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Sources and radiocarbon ages of aerosol organic carbon along the east coast of China and implications for atmospheric fossil carbon contributions to China marginal seas

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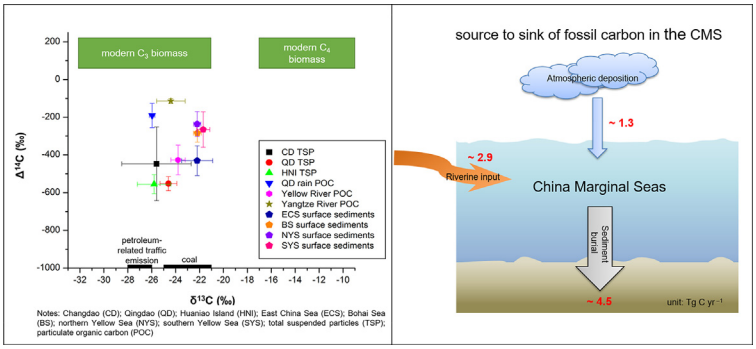
HIGHLIGHTS

- ^{14}C and ^{13}C of aerosol samples from the east coast of China were analyzed.
- Fossil carbon was an important component of coastal aerosols.
- Strong seasonal variations of fossil carbon contribution were shown at Changdao.
- Atmospheric deposition is important for fossil carbon burial in the CMS.

GRAPHICAL ABSTRACT



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ABSTRACT

Aerosol deposition is an important mechanism for the delivery of terrestrial organic carbon (OC) to marginal seas, but OC age characteristics of aerosols are not well constrained and their contributions to sediment OC burial have not been quantified. Total suspended particle samples were collected along the east coast of China at Changdao (CD), Qingdao (QD) and Huaniao Island (HNI), and were analyzed for total organic carbon (TOC) isotopes (^{13}C and ^{14}C) in order to bridge this information gap. TOC $\delta^{13}C$ and $\Delta^{14}C$ values ranged from −23.6 to −30.5‰, and −153 to −687‰, respectively, with the latter corresponding to ^{14}C ages ranging from 1280 to 9260 yr. Estimated contributions of fossil carbon to TOC based on ^{14}C mass balance approach ranged from 26 to 73%, with strong seasonal variations in fossil carbon observed at CD. Fossil carbon at CD showed the highest proportion (73%) in winter, reflecting anthropogenic emissions and the lowest proportion (26%) in summer, caused by biomass contribution (annual ave., 52% ± 17%). In contrast, the fossil carbon at both QD (57–64%) and HNI (57–67%) dominated throughout the year, reflecting local anthropogenic influences and long-range transport. Mass balance estimates indicate that atmospheric deposition and riverine export accounted for 31% and 69% of fossil carbon inputs to the China marginal seas (CMS) respectively, with fossil carbon burial efficiencies approaching 100% in the CMS. On a global scale, an atmospheric fossil carbon deposition flux of 17.2 Tg C yr^{-1} was estimated, equivalent to 40% of the estimated fluvial flux to the ocean, and potentially accounting for 24–41% of fossil OC burial in

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marine sediments. Therefore, the atmospheric deposition constitutes an important source of fossil carbon to marine sediments, and could play a key role in regional and global scale OC budgets and biogeochemical cycles.

1. Introduction

Atmospheric transport represents a significant pathway for the transfer of natural and anthropogenic materials from land to oceans, augmenting riverine input. Atmospheric deposition of nutrients, trace metals and pollutants has influenced coastal and open ocean biogeochemical cycles (Duce et al., 1991; Mahowald, 2011). Aerosol deposition also plays a key role in the global carbon cycle (Jurado et al., 2008; Willey et al., 2000). A total of 58 Tg C yr^{-1} of particulate organic carbon (POC) is delivered to the global ocean through dry and wet deposition (Jurado et al., 2008), equivalent to almost 30% of the annual river POC flux (~200 Tg C yr^{-1}) (Galy et al., 2015) and also to ~40% of total OC (TOC) burial (~160 Tg C yr^{-1}) in marine sediments (Burdige, 2005). Besides the riverine inputs, ^{14}C data suggest that carbonaceous aerosols may also entrain a significant portion of pre-aged and fossil carbon (Heal, 2014; Matsumoto et al., 2001), and once buried in marine sediments, both carbon inputs may represent a long-term carbon sink. The transport and reburial of the non-modern carbon exerts minimal short-term influence on atmospheric CO_2 concentrations (Galy et al., 2008), however its mineralization – both in the terrestrial and marine environments – would result in an increase atmospheric CO_2. Therefore, it is important to constrain the different sources and fate of OC and their influence on atmospheric CO_2 and climate forcing on different timescales. Fossil carbon may derive from natural weathering processes of continental rocks that is then transported oceanwards via riverine or atmospheric processes (Blair et al., 2003) or may be emitted as carbonaceous aerosols from fossil fuel combustion stemming from anthropogenic activities (Liu et al., 2013; Huang et al., 2014). Thus, increasing anthropogenic activity may enhance both the transport and burial of fossil carbon to the ocean.

Marginal seas are major loci of carbon sequestration, accounting for up to 90% of sediment OC burial in the global ocean (Hedges and Keil, 1995). The China marginal seas (CMS) in the western Pacific Ocean, including the Bohai Sea (BS), Yellow Sea (YS) and East China Sea (ECS), are important carbon sinks due to large-scale riverine and atmospheric inputs. With respect to the latter, the CMS are located in the downwind of the Asian continental outflow in spring and winter when the northerly wind prevails, during which atmospheric deposition of nutrients, heavy metals, toxic organic pollutants derived from anthropogenic activity could significantly influence marine ecosystems and biogeochemical processes (Shang et al., 2017; F. Wang et al., 2016; F.J. Wang et al., 2017). From a carbon cycle perspective, aerosol deposition has been also shown to be a significant source of carbon to the CMS, as indicated by studies of polycyclic aromatic hydrocarbons (PAHs, Lin et al., 2011; C. Wang et al., 2017) and black carbon (BC, Fang et al., 2015; Huang et al., 2016). For example, a study of BC budget in the BS suggested that contributions from atmospheric deposition were as important as those from riverine transport (Fang et al., 2015); and that atmospheric deposition contributed nearly 72% of PAHs to the CMS (C. Wang et al., 2017).

Natural abundance variations in radiocarbon (^{14}C) provide a powerful diagnostic for distinguishing fossil and modern (biomass) carbon sources. ^{14}C-based source apportionment studies have also indicated that fossil carbon can comprise an important fraction of BC and PAHs in carbonaceous aerosols and sediments (Hanke et al., 2017; Huang et al., 2016; Uchida et al., 2010). The deposition of fossil carbon may thus also influence marine ecosystems, biogeochemical processes and carbon cycling. However, previous OC budgets for CMS sediments have primarily focused on riverine inputs. For example, Wu et al. (2013) estimated that about 2 Tg C yr^{-1} of fossil OC was buried in the ECS inner shelf, exceeding annual inputs from the Yangtze River. Tao et al. (2016) estimated an unidentified contribution of 0.72 Tg C yr^{-1} of pre-aged OC in the BS and YS. It could be inferred from both of the studies that atmospheric aerosols could serve as an important source of non-modern carbon to CMS sediments. Nevertheless, the importance of aerosol carbon contributions to the ocean carbon cycle remains poorly constrained. It is therefore necessary to characterize the fluxes and sources of aerosol OC in order to assess contributions to both regional and global ocean carbon budget.

In this study, aerosol total suspended particle (TSP) samples were collected along the east coast of China at Changdao (CD), Qingdao (QD) and Huaniao Island (HNI). There have been numerous prior studies on the composition, transport and deposition of major ions, trace elements and organic compounds in total suspended particulates and fine particulates at these sites (Feng et al., 2007, 2012; Guo et al., 2003; F. Wang et al., 2016), however, there has been no study of seasonal variations in ^{13}C and ^{14}C isotopic characteristics and no assessments of fossil carbon contributions to the CMS via atmospheric deposition. Hence, the main objectives of this study are to identify sources, to quantify radiocarbon ages of aerosol OC at these sites, and to estimate the contributions of aerosol-derived fossil carbon to the CMS sediment carbon budget.

2. Materials and methods

2.1. Study sites and sample collections

Aerosols were collected seasonally as total suspended particle (TSP) samples at CD, QD and HNI sites along the east coast of China (Fig. 1). Changdao (area, 56 km^2) is near the demarcation line of the BS and YS and is located ~7 km north of the Shandong Peninsula, with limited local industrial activities. The sampling site at CD (37.90°N, 120.76°E, 90 m above sea level) was located on the rooftop of a radar station near the coast. Qingdao is a major coastal city situated in the southern tip of the Shandong Peninsula and the second largest city in Shandong province along the Yellow Sea coast with an urban population of ca. 4 million. The sampling site at QD (36.16°N, 120.50°E, 85 m above sea level) was on the rooftop of a building on the Ocean University of China campus. Huaniao Island (area, 3.28 km^2) is located 66 km to the east of Shanghai coast, with 1000 inhabitants and no industrial activity. The sampling site of HNI (30.86°N, 122.67°E, 50 m above sea level) was located on the roof of a three-storey building, ~2 km from the population center. Thus, local anthropogenic inputs at CD and HNI are minor, while at QD local anthropogenic emissions may be substantial. All three sites are influenced by East Asian continental outflow toward to the Pacific Ocean, especially for CD and HNI since they have been classified as the background sites to monitor continental aerosol transport to the CMS (Feng et al., 2007; F.J. Wang et al., 2017).

Samples from CD and QD were collected on pre-combusted quartz filters (Whatman, QM-A, 20 × 25 cm^2) by using a high volume sampler at a flow rate of 1 m^3 min^{-1} for 24 h. Samples from HNI were collected on quartz filters (Pall, 2500QAT, 20 × 25 cm^2) at a flow rate of 0.3 m^3 min^{-1} for 23.5 h. All filters and aluminum foil were pre-combusted at 450 °C for 4 h to remove residual OC. After collection, filters were stored at −20 °C until analysis.

2.2. Carbon isotopic analysis

For TOC ^{13}C and ^{14}C analysis, freeze-dried samples were acidified by using 4 M HCl at room temperature to remove inorganic carbon and