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Historical variation in black carbon deposition and sources to Northern China sediments

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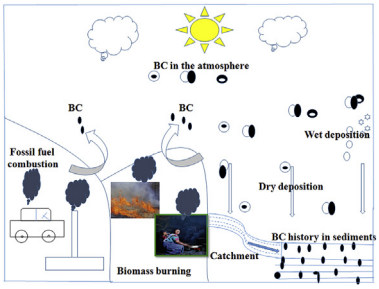
HIGHLIGHTS

- A 100-year history of sedimentary BC in the Northern China Plain was reconstructed.
- The BC deposition has increased tenfold since the pre-industrial era.
- Two peaks in the BC deposition occurred in the 1970s and 2010s.
- Residential energy consumption and biomass burning contributed to the BC deposition peak in the 1970s.
- The BC from fossil fuel combustion was negligible before 1990, but subsequently increased to 70% of all deposited BC.

GRAPHICAL ABSTRACT



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ABSTRACT

Black carbon (BC) in fine particulate matter ($PM_{2.5}$) is an important air pollutant in a large area of China. We have reconstructed a 100-year-long history of BC deposition based on analyses of sediment samples in the coastal area of the Northern China Plain (NCP). During 1900–2010, the sedimentary BC concentrations at three cores increased from 0.2 to 1.3, from 0.2 to 2.3, and from 0.2 to 1.9 mg g^{-1}, and the ranges for the BC deposition fluxes were 0.1–4.7, 0.1–8.2, 0.2–7.4 g m^{-2} a^{-1}, suggesting the increase of ten times from the pre-industrial era. The BC deposition fluxes showed abrupt variation with two peaks in the 1970s and 2010s. Residential energy consumption and biomass burning (i.e., low-temperature combustion sources; thus, large-scale wildfires with high temperature may not be included) were responsible for the BC increase in the 1970s. Fossil fuel combustion generated by the industrial sectors, including industry, power plants, and transportation, was negligible before 1990 but significantly increased during 1990–2010. The historical increase in the BC deposition was accurately predicted by climate models, specifically the Coupled Model Intercomparison Project Phase 5 (CMIP5). However, the

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BC fluxes in the NCP sediments were an order of magnitude greater than those of the simulated depositions, suggesting an underestimation of the BC deposition in the severely polluted area in China.

1. Introduction

China has suffered from extremely high levels of particulate air pollution in recent years, particularly in the mega-cities of Beijing (Han et al., 2016; Zheng et al., 2016) and Tianjin (Zhou et al., 2016) and the associated industrial center (Andersson et al., 2015; Xie et al., 2016) in the Northern China Plain (NCP). The incomplete combustion of fossil fuels and biomass emits significant fractions of black carbon (BC) aerosols that contribute to primary pollutants as fine particulate matter ($PM_{2.5}$). Carbonaceous aerosols (including BC) may be approximately five times the toxicity of inorganic aerosols such as sulfates and nitrates; thus, carbonaceous aerosols may be the key drivers of ~3 million premature deaths attributed to air pollution (Apte et al., 2015; Lelieveld et al., 2015; Lim et al., 2012). Moreover, BC plays a leading role in the short-lived climate pollutants that strongly influence the Earth's climate (Baker et al., 2015; Stohl et al., 2015). Mitigating the BC emissions in Asia could effectively combat CO_2 climate impacts in the short term (Li et al., 2016; Shindell et al., 2012).

Identifying the sources, emissions, and concentrations of the BC in China is the foundation for an effective air pollution mitigation strategy, and is required for the accurate parameterization of climate models (Zhang et al., 2015). Emission inventory suggests that the anthropogenic activities in China might account for 25% of the global BC emissions and that the uncertainties in the BC emissions for China are estimated to be in the range of 100–400% (Bond et al., 2004; Zhao et al., 2011). In addition to the large uncertainties in the emission inventory, the estimate of the BC impact on climate and human health needs to resolve uncertainties in the global models for aerosol microphysical and chemical processes, atmospheric transport, and interactions with clouds, including precipitation scavenging. The processes governing the deposition of carbonaceous aerosols are broadly parameterized in models (Lamarque et al., 2013). To constrain the models to the scavenging processes of the atmospheric BC, long-term historical deposition data are useful for comparison with the results of simulations (Koch et al., 2009; Lee et al., 2013).

Sediments are commonly used to reconstruct historical BC deposition because the stable and recalcitrant nature of the BC causes it to remain in the sediments for hundreds of years (Fang et al., 2015; Rose and Ruppel, 2015; Ruppel et al., 2014). Previous studies have reconstructed historical variations of the BC deposition onto background areas such as the Tibetan Plateau (Cong et al., 2013; Han et al., 2015), northeastern China's Sanjiang Plain (Gao et al., 2014), and southern China's coastal areas (Bao et al., 2015; Han et al., 2011). However, although it is the core area for strong BC emissions, the severely polluted industrial center in the NCP has scarce observations of historical BC variation.

In this study, we analyzed the BC contents in sediment samples from three sites in the coastal areas of the NCP. The 100-year history of the BC profiles, spanning from the pre-industrial to the contemporary era, was characterized in the NCP. The critical periods of the BC increase were identified. The major sources and causes of the historical variation of the BC deposition were discussed. Furthermore, these long-term historical data add useful constraints to the emission inventory and modeling of the BC deposition in this severely polluted area of China.

2. Materials and methods

2.1. Site description and sediment cores

A thick haze frequently shrouds Beijing-Tianjin-Hebei, a densely populated and industrialized area in China. Sediment samples were collected in the coastal and rural areas in the Bohai Sea (Fig. 1). Three sediment cores, S4, S5, and S8, were sampled on a wild salt marsh. S4 and S5 were sampled at an interval of 1 cm for 1-m-deep sediments. S8 was a parallel sample of S4, and S8 was collected with 0.5-cm interval sampling. The ages of the S4 and S5 samples were determined by radioisotope dating for ^{210}Pb and ^{137}Cs (Wang et al., 2015). The S8 age was calibrated from the S4 age profile because the two cores were parallel samples with similar sedimentation environments.

In our previous investigation, more than 50 sediment cores were collected in Bohai Bay. The sedimentation rates were estimated by the excess ^{210}Pb ($^{210}Pb_{exc}$) and ^{137}Cs in the sediment (Andersen et al., 2000). The average sedimentation rates of S4 and S5 were 0.29 and 0.26 cm yr^{-1}, respectively, which was lower than that of the other cores (1.1–3.5 cm yr^{-1}) in Bohai Bay (Fig. S1), indicating few transported sediments into the sampling area. Both the $^{210}Pb_{exc}$ and ^{137}Cs values suggest that there is no sediment mixing layer and no erosion in the upper half of the S4 (S8) and S5 cores (Wang et al., 2015). Consequently, the sediments should have continuous records of atmospheric depositions with few disturbances; thus, the three cores were selected for BC measurements.

2.2. Measurements of black carbon

The sediment samples were pretreated according to a previously published method (Han et al., 2007, 2015). In brief, the sediment samples were freeze-dried and ground into fine particles and treated with 10 ml of 2 N hydrochloric acid (HCl) to remove carbonate and some metals. Then, a 15-ml mixture of concentrated 6 N HCl and 48% hydrofluoric acid (HF) was added to remove silicates and residue metals in the sediments (Han et al., 2011). Finally, the sample was treated with 4 N HCl to remove fluorite minerals. The demineralized sediments were rinsed and diluted with 200 ml of water, followed by filtering with pre-combusted quartz filters for the subsequent BC measurements.

A thermal-optical transmittance (TOT) carbon analyzer (Sunset Laboratory, Tigard, OR, USA) was used to determine the elemental carbon (EC, the instrumental-mass of BC) and organic carbon (OC) loadings on the filter. A protocol of the National Institute of Occupational Safety and Health (NIOSH) 870 TOT program was used for the analysis (Cui et al., 2016; Panteliadis et al., 2015). Table S1 shows the NIOSH 870 program that was slightly adjusted from NIOSH 5040 (Birch and Cary, 1996; Chen et al., 2013). First, the oven temperature was increased to 870 °C in four steps in a pure helium atmosphere to thermally volatilize the OC in the filter samples. Then, the oven temperature was reduced to 550 °C, and an oxygen/helium (10:90) atmosphere was introduced. The oven was heated to 870 °C in six steps, which enabled the thermal oxidization of the EC (Yang and Yu, 2002). The OC might be pyrolyzed (PC) to EC at the first stage in a helium atmosphere, resulting in a decrease in the online laser transmission signal, which was monitored through the