Introduction

Rapid development and dense population have exacerbated air pollution problems in China’s medium and large cities. In response, China is intensifying its air pollution abatement efforts. Since October 1998, Beijing has initiated clean air programs due to mounting public and official concern about the capital’s poor air quality. While gaseous pollutants such as sulfur dioxide, carbon monoxide, and oxides of nitrogen (NOx) have been effectively reduced, the concentrations of PM are still high in Beijing. PM is not monitored routinely in urban areas and there are sparse researches on it till now. As a result, relatively little is known about the status and trends of fine particle mass and composition over time in these areas. However, there is substantial concern about the visibility deterioration in Beijing since it is highly correlated with PM.

Weekly PM measurements were made continuously at two sampling sites for over one year starting in July 1999 with the goal of establishing a comprehensive database to describe fine particulate pollution in Beijing. Mass, ions, carbon, and 40 elements were measured. This paper will summarize the major findings for mass and composition of PM in Beijing with a focus on the seasonal variations of the major components.

Experimental

One week integrated PM samples on filters were taken simultaneously at two sites in Beijing: one located downtown at an air quality monitoring station in Chegongzhuang, and one on the campus of Tsinghua University in a residential area (Figure1). The Chegongzhuang site lies between the western 2nd and 3rd ring roads, both artery roads in the urban area with busy traffic. The Tsinghua site lies outside of the northern 4th ring road also with busy traffic. Around the site, many residents still use small coal-burned ovens for cooking and heating. The distance between the two sites is 10 km.

Figure 1. Beijing airshed and location of the sampling sites.

A low-flow rate sampler was deployed at each of the two sites to collect airborne PM. At each site, the sampler was placed on the roof of a 3m-tall building, resulting in an effective inlet height above the ground of about 4.5m. The sampler is a chemical speciation one for PM, which was designed to minimize sampling artifacts for nitrate via a carbonate solution coated denuder followed by a Nylon filter. It runs at a flow rate of 0.4 l/min with a sampling duration of one week. X-ray fluorescence (XRF), ion chromatography (IC), and thermal/optical reflectance (TOR) were employed to analyzed 40 elements (from Na to U), water-soluble ions, and organic and elemental carbon (OC and EC), respectively. Sampling system, chemical analysis, and quality control for this study has been introduced elsewhere.

Results and Discussion

Weekly PM concentrations ranged from 37 to 357 µg.m$^{-3}$ with annual mean of 115 and 127 µg.m$^{-3}$ in 2000 at the Chegongzhuang and Tsinghua sites, respectively. PM concentrations were highest during the winter, decreased through the spring, and tended to be lowest during late spring, summer, and early autumn. There were similar weekly and seasonal trends in PM concentrations for the two sites, and modest differences were found for the PM concentrations between the two sites during most of sampling periods.

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Figure 2. Variations of PM, PM, and TSP concentrations with time between 11 September 1999 and 16 September 2000 at the Chegongzhuang site.

The most abundant species (generally >1 µg.m$^{-3}$) were OC, EC, sulfate, nitrate, ammonium, potassium, silicon, calcium, and iron. Of these species, carbon and ions accounted for over half of the measured mass. Soil related crustal species (Al, Si, K, Ca, Ti, Fe, and Zn), without counting their oxides, account for about 8% of the mass. Further investigation on PM speciation at the two sites showed PM compositions were similar between the two sites with divergence coefficient CD=0.064.

Carbonaceous PM represented a significant fraction of PM at the two sites. OC was the most abundant species in PM, constituting more than 20%, and total carbon (also termed
carbonaceous aerosol, is the sum of the OC and EC) averaged 31% of PM$_{2.5}$ mass at the two sites. At the Chegongzhuang site, OC and EC seasonal patterns (Figure 3) were similar to those for PM$_{2.5}$, i.e., the highest concentration occurred in winter and the lowest in summer. The winter average values of OC and EC concentrations were 135% and 77% higher than their summer averages, respectively. On the other hand, OC/EC seasonal ratios were much stable, averaging 2.6-3.0, with annual mean amounting to 2.9. As shown in Figure 3, the OC and EC values were highly correlated, suggesting that EC is present along with OC. There were similar results at the Tsinghua site.

Figure 3. Seasonal variations and correlations of OC and EC concentrations at the Chegongzhuang site.

Sulfate, nitrate, and ammonium in PM$_{2.5}$ are primarily secondary particles, with their abundances mainly determined by their precursor gases concentrations and transformation rates. The sum of the ammonium, nitrate, and sulfate ions accounted for 37% of the seasonal average PM$_{2.5}$ mass in summer, and for about 25% in three other seasons, implying secondary particles were most abundant in PM$_{2.5}$ in urban area of Beijing. As shown in Figure 4, seasonal variations of sulfate were quite different from that of SO$_2$ gas. Contrary to the seasonal patterns of SO$_2$ gas, summer average of sulfate was much higher than those in the spring and autumn. The seasonal fractions of sulfate to total sulfur ([SO$_4^{2-}$]/([SO$_2$]+ [SO$_4^{2-}$])) were the following: summer (56%) > autumn (31%) > spring (21%) > winter (11%). The highest value was during the summer, suggesting that SO$_2$-to-sulfate transformation rates peaked in the summer due to enhanced summertime photochemical oxidation and SO$_2$ oxidation in clouds. On the other hand, the abundance of sulfate in winter could be related to high concentrations of SO$_2$, which are likely due to increased coal consumption during heating period combined with poor dispersion. The sulfate versus total sulfur gave a summer average ratio of 3, implying that nearly all of the PM$_{2.5}$ sulfur was present as sulfate in this season.

Figure 4. Seasonal patterns of sulfate in PM$_{2.5}$, SO$_2$, sulfate to total sulfur ratios, and relative humidity at the Chegongzhuang site.

At the Chegongzhuang site, nitrate concentrations exhibited strong fluctuation on a seasonal basis (Figure 5), with the seasonal mean concentrations proceeding in the following manner: winter > fall > spring > summer, which were similar to the seasonal patterns of PM$_{2.5}$ mass. The highest is 13.2 µg/m$^3$ in winter and lowest 5.5 µg/m$^3$ in summer, with a factor of 2.4 difference. Note that NO$_X$ concentrations only had a factor of near 2 difference for the same periods. This could be related to the low temperature (<15 °C) in late fall and winter that favors a shift from the gas phase as nitric acid to the particle phase as ammonium nitrate, and that most nitrate will be in the gas phase at temperature greater than 30 °C. The amount of nitrate present on the backup nylon filters was 47, 23, 19, and 20% for the summer through spring, respectively. This nitrate is due to the volatilization of ammonium nitrate from the front Teflon filter.

Figure 5. Seasonal patterns of nitrate in PM$_{2.5}$, NO$_X$, temperature, and relative humidity at the Chegongzhuang site.

Figure 6 gives a comparison of the main crustal-related elements and some trace elements at the Chegongzhuang site between the winter and spring. In contrast to the PM$_{2.5}$ mass decreasing sharply from the peak in the winter to a much lower value in the spring, concentrations of crustal species such as aluminum, silicon, calcium, magnesium, and iron elevated sharply from winter to spring and peaked then. The spring to winter average concentration ratios for these species were 1.3-1.9, while those for PM$_{2.5}$ and several trace elements such as copper, selenium, and lead, which arise mainly from anthropogenic sources, were about 0.5. It probably implied frequent dust storms had much more impact on crustal-related elements than trace elements during the spring of 2000 when twelve major dust storms swept Beijing, the worst frequency and severity in 50 years. The weekly peak of silicon (16.2 µg/m$^3$) during the spring exceeded the winter value by a factor of 3.6, which also reflected the impact of dust storms.

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References