Marked isotopic variability within and between the Amazon River and marine dissolved black carbon pools

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Riverine dissolved organic carbon (DOC) contains charcoal byproducts, termed black carbon (BC). To determine the significance of BC as a sink of atmospheric CO2 and reconcile budgets, the sources and fate of this large, slow-cycling and elusive carbon pool must be constrained. The Amazon River is a significant part of global BC cycling because it exports an order of magnitude more DOC, and thus dissolved BC (DBC), than any other river. We report spatially resolved DBC quantity and radiocarbon (Δ14C) measurements, paired with molecular-level characterization of dissolved organic matter from the Amazon River and tributaries during low discharge. The proportion of BC-like polycyclic aromatic structures decreases downstream, but marked spatial variability in abundance and Δ14C values of DBC molecular markers imply dynamic sources and cycling in a manner that is incongruent with bulk DOC. We estimate a flux from the Amazon River of 1.9–2.7 Tg DBC yr−1 that is composed of predominately young DBC, suggesting that loss processes of modern DBC are important.
Biomass burning and fossil fuel combustion release vast amounts of carbon into the atmosphere, causing large changes in Earth’s climate1,2. Up to 27% and 0.2% of carbon from the incomplete combustion of biomass and fossil fuel, respectively, is retained as condensed forms of carbon (called pyrogenic or black carbon, BC, ranging from charcoal to soot) rather than emitted as greenhouse gases. In addition to impacting radiative budgets, BC also influences biogeochemical processes because it is a very large and refractory component of the global carbon cycle.3,4 For example, particulate BC (PBC) acts as a biospheric carbon sink5,6,7 by removing carbon from faster atmosphere–biosphere processes and sequestering this carbon to sedimentary reservoirs. To predict how the carbon cycle may respond to climate change, we need to determine the origin, dynamics, and fate of this abundant and slowly cycling component in the carbon cycle. A large portion of BC is exported to the ocean by rivers as dissolved BC (DBC) (27 Tg year−1), thereby connecting marine and terrestrial carbon cycles.8,9 Atmospheric deposition is another major pathway in which BC, reaches rivers (after mobilization from the landscape)10 and also the ocean (1.8–10 Tg year−1).11,12 Uncertainties in regional and global-scale BC budgets persist due to poor constraints on its fluvial dynamics and export. Current estimates suggest that the input by rivers alone to the ocean is sufficient to sustain the turnover of the entire oceanic BC pool in just 500 14C years given current known losses of BC, yet measured 14C ages of BC in the deep sea are 40 times greater (>20,000 14C years).13–15 Our understanding of the role of BC in the regional and global-scale carbon cycle remains inadequate, due in large part to poor constraints on the processing, quality, and fate of DBC during river export to the ocean.16 Rivers are the primary link by which BC is transferred laterally from terrestrial pools to the ocean.9,16 Currently, large gaps exist with respect to the processes, pathways, and timescales over which DBC is mobilized and transported from land to ocean16–19, leading to challenges in reconciling BC cycling on terrestrial landscapes (modern to 1000 years mean residence time) with its longevity in the deep oceans (>20,000 14C years).14 The annual export of DBC is large (27 Tg/year), and represents a significant fraction (i.e., ~10%) of overall riverine dissolved organic carbon (DOC).9 Surprisingly, riverine DOC and DBC concentrations appear to be coupled,17,18,20 regardless of fire history in upstream catchments, and despite substantial lags between the production of charcoal BC and river DBC export21–23. For example, in the Paraiba do Sul River in Brazil, DBC is continuously mobilized irrespective of fire history, with annual export far exceeding contemporary BC production rates.21 DBC is partially removed during mobilization from soils during the wet season,22 implying storage of BC in intermediate reservoirs (such as soils) prior to release to the river network.24 BC has residence times of centuries in soils,25 while turnover times are on the order of millennia in the deep ocean.13,14 These contrasting turnover times suggest that aging may occur along the land–river–ocean transport continuum. Alternatively, more reactive DBC pools could be selectively removed during storage and transport, resulting in an apparent increase in age of residual DBC. For example, low-temperature combustion products derived from modern wildfires are re-mineralized during transport in Arctic river systems on the timescale of 20–40 days.26 However, analyzing the DBC radiocarbon composition (Δ14C) is needed to understand how these remineralization processes influence the age distribution and recalcitrance as DBC is transported from river to ocean reservoirs. On a global scale, PBC in rivers is refractory, but Δ14C measurements on different river systems suggest that the extent of storage within river catchments varies widely for PBC pools.8 Information on the radiocarbon composition of riverine DBC is currently limited to a single study17.

The Amazon River accounts for one-fifth of global freshwater discharge to the ocean,27,28 and is the largest single source of terrestrial organic matter to the ocean (with an average annual DOC export of 22–27 Tg).29,30 Thus, the Amazon River is a crucial system in which to understand DBC cycling and transport and to develop constraints on global BC dynamics. The Amazon Basin transitions between pristine forest and urban influenced aerosol polluted plumes due to rapid developments in energy, agriculture expansion, and deforestation.31,32 Here, we collected dissolved organic matter (DOM) and DBC samples for molecular characterization and radiocarbon analysis in four tributaries (Negro, Madeira, Trombetas, and Tapajós Rivers) and the Amazon River mainstem in November 2015 during one of driest seasons following a strong El Niño (Methods Sampling and Site Locations, Supplementary Fig. 1). This period represents the low flow of water during which the floodplain complexity and connectivity is limited, as we sampled only permanent waters.31 Although DOC export is greatest during intervals of peak discharge,32 we selected this low flow period for analysis to reduce complexity in watershed DBC sources associated with floodplain dynamics. We measured the concentration and radiocarbon content (Δ14C values) of DBC in solid phase-extracted (SPE) DOC using molecular proxies (benzene polycarboxylic acids, BPCAs),33 released through chemical oxidation from the polycyclic condensed aromatic structure of BC. We pair these quantitative measurements of DBC molecular markers with DOM molecular characterization using ultrahigh-resolution mass spectrometry (Fourier transform ion cyclotron resonance mass spectrometry; FT-ICR-MS).34–36 DBC Δ14C measurements reveal that DBC within the Amazon River and its tributaries generally are modern in age, but considerable spatial heterogeneity exists. Notably, there are very low DBC Δ14C values at Trombetas-Oriximiná, Amazonas-Santarém, Óbidos, and near Manaus. However, further downstream, the Amazon River exports modern DBC to the ocean.

**Results**

**Spatial decoupling of DBC and DOC concentrations and trends.** We observe incongruent dynamics of DBC and DOC concentrations. DOC concentrations along the mainstem range from 3.3 ± 0.3 mg L−1 upstream to 2.5 ± 0.2 mg L−1 downstream at Manacapuru (station 1) to Almeirim (station 1), respectively (Supplementary Fig. 2). Tributary concentrations range from 1.6 ± 0.5 to 6.8 ± 0.5 mg L−1 in the Tapajós River (station 2) to Negro River (station 12), respectively. The DOC flux along the Amazon River mainstem increases from 183 kg C s−1 at Manacapuru (station 11) to 229 kg C s−1 at Almeirim (station 1) (Supplementary Table 1, Supplementary Fig. 2). With the exception of an Amazon River mainstem sample near Parintins that has a significantly higher DOC concentration (802 ± 160 μg L−1, station 6), DBC concentrations range from 103 ± 21 μg L−1 in the Tapajós River tributary (station 2), to 181 ± 36 μg L−1 at Almeirim (station 1) to 495 ± 90 μg L−1 at Santarém (station 3) (Fig. 1). The weighted average DBC concentration is 264 ± 20 μg L−1 (22 ± 4 μM) along the mainstem (n = 8). There is also a general increase in DBC fluxes downstream from Manacapuru (station 11) to Almeirim (station 1) from 13.3 to 16.6 kg s−1, respectively (Supplementary Table 2, Supplementary Fig. 2). This lack of covariation between DBC and DOC concentrations along the river (p = 0.59) during low flow contrasts with observations from other rivers globally.9,20,37 Although documented in other river catchments, this decoupling between DBC and DOC concentrations may be a consequence of the extreme drought conditions throughout the
Amazon basin in 2015, which may have affected the dynamics of DOC in this catchment. The lack of correlation between DBC and DOC concentrations in tropical rivers ($p < 0.6023$) may result from the divergent effects of soil properties, temperature, rainfall, and aerosol deposition on bulk DOC and its DBC mobilization from catchments.

**Isotopic heterogeneity of DBC.** SPE-DOC shows $\Delta^{14}$C values ($−10 ± 24\%_{o}$ to $+55 ± 30\%_{o}$) consistent with modern biospheric inputs at all stations (Supplementary Fig. 3). The latter coupled with corresponding stable carbon isotopic compositions ($\delta^{13}$C values $−28.5 ± 0.8\%_{o}$ to $−31.5 ± 0.1\%_{o}$) (Supplementary Table 1) suggests contemporary lowland C3 plants as the dominant source of DOC. Also, DBC $\Delta^{14}$C values are mostly consistent with a modern river source ($−46 ± 15\%_{o}$, $n = 7$). However, DBC $\Delta^{14}$C values are markedly lower at four sites (station 10, Amazonas-20 km downstream of Manaus $−720 ± 8\%_{o}$; station 4, Amazonas-Óbidos, $−658 ± 7\%_{o}$; station 3, Amazonas-Santarém $−431 ± 14\%_{o}$; station 2, Tapajós-Alto do Chão, $−771 ± 16\%_{o}$ (Fig. 1, Supplementary Table 2)). The very low DBC $\Delta^{14}$C values suggest that DBC is not stored in short-term intermediate reservoirs prior to export. The DBC $\Delta^{14}$C values are not correlated to DOC flux ($p = 0.260$), discharge ($p = 0.36$), or other catchment-specific parameters, such as land cover ($p = 0.385$ for wetlands, $p = 0.094$ for croplands, $p = 0.516$ for natural vegetation) burned ($p = 0.283$) or urbanized area ($p = 0.985$) (Supplementary Fig. 4, Supplementary Table 3). The low DBC $\Delta^{14}$C values are also not reflected in abundances of DBC molecular markers (Supplementary Fig. 5). There are several potential explanations for the presence of these four strongly $14^{C}$-depleted riverine DBC values. For example, there is an anthropogenic aerosol plume 8–70 km downwind of Manaus from regional urbanization that may contribute to the low $\Delta^{14}$C DBC values we observe at station 10 (20 km downwind). A second possible explanation for low DBC $\Delta^{14}$C values in mainstem sites just downstream of tributaries (e.g., Santarém) is that the collected water represented an impartial mixture of tributary and mainstem water considering that tributaries in the Amazon have been shown to be poorly mixed up to 100 km downstream of their confluence. Additionally, past measurements show that suspended POC in the lowland rivers studied here have modern radiocarbon signatures similar to DOC, PBC in the Amazon River has a $\Delta^{14}$C value of $−386 ± 43\%_{o}$ (3900 ± 770 $\Delta^{14}$C years). This suggests that the old DBC values we observe here may have some contribution derived from sedimentary material desorbed into the dissolved phase. Overall, the sharp isotopic variability within the DBC brings up more questions than answers. However, in absence of further data we cannot reach a conclusion (see Supplementary Discussion for further information). Future field, laboratory and modeling studies to map urban and biomass burning emissions at different locations in the Amazon paired directly with $\Delta^{14}$C aerosol BC, river PBC, sediments and molecular composition directly need to be conducted to fully determine the primary driver of the observed low DBC $\Delta^{14}$C values at these four sites to test these open hypotheses.

**Compositional variability within DBC.** Of the ~12,000 molecular formulae detected in SPE-DOM using FT-ICR-MS, we approximate ~10% (1272 molecular formulae) contain a polycyclic aromatic (PCA) signature (aromaticity index, $A_{410_{\text{nm}}} ≥ 0.67$, C ≥ 15), consistent with DBC-like sources. These PCA molecular formulae are strongly correlated to the DOM-normalized concentrations of B6CA marker compounds ($p ≤ 0.001$, $r = 0.88$),
inducing a common origin from highly condensed compounds of pyrogenic and combustion sources. The weighted-average aromaticity of PCA molecular formulae decreases downstream (Fig. 2) concomitant with a decrease in more condensed BC structures by higher B6CA marker concentrations and B6CA/B5CA ratios (Supplementary Fig. 3, Supplementary Note 1), suggesting downstream loss of more condensed BC structures by photooxidation \(^{48-50}\). The shift to smaller and less polycondensed DBC structures (Supplementary Fig. 6) may be a consequence of preferential removal of polycondensed PCA compounds due to photo-degradation \(^{48}\) or sorptive interaction processes along the river continuum.

The relative increase of the nitrogen content in the polycondensed aromatic molecular formulae (referred to as dissolved black nitrogen), may also suggest increased fossil fuel inputs \(^{31}\).

The contribution of aerosol fossil fuel inputs that likely caused drastic changes in DBC \(^{14}\)C values along the river continuum is not reflected in the DOM molecular formulae. This suggests either similarities in PCA molecular formulae composition despite contrasting isotopic values and sources (i.e. fossil fuel vs. soils) or that the DBC changes are not detectable in bulk DOM molecular formulae \(^{19}\). The latter may be a consequence of restrictions in the analytical window of FT-ICR-MS due to differences in ionization efficiency of different DBC compounds derived from soot and charcoal inputs \(^{19}\).

We also report significantly lower DOC concentrations (2.5±0.2 mg L\(^{-1}\) compared to 4.2±0.9 mg L\(^{-1}\)) than those annual measurements given by Ward et al. \(^{32}\). Our estimate to the marine DBC pool does not include any fossil fuel aerosol inputs, given that they apparently have only local, ephemeral influence on riverine DBC as fossil fuel signals are removed downstream. Thus, we used the modern DBC values at Almeirim to estimate mass balances between river and the marine DBC pools.

The predominately modern DBC \(^{14}\)C signature (~46±15‰) suggests that DBC is not stored in short-term intermediate reservoirs within the Amazon River, at least during low-flow conditions. Using our measurements as the riverine endmember, a mass balance calculation assuming a background marine DBC pool (~945±6‰) and a freshwater river influence of 20% \(^{13}\), yields a \(^{14}\)C value for Amazon plume marine DBC of ~775±35‰, which agrees within error of the measured BC value (~727±44‰; 10,400±1300 \(^{14}\)C years) in ultra-filtered DOC \(^{13}\). This suggests that modern DBC is exported from the Amazon River, regardless of hydrological state, where it contributes to oceanic DBC.

The marine DBC pool is older and smaller than expected given the riverine DBC signature and input rates (23,000 \(^{14}\)C years and only 12–14 Tg \(^{14,53}\)) suggesting that DBC loss by processes, such as UV oxidation and sedimentation, must be important \(^{48}\). For example, we would expect a larger concentration of DBC in the Amazon River plume (3.3±0.8 \(\mu M\)) than observed (0.3 \(\mu M\), BC in ultra-filtered DOC \(^{13}\)). Thus, along with DOM, a portion of DBC may be decomposed along the river–ocean interface by photochemical degradation both at the mouth–plume interface, and where the clearwater tributaries mix \(^{34}\). Yet, not all DBC is removed at this interface because a smaller signal of recalcitrant DOM, including DBC, persists to the river–mouth interface at the Atlantic Ocean \(^{32,54}\). Medeiros et al. (2015) found that dilution was the primary factor influencing DOM variability in the plume (~60% of total variability), while biodegradation, photo-oxidation, and phytoplankton production all played a smaller, but relevant role (~5–8% of variability each) \(^{32}\).

There are at least two marine DBC pools—younger pool cycling on centennial timescales and a stable pool with residence times >10\(^{3}\) year timescales \(^{14,17}\). Another modern and semi-labile DBC pool from rivers may contain recent biosphere-derived BC that has not accumulated on land due to short continental
residence times, as observed here. Our study suggests that DBC is predominately of modern origin in the Amazon River, but some river DBC does survive to accumulate in the ocean. DBC dynamics appear to be decoupled from those of DOC in this study. Labile DBC may be decomposed along the river–ocean continuum, particularly in clearwater tributaries and beyond the plume where photochemical degradation may occur, while contributions from atmospheric (aerosol) BC deposition may be locally important, but rapidly removed or diluted during downstream transport. Future work is needed to understand the underlying causes of this de-coupling, seasonal and interannual variability in isotopic values and fossil fuel aerosol DBC and PBC contributions in the Amazon during high and low flows.

Methods

Sampling and site locations. DBC samples were collected along the Amazon River in November 2015, during the dry season, at 12 sites from a covered area on the boat. We sampled in the dry season because the floodplain extents are the lowest in November and December55. During the dry season, the hydrological connectivity of the Amazon decreases, as overbank flow paths, and lakes serving reservoirs (for flood waters, rainfall, and saturated water table seepage) decrease.

Surface water samples were collected using deployed 2 L Niskin sampling cylinders from a small ship. The Niskin was deployed and flushed with river water before samples were collected. Samples were collected in the middle of the river when possible. Samples were also collected away from boat traffic, and all sampling was conducted in a covered area on the boat. First, all water from the five Niskin deployments were combined in acid-washed container, rinsed with river water before being filled. Samples were filtered using combusted GF/F filters (Whatman, nominal pore size 0.7 µm) to remove POC. The filtrate river water was subsampled into acid-cleaned, pre-combusted amber glass bottles (100 mL), and acidified for later DOC determination and δ13C analysis. Measurements were taken from different stations. To obtain enough DOC for DBC analysis, DOC (ranging from 8.8–10.1) was loaded onto sorbent phase extraction (SPE) cartridges. Briefly, DOC was concentrated according to Dittmar et al56, as DOC was acidified to pH 2 (around 20 mL high purity HCl) and samples were concentrated via SPE on PPL resin (5 g, Agilent 1225U6087 immediately after collection. 10 L of DOC (placed in two acid-cleaned bottles) was loaded on a pre-washed SPE cartridge,consisting of four SPE 2000 cartridges. DOC was loaded onto a manifold of four SPE cartridges to generate four duplicates per site, stored at −25 °C and shipped back to the University of Zurich before elution. Salt was removed by rinsing all SPE cartridges with 0.1 mol L−1 HCl. The PPL cartridges were dried under a gentle stream of N2 after eluting with 30 mL of high purity methanol. The SPE-DBC recovery (compared to DOC concentrations) was 63 ± 5%.

The molecular DOM composition was analyzed from SPE-DOC samples via 1ST FT-ICR-MS (solarIX XR, Bruker Daltonics) with electrospray ionization (ESI) in negative mode as described in ref.57. Briefly, methanol extracts were diluted 1:1 (v/v) with an aqueous solution of 0.1% formic acid (methanol). Samples were collected over 200 scans, with an ion accumulation time of 0.15 s, in a range of −92–2000 m/z. Molecular formulae were calculated for masses with relative intensities above the method detection limit58 allowing C1−13H21−60O5−90N0−50P0. 13C intensity-weighted averages of aromaticity (modified aromaticity index, Amod,Aromaticity, number of atoms per molecular formula (carbon, C, hydrogen, H, oxygen, O, nitrogen, N, sulfur, S, and phosphorus, P), and molar ratios (hydrogen-to-carbon, H/C and oxygen-to-carbon, O/C) were calculated for each sample by considering the peak intensity of each assigned molecular formula as described in ref.57. Principal coordinate analysis (PCoA) was performed on a Bray–Curtis dissimilarity matrix of the normalized peak intensities of PCA molecular formulae (Amod,Aromaticity ≥ 0.67, C ≥ 15) post-hoc fitted with environmental data and molecular parameters using the envfit function of the vegan package69 within the R statistical platform70.

Dissolved black carbon concentrations. DBC was extracted from the SPE-DOM methanol extracts using the BPCAbenzene polycarboxylic acid (BPCA) method53,54. Briefly, SPE-DOM extracts were dried and lyophilized for 24 h. Concentrated nitric acid was added to the sample in a quartz pressure digestion chamber, 1270 C for 8 h to produce BCAs. After digestion, the solution was filtered, lyophilized, and re-dissolved in methanol. BCAs were separated and collected on a preparative liquid chromatography using an Agilent 1209 infinity HPLC system equipped with a 2.7 µm Agilent Poroshell 120 C-18 column. A reverse phase analytical C-18 column (Agilent, 2.7 µm) was used with two mobile phases of pH 2 Milli-Q (1.7% H3PO4) and acetonitrile (99.98% Scharlab, pH C < 0.004). Quantification of BCAs were made from seven-point calibration curves (2–200 ng mL−1) using commercially available BPCA standards including pentaxyl- carboxylic acid (Aldrich S437107) and hexacarboxylic acid (Aldrich M27025) to quantify the BCAs measured from peak areas obtained from the diode array detector (600 nm path length) chromatography. A BC recovery factor of 23.2 ± 0.4% was used for the conversion of BCAs to estimate BCA54,65 for comparison with published values.

Isotopic analysis. For DBC Δ14C analysis, BSCA and B6CA marker compounds were collected in the fraction collector of the HPLC, according to Wiedemeier et al55. BSCA marker compounds, but no B6CA marker compounds, were detected as peaks may also be derived from aromatic compounds of non-combusted origin (e.g. lignin). Dead (Δ14C = 0.003 ± 0.001) and modern (Δ14C = 1.149 ± 0.004) wood charcoal black carbon standards during the entire BPCA procedure were used to evaluate the extraneous, or non-sample blank carbon added to samples during chemical processing66 (Supplementary Fig. 8). BPCAs in the vials were dried under a gentle stream of ultra-high purity nitrogen on a heating plate (70°C) for 3 h, and stored at −25°C until wet-oxidation to CO2, gas for isotopic analysis67,68.

For DOC Δ14C analysis, and DOC concentration measurements we used a wet-chemical oxidation following Lang et al.56 and Wiedemeier et al.55. Briefly, 8 mL of acidified DOC (pH 2, HCl) was transferred into pre-combusted borosilicate glass Exetainer (septa sealed 4.5-ml extainers vials from Labco Limited, UK) vials, frozen and freeze dried overnight (with pre-combusted aluminum covers). Samples were re-dissolved in Milli-Q water to a final volume of 4 mL. Milli-Q blanks, modern and dead standards (succrose and phthalic acid) were used to evaluate the extraneous carbon added during the wet chemical oxidation procedure.

BPCAs and DOC were then converted to CO2 using the wet oxidation procedure for δ14C measurement using a gas ion source AMS53,54,67. Briefly, 30 µg C BPCA samples, 1 mL of purified sodium persulfate and 3 mL of Milli-Q water (for a total volume of 4 mL) were transferred to gas-tight borosilicate Exetainer vials. All samples were purged with ultra-high purity helium (100 mL min−1, 8 min to remove atmospheric CO2), and oxidized to CO2 in a heating block (95°C, 1 h). Radiocarbon measurements of BDC and DOC were made on the Mini Carbon Dating System (MICADAS) Accelerator Mass Spectrometer coupled to a carbonate system modified with a need for larger sample solutions at the ETH Zurich Ion Beam Laboratory. DBC samples were corrected for extraneous carbon according to Hanke et al.68 (Supplementary Fig. 8, Supplementary Table 2) and all samples were corrected using phthalic acid and succrose standards. Radiocarbon is reported in F14Ct here converted to δ13C (%C) using the equation of sampling. For δ13C concentration measurements, the CO2 gas measured by the AMS was normalized to the volume of DOC used (8 mL). DOC concentration measurements were better than 0.03% based on standards. Radiocarbon measurements were corrected for isotopic fractionation via 12C/13C isotopic ratios. 13C data are reported as δ13C values (%C).

B6C of SPE-DOC was also used the wet-oxidation procedure to prepare samples, following Lang et al.68 at ETH Zurich. The SPE-DOC stable organic isotopic composition (δ13C, %PDB) was measured on the headspace CO2 with a Gas Bench II on-line gas preparation and introduction system (Thermo Fisher Scientific, Bremen, Germany). Samples were prepared 1 day before processing for δ13C. The Gas Bench II is equipped with a CTC autosampler (CTC Analytics AG, Zwingen, Switzerland) and coupled to a ConFlo IV interface and a Delta V Plus mass spectrometer (both Thermo Fisher Scientific). For each sample, three reference gas peaks are measured and the sample gas is introduced four times into the mass spectrometer. The blank was 0.2 µg C. Corresponding δ13C values were determined to an accuracy of ±0.1% based on phthalic acid and succrose standards. BPCA δ13C could not be measured because sample sizes were too small.

Gauge measurements and mass balance hydrological approach. We relied on a combination of gauge records, direct measurements during November 2014, and remote sensing to estimate the river discharge in November 2015. Daily gauge data were taken from the network Agência Nacional de Águas (ANA), from the data portal Sistemas de Informação Hidrográfica e do Ambiente (http://www.sinfra.gov.br/hidroweb/publico/medicoes_historicas_abas.jsf). Rio Madeira and Alter do Chão (Rio Tapajós) and Rio Negro were derived from upstream ANA stations. Almeirim was measured directly by ADCP by the TROCAS project71. The remaining stations were done by mass balance approximations (Supplementary Table 2). Calculated DOC loads (Tg year−1) used these discharge measurements in Eq. (1), where DOC is the DOC concentration (g L−1) of 4.2 ± 0.9 mg L−1 made at the river mouth32 multiplied by 1000 (in units of L m−3), 60, 60 min, 24 h, and 365 days, and the discharge Q (m3 s−1) of 203/2001 recorded from Ward et al.53.

| (DOC) (Tg) | (1000) | (60 + 60 × 24 + 365) | Q |
| --- | --- | --- | --- |
| (DOC + B6CA%) | 1000 | (60 + 60 × 24 + 365) | Q |

We calculated DBC flux in Tg year−1 using Eq. (2), using the same DOC concentration (g L−1) and discharge (m3 s−1) from Ward et al.53. To determine the DBC concentration of 0.004 Tg L−1 measured during this time period (2015) is much lower than the average concentration (4.2 ± 0.9 mg L−1) made at the river mouth32. Future constraints on this first estimate can be made
by sampling multiple cross-channel locations, and at multiple depths, during all seasons across several years. Catchment boundaries corresponding to each sample site were determined using a high-resolution (~500 m) stream drainage direction map for the Amazon River basin. Supplementary Fig. 1c was created with ArcMap 10.6, relief shade from Natural Earth (http://www.naturalearthdata.com), catchments derived from CAMREX (Carbon in the Amazon River Experiment) dataset (https://daac.ornl.gov/LBA/guides/CD06_CAMREX.html) and runoff from GSCD2 (https://water.jrc.ec.europa.eu/).

**Land use, urbanization, and fire history.** Land cover (from Modis 2012, at 15 arc minutes resolution https://modis.gsfc.nasa.gov/data/prod/mod12.php), urban areas (Global Rural-Urban Mapping Project GRUMP)36 and burned area (Global Fire Emission Database GFED4s) for each sample was integrated with the cell area (in km²) for the sample. We used an estimate of fire history from satellite observations using a high-resolution (~500 m) stream drainage direction map for the Amazon River basin. Supplementary Fig. 1c. All panels in Supplementary Fig. 4 were created with ArcMap 10.6, with relief shade from Natural Earth dataset (http://www.naturalearthdata.com) and catchments derived from CAMREX (Carbon in the Amazon River Experiment) dataset (https://daac.ornl.gov/LBA/guides/CD06_CAMREX.html).

**Atmospheric deposition of black carbon aerosols.** Aerosol BC deposition was modeled for 2015 in South America using the UK Met Office Hadley Centre Global Environment Model version 2 earth system model (HadGEM2-ES10,75,76,77. Briefly, HadGEM2-ES represents the life cycle of aerosol species, including from fossil fuel and biofuel emissions and from biomass burning. BC is modeled as an internally mixed component of organic aerosols. Processes such as transport, mixing and deposition are represented explicitly through physically based parameterizations that have been developed and constrained using observations. HadGEM2-ES was run with standard climate resolution (1.875° x 1.25°) in the period 2009–2016. Simulations were driven by a custom biomass burning aerosol emission dataset produced for South America as discussed by Jones et al.10,11. Briefly, published carbon stock consumption factors (kg dry matter −1)29 and BC emission factors (g BC/kg dry matter −1)30 were assigned to burned area cells according to land cover type in the MODIS MCD12Q1 dataset (resolution 500 m) enhanced with information on ecoregion12 and agricultural land use13. Biomass burning emissions outside of South America were taken from the Global Fire Emission Dataset (GFED3) version 3.1.383. Emissions of aerosol from fossil fuel sources followed the dataset employed in the Coupled Model Intercomparison Project phase 5 (CMIP5), based on the historical emissions84 with regional updates following the Representative Concentration Pathway (RCP) 8.585,86. The deposition rates from HadGEM2-ES were interpolated to a 0.05° grid using an empirical Bayesian kriging operation performed in the ArcGIS Geostatistical Analyst toolbox. The approach and performance of the kriging process are reported by Jones et al.10 and summarized in the supplementary material. Rates of biomass and fossil fuel-derived aerosol deposition (kg C km−2 year −1) were averaged within the upstream catchments of all sampling locations on the river network (Supplementary Fig. 4, Supplementary Table 3).

Deposition rates from HadGEM2-ES were transferred to higher-resolution grids using an empirical Bayesian kriging operation performed with the ArcGIS Geostatistical Analyst toolbox. The process was completed using a log-empirical transformation, Whittle de-trended semivariogram, and search radius of 4°. The normalized mean error of the predictions from the kriging operation, when compared to the data from the native HadGEM2-ES grid, was 0.7% for total fossil fuel BC aerosol and 1.7% for biomass burning BC aerosol deposition during 2009–2016. Predictions were mapped to a 0.05° grid. The normalized root mean square error of the predictions from the kriging operation, when compared to the input data from the native HadGEM2-ES, was 5% for total fossil fuel BC aerosol and 15% for biomass burning BC aerosol deposition during 2009–2016.

Although the prevailing wind direction in Amazonia is from East to West, changes in wind direction provide an opportunity for aerosols emitted in southern Brazil to be transported northwards and deposited in the Amazon Basin13. This influences the distribution of BC aerosol deposition across central Brazil and leads to raised deposition rates in the south of the Amazon relative to northern regions that are further from the main population centers of the country. There may be an imprint of sources in southeast Brazil on the background deposition rates of the northern export of BC from cities.

Data availability

The data set will be on the PANGAEA data (www.pangaea.de) repository following publication under the username alyshacoppola (connected to the ORCIDID https://orcid.org/0000-0002-9982-2786). In addition, all data are available from the corresponding author on request. Please contact Alysha Inez Coppola (Alysha.coppola@geo.uzh.ch, or at http://alyshainezcoppola.strikingly.com/) for correspondence and material requests.

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Author contributions
A.I.C., M.W.I.S., T.D. and T.I.E. led efforts in devising the study objectives and design of the work. A.I.C. conducted concentration and isotopic measurements of DOC and DBC, analyzed data, interpreted the data and wrote the paper. G.S. collected samples. B.N.R. coordinated traveling logistics to Brazil. N.H. provided support and quality control with DBC and DOC 14C measurements and radiocarbon corrections. S.A. provided input with discussions. M.S. and T.D. added FT-ICR-MS measurements, associated data analyses and scientific interpretation. D.V., J.E.R. and N.D.W. provided support for hydrology context. N.D.W. and J.E.R. provided river gauge data, hydrological expertise, input on the interpretation of the data and substantially revised the manuscript. D.V. provided discharge, land use, and urbanization catchment-specific data. M.W.J. provided outputs of atmospheric BC deposition from the HadGEM2-ES model and input for the interpretation of the data. All authors provided comments in constructing the final version of the manuscript.

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