | 0.035 | 0.025 | / | / | / | / | (Halstead et al., 2000) |
| Varna, Bulgaria, Black Sea | 2008-2009 | 0.02 | 17.8 | 0.41 | 0.73 | 15.18 | / | 2.01 | 1.1 | (Theodosi et al., 2013) |
| North Sea | 1993–1994 | / | 1.24 | / | 3.52 | 6.5 | 0. 25 | 2.6 | 1.1 | (Injuk et al., 1998) |
| Irish Sea | 1993–1994 | / | 2.6 | / | 1.62 | / | / | 5.07 | / | (Williams et al., 1998) |
| Mediterranean Coast | 1988–1993 | 0.31 | 2.6 | 0.57 | 3.8 | / | / | / | / | (Guieu et al., 1997) |
| Ligurian Sea | 1997–1998 | 0.06 | 1.28 | 1.1 | 1.2 | 41.2 | / | / | / | (Sandroni and Migon, 2002) |

Table 6. Average enrichment (increment) of elemental content in top soil (0−10 cm) relative to deep soil (60−100 cm) vs. atmospheric total deposition flux of metals at agricultural sites on an annual basis (mg m$^{-2}$)

| Site | Item | Mo | Mn | Zn | Cu | Fe | Se | Cd | Pb | Cr | Ni | As |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Increment | 22.3 | -4684.6 | 662.1 | 749.4 | -231178.5 | 43.6 | 0.6 | 420.8 | -838.8 | -349.7 | -217.7 |
| LC | Deposition | 0.5 | 49.7 | 135.0 | 8.4 | 2453.0 | 1.5 | 0.6 | 21.8 | 4.2 | 5.0 | 3.0 |
| | Ratio | **0.02** | **-0.01** | **0.20** | **0.01** | **-0.01** | **0.03** | **1.03** | **0.05** | **0.00** | **-0.01** | **-0.01** |
| | Increment | -12.8 | 3536.9 | 1709.3 | 10.1 | -86889.7 | 13.0 | 2.1 | 347.4 | 232.5 | -190.4 | 35.5 |
| YC | Deposition | 0.6 | 43.0 | 57.0 | 7.9 | 2388.8 | 1.4 | 0.4 | 16.2 | 3.4 | 11.2 | 3.6 |
| | Ratio | **-0.05** | **0.01** | **0.03** | **0.78** | **-0.03** | **0.11** | **0.18** | **0.05** | **0.01** | **-0.06** | **0.10** |

Data shown in bold was the ratio of total deposition to increment of metals in soil.

**Figures**
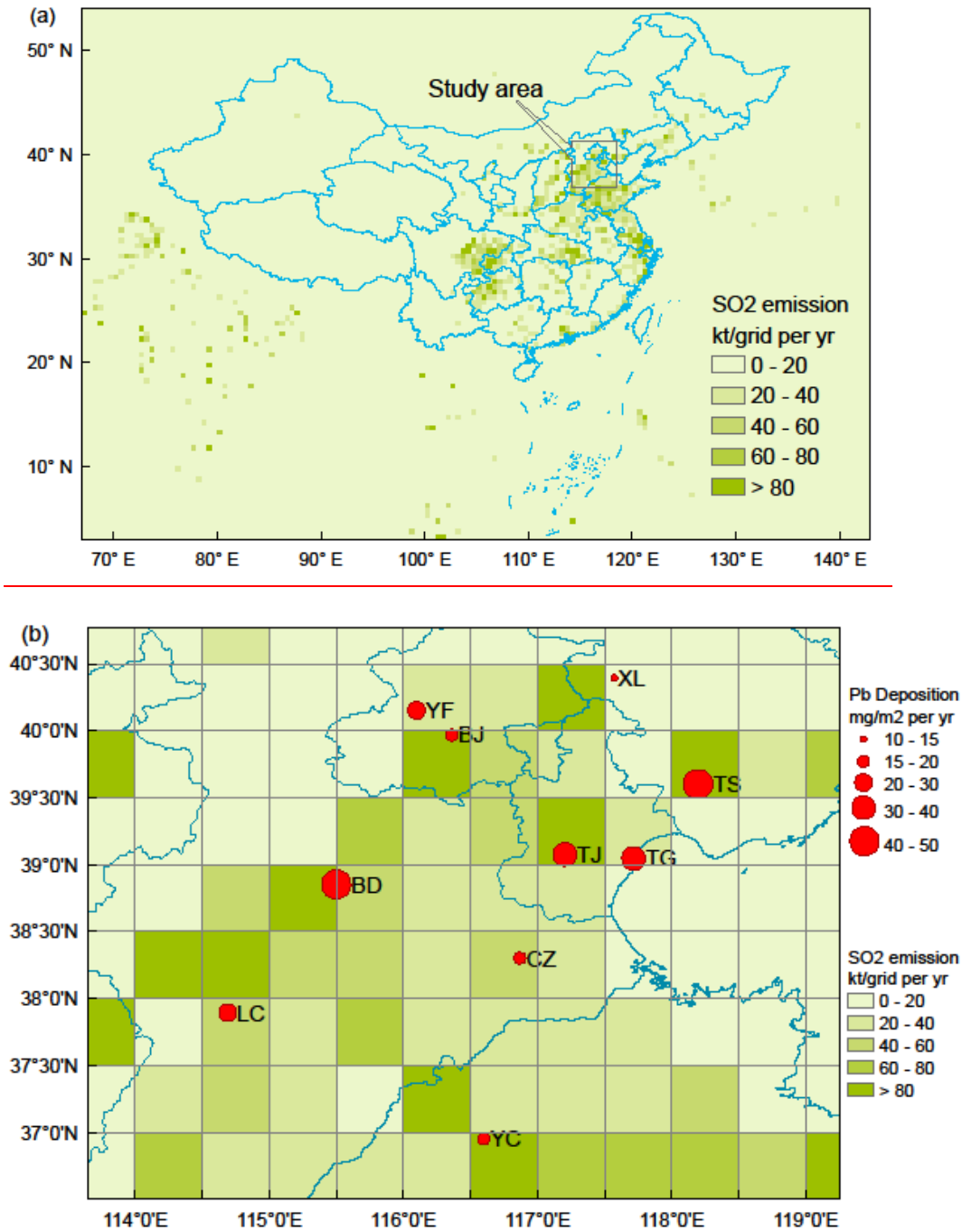


Fig. 1. Locations of the study area (a) and sampling sites (b) in Northern China with lead deposition and SO₂ emission distributions. The total lead deposition data are means of three-year observations from December 2007 to November 2010. The emission data for SO₂ are from 2006 (Zhang et al., 2009) and have a resolution of 0.5°×0.5°. In Northern China, the annual SO₂ emission unit of kt grid⁻¹ is

approximately 400 mg m$^{-2}$.
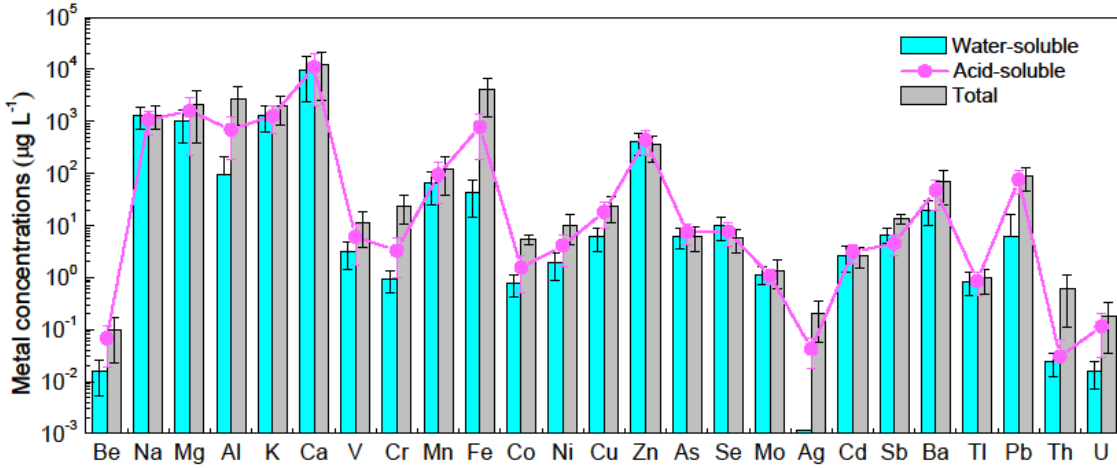
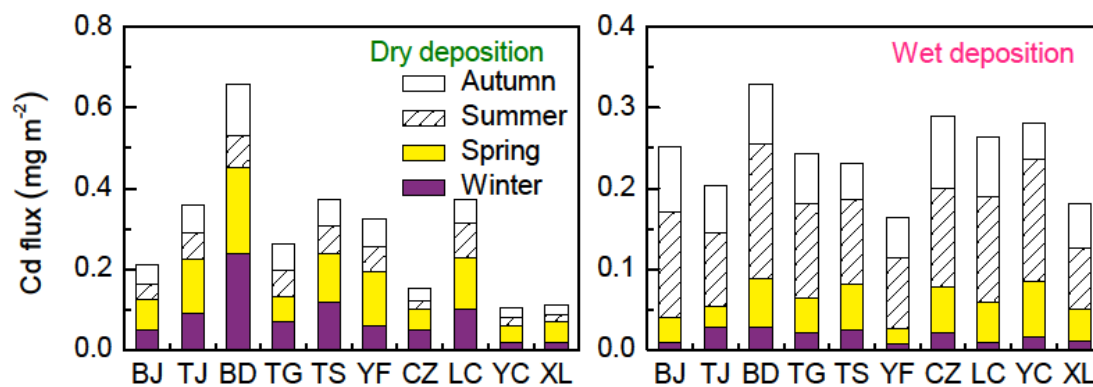Fig. 2. The elemental abundance and fractions of precipitation collected in Beijing.

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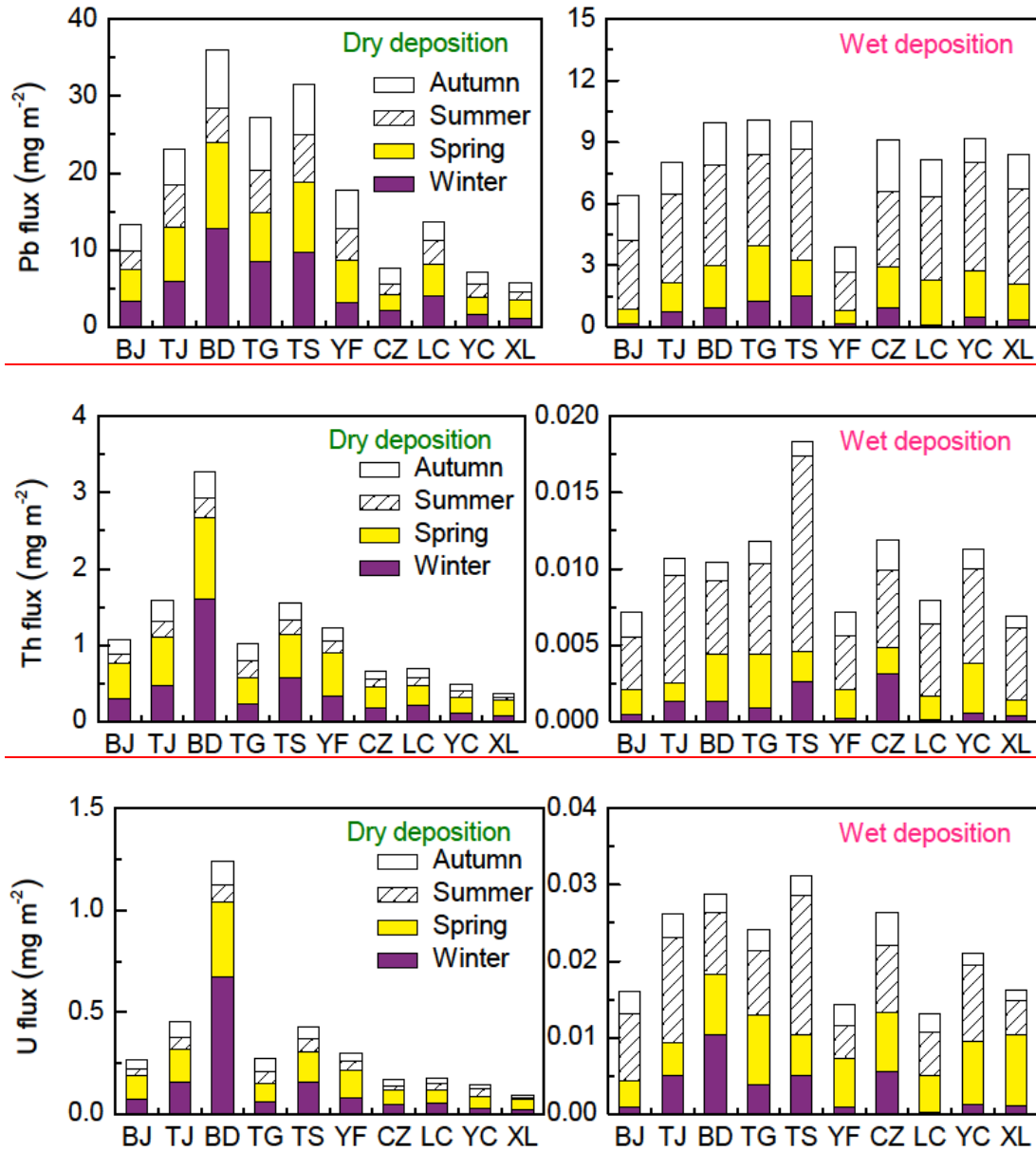
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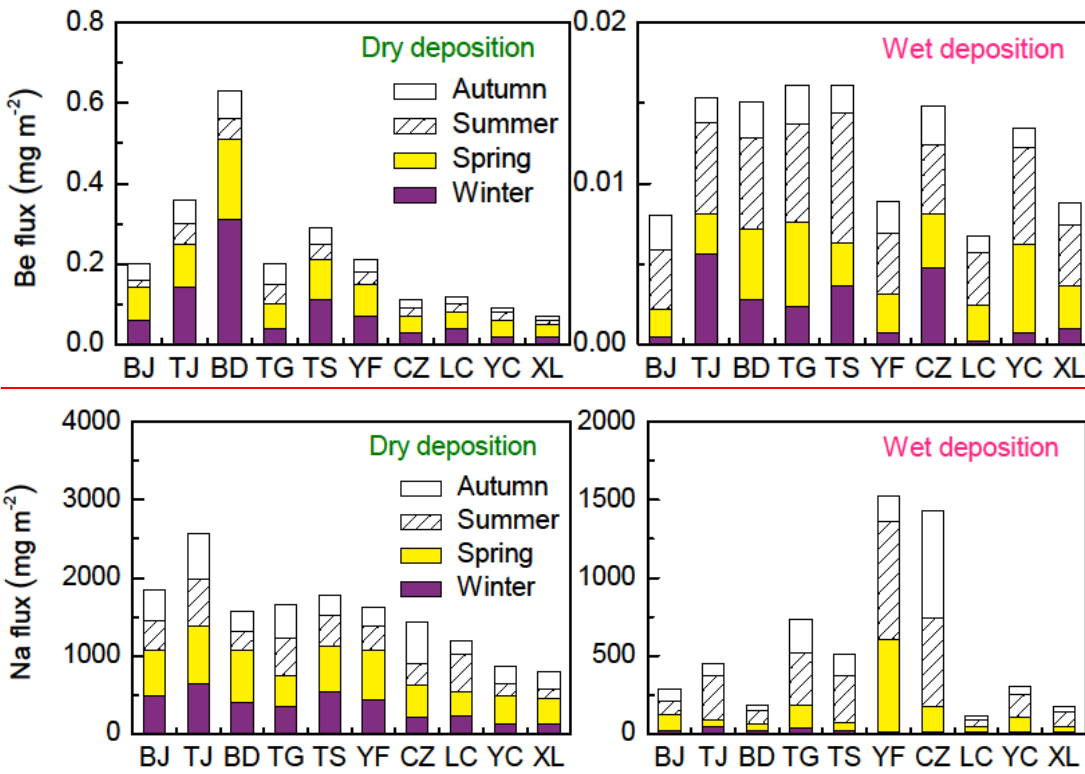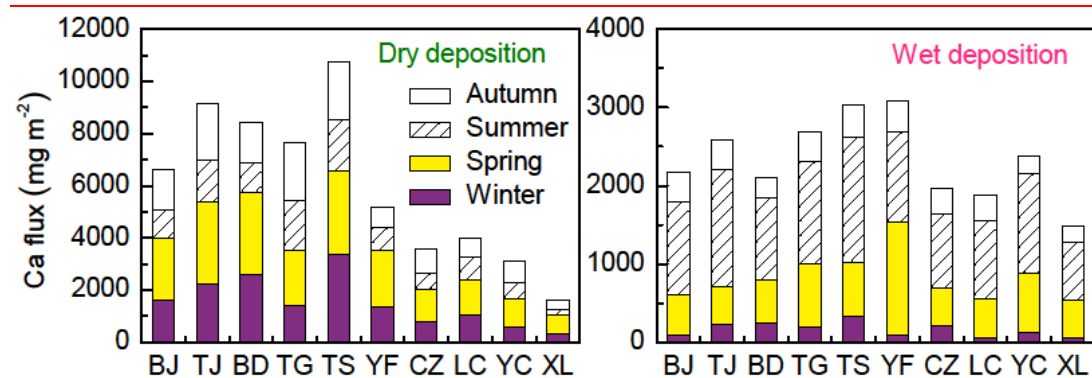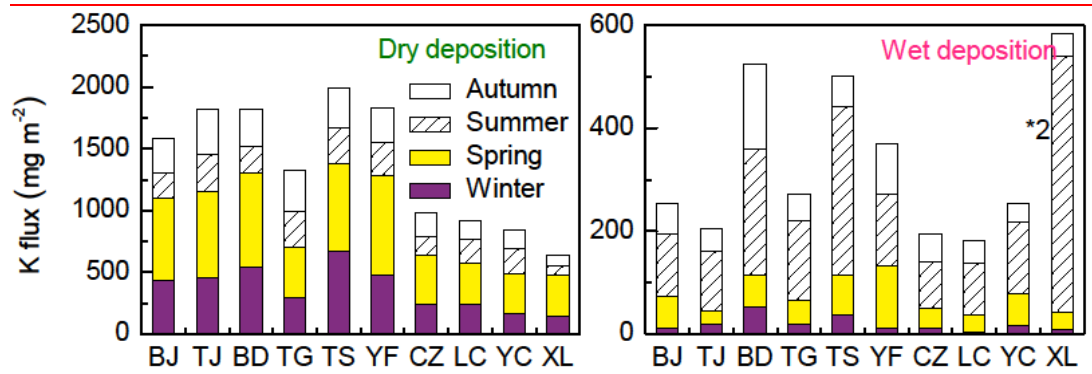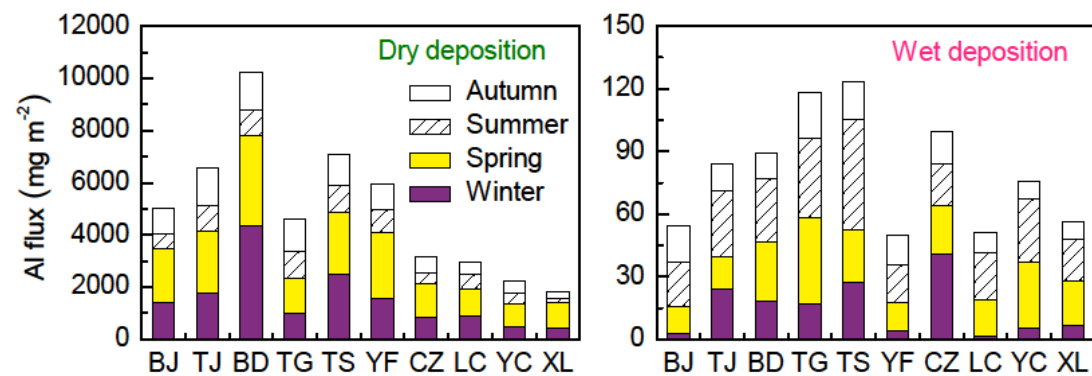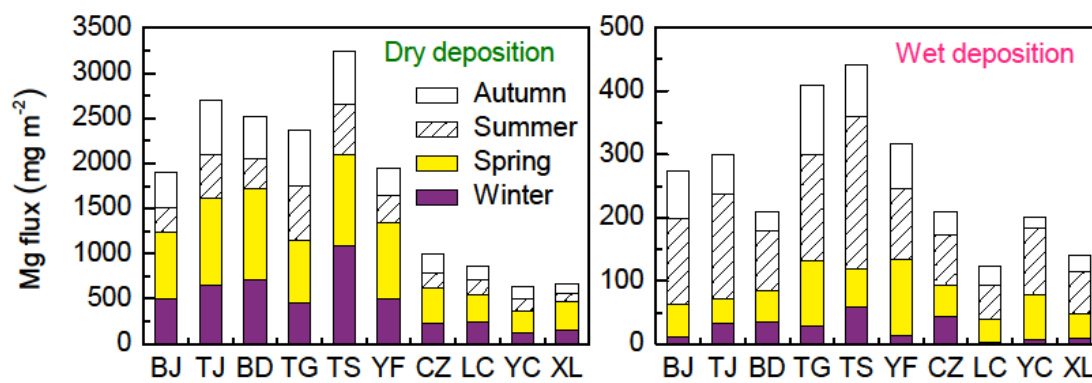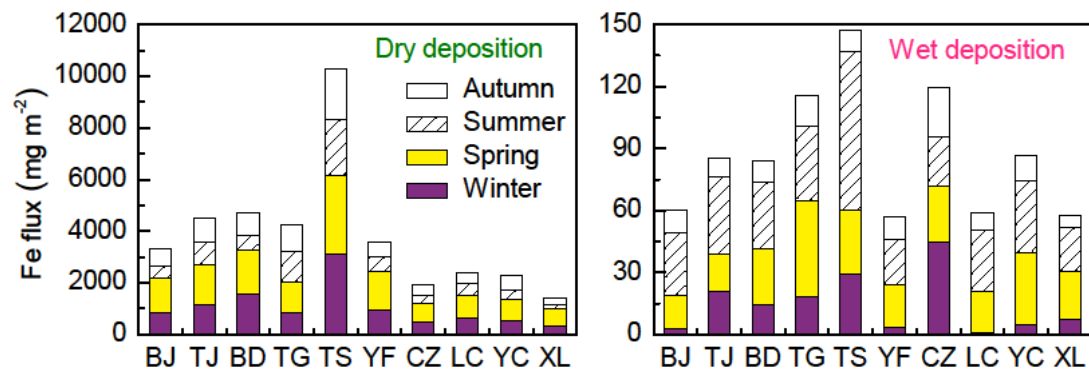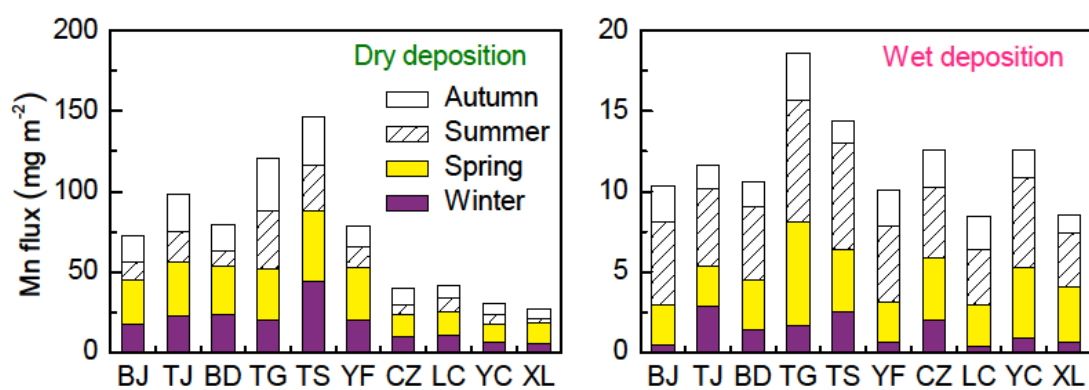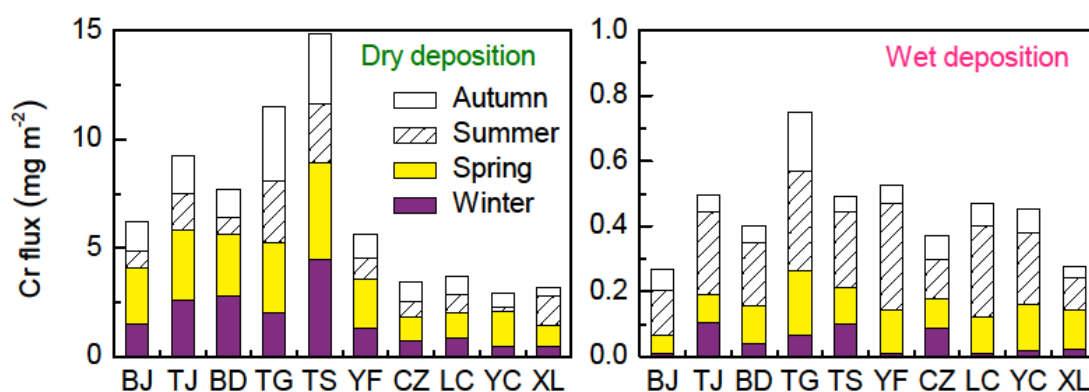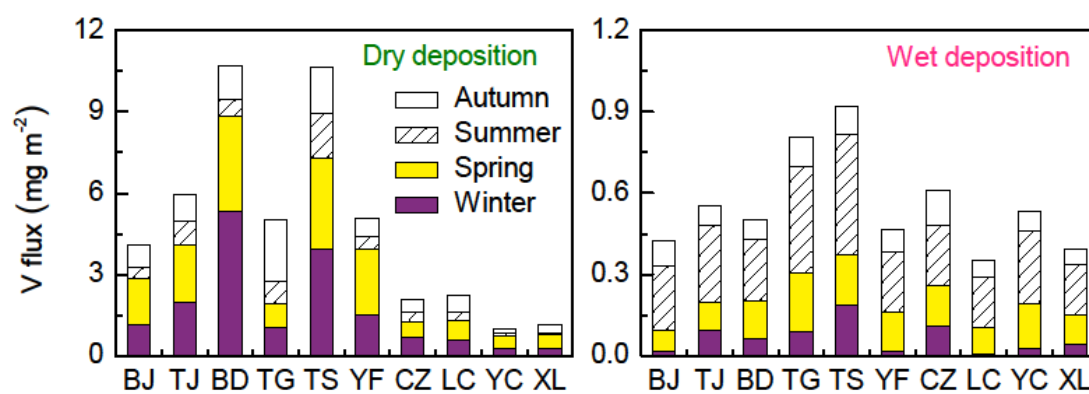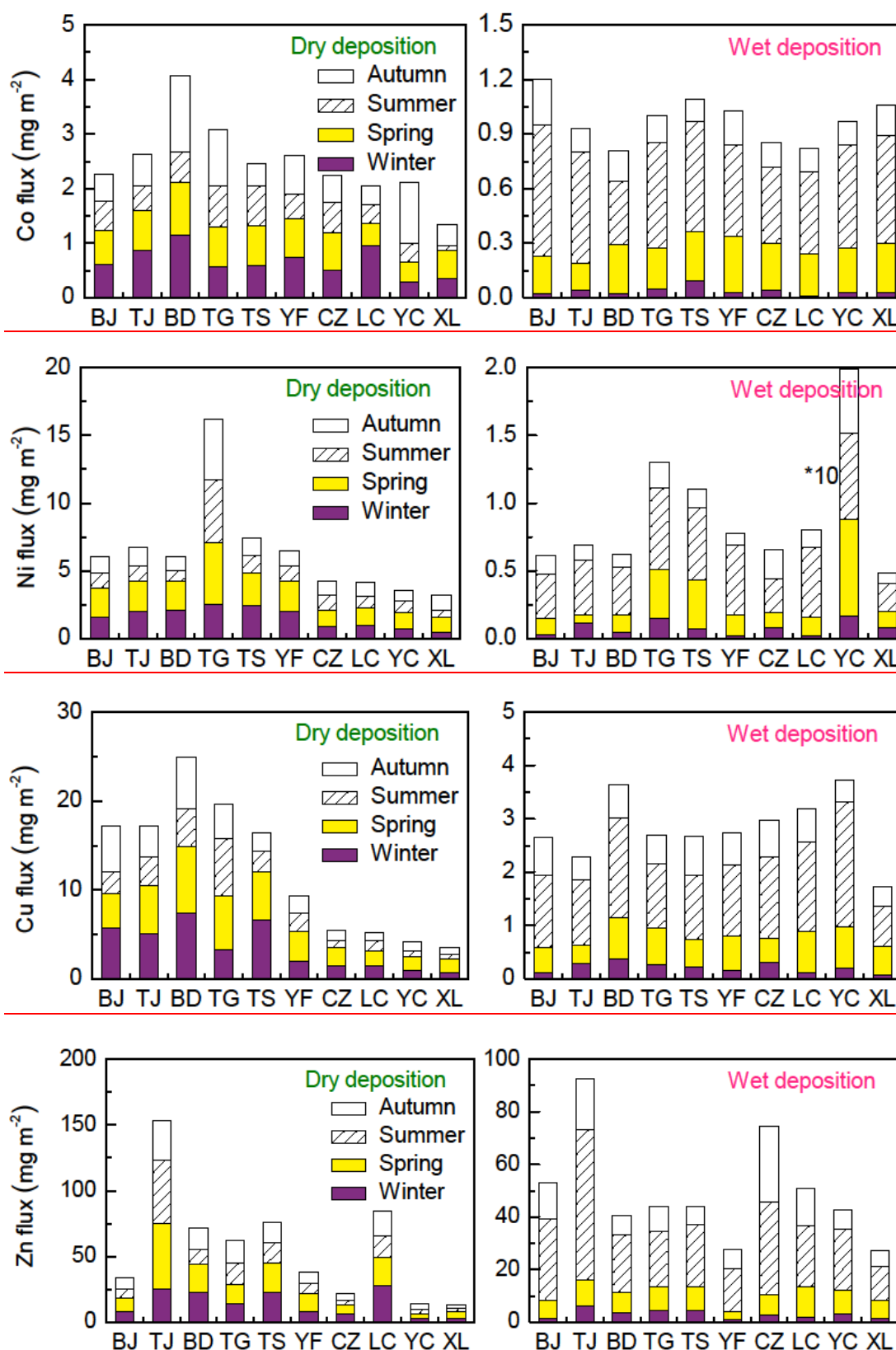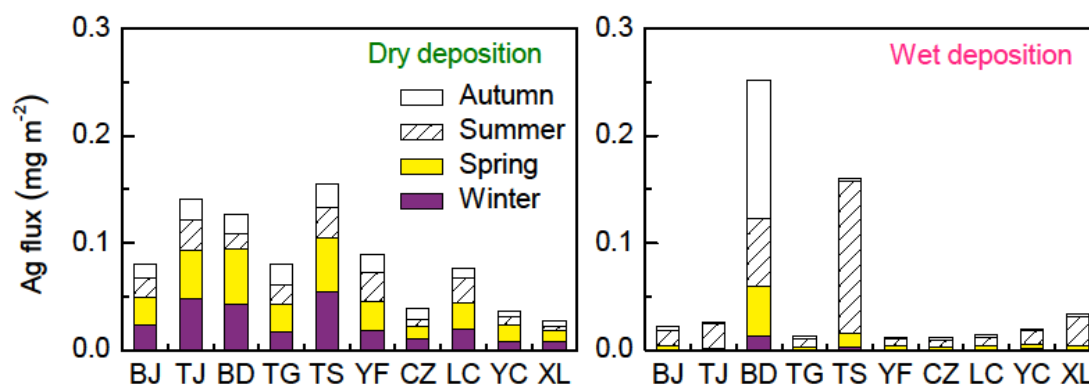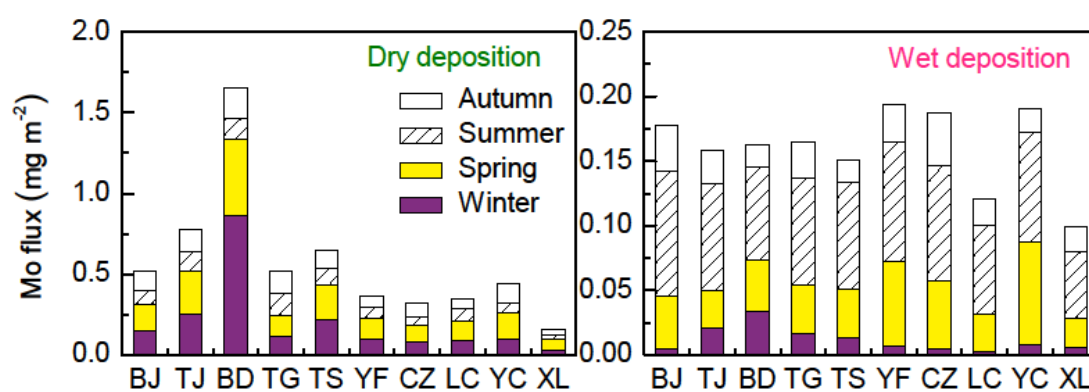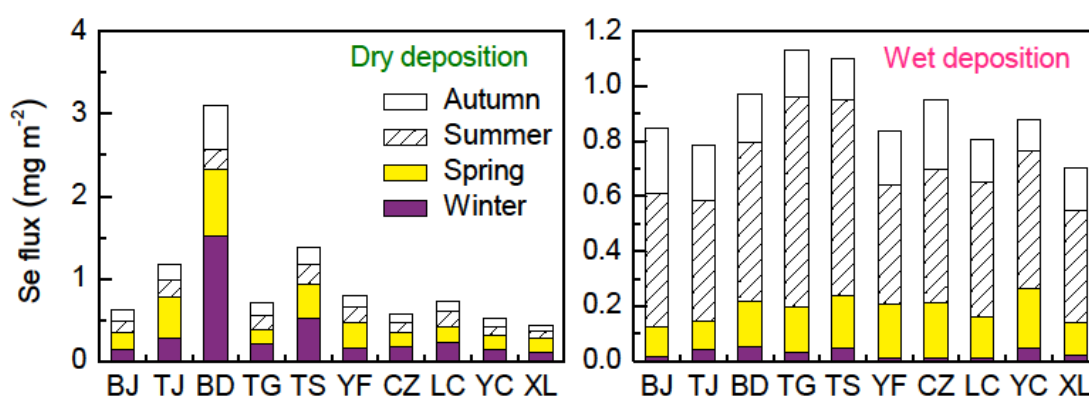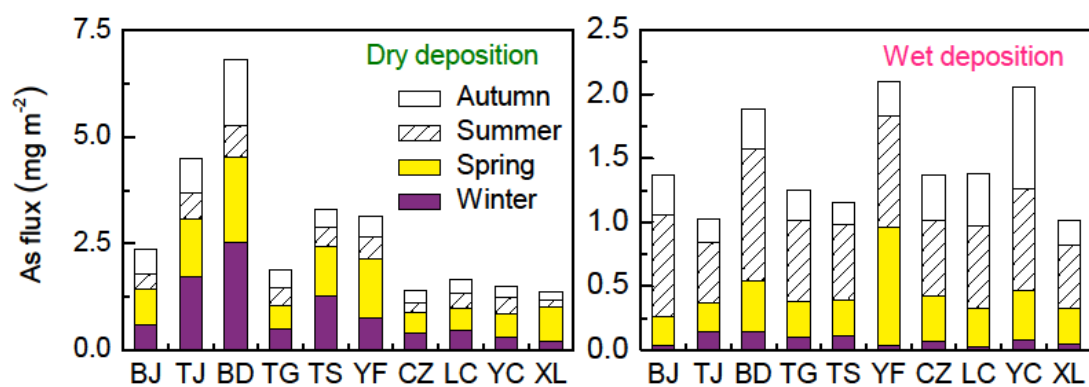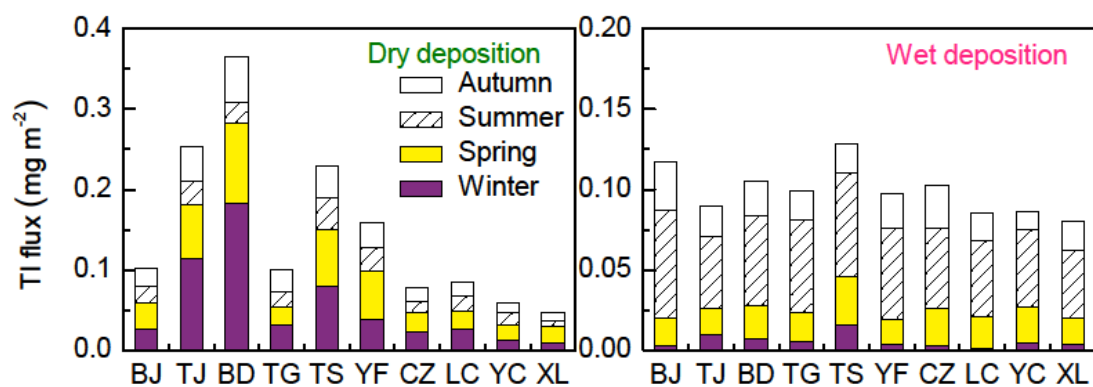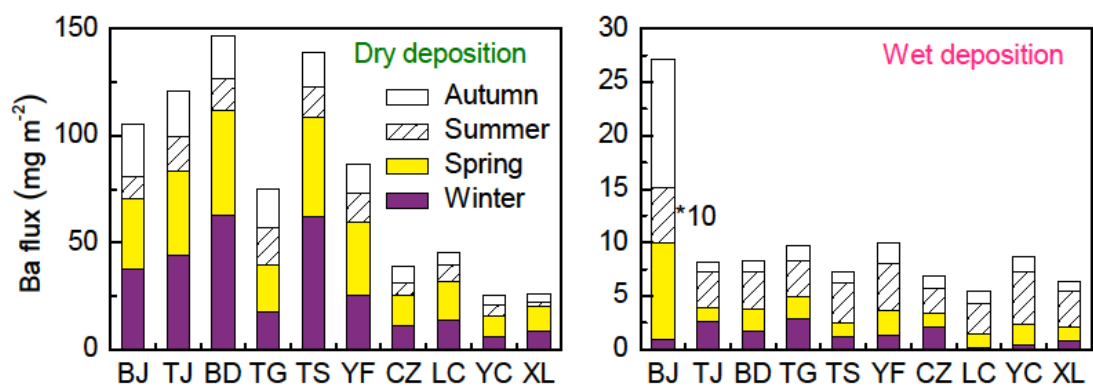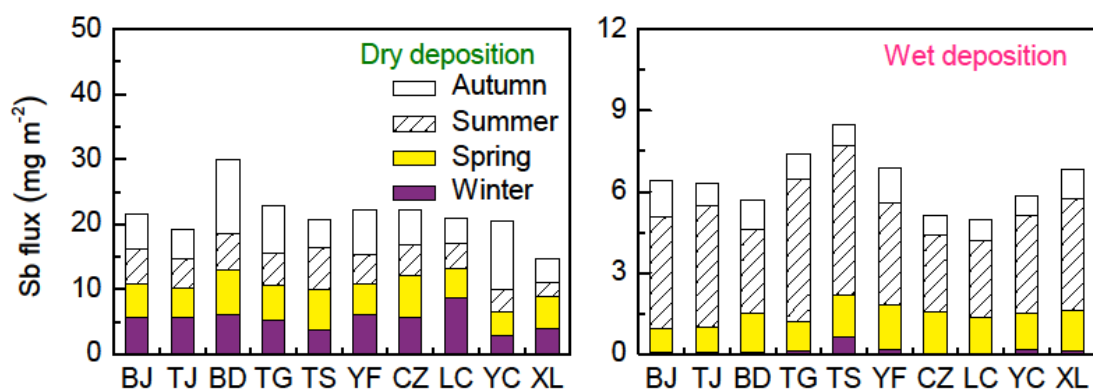
1306 Fig. 3. Spatial distribution and seasonal variations in atmospheric wet and dry

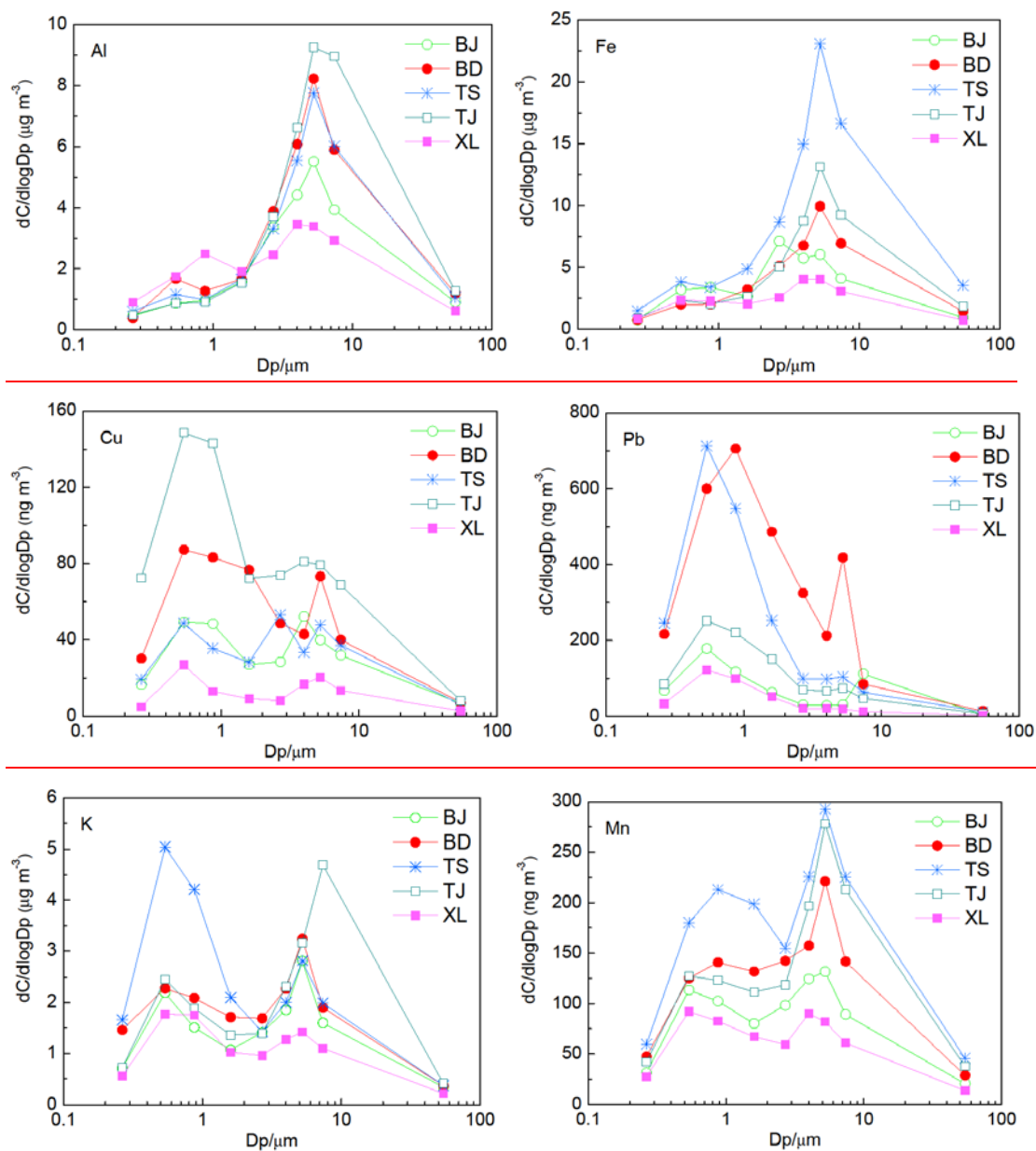1307 deposition fluxes of trace elements in Northern China.

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Fig. 4. Size distribution of aerosol trace elements in Northern China.
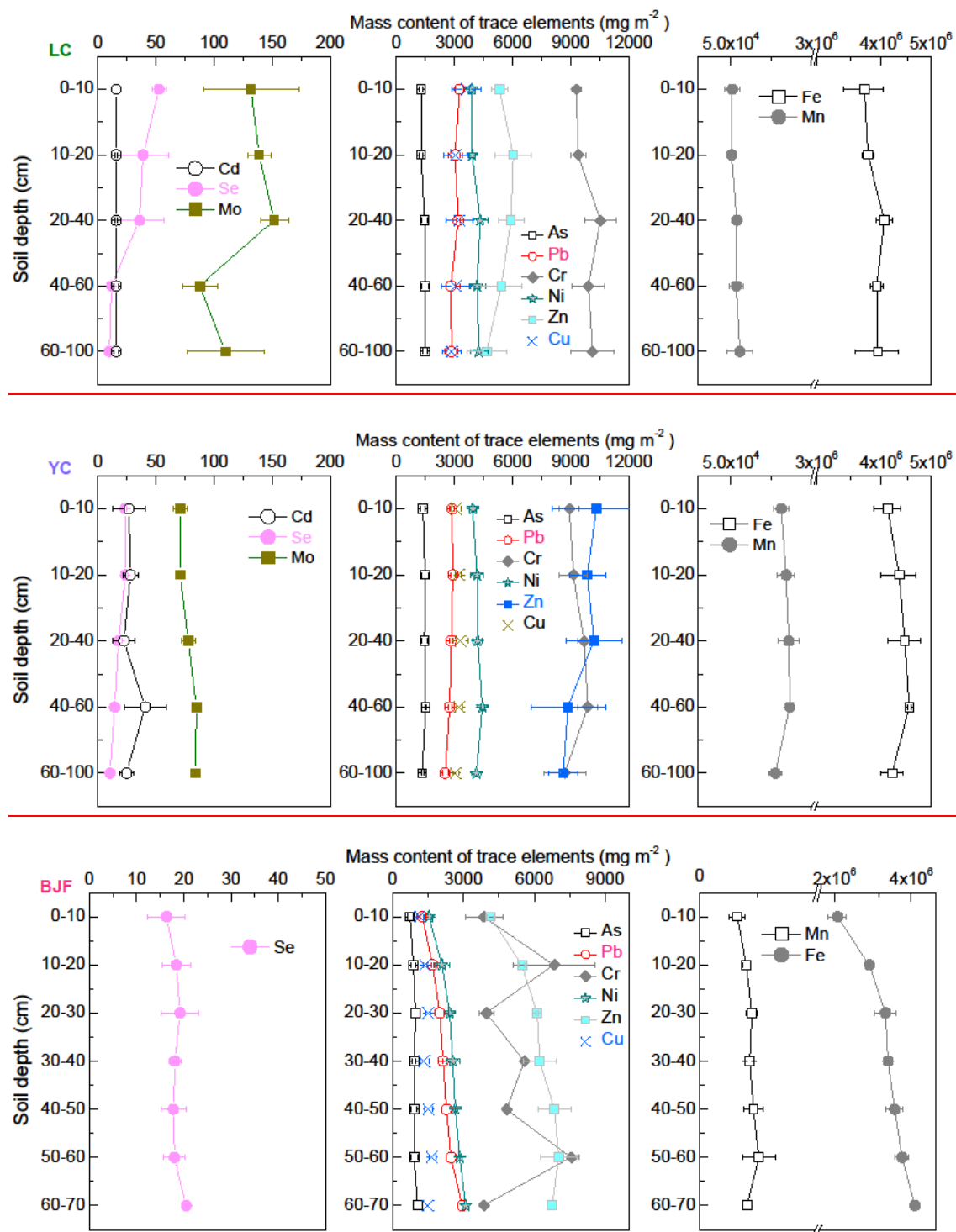
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Fig. 5. Soil profile of selected elements from three typical agricultural and forest sites in Northern China.