

Old aquatic CO₂ in the Amazon contributes to aquatic emissions

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Old carbon contributes to aquatic emissions of carbon dioxide in the Amazon

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Abstract

Knowing the rate that carbon is cycled is crucial to understanding the dynamics of carbon transfer pathways. Recent technical developments now support measurement of the ^{14}C age of evaded CO_2 from fluvial systems, which provides an important “fingerprint” of the source of C. Here we report the first direct measurements of the ^{14}C age of effluxed CO_2 from two small streams and two rivers within the Western Amazonian Basin. The rate of degassing and hydrochemical controls on degassing are also considered. We observe that CO_2 efflux from all systems except the seasonal small stream was ^{14}C -depleted relative to the contemporary atmosphere, indicating a contribution from “old” carbon fixed before ~ 1955 AD. Further, “old” CO_2 was effluxed from the perennial stream in the rainforest, unexpected as here connectivity with the contemporary C cycle is likely greatest. The effluxed gas represents all sources of CO_2 in the aquatic system and thus we used end member analysis to identify the relative inputs of fossil, modern and intermediately-aged C. The most likely solutions indicated a contribution from fossil carbon sources of between 3 and 9 % which we interpret as being derived from carbonate weathering. This is significant as the currently observed intensification of weather has the potential to increase the future release of old carbon, which can be subsequently degassed to the atmosphere, and so render older, slower C cycles faster. Thus ^{14}C fingerprinting of evaded CO_2 provides understanding essential to more accurately model the carbon cycle in the Amazon Basin.

1 Introduction

Aquatic CO_2 outgassing from the Amazon Basin has been estimated as 0.5 GtCyr^{-1} (Richey et al., 2002), equivalent to emissions from South American deforestation (Gloor et al., 2012). When revised gas transfer velocity estimates have been applied to this basin-wide upscaling, the aquatic efflux is likely to be considerably higher, up to $\sim 50\text{--}70\%$ greater in the Amazon main tributaries alone (Alin et al., 2011). The aquatic efflux

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is attributed to rapidly-cycled ecosystem-derived carbon (Richey et al., 2002; Mayorga et al., 2005), rather than slow release from older reservoirs. Recently, in-situ decomposition of lignin (Ward et al., 2013) or CO₂ released by wetland plants (Abril et al., 2013) have been advocated as sources of the effluxed carbon dioxide. However, in samples from mountainous or mixed sites, old carbon can be present (Mayorga et al., 2005) and some fossil particulate carbon can persist into the lowland Amazon (Clark et al., 2013). Young riverine efflux can be considered as internal recycling within the basin (Gloor et al., 2012). However, if the efflux includes oxidation of fossil carbon this constitutes an input of stored CO₂ to the atmosphere (Berner, 2003), and requires adjustment of carbon balance models. Climate change impact models (Huntingford et al., 2013; Bony et al., 2013) do not separate weathering-derived carbon or include rates of carbon movement. To accurately model the response of important carbon landscapes such as the Amazon Basin, to land use and climatic change, the efficacy of slower C cycles and the source of this C must be fully understood.

The C load to a river and its CO₂ efflux can be derived from multiple sources. For example fossil carbon can come from weathering of carbonate and sedimentary rocks (Copard et al., 2007) releasing inorganic and organic carbon, respectively. These sources are millions of years old and “radiocarbon dead” (i.e. so old that the radiocarbon they once contained has decayed to background levels). Younger, but still old carbon could be derived from soil carbon stocks, including black carbon formed in fires (McMichael et al., 2012), from peat deposits (Householder et al., 2012) or erosion of river bank sediments (Rigsby et al., 2009). These aged fractions are mixed with the inputs from contemporaneous vegetation either as dissolved organic carbon (DOC), particulate organic carbon (POC) or dissolved inorganic carbon (DIC).

Fine particulate organic carbon (FPOC < 63 μm) is mainly derived from soils and coarse particulate organic carbon (CPOC, > 63 μm) from plant material (Hedges et al., 1986a, 2000; Townsend-Small et al., 2005), the former being older due to aging in soil (Hedges et al., 1986a). In addition to ecosystem-derived carbon, POC may include kerogen from sedimentary rocks. Once the mineral protected fossil organic matter is

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portant in the Amazon Basin, and thus we need to understand carbon fluxes and the related reservoir residence times. Here, we present the results of a study to investigate controls on the rate of CO₂ efflux through isotopic and hydrochemical measurements. Although ¹⁴C-DIC has been measured in large scale sampling of different parts of the Amazonian Basin (Mayorga et al., 2005), our study is the first to directly measure the age of effluxed CO₂ from the fluvial systems of different sizes in the Amazon.

2 Materials and methods

2.1 Study site

Four drainage systems in the more fertile (Quesada et al., 2010) western part of the Amazon Basin in Tambopata National Reserve, Madre de Dios region, Peru (Fig. 1) were studied. These drainage systems comprised rivers, La Torre and Tambopata, and two small streams draining the local forest area. According to the Amazonian river types classification (Sioli, 1984) the studied rivers are of the white water type that are characterized by high suspended sediment load. One small stream, Main Trail, existed only in the wet season, whereas the other, New Colpita, was perennially present. The seasonality of the former was attributed to the absence of groundwater contribution in this stream. The catchment areas of the small streams were analysed using LiDAR data (Hill et al., 2011; Boyd et al., 2013) and the rivers using USGS ASTER GDEM data.

The climate is warm (average temperature 26 °C) and humid (average rainfall 1600–2400 mm). Elevation above sea level is 210 m. The soils in the area are classed as Haplic Cambisols (Inceptisols in the US Soil Taxonomy) and vary from well-drained to swampy (Quesada et al., 2011). The site has a long history of biomass monitoring within the RAINFOR project (e.g. Malhi et al., 2013) and since 2011 The Ramiro Chacon – SAGES eddy-covariance flux tower has been used to monitor CO₂ and methane flux of the forest ecosystem.

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2.2 Sample analyses

From February 2011–October 2012, pH (Troll 9500, In-Situ Inc.) and stage height (2150Flow module, ISCO Inc.) were monitored in these drainage systems. The small streams were logged continuously at 15 min intervals and campaigns of spot measurements were carried out in the rivers. These systems were regularly sampled for [DIC], $\delta^{13}\text{C}_{\text{DIC}}$ (analysed on a Thermo-Fisher-Scientific Gas Bench/Delta V Plus), DOC (Thermalox TOC 2020, Analytical Sciences), POC (measured by loss on ignition) and CO_2 evasion (floating chamber connected to an infrared gas analyser, Li-840A, LI-COR) across different seasons. Calcium concentration (measured by AAS, Perkin Elmer Analyst 400) was determined on samples collected in 2012. Silicate weathering percentage values were calculated from the bicarbonate concentration data (derived from [DIC] and pH) using the typical values of carbonate and sandstone lithologies (Meybeck, 1987). Evasion CO_2 samples were collected during April–May 2012 for measurement of $\delta^{13}\text{C}$ and ^{14}C content. Each drainage system was sampled three times targeting different stage heights to assess hydrological controls on the ^{14}C content and $\delta^{13}\text{C}$ of the evasion. Evaded fluvial CO_2 was accumulated in a floating chamber (Billett et al., 2006). The chamber was first scrubbed free of atmospheric CO_2 using a soda lime trap, then CO_2 allowed to accumulate in the headspace to yield sufficient material for analysis. In our systems the required accumulation time ranged from 5 to 50 min depending on the sampling point and hydrological conditions. Finally the gas from the headspace was trapped into a cartridge containing 13X zeolite molecular sieve (Hardie et al., 2005). In the laboratory the CO_2 was released by heating the molecular sieve (500°C), the gas purified cryogenically and divided into volumes allocated for $\delta^{13}\text{C}$ and ^{14}C analysis. $\delta^{13}\text{C}$ was measured on a Thermo-Fisher-Scientific Delta V mass spectrometer. The sample fraction for ^{14}C analysis was graphitized and analyzed by accelerator mass spectrometry at the Scottish Universities Environmental Research Centre. Following convention, the ^{14}C results were normalized to $\delta^{13}\text{C} -25\text{‰}$ to account for mass dependent fractionation and the results expressed as % modern and

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conventional radiocarbon age (in yr BP; where 0BP = 1950 AD). % modern and radiocarbon age are related by the following equation:

$$\text{Conventional radiocarbon age (yr BP)} = -8033 \times \text{LN} (\% \text{ modern } 100^{-1}) \quad (1)$$

Radiocarbon concentrations exceeding 100 % modern cannot be assigned a conventional radiocarbon age, but indicate the presence of bomb-¹⁴C and therefore a contribution from carbon fixed from the atmosphere post ~ 1957 AD (when atmospheric ¹⁴CO₂ first exceeded 100 % modern, Levin et al., 2008). In contrast radiocarbon concentrations below 100 % modern unambiguously indicate the presence of pre-bomb (“old”) carbon.

2.3 End member mixing analysis to assign ages to CO₂ efflux

To estimate the source of the effluxed CO₂ we applied the SIAR (Stable Isotope Analysis in R) package developed for stable isotope end-member analysis (Parnell et al., 2010). The DIC pool behaves conservatively within the pH range from 4.6–7.2 (Polse-naere and Abril, 2012), with addition or subtraction of CO₂ only influencing the CO₂ and total DIC concentration, but with no alteration of the bicarbonate pool. However the fractions of DIC pool are open to isotopic exchange. Thus although we have measurement of $\delta^{13}\text{C}_{\text{DIC}}$, outgassing changes the isotopic signatures of all constituents as well as the DIC pool as a whole (Polse-naere and Abril, 2012; Doctor et al., 2008). The adulteration of the $\delta^{13}\text{C}_{\text{DIC}}$ signature can undermine the use of a dual carbon isotope approach for partitioning the carbon sources of CO₂ evasion, although partitioning by hydrological conditions still reveals changing dominance of sources (Waldron et al., 2007). Therefore only the ¹⁴C values were used in SIAR analysis. We chose this approach as the SIAR (Parnell et al., 2010) Bayesian mixing model allows incorporation of uncertainties in the source composition estimates and therefore, mean age estimate and the ranges (as represented by the standard deviation), could be used in the model to derive the potential contributions of mixtures of carbon pools of different ages.

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The ^{14}C age range is constrained by the end members of organic matter containing recently-fixed CO_2 and fossil contributions from weathering of sedimentary rock containing kerogen (Bouchez et al., 2010; Copard et al., 2007) or carbonate rocks, both of which are millions of years in age and hence devoid of radiocarbon. In addition to these end members, carbon aged from hundred years to some millennia could be derived from a variety of sources. We identified the end member components and used isotopic signatures from literature for the mixing model (Table 1) based on the following understanding.

The young end-member: atmospheric nuclear weapons testing in the 1950s–1960s released ^{14}C (bomb- ^{14}C) into the atmosphere resulting in plant material fixed since the mid-1950s having ^{14}C concentrations > 100% modern. Similarly, soil organic matter derived from plants grown since the mid-1950s also has a ^{14}C concentration > 100% modern. Bomb- ^{14}C has also been detected in coarse suspended particulate organic matter (123% modern), whereas it was a very minor component in fine SPOM (102% modern, sampled in 1983) (Hedges et al., 1986b). In Rio Negro and mainstem Amazon, humic and fulvic acid ^{14}C concentrations were 114–118 and 129–134% modern respectively, indicating incorporation of bomb- ^{14}C (Hedges et al., 1986b). Our ^{14}C analyses indicated that the seasonal stream, Main Trail, only effluxed young carbon (Table 2). Main Trail ^{14}C concentrations ($106 \pm 0.6\%$ modern) shows incorporation of bomb- ^{14}C as it is higher than the atmospheric concentration (103.8% modern in 2012, Levin et al., 2008).

The intermediate end-member: soil organic matter (potentially containing black carbon) and erosion of river bank sediments could contribute aged carbon. Compared to the fossil material, these medium-aged fractions are relatively similar in ^{14}C age and were pooled in the model to give our intermediate end-member and assigned an age of $88 \pm 9.5\%$ modern (range 200–2000 yr BP).

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The fossil end-member: weathering-derived organic carbon from sedimentary rocks and inorganic carbon from carbonate bearing rocks, both aged millions of years are characterized by ^{14}C concentration of 0% modern and so is the fossil end member.

2.4 Treatment of stable isotope data

5 Terrestrial C3 plants have $\delta^{13}\text{C}$ between -24 and -34‰ (Faure, 1986), bulk soil organic matter in C3 forested areas $\delta^{13}\text{C}$ is -27 to -29‰ on the surface increasing to -25‰ at depth (Bird et al., 1992), charcoal signature reflects its source (Bird et al., 1992), on average kerogen signature is -27.5‰ (Hoefs, 2004) and marine carbonates, the only inorganic end member, typically have a signature $+1$ to -3‰ (Hoefs, 10 2004).

Whilst degassing can enrich $\delta^{13}\text{C}_{\text{DIC}}$ (Doctor et al., 2008; Polsenaere and Abril, 2012), comparison with expected sources is meaningful as it can confirm when $\delta^{13}\text{C}_{\text{DIC}}$ has been little compromised. We are confident that the C cycle in this area is dominated by C3 vegetation: although $\delta^{13}\text{C}_{\text{DIC}}$ was enriched this is not from C4 vegetation as this 15 is not known in the area and $\delta^{13}\text{C}$ of fluvial dissolved organic matter in La Torre and Tambopata rivers was -29.2‰ ($n = 1$) and -28.7‰ ($n = 1$) respectively. The foliar $\delta^{13}\text{C}$ at the Tambopata site was on average -30.6‰ (Fyllas et al., 2009) and carbon content weighted average composition of the soil organic matter was -26.2‰ , increasing from the -29.4‰ in the A horizon to -25.0‰ in the B2 horizon (Zimmermann et al., 20 2009).

3 Results

Radiocarbon analyses of CO_2 evasion indicated that old carbon was present in all sampled systems except the seasonal small stream (Table 2). In Main Trail, the small stream was present only in the wet season indicating that it was not groundwater 25 fed, and ^{14}C content (106% modern, implying carbon fixed $\sim 4\text{--}5$ yr prior to sampling)

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and $\delta^{13}\text{C}$ of evasion (-26‰) reflect young, C3 plant-derived organic carbon. CO₂ efflux from the adjacent forested small stream, New Colpita, was more ¹³C-enriched (-24.7‰) and older, with ¹⁴C content (99 % modern) indicating a component of carbon fixed before AD 1957. La Torre river efflux had ¹⁴C content intermediate between the two forested streams (102 % modern), suggesting that it contained both pre- and post-bomb carbon, and was more ¹³C-enriched ($\delta^{13}\text{C}$ of -22.1‰). The oldest CO₂ efflux was from the largest river, the Tambopata (97 % modern) which also had the most ¹³C-enriched evasion and DIC (-20.6‰ and -12.9‰ respectively).

In addition to detecting old carbon in effluxed CO₂, spatial variation in ¹⁴C age within a small area and intra-site temporal variation under different hydrological conditions was observed. At higher flow, New Colpita [DIC] was halved due to dilution, $\delta^{13}\text{C}_{\text{DIC}}$ decreased and approached the composition of Main Trail, and the ¹⁴C content of evasion increased, suggesting increased post-bomb C and indicating greater connection with the younger C cycle. In La Torre river during high water (15 May 2012), both $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}$ of evasion decreased, but the ¹⁴C content remained similar. In Tambopata river the $\delta^{13}\text{C}$ and ¹⁴C content of evasion, and $\delta^{13}\text{C}_{\text{DIC}}$ remained consistent across different water levels targeted in the sampling. The CO₂ evasion rates measured here were comparable to the range ($0.18\text{--}24.3\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$) determined in previous studies within the basin (Alin et al., 2011; Salimon et al., 2013; Neu et al., 2011; Rasera et al., 2008) apart from New Colpita which had higher evasion rates probably resulting from greater turbulent flow, since evasion rate is strongly controlled by flow conditions (Alin et al., 2011).

With many sources that could contribute to CO₂ efflux, it is challenging to identify and thus quantify the sources of old carbon. Using ¹⁴C and $\delta^{13}\text{C}$ data simultaneously in mass balance equations to derive unique solutions of end member contributions (Table 2) is precluded by adulteration of the end member $\delta^{13}\text{C}$ through outgassing. The SIAR output for the three drainage systems (excluding Main Trail) shows that the maximum fraction of the contemporary carbon end member was less than 1, indicating

that older carbon was being outgassed from these drainage systems. Further, the total of intermediately aged fraction can be as high as 0.45–0.6 depending on the age of the end member (Fig. 2).

Main Trail had the highest [DOC] and a modern ^{14}C evasion signature. During event flow, in New Colpita, [DOC] increased and the age of CO_2 evaded became younger than other sampling occasions at lower flow. [POC] in all the four drainage systems was approximately constant (Main Trail: $2.2\text{--}2.5\text{ mgL}^{-1}$; New Colpita: $1.9\text{--}3.9\text{ mgL}^{-1}$; La Torre (excluding the event): $1.4\text{--}2.4\text{ mgL}^{-1}$; Tambopata: $4.1\text{--}4.6\text{ mgL}^{-1}$) except for La Torre river where [POC] increased to 19.6 mgL^{-1} during high water. There was no relationship between POC and the ^{14}C content of outgassed CO_2 .

The dissolved calcium concentration ([Ca]) was negatively correlated with ^{14}C content of evasion (Spearman rho 0.83, p value < 0.001 , Fig. 3a) and positively with calculated silicate weathering percentage (rho -0.88 , p value < 0.001 , Fig. 3b). In New Colpita and La Torre there were positive correlations between [DIC] and [Ca], and [DIC] with $\delta^{13}\text{C}_{\text{DIC}}$ when a larger set of data beyond the ^{14}C field campaign was analysed (Table 3). Positive [DIC]–[Ca] correlation was also significant for Tambopata river and the [DIC]– $\delta^{13}\text{C}_{\text{DIC}}$ correlation for Main Trail, albeit weak (p value 0.03).

4 Discussion

Our end-member analysis identifies multiple possible solutions for the proportional mixing of modern, intermediate and old carbon to CO_2 efflux. However, in turn this reveals that there are multiple sources of old C that could contribute to CO_2 efflux, and their relative contribution may change with time and environmental drivers. This temporal and spatial heterogeneity is apparent when we consider from where old carbon may be generated.

The soils at the study site have pH below 6.5 (Quesada et al., 2010), excluding solid soil carbonates as a source of older carbon efflux from the New Colpita stream that drains the local forest. Carbonate lithologies are found mainly in the northern Andes

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in Marañon and Ucayali River catchments but smaller amounts of carbonate-bearing minerals are found in the Madre de Dios region (Moquet et al., 2011). The age of evasion became older as the calcium concentration increased and silicate weathering percentage decreased (Fig. 3), indicating a contribution from carbonate weathering (Fig. 3). As the surface water fed seasonal stream had a contemporary ¹⁴C signature and the local soils do not contain carbonate, the fossil carbonate contribution likely originates from weathering of carbonate minerals in the bed rock that enter the aquatic systems via groundwater flow. Further, the correlations observed between [DIC], [Ca] and $\delta^{13}\text{C}_{\text{DIC}}$ are consistent with the influx of carbon from carbonate weathering (Doctor et al., 2008; Bullen and Kendall, 1998). As dilution of [DIC] is observed during event flow, the aged carbon is likely to enter the perennial New Colpita stream in groundwater. Furthermore, [Ca] were close to zero in the surface-water fed seasonal stream (Main Trail) and here ¹⁴C content was modern, consistent with the lack of an old carbon component due to the absence of groundwater inputs.

Samples taken at different stage heights from La Torre showed changes in $\delta^{13}\text{C}$ indicative of differing contributions of C3 plant-derived material, with higher water level characterized with more depleted DIC and evasion signatures, but little change in ¹⁴C content implying no change in the age of carbon. Tambopata did not show a clear change in carbon isotopic signatures with water level. In the New Colpita stream there was an increase in ¹⁴C content of evasion with higher water levels. The dataset collected is limited in size and includes one season only but reveals that there are hydrological controls on the age of CO₂ evasion, and these can be site specific. Further studies are needed to establish these controls.

We did not directly measure the ¹⁴C concentration in DOC, however, the Main Trail had the highest DOC concentrations and evasion had a young ¹⁴C signature suggesting that in-situ respiration of DOC is not contributing significant quantities of aged carbon to these afforested streams. Furthermore, [DOC] increased with water level in New Colpita, but the age of evasion decreased when [DOC] were highest. These observations are consistent with the dissolved component of soil-derived material in these

forested streams being young, and most likely derived from surface run-off. However, the rivers sampled drain a much wider area where more aged carbon could be encountered and hence aged soil organic matter could contribute to the age of evasion in the rivers.

5 Chemical weathering within the Amazon Basin is estimated to produce one quarter of fossil organic carbon (43 Mtyr^{-1}) delivered to the oceans globally (Copard et al., 2007). For example, sedimentary rocks, mainly shale in the Western Amazon Basin (Copard et al., 2007), may be a source of aged effluxed CO_2 . In our study region Palaeozoic shale dominates with some evaporites present (Quesada et al., 2011). In
10 small mountainous rivers in temperate regions POC has been found to comprise 7–75% of kerogen, with increased sediment yield (more erosion) resulting in older POC (Leithold et al., 2006). In the Amazon Basin, fossil organic matter has been found as aggregates with minerals or as free particles (Bouchez et al., 2010) in sufficient quantities that $\sim 0.25 \text{ MtCyr}^{-1}$ of old organic material from sedimentary rocks is oxidized
15 along the Amazonian rivers (Bouchez et al., 2010). When exposed to oxygen rich waters, organic matter in black shales is extremely labile (Petsch et al., 2000) and the resulting DOM is rapidly degraded (Schillawski and Petsch, 2008). Oxidation of Cretaceous kerogen can also take place at depth in soils developed on shale parent material (Keller and Bacon, 1998). Thus old carbon delivered from weathering of rock kerogen
20 (Petsch et al., 2000; Schillawski and Petsch, 2008) can also be a source and could be a component in the evasion samples which would explain the ^{14}C -depleted values.

Old POC (1258 yrBP, $n = 1$) has been observed at the mouth of the Amazon, whereas DOC was modern (Raymond and Bauer, 2001). In the mountainous head-water region the oldest POC samples analysed were approximately 7600 BP (Mayorga et al., 2005) and 9900 BP (Clark et al., 2013). Erosion of these riverbank sediments
25 can reintroduce trapped older material to the rivers, which if respired may result in efflux of aged CO_2 . Furthermore black carbon can persist in soils for long periods and enter streams via erosion, providing a further aged carbon fraction. Charcoal is usually a minor fraction in the total POC budget (Bird et al., 1992) but charcoal from Holocene

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just transfer between reservoirs. Without this we are neither identifying the significance of differing C contributions to atmospheric CO₂ efflux, nor have the secure foundations to impose a driver of change.

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Table 1. Estimated average ¹⁴C concentrations (% modern) and δ¹³C signatures of the potential end members at the Tambopata site. Intermediately aged carbon age range is ~ 200–2000 yrBP (where 0BP = 1950 AD) which represents the age of material that could be derived from aged soil carbon, Holocene fire black carbon and reworking of the Tambopata river bank terraces. Therefore the Main Trail concentration was selected to represent the recent carbon inputs in the mixing model to solve the end members for the other three drainage systems.

Carbon source	Typical ¹⁴ C (% modern)	Typical δ ¹³ C (‰)
Young (C3 vegetation derived)	106 ± 0.6	–24 to –34
Intermediately aged carbon	88 ± 9.5	–25 to –29
Fossil carbon – Kerogen	0	–27.5
Fossil carbon – marine carbonates	0	+1 to –3

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Table 2. The mean evasion ¹⁴C and δ¹³C signatures, total DIC pool concentration, δ¹³C-DIC, pH, fraction of the DIC pool in the form of CO₂, DOC, POC and Ca concentrations in the studied drainage systems in Tambopata region, Peru. The drainage systems were sampled three times targeting different hydrological conditions: baseflow, rising water and falling water. In the case of the small streams water level is the stream depth, in larger rivers the measurement is a relative change in water level. At the time of sampling, April–May, 2012, the estimated ¹⁴C of atmosphere was ~ 103.8 % modern (Levin et al., 2008). The analytical uncertainty was ±0.1 ‰ and ± < 0.5 % modern for evasion δ¹³C and ¹⁴C measurements, respectively.

Sampling site	Catchment size (km ²)	Date	Water level (m)	Evasion ¹⁴ C % modern	Evasion δ ¹³ C (‰)	DIC (mg L ⁻¹)	δ ¹³ C _{DIC} (‰)	pH	% DIC-CO ₂	CO ₂ evasion (μmol m ⁻² s ⁻¹)	DOC (mg L ⁻¹)	POC (mg L ⁻¹)	Ca (mg L ⁻¹)
Main Trail – seasonal Stream	~ 5	4 Apr 2012	0.23	106.4	-25.9	0.7	-25.6	5.1	95	5.6	6.1	2.5	0
		9 Apr 2012	0.55	105.5	-26.4	1.5	-25.1	5.0	96	7.6	6.2	2.4	0
		11 Apr 2012	0.34	106.7	-25.9	1.2	-23.6	5.0	95	6.3	6.4	2.2	0.1
		Mean	0.37	106.2	-26.0	1.2	-24.4	5.0	95	6.5	6.2	2.4	0.04
		Std dev	0.16	0.6	0.3	0.4	0.8	0.1	0.6	1.0	0.2	0.2	0.08
New Colpita – perennial Stream	~ 7	6 Apr 2012	0.51	98.1	-25.7	3.9	-19.6	6.4	44	15.9	2.5	2.5	1.0
		9 Apr 2012	0.64	101.5	-23.9	1.8	-21.9	6.1	63	64.9	3.9	3.9	0.2
		23 May 2012	0.48	98.6	-24.5	6.3	-18.8	6.5	40	79.6	0.7	1.9	1.7
		Mean	0.54	99.4	-24.7	4.0	-20.1	6.4	49	53.5	2.6	2.8	1.0
		Std dev	0.09	1.8	0.9	2.2	1.6	0.2	12	33.4	2.7	1.0	0.8
La Torre – River	~ 2000	1 May 2012	-1.0	102.8	-21.1	2.4	-15.2	6.5	44	7.0	1.9	3.4	1.4
		9 May 2012	-1.6	102.2	-21.5	3.6	-14.4	6.4	43	18.4	1.5	2.1	2.4
		15 May 2012	1.3	101.4	-23.6	2.7	-18.4	6.5	41	6.7	2.0	19.6	0.5
		Mean	-1.4	102.1	-22.1	2.9	-16.0	6.5	42	10.7	1.8	8.4	1.4
		Std dev	0.3	0.7	1.3	0.6	2.1	0.03	1.6	6.7	0.3	9.7	1.0
Tambopata-River	~ 14000	4 May 2012	-1.6	97.7	-20.8	3.3	-13.1	6.8	27	5.6	1.2	1.5	4.1
		11 May 2012	-2.1	96.5	-21.2	3.7	-13.0	6.9	22	1.8	0.9	1.2	4.6
		13 May 2012	-1.2	95.7	-20.1	3.1	-12.4	7.1	13	5.1	1.3	2.2	4.4
		Mean	-1.6	96.6	-20.6	3.4	-12.9	6.9	21	4.2	1.2	1.6	4.4
		Std dev	0.5	1.0	0.5	0.3	0.4	0.2	7.0	2.1	0.2	0.5	0.2

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Table 3. Spearman rho, p values and sample sizes (n) for correlations that indicate carbonate weathering contributions.

Drainage system	[DIC], [Ca]			[DIC], $\delta^{13}\text{C}_{\text{DIC}}$		
	Spearman rho	p value	n	Spearman rho	p value	n
Main Trail	0	1*	39	0.21	0.033	103
New Colpita	0.86	< 0.001	53	0.86	< 0.001	172
La Torre	0.89	< 0.001	14	0.51	< 0.001	126
Tambopata	0.65	< 0.001	30	0.11	0.32	77

* Due to multiple ties in ranks (no calcium detected) an accurate p value could not be computed for Main Trail [DIC]–[Ca] correlation.

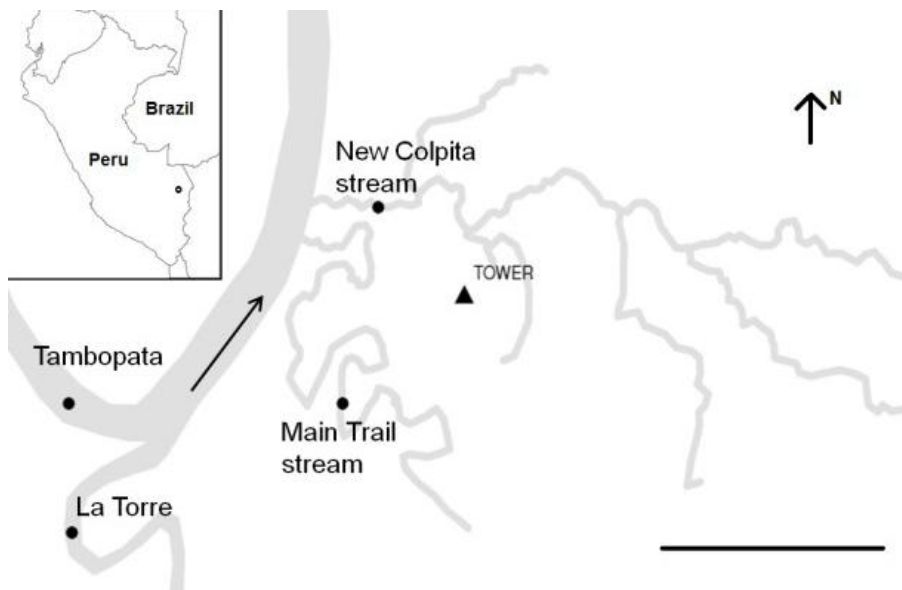


Fig. 1. Location of the study area. The circle in the inset map notes the location of the study site, Tambopata National Reserve, Madre de Dios, Peru. At the study area four independent drainage systems were sampled 2011–2012. These included two small streams in the foot print of an eddy-covariance flux tower and two rivers. The scale bar is 1 km.

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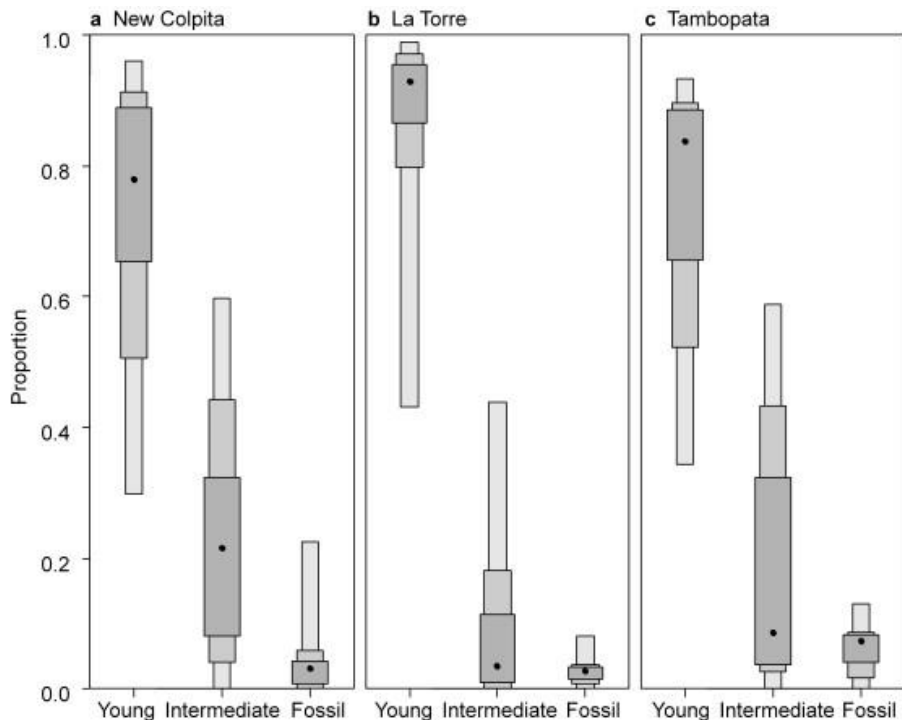


Fig. 2. Potential contributions of different carbon age groups in the three drainage (a–c) systems with old carbon. The intermediate-aged class includes carbon aged 200–2000 yr BP that could be derived from soil organic matter, black carbon or cutting of the river sediment packs. The black dot represents the most likely solution. The dark, light and lightest grey boxes represent respectively the 50%, 75% and 95% confidence intervals of the estimates. All samples had to contain some aged C, but least so in La Torre (b).

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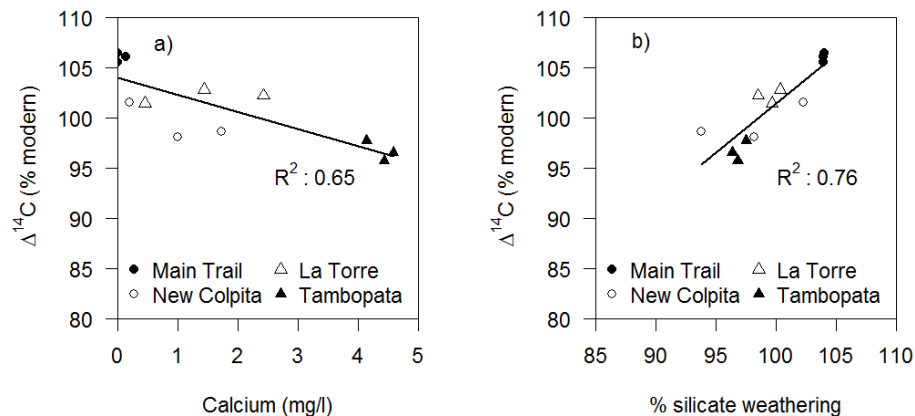


Fig. 3. Across the drainage systems, ^{14}C concentration (% modern) was significantly correlated with calcium concentration (a) and percentage silicate weathering (b).