

## RESEARCH ARTICLE

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## Key Points:

- Quantify discharge of suspended sediment and particulate organic carbon (biospheric and petrogenic) by an Andean River
- The fate of river biospheric particulate organic carbon determines whether Andean forest is a carbon dioxide source or sink
- Oxidation of petrogenic particulate organic carbon eroded from the Andes counters CO<sub>2</sub> drawdown by silicate weathering in the lowlands

## Supporting Information:

- Supporting Information S1
- Data Set S1

## Correspondence to:

K. E. Clark,  
kathryn.clark23@gmail.com

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## Erosion of organic carbon from the Andes and its effects on ecosystem carbon dioxide balance

K. E. Clark<sup>1,2</sup>, R. G. Hilton<sup>3</sup>, A. J. West<sup>4</sup>, A. Robles Caceres<sup>5</sup>, D. R. Gröcke<sup>6</sup>, T. R. Marthews<sup>1,7</sup>, R. I. Ferguson<sup>3</sup>, G. P. Asner<sup>8</sup>, M. New<sup>9,10</sup>, and Y. Malhi<sup>1</sup>
<sup>1</sup>Environmental Change Institute, School of Geography and the Environment, University of Oxford, Oxford, UK,

<sup>2</sup>Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, Pennsylvania, USA,

<sup>3</sup>Department of Geography, Durham University, Durham, UK, <sup>4</sup>Department of Earth Sciences, University of Southern California, Los Angeles, California, USA, <sup>5</sup>Facultad de Ciencias Biológicas, Universidad Nacional de San Antonio Abad del Cusco, Cusco, Peru, <sup>6</sup>Department of Earth Sciences, Durham University, Durham, UK, <sup>7</sup>Centre for Ecology and Hydrology, Wallingford, UK, <sup>8</sup>Department of Global Ecology, Carnegie Institution for Science, Stanford, California, USA, <sup>9</sup>African Climate and Development Initiative, University of Cape Town, Rondebosch, South Africa, <sup>10</sup>School of International Development, University of East Anglia, Norwich, UK

**Abstract** Productive forests of the Andes are subject to high erosion rates that supply to the Amazon River sediment and carbon from both recently photosynthesized biomass and geological sources. Despite this recognition, the source and discharge of particulate organic carbon (POC) in Andean Rivers remain poorly constrained. We collected suspended sediments from the Kosñipata River, Peru, over 1 year at two river gauging stations. Carbon isotopes (<sup>14</sup>C, <sup>13</sup>C, and <sup>12</sup>C) and nitrogen to organic carbon ratios of the suspended sediments suggest a mixture of POC from sedimentary rocks (POC<sub>petro</sub>) and from the terrestrial biosphere (POC<sub>biosphere</sub>). The majority of the POC<sub>biosphere</sub> has a composition similar to surface soil horizons, and we estimate that it is mostly younger than 850 <sup>14</sup>C years. The suspended sediment yield in 2010 was 3500 ± 210 t km<sup>-2</sup> yr<sup>-1</sup>, >10 times the yield from the Amazon Basin. The POC<sub>biosphere</sub> yield was 12.6 ± 0.4 t C km<sup>-2</sup> yr<sup>-1</sup> and the POC<sub>petro</sub> yield was 16.1 ± 1.4 t C km<sup>-2</sup> yr<sup>-1</sup>, mostly discharged in the wet season (December to March) during flood events. The river POC<sub>biosphere</sub> discharge is large enough to play a role in determining whether Andean forests are a source or sink of carbon dioxide. The estimated erosional discharge of POC<sub>petro</sub> from the Andes is much larger (~1 Mt C yr<sup>-1</sup>) than the POC<sub>petro</sub> discharge by the Madeira River downstream in the Amazon Basin, suggesting that oxidation of POC<sub>petro</sub> counters CO<sub>2</sub> drawdown by silicate weathering. The flux and fate of Andean POC<sub>biosphere</sub> and POC<sub>petro</sub> need to be better constrained to fully understand the carbon budget of the Amazon River basin.

## 1. Introduction

Tropical forests and soils contain ~430 Pg C stored within organic matter [Dixon *et al.*, 1994; Houghton, 2005; Saatchi *et al.*, 2011], which is >70% of the carbon dioxide (CO<sub>2</sub>) stock of the preindustrial atmospheric reservoir [Sundquist and Visser, 2004]. Physical erosion can export some of this biospheric carbon and supply it to river systems, which globally deliver 0.16 + 0.07/–0.05 Pg C yr<sup>-1</sup> of particulate organic carbon (POC<sub>biosphere</sub>) to the oceans [Galy *et al.*, 2015]. Over short time scales (10<sup>0</sup>–10<sup>3</sup> years), this is an export of net primary production from ecosystems [Seitzinger *et al.*, 2005; Mayorga *et al.*, 2010; Galy *et al.*, 2015]. If the eroded POC<sub>biosphere</sub> is replaced by new productivity, erosion is a net sink of atmospheric CO<sub>2</sub> [Stallard, 1998; Berhe *et al.*, 2007; Li *et al.*, 2015]. Over longer time scales (>10<sup>3</sup> years), the eroded POC<sub>biosphere</sub> may be buried in continental or marine sedimentary deposits, where it becomes a geological CO<sub>2</sub> sink [Bernier, 1982; France-Lanord and Derry, 1997; Stallard, 1998; Galy *et al.*, 2007b; Kao *et al.*, 2014]. Alternatively, oxidation of POC<sub>biosphere</sub> during transit through river basins can fuel ecosystems downstream [Mayorga *et al.*, 2005] and is a component of heterotrophic respiration, which is not included in ecosystem carbon budgets at the scale of forest plots [Malhi, 2012]. If the carbon is old, such as carbon stored over millennial time scales in soils [Galy and Eglinton, 2011; Hilton *et al.*, 2015] and over longer time scales in sedimentary rocks as “petrogenic” POC (POC<sub>petro</sub>) [Galy and Eglinton, 2011; Hilton *et al.*, 2011a], its oxidation represents a source of CO<sub>2</sub> to the atmosphere not captured in most budgets [Bouchez *et al.*, 2010; Hilton *et al.*, 2014; Vihermaa *et al.*, 2014].

High rates of physical erosion occur in mountains [Milliman, 1995; Kao and Liu, 1997; Hicks *et al.*, 2000; Lyons *et al.*, 2002; Hilton *et al.*, 2008a; Wheatcroft *et al.*, 2010; Milliman and Farnsworth, 2011; Hilton *et al.*, 2012; Goñi

*et al.*, 2013; *Larsen et al.*, 2014], and because of the association between POC and clastic sediment, these locations also experience the highest measured rates of POC discharge [Milliman, 1995; *Kao and Liu*, 1997; *Hicks et al.*, 2000; *Lyons et al.*, 2002; *Hilton et al.*, 2008a; *Wheatcroft et al.*, 2010; *Milliman and Farnsworth*, 2011; *Hilton et al.*, 2012; *Stallard*, 2012; *Goñi et al.*, 2013; *Hilton*, 2017]. Rivers draining mountain islands can export this POC efficiently to ocean basins [Hilton *et al.*, 2008a; *Wheatcroft et al.*, 2010; *Kao et al.*, 2014]. However, many mountain rivers drain to larger continental river systems, and their POC and sediment are instead transported for thousands of kilometers across floodplains [e.g., *Galy et al.*, 2008b; *Blair and Aller*, 2012; *Bouchez et al.*, 2014; *Moreira-Turcq et al.*, 2014].

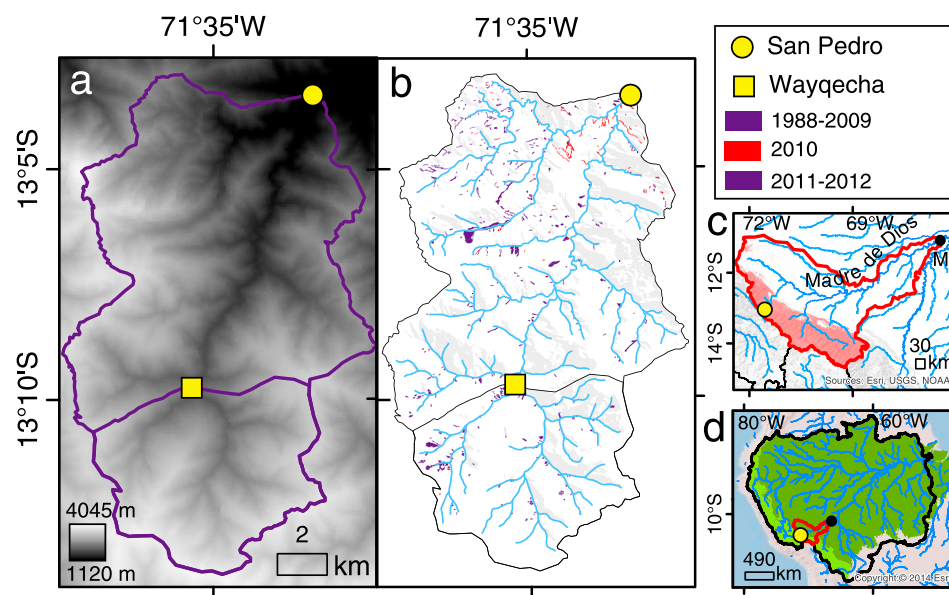
The Amazon Basin ( $\sim 6 \times 10^6 \text{ km}^2$  catchment area) has much of its headwaters in the Andes, which cover  $\sim 600,000 \text{ km}^2$  but are thought to supply most of the  $550\text{--}1550 \text{ Mt yr}^{-1}$  of clastic sediment exported to the Atlantic Ocean [e.g., *Gibbs*, 1967; *Meade et al.*, 1979; *Richey et al.*, 1986; *Allegre et al.*, 1996; *Dunne et al.*, 1998; *Guyot et al.*, 2005; *Filizola and Guyot*, 2009; *Martinez et al.*, 2009]. Many studies have measured POC composition and discharge in the Amazon Basin [e.g., *Richey et al.*, 1990; *Moreira-Turcq et al.*, 2003; *Bouchez et al.*, 2014; *Feng et al.*, 2016] and within Andean tributaries [e.g., *Hedges et al.*, 2000; *Aufdenkampe et al.*, 2007; *Townsend-Small et al.*, 2007; *Townsend-Small et al.*, 2008; *Clark et al.*, 2013]. Recent work has highlighted the importance of rock-derived  $\text{POC}_{\text{petro}}$  input to Andean Rivers [Bouchez *et al.*, 2010; *Clark et al.*, 2013; *Bouchez et al.*, 2014]. However, the rates of  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  discharges in this setting are not well known, hampering efforts to link Andean erosion to carbon budgets over interannual time scales. Quantifying POC discharge is essential in order to understand the context and mechanisms that constrain Andean net ecosystem productivity because the transport of carbon from the Andes to the Amazon Basin and the Atlantic Ocean represents a substantial carbon flux, of similar magnitude to the net carbon balance of the Amazon forest ecosystem, which forest inventory studies suggest accounts for around 25% of global terrestrial carbon sequestration [Malhi, 2010].

We aim to provide new insight into the impact of physical erosion on carbon budgets by quantifying the source and magnitude of river discharge of POC from the steep, eastern flank of the Peruvian Andes, characterized by predominantly sedimentary bedrock with relatively high concentrations of petrogenic organic carbon. We focus on a catchment where previous work has established the hydrological water balance [Clark *et al.*, 2014]; rates of geomorphic processes such as landslides [Clark *et al.*, 2016]; and forest productivity, respiration, and carbon stocks across the landscape [Zimmermann *et al.*, 2009; Zimmermann *et al.*, 2010a; Marthews *et al.*, 2012; Girardin *et al.*, 2014b; Clark *et al.*, 2016; Malhi *et al.*, 2016]. We use a detailed set of suspended sediment samples and hydrometric river gauging measurements over a 12 month period and analyze the stable isotopes of POC ( $\delta^{13}\text{C}_{\text{org}}$ ), the nitrogen to organic carbon ratio ( $[\text{N}]/[\text{OC}_{\text{total}}]$ ), and the radiocarbon activity of POC to distinguish  $\text{POC}_{\text{petro}}$  derived from sedimentary rocks and to study the source and age of  $\text{POC}_{\text{biosphere}}$ . We evaluate how the erosion of carbon from the terrestrial biosphere impacts estimates of Andean net ecosystem productivity and assess the role of Andean  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  in the longer-term carbon cycle.

## 2. Study Area

The Kosñipata River is located in the Eastern Cordillera of the central Peruvian Andes (Figure 1). The steep topography [Montgomery *et al.*, 2001] originated from moderate rates of surface uplift of  $0.2\text{--}0.3 \text{ mm yr}^{-1}$  due to plate convergence and subduction of the Nazca Plate under the South American Plate [Gregory-Wodzicki, 2000]. The South American low-level jet, which carries humid winds westward over the Amazon Basin [Marengo *et al.*, 2004], is redirected by the Andes, driving the high annual precipitation up to  $7000 \text{ mm yr}^{-1}$  in parts of the eastern Andes [Killeen *et al.*, 2007]. The climate and tectonic setting combine to produce moderate-to-high denudation rates of  $\sim 0.4 \text{ mm yr}^{-1}$  in the central Andes according to cosmogenic radionuclide concentrations in detrital quartz [Wittmann *et al.*, 2009] and decadal river gauging [Guyot *et al.*, 1996]. The slopes are steep and prone to landslides, which harvest sediment and POC [Blodgett and Isacks, 2007; Clark *et al.*, 2016]. In this part of the Andes, rivers drain large areas of sedimentary and meta-sedimentary melanges that comprise  $\sim 80\%$  of the Kosñipata River drainage area [Clark *et al.*, 2013].

The Kosñipata River is a tributary of the Madre de Dios River which feeds the Madeira River, a major Amazon tributary (Figures 1c and 1d). The wet climate sustains tropical montane cloud forest over 80% of the Kosñipata Basin (Figure 1a) [Malhi *et al.*, 2010]. The catchment is located in Manu National Park and the adjacent buffer zone (Table 1). The forest contains significant stores of organic carbon (total



**Figure 1.** The Kosñipata River in the Peruvian Andes. (a) San Pedro gauging station (yellow circle) and catchment area (purple line) and the subcatchment at the Wayqecha gauging station (yellow square) overlain on topography from the Shuttle Radar Topographic Mission (SRTM) digital elevation model at  $90 \times 90$  m resolution. (b) Landslides were mapped from satellite imagery at annual resolution from 1988 to 2012, for nontopographic shadow areas (shown in light grey, where landslides were not visible) [Clark *et al.*, 2016]. (c) The Kosñipata River feeds the Madre de Dios River (basin outlined in red), a tributary of the Madeira River draining to the Amazon River. The Miraflones gauging station (MI; black circle) captures a  $124,000 \text{ km}^2$  catchment, of which the Andean portion of the Madre de Dios Basin ( $>550$  m asl red shaded region) is  $35,600 \text{ km}^2$ . The river network was produced from HydroSHEDS [Lehner *et al.*, 2008]. (d) The Amazon River network with the Andes site (yellow circle) and the Miraflones River gauging station. The Andean portion of Amazonia (light green) and Amazonia in a strict sense (dark green) from Eva *et al.* [2005] fall mostly within the Amazon Basin (within black outline) [Lehner *et al.*, 2008].

$35,000 \pm 5000 \text{ t C km}^{-2}$ , with  $28,000 \pm 4000 \text{ t C km}^{-2}$  in soils and  $5300 \pm 800 \text{ t C km}^{-2}$  in vegetation [Clark *et al.*, 2016]. Total carbon stocks increase slightly with elevation due to an increase of soil stocks and woody necromass with elevation, accompanied by a smaller reduction in standing live biomass [Zimmermann *et al.*, 2010b; Gurdak *et al.*, 2014; Clark *et al.*, 2016].

**Table 1.** Characteristics of Gauging Stations on the Kosñipata River, Peru, and Estimates of Suspended Load Yields Over the Water Year of Study (February 2010 to January 2011)

Gauging Station	San Pedro	Wayqecha
Location	$13^{\circ}3'37''$ , $71^{\circ}32'40''$	$13^{\circ}9'46''$ , $71^{\circ}35'21''$
Catchment area <sup>a</sup> ( $\text{km}^2$ )	164.4	48.5
Mean catchment slope <sup>a</sup> (deg)	28	26
Mean catchment elevation <sup>a</sup> (m)	2805	3195
Land cover <sup>b</sup>	TMCF (80%), puna/transition (20%)	TMCF (50%), puna/transition (50%)
Geology <sup>c</sup>	Mudstones (80%), pluton intrusions (20%)	Mudstones (100%)
Number of samples	68	46
Annual runoff <sup>d</sup> ( $\text{mm yr}^{-1}$ )	$2800 \pm 130$	$3000 \pm 1500$
Suspended sediment yield <sup>e</sup> ( $\text{t km}^{-2} \text{ yr}^{-1}$ )	$3500 \pm 210$ ( $2220 \pm 130$ )	$1270 \pm 630$
POC <sub>biosphere</sub> yield <sup>e</sup> ( $\text{t C km}^{-2} \text{ yr}^{-1}$ )	$12.6 \pm 0.4$ ( $7.1 \pm 0.2$ )	$5.3 \pm 2.7$
POC <sub>petro</sub> yield <sup>e</sup> ( $\text{t C km}^{-2} \text{ yr}^{-1}$ )	$16.1 \pm 1.4$ ( $7.2 \pm 0.9$ )	$3.5 \pm 1.8$

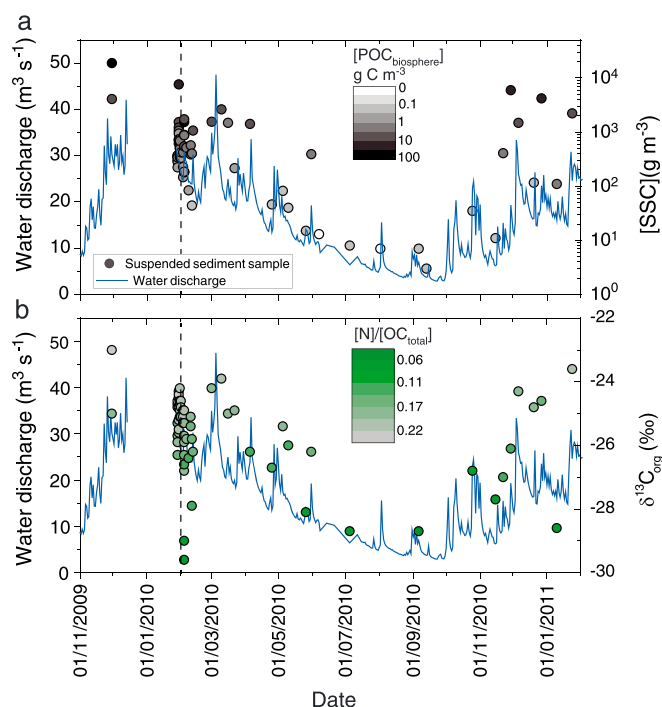
<sup>a</sup>Based on Shuttle Radar Topography Mission (SRTM) data with a  $90 \text{ m} \times 90 \text{ m}$  resolution.

<sup>b</sup>Determined using 2009 Quickbird 2 imagery, where TMCF is the tropical montane cloud forest.

<sup>c</sup>Basin geology derived from Carlotto Caillaux *et al.* [1996].

<sup>d</sup>From Clark *et al.* [2014]. Annual runoff is more uncertain at Wayqecha as it is based on monthly averaged data.

<sup>e</sup>From this study. For San Pedro, yields are derived from rating curves (Figure 5) applied to continuous water discharge data (Figure 2). Values are corrected for log-transformed bias [Ferguson, 1986]. Values in brackets are nonbias corrected. For Wayqecha, yields are derived from monthly averaged data.



**Figure 2.** Sample collection and hydrometric measurements from the San Pedro gauge, Kosñipata River. (a) River water discharge (blue line;  $\text{m}^3 \text{s}^{-1}$ ) over the study period [Clark et al., 2014] with suspended sediment samples (circles) and the corresponding suspended sediment concentration (SSC;  $\text{g m}^{-3}$ ; right axis). The color of the circle corresponds to the estimated biospheric particulate organic carbon concentration ( $\text{POC}_{\text{biosphere}}$ ;  $\text{g C m}^{-3}$ ). (b) Same as in Figure 2a but with the stable isotope composition ( $\delta^{13}\text{C}_{\text{org}}$ ; ‰; right axis) of the samples. The color of the fill is the nitrogen to organic carbon ratio ( $[\text{N}]/[\text{OC}_{\text{total}}]$ ). The vertical dotted line illustrates the start of the year over which annual discharges and yields were calculated (Table 1).

Rainfall in the Kosñipata River valley ranges from  $5300 \text{ mm yr}^{-1}$  around the San Pedro gauging station to  $1560 \text{ mm yr}^{-1}$  in the high elevations of the Wayqecha sub-catchment [Girardin et al., 2014b; Huaraca Huasco et al., 2014]. Average basin-wide rainfall is  $3112 \pm 414 \text{ mm yr}^{-1}$ , with an additional  $\sim 10\%$  cloud water contribution to river runoff [Clark et al., 2014]. The wet season is from December to March, the wet-dry transition season is April, the dry season is May to September, and the dry-wet transition season is October and November [Clark et al., 2014]—although we note that there is still considerable rainfall during the dry season. Stream runoff at the San Pedro gauging station has been calculated over a water year with continuous data spanning 2010–2011, as  $2796 \pm 126 \text{ mm yr}^{-1}$  (Table 1).

### 3. Materials and Methods

#### 3.1. Sample Collection and Hydrometric Measurements

At the San Pedro and Wayqecha catchment outlets (Figure 1a), suspended sediment (SS) samples were collected for geochemical analysis from November 2009 to February 2011, which covers the majority of two wet seasons (Figure 2). Thirty-seven river SS samples were collected from San Pedro and 25 samples from Wayqecha at a weekly to monthly frequency. We combine this new data set with published data from a 2 week intensive sampling scheme in the 2010 wet season, when SS samples were collected every 3 hours at San Pedro ( $n = 31$ ) and Wayqecha ( $n = 21$ ), as described in Clark et al. [2013]. This takes the total number of SS samples used in this study (Table S1 in the supporting information) to 68 at San Pedro and 46 at Wayqecha (Table 1). The sampling strategy was designed to provide suspended sediments from a range of water discharges ( $Q_w$ ;  $\text{m}^3 \text{s}^{-1}$ ), including flood events, in order to quantify SS,  $\text{POC}_{\text{biosphere}}$ , and  $\text{POC}_{\text{petro}}$ .

The geology of the Kosñipata Valley is  $\sim 80\%$  Paleozoic ( $\sim 450 \text{ Ma}$ ) meta-sedimentary mudstones which contain  $\text{POC}_{\text{petro}}$ , with plutonic intrusions contributing the remaining  $\sim 20\%$  of the catchment area [Carlotto Caillaux et al., 1996] (Table 1). The geological characteristics are representative of the Andean portion of the Madre de Dios Basin [Carlotto Caillaux et al., 1996; El Instituto Geológico Minero y Metalúrgico, 2013], covering approximately  $\sim 35,600 \text{ km}^2$ .

Suspended sediment samples were collected between November 2009 and February 2011 from two gauging stations, one capturing the catchment of the Kosñipata River at San Pedro (1360 m above sea level (asl),  $164.4 \text{ km}^2$ ; hereafter the “San Pedro” site) and the other the Wayqecha subbasin (2250 m asl,  $48.5 \text{ km}^2$ ; hereafter the “Wayqecha” site) (Table 1 and Figure 1a). In this study, we greatly expand on the work of Clark et al. [2013], which investigated the source of POC during two storm events in January and February 2010 and demonstrated that  $\text{POC}_{\text{petro}}$  can contribute between  $\sim 10\%$  and  $80\%$  of the total POC [Clark et al., 2013].



discharges, following previous work in mountain rivers [Hilton *et al.*, 2008b; Kao and Milliman, 2008; Townsend-Small *et al.*, 2008].

At the San Pedro site, the  $Q_w$  at the times of sample collection varied from 5.9 to 42.4 m<sup>3</sup> s<sup>-1</sup> [Clark *et al.*, 2014]. The full  $Q_w$  record was determined using an empirical relationship between stage height and  $Q_w$  measured at discrete times; this stage-discharge calibration was applied to the continuous stage height record [Clark *et al.*, 2014]. At the Wayqecha gauging station, the  $Q_w$  varied from 2.3 m<sup>3</sup> s<sup>-1</sup> to 8 m<sup>3</sup> s<sup>-1</sup> [Clark *et al.*, 2014]. At the Wayqecha gauging station all available instantaneous discharge (m<sup>3</sup> s<sup>-1</sup>) measurements ( $n = 59$ ) over the study year were used to determine mean monthly discharge in the absence of a reliable continuous measurement of stream height. The Wayqecha  $Q_w$  record is therefore of lower precision (Table 1) and introduces more uncertainty into flux calculations than at San Pedro [Clark *et al.*, 2014].

Collections of a known volume of river water (from 250 to 6400 mL) were made from the surface of the flow at the middle of the channel, in plastic bottles prerinsed with filtered river water. Larger volumes were collected during the dry season to collect sufficient SS for geochemical analyses. At both sample sites, our samples are likely to be representative of the SS load due to large-scale bed roughness which produces highly turbulent flow and mixed SS in the channel [Lupker *et al.*, 2011]. The known volume of river water was filtered through 0.7  $\mu$ m glass fiber filters (Whatman GF/F, 47 mm) to recover SS. Filters were dried at ~40°C within 2 days and stored in sterile petri dishes.

### 3.2. Geochemical Analyses

The isotopic and elemental compositions of POC were measured with an aim to assess the contribution of POC<sub>biosphere</sub> and POC<sub>petro</sub>. Methods were identical to previous studies in this catchment [Clark *et al.*, 2013], allowing direct data comparison. River SS was rinsed from the glass filter membrane using deionized water in glass beakers, and the samples were dried at 40°C [Hilton *et al.*, 2010; Clark *et al.*, 2013]. This procedure recovered the majority (>95%) of the sediment mass in these turbid samples but may leave behind the very finest sediment. The same procedure was carried out on precombusted quartz powder to quantify procedural blanks. The sediment mass (mg) and known filtered volume (L) were used to calculate the SS concentration (SSC; mg L<sup>-1</sup>). For two SS samples from San Pedro, and four from Wayqecha, there was insufficient material (<10 mg) to process for geochemical analysis (Table S1). Samples were homogenized using an agate mortar and pestle. Inorganic carbon, such as detrital carbonate including dolomite, was removed using a 5 M HCl leach for 4 h at 75°C [Galy *et al.*, 2007a; Hilton *et al.*, 2008a, 2010]. Thus, all analyses reported in this study refer to acid-insoluble POC. The HCl-leach method has been shown by Brodie *et al.* [2011] to be the most robust way to return reliable organic carbon to nitrogen ratios measured in similar materials to those analyzed here. Following several deionized water rinses to remove acid salts, the suspended load samples were dried at 75°C and transferred to clean glass vials.

The weight percent organic carbon ([OC<sub>total</sub>], %) and nitrogen ([N], %; used to determine the [N]/[OC<sub>total</sub>] ratio) was measured using a Costech CHN elemental analyzer (EA). The results were normalized by standards and corrected for an internal and procedural blank [Hilton *et al.*, 2010; Gröcke *et al.*, 2011; Clark *et al.*, 2013]. The stable isotope composition of POC ( $\delta^{13}\text{C}_{\text{org}}$ , ‰) was determined by continuous flow from the EA coupled via CONFLO-III to a Thermo-Delta-V isotope ratio mass spectrometer in the Stable Isotope Biogeochemistry Laboratory, Durham University. Values were normalized based on measured values of International Atomic Energy Agency and laboratory standards, corrected for any internal blank and procedural blank, and reported in  $\delta^{13}\text{C}$  notation relative to Vienna Pee Dee belemnite (VPDB). The precision ( $2\sigma$ ) and accuracy of  $\delta^{13}\text{C}_{\text{org}}$  were determined using standards measured under the same analytical conditions and were both 0.1‰ [Gröcke *et al.*, 2011]. Replicates of the river suspended sediment samples ( $n = 21$ ) returned an average  $2\sigma$  on  $\delta^{13}\text{C}$  of  $\pm 0.1\text{‰}$  and on OC<sub>total</sub> of  $\pm 0.01\%$ , and we take these as the average precision of the analyses.

A set of SS samples (9 from San Pedro and 7 from Wayqecha) were selected to measure <sup>14</sup>C activity, to expand the published measurements ( $n = 21$ ) from the Kosñipata River [Clark *et al.*, 2013]. Following the HCl decarbonation procedure detailed above, carbon in these samples was combusted, prepared to graphite, and measured by accelerator mass spectrometry at the National Ocean Sciences Accelerator Mass Spectrometry Radiocarbon Facility, Woods Hole. The data are presented here in the fraction modern ( $F_{\text{mod}}$ ) terminology, corrected to -25‰  $\delta^{13}\text{C}$ -VPDB based on measured  $\delta^{13}\text{C}_{\text{org}}$  values [Stuiver and Polach, 1977]. The procedural blank for the filtration stage contributed <0.01% of the CO<sub>2</sub> used for each <sup>14</sup>C analysis, meaning that

contamination from GF/F filters was negligible within uncertainty [Hilton *et al.*, 2010; Gröcke *et al.*, 2011; Clark *et al.*, 2013]. The inorganic carbon removal procedure did not alter the  $OC_{total}$ ,  $\delta^{13}C$ , or  $F_{mod}$  values of standards.

### 3.3. Concentration-River Stage Height Relationships

Power law rating curves have been widely used to quantify solid load fluxes using continuous water discharge datasets in mountain rivers, and a growing number of studies have used them to quantify  $POC_{biosphere}$  and  $POC_{petro}$  discharges in tropical [Hilton *et al.*, 2011a; Hatten *et al.*, 2012; Goñi *et al.*, 2013; Lloret *et al.*, 2013; Smith *et al.*, 2013] and temperate locations [Hilton *et al.*, 2011a; Hatten *et al.*, 2012; Goñi *et al.*, 2013; Smith *et al.*, 2013]. First, the fraction of POC derived from petrogenic sources,  $F_{petro}$ , was calculated using an end-member mixing model derived for this catchment [Clark *et al.*, 2013] using  $[N]/[OC_{total}]$  values (see section 4.2). The SS concentrations ( $SSC$ ;  $g\ m^{-3}$ ) were then multiplied by the  $[OC_{total}]$  and  $F_{petro}$  value to calculate the concentrations  $[POC_{biosphere}]$  ( $g\ C\ m^{-3}$ ) and  $[POC_{petro}]$  ( $g\ C\ m^{-3}$ ) in the river (Table 1). These particulate concentrations were compared to stage height ( $h$ ; in m) to examine whether power law rating curves describe patterns in the data set [Cohn, 1995; Vogel *et al.*, 2003; Hilton *et al.*, 2008b; Wheatcroft *et al.*, 2010; Hatten *et al.*, 2012].

### 3.4. Annual SS, $POC_{biosphere}$ , and $POC_{petro}$ Discharges

At San Pedro, the 15 minute resolution stage height ( $h$ ) measurements were used to calculate  $SSC$ ,  $POC_{biosphere}$ , and  $POC_{petro}$  using the rating curve models. Calculated concentrations were then multiplied by  $Q_w$  derived independently from each  $h$  measurement [Townsend-Small *et al.*, 2008; Clark *et al.*, 2013; Clark *et al.*, 2014]. The annual discharge of SS,  $POC_{biosphere}$ , and  $POC_{petro}$  were determined by summing up the 15 minute measurements for each day and then summing for each month. Yields were determined by dividing the discharge by the basin area ( $164.4\ km^2$ ; Table 1 and Figure 1a). Uncertainties in  $SSC$ ,  $POC_{biosphere}$ , and  $POC_{petro}$  discharges were calculated using the standard errors of the rating curve parameters [Turowski *et al.*, 2016]. Error propagation was used to quantify the uncertainty in the 15 minute solid load discharge using these values and the uncertainty in  $Q_w$ . The daily, monthly, and annual uncertainties were then calculated by additive error propagation. All annual solid load discharges were corrected for the bias introduced by fitting a linear regression to log-transformed data [Ferguson, 1986], as described below (see section 4.3.1).

For the Wayqecha Basin, in the absence of high temporal resolution  $h$  and  $Q_w$  measurements [Townsend-Small *et al.*, 2008; Clark *et al.*, 2013; Clark *et al.*, 2014], the mean monthly  $SSC$ ,  $POC_{biosphere}$ , and  $POC_{petro}$  were multiplied by the mean monthly  $Q_w$  to determine monthly discharge. In August there were no river measurements at the Wayqecha gauging station and linear extrapolation was carried out to determine runoff [Clark *et al.*, 2014] and solid load discharge [Clark *et al.*, 2013]. The fluxes were low in the dry season, including in August, so this extrapolation should not substantially affect our estimated annual yield.

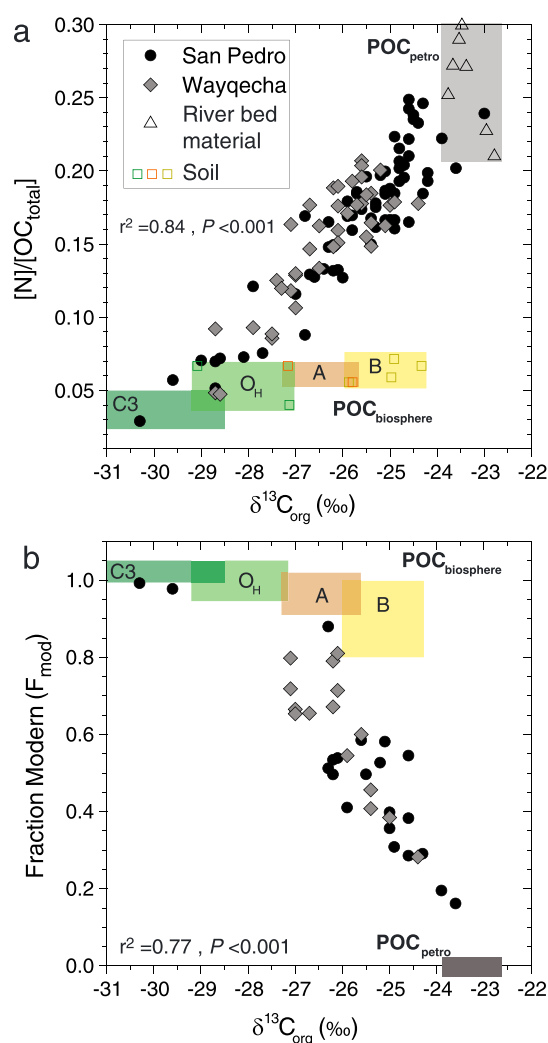
### 3.5. Landslide Mapping

Previous work has established the decadal rates of landsliding in the valley, based on mapping from satellite imagery at an annual resolution from 1988 to 2012 [Clark *et al.*, 2016]. The corresponding rates of  $POC_{biosphere}$  erosion by landslides were quantified as part of this prior work. However, this previous study encompassed a larger catchment area ( $185\ km^2$ ), including regions downstream of the San Pedro gauging station ( $164.4\ km^2$ ) on the Kosñipata River (Figure 1a), and so the results are not directly comparable to those from this study (the larger area was to allow the previous work to link to forest plots further downstream). Here we use the methods and analysis explained by Clark *et al.* [2016], applied to the area of the catchment upstream of the gauging stations used in this study (Figure 1b).

## 4. Results

### 4.1. Elemental and Isotope Geochemistry

The stable isotope composition ( $\delta^{13}C_{org}$ ), elemental composition  $[N]/[OC_{total}]$ , and radiocarbon activity ( $F_{mod}$ ) of POC from the SS samples collected between November 2009 and February 2011 from the Kosñipata River are consistent with the smaller, previously published data set collected over two storm events in January 2010 to February 2010 [Clark *et al.*, 2013] (see Table S1). The  $[OC_{total}]$  at the San Pedro gauging station ranged from 0.48% to 6.8% with a mean of 0.99% and at the Wayqecha gauging station from 0.44% to 4.5% with a



**Figure 3.** Elemental and isotopic compositions of POC in suspended load from the Kosñipata River from the San Pedro gauge (black circles) and from Wayqecha (grey diamonds). Published data from river bed materials (triangles) and soils (squares) from the study area are shown [Zimmermann *et al.*, 2009; Clark *et al.*, 2013]. (a) The stable isotopes of POC ( $\delta^{13}\text{C}_{\text{org}}$ ; ‰) versus the nitrogen to organic carbon ratio ([N]/[OC<sub>total</sub>]). (b) The radiocarbon activity (reported as fraction modern,  $F_{\text{mod}}$ ) versus  $\delta^{13}\text{C}_{\text{org}}$  (‰). The boxes show the ranges of [N]/[OC<sub>total</sub>] and  $\delta^{13}\text{C}_{\text{org}}$  from published sources [Zimmermann *et al.*, 2009; Rao, 2011] and estimates of  $^{14}\text{C}$  activity (not measured on soils), where  $O_H$ , A, and B are the soil horizons and C3 is the C3 vegetation; all of which represent biospheric POC (POC<sub>biosphere</sub>) sources. The grey box shows the rock-derived petrogenic POC (POC<sub>petro</sub>) compositions. Analytical uncertainties are smaller than the point sizes.

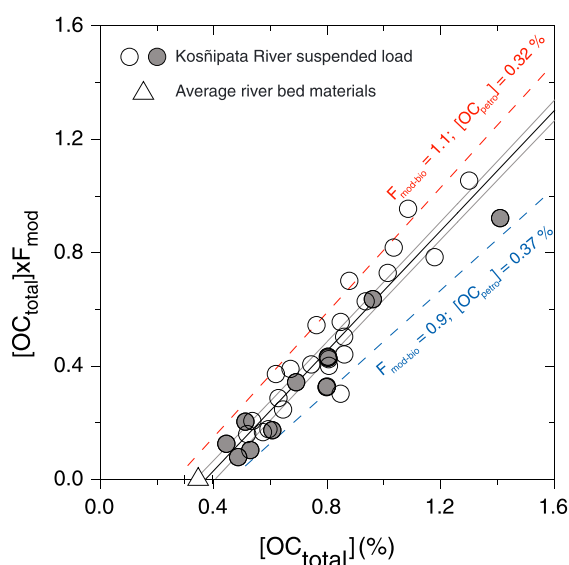
However, their  $\delta^{13}\text{C}_{\text{org}}$  values mean that they do not appear to have been a major input to the river POC<sub>biosphere</sub> during our study (Figure 3). Overall, our findings concur with those from other small mountain river catchments, where POC<sub>petro</sub> and POC<sub>biosphere</sub> are mixed during erosion and fluvial transport [Komada *et al.*, 2004; Hilton *et al.*, 2010; Kao *et al.*, 2014; Hilton, 2017], as well as previous work in the Kosñipata catchment [Clark *et al.*, 2013].

#### 4.2. End-Member Mixing Analysis

Clark *et al.* [2013] found that the  $\delta^{13}\text{C}_{\text{org}}$  and [N]/[OC<sub>total</sub>] values of POC in the Kosñipata River can be quantitatively explained by a mixture of POC<sub>petro</sub> from sedimentary rocks and POC<sub>biosphere</sub> from soil and vegetation. The additional POC samples analyzed here follow the same linear trends described in Clark *et al.* [2013], in

mean of 1.1%. The  $\delta^{13}\text{C}_{\text{org}}$  ranged from  $-23\text{‰}$  to  $-30\text{‰}$ , and the [N]/[OC<sub>total</sub>] ranged from 0.03 to 0.25 (Figure 3a). The  $F_{\text{mod}}$  values ranged from 0.16 to 0.80 (Figure 3b). There were seasonal differences in  $\delta^{13}\text{C}_{\text{org}}$  (‰) evident at both stations (Figure 2b). The wet season had a range in  $\delta^{13}\text{C}_{\text{org}}$  values from  $-27\text{‰}$  to  $-24\text{‰}$ . The dry season had a depleted  $\delta^{13}\text{C}_{\text{org}}$  signal with values mostly between  $-28\text{‰}$  and  $-29\text{‰}$ . The transitional seasons formed a link between the wet season and the dry season with  $\delta^{13}\text{C}_{\text{org}}$  from  $-26\text{‰}$  to  $-28\text{‰}$  (Figure 2b).

The  $\delta^{13}\text{C}_{\text{org}}$  values were linearly correlated with [N]/[OC<sub>total</sub>] and  $F_{\text{mod}}$  (Figure 3). Such trends are consistent with previous work invoking a contribution to POC from rock-derived organic carbon (POC<sub>petro</sub>), which is  $^{14}\text{C}$  depleted ( $F_{\text{mod}} \sim 0$ ), is  $^{13}\text{C}$  enriched, has high [N]/[OC<sub>total</sub>] values, and is well characterized by river bed material samples (Figure 3a). The  $\delta^{13}\text{C}_{\text{org}}$ , [N]/[OC<sub>total</sub>], and  $F_{\text{mod}}$  values can then be explained by variable addition of POC from vegetation and soil (POC<sub>biosphere</sub>), which is  $^{13}\text{C}$  depleted, and has lower [N]/[OC<sub>total</sub>] values (Figure 3). The linear trends described by  $\delta^{13}\text{C}_{\text{org}}$ , N/C, and  $F_{\text{mod}}$  for the suspended load (Figure 3) suggest that the majority of POC<sub>biosphere</sub> has a composition similar to  $O_H$  and A layers of the soil [Zimmermann *et al.*, 2009]. The deeper soil horizons may contribute importantly to the carbon stock on hillslopes [Clark *et al.*, 2016], particularly at lower slope angles. These deeper soils have [N]/[OC<sub>total</sub>] values similar to surface soils and distinct from POC<sub>petro</sub>.



**Figure 4.** Organic carbon concentration  $[OC_{total}]$  versus the  $[OC_{total}]$  multiplied by the fraction modern ( $F_{mod}$ ) from  $^{14}C$ . The circles are the river samples from the Kosñipata River (the grey fills are the samples collected following the large, landslide-triggering storm event of 4 March 2010; the open circles were collected prior), and the triangle is the mean of river bed materials (assumed to have a  $F_{mod} = 0$ ). The black line is the linear fit to the data ( $r^2 = 0.99$ ;  $p < 0.001$ ,  $n = 35$ ), and grey are the 95% confidence intervals. The slope of this line corresponds to  $F_{mod}$  of the biospheric POC ( $F_{mod-bio}$ ) of  $1.05 \pm 0.02$  and the intercept to rock-derived organic carbon concentration,  $[OC_{petro}] = 0.37 \pm 0.03$ . The red and blue lines are the mixing models based on the values of  $F_{mod-bio}$  and  $[OC_{petro}]$  as shown. Analytical errors are smaller than the point sizes.

which  $\delta^{13}C_{org}$  (‰) is correlated with the  $[N]/[OC_{total}]$  ratio and with  $F_{mod}$  (Figure 3). The linear trends between these ratios are consistent with the mixing hypothesis described above. Full details of how these mixing relationships were used to quantitatively partition sources can be found in Clark *et al.* [2013] (though note that  $POC_{biosphere}$  and  $POC_{petro}$  are referred to as  $POC_{nonfossil}$  and  $POC_{fossil}$ , respectively, in this prior paper). To briefly summarize the mixing model calculations, an end-member mixing analysis with  $F_{mod}$  from a subset of river SS samples was first used to determine the fraction of  $POC_{petro}$ , or  $F_{petro}$ , with an estimated uncertainty of 0.02. These results were then used to confirm that the  $[N]/[OC_{total}]$  ratio of the POC samples could be used to reliably quantify  $F_{petro}$  in the absence of  $F_{mod}$  measurements [Clark *et al.*, 2013]. The resulting uncertainty on the calculation of  $F_{petro}$  for the Kosñipata River was found to be 0.08 to 0.14 [Clark *et al.*, 2013].

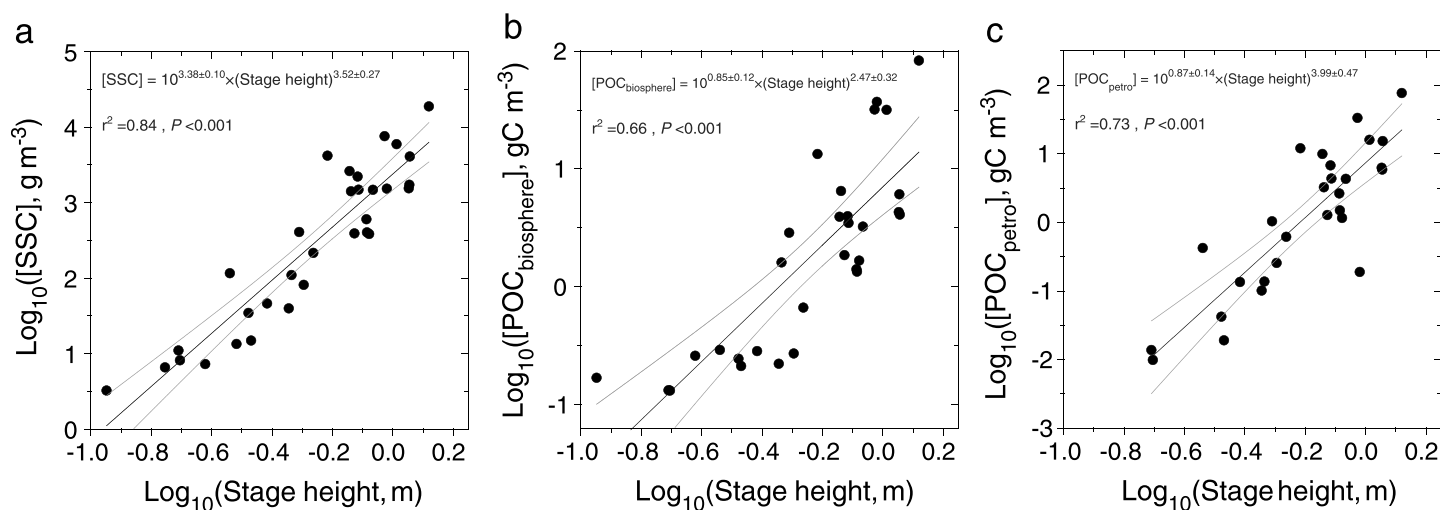
We use the mixing model from Clark *et al.* [2013], the  $[N]/[OC_{total}]$  of the river POC, and the composition of end-members to quantify  $F_{petro}$  in each sample from this study. Although the radiocarbon data were used to validate our approach, the end-member mixing analysis uses  $[N]/[OC_{total}]$  to make the distinction between  $POC_{petro}$  and  $POC_{biosphere}$  (Figure 3a). Therefore, the model used here cannot separate the source of  $POC_{biosphere}$  between different vegetation and soil components which have relatively similar  $[N]/[OC_{total}]$  values compared to the spread of data (Figure 3a). The  $POC_{biosphere}$  calculated for the measured samples (Table S1) comprised on average  $0.53 \pm 0.10\%$  ( $n = 66$ ,  $\pm SE$ ) of the SS at the San Pedro gauging station and  $0.78 \pm 0.14\%$  ( $n = 42$ ,  $\pm SE$ ) at Wayqecha. The  $POC_{petro}$  contribution was on average  $0.37 \pm 0.03\%$  ( $n = 66$ ,  $\pm SE$ ) and  $0.34 \pm 0.02\%$  ( $n = 66$ ,  $\pm SE$ ) of the SS at San Pedro and Wayqecha stations, respectively.

In addition to quantifying contributions from petrogenic versus biospheric carbon to the suspended load samples, we use the  $OC_{total}$  and  $F_{mod}$  measurements to explore the  $^{14}C$  age of the  $POC_{biosphere}$ . Using previously established approaches [Blair *et al.*, 2003; Galy *et al.*, 2008b; Galy and Eglinton, 2011], we plotted  $[OC_{total}]$  against  $[OC_{total}] \times F_{mod}$ . A linear trend in this space suggests that the  $^{14}C$  activity of the biospheric POC ( $F_{mod-bio}$ ) and the petrogenic organic carbon concentration ( $[OC_{petro}]$ , %) are relatively homogeneous in the sample set [Blair *et al.*, 2003; Galy and Eglinton, 2011]. The trend in the samples from the Kosñipata River (Figure 4) suggests that this is the case, with scatter attributable to some variability in  $F_{mod-bio}$  and  $OC_{petro}$  values.

### 4.3. Rating Curve Models

At the San Pedro gauging station, power law rating curves describe the solid load concentrations as a function of stage height,  $h$  (Figure 5). Height ( $h$ ) is used rather than  $Q_w$  [Clark *et al.*, 2014] because stage height represents the measured data, simplifying uncertainty propagation. The San Pedro record includes several published data from a heavily sampled 2 week period [Clark *et al.*, 2013] during which the stage height did not vary by much ( $\log_{10}[\text{stage height}]$  from approximately  $-0.15$  to  $-0.05$ ) when compared to the data set as a whole (Figure 5). This means that a regression model applied to the whole data set (with





**Figure 5.** Relationships between river stage height and solid load constituent concentration for the Kosñipata River at San Pedro. (a) Suspended sediment concentration (SSC), (b) biospheric particulate organic carbon concentration (POC<sub>biosphere</sub>), and (c) petrogenic POC concentration (POC<sub>petro</sub>). The black lines show the linear regressions through log-transformed data and 95% confidence intervals (grey lines). Equations give the forms of rating curves used to quantify solid load discharge.

log<sub>10</sub>[stage height] from approximately −1.0 to +0.1) is potentially biased by these data. Therefore, we average the high-frequency measurements from this time period for each week. However, the storm peak samples were used to help constrain high-flow variability, which is difficult to sample with weekly measurements. The weekly averaging produces a data set totaling 32 data points for SSC, 30 for POC<sub>biosphere</sub>, and 28 for POC<sub>petro</sub>. Linear fits were made to log-transformed data (Figure 5), following common approaches to best describe solid load concentration over a range of flow conditions.

Measured SSC ranged from a minimum of <5 g m<sup>-3</sup> to a maximum of ~19,000 g m<sup>-3</sup> (Table S1). SSC was related to  $h$  and well described by a power law rating curve ( $r^2 = 0.85$ ,  $p < 0.001$ ; Figure 5a). Measured POC<sub>petro</sub> values ranged from <0.01 g C m<sup>-3</sup> up to a maximum of 77 g C m<sup>-3</sup> (Table S1) and were correlated with  $h$  ( $r^2 = 0.73$ ,  $p < 0.001$ ; Figure 5c). POC<sub>petro</sub> was closely linked with SSC as has been previously documented in mountain river-suspended load [Blair *et al.*, 2003; Hilton *et al.*, 2011a], where POC<sub>petro</sub> has not been completely oxidized [Hilton *et al.*, 2014; Hilton, 2017]. Measured samples covered a wide range of POC<sub>biosphere</sub>, with a minimum of ~0.1 g C m<sup>-3</sup> to a maximum of 83 g C m<sup>-3</sup> (Table S1). The POC<sub>biosphere</sub> values were correlated with  $h$ , and a power law rating curve can describe the majority of the variability ( $r^2 = 0.66$ ,  $p < 0.001$ ; Figure 5b). However, there was more overall scatter in the POC<sub>biosphere</sub>- $h$  relationship than for SSC and POC<sub>petro</sub>. In all three cases, the rating curves appear to underestimate the highest measured SSC, POC<sub>biosphere</sub>, and POC<sub>petro</sub> values (Figure 5).

#### 4.3.1. Rating Curve Bias Correction

Rating curves can be subject to known biases if fits are made to log-transformed data and then retransformed back to units of concentration or flux [Ferguson, 1986]. Alternatives include using nonlinear threshold rating curves [Hilton *et al.*, 2008b], linear models [Townsend-Small *et al.*, 2008; Hilton *et al.*, 2012], or flux-weighted averaging methods [Walling and Webb, 1981; Ferguson, 1987; Dadson *et al.*, 2003; Hilton *et al.*, 2012]. Here power law rating curves were used in the first instance because of the known “flashy” nature of river hydrographs in the Peruvian Andes, with storm-induced floods an important feature [Townsend-Small *et al.*, 2008; Clark *et al.*, 2013, 2014]. The observed flux-weighted mean concentrations are used as a cross-check on the rating curve estimates.

The rating curve bias is in the direction of underestimation and increases with the variance of the scatter around the underlying trend. If uncorrected, it can lead to underestimation of river constituent loads by 50% or more [Ferguson, 1986, 1987; Cohn, 1995] even when the underlying trend is of approximately power law form. If the residuals from the log-log regression have an approximately normal distribution, a simple approximate correction for the bias is to multiply  $C_{\text{pred}}$  by  $\exp(2.65 s^2)$ , where  $C_{\text{pred}}$  is the concentration predicted by detransforming the log-log regression equation and  $s^2$  is the variance of the residuals in log<sub>10</sub> units [Walling and Webb, 1981; Duan, 1983; Thomas, 1985; Ferguson, 1986]. An exact correction is given by Cohn *et al.* [1989] and a nonparametric version by Duan [1983]. In most circumstances the three methods give similar results according to Cohn *et al.* [1989] and Cohn [1995], so the simplest one is used here.

For the SSC versus  $h$  rating curve from the Kosñipata River, the standard deviation (SD) of the linear fit to log-transformed data is 0.414, giving a  $(C_{\text{true}}/C_{\text{pred}})$  value of 1.58. The largest bias correction is required for  $\text{POC}_{\text{petro}}$ , with a SD = 0.551 and  $(C_{\text{true}}/C_{\text{pred}}) = 2.23$ . The correction for  $\text{POC}_{\text{biosphere}}$  is between these values, with SD = 0.464 and  $(C_{\text{true}}/C_{\text{pred}}) = 1.77$ . These correction values are within the range of those from the empirical data sets reported by Ferguson [1986]. For completeness, we report both the uncorrected and the bias-corrected solid load discharges (Table 1).

#### 4.4. Annual SS, $\text{POC}_{\text{biosphere}}$ , and $\text{POC}_{\text{petro}}$ Discharges

##### 4.4.1. Kosñipata River at San Pedro

The uncorrected annual SS yield based on the rating curve for the San Pedro catchment ( $164.4 \text{ km}^2$ ) was  $2220 \pm 130 \text{ t km}^{-2} \text{ yr}^{-1}$  over the water year of the study period (1 February 2010 to 31 January 2011; Table 1). Based on the annual river runoff of  $2796 \pm 126 \text{ mm yr}^{-1}$  over the same time period [Clark *et al.*, 2014], this corresponds to an annual average  $\text{SS} \sim 800 \text{ g m}^{-3}$ . This value is considerably lower than both the average measured  $\text{SS} = 1120 \pm 310 \text{ g m}^{-3}$  ( $n = 68$ ,  $\pm \text{SE}$ ) and the water discharge-weighted  $\text{SS} = 1560 \text{ g m}^{-3}$  (i.e., the flux-weighted  $\text{SS}$ ) over the sampling period. The rating curve therefore appears to underestimate the solid load concentrations measured in this river, as expected given the known bias described above (section 4.3.1). After correcting for this bias, we calculate an annual SS yield of  $3500 \pm 210 \text{ t km}^{-2} \text{ yr}^{-1}$  over the water year (Table 1). The corresponding annual average  $\text{SS} = 1260 \text{ g m}^{-3}$  is in better agreement with the measurements. We therefore conclude that the bias correction produces a robust quantification of SS discharge, and by inference also  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  yields for this catchment.

The SS yield for the Kosñipata River at San Pedro over the sampled water year (Figure 2) is larger than that reported for the Chorobamba River of the eastern Andes of Peru at  $\sim 120$  to  $620 \text{ t km}^{-2} \text{ yr}^{-1}$  [Townsend-Small *et al.*, 2008]. This difference is expected given the steeper slopes and higher annual runoff in the Kosñipata study region. The SS yield for the water year is consistent with gauging measurements made downstream of the Kosñipata River, in the Madre de Dios River at Miraflores ( $124,000 \text{ km}^2$ ) from 1983 to 1990, where an estimated  $71 \text{ Mt yr}^{-1}$  of suspended sediment were transported [Guyot *et al.*, 1996]. If this sediment is dominantly sourced from the Andes [e.g., Gibbs, 1967; Meade *et al.*, 1979; Richey *et al.*, 1986; Allegre *et al.*, 1996; Dunne *et al.*, 1998; Guyot *et al.*, 2005; Filizola and Guyot, 2009; Martinez *et al.*, 2009], which cover  $35,600 \text{ km}^2$  (defined here as the area  $> 550 \text{ m asl}$ ) [Wittmann *et al.*, 2009], the corresponding SS yield was  $\sim 2000 \text{ t km}^{-2} \text{ yr}^{-1}$ . Based on Tropical Rainfall Measuring Mission satellite rainfall data from 1998 to 2012, 2010 was a wetter than average year [Clark *et al.*, 2014] and the SS discharge is therefore also likely to be higher than average. Therefore, the Kosñipata River SS discharge is consistent with downstream data.

The annual  $\text{POC}_{\text{biosphere}}$  yield was  $12.6 \pm 0.4 \text{ t C km}^{-2} \text{ yr}^{-1}$  over the study period, when corrected for log-transformed bias using the method of Thomas [1985] and Ferguson [1986] (Table 1). Based on the measured runoff and SS yield, this corresponds to an annual average  $\text{POC}_{\text{biosphere}}$  of  $4.5 \text{ g C m}^{-3}$  and weight percent of  $\text{POC}_{\text{biosphere}}$  in the suspended load of 0.35%. These values are consistent with the measured averages ( $4.0 \pm 1.3 \text{ g C m}^{-3}$ ,  $0.53 \pm 0.10\%$ ) and water-discharge-weighted averages ( $5.5 \text{ g C m}^{-3}$ ,  $0.39\%$ ), suggesting that the bias-corrected yield is a robust estimation of annual  $\text{POC}_{\text{biosphere}}$  yield.

The annual  $\text{POC}_{\text{petro}}$  yield was  $16.1 \pm 1.4 \text{ t C km}^{-2} \text{ yr}^{-1}$ , corrected for log-transformed bias (Table 1). This corresponds to an annual average  $\text{POC}_{\text{petro}}$  of  $5.8 \text{ g m}^{-3}$  and weight percent of  $\text{POC}_{\text{petro}}$  in the suspended load of 0.45%. Again, these values are consistent with the measured averages ( $5.0 \pm 1.4 \text{ g C m}^{-3}$ ,  $0.37 \pm 0.03\%$ ) and water-discharge-weighted averages ( $6.5 \text{ g C m}^{-3}$ ,  $0.41\%$ ).

##### 4.4.2. Kosñipata River at Wayqecha

The annual SS yield for the Wayqecha subcatchment ( $48.5 \text{ km}^2$ ) was estimated to be  $1270 \pm 630 \text{ t km}^{-2} \text{ yr}^{-1}$  over the water year of study, based on the monthly averaging method (Table 1). The sediment yield is therefore lower in this upstream subcatchment compared to the larger catchment at San Pedro, which is consistent with the lower rates of landsliding occurring upstream of the Wayqecha gauging station [Clark *et al.*, 2016], since landslides often supply a large amount of sediment to mountain rivers [Hovius *et al.*, 2000]. The lower SS yield at Wayqecha in comparison to San Pedro is also consistent with a lower average catchment slope [Clark *et al.*, 2014; Torres *et al.*, 2015; Clark *et al.*, 2016]. The Wayqecha  $\text{POC}_{\text{biosphere}}$  yield was estimated to be  $5.3 \pm 2.7 \text{ t C km}^{-2} \text{ yr}^{-1}$  and the  $\text{POC}_{\text{petro}}$  yield  $3.5 \pm 1.8 \text{ t C km}^{-2} \text{ yr}^{-1}$ . These values correspond to a  $\% \text{POC}_{\text{biosphere}}$  in SS of 0.46% and  $\% \text{POC}_{\text{petro}}$  in SS of 0.28%.

#### 4.5. Landslide Mobilization of $\text{POC}_{\text{biosphere}}$

We use the methods of *Clark et al.* [2016] to quantify the rate of landsliding and corresponding mobilization of  $\text{POC}_{\text{biosphere}}$  from soil and vegetation. Across the catchment area upstream of San Pedro, the 25 year average landslide rate mobilized  $23 \pm 4 \text{ t C km}^{-2} \text{ yr}^{-1}$  of  $\text{POC}_{\text{biosphere}}$ . Of this,  $4.7 \pm 0.8 \text{ t C km}^{-2} \text{ yr}^{-1}$  was derived from vegetation (aboveground and belowground biomass) and  $18 \pm 3 \text{ t C km}^{-2} \text{ yr}^{-1}$  from soil. These yields are lower than the previously published work based on a larger catchment area ( $184 \text{ km}^2$  compared to  $164.4 \text{ km}^2$  in this study) because landsliding rates increase downstream of a river knickpoint in the valley [*Clark et al.*, 2016]. In the Wayqecha subcatchment, the 25 year average landslide rate mobilized  $17 \pm 3 \text{ t C km}^{-2} \text{ yr}^{-1}$  of  $\text{POC}_{\text{biosphere}}$ ,  $3.2 \pm 0.8 \text{ t C km}^{-2} \text{ yr}^{-1}$  of vegetation, and  $14 \pm 3 \text{ t C km}^{-2} \text{ yr}^{-1}$  of soil.

On 4 March 2010, a large storm delivered intense precipitation [*Clark et al.*, 2014] and triggered landslides which contributed importantly to the 25 year average  $\text{POC}_{\text{biosphere}}$  yield [*Clark et al.*, 2016]. Within the whole basin captured by the San Pedro gauge, the 2010 landslides, mostly triggered during a single storm event on 4 March 2010, mobilized  $71 \pm 12 \text{ t C km}^{-2}$ , of which  $17 \pm 2 \text{ t C km}^{-2}$  derived from vegetation and  $54 \pm 12 \text{ t C km}^{-2}$  from soil. The storm had less impact further upstream [*Clark et al.*, 2014; *Clark et al.*, 2016]. In the Wayqecha catchment, the 2010 landslide  $\text{POC}_{\text{biosphere}}$  yield was  $10 \pm 2 \text{ t C km}^{-2}$  ( $1.9 \pm 0.6 \text{ t C km}^{-2}$  derived from vegetation and  $8.5 \pm 2.4 \text{ t C km}^{-2}$  from soil).

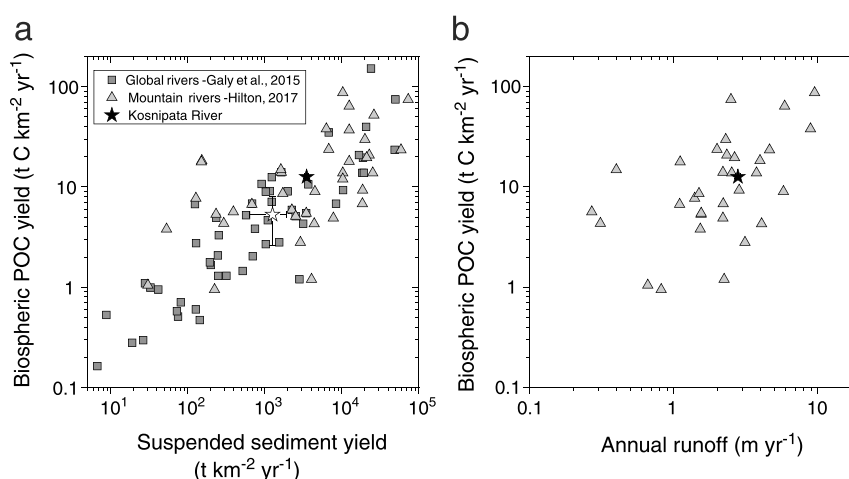
### 5. Discussion

The lateral carbon transfer from the terrestrial biosphere to  $\text{POC}_{\text{biosphere}}$  in rivers is important for carbon budgets both at the forest plot scale over annual time scales [*Berhe et al.*, 2007; *Restrepo et al.*, 2009; *Malhi*, 2012; *Li et al.*, 2015] and at regional to global scale, over longer periods of time [*Galy et al.*, 2015; *Hilton*, 2017]. Mountain rivers have been shown to have high  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  discharges, particularly in regions which experience high runoff [*Hilton*, 2017], and distinguishing between these sources is vital to evaluate the impact of river transport on carbon budgets. Here we shed new light on the discharge of  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  by mountain rivers, by quantifying annual yields in an Andean catchment where a suite of hydrometric, geomorphic, and ecological data sets are available [*Girardin et al.*, 2010; *Malhi et al.*, 2010; *Marthews et al.*, 2012; *Clark et al.*, 2014, 2016]. First, we assess the intraannual variability of  $\text{POC}_{\text{biosphere}}$  discharge and, for the first time, directly compare annual river fluxes to estimates of landslide-mobilized  $\text{POC}_{\text{biosphere}}$  inputs made over the same time window. Second, we discuss the degree to which the erosion and discharge of  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  impact the net carbon balance of Andean forest ecosystems. Finally, we consider the fate of eroded organic carbon in the wider Amazon Basin and its role in larger-scale carbon budgets.

#### 5.1. Fluvial Transport of $\text{POC}_{\text{biosphere}}$

The annual  $\text{POC}_{\text{biosphere}}$  yields of the Kosñipata River are consistent with patterns revealed by recently published global compilations in catchments around the world [*Galy et al.*, 2015; *Hilton*, 2017]. These data confirm the important role of physical erosion rate (which sets SS yield) in determining the  $\text{POC}_{\text{biosphere}}$  yield (Figure 6a) [*Hilton et al.*, 2012; *Galy et al.*, 2015]. They also suggest that annual runoff controls the variability in  $\text{POC}_{\text{biosphere}}$  yield (Figure 6b), confirming an important role of climate in regulating carbon export from the terrestrial biosphere [*Hilton*, 2017].

These global patterns arise because high catchment-average physical erosion rates are often accompanied by steep slopes in mountain environments [*Larsen et al.*, 2014]. Steep slopes can enhance the erosion and supply of  $\text{POC}_{\text{biosphere}}$  from soil and vegetation via two main geomorphic processes. First, bedrock landslides can clear entire tracts of mountain forest and deliver this material to the river channel network [*Hilton et al.*, 2008a; *West et al.*, 2011; *Clark et al.*, 2016]. This process mobilizes  $\text{POC}_{\text{biosphere}}$  ranging from fine-grained, mineral-associated  $\text{POC}_{\text{biosphere}}$  to entire tree trunks [*Hilton et al.*, 2011b; *West et al.*, 2011]. Second, overland surface flow and shallow landsliding can mobilize loose material and  $\text{POC}_{\text{biosphere}}$  from surface soils [*Gomi et al.*, 2008], with the rate of transport depending on hillslope steepness [*Roering et al.*, 2001]. Rainfall can drive both landslide activity and overland surface flow, resulting in more efficient hillslope-channel coupling and delivery of  $\text{POC}_{\text{biosphere}}$  to river channels [*Hilton et al.*, 2012]. We discuss these processes in more detail in the following sections.



**Figure 6.** Biospheric POC yields for the Kosñipata River (stars) at San Pedro (black star) and Wayqecha (white star) in comparison to data from global compilations [Galy *et al.*, 2015; Hilton, 2017] as a function of (a) suspended sediment yield and (b) annual runoff (Wayqecha not shown).

### 5.1.1. Intraannual Variability in $\text{POC}_{\text{biosphere}}$ Discharge

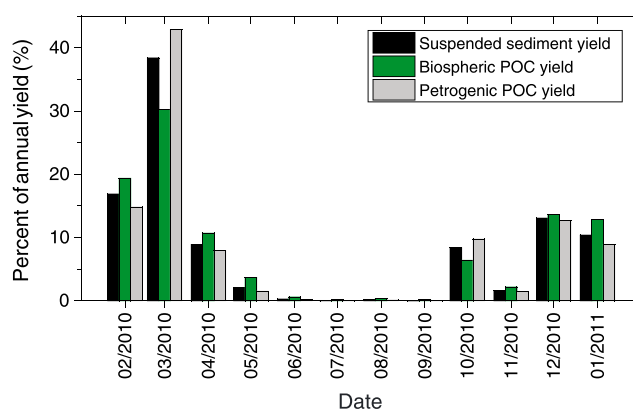
Seasonality played an important role in the erosion and discharges of SS,  $\text{POC}_{\text{biosphere}}$ , and  $\text{POC}_{\text{petro}}$  at the San Pedro gauging station, reflecting the geomorphic and hydrological processes operating in mountain catchments. The wet season, covering 4 months from December to March, was responsible for most of the discharges of SS (77%),  $\text{POC}_{\text{biosphere}}$  (73%), and  $\text{POC}_{\text{petro}}$  (78%) (Figure 7). In the dry season (5 months from May to September), the river transported <5% of the annual discharge of these solid constituents.

The low  $Q_w$  values during the dry season (Figure 2) result in reduced turbulent kinetic energy, allowing fine suspended sediment and POC to settle [Garcia and Parker, 1991; Hamm *et al.*, 2011]. The hydrological budget of this catchment shows that the majority of the river water during the dry season is sourced from delayed runoff via groundwater [Clark *et al.*, 2014]. When combined with the low rainfall, this results in minimal overland flow and mass-wasting processes such as landslides, which deliver  $\text{POC}_{\text{biosphere}}$  to rivers [Hilton *et al.*, 2012; Clark *et al.*, 2013; Smith *et al.*, 2013], explaining the low  $\text{POC}_{\text{biosphere}}$  discharge (Figure 7).

These geomorphic processes can also explain seasonality in the  $\delta^{13}\text{C}$  and  $[\text{N}]/[\text{OC}_{\text{total}}]$  values (Figure 2b). In general, in the dry season the  $\delta^{13}\text{C}$  values were more depleted at  $\sim -28\text{‰}$ , and these samples also carry the more  $^{14}\text{C}$ -enriched  $\text{POC}_{\text{biosphere}}$  component of the POC (Figure 3b) [Clark *et al.*, 2013]. With low  $Q_w$  and low rainfall, landslide activity is greatly reduced [Clark *et al.*, 2016], driving less input of clastic sediment (Figure 2a) and  $\text{POC}_{\text{petro}}$ . As a result, the ratio of  $\text{POC}_{\text{petro}}$  to  $\text{POC}_{\text{biosphere}}$  is lower in the dry season, explaining the bulk elemental and isotopic composition (Figures 2b and 3).

These observations contrast with previous work in the Peruvian Andes in a less steep and much less erosive catchment of the Chorobamba River [Townsend-Small *et al.*, 2007; Townsend-Small *et al.*, 2008]. There, in-stream photosynthesis by aquatic autotrophs is thought to be responsible for depleted  $\delta^{13}\text{C}$  values during the dry season. While POC from this source could be present in the Kosñipata River during the low-turbidity dry season, we note that the dry season  $[\text{N}]/[\text{OC}_{\text{total}}]$  values are 0.04–0.07, consistent with a source from vegetation and soil (Figure 3a) rather than aquatic biomass ( $[\text{N}]/[\text{OC}_{\text{total}}] > 0.1$ ) [Townsend-Small *et al.*, 2007].

Individual storm events and the associated rainfall-driven changes in SS load and POC transport [e.g., Hilton *et al.*, 2012] influenced the mobilization and transport of material in this catchment. The largest storm in the sampling period (4–7 March 2010) had a stream runoff of  $1.3 \text{ mm h}^{-1}$  over the peak when  $Q_w > 50 \text{ m}^3 \text{ s}^{-1}$ . This storm contributed only  $\sim 2\%$  of the annual water discharge but was responsible for 24% of the SS yield, 14% of the  $\text{POC}_{\text{biosphere}}$  yield, and 31% of the  $\text{POC}_{\text{petro}}$  yield based on the rating curve estimates. Intense runoff during such storm events can allow erosion thresholds to be surpassed at a time when fluvial transport capacity is high, explaining why these events play an important role in the erosion and transfer of soil and standing biomass to the river.



**Figure 7.** Annual breakdown by month of yields of suspended sediment,  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  for the San Pedro catchment, as a percentage of the annual yield. The wet season typically represents the period from December to March.

### 5.1.2. Comparison Between $\text{POC}_{\text{biosphere}}$ Discharge and Landslide Inputs

Previous studies have suggested that bedrock and shallow-soil landslides can supply  $\text{POC}_{\text{biosphere}}$  to mountain rivers [Hilton *et al.*, 2008b, 2011b; Hovius *et al.*, 2011; West *et al.*, 2011; Larsen, 2012; Stallard, 2012; Smith *et al.*, 2013]. In the Kosñipata Valley, landslides have been shown to play an important role in mobilizing  $\text{POC}_{\text{biosphere}}$  from hillslopes [Clark *et al.*, 2016]. In the San Pedro catchment, the 25 year average landslide activity mobilized  $23 \pm 4 \text{ t C km}^{-2} \text{ yr}^{-1}$  of  $\text{POC}_{\text{biosphere}}$  from soil and vegetation, which is higher than the river

$\text{POC}_{\text{biosphere}}$  discharge ( $12.6 \pm 0.4 \text{ t C km}^{-2} \text{ yr}^{-1}$ ). The difference is even larger when we compare the 2010 landslide  $\text{POC}_{\text{biosphere}}$  yield of  $71 \pm 12 \text{ t C km}^{-2} \text{ yr}^{-1}$ , which covers the same time period as the river gauging. The 2010 landslides were mostly triggered during the 4 March rainfall event, when an estimated  $\sim 1.8 \text{ t C km}^{-2}$  of  $\text{POC}_{\text{biosphere}}$  was discharged by the river-suspended load. Before now, it has not been possible to compare landslide and river  $\text{POC}_{\text{biosphere}}$  discharge over the same time window for more than one storm event [Hilton *et al.*, 2008b].

Two reasons for the difference between landslide-mobilized  $\text{POC}_{\text{biosphere}}$  and river  $\text{POC}_{\text{biosphere}}$  discharge may relate to the methods employed. Landslides can mobilize coarse materials which are not collected by most river POC sampling methods [Turowski *et al.*, 2016]. The differences between the yields in the Kosñipata catchment can be explained if  $\sim 80\%$  of the landslide-mobilized  $\text{POC}_{\text{biosphere}}$  were coarse grained (i.e., coarser than sand) and thus were not sampled using our methodology. Coarse  $\text{POC}_{\text{biosphere}}$  transport in rivers remains difficult to measure but can be an important component of  $\text{POC}_{\text{biosphere}}$  discharge in mountain catchments [Turowski *et al.*, 2013, 2016]. The second methodological issue relates to the underestimation of river  $\text{POC}_{\text{biosphere}}$  discharge during the March 2010 flood, resulting from (i) underestimation of  $Q_w$  at high flow [Clark *et al.*, 2014] and (ii) lacking  $\text{POC}_{\text{biosphere}}$  measurements at this storm peak to validate the rating curve (Figure 2a). Both factors are likely to play some role.

Another explanation for the observed difference between estimates of landslide  $\text{POC}_{\text{biosphere}}$  inputs and river  $\text{POC}_{\text{biosphere}}$  discharge is process based. Some of the material mobilized by landslides can be stored within landslide deposits over decades, in analogy to clastic sediment [Korup *et al.*, 2004; Hovius *et al.*, 2011; Wang *et al.*, 2015]. Almost all ( $\sim 90\%$ ) of the landslides in the Kosñipata catchment are connected to channels that are visibly identifiable in satellite imagery [Clark *et al.*, 2016]. However, not all of the landslide material may have been rapidly transported out of the catchment by the river. At high to middle elevations, landslide deposits reached small streams where the transport capacity is low. Additionally, in the lower elevations of the San Pedro catchment, alluvial sediment deposits are evident. Eroded material could remain in these deposits, contributing to a transient carbon sink, and subsequently be transferred out of the valley over an extended period of time [Ramos Scharrón *et al.*, 2012]. Alternatively, carbon in landslide deposits may contribute to dissolved organic carbon after partial degradation, or be degassed from deposits, releasing  $\text{CO}_2$  back to the atmosphere. To fully understand this component of the C erosion budget, more research needs to be done to evaluate the fate of landslide-mobilized carbon in landslide deposits, evaluating debris C stocks,  $\text{CO}_2$  respiration, and C residence time.

### 5.1.3. Source and Age of $\text{POC}_{\text{biosphere}}$

In the Kosñipata River valley, the stocks of carbon in soil are large relative to lowland tropical forest [Clark *et al.*, 2016]. At high elevations in the Kosñipata catchment, where temperatures are lower and hillslopes have lower slope angles [Clark *et al.*, 2016],  $\text{POC}_{\text{biosphere}}$  may be stored over centuries or millennia in deep B soil



horizons [Rumpel and Kögel-Knabner, 2011; Schmidt *et al.*, 2011], although the  $^{14}\text{C}$  activity of soils in this valley has not been measured (Figure 3b).

The isotopic and elemental compositions of POC in the Kosñipata River suggest that the  $\text{POC}_{\text{biosphere}}$  is mostly derived from surface soil horizons ( $O_H$  and  $A$  layers; Figure 3a). The deeper  $B$  soil horizons have  $\delta^{13}\text{C}_{\text{org}}$  and  $[\text{N}]/[\text{OC}_{\text{total}}]$  values [Zimmermann *et al.*, 2009] which are distinct from the linear trend defined by the suspended load data (Figure 3a), indicating that the relative contribution of carbon from the deeper soil horizons to the river  $\text{POC}_{\text{biosphere}}$  is small. This inference is consistent with the  $^{14}\text{C}$  activity (Figure 3b), which suggests that the majority of samples have a  $F_{\text{mod-bio}}$  value (i.e., the  $^{14}\text{C}$  activity of the  $\text{POC}_{\text{biosphere}}$ ) between 1.1 and 0.9 (Figure 4). These values correspond to carbon which is younger than  $\sim 850$   $^{14}\text{C}$  years. Interestingly, the data suggest that following the 4 March 2010 storm, which triggered a large number of bed-rock landslides in the catchment [Clark *et al.*, 2016], the  $F_{\text{mod-bio}}$  values may have been lower (between 1.0 and 0.9) than prior to the storm (Figure 4). Deep-seated landslides are capable of mobilizing deep soils and supplying this material to river channels, and the associated addition of older carbon could explain changing  $F_{\text{mod-bio}}$ . However, the role of aged  $\text{POC}_{\text{biosphere}}$  input is hard to resolve from the bulk measurements alone. Further investigation into the age structure of POC [Rosenheim and Galy, 2012] and/or the  $^{14}\text{C}$  activity of plant- and soil-derived biomarkers [Galy and Eglinton, 2011] could provide additional insight.

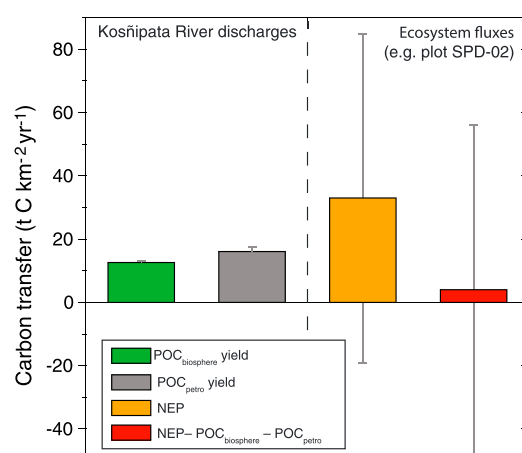
## 5.2. $\text{POC}_{\text{biosphere}}$ Discharge and the Carbon Budget of Andean Forest

Erosion and river transport of  $\text{POC}_{\text{biosphere}}$  represents export of carbon from forest ecosystems [Hilton *et al.*, 2012; Ciais *et al.*, 2014; Galy *et al.*, 2015]. This component of ecosystem carbon budgets is not often considered at the forest plot scale [Iwata *et al.*, 2005; Ciais *et al.*, 2014; Vihermaa *et al.*, 2016]. In the Kosñipata River valley, the net primary production of forests (NPP—the carbon equivalent of above and belowground biomass production) is  $\sim 1000 \text{ t C km}^{-2} \text{ yr}^{-1}$  [Malhi *et al.*, 2016]. The river  $\text{POC}_{\text{biosphere}}$  discharge of  $12.6 \pm 0.4 \text{ t C km}^{-2} \text{ yr}^{-1}$  represents  $\sim 1.0\%$  of the NPP of the forest, a similar proportion as reported elsewhere [Hilton *et al.*, 2008a, 2008b; Galy *et al.*, 2015].

While the  $\text{POC}_{\text{biosphere}}$  flux is small compared to NPP, it is more significant when compared to the net carbon balance of the ecosystem. Net ecosystem productivity (NEP) quantifies the medium-term net carbon uptake/storage [Marthews *et al.*, 2012] by accounting for heterotrophic respiration,  $R_h$  (respiration not derived from plants), where  $\text{NEP} = \text{NPP} - R_h$  [Marthews *et al.*, 2012]. Respiration from coarse woody material represents a significant source of uncertainty in Andean forest plots [Girardin *et al.*, 2010, 2014a; Gurdak *et al.*, 2014; Huaraca Huasco *et al.*, 2014]. In the Kosñipata Valley, NEP has been estimated at four sites, with values ranging from  $+33 \pm 52 \text{ t C km}^{-2} \text{ yr}^{-1}$  (positive values reflecting the ecosystem being a  $\text{CO}_2$  sink) to  $-172 \pm 81 \text{ t C km}^{-2} \text{ yr}^{-1}$  (a  $\text{CO}_2$  source) [Marthews *et al.*, 2012; Girardin *et al.*, 2014b; Huaraca Huasco *et al.*, 2014].

Since these NEP values hover around zero, the export of  $12.6 \pm 0.4 \text{ t C km}^{-2} \text{ yr}^{-1}$  of  $\text{POC}_{\text{biosphere}}$  by the Kosñipata River has the potential to tip the net carbon balance of the Andean montane forest (Figure 8). The role of erosion is more significant if we also consider the higher  $\text{POC}_{\text{biosphere}}$  removal by landslides [Clark *et al.*, 2016]. If  $\text{POC}_{\text{biosphere}}$  in Andean Rivers such as the Kosñipata avoids respiration as it is transported downstream, and if eroded  $\text{POC}_{\text{biosphere}}$  is replaced by new productivity on hillslopes, the carbon removed by rivers would strengthen the role of Andean ecosystems as a net sink of  $\text{CO}_2$  over years to decades. The revegetation of landslide scars takes  $\sim 20$ – $30$  years [Clark *et al.*, 2016], which is rapid enough to replace carbon lost to rivers, although soil carbon stocks may take longer to reestablish following landsliding [Restrepo *et al.*, 2009].

Although efficient preservation of eroded  $\text{POC}_{\text{biosphere}}$  could shift the Andean forest NEP to a  $\text{CO}_2$  sink, some work suggests that Andean riverine POC is efficiently oxidized during its transit through the lowland Amazon Basin [Quay *et al.*, 1992; Hedges *et al.*, 2000]. If this is the case, river  $\text{POC}_{\text{biosphere}}$  contributes to an increase in Andean heterotrophic respiration and reduces estimated local stand NEP by the equivalent amount (Figure 8). Some of this Andean  $\text{POC}_{\text{biosphere}}$  may be many centuries old, if derived from deep soils (Figure 4 and section 5.1.3). If this older carbon and/or rock-derived  $\text{POC}_{\text{petro}}$  is also oxidized downstream [Bouchez *et al.*, 2010; Hilton *et al.*, 2014] (see section 5.3), and if we consider this as part of the C budget of the Andean forest plots, the impact is larger. Assuming oxidation of riverine  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  would shift the overall NEP balance in favor of a reduced sink (or increased source) of  $\text{CO}_2$  (Figure 8).



**Figure 8.** Kosñipata River POC<sub>biosphere</sub> and POC<sub>petro</sub> discharges compared to net ecosystem productivity (NEP), where positive values indicate a CO<sub>2</sub> drawdown from the atmosphere and negative values a CO<sub>2</sub> source. Data from the SPD-02 plot [Marthens *et al.*, 2012] are shown for illustrative purposes. The NEP minus the POC<sub>biosphere</sub> and POC<sub>petro</sub> discharges (i.e., assuming complete oxidation of Andean POC during riverine transit) is shown. The whiskers show the uncertainties. The red bar assumes that POC<sub>biosphere</sub> is oxidized. If it is instead preserved, its erosion and export would strengthen the role of Andean ecosystems as a C sink, rather than tipping the balance toward C source—emphasizing the importance of understanding the fate of eroded POC for quantifying carbon budgets.

While the fate of eroded POC from mountains reaching floodplains needs to be better constrained [Clark *et al.*, 2013; Bouchez *et al.*, 2014; Ponton *et al.*, 2014], the uncertainties on the NEP values at the plot scale are large (Figure 8) compared to the uncertainties on river discharge of POC<sub>biosphere</sub> and POC<sub>petro</sub> [Marthens *et al.*, 2012; Girardin *et al.*, 2014b; Huaraca Huasco *et al.*, 2014]. The uncertainties on plot-scale NEP mainly relate to the challenges of measuring  $R_h$  over a representative time period, while accounting for respiration and degradation of dead coarse woody debris [Malhi, 2012; Gurdak *et al.*, 2014].

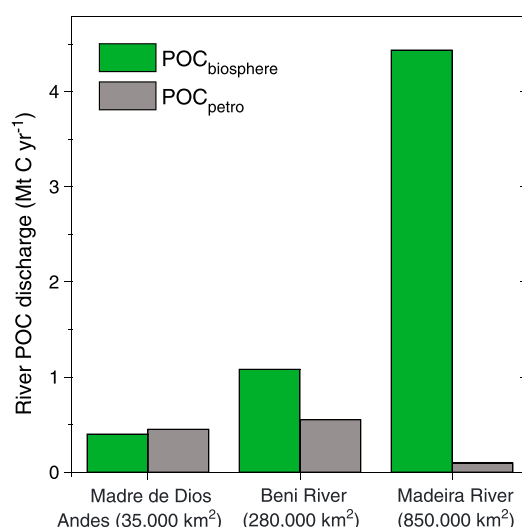
### 5.3. Andean POC<sub>biosphere</sub> Discharge and Contribution to the Amazon Basin Carbon Budget

The Kosñipata River drains to the Madre de Dios River (124,000 km<sup>2</sup>), which joins the Beni River to form

the Madera River, a major tributary of the Amazon River (Figures 1c and 1d). The POC<sub>biosphere</sub> and POC<sub>petro</sub> discharges from the Peruvian Andes have remained poorly constrained, and our measurements from a complete water year provide new insight into this component of the larger Amazon River system. If the short-term Kosñipata River POC<sub>biosphere</sub> yield at San Pedro is representative of the wider Andean area in the Madre de Dios Basin, where steep slopes, high rainfall, and productive forests coincide [Killeen *et al.*, 2007; Marthens *et al.*, 2012; Asner *et al.*, 2014; Mitchard *et al.*, 2014], then POC<sub>biosphere</sub> discharge from the Andean portion of the Madre de Dios (an area of 35,600 km<sup>2</sup>) may reach  $0.4 \pm 0.2$  Mt C yr<sup>-1</sup>. This is 10% of the Madeira River POC<sub>biosphere</sub> discharge, estimated to be  $4.4$  Mt C yr<sup>-1</sup> (Figure 9), coming from 4% of the catchment area [Galy *et al.*, 2015].

The neighboring Beni River catchment, which has a larger Andean source area, has a total POC<sub>biosphere</sub> discharge estimated to be  $1.1$  Mt C yr<sup>-1</sup> [Galy *et al.*, 2015]. The corresponding %POC<sub>biosphere</sub> in the suspended load of the Beni River is ~0.5%, similar to that measured in the Kosñipata River. These observations together suggest that Andean POC<sub>biosphere</sub> can contribute a significant flux to downstream Amazon tributaries. However, the overall Madeira POC<sub>biosphere</sub> discharge is much larger, which means that Andean River POC<sub>biosphere</sub> discharge cannot dominate the Amazon flux in the same way it is thought to do for clastic sediment (Figure 9). This observation is consistent with a substantial contribution of lowland-derived organic material to the suspended load of the larger Amazon tributaries, as inferred in the Madre de Dios from the H-isotope composition of plant-derived biomarkers [Ponton *et al.*, 2014].

The average age of biospheric POC carried by the Madeira River downstream of the Madre de Dios and Beni Rivers has been quantified as 2850 <sup>14</sup>C years [Bouchez *et al.*, 2014], much older than Andean POC<sub>biosphere</sub> from the Kosñipata River which is mostly <850 <sup>14</sup>C years (Figure 4). The older ages downstream could be a consequence of mixing older, floodplain-derived POC<sub>biosphere</sub> [Lähteenoja *et al.*, 2009] with younger, Andean-sourced POC<sub>biosphere</sub>. Alternatively, Andean POC<sub>biosphere</sub> may be deposited and stored for hundreds to thousands of years during the exchange of sediment with the floodplain [Aalto *et al.*, 2003; Moreira-Turcq *et al.*, 2013], which represents a significant sediment flux in the rapidly meandering Beni and Madre de Dios Rivers [Constantine *et al.*, 2014]. The potential aging of Andean POC<sub>biosphere</sub> imposed by channel migration and floodplain storage remains to be assessed in more detail.



**Figure 9.** Estimated annual river discharge of POC<sub>biosphere</sub> (green) and POC<sub>petro</sub> (grey) from the Madre de Dios Andes (this study) alongside published estimates from the Beni River and Madeira River [Galy et al., 2015].

#### 5.4. Andean POC<sub>petro</sub> Discharge and Contribution to the Amazon Basin Carbon Budget

Erosion in the Peruvian and Bolivian Andes mobilizes POC<sub>petro</sub> [Bouchez et al., 2010; Clark et al., 2013]. Over geological timescales, the oxidation of POC<sub>petro</sub> represents a major source of CO<sub>2</sub> to the atmosphere alongside volcanic degassing [Berner and Canfield, 1989; Derry and France-Lanord, 1996]. The global fluxes are still uncertain [Petsch et al., 2000; Hilton et al., 2014] but are likely to be between 40 and 100 Mt C yr<sup>-1</sup> [Petsch, 2014]. This CO<sub>2</sub> source counters geological CO<sub>2</sub> drawdown during the weathering of silicate minerals by carbonic acid [Gaillardet et al., 1999; Torres et al., 2016] and

the burial of new organic matter in sediments [Derry and France-Lanord, 1996].

In the Kosñipata River during our study, POC<sub>petro</sub> comprised ~0.45% of the SS load. Assuming that the POC<sub>petro</sub> component remains coupled with the SS load [Hilton et al., 2011a], the Madre de Dios River sediment flux of 71 Mt yr<sup>-1</sup> [Guyot et al., 1996] would equate to a POC<sub>petro</sub> discharge of ~0.3 Mt C yr<sup>-1</sup>. Another way to estimate the POC<sub>petro</sub> discharge is using the measured annual POC<sub>petro</sub> yield for the Kosñipata River ( $16.1 \pm 1.4 \text{ t C km}^{-2} \text{ yr}^{-1}$ ) over the Andean source area (35,600 km<sup>2</sup>), giving a POC<sub>petro</sub> discharge of ~0.6 Mt C yr<sup>-1</sup>. For comparison, the estimate of POC<sub>petro</sub> discharge in the neighboring Beni River is 0.55 Mt C yr<sup>-1</sup> [Bouchez et al., 2010; Galy et al., 2015]. Interestingly, the ratio of POC<sub>biosphere</sub> to POC<sub>petro</sub> discharge by these two Andean tributaries of the Madeira River appear to differ (Figure 9), which may relate to the higher proportion of POC<sub>petro</sub>-bearing shales in the Madre de Dios Basin [Carlotto Caillaux et al., 1996; Clark et al., 2013]. The combined POC<sub>petro</sub> discharge from the Beni and Madre de Dios Rivers is larger than that exported to the Bay of Bengal by the Ganges-Brahmaputra Rivers [Galy et al., 2007b; Galy et al., 2008a].

At the outlet of the Madeira River, Bouchez et al. [2010] estimate that 0.02% of the SS is POC<sub>petro</sub>, with a corresponding POC<sub>petro</sub> discharge of 0.1 Mt C yr<sup>-1</sup> [Galy et al., 2015]. The Madeira River's sediment load comprises sediments from the Madre de Dios, Beni, and Mamoré Rivers. Combining the estimates of the Andean POC<sub>petro</sub> discharge from the Beni and Madre de Dios gives ~0.9–1.1 Mt C yr<sup>-1</sup>, and therefore, there is a marked discrepancy of ~1 Mt C yr<sup>-1</sup> between the Andean POC<sub>petro</sub> input and Madeira River output, without even accounting from any additional contribution from the Mamoré (Figure 9). POC<sub>petro</sub> may be preferentially buried in the lowland floodplain during overbank deposition [Dunne et al., 1998; Aalto et al., 2003]. Alternatively, POC<sub>petro</sub> may have been oxidized during floodplain transit [Bouchez et al., 2010]. Supporting this interpretation, <sup>14</sup>C measurements of CO<sub>2</sub> degassing from the Tambopata River, a small tributary of the Madre de Dios with Andean headwaters, suggest a role of geological sources [Vihermaa et al., 2014]. The total difference between the Madeira River output and its Andean sources suggest a potential release of ~1 Mt C yr<sup>-1</sup> of geological CO<sub>2</sub> to the atmosphere [Bouchez et al., 2010]. This flux is larger than the CO<sub>2</sub> drawdown via silicate weathering in the Madeira Basin, of ~0.8 Mt C yr<sup>-1</sup> [Gaillardet et al., 1999], providing a strong impetus to better constrain the flux and fate of POC<sub>petro</sub> in the Amazon Basin and its contribution to CO<sub>2</sub> degassing.

## 6. Conclusions

We quantify the SS, POC<sub>biosphere</sub>, and POC<sub>petro</sub> yields for the Kosñipata River, in the Peruvian Andes (Figure 1), where we draw from parallel data sets on hydrology, ecology, and rates of geomorphic processes to understand these yields and to assess their impact on local to regional carbon cycles. We use carbon isotopes (<sup>14</sup>C,

$^{13}\text{C}$ , and  $^{12}\text{C}$ ) and  $[\text{N}]/[\text{OC}_{\text{total}}]$  ratios to distinguish POC from sedimentary rocks ( $\text{POC}_{\text{petro}}$ ) and POC from the terrestrial biosphere ( $\text{POC}_{\text{biosphere}}$ ) (Figure 3). At the San Pedro gauging station ( $164.4\text{ km}^2$ ), the SSC,  $\text{POC}_{\text{biosphere}}$ , and  $\text{POC}_{\text{petro}}$  (instantaneous concentrations in the river) are well described by power law rating curves as a function of river stage height. These rating curves are applied to a continuous water stage record to quantify daily, monthly, and annual yields. We correct for the known underestimation of river loads due to statistical bias in the rating curve method, correcting yields by a factor of 1.58 for SS, 1.77 for  $\text{POC}_{\text{biosphere}}$ , and 2.23 for  $\text{POC}_{\text{petro}}$ .

Over the water year of study (1 February 2010 to 31 January 2011), we calculate a SS yield of  $3500 \pm 210\text{ t km}^{-2}\text{ yr}^{-1}$ ,  $>15$  times the Amazon Basin average. The bias-corrected rating curve estimates return a  $\text{POC}_{\text{biosphere}}$  yield of  $12.6 \pm 0.4\text{ t C km}^{-2}\text{ yr}^{-1}$  and a  $\text{POC}_{\text{petro}}$  yield of  $16.1 \pm 1.4\text{ t C km}^{-2}\text{ yr}^{-1}$ . The yields are lower at the upstream Wayqecha gauging station, where catchment average slope, rainfall, and landslide rates are lower (Table 1 and Figure 1b). The erosional transfers of  $\text{POC}_{\text{biosphere}}$  confirm the global importance of SS yield and annual runoff for setting carbon export from the biosphere (Figure 6). The  $\text{POC}_{\text{biosphere}}$  discharge is large enough that it can play an important role in the NEP of Andean forest. If one also considers eroded  $\text{POC}_{\text{petro}}$ , the river POC is even more significant. For example, if river  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  were efficiently oxidized following export from the Andes, the NEP at Andean sites would be reduced to  $<+4 \pm 52\text{ t C km}^{-2}\text{ yr}^{-1}$  (Figure 8). However, the river POC discharges are within the uncertainty on the NEP estimates.

We use our measurements to provide a first estimate of Andean  $\text{POC}_{\text{biosphere}}$  discharge delivered to the Madre de Dios River (Andean area =  $35,600\text{ km}^2$ ) of  $0.4 \pm 0.2\text{ Mt C yr}^{-1}$ , which is  $\sim 10\%$  of the Madeira River  $\text{POC}_{\text{biosphere}}$  discharge, from 4% of the catchment area (Figure 9). Consequently, while Andean erosion is thought to supply the vast majority of SS to the lowland Amazon, lowland sources must also be important for riverine  $\text{POC}_{\text{biosphere}}$ . In contrast, the estimated Andean  $\text{POC}_{\text{petro}}$  discharge delivered to the Madre de Dios River ( $0.3\text{--}0.6\text{ Mt C yr}^{-1}$ ) is 300% of the Madeira River  $\text{POC}_{\text{petro}}$  discharge. Net oxidation of Andean  $\text{POC}_{\text{petro}}$  during lowland transit may release significant amounts of  $\text{CO}_2$  to the atmosphere, while transient storage of  $\text{POC}_{\text{biosphere}}$  and its contribution to oceanic POC export represent an important  $\text{CO}_2$  sink. The fate of Andean  $\text{POC}_{\text{biosphere}}$  and  $\text{POC}_{\text{petro}}$  in the lowland rivers of the Amazon basin needs to be better constrained in order to fully quantify the impact of erosion and lateral carbon fluxes on the  $\text{CO}_2$  budget of the Amazon ecosystem.

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