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Heavy Metal Concentration in PM2.5 from Firework Displays is a Major Factor of Atmospheric Pollution during Spring Festival in Chengdu, China

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Abstract

Firework displays have been reported to dramatically increase atmospheric pollution during the annual Spring Festival in Chengdu, China. It is unclear, however, whether the atmospheric pollution caused by the displays is associated with specific heavy metal elements. To investigate the matter of firework induced atmospheric pollution during Spring Festival in Chengdu in 2017. We determined the major measurement factors of air quality include PM10, PM2.5, PM1.0, meteorological phenomena, and heavy metal elements with the conditions and characteristics of atmospheric pollution. All data was measured under atmospheric quality monitoring and quality control in accordance with the relevant standard of China. On the one hand, we observed the first heavy atmospheric pollutions were impacted by unfavorable meteorological conditions which led to constant generation and accumulation of PM1.0, and an increased concentration of PM2.5. The maximum value of concentration of PM10, PM2.5 and PM1.0 was 302 μg/m3, 222 μg/m3 and 131 μg/m3 respectively. On the other hand, we measured the maximum value of concentration of PM10, PM2.5 and PM1.0 as 408 μg/m3, 275 μg/m3 and 191 μg/m3, respectively during the second heavy atmospheric pollution. We found that while the concentration of PM2.5 was decreased to 78μg/m3, the heavy metal elements in PM2.5 also declined to 10.6 μg/m3, which was almost the same as the concentration of heavy metal elements before the displays. Moreover, the concentrations of heavy metal elements K, Ca, Cu and Ba were obviously changed in different weather conditions. We observed that the concentrations of K, Ca, Cu and Ba can be decreased to a large extent in the transition from pollution to cleaners, suggesting that the concentration of heavy metal elements in PM2.5 was significantly increased by fireworks during Spring Festival in Chengdu, China. Taken together, firework displays were a major factor of atmospheric pollution, causing the concentration of heavy metal elements in PM10, PM2.5 and PM1.0 to dramatically increase during Spring Festival in Chengdu, China.

Keywords: Atmospheric pollution; PM2.5; Heavy metal elements; Spring Festival

Introduction

Heavy metal *pollution is* a serious environmental danger because of its direct effect *on* ecosystems and human health [1]. PM2.5 is a complex mixture of extremely small particles (having a diameter of no more than 2.5 μm) and liquid droplets composed of multiple heavy metal components which causes serious harm to human health [2]. A number of studies have shown that heavy metal pollutants are the major component of the atmospheric aerosol system, and that these metals can enter the atmosphere from different sources such as industrial and agricultural activities [3,4]. PM2.5 contains high concentrations of heavy metal elements, such as chromium (Cr), cadmium (Cd), titanium (Ti), manganese (Mn), nickel (Ni), lead (Pb), arsenic (As), zinc (Zn), etc., [5]. If these heavy metal elements, incorporated with atmospheric PM2.5, enter the human vascular or respiratory system, then the probability of developing cancer, malformation and mutation will be increased [6].

The Lunar New Year's Eve and Spring Festival are two of the most important events in China every year. Many cities celebrate these events by setting off firework displays to ward off bad luck. Although firework displays have been gradually prohibited in most urban areas, the influence of traditional fireworks still exists. During the Lunar New Year's eve and Spring Festival, the air quality is often greatly worsened and the probability of haze days occurring is also increased substantially. Many studies on PM2.5 have been studied in China are focused on emissions from traffic and industry in megacities and developed economic areas [7-9]. However, pollution caused by heavy metals in PM2.5 emitted during firework displays during Spring Festival in China has rarely been reported.

The objectives of this study were:

To investigate characteristics of atmospheric particulate matters on meteorological change;

To investigate characteristics of change in indicative metal elements of fireworks in PM2.5 and

To identify how heavy metal elements affect human health during Spring Festival in Chengdu, China in 2017.

Materials and Methods

Measurement of the area and site

The city of Chengdu is located west of Sichuan Basin, bordered by Longmen Mountain and Qionglai Mountain, sitting on the transition zone between Chengdu Plain and the Hilly area of Central Sichuan Basin and covering an area of 12121 km^2. Monitoring equipment was installed at the roof of the seven-storey Huanbao Building, No.8, Fanglin Road, Qingyang District, Chengdu (Coordinates: 30.66°N,

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104.04°E), surrounded by a park, residential area and commercial area, as shown in Figure 1.

The monitoring site has typical urban characteristics, with a well-developed transportation system and a dense population. However, there is no obvious local source of pollutant emission. The site is a year-round observation site of Chengdu Municipal Environmental Protection Bureau for multi-parameter online comprehensive observation. It can well reflect the ambient air quality level of Chengdu.

Monitoring and data quality control

Monitoring method

The monitoring on particulate matters was carried out strictly in accordance with Technical Specifications and Test Procedures of Continuous Automated Monitoring System for Ambient Air Particulate Matters (PM10 and PM2.5) (HJ 653-2013) issued by the Ministry of Environmental Protection. China has lagged behind in promulgating the atmospheric environmental protection standards on heavy metal elements in ambient air. In this study, the monitoring on heavy metal elements in ambient air was conducted in pursuance of USEPA 103.3, the U.S. determination of metals in ambient particulate matters. The X-ray Fluorescence (XRF) Spectroscopy was adopted to monitor the amount of heavy metals in PM2.5 of ambient air. Refer to Literature 7 for the analysis and test standards on heavy metal elements in effect [10].

Monitoring equipment

In this study, METONE BAM 1020, the U.S. online particulate matter monitor with dynamic intelligent heating device, was adopted for PM2.5 monitoring. The principle of measurement was beta absorption, the sampling flow rate was 16.7 L/min, the measurement range was 0~1000 μg/m^3 and the precision was 8 μg/m^3. Thermo Fisher TEOM 1405, the U.S. thermoelectric monitor on atmospheric particulate matters was adopted for PM1.0 monitoring. The principle of measurement of TEOM, i.e. PM1.0 in ambient air was pulled into the equipment through the sample cutter at a constant flow rate and then the mass concentration of PM1.0 was measured on the basis of FDMS and TEOM. The main flow rate was 3 L/min, the bypass flow rate was 13.67 L/min, the measurement range was 0-1000 μg/m^3 and the precision was ± 2.0 μg/m^3 (1-hour average) and ± 1.0 μg/m^3 (24-hour average). Metal elements were monitored by using the online monitor on heavy metal elements Xact™ 625 of U.S. Cooper Environmental Services LLC (CES) (whose business has been acquired by Hebei Sailhero Environmental Protection Hi-tech Co., Ltd.). The principle was EDXRF and the sample flow rate was 16.7 L/min. With the function of temperature and humidity correction and quality tracking control that met the relevant standards of U.S. NIST, the monitor could be used to measure 23 heavy metal elements including Cr, Mn, V, Fe, Cu, Zn, Ag, Ni, Cd, Sn, Ba, Hg and Pb with the precision of 10 ng/m^3. Refer to Literature 8 for the measurement principle of beta absorption and EDXRF [11,12].

Figure 1: Surroundings of observation site.

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Data Quality Control

In this study, the data quality control was carried out strictly in accordance with Ambient Air Quality Standards (GB3095-2012). Sampling was conducted for at least 45 minutes per hour. The average concentration value of no less than 20 hours was measured per day. Otherwise, the data was regarded invalid. In this study, 86 groups of hourly valid data on PM2.5 and heavy metal elements (23) were acquired through data quality control. The aforementioned data was measured from 11:00 on January 26, 2017 to 23:00 on January 29, 2017.

Heavy metal element online monitor Xact^{TM} 625 stably ran during the observation as shown in Figure 2. The sample flow rate was maintained at 16.7 ± 0.4 L/Min, the temperature of the x-ray tube was kept at 35 ± 0.5°C and the tape pressure was constantly at 560 ± 40 mmHg when the sample was collected, which satisfied the requirement for sample collection and analysis.

Results and Discussion

Characteristics of atmospheric particulate matters on meteorological change

The Eve of the Lunar New Year and Spring Festival are celebrated traditional Chinese festivals. Firework displays are a thousand-year-old tradition to celebrate Chinese New Year. The Lunar New Year's Eve in 2017 was from January 27, 2017 to January 28, 2017. Most of the firework displays occurred at night on January 27, 2017 and in the early morning on January 28, 2017. This study analyzed the hour-by-hour data on particulate matter from January 26, 2017 to January 29, 2017, such as the data on PM10, PM2.5 and PM1.0 and meteorological conditions including extinction coefficient, temperature, humidity, wind speed, wind direction and precipitation.

Chengdu suffered from PM10 and PM2.5 pollution since January 26, 2017. From the Lunar New Year's Eve (January 27, 2017) to Spring Festival, the concentration of PM10 and PM2.5 was further increased to a large extent. It can be found, based on laser radar, that the boundary-layer height in the process of the two pollution events was around 1km. The change in the extinction coefficient also clearly reflects the occurrence and disappearance of the two pollution events, as shown in Figure 3.

Two heavy pollution events occurred in Chengdu around Spring Festival and there was little precipitation during that period. The first heavy pollution occurred at night on January 26, 2017 and in the early morning on January 27, 2017. In the aforementioned two days, the maximum temperature was 12°C, occurring at 16:00 on January 26, 2017. As night fell, the temperature regularly decreased while the humidity regularly increased, which was favorable for the generation and increase of the aerosol condensation nucleus. The heavy pollution occurred basically under calm wind condition, which was unfavorable to atmospheric diffusion. The concentration of PM10 and PM2.5 reached a peak at 1:00 on January 27, 2017. The maximum value of concentration of PM10, PM2.5 and PM1.0 was 302 μg/m^3, 222 μg/m^3 and 131 μg/m^3, respectively (Figure 4).

The second heavy pollution occurred from the night of the Lunar New Year's Eve to Spring Festival. The temperature and humidity were at the same level as those of the previous heavy pollution. However, there was a wind field with a maximum wind speed of 2.79 m/s. Nevertheless, under the influence of cultural tradition, firework displays were set off in scattered amounts for a long time so that the maximum value of the particulate matter concentration was much higher than that in the previous pollution. The concentration of PM10 and PM2.5 reached a peak at 7:00 on January 28, 2017. The maximum value of concentration of PM10, PM2.5 and PM1.0 was 408 μg/m^3, 275 μg/m^3 and 191 μg/m^3 respectively. During the two pollution events, there was a large proportion of PM1.0, which shows that the newly generated particulate matter was very active.

After 7:00 on January 28, 2017, the sun regularly rose and the firework displays stopped so that the concentration of particulate

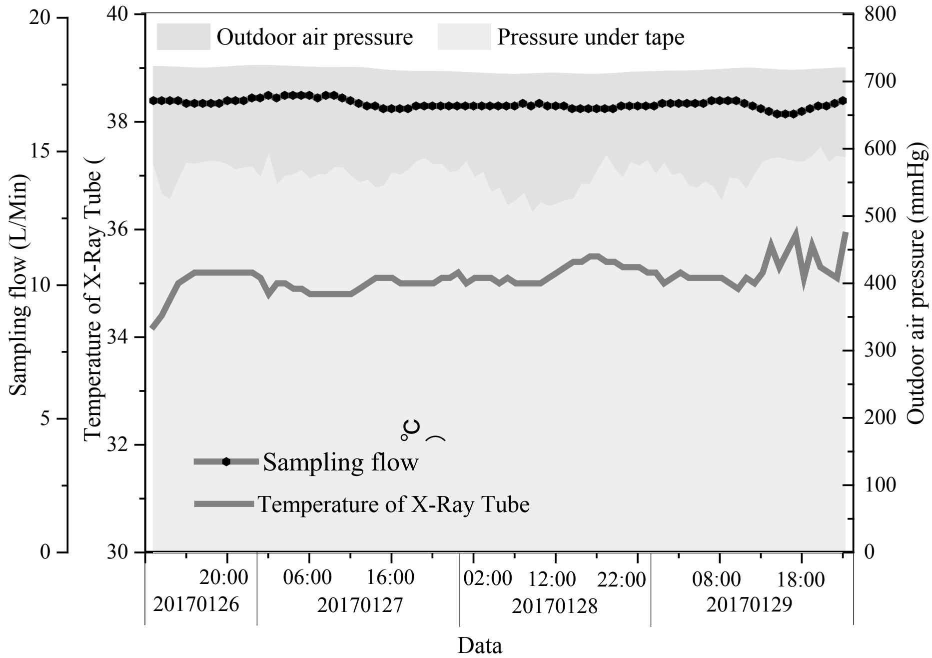

Figure 2: Status of running stability of equipment for observing heavy metal elements in atmospheric PM2.5.

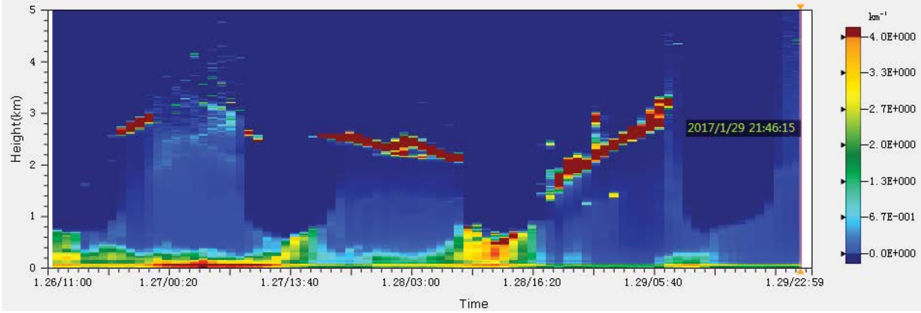

Figure 3: Time-varying extinction coefficient of Laser Radar.

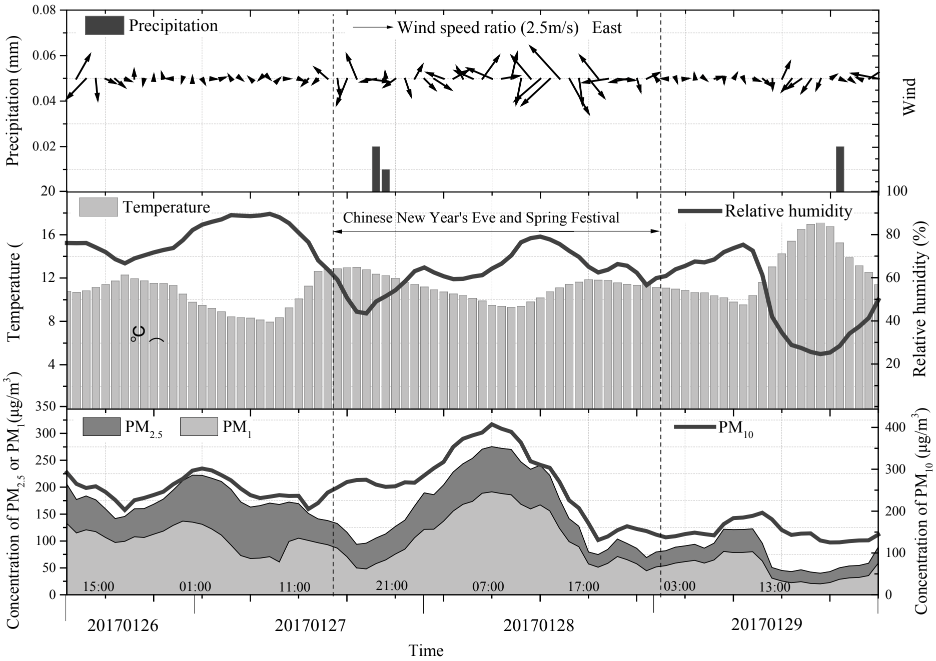

Figure 4: Characteristics of atmospheric particulate matters (PM10, PM2.5 and PM1.0) and change in meteorological conditions during the lunar New Year's Eve and spring festival in Chengdu in 2017.

matter was regularly declined until it reached the level of cleanness. Subsequently, the temperature grew to a certain extent and reached 16℃ at 16:00 on January 29, 2017, while the relative humidity substantially decreased to 20 % and the concentration of particulate matter further declined. The minimum value of concentration of PM10, PM2.5 and PM1.0 was 125 μg/m³, 40 μg/m³, and 20 μg/m³, respectively.

Characteristics of change in indicative metal elements of fireworks in $PM_{2.5}$

Characteristics of concentration level

Under the influence of Chinese tradition, firework displays are widespread. The major raw material of fireworks is black powder. When it explodes, a great amount of dust, heat and light can suddenly be emitted. Different metallic vapors have different kinds of spectrums. Fireworks often contain pyrotechnic stars to make the display more colorful. For example, the metals that contain Sr such as $SrCO_3$ or the ore that contains Ca are used as pyrotechnic stars of red light in red spectrum. $BaCl_2$ and Ba $(NO_3)_2$, etc. are often used as pyrotechnic stars of green-and-yellow light in green spectrum. $CuCO_3$, malachite green or the ore that contains impurities with Co are used as pyrotechnic stars in blue-and-green spectrum. Those metallic salts will undergo instant pyrolysis as fireworks explode. Accordingly, the colorful spectrum will be generated. Due to the aforementioned substances added to fireworks, the concentration of PM2.5 in the atmosphere rises sharply. During the peak period of firework displays in Spring Festival, the concentration of PM2.5 and the heavy metal elements therein increased to different degrees, as shown in Table 1.

In the week preceding Spring Festival, there were two heavy pollution events and one transition from heavy pollution to cleanness. Table 1 shows that in the process of the first heavy pollution (from 11:00 on January 26, 2017 to 17:00 on January 27, 2017), the average value of concentration of PM2.5 reached 170 μg/m³ and the concentration of heavy metal elements in PM2.5 was 10.8 μg/m³. There were not any firework displays in the aforesaid process. In the process of the second heavy pollution (from 18:00 on January 27, 2017 to 18:00 on January 28, 2017), the traditional the Lunar New Year's Eve and Spring Festival of China, there were widespread firework displays in the urban area and the peripheral area. The average value of concentration of PM2.5 soared to 187 μg/m³ and the concentration of heavy metal elements in

Air pollution process	Time (2017)	PM2.5		Concentration of heavy metal elements in PM2.5		Remarks
		Range	Average value	Range	Average value	
The first heavy pollution process	01/26, 11:00-01/27, 17:00	94-222	170	9.2-13.3	10.8	No fireworks and firecrackers
The second heavy pollution process	01/27, 18:00-01/28, 18:00	74-275	187	10.5-44.7	24.1	Fireworks and firecrackers
The cleaning process	01/28, 19:00-01/29 23:00	40-122	78	9.0-12.4	10.6	No fireworks and firecrackers

Table 1: Change in concentration of PM2.5 and the heavy metal elements there in different kinds of atmospheric pollution process.

Air pollution process	K		Ca		Cu		Ba	
	Range	Average value	Range	Average value	Range	Average value	Range	Average value
The first heavy pollution process	2734.0-6483.0	3891.0	74.7-2135.0	333.8	26.8-85.1	43.1	68.2-214.5	118
The second heavy pollution process	2390.0-31576.0	14464.7	235.8-2202.0	1042.1	23.0-547.0	199.3	126.2-2729	1137.1
The cleaning process	1467.0-5033.0	3205.6	367.7-1208.0	730.6	19.5-89.1	40.2	100.7-324.6	214.3

Table 2: Change in concentration of indicative elements of fireworks in PM2.5 in the process of different atmospheric pollution events (ng/m^3).

PM2.5 reached 24.1 μg/m^3. In the subsequent transition from heavy pollution to cleanness, the concentration of PM2.5 decreased to 78 μg/m^3 and that of the heavy metal elements in PM2.5 declined to 10.6 μg/m^3, which was almost the same as the atmospheric concentration of heavy metal elements before the firework displays. This indicates that the increase in concentration of the heavy metal elements in PM2.5 during Spring Festival was totally caused by firework displays.

In the process of the two heavy pollution events and one transition herein, the resulting pollution from firework displays was obviously varied. The concentration of heavy metal elements such as K, Ca, Cu and Ba grew the most. The change in their concentration is shown in Table 2.

Table 2 shows that in the process of the second heavy pollution, the concentration of the heavy metal elements K, Ca, Cu and Ba in PM2.5 was higher than the first heavy pollution. In the process of the first heavy pollution, the average value of concentration of K, Ca, Cu and Ba was 3891.0 ng/m^3, 333.8 ng/m^3, 43.1 ng/m^3 and 118.0 ng/m^3, respectively. However, during Spring Festival (in the process of the second heavy pollution), the average value of concentration of K, Ca, Cu and Ba soared to 14464.7 ng/m^3, 1042.1 ng/m^3, 199.3 ng/m^3 and 1137.1 ng/m^3, respectively. It is clear that firework displays can cause severe atmospheric pollution. Subsequently, due to the change in meteorological conditions at the end of firework displays, the concentration of K and Cu dropped but the concentration of Ca and Ba rose to some extent. On the one hand, the traditional relative-and-friend visit caused road dust to increase the concentration of Ca and Ba. On the other hand, differences exist in the time required for different kinds of metallic salts.

Characteristics of time series

To further analyze the change in concentration of the indicative elements of fireworks in PM2.5 in the process of the aforementioned heavy pollution and transition, a graph on the time-series change in the concentration of K, Ca, Cu and Ba is drawn, as shown in Figure 5.

As shown in Figure 5, around Spring Festival in 2017 in Chengdu, China, there was an obvious time-series variation in the concentration of the indicative elements of fireworks: K, Ca, Cu and Ba in PM2.5. Beginning 16:00 on January 27, 2017, there was no obvious variation in the concentration of K, Cu and Ba, but the concentration of Ca rose sharply, which was connected with the increase in road dust that was caused by the migration of urban residents who went back to their hometown to celebrate the Lunar New Year. At 23:00, the concentration of Ca declined a little. As night fell, firework displays started at night on the Lunar New Year's eve and Spring Festival started at 00:00 on January 28, 2017, so the concentration of the indicative elements of fireworks K, Ca, Cu and Ba surged. At dawn on January 28, 2017 (around 6:00), the concentration of K, Ca, Cu and Ba reached a peak at the same time. However, at 18:00, it dropped to the same level as that before January 27, 2017. Because of the nationwide Spring Festival holiday, industrial activities were reduced to the minimum, so the concentration of K, Ca, Cu and Ba started to surge at night and dropped after several hours. This indicates that the tradition of firework displays has a huge influence on the air quality. The constant increase in the concentration of Ca from 8:00 on January 29, 2017 reflects the impact of road dust caused by the traditional relative-and-friend visit beginning on the second day of Spring Festival.

Conclusions

In this study, we observed two heavy pollution events and one transition from heavy pollution to cleanness occurring around Spring Festival in Chengdu in 2017. The first heavy pollution was impacted by unfavorable meteorological conditions, which resulted in the constant generation and accumulation of PM1.0 and the further increase in the concentration of PM2.5. The second heavy pollution was determined to be caused by the firework displays. In addition, there was obvious variation in the concentration of heavy metal elements in PM2.5 during the two heavy pollution events. In the transition from heavy pollution to cleanness, the concentration of PM2.5 was decreased to 78 μg/m^3 and that of the heavy metal elements in PM2.5 was declined to 10.6 μg/m^3, which was nearly the same as the concentration of heavy metal elements before the firework displays. Therefore, the concentration of the indicative heavy metal elements of fireworks K, Ca, Cu and Ba was obviously varied in different weather processes.

Our data has shown that firework displays can lead to atmospheric pollution in a short time, which is a major cause of the heavy atmospheric pollution in Chengdu during Spring Festival in 2017. The regulation of firework displays in Chengdu is not strict enough. We shall appeal for decreasing the number of firework displays in festivals to improve air quality. The data suggested that the relevant governmental department should work on reduction of atmospheric pollution by conducting the corresponding research and development for improving the manufacturing technique of traditional fireworks. Further, the substitute of fireworks should be used so that the health hazards caused by atmospheric pollution will be reduced and people's desire to celebrate festivals will still be satisfied.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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