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Characterization of airborne individual particles collected in an urban area, a satellite city and a clean air area in Beijing, 2001

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Abstract

Collection campaigns for PM_{10} and $PM_{2.5}$ have been conducted in a northwestern Beijing urban area in monthly periods over 2001, with 7 days collection per month. The samples were also collected simultaneously in a satellite city, Nankou, and a clean air area near the Ming Tombs Reservoir (MTR) over the domestic heating (March) and non-heating (July/August) periods in 2001 (both for one week). To assist the analysis, three types of 'source' particulate matter (PM) samples were taken. These consisted of coal combustion ash collected on top of a coke oven; dust storm particles collected during dust storm periods; and roadside PM_{10} collected on a major road in Beijing. Monitoring results reveal that, in the urban area, particle mass levels were higher in winter than in other seasons. The 1-week/month average PM_{10} mass levels were over 250 μg m^{-3} in winter. The particle mass levels in the satellite city were slightly lower than those at the urban site, and the lowest mass levels occurred at the MTR site. The morphology and chemical composition of individual airborne particles were determined by scanning electron microscopy, and image analysis was employed to study the number-size distributions. The number-size distributions of mineral particles showed that those in the Asia-Dust storm (ADS) collections are mostly coarser than 1 μm, while mineral particles of the non-ADS collections are predominately finer than 1 μm. The particles in the respirable (<2.5 μm) fraction accounted for 99% of the total particles in airborne PM samples. Soot aggregates were generally the most abundant components in airborne PM samples at all three sites. The fly ash (spherical) particles at the MTR site were significantly enriched over the heating period, indicating a domestic coal-burning source.

Keywords: Airborne particles; Beijing air; Minerals; Size distribution; PM_{10}

1. Introduction

Many epidemiological studies provide evidence of a causal association between exposure to airborne particles, measured as PM_{10} (particulate matter less than 10 μm) and increased daily mortality and morbidity in adults (Schwartz, 1994; Pope III et al., 1995; Ostro et al., 1999), especially elderly adults (age 65 years and older) with cardiopulmonary illness (Chapman et al., 1997). Studies in Beijing have shown that increases in airborne particulate pollution can cause increases in mortality and hospital visits (Xu et al., 1994, 1995). It was reported that the hourly average PM_{10} mass levels could be as high as 400 μg m^{-3} in urban Beijing (Ando et al., 1994; Ning et al., 1996; He et al., 2001; Shi et al., 2002).

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During recent years the Beijing government has imposed strong measures to counteract atmospheric pollution, especially particulate pollution. Amongst other measures, these include the gradual replacement of coal by gas for domestic heating from 2000 onwards, and the prohibition of the burning of high sulphur and high ash coal. However, the clean air days (i.e. daily PM_{10} mass level lower than 150 μg m^{-3}, the Class II National Air Quality Standard of China for PM_{10} (GB3095-1996)) only account for half of year 2001 (http://www.bjepb.gov.cn).

Coal burning particles were recognized as a major source of Beijing PM_{10} (e.g. Winchester and Bi, 1984; Dod et al., 1986; Ando et al., 1994). However, recent studies suggest that automobile exhaust particles, particularly diesel exhaust particles, are becoming a more prominent component in Beijing PM_{10} (Zhang et al., 1998). Mineral dusts, though one of the main components in Beijing PM_{10}, have not been extensively studied to date. Winchester and Bi (1984) suggest that the main source of coarse mineral particles is local surface dust being re-suspended by vehicle traffic. In spring the particulate pollution in Beijing is occasionally exacerbated by the ADS (Asia-Dust Storm) (Iwasaka et al., 1988). Dust storm particles and coal burning particles are characteristic of Beijing air, which are very different from source profiles of airborne particles in large cities of western countries as reported by Chow et al. (2000), Harrison and Yin (2000), Watson and Chow (2001) and Watson et al. (2002).

With complicated and multiple emission sources, individual particle characterization of sources and receptor samples have become a necessary means for accurate source apportionment (Watson et al., 2002). Electron microscopy has proved to be an ideal tool for characterization of individual particles (Anderson et al., 1988; Iwasaka et al., 1988; Katrinak et al., 1995; Querol et al., 1996; Pooley and de Mille, 1999; Bérubé et al., 1999; Zhang and Iwasaka, 1999; Jones et al., 2001; Shi et al., 2002). Electron microscopy, coupled with Energy Dispersive X-ray Spectrometer (EDX), can provide valuable information on the composition, sources, and atmospheric transformations as well as the number and volume-size distribution of atmospheric aerosols (Bérubé et al., 1999; McMurry, 2000). These data are essential for the assessment of health effects of airborne particles (Bérubé et al., 1999), but cannot be obtained by mass measurement alone (Pooley and de Mille, 1999). Previous studies of Beijing airborne particulate matter (PM) have mainly concentrated on mass and bulk chemical measurements (Winchester and Bi, 1984; Dod et al., 1986; Huebert et al., 1988; Ando et al., 1994; Chen et al., 1994; Ning et al., 1996; He et al., 2001; Yao et al., 2002). Although there are some studies that are concerned with morphological features and chemical compositions of PM from ADS (Fan et al., 1996; Zhou et al., 1996; Zhang and Iwasaka, 1999), few studies have been undertaken to study the microscopic characteristics and number-size distributions of Beijing PM_{10} and its 'source' samples.

The objective of this study was to monitor the mass levels of airborne PM in urban Beijing, a satellite city (Nankou) and a clean air area (Ming Tombs Reservoir; MTR). In addition, the study aims to characterize individual particles in these PM_{10} samples along with three 'source' samples (coal combustion ash, ADS and roadside PM_{10}) in order to determine the likely sources.

2. Materials and measurement

2.1. Sample collection

Three sites were selected for collection of PM_{10} and $PM_{2.5}$, an urban site, a satellite city and a clean air site (Fig. 1). The urban collection site was located in northwestern Beijing around 1 km from the fourth ring road of Beijing city. The samplers were mounted on the fifth floor of the main building in China University of Mining and Technology, 100 m west from the Xueyuan Road (a major road in Beijing). The satellite city collection site was located in Nankou, a town around 45 km northwest from central Beijing. The samplers were installed in a local factory. The clean air collection site was located at the MTR site, around 40 km northeast from central Beijing. The Ming Tombs area is currently the background air quality monitoring site for the Beijing Environmental Monitoring Network. The sample information is shown in Table 1. At the urban site (Beijing), 12-h PM_{10} and $PM_{2.5}$ were collected for 7 days per month over 2001. During the heating

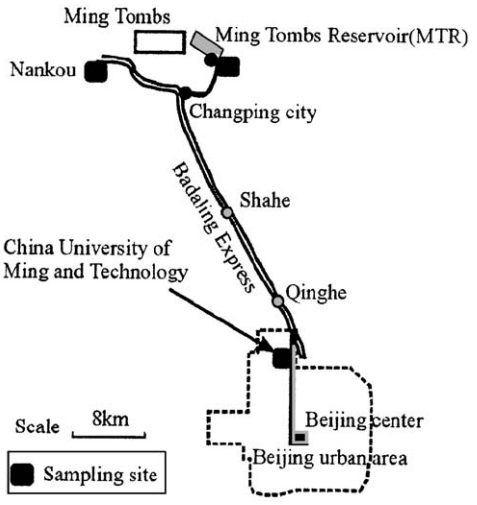

Fig. 1. Sketch map of collecting sites.

Table 1
Summary of sample collection information

Type	'Source' samples			Airborne PM_{10} and $PM_{2.5}$				
Collection site	Coal fly ash Coking oven	ADS Beijing	Roadside PM Xueyuan Rd.	Nankou		MTR		Beijing
Collection date	July	Spring	Sep.	Mar.	Aug.	Mar.	July–Aug.	Jan–Dec.
Sample number	16	5	4	28	18	15	40	About 40 each month

(March) and non-heating (July/August) periods, the samples were collected simultaneously in a satellite city, Nankou, and a clean air area near the Ming Tombs Reservoir (MTR). Three types of 'source' samples, coal combustion ash, dust storm particles and roadside PM_{10}, were also taken. Two kinds of coal combustion ash samples were collected; one was collected during coal feeding process (rapid combustion of coal with air) and another during charcoal pushing (ash is formed in the oven without air).

TSP-PM_{10}-$PM_{2.5}$ ~2 samplers (Beijing Geologic Instruments Factory) and a high volume XH-1000 sampler (Hebei Sailhero High-tech Co., Ltd), both using glass fibre filters, were employed to collect $PM_{2.5}$ and PM_{10} for mass measurements. A Negretti selective head (UK), with polycarbonate filters (Millipore, UK), was used to collect particles for microscopic analysis.

2.2. Measurement

2.2.1. Gravimetric analysis

The glass fibre and polycarbonate filters were weighed before and after collection with a 0.01mg precision microbalance after preconditioning for 48 h at constant humidity (40–42%) and temperature (20–22°C).

2.2.2. Electron microscopy

A 4 mm (internal diameter) copper washer was fixed on the standard 12.5 mm aluminum SEM stub using epoxy resin (Araldite). Approximately one eighth of the polycarbonate filter was cut and mounted onto the copper washer using epoxy resin (Bérubé et al., 1999). The stubs were gold coated to a thickness of 20 nm using a sputter coater (Cressington 208HR). The specimens were analysed using a XL30 Field Emission Scanning Electron Microscope (FESEM, Philips Electron Optics, NL) at the Natural History Museum (London, UK). A Philips XL30 Environmental Scanning Microscopy (ESEM) coupled with an Energy Dispersive X-ray Spectrometry (EDX) at Cardiff University (UK) was also used to obtain the morphology and chemical composition of individual particles. For the ESEM analyses the samples were carbon coated.

2.2.3. Image analysis

Images from the FESEM were further analysed with the Quantemet 500MC image processing and analysis system (Leica, UK). By targeting each of the particle groups the custom-written program automatically calculated the equivalent spherical diameter (ESD) of the particles. The data was then downloaded into Microsoft Excel for further processing. Image analysis is only reliable when the particles on the filter are sparse enough for individual particles to be identified. In our study, about one third of collected samples, from different seasons and sites, are chosen for microscopic analysis, of which about two thirds are appropriate for image analysis. Samples during very high PM pollution episodes, for example, PM_{10} mass levels larger than 250 μg m^{-3}, are not analysed in this study.

3. Results

3.1. Mass concentrations

In 2001, seasonal differences were apparent (Fig. 2). The wintertime collections from December to March had the highest particle mass levels, with the 1-week/month average PM_{10} mass concentrations over 250 μg m^{-3}. One-week/month average PM_{10} mass levels in March even reached 365 μg m^{-3} and a 12 h average PM_{10} mass concentration reached 655 μg m^{-3}. This was possibly due to increased emissions from heating sources coupled with meteorological conditions that limit dispersion (Dod et al., 1986; He et al., 2001). From April to June, high particle mass levels were also recorded; this was attributed to low precipitation and high average wind speed. The summer and early autumn collections from July to September had the lowest PM mass levels.

$PM_{2.5}$ constituted 46% of the PM_{10} in the urban area during 2001. The annual average (1-week/month) $PM_{2.5}$ mass concentration is 106 μg m^{-3}, which is approximately seven times higher than the annual average National Ambient Air Quality Standard of the United States (NAAQS) for $PM_{2.5}$. And the annual average (1-week/month) PM_{10} mass concentration at the urban Beijing site was 230 μg m^{-3}, which is 130% higher than

the annual average National Ambient Air Quality Standard of China (GB3095-1996) for PM_{10}.

During heating (March) and non-heating (July/August) periods, PM_{10} and $PM_{2.5}$ samples were collected at Nankou and the MTR site. The results are summarized in Table 2. The weekly average PM_{10} and $PM_{2.5}$ mass concentrations in Nankou were 334 ± 96 and $177\pm53\ \mu g\ m^{-3}$ during the heating period, and 44 ± 14 and $25\pm11\ \mu g\ m^{-3}$ during non-heating period. Particle mass levels during the heating period in Nankou were lower than those at the urban site. The weekly average PM_{10} mass concentration at the clean air site was $119\pm42\ \mu g\ m^{-3}$ during the heating period compared to $313\pm101\ \mu g\ m^{-3}$ at the urban Beijing site. Both $PM_{2.5}$ and PM_{10} mass concentrations during the non-heating period at the clean air site were lower than $50\ \mu g\ m^{-3}$, whereas the 5-day 24-h average PM_{10} mass concentration during heating period exceeded $100\ \mu g\ m^{-3}$.

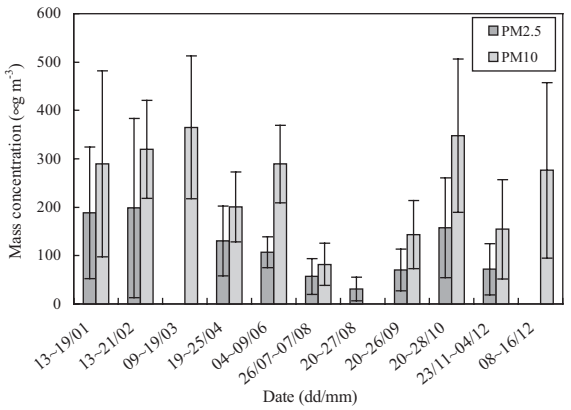

Fig. 2. One-week/month average mass concentrations of $PM_{2.5}$ and PM_{10} in urban Beijing air during 2001.

3.2. Particle types and morphology

Analyses of particle morphologies are based on the FESEM observation. Different types of particles collected from both ambient air and 'sources' were determined.

3.2.1. Soot aggregates

The soot aggregates readily aggregate together, developing from small groups or chains into larger chains (Fig. 3a). When the soot is wetted, the morphology changes further (Fig. 3b), losing its 'fluffy' appearance. Any of the soot aggregates described above are put into 'soot' type in image analysis.

3.2.2. Coal fly ash

In this study, the 'coal fly ash' is defined as the spherical particle (Fig. 3c), which is larger than 100 nm. Some of the spheres found in Beijing are coated with fine particles ($<2.5\ \mu m$, Fig. 3d). These fine particles may be the solid products of atmospheric chemical reaction (usually involving SO_2) (Querol et al., 1996), or may be emitted along with the fly ash particles and adhered to the surfaces of the sphere, a process called the self-absorption effect. The fly ash particles examined in this study were predominately aluminosilicates in composition.

3.2.3. Mineral matter

Mineral dusts are common in Beijing air. The irregular shaped grains are geologically sourced (Fig. 3e), while the elongated particles (Fig. 3f) and the bar-shaped particles (Fig. 3g) are possibly formed by secondary atmospheric reactions. The EDX spectra of these elongated crystals show that they contain significant amounts of K and/or Al in addition to $CaSO_4$. This suggests that these crystals may comprise two or more phases of sulphates or sulphates and non-sulphates,

Table 2
Comparison of particle mass levels in ambient air of Beijing, MTR and Nankou during the heating and non-heating periods over 2001

Particle type	avg. ± S.D. ($\mu g\ m^{-3}$)	Sample number	Collection date	Urban		
				avg. ± S.D. ($\mu g\ m^{-3}$)	Sample number	Collection date
MTR						
PM_{10}	119 ± 42	5	14–19 March	313 ± 101	10	14–19 March
$PM_{2.5}$	32 ± 30	17	27 July–5 Aug.	46 ± 28	17	27 July–5 Aug.
PM_{10}	49 ± 23	17	27 July–5 Aug.	68 ± 33	15	27 July–5 Aug.
Nankou						
$PM_{2.5}$	177 ± 53	9	9–14 March			
PM_{10}	334 ± 96	10	9–14 March	417 ± 181	10	9–14 March
$PM_{2.5}$	25 ± 11	13	20–27 Aug.	25 ± 13	13	20–27 Aug.
PM_{10}	44 ± 14	13	20–27 Aug.			

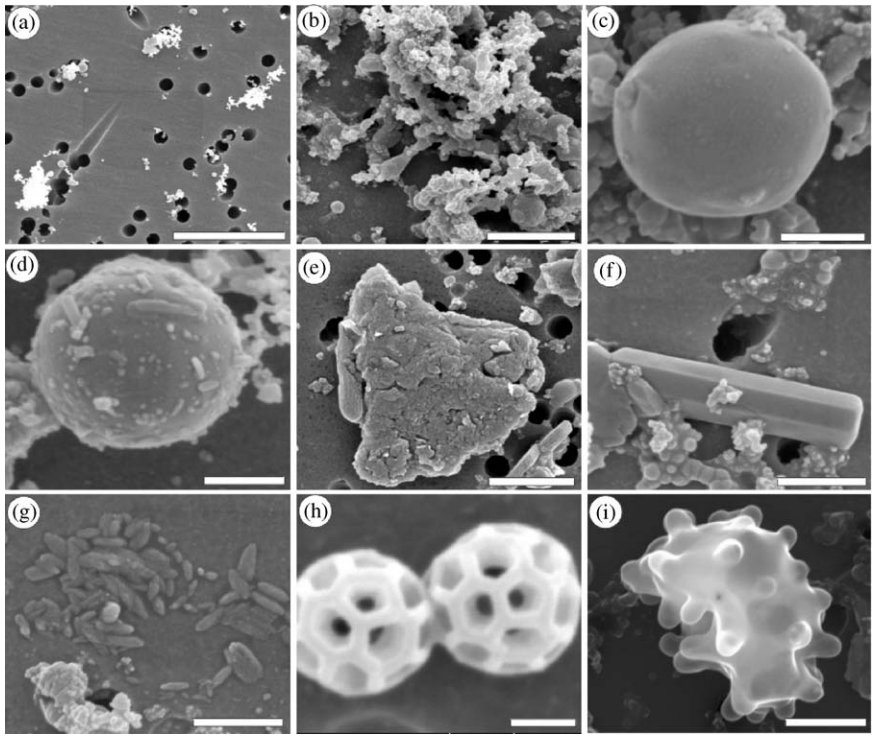

Fig. 3. Typical particle types in Beijing air. (a) Soot aggregates, developing from small groups or chains into larger chains (scale bar 5 μm). (b) 'Wet' soot aggregates, having lost their 'fluffy' appearance (scale bar 1 μm). (c) A smooth coal fly ash particle (scale bar 500 nm). (d) A coal fly ash particle coated with fine particles (scale bar 500 nm). (e) Irregular mineral particle that is geologically sourced (scale bar 2 μm). (f) Elongated particle observed in some samples at all three sites (scale bar 2 μm). (g) Bar-shaped gypsums observed at the urban site only (scale bar 2 μm). (h) Biological particles. Large amounts of these particles are observed in groups only on one July collection at the MTR site (scale bar 200 nm). (i) A biological particle. Only observed on one July collection at the MTR site (scale bar 3 μm).

similar to particles seen in a case study in Phoenix, Arizona reported by Katrinak et al. (1995).

3.2.4. Other particles

Biological particles, coal debris, some unrecognized particles and ultrafine particles (<100 nm) were also observed in the collections. Figs. 3h and i show two distinct biological particle types. Large numbers of ultrafine particles (<100 nm) were seen in certain samples. Some ultrafine particles, which are near-cubic or bar-shaped, rather than spherical shapes, are most likely secondary particles such as sulphates or nitrates (Fig. 4). These have been identified as an important fraction of Beijing airborne particles from bulk chemical analysis (Huebert et al., 1988; He et al., 2001; Yao et al., 2002). This hypothesis is supported by comparison of backscatter and secondary electron images of the same field, which show that some ultrafine particles are bright in backscattering mode, indicating the presence of elements with an atomic weight larger than 11.

3.2.5. Particle morphology of 'source' samples and PM_{10} in ambient air

As one of the major stationary industrial sources, a coking plant may emit three types of particles, spherical fly ash (Fig. 5a) produced during coal feeding, soot aggregates (Fig. 5b) emitted during coke pushing, and ultrafine particles (Figs. 5a and b) produced from both processes. Irregular mineral particles predominate the dust storm particles (Fig. 5c). Although morphological modification of ADS particles originated from China has been observed in Japan by Iwasaka et al. (1988) and Zhou et al. (1996), almost all ADS particles in Beijing exhibited no sign of this kind of modification. Roadside PM_{10} samples are dominated by fine soot aggregates with small amounts of mineral particles and rare fly ash particles (Fig. 5d). Most of these soot aggregates are fine chains. During the high pollution periods, the airborne PM samples were complex mixtures of soot aggregates, coal fly ash, minerals and ultrafine particles as well as some unidentified particles (Fig. 5e). Heating period collections at the MTR site were special in that they contained large amounts of coal fly ash (Fig. 5f).

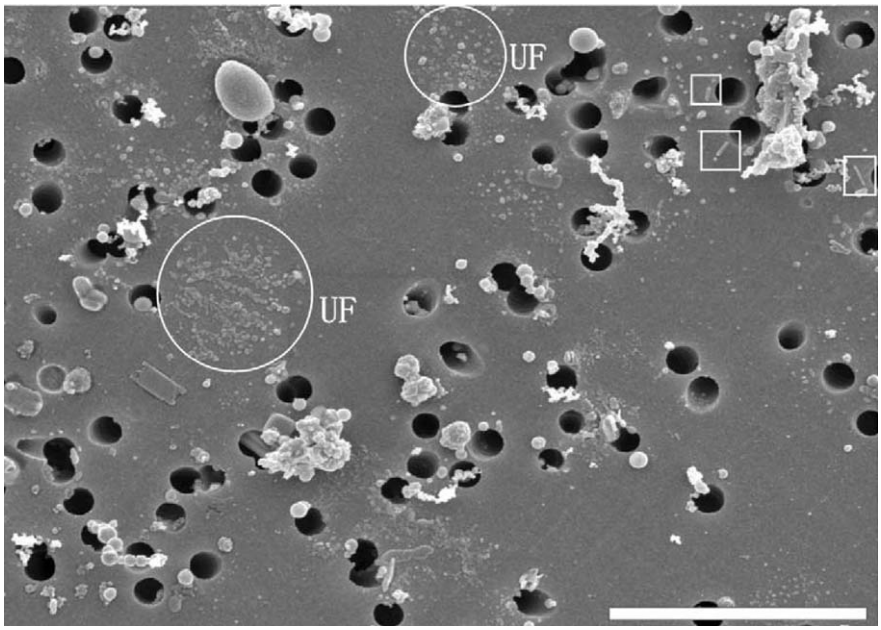

Fig. 4. Ultrafine particles (UF). They are near-cubic or bar-shaped rather than spherical. These are most likely secondary particles such as sulphates or nitrates. Note the bar-shaped particles in rectangles (scale bar 5 μm).

3.3. Number-size distributions

For each sample, more than 1200 particles on ten images were measured. Three types of particles are classified in number-size distributions: soot aggregates, coal fly ash and minerals. The elongated and bar-shaped particles are put into the mineral category in the number-size distributions. Biological particles are not considered in the number-size distribution due to their low frequency. Ultrafine particles are also not considered in image analysis because of the technical limitation in obtaining the accurate sizes. For some 'fluffy' soot aggregates, the circumscribed area was used as substitute of the surface area.

3.3.1. Coal fly ash

The number-size distribution of coal fly ash that was collected on top of the coke oven during coal feeding (Fig. 6a) was determined by analysing a total of 838 individual particles. All the fly ash particles were less than 1 μm with approximately 68% less than 0.3 μm. The particle number frequency decreases from 0.2 to 1 μm.

3.3.2. ADS collections

The number-size distribution of the mineral particles in the ADS collection showed that mineral particles in 1–2.5 μm size range accounts for about 32% of the total particles (Fig. 6b). The frequency of minerals larger than and less than 1 μm in diameter was 47% and 53%, respectively. About 94% of the particles were in the respirable fraction (<2.5 μm), an important result when considering the potential health hazards of dust storms.

3.3.3. Roadside collections

The predominant size range of the soot aggregates in roadside PM_{10} (Fig. 6c) was between 0.1 and 0.4 μm. The number frequency of the soot aggregates decreased with ESD. Particles less than 1 μm accounted for 98% of PM_{10}. The number-size distribution of soot aggregates in the roadside PM_{10} samples is similar to that of diesel exhaust particles reported by Bérubé et al. (1999) for the UK.

3.3.4. Minerals in PM_{10} and $PM_{2.5}$ collections

The number-size distributions of minerals in non-ADS PM_{10} samples often showed a peak in 0.4–0.5 μm size range (Figs. 7a–d). Mineral particles that are larger than 1 μm accounted for 10–30% of the total mineral particles in PM_{10} samples. Particles larger than 2.5 μm (mostly minerals) were often less than 5% of the total number of the PM_{10} collections.

3.3.5. PM_{10} and $PM_{2.5}$ in ambient air

The number-size distributions of whole PM_{10} and $PM_{2.5}$ samples revealed that more than 99% of the particles analysed are in the respirable fraction, with a peak being in 0.2–0.3 μm size range (Fig. 7a–d). Ning et al. (1996) reported that the peak size range of Beijing aerosol (0.5–15 μm) was between 0.5 and

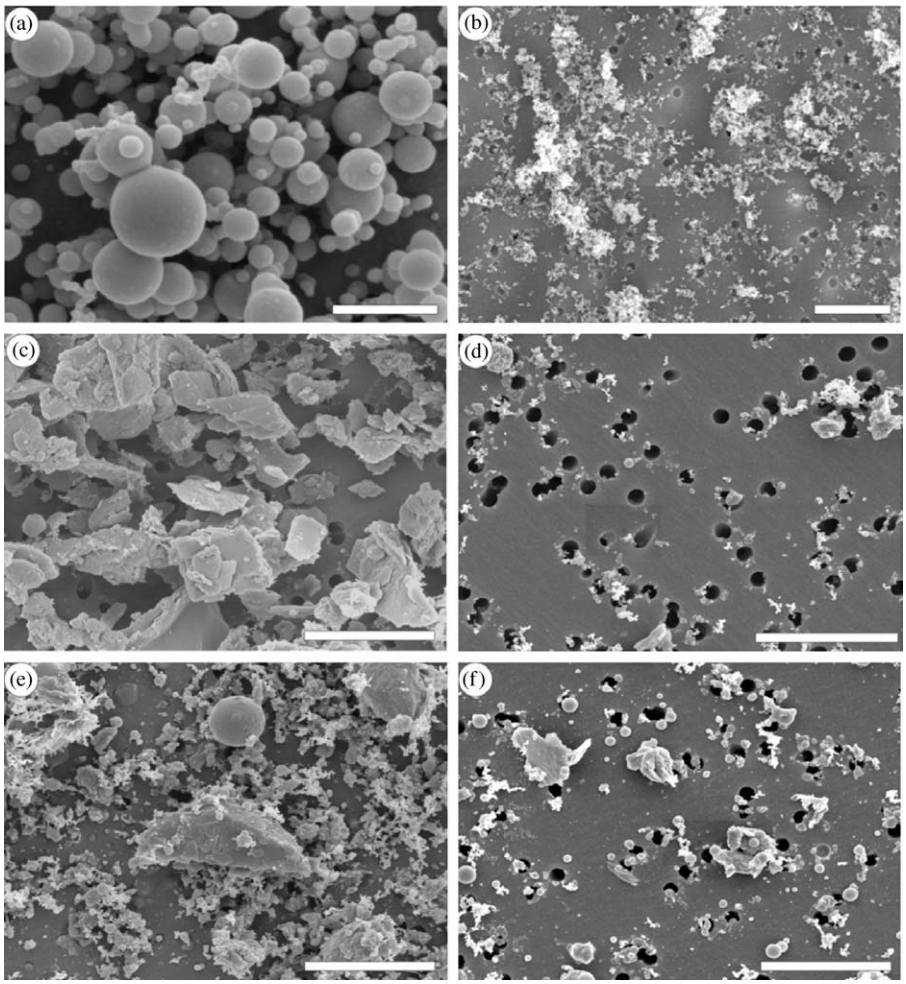

Fig. 5. FESEM images of 'source' and airborne PM samples. (a) Coal fly ash collected on top of the coking oven during a coal feeding operation (scale bar 1 μm). (b) Particles collected on top of the coking oven during coke pushing process. These particles are soot aggregates formed in the coke oven without air (scale bar 5 μm). (c) Dust storm particles collected at the urban site in March 2001. They are mostly geologically sourced irregular mineral particles (scale bar 5 μm). (d) PM_{10} collected on a major road of Beijing in September 2001. Dominated by freshly emitted fine soot aggregates with small amounts of mineral particles and rare fly ash particles (scale bar 5 μm). (e) Typical PM_{10} collected during a high pollution episode (scale bar 5 μm). (f) $PM_{2.5}$ collected during heating period at the MTR site showing large amounts of fly ash particles (scale bar 5 μm).

1.0 μm. Zhang et al. (2000) demonstrated that Beijing PM_{10} has a unimodal size distribution with the peak value in the range of 0.5–0.7 μm.

3.4. Percentage of soot aggregates, coal fly ash and minerals by number and area

Only soot aggregates, coal fly ash, minerals and elongated or bar-shaped particles are used for source analysis. Other particles, such as the biological particles are not considered in source analysis because of their low frequency.

3.4.1. Dust storm, coal fly ash particles and roadside PM_{10}

The three 'source' samples, coal fly ash, dust storm and roadside PM_{10}, were dominated by fly ash particles (99% by number and 94% by area), mineral particles (71% by number and 96% by area) and soot aggregates (88% by number and 70% by area), respectively (Table 3).

3.4.2. Soot aggregates

The presence of soot aggregates in most collections was over 50%, indicating that soot had a regional distribution in Beijing air. A few exceptions were found in some samples in which the contribution of soot

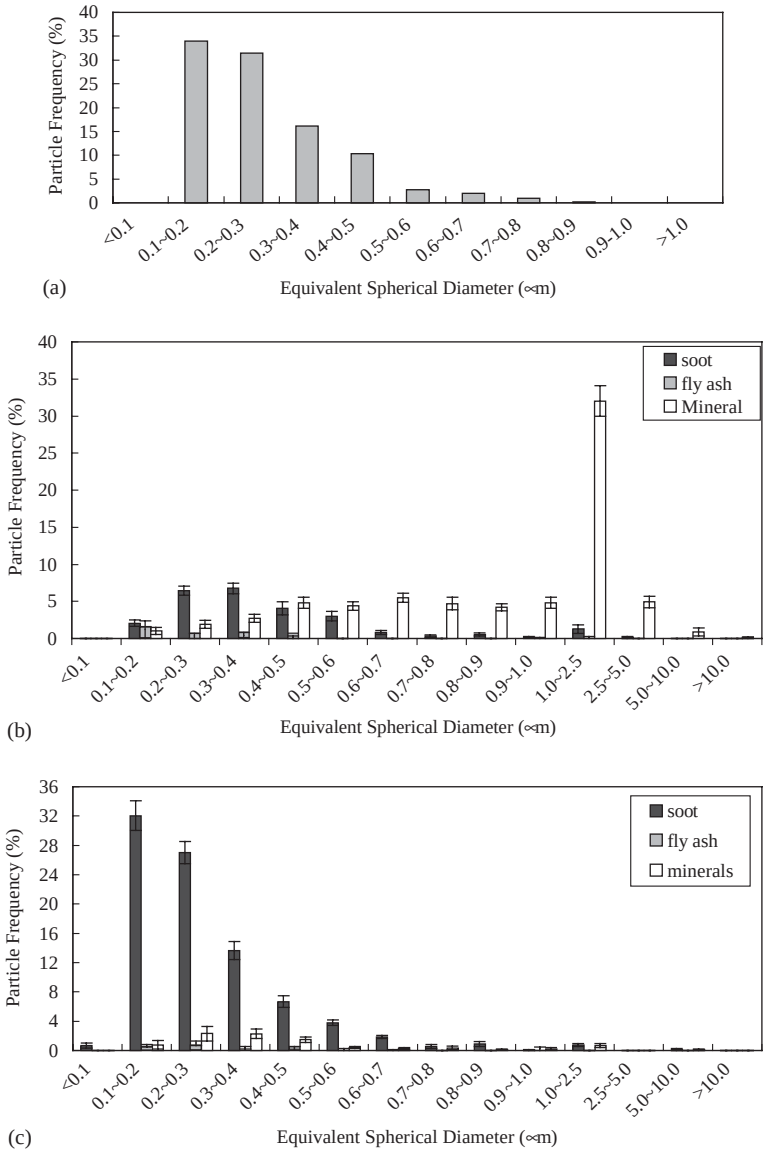

Fig. 6. Number-size distributions of three 'source' particles. (a) Coal fly ash collected on top of the coke oven during one coal feeding operation. Nearly all the fly ash particles are less than 1 μm in diameter. The frequency of fly ash decreases with ESD from 0.1 to 1.0 μm; (b) PM_{10} collected during a dust storm episode. Mineral particles predominate; (c) Roadside PM_{10}. Soot aggregates predominate, with the frequency decreasing with ESD.

aggregates was below 50%, possibly due to a higher proportion of fly ash particles (No. 6 and 7, Table 3), or a higher level of gypsum (No. 4, Table 3). Compared with percentage by number, the percentage by area of the soot aggregates is lower due to the smaller sizes of the soot aggregates.

3.4.3. *Coal fly ash particles*

The percentage of fly ash particles showed a large variation among the three sites from 2% to 41% in this study. The percentage of fly ash particles was consistently lower in the urban area than that in Nankou and MTR areas. Except for the heating period collections at the MTR site, the percentage by area of fly ash particles in all other samples is below 10%, suggesting that the mass contribution of fly ash particles should be quite low. Seasonal variations of fly ash particles are observed at the MTR site. In the samples collected during heating period at this site, the contribution of fly ash particles was as high as 41% (No. 7, Table 3), while in non-heating period samples, the contribution of fly ash particles was as low as 9% (No. 10, Table 3).

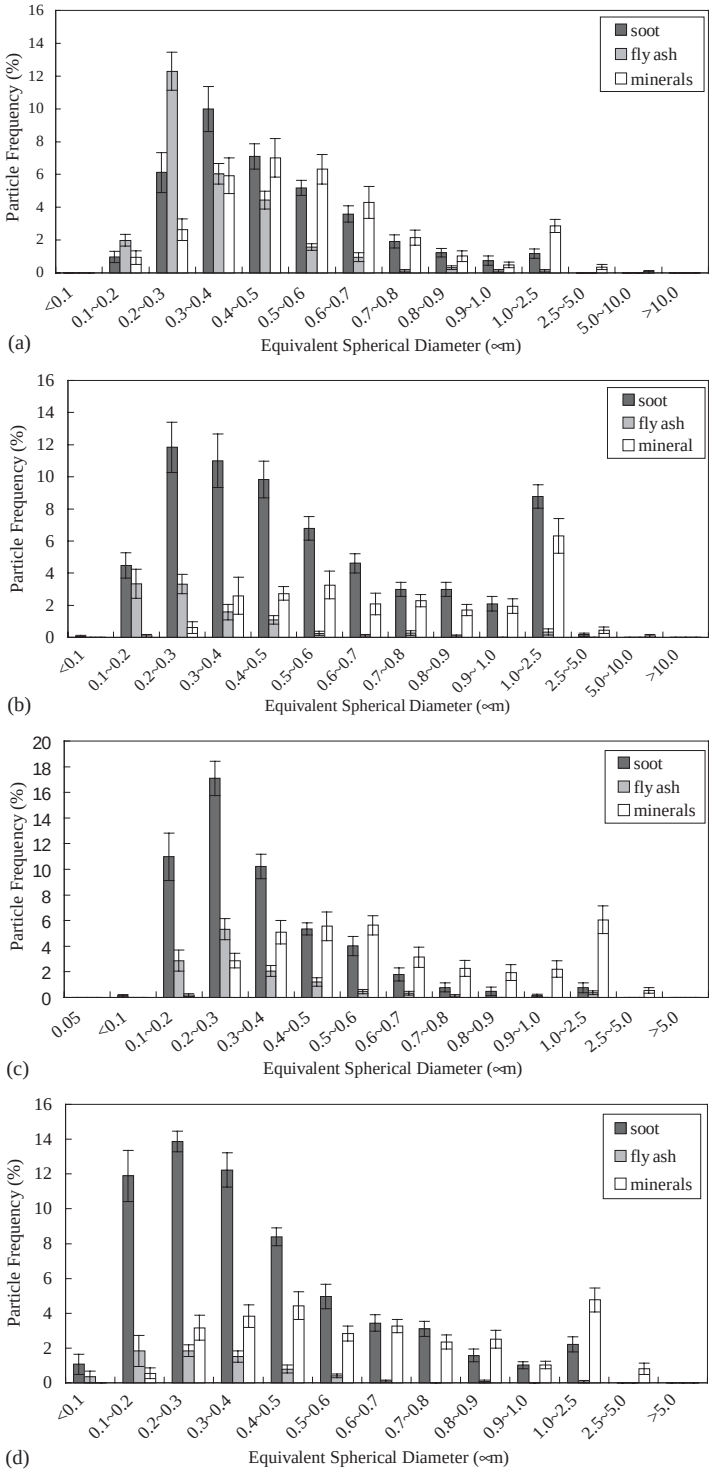

Fig. 7. Number-size distributions of airborne PM at the three collection sites. (a) Representative $PM_{2.5}$ collected during heating period at the MTR site. The contribution of fly ash particles to all the particles analysed is 28%. (b) Representative PM_{10} collected over non-heating period at the MTR site. The contribution of fly ash particles to all the particles analysed is much lower than that in the March collections. (c) $PM_{2.5}$ collected during the heating period in Nankou. The soot particles are predominately in 0.1–0.4 μm size range. (d) PM_{10} collected in July in urban Beijing. The soot particles are predominately in 0.1–0.4 μm size range.

Table 3
Area and number percentage of different types of particles

No.	Site	Date	Time (min)	Type	Soot		Coal fly ash		Mineral		Elongated or bar-shaped particles	
					Area	Number	Area	Number	Area	Number	Area	Number
1	Beijing	Mar-01	480	ADS	4±1	27±5	0±0	2±3	96±1	71±5		
2	Roadside	Sep-01	150	PM_{10}	70±21	88±4	1±1	2±1	29±22	9±5		
3	Beijing	Jul-00	710	PM_{10}	37±6	64±6	2±1	7±3	61±6	29±6		
4	Beijing	Sep-01	720	PM_{10}	34±11	45±10	4±4	5±4	55±16	29±11	7±7	21±22
5	Beijing	Sep-01	720	$PM_{2.5}$	79±7	74±4	3±2	5±3	18±6	21±3		
6	MTR	Mar-01	1440	$PM_{2.5}$	34±14	38±11	11±3	28±6	55±17	34±13		
7	MTR	Mar-01	1020	$PM_{2.5}$	40±11	42±6	28±10	41±8	32±16	17±5		
8	MTR	Jul-01	720	PM_{10}	54±9	66±11	3±2	10±4	34±13	19±13	10±8	6±5
9	MTR	Jul-01	720	$PM_{2.5}$	70±11	76±6	7±4	13±2	21±12	8±5	2±2	4±4
10	Nankou	Mar-01	720	$PM_{2.5}$	57±10	64±5	6±6	9±3	36±15	26±6		
11	Nankou	Mar-01	720	$PM_{2.5}$	22±9	52±11	5±5	13±4	64±14	31±12	9±6	4±2
12	Nankou	Aug-01	720	$PM_{2.5}$	72±15	73±10	9±6	14±6	19±15	13±9		

Note: Uncertainty means standard deviation from ten images.

3.4.4. Mineral matter

The presence of mineral particles varies significantly in different samples and this is possibly due to the complexity of the ambient conditions such as temperature, wind speed and humidity. Contrary to soot aggregates and coal fly ash particles, the percentages by area of mineral particles (from 18% to 64%) in the samples are much higher than the corresponding values of the percentage by number.

4. Discussion

4.1. Source analysis of fly ash

In 2001, some 26.75 million tons of coal were consumed and more than 90,000 tons of combustion ash were emitted in Beijing (http://www.bjepb.gov.cn). However, as one of the major components in coal combustion ash, the spatial and temporal distributions of fly ash particles were not homogenous. The Ming Tombs Region is regarded as the clean air site for Beijing air quality monitoring network. However, this study showed that airborne PM mass levels at this site, though lower than those at the urban collection site, were greatly influenced by anthropogenic activities (coal combustion), especially during the heating period. The temporal and spatial distribution of fly ash percentage in samples at the three collection sites suggested that the higher fly ash content (up to 41%) in airborne PM samples collected during heating period at the MTR site is probably the result of local coal-burning sources for domestic heating.

4.2. Contribution of mineral matter to airborne PM

Characteristics of the number-size distribution of mineral particles during non-ADS episodes (Figs. 7a–d) showed that minerals in 0.4–0.5 μm and 1–2.5 μm size ranges may have different sources. In general, mineral particles in 1–2.5 μm size range are irregular in shape, indicating their geological origins, while many of the mineral particles in 0.3–0.5 μm size range show regular shapes, indicating their secondary reaction origin.

On average the $PM_{2.5-10}$ mass accounts for approximately 54% of the PM_{10} mass. Volume-size distributions of PM_{10} samples also demonstrated that, volume of particles larger than 1 μm often accounted for more than 50% of the total volume of all particles analysed (Shao and Shi, 2003). Therefore, a small number of larger particles must have contributed towards a significant percent of the PM_{10} mass.

5. Conclusions

(1) Distinct seasonal variations in particle mass levels were observed at the urban site, with highest mass level recorded in winter and lowest in summer and early autumn. For both heating and non-heating periods, weekly average particle mass levels were higher at the urban site compared to those at Nankou, with the lowest particle mass levels occurred at the MTR site.

(2) Image analysis showed that more than 99% of airborne particles in PM_{10} and $PM_{2.5}$ and about 94% of dust storm particles are in the respirable fraction. In the roadside PM_{10} samples, particles less than 1 μm accounted for 98% of the total particulate matter. This is of great health concern considering the high PM mass levels in Beijing and the ability of $PM_{2.5}$ to penetrate into the human lung.

(3) Mineral particles are mainly concentrated in two size ranges, 0.4–0.5 μm and 1–2.5 μm. The first one is dominated by minerals of secondary origin and the

second one is represented by minerals of geological sources.

(4) The 'source' samples have their distinct compositions. Mineral matter predominated the ADS collections. Soot aggregates accounted for 88% by number and 70% by area of all the particles analysed. In the coking plant, coal fly ash was produced at the coal feeding mouth, whereas soot aggregates were emitted at the coke-pushing exit.

(5) The presence of soot aggregates in airborne PM samples is generally higher than that of minerals and fly ash. However, although mineral matter is not a dominant component by number in non-ADS PM_{10} and $PM_{2.5}$ samples, its contribution to the total area, therefore, the volume (mass) of the total particles is significant.

(6) Microscopic analysis demonstrated that, Ming Tombs area as the background monitoring site for Beijing Air Quality Monitoring Network is highly polluted by domestic coal burning during the heating period.

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