



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 CO<sub>2</sub> released by wetland plants (Abril et al., 2013) have been advocated as sources of the effluxed carbon dioxide. However, in  
5 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 CO<sub>2</sub> to the atmosphere (Berner, 2003), and requires ad-  
10 justment 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.

15 The C load to a river and its CO<sub>2</sub> 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  
20 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).

25 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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released to the aquatic system it is labile and can be respired quickly (Petsch et al., 2000) and hence contribute to the outgassed CO<sub>2</sub>. In Madre de Dios headwaters, in the western part of the Amazon Basin where our study site is located, <sup>14</sup>C age of POC ranged from approximately 120–9900 yrBP (98.5 to 28.9 % modern) with fossil POC  
5 found to constitute up to 80 % of the total POC (Clark et al., 2013).

The floodplain soils of Western Amazonia are not much older than 5000 yr (Quesada et al., 2011) and the soils’ organic matter probably considerably younger. In the upper part of the Amazon mainstem fine suspended particulate organic matter (FPOM), that is thought to originate from soils (Hedges et al., 2000; Townsend-Small et al., 2005),  
10 had a <sup>14</sup>C content of 101.9 ± 1.9 % modern (measured in 1983, Hedges et al., 1986b) – a mixture of pre and post-bomb material most likely dominated by pre-bomb contributions indicating an aged soil derived component. Some wildfire-derived black carbon aged 1100–4000 yrBP (0BP = 1950 AD) has been detected in soils of southeastern Peru, with the ages older than 500 yr below 20 cm depth (McMichael et al., 2012).  
15 The Quaternary Madre de Dios basin, in which the Tambopata catchment is nested, has undergone several sedimentation and under-cutting sequences, with the most recent bank sediment deposition starting approximately 870 yr ago: wood samples from Tambopata floodplain deposits were dated as 690 ± 20 and 870 ± 50 yrBP old (Rigsby et al., 2009). Cutting of these river banks can contribute carbon predominantly from  
20 this period, with additionally some sedimented older carbon.

The magnitude of the different source fluxes will vary in space and time in response to environmental drivers. For example, over the last few decades the Amazon has become wetter, with larger differences in minimum and peak river discharge, resulting in the increased occurrence of extreme events in the wet season (Gloor et al., 2013).  
25 Higher storm frequency increases the erosion rate and POC delivery (Hilton et al., 2008; Leithold et al., 2006; Townsend-Small et al., 2008). Storm-induced landslides contribute significantly to fluvial POC in mountainous watersheds and increase the rock-derived “fossil” carbon fraction (Hilton et al., 2008). If the observed wetting trend continues, geomorphological controls of fluvial C influx are likely to become more im-

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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 CO<sub>2</sub> efflux through isotopic and hydrochemical measurements. Although <sup>14</sup>C-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 CO<sub>2</sub> 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 CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> samples were collected during April–May 2012 for measurement of  $\delta^{13}\text{C}$  and <sup>14</sup>C content. Each drainage system was sampled three times targeting different stage heights to assess hydrological controls on the <sup>14</sup>C content and  $\delta^{13}\text{C}$  of the evasion. Evaded fluvial CO<sub>2</sub> was accumulated in a floating chamber (Billett et al., 2006). The chamber was first scrubbed free of atmospheric CO<sub>2</sub> using a soda lime trap, then CO<sub>2</sub> 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<sub>2</sub> was released by heating the molecular sieve (500 °C), the gas purified cryogenically and divided into volumes allocated for  $\delta^{13}\text{C}$  and <sup>14</sup>C analysis.  $\delta^{13}\text{C}$  was measured on a Thermo-Fisher-Scientific Delta V mass spectrometer. The sample fraction for <sup>14</sup>C analysis was graphitized and analyzed by accelerator mass spectrometry at the Scottish Universities Environmental Research Centre. Following convention, the <sup>14</sup>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-<sup>14</sup>C and therefore a contribution from carbon fixed from the atmosphere post ~ 1957 AD (when atmospheric <sup>14</sup>CO<sub>2</sub> 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 CO<sub>2</sub> efflux

To estimate the source of the effluxed CO<sub>2</sub> 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 CO<sub>2</sub> only influencing the CO<sub>2</sub> 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 δ<sup>13</sup>C<sub>DIC</sub>, 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 δ<sup>13</sup>C<sub>DIC</sub> signature can undermine the use of a dual carbon isotope approach for partitioning the carbon sources of CO<sub>2</sub> evasion, although partitioning by hydrological conditions still reveals changing dominance of sources (Waldron et al., 2007). Therefore only the <sup>14</sup>C 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 <sup>14</sup>C age range is constrained by the end members of organic matter containing recently-fixed CO<sub>2</sub> 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 <sup>14</sup>C (bomb-<sup>14</sup>C) into the atmosphere resulting in plant material fixed since the mid-1950s having <sup>14</sup>C concentrations > 100% modern. Similarly, soil organic matter derived from plants grown since the mid-1950s also has a <sup>14</sup>C concentration > 100% modern. Bomb-<sup>14</sup>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 <sup>14</sup>C concentrations were 114–118 and 129–134% modern respectively, indicating incorporation of bomb-<sup>14</sup>C (Hedges et al., 1986b). Our <sup>14</sup>C analyses indicated that the seasonal stream, Main Trail, only effluxed young carbon (Table 2). Main Trail <sup>14</sup>C concentrations (106 ± 0.6% modern) shows incorporation of bomb-<sup>14</sup>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 <sup>14</sup>C age and were pooled in the model to give our intermediate end-member and assigned an age of 88 ± 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  $^{14}\text{C}$  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, 2004).

10 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 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., 2009).

### 3 Results

Radiocarbon analyses of  $\text{CO}_2$  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 fed, and  $^{14}\text{C}$  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.  $\text{CO}_2$  efflux from the adjacent forested small stream, New Colpita, was more  $^{13}\text{C}$ -enriched ( $-24.7$ ‰) and older, with  $^{14}\text{C}$  content (99% modern) indicating a component of carbon fixed before AD 1957. La Torre river efflux had  $^{14}\text{C}$  content intermediate between the two forested streams (102% modern), suggesting that it contained both pre- and post-bomb carbon, and was more  $^{13}\text{C}$ -enriched ( $\delta^{13}\text{C}$  of  $-22.1$ ‰). The oldest  $\text{CO}_2$  efflux was from the largest river, the Tambopata (97% modern) which also had the most  $^{13}\text{C}$ -enriched evasion and DIC ( $-20.6$ ‰ and  $-12.9$ ‰ respectively).

10 In addition to detecting old carbon in effluent  $\text{CO}_2$ , spatial variation in  $^{14}\text{C}$  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  $^{14}\text{C}$  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  $^{14}\text{C}$  content remained similar. In Tambopata river the  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  content of evasion, and  $\delta^{13}\text{C}_{\text{DIC}}$  remained consistent across different water levels targeted in the sampling. The  $\text{CO}_2$  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).

20 With many sources that could contribute to  $\text{CO}_2$  efflux, it is challenging to identify and thus quantify the sources of old carbon. Using  $^{14}\text{C}$  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

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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 ( $43 \text{ Mt yr}^{-1}$ ) 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  $\text{CO}_2$ . 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  $\sim 0.25 \text{ Mt C yr}^{-1}$  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  $^{14}\text{C}$ -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-  
25 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 can reintroduce trapped older material to the rivers, which if respired may result in efflux of aged  $\text{CO}_2$ . 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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fires has been observed in soils of southeastern Peru (McMichael et al., 2012). Further, tropical forest burning can contribute dissolved black carbon or particulate matter for centuries to millennia after burning: in the Paraíba do Sul River, export from  
5 previously-burned Atlantic forest dissolved black carbon accounted for 7 % of bulk DOC during peak flow conditions (Dittmar et al., 2012). Priming effects can render complex molecules, previously considered inherently recalcitrant, labile (Bianchi, 2011; Schmidt et al., 2011; Ward et al., 2013). Both fine and coarse POC and DOM are increasingly degraded further downstream in the Amazon indicating sufficient residence times for  
10 decomposition to occur (Hedges et al., 2000). In our studied drainage systems there was no relationship between POC concentration and the age of evasion, indicating that in-situ decomposition of POC-containing kerogen is an unlikely source of aged carbon in these systems. However, decomposition of POC could take place upstream in the catchment, be transported to the site and still potentially contribute to aged evasion  
15  $\text{CO}_2$  detected in the rivers in this study.

Our study confirms for the first time using direct  $^{14}\text{CO}_2$  analyses that aged carbon is outgassed from Amazonian river systems ranging in size from  $7 \text{ km}^2$  to  $14\,000 \text{ km}^2$ . This phenomena had previously been inferred from indirect measurements of  $^{14}\text{CO}_2$ , with estimations of average  $^{14}\text{CO}_2$  concentration of 75 % modern  
20 ( $\sim 2300 \text{ yrBP}$ ) in mountain rivers and 97 % modern ( $\sim 250 \text{ yrBP}$ ) in mixed catchments within the Amazon Basin (Mayorga et al., 2005). However, the interpretative focus was on the Amazonian fluvial carbon cycle being fast (Mayorga et al., 2005) and in balance (Gloor et al., 2012). Now, confirmation of old C in effluxed  $\text{CO}_2$ , indicates that we must consider the slow turnover carbon cycle processes, such as sedimentary rock and carbonate weathering, in order to understand the controls of long term carbon balance  
25 within the basin.

If the aged carbon originates from carbonate weathering, as indicated for our study site by the correlations with [Ca], then the efflux of this aged component is likely to be more significant in areas closer to the Andean headwaters to which also our Tambopata study site belongs. Therefore the fraction of aged carbon in  $\text{CO}_2$  efflux from the main

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stem and major tributaries further downstream is likely to be lower as indicated by  $^{14}\text{C}$  analysis of DIC from these systems (Mayorga et al., 2005). However, even if the efflux of weathering-derived aged  $\text{CO}_2$  would be limited to the headwater regions, it still forms an important pathway of returning stored fossil carbon to the atmosphere and hence should not be disregarded. Rather, its significance within the Amazon Basin needs to be assessed to correctly describe models of carbon flux pathways on which are often imposed a land use or environmental change.

Furthermore, if aged carbon is being delivered in groundwater to the streams then the fractional contribution from these carbon sources will be higher in the dry season and the gas evaded will be older. Such a response in New Colpita stream was evident as water level dropped. However, further investigation of the age of evasion over different season is needed to verify this seasonality in flux source. This investigation requires end member characterisation including dating of DOC, POC (separating the fine and coarse fractions that have different origins, Hedges et al., 2000, 1986a; Bird et al., 1992; Townsend-Small et al., 2005) and soil carbon to verify the origin and age of older fractions.

We need more secure understanding: turnover times have recently been identified as the key model inputs in terrestrial ecosystems (Keenan et al., 2013); knowing the speed of carbon cycling of different aquatic pools is equally as crucial as links from terrestrial to marine and atmospheric C reservoirs, and the sensitivities of each to environmental drivers of change are likely to differ. The DyDOC model uses  $^{14}\text{C}$  data to simulate the soil carbon cycle and DOC production, and considers pool turn over times (Tipping et al., 2007) but larger ecosystem scale models lack age as a constraint on pool residence time or rate of C transfer (Schmidt et al., 2011; Huntingford et al., 2013; Bony et al., 2013). Future projections of the importance of the Amazon as a global C sink focus largely on an ecosystem response to land use e.g., burning and clearing, or to acute meteorological events e.g., drought, and of this we cannot be certain without knowing the significance of older carbon contributions. The carbon cycling models need to be revised to incorporate the rates of carbon flow and residence times, rather than

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just transfer between reservoirs. Without this we are neither identifying the significance of differing C contributions to atmospheric  $\text{CO}_2$  efflux, nor have the secure foundations to impose a driver of change.

*Acknowledgements.* This study was funded by UK NERC Amazonica grant NE/F005482/1. We thank Eric Cosio and Eliana Esparza Ballón for help with logistics and research permits, Rosa Maldonado Maldonado, Susanne Wörner and Fabian Limonchi Tamamoto for assistance with fieldwork, Kenneth Roberts for the help with GIS analysis, Alison McDonald for assistance with DIC analysis, Valeria Donets and Karen-Jane Miller for the calcium analyses. We are grateful to Bryan Mark of Ohio State University, USA for collecting the LiDAR data, and to Chris Hopkinson of the University of Lethbridge, Canada, Ross Hill of Bournemouth University, UK, and Doreen Boyd of the University of Nottingham, UK for processing and supplying the LiDAR data in the format of digital terrain and canopy models, which allowed the detection of small streams. We thank NASA LP DAAC for ASTER GDEM data that allowed analysis of river catchment areas.

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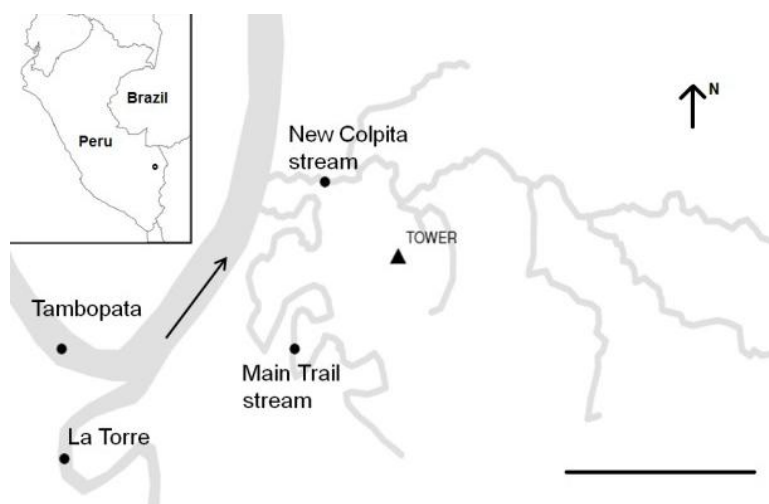


**Table 3.** Spearman rho,  $\rho$  values and sample sizes ( $n$ ) for correlations that indicate carbonate weathering contributions.

Drainage system	[DIC], [Ca]			[DIC], $\delta^{13}\text{C}_{\text{DIC}}$		
	Spearman rho	$\rho$ value	$n$	Spearman rho	$\rho$ 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

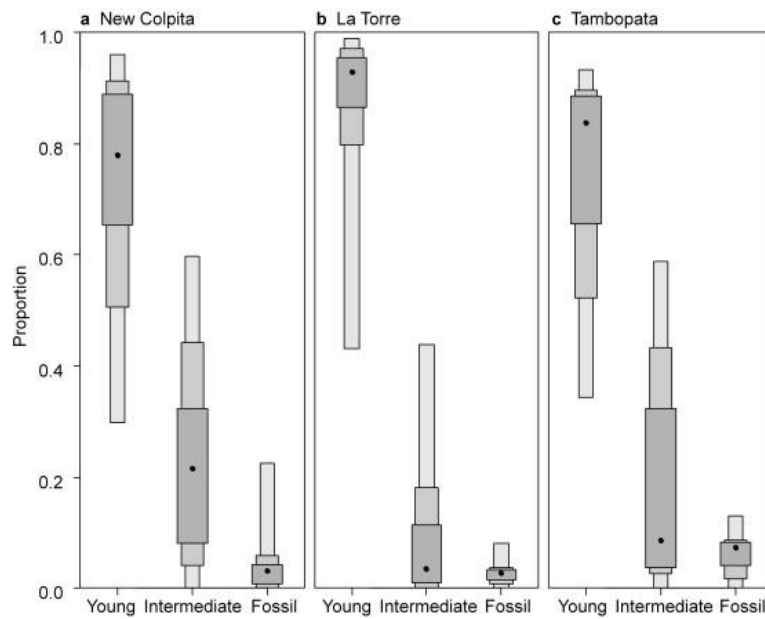
\* Due to multiple ties in ranks (no calcium detected) an accurate  $\rho$  value could not be computed for Main Trail [DIC]–[Ca] correlation.

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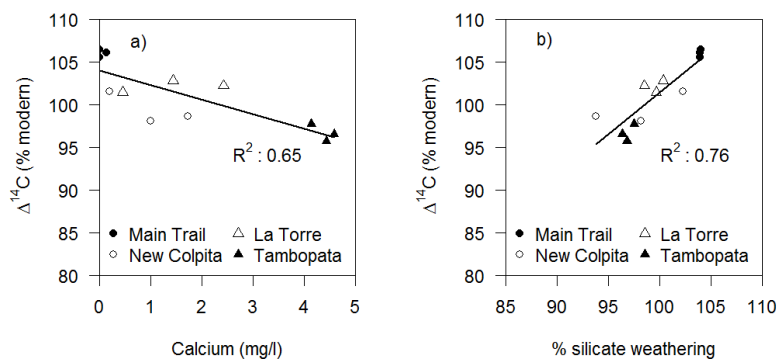
**Fig. 1.** Location of the study area. The circle in the inset map notes the location of the study site, Tambopata National Reserve, Madre de Dios, Peru. At the study area four independent drainage systems were sampled 2011–2012. These included two small streams in the foot print of an eddy-covariance 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,  $^{14}\text{C}$  concentration (% modern) was significantly correlated with calcium concentration (a) and percentage silicate weathering (b).

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