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Daily variations of size-segregated ambient particulate matter in Beijing

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ABSTRACT

Daily, size-segregated particulate matter (PM) samples were collected at Peking University from March 2012 to April 2013. Seventeen indoor air samples were also collected over this period. Winter PM concentrations decreased compared with those reported a decade ago, but summer PM concentrations increased over the same time period. Increasing summer PM concentrations likely resulted from a shift in the major source of PM from primary coal burning to vehicle-associated secondary particle formation. A multiple regression model explained 62% of daily PM concentration variations, and wind direction was the most important factor controlling PM concentrations. Severe pollution was often associated with southeasterly winds, while westerly and northwesterly winds brought relatively clean air. Temperature, precipitation and relative humidity also affected PM concentrations. PM concentrations indoors were generally lower than, but significantly correlated with ambient concentrations. Indoor PM concentrations were also affected by wind speed and temperature.

1. Introduction

For decades China has been suffering from severe air pollution, and particulate matter (PM) is among the most important pollutants (He et al., 2001; Chan and Yao, 2008). This is particularly true in northern China where heating is needed (Li et al., 2014). A recent campaign conducted in seven cities across northern China revealed that annual mean concentrations of PM less than 10 μm in aerodynamic diameter (PM_{10}) reached 180 $\mu g/m^3$ (Li et al., 2014).

Robust associations between inhalation exposure to PM and a number of respiratory and cardiovascular diseases have been reported (Pope et al., 2002). According to the latest estimate, the population attributable fraction of total mortality from ambient PM pollution was as high as 16.2% in China, ranking fourth among major factors contributing to death (Global Burden of Disease (2014)).

The adverse health effects of PM are size dependent and it is believed that fine particles ($PM_{2.5}$), particularly ultrafine PM (<0.1 μm, $PM_{0.1}$), can penetrate deep into the lungs and even into the bloodstream (Brook et al., 2010; Dockery et al., 1993; Englert, 2004). Ambient PM in Beijing is generally from primary sources such as motor vehicles and coal combustion. Re-suspended soil and secondary particles are also important (Sun et al., 2004; He et al., 2001). PM from different sources tend to have different size distributions. For example, coarse PM observed in Beijing is often from the long-range transport of dust storms (Shi et al., 2003) and fugitive sources (Huang et al., 2010). Fine particles usually originate from combustion and secondary formation (Tan et al., 2014). A previous study showed that the annual mean mass fractions of $PM_{2.5}$, $PM_{2.5-10}$, and $PM_{>10}$ in Beijing were 31.8, 21.8, and 46.4%, respectively (Zhang et al., 2010). The contributions from different particle size fractions varied significantly among seasons, with relatively high $PM_{>10}$ (55.2%) during spring and high $PM_{2.5}$ (37.9%) during winter (Zhang et al., 2010).

Ambient PM in Beijing varies diurnally, daily, and seasonally because of the mixture of particle sources and varying meteorological conditions (Wang et al., 2005; Huang et al., 2010). It was suggested that 30% of $PM_{2.5}$ at an urban background site could be attributed to sources outside Beijing, particularly the highly contaminated regions to the south. Therefore, daily concentrations of PM in Beijing are strongly influenced by wind direction (Streets et al., 2007). According to results of a study conducted in 2002, primary $PM_{2.5}$ concentrations in Beijing were higher during winter than summer, mainly because of intensive emissions from coal

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burning for domestic heating (Sun et al., 2004). Concentrations of ions associated with secondary particles were high during summer, indicating secondary particle formation often occurred under the conditions of high humidity and strong solar radiation (Sun et al., 2004; Wang et al., 2005).

Emissions of primary PM and precursor gases for secondary PM formation in Beijing and the surrounding areas have changed rapidly. Household coal cooking stoves were previously popular in urban areas, but have gradually been replaced with piped natural gas and liquefied petroleum gas. Residential and commercial heating demands are now predominantly provided by centralized heating systems (National Bureau of Statistics of China, 2002–2013). As a result, emissions of primary PM from coal combustion have decreased significantly (Tan et al., 2014). Despite these improvements, the number of motor vehicles has increased from 1.63 million in 2003 to 5.37 million, which has increased both the primary particle and secondary particle precursor gas emissions from the transportation sector (Editorial Board of China Auto Market Almanac (2012)).

The objectives of this study were to collect data on the daily concentrations of size-segregated PM over one year to address: 1) the concentrations and size distributions of PM in ambient air and to compare the results with those reported previously; 2) the major factors affecting daily variations in PM concentrations and size distributions; and 3) the relationship between indoor and outdoor PM concentrations using data from only one household as a preliminary survey.

2. Materials and methods

2.1. Sample collection

PM samples were collected on the roof of a seven-storey building at the Peking University main campus. The campus is located within the urban area of Beijing (39.991°N/116.308°E). Daily (24-h) samples were collected on quartz fiber filters (25 mm in diameter), typically beginning at 6:00 pm, from March 5, 2012 to April 12, 2013. Because of student vacations, equipment failures, and power outages, samples were not collected every day. A total of 312 samples were obtained in this study. Low-volume Leland Legacy sampling pumps (SKC, USA) coupled with Sioutas Cascade Impactors (SKC) were used at a flow rate of 9.0 L/min. The five fractions collected by the impactors were those smaller than 0.25 μm ($PM_{0.25}$), between 0.5 and 0.25 μm ($PM_{0.25-0.5}$), between 0.5 and 1.0 μm ($PM_{0.5-1.0}$), between 1.0 and 2.5 μm ($PM_{1.0-2.5}$), and larger than 2.5 μm ($PM_{>2.5}$).

In addition to the ambient samples, 17 indoor air samples (April 1, 9, 16; May 10, 26; June 21, 30; July 19; Sept. 5, 9, 18, 23; Nov. 11, 12; and Dec. 22, 23, 25, 2012) were also collected for 24 h in a non-smoking, non-cooking residence flat (15th floor, located at the northeast corner of an apartment building several hundreds meters from the ambient air sampling building). The indoor samples were collected to investigate the relationship between PM concentrations indoors and outdoors for this particular household. The samples were collected using the same equipment and procedures. The indoor air sampling days were chosen to cover different seasons and a wide range of ambient PM concentrations.

Table 1
Concentrations and statistical parameters for different PM size fractions (μg/m^3).

	Mean	Std. dev.	P5	P25	P50	P75	P95
TSP	147	96	23	73	130	196	331
$PM_{2.5}$	102	72	16	47	87	144	232
$PM_{1.0}$	83	61	9.9	35	72	118	194
$PM_{0.5}$	68	49	11	30	61	98	153
$PM_{0.25}$	33	26	5.5	17	29	42	78

2.2. Sample analysis

The filters were stored in desiccators for at least 24 h prior to weighing, and then weighed using a five-digit balance (XS-105, Mettler Toledo, Switzerland; Accuracy 0.01 mg) in a temperature-controlled room. At least three readings were obtained for reporting an average value. After sampling, the filters were stored in desiccators for at least 24 h and weighed under the same conditions as the unloaded filters. The gravimetric masses were calculated based on their pre- and post-weights.

Duplicate sampling and gravimetric weighing were conducted randomly and a total of 18 ambient sample pairs and four indoor sample pairs were analyzed. The average coefficients of variations were 7.2, 8.1, 8.5, 5.7, and 9.4% for the ambient duplicate samples and 10, 7.3, 3.6, 6.3, and 5.7% for the indoor samples.

2.3. Meteorological conditions

Meteorological parameters were collected using a weather station (DT80, Rainroot, China) set up on the top of the same building as the sampler. Readings of temperature (*T*), relative humidity (*RH*), wind direction, wind speed (*WS*) and precipitation (*R*) were recorded at 10-min intervals. Daily averages were calculated according to the exact sampling periods. For each 24-h sampling period, the calculated daily mean wind speeds were broken into eight direction components: north (WS_N), northeast (WS_{NE}), east (WS_E), southeast (WS_{SE}), south (WS_S), southwest (WS_{SW}), west (WS_W), and northwest (WS_{NW}), for further data analysis.

2.4. Trajectory calculation

Backward air mass trajectories over 120 h were calculated in 6-h intervals using the NOAA hybrid single-particle Lagrangian integrated trajectory model, driven by meteorological variables from global NOAA-NCEP/NCAR pressure level reanalysis data (Draxler and Rolph, 2003). A probabilistic function was derived and normalized based on the geographical locations of the trajectories.

2.5. Data analysis

The five size fractions were converted into TSP (total suspended solids), $PM_{2.5}$ (<2.5 μm), $PM_{1.0}$ (<1.0 μm), $PM_{0.5}$ (<0.5 μm) and $PM_{0.25}$. Statistica (StatSoft, USA) was used for statistical analysis. A significance level of 0.05 was used. For multiple regression analysis, a forward stepwise method was applied.

3. Results and discussion

3.1. Concentrations

The measured concentrations of the five size fractions are presented in Table 1 as annual means, standard deviations, and several percentiles based on daily concentrations. The measured $PM_{2.5}$ concentration range is similar to those reported previously. For instance, He et al. (2001) measured $PM_{2.5}$ at two stations in Beijing in 1999 and 2000 and the annual mean concentration at one station located approximately 1 km east of our site was 127 μg/m^3. An annual mean $PM_{2.5}$ concentration slightly higher than 100 μg/m^3 has been reported (Zheng et al., 2005). The $PM_{2.5}$ concentration was also very close to that (100 ± 80.3 μg/m^3) measured at Wanliu Station during the same period by the Beijing Municipal Monitoring Center (Beijing Municipal Environmental Monitoring Center, 2014),

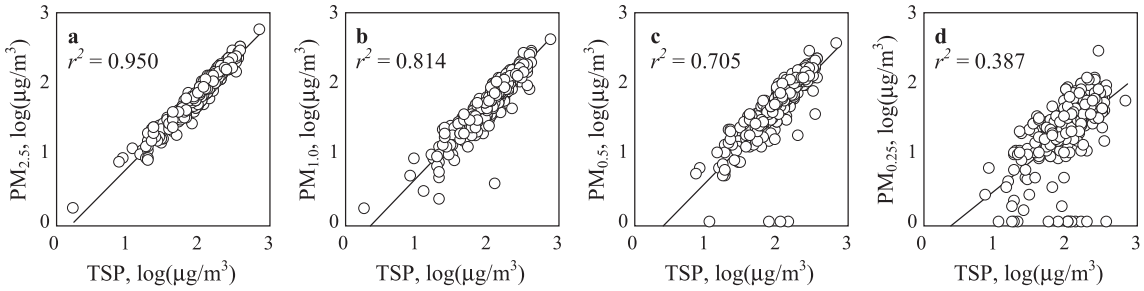

Fig. 1. Relationships between ambient TSP concentrations and a) $PM_{2.5}$, b) $PM_{1.0}$, c) $PM_{0.5}$ and d) $PM_{0.25}$.

despite the differences in the methods (gravimetric vs oscillating microbalance) and locations (2.2 km southwest of our site).

Until recently, $PM_{2.5}$ was not regulated or routinely monitored in China; and only PM_{10} is listed in the ambient air quality standards. According to the newly-issued third amendment of the Ambient Air Quality Standards of China (GB 3095-2012), which will not be enforced until 2016, annual and daily average concentrations of $PM_{2.5}$ should not exceed 35 and 75 μg/m^3, respectively. The measured annual mean concentration in this study was almost three times greater than the annual mean standard, and daily concentrations in 176 out of 312 days (56%) exceeded the daily mean standard. This is comparable to the exceedance rate of 53% reported at the Wanliu Station during the same period. If stricter World Health Organization (WHO) air quality guidelines, based on the lowest concentrations causing cardiopulmonary and lung cancer mortality were taken into consideration (World Health Organization, 2006), the measured annual mean concentration of $PM_{2.5}$ would be more than 10 times higher (WHO annual average 10 μg/m^3), and the percentage of daily exceedances (daily mean above 35 μg/m^3) would be 83%.

The daily concentrations of all size fractions varied widely. Fig. S1 presents a time series of $PM_{2.5}$ concentrations. It is apparent that $PM_{2.5}$ concentrations rapidly increased or decreased throughout the year, regardless of the season. More severe and frequent pollution episodes were observed in April 2012 and March 2013. For example, the highest 24-h average $PM_{2.5}$ concentration (565 μg/m^3) was recorded on March 16, 2013, and daily average $PM_{2.5}$ concentrations for 17 days in April 2012 were higher than 110 μg/m^3. As expected, concentrations of the five size fractions increased and decreased in unison, resulting in significant correlations among them ($p < 0.05$). Correlations of daily PM concentrations were more significant among the fractions with similar sizes. For instance, the Pearson correlation coefficients of log-transformed daily PM concentrations were 0.97, 0.93, 0.90, and 0.50 between TSP and $PM_{2.5}$, TSP and $PM_{1.0}$, TSP and $PM_{0.5}$ and TSP and $PM_{0.25}$, respectively (Fig. 1). A study carried out in Turkey also revealed that TSP, PM_{10}, and $PM_{10-2.5}$ from similar sources were highly correlated, while combustion-sourced $PM_{2.5}$ was only moderately correlated with other size fractions (Hanefi et al., 2010).

For all size fractions, the distributions of the measured concentrations were right-skewed and leptokurtic. For example, the coefficients of skewness and kurtosis for the measured $PM_{2.5}$ concentrations were 1.5 and 4.8, respectively, both of which were significant ($p < 0.05$). The two coefficients were −0.8 and 0.9 ($p > 0.05$) after log-transformation, showing typical log-normal distributions. Similarly, the coefficients of skewness and kurtosis for $PM_{2.5}$ at Wanliu (Beijing Municipal Monitoring Center operated station) were 1.68 and 3.94, respectively, before log-transformation, and −0.79 and 0.22 after log-transformation, respectively. A histogram of $PM_{2.5}$ concentrations is shown in Fig. S2, which was well-fit using a log-normal distribution curve. The frequency distributions of the other four size fractions were very similar to that of $PM_{2.5}$.

3.2. Seasonality

Seasonal variations in $PM_{2.5}$ concentrations have previously been reported. Based on the results of yearlong measurements at two stations in Beijing from 1999 to 2000, $PM_{2.5}$ concentrations varied among seasons and weekly averages during the wintertime were significantly higher than those during the summertime (He et al., 2001). It was suggested that the high concentrations during winter were from high domestic heating emissions combined with local meteorological conditions that were unfavorable for pollutant dispersion (He et al., 2001). Average concentrations of the five size fractions measured in this study are presented in Fig. S3 as stacked bars. Generally the concentrations were highest from January to June and lowest from September to December. Compared with the seasonal trend reported more than a decade ago (He et al., 2001), the winter peak has declined and $PM_{2.5}$ concentrations during

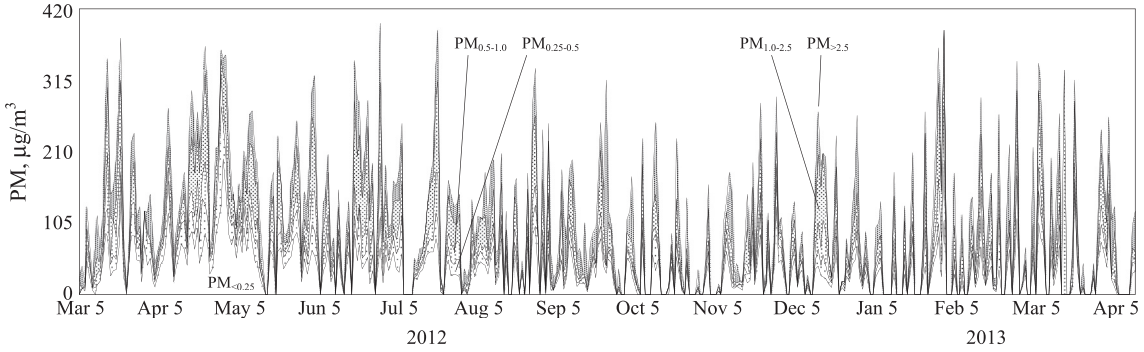

Fig. 2. Time series of measured daily concentrations of the five PM size fractions ($PM_{<0.25}$, $PM_{0.25-0.5}$, $PM_{0.5-1.0}$, $PM_{1.0-2.5}$ and $PM_{>2.5}$) as a stacked area chart. Data were collected from March 5, 2012 to April 12, 2013. Missing data were recorded as zero (an enlarged color figure can be see as Fig. S14 in the Supplementary Material).

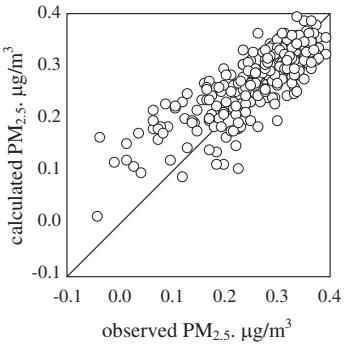

Fig. 3. Comparison between the multiple regression model predicted and measured concentrations of $PM_{2.5}$ over the sampling period.

summer have increased. Traditionally, coal was the major fuel for household cooking and heating in Beijing. Over the past two decades however, household coal stoves in downtown Beijing have gradually been replaced with liquefied petroleum gas (Baidu Encyclopedia, 2014), pipeline natural gas (International Energy Agency, 2012) and centralized heating systems (Guo et al., 2010). Coal is still commonly used for cooking and heating by households in suburban and rural areas around Beijing, and in the areas surrounding Hebei (Tan et al., 2014). As a result, there is still a winter peak in PM concentrations, but concentrations are not as high as those reported over a decade ago (He et al., 2001). Conversely, fractions of $PM_{2.5}$ in TSP during summer increased. This is likely because of increased formation of secondary aerosols from gaseous precursors emitted by the rapidly growing motor vehicle fleet in hot summer (Xie, 2014). A recent study reported that concentrations of inorganic ions in aerosol samples collected in Beijing were highest during summer, suggesting enhanced secondary particle formation under favorable meteorological conditions (Zhao et al., 2013).

Meteorological conditions are also important factors affecting particle concentrations in ambient air. Fig. S4 presents monthly statistics for *T*, *RH*, *WS*, and *R*. High *RH* could be responsible for high PM concentrations during summer because it can accelerate the formation of secondary aerosols under high solar radiation (Wang et al., 2005). PM emissions related to cold weather and heating demand led to elevated PM concentrations during winter, but this was not as substantial as a decade ago (Wang et al., 2005). Despite the potential influences of *RH* and *T*, wind direction was the most significantly correlated with PM concentrations. The correlation coefficients between TSP concentrations and wind speed ratios from the averages of northeast-north-northwest winds and southwest-west winds were as low as −0.63 (Fig. S5), indicating

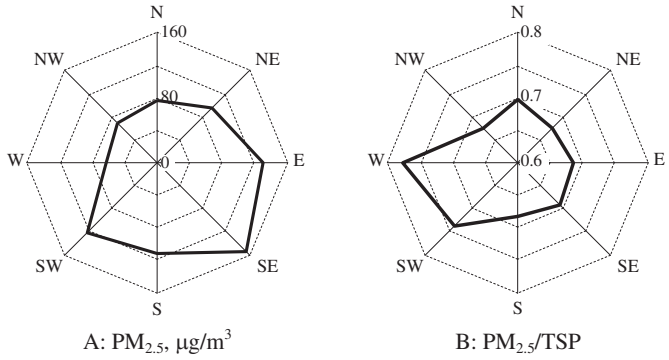

Fig. 4. Average concentrations of $PM_{2.5}$ (A) and $PM_{2.5}$/TSP ratios (B) for days with eight prevailing wind directions.

that westerly winds were favorable for pollutant dispersion. Easterly winds were associated with increased PM concentrations. Beijing is located in the northwest corner of the China Northern Plain, surrounded by the Yanshan Mountains to its north and west. Winds from mountain areas often bring clean air masses, while pollutants emitted in surrounding areas to the south and east can be transported to Beijing (Xu et al., 2008). It was also previously reported that heavy pollution episodes in northern China are strongly affected by synoptic patterns, and wind is one of several important meteorological factors (Ji et al., 2012). In addition to wind direction, many other meteorological variables as well as emission activities can play important roles.

Although private cars in Beijing are not to be used one weekday per week, according to a roster system, by municipal government regulation, one-way analysis of variance showed no significant differences in ambient concentrations of $PM_{2.5}$ or other size fractions between weekdays and weekends. Similarly, there was no significant reduction in PM concentrations during the spring festival, when traffic in Beijing was much lighter than other months.

3.3. Size distribution

Particle size distribution is critical in terms of health impacts of airborne particles (Oberdorster et al., 2005). Although data on $PM_{2.5}$ concentrations in Beijing have been extensively reported (Zheng et al., 2005; Zhao et al., 2013; Quan et al., 2014), limited information is available on long-term PM size distributions. The data for five size fractions of PM measured in this study provide important information in this regard. The average contributions of various size fractions are presented in Fig. S6. On average, as much as 69.5% of PM was smaller than 2.5 μm, and 56.8% was smaller than 1 μm in this study. A study conducted in several cities in eastern China, including Beijing, also revealed that most of the ambient particle mass was in the submicron size range (Davis and Guo, 2000). The fraction of $PM_{2.5}$ to TSP in our study was higher than those reported previously. Kan et al. (2005) estimated that $PM_{2.5}$ contributed to 42% of PM_{10} in Shanghai based on the measured concentration ratio of PM_{10} to TSP (65%), leading to a concentration ratio of $PM_{2.5}$ to PM_{10} of 65%. A review based on data published 10–20 years ago indicated that the average TSP and $PM_{2.5}$ concentrations in Beijing were approximately 340 and 100 μg/m^3, respectively, suggesting less than 30% of TSP is in the $PM_{2.5}$ size fraction (Laakso et al., 2006). The relatively high ratio of $PM_{2.5}$ found in this study can be explained by a decreasing trend in the occurrence of spring sandstorms in Beijing (Zhang et al., 2012), and increasing secondary aerosol concentrations. Emissions from coal combustion, especially residential coal stoves, dominated PM emissions in the past (Shi et al., 2003), but now secondary aerosol concentrations have increased, associated with increased vehicular use (Tan et al., 2014; Xie, 2014). Secondary aerosols produced from vehicular emissions are predominantly fine particles (Weitkamp et al., 2007).

Time series of ratios of $PM_{2.5}$/TSP, $PM_{1.0}$/TSP, $PM_{0.5}$/TSP, and $PM_{0.25}$/TSP over the study period are shown in Fig. 2. Like the size-segregated concentrations, the relative contributions of various size fractions to TSP varied widely over time. The coefficients of variation were 18, 28, 31, and 59% for the four ratios, respectively, indicating an increasing trend in variation from ultrafine particles to fine ones. $PM_{2.5}/PM_{10}$ ratios in UK urban background sites have been summarized, and a seasonal trend of relatively low ratios during summer was revealed (Deacon et al., 1997). A similar trend with a high $PM_{2.5}$/TSP ratio during summer was identified in this study, though it was not as pronounced as that in the UK. It is believed that higher and lower mass concentration ratios of $PM_{2.5}$/

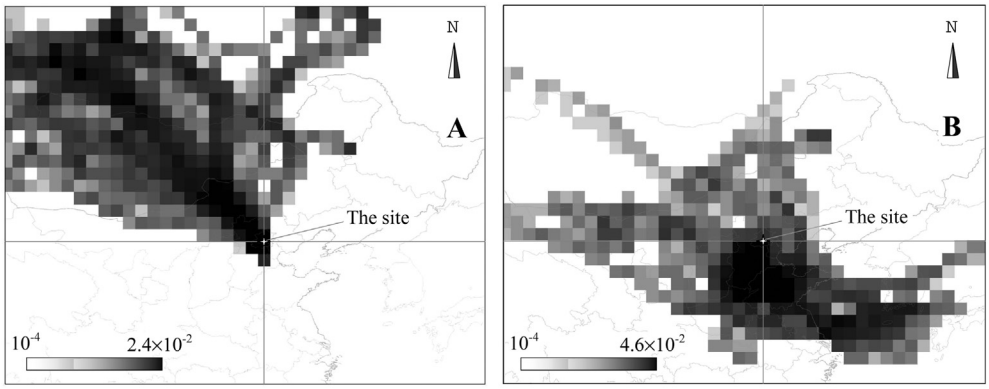

Fig. 5. Probabilistic maps of 20-h backward trajectories of air mass during the 20 least polluted (A) and 20 most polluted (B) days over the study period. All trajectories started from the sampling sites marked with an open circle. The probabilities were normalized and log-scaled.

TSP indicate anthropogenic and mineral load contributions, respectively (Hanefi et al., 2010). Slight decreases in the ratios during spring months indicated more mineral load input (Querol et al., 2004).

A significant negative correlation ($p < 0.05$) was found between the $PM_{0.25}$/TSP ratio and TSP concentrations, indicating that as PM mass increased, ultrafine particles had less contribution to TSP. This relationship was seasonally dependent. As shown by monthly correlations between the $PM_{0.25}$/TSP ratio and TSP concentrations in Fig. S7, the negative correlations were significant ($p < 0.05$) for eight months (March, April, May, August, 2002 and January through April, 2003; solid dots in the figure), when TSP concentrations were generally high. Such a relationship, together with no correlation between TSP and $PM_{0.25}$, suggests that coarse and ultrafine particles are from totally different sources.

Significant correlations were also found between size ratios and a number of meteorological conditions based on a non-parametric test (Spearman *R* calculation, to avoid influence of outliers). As examples, log-transformed $PM_{2.5}$/TSP ratios are plotted against *RH*, *R* and *WS* in descending order from left to right in Fig. S8. The $PM_{2.5}$/TSP ratios were positively correlated with *RH* and *R*, and negatively correlated with *WS*. All three correlations were significant ($p < 0.05$), suggesting that high humidity and rain are favorable for the accumulation of fine particles and that strong winds increased coarse particle concentrations. Similar results for other size ratios were found. The mean *RH*, *R*, and *WS* during the study period were 53.6%, 9.63 mm and 1.10 m/s, respectively, when $PM_{2.5}$/TSP ratios were very high (>0.88), and were 32.7%, 0 mm and 1.54 m/s, respectively, when $PM_{2.5}$/TSP ratios were very low (<0.46). Significant correlation between mass concentrations of $PM_{2.5}$ and *RH* in Beijing has also been reported previously (Wang et al., 2005). High concentrations of coarse particles in the UK were believed to be caused by soil re-suspension associated with strong winds (Harrison et al., 2001).

3.4. Influence of meteorological conditions

A stepwise multiple regression was conducted to evaluate the influences of various meteorological factors on daily $PM_{2.5}$ concentrations. The independent variables included: *T*, *RH*, *WS*, *R*, WS_N, WS_{NE}, WS_E, WS_{SE}, WS_S, WS_{SW}, WS_W and WS_{NW}, as daily averages for the same day that the $PM_{2.5}$ was measured and one day immediately before the measurement (a superscript of 0 added to the variables). The objective of the modeling was to understand the influcence of various meterological conditions on ambient PM concentrations in Beijing, rather than to develop a predictive tool. Therefore, all independent variables were normalized.

Among the 24 meteorological variabes, 12 entered the regression equation with *p* values lower than 0.05. The model calculated $PM_{2.5}$ concentrations are plotted against the measured concentrations in Fig. 3. The coefficient of determination (R^2) was 0.624, indicating that more than 62% of the variation can be explained by these variables. In terms of regression coefficients, seven wind vectors, including WS_{SE} (0.667, $p = 0.0000$), WS_W (−0.527, $p = 0.0000$), WS_E (−0.416, $p = 0.0027$), WS^0_{SE} (0.263, $p = 0.0026$), WS^0_E (0.210, $p = 0.0381$), WS^0_W (−0.169, $p = 0.0001$), and WS_{NW} (0.093, $p = 0.0286$) were significant. The coefficients for south and southeast wind vectors were all positive, suggesting strong contributions from PM emissions in areas to the south and southeast. The coefficents for westerly and northerly wind vectors were generally negative because northerly and westerly winds often bring in clean air masses from mountain areas and highlands. Streets et al. (2007) estimated that under sustained wind flow from the south, nearly 70% of $PM_{2.5}$ in Beijing was from emissions in the Hebei Province. Alongside wind, other significant variables included: T^0 (−0.943, $p = 0.0000$), *T* (0.041, $p = 0.0000$), *RH* (0.010, $p = 0.0000$), *R* (−0.004, $p = 0.0195$), and RH^0 (−0.004, $p = 0.0002$). High *T* and *RH* on the sampling day were favorable for the formation of $PM_{2.5}$ because high *RH* combined with strong solar radiation can

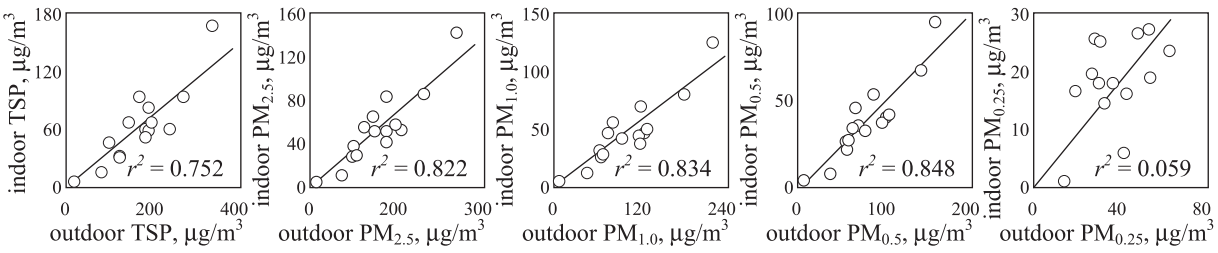

Fig. 6. Relationships between concentrations of TSP, $PM_{2.5}$, $PM_{1.0}$, $PM_{0.5}$ and $PM_{0.25}$ in indoor and outdoor air.

accelerate secondary aerosol production (Wang et al., 2005). It was previously reported that because of high *T* and *RH*, the contributions of SO_4^{2-}, NO_3^- and NH_4^+ to total $PM_{2.5}$ mass concentrations during summer were much higher than those during winter in Beijing (Sun et al., 2004). Similarly, increased concentrations of ambient secondary pollutants were found to be associated with increased *T* and *RH* during summer (Wang et al., 2010). The *T* and *RH* of the previous day were negatively correlated with $PM_{2.5}$ concentrations. *R* (−0.004, $p = 0.0195$) also had a significantly negative influence on $PM_{2.5}$ concentrations during the same day. It is noteworthy that the meteorological conditions of the day prior to sampling had a similar influence to those on the sampling day, indicating that the influence of wind can last for more than 24 h, highlighted by the fact that wind speeds for consecutive days were positively correlated ($p < 0.05$). It was previously reported that pollutants can build up in Beijing for several days because of the surrounding hills and restricted ventilation (Streets et al., 2007).

In Fig. 4A, mean concentrations of $PM_{2.5}$ for all days with one of the eight prevailing wind directions are presented. Mean $PM_{2.5}$ concentrations ranged from 112 to 155 μg/m^3 when the prevailing winds were from the east, southeast, south, or west. When winds were from the other directions, the $PM_{2.5}$ concentrations ranged from 62 to 96 μg/m^3. If the ratio of $PM_{2.5}$/TSP is examined (Fig. 4B), the highest ratios occurred when prevailing winds were from the west or southwest.

Backward air mass trajectories of the 20 most polluted (daily $PM_{2.5}$ concentrations ranging from 210 to 565 μg/m^3) and the 20 least polluted days (daily $PM_{2.5}$ concentrations ranging from 8.4 to 18.5 μg/m^3) were calculated and are shown in Fig. S9 (four 6-h trajectories each day). During the pollution episodes, air masses moved in from south of Beijing, while winds from the north and northwest were associated with clean air. The 40 trajectories were combined into two probabilistic maps for the 20 least polluted and 20 most severely polluted days in Fig. 5. Fig. 5 shows that the major pollutant source regions were Hebei to the south and Shandong to the southeast.

3.5. Indoor air

Knowledge on PM concentrations in indoor air is critical for health impact assessments because people spend most of their time indoors (Duan et al., 2013). During the study period, 17 daily (24-h, April 1, 9, and 16, May 10 and 26, June 21 and 30, July 19, Sept. 5, 9, 15, 18, 23, and 29, Nov. 12, and Dec. 23 and 25) indoor samples were collected alongside ambient air samples. The indoor sampling dates were chosen to cover different seasons and a wide range of concentrations, from unpolluted (e.g., Nov. 12, 2012, ambient $PM_{2.5}$ concentration = 11 μg/m^3) to heavily polluted (e.g., July 19, 2012, ambient $PM_{2.5}$ concentration = 255 μg/m^3) days. For the 17 days, the average concentrations of TSP, $PM_{2.5}$, $PM_{1.0}$, $PM_{0.5}$, and $PM_{0.25}$ were 57 ± 38, 48 ± 34, 42 ± 29, 35 ± 23, and 17 ± 8 μg/m^3, respectively, indoors and 155 ± 86, 107 ± 64, 89 ± 56, 71 ± 42 and 33 ± 18 μg/m^3, respectively, outdoors. The means and standard deviations of the ambient air measurements for the 17 days were very close to those over the whole year (147 ± 96, 102 ± 72, 83 ± 61, 68 ± 49, and 33 ± 26 μg/m^3 for TSP, $PM_{2.5}$, $PM_{1.0}$, $PM_{0.5}$, and $PM_{0.25}$, respectively), confirming the representativeness of the indoor sampling. The indoor concentrations were significantly lower than outdoor ones. In a previous study on indoor PM sources in three residential flats in Athens, it was also found that indoor concentrations of PM_{10} and $PM_{2.0}$ were generally lower than the corresponding outdoor concentrations; and elevated indoor concentrations were mainly caused by penetration of ambient PM (Diapouli et al., 2011). The coefficients of variation for PM concentrations indoors were higher than those outdoors ($PM_{0.25}$ was the only exception) because very low concentrations were measured indoors.

One direct result of the relatively low concentrations in indoor air compared with those outdoors is that the indoor/ourdoor (I/O) ratios were generally below 1. Fig. S10 presents a comparison of the ratios of $PM_{2.5}$/TSP, $PM_{1.0}$/TSP, $PM_{0.5}$/TSP, and $PM_{0.25}$/TSP between indoors and outdoors. From Fig. S10, it is apparent that fine particles make up a greater proportion of the PM indoors than outdoors. On average, the I/O ratios of TSP, $PM_{2.5}$, $PM_{1.0}$, $PM_{0.5}$, and $PM_{0.25}$ were 0.34 ± 0.11, 0.42 ± 0.12, 0.48 ± 0.15, 0.50 ± 0.15 and 0.50 ± 0.25, respectively. The increasing I/O ratios with decreasing particle size indicate that fine, especially ultrafine particles, behave like gaseous-phase components and can penetrate the indoor environment more freely. The size selective penetration of outdoor aerosols in favor of fine particles has also been revealed by a tracing penetration study for PM of different sizes using Po-210/Pb-210 (Hovorka et al., 2005). The measured concentrations of various PM size fractions indoors are plotted against those measured at the same time outdoors in Fig. 6. The calculated slopes of 'force-to-origin' regressions were all below 1. These slopes are similar, but not exactly equal to the calculated average I/O values, and they also show a general increasing trend as particle sizes decrease (0.37, 0.46, 0.47, 0.50, and 0.49 for TSP, $PM_{2.5}$, $PM_{1.0}$, $PM_{0.5}$, and $PM_{0.25}$, respectively).

Although the PM concentrations indoors and outdoors shown in Fig. 6 appear to be linearly correlated, deviations from the linearity were revealed by examing the data in detail. In Fig. S11, I/O ratios of different size fractions are plotted against ambient PM concentrations. Significant ($p < 0.05$) positive relationships for TSP and $PM_{2.5}$, and a significant negative relationship for $PM_{0.25}$ ($PM_{1.0}$ and $PM_{0.5}$ were not significant at the 0.05 level) were evident. Such trend suggests a non-linear relationship between indoor and ambient particle concentrations that cannot be revealed by simple plots of the two. Differences in meteorological conditions between high and low concentration days could be a reason.

As expected, the I/O ratios depend on meteorology. It was reported that increased natural ventilation is associated with increases in *T* and wind speed, consequently I/O ratios (Isaacs et al., 2013). Among various meteorological parameters, northeast wind speed was positively correlated with I/O values for all five fractions (Fig. S12). This is because the residential flat where the indoor samples were collected is located in the northeast corner of the building, with most of the windows facing the north or east. For TSP and $PM_{0.5}$, the I/O ratios were also positively correlated with *T* ($p < 0.05$). As shown in Fig. S13, the winter samples were all collected on cold days with daily *T* below 10 °C when all windows were closed, reducing the penetration of particles.

4. Conclusions

Both concentrations and size distribution of PM in ambient air in Beijing are strongly meteorological condition dependent with wind direction as the dominant influencing factor. There was strong seasonality and the patterns of the seasonality and source contributions were different from those reported years ago. Indoor PM concentrations were lower than but significantly correlated with outdoor PM concentrations.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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