Global scale evidence for the refractory nature of riverine particulate black carbon

Supplementary Information

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References

1. RESULTS

1.1. Concentrations and relative structure of particulate black carbon

PBC concentrations ranged widely from 6.9 to 77.5 g BPCA/kg POC in the Pettaquamscutt to Collville River, respectively (Supplementary Table 1, Supplementary Figure 2a). The average BPCA content was 40±22 g BPCA/kg POC. Using the conversation factor [1] to estimate of original BC mass from BPCA marker compounds, this corresponds to a range from 2.7±0.4 (Pettasquamscutt) to 32.9±2.9 (Eel) PBC% for these same samples (Table 1). The weighted mean of PBC% was 15.8±0.9% (wtd error) (Supplementary Table 1). The weighted mean μ and weighted error σ_μ were calculated from individual river BC means μ_j and the standard deviation σ_j [2]. We used Equation 1 to calculate the weighted mean μ and weighted error σ_μ of BC, where

$$\mu = \frac{\sum \mu_j/\sigma_j^2}{\sum 1/\sigma_j^2} \quad \text{where } \sigma_\mu^2 = \frac{1}{\sum(1/\sigma_j^2)} \qquad (1)$$

The study of BC in POC is challenged by the presence of a mineral matrix, which dilutes organic carbon, making it difficult to collect enough material for $\Delta^{14}C$ measurements. HF demineralization eliminates minerals and concentrates organic carbon and BC. HF does not alter the chemical composition of organic matter [3] nor PBC structures (Supplementary Figure 3) which is supported by findings of a previous study [4]. Carbon loss was not accompanied by isotopic fractionation, as the $\Delta^{14}C$ values showed similar values before and after HF treatment (Supplementary Figure 3b). Similar results were obtained by Schmidt et al.,(2005)[5]. PBC concentrations are reported on non-HF treated POC samples. Total sediment mass balance recoveries after HF treatment were between 3 and 23% of the initial mass. Thus, BPCA

concentrations increased from an average of 17.3±0.8 g BPCA/kg POC to 77±15 g BPCA/kg POC to allow for sufficient material (30 µg C) for HPLC collection and subsequent ^{14}C analysis (Supplementary Table 1).

The aromatic carbon analytical window implies that the mass weighted fluxes are conservative underestimates based on the highest refractory components in PBC because it does not include by-products of low temperature fires (i.e. levoglusan). Our PBC concentrations in the Santa Clara River (27±1.8%) are significantly higher compared to estimates by Masiello and Druffel (16.7%) [6] using the dichromate-sulfuric acid oxidation method. In the Yellow River, our PBC content (11.5±1.5% and 9.4±1.5%) is in the lower range of seasonality reported PBC% (9.0-45%) [7] using Chemical Thermal Oxidation (CTO) method. These differences may be reflected in river seasonal/annual variability of PBC flux. The analytical window captured by each the BC methods varies significantly and likely explains the variability [8,9].

Although Hindersmann and Achten (2017)[10] report recoveries of BPCAs for coal, oil and lignite samples, we do not consider petrogenic components of BPCA contributions in these samples. Oil, coal and lignite are present in negligible amounts in the rocks eroded in the catchments we studied. Reference standard Green River Shale is a good analog of riverine petrogenic carbon, yet only showed very low recoveries of BPCAs (<2%) in Hammes et al., (2007)[9]. Thus, the BPCAs are largely dominated by pyrogenic (biospheric) inputs.

1.2. Isotopic signatures of particulate black carbon

We report the $\Delta^{14}C$ values for PBC in Supplementary Table 1. The error-weighted PBC

$\Delta^{14}C$ average is -589±20‰ (7,100±300 ^{14}C yrs). To get estimates of the global significance of BC export, we estimated a global river BC ^{14}C age. First, $F^{14}C$ values for individual rivers were weighted according to the flux of BC from that specific river (Supplementary Table 2). Then, the mean $F^{14}C$ value was converted to $\Delta^{14}C$ values and ^{14}C ages.

We find a large variability in PBC $\Delta^{14}C$ values. The range in values could be driven by the relative amount of fossil fuel derived PBC. If we assume all BC produced from biomass burning has a post-bomb $\Delta^{14}C$ value of +100‰ [11] and BC derived from fossil fuels has a $\Delta^{14}C$ value of -1000‰, we can use a two-end member isotopic mass balance approach. For PBC, we calculate a range in biomass burning contributions based on the two Colville and Congo extremes from 10 to 98% of biomass derived and 2 to 90% of fossil fuel contributions, respectively. For all PBC samples, this simple two endmember mixing model suggests that the biomass burning contributions can be 56±29% of PBC, and 44±28% is from fossil fuel contributions. However, these calculations are overly simplistic by assuming only 2 end members and do not agree with estimates from Mitra et al., (2002) who reported that 27% of PBC from the Mississippi River is from fossil fuel origin. Here, we find a larger contribution of 63±10% of fossil fuel BC to PBC from the Mississippi River which suggests the two end member estimation is overly simplified. Using only two end members, we also estimate the fossil fuel contribution to PBC in the Yellow (Huanghe) River to be 88±10%. Wang et al., [12] reported a contribution of 52±19% of fossil fuel contribution to PBC in the Yellow River. There may be seasonality associated with the $\Delta^{14}C$ of PBC. The range in PBC $\Delta^{14}C$ values suggests that BC exported by rivers cannot be assumed to be composed

of only modern biomass BC. Instead there is likely a pre-aged PBC component in which biomass derived PBC ages in the river catchment before export [13].

The riverine POC pool includes modern C from terrestrial primary producers, aged C from deeper soil horizons and contributions from weathering ^{14}C-free sedimentary rocks [14]. The contribution of BC to the riverine POC pool has been investigated on a per-site basis [6], but not yet on a global scale. Here, we find no correlation of river basin size with BC content (Supplementary Figure 4a) nor river particulate BC Δ^{14}C values. We find the Δ^{14}C content in PBC is significantly correlated to POC Δ^{14}C values (Figure 2b). Also, dissolved BC concentration has been found to be coupled to riverine dissolved organic carbon (DOC) export [15,16], yet are decoupled from the POC pool [12,17].

1.3. Normalization of river particulate black carbon to biospheric POC

PBC fluxes from each river were estimated by multiplying the relative PBC concentration (derived from BPCA concentrations) with the reported biospheric particulate organic carbon (POC) yield of each river given by Galy et al., [18] (2015) (Supplementary Table 2). This way, PBC was normalized to biospheric OC export to compare and contrast BC to other components of POC produced by the biosphere in a manner that is unaffected by interference from non-biospheric (petrogenic) OC. First, the reported biospheric POC yields were used from Supplementary Table 1 in Galy et al., (2015). However, for 4 rivers, there were no previous determinations of biospheric POC yield, (Pettaquamscutt, Cagayan, Colville and Danube, Supplementary table 2, marked *). For these rivers, we calculated the biospheric POC yield based on the linear relationship with suspended sediment yield (Fig 2 Galy et al., $Y_{bios} = 0.081 \times Y^{0.56}_{sed}$).

123 The flux of PBC was normalized to the biospheric organic carbon yield. Cagayan POC
124 river flux was not available in the literature, so PBC flux was upscaled for Luzon, given
125 by Liu et al., (2016).
126
127 **1.4 Fluxes of riverine particulate black carbon**
152 In comparison, our PBC estimates are larger than published PBC values. Our
153 estimates for the Santa Clara, Ob, Mackenzie and Yukon Arctic rivers of 11±2, 28±6,
154 296±60, and 85±17 Gg yr^{-1} are larger than published values of 5.9, 18, 99 and 29 Gg
155 yr^{-1}, respectively [19,20]. These studies use a BC method, which isolates only soot-BC
156 across the char to soot BC continuum [9,21]. In addition, the sample collection time may
157 not have captured the temporal variability, as small mountainous rivers have few high
158 flux events. For the Amazon, we calculate 1162±218 Gg yr^{-1} PBC flux which is
159 significantly smaller than the dissolved BC estimated by Dittmar et al.,[22] of 2799 Gg
160 yr^{-1}.
161
162 Climate seasonality may play a central role in setting the magnitude of the negative
163 BC feedback on the global carbon cycle. A high seasonality environment would favor
164 fires during the dry season, and high physical erosion rates during the wet season
165 would balance the potential competing effect of changing physical erosion rates in
166 favor of a negative feedback. The interplay of these two factors would need to be
167 evaluated in detail on process-oriented basin scales studies to determine the
168 sensitivity of riverine PBC export.
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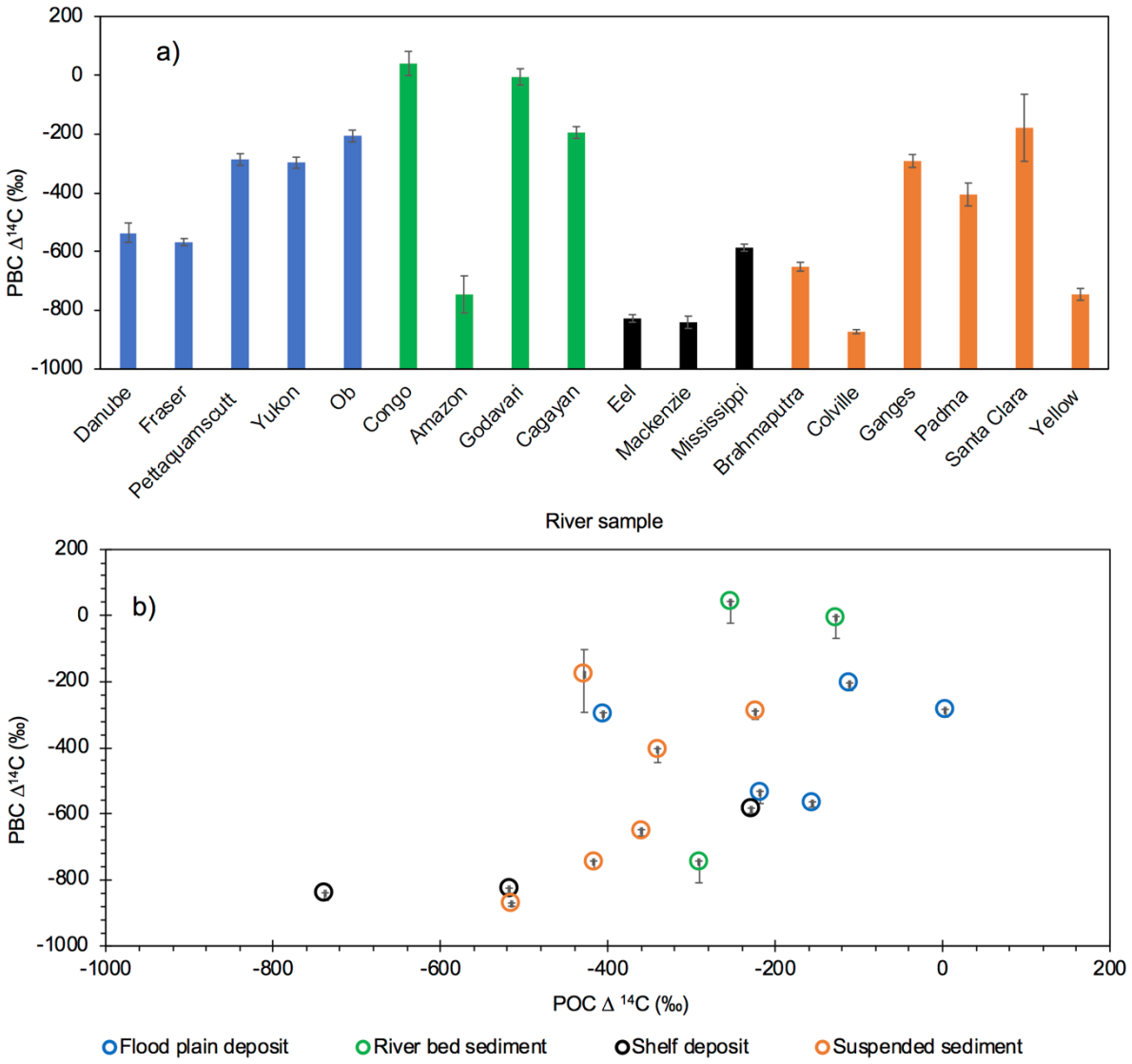
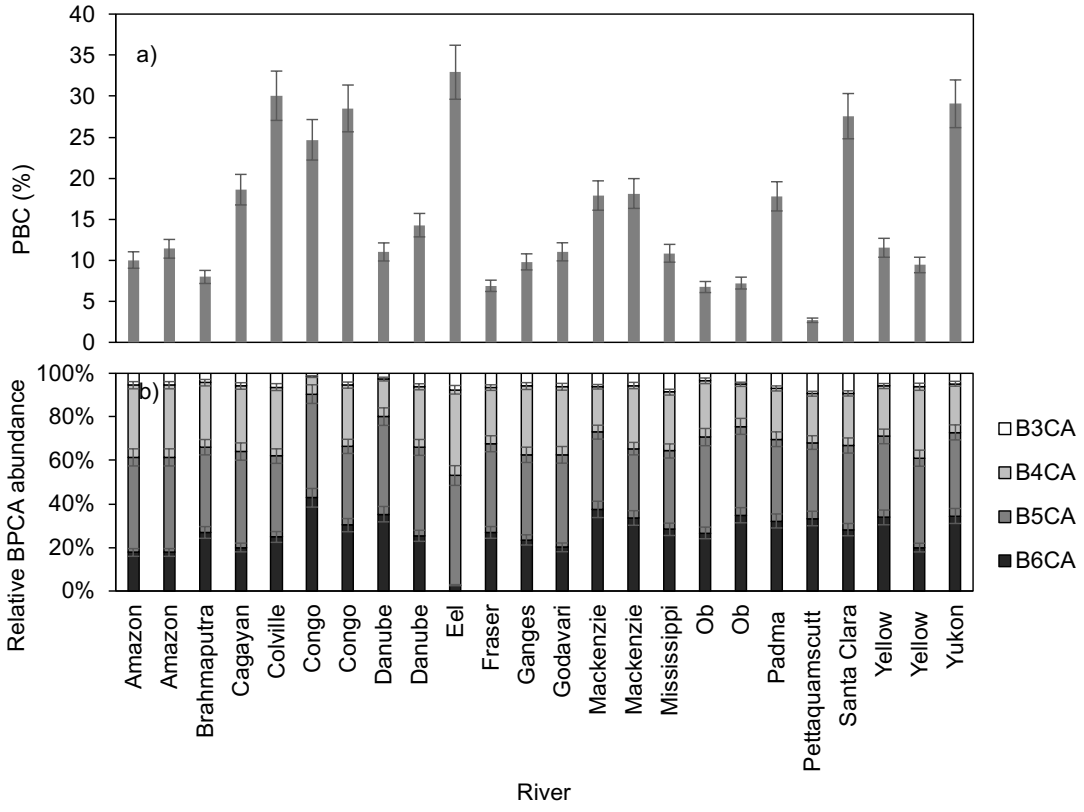


Supplementary Figure 1. River sample types used in this study. Blue, green, black and orange values represent flood plain deposits, river bed sediments, shelf deposits and suspended sediments, respectively. River $\Delta^{14}C$ for a) PBC and grouped by sample type. b) relationship of PBC and POC $\Delta^{14}C$ for river samples used in this study.



Supplementary Figure 2. a) PBC as a percentage of biospheric POC b) Relative BPCA abundances for all rivers in this study.

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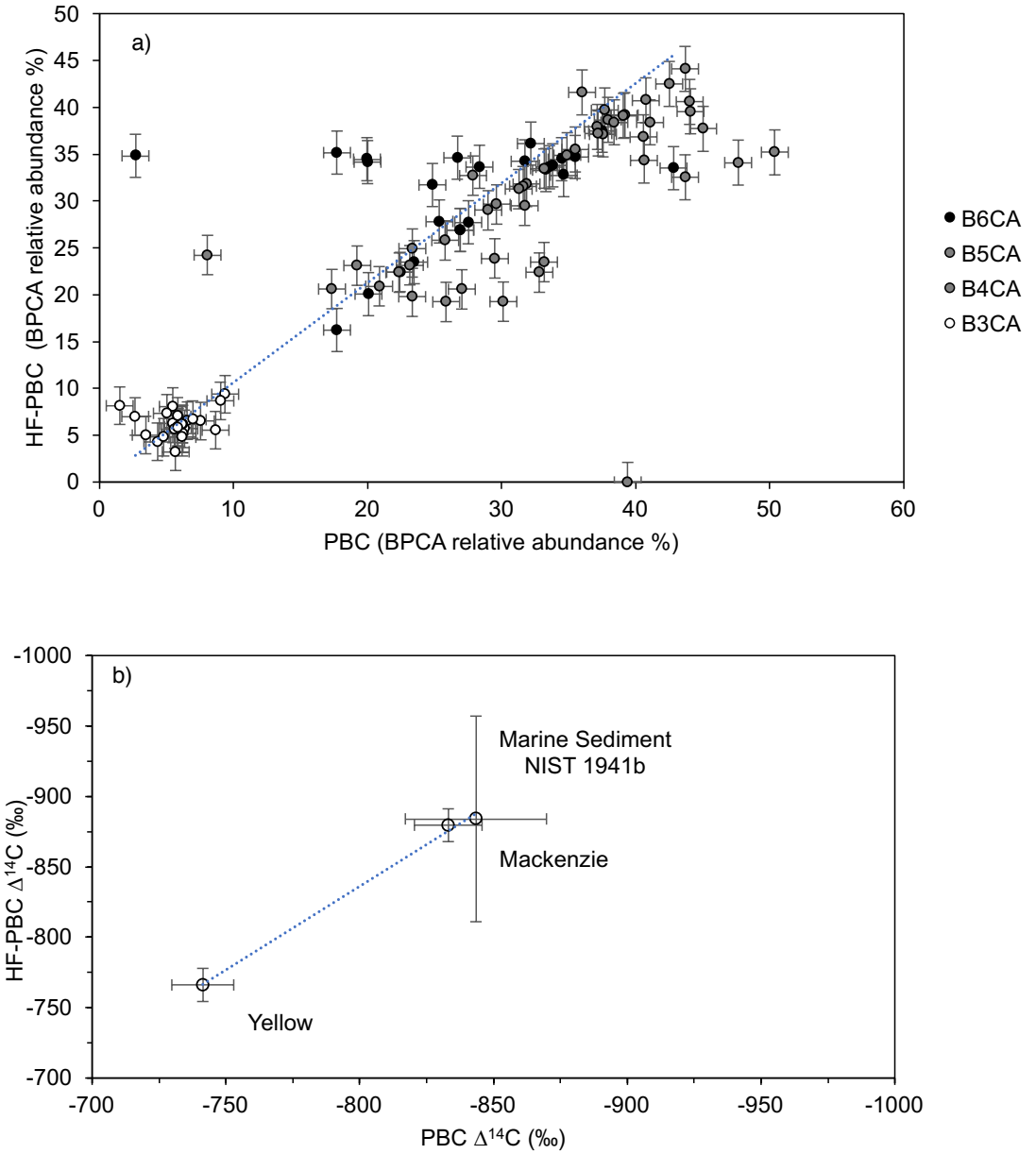

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201 Supplementary Figure 3. a) BPCA distribution for all BPCA isomers between HF

202 treated and non-HF treated samples. b) Radiocarbon values for B6CA and B5CAs

203 between HF-treated and non-HF treated samples and NIST 16491b Marine Sediment.

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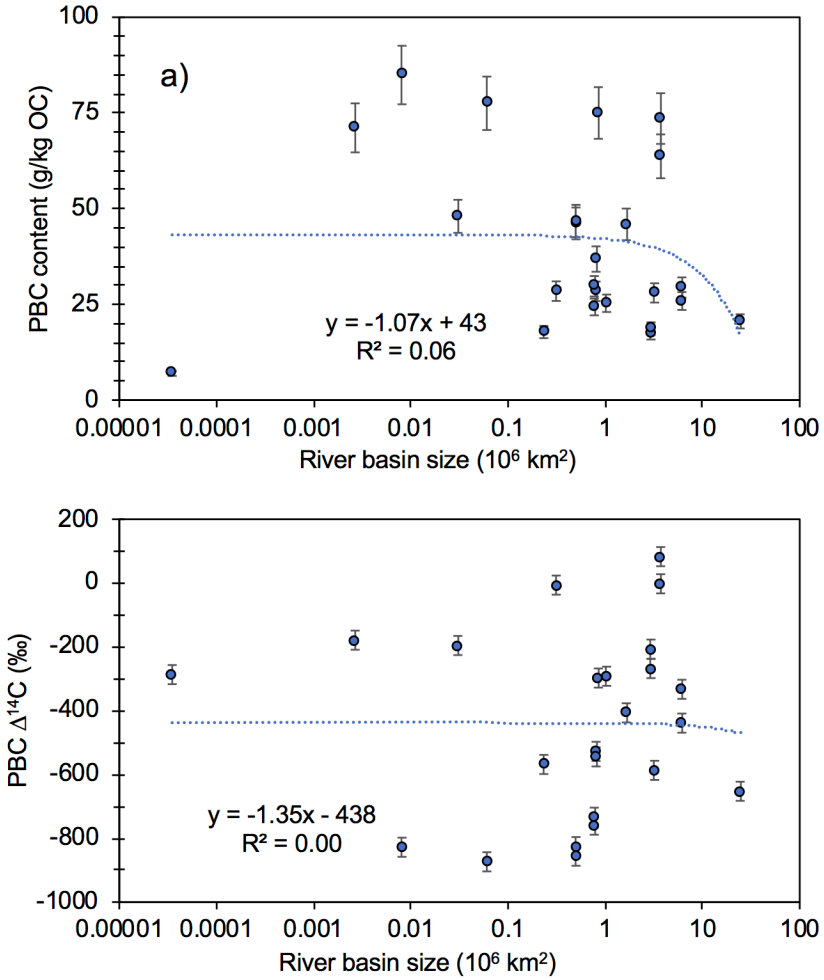

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208 Supplementary Figure 4. Relationship of drainage basin with river a) PBC content and

209 b) PBC $\Delta^{14}C$. We find no correlation.

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River	POC		PBC				BPCA	Degree of condensation	sample type	Year of collection	sample source(s)
	Δ14C	±	Δ14C	±	14C age	±	BPCA g/kg OC	B6CA+B5CA/ sum BPCAs			Origin
Amazon	-291	3	-333	63	3'250	770	25.9	0.61	River bed sediment	2015	Moreira-Turcq 2003
			-439	40	4'640	580	29.4	0.61	River bed sediment	2015	Moreira-Turcq 2003
Brahmaputra	-360	4	-653	16	8'500	370	20.6	0.66	River bed sediment	2007	Galy et al., 2015
Cagayan	no data		-196	20	1'750	210	48.0	0.64	River bed sediment	2016	this study
Colville	-515	3	-874	7	16'620	450	77.5	0.62	Suspended sediment	2007	McClelland et al. 2014
Congo	-254	4	83	33	bomb	250	63.7	0.90	River bed sediment	1978	Eisma et al., 1978
			-2	30	20	250	73.5	0.66			
Danube	-218	4	-528	9	6'020	150	28.4	0.80	Floodplain deposit	2013	Freymond et al., 2018
			-545	7	6'320	130	36.8	0.66	Floodplain deposit	2013	
Eel	-518	3	-828	13	14'150	630	84.9	0.53	Shelf deposit	2010	Goni et al 2013
Fraser	-155	3	-569	20	6'750	380	17.8	0.68	Floodplain deposit	2010	this study
Ganges	-224	3	-292	22	2'780	260	25.3	0.63	Suspended sediment	2007	Galy et al., 2015
Godavari	-127	3	-7	29	50	240	28.5	0.63	Floodplain deposit	2015	this study
Mackenzie	-738	2	-826	20	14'060	930	46.2	0.73	Shelf sediment	1987	Guo and Macdonald, 2006
			-856	20	15'580	1'120	46.8	0.65	Shelf sediment	1987	Guo and Macdonald, 2006
Mississippi	-229	4	-587	12	7'110	230	28.0	0.64	Flood plain deposit	2004	Duan and Bianchi, 2007
Ob	-111	4	-207	41	1'860	420	17.4	0.71	Flood plain deposit	2000	Stein and Macdonald, 2004
			-268	25	2'510	280	18.6	0.76	Flood plain deposit	2000	Stein and Macdonald, 2004
Padma	-341	3	-407	39	4'200	530	45.9	0.70	Suspended sediment	2007	Galy et al., 2015
Pettaquamscutt	3	4	-287	19	2'720	220	6.9	0.68	Floodplain deposit	1999	Hanke et al., 2017
Santa Clara	-428	76	-179	114	1'580	1'120	71.1	0.67	Suspended sediment	1997	Masiello and Druffel 2001
Yellow	-417	3	-759	20	11'430	670	29.7	0.71	Suspended sediment	2011	Tao et al., 2015
			-734	20	10'640	610	24.3	0.61	Suspended sediment		Tao et al., 2015
Yukon	-406	3	-298	20	2'840	230	75.0	0.73	Floodplain deposit	2007	Guo and Macdonald, 2006

Supplementary Table 1. River POC and PBC $\Delta^{14}C$ content. The relative structure of PBC is given by the relative abundance of BPCA marker compounds and the degree of condensation. Orgion of supporting POC $\Delta^{14}C$ data comes from references [6,12,13,18,23-33].

Basin	Catchment size		Suspended sediment yield		Biospheric POC yield	PBC content		PBC yield **	PBC flux	
	10^6 km^2	±10^6 km^2	t/km^2/yr	± t/km2/yr	t/km^2/yr	%	±%	t/km^2/yr	kton/yr	± kton/yr
Ganges	1.1	0.032	519	104	1.45	9.8	1.7	0.142	151	30
Brahmaputra	5.8E-1	0.017	1034	207	2.69	8.0	0.3	0.215	125	25
Fraser	2.3E-1	0.007	75	15	0.51	6.9	0.5	0.035	8	2
Amazon	6.1	0.184	195	39	1.77	10.0	1.0	0.177	1088	218
Eel	8.1E-3	0.000	1987	397	9.02	32.9	2.9	2.969	24	5
Santa Clara	4.2E-3	0.000	1167	233	9.08	27.6	1.8	2.506	11	2
Huanghe	7.7E-1	0.023	144	29	0.47	11.5	1.5	0.054	42	8
						9.4	1.5	0.044	34	7
Mackenzie	5.0E-1	0.015	254	51	3.30	17.9	0.2	0.591	295	59
						18.1	0.2	0.597	298	60
Ob	3.0	0.089	5	1	0.14	6.7	0.3	0.009	27	5
						7.2	0.3	0.010	29	6
Godavari	3.1E-1	0.009	544	109	1.47	11.0	1.2	0.162	51	10
Mississippi	3.2	0.097	19	4	0.28	10.9	1.0	0.030	98	20
Congo	3.7	0.111	9	2	0.53	24.7	2.7	0.131	485	97
					0.53	28.5	2.7	0.151	560	112
Padma	1.6	0.049	702	140	2.04	17.8	0.9	0.363	597	119
Pettaquamscutt	0.0	1E-06	no data	no data	no data	2.7	0.4	no data	no data	no data
Cagayan*	0.1	0.003	428	86	6.06	18.6	2.1	1.128	118	24
Colville*	0.06	0.002	99.28	20	1.20	30.0	1.5	0.359	22	4
Danube*	0.8	0.024	12	2	0.14	11.0	2.3	0.016	13	3
						14.3	2.3	0.021	17	3
Yukon	5.1E-1	0.015	73	15	0.58	29.10	2.0	0.168	85	17

Supplementary Table 2. River catchment size, suspended sediment yield, biospheric POC yield from Galy et al., (2015)[18]. Rivers with a "*" mark represent rivers that did not already have supplementary data from Galy et al., (2015). Thus, for these rivers the correlation between suspended sediment yield and biospheric POC yield was used. PBC yield (**) was normalized to biospheric POC. The flux of PBC was normalized to the biospheric POC yield. The source of the data used to calculate biospheric POC yield was calculated from Galy et al., [18] for the Padma, Pettaquamscutt, Cagayan, Colville and Danube. Cagayan POC river flux was not available in the literature, so PBC flux was upscaled for Luzon, given by Liu et al., (2016)[23].

BC Fluxes		Flux (Tg/yr)	Reference
Biomass burning	annual production	114-383	Santin et al., 2015
	to the atmosphere	2.8-6.2	Bond et al., 2013
	to the terrestrial biosphere	56-123	Bond et al., 2016
Fossil Fuel combustion	annual production	2-29	Bond et al., 2016
	to the atmosphere	0.08-13.8	
	to the terrestrial biosphere	<1	Bird et al., 2015
River Dissolved	land to the ocean	27	Jaffe et al., 2014
River Particulate	land to the ocean	16-34	this study
Sinking Particulate	surface to deep	16	Coppola et al., 2014
Atmospheric Deposition	Global	2-10	Jurado et al., 2008
	to the terrestrial biosphere	2.1-4.9	Bird et al., 2015
	to the ocean	5.4-12.1	Bird et al., 2015
	to the ocean	2-10	Jurado et al., 2008
	to the ocean dissolved PyC pool	1.8±0.83	Bao et al., 2017
UV Oxidation	surface ocean	2-4	Stubbins et al., 2012

Supplementary Table 3. Literature values for BC fluxes used in the schematic summary Figure 1. Schematic overviews of radiocarbon values measured in this study and other systems are from estimates in [15,21,34-41].

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