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Horizontal distribution and levels of heavy metals in the biggest snowstorm in a century in Shenyang, China

AN Jing[1,2], ZHOU Qixing[1,3,*], LIU Weitao[1,2], REN Liping[1]

1. Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China. E-mail: anjing.china@yahoo.com.cn
2. The Graduate School of the Chinese Academy of Sciences, Beijing 100039, China
3. Key Laboratory of Pollution Processes and Environmental Criteria (Ministry of Education), College of Environmental Science and Engineering, Nankai University, Tianjin 300071,China

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Abstract

The horizontal distribution and levels of heavy metals in the biggest snowstorm in Shenyang since 1904 were investigated by analyzing 4 metals (As, Cd, Pb, and Cu) in a series of ultraclean samples collected from 17 sites distributed in different regions of the Shenyang area, China. The results showed that the concentrations of all the 4 heavy metals in snow from the industrial regions were high, up to 7.3 (As), 2.2 (Cd), 850.0 (Pb), and 0.197–20.2 (Cu) μg/kg, respectively. In the suburb, in contrast, their concentrations were not detected, except for As. Because of the long-term application of arsenical pesticides and herbicides, As was detected in the snow samples which collected on the farm. As, Cd, and Pb were also detected in the snow samples collected from the parks, the residential areas, and the commercial districts mainly by reason of human activities. In a sense, long-term industrial activities, traffic activities, coal combustion, and agricultural activities affected the horizontal distribution and levels of these heavy metals in snow differently. The data relating to the horizontal distribution and concentrations of heavy metals in the snow under extreme climatic conditions can provide with a unique snapshot of environmental pollution situation and behaviors in urban areas.

Key words: heavy metal; distribution; pollution level; snowstorm; extreme climate

Introduction

In recent years, heavy metals in atmospheric wet precipitation and their environmental pollution behaviors have received global interest (Zhou and Huang, 2001; Bragazza, 2006; Temme *et al*., 2007), mainly because heavy metals have strong toxicity to human health and other living organisms at global levels. Cases had documented that heavy metals in the body cells elicit inflammatory injuries in the airway and lungs (Nel, 2005). Furthermore, heavy metals can accumulate in human tissues through the food chain, and cause damage to human nervous systems and internal organs (Lee *et al.*, 2006). They also act as potentially derivational factors of cardiovascular diseases, reproductive impairments, and cancers (Dockery and Pope, 1996; Willers *et al*., 2005).

Atmosphere is an important environmental compartment in the biogeochemical cycle of heavy metals, which can be deposited on the land by wet precipitation such as snowfall, frosting, and rainfall. Heavy metals are emitted to the atmosphere largely from burning of fossil fuels, incineration of waste, smelting of metals, and metallic sand blown by the wind (Pirrie *et al*., 2002; Sezgin *et al*., 2004; Sanchez-Rodas *et al*., 2007). They can be adsorbed on the aerosol and drop to the ground with the aerosol by wet or dry precipitation (Hu *et al*., 2005). Usually, the high concentration of heavy metals occurs in impacted areas. Monitoring the concentration and determining the horizontal distribution of heavy metals in the wet precipitation can, thus, provide important information about the sources and behaviors of these metals in the atmosphere. Several studies (Galloway *et al*., 1982; Barrie *et al*., 1987; Atteia, 1994; Riemann *et al*., 1996; Gregurek *et al.*, 1999; Simonetti *et al*., 2000; Veyssere *et al*., 2001) had examined heavy metals in snow depositions and showed that heavy metals in a big snowstorm can reflect and indicate environmental pollution situation in urban areas.

Heavy metals in the snowfall in Shenyang area represent a very interesting case because it is characterized by rather unique parameters. There is almost no information available from the published literatures discussing about the concentration and horizontal distribution of heavy metals in the biggest snowstorm in a century in this area. Shenyang is not only a big city with large numbers of population, but also an important base for old heavy industries in China. Local emissions of heavy metals to the atmosphere are indeed very significant as a consequence of dense population and continual human activities, such

* Corresponding author.
E-mail: zhouqx@iae.ac.cn; zhouqx@nankai.edu.cn.

as long-term industrial activities, heavy traffic activities, and coal combustion. Thus, it is of great significance in environmental science to investigate horizontal distribution and levels of heavy metals in the biggest snow event since 1904 in the Shenyang area.

1 Materials and methods

1.1 Snowfall events and sampling sites

The snow that covered the whole Shenyang Area fell on 4th–5th March 2007 and lasted about 24 h with great intensity. The snowfall was up to the extreme value during the recent century. Under this extreme climatic condition, the average thickness of the snow layer was more than 36 cm and the maximum depth of the snow was 49 cm, which was the highest record since 1904 in the Shenyang Area, China.

The snow samples were selectively collected on 7 March 2007 before restarting human activities on a large scale. The sampling sites for snow depositions were depicted in Fig.1. To find out the horizontal distribution of heavy metals distinctly, 17 locations were divided into 5 districts according to their major application function. They were commercial districts, industrial region, residential areas, park, and suburb. The Wuai Market (site 1), the Middle Street (site 2), and the Taiyuan Street (site 3) were the busiest emporium in Shenyang, so they belonged to the commercial district. Most of heavy industrial enterprises in Shenyang were centralized in the Tiexi District. Thus, 2 sites in the Tiexi District were selected as the representation of the industrial region, including the Shenyang Smelting Plant (site 4) and the Shenyang Cable Incorporated Company (site 5). In residential area, sampling sites were selected near the Northeast Road (site 6), the Huaihe Street (site 7), the Baogong Street (site 8), the Mukden Street (site 9), and the Youth Street (site 10). The Youth Park (site 11), the Laboring Park (site 12), and the North Mausoleum Park (site 13) were situated in the urban areas. Barrie *et al*. (1987) defined the "suburb" as an area outside urban centers but within populated regions. According to this definition, the 21 Century Square (site 14) and the International Horticultural Exposition Park (site 15) were the park that were constructed in the suburb. Furthermore, the Taoxian International Airport (site 16) and the Tonggou Village (site 17) in the suburb were also chosen as sampling sites and were compared with the urban sites.

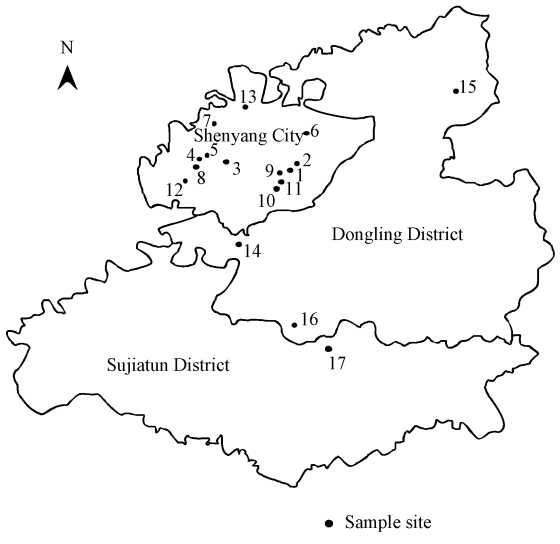

Fig. 1 Sketch showing the location of the sampling sites.

1.2 Sampling and analytical procedures

To provide a reliable data, proper precautions were taken to avoid sample contamination. The sampling sites were selected carefully to ensure that the snow samples were not trampled by people and automobiles. At each sampling site, two parallel samples were collected within a horizontal distance of 1.0 m. Snow samples were excavated using a stainless steel spade, and care was taken not to touch the ground lest the soil enters into the snow. In addition, the surface snow was not selected to decrease the contamination from the surrounding after the snowfall. Each snow sample was collected in a low density polyethylene (LDPE) bag and compressed by a piece of clean LDPE sheet (Walker *et al*., 2003). The bags were then tightly sealed to avoid evaporation or diffusion. Sample bags, the polytetrafluoroethylene sheet, and spade were all previously cleaned by rinsing in two hot washes of deionised water. The samples were kept frozen until analysis.

Snow samples were melted gradually at room temperature, and digested with a solution containing 87% concentrated HNO_3 and 13% concentrated $HClO_4$ (*V/V*). The concentrations of heavy metals in digested solution were determined using the atomic absorption spectrophotometric (WFX-120, China) method.

1.3 Statistical analysis

All measurements were performed in triplicate in independent experiments and the determination of heavy metals concentration was carried out with 2 parallel samples in all samples. The data from these experiments were statistically processed using the Microsoft Excel 2003, including calculation of average values and standard deviation. Data were presented as mean ± standard deviation.

2 Results and discussion

2.1 Horizontal distribution and levels of 4 heavy metals in snow

There was a big difference in the concentration of heavy metals in snow from various sites in the heavy industrial city. It can be seen that there were some resemblances in the horizontal distribution of As, Cd, and Pb in the sampled sites (Fig.2). A striking feature of the horizontal distribution was that the As, Cd, and Pb concentrations measured in the snow from the industrial region were extremely high, especially in the Shenyang Smelting Plant (site 4). It was found that the concentration of As, Cd, and Pb in the snow was high, reaching a maximum of

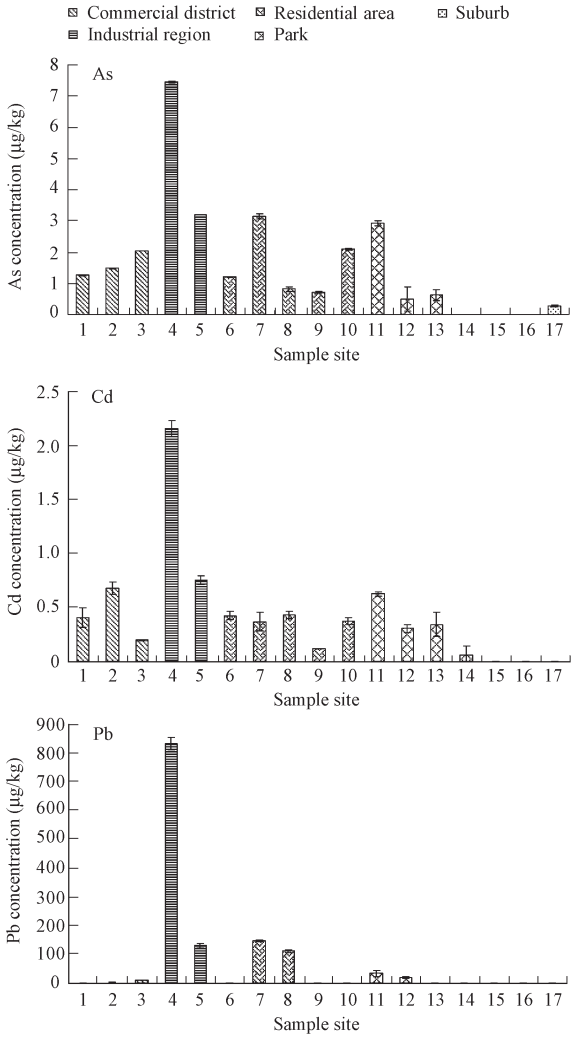

Fig. 2 As (a), Cd (b), and Pb (c) concentrations measured in fresh snow collected at various sites.

7.3, 2.2, and 850.0 μg/kg, respectively. In contrast, the concentrations of these three heavy metals were low and even can not detected in the suburb areas. Moreover, Cu was not detected in most of the collected snow samples except that in the industrial region. But, there was a big difference in the concentration of Cu in the snow between the two sites from the industrial region. The Cu concentration in site 4 was quite high, reaching up to 20.2 ± 7.1 μg/kg, and the concentration of Cu in the snow from site 5 was only 0.197 ± 0.066 μg/kg. Although most heavy metals in the snow from suburb areas were not detected, the metalloid As could be detected in the snow collected from the Tonggou Village (site 17) and its concentration was 0.5 μg/kg.

Among the parks, the snow collected in the urban parks contained higher concentrations of heavy metals than that in the suburb parks, especially the parks surrounded by the vital communication lines such as the Youth Park (site 11). It was found that the concentration of As, Cd, and Pb in the snow sampled from the Youth Park reached up to 3.0, 0.65, and 33.0 μg/kg, respectively. In the suburb parks, extremely low Cd concentration was detected only in the snow sampled from the 21 Century Square (site 14). Heavy metals were not detected in the snow sampled from the International Horticultural Exposition Park.

In the commercial district, there was no obvious difference in the concentration of As between the 3 sites. The snow that was sampled from the Taiyuan Street (site 3) contained the highest As concentration (2.0 μg/kg), and the lowest As concentration appeared in the snow that was sampled from the Wuai Market (site 1) (1.4 μg/kg). However, the concentration of Cd in the snow collected from the Middle Street site 2 was obviously higher than that from the other two sites. Noticeably, there was scarcely any Pb present in the commercial districts.

In residential area, the concentration of As in the snow collected near the Huaihe Street (site 7) and the Youth Street (site 10) was obviously higher than that collected at other 3 sites. The As concentration in the snow sampled near the Huaihe Street was high, up to 3.14 μg/kg, which was near to the As concentration in the snow that collected at the Shenyang Cable Incorporated Company. The concentration of Cd in all the snow samples collected from the residential areas was approximately 0.50 μg/kg, except that in the snow sampled near the Mukden Street (site 9) (0.12 μg/kg). Pb could be only detected in the snow collected near the Huaihe Street and the Baogong Street (sites 7 and 8) with concentrations which are lower than 200 μg/kg.

2.2 Influences of long-term industrial activities and wind direction

Industrial activities were one of the main routes to increase the concentration of heavy metals in the atmosphere (Kavouras *et al*., 2001; Mandal and Suzuki, 2002). Long-term industrial activities can make the particles of the aerosol with some heavy metals to be suspended in the atmosphere. In addition, heavy metals generated from industrial activities often remained in the soil. Soil particles subsequently entered into the atmosphere as dust. Both the aerosol and the dust can drop with the snow.

Shenyang was a famous heavy industrial city in China since 1930s. Thus, heavy metals including As, Cd, Pb, and Cu emitted from anthropogenic activities were mainly derived from industrial inputs, especially in the Tiexi District. The Tiexi District was a highly industrialized area in Shenyang with a potential and important heavy metal emission source such as industrial and incinerator emissions and smelting of metals. Lots of chimneys can be seen in the Tiexi District. The black smoke and unidentified gases escaped from the chimney continuously. However, it is a pity that there is no available information about the distribution of heavy metals in the air from this area.

In this experiment, it is found that the concentrations of the 4 heavy metals As, Cd, Pb, and Cu were extremely high in sites 4 and 5 situated in the Tiexi District, especially in site 4. The Shenyang Smelting Plant (site 4) was a large integrated smeltery, built in 1936 and moved in 2002. During the past 66 years, dangerous waste from this factory contained high concentrations of As, Cd, and Pb (Yu *et al*., 2005). Although the Shenyang Smelting Plant had stopped its industrial production, the heavy metal concentration was still high in the soil. The Cd,

Pb, and Cu concentrations in the soil were a maximum of 8.78, 1,051.8, and 1,672.0 μg/kg, respectively (Chao *et al*., 2007). Thus, one important reason for the high concentration of heavy metals was that little vegetation was well grown in and around the industrial region, and more soil granules with the heavy metals were blown to the atmosphere by wind.

Noticeably, Cu can be detected only in the industrial area, in particular, the concentration of Cu in the snow samples collected from the Shenyang Smelting Plant was as high as 20.2 μg/kg. This indicated that the primary environmental sources of Cu were a result of industrial activities, especially metal smelting.

Combined with various industrial activities, wind direction was an important influencing factor related to the horizontal distribution and levels of heavy metals in snow, in particular, when the snowstorm was caused by the cold air from the Lake Baikal. The wind force in that day reached a maximum of 8.0 (the Chinese rating system, corresponding to hurricane) or more, wind speed was 17.2–20.7 m/s, and the wind direction was northwest by north. The metallic granules in the atmosphere or the soil blew up and moved with the wind, thus, increasing the levels of the heavy metals in snow of the south part in the city to a certain extent. For example, Cd could be only detected in the snow samples which collected in the 21 Century Square (site 14) located in the south of the urban area. Moreover, Cd concentration in the snow sampled at site 9 was 0.11 μg/kg, much lower than that in site 10 (0.40 μg/kg). In addition, the Mukden Street (site 9) was located in the northeast of the Youth Park, whereas the Youth Street (site 10) was located in the south of the Youth Park. Thus, As concentration in the snow sampled at site 9 (0.72 μg/kg) was lower than that in the snow sampled at site 10 (2.1 μg/kg).

2.3 Influences of traffic activities and coal combustion

Rapid economic development had taken place in Shenyang in the past decades. Subsequently, the population increased rapidly, the business activity flourished, and the vehicles expanded strikingly. All this led to severe deterioration of the local environment.

Many significant parameters affected air pollution levels, especially in urban areas due to the large number and types of vehicles. Vehicular traffic was accepted as an important and increasing source of the atmospheric pollution (Colvile *et al*., 2001; Lonati *et al*., 2006). Pb was the most reliable indicator of traffic-induced (Lewis, 1985) pollution. The usage of Pb-containing petrol as the fuel for automobiles had been practiced in Shenyang for years. Although the Pb-free fuel was available on the market, Pb-containing gasoline still occupied the fuel market in Shenyang to a certain extent (Qiao and Zhang, 2003).

In the present work, the atmospheric quality influenced by the vehicular traffic can be known through the observation of Pb concentration in the snow in the residential area and the park. It is found that, except sites 4 and 5, Pb concentration was quite high in the snow sampled near the Huaihe Street and the Baogong Street (sites 7 and 8). Both these streets were important traffic roads in which lots of automobiles passed through everyday. Similarly, the Youth Park and the Laboring Park were both opening parks. Unlike other parks, these two parks were encircled by the busy traffic roads and high buildings. Large numbers of people and automobiles passed along the parks, especially at the rush hours. The gases released by the automobiles might be responsible for the high Pb in the snow sampled in the two parks. Thus, the Pb concentration at these four sites was high.

Moreover, coal combustion was also one of the main factors which influenced atmospheric quality. Because it contained nearly all elements. Coal combustion could result in an increasing release of trace metals into environment, for example, As and Cd were of great concern as potentially hazardous trace elements (Swaine *et al*., 1995). Some examples of drastic poisoning by As from domestic heating of high As coals are known from southwestern China (Ding *et al*., 2001). Coal combustion was the main contamination source of heat and power for Chinese northeasterners to weather through the winter. Thus, during winter the concentration of heavy metals in atmosphere was higher than that during other seasons (Yan and Du, 2007). It is, thus, unavoidable that the snow contains high concentration of heavy metals.

In this work, As and Cd were used as the fingerprints of coal combustion (Ölmez *et al*., 2004). The growth of human population had resulted in an increased demand of the coal for heat. Thus, the gases emitted by the coal combustion were overabundant in the impacted area. The Wuai Market, the Middle Street, and the Taiyuan Street were the biggest emporia in Shenyang. Many people served or did shopping in this area. These influencing factors could attribute to the detection of As and Cd in the snow of this area. Namely, As concentration was 1.4–2.1 μg/kg, and Cd concentration was 0.2–0.7 μg/kg in snow of the commercial district. Similar to the commercial district, there was a large population living in the residential areas and around the urban parks. Thus, As and Cd were both detected in these areas.

In Shenyang, the affected area was situated around the traffic artery. Thus, the dense population and frequent traffic activities, jointly, had influences on the atmospheric quality. In this work, for example, the snow sampled at the Youth Park and the residential area near the Huaihe Street was both influenced by the two factors, thus resulting in higher concentrations of As, Cd, and Pb than other samples in the same district.

2.4 Influences of agricultural activities

Scarcely any heavy metals had been detected in the snow sampled from the suburb area. Sparse population might be the main reason. Moreover, the terrain is flat and wide in this area, and the heavy metals can diffuse quickly into the atmosphere. Thus, the pollutants, such as heavy metals, hardly remained in this area. However, unlike Cd and Pb, As occurred in the snow sampled at the Tonggou Village. This might relate to the use of arsenical pesticides and herbicides.

In air, the adverse effect of As that absorbed on the particulate matters with organic species was not remarkable, but the use of As-containing pesticides or herbicides cannot be negligible (Davidson *et al*., 1985). China was the main producer of As-containing pesticides and herbicides. To date, a mass of As-containing pesticides or herbicides were used in agriculture, although the toxicity of As-containing pesticides or herbicides was known to human. Thus, As may accumulate in soil through use of As-containing pesticides and application of As-containing fertilizers. The concentration of As in the soil in the suburb areas of Shenyang was 8.6–13.8 mg/kg (Zhang, 2001). The soil granules containing As were blown to the atmosphere by powerful wind, and then dropped with the snow. This might be the main reason for As to be detected in the farmland in suburb area.

3 Conclusions

The concentrations of As, Cd, and Pb in the snow from the industrial regions were up to 7.3, 2.2, and 850.0 μg/kg, respectively. Conversely, most heavy metals in the snow from suburb areas could not be detected, except for the concentration of As in the snow collected from the Tonggou Village (0.5 μg/kg). Moreover, Cu was not detected in most of the collected snow samples except for the snow that collected at the Shenyang Smelting Plant and the Shenyang Cable Incorporated Company. The concentration of Cu in these 2 sites was 20.2 and 0.197 μg/kg, respectively. Among the parks, the snow collected in the urban parks contained higher concentrations of heavy metals than that in the suburb parks. There was no obvious difference in the concentration of As between the 3 sites in the commercial district. However, the concentration of Cd in the snow collected from the Middle Street was obviously higher than that from the other two sites. The snow sampled in the industrial region contained high concentrations of As, Cd, Pb, and Cu due to the long-term industrial activities, especially in the Shenyang Smelting Plant. In brief, human activities were the main environmental sources of the heavy metals, such as the long-term industrial activities, traffic activities, coal combustion, and agricultural activities. In addition, the horizontal distribution and levels of heavy metals in the big snowstorm in Shenyang can reflect and indicate the level of environmental pollution.

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