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Atmospheric wet and dry deposition of trace elements at ten sites in Northern China

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Abstract

Atmospheric deposition is considered to be a major process that removes pollutants from the atmosphere and an important source of nutrients and contaminants for ecosystems. Trace elements (TEs), especially toxic metals deposited on plants and into soil and water, can cause substantial damage to the environment and human health due to their transfer and accumulation in food chains. Despite public concerns, quantitative knowledge of metal deposition from the atmosphere to ecosystems remains scarce. To advance our understanding of the spatio-temporal variations in the magnitudes, pathways, compositions and impacts of atmospherically deposited TEs, precipitation (rain and snow) and dry-deposited particles were collected simultaneously at ten sites in Northern China from December 2007 to November 2010. The measurements showed that the wet and dry depositions of TEs in the target areas were orders of magnitude higher than previous observations within and outside China, generating great concern over the potential risks. The spatial distribution of the total (wet plus dry) deposition flux was consistent with that of the dry deposition, with a significant decrease from industrial and urban areas to suburban, agricultural and rural sites. In contrast, the wet deposition exhibited less spatial variation. The seasonal variation of wet deposition was also different from that of dry deposition, although they were both governed by the precipitation and emission patterns. For the majority of TEs that exist as coarse particles, dry deposition dominated the total flux at each site. This was not the case for K, Ni, As, Pb, Zn, Cd, Se, Ag and Tl, for which the relative importance between wet and dry deposition fluxes varied by site. Whether wet deposition is the major atmospheric cleansing mechanism for the TEs depends on the size distribution and solubility of the particles. We found that atmospheric inputs of Cu, Pb, Zn, Cd, As and Se were of the same magnitude as their increases in the topsoil of agricultural systems. In addition, the total deposition flux of Pb observed at a forest site in this study was twice that of the critical load ($7.0 \text{ mg m}^{-2} \text{ yr}^{-1}$) calculated for temperate forest ecosystems in Europe. These findings provide baseline data needed for future

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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 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). 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, dry deposition as a cleansing mechanism is more important than wet deposition on an annual basis. Thus, the relative importance of wet vs. 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). In regions where natural biogeochemical cycles are perturbed by human activities, atmospheric deposition can be important sources of either toxic substances or nutrients for the

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ecosystems (Hovmand et al., 2009; Meng et al., 2008). Thus, the interest in atmospheric deposition results mostly from concerns regarding the effects of the deposited materials entering the terrestrial and aquatic environments as well as their subsequent health effects (Sakata et al., 2006). When estimating atmospheric deposition flux, it is also important to consider the global biogeochemical cycle. For example, when compared with the riverine input, atmospheric dry deposition is one of the major paths for the transport of chemical species from the continents to coastal and open marine ecosystems (Duce et al., 1991). On the regional scale, the dry deposition process may be particularly important near urban/industrial areas where particle concentrations and sizes are large, such as sites near the Great Lakes (Sweet et al., 1998). Compared with developed regions in the US and Europe, however, relatively little is known about the magnitude and potential impacts of atmospheric deposition in the vast areas of Asia.

Northern China is subject to large quantities of emissions. However, measuring the atmospheric deposition flux, particularly the dry deposition of aerosols and their precursors, has thus far received little attention. The components of aerosols in Northern China are characterized by high levels of crustal elements (e.g., Al, Si and Ca) that are mainly generated over upstream arid/semi-arid areas (specifically, episodic dust storms in the springtime); the aerosols also contain abundant acids and heavy metals that are emitted directly from local anthropogenic sources (e.g., power plants, motor vehicles and industrial facilities) (Chen et al., 2014; Zhao et al., 2013). In addition to the complex emissions, the topography (surrounded by mountains) and climate (lack of rain) are not favorable for the diffusion and wet deposition of pollutants (e.g., SO₂, NO₂ and NH₃) in Northern China (Yang et al., 2012). Although previous studies have defined the aerosol/precipitation chemistry at a number of sites in the target areas, spatial and temporal information regarding wet and dry deposition derived from local and regional emissions in this complex air shed is limited. To advance our understanding of the transportation and transformation of pollutants from the local to the regional and global scales, our knowledge of the quantitative aspects of atmospheric deposition must be updated with detailed spatio-temporal descriptions. Therefore, a new

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monitoring network including ten well-distributed sites within the target areas was established in late 2007. The focus of the program was to evaluate the wet and dry deposition of the important trace species, including carbon, nitrogen, sulfur, phosphorus, heavy metals, and polycyclic aromatic hydrocarbons. The observations of this monitoring network have recently been presented, with an emphasis on acids and nutrients that most affect natural ecosystems (Pan et al., 2010, 2012, 2013b; Wang et al., 2012). With the substantial anthropogenic emissions, toxic metals deposited into ecosystems have led to increasing public concerns due to their transfer and accumulation in food chains (Luo et al., 2009).

In this paper, we further investigate the atmospheric wet and dry deposition fluxes of 25 trace elements (TEs) to complement the previous studies. The measurements were conducted during a three-year observation campaign at 10 selected sites. This study is the first attempt to conduct long-term direct measurements of the atmospheric deposition flux of crustal and anthropogenic metals in such a vast geographical area of China. The objectives of this research were (i) to clarify the spatial and seasonal variations in the wet and dry deposition fluxes across Northern China, (ii) to examine the relative importance of wet and dry deposition in removing airborne metals, and (iii) to compare the atmospheric deposition flux of TEs to other measurements in the literature and to the anthropogenic metal input to various ecosystems.

2 Materials and methods

2.1 Site description

Ten sites representing a range of conditions (coast-inland, forest-cropland, source-receptor, urban-rural, etc.) encountered in Northern China were selected for this study (Fig. S1). The observations of atmospheric deposition at all of the monitoring stations were conducted from December 2007 to November 2010. The monitoring network was operated and managed by the Institute of Atmospheric Physics, Chinese Academy

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of Sciences. The 10 sites are abbreviated using the names of the town/county/city in which they are located, and they are organized according to their urban geographies, energy structures and ecosystem types (Table 1). The types include urban (Beijing-BJ and Tianjin-TJ), industrial (Baoding-BD, Tanggu-TG and Tangshan-TS), suburban (Yangfang-YF and Cangzhou-CZ), agricultural (Yucheng-YC and Luancheng-LC) and rural (Xinglong-XL).

2.2 Sampling and analysis

2.2.1 Wet and dry deposition sampler

Wet-only rainwater and dry-deposited particles were collected using a custom wet-dry automatic collector (APS-2B, Changsha Xianglan Scientific Instruments Co., Ltd., China). The wet-dry sampler was equipped with a 707 cm² aperture and a 177 cm² polyurethane foam (PUF)-based glass bucket in separate containers to sample daily rainfall and monthly particulate dry deposition, respectively. Because the rainwater sensor allows the collection funnel of the cover device to open/close automatically when rainfall begins/ceases, wet and dry deposition can be collected separately with minor mixing between the two. A schematic of the sampler used is shown in Fig. S2. 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 mL 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

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Chemistry (LAPC, Beijing) by routine monthly site-maintenance visits. In the laboratory, the precipitation (rainwater and snow) samples were acidified with HNO_3 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.

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 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 min. 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 , $\text{H}_2\text{O}_2/\text{HCl}$ and HF. The results showed that the optimal combination was 5 mL

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of concentrated HNO_3 , 2 mL H_2O_2 and 0.2 mL HF. The filter was cut into ten to twenty equal portions to obtain a sample mass below 0.5 g, which is the working limit of the microwave vessels. This procedure also allowed for a comparison of the analysis results from multiple strips per filter. To ensure analytic quality, certified soil (GBW07401) and fly ash (GBW08401) materials were employed. Approximately 10 mg of these reference materials was accurately weighed and placed into a Teflon vessel along with the HNO_3 , H_2O_2 and HF. Subsequently, the vessels were capped, fastened on the rack and placed in the microwave oven to undergo the digestion procedure; the temperature-controlled digestion procedure is illustrated in Fig. S3. After cooling to room temperature, the digests were carefully transported to PET vials and diluted with Mini-Q water to a final volume of 50 mL. All samples were stored in the dark at 4°C prior to analysis. All observed results were blank corrected.

2.2.4 Trace metal analysis

A multi-element analytical program was run at LAPC using an Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Tokyo, Japan). The instrument was optimized daily in terms of sensitivity (Li, Y, and Tl), level of oxide (Ce) and doubly charged ion (Ce) using a tuning solution containing $10\text{ }\mu\text{g L}^{-1}$ of Li, Y, Tl, Ce, and Co in 2 % HNO_3 . The standard optimization procedures and criteria specified in the manufacturer's manual were followed. The concentrations of 25 TEs were determined by ICP-MS after calibration using external standards (Agilent Technologies, Environmental Calibration Standard, Part# 5183-4688) and internal standards (^{45}Sc , ^{73}Gd , ^{115}In and ^{209}Bi at $20\text{ }\mu\text{g L}^{-1}$ in 2 % HNO_3) added online during TEs analysis. The multi-element standard stock solution containing 10 or 1000 mg L^{-1} of TEs in nitric acid was diluted in 2 % HNO_3 to obtain five calibration standards ($1, 5, 10, 20$ and $50\text{ }\mu\text{g L}^{-1}$ for Cu, Pb, Zn, Cd, As, Be, Al, Mn, Ba, Co, Ni, Cr, Se, V, Mo, Ag, Sb, Tl, Th and U; $100, 500, 1000, 2000$ and $5000\text{ }\mu\text{g L}^{-1}$ for Fe, K, Na, Ca and Mg) plus a blank that covered the expected range for the samples. The analytical reproducibility of the extract concentrations was assessed by replication (the same sample was analyzed three times).

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The relative percent differences for replicate samples were less than 5 %. A check standard was analyzed after the initial calibration and again after every 12 samples. If the relative difference between the measured and actual concentrations was not within 10 %, the instrument was recalibrated and the previous 12 samples were re-analyzed.

As noted above, two certified materials were prepared in parallel to ensure the quality of the obtained results. The recoveries of the target elements ranged between 78 % and 115 % with the exception of Al (75 %). In all experiments, reagent blanks were measured separately. The filter blanks and the final concentrations of metals in the samples are reported after the field blank correction. The detection limits were better than 10 ng L^{-1} for most of the metals determined through analyses of blank samples. The average metal concentrations in the field blanks were well below the detection limits, indicating that no significant contamination occurred during the sampling, handling, delivery or measurement steps.

2.3 Statistics

The monthly wet deposition fluxes of TEs ($_{\text{wdf}}$ TEs) were obtained by multiplying the volume-weighted concentrations of TEs in the precipitation and the volume of precipitation measured by a standard rain gauge at each site during the sampling period. The monthly dry deposition fluxes of TEs ($_{\text{ddf}}$ TEs) were calculated by dividing the amount of TEs loaded on the PUF-filter by the surrogate surface area during the corresponding period. One-way analysis of variance (ANOVA) and nonparametric tests were conducted to examine the significance of the differences in the annual $_{\text{wdf}}$ TEs and $_{\text{ddf}}$ TEs for all ten sites. All analyses were conducted using the software SPSS 11.5 (SPSS Inc., Chicago, IL, USA) and Origin 8.0 (Origin Lab Corporation, Northampton, MA, USA). Statistically significant differences were defined as $P < 0.05$ unless otherwise stated.

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3 Results and discussion

3.1 Dry deposition of TEs

3.1.1 Profile of dry-deposited TEs

Figure 1 shows the annual mean $_{\text{ddf}}$ TEs at the ten sites during the observation period. In general, the magnitude of $_{\text{ddf}}$ TEs for each element at one station varied substantially, ranging from $0.03 \text{ mg m}^{-2} \text{ yr}^{-1}$ for Ag at the XL site to $10.3 \text{ g m}^{-2} \text{ yr}^{-1}$ 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 above 10, suggesting that the fluxes of these TEs were substantially affected by human activities. The primarily crustal elements with EFs lower than 10 (e.g., Al, Ca and Fe) had the highest flux among the 25 TEs. These TEs had fluxes similar to each other; the next highest fluxes were attributed to Na, Mg, K, Mn and Ba. Among dry-deposited particles, Zn was the most abundant anthropogenic metal, followed by Pb, Sb, Cu, Ni, Cr, As, Co, V, Se, Mo, Cd and Tl. Ag had the lowest measured flux among the heavy metals. In general, the average fluxes of the above crustal elements excepting Mn and Ba were 2–4 orders of magnitude higher than those of anthropogenic elements (e.g., Zn, As and Tl). The profile of TEs in dry-deposited particles agrees closely with those described in previous studies (Odabasi et al., 2002; Tasdemir and Kural, 2005). In addition, the dry deposition fluxes of most of the TEs in Northern China as shown in Fig. 1 fell within the range of values reported within and outside China (Table S1), with the exception of some crustal elements (e.g., Na, Mg and Al). The relatively high dry deposition fluxes of crustal elements are not surprising because these elements are commonly found in the bare soil of the study area, which constitutes the major proportion of the particulate matter (Chen et al., 2014). Although accounting for only a small fraction of the particles, heavy metals are of great environmental importance due to their toxicity and anthropogenic origins (Almeida et al., 2006). In conclusion, the dry deposition of

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TEs originating from both regional natural and local anthropogenic sources is closely linked to the dry nature of the soil and the intensive human activities in Northern China.

3.1.2 Spatial variation in $_{\text{ddf}}$ TEs

Generally, the values of $_{\text{ddf}}$ TEs were significantly higher for urban and industrial sites (e.g., BD, TJ and TS) compared with suburban, agricultural and rural sites (e.g., CZ, YC and XL). For example, the three-year mean $_{\text{ddf}}$ Pb was largest at BD ($35.6 \text{ mg m}^{-2} \text{ yr}^{-1}$), followed by TS, TG and TJ (31.4 , 27.3 , $23.1 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively). The $_{\text{ddf}}$ Pb was similar at YF, LC and BJ, with high values of 17.8 , 13.6 and $13.2 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively. At CZ, YC and XL, the $_{\text{ddf}}$ Pb was relatively low (7.1 , 7.1 and $5.7 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively). This spatial pattern was closely linked with local emissions, implying that human activities have affected the dry deposition of TEs and altered their regional budget, particularly for heavy metals. The human impact is more pronounced at the industrial sites of BD and TS. As shown clearly in Fig. 1, the dry deposition of some elements was significantly elevated at BD (Al, Be, Pb, Se, Th, Tl, U, V, Cd, Co, As, Mo, Ba, Sb and Cu) or TS (Fe, Mn, Mg, V, K, Ca, Ag and Cr) compared with at other urban or industrial sites. This finding suggests the presence of substantial metal emissions near these two sites. At TS, for example, the highest depositions of Fe, Mn and Cr were observed, which can be attributed primarily to the iron and steel processing industry, particularly the relocation of the Capital Steel Company from Beijing to Tangshan City during the observation period. After this relocation, a substantial decline in airborne steel-related elements has been observed in Beijing (Chen et al., 2014).

The two pairs of urban-suburban sites located in the Beijing and Tianjin metropolitan areas allowed us to assess the spatial variation in dry deposition along the environmental gradient. As expected, the dry deposition fluxes of most elements in the megacity, TJ, were higher than those in its suburban counterpart, TG, excepting certain elements such as Mn, Pb, Sb, Cu, Co, Ni and Cr. The relatively high $_{\text{ddf}}$ TEs observed at TG reflect the industrial activities in the coastal regions near Tianjin Harbor. This pattern is

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supported by the fact that the pre-2001 Pb level in the coastal waters of Bohai Bay originated primarily from river discharge; after 2001, a declining trend has not been observed due to additional contributions from atmospheric deposition, although the annual runoff levels have declined (Meng et al., 2008). Another recent geochemical study also suggested the contribution of atmospheric inputs of harmful elements to the surface sediments of Bohai Bay (Duan et al., 2010). These findings further indicate the human impact on regional element cycling, particularly on the transport and deposition from inland to coastal areas.

Compared with other sites, certain elements were found at the highest or second highest levels at TJ (Zn, Na, As, Cr and Tl) and TG (Ni, Cr, Pb and Mn). Wet deposition of Zn at TJ and Ni at TG was also higher than at other sites (Fig. 1). 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 $_{\text{ddf}}$ 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, the capital of

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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 $_{\text{ddf}}\text{TEs}$ 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 S1. This finding indicates that the $_{\text{ddf}}\text{TEs}$ 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 $_{\text{ddf}}\text{TEs}$

The seasonal mean $_{\text{ddf}}\text{TEs}$ during the three-year period are also shown in Fig. 1. The $_{\text{ddf}}\text{TEs}$ 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. This effect is more pronounced at the rural and agricultural sites XL, YC, CZ and YF, where natural sources dominated the fluxes.

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 episodic dust-storms originating from the northwest (Chen et al., 2014). At industrial and urban sites such as BD, 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. The enhanced fluxes of heavy metals (e.g., Pb and Ti) in winter at TG and LC are also related to coal consumption.

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 $_{\text{ddf}}\text{TEs}$ varied from one season to another due to changes in meteorological

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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

Figure 1 shows the annual mean $_{\text{wdf}}\text{TEs}$ at the ten sites during the observation period. The magnitude of $_{\text{wdf}}\text{TEs}$ for each element at one station varied significantly, from $0.01 \text{ mg m}^{-2} \text{ yr}^{-1}$ for Th at the XL site to $3.1 \text{ g m}^{-2} \text{ yr}^{-1}$ 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 Ti. 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 Ti). 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 was comparable to that observed in other sites listed in Table S2. In contrast, the wet deposition of Fe, Al, Mn and Zn was higher in Northern China as shown in Fig. 1 than in other regions of the world. The $_{\text{wdf}}\text{Pb}$ was also higher in this study than previously reported, with the exception of the North Sea and Singapore (Table S2). The relatively high $_{\text{wdf}}\text{TEs}$ 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.

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3.2.2 Seasonal variations in w_{df} TEs

The seasonal variations in w_{df} TEs showed similar trends at each site (Fig. 1), 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 w_{df} TEs and precipitation. 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 w_{df} 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 the sites.

3.2.3 Spatial variations in w_{df} TEs

In general, the spatial distribution of w_{df} TEs exhibited less variation. For example, the three-year mean w_{df} Pb was highest at TG ($10.1 \text{ mg m}^{-2} \text{ yr}^{-1}$), followed by TS, BD and YC (10.0 , 9.9 and $9.2 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively). The w_{df} Pb was similar at CZ, XL, LC, TJ and BJ, with high results of 8.8 , 8.4 , 8.2 , 8.0 and $6.4 \text{ mg m}^{-2} \text{ yr}^{-1}$, respectively. The lowest value occurred at YF ($3.9 \text{ mg m}^{-2} \text{ yr}^{-1}$). This pattern is different from the dry-deposited TEs, for which higher values were found at industrial and urban sites than at suburban, agricultural and rural areas. The wet deposition of certain elements (e.g., Al, Mg, Mn, Se, Th, U, V, Ca, Cd, Ag, Ni, Zn and Cr), however, was somewhat higher at the industrial sites compared with the other sites, indicating that these TEs were

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affected by local emissions. In Germany, heavy metals were also found to be higher in precipitation in urban-industrial areas than at rural measurement sites (Grömping et al., 1997). Surprisingly, unlike the dry-deposited TEs found in low values at XL, the wet deposition of certain TEs (e.g., Ag, Co, K, Be, Pb, Sb, Th and U) at XL was comparable to or higher than that at other sites, including industrial sites. Since there were no local emission sources near XL, the higher w_{df} TEs most likely resulted from the long-range transport from upwind areas of Northern China (Pan et al., 2013a).

3.2.4 Factors influencing the regional distribution of w_{df} TEs

To investigate the factors controlling the regional distributions of w_{df} 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:

$$S_r = C_p / C_a. \quad (1)$$

When the precipitation volume is expressed as P , the w_{df} TEs depend on S_r , C_a and P :

$$w_{df}\text{TEs} = S_r C_a P. \quad (2)$$

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

The statistical analysis of data from the three-year period revealed a positive relationship between the annual wet deposition fluxes of 12 trace elements (As, Cd, Co, Cu, Fe, Mn, Pb, Sb, Se, Th, Ti and V) and the corresponding precipitation volume ($0.11 < r^2 < 0.38$; Fig. S4). For most of these TEs that exist entirely as fine particles

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that can act as condensation nuclei, this finding may indicate that wet deposition represents a large contribution of their long-range transport during in-cloud processes. However, only approximately 20 % of the variance in the wet deposition fluxes for these TEs is explained by the volume of precipitation. The aforementioned percentage is significantly lower than that estimated in Japan, e.g., 68 % and 80 % of the variance in $w_{\text{df}}\text{Sb}$ and $w_{\text{df}}\text{V}$ is explained using the precipitation volume (Sakata et al., 2006), suggesting marked differences in the S_r and C_a of TEs across Northern China. For example, the $w_{\text{df}}\text{Pb}$ values at the BD, LC and TS sites in certain years was much higher than expected based on the precipitation amount, indicating a large contribution from anthropogenic emissions. However, the relatively low $w_{\text{df}}\text{Pb}$ values at the YC, CZ and YF sites compared with those expected from the precipitation amount may be due to the lower number of anthropogenic sources in suburban areas.

In contrast, the relationship between the annual wet deposition fluxes and the precipitation amount for the rest of the 13 TEs (Zn, U, Ni, Na, Mo, Mg, K, Cr, Ca, Ba, Be, Al and Ag) is not significant (Fig. S4). The results demonstrate that the annual values of these TEs were most likely dominated by the scavenging ratio and atmospheric concentrations across Northern China. Clearly, there is marked difference in the atmospheric concentrations of these TEs throughout the study region (Pan et al., 2013a; Zhao et al., 2013), although the available data are not sufficient. Considering that these TEs exist entirely in coarse particulate form, their wet deposition depends on the below-cloud scavenging of local emissions rather than regional contributions. For TEs in fine particles, however, wet deposition is mainly governed by regional transport (most of which might be from in-cloud scavenging) rather than local emissions.

3.3 Total deposition of TEs

3.3.1 Wet vs. dry deposition of TEs

A comparison of the w_{df} TEs and d_{df} TEs at each site provided in Fig. 1 shows that the dry deposition fluxes of most TEs were significantly higher than their wet deposition

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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 Northern China.

The relative difference between w_{df} TEs and d_{df} 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 deposition velocities (Sakata and Marumoto, 2004). In contrast, wet deposition may dominate the total flux for TEs exist as fine particles, which act as condensation nuclei for the formation of precipitation.

To confirm the above hypothesis, we performed elemental analyses on size-resolved particles collected at five selected sites (BD, BJ, TJ, TS and XL). The results showed that Al, Fe, Th and U were concentrated in coarse particles, whereas Cu, Pb, Zn, Cd,

As, Se, Ag and Tl existed as fine particles. In addition, the size distributions of Be, Na, K, Ca, Ba, Mg, Co, V, Mo, Ni, Sb, Cr and Mn were bimodal at all sites, with two peaks at 0.43–0.65 μm and 4.7–5.8 μm and a valley at 1.1–2.1 μm . The above premise proposed by Sakata et al. (2008) is partially supported by our measurements indicating that the dry deposition fluxes of TEs associated with larger particles (e.g., Al, Mn and Fe) are larger than their wet deposition fluxes. Similarly, the TEs accumulated in fine particles (e.g., As, Pb and Cd) have much larger wet deposition than dry deposition fluxes.

Interestingly, however, some metals have a similar size distribution but different deposition mechanisms (e.g., Cu and Pb). This circumstance may be due to the different solubilities of these TEs because the solubility determines the release of metals from particles and their subsequent incorporation into rainwater (Desboeufs et al., 2005). Although the solubility of Cu (43–93 %) is comparable to that of Pb (40–93 %) in most studies, only 8.4 % of Cu was soluble in rainwater sampled at Istanbul (Cizmecioglu and Muezzinoglu, 2008). Thus, the low solubility of Cu may be the reason for the low wet deposition fluxes in this study, although the premise must be verified in the future.

3.3.2 Wet plus dry deposition of TEs

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

The spatial variation in $_{\text{tdf}}$ 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 $_{\text{tdf}}$ 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 $_{\text{tdf}}$ TEs type by type due to the limited available measurement data for the study region, the relatively high $_{\text{tdf}}$ TEs observed for land use types other than rural

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areas stem from increased TEs emissions. Most importantly, the $_{\text{tdf}}$ 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 S3). Thus, the extremely high $_{\text{tdf}}$ 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 1), which is located in a forest area surrounded by few villages, exceeds the critical load of Pb ($7.0 \text{ mg m}^{-2} \text{yr}^{-1}$) 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 potential effects of substantial metal deposition on different ecosystems. Therefore, it is important to further reduce the emissions to mitigate the environmental risks posed by TEs in Northern China.

3.3.3 Atmospheric deposition of TEs into ecosystems

To quantify the contribution of atmospheric deposition to the elemental level in receiving ecosystems, it is necessary to know the metal content of a specific surface area for comparison with the atmospheric deposition in the same area. The mass content (M_c , mg m^{-2}) of TEs in the vertical soil profile is determined according to the following equation:

$$M_c = 10D_1B_dC_s. \quad (3)$$

where 10 is the conversion coefficient and D_1 , B_d and C_s are depth (cm), bulk density (g cm^{-3}) and the metal concentration (mg kg^{-1}) in each vertical layer, respectively.

In this study, we selected two agricultural sites (LC and YC) and a forest site approximately 100 km to the west of Beijing, where the elemental content of a typical soil

profile (0–100 cm) was measured in 2005. Only 11 TEs (Mo, Mn, Zn, Cu, Fe, Se, Cd, Pb, Cr, Ni and As) were selected because the other TEs were not available in the soil profile. The distribution of M_c for each metal vs. soil depth was first examined (data not shown). At the YC site, the M_c of Mn, Fe and As increased with depth, whereas that of Mo, Zn, Cr and Ni was enriched at 20–40 cm. In addition, Cu, Se and Pb were slightly accumulated in the top soil of 0–10 cm. No systematic pattern was found for Cd, which was rather stable within the profile. At the LC site, Zn, Se and Pb contents were found highest in the surface soil and decreased generally with depth. Mo, Mn, Cu, Fe, Cd, Cr, Ni and As were enriched in the plow horizon from 40–60 cm, which is deeper than that for Mo, Zn, Cr and Ni found at YC. Note that the M_c of each metal in the forest soils of Beijing increases with depth.

For TEs whose M_c increase with depth, the trend appears to be largely related to the parent materials of the soils at each site. Alternatively, the enrichment of TEs in the top soil may suggest important sources (e.g., atmospheric deposition) other than the mineralization of indigenous minerals. Presuming that the top soil (0–10 cm) and deep soil (60–100 cm) had the same initial elemental content when riverine alluvial soil was formed at the location, the significant enrichment of TEs in the upper soil layer indicates an anthropogenic origin such as atmospheric deposition, plant litter decomposition, fertilizer application or sewage irrigation.

The increase in elemental content (mg m^{-2}) in the topsoil (0–10 cm) relative to the deep soil (60–100 cm), which indicates the total anthropogenic input, is calculated and listed in Table S4. The ratio of atmospheric deposition to the total anthropogenic input (R_{at}) varied among sites and TEs. Negative values may indicate negligible anthropogenic input compared with the mineralization input. The R_{at} values for Mo, Zn, Cu, Se, Cd and Pb at YC were 0.02, 0.20, 0.01, 0.03, 1.03 and 0.05, respectively, indicating that atmospheric deposition contributed 20 % of anthropogenic Zn and almost all of the Cd in the topsoil. The explanation for the R_{at} values lower than 0.05 are not clear at present and require further study.

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At another agricultural site (YC), the R_{at} values of Mn, Zn, Cu, Se, Cd, Pb, Cr and As were 0.01, 0.03, 0.78, 0.11, 0.18, 0.05, 0.01 and 0.10, respectively. Thus, atmospheric deposition accounted for 10–78 % of the anthropogenic Cu, Se, Cd and As input. Although the R_{at} of some TEs was lower than 0.05, the contribution of atmospheric input cannot be overlooked when considering a longer accumulation period. A national inventory estimated that the inputs of TEs (As, Cr, Ni and Pb) to agricultural soils via atmospheric deposition were 43–85 % (Luo et al., 2009). Thus, long-term parallel measurements of atmospheric deposition and soil profile physico-chemical properties are required to detect the accumulated impacts. In addition, the chemical speciation and bioavailability of atmospheric deposited TEs should be considered given that the mobility of TEs determines their transformation and accumulation from soil and water to plants and humans.

As fertilization practices are not applicable in natural ecosystems, forest, for example, may be an ideal upland ecosystems in which to track atmospheric deposition (Hovmand et al., 2008). However, the increasing elemental M_c with depth in the forest soils of Beijing makes it difficult to quantify the anthropogenic input using the method described above. Nevertheless, impacts of atmospheric deposition on the urban park and agricultural soils were identified in Beijing (Chen et al., 2005; Lu et al., 2012). Evidence can also be found at the rural forest site of XL, where elevated elemental concentrations were observed in fine particles transported via southern winds from industrial and urban areas in Northern China (Pan et al., 2013a).

4 Conclusions

To our knowledge, this study provides the first long-term direct measurements of atmospheric wet and dry deposition fluxes of crustal and anthropogenic metals on a regional scale across China. The dataset provides a basis for the validation of regional emission inventories and biogeochemical or atmospheric chemistry models. It also facilitates the

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effective targeting of policies to protect ecosystems (e.g., water and soils) from long-term heavy metal accumulation. Three major findings and conclusions can be drawn:

1. Significantly higher $_{ddf}$ TEs were observed at industrial and urban areas than at suburban, agricultural and rural sites, corresponding to the urban-rural land use gradient. The minimum $_{ddf}$ TEs that occurred in summer/autumn were attributable to an increase in precipitation, whereas the maximum in winter/spring were due to the additional emissions from coal burning and sandstorms. Elevated $_{ddf}$ TEs, most of which originated from coarse particles, are closely linked with the regional dry nature of the soil and the intensive local human activities in Northern China.
2. Due to the precipitation pattern in Northern China, summer contributed the most to annual wet deposition flux, followed by spring, autumn and winter. Although the precipitation in winter was comparable at each site, the spatial variation in the wet deposition fluxes of several TEs in cold season was evident due to the local emissions from house heating. Compared with $_{ddf}$ TEs, however, the annual $_{wdf}$ TEs had less spatial variation and were influenced by the regional patterns of precipitation and emissions. The wet deposition of TEs that exist as fine particles was mainly governed by regional transport rather than local emissions. However, for coarse particulate TEs, wet deposition was attributed mainly to below-cloud scavenging (most of which might be from local emissions).
3. The relative importance between wet and dry deposition flux varied among sites and TEs. Nevertheless, dry deposition flux was significantly higher than the wet deposition flux for most TEs, signifying the dominance of self-cleansing mechanisms in the atmosphere. In addition to the local availability of precipitation, size distribution and solubility of TEs in particles are important factors determining the relative importance of wet vs. dry deposition. Compared with other measurements around the world, the atmospheric deposition flux in Northern China was very high, indicating that the mitigation of metal emissions is greatly needed in the future.

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The case study demonstrates that a comparison of atmospheric deposition and vertical soil profile is an appropriate tool with which to characterize the atmospheric input of toxic metals to ecosystems and to differentiate their contributions from other anthropogenic sources. The atmospheric deposition of Cu, Pb, Zn, Cd, As and Se is of the same magnitude as the increase of these TEs in the topsoil; this type of atmospheric deposition may dominate the anthropogenic input to agricultural systems in the future. Our study further highlights the need to focus on the chemical speciation and bioavailability of atmospherically deposited materials and demonstrates the importance of establishing long-term observation studies on the accumulation of heavy metals in food chains as a result of substantial atmospheric deposition.

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Table 1. 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
TI	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.

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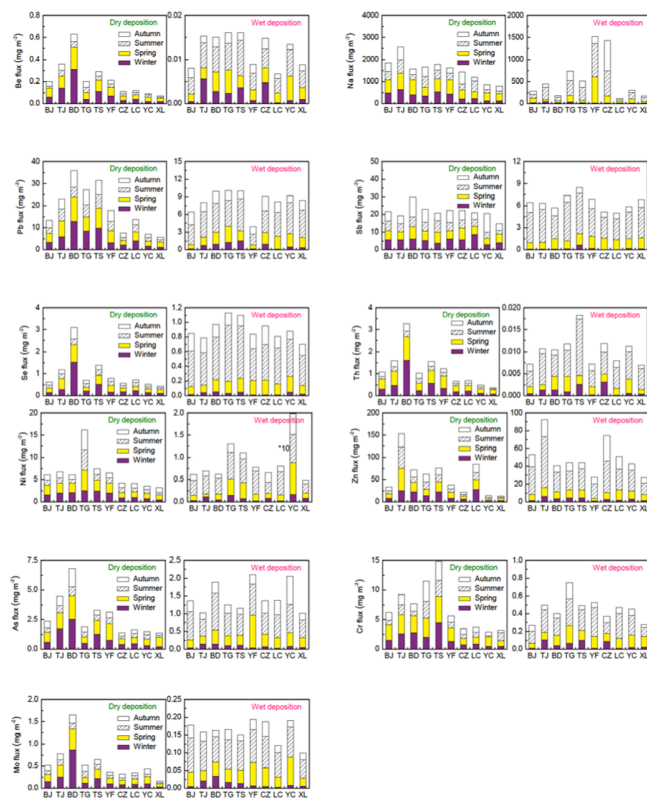


Figure 1. Spatial distribution and seasonal variations in atmospheric wet and dry deposition fluxes of trace elements in Northern China.

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