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Single particle characterization of spring and summer aerosols in Beijing: Formation of composite sulfate of calcium and potassium

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Abstract

Scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDX) was used for the analysis of 2500 single particles in five atmospheric aerosol samples collected during the spring and summer of 2000 in Beijing, China. Mineral dust appeared to be the dominant particles during an Asian dust episode, while in other circumstances mineral dust and S-containing particles constituted the major particle components. During anthropogenic pollution episodes in the summer, a large abundance of S-containing particles featured the atmospheric aerosol. Chemical and size distribution characteristics are discussed for Ca–S, K–S and Ca–K–S particle classes. Formation of Ca–K–S and other S-containing particle classes with high abundance was closely related to meteorological conditions such as relative humidity and cloud coverage. Simple and composite sulfate particles with an elongated crystalline morphology were detected which appear to be indicative of aqueous phase oxidation, such as in-cloud processing for sulfate formation pathway.

Keywords: Atmospheric aerosol; Single-particle analysis; Scanning electron microscopy–energy dispersive X-ray analysis; Sulfate formation; In-cloud processing; Beijing

1. Introduction

The application of single particle analysis with methods such as scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDX) provides complementary and more detailed information than that available through bulk analysis. In recent years SEM–EDX has been used to study aerosol particles collected over the North Sea (Van Malderen et al., 1996a; Hoornaert et al., 1996), the Atlantic Ocean (Posfai et al., 1995; Anderson et al., 1996), the Antarctic (Artaxo et al., 1992), and Siberia (Van Malderen et al., 1996b). Urban areas around the world were also investigated by such single particle analysis methods as e.g., in Phoenix, Arizona, USA (Katrinak et al., 1995), Antwerp, Belgium (Van Borm and Adams, 1989), Seoul and other cities in Korea (Ro et al., 2002). The study of

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urban aerosols is important due to their complexity; many anthropogenic sources are involved. Their study is also important for health effect studies tracing the effects of atmospheric pollution. In general, there appears to be a similarity in aerosol composition and size distribution for urban areas around the world but specific compositional characteristics occur according to population size, energy consumption pattern, industrial structure, geographic location and topography/economic situation.

The Beijing site is featured by its rapidly expanding population, increasing traffic density, a high consumption of coal and flourishing construction activities. Beijing is situated in a semi-arid region in North China and surrounded by mountains in the west and north. The weather conditions usually do not favor dispersion and transport of air pollutants. At present, the concentration of inhalable particles exceeds the national air quality standards during extended periods of time each year. The municipal government recently implemented pollution control measures, policies and various action plans. An in-depth understanding of air pollution and aerosol chemistry in Beijing is urgently needed, justifying intensive aerosol research in the area. The urban aerosol in Beijing has been the topic of several recent studies (He et al., 2001; Shi et al., 2003; Yao et al., 2002, 2003).

In their study Yao et al. (2002) focused on the ionic composition of PM2.5 particles. The major route of sulfate formation in Beijing was identified as gas-phase oxidation of SO_2 in winter and in-cloud processing in summer, but insufficient ammonium was present to totally neutralize the aerosol. Based on the size distribution of ionic species and the mole ratio of sulfate to SO_2, more evidence on the formation mechanisms of secondary aerosol in Beijing was provided by Yao et al. (2003). During the summer, sulfate was mainly in the fine particles with a mass median aerodynamic diameter (MAD) of $0.7 \pm 0.1\,\mu m$. Sulfate formation was attributed to in-cloud processing. Sulfate formation in the spring was attributed to non-cloud heterogeneous processes, as sulfate had a MAD of $0.45 \pm 0.05\,\mu m$ (Yao et al., 2003).

Shi et al. (2003) examined a variety of particles collected in Beijing in 2001 by using SEM and image analysis. These included mineral dust, coal fly ash, soot aggregates as well as sulfates. Some sulfate particles were crystalline and contained S, Ca, K and Al and there were indications that two or more phases of sulfates were present.

In this study, aerosol samples collected in the spring and summer in Beijing were analyzed with SEM–EDX. The aerosol composition, pollution characteristics and the formation mechanism of secondary sulfate aerosol were investigated. For the spring samples, the difference between Asian dust and normal urban aerosols was investigated. For the summer samples, the number variation of major particle classes and their relation with aerosol pollution situation and meteorological conditions was observed. The focus of the study was largely put on the formation of sulfate particle classes, which showed close relationship with the urban air quality in the summer.

2. Experimental

2.1. Aerosol samples

The sampling site is located in an urban area, under the influence of the traffic, of the north part of the urban fourth ring of Beijing. PM10 aerosol samples were collected for 24 h on the roof of the 11 floor main building of the Sino-Japan Friendship Center for Environmental Protection on 25 April , 15 May (spring samples) and on 21, 24 and 25 July (summer samples), 2000. PM10 concentration was 386, 70, 153, 70 and $124\,\mu g\,m^{-3}$, respectively. An Asian dust event occurred on 25 April, while air quality was reasonably good on 15 May and 24 July, and showed light pollution on 21 and 25 July, all this according to National Standard of Ambient Air Quality and the Air Quality Index System in China. Nuclepore (polycarbonate) membrane with $0.4\,\mu m$ pores was used as aerosol sampling filter as it provides a flat surface for SEM observation. The particulate aerosol sampler with flow rate of $16.7\,l\,min^{-1}$ was the stacked filter unit (SFU) of Gent type recommended by IAEA for a number of projects (Maenhaut et al., 1994), but only the PM10 size particles (with aerodynamic size less than or equal to $10\,\mu m$) were collected. In this work, particles with sizes from 2.5 to $10\,\mu m$ are defined as coarse particles, those less than $2.5\,\mu m$ are defined as fine particles, and those less than $1\,\mu m$ are listed as sub-micrometer.

2.2. SEM–EDX measurements

Sections of the 47-mm diameter filter sample were mounted on electron microprobe stubs and vacuum coated with a carbon layer of about 40 nm. The individual particle analyses were carried out with a