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Original Research

Size Distribution of Atmospheric Particulates and Pb Concentrations in TSP During the Cold-Weather Heating Period

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

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

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Abstract

We collected and analyzed atmospheric particulates in Changji, China, in order to investigate size distribution of atmospheric particulates and Pb concentrations in TSP during cold-weather heating periods. The results indicated that during such periods, contamination increased as particle size decreased. As compared with the non-heating period, the concentrations of atmospheric particulates were relatively higher during the heating period. The concentrations of TSP, PM_{10}, PM_5, and $PM_{2.5}$ had two peaks during this time. Coal combustion and meteorological variables – especially temperature – could be the main contributing factors. The size distribution of atmospheric particulates had certain regularity. The ratio of atmospheric particulates with size under 2.5 μm in TSP first increased and then decreased during the heating period. Atmospheric particulates with size between 2.5 to 5, 5 to 10, and 10 to 100 μm in TSP had the same change trend of first decreasing and then increasing. The change in the Pb trend was contrary to the temperature during the heating period, which may be caused by the fact that as temperature decreased, the intensity of coal combustion for heating increased, which emitted a lot of Pb. Conducting this study plays a significant role in prevention and control of atmospheric pollution and ecological environmental protection.

Keywords: cold-weather heating period, atmospheric particulates, size distribution, Pb

Introduction

The atmosphere is subjected to large inputs of contaminants in China [1-4]. As one of the atmospheric contaminants, atmospheric particulates have received considerable attention because of the health implications and effects of atmospheric particulates on global climate change [5]. The study about size distribution of atmospheric particulates is essential [6-8]. It provides information related to the concentration of particulates that can be retained in the different zones of the respiratory tract and, on the other hand, it contributes to knowledge on atmospheric particulate sources, formation, and growth

*e-mail: 824462939@qq.com

mechanisms [9]. Generally, particulates that can reach the different zones of the human respiratory tract are classified as: particulates larger than 10 μm in diameter, which are retained in the extrathoracic region; particulates smaller than 10 μm, which may pass into the tracheobronchial region; and particles smaller than 2.5 μm which can reach the alveoli and consequently the bloodstream, which may endanger human health [9]. The smaller the particulates, the greater the adverse effect. In recent years, the ratio of fine particulates in atmospheric particulates has increased [10].

Atmospheric particulates can carry toxic or hazardous pollutants such as heavy metals [11]. Some studies have established the fact that the accumulation of heavy metals in the body by inhalation or ingestion can be responsible for a wide range of health problems such as cancer, respiratory disease, and cardiovascular disease causing increased morbidity/mortality in populations [12]. Among heavy metals, Pb is a non-essential and toxic metal to plants, animals, and humans, and thus it is a kind of heavy metal that poses a risk to ecology and health. In recent years, with rapid industrialization and urbanization, a lot of Pb is put into the atmosphere, which has greatly increased the Pb burden in the environment in China, where Pb pollution has been recognized as a major problem [13, 14].

Heating processes using coal combustion make a sizable contribution to concentrations of atmospheric pollutants, so atmospheric pollutant characteristics during the heating period are very different from those during the non-heating period. In addition, due to the presence of different meteorological conditions (low temperature, prevailing wind, and a stable atmospheric structure) in winter, it is difficult for atmospheric pollutants to disperse, and it accumulates gradually, so that the characteristics of atmospheric pollutants during the heating period are different from that during the non-heating period [15, 16].

In this work, we discussed size distribution of atmospheric particulates and concentrations of Pb in TSP during the heating period in Changji.

Materials and Methods

Sampling Site Description

The study was carried out in Changji, China, (44.05 N, 87.31 E) which has a typical continental arid climate. The annual precipitation is only about 200 mm. Changji also has four distinct seasons, but winter is cold and long, and the period when living and work spaces need to be heated lasts six months. Due to western development, Changji has experienced a rapid increase in urbanization in recent years with increased emissions of pollutants and decreased air quality, and the urban ecological environment is facing unprecedented pressure. However, Changji is located approximately 100 km southeast of Manas, where the thermal power industry is major industry; therefore, air pollutants emitted in Manas can be transported to Changji when there is a prevailing northwest wind.

The sampling site was 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.

Sample Collection

In order to investigate the impact of heating on size distribution of atmospheric particulates and Pb concentration in TSP, monthly atmospheric particulate samples (including TSP, PM_{10}, PM_5, and $PM_{2.5}$) were continuously collected from October 2013 to September 2014. According to the heating period of Changji, the sample collection was conducted in two periods, including "heating period" from October 2013 to April 2014, and "non-heating period" from May 2014 to September 2014. The samples were collected unless it was raining, snowing, too dusty, and in other various conditions. After these abnormal days, sampling was also stopped for one day, because atmospheric particulate characteristics were affected by weather [15].

At least seven samples were collected every month. There were 49 samples for TSP, PM_{10}, PM_5, and $PM_{2.5}$ during the heating period and there were 35 samples for TSP, PM_{10}, PM_5, and $PM_{2.5}$ during the non-heating period. Atmospheric particulate samples were collected on the roof of No. 7 apartment approximately 12 m above ground level using a middle volume sampler (TH-150, Wuhan Tianhong, China) at approximately 0.1 m^3 min^{-1} through glass fiber filters (9-cm diameter, Wuhan Tianhong, China). In order to remove the water in the samples, the filters were put into dry dishes for 48 h and weighed before and after sampling.

Analytical Instruments

An atomic absorption spectrometer (AA-7000, SHIMADZU, JPN) was used for quantifying Pb. Measurements were made at a wavelength of 283.3 nm for Pb with a slit width of 0.7 nm.

Reagents and Standard Solution

Guaranteed reagent-grade chemicals and ultra-pure water were used for all procedures unless stated otherwise. Nitric acid (65-68%, Sichuan Xilong Chemical Industry, China) and perchloric acid (70-72%, Tianjin Zhengcheng Chemical Industry, China) were used for the digestion of TSP filter samples. Ultra-pure water was used for washing, diluting, and digesting. Pb calibration standards were prepared by diluting single element atomic absorption standard solutions (Shanghai Chemical Reagent Research Institute, China) containing 1mg mL^{-1} metal ion.

Extraction and Quantification of Pb in TSP

TSP sampling and control glass fiber filters were processed separately to extract the heavy metals by acid

digestion. The filter papers were cut into small pieces by using polyethylene scissors and placed in a breaker. Then, 2-mL perchloric acid and 18-mL nitric acid were added to the breaker. After a night of room temperature digestion, samples were further digested at 200ºC on a hot plate for 2 h. Then the suspensions were filtered, and the filtrates were diluted to a final volume of 100 mL with 0.5 M nitric acid prior to analysis.

The quantitative analysis of Pb was performed using an atomic absorption spectrometer. For quality assurance and quality control of Pb, GSS-3 (National Standard Substances Center) was measured and the measured values were in good agreement with the certified values (the recoveries were between 90% and 110%). The relative standard deviation (RSD) in the concentration of Pb measured using the prepared standard solution was less

Fig. 1. Map of the study area (44°05′N, 87°31′E).

than 5%. Each sample was measured at least two times to obtain the concentration values of Pb. The detection limit of the atomic absorption spectrometer for Pb was 0.05 μg L^{-1}. The average Pb value in the blank glass fiber filters was 0.23 μg m^{-3}.

The whole process of the experiment was carried out in a laboratory with air cleanliness of 1,000 grade.

Results and Discussion

Variation of Atmospheric Particulate Concentrations during the Heating Period

The average daily concentrations of collected atmospheric particulates were 282.54 (81.25-1254.86) μg m^{-3}, 244.04 (61.11-968.75) μg m^{-3}, 201.24 (50.00-654.17) μg m^{-3}, and 162.31 (36.11-611.81) μg m^{-3} for TSP, PM_{10}, PM_5, and $PM_{2.5}$, respectively, during the heating period. According to National Ambient Air Quality Standards (GB 3095-2012) made by the Chinese Ministry of Environmental Protection, the national daily average concentration limits were 300 μg m^{-3}, 150 μg m^{-3}, and 75 μg m^{-3} for TSP, PM_{10}, and $PM_{2.5}$, respectively [17]. The number of days up to the standards account for 64.29, 26.79, and 16.07 percent of the whole heating period for TSP, PM_{10}, and $PM_{2.5}$, respectively. The average daily concentrations of atmospheric particulates during the heating period were higher compared to the non-heating period (Table 1).

The variation trends of daily concentrations of TSP, PM_{10}, PM_5, and $PM_{2.5}$ had two peaks, respectively, during the heating period (Fig. 2). Emissions from coal combustion and favorable meteorological conditions such as humidity caused the concentrations of atmospheric particulates to reach the first peaks in January [18]. In April, the concentrations of atmospheric particulates reached the second peak. However, except for TSP, the concentrations of PM_{10}, PM_5, and $PM_{2.5}$ in April were lower, as compared to those in January. Some studies have reported that the primary atmospheric particulates from emissions of coal combustion was fine particulate [19]. In April, the intensity of heating by coal combustion decreased, which led to a decreased amount of fine particulate. In addition, in the early spring the vegetation coverage was low and windy conditions and sandstorms were frequent in Changji, which resulted in an increase of big size particulates, which explains the characteristics of concentrations of atmospheric particulates in April.

Characteristics of Size Distribution of Atmospheric Particulates during the Heating Period

Atmospheric particulates (Sap) were divided into four categories according to size: Sap≤2.5 μm, 2.5 μm<Sap≤5 μm, 5 μm<Sap≤10 μm, and 10 μm<Sap≤100 μm, and we discussed the size distribution of atmospheric particulates during the heating period.

For atmospheric particulates with Sap≤2.5 μm: their average ratio in TSP was 59.40% during the heating period. In detail, their ratio in TSP was 47.49% in October, which increased to 52.81% in November, and then increased to 66.86% in December. Their ratio in TSP reached maximum (81.83%) in January. Afterward, their ratio in TSP decrease to 68.91%, 69.62%, and 34.97% for February, March, and April, respectively (Fig. 3).

For atmospheric particulates with 5 μm<Sap≤10 μm, their average ratio in TSP was 14.59% during the heating period. In detail, their ratio in TSP was 21.79% in October, decreasing to 19.37% in November and then 11.82% in December. Their ratio in TSP reached the minimum (5.79%) in January. Afterward, their ratio in TSP began to increase to 6.89%, 9.99%, and 23.89% for February, March, and April, respectively (Fig. 3).

For atmospheric particulates with 10 μm<Sap≤100 μm, their average ratio in TSP was 13.99% during the heating period. In detail, their ratio in TSP was 15.43% in October and started to decrease to 10.45% in November. In December, the change of the ratio in TSP was small and reached minimum (7.97%) in January. Afterward, their ratio began to increase to 13.04%, 14.09%, and 23.04% for February, March, and April, respectively (Fig. 3).

Compared with the non-heating period, the average concentrations of atmospheric particulates with Sap≤2.5 μm increased, but average concentrations of atmospheric particulates with 2.5 μm<Sap≤5 μm, 5 μm<Sap≤10 μm, and 10 μm< Sap≤100 μm slightly decreased during the heating period (Table 1).

Table 1. Comparison of concentrations of atmospheric particulates during the heating and non-heating period.

Time	TSP Ave[a]±SD[b] (μg m^{-3})	PM_{10} Ave[a]±SD[b] (μg m^{-3})	PM_5 Ave[a]±SD[b] (μg m^{-3})	$PM_{2.5}$ Ave[a]±SD[b] (μg m^{-3})
Heating period (n=49)	282.54±214.32	244.04±181.88	201.24±148.58	162.31±127.13
Non-heating period (n=35)	221.43±80.42	177.24±69.23	133.17±61.31	89.74±45.24
National Ambient Air Quality Standards[c]	300	150	_	75

T test for atmospheric particulates during the heating period and non-heating period were carried out. The results indicated that the values of P were less than 0.05.

[a] Average concentration

[b] Standard deviation

[c] Provided by Ministry of Environmental Protection of the People's Republic of China and General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China.

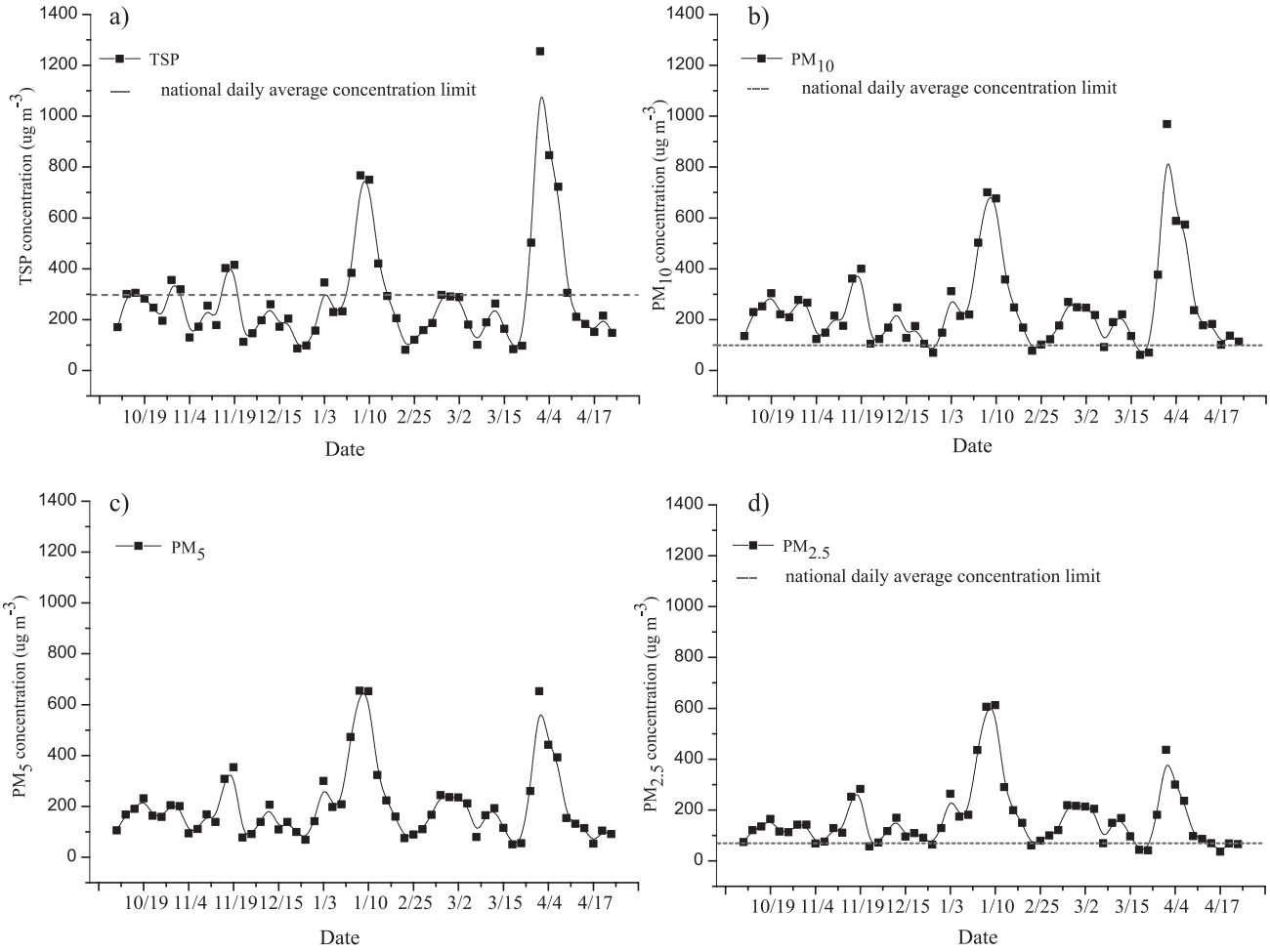

Fig. 2. Variation of atmospheric particulate concentrations during the heating period: a) TSP, b) PM_{10}, c) PM_5, d) $PM_{2.5}$

During the heating period, TSP mainly consisted of $PM_{2.5}$ and the increase of TSP was dominated by the increase of $PM_{2.5}$, which demonstrated that the primary atmospheric particulate from coal combustion for heating in winter was $PM_{2.5}$. The size distribution of atmospheric particulates had a certain regularity. The ratio of atmospheric particulates with Sap≤2.5 μm in TSP first increased and then decreased during the heating period. For atmospheric particulates with 2.5 μm<Sap≤5 μm, 5 μm<Sap≤10 μm, and 10 μm<Sap≤100 μm, they had same

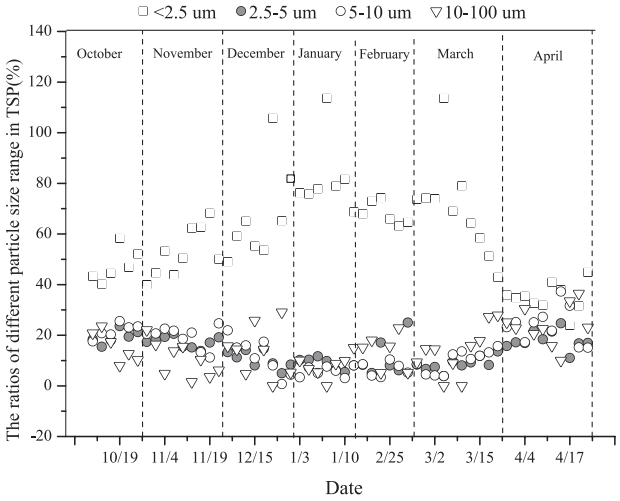

Fig. 3. Characteristics of size distribution of atmospheric particulates during the heating period.

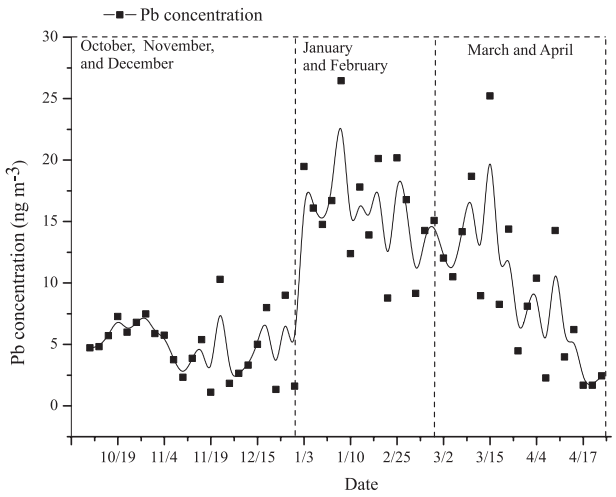

Fig. 4. Variations in Pb concentrations in TSP during the heating period.

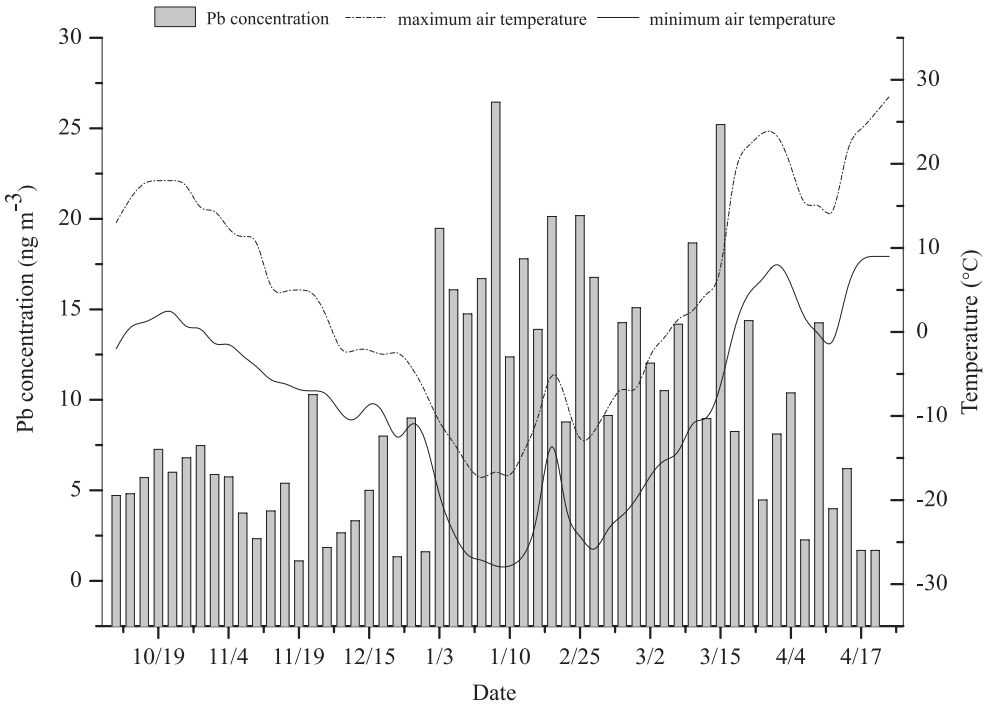

Fig. 5. Relationship between Pb concentrations and temperature during the heating period.

change trend that first decreased and then increased. The ratios of four categories in TSP reached their maximum in January.

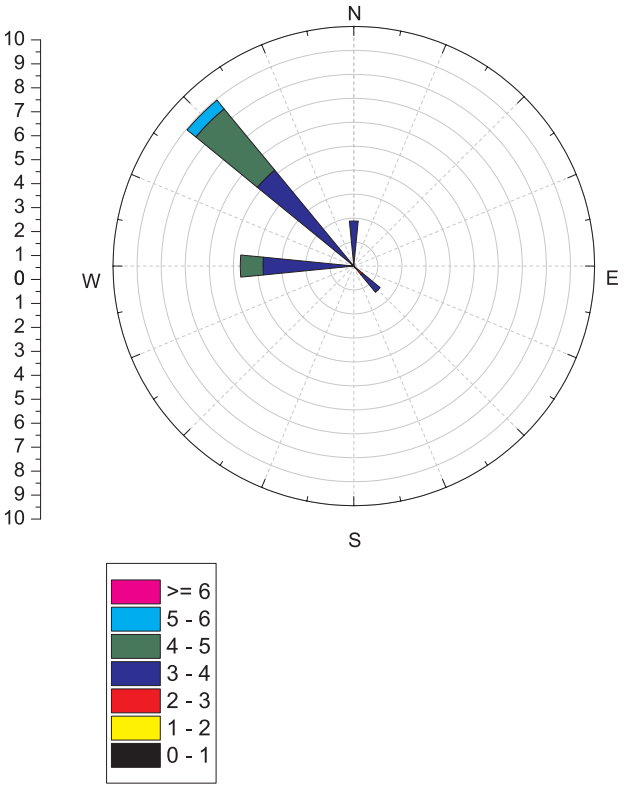

Fig. 6. Changji wind rose diagram during the heating period (October 2013 to April 2014).

Pb Concentration in TSP and Its Influence Mechanism during the Heating Period

The average daily concentration of Pb in TSP was 9.35 ng m^{-3} during the heating period. The maximum daily concentration of Pb in TSP appeared on 10 January 2014 at 26.44 ng m^{-3}, and the minimum daily concentration of Pb in TSP appeared on 19 November 2013 at 1.11ng m^{-3}. The average daily concentration of Pb in TSP was 3.25 ng m^{-3} during the non-heating period. The average daily concentration of Pb in TSP during the heating period was about 1.5 times higher compared to the non-heating period.

During the heating period, a variation of Pb concentrations in TSP had obvious regularity – first increasing and then decreasing. In detail, Pb concentrations in TSP started to increase in a wave at the beginning of the heating period (October), reached the maximum between January and February, and then began to decrease in a wave. At the end of April, the Pb concentration in TSP was restored to its original level before the heating period (Fig. 4).

We investigated the relationship between variation tendency of Pb concentrations in TSP and temperature during the heating period. The results indicated that variation tendency of Pb concentrations in TSP and temperature during the heating period were opposite (Fig. 5). Some studies have identified that coal contained Pb [20, 21]. In Changji, the winter was cold and long, causing a long heating period during which heating relied mainly on coal combustion. In the whole heating period, with temperature decreasing, the intensity of heating was enhanced, which led to more Pb being emitted from

coal combustion being put into the atmosphere. The result also showed that coal combustion was the main air pollution source of Pb in the northern city of China during the heating period [22]. Recently, the average daily concentration of Pb in TSP was low during the heating period in Changji [23]. However, with urban sprawl, the amount of coal combustion for heating will increase and pollution of Pb in the atmosphere is not optimistic.

Furthermore, the winter prevailing wind was northwest in Changji. Therefore, Pb emitted in Manas can be transported to Changji when there is prevailing northwest wind, which may be one reason for increasing Pb concentrations in TSP during the heating period in Changji (Fig. 6).

Conclusions

1. During the heating period, as particle size decreased contamination was aggravated. Compared with the non-heating period, the average daily concentrations of atmospheric particulates were relatively higher during the heating period. The concentrations of TSP, PM_{10}, PM_5, and $PM_{2.5}$ had two peaks during the heating period.
2. The size distribution of atmospheric particulates had certain regularity during the heating period. The ratio of atmospheric particulates with size under 2.5 μm in TSP first increased and then decreased during the heating period. For atmospheric particulates with size between 2.5 to 5, 5 to 10, and 10 to 100 μm they showed the same change trend of first decreasing and then increasing.
3. The average daily concentration of Pb in TSP during the heating period was about 1.5 times higher compared to the non-heating period. During the heating period, the concentration of Pb in TSP first increased and then decreased, and the change trend of Pb concentration in TSP was contrary to the temperature.

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