

LETTERS

Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers

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Rivers are generally supersaturated with respect to carbon dioxide, resulting in large gas evasion fluxes that can be a significant component of regional net carbon budgets^{1,2}. Amazonian rivers were recently shown to outgas more than ten times the amount of carbon exported to the ocean in the form of total organic carbon or dissolved inorganic carbon¹. High carbon dioxide concentrations in rivers originate largely from *in situ* respiration of organic carbon^{1–3}, but little agreement exists about the sources or turnover times of this carbon^{2,4,5}. Here we present results of an extensive survey of the carbon isotope composition (¹³C and ¹⁴C) of dissolved inorganic carbon and three size-fractions of organic carbon across the Amazonian river system. We find that respiration of contemporary organic matter (less than five years old) originating on land and near rivers is the dominant source of excess carbon dioxide that drives outgassing in medium to large rivers, although we find that bulk organic carbon fractions transported by these rivers range from tens to thousands of years in age. We therefore suggest that a small, rapidly cycling pool of organic carbon is responsible for the large carbon fluxes from land to water to atmosphere in the humid tropics.

Riverine CO₂ concentrations in Amazonian lowlands are 5–30 times supersaturated with respect to atmospheric equilibrium¹; such conditions may be prevalent throughout the humid tropics. *In situ*

respiration is the primary source of CO₂ sustaining supersaturation in rivers, although inputs from groundwater supersaturated by soil respiration can be important in small systems and from submerged root respiration in floodplain-influenced systems^{1–3,6–8}. Although air–water gas exchange is a bi-directional process, atmospheric CO₂ invasion has a negligible role compared to the large CO₂ evasion fluxes, except at low supersaturation^{2,3,6,7}. ¹³C and ¹⁴C isotopes can provide constraints on sources and turnover times of organic carbon fuelling river respiration, but no previous tropical study has used a dual-isotope approach to address these questions. Studies in temperate eastern USA provide contrasting findings. In the Hudson River, up to 70% of the centuries-old terrestrial organic carbon entering the river is respired in transit, and the average age of riverine organic carbon decreases downstream². However, the youngest components of dissolved organic carbon (DOC) are preferentially respired in the York River⁵, and modern dissolved inorganic carbon (DIC) in the Parker River may be explained by respiration of young DOC produced within the estuary⁴. Documenting key patterns and controls on CO₂ sources in diverse ecosystems is critical to advance our understanding of CO₂ outgassing from rivers and its contribution to regional net carbon budgets.

To identify dominant sources and turnover times of riverine carbon throughout the Amazon basin, we analysed ¹⁴C and ¹³C of

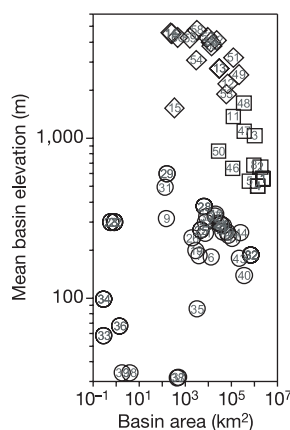
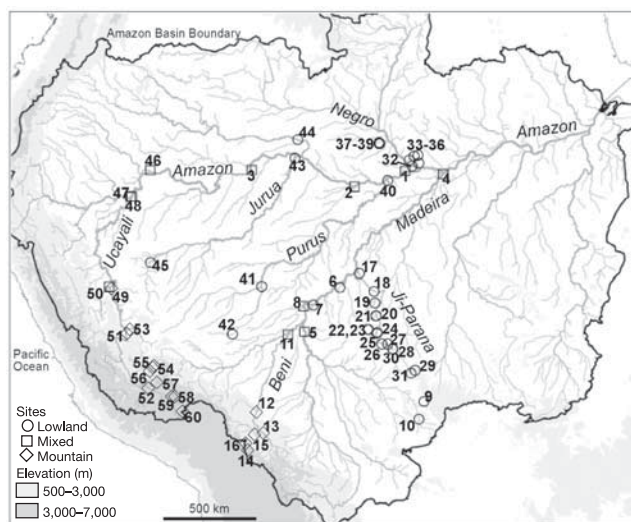


Figure 1 | Amazon basin and river sites sampled for carbon isotopes. We used GTOPO30 elevation²⁸ and a regional river network data set²⁹ to categorize each site by topography according to the percentage of the drainage area above 1,000 m elevation: mountain (diamond), $\geq 50\%$ (16 sites); mixed (square), $\geq 10\%$ (11 sites); and lowland (circle), $< 10\%$ (33 sites). Mountain sites are found only in the Andean Cordillera, while mixed sites are large rivers draining both mountain and lowland areas. Site numbers are displayed. Distribution of sites by drainage area (river size) and mean basin elevation is shown. Additional information is in Supplementary Table S1.

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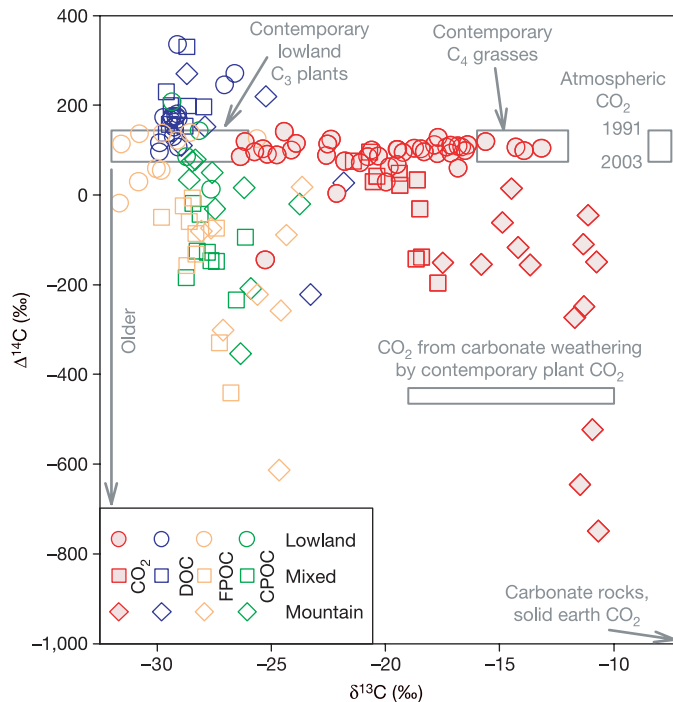


Figure 2 | Distribution of ^{14}C and ^{13}C isotopes. Lower $\Delta^{14}\text{C}$ values indicate older carbon. Symbol shapes are as in Fig. 1; Red (shaded), blue, orange, and green symbols represent CO_2 , DOC, FPOC and CPOC respectively. Isotopic ranges of carbon sources are shown by grey boxes. Plant $\delta^{13}\text{C}$ ranges from -32‰ to -26‰ for lowland plant material fixed via the C_3 photosynthetic pathway dominant among plants, to -16‰ to -12‰ for tropical C_4 grasses^{24,30}. Phytoplankton take up H_2CO_3 and impose ^{13}C fractionations of $\sim -20\text{‰}$, leading to biomass $\delta^{13}\text{C}$ values of -32 to -45‰ in mixed and lowland rivers^{8,10,30}, beyond the range found in our lowland organic carbon and CO_2 observations. Carbonate rocks and CO_2 from solid earth degassing are ^{14}C -free ($\Delta^{14}\text{C} = -1,000\text{‰}$; ref. 10). $\delta^{13}\text{C}$ of carbonate rocks is $\sim 0\text{‰}$; degassed CO_2 ranges from -6‰ for volcanic to 10‰ for metamorphic sources¹⁰. The carbonate weathering region represents CO_2 in equilibrium with HCO_3^- resulting from weathering by CO_2 derived from respired, contemporary C_3 or C_4 plant material¹⁰.

DIC, DOC, and suspended fine and coarse particulate organic carbon fractions (FPOC and CPOC), grouping sites topographically (Fig. 1). This survey represents the most extensive dual carbon isotope inventory so far in a large, diverse basin, and the first ^{14}C analysis of DIC in Amazonian rivers. It complements but greatly exceeds previous carbon isotope surveys^{5,7,9}, enabling an integrated assessment of carbon cycling.

DIC is composed of dissolved CO_2 and bicarbonate and carbonate ions in pH-dependent chemical and isotopic equilibrium¹⁰. In studies of marine and homogeneous river systems, where pH is nearly uniform, it has been the convention to report the isotopic composition of total DIC, which is directly measured. However, when the turnover of DIC by CO_2 fluxes is as rapid as in many of these tropical rivers, a quasi-steady-state condition constrains the isotopic composition of outputs by CO_2 outgassing to equal that of inputs by CO_2 production from respiration^{7,8}. In response to this pre-eminence of CO_2 sources and the large range of observed pH (3.8 to 8.7), we base our analysis on the calculated isotopic values of CO_2 gas in equilibrium with DIC, avoiding the need to discuss the isotopic variation in ^{13}C of DIC caused by changes in pH alone (see Methods and Supplementary Discussion). We report measured $\delta^{13}\text{C}$ -DIC in Supplementary Table S3. For ^{14}C we use $\Delta^{14}\text{C}$ notation, which includes a correction for ^{13}C such that $\Delta^{14}\text{C}$ of CO_2 and DIC are equal at any pH (ref. 11).

CO_2 in nearly all lowland rivers had a $\Delta^{14}\text{C}$ signature bound within the range of local atmospheric $\Delta^{14}\text{C}$ - CO_2 estimated for the lowland

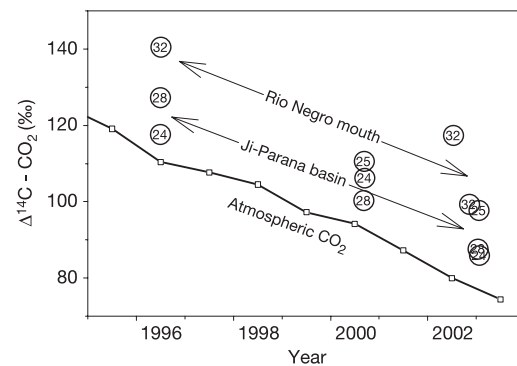


Figure 3 | Temporal evolution of ^{14}C - CO_2 at four lowland sites from medium to large rivers in the Ji-Parana basin and Rio Negro. Legend is as in Fig. 1. These sites drain continental shields and were analysed for ^{14}C -DIC 2–3 times between 1996 and 2003.

DIC sampling period (1996–2003, Fig. 2; Methods). Testing of thermonuclear bombs resulted in a large increase in atmospheric ^{14}C , reaching a peak in the late 1960s and steadily decreasing afterwards^{12,13}. Continual changes in atmospheric radiocarbon content means that we need to assess the mean age for modern carbon samples by the offset between riverine $\Delta^{14}\text{C}$ and the sampling year's annual mean atmospheric $\Delta^{14}\text{C}$ - CO_2 (ref. 14). From 1996 to 2003, $\Delta^{14}\text{C}$ - CO_2 at four supersaturated sites in medium to large lowland rivers decreased by 32–42‰, equivalent to the annually averaged atmospheric $\Delta^{14}\text{C}$ - CO_2 decrease of 36‰ ($-5.6 \pm 2.3\text{‰ yr}^{-1}$) (Fig. 3). Thus, atmospheric offsets remained roughly constant, suggesting constant respiratory organic carbon turnover times for each basin. The range of these offsets suggests rapid turnover of photosynthetically sequestered atmospheric CO_2 ; outgassed CO_2 is derived from atmospheric CO_2 sequestered within <4 yr in the medium-sized Ji-Parana basin ($\Delta^{14}\text{C}$ offsets: $14 \pm 6\text{‰}$, $n = 8$) and 4–7 yr previously at the Rio Negro mouth ($\Delta^{14}\text{C}$ offsets: $29 \pm 9\text{‰}$, $n = 3$).

Rapid carbon turnover is probably widespread across Amazonian rivers. However, DIC from carbonate mineral weathering, with its typically enriched $\delta^{13}\text{C}$ and highly depleted $\Delta^{14}\text{C}$ (Fig. 2), commonly obscures the influence of respiration. To focus on sites where DIC originates largely as respired CO_2 , we identified sites draining substantial carbonate lithologies through their inorganic solute composition¹⁵ (Methods and Supplementary Discussion). Only lowland sites had little potential for direct, substantial carbonate contributions to DIC (38 samples in 25 lowland sites, Supplementary Fig. S1). Observations in carbonate-free lowlands contained supersaturated, predominantly contemporary CO_2 (Table 1, Fig. 2) and could be divided into two groups based on atmospheric $\Delta^{14}\text{C}$ - CO_2 offsets. The largest group (32 samples from 21 sites) encompassed first-order streams and large rivers carrying contemporary CO_2 with atmospheric $\Delta^{14}\text{C}$ - CO_2 offsets ranging from -3 to 38‰ ($14 \pm 11\text{‰}$), indicating a mean CO_2 age of approximately 2 yr (and <5 yr in 87% of the observations); enriched $\delta^{13}\text{C}$ - CO_2 in the Ji-Parana region ($-17.5 \pm 2.2\text{‰}$, $n = 21$) suggest a C_4 plant influence. The second group of carbonate-free observations consisted of six samples in three small and two medium-sized rivers in the Ji-Parana region having considerable negative $\Delta^{14}\text{C}$ offsets ($-32 \pm 21\text{‰}$), indicating a mean source age of several decades. Relatively depleted $\delta^{13}\text{C}$ - CO_2 values ($-20.0 \pm 1.7\text{‰}$) compared to Ji-Parana rivers from the first group suggest an influence from groundwater influx of aged soil CO_2 with a significant terrestrial C_3 plant source relative to other rivers in that highly deforested region. In both groups, respiration of submerged tree and grass roots can be excluded as important CO_2 sources because our data set was predominantly collected during low water.

Isotopic signatures in carbonate-free lowland rivers demonstrate

Table 1 | ^{14}C and ^{13}C isotopic composition for each carbon fraction

Site	CO_2		DIC	DOC		FPOC		CPOC	
	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$
Mountain	-240 ± 233 (14)	-12.9 ± 2.2	-4.9 ± 2.7	94 ± 176 (6)	-26.0 ± 3.0	-202 ± 198 (8)	-25.7 ± 1.7	-39 ± 146 (9)	-27.0 ± 1.6
Mixed	-14 ± 99 (11)	-19.4 ± 1.2	-14.2 ± 2.9	196 ± 59 (9)	-29.0 ± 0.6	-135 ± 141 (10)	-28.2 ± 0.9	-124 ± 66 (9)	-27.7 ± 0.9
Lowland	89 ± 44 (43)	-20.1 ± 3.6	-17.0 ± 5.9	177 ± 64 (15)	-29.0 ± 0.9	90 ± 55 (10)	-29.8 ± 1.8	112 ± 83 (4)	-28.5 ± 0.7
Carbonate-free	98 ± 20 (38)	-19.8 ± 3.7	-17.1 ± 6.2	175 ± 67 (11)	-29.1 ± 0.7	129 ± 10 (6)	-29.2 ± 2.1	121 ± 100 (3)	-28.4 ± 0.9

All carbonate-free sites are in the lowlands. Data are reported as mean \pm s.d. (number of samples), in per mil (‰). The number of samples for ^{13}C is the same as that shown for ^{14}C . The number of samples for DIC is the same as for CO_2 .

that CO_2 originated from heterotrophic respiration of contemporary C_3 and C_4 organic carbon (Fig. 2), yet CO_2 appears isotopically distinct from the associated bulk organic carbon load. All organic carbon fractions were considerably depleted in ^{13}C relative to CO_2 (Table 1, Fig. 2 and Supplementary Discussion). Furthermore, DOC was generally older than CO_2 , FPOC showed a bimodal distribution with ages similar to CO_2 in non-turbid rivers and older carbon in high-sediment rivers, and CPOC exhibited a wide range of ages. We conclude that *in situ* respiration is fuelled largely by an unmeasured organic subfraction that cycles over a period of less than about five years and typically makes up a small component of the riverine organic carbon load. ^{13}C enrichment of CO_2 relative to organic carbon indicates that this missing organic carbon source fuelling river respiration is disproportionately composed of river-corridor and floodplain C_4 grasses, which may be intrinsically more biodegradable^{7,16}.

Mountain and mixed rivers contain older dissolved CO_2 ($\Delta^{14}\text{C} = -749$ to 96‰) with clear carbonate mineral dissolution signatures. However, observed CO_2 supersaturation in these rivers must be generated by CO_2 sources other than carbonates (Supplementary Discussion). These CO_2 fluxes gradually flush out geologically derived DIC, replacing its isotopic signature. Indeed, a CO_2 trend of increasing $\Delta^{14}\text{C}$ and decreasing $\delta^{13}\text{C}$ is observed from the Peruvian Andes to the Amazon mainstem, with $\Delta^{14}\text{C}$ - CO_2 reaching 30–76‰ in the central mainstem, still below atmospheric levels (Fig. 2). Along the Ucayali and western-central mainstem, inputs of probably young CO_2 from *in situ* respiration and lowland tributaries drive large evasion fluxes of ^{14}C -depleted CO_2 derived from carbonate dissolution. In the more arid Ucayali mountain headwaters, highly depleted $\Delta^{14}\text{C}$ - CO_2 ($< -500\text{‰}$), enriched $\delta^{13}\text{C}$ - CO_2 ($\sim -11\text{‰}$), and considerable CO_2 supersaturation point to solid-earth degassing as a large dry-season CO_2 source, as documented in other tectonically active mountain ranges¹⁷.

Control of respiration by a small fraction of organic carbon does not imply that bulk organic carbon is unreactive. On the contrary, measured organic carbon fractions appear to be mineralized throughout the river system. The strongest evidence is that FPOC generally becomes younger and more depleted in ^{13}C downstream from mountain sites (Fig. 2, Table 1), where all organic carbon fractions mirror the high-altitude ^{13}C enrichment in plants of $\sim 1\text{‰}$ per 1,000 m elevation^{18,19}. Within 1,000 km from mountain headwaters, $\delta^{13}\text{C}$ -FPOC becomes nearly indistinguishable from lowland carbon. With FPOC tightly associated with mineral surfaces^{19,20}, no downstream changes in the ratio of FPOC to fine suspended sediment concentration (0.8–1.5%, Supplementary Table S2), and $>85\%$ of the Amazon mainstem mineral load ultimately originating in the Andes²¹, this observation implies nearly complete mineralization of old Andean FPOC and replacement with new lowland organic carbon during transit within the river or during long-term floodplain storage⁷. Even if all FPOC leaving the Andes were mineralized within the river channel, the resulting CO_2 flux would be 1/40 of total CO_2 evasion fluxes¹, hardly affecting the isotopic signature of CO_2 . CPOC and DOC descending from the Andes follow identical trends of gradual ^{13}C depletion to lowland values (Fig. 2), although without a conservative mineral carrier as for FPOC, simple dilution by lowland

organic carbon cannot be ruled out. DOC is generally modern (<50 yr old) everywhere, demonstrating that old DOC does not escape from the basin.

Isotopic evidence for dominance of respiration fluxes by a rapidly cycling, typically small fraction of total organic carbon confirms the hypothesis previously posited for the Amazon mainstem from respiration^{8,16}, ^{13}C (ref. 7), and mass balance studies^{1,7}. It implies that gradual consumption or replacement of old fractions in bulk organic carbon can occur in parallel with high rates of respiration of a highly labile organic carbon subfraction. This paradigm has been advanced for tropical and temperate soils²², providing strong conceptual linkage between aquatic and terrestrial carbon dynamics²³. It suggests that deforestation in the Amazon leads to immediate changes to the organic sources of riverine heterotrophic energy and argues that such impact is not inconsistent with apparent lag times observed in bulk organic carbon composition²⁴. Although the mechanism proposed here may be widespread across the humid tropics¹ and appears consistent with radiocarbon observations from temperate rivers^{2,4,5}, it is probable that certain river systems, such as those draining eroding peats, are fuelled by old organic carbon. Explicit accounting of isotopic signatures of CO_2 outgassing from different river types may be required to accurately interpret isotope-based regional tropospheric CO_2 inversions.

METHODS

Sample collection and analysis. Samples analysed for ^{14}C -DIC were collected between 1991 and 2003, whereas organic-carbon ^{14}C samples are from 1995–1996. All samples were preserved with mercuric chloride immediately after collection at mid-depth from the deepest section of the channel. DIC samples were prepared as described in ref. 7 and stored in tightly capped glass bottles for up to 24 months; in the lab, the top half of the bottle was drawn into a vacuum line (eliminating particles) and stripped of CO_2 after acidification⁷. CPOC (63–2,000 μm) was isolated either by sieving or with a plankton net, FPOC (0.1–63 μm) by tangential flow microfiltration, and DOC (1,000 atomic mass units to 0.1 μm) by tangential flow ultrafiltration¹⁹. Final concentration and drying was achieved by centrifugal evaporation or freeze drying¹⁹, and the dried powder stored in the dark at ambient temperature for up to 6 yr. Ultrafiltration yields ranged from 40% in the Andes to 80% in the lowlands^{19,25}. Organic samples were combusted as in ref. 7.

Cryogenically purified CO_2 from organic carbon and DIC was analysed for stable isotope and radiocarbon by dual-inlet Isotope Ratio Mass Spectrometry and Accelerator Mass Spectrometry (AMS)²⁶, respectively; $>90\%$ of ^{14}C analyses were carried out at the Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry, and the rest at the University of Arizona AMS Laboratory. CO_2 extracted from DIC was stored in sealed glass ampoules for up to 8 yr. ^{13}C is reported in $\delta^{13}\text{C}$ notation versus the PDB standard¹⁰. Radiocarbon values are reported as age-corrected $\Delta^{14}\text{C}$ adjusted for sample $\delta^{13}\text{C}$ (ref. 11); carbon is defined as modern when it originates after 1890 (ref. 11). Absolute $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analysis errors (1σ) are typically $<6\text{‰}$ and $<0.2\text{‰}$, respectively. Isotopes for all carbon fractions were not always analysed at each site. Additional analyses include pH, major ions, alkalinity and total carbon fraction concentrations (Supplementary Table S2). Major ions were quantified by ion chromatography. Alkalinity was measured by Gran titration, or estimated from temperature, pH and DIC when not measured. CO_2 concentrations were either measured directly by headspace equilibration (A.K.A., manuscript in preparation) or estimated from temperature, pressure, pH, DIC, and alkalinity. Sampling sites are grouped by topographic characteristics (Fig. 1). In the discussion, grouped observations are reported as mean \pm standard deviation

(number of samples) and compared only qualitatively owing to low number of samples per group.

Isotopic calculation of CO₂ gas in equilibrium with DIC. DIC is composed of dissolved carbonate species (H₂CO₃(aq), HCO₃⁻(aq), and CO₃²⁻(aq)) in temperature- and pH-dependent equilibrium with one another. Isotopic fractionation occurs during conversion from one species to another and dissolution of CO₂ gas¹⁰; CO₂ gas is hereafter referred to as simply CO₂. δ¹³C of CO₂ gas in equilibrium with DIC is calculated from measured δ¹³C-DIC and pH, and from temperature-dependent isotopic equilibrium fractionations between CO₂ and DIC species^{10,27}. pH can vary dramatically in a large basin and is largely a function of weathering lithologies (Supplementary Table S2). Δ¹⁴C is defined to be insensitive to mass-dependent fractionation¹¹; as a result Δ¹⁴C-CO₂ = Δ¹⁴C-DIC. Although a focus on isotopes of CO₂ instead of DIC is unconventional, it yields more straightforward assessments of the impact of respiration and air–water gas exchange on DIC across geochemically diverse rivers.

Radiocarbon trends in atmospheric CO₂. Measurements from Schauinsland Station, Germany, were used to characterize atmospheric Δ¹⁴C-CO₂ from 1991 to 2003 (refs 12, 14). The uncharacterized effect of seasonal and short-term atmospheric variability is minimized by comparing river ¹⁴C only against time-weighted annual means¹⁴. A constant +8‰ offset was added to Schauinsland annual means to account for a 5‰ depletion from regional fossil-fuel emissions at Schauinsland relative to the well-mixed, mid-latitude European troposphere (Jungfraujoch site¹⁴), and approximately 3‰ further depletion at the mid-latitude troposphere relative to tropical South America^{12,13}. Atmospheric Δ¹⁴C-CO₂ composition within the Amazon basin is unknown, but seasonal and regional variability may be as large as 10‰ (ref. 13). Riverine Δ¹⁴C values within 5‰ of our estimated atmospheric annual average for the sampling year probably represent carbon turnover times of one year or less. Mid-1990s tropospheric CO₂ can be characterized by a partial pressure (p_{CO₂}) of 370 p.p.m. and δ¹³C composition of -8‰ (refs 10, 12, 13).

Carbonate mineral dissolution and DIC. Carbonate weathering is a source of high DIC concentrations enriched in δ¹³C and highly depleted in Δ¹⁴C when, as is most common, it involves the dissolution of ¹⁴C-dead carbonate minerals (CaCO₃(s)) by carbonic acid (H₂CO₃(aq)) from respired modern plant matter in soils (Fig. 2 and Supplementary Discussion). We used alkalinity and dissolved inorganic cation composition to identify sites draining substantial carbonate lithologies¹⁵ (Supplementary Fig. S1). Although exchange with the atmosphere or input of respired CO₂ may erase the isotopic signature of carbonate dissolution, we identified and excluded carbonate-influenced sites in order to focus unambiguously on the isotopic relationship between organic carbon and DIC.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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