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The influence of terrestrial transport on visibility and aerosol properties over the coastal East China Sea

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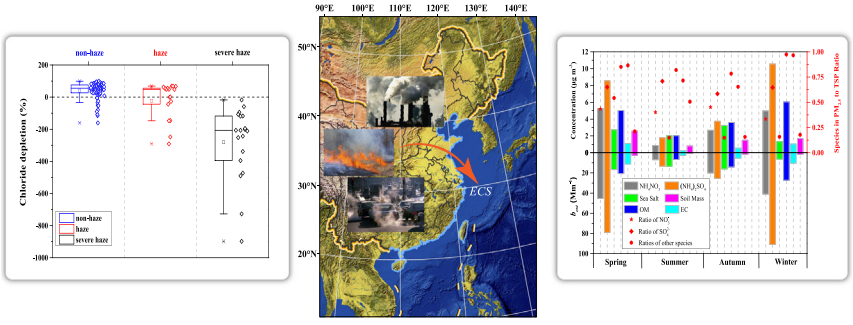
HIGHLIGHTS

- The highest haze frequency occurs around noon over the coastal ECS, implying the importance of terrestrial transport.
- Chloride depletion over the coastal ECS may be converted to Cl^- enrichment influenced by the severe haze.
- The underestimated b_{ext} of aerosols over the coastal ECS was largely related to large mode components and excluding NH_4Cl.

GRAPHICAL ABSTRACT



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ABSTRACT

Air pollutants from East Asia continent can affect the physio-chemical and optical properties of marine aerosols under seasonal winds. We investigated the change of visibility and haze frequency from 1974 to 2017 over the coastal East China Sea (ECS), and reconstructed the light extinction coefficients according to the chemical compositions of $PM_{2.5}$ samples collected at Huaniao Island in the ECS. The annual average visibility significantly decreased from over 25 km in the early 1970s to <18 km in recent 4 years. The occurrence of daily maximum haze frequency was approximately 3-h later with respect to land sites, which could be explained by the diffusion of air pollutants from nearby cities (haze peak around rush hour) to the coastal ECS as well as the formation of secondary aerosols enhanced by photochemical reactions around noon at the condition of affluent gaseous precursors. Meanwhile, anthropogenic chloride transported from the land could increase the concentration of Cl^- in marine aerosol, which may weaken the Cl^- depletion phenomenon over coastal ECS and even induced considerable Cl^- enrichment during the severe haze event in Jan. 2013. The largest contributor to the light extinction was $(NH_4)_2SO_4$ followed by NH_4NO_3 and OM in almost all seasons. Especially in winter and spring, $(NH_4)_2SO_4$ accounted for 45% and 52% of total light extinction, respectively. The estimated b_{ext} was lower than the monitored values, suggesting that the contribution of some aerosol components (e.g. NH_4Cl and large mode components) might be underestimated. Further study on the combination of observation and estimation of specific aerosol contribution to the visibility impairment are needed.

1. Introduction

With a rapid development of Chinese economy, the pollutants' emission from industry, transportation, agriculture and residence increased

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enormously leading to frequently hazy weather in the mid-east region of China in recent decades (Chang et al., 2009; Che et al., 2007; Chen and Wang, 2015). Atmospheric visibility is impaired by the extinction of abundant gaseous pollutants (e.g. Rayleigh scattering of NO_2) and fine particles ($PM_{2.5}$) in the air. Exposure to the high concentration of $PM_{2.5}$ was associated with the increased risk of mortality from lung cancer and cardiovascular diseases (Chen et al., 2008), which caused 7.6% of total global deaths and 4.2% of disability-adjusted life-years in 2015, making it the fifth-ranked global risk factor (Cohen et al., 2017) Atmospheric aerosols also influence the Earth's energy budget by absorbing or scattering solar radiation. Black carbon (BC) is the major absorbing component in aerosols, and the mitigation of greenhouse effect by cutting BC emission may achieve or even exceed that from controlling methane (Jacobson, 2001). Besides, aerosols can act as cloud condensation nuclei (CCN) affecting the radiative properties and lifetimes of clouds, leading to the change of regional climate (Leng et al., 2014).

Many studies have been done on the mechanisms of haze formation and the extinction capability of $PM_{2.5}$ components in Chinese cities. Sulfate was found to be the major contributor (39.8% of total extinction) to visibility reduction followed by organic matter (OM, 23.8%), nitrate (23.1%) and elemental carbon (EC, 9.1%) in Xi'an (Cao et al., 2012). Ammonium sulfate accounted for about 41% of the aerosol extinction coefficient followed by organic carbon (OC, 22%), ammonium nitrate (20%) and BC (18%) in Ji'nan (Yang et al., 2012). Ammonium sulfate was also the main component impairing visibility in the Pearl River Delta (PRD) and accounted for 45%, 47% and 70% of the light extinction with the prevailing northeasterly, northerly and easterly winds, respectively (Cheung et al., 2005). In the Yangtze River Delta (YRD), three typical haze types were observed with $PM_{2.5}$ mass dominated by secondary inorganic pollutants, mineral dust, and biomass burning emissions (Huang et al., 2012a). The light scattering coefficient of aerosols during the day showed a bimodal distribution with the maximal 319.8 Mm^{-1} at 8:00 and a submaximal 280.7 Mm^{-1} at 20:00 in the winter of Shanghai (Xu et al., 2012). A study in Nanjing found that ammonium sulfate (37%), ammonium nitrate (16%), organic matter (15%) and light absorption carbon (10%) in $PM_{2.5}$ contributed significantly to the total light extinction of PM, whereas soil (5–7%) and sea salt (2–4%) in $PM_{2.5}$ and coarse PM (6–11%) had relatively minor influence (Shen et al., 2014). It can be seen that major components affecting the light extinction ability of aerosols are very similar in the Chinese cities probably due to strong influence of anthropogenic air pollutants. Nonetheless, marine aerosols affected significantly by oceanic sources (e.g. sea salt and marine biogenic substances) may have different chemical composition and light extinction components and such studies are limited.

The severe haze and high concentration of $PM_{2.5}$ can be transported from the land to adjacent oceans, which may alter the physiochemical and optical properties of marine aerosols and affect primary productivity and biogeochemistry by depositing nutrients and toxic substances to the surface ocean (Duce et al., 2008; Mahowald, 2011; Mahowald et al., 2008). The East China Sea (ECS) is one of the largest marginal seas of western North Pacific (WNP) and neighboring to the eastern China. Uematsu et al. (2010) found that air pollutants in East Asia including heavy metals and major ions could be transported to the ECS during non-dusty periods. The continental outflow controlled the chemical composition and concentrations of organic aerosols over the ECS including lipids, PAHs and phthalates with the main sources of biomass burning, fungal activities and fossil fuel combustion (Kang et al., 2017). Over 50% of resolved aerosol mass in the coastal ECS was contributed by the anthropogenic sources, and the relevant contributing factors apportioned by Positive Matrix Factorization (PMF) included primary industrial emission, secondary aerosol (high loadings of sulfate and nitrate), oxalate-associated aerosol (high loading of oxalate) and ship emission (Wang et al., 2016). Although the chemical composition (Ji et al., 2015; Li et al., 2015) and source apportionment (Wang et al., 2014) of aerosols have been studied, the haze characters over the ECS and associated radiative properties of marine aerosols have rarely been reported.

This study investigates the haze frequency in the coastal ECS and its correlation with the haze occurrence at adjacent land sites based on the 45-year (1973–2017) meteorological and visibility data. Concentrations of $PM_{2.5}$ components were measured at Huaniao Island during Dec. 2011–Jan. 2013, and their difference between the haze and non-hazy days and contributions to the light extinction were analyzed, which may help to understand the haze diffusion from the land to coastal seas and its influence on the chemical and optical properties of marine aerosols.

2. Methods

2.1. Meteorological data collection

The meteorological data between 1973 and 2017 were obtained from the National Climatic Data Center (NCDC, https://www.ncdc.noaa.gov/isd) for the weather stations at Shengsi (30.73° N, 122.45° E, altitude 81 m and station number 584720, Zhejiang province), Dinghai (30.03° N, 122.11° E, altitude 37 m and station number 584770, Zhejiang province), Xiaoshan (30.23° N, 122.43° E, altitude 7 m and station number 584570, Zhejiang province) and Hongqiao (31.20° N, 121.34° E, altitude 3 m and Station number 584570, Shanghai), of which Shengsi is closest (about 20 km) to our sampling site at Huaniao Island (30.86°N, 122.67°E, Fig. S1). The data used in this study include temperature, dew point, visibility, wind speed and relative humidity.

The TSP data was from the previous study (Wang et al., 2016) focusing the contribution of anthropogenic sources to the aerosols over the ECS. OC and EC data were from another previous study (Wang et al., 2015a) which focuses the characterization of carbonaceous aerosols over the ECS.

2.2. Aerosol sampling and analysis

About 100 individual $PM_{2.5}$ samples were collected in the four seasons between Dec. 2011 and Jan. 2013 at Huaniao Island (altitude ~60 m) in the coastal ECS (Table S1). This site was approximately 80 km away from the nearest shore and influenced significantly by the continental outflow and ship emission from two largest container ports (Fig. S1). The $PM_{2.5}$ were collected on Whatman® 41 cellulose filters (diameter 90 mm) using a medium flow sampler (100 L min^{-1}, Qingdao Hengyuan® HY-120) with the duration of 23.5 h. The cellulose filters were weighted before and after aerosol collection by an analytical balance with reading precision of 10 μg (Sartorius 2004 MP®) after stabilizing under constant temperature (20 ± 1 °C) and relative humidity (40 ± 1%) for >24 h.

A quarter (1/4) of each $PM_{2.5}$ sample and operational blank filter was cut and extracted ultrasonically with 20 mL deionized water (18.25 MΩ cm^{-1}). The extracted solution was filtered through 0.45 μm microporous membrane and analyzed for major ions (Na^+, NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) using an Ion Chromatography (Dionex ICS 3000). The analysis of elements was conducted on 1/2 of each $PM_{2.5}$ sample after a strong-acid microwave digestion. The digestion was performed in a MARS Xpress microwave digestion system with 8 mL of ultrapure HNO_3 and 0.6 mL of ultrapure HF (purified from GR HNO3 and GR HF by a sub-boiling distillation apparatus) per sample. The concentrations of 22 elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Ti, V and Zn) were determined by an Optical Emission Spectrometer with Inductively Coupled Plasma excitation (ICP-OES, SPECTRO ARCOS). The digestion recoveries for all of the certified elements were about 100 ± 15% and the average repeatability for ions and elements were <5% and 10% respectively. Detailed analytical procedures were provided in previous papers (Guo et al., 2014; Wang et al., 2016; Zhu et al., 2013).