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Pre-aged soil organic carbon as a major component of the Yellow River suspended load: Regional significance and global relevance

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A B S T R A C T

Large rivers connect the continents and the oceans, and corresponding material fluxes have a global impact on marine biogeochemistry. The Yellow River transports vast quantities of suspended sediments to the ocean, yet the nature of the particulate organic carbon (POC) carried by this system is not well known. The focus of this study is to characterize the sources, composition and age of suspended POC collected near the terminus of this river system, focusing on the abundance and carbon isotopic composition (^{13}C and ^{14}C) of specific biomarkers.

The concentrations of vascular plant wax lipids (long-chain ($\geq C_{24}$) *n*-alkanes, *n*-fatty acids) and POC co-varied with total suspended solid (TSS) concentrations, indicating that both were controlled by the overall terrestrial sediment flux. POC exhibited relatively uniform $\delta^{13}C$ values (-23.8 to -24.2‰), and old radiocarbon ages (4000–4640 yr). However, different biomarkers exhibited a wide range of ^{14}C ages. Short-chain (C_{16}, C_{18}) fatty acid ^{14}C ages were variable but generally the youngest organic components (from 502 yr to modern), suggesting they reflect recently biosynthesized material. Lignin phenol ^{14}C ages were also variable and relatively young (1070 yr to modern), suggesting rapid export of carbon from terrestrial primary production. In contrast, long-chain plant wax lipids display relatively uniform and significantly older ^{14}C ages (1500–1800 yr), likely reflecting inputs of pre-aged, mineral-associated soil OC from the Yellow River drainage basin. Even-carbon-numbered *n*-alkanes yielded the oldest ^{14}C ages (up to 26 000 yr), revealing the presence of fossil (petrogenic) OC.

Two isotopic mass balance approaches were explored to quantitively apportion different OC sources in Yellow River suspended sediments. Results indicate that the dominant component of POC (53–57%) is substantially pre-aged (1510–1770 yr), and likely sourced from the extensive loess-paleosol deposits outcropping within the drainage basin. Of the remaining POC, between 10 and 31% is fossil in origin (>26 000 yr), resulting from the physical erosion of ancient sedimentary rock and input of fossil fuel residues from anthropogenic activity, and 16–33% is modern carbon derived from terrestrial and aquatic productivity. These findings have implications both regarding the provenance and vintage of organic matter signatures emanating from the Yellow River basin and similar catchments containing extensive paleosol sequences, as well as for the reactivity and fate of this POC upon supply to adjacent marginal seas.

1. Introduction

Organic carbon (OC) in recently biosynthesized terrestrial biomass and soil humus is at least 3–5 times greater than that as CO_2 in the atmosphere (Hedges, 1992; Tarnocai et al., 2009). Small changes in the rate of carbon exchange between these terrestrial reservoirs and the atmosphere can thus influence atmospheric CO_2

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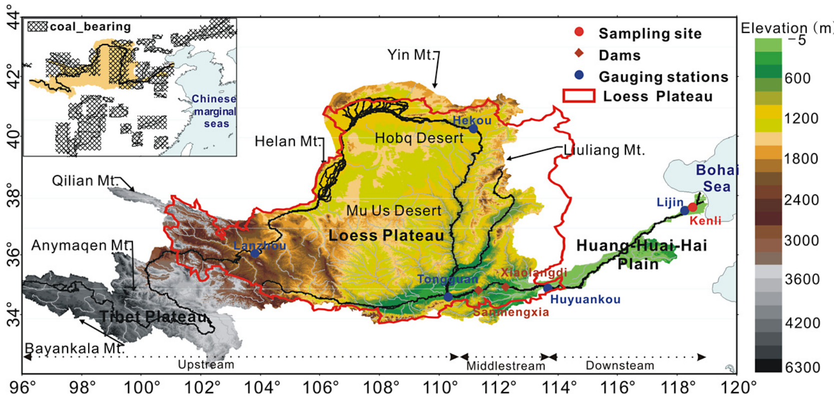

Fig. 1. Elevation map of the Yellow River drainage basin with the sampling site of Kenli (37.68°N, 118.52°E, Kenli) and morphological features. The up-left panel is a map of East Asia showing the location of the Yellow River and Chinese marginal seas and coal-bearing areas within the watershed. (For interpretation of the reference to color in this figure legend, the reader is referred to the web version of this article.)

inventories. Understanding the composition, reactivity and mobilization of terrigenous OC is therefore of key importance given their impact on the biogeochemical properties of terrigenous OC (Blair and Aller, 2012; Feng et al., 2013a, 2013b; Galy and Eglinton, 2011).

Rivers link about 87% of the continental surface to the ocean (Ludwig and Probst, 1998; Schlünz and Schneider, 2000), and fluvial systems can offer an integrated perspective on processes determining the flux and nature of terrigenous OC export to the ocean. Natural riverine OC derives from three primary sources: detritus of recently biosynthesized biomass, soils, and sedimentary rocks (Hedges et al., 1986). The two latter components may contain relatively refractory organic matter, having previously experienced degradation and modification during their formation, and hence influence carbon cycling over longer time scales (thousands to millions of years). River-exported OC display a very wide range of ages from modern to over 30 000 ^{14}C yr (e.g., Bouchez et al., 2014; Feng et al., 2013b; Galy and Eglinton, 2011; Goñi et al., 2014; Hilton et al., 2010; Martin et al., 2013; Raymond and Bauer, 2001; Wang et al., 2012), underlining the diversity of sources, compositions and storage times of riverine OC that reflect geologic and environmental characteristics of the respective catchments (Blair and Aller, 2012). Thus, it is necessary to establish watershed-specific properties in order to develop accurate assessments of fluvial influences on biogeochemical processes over regional and global scales.

Terrigenous OC sources are assessed using a range of approaches, such as elemental and bulk carbon isotopic compositions and molecular characteristics (e.g., Collister et al., 1994a; Drenzek et al., 2009; Galy and Eglinton, 2011; Hedges et al., 1997; Weijers et al., 2009). A key issue for quantifying different riverine OC components is to constrain their respective end-member characteristics within inherently complex and heterogeneous drainage basins. Individual biomarker δ^{13}C and Δ^{14}C measurements provide a means to directly constrain end-member values of source-specific carbon inputs (Eglinton et al., 1997; Freeman et al., 1990). Higher plant biomarker Δ^{14}C contents have been examined to study sources and storage times of terrestrial OC in several river/estuary systems including tropical/sub-tropical (e.g. Ganges–Brahmaputra, Mekong; Galy and Eglinton, 2011; Martin et al., 2013), temperate (e.g., Eel, Danube, Columbia; Drenzek et al., 2009; Feng et al., 2013a; Kusch et al., 2010), and high latitude (e.g., Mackenzie, and several Eurasian Arctic rivers; Drenzek et al., 2007; Feng et al., 2013b; Gustafsson et al., 2011). In tropical rivers, young ^{14}C ages of higher plant biomarkers indicate short average residence times (years to centuries) of terrestrial vegetation, whereas OC storage and transfer in high latitude catchments appears more complex and heterogeneous, with ^{14}C ages of different components ranging from decades to millennia. At present, however, we are lacking a comprehensive understanding of the factors that influence the sources and storage times of terrestrial OC pools within river basins.

As amongst the world's most turbid major rivers, the Yellow River represents a regionally important and globally significant fluvial system. Over the past millennium, estimated sediment discharge (1×10^9 t/yr; Milliman and Syvitski, 1992) and OC export (4.5 Tg OC/yr; Cauwet and Mackenzie, 1993) from the Yellow River account for roughly 89% of sediment flux to the adjacent Bohai and Yellow Sea, and ∼6% and ∼1% of global fluvial sediment and organic carbon flux to the ocean, respectively (Bianchi and Allison, 2009; Milliman and Syvitski, 1992). Sediment load and carbon flux dramatically declined to 1.51×10^8 t/yr and 0.47 Tg/yr in the past 50 years due to drought and enhanced human intervention (Peng et al., 2010; Ran et al., 2013). About 90% of the OC carried by the Yellow River is in particulate form (Cauwet and Mackenzie, 1993; Zhang et al., 2013) as a consequence of intense soil erosion within the drainage basin, with POC flux (0.41 Tg/yr) comparable to other large river systems (Mississippi 0.8 Tg/yr, Lena 0.46 Tg/yr and Niger 0.66 Tg/yr; Dagg et al., 2004). High burial efficiencies (up to 80%) for the Yellow River POC contrast sharply with other river systems developed on passive margins, which are typically <50% (Blair and Aller, 2012; Keil et al., 1997), but are similar to the that reported for the Ganges–Brahmaputra system (Galy et al., 2007). While the Yellow River is known as a major contributor of clastic sediment and POC to the ocean, the characteristics of the Yellow River POC remain only partially determined. Wang et al. (2012) utilized a binary model based on bulk ^{14}C values to estimate that 66–93% of POC in the Yellow River were comprised of old components, which may explain its refractory nature. However this study did not distinguish between pre-aged soil and ancient (fossil) OC, yet these two pools have quite different implications for carbon cycle and associated biogeochemical processes.

The focus of this study is to develop robust constraints of the sources, composition and age of POC carried by the Yellow River and supplied to the adjacent Bohai Sea and Yellow Sea. In addition to bulk properties, the abundance and carbon isotopic composition of specific biomarkers were measured in order to characterize and quantify sources of OC.

2. Materials and methods

2.1. Study area

The Yellow River (Huanghe) is the world's fifth longest river (5464 km), originating on the Qinghai–Tibet Plateau at an altitude >5000 m and encompassing a drainage area of 75.2×10^4 km^2 (Fig. 1). Its basin spans the entire semi-arid and arid region of northern China and flows through extensive prairies