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Effects of continental anthropogenic sources on organic aerosols in the coastal atmosphere of East China

Dongjie Shang [a], Min Hu [a, b, *], Qingfeng Guo [a], Qi Zou [a], Jing Zheng [a], Song Guo [a]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
[b] Beijing Innovation Center for Engineering Sciences and Advanced Technology, Peking University, Beijing, China

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ABSTRACT

Although organic compounds in marine atmospheric aerosols have significant effects on climate and marine ecosystems, they have rarely been studied, especially in the coastal regions of East China. To assess the origins of the organic aerosols in the East China coastal atmosphere, $PM_{2.5}$ samples were collected from the atmospheres of the Yellow Sea, the East China Sea, and Changdao Island during the CAPTAIN (Campaign of Air PolluTion At INshore Areas of Eastern China) field campaign in the spring of 2011. The marine atmospheric aerosol samples that were collected were grouped based on the backward trajectories of their air masses. The organic carbon concentrations in the $PM_{2.5}$ samples from the marine and Changdao Island atmospheres were 5.5 ± 3.1 μgC/m^3 and 6.9 ± 2.4 μgC/m^3, respectively, which is higher than in other coastal water atmospheres. The concentration of polycyclic aromatic hydrocarbons (PAHs) in the marine atmospheric $PM_{2.5}$ samples was 17.0 ± 20.2 ng/m^3, indicating significant continental anthropogenic influences. The influences of fossil fuels and biomass burning on the composition of organic aerosols in the coastal atmosphere of East China were found to be highly dependent on the origins of the air masses. Diesel combustion had a strong impact on air masses from the Yangtze River Delta (YRD), and gasoline emissions had a more significant impact on the "North China" marine atmospheric samples. The "Northeast China" marine atmospheric samples were most impacted by biomass burning. Coal combustion contributed significantly to the compositions of all of the atmospheric samples. The proportions of secondary compounds increased as samples aged in the marine atmosphere indicating that photochemical oxidation occured during transport. Our results quantified ecosystem effects on marine atmospheric aerosols and highlighted the uncertainties that arise when modeling marine atmospheric $PM_{2.5}$ without considering high spatial resolution source data and meteorological parameters.

1. Introduction

Long-range transport of continent-derived atmospheric aerosols has recently become an active research area (Law et al., 2013). The chemical compositions of atmospheric aerosols in the marine boundary layer (MBL) contribute significantly to climate effects (Carslaw et al., 2013; Evan et al., 2009; Fu et al., 2011; King et al., 2012; Quinn and Bates, 2011). It has been shown that dust storms, burning of biomass, coal combustion, and exhausts from ships on coastal harbors are key contributors of aerosols in the marine atmosphere (Fu et al., 2013; Lelieveld et al., 2001), and the terrestrially generated particles contain carbon, nitrogen, and other nutrients. Deposition of these particles in oceanic areas will affect their circulation and will disturb the biogenics of the ocean by increasing nutrient availability (Cassar et al., 2007; Hsu et al., 2009; Krishnamurthy et al., 2009). Furthermore, deposition of toxic anthropogenic aerosols, such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals, can harm marine organisms (Offenberg et al., 2005). Therefore, the continental outflow of anthropogenic aerosols, including primary emissions and secondary formations, can influence the marine environment and the global climate.

The organic compounds found in atmospheric particles in the marine environment come from a variety of sources and were

* Corresponding author. State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China.
E-mail address: minhu@pku.edu.cn (M. Hu).

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found to constitute 48% and 76% of the mass of ambient aerosols in the marine atmospheres in the Aerosol Characterization Experiment-Asia and a study at the Mace Head Global Atmospheric Watch station, respectively (O'Dowd and de Leeuw, 2007; Shank et al., 2012). It has been shown that large amounts of atmospheric water-soluble organic carbon (WSOC) can be emitted by sea spray during high bioactivity periods in marine environments (O'Dowd et al., 2004; O'Dowd et al., 2002). Biogenic secondary organic aerosols (SOA) also contribute to the levels of organic aerosols in marine environments via iodine-induced nucleation, heterogeneous reactions, and other secondary transformations of biogenic volatile organic compounds (BVOCs) (O'Dowd and de Leeuw, 2007). In addition, aerosols and gas precursors from inland anthropogenic processes, such as coal combustion and burning of biomass, may be transported long distances and may have strong impacts on the presence of particulate organic matter in marine atmospheres, especially in coastal water environments (Doney, 2010; Fu et al., 2013; Krishnamurthy et al., 2009; Simoneit et al., 2004).

Although, based on current cutting-edge methods, quantifiable organic species in ambient aerosols only account for a small proportion of total organics, these quantifiable organic molecules still provide valuable information regarding the sources of the aerosols. Source profiles have shown that some organics can be linked to primary emissions, such as hopanes from vehicle emissions and levoglucosan from biomass burning (Schauer et al., 1999; Simoneit, 2002). Several organic species, such as cholesterols, have been shown to originate from marine organisms (Simoneit and Elias, 2000). It is important to quantify the organic components in aerosols at the molecular level to better determine the sources of the atmospheric aerosols in marine environments, however, most studies have only analyzed bulk concentrations of organics and ions in aerosols in marine atmospheres (Fu et al., 2011).

East Asia, especially the coastal area along the Pacific Rim, is thought to be a major source of worldwide particulates in recent years because of its rapid urbanization and industrialization. This study focuses on an ~1 million km^2 coastal region of East China, including the East China Sea and the Yellow Sea (~25–37°N, 117–125°E). In recent years, there have been frequent and severe haze problems in Eastern China (Guo et al., 2014; Hu et al., 2015), and organic pollutants were a significant portion of the particle mass (Gao et al., 2009; Hu et al., 2012; Huang et al., 2013). High levels of fine particles and volatile organic compounds (VOCs) in the atmosphere could increase the levels of primary organic aerosols (POA) and secondary organic aerosols (SOA) in the marine atmosphere via long-range-transport and secondary transformation (Fu et al., 2013). Because meteorological conditions vary considerably in the marine atmosphere, the transport routes and sources of pollutants also vary considerably, thus the composition of aerosols in marine atmospheres are complex.

In this study, we firstly characterized the compositions of organic aerosols in the coastal atmospheres of East China. In addition, we identified the sources of the aerosols and determined their effects on marine aerosols.

2. Methods

2.1. Sample collection

To study the transport of terrestrial aerosols and their impacts on the marine atmosphere, coastal atmospheric aerosols were sampled. A 22 day sampling cruise was conducted in most of the Yellow Sea and the northern part of the East China Sea (27–37°N and 120–126°E) from March 17-April 9, 2011 during the East Asian monsoon when winds were primarily northwesterly and from the eastern parts of the Chinese mainland (Fig. S1).

During each cruise segment, samples of particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) were collected on prebaked quartz filters with a high-volume sampler (Anderson Inc., USA) for the particulate organic matter (POM) study. Each cruise segment took approximately a half-day and covered 30–100 km. A total of 35 aerosol samples were collected, which provided credible meterological variations, and 11 of the samples were collected at night (Table S1). Samples were only collected when the ship was moving and the inlet of the sampler was placed in the bow of the ship to avoid contamination from the ship's exhaust. A low-volume (16.7 L/min) honeycomb sampler (Thermo Scientific, USA) was also used during the cruise to obtain 28 cm^2-filter samples along with the high-volume samples. Elemental carbon (EC), organic carbon (OC), and ion concentrations were analyzed with honeycomb filters. During four of the cruise segments in the East China Sea, the direction of the wind was from the exhaust port to the sampling inlet and the wind speed was higher than the speed of the ship, and the EC:OC ratios of the samples from these segments were unusually high, thus these contaminated samples were not included in further analyses.

Changdao Island (38.0°N, 120.7°E), which is located 7 km north of the Shangdong peninsula, was selected as a collection site on the continent to sea transport route (Fig. 1). This site was described in a CAPTAIN campaign study (Hu et al., 2013). A four-channel sampler (Tianhong, China) was used to collect aerosol samples every 24 h from March 18–April 24, and 39 quartz filter samples were obtained. These samples were analyzed for organic aerosols in the continent boundary atmosphere and were compared with samples from the marine atmosphere.

2.2. Backward trajectories analysis

Although the east wind was dominant during the monsoon in eastern China, the continental origins of the air masses in the Yellow Sea and the East China Sea varied considerably, for example, the origins of the air masses ranged from northeast China to the Yangtze River Delta (YRD). Back trajectory analysis was performed using the HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT4) model developed by the U.S. National Oceanic and Atmospheric Administration/Air Resources Laboratory (NOAA/ARL) (Draxier and Hess, 1998). A cluster analysis at the midpoint of the Yellow Sea and the East China Sea was conducted to get a brief understanding of air mass features in this area. Forty-eight hour back trajectories starting at 100 m above sea level at two points (34.5°N, 122.6°E and 30.2°N, 124.2°E) were firstly calculated every 2 h. The trajectories were then clustered according to similarities in spatial distributions by the HYSPLIT software. The air mass trajectory clusters for the Yellow Sea (YS) and the East China Sea (ES) during the CAPTAIN cruise are shown (Fig. 1). The Yellow Sea was influenced by two continental air masses, which originated in the Shangdong Peninsula (Y1) and in Northeast China (Y2), and one marine air mass (Y3). The East China Sea was mainly influenced by the marine air masses E1 from the north and E3 from the south. An air mass from north China (E2) also impacted the East China Sea.

All of the 31 marine samples were categorized into 6 groups according to their individual 48 h back trajectories (Fig. 2). We named those samples based on continental regions their trajectories past. Four of the samples had air masses from deep in north China (the Beijing-Tianjin-Hebei city cluster), were categorized as “North China”, and aged less than 1 day in the MBL. Those samples corresponded to Y1 and E2 air masses in Fig. 1. Seven of the samples, corresponding to Y2 air masses in Fig. 1, originated from northeast China, which is a primarily agricultural area where biomass is burned heavily in the spring. Among the 7 samples, 4