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Environmental effect of heavy metals deposition in arid city

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Abstract

This paper analysis the contents and variation of heavy metals in wet and dry deposition in Changji (Xinjiang, China) revealed their reducing regularity for heavy metals in atmosphere in arid area. Samples (including 84 dry deposition samples and 16 wet deposition samples) were collected from January 2016 to December 2016, and the contents of heavy metals (Ni, Cu, Cd and Pb) were analyzed by AA-7000 atomic absorption spectrophotometer. The dry deposition fluxes of Ni, Cu, Cd and Pb are 3.70 mg/(m^2 a), 4.81 mg/(m^2 a), 0.53 mg/(m^2 a) and 22.74 mg/(m^2 a), respectively; the wet deposition fluxes of Ni, Cu, Cd and Pb are 0.77 mg/(m^2 a), 3.25 mg/(m^2 a), 0.04 mg/(m^2 a) and 0.11 mg/(m^2 a), respectively. Each of the four heavy metals deposition fluxes during heating period was higher than non-heating period, especially for Pb and Cd, which is mainly due to the emission of coal combustion for heating. During sampling periods, the ratio of wet deposition flux to total for Ni, Cu, Cd and Pb are 17.21%, 40.33%, 7.67% and 0.48%, respectively; the wet deposition flux is far less than dry deposition, especially for Pb. The rate of dry deposition is lower than wet deposition, however dry deposition plays an important role in scavenging heavy metals in arid region. Arid region has a low intensity and frequency of rain event, heavy metals were mainly scavenging by dry deposition attribute to its continuous and dependable process. Dry deposition has much more environmental effect on heavy metal in arid region.

Keywords: Arid area; heavy metal; dry deposition; wet deposition; environmental effect.

1. Introduction

Heavy metal is a kind of contaminant with non-biodegradable, teratogenicity and carcinogenicity. Heavy metal in atmospheric particulates can be breathed into human body directly, then cause a variety of diseases and dysfunction, and harm to health. Dry and wet deposition is an important way to remove heavy metals from atmospheric particulates (Susan *et al.*, 2014). Dry and wet deposition can decrease the contents of heavy metals in the air, keep the air quality relatively stable. However, a large amount of heavy metals can deposit in the water and soil with dry and wet deposition continuously and pollute directly. The pollutants are able to make negative effect on biogeochemical cycle permanently in ecological system (Connan *et al.*, 2013; Grantz *et al.*, 2003). Therefore, it is significant to study on the dry deposition of heavy metals.

The airborne pollutant reducing rate of wet deposition is higher than dry deposition, so the reduction effects of wet deposition has been considered much better than dry deposition (Omrani *et al.*, 2017). Researcher found that the ratio of wet deposition flux to total is 90%, wet deposition can strongly influence heavy metal reduction (Muezzinoglu and Cizmecioglu, 2006). On the contrary, some researchers consider that, although the rate of dry deposition is lower than wet deposition, dry deposition is a much more continuous and stable airborne pollutant reducing process (Grantz *et al.*, 2003). Although the rate of wet deposition is higher than dry deposition, dry deposition flux is higher than wet deposition during the sample period due to low annual precipitation in arid region. Heavy metals were mainly scavenged by dry deposition, dry deposition has much more environmental effect on heavy metal in arid region. The reduction effects on heavy metal depend not only on the rate of dry and wet deposition, but also on regional annual precipitation strongly (Gunawardena *et al.*, 2013).

Researchers mainly focused on studies about dry and wet deposition rate and deposition flux of heavy metals. However, the research on reduction of heavy metals in atmosphere is rare in arid area (Connan *et al.*, 2013; Omrani *et al.*, 2017; Liu *et al.*, 2016), research on comparison of environmental effect of dry and wet deposition is much fewer. The study was carried out in Changji (Xinjiang, China), which is a satellite city (about 420,000 population) of Urumqi in the center of Eurasian continents and is known as the 'Silk Road' of the new North Road. Changji has a typical continental arid climate and an annual precipitation of approximately 200 mm, and the main form of wet deposition was snow in winter

and rain in the other seasons. Owing to the development of the western region in China, Changji has experienced rapid increase in urbanization in recent years with increased emissions of pollutants and sacrificed air quality. The urban ecological environment is facing unprecedented pressure. Building on this background, research was carried out to analyze the variation of dry and wet deposition of heavy metals (Ni, Cu, Cd, and Pb), and to illustrated the reducing regularity and influencing factors. In order to provide a reference for the in-depth study of environmental geochemical processes of heavy metals and theoretical support for air pollution prevention and ecological protection for urban air environment, we choose Changji (Xinjiang, China) as a study area for the research of the dry and wet deposition characteristics of heavy metals in an arid urban atmosphere.

2. Materials and methods

2.1. Sample collection

Dry deposition samples were monthly collected from January 2016 to December 2016. A total of 84 samples were continuously collected for 24 h from the roof of the No.3 apartment of Changji University at approximately 15-20 m above ground using a middle volume sampler (TH-150, Wuhan Tianhong, China) at approximately 0.1 m^3/min through a glass fiber filter (90 mm diameter, 0.65 μm aperture). The filters were placed in a seal dry dish for 48 h and contrast weighed before and after sampling, then weighted via an Analytical Balance (10^{-6} g minimum). Weather data (atmospheric pressure, relative humidity, temperature, wind speed, and wind direction) were recorded during the sampling period. Samples were continuously collected each day for 7 days at the beginning of every month in sampling period. If it was raining, snowing, or there was a large amount of dust in the air, sampling would cease for 24 h following the event.

The sampling period and site of wet deposition are same as dry deposition. During the period, there were 75 precipitation events (39 rainy days and 36 snowy days). Based on factors such as precipitation amount, drying time, total precipitation hours, etc., 6 snowfall events and 10 rainfall events were selected for samples. The sampling container was polyethylene bucket. It was washed with dilute nitric acid before precipitation to ensure that each sampling tool was free of pollution, and the container was secured when sampling. After the end of each precipitation, samples were transferred to polyethylene bottles and frozen at -1°C. A total of 16 samples were collected. The weather dates and samples details such as sample quality were recorded and carefully maintained.

2.2. Sample analysis

2.2.1. Main instruments and reagents

An AA-7000 atomic absorption spectrophotometer with graphite furnace (SHIMADZU, Japan), a TH-150 Middle-Volume sampler (Pall, Port Washington, NY, USA), a Laoying 2030 medium flow rate intelligent TSP sampler (Laoying Institute), a CEM microwave digestion instrument (CEM Corporation, Charlotte, NC, USA), and a Milli-Q water purification system (EMD Millipore, Billerica, MA, USA) were used. Guaranteed reagent–grade chemicals and ultra–pure water were used for all procedures, unless stated otherwise. An environmental mixed calibration standard of Ni, Cu, Cd, and Pb (10 μg/mL, Agilent, Part#5183-4688) were diluted to produce a standard solution series in stages with 5% nitric acid (Merck, Germany).

2.2.2. Experiment methods

The dry samples were cut up using a PVC scissors and placed in the beakers, respectively. Each sample was digested using 20 mL mixed solution (2 mL HNO_3 and 18 mL $HClO_4$) and heated on an electric stove in the fume hood. Lower the temperature after digesting the samples completely, then transfer from the beakers to the volumetric flasks. Distilled water was added to fill the volumetric flasks, then shake up and transfer to the PVC bottle before analyzed. The wet samples were removed from the freezer floor, melted naturally at room temperature. Then, the wet samples were added 0.1 mL HNO_3, and analyzed after standing 8 h.

Heavy metals concentrations (Ni, Cu, Cd, and Pb) of samples were examined by AA-7000 Atomic absorption spectrometer (SHIMADZU, Japan). Under optimum conditions, blank and standard solution series were measured and the standard curves were automatically drawn by the instrument (r≥0.9999). For quality assurance and quality control of heavy metals, national geochemical standard sample was measured. Every sample was examined three times, and the relative standard deviation for each metal was <5%, and the recovery rates for metals ranged from 85% to 110%. Every 30 samples made a group standard curves and every 15 samples made a standard calibration. Reagent blanks were also employed to detect potential contamination during the digestion and analytical procedure.

3. Results and discussion

3.1. Dry deposition

3.1.1. Heavy metals concentrations in dry deposition

The results showed that the mean concentrations of Ni, Cu, Cd, and Pb in TSP were 22.39 (n.d.-56.77) ng/m^3, 50.89 (0.07-129.60) ng/m^3, 1.10 (n.d.-6.11) ng/m^3, and 142.61 (n.d.-301.85) ng/m^3, respectively.

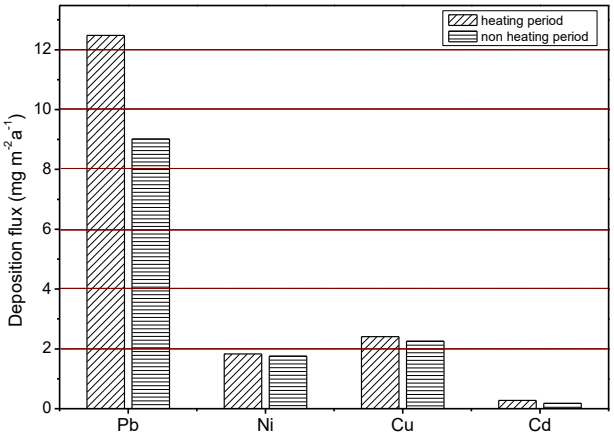

Figure 1. Dry deposition fluxes of heavy metals in heating period and non-heating period

The rate of dry deposition is depended on wind speed, humidity, temperature and particulate diameter and so on, however the rate is hard to evaluate accurately. The value 0.5 cm/s in this paper is referenced to some empirical researchers calculated before (Fang *et al.*, 2001; Davidson *et al.*, 1985; Connan *et al.*, 2013; Lamborg *et al.*, 1995). The dry deposition flux of heavy metals in TSP was calculated using Eq. (1) (Fang *et al.*, 2001; Qin *et al.*, 2011).

$$F_d = V_d \times C_a \quad (1)$$

where F_d is dry deposition flux, and the annual flux unit is mg/(m^2 a), C_a is concentration of the given heavy metal in atmospheric particulates (mg/m^3), and V_d is the dry deposition rate.

The results indicated that the annual dry deposition fluxes of Ni, Cu, Cd, and Pb were 3.70 mg/(m^2 a), 4.81 mg/(m^2 a), 0.53 mg/(m^2 a), and 22.74 mg/(m^2 a), respectively. The annual dry deposition flux of Pb is the highest, followed by Cu, Ni, and Cd (Figure 1).

3.1.2. Heavy metals variations in dry deposition

The result showed that the dry deposition fluxes of Ni, Cu, Cd and Pb in heating period are 1.83 mg/m^2, 2.41 mg/m^2, 0.28 mg/m^2, and 12.48 mg/m^2, respectively. The dry deposition fluxes of Ni, Cu, Cd and Pb in non heating period are 1.76 mg/m^2, 2.26 mg/m^2, 0.18 mg/m^2, and 9.02 mg/m^2, respectively. The winter in Xinjiang is cold and long and the mean temperature of the coldest month (January) was about -15.6 °C, which made the local heating period last 6 months (October 15 to April 15) include three seasons (autumn, winter, and spring). The heating method relied on coal in Changji. There were studies reported that coal contains a lot of heavy metals such as Cd, As, Cu, Pb, Ni, Zn, and Hg (Liu *et al.*, 2015). By comparing, the deposition fluxes of heavy metals in heating period are generally higher than those in non-heating period, and Cd and Pb are most prominent, which may attribute to large number of coal burning in heating period (Figure 1) (Yang, *et al.*, 2013).

3.2. Wet deposition

3.2.1. Heavy metals concentrations in wet deposition

The average concentrations of Ni, Cu, Cd, and Pb in wet deposition are 22.39 (0-56.77) ng/m^3, 50.89 (0.07-129.60) ng/m^3, 1.10 (0-6.11) ng/m^3, and 142.61 (0-301.85) ng/m^3, respectively. Moreover, the average concentrations of the four heavy metals in rain are 2.08 (0.36-12.09) ng/mL, 9.59 (2.98-33.09) ng/mL, 0.11 (0.05-0.14) ng/mL, and 0.28 (0.09-1.10) ng/mL, respectively; those metals in snow are 6.75 (3.11-17.02) ng/mL, 26.12 (8.75-81.68) ng/mL, 0.45 (0.11-0.84) ng/mL, and 0.96 (0.18-1.51) ng/mL, respectively (Figure 2).

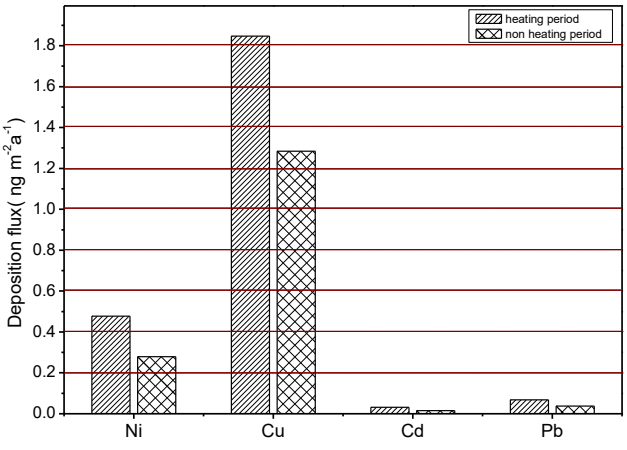

Figure 2. Wet deposition fluxes of heavy metals in heating period and non-heating period

The results indicated that the concentrations of Ni, Cu, Cd, and Pb in snow were about 3-4 times higher than in rain. The higher concentrations of heavy metals in snow are attributed to coal combustion emitting a large amount of heavy metals in winter, and the slower fall speeds and larger specific surface area compare to rain. Moreover, the crystal shape of snow has been proven to provide an effective filtering effort to atmospheric particulate matters (Liu *et al.*, 2015).

3.2.2. Heavy metals variations in wet deposition

The wet deposition flux of a given heavy metal was calculated using Eq. (2) (Yang *et al.*, 2009).

$$F_i = C_i \times P \times 10^{-3} \quad (2)$$

where F_i is wet deposition flux, and the annual flux unit is mg/(m^2 a), C_i is the concentration of the given heavy metals in precipitation (mg/m^3), and P is total precipitation (mm). For this study, the value 204.6 mm was provided by Meteorological Bureau, Changji is taken as P to calculate wet deposition fluxes of heavy metals.

The results indicated that the annual wet deposition fluxes of Ni, Cu, Cd, and Pb were 0.77 mg/(m^2 a), 3.25 mg/(m^2 a), 0.04 mg/(m^2 a), and 0.11 mg/(m^2 a), respectively. The annual wet deposition flux of Cu is the highest, followed by Ni, Pb, and Cd. The wet deposition fluxes of Ni, Cu, Cd and Pb during heating period were 0.48 mg/m^2, 1.85 mg/m^2, 0.03 mg/m^2, and 0.07 mg/m^2, respectively. Moreover, the wet deposition fluxes of Ni, Cu, Cd and Pb during non-heating period were 0.28 mg/m^2, 1.29 mg/m^2, 0.02 mg/m^2, and 0.04 mg/m^2, respectively. By comparing, the wet deposition fluxes of heavy metals in heating period were generally higher than in non-heating period, especially for Cd and Pb (Figure 2). The study area has a typical continental arid climate with drought and less rainfall. The precipitation events mainly happened in spring, summer and autumn, while it is less in winter. Although the precipitation is low in heating period, the main wet deposition form is snow which contains much more heavy metals than rain.

The deposition flux of heavy metals is very high in one snowfall event. Those are the main reason for the high wet deposition flux of heavy metals during heating period. In contrast, the precipitation is relatively higher in non-heating period, whereas, the main wet deposition form is rain which contains less heavy metal. Hence, wet deposition flux of heavy metals during non-heating period is less than heating period.

3.3. Environmental effect of heavy metal reduction by dry and wet deposition

Atmospheric deposition is one of the most important pathways for scavenging of atmospheric heavy metals, which can be in the form of either dry or wet deposition.

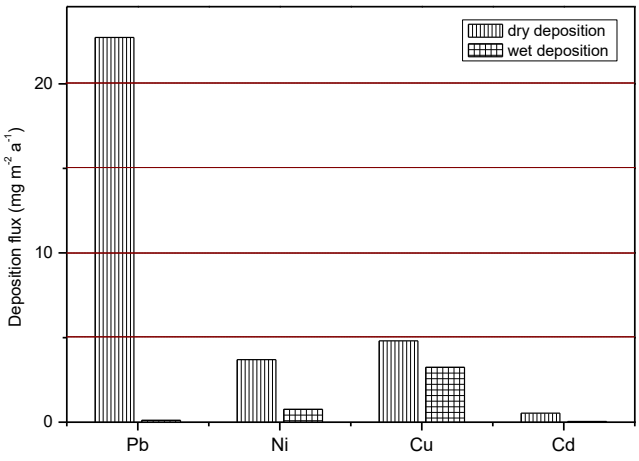

Figure 3. Annual dry deposition fluxes and wet deposition fluxes of heavy metals

The results indicated that the total dry and wet deposition fluxes of Ni, Cu, Cd, and Pb were 4.47 mg/(m^2 a), 8.06 mg/(m^2 a), 0.58 mg/(m^2 a), and 22.85 mg/(m^2 a), respectively. Researchers generally considered that wet deposition play a more important role than dry deposition in scavenging atmospheric particulate heavy metals due to the faster reducing rate of wet deposition and the more intuitive and obvious scavenging effect. Groempling *et al.* believed that heavy metal in wet deposition accounted for more than 90% of the total deposition flux (Groempling *et al.*, 1997). But, the results of this study indicated that the wet deposition flux was far less than dry deposition. The ratio of wet deposition flux to total deposition for Ni, Cu, Cd and Pb are 17.21%, 40.33%, 7.67% and 0.48%, respectively; the ratio of wet deposition flux to total deposition for Ni, Cu, Cd and Pb are 82.79%, 59.67%, 92.33% and 99.52%, respectively. Pb in atmosphere particulates is mostly cleaned by dry deposition, therefore wet deposition has a very weak effect on scavenging Pb (Figure 3). Although the rate of dry deposition slower than wet deposition, it is a continuous and dependable process for atmospheric scavenging. Therefore, dry deposition flux is higher than wet deposition during the whole study period and dry deposition has stronger effect on scavenging heavy metals in arid areas. Besides, the result was the same with the research of Grantz, Muezzinoglu, etc. (Grantz *et al.*, 2003; Muezzinoglu *et al.*, 2006). The reduction effects on heavy metal depend not only on the rate of dry and wet deposition, but also on regional annual precipitation strongly (Melaku *et al.*, 2008; Sakata *et al.*, 2011). In summary, it is relative significance for dry deposition in arid area with a low intensity and frequency of rain event, and low humidity in the air. In addition, the dry and wet deposition fluxes of heavy metals during heating period were higher than non-heating period, which were mainly attribute to emission of coal combustion for heating.

4. Conclusion

(1) The annual dry deposition fluxes of heavy metals tends to decrease in the following order: Pb>Cu>Ni>Cd, in which the value of Pb is much higher than others. Moreover, the annual wet deposition fluxes of heavy metals tends to decrease in the following order: Cu>Ni>Pb>Cd.

(2) The dry and wet deposition fluxes of heavy metals in heating period were higher than non-heating period, and Pb and Cd were the most obvious, which was mainly due to emission of coal combustion for heating.

(3) The ratio of wet deposition flux was far less than dry deposition in the whole sampling period, especially for Pb. Dry deposition is more important on scavenging heavy metals attribute to its continuous and dependable process, low intensity and frequency of rain event and low humidity in the air in arid areas.

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