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Physico-chemical characterization and source tracking of black carbon at a suburban site in Beijing

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ABSTRACT

Particles from ambient air and combustion sources including vehicle emission, coal combustion and biomass burning were collected and chemically pretreated with the purpose of obtaining isolated BC (black carbon) samples. TEM (transmission electron microscopy) results indicate that BC from combustion sources shows various patterns, and airborne BC appears spherical and about 50 nm in diameter with a homogeneous surface and turbostratic structure. The BET (Barrett–Emmett–Teller) results suggest that the surface areas of these BC particles fall in the range of 3–23 m^2/g, with a total pore volume of 0.03–0.05 cm^3/g and a mean pore diameter of 7–53 nm. The nitrogen adsorption–desorption isotherms are indicative of the accumulation mode and uniform pore size. O_2-TPO (temperature programmed oxidation) profiles suggest that the airborne BC oxidation could be classified as the oxidation of amorphous carbon, which falls in the range of 406–490°C with peaks at 418, 423 and 475°C, respectively. Generally, the BC characteristics and source analysis suggest that airborne BC most likely comes from diesel vehicle emission at this site.

Introduction

Black carbon (BC) is usually defined as particles, black in color, and composed mostly of elemental carbon with oxygen and hydrogen as minor components. In most cases, BC comes from the incomplete combustion of fuel oil, coal, biomass and so on. Processes including nucleation, increase of surface area, accumulation, agglomeration and oxidation take place during the combustion before BC particles are emitted to atmosphere (Richter and Howard, 2000). During the past decades, BC has been released in increasing quantities into the atmosphere and dispersed over wide areas by long-distance transport (Cachier et al., 1988; Chylek et al., 1992; Rose, 1995). BC possesses characteristics different from those of other atmospheric

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aerosols, and has been shown to absorb sunlight, heat the air, and contribute to global warming (Hansen et al., 2000; Jacobson, 2002; Menon et al., 2002). BC was found to strongly adsorb pesticides, polyaromatic hydrocarbons (PAHs), biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and so on (Lohrnann et al., 2002; Yang and Sheng, 2003a, 2003b; Yang et al., 2004). BC in accumulation mode with absorbed PAHs, heavy metals and other toxic matters could enter the human body by inhalation and threaten public health. In addition, BC also plays an important role in photochemical reactions, heterogeneous reactions and gas-to-particle conversion (Decesari et al., 2002).

Due to its significant impact on climate, public health and the environment, BC has been widely studied in terms of concentration measurement, optical properties, size distribution, climate forcing and so on. Since the 1990s, several large-scale international aerosol observation experiments have been carried out, such as ACE (Aerosol Characterization Experiment) (Alfaro et al., 2003), RACE (Radiative Aerosol Characterization Experiment) and INDOEX (the Indian Ocean Experiment) (Lelieveld et al., 2001). BC observation is regarded as an important component in these plans. In addition, continuous observation of BC has also been carried out in the worldwide monitoring stations of WMO/GAW (World Meteorological Organization/Global Atmosphere Watch) and numerous data have been obtained (Zheng et al., 2007). In China, BC from household stoves, coal combustion and ambient air in the Pearl River Delta, Beijing and other sites has been studied (Zhi et al., 2008; Li et al., 2009; Wu et al., 2009; Shen et al., 2010; Yan et al., 2010). In recent years, BC online concentration, possible emission sources and relationship with climate factors has been well reported based on a three-year monitoring at the QilianShan Station of Glaciology and Ecologic Environment (Zhao et al., 2012).

However, those macroscopic studies usually consider BC as a part of atmospheric particles, and detailed characteristics including morphology, textural properties, thermal stability of airborne BC are scarcely reported. Only BC particles collected from sediments and fly ash have been researched (Griffin and Goldberg, 1979; Stoffyn-Egli et al., 1997). Usually, it is difficult to separate BC from other atmospheric particles and also difficult to obtain enough BC for analysis. By contrast, in this study, atmospheric particles in a suburban site were sampled with a large volume sampler and for a long enough time to obtain sufficient sample volume, and then BC particles were isolated and characterized by physico-chemical methods. To further identify the possible sources, samples from mobile vehicle emission (including gasoline and diesel vehicles), and coal and biomass burning were also collected and analyzed. The aims of this study are to establish the major morphology and chemical characteristics of airborne BC and to identify their major sources at the sampling site.

1. Materials and methods

1.1. Particle samples

A high volume TSP (total suspended particles, diameter less than 100 μm) sampler (HV-1000F, Sibata Scientific Technology Ltd., Tokyo, Japan) was used to gather the data. The sampler was set at an approximate altitude of 16 m, located on the roof of a building in the Research Center for Eco-Environmental Sciences (RCEES) in Beijing, China (40°00′N and 116°20.240′E). More information about the sampling location was given in our previous study (Wang et al., 2009). Aerosol samples were collected once a week and every sampling lasted for 24 hr at a flow rate of 1000 L/min. Quartz filters were used in the experiments (QR100, Advantec Corporation, Tokyo, Japan) with a collection efficiency of 99.99% for 0.3 μm particles. Besides the airborne particles, samples were also collected from four main combustion sources. Vehicle emission particles were collected from the tail pipes of gasoline and diesel-powered vehicular internal combustion engines during normal tests. Particles from coal and biomass burning were collected from the top inner surface of the chimney in nearby household stoves.

1.2. Pre-treatment and analysis

As mentioned above, in most cases BC is mixed with other components in particles and its content is not so high that isolation and concentration of samples are necessary. There are methods for BC exaction from sediment samples. Generally, those methods consist of steps designed to eliminate carbonate, silicate minerals and organic matter, and the residue is regarded as BC. The difference is that in some literature studies, H_2O_2/KOH was chosen for the oxidation of organic matter (Rose, 1990; Emiliani et al., 1991), and $K_2Cr_2O_7/H_2SO_4$ was selected as the oxidation agent in other references (Wolbach and Anders, 1989; Lim and Cachier, 1996; Bird and Grocke, 1997). In this work, we chose the latter because dichromate has been shown to be the most effective for oxidizing organic matter with minimal effect on BC, including charred materials. For the samples from ambient air, particles were scraped carefully from the surface of the quartz filter, and then about four samples were mixed together for analysis at one time. The emission source samples were collected in the form of powder, so they were directly ready for analysis. All samples were treated following Lim's method.

A scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) and a transmission electron microscope (TEM, H-7500, Hitachi, Tokyo, Japan) were employed to analyze the morphology of BC separated from the above samples. The SEM has an Energy Dispersive X-ray Spectrometer (EDX) attachment, which was used to measure the composition of BC particles. All samples were dispersed in ethanol, and deposited on a copper microgrid prior to the morphology observation.

A gas sorption analyzer (NOVA 2100, Quantachrome, Boynton Beach, Florid, US) was used to calculate the BET surface areas based on the linear part of the BET plot. The samples were all degassed under vacuum at 100°C for more than 4 hr before the measurement. The total pore volumes were estimated according to nitrogen uptake at a relative pressure ratio of 0.99 (P/P_0).

Based on the fact that BC from different sources could be oxidized at different temperatures, the temperature programmed oxidation (TPO) method was adopted to identify the possible oxidation stages of BC from different sources. TPO tests were carried out in a TPx analyzer (Chem 2720, Micromeritics, Norcross, GA, USA). During each test, a certain mass of BC was used (20 mg), and the room temperature was raised to 1100°C under a gas flow of pure O_2 (≥99.99%), with a heating rate of 10°C/min.