Effect of human-controlled hydrological regime on the source, transport, and flux of particulate organic carbon from the lower Huanghe (Yellow River)

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ABSTRACT: Evaluating the role of fluvial transfer of terrestrial organic carbon (OC) and subsequent burial in the global carbon cycle requires the sources and fluxes of fluvial OC to be assessed, which remains poorly constrained in the Huanghe (Yellow River). Here, we report the elemental, stable isotopic, and radiocarbon activity of particulate organic carbon (POC) sampled at the outlet of Huanghe in 2012–2013. We show that the Huanghe riverine POC can be explained by binary mixing of fossil (POCfossil) and non-fossil (POCnon-fossil) components, the former may reach ~40% of the total POC. The Huanghe POCnon-fossil is mostly sourced from C3 plants, with a mean residence time of ~2200 years. The current human-controlled hydrological regime strongly influenced the POC sources, transport modes, and fluxes. In 2012–2013, the Huanghe delivered 0.73 Tg (1 Tg = 10^12 g) of POC to the sea, and about 28% of the annual POC flux occurred within a short human induced flood event. Globally, the Huanghe should be one of the largest rivers in the transfer and re-burial of fossil OC. However, the fate of Huanghe fossil OC is still unconstrained and needs to be further investigated. Copyright © 2015 John Wiley & Sons, Ltd.

KEYWORDS: particulate organic carbon; stable isotope geochemistry; Huanghe (Yellow River); carbon export; water–sediment regulation scheme

Introduction

Fluvial transfer of terrestrial organic carbon (OC) links terrestrial, atmospheric, and oceanic carbon pools and plays an integral role in the global carbon cycle over geologic timescales (Berner, 1982, Burbidge, 2005, 2007; Audidenkepe et al., 2011; Bauer et al., 2013). Globally, rivers export ~400 Tg (1 Tg = 10^12 g) OC per year to the coastal ocean margins, of which ~250 Tg is dissolved organic carbon (DOC) and ~150 Tg is particulate organic carbon (POC) (Meybeck, 1993; Ludwig et al., 1996; Schlünz and Schneider, 2000). About ~70% of this terrestrial OC is thought to be oxidized and thus returns back to the atmosphere, the remains may be buried in deposited sediment leading to atmospheric carbon dioxide (CO2) sequestration (Berner, 1982; Burbidge, 2005, 2007; Blair and Aller, 2012). This burial represents the second largest sink of atmospheric CO2, and thus plays an important role in regulating long-term climate changes (e.g. the glacial–inter-glacial cycles) (Berner, 1990). However, in many river systems, the POC eroded from the terrestrial biosphere (vegetation, soil, and riverine autotrophic living organisms, hereafter POCnon-fossil) can be mixed with POC derived from sedimentary rocks or ‘petrogenic’ OC (hereafter POCfossil) (e.g. Raymond and Bauer, 2001; Blair et al., 2003; Komada et al., 2004; Komada et al., 2005; Leithold et al., 2006; Galy et al., 2007; Galy et al., 2008a; Blair et al., 2010; Bouchez et al., 2010; Gomez et al., 2010; Hilton et al., 2010, 2011; Graz et al., 2012; Hilton et al., 2012; Bouchez et al., 2014). Erosion and burial of POCnon-fossil is a long-term sequestration of atmospheric CO2, whereas the reinterment of POCfossil only lengthens the residence time of OC in the lithosphere and thus has no effect on recent atmospheric CO2 (Galy et al., 2007; Galy et al., 2008a; Hilton et al., 2008b; Hilton et al., 2011; Kao et al., 2014). POCfossil, if oxidized, consumes O2 from and returns CO2 to the atmosphere, thereby countering contemporaneous CO2 drawdown (Galy et al., 2008a; Bouchez et al., 2010). For these reasons, it is important to quantify the...
proportions of POC_{fossil} and POC_{non-fossil} in the riverine OC, and then to determine the effective conditions for their transfer and burial (Wheatcroft et al., 2010).

A recent review by Blair and Aller (2012) suggests there are two end-member fluvial systems, one is small mountainous rivers (SMRs) and the other is large rivers. The terrestrial OC in the SMRs is typically characterized by a bimodal mixture of fossil and modern OC, resulting from high erosion rates and relative short residence times for sediment particles (Blair et al., 2003; Komada et al., 2004; Hilton et al., 2008b; Hilton et al., 2011). Duringaperiodic intense rainfall events (cyclones and/or tropical storms), SMRs can rapidly deliver a huge amount of sediment to the ocean, notably if floodplain transits are short (Milliman and Farnsworth, 2011). This, in turn, provides favorable conditions for higher burial rates and more efficient preservation of terrestrial OC (Hilton et al., 2008a; Hilton et al., 2008b; Gomez et al., 2010; Wheatcroft et al., 2010; Hilton et al., 2011; Lloret et al., 2013; Kao et al., 2014). In contrast, studies focused on the Amazon and Ganges-Brahmaputra Rivers indicated that riverine OC is dominated by the non-fossil component (contemporary plus aged soil OC) and the fossil OC is a relatively small component (Galy et al., 2007; Galy et al., 2008a; Bouchez et al., 2010; Galy and Eglinton, 2011; Bouchez et al., 2014). With a large watershed and a well-developed floodplain, large rivers have more reactive behavior than SMRs (Aucour et al., 2006; Blair and Aller, 2012; Bouchez et al., 2014). A series of chemical, physical and biological processes within the large river system could have great impacts on the source, composition, and flux of terrestrial OC and thus on its fate in the coastal ocean margins (Cole et al., 2007; Bianchi, 2011; Blair and Aller, 2012; Fichot and Benner, 2014). This situation may be further complicated by the basin-scale regional environment, climate change, and human activities (e.g. Bianchi et al., 2004; Bianchi et al., 2007; Zhang et al., 2009; Yu et al., 2011; Regnier et al., 2013). More information about the processes that influenced the terrestrial OC behaviors are urgently needed to better predict the response of the coupled watershed-ocean system to future climate change and its possible feedback (Bianchi, 2011; Galy and Eglinton, 2011; Feng et al., 2013; Bauer et al., 2013).

The Huanghe (Yellow River), one of the largest rivers in terms of annual OC flux, historically delivered a total of 4.56 to 6.81 Tg C \textsuperscript{-1} OC (POC + DOC) to the sea (Zhang et al., 1992; Cauwet and Mackenzie, 1993), and thus it plays an important role in the global carbon cycle and regional biogeochemical processes. Nearly 90% of the Huanghe OC is transported in particulate form, which is different from other major world large rivers (e.g. Amazon, Congo, Mississippi, and Mekong) (Dagg et al., 2004; Cynel et al., 2005), but similar to SMRs (e.g. Taiwan) (Kao and Liu, 1997). The extreme low DOC/POC ratio for the Huanghe, together with the highly depleted \Delta^{13}C values of POC, confirmed that the Huanghe riverine POC must be refractory and bound tightly to minerals particles (Wang et al., 2012; Ran et al., 2013a; Zhang et al., 2013). However, detailed information about the different components of the Huanghe riverine POC and their respective transport modes is still unavailable. Furthermore, human activities have totally changed the hydrological cycle of the lower Huanghe after the operation of Xiaolangdi Reservoir in 1999 (Figure 1) (Wang et al., 2010; Yu et al., 2013a; Yu et al., 2013b). Since 2002, the implement of the Water–Sediment Regulation (WSR) Scheme has introduced a new hydrological regime to the lower Huanghe (Yu et al., 2013b). The WSR Scheme has changed the natural variation in the water and sediment, caused significant erosion of the channel in the lower reaches, and modified the morphological features at the river mouth (Wang et al., 2010; Yu et al., 2013a; Bi et al., 2014). However, our knowledge of the source, transport, and flux of terrestrial OC in the Huanghe, how and to what extent it has responded to the anthropogenic disturbances, is rather limited.

In this study, we sampled the suspended particulate matter (SPM) from the outlet of Huanghe (Lijin) over a wide range of water discharges during the 2012–2013 hydrological year (September 2012–September 2013). Our main objectives are (1) to make the first assessment of the contributions of POC_{fossil} to the Huanghe POC flux, (2) to reveal the transport modes of Huanghe POC under a new hydrological regime, and (3) to examine the impact of human activity on the basin-scale carbon cycle.

### The Huanghe Basin

The Huanghe originates in the Bayankala Mountains of the eastern Tibetan Plateau at an elevation of 4600 m, drains a basin area of 795 000 km\textsuperscript{2} through nine provinces, and discharges into the Bohai Sea. The Huanghe, with a length of 5464 km, can be divided into the upper (above Toudaoguai), middle (between Toudaoguai and Huayuankou) and lower reaches (below Huayuankou) based on distinctive geomorphology and climatic conditions (Figure 1a). Geologically, the Huanghe basin is located on the North China carton, most of the outcropping rocks formed during the Precambrian to Quaternary. About 44% of the Huanghe watershed is covered by the Loess Plateau (~440 000 km\textsuperscript{2}), which is one of the largest and thickest loess deposits in the world. Additionally, outcrops of Archean to Tertiary granites and metamorphic rocks are scattered in the south and north-northwest boundaries of the watershed, as well as near the Dawn River of the lower Huanghe (Chen et al., 2005; Zhang et al., 1995). Climatically, the Huanghe basin spans the arid (Zone A), semi-arid (Zone SA), and sub-humid (Zone SH) climate zones, with mean annual precipitation increasing from 200 mm in Zone A to 700 mm in Zone SH from northwest to southeast (Xu et al., 2006). The upper, middle and lower Huanghe basins have distinct climates with mean annual temperatures of 1 to 4 °C, 8 to 14 °C, and 12 to 14 °C, respectively, and mean annual precipitations of 368 mm, 530 mm and 670 mm, respectively (Chen et al., 2005). On the Loess Plateau, modern vegetation in the south-eastern region is dominated by C3 trees and C4 grasses, with the annual temperature and precipitation reducing toward the northwest, the proportion of C3 trees and C4 grasses reducing, but the cold season C3 grasses and C3 shrubs increasing gradually (Wang et al., 2003; Wang et al., 2006a).

The Huanghe is well known for its low water discharge (<60 km\textsuperscript{3}/a \textsuperscript{-1}), high sediment load (>1000 Mt a\textsuperscript{-1}), and extremely high suspended sediment concentration (SSC) (>50 kg m\textsuperscript{-3}) (Figure 1b). The upper Huanghe supplies 60% of the total water but only 10% of the sediment, whereas roughly 90% of the Huanghe sediment originates from the Loess Plateau in the middle reaches (Wang et al., 2007; Hu et al., 2012b), due to its highly erodible loess particles. Seven major tributaries flow through the Loess Plateau and are characterized by extremely high sediment yield (3000–20 000 t km\textsuperscript{-2} a\textsuperscript{-1}) (Ran et al., 2013b). These seven major tributaries collectively contributed 977 Mt a\textsuperscript{-1} to the mainstream, accounting for 95% of the annual sediment load at Huayuankou (Wang et al., 2007; Hu et al., 2012b). The water discharge, and therefore the sediment load of the tributaries in the Loess Plateau show higher seasonal variations, as the entire water discharge in a year may be due to a few storm events, and high SSC values of more than 100 kg m\textsuperscript{-3} have been frequently recorded (Xu, 1999). A recent gully survey indicated that there were about
660,000 gullies with lengths greater than 500 m and gully channel areas larger than 5 km² in the Loess Plateau, and thus gully erosion accounts for about 60–80% of total soil erosion (Zheng and Wang, 2014). As the river flows over the flat North China Plain, huge amounts of suspended sediment deposits occur within the channel or on the floodplains (Wang et al., 2007). The lower Huanghe is a naturally aggrading river in the long-term, with a total of ~5.52 billion m³ sediment deposited in 1950–1999 (Xia et al., 2010). Rapid aggradation (20–80 mm a⁻¹) has raised the riverbed to a height of 4 to 6 m above the surrounding floodplain outside the levees. As of 2007, there were more than 3100 reservoirs in the Huanghe basin, with a total storage capacity of 72 km³ (Ran et al., 2013b), amounting to three times of the annual water discharge measured in recent years. Four major reservoirs (Sanmenxia, Lijiaxia, Longyangxia, and Xiaolangdi) (Figure 1a), located in the mainstem, make the greatest contribution to water regulation and sediment trapping (Wang et al., 2006b; Wang et al., 2007; Miao et al., 2011; Ran et al., 2013b) (Figure 1b).

**Materials and Methods**

**Sampling**

Lijin Hydrographic Station is located about 110 km upstream of the Huanghe mouth and is free of tidal influences. Records at Lijin Hydrographic Station thus represent the Huanghe material fluxes delivery to the sea. Biweekly water samples were collected at the Lijin Hydrographic Station from September 2012 to October 2013, with more intensive sampling during the period of WSR (June 25, 2013–July 16, 2013). Since the water depth of the main channel was much shallower (~1.5 m) during most months in recent years, we took five samples from cross-section at ~0.5 m beneath the water surface using acid-washed but carefully neutralized 1.5-l high density polyethylene containers, and then mixed them to obtain representative samples for the whole water column. A total of 41 water samples were obtained throughout the study period. All water samples were filtered through pre-combusted and pre-weighed glass fiber
filters (Whatman GF/F, 0.45 μm, 47 mm) three times, and then the filters were dried at 60 °C, re-weighed to obtain mean value. Suspended particulate material retained on the filters was carefully removed by scraping and kept frozen until further laboratory analysis. Daily and monthly records of water discharge and sediment load at the Lijin station were provided courtesy of the Huanghe Conservancy Commission.

Analytical methods

Grain-size analyses were conducted using a Mastersizer-2000 laser particle-size analyzer at the Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, China, with a measurement range of 0.02 to 2000 μm and a size resolution of 0.01 μm. The measuring error was within 3%. Before the grain-size analyses, the samples were pretreated with 10% hydrogen peroxide (H₂O₂) for 24 hours to remove organic matter. Grain sizes were divided into three groups: < 4 μm for clay, 4–63 μm for silt, and > 63 μm for sand, according to Folk classification system.

Elemental (POC%) and isotopic (δ¹³C‰) carbon analyses were undertaken using a GV IsoPrime 100 IRMS coupled with an Elementar Vario PYRO Cube elemental analyzer at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Briefly, the samples were freeze-dried, homogenized and powdered, and then decalcified using 10% hydrogen chloride (HCl) at room temperature for 24 hours. After rinsing with deionized water three times and drying overnight at 60 °C, the samples were ground into powder in an agate mortar and dried again at 60 °C. The δ¹³C‰ is expressed in the standard delta notation with respect to PeeDee Belemnite (PDB). Reproducibility based on six replicates was within ±0.002‰, with a standard deviation of replicate measurements being better than 3‰ for POC and 0.15‰ for δ¹³C‰. When duplicates were measured, the average value was calculated and used in plots and statistical analyses.

Radioisotope analyses were carried out by the Beta Analyses Company, USA. Briefly, CO₂ samples were obtained by the combustion of bulk OC from pre-acidified sediments. The evolved CO₂ was cryogenically purified and reduced to graphite using hydrogen on a cobalt catalyst. The graphite was then pressed into targets, which were analyzed on the accelerator mass spectrometer (AMS) at the State Key Laboratory of Isotope Geochemistry, Chinese Academy of Sciences. The carbon-14 (14C) values were corrected for instrumental mass dependent fractionation (normalization to a δ¹³C‰ = −25‰) and expressed as fraction modern carbon (Fm‰) based on modern reference material used and conventional radiocarbon ages. NIST SRM-4990B was the primary standard used for all ¹⁴C measurements, with an analytical 2σ-uncertainty of 0.002‰ was estimated for Fm‰ values.

Results

Water discharge and suspended load

Monthly water discharge and sediment load during the overall studied period are shown in Table I and Figure 1c. From September 2012 to September 2013, a total of 30.3 km³ of water and 201 Mt of sediment were exported from the Huanghe to the sea, with 50% of water and 82% of sediment concentrated in the period June to August 2013. Daily water discharge (Q) and SSC during the overall studied period varied from 200 m³ s⁻¹ to 4130 m³ s⁻¹ and from 0.2 to 15.9 kg m⁻³, with a mean of 1630 m³ s⁻¹ and 3.6 kg m⁻³, respectively (Figure 2a). The new hydrological regime of lower Huanghe is characterized by small Q (200–1600 m³ s⁻¹) and low SSC (0.2–1.7 kg m⁻³) during the normal period, with elevated Q (mean of 3000 m³ s⁻¹) and high SSC (mean of 7.6 kg m⁻³) during the WSR periods (June 25–July 16, 2013). About 5.4 km³ (60 Mt) of water (sediment) was delivered to the sea during this human-made flood event, implying that 18% (29%) of annual water (sediment) flux occurred in only 6% of the time.

Grain size

The Huanghe suspended sediment can be classified as silt and clayey silt according to the Folk classification system, with an average by fraction of 4 ± 4% sand, 75 ± 5% silt, and 21 ± 5% clay (Figure 2b). The grain size of suspended sediment (expressed as D₅₀) ranged from 5.8 μm to 24.4 μm, with maximum values (c. 18 μm) recorded during the early stage of the WSR (WSR-1) and minimum values (c. 8 μm) during the late stage of the WSR (WSR-2) (Figure 2b).

POC content (%) and concentration (in mg l⁻¹)

POC contents in the Huanghe suspended sediment vary from 0.3% to 1.8%, with a mean of 0.75 ± 0.34% (n = 41) (Table I). No seasonal variations in POC% can be found in the overall studied period, but POC contents are relative higher during the normal period (0.89 ± 0.34%, n = 25) than the WSR period (0.52 ± 0.20%, n = 16) (Figure 2c). POC concentrations ranged from 2 mg l⁻¹ to 116 mg l⁻¹, with a mean of 22 mg l⁻¹ (Figure 3), and display a temporal pattern similar to that of SSC. When we excluded the samples collected during the WSR-2 period, POC contents generally decreased with increasing Q and SSC (Figures 3a and 3b) whereas POC concentrations increased as a power function of Q and SSC (Figures 3c and 3d). These relationships have been observed in previous studies in the Huanghe (Ran et al., 2013a; Zhanget al., 2013) and other river systems (Ludwig et al., 1996; Coynelet al., 2005; Zhang et al., 2009), and likely resulted from: (1) dilution of mineral-like material coming from soil erosion and riverbed scour, (2) mechanical erosion of deeper horizons of soil profiles with lower POC%, and (3) high SSC reducing light availability and thus restricting the growth of phytoplankton. Nevertheless, these results suggest that the transport dynamics of Huanghe POC are largely hydrological controlled. In contrast, samples collected during the WSR-2 period display distinctively elevated values of POC content and concentration for a given Q or SSC, indicating strong human disturbance of the POC transport processes (Figure 3).

Isotope compositions

The mean δ¹³C of Huanghe POC was −24.9 ± 1.2‰ (n = 41) and ranged from −27.4% to −22.6‰ (Figure 2c). The δ¹³C values of suspended POC in this study were within the range previously reported for the riverine POC elsewhere in the Huanghe (Liu et al., 2003; Liu and Xing, 2012; Wang et al., 2012), but higher than those of riverbed sediment in the lower reaches (−23.8 ± 0.4‰, n = 12) (Wu et al., 2014). Depleted δ¹³C values of the suspended POC are observed from March 2013 to May 2013 and in September 2013 (mean of −26.6 ± 0.5‰, n = 10), whereas samples from June 2013 to August 2013 are generally characterized by elevated δ¹³C values (mean of −24.2 ± 0.9‰, n = 19) (Figure 2c).
The mean $\Delta^{14}\mathrm{C}$ of the selected samples during the WSR period was $-630 \pm 50$\%o ($n = 6$), ranged from $-681$\%o to $-553$\%o (Table I). Four $\Delta^{13}\mathrm{C}$ values (mean of $-660$\%o) in the WSR-1 are more depleted than those two (mean of $-570$\%o) of the WSR-2. However, these values were all lower than those measured during the normal period ($-530 \pm 100$\%o, $n = 4$) with low $Q$ and SSC in 2009 (Wang et al., 2012).

**Discussion**

**Sources of POC in the Huanghe basin**

The origin of riverine POC can be assigned to autochthonous and allochthonous sources. However, light limitation due to the high turbidity water of the Huanghe (minimum SSC $>200$ mg l$^{-1}$ during the sampling period) may restrict in situ production. Thus, the autochthonous contribution provided by riverine phytoplankton is very limited, evidenced by much high POC/chlorophyll a (Chl a) ratio (averaged 4000) in the Huanghe mainstream (Zhang et al., 2013). Even in the large reservoirs (i.e. Sanmenxia, Xiaolangdi, see locations in Figure 1a) in the middle Huanghe, the POC/Chl a ratio is averaged at 964 (Zhang et al., 2013) much higher than those typically found in phytoplankton ($<50$), suggesting that the contribution of reservoir phytoplankton should be insignificant. Furthermore, in several small tributaries of the middle Huanghe, more negative $\delta^{13}\mathrm{C}$ values of riverine SPM in summer than that in winter was explained as seasonal variation of C3/C4 vegetation (Liu et al., 2003). However, there is no evidence that this seasonal change in the C4/C3 vegetation has modified the elemental and isotopic signal of POC in this study (Figure 2). Therefore, the elemental and isotopic signals of Huanghe POC may be dominated by the mixing of different allochthonous POC sources, such as soil and plant debris of various ages and types, as well as sedimentary rock (Figure 4).

Recent studies suggested that the grain size of SPM plays an important role in determining the Huanghe POC contents, with over 85\% of the Huanghe POC concentrated in fine-grained sediment ($<32$ $\mu$m) (Zhang et al., 2013). In this study, we also found a significant non-linear negative relationship between POC content and median grain size ($D_{50}$) (Figure 5a). These results suggest that POC loading in the Huanghe is mainly related to hydrodynamic sorting of organic particles and/or various
degrees of organo-mineral aggregation, similar to that in the Ganga-Brahmaputra (Galy et al., 2008b) and Amazon Rivers (Bouchez et al., 2014). Moreover, the δ13C and POC% of Huanghe suspended and riverbed sediments broadly defined a binary mixing of two distinct end-members (Figure 5b). One end-member is isotopically light and enriched in POC%. The other is isotopically heavy and depleted in POC%. This is further confirmed by an inverse relationship between δ13C and Fmod in the Huanghe POC, implying a bimodal mixing of 13C-enriched POCfossil (14C-dead) and 13C-poor POCnon-fossil (14C-containing) (Figure 5c).

The sources of Huanghe POCfossil are more complicated than other river systems, where it is mainly sourced from sedimentary rocks (Blair et al., 2003; Komada et al., 2005; Leithold et al., 2006; Galy et al., 2008a; Hilton et al., 2010, 2011; Göh et al., 2013; Bouchez et al., 2014). Because the Huanghe materials are mostly eroded from the Loess Plateau, the Huanghe POCfossil likely includes fossil OC inherited from dust source regions (Liu et al., 2007) and OC eroded from gully incision of the loess-paleosol sequences (which may be older than 60 ka and thus 14C free). It is not appropriate to obtain the isotopic composition of fossil OC (δ13Cfossil) using the reference data, resulting from the large variability of δ13C in potential fossil OC sources (Vidic and Montañez, 2004; Sun et al., 2012).

Accordingly, we have to infer the δ13Cfossil in the Huanghe basin by extrapolating the linear trend in Figure 5c to Fmod = 0. The estimated δ13Cfossil value ranges from −22.1‰ to −18.4‰, with a mean of −20.2 ± 0.8‰ at 95% confidence levels (Figure 5c). These values fall in the range of the potential fossil sources in the Huanghe basin, further validating this approach. To evaluate the age and composition of POCnon-fossil, we employed an end-member mixing analysis assuming the rivers carry a well-mixed sample of POC sources (fossil versus non-fossil) (Blair et al., 2003; Galy et al., 2008a):

\[
F_{\text{riverine}}C_{\text{riverine}} = C_{\text{fossil}}F_{\text{fossil}} + C_{\text{non-fossil}}F_{\text{non-fossil}}
\]

(1)

\[
C_{\text{riverine}} = C_{\text{fossil}} + C_{\text{non-fossil}}
\]

(2)

where \(F_{\text{riverine}}, F_{\text{fossil}}, \) and \(F_{\text{non-fossil}}\) are the Fmod values of riverine suspension, fossil and non-fossil POC, respectively; \(C_{\text{riverine}}, C_{\text{fossil}}, \) and \(C_{\text{non-fossil}}\) are the weight percent values of POC in the river suspended sediment and that sourced from these two end-members. Combining and rearranging Equations (1) and (2) yields

\[
F_{\text{riverine}}C_{\text{riverine}} = C_{\text{riverine}}F_{\text{non-fossil}} = C_{\text{fossil}}F_{\text{non-fossil}} - C_{\text{non-fossil}}F_{\text{non-fossil}}
\]

(3)

Figure 2. (a) Daily water discharge (Q) and suspended sediment concentration (SSC) during the sample period. (b) Grain size compositions and median grain size (D50) of the Huanghe suspended particulate materials. (c) Particulate organic carbon content (POC%) and stable isotopic composition (δ13C) of the Huanghe suspended particulate materials. This figure is available in colour online at wileyonlinelibrary.com/journal/espl
If the end-member isotopic compositions are reasonably invariant and well mixed, plotting POC% versus the Modern $C_{\text{mod}}$ ($C_{\text{mod}} \times \text{POC}\%$) should define a linear relationship (Figure 6a). This linear trend can principally provide information of the average POCfossil content ($x$-intercept) and the average $F_{\text{mod}}$ of eroded biosphere of POCnon-fossil (slope) (Galy et al., 2008a; Blair et al., 2010; Bouchez et al., 2010; Galy and Eglinton, 2011; Clark et al., 2013; Bouchez et al., 2014). In the case of Huanghe, the approximately linear trend suggests an average POCfossil% of $0.21 \pm 0.09\%$ and an average $F_{\text{mod}}$ of eroded biosphere of $0.763 \pm 0.126$ ($^{14}C$ ages of c. 2200 years) in the Huanghe basin (Figure 6a). The estimated POCfossil% of $0.21 \pm 0.09\%$ is supported by the relationships between POC% and $Q$ or SSC, which indicated that most of POC% values in the Huanghe SPM are above ~0.2% regardless of the large variations of $Q$ and SSC (Ran et al., 2013a; Zhang et al., 2013). Compared with the POC% of dust rock samples ($0.11 \pm 0.07\%$) (Liu et al., 2007), additional OC must have been added into the Huanghe fossil OC pools. The POCfossil% of Huanghe is much higher than that exported by the Ganges-Bangladesh and Amazon Rivers (only $0.02 \sim 0.06\%$), where the oxidation of fossil OC is thought to be significant during the fluvial transport process (Galy et al., 2008a; Bouchez et al., 2010). As the original fossil OC content is unclear, we cannot evaluate the status of fossil OC oxidation in the Huanghe basin here. Moreover, recent studies indicate that, in rivers with high physical erosion rates (e.g. Taiwan), it is difficult to quantify fossil OC oxidation in the watershed using the solid products of weathering (Hilton et al., 2011; Hilton et al., 2014). This is also the case for the Huanghe, where the specific sediment yields of several small tributaries located in the Loess Plateau exceed 20 000 t km$^{-2} \text{a}^{-1}$ (Ran et al., 2013b).

With the time series data used in this study, the errors of the estimated $F_{\text{mod}}$ of the eroded biosphere are relatively larger than previous studies focused on other large rivers, where the depth profile data were used (Galy et al., 2008a; Bouchez et al., 2010; Bouchez et al., 2014). Indeed, the scatter of Figure 6a is likely to originate from variable POCfossil contents due to the mixed sources of fossil OC as discussed earlier and/or the variable mean ages of POCfossil during the
seasonal hydrological cycle. To get more detailed information about these different carbon pools, the $^{14}$C activities of specific components at molecular level (e.g. Galy and Eglinton, 2011; Martin et al., 2013) or direct ramped-pyrolysis radiocarbon analysis of SPM (e.g. Rosenheim and Galy, 2012; Rosenheim et al., 2013) are urgently needed. Nevertheless, the estimated bulk age of biogenic OC ($c. 2200$ years) in the Huanghe basin can be validated by a partial ‘residence time’ for the POC in soil ($\text{Time}_{\text{SOC}}$), which only takes into account the physical erosion processes (Lloret et al., 2013). According to Ran et al. (2014), the Huanghe annually exported $4.11$ Tg of POC ($i.e. 5.17$ t km$^{-2}$ a$^{-1}$) to the sea in 1950–2010, accounting for only $0.05\%$ of the total soil organic carbon (SOC) stock of $10\ 641$ t km$^{-2}$ (Yu et al., 2007), and exhibiting a long $\text{Time}_{\text{SOC}}$ of $c. 2058$ years in the Huanghe basin. This long OC residence time of the Huanghe is in the range of other large river systems (e.g. Amazon, Mekong, and Orinoco) but indeed shorter than SMRs (e.g. Taiwan, New Zealand) (Lloret et al., 2013). Therefore, despite very strong physical erosion occurring in the Loess Plateau, the POC$_{\text{non-fossil}}$ delivered from the biosphere is dominated by pre-aged OC, reflecting a composite of residence times for the different components of the biospheric carbon pool (Galy and Eglinton, 2011; Martin et al., 2013). Similarly,
Chen et al. (2003, 2004) indicated that the Huanghe POC is mainly composed of refractory natural humus with low degradability, resulting from a large portion of modern and labile OBC being decomposed within the Huanghe systems.

Similarly, we can obtain the $\delta^{13}C$ value of the POC$_{non-fossil}$ component by substituting $\delta^{13}C$ values for $F_{mod}$ in Equation (3), i.e. the slope of the linear trend in Figure 6b. This $\delta^{13}C_{non-fossil}$ value ($-28.1 \pm 0.8\%$) is comparable to that of C3 plant in the Loess Plateau (ranging from $-24.5$ to $-29.6\%$, mean of $-27.3\%$) (Liu et al., 2005) (Figure 4). Thus, it reflects the dominant contribution of C3 plant-derived organic matter to the Huanghe POC, consistent with the vegetation patterns in the Loess Plateau. Given the simple binary mixing of the Huanghe basin, we can extend the determination of $F_{fossil}$ and $F_{non-fossil}$ to each sample, using the fossil ($\delta^{13}C_{fossil} = -20.2 \pm 0.8\%$) and non-fossil ($\delta^{13}C_{non-fossil} = -28.1 \pm 0.8\%$) end-members determined earlier:

$$F_{fossil} = \frac{\delta^{13}C_{riverine} - \delta^{13}C_{non-fossil}}{\delta^{13}C_{fossil} - \delta^{13}C_{non-fossil}}$$  \hspace{1cm} (4)

$$F_{non-fossil} = 1 - F_{fossil}$$  \hspace{1cm} (5)

Combining the errors of two end-members, $F_{fossil}$ was found to have an average precision of 0.07 (Figure 7a). To test the mixing model, the $F_{non-fossil}$ of suspended POC was compared with the $F_{mod}$ measured for the same samples. These 10 samples gave averaged values of $0.41 \pm 0.09$ (ranging from 0.32 to 0.60) for $F_{mod}$ and $0.44 \pm 0.11$ (ranging from 0.3 to 0.68) for $F_{non-fossil}$, respectively, suggesting this estimation provides a robust quantification of different POC source inputs. Our results thus demonstrate the significant contribution of POC$_{fossil}$ to the Huanghe POC, with an average $F_{mod}$ of $0.41 \pm 0.15$ ($n=41$). The $F_{non-fossil}$ values ranged from 0.09 to 0.70 and generally increased with increasing Q during the normal period, but the relationship between them is not straightforward during the WSR-flood period (Figure 7a). This is broadly in accordance with findings from Taiwan mountain rivers (Hilton et al., 2012). However, the underlying mechanisms may be substantially different between SMRs (e.g. Taiwanese rivers) and large rivers (e.g. the Huanghe), because large rivers have multiple source signals and attenuated hydrology (Blair and Aller, 2012).

Transport dynamics of POC in the lower Huanghe

Because distinct terrestrial carbon pools behave differently, their mobilization and transfer conditions also differ (Hilton et al., 2008b; Wheatcroft et al., 2010; Hilton et al., 2012; Feng et al., 2013; Smith et al., 2013). It is therefore important to determine the optimized conditions for the transport and burial of not only the total POC, but of non-fossil and fossil POC separately (Wheatcroft et al., 2010; Smith et al., 2013). In this study, a high frequency sampling strategy and the geochemical quantification of POC sources (POC$_{non-fossil}$ and POC$_{fossil}$) allowed us to assess the transport dynamics of POC in the lower Huanghe, in relation to the hydrological and geomorphic controls.

Based on the calculated $F_{fossil}$ values using the two end-members mixing model (Figure 7a), the rating curves between $Q_e$ and four constituent loads (i.e. SSC in kg m$^{-3}$, POC, POC$_{fossil}$, and POC$_{non-fossil}$ in mg l$^{-1}$) were obtained in the form of power laws (Figure 7b). Due to strong human interference on the hydrological regime during the WSR-2 period (Figure 3), we excluded these WSR-2 samples when fitting the rating curves. Subsequently, the effective discharges for these four constituent loads were estimated following the method of Wheatcroft et al. (2010). All of these four constituent loads were significantly positively correlated with $Q_e$ ($r^2 = 0.55 - 0.85, p < 0.001$), however, the exponents of four rating curves varied largely (Figure 7b). The exponent for SSC ($b_{SSC} = 1.07 \pm 0.18$) is much higher than that of POC ($b_{POC} = 0.72 \pm 0.09$), suggesting that relatively less POC is exported during the higher $Q$ periods than suspended sediment, consistent with the situations reported elsewhere, such as the Waipaoa and Alsea Rivers (Komada et al., 2005). This effect is more conspicuous for POC$_{non-fossil}$ ($b_{POC}_{non-fossil} = 0.53 \pm 0.07$) than for POC. In contrast, the exponents for POC$_{fossil}$ ($b_{POC}_{fossil} = 1.08 \pm 0.17$) and SSC ($b_{SSC} = 1.07 \pm 0.18$) are nearly identical, reflecting their shared elastic origin. These distinct exponents of different constituents lead to different effective discharges ($Q_e$), which are greatest for POC$_{fossil}$ (2800 m$^3$ s$^{-1}$) and least for POC$_{non-fossil}$ (1600 m$^3$ s$^{-1}$) (Figure 7b). A threshold value of $Q$ can be roughly estimated as 2300 m$^3$ s$^{-1}$, below which the Huanghe delivered POC$_{fossil}$ to the sea more efficiently (Figure 7b). Due to the buffering effects of large storage capacity and numerous reservoirs in the Huanghe basin, the transport process of POC in the lower Huanghe cannot be directly connected with the erosion processes operated in the catchment.

Rather, we suggest that changes in the sources and transfer modes of POC from the Huanghe to the sea are a dynamic response to the human-controlled hydrological regime in the lower Huanghe (Wang et al., 2010; Yu et al., 2013b). Since 1999, when the Xiaolangdi Reservoir (storage capacity of...
begin operation, the flows and sediments entering the lower Huanghe have been totally altered. On the one hand, extreme flood peaks in the lower Huanghe have been completely controlled, low and constant flow (mostly < 2000 m³ s⁻¹) dominates the discharge pattern for most of the year, and relatively-higher flows (2000–4000 m³ s⁻¹) are mainly concentrated in a human-made flood (WSR) since 2002 (Yu et al., 2013a). On the other hand, the majority of sediment (about 80%) from the middle reaches is now trapped in the Xiaolangdi Reservoir. Besides reducing sediment supply, the reservoir trapping effect also changes the compositions of sediment entering the lower Huanghe, and only the fine sediment can be expelled from the reservoir (Wang et al., 2010). Consequently, the lower Huanghe riverbed is being scoured by the clear water flow with low SSC released from the reservoir (Yu et al., 2013a). The accumulated sediment eroded from the lower Huanghe channel is estimated up to c. 1.36 km³ (average ~100 Mt a⁻¹) in 1999–2010 (Xia et al., 2014b), which accounts for about 60% of the fluvial sediment flux to the sea during this period. As a result of continuous scouring in the lower Huanghe, the median grain size of the riverbed material gradually increased from 36 ~ 56 μm in 1999 to about 151 μm in 2012 (Xia et al., 2014a).

Accordingly, two different POC transport processes can be recognized in the study period. During the normal and WSR-1 periods, freshwaters with low SSC and finer reservoir-origin sediment were released from the Xiaolangdi Reservoir, and thus tend to scour the riverbed sediments. In this case, increased Q will enhance the erosion capacity of flow, resulting in much more coarse riverbed sediments being entrained and transported to the sea. Hydrodynamic sorting therefore controlled the relative contributions of coarse-grained riverbed-scoured (dominated by fossil OC) and fine-grained reservoir-originated (dominated by non-fossil OC) sediments to the Huanghe SPM (Figure 5), and ultimately defined the different exponents and effective discharges (Figure 7b). This is supported by a negative correlation between the Δ¹³C values and Q of the samples measured by Wang et al. (2012) (data not shown). However, scenarios are totally different during the WSR-2 period, when the muddy flow with extremely high SSC (~40 kg m⁻³) was expelled from the Xiaolangdi Reservoir and delivered by sustained high water discharge (2000 ~ 4000 m³ s⁻¹) to the sea. Riverine SPM of the lower Huanghe has changed from the mix-sources to the predominant reservoir-originated during the WSR-2 period. This is testified by the finer grain size compositions (Figure 2b) and younger POC ages of the WSR-2 samples than those of WSR-1 (Table I). Similar results are also founded during the 2008-WSR period, showing that the SPM at Lijin station originated mainly from the coarse sediment in the channel in WSR-1, whereas that in WSR-2 mainly came from the upstream reservoir (Zhang et al., 2013).

Fluxes of POC from the Huanghe to the sea

To evaluate an order of magnitude of the Huanghe POC exports, we calculated the monthly, WSR flood event, and annual fluxes of POC, POC_fossil, and POC_non-fossil at Lijin station using the discharge-weighted contents method (Phillips et al., 1999):

\[
F_M = Q_M \cdot \sum Q_i \cdot SSC_i \cdot C_i \sum Q_i
\]

\[
F_{WSR} = F_{WSR-1} + F_{WSR-2} = Q_{WSR-1} \cdot \sum Q_i \cdot SSC_i \cdot C_i \sum Q_i
\]

\[
F_{WSR-2} = \frac{Q_i \cdot SSC_i \cdot C_i}{Q_i \cdot C_i}
\]

\[
F_A = \sum_{Aug.-2011}^{Sep.-2012} F_M
\]

where \(F_M\), \(F_{WSR}\), and \(F_A\) are monthly, WSR flood event (WSR-1 and WSR-2), and annual fluxes of POC, respectively; \(Q_M\), \(Q_{WSR-1}\), and \(Q_{WSR-2}\) are monthly water discharge, total WSR-1 water discharge, and total WSR-2 water discharge, respectively; \(Q_i\), \(SSC_i\), and \(C_i\) are daily water discharge, daily suspended sediment concentration, and daily particulate carbon content of sampling time, respectively. As the bedload component usually contributes less than 1% to the total sediment load in the Huanghe, we do not consider the impact of bedload on the POC flux in this study.

During the 2012–2013 hydrological year (September 2012–August 2013), about 0.73 Tg a⁻¹ POC was delivered by the Huanghe to the sea (Table II). This value is nearly twice those of two recent studies, that is, 0.39 Tg a⁻¹ in 2009 (Wang et al., 2012) and 0.41 Tg a⁻¹ in 2008–2012 (Ran et al., 2013a). These discrepancies can be ascribed to (1) different water and sediment flux during the sampling campaigns (Table II) and (2) different sampling strategies. For the latter, our sampling strategy, i.e., biweekly sampling during the normal period and additional samplings during the WSR flood event, should provide more accurate and reliable results.

Table II. Comparison of the organic carbon fluxes from the Huanghe to the sea and other global large rivers

<table>
<thead>
<tr>
<th>River</th>
<th>Area (10³ km²)</th>
<th>Water discharge (km³ a⁻¹)</th>
<th>Sediment load (Mt a⁻¹)</th>
<th>POC flux (Tg a⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huanghe (2012–2013)</td>
<td>795</td>
<td>29.4</td>
<td>201</td>
<td>0.73</td>
<td>This study</td>
</tr>
<tr>
<td>Huanghe (1950–1968)</td>
<td>48.9</td>
<td>1330</td>
<td>7.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huanghe (1983)</td>
<td>49.8</td>
<td>1024</td>
<td>4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huanghe (1987)</td>
<td>10.8</td>
<td>96</td>
<td>6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huanghe (2009)</td>
<td>13.3</td>
<td>56</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Huanghe (2008–2012)</td>
<td>18.8</td>
<td>115</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Changjiang (2009)</td>
<td>1705</td>
<td>111</td>
<td>1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mississippi (2004–2007)</td>
<td>3423</td>
<td>80</td>
<td>0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amazon</td>
<td>5903</td>
<td>6600</td>
<td>600–1150</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Irrawaddy-Salween</td>
<td>680</td>
<td>638</td>
<td>379–576</td>
<td>4.6 ~ 7.7</td>
<td></td>
</tr>
<tr>
<td>Congo</td>
<td>3700</td>
<td>1325</td>
<td>32</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Ganges-Brahmaputra</td>
<td>1630</td>
<td>1003</td>
<td>1250</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

over the past 60 years, the Huanghe water and sediment fluxes have decreased sharply (Figure 1b), mainly resulting from human activities (e.g., reservoir trapping, soil-conservation practices, water consumption) (Wang et al., 2007; Miao et al., 2011). For a first-order estimation of the Huanghe POC exports under natural conditions, we recalculated the Huanghe POC flux (7.63 Tg a⁻¹) by multiplying the discharge-weighted POC of 0.57% (this study) by the averaged sediment load of 1330 Mt a⁻¹ in 1950–1968 (Wang et al., 2007). This estimation should be reasonable because the Huanghe POC content is relative constant at decadal timescale (Ran et al., 2013a). Presently, the Huanghe POC flux (0.39 – 0.73 Tg a⁻¹) only represents 0.2 – 0.4% of the global riverine POC input to the oceans (170 – 200 Tg a⁻¹) (Ludwig et al., 1996; Schlunz and Schneider, 2000). Obviously, human activities in the Huanghe basin have led to a >90% drop of POC flux to the sea during recent years (Table II). As a large part of Huanghe POC associated with sediments were trapped within the reservoirs (Ran et al., 2013b), where the OC burial efficiency might be much higher than that of the delta/basin area, the reservoirs thus have been an important POC sink at short-term timescales (Zhang et al., 2013; Ran et al., 2014). The POC fossil fluxes may be more significantly influenced by human activities in the Huanghe basin, because the Huanghe POC fossil is mostly associated with coarse sediments (Figure 5), which tended to be trapped by numerous reservoirs. Furthermore, the influences of human activities have transferred downstream, and ultimately shifted the suspended sediment transport mode from hyporheic to hyporheic flow (Wang et al., 2010). This transition potentially decreased the burial efficiency of terrestrial organic matter in the Huanghe estuary/delta area.

Finally, we would like to highlight here the role of Huanghe fossil OC and its implications for global and regional carbon cycle. Given the averaged POC fossil of 0.41 ± 0.15 (n = 41) obtained in this study, the export fluxes of Huanghe POC fossil can be estimated as 3.13 Tg a⁻¹ under natural conditions, representing c. 5% of the global riverine POC fossil input to the oceans (40 – 80 Tg a⁻¹) (Meybeck, 1993; Blair et al., 2003). Comparatively, the natural Huanghe POC fossil flux is much higher than that of the Taiwanese Rivers (~1.7 Tg a⁻¹) (Hilton et al., 2011) and the Ganges-Brahmaputra system (0.4 – 0.6 Tg a⁻¹) (Galy et al., 2008a). Although the fate of huge amounts of Huanghe POC fossil to the sea is still unconstrained, it should be largely re-buried in the estuary/delta area, resulting from rapid accumulation due to the frequent hyporheic events before 1999 (averaged 33 days each year) (Wang et al., 2010). Therefore, the exports of POC fossil from the Huanghe may be historically important in the transfer and re-burial of fossil OC in marine sediments. Additionally, some of these Huanghe materials can be resuspended by strong winter storms and then dispersed by strong winter coastal current (Bi et al., 2011; Yang et al., 2011; Hu et al., 2012a). When using a δ¹³C-based two-end-member mixing model (i.e. terrestrial versus marine) in the adjacent marine settings, the overlapped δ¹³C values of Huanghe POC fossil (~22.1% to ~18.4%) and marine organic matter (~22% to ~20%) can overestimate the contribution of marine organic matter. To overcome this short-age, a three-end-member model (fossil, terrestrial biospheric, and marine) with multiple isotopic (δ¹³C and δ¹⁴C) compositions should be carried out (Cathalot et al., 2013; Tesi et al., 2013; Wu et al., 2013). This will help us to address the fate of Huanghe fossil OC and to better understand the regional biogeochemical cycle of East China Seas.

Conclusion

We present the grain size, POC contents and isotopic composition of the Huanghe SPM collected from the outlet during September 2012–September 2013. Our samples cover a range of water discharges, including human-made flood events, thus provide a first comprehensive characterization of POC exported by the Huanghe under a new human-controlled hydrological regime. The Huanghe POC loadings are controlled by the hydrological sorting and organo-mineral aggregates. The Huanghe riverine POC is a mixture of two distinct end-members (fossil versus non-fossil), and fossil OC is a significant component of the Huanghe POC (~40%). The non-fossil OC of Huanghe is most likely sourced from C3-plants, with a long residence time (c. 2200 years). The source and transport of Huanghe POC is controlled by different hydrological processes that, in turn, changed the relative contributions of coarser riverbed-scoured and finer reservoir-terminated sediments. Using the discharge-weighted method, a total of 0.73 Tg a⁻¹ of POC was exported by the Huanghe in 2012–2013, of which 0.35 Tg a⁻¹ is fossil and 0.38 Tg a⁻¹ is non-fossil. Human-made flood events play a significant role in POC export, with 28% of annual POC flux occurred within the short WSR period (5% of one year).

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