Fluvial Carbon Dynamics across the Land to Ocean Continuum of Great Tropical Rivers: the Amazon and Congo

Jeffrey Richey[1], Robert Spencer[2], Travis Drake[3], and Nicholas Ward[4]

[1]University of Washington
[2]Florida State University
[3]ETH Zurich
[4]Pacific Northwest National Laboratory

November 23, 2022

Abstract

Many rivers systems of the world are super-saturated in dissolved CO2 (pCO2) relative to equilibrium with the atmosphere — why? Here we compare the coupled organic matter and pCO2 dynamics of the world's two largest river systems, the Amazon and Congo, where data sets enable insights into the overall functioning of the respective basins. Discharge is the primary control on particulate (POC) and dissolved organic carbon (DOC) export in both the Amazon and Congo Rivers. Total suspended sediments (TSS) yield from the Amazon is twenty times greater per unit area than the Congo. However, despite low TSS concentrations, the Congo has a POC content approximately five times higher than the Amazon. The organic rich character of both watersheds is reflected in the DOC export, with the Amazon exporting ˜ 11% and the Congo ˜ 5% of the global land to ocean flux, based on measurements from the last discharge gauging stations. But care should be taken when describing estimates of TSS and carbon to the ocean. Processing and sequestration in tidal and coastal areas can significantly alter TSS and carbon delivery, and last discharge gauging stations are typically hundreds of kilometers from the sea. pCO2 in the Amazon mainstem ranges from 1,000 to 10,000 µatm, with floodplain lakes ranging from 20 to 20,000 µatm. Concentrations in the Congo mainstem are lower, with maximum values of ˜5,000 µatm observed. The elevated level of pCO2 even as far as the mouth of such major rivers as the Amazon and Congo, up to thousands of kilometers from CO2-rich small streams, poses a most interesting question — what set of processes maintains such high levels? The answer is presumably some combination of instream metabolism of organic matter of terrestrial and floodplain origin, and/or injection of very high pCO2 water from local floodplains or tributaries.

Hosted file

`acknowledgments.docx` available at https://authorea.com/users/544696/articles/601796-fluvial-carbon-dynamics-across-the-land-to-ocean-continuum-of-great-tropical-rivers-the-amazon-and-congo

AGU Books

Fluvial Carbon Dynamics across the Land to Ocean Continuum of Great Tropical Rivers: the Amazon and Congo

Journal:	*AGU Books*
Manuscript ID	2020-May-CH-1259.R1
Wiley - Manuscript type:	Chapter
Date Submitted by the Author:	n/a
Complete List of Authors:	Richey, Jeffrey; University of Washington, School of Oceanography Spencer, Rob; Florida State University, Earth, Ocean and Atmospheric Sciences Drake, Travis; ETH Zürich, Environmental Systems Science Ward, Nicholas; University of Washington, School of Oceanography; Pacific Northwest National Laboratory Marine Sciences Laboratory
Primary Index Term:	428 - Carbon cycling (4806) < 400 - BIOGEOSCIENCES
Index Term 1:	1806 - Chemistry of fresh water < 1800 - HYDROLOGY
Index Term 2:	9305 - Africa < 9300 - GEOGRAPHIC LOCATION
Index Term 3:	9345 - Large bodies of water (e.g., lakes and inland seas) (0746) < 9300 - GEOGRAPHIC LOCATION
Index Term 4:	9360 - South America < 9300 - GEOGRAPHIC LOCATION
Keywords:	metabolism, rivers, Congo, Amazon, organics, pCO2
Abstract:	Many rivers systems of the world are super-saturated in dissolved CO2 (pCO2) relative to equilibrium with the atmosphere — why? Here we compare the coupled organic matter and pCO2 dynamics of the world's two largest river systems, the Amazon and Congo, where data sets enable insights into the overall functioning of the respective basins. Discharge is the primary control on particulate (POC) and dissolved organic carbon (DOC) export in both the Amazon and Congo Rivers. Total suspended sediments (TSS) yield from the Amazon is twenty times greater per unit area than the Congo. However, despite low TSS concentrations, the Congo has a POC content approximately five times higher than the Amazon. The organic rich character of both watersheds is reflected in the DOC export, with the Amazon exporting ~ 11% and the Congo ~ 5% of the global land to ocean flux, based on measurements from the last discharge gauging stations. But care should be taken when describing estimates of TSS and carbon to the ocean. Processing and sequestration in tidal and coastal areas can significantly alter TSS and carbon delivery, and last discharge gauging stations are typically hundreds of kilometers from the sea. pCO2 in the Amazon mainstem ranges from 1,000 to 10,000 µatm, with floodplain lakes ranging from 20 to 20,000 µatm. Concentrations in the Congo mainstem

	are lower, with maximum values of ~5,000 µatm observed. The elevated level of pCO2 even as far as the mouth of such major rivers as the Amazon and Congo, up to thousands of kilometers from CO2-rich small streams, poses a most interesting question — what set of processes maintains such high levels? The answer is presumably some combination of instream metabolism of organic matter of terrestrial and floodplain origin, and/or injection of very high pCO2 water from local floodplains or tributaries.

1. Introduction

The Amazon and the Congo combined account for ~25% of global river discharge to the oceans. Understanding the flow of pCO_2 and organic matter (OM) in these humid tropical basins is an important part of understanding the role of fluvial systems in the global carbon cycle. The classic perspective for the role of rivers is that they simply export terrestrially-derived OM to the world's oceans, where long-term preservation occurs largely along continental margins. However, rivers are now conceptualized as an 'active pipe' (Cole et al., 2007) with inputs sequestered in sediments, evaded to the atmosphere or exported to the ocean (Cole et al., 2007; Ward et al., 2017). This paradigm shift results from knowledge that rivers and other inland waters outgas immense quantities of CO_2 to the atmosphere. While Wissmar et al. (1981) were the first to call attention to this for the Amazon River, it took years for the consequences to be more fully understood. Richey et al. (2002) estimated that the Amazon River Basin emits roughly 0.5 Pg C yr^{-1} from aquatic systems to the atmosphere as CO_2 and scaled these rates to a global estimate of ~1 Pg C yr^{-1}. To put the Amazon River value in context, it is roughly comparable to net ecosystem exchanges in non-inundated upland forests derived from eddy covariance measurements (Malhi and Grace, 2000). New global estimates of the surface area of aquatic systems (Allen and Pavelsky, 2018), models for gas transfer velocities, and observations of aquatic CO_2 concentrations have resulted in a 2-3 fold increase in global estimates of inland water CO_2 emissions (Raymond et al., 2013; Drake et al., 2017; Sawakuchi et al., 2017).

These observations pose three primary questions – (1) what are the geographic distributions and magnitude of aquatic CO_2 outgassing, (2) what are the biological and physical processes that ultimately drive the outgassing, and (3) how should the cycles producing such fluxes be incorporated into the overall carbon cycle of a large river basin, among water, land, and

atmosphere? Addressing these questions is very complicated. To assess the overall outgassing dynamics for a river basin requires examining much more than just the main channel. Melack (2016) identifies small streams, medium tributaries, river mainstem, lakes, river-adjacent floodplains and other wetlands as having their own respective dynamics. Further, each of these environments change dramatically over the course of the annual hydrograph and from year to year. River impoundments can also substantially modify the hydrological and biogeochemical behavior of aquatic ecosystems (St. Louis et al., 2000; Tranvik et al., 2009; Araújo et al., 2019).

While the Amazon River has been relatively well-studied, there is much less information for the Congo River. Alsdorf et al. (2016) summarized what was known at the time on the fluxes of total suspended sediments (TSS), particulate and dissolved organic carbon (POC, DOC), and dissolved greenhouse gases (CO_2 and CH_4) in the Congo River. They posed the hypothesis that "the annual-average amount of CO_2 and CH_4 evasion from all Congo Basin waters is more than 480 Tg C yr^{-1}, i.e., more than a value comparable to that of the Amazon per unit area."

The emerging data sets for the Congo River, joint with Amazon River data, enable us to begin to think more generally about the overall functioning of the world's two largest river basins. Our primary intent here is to examine in more detail the relative magnitudes and composition of pCO_2 and OM in the Congo River relative to the Amazon River, with an emphasis on the main channel of each river. Studies of large river systems typically stop at the last discharge gauging station, which may be many kilometers upstream from the ocean. Here we will extend the analysis to the full complement of the river to ocean continuum, recognizing that a river plume extending out into the ocean is still an integral part of the river system.

To keep track of all components of the fluvial carbon cycle for a river reach, it is useful to track the processes controlling pCO_2 and OM through the lens of Net Ecosystem Exchange (NEE, *sensu*

Lovett et al., 2006; Cole et al., 2000; Butman and Raymond, 2011). NEE, the change in pCO_2 over time and distance, can be expressed mathematically (following Devol et al., 1995) as:

$$d(pCO_2)/dt = NEE = \text{Net advection } [I + T \pm F - O] + \text{Net Metabolism } [R - GPP] - G + NB$$

where I is upstream input (discharge x concentration), T is tributary inputs, F is floodplain exchange, O is downstream output, R is respiration (as a function of OM substrates), GPP is gross primary production, G is gas exchange, and NB is non-biological reactions (e.g., photo-oxidation). While the existing data are far from complete enough to compute NEE for each river, it does provide a useful organizing framework.

While we focus our discussion of inland water greenhouse gases specifically on CO_2, methane (CH_4) is certainly also important. Information on methane cycling in the Amazon River and its wetlands have been presented in studies such as Sawakuchi et al. (2014, 2016), Melack et al. (2004), Pangala et al. (2017), Barbosa et al (2009, 2020), with fewer studies available for the Congo River (e.g., Borges et al., 2015; 2019).

2. The Regions

The Amazon and Congo Rivers (Figure 1) are the two largest rivers on Earth in terms of their discharge (~6,590 $km^3\ yr^{-1}$ at the last discharge gauging station and ~7,600 $km^3\ yr^{-1}$ to the sea, and ~1,325 $km^3\ yr^{-1}$, respectively), and their watershed areas (6.1 Mkm^2 and 3.7 Mkm^2, respectively). These two massive rivers drain large areas of predominantly tropical rainforest and savannah. The Congo River Basin contains some of the most pristine areas of rainforest remaining on Earth, as

well as fewer dams in comparison to the Amazon River Basin (Laporte et al., 2007; Duveiller et al., 2008; Winemiller et al., 2016). A major feature of the central Congo is the Cuvette Centrale, a shallow depression overlain by swamp forest, with extensive peat deposits (Darghie et al., 2017). The mainstem of the Amazon River is bordered by an extensive floodplain (or várzea), with seasonally flooded savannas across the basin. There are marked distinctions in topography (with the Amazon receiving significant TSS inputs from the Andes), and land cover (with more abundant savannah-mosaic and perennially flooded wetlands in the Congo Basin compared to the Amazon, which has less savannah and the strongly seasonal floodplain).

Óbidos has been the traditional terminal measuring point for the Amazon River. Between Óbidos and the ocean, an additional ~20% discharge is added by lowland tributaries (roughly double the volume of the Mississippi River). The lower part of the reach is split around the island of Marajó, where tides of ~3 m (detectable nearly 600km upstream) produce semi-diurnal fluxes to and from floodplains and channels, resulting in complete flow reversal (though no salinity intrusion).

Although these two immense rivers drain tropical watersheds, there are clear differences in annual precipitation between them resulting in higher specific discharge (discharge per unit upstream area) in the Amazon River. Fluctuations in the Intertropical Convergence Zone induce wet and dry seasons in alternating seasons in the northern and southern sides of the Amazon Basin, resulting in a single peak of maximum flow at Óbidos in May-July, with a minimum in October-November (Richey et al. 1989, multiple sources). Precipitation ranges from less than 2,000 mm/yr in the extreme northeastern and southern parts of the Basin, to more than 3,500 mm/yr in the northwest lowlands and increases to 7,000 mm/yr on the east side of the Andes. South of the

equator there is a distinct dry period from June to August, whereas north of the equator the dry period lasts from January to March.

The Congo River exhibits less seasonal and interannual variability in river discharge than the Amazon River (Coynel et al., 2005; Richey et al., 1989; Spencer et al., 2012). Due to its position straddling the Equator, the Congo River near its mouth at Kinshasa-Brazzaville exhibits a bimodal hydrologic cycle with maximum flows in November-December and May, and minimum flows in August and March. The largest discharge maximum in November-December is due to increased discharge from the northern tributaries and is complemented by southern tributaries where water discharge begins to increase around the same time. The smaller May discharge maximum is driven by an increase from the southern part of the Basin by savannah draining tributaries (Coynel et al., 2005; Spencer et al., 2012). Given an estimated total global discharge to the ocean of 36,000 km^3 yr^{-1}, the Amazon and the Congo Rivers are responsible for ~21% and 3.5% of freshwater discharge to the world's oceans, respectively.

3. Advective Fluxes

3.1. pCO_2 Distributions in the Mainstem, Tributaries, and Floodplains

Borges et al. (2015; 2019) report on a series of ten field expeditions between 2010 and 2015 in the Congo River. Transects in the lowland reaches of the river network in the eastern and central part of the Basin, predominantly between Kisangani and Kinshasa were conducted at high water (HW, December 2013) and at falling water (FW, June 2014). The pCO_2 values in the mainstem increased from upstream to downstream, with typically elevated tributary values. pCO_2 ranged from 2,400 (HW) and 1,700 (FW) µatm in Kisangani to 5,350 (HW) and 2,900 (FW) µatm in Kinshasa, with an average in tributaries of 8,300 ± 4,100 (HW) and 8,050 ± 5,300 (FW) µatm.

pCO_2 in tributaries was in general higher than in the mainstem with a few exceptions, namely in rivers close to Kinshasa (1,600 to 1,900 HW and 1,100 to 2,500 FW µatm), due to degassing at waterfalls upstream of the sampling stations. The highest pCO_2 values (up to 16,950 µatm) were observed in streams draining the Cuvette Central.

There are several studies of the longitudinal distribution of pCO_2 in the Amazon River. The first recognition that pCO_2 was supersaturated was by Wissmar et al. (1981), in a transect of the *R/V Alpha Helix*, from upstream of the Napo River (Peru) to Óbidos, at high water in May 1977. They reported increasing pCO_2 values from upstream to downstream of 4,900 to 6,900 µatm, with a range of concentrations in tributaries and lakes, from 2,500 to 15,000 µatm. They hypothesized that the respiratory input of CO_2 was balanced by outgassing but commented that this needed further examination.

The next systematic evaluation of pCO_2 (and related carbon species) was conducted by the *CAMREX* program, resulting in eight synoptic "snapshots" of the spatial and temporal variability of the chemical species measured, from Santo Antônio do Ica to Óbidos (Richey et al., 1990). The mainstem was supersaturated in CO_2 with respect to the atmosphere by 10-20 times, with an overall mean of 3,800 µatm. In contrast to dissolved inorganic carbon (DIC) concentrations, pCO_2 did not change downstream at rising water (mean 3,000 µatm) and increased downstream at falling water from 3,200 to 5,300 µatm; downstream, increases in pCO_2 were accompanied by decreases in pH. At rising water, the tributaries were either comparable in pCO_2 to the mainstem (Madeira, Negro, Japurá Rivers), up to 5,900 µatm more enriched (Iça, Juruá, and Purus Rivers), or from 5,900 to 14,800 µatm more enriched (Jutaí River). At falling water, the maxima for the Jutaí and Purús rivers were comparable to rising water, while the Iça, Jurua, and Japura rivers increased by 3,000-4,400 µatm. The Negro River increased slightly and the Madeira River decreased slightly.

Abril et al. (2014) conducted a series of transects along an 800 km section of the Central Amazon, between 2007-2011, reporting that values in the mainstem were consistent with the previous reports of 1,000 to 10,000 µatm, with floodplain lakes ranging from 20 to 20,000 µatm. Borges et al. (2015) conducted a series of five cruises along the Amazon River mainstem and mouths of tributaries between 2007 and 2010. Results were presented as aggregated bins, representing mainstem, tributaries >100 m and tributaries <100 m in width. With this lumped binning, it was not possible to see spatial or seasonal trends. The pCO_2 values were consistent with the previous measurements, averaging 4,500 µatm in the mainstem, with values to 16,900 pm in streams <100 m. These values are higher than the Congo mainstem, which was attributed to higher wetland coverage. Amaral et al (2019) reported on pCO_2 at multiple environments across the Negro River and Amazon during different periods of the fluvial hydrological cycle, with values that ranged from 307 to 7,527 µatm.

Sawakuchi et al. (2017) measured pCO_2 and outgassing from Óbidos to the lower river near the region of Macapá, with extrapolations to the ocean, from 2014 to 2016, at low, rising, high, and falling water. pCO_2 and outgassing were measured directly. Concentrations decreased from Óbidos towards Macapá, as the channels widened, and wind fetch increased, and increased from low water to high water. The average pCO_2 including all seasons and sites measured in the lower Amazon River and its tributaries was 2,914 ± 1,768 µatm. The mainstem (averages of Óbidos, Almeirim, and Macapá) averaged 3,218 ± 1,656 µatm. The tributaries (Rios Xingu and Tapajós), had significantly lower pCO_2 compared to the mainstem stations with values of 1,322 ± 1,545 µatm. Concentrations decreased from Óbidos to Macapá and decreased from 5,500 µatm at high water to 1,800 µatm at low water.

3.2. POC Fluxes

The Congo River has low TSS concentrations resulting in a flux to the Atlantic Ocean of ~ 30 Tg yr^{-1} (Coynel et al., 2005; Spencer et al., 2016), much lower than that estimated from the Amazon River (600 - 1,150 Tg yr^{-1}; Meade et al., 1985; Richey et al., 1986; Filizola and Guyot, 2009). Therefore, even though the Congo Basin is ~ 40% smaller than the Amazon, the TSS yield (flux per unit area) from the Amazon is still proportionally twentyfold greater (~ 90-180 versus ~8.5 t km^{-2} yr^{-1} for the Amazon and Congo Rivers, respectively; Meade et al., 1985; Richey et al., 1986; Coynel et al., 2005; Filizola and Guyot, 2009). The relatively low TSS yield from the Congo is due to the comparative lack of mountainous headwaters, generally low relief topography, lack of highly erodible sedimentary rocks, limited fluctuation in seasonal discharge, and large lakes as well as the world's largest swamp forest in the central depression (Cuvette Centrale) that act as giant sediment traps (Laraque et al., 2009; Spencer et al., 2016).

However, despite low concentrations, Congo River TSS has been reported to have a high POC content (6.05 - 7.25 %), which is approximately five times higher than the Amazon River at its furthest downstream discharge gaging station, Óbidos (Hedges et al., 1986; Aufdenkampe et al., 2007; Spencer et al., 2012; 2016). Thus, the Congo River exports ~ 2 Tg C yr^{-1} as POC to the Atlantic Ocean, resulting in a POC yield of ~ 0.6 g C m^{-2} yr^{-1} (Coynel et al., 2005; Spencer et al., 2016). Although this is lower than POC yield estimates from the Amazon (~ 0.9 - 1.0 g C m^{-2} yr^{-1}), it highlights the organic rich nature of Congo River TSS as the yield is comparable between the basins despite the POC flux being approximately three times greater from the Amazon (~ 6 Tg yr^{-1}; Moreira-Turcq et al., 2003; Coynel et al., 2005).

Upstream processes set the seasonally varying template for what is propagated downstream. Care should be taken when describing estimates of TSS and POC "to the ocean" since inputs below

the last measuring station and processing and sequestration in tidal and coastal areas can significantly alter TSS and POC delivery. Estimates of TSS and POC fluxes for both rivers have typically been made upstream of any tidal influence (i.e., at Óbidos in the case of the Amazon River and at Kinshasa-Brazzaville for the Congo River). However, POC concentrations are about two times higher upstream at Óbidos compared to near the river mouth at Macapá (Ward et al., 2015), suggesting both that POC is lost in transit due to processes such as degradation and/or burial of suspended sediments along the tidal tributary network (Fricke et al., 2017). This highlights the need to study large rivers in their lower reaches, downstream of the head of tides, to accurately account for material fluxes to the ocean (and atmosphere).

3.3. DOC Fluxes

With respect to DOC fluxes, the Amazon River at Óbidos has been estimated to export ~ 22-27 Tg C yr^{-1} (Richey et al. 1990; Moreira-Turcq et al., 2003) which amounts to 11% of the global DOC flux from river mouths, or more accurately the last gauging stations, to the ocean. If downstream major lowland tributaries are also included (e.g., the Tapajós and Xingu rivers; 1.5 and 1.0 Tg C yr^{-1} respectively), the total flux of the Amazon to the Atlantic is ~ 29.4 Tg C yr^{-1} (Moreira-Turcq et al., 2003; Coynel et al., 2005). Indeed, measurements made near the mouth of the Amazon River at Macapá show an increase in DOC concentrations of 1.2 times compared to concentrations at Óbidos as a result of the tributary inputs and floodplain interactions along the tidally-influenced reaches of the river (Ward et al., 2015; Seidel et al., 2016).

The Congo River represents the second largest fluvial DOC flux to the ocean at ~ 12.4 Tg C yr^{-1}, or 5% of the global land to ocean flux (Coynel et al., 2005; Spencer et al., 2016). Interestingly, despite the extensive wetlands in the center of the Congo Basin, the Amazon has a higher DOC

yield (4.4 versus 3.4 g C m^{-2} yr^{-1}), but the organic rich character of both watersheds is apparent when compared to the global average DOC yield from the world's 30 major rivers (2.3 g C m^{-2} yr^{-1}; Raymond and Spencer, 2015). In total, the Amazon River exports ~ 36 Tg C yr^{-1} of organic carbon (OC, both POC and DOC) and the Congo River exports ~14 Tg C yr^{-1} to the Atlantic Ocean, with both rivers exporting OC predominantly as DOC.

3.4. Floodplain Exchange

The literature on floodplain exchange in the Congo is very sparse, relative to the Amazon. These floodplains represent regions of significant *in situ* primary production, dominated by phytoplankton, periphyton, aquatic herbaceous plants, and flooded forests (Sioli 1984; Junk and Howard-Williamson, 1984; Melack and Forsberg, 2001), and are thought to provide a seasonal source of organic matter (OM) to the mainstem (Bourgoin et al., 2007; Bonnet et al., 2005). The contribution of large floating macrophytes, produced primarily in floodplains, may be important relative to the Basin's overall carbon budget, but the magnitude of their production and export is highly understudied (Melack and Engle, 2009). During the falling water period, Amazon River floodplains drain dissolved and particulate material including intact aquatic vegetation (i.e., macrophytes) into the mainstem as the floodplains become dry at low water. In addition to exporting freshly produced OM to the mainstem, productive floodplains can also represent sinks for sedimentary OM (Moreira-Turcq et al.; 2003). Algal biomass derived from floodplain lakes and clearwater tributaries has been estimated to represent only 2-8% of Amazon River POC (Meybeck et al., 1982; Saliot et al., 2001). While they are major bio-reactors in their own right, the actual magnitude of exchange with the Amazon mainstem remains ambiguous.

4. Organic Matter Sources and Metabolic Potential

The composition of the OM fractions not only contains signals of not only the origin of the material, but the potential for degradation by metabolic processes.

4.1. OM Composition

Discharge is the primary control on POC and DOC export in both the Amazon and Congo Rivers (Moreira-Turcq et al., 2003; Coynel et al., 2005; Spencer et al., 2016). Concurrent with elevated concentrations of POC and DOC in the Congo River at high discharge (Figure 2a) a shift in the source of organic matter is apparent (Spencer et al., 2016). More depleted δ^{13}C-POC and δ^{13}C-DOC values are generally observed with peaks in discharge and along with elevated lignin carbon-normalized yields (Λ_8) at these times suggest increasing vascular plant inputs derived from litters and surface soils. Likewise, Λ_8 (total yield of eight lignin-derived phenols indicative of vascular plant tissues. normalized to weight of bulk sample) for POC is generally highest during peak discharge both at Óbidos and the river mouth near Macapá, but significant seasonal variability in the dissolved phase was not observed (Ward et al., 2015).

Particulate OM (POM) in the Congo mainstem is comparable to fine particulate OM (FPOM; < 63µm > 0.7 µm) in the Amazon at Óbidos with respect to its C:N ratio (9.9-12.4 versus 10.0; Hedges et al., 1986; 1994) and the Congo River is dominated by FPOM (Spencer et al., 2012; 2016; Figure 2b). Congo River FPOM (C:N 11.4-12.5) is also enriched in nitrogen relative to the coarse POM (CPOM; > 63 µm) fraction (17.2-20.4), as also observed in the Amazon at Óbidos (20.2) (Hedges et al., 1986; Spencer et al., 2012; Figure 2b). This nitrogen enrichment in the fine fraction of POM is likely due to nitrogen enriched microbial biomass as well as preferential

sorption of nitrogen containing compounds (e.g., amino acids) to the suspended sediments in the rivers (Aufdenkampe et al., 2001; Marin-Spiotta et al., 2014).

Both Congo River δ^{13}C-POC (-26.1 to -28.0 ‰) and δ^{13}C-DOC (-29.0 to -29.8 ‰) reflect the dominance of terrestrial inputs but with a systematic depletion in δ^{13}C-DOC values due to different sources between these two components of the OC pool. The enrichment in the δ^{13}C-POC pool may be due to a variety of factors such as potential phytoplankton inputs or contributions from C4 plants in certain headwaters (Bouillon et al., 2012; Balagizi et al., 2015; Descy et al., 2016). On the other hand, since POC is typically soil-derived, the relative enrichment of δ^{13}C-POC compared to δ^{13}C-DOC may be linked to preferential remineralization of δ^{13}C depleted organic carbon in soils prior to export to the aquatic environment; the older radiocarbon age reported for riverine POC compared to DOC provides further evidence for this interpretation (Marin-Spiotta et al., 2014). The depleted signature of δ^{13}C-DOC reflects its source in surface litters and organic-rich upper soil horizons and also by the predominantly modern radiocarbon age of DOC in major rivers including the Amazon and Congo Rivers (Mayorga et al., 2005; Spencer et al., 2012; Marwick et al., 2015). The Congo River δ^{13}C-POC values are comparable to values reported for the Amazon River at Óbidos (-27.1 to -28.0 ‰; Bouchez et al., 2014), and Congo River δ^{13}C-DOC values are comparable to those reported for a host of global rivers dominated by terrestrial inputs (Raymond and Bauer, 2001; Raymond et al., 2007; Mann et al., 2015).

A plethora of research in both the Congo and Amazon Rivers has utilized biomarkers to assess sources of OM (e.g., Hedges et al., 1986; 1994; 2000; Aufdenkampe et al., 2007; Spencer et al., 2012; 2016). Combining OM C:N and Λ_8 has historically been undertaken to examine OM sources and transformations in both the Congo and Amazon Rivers. Examination of vascular plant contributions to the OM pool using Λ_8 has shown that Congo River POM is high in vascular plant

content (2.79 to 3.54 mg 100mg OC^{-1}) in comparison to Amazon FPOM at Óbidos (1.68 mg 100mg OC^{-1}) (Hedges et al., 2000; Spencer et al., 2016; Figure 2b). Congo dissolved OM (DOM) Λ_8 values (0.50 to 0.76 (mg 100mg OC^{-1}) are also high in comparison to major global rivers (Spencer et al., 2016), highlighting the organic rich nature of the Congo River in both dissolved and particulate phases.

4.2. Degradation Potential of OM

Λ_8 values from CPOM to FPOM have been attributed to degradative loss of lignin in the source materials, and dilution with nitrogen enriched microbial and fungal derived OM (Hedges et al., 1986; Aufdenkampe et al., 2001; Spencer et al., 2016; Figure 2b). When both the Congo and Amazon River POM C:N and Λ_8 data are compared to Mississippi River POM, the organic rich nature of the tropical systems dominated by terrestrial inputs is apparent. For instance, compared to the Mississippi River, Amazon River FPOM and Congo River POM Λ_8 values are almost double and roughly three to four times higher, respectively (Figure 2b). This marked terrestrial footprint has been shown to be an important source of energy fueling the foodweb and critical fisheries in both the Congo and Amazon Basins (Araujo-Lima et al., 1986; Forsberg et al., 1993; Soto et al., 2019). Likewise, decomposition of lignin phenols in the Amazon River fuels 30-50% of bulk microbial respiration in the Amazon River mainstem (Ward et al., 2013). The ratio of lignin acids to aldehydes (Ad:Al) is an indicator of the decay state of terrestrially-derived OM. The Ad:Al ratio of POM systematically increases along the lower Amazon River, confirming degradation of POM in transit (Ward et al., 2015). This downstream shift in degradation state is not as apparent in the dissolved pool, leading to the hypothesis that DOM is remineralized at similar rates as fresh inputs

to the river system from the landscape and floodplains until there is no longer a source, i.e., beyond the river mouth (see Section 5; Seidel et al., 2015).

4.3. Deforestation and Agricultural Land-Use Change

Deforestation and forest alteration caused by logging, agricultural expansion, human settlement, and hunting proceeds at an unrelenting pace throughout the tropics. The epicenter of tropical deforestation is the Brazilian Amazon Basin, where in recent years an average of ~6,700 km^2 of forest has been lost per year to industrial logging and agricultural land-use change. Recent rollbacks of environmental protections in Brazil, where more than half of the Amazon's deforestation occurs, has led to further forest loss by opening new swathes of protected lands to industrial logging and agriculture. Meanwhile, in the Congo Basin, deforestation continues similarly unabated, albeit primarily in the form of shifting agriculture (Curtis et al., 2018). Chronic instability, poor infrastructure, and limited governance in the Congo have so far provided a form of "passive protection" from the kind of industrial or mechanized deforestation taking place in the Amazon Basin (De Wasseige et al., 2012). As a result, the rate of forest loss in the Congo Basin has been relatively lower. However, given the current expansion of mineral extraction, road development, agribusiness, biofuels, and additional shifting agriculture and charcoal production in the Congo Basin, its forests may lie at a turning point. Indeed, the population of Democratic Republic of Congo, the largest country within the Basin, is expected to grow five-fold by 2100 (Gerland et al., 2014). And if recent trends hold, increased mining and infrastructure investments from China and elsewhere into Central Africa also threaten to accelerate industrial logging. In short, intensive deforestation promises to be a fixture in both Basins for the foreseeable future.

The effect of this rampant tropical deforestation on the local and regional carbon cycle depends on the original vegetation, soil type, topography, climate, and replacement land-use. Generally, the net effect of deforestation is to transform ecosystems from a sink into a source of carbon to the atmosphere through the loss of above-ground biomass, decrease in photosynthetic capacity, burning of cleared vegetation, and the enhancement of soil carbon respiration.

While the loss of carbon as CO_2 released from OC respiration in deforested soils is well documented, a relatively understudied effect of soil disturbance is the leaching and mobilization of soil OC (SOC) to rivers and streams. Deforestation has the potential to dramatically augment this flux in multiple ways. First, the loss of root structure following tree removal destabilizes soils, leading to erosion and the exposure of deeper, previously stable soil horizons to precipitation. Second, on the micro to meso-scale (1-100 km^2), deforestation reduces evapotranspiration and increases runoff to rivers and streams (Bruijnzeel, 2004; Cavalcante et al., 2019; Costa, 2005). This post-deforestation increase in the ratio of runoff to precipitation has been observed and modelled in both the Amazon and Congo Basins (Coe et al., 2009; Drake et al., 2019a; Trancoso, 2006). With more water available to infiltrate into degraded or exposed soil, enhanced leaching of SOC and rock weathering are likely to increase soil carbon fluxes to streams.

In the Amazon, deforestation and agricultural conversion have been shown to impact water, solute, nutrient, and soil-derived OM export to rivers (Farella et al., 2001; Spencer et al., 2019; Thomas et al., 2004; Williams and Melack, 1997). Stable carbon isotopic signatures of riverine DOC and POC in both the Amazon and Congo Rivers exhibit a relative enrichment in deforested and pasture-influenced catchments, suggesting the export of either soil or C4-dominant OC, or both (Bernardes et al., 2004; Drake et al., 2019a; Richey et al., 1990). Using paired stable and radiocarbon isotopic measurements can often resolve whether carbon is sourced from modern C4

plants or aged soil OC (which itself could be originally derived from C4 biomass). In Eastern Congo, the radiocarbon age of DOC from deforested catchments was found to be ~1,500 years old, indicating the loss of aged and previously stabilized soil OC from deeper horizons rather than modern C4-derived vegetation (Drake et al., 2019a).

The effect of this mobilization and re-introduction of aged and previously stabilized tropical SOC into the modern carbon cycle depends, in part, on its composition. Recent studies into the molecular composition of DOM in both the Amazon and Congo Rivers have uniformly shown that DOM leached from deforested catchments into rivers is energy-rich (high hydrogen to carbon ratios) and chemo-diverse (enriched in nitrogen and sulfur compounds) (Drake et al., 2019a; Drake et al., 2019b; Spencer et al., 2019). The molecular signature of deforestation is readily apparent when the peak intensities of specific formulae are correlated with the proportion of cropland within a catchment and plotted in van Krevelen space (Figure 3). Although differences are present, the overall pattern shows how aliphatic (hydrogen-rich) and reduced (low O/C ratio) DOM (red points, Figure 3) is strongly correlated with deforestation and consistent across the pan-tropics. Such compositional signatures are consistent with deeper soil OM, which often contains low-molecular weight OM sourced from bacteria and stabilized on mineral surfaces (Dungait et al 2012, Lützow et al. 2006).

Together, the carbon isotopic and compositional signatures of deforestation derived DOM in both the Amazon and Congo Basins indicates microbial bio- or necromass from soils as a source, given the enriched ^{13}C and depleted ^{14}C signatures, high H/C ratios (aliphatic), high N content, and low aromaticity (Kaiser and Kalbitz, 2012; Kellerman et al., 2018). The ultimate fate of this mobilized SOC, i.e., whether it is exported downstream to the ocean or mineralized and outgassed to the atmosphere, depends on its lability and environmental conditions. Bioincubation data from

the Eastern Congo show that the aged DOC derived from deforested soils was more biolabile than younger DOC derived from surface vegetation in the forest and corresponded with higher in-stream CO_2 concentrations (Figure 4). Assuming that this high biolability is driven primarily by the highly aliphatic and N-rich chemical composition, as has been observed to be the scenario in other terrestrial and aquatic systems (Berggren et al., 2010; van Hees et al., 2005; Kalbitz et al., 2003; Spencer et al., 2015), then we can assume similar patterns of high biolability of OC mobilized to catchments by deforestation and soil disturbance in both Basins.

If tropical deforestation and conversion to agriculture reverses the microbially-mediated stabilization of OC in soils by venting biolabile and aged OC to the atmosphere via microbial respiration and outgassing in the aquatic network, then rivers draining impacted landscapes may represent an important and understudied anthropogenic carbon source. In short, the lateral flux of disturbed soil carbon to rivers exemplifies an additional mechanism by which deforestation converts these tropical ecosystems from sinks to sources. For now, this flux appears to be small relative to the natural fluxes of carbon from tropical rivers, given the modern age of DOC, CO_2, and DIC in the mainstem and larger tributaries of the Amazon and Congo Rivers (Hedges et al., 1986; Marwick et al., 2015; Mayorga et al., 2005; Spencer et al., 2012). Organic matter rich peat deposits across the majority of Congo wetlands and wetlands in the Peruvian Amazon are another potential source of aged carbon that is vulnerable to being mobilized into the modern aquatic carbon cycle due to a variety of disturbances (Dargie et al., 2017; Draper et al., 2014; Moore et al., 2013). Future work might aim to better quantify the riverine flux of aged OC from deforested landscapes and to trace its fate downstream before it is masked by mixing with waters draining pristine or relatively undisturbed areas. In addition to anthropogenic deforestation, the tropical forest carbon sink in the Amazon is also declining relative to the Congo due to increasing rates of

tree mortality linked to hydrologic variability (Hubau et al., 2020). In addition to influencing forest productivity, hydrologic variability also plays a direct role in the balance between carbon sequestration in terrestrial environments and mobilization into aquatic ecosystems (Schefuß, et al., 2016). For example, model results suggest that while terrestrial net ecosystem productivity and carbon sequestration is highest during wetter years, the percentage of net primary production lost to aquatic CO_2 evasion is also highest (Hastie et al., 2019).

5. Metabolism

The elevated level of pCO_2 even as far as the mouth of such major rivers as the Amazon and Congo, up to thousands of kilometers from CO_2-rich small streams, poses a most interesting question — what set of processes maintains such high levels? The answer is presumably some combination of instream metabolism of OM of terrestrial and floodplain origin, and/or injection of high pCO_2 water from local floodplains or tributaries.

5.1. Metabolic Rates

Metabolic parameters in large rivers are typically measured by dissolved oxygen changes in 60-ml BOD (Biological Oxygen Demand) bottles over 24 hours, where the bottle is stationary and in the dark. This technique may inject a critical methodological bias in traditional respiration experiments—the role of flowing water on biological activity is typically ignored. Ward et al. (2018a) reported on results from a rotating incubation system that monitors O_2 drawdown in real-time to evaluate respiration under different flow rates, capable of directly measuring heterotrophic respiration rates under variable flow velocities. Respiration rates in these rotating chambers were on the order of 2 to 3 times higher than traditional experiments performed simultaneously, and

depth integrated river velocity-normalized respiration rates actually exceeded CO_2 outgassing rates by ~30%. This excess CO_2 is balanced by new estimates of primary production in the lower Amazon River based on an O_2 stable isotopic mass balance showing that photosynthesis occurs at 25-50% the rate of respiration (Gagne-Maynard et al., 2017). They conclude that river velocity and hydrodynamic conditions are key physical factors controlling microbial metabolism of river-borne OM that has not been appropriately considered either conceptually or quantitatively. Another important pathway for organic matter remineralization is photo-oxidation and its interactions with metabolic activity (Cory et al., 2018) are discussed in more detail below.

In rivers of the Congo Basin lowlands, Borges et al. (2019) measured primary production (PP) during 2-hour incubations using $^{13}C\text{-}HCO_3^-$ as a tracer and pelagic community respiration (CR) using the 60 mL BOD bottle technique. On average the PP:CR ratio was 0.28. Volumetric rates of CR ranged between 0.7 and 46.6 mmol m^{-3} d^{-1}, while integrated rates of CR ranged between 3 and 790 mmol m^{-2} d^{-1}. They concluded that CO_2 outgassing was on average about 10 times higher than the flux of CO_2 produced by aquatic net heterotrophy, indicating that the CO_2 emissions from the river network were sustained by lateral inputs of CO_2 (either from terra firme or from wetlands). The authors acknowledge that their CR results might be underestimates based on finding by Ward et al. (2018a), but consider it unrealistic to assume an underestimation of 10-fold necessary to bring the balance of CR and PP in balance with outgassing, given that TSS concentrations are considerably lower in the Congo River than in the Amazon River. However, Ward et al. (2018a) found the same order of magnitude difference between stationary and rotating experiments in the clearwater Tapajós River, which has similar TSS levels as the Congo River.

5.2. Substrates for Metabolism

The previous discussion is underpinned by the concept of rivers no longer being considered passive pipes (Cole et al., 2007) and opens a new avenue for research: what organic substrates fuel heterotrophic respiration? Historically, OM in transit in a large river is considered to be stable. But Ward et al. (2013) showed that the degradation of lignin and associated macromolecules in the Amazon River corresponds to 30–50% of bulk river respiration. As discussed in the previous section, these results present strong evidence of the biodegradability of terrestrially derived macromolecules in the aquatic setting.

A process that may be involved is "priming," whereby the decomposition of less reactive OM is stimulated by the presence of highly reactive material such as algal exudates. Ward et al. (2016; 2019) showed this potential with the impact of mixing Rios Tapajós and Xingú water in the mixing zones with the main channel. It is conceivable that this is a pathway by which floodplain waters could influence respiration in the main channel. Another potential fuel for river respiration and direct source of CO_2 to tropical waters are the by-products of photo-oxidized OM.

Terrestrially derived OM in tropical rivers can be subject to intense solar radiation, which can directly oxidize organic compounds to CO_2 and photodegrade other aromatic compounds into potentially more biolabile forms. Indeed, irradiation experiments conducted on Congo River water produced new compounds that were highly aliphatic (hydrogen-rich), a characteristic common to highly biodegradable OM (Stubbins et al. 2010). Initial conservative estimates suggest that photo-oxidation only contributes to ~0.5% of CO_2 emission rates in the Amazonian Negro River (Remington et al., 2011). Other experiments in the Negro River have shown that solar irradiation contributes to ~7% of DOC mineralization in tropical blackwater systems and that exposure to sunlight produces bio-labile DOC, stimulating microbial respiration (Amaral et al. 2013). Along the lower reaches of the Amazon River mainstem, rates of dissolved lignin decay via photo-

oxidation are on the same order of magnitude as microbial degradation (Ward et al., 2013; Seidel et al. 2016). However, a remaining challenge is quantifying the importance of depth-integrated photo-oxidation across the diversity of river types. For example, the abundance of suspended sediments in the deep channels of the Amazon River mainstem likely limit the importance of photo-oxidation, while photo-oxidation may play a significant role in transforming OM in less turbid systems such as Amazonian clearwater tributaries.

Other potential sources of pCO_2 in the mainstem rivers could be direct inputs from soils or the injection from floodplains of high pCO_2 directly, or DOC and POC as substrates for riverine respiration. While the majority of CO_2 emissions from headwater streams is derived from soil respiration (Johnson et al., 2008), contributions from this pathway diminish at increasing stream orders (Raymond et al., 2016). With respect to floodplain CO_2 contributions to the main river channel, Abril et al. (2014) developed a simple one-dimensional model that simultaneously calculates the floodplain-derived CO_2 lost by outgassing and the CO_2 that remains dissolved in water and is transported downstream based on extensive measurements across the floodplain and mainstem in different locations. Their model computed that water movement is fast enough relative to gas exchange to maintain high supersaturation of the floodplain pCO_2 over dozens to hundreds of kilometers without requiring heterotrophic metabolism. They estimated that Amazonian wetlands export half of their GPP to river waters as dissolved CO_2 and OC, compared with only a few percent of GPP exported in upland (non-flooded) ecosystems, concluding that the input of strictly upland terrestrial carbon to river CO_2 outgassing is potentially minor compared to the wetland carbon contribution. A similar argument is made for the Congo (Borges et al. 2019).

That said, it is not clear what the impacts of the floodplain export to the main channel actually are. To be significant, a mass balance (e.g., NEE) has to be demonstrated, on the flux to, by season,

relative to the mass being transported in the river; i.e., how many m^3 s^{-1} of water with what chemical load is being exported to the mass of the main river? Alsdorf et al (2010) computed that water stored on and subsequently drained from the mainstem Amazon floodplain each year represents only about 5% of the total volume of water discharged from the Amazon River, and that the contribution to the floodplain from local upland runoff represents less than 20% of the floodplain water volume for any given time. The Abril et al. (2014) model tracks only a parcel of water from the floodplain, not accounting for the mass of water and the pCO_2 of the main channel. Further, the assumption that heterotrophic respiration in the main channel is much less than outgassing, hence requiring lateral inputs, is based in large part on the classic BOD bottle techniques. Most all previous balances using respiration measured with the classic small bottle need re-evaluation, in light of the Ward et al. (2018a) results.

6. Gas Exchange

As summarized by Melack (2016), gas exchange between surficial water and overlying atmosphere depends on the concentration gradient between air and water and on physical processes at the interface, usually parameterized as a gas transfer velocity (k_{600}), also called a piston velocity or gas exchange coefficient: $F_{CO2} = k_{600} (C_s - C_o)$, where F is the evasive flux, C_s is the surface water concentration, and C_o is the atmospheric equilibrium. The challenge is that k_{600} varies widely and is difficult to measure directly. Melack (2016) and MacIntyre et al. (2019) summarized direct techniques involving floating chambers, surface renewal models, eddy covariance, and tracers such as ^{222}Rn. The measurement is especially problematic on large rivers. Studies frequently default to literature or modelled values for k_{600}. It should also be noted that k_{600} and pCO_2 may not be entirely independent. For example, highly elevated pCO_2 levels (e.g., > 20,000 µatm) are

generally only observed in settings with low k_{600} values (e.g., floodplains) due to gas exchange limitations. On the other hand, turbulent settings with high k_{600} values typically do not become highly saturated in pCO_2 as exchange occurs more rapidly than production (Rocher-Ros et al., 2019).

For the Congo River, Borges et al. (2019) used a parameterization for k_{600} of stream slope and stream water velocity, as a function of Strahler stream order, where k_{600} becomes smaller as stream order gets larger. Computed values were in the range of 12-30 cm hr^{-1} for streams greater than stream order 3, generally in the range reported by Alin et al. (2011), for the Amazon and Mekong rivers. The calculated F_{CO2} ranged between 86 and 7,110 mmol m^{-2} d^{-1}, averaging 2,500 mmol m^{-2} d^{-1} (weighted by surface area of Strahler stream order). The F_{CO2} decreased with increasing Strahler order. Strahler orders 1–4 accounted for > 90 % of the integrated F_{CO2}, while Strahler orders 5–10 only accounted for 9.3% of integrated F_{CO2}. The rivers draining the Cuvette Central contributed to 6 % of the basin-wide emissions for CO_2.

For the Amazon, Melack (2016) summarizes a wide range of k_{600} and outgassing fluxes across different Amazonian environments, from small streams to flooded lakes to large rivers. Values ranged from 40 mmol m^{-2} d^{-1} to 6,700 mmol m^{-2} d^{-1}. For the lower Amazon, i.e., Óbidos to Macapá, Sawakuchi et al. (2017) estimated an average k_{600} (based on direct measurements of fluxes and concentrations) for all stations of 34 ± 16 cm hr^{-1}, slightly higher than the maximum Congo River k_{600} values computed by Borges et al. (2019). Sawakuchi et al. (2017, corrigendum) calculated the total flux of CO_2 from the main channel of the lower Amazon River from Óbidos to Macapá, which had an average wetted surface area of 7,118 km^2, as 0.02 Pg C yr^{-1}. They then extrapolated from Macapá to the actual river mouth, which has an additional surface area of 11,261 km^2, producing a CO_2 flux of 0.03 Pg C yr^{-1}. The sum of fluxes for these two zones, or the total

emissions from Óbidos to the actual river mouth was 0.05 Pg C yr^{-1}. This flux is roughly 10% of the first estimations of CO_2 outgassing from the entire Amazon River Basin that conservatively extrapolated measurements from the central Amazon River (Richey et al., 2002).

Overall, it is clear that the original Richey et al. (2002) estimate of 0.5 Pg C yr^{-1} is a considerable underestimate of total outgassing from the aquatic habitats of the Amazon Basin. Re-evaluating new data and understanding, Melack (2016) estimated an updated value for annual CO_2 emission from aquatic habitats in the lowland Amazon Basin of 1.8 Pg C yr^{-1}, with 90% of this flux likely being associated with lakes, floodplains, and other wetlands. It does not include Sawakuchi et al. (2017) calculations for the lower river to the mouth, nor does it include likely outgassing from the Amazon plume, as the CO_2-rich water enters the ocean. Borges et al. (2019) gives an updated integrated CO_2 outgassing flux for the Congo River network of 0.25 ± 0.05 Pg C yr^{-1}. They conclude that the primary sources are almost certainly not terrestrial carbon being decomposed in the river, with the most likely alternative source being wetlands (flooded forest and aquatic macrophytes).

7. The River-to-Ocean Continuum

Unsurprisingly, both plumes of the Amazon and Congo Rivers exert a strong influence onto the Atlantic Ocean and, as highlighted earlier, export substantial amounts of terrestrially derived pCO_2 and OM. Here we consider their respective marine fates.

7.1. Marine Fate of Riverine CO_2

Do signals of elevated river pCO_2 then propagate beyond the mouth of large rivers? Integrated *in situ* measurements at the mouth of the Amazon River and out into the plume with satellite

observations from the Soil Moisture and Ocean Salinity (SMOS) satellite suggest that, including the plume area near the mouth, the plume is a net source of CO_2, with an average annual flux of 5.6 ± 7.2 Tg C y^{-1} (Valerio et al., in press; Ward et al., 2018b). This is contrary to past studies (e.g., Cooley et al., 2007; Ibánhez et al., 2015) that estimated the region to be a net sink of atmospheric CO_2. The inclusion of lower salinity waters has shifted these estimates to near net neutral (Valerio et al., in press). This calculation is likely an underestimate, as SMOS coverage is not valid within 100 km offshore. Intra-annual variability was related to discharge patterns at the river mouth and ocean currents plus trade winds in the plume, as a consequence of climatic events such as the severe drought throughout the Amazon Basin in 2010, and record flood in 2012-2014. The immediate question is, how far does the extension of the Congo plume result in CO_2 outgassing and at what magnitude? In the case of the Amazon, freshwaters extend up to 100 km beyond the actual river mouth, covering a significant amount of surface area relative to the river channel (Sawakuchi et al., 2017).

The previous discussion highlights a critical gap in observational data—the nearshore plume environments of large rivers, which are logistically difficult to measure. While oceanographic cruises typically do not make measurements directly adjacent to river mouths, river studies typically do not extend beyond the river mouth. These observational gaps are a byproduct of both logistical constraints and traditional disciplinary boundaries not crossed by limnologists and oceanographers until relatively recently. Addressing this gap requires careful collaboration between riverine and marine scientists, and nimble research vessels capable of sampling in these difficult nearshore regions. Great progress has been made in this regard over the last several decades and we advocate for increased efforts to sample across the river-ocean continuum.

7.2. Marine Fate of Organic Matter

Historic estimates of the residence time of terrestrial DOM in the Atlantic Ocean were derived from lignin concentrations measured in the open ocean and scaling average lignin fluxes from the Amazon and Mississippi Rivers to all other rivers draining into the Atlantic Ocean (Opsahl and Benner, 1997; Hernes and Benner, 2006). However, both the Amazon and Mississippi exhibit lower Λ_8 values than the Congo River (i.e., they are not as efficient at exporting lignin per mg of DOC as the Congo). Additionally, the Congo River is more efficient than the Amazon River at exporting lignin per unit volume as the Congo exports ~ 50% of the lignin load in ~ 20% of the volume of the Amazon River at Óbidos (i.e., 2.5 times more efficient) (Spencer et al., 2016). If the Congo River flux of dissolved lignin is extrapolated to the freshwater input of the Atlantic Ocean, the result is a much-reduced residence time for terrestrial DOM (~ 13 years versus ~ 35 years). Although it is unrealistic to extrapolate the Congo River lignin flux data to all other Atlantic Ocean draining rivers, this clearly highlights the sensitivity to the original calculations derived solely from the Amazon and Mississippi rivers, and emphasizes the disproportionate role organic rich systems like the Congo can play on overall ocean residence time estimates (Spencer et al., 2016). Regardless of how these lignin fluxes are represented, the residence time of terrestrial DOM is substantially lower than the mixing time of the world's oceans (500-1000 years) and apparent age of bulk DOC in the ocean (4,000 to 6,000 years; Williams and Druffel, 1987).

With respect to the fate of Amazon River DOM in the Atlantic Ocean, recent research suggests that a large fraction is stable over the continental margin, potentially due to extensive prior biodegradation in soils and the Amazon fluvial network (Ward et al., 2013; Medeiros et al., 2015; Seidel et al., 2015). Also, Amazon River plume waters are exported from the continental margin quickly (≤ 2 months) and thus a major fraction may survive export across the margin due to the

short residence time, particularly as this is coupled with high TSS concentrations that decreases photo-oxidation (Medeiros et al., 2015). Conversely with respect to the Congo River, the low TSS concentrations, its outflow position near the Equator, and its extensive surface plume in which Congo freshwater has been shown to be confined to the surface 15 m for the initial 200 km of the plume, and low salinity waters extend for 700 to 800 km from the mouth provide an ideal location for photo-oxidation (Eisma and Van Bennekom, 1978; Pak et al., 1984; Spencer et al., 2009). To date the proportion of DOC exported from the Congo River that is photo-mineralized remains unknown, but laboratory based photo-oxidation experiments have shown loss of ~ 45 % of Congo River DOC with simulated sunlight (Spencer et al., 2009). As discussed previously, these experiments also changed the composition of Congo River DOM, preferentially degrading the chromophoric fraction (CDOM) and lignin, enriching the δ^{13}C-DOC toward marine endmember values and shifting the molecular composition of DOM toward a less condensed, less aromatic composition (Spencer et al., 2009; Stubbins et al., 2010). This selective removal of the characteristics of terrestrial DOM resulted in a photo-resistant and altered pool that although sourced from the Congo would be difficult to trace back to its origins.

The fate of POM exported by the Amazon River has been well-studied and highlights low preservation of OM in high energy, mobile muds that receive extensive oxygen exposure and are home to diverse microbial communities (Hedges et al., 1997; Blair and Aller, 2012). At the mouth of the Congo River, the Congo Canyon facilitates burial of POC to the abyssal plain. Recent studies underscore efficient transport from the Canyon to the Congo Fan and across the depocenter a fan-wide deposition rate of ~ 0.7 Tg C yr^{-1}, and a burial rate of ~ 0.4 Tg C yr^{-1} (Rabouille et al., 2009; Savoye et al., 2009). Comparing this to the Congo River POC flux of 2 Tg C yr^{-1} suggests that ~ 36 % of exported POC reaches the depocenter and approximately one-fifth is ultimately buried

(Spencer et al., 2016). When compared to depocenters with extensive particle residence time in oxygenated waters like the Amazon and Mississippi which exhibit greater remineralization of POC (Aller et al., 1996; Allison et al., 2007) it is apparent the Congo River is a highly efficient site of POC preservation. Thus despite its comparably low POC flux, ultimately the Congo represents a sizeable fraction of the estimated POC burial term for the South Atlantic (~ 1.8 Tg C yr^{-1}; Mollenhauer et al., 2004) and even of global deep-sea POC burial (10-20 Tg C yr^{-1}; Berner, 1989; Hedges and Keil, 1995) due to the efficient injection of POC via the Congo Canyon to the Congo Fan.

8. Conclusion

Together the Amazon and Congo represent the end-member of the River Continuum (*sensu* Vannote et al., 1980), and illustrate the important role of fluvial systems in the global carbon cycle. Examining the interdependence of pCO_2, DOM, and POM within the construct of NEE in these large aquatic systems, while incomplete, provides a quantitative perspective on the dynamics of the respective C fractions.

A major difference between the basins, other than size and rainfall regime, is that the Amazon has origins in the high Andes, producing a much higher sediment load than the Congo. But organic loading on the sediments is ~ 5x greater in the Congo than the Amazon, so the total flux of OM in the Amazon is only ~ 3x greater than the Congo despite the fact that the Amazon discharges ~ 5x as much water. Hydrology governs carbon in both rivers, with both the greatest concentration of dissolved and particulate carbon at high water, and with biomarkers indicating increasing vascular plant inputs derived from litters and surface soils relative to low water. While the $\delta^{13}C$ and C:N signatures of OM between the two rivers are comparable, Λ_8 values indicate that the vascular plant

contribution to POM in the Congo is ~ 2x greater than in the Amazon. Overall, the organic rich nature of the tropical systems dominated by terrestrial inputs is readily apparent, especially compared to the Mississippi River and other global rivers. Landuse change in both basins leads to changes in the molecular composition of POM from deeper soil horizons and DOM leached from deforested catchments in both the Amazon and Congo Rivers. These energy-rich OM sources would presumably be more reactive in oxygenated river settings compared to deep soil environments, leading to enhanced metabolism and reintroduction of pre-aged carbon into the modern carbon cycle.

Terrestrially-derived OM feeds foodwebs in both the Congo and the Amazon, from fisheries to microbes. Decomposition of lignin phenols during transit appears to support a significant percentage of in situ respiration in the Amazon. While data are lacking, it would be reasonable to assume the same for the organic-rich Congo River. The process of priming may also expedite this OM remineralization. Combined with recent measurements indicating that traditional static BOD bottle measured respiration produces results 2-3x lower than more realistic rotating chambers suggests that in situ respiration may play a major role in sustaining the high levels of supersaturation of pCO_2 far downriver. In the lowermost Amazon, pCO_2 begins to decrease, with turbulence from winds and tides.

The marine fate of the river-borne materials is quite different. The Congo Canyon facilitates burial of POM to the abyssal plain. In contrast, POM exported by the Amazon River is minimally preserved in the high energy, mobile muds of the plume that receive extensive oxygen exposure. A large fraction of DOM is stable over the continental margin, potentially due to extensive prior biodegradation in soils and the Amazon fluvial network, and short residence time across the shelf. DOM exported by the low-sediment Congo River is subject to considerably more photoxidation

and selective removal of terrestrial signals. The greater fraction of lignin in the Congo relative to the Amazon and Mississippi leads to estimates of reduced residence time for terrestrial DOM. Depending on the season, the CO_2 discharged by the Amazon River into the plume persists to the extent that the plume can be considered a net source, rather than sink, of pCO_2. Comparable data are not available for the Congo.

Based on the data summarized here, it would appear that the Alsdorf et al. (2016) hypothesis that the annual-average amount of CO_2 evasion from the Congo Basin is greater than the Amazon per unit area is not supported. As was the case with the Amazon, further information in this data-sparse region would certainly modify these results, both for magnitude and possibly for dynamics. Regardless of absolute magnitude the key finding with the Congo is that it too is a highly dynamic region of aquatic carbon cycling. It is too early to conclude how these outgassing results relate to the overall carbon balance of these largest river basins, and how this carbon balance will shift under future scenarios. Model results suggest that the export of carbon and emission of CO_2 from the Amazon River vary systematically with climate (e.g., more CO_2 evasion during wet years; Hastie et al., 2019) and that these fluxes have steadily increased by ~ 25 % since 1861 in the Congo River (Hastie et al., 2020). However, such representation of river and coastal carbon fluxes are not currently deployed in global scale models, limiting our ability to interpret potential feedbacks among these interconnected components of the Earth system (Ward et al., 2020). Thus, disentangling the natural drivers of large riverine carbon cycling remains a challenge, and the complexity and importance of this effort is becoming increasingly compounded by human disturbances discussed. One interpretation is that there is an aquatic-based carbon cycle that is not accounted for in terrestrially focused carbon budgets.

References

Abril, G., Martinez, J.-M., Artigas, L.F., Moreira-Turcq, P., Benedetti, M.F., Vidal, et al. (2014). Amazon River carbon dioxide outgassing fuelled by wetlands. *Nature* 505: 395–398. doi:10.1038/nature12797

Alin, S. R., M.D.F.L. Rasera, C. I. Salimon, J. E. Richey, G. W. Holtgrieve, A. V. Krusche, and A. Snidvongs. (2011). Physical controls on carbon dioxide transfer velocity and flux in low-gradient river systems and implications for regional carbon budgets. *Journal of Geophysical. Research. Biogeosciences.* 116:G01009. doi:10.1029/2010JG001398

Allen, G. H., and Pavelsky, T. M. (2018). Global extent of rivers and streams. *Science*, 361(6402), 585-588.

Aller, R.C., Blair, N.E., Xia, Q. and Rude, P.D. (1996). Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments. *Continental Shelf Research, 16(5-6*), pp.753-786.

Allison, M.A., Bianchi, T.S., McKee, B.A. and Sampere, T.P. (2007). Carbon burial on river-dominated continental shelves: Impact of historical changes in sediment loading adjacent to the Mississippi River. *Geophysical Research Letters, 34(1)*.

Alsdorf, D., Han, S-C., Bates, P., and Melack, J. (2010). Seasonal water storage on the Amazon floodplain measured from satellites. *Remote Sensing of Environment* 114: 2448-2456.

Alsdorf, D., Beighley, E., Laraque, A., Lee, H., Tshimanga, R., O'Loughlin, F., Mahé, G., Dinga, B., Moukandi, G., and Spencer, R. (2016), Opportunities for hydrologic research in the Congo Basin, *Rev. Geophys., 54*, doi:10.1002/2016RG000517.

Amaral, J. H. F., Suhett, A. L., Melo, S., and Farjalla, V. F. (2013). Seasonal variation and interaction of photodegradation and microbial metabolism of DOC in black water Amazonian ecosystems. *Aquatic Microbial Ecology, 70(2),* 157-168.

Amaral, J.H.F., Farjalla, V.F., Melack, J.M., Kasper, D., Scofield, V., Barbosa, P.M., and Forsberg, B.R. (2019). Seasonal and spatial variability of CO_2 in aquatic environments of the central lowland Amazon basin. *Biogeochemistry* 143:133–149.

Araújo, K.R., Sawakuchi, H., Bertassoli Jr, D.J., Sawakuchi, A.O., da Silva, K.D., Vieira, T.B., Ward, N.D. and Pereira, T.S. (2019). Carbon dioxide (CO2) concentrations and emission in the newly constructed Belo Monte hydropower complex in the Xingu River, Amazonia. *Biogeosciences, 16(18),* pp.3527-3542.

Araujo-Lima, C.A.R.M., Forsberg, B.R., Victoria, R., Martinelli, L. (1986) Energy sources for detritivorous fishes in the Amazon. *Science, 234*, 1256-1258.

Aufdenkampe, A.K., Hedges, J.I., Richey, J.E., Krusche, A.V., and Llerena, C.A. (2001) Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. *Limnology and Oceanography, 46*, 1921-1935.

Aufdenkampe, A.K., Mayorga, E., Hedges,J.I., Llerena, C.A., Quay, P.D., Gudeman, J., Krusche, A.V., and Richey, J.E. (2007) Organic matter in the Peruvian headwaters of the Amazon: Compositional evolution from the Andes to the lowland Amazon mainstem. *Organic Geochemistry*, 38, 337-364.

Balagizi, C.M., Darchambeau, F., Bouillon, S., Yalire, M.M., Lambert, T., Borges, A.V. (2015) River geochemistry, chemical weathering, and atmospheric CO2 consumption rates in the Virunga Volcanic Province (East Africa). *Geochemistry, Geophysics, Geosystems*, 16, 2637-2660.

Barbosa, P.M., Melack, J.M., Amaral, J.H.F., Scofield, V., Farjalla, V., and Forsberg., B.R. (2016). Methane concentrations and fluxes from rivers and lakes in the Amazon basin. *Limnology and Oceanography* 61, S221-237.

Barbosa, P.M., Melack, J.M., Amaral, J.H.F., MacIntyre, S., Kasper, D., Cortes, A.C., Farjalla V.F., and Forsberg, B.R. (2020). Dissolved CH_4 concentrations and fluxes to the atmosphere from a tropical floodplain lake. *Biogeochemistry,* doi.org/10.1007/s10533-020-00650-1.

Berggren, M., Laudon, H., Haei, M., Ström, L., and Jansson, M. (2010). Efficient aquatic bacterial metabolism of dissolved low-molecular-weight compounds from terrestrial sources. *The ISME Journal*, 4(3), 408–416.

Bernardes, M. C., Martinelli, L. A., Krusche, A. V., Gudeman, J., Moreira, M., Victoria, R. L., et al. (2004). Riverine organic matter composition as a function of land use changes southwest Amazon. *Ecological Applications* 14(sp4), 263–279.

Berner, R.A. (1989), Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanearozoic time. *Global and Planetary Change* (1): 97-122. doi.org/10.1016/0921-8181(89)90018-0

Blair, N.E., and Aller (2012), The fate of terrestrial organic carbon in the marine environment. *Annual Review of Marine Science*, 4, 401-423.

Bonnet, M.-P., G. Barroux, P. Seyler, G. Pecly, P. Moreira-Turcq, C. Lagane, G. Cochoneau, J. Viers, F. Seyler, and J.-L. Guyot (2005), Seasonal links between the Amazon corridor and its flood plain: The case of the varzea of Curuai, in Dynamics and Biogeochemistry of River Corridors and Wetlands, *Proceedings of symposium S4 held during the Seventh IAHS Scientific Assembly* at Foz do Iguaçu, Brazil, April 2005), IAHS Publ., 294.

Borges, A., G. Abril, F. Darchambeau, C.R. Teodoru, J., Deborde, L.O. Vidal, T. Lambert, and S. Bouillon (2015), Divergent biophysical controls of aquatic CO2 and CH4 in the world's two largest rivers. *Scientific Reports*, 5, 15614.

Borges, A.V., Darchambeau, F., Lambert, T., Morana, C., Allen, G.H., Tambwe, E., Sembaito,

A.T., Mambo, T., Wabakhangazi, J.N., Descy, J-P, Teodoru, C.R. and Bouillon, S. (2019). Variations in dissolved greenhouse gases (CO_2, CH_4, N_2O) in the Congo River network overwhelmingly driven by fluvial-wetland connectivity. *Biogeosciences*, 16, 3801–3834, https://doi.org/10.5194/bg-16-3801-2019

Bouchez, J., Galy, V., Hilton, Gaillardet, J., Moreira-Turcq, P., Perez, M.A., France-Lanord, C., and Maurice (2014), Source, transport and fluxes of Amazon River particulate organic carbon: Insights from river sediment depth-profiles. *Geochimica et Cosmochimica. Acta*, 133, 280-298.

Bouillon, S., Yambélé, A., Spencer, R.G.M., Gillikin, D.P., Hernes, P.J., Six, J., et al. (2012). Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo River Basin). *Biogeosciences* 9, 2045–2062.

Bourgoin, L.M., Bonnet, M.P., Martinez, J-M, Kosuth, B., Cochonnea, G., Moreira-Turcq, B., Guyot, J-L., Vauchele, P., Filizola, N., and Seyler, P. (2007). Temporal dynamics of water and sediment exchanges between the Curuaı́floodplain and the Amazon River, Brazil. *Journal of Hydrology* 335, 140–156.

Bruijnzeel, L. A. (2004). Hydrological functions of tropical forests: not seeing the soil for the trees? *Agriculture, Ecosystems and Environment*, 104(1), 185–228.

Butman, D., and Raymond, P. (2011). Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience*. DOI: 10.1038/NGEO1294

Cavalcante, R. B. L., Pontes, P. R. M., Souza-Filho, P. W. M., and Souza, E. B. (2019). Opposite Effects of Climate and Land Use Changes on the Annual Water Balance in the Amazon Arc of Deforestation. *Water Resources Research*, 55(4), 3092–3106.

Coe, M. T., Costa, M. H., and Soares-Filho, B. S. (2009). The influence of historical and potential future deforestation on the stream flow of the Amazon River--Land surface processes and

atmospheric feedbacks. *Journal of Hydrology*, 369(1-2), 165–174.

Cole, J. J., Pace, M.L., Carpenter, S.R., Kitchell, J.F. (2000). Persistence of Net Heterotrophy in Lakes during Nutrient Addition and Food Web Manipulations. *Limnology and Oceanography*. 45 (8), 1718-1730

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., et al. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10(1), 172-185.

Cooley, S.R., Coles, V.J., Subramaniam, A. and Yager, P.L. (2007). Seasonal variations in the Amazon plume-related atmospheric carbon sink. *Global Biogeochemical Cycles*, 21(3).

Cory, R. M., Ward, C. P., Crump, B. C., and Kling, G. W. (2014). Sunlight controls water column processing of carbon in arctic fresh waters. *Science*, 345(6199), 925-928.

Costa, M. H. (2005). Large-scale hydrological impacts of tropical forest conversion. Pp. 590-597. In M. Bonell and L. A. Bruijnzeel (eds), *Forests, Water and People in the Humid Tropics*, Cambridge University Press.

Coynel, A., Seyler, P., Etcheber, H., Meybeck, M., and Orange, D. (2005), Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River. *Global Biogeochemical Cycles* 19, GB4019, doi:10.1029/2004GB002335.

Curtis, P. G., Slay, C. M., Harris, N. L., Tyukavina, A., and Hansen, M. C. (2018). Classifying drivers of global forest loss. *Science*, 361(6407), 1108–1111.

Dargie, G. C., Lewis, S. L., Lawson, I. T., Mitchard, E. T., Page, S. E., Bocko, Y. E., and Ifo, S. A. (2017). Age, extent and carbon storage of the central Congo Basin peatland complex. *Nature*, 542(7639), 86-90.

De Wasseige, C., De Marcken, P., Bayol, N., Hiol, F., Mayaux, P., Desclée, B., et al. (eds) (2012).

The forests of the Congo basin: state of the forest 2010. Publications Office of the European Union. Luxembourg. 276 p. ISBN: 978-92-79-22716-5, doi:10.2788/47210

Descy, J.P., Darchambeau, F., Lambert, T., Stoyneva-Gaetner, M.P., Bouillon, S., Borges, A.V. (2016). Phytoplankton dynamics in the Congo River. *Freshwater Biology*, 62, 87-101.

Drake, T.W., Raymond, PA. and Spencer, R.G.M. (2017). Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. *Limnology and Oceanography Letters* https://doi.org/10.1002/lol2.10055

Drake, T. W., Podgorski, D. C., Dinga, B., Chanton, J., Six, J., and Spencer, R. G. M. (2019a). Land-use controls on carbon biogeochemistry in lowland streams of the Congo Basin. *Global Change Biology*. https://doi.org/10.1111/gcb.14889

Drake, T. W., Van Oost, K., Barthel, M., Bauters, M., Hoyt, A. M., Podgorski, D. C., et al. (2019b). Mobilization of aged and biolabile soil carbon by tropical deforestation. *Nature Geoscience*, 12(7), 541–546.

Draper, F. C., Roucoux, K. H., Lawson, I. T., Mitchard, E. T., Coronado, E. N. H., Lähteenoja, O., et al. (2014). The distribution and amount of carbon in the largest peatland complex in Amazonia. *Environmental Research Letters*, 9(12), 124017.

Dungait, J. A., Hopkins, D. W., Gregory, A. S., and Whitmore, A. P. (2012). Soil organic matter turnover is governed by accessibility not recalcitrance. *Global Change Biology*, 18(6), 1781-1796.

Duveiller, G., Defourny, P., Desclee, B. and Mayaux, P. (2008), Deforestation in central Africa: estimates at regional, national and landscape levels by advanced processing of systematically-distributed Landsat extracts. *Remote Sensing of Environment*, 112, 1969- 1981.

Eisma, D. and Van Bennekom, A.J. (1978). The Zaire river and estuary and the Zaire outflow in

the Atlantic Ocean. *Netherlands Journal of Sea Research*, 12, 255–272.

Empresa de Pesquisa Energética (2013). Plano Decenal de Expansão de Energia 2022. Ministério de Minas e Energia. Brasília: Ministério de Minas e Energia.

Farella, N., Lucotte, M., Louchouarn, P., and Roulet, M. (2001). Deforestation modifying terrestrial organic transport in the Rio Tapajos, Brazilian Amazon. *Organic Geochemistry*, 32(12), 1443–1458.

Fearnside, P.M. (2002). Greenhouse gas emissions from a hydroelectric reservoir (Brazil's Tucuruí Dam) and the energy policy implications. *Water, Air, and Soil Pollution*, 133(1-4), pp.69-96.

Filizola, N., and Guyot, J.L. (2009), Suspended sediment yield in the Amazon basin. An assessment using the Brazilian national data set. *Hydrological Processes*, 23, 3207 – 3215.

Forsberg, B.R., Araujo-Lima, C.A.R.M., Martinelli, L.A., Victoria, R.L., Bonassi, J.A. (1993). Autotrophic carbon source for fish of the central Amazon. *Ecology*, 73, 643-652.

Fricke, A.T., Nittrouer, C.A., Ogston, A.S., Nowacki, D.J., Asp, N.E., Souza Filho, P.W., da Silva, M.S. and Jalowska, A.M. (2017). River tributaries as sediment sinks: Processes operating where the Tapajós and Xingu rivers meet the Amazon tidal river. *Sedimentology*, 64(6), pp.1731-1753.

Gagne-Maynard, W.C., Ward, N.D., Keil, R.G., Sawakuchi, H.O., Da Cunha, A.C., Neu, V., Brito, D.C., Da Silva Less, D.F., Diniz, J.E., De Matos Valerio, A. and Kampel, M. (2017). Evaluation of primary production in the Lower Amazon River based on a dissolved oxygen stable isotopic mass balance. *Frontiers in Marine Science*, 4, p.26.

Gerland, P., Raftery, A. E., Ševčíková, H., Li, N., Gu, D., Spoorenberg, T., et al. (2014). World population stabilization unlikely this century. *Science*, 346(6206), 234–237.

Hastie, A., Lauerwald, R., Ciais, P., and Regnier, P. (2019). Aquatic carbon fluxes dampen the overall variation of net ecosystem productivity in the Amazon basin: An analysis of the

interannual variability in the boundless carbon cycle. *Global Change Biology*, 25(6), 2094-2111.

Hastie, A., Lauerwald, R., Ciais, P., Papa, F., and Regnier, P. (2020). Historical and future contributions of inland waters to the Congo basin carbon balance. *Earth System Dynamics Discussions*, 1-49.

Hedges, J. I., Ertel, J. R., Quay, P. D., Grootes, P. M., Richey, J. E., Devol, A. H., et al. (1986a). Organic carbon-14 in the Amazon river system. *Science*, 231(4742), 1129–1131.

Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., and Santos, U.D.M. (1986b). Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography*, 31, 717- 738.

Hedges, J.I., Cowie, G.L., Richey, J.E., Quay, P.D., Benner, R., Strom, M., and Forsberg, B.R. (1994), Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. *Limnology and Oceanography*, 39, 743-761.

Hedges, J. I., and Keil, R.G. (1995), Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry*, 49, 81-115.

Hedges, J. I., Keil, R.G., and Benner, R. (1997), What happens to terrestrial organic matter in the ocean? *Organic Geochemistry*, 27, 195-212.

Hedges, J.I., Mayorga, E., Tsamakis, E., McClain, M.E., Aufdenkampe, A.K., Quay, P.D., Richey, J.E., Benner, R., Opsahl, S., Black, B., Pimental, T., Quintanilla, J. and Maurice, L. (2000). Organic matter in Bolivian tributaries of the Amazon River: A comparison to the lower mainstream. *Limnology and Oceanography* 45, 1449-1466.

van Hees, P. A. W., Jones, D. L., Finlay, R., Godbold, D. L., and Lundström, U. S. (2005). The carbon we do not see—the impact of low molecular weight compounds on carbon dynamics

and respiration in forest soils: a review. *Soil Biology and Biochemistry*, 37(1), 1–13.

Hernes, P.J., and Benner, R. (2006), Terrigenous organic matter sources and reactivity in the North Atlantic Ocean and a comparison to the Arctic and Pacific oceans. *Marine Chemistry* 100, 66-79.

Hubau, W., Lewis, S.L., Phillips, O.L. *et al.* (2020). Asynchronous carbon sink saturation in African and Amazonian tropical forests. *Nature* 579**,** 80–87 https://doi.org/10.1038/s41586-020-2035-0

Ibánhez, J. S. P., Diverrès, D., Araujo, M., and Lefèvre, N. (2015). Seasonal and interannual variability of sea-air CO_2 fluxes in the tropical Atlantic affected by the Amazon River plume. *Global Biogeochemical Cycles*, 29(10), 1640-1655.

Johnson, M. S., Lehmann, J., Riha, S. J., Krusche, A. V., Richey, J. E., Ometto, J. P. H., and Couto, E. G. (2008). CO2 efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. *Geophysical Research Letters*, 35(17).

Junk, W. J. and C. Howard-Williams, C. (1984). Ecology of aquatic macrophytes in Amazonia. In: Sioli, H. (ed.), The Amazon: limnology and landscape ecology of a mighty tropical river and its basin. Dr W. Junk Publishers, Dordrecht: 269–293.

Kaiser, K., and Kalbitz, K. (2012). Cycling downwards--dissolved organic matter in soils. *Soil Biology and Biochemistry*, 52, 29–32.

Kalbitz, K., Schwesig, D., Schmerwitz, J., Kaiser, K., Haumaier, L., Glaser, B., et al. (2003). Changes in properties of soil-derived dissolved organic matter induced by biodegradation. *Soil Biology and Biochemistry*, 35(8), 1129–1142.

Kellerman, A. M., Guillemette, F., Podgorski, D. C., Aiken, G. R., Butler, K. D., and Spencer, R. G. M. (2018). Unifying Concepts Linking Dissolved Organic Matter Composition to

Persistence in Aquatic Ecosystems. *Environmental Science and Technology*, 52(5), 2538–2548.

Laporte, N., Stabach, J.A., Grosch, R., Lin, T.S., and Goetz, S.J. (2007), Expansion of industrial logging in Central Africa. *Science* 316, 1451.

Laraque, A., Bricquet, J.P., Pandi, A., and Olivry, J.C. (2009), A review of material transport by the Congo River and its tributaries. *Hydrological Processes* 23, 3216-3224.

Lovett, G.M., Cole, J.J., Pace, M.L. (2006). Is Net Ecosystem Production Equal to Ecosystem Carbon Accumulation? Ecosystems Volume 9, Number 1, 152-155, DOI: 10.1007/s10021-005-0036-3

Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., and Flessa, H. (2006). Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions–a review. *European Journal of Soil Science*, 57(4), 426-445.

MacIntyre, S., Amaral, J.H.F., Barbosa, P.M., Cortés, A., Forsberg, B.R., and Melack, J.M. (2019). Turbulence and gas transfer velocities in sheltered flooded forests of the Amazon basin. Geophysical Research Letters. doi.org/10.1029/2019GL083948

Malhi, Y., and Grace, J. (2000). Tropical forests and atmospheric carbon dioxide. *Trends in Ecology and Evolution*, 15(8), 332-337.

Mann, P.J., Eglinton, T.I., McIntyre, C.P., Zimov, N., Davydova, A., Vonk, J.E., Holmes, R.M., and Spencer, R.G.M. (2015), Utilization of ancient permafrost carbon in headwaters of Arctic fluvial networks. *Nature Communications*, 6, doi:10.1038/ncomms8856.

Marin-Spiotta, E., Gruley, K.E., Crawford, J., Atkinson, E.E., Miesel, J.R., Greene, S., Cardona-Correa, C., and Spencer, R.G.M. (2014), Paradigm shifts in soil organic matter research affect interpretations of aquatic carbon cycling: transcending disciplinary and ecosystem boundaries.

Biogeochemistry, 117, 279-297.

Marwick, T. R., Tamooh, F., Teodoru, C.R., Borges, A.V., Darchambeau, F., and Bouillon, S. (2015), The age of river-transported carbon: A global perspective, *Global Biogeochemical Cycles*, 29, 122–137, doi:10.1002/2014GB004911

Mayorga, E., Aufdenkampe, A. K., Masiello, C. A., Krusche, A. V., Hedges, J. I., Quay, P. D., et al. (2005). Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. *Nature*, 436(7050), 538–541.

Meade, R. H., Dunne, T., Richey, J.E., Santos, U.M.m and Salati, E. (1985), Storage and remobilization of sediment in the lower Amazon River of Brazil, *Science*, 228, 488–490.

Medeiros, P.M., Seidel, M., Ward, N.D., Carpenter, E.J., Gomes, H.R., Niggemann, J., Krusche, A.V., Richey, J.E., Yager, P.L., Dittmar, T. (2015) Fate of the Amazon River dissolved organic matter in the tropical Atlantic Ocean. *Global Biogeochemical Cycles*, 29, 677-690.

Melack, J.M, and Forsberg, B. (2001) Biogeochemistry of Amazon floodplain lakes and associated wetlands. In: McClain, M.E., Victoria R.L., and Richey J.E. (eds) Biogeochemistry of the Amazon Basin and its role in a changing world. Oxford University Press, Oxford, pp. 235–276

Melack, J.M,. Hess, L.L, Gastil, M, Forsberg, B.R., Hamilton, S.K., Lima, I.B.T., Novo, E.M.L.M. (2004). Regionalization of methane emissions in the Amazon basin with microwave remote sensing. *Global Change Biology* 10:530–544.

Melack, J. M., Hess, L. L., Gastil, M., Forsberg, B. R., Hamilton, S. K., Lima, I. B., and Novo, E. M. (2004). Regionalization of methane emissions in the Amazon Basin with microwave remote sensing. *Global Change Biology*, 10(5), 530-544.

Melack, J.M., and Engle, D (2009). An organic carbon budget for an Amazon floodplain lake. *Verhandlungen des Internationalen Verein Limnologie* 30:1179–1182

Melack, J.M. (2016). Aquatic Ecosystems. In L. Nagy et al. (eds.), *Interactions Between Biosphere, Atmosphere and Human Land Use in the Amazon Basin*, Ecological Studies 227, Springer-Verlag Berlin Heidelberg DOI 10.1007/978-3-662-49902-3_7

Meybeck M. (2002), Riverine quality at the Anthropocene: Propositionsfor global space and time analysis, illustrated by the Seine River, *Aquatic Sciences*, 64, 376-393.

Mollenhauer, G., Schneider, R.S., Jennerjahn, T.C., Muller, P.J., and Wefer, G. (2004), Organic carbon accumulation in the South Atlantic Ocean: Its modern, mid- Holocene and last glacial distribution. *Global and Planetary Change*, 40, 249-266.

Moore, S., Evans, C. D., Page, S. E., Garnett, M. H., Jones, T. G., Freeman, C., et al. (2013). Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes. *Nature*, 493(7434), 660-663.

Moreira-Turcq, P., Seyler, P., Guyot, J.L., Etcheber, H., (2003). Exportation of organic carbon from the Amazon river and its main tributaries. *Hydrological Processes*, 17, 1329–1344.

Onstad, G.D., Canfield, D.E., Quay, P.D., Hedges, J.I. (2000), Sources of particulate organic matter in rivers from the continental USA: Lignin phenol and stable carbon isotope composition. *Geochimica et Cosmochimica Acta*, 64, 3539-3546.

Opsahl, S., and Benner, R. (1997), Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature*, 386, 480-482.

Pak, H., Zaneveld, J.R.V., and Spinrad, R.W. 1984. Vertical distribution of suspended particulate matter in the Zaire river, estuary and plume. *Netherlands Journal of Sea Research*, 17, 412–425.

Pangala, S., Enrich-Prast, A., Basso, L. *et al.* (2017). Large emissions from floodplain trees close the Amazon methane budget. *Nature* 552**,** 230–234 https://doi.org/10.1038/nature24639

Rabouille, C., Caprais, J.C., Lansard, B., Crassous, P., Dedieu, K., Reyss, J.-L., and Khripounoff, A. (2009), In situ measurements of sediment oxygen consumption and organic matter budget in the Southeast Atlantic continental margin close to the Congo Canyon. *Deep-Sea Research*, II, 56, 2223–2238.

Raymond, P.A., and Bauer, J.E. (2001), Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. *Nature*, 409, 497-500.

Raymond, P. A., McClelland, J. W. , Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., Striegl, R. G., Aiken, G. R., and Gurtovaya, T. Y. (2007), Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest rivers. *Global Biogeochemical Cycles*, 21, GB4011, doi:10.1029/2007GB002934.

Raymond, P.A., Hartmann,J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., et al. (2013).Global carbon dioxide emissions from inland waters. *Nature* 503,355–359.doi:10.1038/nature12760

Raymond, P.A., and Spencer, R.G.M. (2015), Riverine DOM. In Hansell, D.A. and C.A. Carlson (eds) *Biogeochemistry of Marine Dissolved Organic Matter* (2nd Edition), AP, pp. 509-535.

Raymond, P. A., Saiers, J. E., and Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology*, 97(1), 5-16.

Remington, S., Krusche, A., and Richey, J. (2011). Effects of DOM photochemistry on bacterial metabolism and CO 2 evasion during falling water in a humic and a whitewater river in the Brazilian Amazon. *Biogeochemistry*, 105(1-3), 185-200.

Richey, J. E., Meade, R.H., Salati, E., Devol, A.H., Nordin, C.F., and dos Santos, U. (1986), Water discharge and suspended sediment concentrations in the Amazon River: 1982–1984,

Water Resources Research, 22, 756– 764.

Richey, J. E., Nobre, C., and Deser, C. (1989). Amazon River discharge and climate variability: 1903 to 1985. *Science*, 246 (4926), 101-103. Richey, J. E., Hedges, J. I., Devol, A. H., Quay, P. D., Victoria, R., Martinelli, L., and Forsberg, B. R. (1990). Biogeochemistry of carbon in the Amazon River. *Limnology and Oceanography*, 35(2), 352–371.

Richey, J. E., J. I. Hedges, A. H. Devol, P. D. Quay, R. Victoria, L. Martinelli, and B. R. Forsberg. (1990). Biogeochemistry of carbon in the Amazon River. *Limnology and Oceanography*, 35: 352-371.

Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., and Hess, L.L. (2002). Carbon dioxide evasion from central Amazonian wetlands as a significant source of atmospheric CO2 in the tropics. *Nature* 416,617–620. doi:10.1038/416617a

Rocher-Ros, G., Sponseller, R. A., Lidberg, W., Mörth, C. M., and Giesler, R. (2019). Landscape process domains drive patterns of CO_2 evasion from river networks. *Limnology and Oceanography Letters*, 4(4), 87-95.

Saliot, A., Mejanelle, L., Scribe, P., Fillaux, J., Pepe, C., Jabaud, A., and Dagaut, J. (2001). Particulate organic carbon, sterols, fatty acids andpigments in the Amazon River system. *Biogeochemistry* 53:79–103.

Savoye, B., Babonneau, N., Dennielou, B. and Bez, M. (2009). Geological overview of the Angola- Congo margin, the Congo deep-sea fan and its submarine valleys. *Deep Sea Research Part II*, 56, 2169-2182.

Sawakuchi, H.O., Bastviken, D., Sawakuchi, A.O., Krusche, A.V., Ballester, M.V. and Richey, J.E. (2014). Methane emissions from Amazonian Rivers and their contribution to the global methane budget. *Global Change Biology*, 20(9), pp.2829-2840.

Sawakuchi, H.O., Bastviken, D., Sawakuchi, A.O., Ward, N.D., Borges, C., Tsai, S.M., Richey, J.E., Ballester, M.V.R., Krusche, A.V. (2016). Oxidative mitigation of methane evasion in large Amazonian rivers. *Global Change Biology*. 22 (3), 1075-1085.

Sawakuchi, H.O., Neu, V., Ward, N.D., Barros, M.D.L.C., Valerio, A.M., Gagne-Maynard, W., Cunha, A.C., Less, D.F., Diniz, J.E., Brito, D.C. and Krusche, A.V. (2017). Carbon dioxide emissions along the lower Amazon River. *Frontiers in Marine Science*, 4, p.76.

Schefuß, E., Eglinton, T.I., Spencer-Jones, C.L., Rullkötter, J., De Pol-Holz, R., Talbot, H.M., Grootes, P.M. and Schneider, R.R., (2016). Hydrologic control of carbon cycling and aged carbon discharge in the Congo River basin. *Nature Geoscience*, 9(9), 687-690.

Seidel, M., Yager, P.L., Ward, N.D., Carpenter, E.J., Gomes, H.R., Krusche, A.V., Richey, J.E., Dittmar, T. and Medeiros, P.M. (2015). Molecular-level changes of dissolved organic matter along the Amazon River-to-ocean continuum. *Marine Chemistry*, 177, pp.218-231.

Seidel, M., Dittmar, T., Ward, N.D., Krusche, A.V., Richey, J.E., Yager, P.L. and Medeiros, P.M. (2016). Seasonal and spatial variability of dissolved organic matter composition in the lower Amazon River. *Biogeochemistry*, 131(3), pp.281-302.

Sioli, H. (ed). 1984. The Amazon. Springer Netherlands. DOI10.1007/978-94-009-6542-3. 800p.

Soto, D.X., Decru, E., Snoeks, J., Verheyen, E., de Walle, L.V., Bamps, J., Mambo, T., and Bouillon, S. (2019). Terrestrial contributions to Afrotropical aquatic food webs: The Congo River case. *Ecology and Evolution*, 9, 10746-10757.

Spencer, R.G.M., Stubbins, A., Hernes, P.J., Baker, A., Mopper, K., Aufdenkampe, A.K., Dyda, R.Y., Mwamba, V.L., Mangangu, A.M., Wabakanghanzi, J.N., and Six, J. (2009). Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. *Journal of Geophysical Research: Biogeosciences*. 114, G03010, doi:

10.1029/2009JG000968.

Spencer, R. G. M., Hernes, P. J., Aufdenkampe, A. K., Baker, A., Gulliver, P., Stubbins, A., et al. (2012). An initial investigation into the organic matter biogeochemistry of the Congo River. *Geochimica et Cosmochimica Acta*, 84, 614–627.

Spencer, R. G. M., Mann, P. J., Dittmar, T., Eglinton, T. I., McIntyre, C., Holmes, R. M., et al. (2015). Detecting the signature of permafrost thaw in Arctic rivers. *Geophysical Research Letters*, 42(8), 2015GL063498.

Spencer, R.G.M., Hernes, P.J., Dinga, B., Wabakanghanzi, J.N., Drake, T.W., and Six, J. (2016). Origins, seasonality and fluxes of organic matter in the Congo River. *Global Biogeochemical Cycles*, 30 (7), 1105-1121.

Spencer, R. G. M., Kellerman, A. M., Podgorski, D. C., Macedo, M. N., Jankowski, K., Nunes, D., and Neill, C. (2019). Identifying the Molecular Signatures of Agricultural Expansion in Amazonian Headwater Streams. *Journal of Geophysical Research: Biogeosciences*, 124(6), 1637–1650.

St. Louis, V.L., Kelly, C.A., Duchemin, É., Rudd, J.W. and Rosenberg, D.M., 2000. Reservoir surfaces as sources of greenhouse gases to the atmosphere: A global estimate. *BioScience,* 50(9), pp.766-775.

Stubbins, A., Spencer, R. G., Chen, H., Hatcher, P. G., Mopper, K., Hernes, P. J., Mwamba, V.L., Mangangu, A.M., Wabakanghanzi, J.N., and Six, J. (2010). Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. *Limnology and Oceanography*, 55(4), 1467-1477.

Thomas, S. M., Neill, C., Deegan, L. A., Krusche, A. V., Ballester, V. M., and Victoria, R. L. (2004). Influences of land use and stream size on particulate and dissolved materials in a small

Amazonian stream network. *Biogeochemistry*, 68(2), 135–151.

Trancoso, R. (2006). Land cover changes, and disturbances in hydrological response of Amazonian watersheds, *Master's thesis*, Manaus: INPA.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., et al. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54(6part2), 2298-2314.

Valerio, A.M., Kampel, M., Ward, N.D., Sawakuchi, H.O., Cunha, A.C., Krusche, A.V., Richey, J.E. (in press) Seasonal and inter-annual variability of carbon dioxide fluxes in the Amazon River plume based on Soil Moisture and Ocean Salinity satellite data. *Continental Shelf Research*

Vannote, R. L, Minshall, G.W., Cummins, K.W., Sedell, J.R, and Cushing, C.E. 1980. The river continuum concept. *Canadian. Journal of Fisheries and Aquatic Sciencews*. 37: 130-137.

Ward, N.D., Keil, R.G., Medeiros, P.M., Brito, D.C., Cunha, A.C., Dittmar, T., Yager, P.L., Krusche, A.V., Richey, J.E. (2013). Degradation of terrestrially derived macromolecules in the Amazon River. *Nature Geoscience*, 6, 530-533.

Ward, N.D., Krusche, A.V., Sawakuchi, H.O., Brito, D.C., Cunha, A.C., Moura, J.M.S., da Silva, R., Yager, P.L., Keil, R.G. and Richey, J.E. (2015). The compositional evolution of dissolved and particulate organic matter along the lower Amazon River—Óbidos to the ocean. *Marine Chemistry*, 177, pp.244-256.

Ward, N.D., Bianchi, T.S., Sawakuchi, H.O., Gagne-Maynard, W., Cunha, A.C., Brito, D.C., Neu, V., de Matos Valerio, A., da Silva, R., Krusche, A.V. and Richey, J.E. (2016). The reactivity of plant-derived organic matter and the potential importance of priming effects along the lower Amazon River. *Journal of Geophysical Research: Biogeosciences*, 121(6), pp.1522- 1539.

Ward, N.D., Bianchi, T.S., Medeiros, P.M., Seidel, M., Richey, J.E., Keil, R.G. and Sawakuchi, H.O. (2017). Where carbon goes when water flows: carbon cycling across the aquatic continuum. *Frontiers in Marine Science*, 4, p.7.

Ward, N.D., Sawakuchi, H.O., Neu, V., Less, D.F., Valerio, A.M., Cunha, A.C., Kampel, M., Bianchi, T.S., Krusche, A.V., Richey, J.E. and Keil, R.G. (2018a). Velocity-amplified microbial respiration rates in the lower Amazon River. *Limnology and Oceanography Letters*, 3(3), pp.265-274.

Ward, N.D., Sawakuchi, H.O., Richey, J.E. (2018b) The Amazon River's ecosystem—where land meets the sea. *Eos*. 99. https://doi.org/10.1029/2018EO088573

Ward, N.D., Sawakuchi, H.O., Richey, J.E., Keil, R.G., and Bianchi, T.S. (2019). Enhanced aquatic respiration rates associated with mixing of clearwater tributary and turbid Amazon River waters. *Frontiers Earth Science Section Marine Biogeochemistry*. DOI: 10.3389/feart.2019.00101

Ward, N. D., Megonigal, J. P., Bond-Lamberty, B., Bailey, V. L., Butman, D., Canuel, E. A., et al. (2020). Representing the function and sensitivity of coastal interfaces in Earth system models. *Nature Communications*, 11(1), 1-14.

Williams, P. M., and Druffel, E. R. (1987). Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature*, 330(6145), 246-248.

Williams, M. R., and Melack, J. M. (1997). Solute export from forested and partially deforested catchments in the central Amazon. *Biogeochemistry*, 38(1), 67–102.

Winemiller, K.O., McIntyre, P.B., Castello, L., et al. (2016), Balancing hydropower and biodiversity in the Amazon, Congo and Mekong. *Science*, 351, 128-129

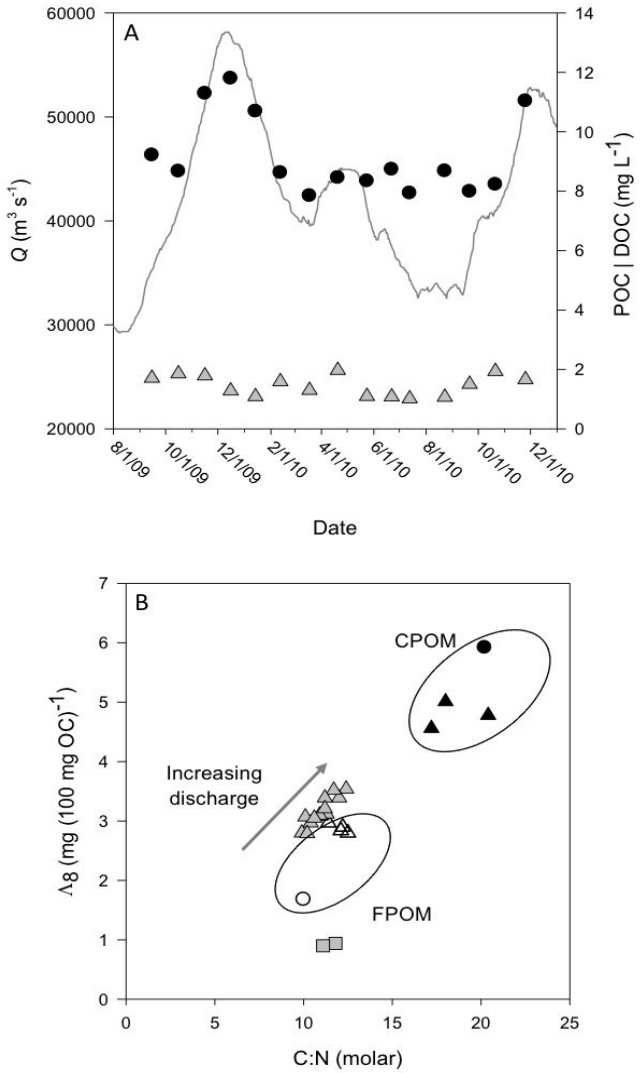
Wissmar, R. C., Richey, J.E., Stallard, R.F., and Edmond, J.M. (1981). Plankton metabolism and

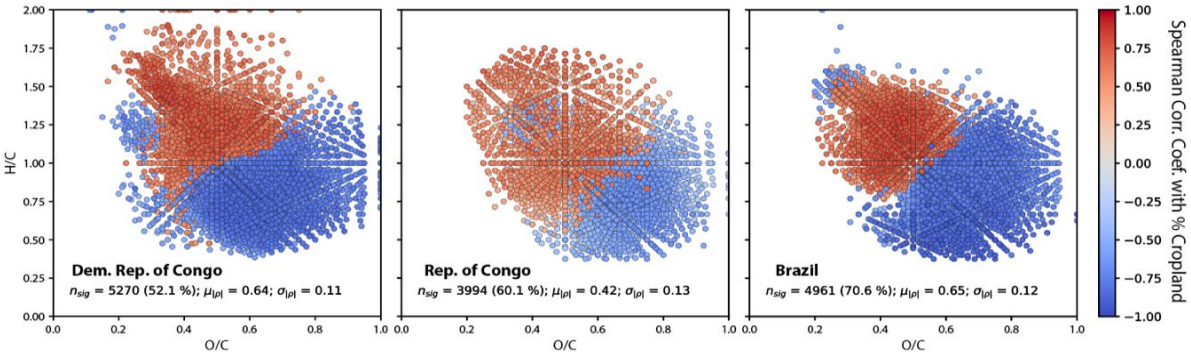
carbon processes in the Amazon River, its tributaries, and floodplain waters, Peru-Brazil, May-June 1977. *Ecology*, 62: 1622-1633.

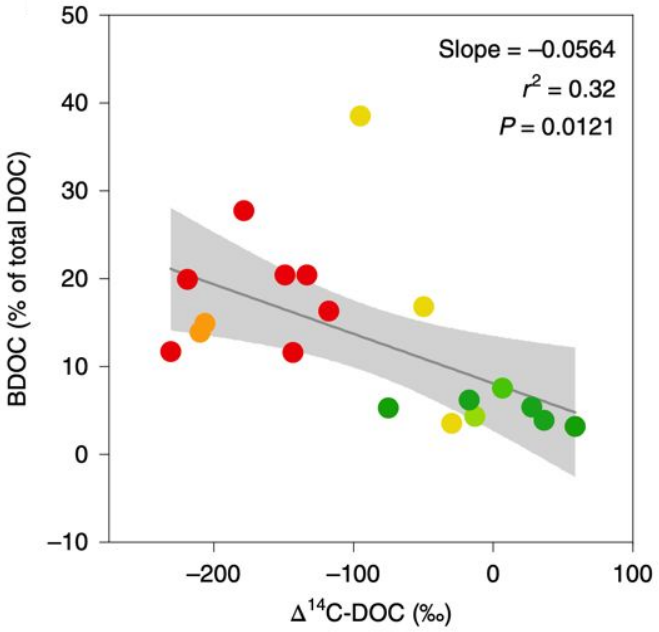
Zarfl, C., Lumsdon, A.E., Berlekamp, J., Tydecks, L. and Tockner, K. (2015). A global boom in hydropower dam construction, *Aquatic Sciences* 77:161– 170.

Acknowledgments

This work was partially supported by funding provided by the São Paulo Research Foundation (FAPESP 2018/18491-4), US National Science Foundation DEB- 1754317 and OCE 1464396 and DMR-1157490 and DMR-1644779 to the National High Magnetic Field Laboratory.


A
Q (m3 s-1)
POC | DOC (mg L-1)
Date
8/1/09
10/1/09
12/1/09
2/1/10
4/1/10
6/1/10
8/1/10
10/1/10
12/1/10
B
CPOM
FPOM
Increasing discharge
Λ8 (mg (100 mg OC)-1)
C:N (molar)




Slope = –0.0564
r^2 = 0.32
P = 0.0121
BDOC (% of total DOC)
50
40
30
20
10
0
–10
–200
–100
0
100
Δ^{14}C-DOC (‰)