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Characterization of carbonaceous aerosols over the East China Sea: The impact of the East Asian continental outflow

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HIGHLIGHTS

- An obvious seasonal variation of carbonaceous aerosols was observed.
- PM2.5 contained approximately 84% of carbonaceous aerosols in TSP.
- The sea spray aerosol (SSA) played a key role on *n*-alkanes in winter.
- POC and EC dominated in cold season due to Asian continental outflow.

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ABSTRACT

Seventy-five paired PM2.5 (aerodynamic diameter less than 2.5 μm) and TSP (total suspended particle) samples collected from a pristine island in the East China Sea (ECS) between October 2011 and August 2012 were analyzed for organic carbon (OC), elemental carbon (EC), and *n*-alkanes. The island lies in the pathway of continental outflow from Mainland China to the northwest Pacific Ocean driven by the East Asian Monsoon. The concentrations of OC, EC (in $\mu g/m^3$), and *n*-alkanes (in ng/m^3) were highest in winter (means: 4.7, 1.3, 140.1, respectively) and lowest in summer (means: 1.1, 0.3, 17.0, respectively). PM2.5 contained approximately 88% of the OC, 80% of the EC, and 61% of the *n*-alkanes in TSP. Petroleum residue was the dominant contributor to the *n*-alkanes. C_{12}–C_{22} *n*-alkanes with strong even-to-odd predominance observed in winter were attributed to the microbial contribution from sea spray aerosol (SSA) driven by the higher wind speed. There was a higher secondary organic carbon (SOC)/OC ratio in warm seasons (summer and fall) than that in cold seasons (spring and winter). The dominance of primary organic carbon (POC) and EC in cold seasons was possibly mainly due to the influence of the East Asian continental outflow. Three episodes of high concentrations of carbonaceous aerosols were observed, and we focused on the impact of these pollutants from East Asia on the air quality over the ECS. Carbonaceous pollutants were more concentrated in PM2.5 during the fall episode triggered by biomass burning in East China. The winter haze associated with intensive indoor heating in North China brought substantial carbonaceous pollutants, with a minor influence on their size distribution. The dust episode in spring was related to coarse particles (i.e., TSP–PM2.5), yielding a distinctly different size distribution.

1. Introduction

Carbonaceous species, which are a mixture of substances containing carbon atoms, comprise a large but highly variable fraction of the aerosol burden in the atmosphere. In general, in the

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atmosphere, these compounds can be classified into two groups: organic carbon (OC) and elemental carbon (EC). OC, formed by a variety of processes including combustion and secondary organic carbon (SOC) formation, is a mixture of hundreds of organic compounds spanning a wide range of chemical and thermodynamic properties. *N*-alkanes are important components of the OC fraction, and they are derived from both natural origins and anthropogenic activities (Simoneit, 1986). Waxes from higher plants and two commercial sources, crude oil and natural gas, have been shown to be common sources for *n*-alkanes. EC, produced by incomplete combustion of fossil fuels and biomass burning, is a mixture of graphite-like particles and light-absorbing organic matter.

Carbonaceous aerosols have received increasing attention in recent years due to their adverse effects on human health and climatic change (Highwood and Kinnersley, 2006; Menon et al., 2002), potential importance in a wide range of biogeochemical processes (Schmidt et al., 2001), and possible representation of a notable sink in the global carbon cycle (Jurado et al., 2008). In recent decades, the concentrations of atmospheric carbonaceous pollutants (e.g., OC and EC) in China have been increasing with the rapid industrialization and urbanization, especially in the Yangtze River Delta (YRD) region (Feng et al., 2009). The YRD, covering 1.1% of the area of China (~99,600 km^2), is home to 108 million people (8.1% of the total population of China). The GDP of the YRD was 8214 billion yuan (renminbi, a Chinese currency unit) in 2011, which represents 17.4% of the entire Chinese economy (www.hktdc.com). The East China Sea (ECS), located near highly developed regions of China (i.e., the YRD), has been receiving a large influx of pollutants from the Yangtze River and atmospheric deposition (Lin et al., 2013). The air circulation pattern of this region is influenced by the East Asian Monsoon, rendering the ECS a sink of the pollutants transported not only from the YRD but also from North China (Lin et al., 2011; Zhang and Gao, 2007). Therefore, knowledge of the characteristics of anthropogenic pollutants in the aerosols over the ECS would provide useful information to explore the significant role of Asian continental outflow on the ECS and even the northwest Pacific Ocean.

The outflow of East Asian continental pollutants such as dust and organic compounds to the Bohai Sea and Yellow Sea has been investigated in previous studies (Duce et al., 1980; Gao et al., 1997; Feng et al., 2007). There have also been several studies on the occurrence and sources of nutrients, heavy metals in dust, and trace elements in the atmosphere over the ECS (Hsu et al., 2009, 2010; Zhang et al., 2010; Guo et al., 2014). The occurrence of organic and elemental carbon associated with the East Asian outflow was also measured during a cruise campaign in the ECS (Huebert et al., 2004). Nevertheless, the seasonal sources and size of carbonaceous aerosols over the ECS have scarcely been documented. In this study, PM2.5 (aerodynamic diameter less than 2.5 μm) and TSP (total suspended particle) samples were simultaneously collected over four seasons from October 2011 to August 2012 at a remote island in the ECS. Driven by the East Asian Monsoon, the wind pattern arriving at this island (Huaniao Island) is mostly from west to east and north to south. This makes the island an ideal receptor site to explore the effects of continental outflow on the ECS and northwest Pacific Ocean. The objectives of this study are to determine the occurrence and sources of carbonaceous pollutants (i.e., OC, EC, and *n*-alkanes) over four seasons, and to demonstrate the role of continental outflow on carbonaceous aerosols over the ECS.

2. Materials and method

2.1. Sampling site and sample collection

The aerosol samples were collected at Huaniao Island (30.86°N, 122.67°E), located 66 km to the east of the Shanghai coast (Fig. 1). The island has a land area of 3.28 km^2 and a population of less than 1000, most of which is concentrated on the southeast of the island where a wharf is situated. To minimize the influence of local anthropogenic emissions, the sampling apparatus was placed on the rooftop of a three-story building on the northwest side of the island, ~2 km from the center of population. The elevation of the instrument station was ~50 m above sea level.

PM2.5 samples were collected using a sampler (Guangzhou Mingye Huanbao Technology Company) (Wang et al., 2014) on quartz filters (20 × 25 cm^2, 2500QAT, PALL, USA) at a flow rate of 18 m^3/h. TSP samples were collected using a sampler (Beijing Geological Institute) (Guo et al., 2009) on quartz filters (9 cm in diameter, QM-A, Whatman, UK) at 4.1 m^3/h. A total of 75 paired PM2.5 and TSP samples were obtained from October 23, 2011 to August 20, 2012. Each paired sampling campaign consisted of a 23.5-h sampling period, starting at 9:00 am on the first day to 8:30 am of the following day. At least two parallel operational sampling blanks were measured for each season. Sample media for OC and EC were prepared as follows: the filters were wrapped in aluminum foil and baked at 450 °C for 4 h to remove residual OC. Subsequently, they were sealed in a marked valve bag and stored in the laboratory prior to sample collection. All post-sampling filters were stored at −20 °C for later analysis.

2.2. Sample analysis

OC and EC were detected in the aerosol samples using the IMPROVE thermal/optical reflectance (TOR) method using the Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Chow et al., 1993). For each sample, a 0.544-cm^2 punch area was taken to analyze the targeted carbon fractions including four OC (OC1, OC2, OC3, and OC4) and three EC (EC1, EC2, and EC3) fractions, and a pyrolyzed carbon fraction (OP). These fractions were produced under various temperature and oxidation conditions. OC1, OC2, OC3, and OC4 were formed in a helium atmosphere under a temperature of 140 °C, 280 °C, 480 °C, and 580 °C, respectively. EC1, EC2, and EC3 were formed in a 2% oxygen/98% helium atmosphere under a temperature of 580 °C, 740 °C, and 840 °C, respectively. OC was operationally defined as total carbon in the sample when heated to 550 °C in a 100% helium atmosphere. EC was defined as the total remaining carbon when heated to 800 °C in an atmosphere of 2% oxygen and 98% helium after removal of OC. OP is defined as the amount of carbon measured after the oxygen is added until the reflectance achieves its original value. Therefore, OC and EC were obtained as:

$$\mathrm{OC1} + \mathrm{OC2} + \mathrm{OC3} + \mathrm{OC4} + \mathrm{OP},\ \text{and EC1} + \mathrm{EC2} + \mathrm{EC3} - \mathrm{OP},\ \text{respectively}. \quad (1)$$

The analytical procedure of measurement of *n*-alkanes in aerosols has been described previously (Guo et al., 2009). In brief, half of each filtrate was used for Soxhlet extraction. The extraction lasted 48 h with dichloromethane (DCM) spiked with mixture of 200 ng of deuterated naphthalene (Nap-d_8, *m*/*z* 136), deuterated acenaphthene (Ace-d_{10}, *m*/*z* 164), deuterated phenanthrene (Phe-d_{10}, *m*/*z* 188), deuterated chryene (Chr-d_{12}, *m*/*z* 240), and deuterated perylene (Per-d_{12}, *m*/*z* 264) for the recovery rate. The sample extracts were concentrated to ~5 ml using a vacuum rotary evaporator at 40 °C, 50 rpm. Subsequently, the solvent was exchanged into *n*-hexane (HEX) and was rotary evaporated to approximately 2 ml. All samples were then transferred into 22-ml glass cylinder tubes and concentrated to ~2 ml under soft purified N_2. The concentrated extracts were sequentially cleaned in a chromatography column filled with 3-cm deactivated alumina (Al_2O_3), 3-cm silica gel (SiO_2)