Part IV
Sediments and Carbon

20

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

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ABSTRACT

Many river systems of the world are super-saturated in dissolved CO_2 (pCO_2) relative to equilibrium with the atmosphere. Here we compare the coupled organic matter and pCO_2 dynamics of the world's two largest and most organic-rich river systems. 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. Discharge is the primary control on POC and DOC export in both the Amazon and Congo Rivers. TSS yield from the Amazon is twentyfold 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 (but care should be taken when describing estimates of TSS and carbon to the ocean since processing and sequestration in tidal and coastal areas can significantly alter TSS and carbon delivery, and last measuring stations are typically hundreds of kilometers from the sea). pCO_2 in the Amazon mainstem range from 1,000 to 10,000 ppm, with floodplain lakes ranging from 20 to 20,000 ppm. Concentrations in the Congo are lower, with high values of 5,000 ppm. 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 organic matter of terrestrial and floodplain origin, and/or injection of very high pCO_2 water from local floodplains or tributaries.

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20.1. 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

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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 from aquatic systems to the atmosphere as CO_2 and scaled these rates to a global estimate of ~1 Pg C/yr. 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 & Grace, 2000). New global estimates of the surface area of aquatic systems (Allen & 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 (Drake et al., 2017; Raymond et al., 2013; 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, between 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 (Araújo et al., 2019; St. Louis et al., 2000; Tranvik et al., 2009).

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

$$\begin{aligned} d\left(pCO_2\right)/dt = NEE = {} & \text{Net advection} \\ & \left[I + T \pm F - O\right] + \text{Net Metabolism}\left[R - GPP\right] - G + NB \end{aligned} \tag{20.1}$$

where I is upstream input (discharge × 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), and Barbosa et al (2009, 2020), with fewer studies available for the Congo River (e.g., Borges et al., 2015, 2019).

20.2. THE REGIONS

The Amazon and Congo Rivers (Figure 20.1) are the two largest rivers on Earth in terms of their discharge (~6,590 km^3/yr at the last discharge gauging station and ~7,600 km^3/yr to the sea, and ~1,325 km^3/yr, 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 (Duveiller et al., 2008; Laporte et al., 2007; Winemiller et al., 2016). A major feature of the central Congo is the Cuvette Centrale, a shallow depression overlain by swamp forest,

Figure 20.1 Map of the Amazon (left) and Congo (right) Basins. Rivers and oceans are labeled in italic font and sampling points (i.e., city names) discussed in the main text are displayed in normal text. Map was created using ArcGIS 10.5 software (ESRI, 2017). Coordinate system: GCS WGS 1984.

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 savannahs 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 600 km 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, the Amazon and the Congo Rivers are responsible for ~21% and 3.5% of freshwater discharge to the world's oceans, respectively.

20.3. ADVECTIVE FLUXES

20.3.1. 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.

20.3.2. POC Fluxes

The Congo River has low TSS concentrations resulting in a flux to the Atlantic Ocean of ~30 Tg/yr (Coynel et al., 2005; Spencer et al., 2016), much lower than that estimated from the Amazon River (600–1,150 Tg/yr; Filizola & Guyot, 2009; Meade et al., 1985; Richey et al., 1986). 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 for the Amazon and Congo Rivers, respectively; Coynel et al., 2005; Filizola and Guyot, 2009; Meade et al., 1985; Richey et al., 1986). 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 gauging station, Óbidos (Aufdenkampe et al., 2007; Hedges et al., 1986; Spencer et al., 2012, 2016). Thus, the Congo River exports ~2 Tg C/yr as POC to the Atlantic Ocean,

resulting in a POC yield of ~0.6 g C/m^2/yr (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), 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; Coynel et al., 2005; Moreira-Turcq et al., 2003).

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).

20.3.3. DOC Fluxes

With respect to DOC fluxes, the Amazon River at Óbidos has been estimated to export ~22–27 Tg C/yr (Moreira-Turcq et al., 2003; Richey et al. 1990), 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, respectively), the total flux of the Amazon to the Atlantic is ~29.4 Tg C/yr (Coynel et al., 2005; Moreira-Turcq et al., 2003). 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 (Seidel et al., 2016; Ward et al., 2015).

The Congo River represents the second largest fluvial DOC flux to the ocean at ~12.4 Tg C/yr, 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), 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; Raymond & Spencer, 2015). In total, the Amazon River exports ~36 Tg C/yr of organic carbon (OC, both POC and DOC) and the Congo River exports ~14 Tg C/yr to the Atlantic Ocean, with both rivers exporting OC predominantly as DOC.

20.3.4. 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 (Junk & Howard-Williamson, 1984; Melack & Forsberg, 2001; Sioli 1984), and are thought to provide a seasonal source of OM to the mainstem (Bonnet et al., 2005; Bourgoin et al., 2007). 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 & 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.

20.4. ORGANIC MATTER SOURCES AND METABOLIC POTENTIAL

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

20.4.1. OM Composition

Discharge is the primary control on POC and DOC export in both the Amazon and Congo Rivers (Coynel et al., 2005; Moreira-Turcq et al., 2003; Spencer et al., 2016). Concurrent with elevated concentrations of POC and DOC in the Congo River at high discharge (Figure 20.2) 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

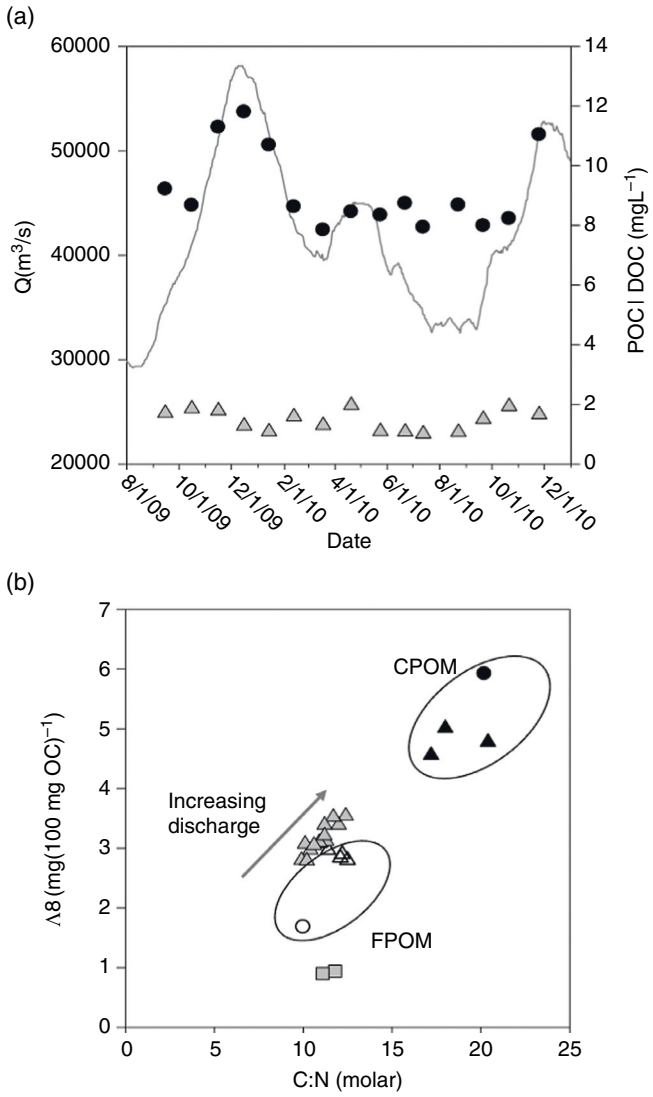

Figure 20.2 (a) Congo River at Kinshasa-Brazzaville discharge (Q) (grey line), DOC (black circles) and POC (gray triangles) concentrations (modified from Spencer et al., 2016). (b) Congo River at Kinshasa-Brazzaville POM lignin carbon-normalized yields (Λ8) versus C:N (molar) (gray circles) in relation to Congo and Amazon CPOM (black triangles and black circle, respectively), FPOM (white triangles and white circle, respectively), and Mississippi POM (gray squares) data (modified from Onstad et al., 2000, and Spencer et al., 2012, 2016).

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; < 63 μm > 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 20.2b). 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 20.2b). 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 (Balagizi et al., 2015; Bouillon et al., 2012; 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 (Marwick et al., 2015; Mayorga et al., 2005; Spencer et al., 2012). 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 (Mann et al., 2015; Raymond & Bauer, 2001; Raymond et al., 2007).

A plethora of research in both the Congo and Amazon Rivers has utilized biomarkers to assess sources of OM (e.g., Aufdenkampe et al., 2007; Hedges et al., 1986, 1994, 2000; 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/100 mg OC) in comparison to Amazon FPOM at Óbidos (1.68 mg/100mg OC) (Hedges et al., 2000; Spencer et al., 2016; Figure 20.2b). Congo dissolved OM (DOM) Λ_8 values (0.50 to 0.76 mg/100mg OC) 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.

20.4.2. 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 (Aufdenkampe et al., 2001; Hedges et al., 1986; Spencer et al., 2016; Figure 20.2b). 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 20.2b). 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 20.5; Seidel et al., 2015).

20.4.3. 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 swaths 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 aboveground 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 modeled 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 & 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 reintroduction 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, b; 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 20.3). Although differences are present, the overall pattern shows how aliphatic (hydrogen-rich) and reduced (low O/C ratio) DOM (red points, Figure 20.3) 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

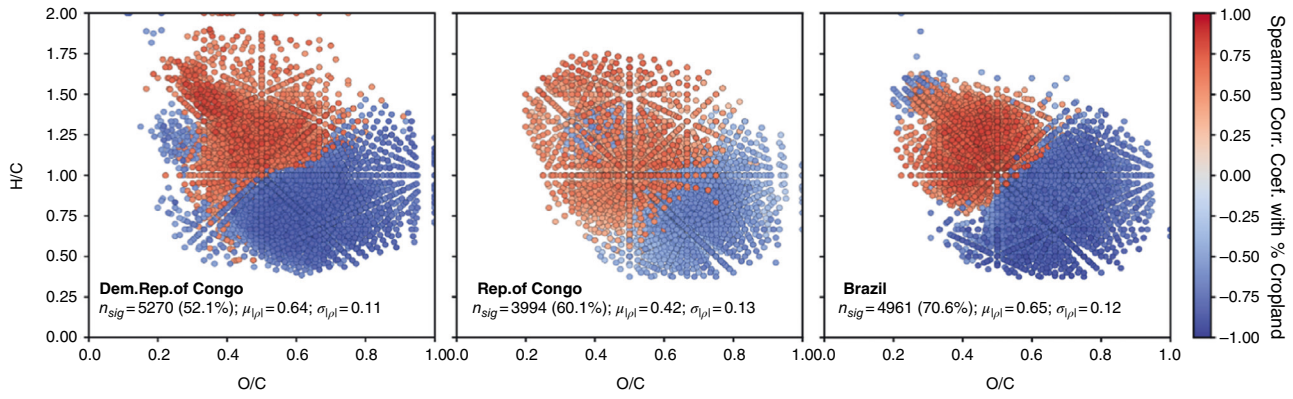

Figure 20.3 van Krevelen diagrams of molecular formulae derived from river samples as a function of deforestation/cropland extent. Spearman-rank correlations of relative intensities for each molecular formulae and cropland/deforestation extent in Bukavu, Democratic Republic of Congo; Ouesso, Republic of Congo; and Tanguro, Brazil (Figure 20.1). Modified from Drake et al., 2019a; Drake et al., 2019b; and Spencer et al., 2019, respectively. Colors represent the correlation coefficient between the relative intensity of each molecular formulae and cropland/deforestation extent in the catchment, such that red formulae are more abundant in samples where cropland/deforestation extent is high and vice versa. All samples were run using negative electro-spray ionization on a 21 Tesla Fourier transform ion cyclotron resonance mass spectrometer.

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 indicate 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 & 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 20.4). 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; Kalbitz et al., 2003; Spencer et al., 2015; van Hees et al., 2005), 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).

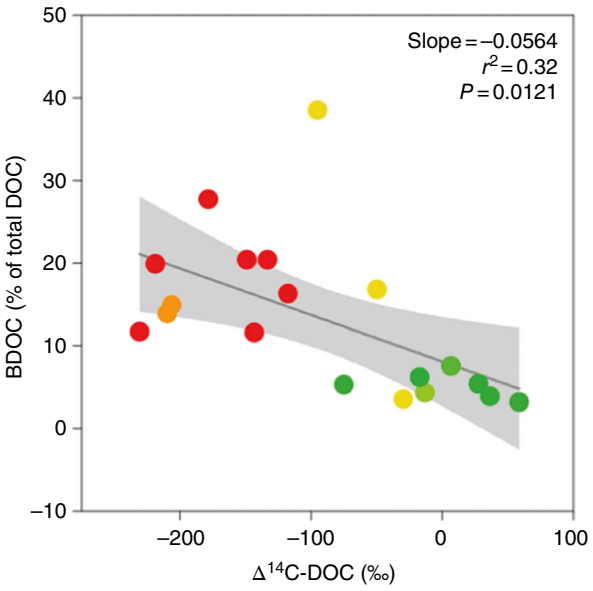

Figure 20.4 Linear regression between Δ14C-DOC and biodegradable dissolved organic carbon (BDOC) for 19 catchments in Eastern Congo. Red to green color gradient indicates the proportion of deforestation in the catchment, such that red = 100% and green = 0%. Gray bands indicate 95% confidence interval. Reproduced from Drake et al., 2019a.

20.5. 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.

20.5.1. 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 riverborne 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) (as 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, while integrated rates of CR ranged between 3 and 790 mmol/m^2/d. 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 findings 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.

20.5.2. 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 (Seidel et al. 2016; Ward et al., 2013). 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 with 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 calculated 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, the actual impacts of the floodplain export to the main channel are not clear. 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 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.

20.6. 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 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 to 6,700 mmol m^2/d. 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, 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. 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. 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. 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 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, with 90% of this flux likely

being associated with lakes, floodplains, and other wetlands. It does not include the calculations of Sawakuchi et al. (2017) 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. 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).

20.7. 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.

20.7.1. 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/yr (Valerio et al., 2021; 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.

20.7.2. 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 (Hernes & Benner, 2006; Opsahl & Benner, 1997). 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 & 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 (Medeiros et al., 2015; Seidel et al., 2015; Ward et al., 2013). 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 decrease 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 & 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 end-member 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 (Blair & Aller, 2012; Hedges et al., 1997). 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, and a burial rate of ~0.4 Tg C/yr (Rabouille et al., 2009; Savoye et al., 2009). Comparing this to the Congo River POC flux of 2 Tg C/yr 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; Mollenhauer et al., 2004) and even of global deep-sea POC burial (10–20 Tg C/yr; Berner, 1989; Hedges & Keil, 1995) due to the efficient injection of POC via the Congo Canyon to the Congo Fan.

20.8. CONCLUSION

Together the Amazon and Congo represent the end-members 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 ~5× greater in the Congo than the Amazon, so the total flux of OM in the Amazon is only ~3× greater than the Congo despite the fact that the Amazon discharges ~5× 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 δ^{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 ~2× 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. Land-use 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 2–3× 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 riverborne 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 photo-oxidation 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 representations 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.

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