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Diurnal variation of number concentration and size distribution of ultrafine particles in the urban atmosphere of Beijing in winter

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Abstract

Number concentration and distribution of airborne particles in the size range 5.6 to 560 nm diameter were measured in Beijing for a 15-d period in winter 2005. Daily average number concentrations of nucleation mode (5.6–20 nm), Aitken mode (20–100 nm), and accumulation mode (100–560 nm) particles, and total particles were 17500, 32000, 4000, and 53500 cm^{-3}, respectively. Average particle size distribution was monomodal with a mode diameter of about 40 nm at night and bimodal with mode diameters of about 10 and about 40 nm during the daytime. New particle formation events, which were connected to diurnal variation of nucleation mode particles, were observed in more than half of the observation days. The events often started around 10:00–11:00 Chinese Standard Time (CST) and ended up after 3–4 h. Concentrations of Aitken and accumulation mode particles increased from midnight and reached their maxima at about 10:00 CST, and then decreased and became the lowest in the afternoon. Analysis of diurnal cycles in traffic volume and meteorological parameters revealed that the accumulation of the particles in Aitken and accumulation modes in the morning was influenced by formation of an inversion and increase in vehicle emission, and dispersion of such particles in the afternoon was associated with more effective vertical mixing and higher wind speed.

Key words: fine particles; nucleation mode; Aitken mode; new particle formation

Introduction

Ultrafine particles are particulate matter less than 100 nm in diameter. They account for a small percentage of PM_{10} (particulate matter with aerodynamical diameter less than 10 μm) mass but are very high in number concentrations. Previous researches have suggested that there are correlations between ultrafine particle number concentration and adverse human health effects (Peters *et al*., 1997; Donaldson *et al*., 1998). Recently, Nemmar *et al*. (2002) showed that the particles could pass rapidly into the systematic circulation, leading to direct and indirect damage to human health.

Physical properties of ultrafine particles in the atmosphere were intensively investigated in Europe (Shi *et al*., 2001; Ruuskanen *et al*., 2001; Wehner *et al*., 2002; Tuch *et al*., 2003; Kreyling *et al*., 2003; Laakso *et al*., 2003), North America (Woo *et al*., 2001; Noble *et al*., 2003), and Australia (Morawska *et al*., 1998). Chemical compositions of ultrafine particles were also examined (Wehner, 2004a; Hasegawa *et al*., 2004). These studies showed that environmental behaviors of ultrafine particles are affected by many factors such as emission sources, physical and chemical processes in the atmosphere, and weather conditions.

Although a series of control measures have been implementing since 1998, particulate pollution still maintained a high level in Beijing. For example, annual average PM_{10} mass concentration in 2004 was as high as 149 $\mu g/m^3$ (Beijing Environmental Protection Bureau, http://www.bjepb.gov.cn/news/2005-6/2005651950 34.htm). In Beijing, researches on particulate matter focused on bulk chemical analysis (He *et al*., 2001; Yu *et al*., 2004; Huang *et al*., 2005) and individual particle analysis (Shi *et al*., 2003; Liu *et al*., 2005). Less attention has been paid to size distribution of atmospheric particles. Recently, Zhang *et al*. (2001) and Jiang *et al*. (2003) reported number size distribution of particles larger than 300 nm, and Wehner *et al*. (2004b) showed the differences in particle size distributions under three typical weather conditions in Beijing. However, little information is available to evaluate the factors affecting diurnal variation of number concentration and size distribution of ultrafine particles in the urban atmosphere of Beijing.

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In this study, distribution of particles in the size range 5.6–560 nm was measured with Engine Exhaust Particle Sizer™ (EEPS™, TSI incorporated) in an urban area of Beijing. Diurnal variation of concentration of particles in different modes is reported and factors potentially responsible for the variation are discussed.

1 Materials and methods

In this study, EEPS™ was used to measure the size distribution of ultrafine particles. It measures particle size from 5.6 to 560 nm with a sizing resolution of 16 channels per decade (a total of 32 channels) and a time resolution of 0.1 s. Like the Scanning Mobility Particle Sizer (SMPS) system, EEPS™ uses a measurement based on electrical mobility. Particles entering the instrument are charged to a predictable level, then they are passed through an annular space where they are repelled outward by the voltage from a central column. When the particles reach electrodes on the outer cylinder (a column of rings), they create a current that is measured by an electrometer on one or more of the rings. The currents are converted to particle size and concentration for immediate display using a real-time inversion algorithm.

The EEPS™ was installed on the second floor of environmental building on campus of Tsinghua University. It is located at northwest border of the Beijing urban area. This site has been described in detail in our previous study (He *et al*., 2001). Particle size distribution were measured from February 18 to 27, 2005 and March 1 to 10, 2005 except for maintenance and power failure. In total, particle size distributions in 15 d were recorded at the site. The distributions at a roadside site near West Fourth Ring Road in Beijing were measured on February 28, 2005. In addition, hourly average concentrations of PM_{10}, CO, NO, NO_2, O_3, and SO_2 were monitored at an air quality auto-monitoring station on campus of Tsinghua University. Hourly average wind speed, wind direction, temperature, and humidity were also recorded at the station.

During the observation period, the daily average temperature ranged from –7.2 to 6.5 °C with an average of –0.4 °C; the average relative humidity was 47%. In addition, domestic heating was continuously provided to offices and residential buildings in Tsinghua University during this period. This was also expected all over Beijing because of the cold weather. Therefore, the observation period could represent a typical wintertime in Beijing.

2 Results

2.1 Number concentration of particles in different modes

Number concentrations of particles in different size ranges are listed in Table 1. In this study, definitions of different modes by Kulmala *et al*. (2004) are followed, but slightly modified. The nucleation, Aitken, and accumulation mode partiles are those in the size ranges of 5.6–20 nm, 20–100 nm, and 100–560 nm, respectively. Daily average concentrations of nucleation mode particles were in the range of 0.52×10^4–2.88×10^4 cm^{-3} with an average of 1.75×10^4 cm^{-3}; those of Aitken mode particles were 1.12×10^4–4.40×10^4 cm^{-3} with an average of 3.20×10^4 cm^{-3}; those of accumulation mode particles were 0.04×10^4–1.14×10^4 cm^{-3} with an average of 0.40×10^4 cm^{-3}; and those of 5.6–560 nm were 2.50×10^4–7.51×10^4 cm^{-3} with an average of 5.35×10^4 cm^{-3}. Number of Aitken particles was dominant, and accounted for approximately 60% that of total particles. Diameter of more than 93% of the particles was less than 100 nm.

Table 1 also shows that concentrations of ultrafine particles were much higher in cloudy days than in clear days. Concentrations of ultrafine partiles measured at the roadside site are also listed in Table 1. Those of nucleation and Aitken mode particles, and total particles were several to 10 times higher in the roadside atmosphere.

2.2 Diurnal variation of number concentration of ultrafine particles, mixing ratios of SO_2, NO_x, CO, and O_3, and mass level of PM_{10}

During the observation period, there were mainly two types of diurnal variation patterns in particle distribution. The first one was characterized by presence of new particle formation event (nucleation event, Fig.1a). The event often started around 10:00–11:00 CST (Chinese Standard Time) and ended up after 3–4 h (Fig.1a). Concentration of nucleation mode particles then decreased substantially without an observable increase in mode diameter of the particles. This is different from the typical new particle formation events reported by Kulmala *et al*. (2004) and Wehner *et al*. (2004b). During the observation period, nucleation events were observed in 8 d. The second pattern was characterized by continuous high number concentration of Aitken mode particles (Fig.1b). This pattern was observed in 5 d.

Diurnal variation of particle size distribution averaged over the observation period is shown in Fig.1c. Number concentration and mode diameter of Aitken and accumulation mode particles increased from midnight to 06:00 CST. Concentrations of Aitken and accumulation mode particles reached their maxima during 08:00–09:30 CST, and decreased substantially after 10:00 CST. Their concentrations were the lowest in the afternoon, and increased slightly

Table 1 Average number concentration of particles (unit: 10^4 cm^{-3})

Mode	Campus of Tsinghua University						Roadside
	All day[1]	Clear day[2]	Clear/cloudy day[3]	Cloudy day[4]	Daily min.	Daily max.	hourly average
Nucleation (5.6–20 nm)	1.75	1.51	1.65	2.43	0.52	2.88	17.99
Aitken (20–100 nm)	3.20	3.05	3.05	3.81	1.12	4.40	11.46
Accumulation (100–560 nm)	0.40	0.34	0.38	0.56	0.04	1.14	0.32
Total particle (5.6–560 nm)	5.35	4.91	5.07	6.79	2.50	7.51	29.78

[1] 15 d average; [2] 6 d average; [3] 6 d average; [4] 3 d average.

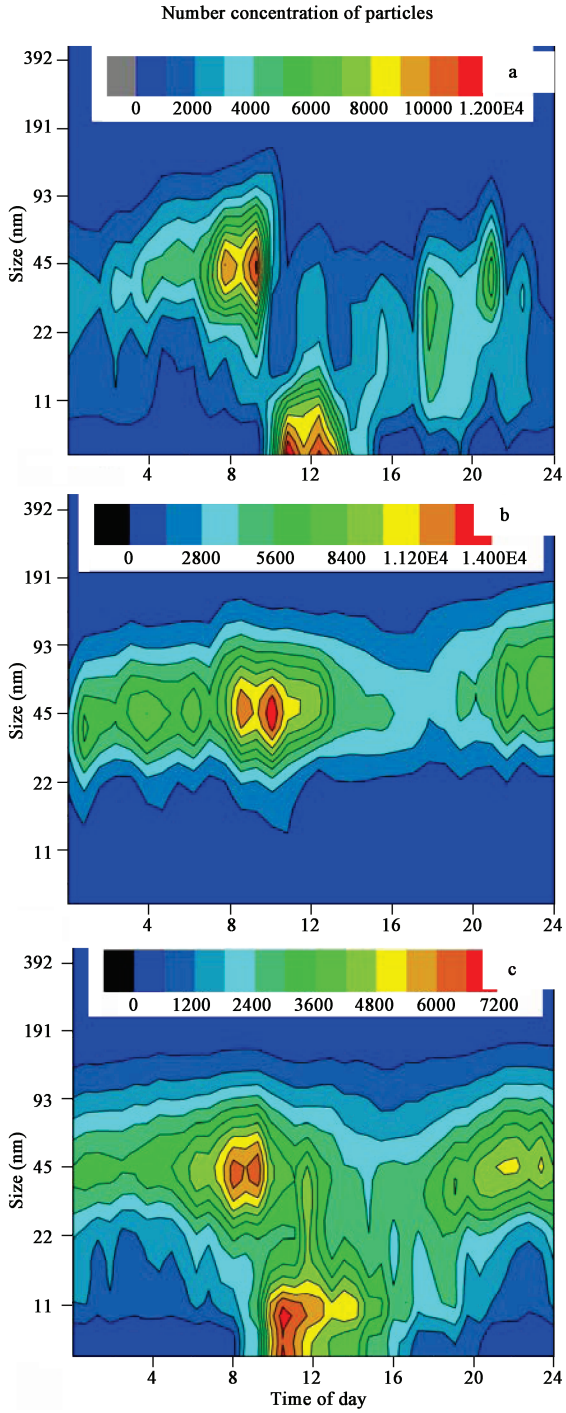

Fig. 1 Diurnal variation of particle size distribution in a day with new particle formation event (a), in a day with continuous high number concentration of Aitken particles (b), and averaged over the observation period (c) (Unit: cm^{-3}).

after 18:00 CST. In contrast, concentration of nucleation mode particles increased significantly after 10:00 CST and maintained a high level until about 14:00 CST. Their concentrations were low at other times.

Concentration of total particles had a maximum during 09:00–10:00 CST (Fig.2) and maintained a high level during 08:00–12:00 CST. The concentrations were lower in the afternoon, especially during 16:00–17:00 CST. Fig.2 also shows that diurnal variation of concentration of total particles averaged over the workdays was similar to that over the nonworkdays. This is different from those reported in some cities in developed countries (Pekkanen *et al*., 1997; Wehner *et al*., 2002; Laakso *et al*., 2003).

Diurnal variations of mixing ratios of SO_2, NO_x, CO, and O_3 and mass level of PM_{10} are shown in Fig.3. PM_{10} mass and SO_2 mixing ratio were the highest at about 10:00 CST. NO_x mixing ratio was the highest at about 09:00–12:00 CST (Fig.3). CO concentration kept its high level from midnight to about 09:00: CST. Concentrations of SO_2, NO_x, CO, O_3, and PM_{10} all decreased substantially after reaching their maximum levels. These characteristics were similar to those of Aitken and accumulation mode particles but were different to that of nucleation mode particles (Fig.1c).

2.3 Diurnal variation of particle size distribution

The particle size distribution averaged over the observation period was bimodal (Fig.4). One mode was about 10 nm, and another is about 40 nm. The former mode was newly-nucleated particles (Charron and Harrison, 2003); whereas the latter one was primary particles emitted from combustion sources (Shi and Harrison, 1999) or the particles formed by coagulation of newly-nucleated ones (Wehner *et al*., 2004a; Hasegawa *et al*., 2004). It is also noted that concentration of particles was the lowest at about 20 nm, which is the reason why we divide the nucleation and Atiken mode particles at this size.

As shown in Fig.4, distribution of particles during the daytime was different from that at night. During the daytime, it was bimodal with mode diameters of about

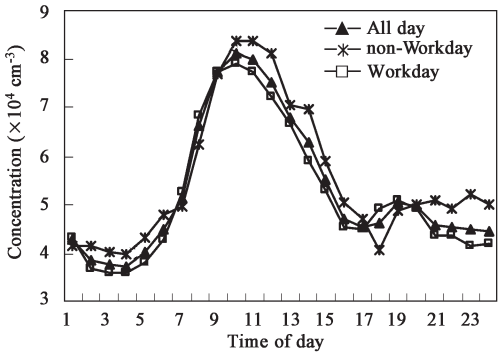

Fig. 2 Diurnal variation of number concentration of total particles averaged over the workdays, the non-workdays, and the observation period.

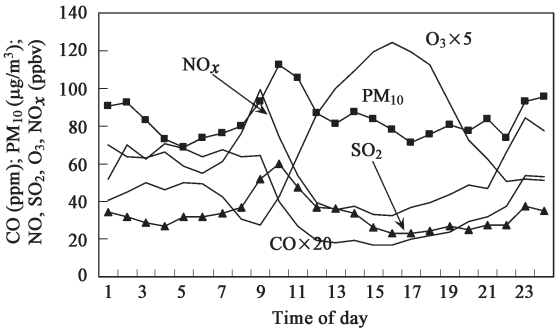

Fig. 3 Diurnal variations of mixing ratios of CO, NO, NO_x, SO_2, and O_3, and mass level of PM_{10} averaged over the observation period.

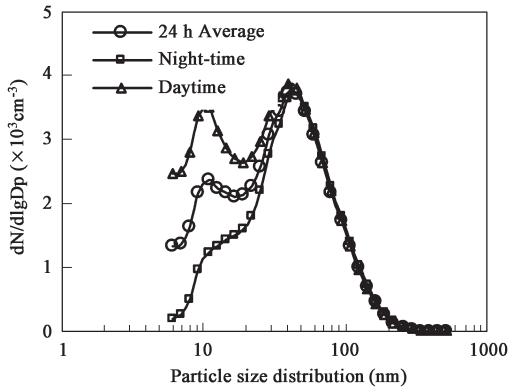

Fig. 4 Daily, daytime, and nighttime averaged number size distributions of particles during the observation period. dN/dlg Dp displays differential or normalized particle size distribution.

10 and about 40 nm. However, the distribution became monomodal with a mode diameter of about 40 nm at night.

3 Discussion

3.1 Comparison of particle number concentration in Beijing and some cities in developed countries

Number concentration of particles larger than 10 nm in Beijing was compared to those in some cities in developed countries. Upper limits of the size ranges were different in literature. Fortunately, their influence on the comparison should be small because concentration of particles larger than 560 nm is low. During the observation period, the concentration of particles larger than 10 nm in Beijing was 4.7×10^4 cm^{-3}, which was much higher than those in Alkmaar of Holland (Ruuskanen *et al*., 2001), Erfurt of Germany (Ruuskanen *et al*., 2001; Tuch *et al*., 2003; Kreyling *et al*., 2003), Helsinki of Finland (Ruuskanen *et al*., 2001; Laakso *et al*., 2003), and Leipzig of Germany (Tuch *et al*., 2003).

3.2 Occurrence of nucleation events

The nucleation events often occurred after a sharp decrease in concentrations of Aitken and accumulation mode particles (Fig.1a). This suggests that the decrease in particle number, and thus surface area, favors new particle formation (Kulmala *et al*., 2004; Wehner *et al*., 2004b). The nucleation events did not occur at the time under the strongest solar radiation and highest atmospheric temperature. Lower concentration of SO_2 (Fig.3), which is the precursor gas of H_2SO_4, and higher temperature in the afternoon may partly account for this trend (Wehner *et al*., 2002; Kulmala *et al*., 2004).

The SO_2 and PM_{10} mass levels during the days with nucleation events were mostly less than 100 and 80 $\mu g/m^3$ with an average of 60 and 69 $\mu g/m^3$, respectively. On the contrary, those during the days with continous high concentration of Aitken particles were mostly higher than 100 and 80 $\mu g/m^3$ with an average of 146 and 137 $\mu g/m^3$, respectively. This suggests that higher pollution suppresses new particle formation.

3.3 Vehicle emission and diurnal variation of particle number concentration

Vehicle emission is considered to be one of the major sources of ultrafine particles in the urban atmosphere in developed countries (Shi *et al*., 2001; Molnár *et al*., 2002; Wehner *et al*., 2002; Laakso *et al*., 2003; Hasegawa *et al*., 2004). The conclusion was frequently made by comparing diurnal variations in particle concentration and traffic volume in workdays with those in nonworkdays. However, this approach was not applicable in this study because the diurnal variation of traffic volume in workdays did not show large difference to that in nonworkdays in Beijing.

In this study, dirunal variation of ultrafine particle concentrations did not correspond with that of total traffic volume except in the early morning. As shown in Fig.1c, concentration of Aitken particles increased from 06:00–10:00 CST with a decrease in mode diameter. This corresponded with an increase in traffic volume during the period, suggesting that vehicle emission contributed to the accumulation of Aitken particles. The increase in NO_x concentration during this period supported the influence of vehicle emission on accumulation of air pollutants. While traffic volume decreased slightly from 09:00–12:00 CST and maintained a high level from 15:00 until 19:00 CST, concentrations of Aitken and accumulation mode particles substantially decreased after 10:00 CST and were lower in the afternoon (Fig.1c). After 18:00 CST, their concentrations increased, while traffic volume decreased. Therefore, variation in concentrations of Aitken and accumulation mode particles after 10:00 CST could not be explained by variation in traffic volume. This indicates that there were factors other than vehicle emission affecting their variation. The argument is supported by the weak correlation of hourly average mixing ratios of CO and NO with concentrations of nucleation, Atiken, and accumulation mode particles (all correlation coefficients are less than 0.65).

3.4 Meteorological condition and diurnal variations of particle number concentrations

That concentrations of Aitken and accumulation mode particles, mixing ratios of SO_2, NO_x and CO, and mass level of PM_{10} all maximized in the morning and minimized in the afternoon, pointing to common factors affecting their diural variations. Meteorological condition was most likely the driving factor. In Beijing, an inversion in the surface layer often formed at night and became stronger in the morning in winter, resulting in air stagnation. This could contribute to accumulation of Aitken and accumulation mode particles. The inversion disappeared as ground temperature increased. This facilitated dispersion of air pollutants including Aitken and accumulation mode particles (Fig.1c and Fig.3). In addition, concentrations of Aitken and accumulation mode particles were the lowest when wind speed was the largest, suggesting that wind speed may be another important factor affecting the concentrations of such particles. This is confirmed by the data

Table 2 Influence of wind speed and wind direction on hourly average concentrations of particles in different modes (Unit: 10^4 cm^{-3})

Mode	Wind speed (m/s)				Wind direction* (°)			
Range	0–1.0	1.0–2.0	2.0–3.0	>3.0	0–90	90–180	180–270	270–360
Frequency (%)	38	31	15	16	16	8	15	62
Nucleation (5.6–20 nm)	0.97	1.77	2.67	2.24	1.48	0.84	0.76	2.08
Aitken (20–100 nm)	5.19	3.21	2.66	1.60	3.37	3.88	3.94	2.91
Accumulation (100–560 nm)	0.67	0.39	0.24	0.09	0.48	0.74	0.55	0.33
Total particle (5.6–560 nm)	5.86	5.37	5.57	3.92	5.33	5.46	5.27	5.32

*North is 0°; south is 180°.

in Table 2, which shows that the higher the wind speed, the lower the concentrations of Aitken and accumulation mode particles. Dependency of concentrations of ultrafine particles on wind speed has also been indicated in other studies (Molnár *et al*., 2002; Wehner *et al*., 2002; Hasegawa *et al*., 2004). Thus, dispersion of Aitken and accumulation mode particles in the afternoon was associated with more effective vertical mixing and higher wind speed.

Wind direction moderately affected concentration of total particles but greatly affected those of nucleation, Aitken, and accumulation mode particles (Table 2). Concentration of nucleation mode particles was higher when the wind blew from the northwest, whereas those of Aitken and accumulation mode particles were higher when the wind blew from the southwest and southeast. This is because the northwest wind brought cleaner air masses, whereas southwest and southeast winds brought polluted air masses to the measurement site. The above results further supported the argument that higher pollution suppresses new particle formation.

4 Conclusions

Number concentration and distribution of airborne particles in the size range 5.6 to 560 nm were measured in an urban area of Beijing in winter 2005. Daily average number concentrations of nucleation, Aitken, and accumulation mode particles, 10–560 nm and 5.6–560 nm particles were 17500, 32000, 4000, 47000 and 53500 cm^{-3}, respectively. Diurnal variation of nucleation mode particles were connected to new particle formation events. The difference in diurnal variations of traffic volume and ultrafine particle concentrations suggested that vehicle emission was not the dominant factor affecting concentrations of ultrafine particles. The concentrations of nuclation, Aitken and accumulation mode particles showed strong dependency on wind speed and wind direction.

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