Global Biogeochemical Cycles

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Key Points:
- Combined $^{14}$C and $^{13}$C study to quantify black carbon in both dissolved and particulate phases for two largest rivers in China
- We identified two black carbon pools with distinct C-14 ages transported in the rivers
- River dissolved BC was younger and mainly derived from biomass burning; particulate BC was largely from the fossil fuel combustion

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Abstract

Major rivers play important roles in transporting large amounts of terrestrial organic matter from land to the ocean each year, and the organic matter carried by rivers contains a significant fraction of black carbon (BC). A recent study estimated that 0.027 Gt of BC is transported in the dissolved phase by rivers each year, which accounts for ~10% of the global flux of dissolved organic carbon. The relative sources of this large amount of riverine dissolved black carbon (DBC) from biomass burning (young, modern $^{14}$C) and fossil fuel (old, $^{13}$C free) combustion are not known. We present radiocarbon measurements of BC in both dissolved and particulate phases transported by the Changjiang and Huanghe Rivers, the two largest rivers in China, during 2015. We show that two, distinct BC pools (young and old) were carried by the rivers. The DBC pool was much younger than the particulate BC (PBC) pool. Mass balance calculations indicate that most (78–85%) of the DBC in the Changjiang and Huanghe Rivers was derived from biomass burning, and only 15–22% was from fossil fuel combustion. In contrast, PBC from biomass burning and fossil fuel combustion were approximately equal in these two rivers. Export of PBC and DBC by the rivers are decoupled, and fluxes of PBC were 4.1 and 6.7 times higher than DBC in the Changjiang and Huanghe Rivers, respectively. The $^{14}$C age differences of the two BC pools suggest that BC derived from biomass burning and fossil fuel combustion are mobilized in different phases and on different time scales in these rivers.

1. Introduction

Black carbon (BC) is a group of combustion-derived, organic compounds that is widely dispersed in the natural environment, particularly in soils and marine sediments [Laflamme and Hites, 1978; Goldberg, 1985; Masiello and Druffel, 1998]. BC is defined as condensed carbonaceous residue produced from incomplete combustion of fossil fuel and biomass [Goldberg, 1985]. It is estimated that globally, about 0.05–0.27 Gt (1 Gt = 1 × 10^15 g) BC is produced annually by fossil fuel combustion [Kuhlbusch and Crutzen, 1995] and 0.012–0.024 Gt BC by biomass burning [Penner et al., 1993]. In their recent study, Santin et al. [2015] reported that production of pyrogenic BC from boreal forest wildfires alone could reach 0.1 Gt yr and that is much higher than the values previously estimated. After production, some of the BC is preserved in soils [Czimczik and Masiello, 2007; Ohlson et al., 2009; Cusack et al., 2012], and some very fine particulate BC is transported long distances by rivers and as atmospheric aerosols, eventually being deposited in the ocean [Masiello and Druffel, 1998; Mitra et al., 2002; Dittmar et al., 2012; Singh et al., 2012; Coppola et al., 2015].

Concerns regarding BC in the environment are largely based on its effects on natural ecosystems [Rust et al., 2004; Lohmann et al., 2005; Moermond et al., 2005; Shrestha et al., 2010], health risks to humans [Na et al., 2011], impact on climate, and importance as a sink for the global carbon cycle [Masiello and Druffel, 1998; Druffel, 2004; Shrestha et al., 2010]. Because BC is chemically stable [Bird et al., 1999], it is believed to be transported mainly as fine particulate matter and aerosols. However, recent studies have suggested that a major fraction of charcoal produced annually is lost from soils by dissolution and is transported in rivers [Dittmar et al., 2012; Ding et al., 2013; Jaffé et al., 2013; Wagner et al., 2015]. Jaffé et al. [2013] estimated that about 0.027 Gt yr of BC is transported in the dissolved phase by rivers, accounting for ~10% of the global flux of dissolved organic carbon (DOC) via rivers. Clearly, rivers play an important role in mobilizing BC and transporting it from the land to the oceans. However, the sources of this large amount of riverine dissolved BC (DBC), whether from recent biomass burning or fossil fuel combustion, are not known.

Radiocarbon measurement of BC is powerful for identifying the sources of BC produced from biomass burning (modern $^{14}$C age) compared with BC generated from fossil fuel combustion (>50,000 $^{14}$C years).
Ziolkowski and Druffel [2010] reported $\Delta^{14}C$ values of BC in high molecular weight DOC (HMW-DOC) isolated from the Suwannee River in Florida (USA) in 1999 and the ocean. They found that the $^{14}C$ age of DBC in the Suwannee River (410 ± 280 years B.P.) was much younger than the DBC age (18,000 ± 3000 years B.P.) in the Atlantic and Pacific Oceans. This suggests that the DBC transported by rivers could be more labile than presently believed [Ziolkowski and Druffel, 2010]. However, since there was only a single sample from a local small river, it remains unknown whether this is representative of larger river systems.

In this paper, we present the results of $^{14}C$ measurements of BC in both dissolved and particulate phases transported by the Changjiang and the Huanghe Rivers. Two BC pools with distinct $^{14}C$ ages were identified, and their sources and geochemical cycling in the rivers are discussed.

2. Methods

2.1. Study Site and Sample Collection

Water samples were collected from the Changjiang (Yangtze) River Estuary and the lower reach of the Huanghe (Yellow) River (Figure 1). The Changjiang and Huanghe Rivers are the two largest rivers in China and the third and sixth longest rivers in the world [Milliman and Meade, 1983; Cai et al., 2008]. Together, they drain one third of China’s land (~3.0 × 10^6 km^2) and deliver about 0.0019 and 0.0016 Gt of particulate organic carbon (POC) and DOC annually to the coasts of the East China Sea (ECS) and Bohai Sea, respectively [X. C. Wang et al., 2012].

Water samples (15–50 L) were collected in the lower reach of the Changjiang River, its estuary, and the coast of ECS in July and October 2015. Monthly water samples (15 L) were collected from the lower reach of the
Huanghe River during 2015. Subsurface (1.5 m) water samples from the Changjiang River Estuary and the coast were collected using an in situ pump (SFP-900P) on board the RV Dongfanghong-2 (a fishing boat used for the river water collection), filtered immediately through 0.7 μm Whatman GF/F filters (precombusted at 550°C for 4 h), and acidified with high-purity HCl to pH 2. The acidified water samples were stored in pre-cleaned polyethylene bottles at low temperature for further processing. The suspended particles retained on the filter were kept frozen for solid phase BC analysis. The river water was transported back to the laboratory within 1 day and extracted immediately, and the acidified coastal water samples were extracted within 1 week [Xu et al., 2016].

2.2. DBC and PBC Measurement

To determine DBC, water samples were first extracted for DOC using the solid phase extraction (SPE) method based on Dittmar et al. [2008] and Coppola et al. [2015]. We used prepacked PPL cartridges (Agilent Technologies Mega Bond Elute) that contained 5 g styrene divinyl benzene polymer as sorbent (pore size 150 Å). The extraction efficiency and detailed description of the sample processing are described in Xu et al. [2016]. For the dissolved phase, we measured 14C of total DOC, SPE-extracted DOC (SPE-DOC), DBC et al. [2016] and permeate-DOC (the filtrate passing through the sorbent for two Huanghe River samples). For the solid phase, we measured 14C of POC and PBC (particulate BC).

Both DBC and PBC were determined using the thermal oxidation method based on Gustafsson et al. [2001]. Previous studies have shown that this method is reproducible for BC analyses of standards, marine sediment, and particles [Gustafsson et al., 2001; Reddy et al., 2002; Hammes et al., 2007; Wang and Li, 2007]. The thermal oxidation method has also been used to determine DBC in HMW-DOM samples [Mannino and Harvey, 2004]. However, it should be stated that there is no single standard method used to separate and quantify BC in both particulate and dissolved phases. Different techniques used in different studies give a wide range of BC concentrations [Currie et al., 2002; Hammes et al., 2007]. For BC determination in the dissolved phases, a chemical oxidation method using benzene polycarboxylic acids (BPCAs) has been used recently [Dittmar, 2008; Ziolkowski et al., 2011; Coppola et al., 2015]. The BPCA method chemically oxidizes condensed aromatic BC in SPE-DOC to produce individual BPCAs that are subsequently analyzed using high-performance liquid chromatography [Dittmar, 2008] or preparative capillary gas chromatography [Ziolkowski et al., 2011]. For the thermal oxidation method, highly condensed aromatic structures in BC are measured, usually giving lower BC concentrations [Hammes et al., 2007].

For our study, 1.0–2.0 mL of SPE-DOC was put into a 9 mm OD × 200 mm quartz tube (precombusted at 850°C for 2 h) and dried with high purity N2 gas. The quartz tube was then placed in an oven and thermally oxidized at 375°C for 24 h with a continuous air supply to remove non-BC OC. The organic carbon that remained after thermal oxidation was operationally defined as DBC. For PBC, suspended particles were dried at 60°C and ground to a fine powder. About 1.0 g powder was placed in a very thin layer (2–3 mm) in a petri dish and heated at 375°C for 24 h in an oven with a continuous air supply. Before and after thermal oxidation, particles were acidified with 10% HCl to remove inorganic carbon. DBC, PBC, and POC were combusted in evacuated 9 mm OD quartz tubes (with CuO and Ag wire added) at 850°C for 2 h [Druffel et al., 1992]. The resultant CO2 was collected cryogenically and quantified manometrically on a vacuum line. The purified CO2 was flame sealed in a 6 mm OD glass tube for isotope analysis.

2.3. DOC Oxidation, DOC Concentration, and Isotope Measurements

Total DOC and permeate-DOC of the samples were processed separately using a modified UV-oxidation method for carbon isotope measurement [Xue et al., 2015]. Briefly, about 200 mL (river) or 400 mL (coast) of filtered and acidified water was placed into 2 to 4 custom-made 150 mL quartz reaction tubes specially designed to interface directly with a vacuum extraction line. Samples were first purged with ultrahigh purity (UHP) helium gas for 30 min to remove dissolved inorganic carbon and then irradiated using a 1.2 kW medium-pressure mercury arc UV lamp (Hanovia Co.) for 5 h. Following UV-irradiation, CO2 generated from UV oxidation of DOC was purged again with UHP helium gas through the vacuum line and collected cryogenically and measured manometrically. The purified CO2 was flame sealed in 6 mm OD Pyrex tubes for δ13C and Δ14C analyses. The oxidation efficiency and blanks associated with the UV-oxidation of DOC were tested using high purity Milli-Q water and a DOC standard (oxalic acid OXI) solution, yielding high oxidation efficiency (~95%) of DOC and considerably low blanks (<5 μg C) [Xue et al., 2015]. The concentrations of DOC
were analyzed by the high-temperature combustion method using a Shimadzu total organic carbon (TOC)-L analyzer equipped with an ASI-V autosampler. DOC concentration was calibrated using a five-point calibration curve generated from a DOC standard prepared using potassium hydrogen phthalate and UV-oxidized, high purity Milli-Q water. Instrument blank and standard validation for DOC were checked against low-carbon, reference water, and deep seawater reference material (University of Miami, Rosenstiel School of Marine and Atmospheric Sciences). Blank subtraction was carried out using high purity Milli-Q water that was analyzed before each sample. The average blank associated with DOC concentration measurements was about 5 μM, and the analytic precision on triplicate injections was ±3%.

$\delta^{13}C$ and $\Delta^{14}C$ measurements were made at the National Ocean Sciences accelerator mass spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution. A small split of CO$_2$ was analyzed for $\delta^{13}C$ using a VG isotope ratio mass spectrometer, and the rest of the CO$_2$ was graphitized for $^{14}C$ analysis using AMS. Values of $\delta^{13}C$ are reported in ‰ relative to the Vienna PeeDee belemnite standard and the $^{14}C$ measurements were reported as modern fraction [McNichol et al., 1994]. The conventional radiocarbon ages (years before present, B.P.) were calculated based on Suess and Polach [1977]. The errors of $\Delta^{14}C$ ($\sigma$) measurements determined from duplicate sample analyses are ±6.0‰ and ±3.5‰ for DOC and POC [Xue, 2016], respectively; errors were ±5.0‰, ±7.0‰, and ±4.5‰ for SPE-DOC, DBC and PBC measurements, respectively.

3. Results and Discussion
3.1. SPE-DOC, DBC, and PBC Concentrations

The SPE extraction efficiency of DOC using a PPL cartridge was 59–61% ($n = 16$) for river water and 42 ± 2% ($n = 3$) for seawater [Xu et al., 2016]. These values are in good agreement with the results reported by Dittmar [2008] and Coppola et al. [2015] using the same resin. In Table 1, we summarize the DOC and POC concentrations and the DBC/DOC and PBC/POC ratios determined for the Changjiang and Huanghe Rivers. The average distributions of SPE-DOC, DBC, permeate-DOC, POC (non-BC fraction), and PBC determined for the total DOC and bulk POC samples in the Changjiang and Huanghe Rivers, and ECS coastal samples are plotted in Figure 2. The DBC accounted for (with standard deviation) $3.0 ± 0.4\%$ and $4.8 ± 3.6\%$ of the DOC pools, and PBC accounted for $13 ± 0.4\%$ and $22 ± 11\%$ of the POC in the Changjiang and Huanghe Rivers, respectively (Table 1). Detailed discussion of the concentrations of DOC and POC and the concentrations and fluxes of DBC and PBC in the two rivers is presented in a separate publication [Xu et al., 2016].

Our results are comparable to those reported in earlier studies. Surface seawater was reported to contain 2.6% and 0.9% of DBC from the Gulf of Mexico and the Atlantic Ocean [Dittmar, 2008] and 4.2 ± 1.0% DBC in the northeast Pacific [Coppola and Druffel, 2016]. Also, using the SPE and BPCA methods, Wagner et al. [2015] reported that 3.2–6.6% of the riverine DOC pool was DBC in the Cache La Poudre River in the Colorado Rocky Mountains (USA). Using an ultrafiltration technique and thermal oxidation method, Mannino and Harvey [2004] reported that DBC comprised 8.9 ± 6.5% of the DOC in the Delaware Estuary and 4–7% in the Atlantic coastal waters. Using ultrafiltered DOC and BPCA methods, Ziolkowski and Druffel [2010] reported that DBC accounted for 0.5–3.5% of the DOC pool in the Suwannee River and Atlantic seawater. These similarities in DBC abundance in different aquatic environments may suggest that similar mechanisms or processes control the dissolution and cycling of BC in the DOC pool. As demonstrated by Jaffé et al. [2013], a strong, linear correlation ($r^2 = 0.95$) exists between DBC and DOC concentrations in the 15 large rivers they studied, suggesting that rivers play an important role in mobilizing and transporting soil BC to the ocean.

The PBC/POC abundances in the Changjiang (12.2–13.0%) and Huanghe (9.0–45.2%) rivers were higher than the DBC/DOC abundances (Table 1 and Figure 2). This is in good agreement with the results reported previously for the BC content in the coastal sediments of China’s marginal seas [Wang and Li, 2007; Kang et al., 2009]. In the Bohai Sea, which is influenced largely by the Huanghe River, BC content in the surface sediments ranged from 27 to 41% of the sedimentary TOC, higher than values (5–26%) in the ECS coastal sediments [Kang et al., 2009]. This indicates that most PBC transported by the rivers was deposited and preserved in the coastal sediments and is consistent with the recent study of Tao et al. [2016]. In their earlier study, Masiello and Druffel [2001] measured BC in POC samples collected in the Santa Clara River in California...
We report... of DBC and PBC... adsorption of BC onto particles could be an important process. Association with minerals is a major control of... SPE-DOC and permeate-DOC showed 94.5 ± 0.7% recovery of bulk DOC and offsets of 0.6 ± 0.2‰ and 14 ± 4‰ from the bulk δ13C-DOC and Δ14C-DOC values, respectively. Figure 3 shows δ13C versus Δ14C values for DBC and PBC samples, and distinct BC pools transported by the Changjiang and Huanghe Rivers are...
River DBC with high $\Delta^{14}C$ and low $\delta^{13}C$ values is in one pool (yellow shaded area), which is different from the river PBC that has lower $\Delta^{14}C$ values (green shaded areas). The Huanghe River PBC is separated into two isotopic groups: PBC-1 with relatively high $\Delta^{14}C$ and $\delta^{13}C$ values and PBC-2 with low $\Delta^{14}C$ and $\delta^{13}C$ values. DBC in the offshore seawater had low $\Delta^{14}C$ and high $\delta^{13}C$ values, quite different from the river DBC (Figure 3), and consistent with the study of Ziolkowski and Druffel [2010].

In Figure 4, we compare the $\delta^{13}C$ values and $^{14}C$ ages for total DOC, SPE-DOC, DBC and permeate-DOC fractions separated for two Huanghe River samples and find three interesting differences. First, the SPE-DOC had similar $\delta^{13}C$ values but were significantly younger (average $1060^{14}C$ years B.P.) than the total DOC ($1380^{14}C$ years). Second, the permeate-DOC had high $\delta^{13}C$ values (average $-22.4\%$) but much older $^{14}C$ ages ($2070$–$3200^{14}C$ years) than both total DOC and SPE-DOC. Third, DBC had similar $\delta^{13}C$ values but was younger ($1030^{14}C$ years) than total DOC and similar to the ages of SPE-DOC. These patterns were similar for all of the samples we measured for $\Delta^{14}C$ of DOC, SPE-DOC, and DBC (Table 2).

In Figure 5, we compare the monthly $^{14}C$ ages of DOC and DBC, POC and PBC, and DBC and PBC in the Huanghe River. We note that the ages of DBC ($945$–$1510^{14}C$ years) are younger than those of DOC ($1320$–$1680^{14}C$ years) during all months (Figure 5a). The PBC, however, shows different seasonal patterns (Figure 5b). PBC samples collected in the winter months (December–March) were much older ($9290$–$12,600^{14}C$ years) than the bulk POC ($4300$–$4630^{14}C$ years), and PBC collected from April to July and September were younger ($3100$–$3970^{14}C$ years) than the POC ($4520$–$5060^{14}C$ years). Comparison between DBC and PBC indicates that PBC samples were much older than DBC during all months, with an even larger difference during the winter months in the Huanghe River (Figure 5c). These are consistent with the isotopic results shown in Figure 3, where PBC in the four winter months had low $\delta^{13}C$ ($-24.1\%$ to $-24.4\%$) and low $\Delta^{14}C$ ($-688\%$ to $-794\%$) values (PBC-2 group), whereas PBC in the nonwinter months had relatively high $\delta^{13}C$ ($-20.5\%$ to $-22.0\%$) and high $\Delta^{14}C$ ($-278\%$ to $-395\%$) values (PBC-1). Based on the isotopic values,
Table 2. Radiocarbon (Δ^{14}C) and Stable Carbon (δ^{13}C) Isotopic Values Measured for the Samples From the Changjiang and Huanghe Rivers and ECS^{a}

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>DOC</th>
<th>SPE-DOC</th>
<th>DBC</th>
<th>POC</th>
<th>PBC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ^{13}C</td>
<td>δ^{14}C</td>
<td>Age</td>
<td>δ^{13}C</td>
<td>δ^{14}C</td>
</tr>
<tr>
<td>Changjiang (CR03)</td>
<td>-26.2</td>
<td>-137</td>
<td>1120</td>
<td>-25.9</td>
<td>-64.9</td>
</tr>
<tr>
<td>ECS-P02</td>
<td>-26.4</td>
<td>-277</td>
<td>2540</td>
<td>-25.2</td>
<td>-166</td>
</tr>
<tr>
<td>ECS-P04</td>
<td>-27.9</td>
<td>-269</td>
<td>2460</td>
<td>-22.7</td>
<td>-293</td>
</tr>
</tbody>
</table>

DBC, PBC-1, and PBC-2 were derived from different sources. BC produced from biomass burning should have modern $^{14}$C ages compared with BC generated from fossil fuel combustion (>50,000 $^{14}$C years) [Ziolkowski 2016].

**Figure 3.** Plot of $^{14}$C (%) versus $^{13}$C (%) values for DBC and PBC in the Changjiang and Huanghe Rivers and ECS seawater (DBC only). For the river DBC: (solid triangle) DBC in the Huanghe River; (open triangle) DBC in the Changjiang River; (diamond) DBC in the nearshore water (P02). The errors of $^{14}$C (1σ) measurements, derived from duplicate sample analyses, are ±7.0‰ and ±4.5‰ for DBC and PBC, which are in general smaller than the symbols. And the errors of $^{13}$C (1σ) measurements are ±0.5‰ and ±0.3‰ for DBC and PBC, respectively.
and Druffel, 2010]. Because river DBC had relatively high \( \Delta^{14}C \) (average \(-139\)‰, 1140 years B.P.) and low \( \delta^{13}C \) values, it originated mostly from biomass burning likely from C3 plants that have similar \( \delta^{13}C \) values (\(-22\)‰ to \(-34\)‰) [Vogel, 1993]. This BC could have been stored in soils and preaged before entering the riverine DBC pool. For the PBC-2 group, which had old \( ^{14}C \) ages (average 11,100 years) and low \( \delta^{13}C \) values (average \(-24.2\)‰ similar to fossil fuels, mainly coals used in China) [Xu and Shen, 1990], it is evident that fossil fuel combustion generated BC is a major contributor to PBC-2. For PBC-1, these samples likely contained a mixture of BC from both fossil fuel combustion and biomass burning.

If we assume that all BC produced from biomass burning had a postbomb \( \Delta^{14}C \) value of 100‰ [Ziolkowski and Druffel, 2010] and BC derived from fossil fuel combustion had a \( ^{14}C \)-free \( \Delta^{14}C \) value of \(-100\)‰, we can estimate the contribution of each source to the DBC and PBC pools using an isotopic mass balance approach. By doing this, we calculate that 85 ± 5% and 78 ± 12% (\( n = 12 \)) of the DBC in the Changjiang and Huanghe Rivers, respectively, were derived from biomass burning, and 15 ± 4% and 22 ± 12% of the DBC were derived from fossil fuel combustion. For all PBC samples, we estimate that 51 ± 7% and 48 ± 19% were from biomass burning, and 49 ± 6% and 52 ± 19% were from fossil fuel combustion in the Changjiang and Huanghe Rivers, respectively. If we calculate the percentages for the PBC-1 and PBC-2 groups separately, we find that 34–45% is from fossil fuel produced BC, and 55–66% is from biomass burning-produced BC for PBC-1 (nonwinter), and 72–81% is from fossil fuel BC, and 19–28% is from biomass burning BC for PBC-2 (winter), respectively. For the Changjiang River and offshore (P02) DBC samples (Figure 3), they originated mainly from biomass burning-produced BC as well (85% and 77%, respectively). These calculations are overly simplistic. We assumed only two end-members (modern BC from biomass burning and old BC from fossil fuel combustion) and did not take into account other sources, such as BC from soils or groundwater. The Changjiang River and offshore DBC samples had high \( \delta^{13}C \) values (\(-19\)‰), not consistent with others, and we are not able to provide an adequate explanation. More isotopic data for DBC and PBC are needed for the Changjiang River and ECS to resolve this issue.

The fossil fuel BC contributions to POC in the Huanghe and Changjiang Rivers were higher compared with the Mississippi River (USA), for which Mitra et al. [2002] reported that 27% of POC-BC was from fossil fuel origin. In China, fossil fuel consumption, especially coal burning, has increased dramatically in the last 20 years. Data from the National Bureau of Statistics of China (www.stats.gov.cn) indicated that in 2015, 4.3 Gt coal C were combusted in China. In the northern region of China, coal is the major source of heating fuel during winter, so large amounts of BC are produced from coal combustion. The fine BC particles that are produced could enter rivers via wind deposition, wet deposition, and runoff [Raymond, 2005; Avery et al., 2013; Chen et al., 2015; Wang et al., 2016]. This is clearly demonstrated in the very old PBC (average 11,100 ± 1500 \( ^{14}C \) years) measured in the Huanghe River during the four winter months (December, January, February, and March) compared to the rest of the months in 2015 (average 3240 ± 520 \( ^{14}C \) years) (Figure 5b). During the nonwinter months, more biomass was burned than coal, producing younger BC that was added to the PBC pool in
the Huanghe River. During the field sampling in the late summer and fall seasons, we observed that agriculture residue stalk burning in the farm lands along both sides of the river is a very common phenomenon. In their recent study, Zhao et al. [2011] estimated that 0.033 Gt biomass carbon emission was produced from the farm land grain crop residues each year in China. R. Wang et al. [2012] reported that about 0.00196 Gt BC was produced annually in China in recent years. They estimated that 22.2%, 3.1%, and 0.14% were from residential biomass (firewood and crop residue) burning, open agricultural crop waste burning, and wildfire burning, respectively. Residential coal combustion that occurred mostly in the winter months contributed 27.5% of the BC produced each year. This trend has been clearly demonstrated by our $^{14}$C results. The relatively high $\delta^{13}$C values ($-20.7\%$ to $-22.0\%$) of the PBC in the spring, summer, and fall months may suggest that some BC is from $C_4$ plants, such as corn stalk burning.

As the largest two rivers in China, the Changjiang and Huanghe are impacted by human activities, such as anthropogenic inputs and dam construction. The flow rate of the Changjiang River is usually 40–50 times...
higher than that of the Huanghe River throughout the year, and the fluxes of DOC and POC in the two rivers were determined to be 50 and 4 times higher, respectively, in the Changjiang River than in the Huanghe River (Table 1) [X. C. Wang et al., 2012]. Despite the large flux differences, the comparable 14C ages of DBC and PBC determined in the two rivers may suggest similar processes and mechanisms of mobilization of BC from land to the ocean by rivers [Dittmar et al., 2012; Jaffé et al., 2013; Wagner et al., 2015].

3.3. Fluxes of DBC and PBC in the Rivers

Based on the flow rates of water and concentrations of DOC, POC, DBC, and PBC determined for the Changjiang and Huanghe Rivers, we calculated the fluxes of DBC and PBC for the rivers (see Table 1). For the Huanghe River, the monthly fluxes of DBC and PBC ranged from $0.01$ to $0.59 \times 10^9$ g C and $0.01$ to $3.27 \times 10^9$ g C, respectively. The monthly flux variations were likely affected by the hydrological differences. Higher flow rate in the Huanghe River usually occurs in the later spring and summer (rainy season), and rainwater runoff could mobilize soil BC into the river and result in relatively higher DBC and PBC fluxes (Table 1). The annual fluxes of DBC and PBC in the Huanghe River in 2015 were $1.7 \times 10^9$ g C and $11.5 \times 10^9$ g C, which accounted for 5.5% and 28% of the annual fluxes of DOC and POC in the river, respectively. The PBC flux was 4.1 and 6.7 times higher than the DBC fluxes in the Changjiang and Huanghe Rivers, suggesting that the PBC flux was the dominant process for mobilization and transport of BC from land to the ocean by the two rivers. We calculated that together, the Changjiang and Huanghe transported 12.7% of the 0.00196 Gt BC produced annually in China [R. Wang et al., 2012]. These large fluxes of DBC and the great age of PBC transported by the Changjiang and Huanghe Rivers demonstrate a significant sink of anthropogenic carbon, which likely plays an important role in the cycling of carbon in China’s marginal seas.

Figure 6. Plot of fluxes of DBC versus DOC, PBC versus POC, and DBC versus PBC for the Huanghe River. Solid lines are liner regression of the data.

(Table 1). For the Changjiang River, we used the average DBC and PBC values of the two river samples and the annual flux values of DOC and POC in 2009 determined in our previous study [X. C. Wang et al., 2012]. The annual fluxes of DBC and PBC are calculated to be $47.4 \pm 6.3 \times 10^9$ g C and $19.2 \pm 6.1 \times 10^9$ g C, which accounts for 3% and 13% of the annual DOC and POC fluxes in the Changjiang River, respectively. The PBC flux was 4.1 and 6.7 times higher than the DBC fluxes in the Changjiang and Huanghe Rivers, suggesting that the PBC flux was the dominant process for mobilization and transport of BC from land to the ocean by the two rivers. We calculated that together, the Changjiang and Huanghe transported 12.7% of the 0.00196 Gt BC produced annually in China [R. Wang et al., 2012]. These large fluxes of DBC and the great age of PBC transported by the Changjiang and Huanghe Rivers demonstrate a significant sink of anthropogenic carbon, which likely plays an important role in the cycling of carbon in China’s marginal seas.
In Figure 6, we examined the relationships between DBC and DOC fluxes, PBC and POC fluxes, and DBC and PBC fluxes in the Huanghe River. It appears that a significant positive correlation ($r^2 = 0.73$, $p < .0002$) exists between DBC and DOC fluxes if we eliminate the highest DOC flux in July (Figure 6a). This high DOC flux was caused by a man-made flood event. Since 2002, annual water management regulations for the Huanghe River require opening the dam gate at the Xiaolangdi Reservoir (600 km upstream) during June–July, to remove the sediment deposited on the river bed during previous months [Xu et al., 2016]. We did not see a high DBC flux during this high flow period. It is possible that some DBC could be adsorbed onto sediment particles because the flux of particles was the highest during July (Table 1). For PBC and POC fluxes (Figure 6b), there is a strong positive correlation ($r^2 = 0.84$, $p < .0001$) showing that the flux of PBC increased with the flux of POC in the river. The fluxes of DBC and PBC, however, were not significantly correlated ($r^2 = 0.20$, $p < .11$). This supports our observations indicating that the DBC and PBC transported in the river were derived from different sources; therefore, the fluxes of DBC and PBC are decoupled in the Changjiang and Huanghe Rivers. This finding is consistent with the conclusion made by Wagner et al. [2015].

### 4. Implications

Our study reveals evidence that two BC pools were transported by the Huanghe and Changjiang Rivers during 2015. BC transported in the riverine dissolved phase (DBC) is significantly younger than BC in the solid phase (PBC), indicating a higher percentage of BC from biomass burning. Though $\Delta^{14}C$ measurements of DBC in rivers are few, we compare results from three rivers (Changjiang, Huanghe, and Suwannee Rivers in the USA) in Figure 7. DBC in the Changjiang River (475 ± 150 years B.P.) had a similar $^{14}C$ age to that in the Suwannee River (450 ± 280 years B.P.) collected in 1999 [Ziolkowski and Druffel, 2010]. The DOC in the Suwannee River is modern ($\Delta^{14}C = 153‰$) and likely derived from terrestrial plants that are concentrated along the river basin. This compared with the old ages of DOC in the Changjiang (900 ± 282 $^{14}C$ years) and Huanghe (1489 ± 133 $^{14}C$ years) rivers, which were heavily influenced by preaged OM in soils [X. C. Wang et al., 2012; Tao et al., 2015; Xue, 2016] and anthropogenic inputs [Zhang et al., 2013]. The young DBC found in these rivers also supports the speculation of Ziolkowski and Druffel [2010] that riverine DBC could be more labile than presently believed.

Another interesting finding in our study is that the $^{14}C$ ages of permeate-DOC (average 2640 ± 560 $^{14}C$ years) were much older than the total DOC, SPE-DOC, and DBC in the Huanghe River, while their $\delta^{13}C$ value ($-22.4 ± 0.5‰$) was higher and close to that of marine DOC ($-20.4‰$ to $-22.4‰$) [Druffel et al., 1992; Bauer et al., 1998]. Because the PPL cartridge uses a more polar sorbent, the 42% of the riverine DOC that passed through the resin could contain a significant fraction of nonpolar, smaller-sized DOC molecules. It is not clear why the permeate-DOC fraction is so old. We expect that the SPE-DOC fraction is younger and more labile and could be decomposed more rapidly by both bacteria [Amon and Benner, 1996; Benner and Biddanda, 1998] and photodegradation [Spencer et al., 2009] during river transport and in estuarine and coastal waters. The nonpolar, smaller-sized riverine DOC thus could be more refractory and possibly contribute to the very old oceanic DOC pool (4900–6400 years B.P.) [Druffel and Griffin, 2015]. In their recent study,
Coppola and Druffel [2016] reported that at least two distinct DBC pools exist in the ocean. A younger pool of DBC (4800 ± 620 14C years) cycles on centennial time scales, and an ancient DBC pool (23,000 ± 3000 14C years) cycles on > 105 year time scales. They suggest that river input of DBC is an important process, though most DBC delivered via rivers is not accumulating in the ocean. Riverine DBC could be removed by processes such as UV oxidation [Stubbs et al., 2012] and microbial degradation [Coppola and Druffel, 2016]. Nevertheless, our study brings up more questions than it answers. Considering the limited data base for 14C measurements of DBC and DOC in rivers, larger data sets for more rivers are crucial to nail down the sources and geochemical cycling of river transported DOC and their roles in oceanic DOC cycling and its budget.

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