Morphology of single inhalable particle in the air polluted city of Shijiazhuang, China

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Abstract

In the typical air polluted city of Shijiazhuang, single inhalable particle samples in non-heating period, heating period, dust storm days, and snowy days were collected and detected by SEM/EDS (scanning electron microscopy and energy dispersive X-ray spectrometry). The particle morphology was characterized by the 6 shape clusters, which are: irregular square, agglomerate, sphere, floccule, column or stick, and unknown, by quantitative order. The irregular square particles are common in all kinds of samples; sphere particles are more, and column or stick are less in winter samples; in the wet deposit samples, agglomerate and floccule particles are not found. The surface of most particles is coarse with fractal edge, which can provide suitable chemical reaction bed in the polluted atmospheric environment. New formed calcium crystal is found to demonstrate the existence of neutralized reaction, explaining the reason for the high SO2 emission and low acid rain frequency in Shijiazhuang. The three sorts of surface patterns of spheres are smooth, semi-smooth, and coarse, corresponding to the element of Si-dominant, Si-Al-dominant, and Fe-dominant. The soot particle is present as floccule with average size around 10 µm, considerably larger than the former reported results, but wrapped or captured with other fine particles to make its appearance unique and enhance its toxicity potentially. The new formed calcium crystal, the 3 sorts of sphere surface patterns, and the unique soot appearance represent the single inhalable particle’s morphology characteristics in Shijiazhuang City.

Key words: single particle; morphology; new formed calcium crystal; spheres; soot

Introduction

Air pollution is the major focus of attention in Chinese cities, and suspended particulate matter of aerodynamic diameter less than 10 µm (PM$_{10}$) is reckoned as the first pollutant (Florig et al., 2002). Studies of ambient particulate pollution have been carried out in some big cities in China in the recent years (Ning et al., 1996; Davis and Guo, 2000; Kim et al., 2006). Single particulate of PM$_{10}$ in Beijing (Shi et al., 2003), Qingdao (Zhang et al., 2000), Guiyang (Xie et al., 2005), and Shanghai (Li et al., 2003), has been invested with the results showing that mineral dust and soot are dominant, which derive mainly from anthropogenic influence and discharge. Aerosols produced locally can influence far-reaching areas by transportation mechanisms (Prospero and Savoie, 1989; Heintzenberg et al., 2000; Teinila et al., 2000). According to Han et al. (2005), the non-local sources to the mineral aerosols in Beijing account for 62% in TSP, 69% in PM$_{10}$, and 79% in PM$_{2.5}$. Local air pollution condition cannot be thoroughly explained without taking account of the nearby cities’ atmospheric environment characteristics. The above case researches involved only a few cities with air pollution problems in China, while there still remain other cities, which suffer worse air quality conditions but are rarely discussed.

Shijiazhuang City, located in the north plain of China, 270 km south of Beijing, ranked in the top ten most serious air pollution cities in 2003 by the State Environmental Protection Administration of China, is the only provincial capital city in the blacklist. In 2004, the annual average concentration of the primary pollutant—PM$_{10}$ in Shijiazhuang was 123 µg/m$^3$, exceeding the Chinese national atmospheric quality standard criteria by 23%, considerably higher than that of the cities mentioned above. Nevertheless, characteristics of particulate matter in Shijiazhuang City are unexplored. Meanwhile, the SO2 release amount and the annual average ambient concentration are both high but the occurrence of acid deposits is low in Shijiazhuang City, implying some atmospheric antacid mechanism. Actually, by the dense population and serious atmospheric particulate pollution, Shijiazhuang City can be the typical one for the air pollution research in northern China. Therefore, this article aims at the morphology features of single particulate of Shijiazhuang City by different sampling conditions using SEM/EDS (scanning electron microscopy and energy dispersive X-ray spectrometry)
electron microscopy and energy dispersive X-ray spectrometry) technology, the result of which may be helpful to understand atmospheric particulate characteristics in city cluster of northern China.

1 Materials and methods

1.1 Sampling

PM$_{10}$ samples have been collected at the Environment Monitoring Center of Shijiazhuang City, one of the 6 regular air monitoring stations, on the roof of a five storey building surrounded by residential area. A medium volume sampler (TH-150, Wuhan Tianhong, China) was used under 30 L/min with a cutoff of 10 $\mu$m (aerodynamic diameter), using polycarbonate filters (Millipore, UK, 90 mm in diameter with 0.45 $\mu$m pores) for the microscopic analysis. Five daily samples in June, August, and October 2005 were collected respectively for the period of ordinary days condition (viz. non-heating season) and five daily samples in December 2005 and January 2006 were collected for the period of heating season. All the above samplings were conducted under fine, less windy days, and the collection time of each sample was controlled in 24 h. On March 18–22, 2006, a strong Asian dust storm event occurred in north China and dust float covered Shijiazhuang City. Fortunately, we collected the PM$_{10}$ sample of this typical dust storm process. Also, wet deposit of snow in the winter of 2005 was collected and the unsolvable solid particles were filtered through polycarbonate membranes.

Beside the filter sampling, we hanged vertically a slide covered by a layer of petroleum jelly, which can revolve freely with air turbulence, 1.5 m above roof ground, to collect suspended particles in the air for the particle size and shape detection. Three slide samples of the non-heating period and the heating period were collected in October 2005 and January 2006, respectively. Table 1 presents the records for the three sampling conditions.

1.2 SEM/EDS detection

From the center of the filters and membranes, a portion of 1 cm$^2$ was cut and mounted on a smooth Cu-alloy stub, and sprayed with a thin film of Au for the SEM (scanning electron microscope) analysis. The instrument used was an electronic microscope (Hitachi S-570, Japan), coupled with an Energy Dispersive X-ray Spectrometer (EDAX pV9900, USA) to obtain the morphology and chemical composition of individual particles. Elements with atomic numbers less than 11 were not determined, neither were the super-tiny particulate less than 1 $\mu$m by visual. During the SEM/EDS detection, on each sample portion, around 100 particles were scanned and observed, to get totally 3300 particles data.

1.3 Particle size and shape detection

The particle size and shape analyzer (CIS-50, Holand) was applied, by its visual channel, slide cell of ACM-110, and lens of CW (0.7-$\mu$m pixel and size range of 2–150 $\mu$m). The sampling slide was put into the cell slot and moved up-down and left-right to check all parts of the slide. Around 5,000 particles were detected on each slide. All slides were measured immediately after sampling.

2 Results and discussion

2.1 Particle shape sorts

Based on the images of particle surface shape gained by the SEM/EDS analysis, 6 clusters of particulate morphology of PM$_{10}$ in Shijiazhuang City have been sorted out (Table 2).

The images of the 6 particle shape sorts and the corresponding X-ray spectra in Shijiazhuang City are shown in Fig.1.

Table 1  Conditions of the PM$_{10}$ sampling for the non-heating period, heating period, dust storm days, and wet deposit in Shijiazhuang City

<table>
<thead>
<tr>
<th>Sample sort</th>
<th>Date</th>
<th>Filter/slide number</th>
<th>Weather description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-heating period</td>
<td>10–14 June; 8–12 August; 15–19 October 2005</td>
<td>15/3</td>
<td>Unclouded, average wind speed 1.8–2.1 m/s, with prevailing wind direction of SE, SW, and S</td>
</tr>
<tr>
<td>Heating period</td>
<td>20–24 December 2005; 16–20 January 2006</td>
<td>10/3</td>
<td>Unclouded, average wind speed 1.5–1.9 m/s, with prevailing wind direction of N, NW</td>
</tr>
<tr>
<td>Dust storm days</td>
<td>18–22 March 2006</td>
<td>2/0</td>
<td>Floating dust, average wind speed 2.9 m/s, with prevailing wind direction of NW</td>
</tr>
<tr>
<td>Wet deposit</td>
<td>21–23, 30 December 2004; 5 January 2005</td>
<td>6/0</td>
<td>Snowing, snowfall amount ranging from 3.8 to 21 mm</td>
</tr>
</tbody>
</table>

Table 2  Particle morphology types of PM$_{10}$ of Shijiazhuang City

<table>
<thead>
<tr>
<th>Shape description</th>
<th>Size range ($\mu$m)</th>
<th>Percentage of particle number (%)</th>
<th>Main elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>In the non-heating period</td>
<td>In the heating period</td>
</tr>
<tr>
<td>Irregular square</td>
<td>5–12</td>
<td>+++++*</td>
<td>+++</td>
</tr>
<tr>
<td>Agglomerate</td>
<td>4–16</td>
<td>++++</td>
<td>+++++</td>
</tr>
<tr>
<td>Sphere</td>
<td>1–6</td>
<td>++</td>
<td>++++</td>
</tr>
<tr>
<td>Floccule</td>
<td>2–18</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Column or stick</td>
<td>8–12</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Unknown</td>
<td>3–5</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

* The number of signs “+” indicates the particle relative amount.
2.1.1 Irregular square

Irregular shaped grains (Fig.1a) are primary quantitatively in the samples detected in Shijiazhuang City. The surface of these particles is coarse and holed, with average diameter of 8 µm. EDS (energy dispersive X-ray spectrometry) detection shows that the crust elements of Si, Al, Ca, Mg, K, and Fe are the main components. Some irregular diamonds have rather smooth and flat surface with obvious Ca peak in the elemental spectrum. The amount of particles with holed surface are relatively more in the non-heating period than in the heating period and the most in the dust storm days.

2.1.2 Agglomerate

Agglomerate shaped particles (Fig.1b) are less quantitative than the irregular diamond but are little larger in size. Flexuous fractal edge branches or crinkles present randomly outside the agglomerate grains’ surface form the lump morphology. Element components of agglomerate particles are quite similar to that of the irregular square particles but with different X-ray counts rate. In some particle surface of agglomerate, elements S and Cl are measured by the EDS. The amount of agglomerate does not differ considerably in the three sampling conditions.

Fig. 1 SEM images of single inhalable aerosol particle and corresponding X-ray spectra in Shijiazhuang City. (a) irregular square; (b) agglomerate; (c) sphere; (d) flocule; (e) column or stick; (f) unknown. In the X-ray spectra, element Au is due to the spray dealt for the SEM image observation and the same in the following figures.
2.1.3 Sphere

Sphere particles (Fig.1c) are generally smaller than all other particle types with average diameter under 3 µm. There are three impressed surface patterns of the sphere particles in Shijiazhuang City (Fig.2): smooth, semi-coarse, and coarse. Each pattern corresponds to different elemental components; the smooth sphere to Si-dominant, the semi-coarse to Si-Al-dominant, and the coarse to Fe-dominant, especially when the spheres are separated captured. The spheres conglutinated together do not display such patterns. Obviously, sphere particles appear considerably frequently in the heating-period than in other days.

2.1.4 Floccule

By amplified observation, it is found that these grains are made up of tiny spherical particles normally less than 1 µm (Fig.1d). It seems that these floccule particles are structured loosely and have alterable size, but in this research, most floccule shaped grains possess an apparent size of about 10 µm. Though almost no elemental peaks emerge in the EDS spectrum (except element of Au for the spraying operation), C, O, and other elements with low sequence number cannot be excluded in these samples. The floccule particles are more in the non-heating period, and are not found in the samples of duststorm days and wet deposit, possibly because the loose construction is propitious for these floccule particles to disaggregate in violent current environment.

2.1.5 Column or stick

Shaped long and elliptical, this sort of grain usually bears some physiological texture externally (Fig.1e), and can be found in all samples in Shijiazhuang City. The X-ray detecting counts for these particles are quite low, demonstrating that they are biomass.

2.1.6 Unknown

Some deformed or nondescript particles just account for minority in the samples with elemental spectrum peaks of Si, K, Ca, and Fe (Fig.1f), which may be explored further in the future.

2.2 Sources of the PM$_{10}$

Based on the morphological features, it can be considered that the irregular diamond particles are assuredly derived from soil and surface geological deposit as the product of mechanical abrasion (Kaegi, 2004); the agglomerate and sphere particles are from the combustion of coal (Ramesh and Koziski, 1999; Styszko-Grochowiak et al., 2004; Goodarzi, 2006), while the floccule particles are from the discharge of vehicles (Colbeck et al., 1997; Shi et al., 2003), and the column or stick shaped particles are from bioactivities (Crook and Sherwood-Higham, 1997; Wittmaack et al., 2005), but the numerical ratio of the above particles (Table 2) cannot directly indicate the source apportionment. In Shijiazhuang City, a distinct environmental problem is the fugitive dust derived from bare soil, construction activities, vehicle discharge, industry emission, and street deposit. All through the year, there is always a layer of dust on almost any ground object surface, especially accumulated on the road side. Owing to repeated depositing, accumulating, and re-suspending processes, the particles from the above sources mix together, thus making the dust a serious nuisance. The detection of PM$_{10}$ particles by ambient sampling represents intermingle
of each original discharge source and re-suspension of street dust, and the ratio of particle number percent by calculation under SEM can only indicate source categories.

2.3 Particle surface characteristics and possible atmospheric reaction

Airborne particles play an important catalytic role in the atmospheric chemical reaction (Böke et al., 1999), and the particle surface character is influencing (Dall’Osto and Harrison, 2006; Choël et al., 2007). In the atmospheric environment, only a few particles possess smooth surface, most of them are fractal. With the enlarged surface area by the cracked and holed process, these fractal particles can provide suitable environment and medium for the secondary atmospheric reaction. In this research, a crystal growing process is observed in one of the PM$_{10}$ samples in the heating period in Shijiazhuang City (Fig.3), in which some spiny like substance can be seen growing from the bed particle and a raised peak of Ca and S, companied with other mineral elements such as Al and Si in the EDS spectrum. This demonstrates that an atmospheric reaction has occurred and a new mineral has formed. This newly formed mineral should be the calcium sulfate by the morphological feature according to former studies (Böke et al., 1999). In the reaction, the Ca may be provided by the mineral component of suspending particles such as CaCO$_3$, and the S by the SO$_2$ originally. As mentioned, Shijiazhuang City is characterized by both the high SO$_2$ emission and serious street dust nuisance, and the precursor emission is considerably enough to make the reaction continue thoroughly until new mineral is formed. The former result obtained by the authors also identifies with this outcome, which shows that the high ratio of ($\rho_{Ca^{2+}}$ + $\rho_{NH_4^+}$)/($\rho_{SO_2^{−4}}$ + $\rho_{NO_3^{−3}}$) with the value 1.93 in the sample of snow in Shijiazhuang City is responsible for the restraint of acid deposit, revealing strong antacid ability (Wang and Li, 2006). Thus, the reason for the high SO$_2$ emission but low acid rain frequency in Shijiazhuang City is explained by this neutralization.

2.4 Unique soot morphology

In Fig.1, the floccule particles are usually sized around 10 µm, considerably larger than that in other research reports (Colbeck et al., 1997; Shi et al., 2003; Xie et al., 2005; Chandler et al., 2007), and some floccule even larger by the capturing of other fine particles (Fig.4). These soot particles’ morphology has been seldom described. Considering the sampling condition of continuous calm

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Fig. 3 New formed calcium crystal and its X-ray spectrum.

Fig. 4 Unique soot morphology by capturing other fine particles.
and stable weather days, the unique soot size and shape characteristics should indicate a kind of physical aging process of aerosol by coagulation or impaction.

2.5 Possible particle water-insolubility

In the snow wet deposit samples, irregular mineral particles and spherical particles retain the principle part; some biomass like particles are also present; other particles such as soot or agglomerates are not detected, which demonstrates the water-insolubility of particles derived from fugitive dust and coal combustion.

2.6 Particle size and shape difference in the non-heating and heating period

By the result of CIS-50 measurement (Fig. 5), we can find that the particle size distribution spans wider in the heating period than in the non-heating period, with more coarse mean size value, indicating alternation of ground emission with more coal combustion. Here, the particle shape factor ($S_F$) is given by:

$$S_F = 4\pi A/P^2 \quad (1)$$

where, $A$ is the particle area, and $P$ is the particle perimeter. When the particle is round, $S_F$ equals to 1, and square to 0.785, triangle to 0.604, oblong to 0.436, strip to 0.160. Also, in Fig. 5, particles with $S_F$ close to 1 increase obviously in the heating period, and in the non-heating period, more particles are square like, implying that the irregular and sphere like shape is dominant in the particle shape groups, which is consistent with the estimate by SEM observation.

3 Conclusions

In the typical air polluted city of Shijiazhuang, single inhalable particle’s morphology was characterized by the six shape clusters, which are: irregular square, agglomerate, sphere, floccule, column or stick, and unknown, by quantitative order. The irregular square particles are common in all kinds of samples; sphere particles are more, and column or stick are less in winter samples; in the wet deposit samples, agglomerate and floccule particles are not found in this research. The surface of most particles is coarse with fractal edge, which can provide suitable chemical reaction bed in the polluted atmospheric environment. New calcium crystal is found to demonstrate the existence of neutralized reaction, explaining the reason for the high $SO_2$ emission and low acid rain frequency in Shijiazhuang City. Three sorts of surface patterns of spheres are smooth, semi-coarse, and coarse, corresponding to the element of Si-dominant, Si-Al-dominant, and Fe-dominant. The soot particle here is present as floccule, considerably larger than the former common results, wrapped or captured with other fine particles to make its appearance unique. This mixed process can compound particle components to enhance its toxicity potentially, but to increase its deposit velocity by possible increased weight. The new formed calcium crystal, the three sorts of sphere surface patterns, and the unique soot appearance represent the single inhalable particle’s morphology characteristics in Shijiazhuang City, which are different from those in other cities, and deserve further research. The particle size distribution and shape factor alter considerably in different seasons; when in the heating period, the particles suspended are more coarse and more sphere-like than in the non-heating period.

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