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Diurnal variations of carbonaceous components, major ions, and stable carbon and nitrogen isotope ratios in suburban aerosols from northern vicinity of Beijing

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HIGHLIGHTS

- Diurnal changes of carbonaceous and ionic components were studied in northern Beijing.
- $\delta^{13}C$ and $\delta^{15}N$ of total carbon and nitrogen in aerosols were determined.
- We found diurnal changes of chemical constitutes with day/night air mass transport.
- In daytime pollutants are transported from Beijing to northern vicinity.
- During rainfall events, all chemical components declined with the depletion of nitrate.

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ABSTRACT

We report diurnal variations of organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC) and major ions as well as stable carbon and nitrogen isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) in ambient aerosols at a suburban site (Mangshan), 40 km north of Beijing, China. We found that aerosol chemical compositions were largely controlled by the air mass transport from Beijing in daytime with southerly winds and by relatively fresh air mass in nighttime from the northern forest areas with northerly winds. Higher concentrations of aerosol mass and total carbon were obtained in daytime. Further, higher OC/EC ratios were recorded in daytime (4.0 ± 1.7) than nighttime (3.2 ± 0.7), suggesting that OC is formed by photochemical oxidation of gaseous precursors in daytime. Contributions of WSOC to OC were slightly higher in daytime (38%) than nighttime (34%), possibly due to secondary formation of WSOC in daytime. We also found higher concentrations of Ca^{2+} in daytime, which was originated from the construction dust in Beijing area and transported to the sampling site. $\delta^{13}C$ ranged from −25.3 to −21.2‰ (ave. −23.5 ± 0.9‰) in daytime and −29.0 to −21.4‰ (−24.0 ± 1.5‰) in nighttime, suggesting that Mangshan aerosols were more influenced by fossil fuel combustion products in daytime and by terrestrial C_3 plants in nighttime. This study suggests that daytime air mass delivery from megacity Beijing largely influence the air quality at the receptor site in the north together with photochemical processing of organic aerosols during the atmospheric transport, whereas the Mangshan site is covered with relatively clean air masses at night.

1. Introduction

Carbonaceous aerosols are enriched with organic carbon (OC) rather than elemental carbon (EC). Almost 50% of global EC are emitted from fossil fuel combustion. OC has primary (anthropogenic or biogenic) and secondary sources via atmospheric oxidation of volatile organics (Galbally and Goldstein, 2007). The formation of secondary organic aerosol (SOA) increases atmospheric levels of OC and hence OC/EC ratios are enhanced (Cabada et al., 2004). OC/EC ratio has been used as a tool for the source apportionment of

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carbonaceous aerosol (Gnauk et al., 2008; Plaza et al., 2011).

Significant fraction (20–70%) of organic carbon (OC) or total carbon (TC) is water-soluble (Duarte et al., 2007; Sempéré and Kawamura, 1994). Water-soluble organic carbon (WSOC) plays an important role in the wet scavenging of atmospheric particles, formation of haze, and the impact on human health (Dreher, 2000; Turpin, 1999), and also acts as cloud condensation nuclei (CCN) influencing the global climate (Kanakidou et al., 2005). The emission sources of primary WSOC include biomass burning (Fine et al., 2002; Nolte et al., 2001; Rogge et al., 1998; Schauer et al., 2001), cooking (He et al., 2004; Rogge et al., 1991; Schauer et al., 1999), paved road dust (Nolte et al., 2002) and automobiles (He et al., 2006; Rogge et al., 1993). However, major fraction of WSOC is derived from atmospheric oxidation of volatile organic compounds (VOCs) emitted from the primary sources (Kondo et al., 2007) via chemical aging during atmospheric transport (Rudich et al., 2007).

Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios have been successfully used to better understand the contributions of various sources to organic aerosols (Cachier et al., 1986; Kawamura et al., 2004; Narukawa et al., 1999; Turekian et al., 1998). The contribution of nitrate (NO_3^-) and ammonium (NH_4^+) ions to total aerosol nitrogen could provide additional information on the source types of aerosols (Kundu et al., 2010; Pavuluri et al., 2010). Water-soluble inorganic ions (e.g., K^+, SO_4^{2-}, NH_4^+, Ca^{2+} and NO_3^-) are often considered as indicators of different origins (e.g., biomass burning, coal combustion, agricultural emission, NO_x, and soil/dust) (Wang et al., 2005a,b). Secondary formation of inorganic aerosols and their contribution to fog and haze formation have been discussed. For example, Guo et al. (2010) reported that 55% of summertime fine aerosol mass (<1.8 μm) in Beijing was derived from secondary inorganic aerosols (sum of NH_4^+, NO_3^- and SO_4^{2-}), which were responsible to the regional-scale pollution.

Beijing city is generally considered more polluted than its suburban areas due to geographically closer situation to emission sources, e.g., vehicle exhaust and industrial areas. With continuous economic growth, air quality in Beijing has been deteriorating seriously (Cao et al., 2014; Yu et al., 2013). However, our recent study on dicarboxylic acids in the ambient aerosols from background vicinity site (Mangshan) of Beijing demonstrated that their concentrations were much higher than those previously reported in Beijing (He et al., 2014). Here, we present comprehensive data sets on OC, EC, WSOC, major ions, and stable carbon and nitrogen isotopes in the ambient aerosols from Mangshan site. We discuss aerosol chemical properties to elucidate the source difference following the wind patterns during day and night. The photochemical aging of atmospheric aerosols will also be discussed during the transport from Beijing to the receptor site.

2. Aerosol collection and analytical methods

2.1. Site description and aerosol sampling

Aerosol (TSP) sampling was carried out in a suburban site near the entrance of the Mangshan national forest park (40°16′N, 116°17′E; elevation of 187 m above sea level). The sampling site is 40 km north of the center of Beijing. Forest-surrounded areas expand to the north of Mangshan, while populous, urbanized and industrialized areas including Beijing, Tianjin and Hebei Provinces expand in the south of the sampling site (Fig. 1).

We collected 3-h daytime samples (n = 26), 9-h daytime samples (n = 12), and 15-h nighttime samples (n = 20) together with 4 field blanks from 15th September to 5th October 2007 using a high-volume air sampler and pre-combusted quartz fiber filters (20 × 25 cm). Before and after the sampling, filters were stored in a clean glass jar (150 ml) with a Teflon-lined screw cap. The filter

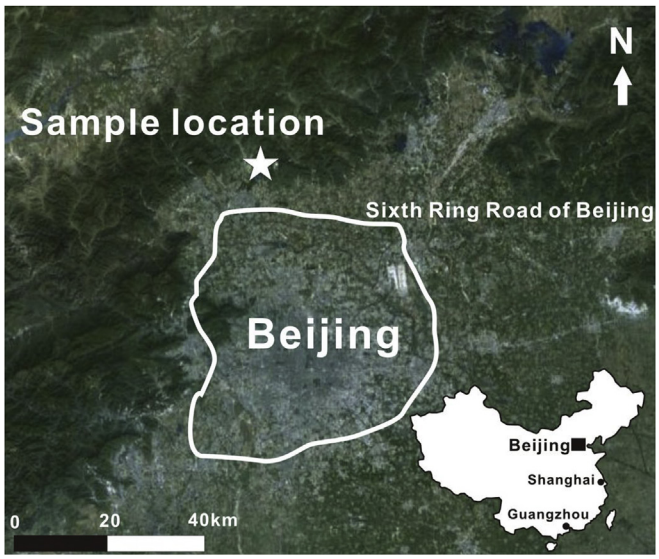

Fig. 1. Location of the sampling site and Beijing city.

samples were stored at −20 °C in a dark freezer room prior to analysis. Meteorological parameters including precipitation, ambient temperature, relative humidity, and wind direction were recorded at the sampling site during the campaign period. The average temperature and relative humidity at Mangshan were 25 °C and 57% in daytime and 17 °C and 78% in nighttime. The dominant wind pattern was characterized by southwesterly wind (205°, on average) during daytime and northeasterly wind (30°, on average) during nighttime, being consistent mostly with air mass back trajectories (He et al., 2014). Rainfall was observed at night of September 17, evening of September 26, and daytime of Oct 1. Light rain lasted from October 4 to the end of the field campaign.

2.2. Chemical analyses

We conducted the measurements of total carbon (TC), total nitrogen (TN), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), stable carbon and nitrogen isotopes of TC and TN, and inorganic ions in the ambient aerosol samples. For TC and TN and their stable isotopes, a filter cut (area 3.14 cm^2) was placed into a pre-cleaned tin cup and shaped into a rounded ball, which was introduced to an elemental analyzer (EA; model: NA 1500 NCS, Carlo Erba Instruments) using an auto-sampler. The sample was oxidized in a combustion column to promote the intensive oxidation of sample materials in an atmosphere of pure oxygen. Excess oxygen is removed and nitrogen oxides coming from the combustion column are reduced to molecular nitrogen (N_2) in the reduction column. The N_2 and CO_2 derived from the samples were isolated on-line using a gas chromatograph and then measured with a thermal conductivity detector.

Aliquots of the N_2 and CO_2 gases were then introduced into an isotope ratio mass spectrometer (Thermo Quest, Delta Plus) through an interface (Thermo Quest, ConFlo II). The isotopic compositions of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) were determined using acetonitrile as a standard and the following isotope conversion equations:

$$\delta^{13}C(‰) = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1\right] \times 1000 \quad (1)$$