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Original Research

Wet Deposition of Heavy Metals in an Arid City

Yuyan Liu[1]*, Cheng Liu[1], Fangfang Tian[1], Haofeng Liu[2], Fengshan Shi[1]

[1]Department of Chemistry and Applied Chemistry, Changji University, Changji 831100, P. R. China
[2]Changji Environmental Monitoring Station, Changji 831100, P.R. China

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Abstract

In order to investigate characteristics of wet deposition of heavy metals in an arid city, precipitation samples were collected for 16 precipitation events in the arid city of Changji. A total of 16 samples were collected and concentrations of principal heavy metals in the atmosphere were examined by inductively coupled plasma-mass spectrometry (ICP-MS) to discuss levels, variation, and wet deposition fluxes of heavy metals. Among these heavy metals in wet deposition, Fe, Zn, and Cu were found to be the highest. Levels of As, Ni, and Cr ranked second, while Pb, Cd, and Hg were found to be the lowest. The concentrations of heavy metals in wet deposition showed distinct seasonal variations, having high values in winter and low values in other seasons. Besides, in general, concentrations of heavy metals in snow were higher than those in rain. Because the winter was cold and long in Xinjiang, emissions from coal-fired heating were high, which was associated with enhanced concentrations of heavy metals. The order of wet deposition fluxes of heavy metals in the whole year was Fe > Cu, Zn > As, Ni, Cr, Pb > Cd, Hg. Compared to other areas, wet deposition fluxes of heavy metals were low in Changji, which may be due to minimal rainfall in the arid city, having a weak scavenging effect of atmospheric pollutants. In addition, because the level of urbanization and industrialization was not high in Changji, emissions of atmospheric pollutants were low.

Keywords: arid city, heavy metals, wet deposition, atmosphere

Introduction

Particulate Matter (PM) is one of the most important atmospheric pollutants in china. The composition of the particulate pollutants such as heavy metals can cause a lot of diseases, for example, allergies, asthma, and lung cancer. The synergy of PM and heavy metals associated with PM may lead to more severe synergistic toxicological effects. This has increased research interest in heavy metals in the environment over the past few decades around the world. However, information on cleansing mechanisms and the fate of heavy metals is very limited. Atmospheric deposition, which can be in the form of either dry or wet deposition, is one of the most important pathways for cleansing air of atmospheric heavy metals. Dry and wet deposition can remove heavy metals from the air, which makes concentrations of heavy metals in the atmosphere maintained at a relatively stable level. At the same time, heavy metals can be deposited into surface water and the terrestrial environment, which are associated with adverse human and wildlife health effects [1, 2]. Migration and transformation of pollutants is unique in arid regions for special meteorological conditions, and studies about cleansing mechanisms and the fate of heavy metals in arid regions are essential [3, 4]. Against this background, research was carried out to determine characteristics of wet deposition of heavy metals in the arid city of Changji.

*e-mail: 824462939@qq.com

Materials and Methods

Site Selection and Sampling Procedures

The study was carried out in Changji (44.05 N, 87.31 E), China, which is in the center of Asia and Europe, and is known as the "Silk Road" of the new North Road. It has a typical continental arid climate. The annual precipitation is only about 200 mm. Precipitation in the form of snow is common during winter and in the form of rain during other seasons. The population of the city is about 420,000. Due to Western development, Changji has experienced a rapid increase in urbanization in recent years with increased emissions of pollutants and decreased air quality; the urban ecological environment is facing unprecedented pressure.

The sampling sites were established on the Changji College North Campus (Fig. 1). Although the sampling site was in the downtown area of the city, it was more secluded and had less human interference than others in the city [5].

The sampling period was one year (December 2011 through December 2012), and there were 87 precipitation events in total (40 rainy days and 47 snowy days). Based on factors such as precipitation characteristics (precipitation amount, drying time, total precipitation hours, etc.), six snowfall events and 10 rainfall events were selected for samples to be taken (Table 1). The sampling container was a 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 -1ºC. A total of 16 samples were collected. The weather data (temperature, atmospheric pressure, wind speed and direction, and relative humidity) and samples details such as sample quality were recorded and carefully maintained through the study.

Instruments

The main instruments were as follows: an Agilent ICP-MS 7 500Ce inductively coupled plasma mass spectrometer and a Milli-Q water purification system.

Reagents and Standard Solution

Guaranteed reagent-grade chemicals and ultra-pure water were used for all procedures, unless stated otherwise. Before use, an environmental mixed calibration standard of Fe, Zn, Cu, As, Ni, Cr, Cd, and Pb (10 µg/mL, Agilent, Part#5183-4688) had to be diluted to mixed standard solution series (0, 0.5, 2, 10, 50 ng/mL) by stage with 5% nitric acid (Merck). Standard stock solution of Hg (1000 µg/mL, Iron and Steel Institute) was diluted to standard solution series (0, 0.5, 2, 10, 50 ng/mL) by stage with 5% nitric acid (Merck). Mixed internal standard stock solution of ^{6}Li, ^{45}Sc,

Fig. 1. Map of the study area.

Table 1. The concentrations of heavy metals in precipitation for each precipitation event.

Ordinal of precipitation	Precipitation data	Precipitation form	Concentrations of heavy metals (ng/mL)								
			Pb	Ni	Cu	Zn	As	Cd	Cr	Fe	Hg
1	2011–12–31	Snow	1.09	3.38	8.78	7.46	6.40	0.83	1.35	104.30	0.17
2	2012–12–17	Snow	1.20	7.29	29.12	22.94	8.56	0.72	5.02	133.70	0.15
3	2012–01–18	Snow	0.82	16.97	82.51	111.60	2.39	0.26	2.55	56.28	0.13
4	2012–02–01	Snow	0.17	5.27	10.02	1.76	16.21	ND	7.92	224.50	0.31
5	2012–02–06	Snow	0.98	3.09	10.99	9.77	4.48	0.31	1.33	62.88	0.13
6	2012–03–07	Snow	1.50	3.30	10.02	8.60	4.00	0.10	0.45	80.80	0.14
7	2012–04–29	Rain	0.36	1.25	9.25	9.96	3.91	0.12	3.85	71.67	0.21
8	2012–05–19	Rain	0.36	0.38	3.05	4.55	1.04	0.08	1.37	20.51	0.16
9	2012–06–03	Rain	0.28	1.19	4.87	5.85	2.81	0.08	1.32	65.52	0.14
10	2012–06–18	Rain	0.09	0.46	3.03	4.71	1.85	0.06	0.67	46.38	0.10
11	2012–06–22	Rain	1.06	2.52	25.83	73.09	4.64	0.12	2.77	141.50	0.16
12	2012–07–01	Rain	0.15	11.90	32.59	17.31	7.66	0.11	3.40	117.60	0.23
13	2012–09–15	Rain	0.09	0.83	3.16	17.74	0.67	0.11	0.17	18.48	0.08
14	2012–09–22	Rain	0.15	1.84	8.27	20.02	1.55	0.13	0.49	27.43	0.09
15	2012–10–07	Rain	0.09	0.40	4.57	14.69	0.39	0.09	0.14	8.73	0.08
16	2012–10–19	Rain	0.11	0.43	3.84	15.17	1.24	0.10	0.47	25.49	0.10
Average			0.53	3.78	15.62	21.58	4.26	0.21	2.08	75.36	0.15

^{72}Ge, ^{89}Y, ^{115}In, ^{159}Tb, and ^{209}Bi (10 μg/mL, Agilent, part#5183-4680) was diluted to 1 μg/mL with 5% nitric acid. Tuning solution was the mixed standard solution of Li, Co, Y, Ce, and Ti (10 ng/mL, Agilent, Part#5184-3566).

Analysis Procedures

Samples were removed from the freezer floor and allowed to melt naturally at room temperature. Then the samples were analyzed directly after going through the 0.45 μm membrane water.

Under the optimum conditions, blank and standard solution series were collected and the standard curves were automatically drawn by instrument (r>=0.9999). Operating parameters of ICP-MS were automatically defined by the tuning optimization that satisfied sensitivity, background, oxide, dual charge, and stability of equipment installation standards. The main operating parameters of the instrument were as follows: RF power 1450 W, cooling gas 15.0 $L \cdot min^{-1}$, auxiliary gas 1.0 $L \cdot min^{-1}$, carrier gas 1.06 $L \cdot min^{-1}$. The isotopes used in the determination were ^{57}Fe, ^{53}Cr, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{111}Cd, ^{202}Hg, and ^{208}Pb. Based on factors such as mass number of elements, ionization energy of elements, and elemental chemical properties, internal standards were selected. Ge was the internal standard element for Fe, Cr, Ni, Cu, and Zn; Y was the internal standard element for As; In was the internal standard element for Cd; Bi was the internal standard element for Hg and Pb. The limits of detection were 2.746 ng/g, 0.504×10^{-1} ng/g, 0.393×10^{-1} ng/g, 1.409×10^{-1} ng/g, 0.273×10^{-1} ng/g, 2.215×10^{-3} ng/g, 8.132×10^{-3} ng/g, 1.038×10^{-3} ng/g, and 7.292×10^{-3} ng/g for Fe, Zn, Cu, As, Ni, Cr, Cd, Pb, and Hg, respectively. Their recoveries were more than 85%, and the relative standard deviation was less than 2.5%.

Results and Discussion

Concentrations of Heavy Metals in Precipitation

The concentrations of heavy metals in precipitation for all precipitation events are shown in Table 1. Based on concentrations, the elements can be divided into three major groups. Fe, Zn, and Cu were found to be the highest, the range of which was 75.36 (8.73-224.50) ng/mL, 21.58 (1.76-111.60) ng/mL, and 15.62 (3.03-82.51) ng/mL, respectively. Levels of As, Ni, and Cr ranked second, the range of which was 4.26 (0.39-16.21) ng/mL, 3.79 (0.38-16.97) ng/mL, and 2.08 (0.14-7.92) ng/mL, respectively. Pb, Cd, and Hg were found to be the lowest, the range of which was 0.53 (0.09-1.50) ng/mL, 0.21 (0.06-0.83) ng/mL, and 0.15 (0.08-0.31) ng/mL, respectively.

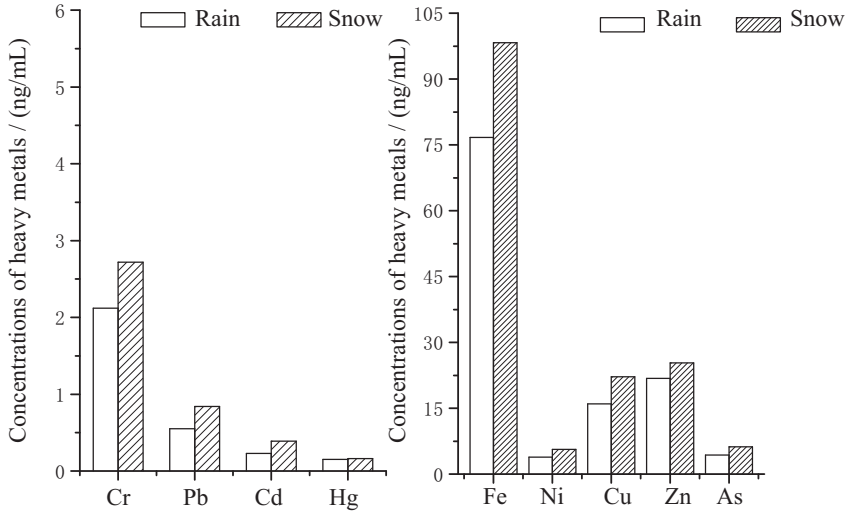

Fig. 2. Concentrations of heavy metals in rain and snow.

Variations on Concentrations of Heavy Metals in Precipitation

Atmospheric cleansing mechanisms involve wet deposition of atmospheric pollutants in rain and snow forms. In the present study, concentrations of heavy metals in snow generally increasedcompared to those in rain, especially for Cd, Pb, Ni, As, and Cu. The higher concentrations of heavy metals in snow were possibly caused by slower fall speeds and higher collection surface area compared with rain. In addition, the crystal shape of snow has been proven to provide an effective filtering effect for aerosols because of their porosity [6, 7]. The average concentrations of the five heavy metals in rain were 0.23 ng/mL, 0.55 ng/mL, 3.89 ng/mL, 4.37 ng/mL, and 16.00 ng/mL, respectively. However, those in snow were 0.39 ng/mL, 0.84 ng/mL, 5.67 ng/mL, 6.23 ng/mL, and 22.1 ng/mL, respectively, which was about 1.7, 1.5, 1.5, 1.4, and 1.4 times higher than those in rain, respectively (Fig. 2). The winter was cold and long and the average temperature of the coldest month (January) was about -15.6ºC in Changji, which made the local heating period last six months. The heating method relied on coal in Changji. There were studies reported that coal contains a lot of heavy metals such as Cd, Cr, As, Cu, Pb, Ni, Zn, Fe, and Hg [8, 9]. Contents of some heavy metals in coal from Xinjiang were higher than the average contents of china and the world [10]. Concentrations of heavy metals in snow were generally higher than those in rain in Changji, which may attribute to large exploitation of coal and rapid urbanization. Because rapid urbanization made the area of the town expand, the area and intensity of heating were increased in winter, which led to increased pollutant emissions making concentrations of some heavy metals in the atmosphere display an increasing trend in winter. A recent study found that particulate Hg was more effectively scavenged by snow than by rain and low temperature was hardly conducive to volatilization of

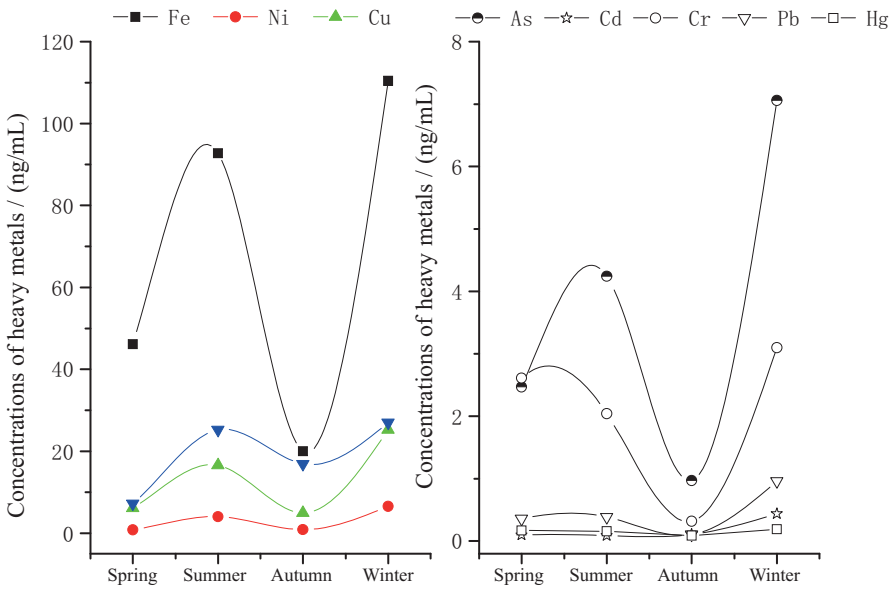

Fig. 3. Seasonal variations of heavy metals in wet precipitation.

Table 2. Comparison of wet deposition fluxes of heavy metals around the world.

Location	Wet deposition fluxes of heavy metals (mg/m²×a)									Data source
	Hg	Cr	Cu	Zn	As	Pb	Cd	Ni	Fe	
Changji	0.03	0.43	3.20	4.42	0.87	0.11	0.04	0.77	15.42	Our study
Changchu	0.02	1.70	3.74	65.78	2.13	6.82	0.21	—	—	[14]
Xian	0.05	0.71	2.11	29.53	0.57	2.40	0.14	1.01	—	[15]
Chongqing	—	2.90	13.00	76.26	4.50	30.25	0.44	2.22	73.03	[16]
Hong Kong	—	—	4.70	33.15	—	87.02	—	—	67.20	[17]
Noshiro	—	0.24-0.61	—	—	0.80-1.60	6.00-12.00	0.19-0.41	0.65-1.07	—	[18]
Nakanoto	—	0.18-0.62	1.40-2.20	19.00-30.00	1.00-2.20	8.00-12.00	0.27-0.35	0.50-2.30	—	[18]
Matsuyama	—	0.27-0.41	0.90-1.60	15.00-29.00	0.79-1.05	6.00-7.80	0.21-0.33	0.73-1.01	—	[18]
Tokyo Bay	—	6.20	16.00	—	2.90	9.90	0.40	6.80	—	[19]
Izmir	—	3.41-152.52	3.10-866.76	54.87-1568.29	—	—	0.62-60.45	5.58-140.43	—	[20]
Marais-Vernier	0.01	—	—	2.85	—	0.10	0.01	0.32	—	[21]
Korean countryside	—	—	1.21	6.93	0.26	1.06	0.05	0.37	—	[22]
Washington	—	0.06-4.62	—	—	—	0.11-3.20	0.06-5.10	—	—	[23]
Recreativo	—	1.60	70.00	—	0.60	3.40	0.10	1.40	—	[24]

Hg in winter, which made relative enrichment of Hg in snow [11, 12]. Besides, there was some correlation between the amount of precipitation and the concentrations of heavy metals. Further studies should be performed to determine a better explanation for the problem.

Seasonal variations of heavy metals in wet precipitation were distinct for all of the elements, showing considerably higher concentrations in winter and lower concentrations in other seasons (Fig. 3). Among these heavy metals, seasonal variations of Cd and Hg were relatively flat, which may be due to low background value of the environment for these two elements (Fig. 3). The main wet deposition form in winter was snow, which mainly occurred annually from December to the next February, and the main wet deposition form in other seasons was rain. The concentrations of heavy metals in snow were high and concentrations of heavy metals in winter were highest compared to other seasons, which mainly was attributed to emissions of heavy metals from coal-fired heating [13].

Characteristics of Wet Deposition Fluxes of Heavy Metals

The wet deposition flux of a given heavy metal can be expressed by:

$$F=C\times P\times 10^{-3} \quad (1)$$

...where F is wet deposition flux of the given heavy metal (mg/(m²×a)), C is concentration of the given heavy metal in precipitation (mg/m³), and P is annual precipitation amount (mm). Based on average annual precipitation of Changji, P in this study was taken as 204.6 mm.

In our study, wet deposition flux of Fe was 15.42 mg/(m²×a), which was found to be the highest among these heavy metals. Wet deposition flux of Cu and Pb was 4.42 mg/(m²×a) and 3.20 mg/(m²×a), respectively. Wet deposition flux of As, Ni, Cr, and Pb was small, with a range of 0.87-0.11 mg/(m²×a). Wet deposition flux of Cd and Hg was smallest, with a range of 0.03-0.04 mg/(m²×a). Some pollutants, even though they exist in the presence of trace or ultra-trace, can seriously threaten human health and the ecosystem, such as Cd, Hg, and Pb.

The results are further compared with the data from various locations (Table 2). The wet deposition fluxes of Hg, As, and Cu are comparable to intermediate level and the wet deposition fluxes of Cr, Zn, Pb, Cd, Ni, and Fe are lower than average level, which may be attributed to a few precipitation amounts of the arid city, having rare rinsing amounts of atmospheric pollutant. Besides, the small urban population, moderate level of urbanization and industrialization, and relatively little emissions of pollutants may be other reasons. However, as Western development rapidly advances, the rapid growth of the economy may bring unprecedented pressure for the urban ecological environment of Changji, which requires enough attention.

Conclusions

1. Among heavy metals in wet deposition in this study, concentrations of Fe, Zn, and Cu were found to be the highest, and levels of As, Ni, and Cr ranked second, while Pb, Cd, and Hg were found to be the lowest.

2. The concentrations of heavy metals in wet deposition showed distinct seasonal variations, having high values in winter and low values in other seasons. Besides, in general concentrations of heavy metals in snow were higher than those in rain. Because the winter was cold and long in Xinjiang, emissions from coal-fired heating was large, which was associated with enhanced concentrations of heavy metals. Meanwhile, Hg was more effectively scavenged by snow than by rain, and low temperature was hardly conductive to volatilization of Hg in winter, which made enrichment of Hg in snow.
3. The order of wet deposition fluxes of heavy metals in the whole year was Fe > Cu, Zn > As, Ni, Cr, Pb > Cd, and Hg. Compared to other areas, wet deposition fluxes of heavy metals were low in Changji, which may be due to small rainfall in the arid city, having a weak scavenging effect of atmospheric pollutants. In addition, because the level of urbanization and industrialization was not high in Changji, emission of atmospheric pollutants was low.

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