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Chemical characteristics and source apportionment of atmospheric particles during heating period in Harbin, China

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ABSTRACT

Atmospheric particles (total suspended particles (TSPs); particulate matter (PM) with particle size below 10 μm, PM_{10}; particulate matter with particle size below 2.5 μm, $PM_{2.5}$) were collected and analyzed during heating and non-heating periods in Harbin. The sources of PM_{10} and $PM_{2.5}$ were identified by the chemical mass balance (CMB) receptor model. Results indicated that $PM_{2.5}$/TSP was the most prevalent and $PM_{2.5}$ was the main component of PM_{10}, while the presence of PM_{10-100} was relatively weak. SO_4^{2-} and NO_3^- concentrations were more significant than other ions during the heating period. As compared with the non-heating period, Mn, Ni, Pb, S, Si, Ti, Zn, As, Ba, Cd, Cr, Fe and K were relatively higher during the heating period. In particular, Mn, Ni, S, Si, Ti, Zn and As in $PM_{2.5}$ were obviously higher during the heating period. Organic carbon (OC) in the heating period was 2–5 times higher than in the non-heating period. Elemental carbon (EC) did not change much. OC/EC ratios were 8–11 during the heating period, which was much higher than in other Chinese cities (OC/EC: 4–6). Results from the CMB indicated that 11 pollution sources were identified, of which traffic, coal combustion, secondary sulfate, secondary nitrate, and secondary organic carbon made the greatest contribution. Before the heating period, dust and petrochemical industry made a larger contribution. In the heating period, coal combustion and secondary sulfate were higher. After the heating period, dust and petrochemical industry were higher. Some hazardous components in $PM_{2.5}$ were higher than in PM_{10}, because $PM_{2.5}$ has a higher ability to absorb toxic substances. Thus $PM_{2.5}$ pollution is more significant regarding human health effects in the heating period.

Introduction

Atmospheric particulate pollution is becoming more and more serious. Many countries and cities have experienced serious ash haze and fog haze weather. This has a significant influence on the urban atmospheric environment and human health, which has received increasing attention in many countries (Godec et al., 2012; Hansen et al., 2010; Kleeman et al., 2009; Tiwari et al., 2012).

Fuel combustion is an important source of atmospheric particulates. Heating processes using coal combustion make a sizable contribution to particulate matter (PM) concentrations, so particulate matter characteristics during the heating period are very different from those during the non-heating period. In addition, due to the presence of a concave terrain, lower wind speeds, and a relatively stable atmospheric structure in winter, it is difficult for atmospheric particulate matter to disperse, and it accumulates gradually, so that the characteristics of atmospheric particulate matter in the heating period is different from that during the non-heating period (Braniš and ělová, 2010; Kong et al., 2012; Qiao et al., 2010; Wang et al., 2012).

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In several major world cities, the characteristics and source apportionment of atmospheric particulate matter during the heating period and the non-heating period have been studied. However, there are differences in air quality characteristics between other cities and Harbin due to its high latitude, cold climate, and frequent inversion phenomena in the winter season (Dong et al., 2012; Dai et al., 2013; Li et al., 2012; Xu et al., 2012; Shen et al., 2011; Zhang et al., 2012). No detailed investigation has been conducted in Harbin thus far. Accordingly, in order to improve atmospheric quality, protect human health, and reduce ecological damage, it is crucial to investigate the characteristics of particulate matter during the heating period and the non-heating period in order to develop effective air pollution control measures in Harbin. Hence, we collected atmospheric particulate matter (TSP, PM_{10}, and $PM_{2.5}$) in Harbin in 2010 and 2011 to analyze the chemical characteristics of the particles and further to apportion their main sources by using chemical analysis and the chemical mass balance (CMB) receptor model (Gummeneni et al., 2011).

1. Sampling and analytical methods

1.1. Sample collection

In order to investigate the impacts of heating on ambient air quality, monthly atmospheric particulate matter data, including TSP, PM_{10}, and $PM_{2.5}$, were continuously collected from August, 2010 to June, 2011. According to the heating period of Harbin, the sample collection was conducted in three stages including "before heating period" from Aug. 2010 to Sep. 2010, "heating period" from Oct. 2010 to Apr. 2011, and "after heating period" from May 2011 to Jun. 2011. The sampling site was located at the South Campus of Harbin University of Commerce as illustrated in Fig. 1. Samples were collected every day, except raining days, snowing days, dust days and other special days. After these abnormal days, sampling was also stopped for one day, because particulate matter characteristics were affected by the weather. At least 15 samples were selected every month for a subsequent chemical and physical analysis. The filters used in this study were 80 mm quartz filters that were initially heated at 900°C before sampling, in order to eliminate the interference of residual organic compounds. Three medium-flow air samplers (Tianhong Intelligent Instrument, Model TH-150, Wuhan, China) were applied to collect TSP, PM_{10}, and $PM_{2.5}$ with the same flow rate of 100 L/min and sampling time of 24 hr every time. Overall sampling volume and duration were automatically recorded. The sampling height was 8 m above the ground. Near the sampling site, there was no substantial pollution source or obvious obstacles. The sampling approach was consistent with the requirements of national standards.

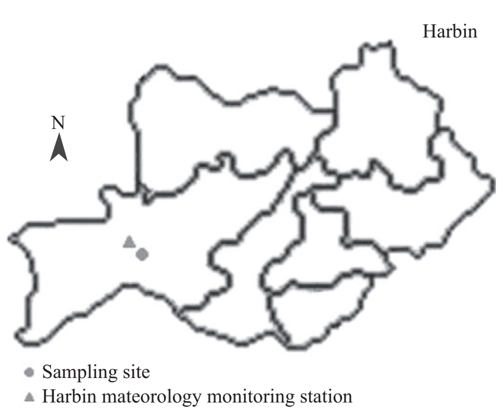

Fig. 1 – Locations of sampling site and meteorology monitoring station in Harbin, China.

1.2. Chemical analysis

1.2.1. Ionic species

Before and after sampling, the quartz filters were temporarily stored at 4°C and then transported back to the Central Laboratory of Harbin Institute of Technology (HIT) for further conditioning, weighing, and chemical analysis. Before conducting the chemical analysis, the filter samples were initially cut into 8 identical parts, four parts of which were used for the analysis of metallic elements, ionic species, total carbon and elemental carbon, respectively, while the remaining parts were used for other chemical analysis (Tsai et al., 2006).

A one eighth segment of the quartz filter to be analyzed for ionic species was put into a 50-mL PE bottle for each sample. Distilled–de-ionized water was added into each bottle for ultrasonic vibration for approximately 120 min. An ion chromatography system (Dionex, Model 100, USA) was used to analyze the concentration of major anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) (Yuan et al., 2004). Method detection limits were obtained from duplicate analysis of predefined quality control solutions. The method detection limits of F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were 0.013, 0.024, 0.033, 0.021, 0.017, 0.04, 0.039, 0.031, and 0.033 μg/mL, respectively. The averaged recovery efficiencies ranged from the lowest of 90% for Na^+ to the highest of 110% for Cl^- with an overall average of 97% (Huang et al., 2011).

1.2.2. Metallic elements

One eighth of the quartz filter was soaked in 15 mL mixed acid (V_{HNO_3}:V_{HClO_4} = 3:7) and placed on an electrical heating plate at 150–200°C for at least 2-hr digestion until the solution boiled and clarified. During the digestion period, distilled–de-ionized water was added into the residual solution twice or more in order to completely dissolve the metallic elements. The residual solution was then diluted to 50 mL with 0.5 mol/L $HNO_{3(aq)}$ and stored in a polyethylene (PE) bottle. After conducting the above steps, the metallic contents were measured with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkins Elmer, Model 400, USA) (Yuan et al., 2004). The metallic elements analyzed for this study included Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, Sr, Ti, V, and Zn, with the detection limits of 0.050, 0.014, 0.002, 0.028, 0.002, 0.007, 0.007, 0.009, 0.050, 0.029, 0.016, 0.030, 0.004, 0.030, 9.000, 1.500, 0.010, 0.009, 0.200, and 0.004 μg/mL, respectively.

1.2.3. Carbonaceous contents

Total and elemental carbon (TC and EC) contents of each quartz filter were determined with an elemental analyzer (EA, Fison, Model CHNS/O 1108, Italy). One eighth of each filter sample was heated in advance in a 340°C oven for 100 min to expel the organic carbon (OC) content, and then fed into the elemental analyzer to obtain the elemental carbon (EC) content. Another one eighth of each filter was fed directly into the