

# The Role of Rivers in the Regional Carbon Balance

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Through the evolution of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia, fluvial systems evolved from being regarded as ecologically interesting, but not necessarily relevant to the carbon budget, to important systems outgassing a volume of CO<sub>2</sub> roughly equal to the carbon sequestered by the forest. Resolving the role of fluvial systems in the carbon balance of the Amazon basin is a problem in scaling, from small seeps and springs to streams to larger rivers. Groundwater discharge of CO<sub>2</sub> and its subsequent evasion is a significant conduit for terrestrially respired carbon in tropical headwater catchments. Hydrologic transport of dissolved CO<sub>2</sub> was equivalent to nearly half the gaseous CO<sub>2</sub> contributions from deep soil (>2 m) to respiration at the soil surface. At larger scales, the dominant feature was a clear relation between discharge and biogeochemical concentrations, with systematic variance among sites. Seasonal distributions of pCO<sub>2</sub> rose and fell almost exactly with the discharge hydrograph, while pH decreased and dissolved organic carbon increased. This suggests a constancy of processes across systems. Gas exchange is greater than previously thought, primarily due to greater outgassing in smaller streams than expected. No single organic matter source consistently fuels respiration; instead, the δ<sup>13</sup>C of respiration-derived CO<sub>2</sub> varies with time and space. Photochemical production of labile bioavailable compounds would appear to be limited to clear water conditions. Based on these results, the original Richey et al. (2002) estimate of outgassing of 1.2 ± 0.3 Mg C ha<sup>-1</sup> a<sup>-1</sup> is conservative; the true value is likely higher.

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## 1. INTRODUCTION

A long-standing paradigm of river networks is that they are minor components in the global carbon cycle, passively connecting the land and ocean reservoirs. As quoted by *Cole et al.* [2007], *Leopold et al.* [1964] described rivers as the “gutters down which flow the ruins of continents.” The major biogeochemical role of river systems is typically considered to be the “carbon leakage” (in the sense of *Malhi and Grace* [2000]), primarily the fluvial export of total organic carbon (TOC) and dissolved inorganic carbon (DIC) to the ocean of ~0.4 Gt C a<sup>-1</sup>, respectively [*Degens et al.*, 1991; *Stallard*, 1998]. While these fluxes are significant compared

to the net oceanic uptake of anthropogenic CO<sub>2</sub> of ~2 Gt C a<sup>-1</sup> [Sarmiento and Sundquist, 1992], they are small components of the global carbon cycle.

These views influenced the initial design for the inclusion of water chemistry within the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) project. Richey *et al.* [1997] reviewed the state of understanding of the fluvial dynamics of the Amazon basin at that time. With regard to carbon cycling, they posed a series of questions, addressing the nature of the transfer of organic matter from terrestrial to river environments as well as the riverine fate of organic material: (1) How does the evolution of CO<sub>2</sub> and CH<sub>4</sub> change with increasing proximity to the riparian zone and streams? (2) How will the composition of organic matter entering streams be altered under different land use change scenarios? (3) To what extent do intact riparian zones buffer streams against changes due to anthropogenic activities in surrounding uplands? (4) How far do sediments, nutrients, and organic matter travel before they are taken up, decomposed, temporarily stored, permanently buried, or degassed to the atmosphere?

Richey *et al.* [1997] noted that the nature of the research required to address these questions crossed multiple scales, from the individual stream to the mouths of major tributaries. Small watershed studies where the export of water, sediments, nutrients, and organic matter can be quantified are as important to understanding “horizontal” carbon fluxes between land and water, as instrumented towers are to vertical fluxes between land and the atmosphere. Sampling transects of soil solution and trace gas fluxes from uplands through riparian zones into streams, in which the partitioning of organic matter and nutrients into gaseous, liquid, and particulate phases is tracked, can help identify the sequence of substrate and oxidation/reduction conditions, which control the partitioning and degradation pathways.

How, then, do the inputs from small streams and their watersheds translate downstream? This is a “mesoscale” question, where it is necessary to understand the distribution of moisture regimes and biogeochemical processes at scales of ~10,000–100,000 km<sup>2</sup>. Within mesoscale areas, a significant problem in analyzing the impacts of land use change on aquatic systems is evaluating how far downstream local changes are detectable. The corollary is that the cumulative impact of change in a series of low-order streams may be manifested in higher-order streams in a significant, but nonadditive manner. Working across scales thus requires integrating a range of approaches. Finding paired basins that are forested/deforested for comparison is difficult. Rather, chemical tracers and computer models are useful. This understanding needs to be evaluated across different land covers and land uses, dominant climatological regimes, and topographic regimes.

For the integration of multiple mesoscale regions into regional, to whole basin perspectives, a functional basin scale is that of major tributaries, e.g., the downstream segments of the major tributaries, such as the Rio Madeira, Rio Tapajós, Rio Xingú, or Rio Tocantins. At this scale, the dynamics of factors controlling basin output from smaller scales would be aggregated, and the subsequent output would be comparable to the whole-basin scale of the hydrology and energy balance studies [Richey *et al.*, 2004]. Time series measurements of dissolved and particulate fractions are necessary to establish the basic composition regime of the river. Emphasis should include those tracers of terrestrial-scale controls that persist through the river system. Basin-scale modeling would be based on hydrologic routing modeling and process-level understanding. The objective is to predict the output hydrographs of water and chemical constituents under different conditions of land use.

These perspectives were then translated into the original Concise Science Plan of LBA, where the central question for the study of surface water chemistry was the following: How do the pathways and fluxes of organic matter, nutrients, and associated elements through river corridors (riparian, floodplain, channels, and wetlands) change as a function of land cover?

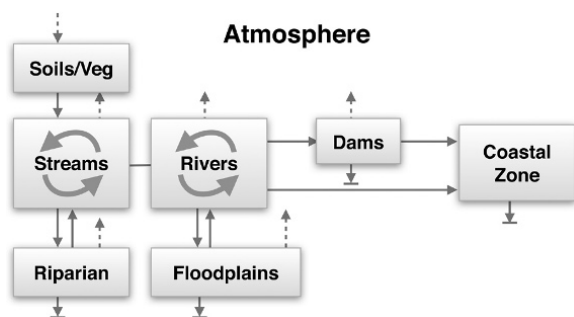
The perspective was that “because the river corridors of a region express the integrated interaction of hydrological processes and the land surface, understanding how the organic matter and nutrient composition of river corridors respond to forest conversion is an essential precursor to assessing the impact of land use change on the ecological functioning and sustainability of the region.” The proposed research plan was to first, study lower-order streams, then to use modeling to consider elemental budgets at larger scales. An important conclusion from the initial setup of LBA is the fluvial system was regarded as an important ecological entity unto itself, but not a priori of the overall carbon cycle of Amazonia. What have we learned since? Our intent in this chapter is to outline the progress toward developing a quantitative understanding of the sequence of carbon processes from small streams to the Amazon main stem. The focus on flowing water here complements the focus of Melack *et al.* [this volume] on inundated areas, to jointly place fluvial systems in the overall LBA context of the role of rivers in the regional carbon cycle of the Amazon basin.

## 2. A HEURISTIC MODEL OF CARBON FLOW THROUGH A RIVER SYSTEM

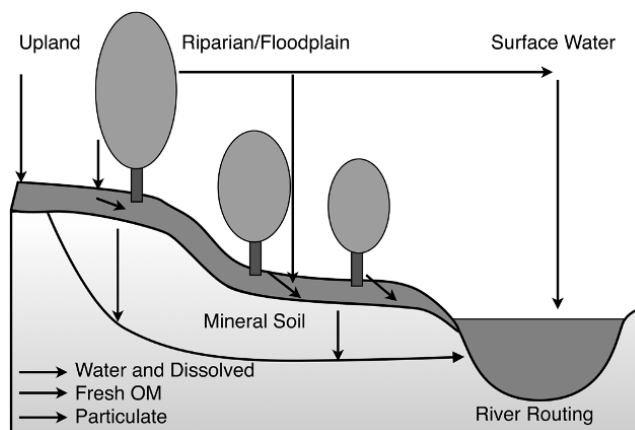
To put our analysis into context, it is useful to evaluate the elements of the work done under LBA in relation to a heuristic river model. Richey [2004] formalized a conceptual

model of river corridors from *Richey et al.* [1997]. Understanding the processes that control the pathways from initial source to final mineralization of riverine organic matter is important on both regional and global scales. At regional scales, river basins are natural integrators of surficial processes (Figure 1). Large rivers owe their flow and chemical loads to a much denser network of small rivers and streams bordered by areas of periodically inundated land, so that upland areas are dissected by corridors of wet soils and flowing water. Hence, understanding the hydrological and chemical patterns observed at the mouths of major rivers requires delineating the sequences of biogeochemical processes operating across multiple scales in time and space. The central premise of a river basin model is that the constituents of river water provide an integrated record of upstream processes whose balances vary systematically depending upon changing interactions of flowing water with the landscape and the interplay of biological and physical processes [Karlsson et al., 1988; Billen et al., 1991]. That is, the chemical signatures of riverine materials can be used to identify different drainage basin source regions and can be tied to landscape-related processes such as chemical weathering and nutrient retention by local vegetation [Meyer et al., 1988]. Because of the dynamic nature and abrupt moisture gradients of river corridors, the cumulative signal from a series of low-order streams may be manifested by higher-order rivers in a nonadditive manner.

Within this framework, there are three primary forms of carbon that are mobilized from land and transported into and through fluvial systems, each with characteristic pathways (Figure 2). Particulate organic carbon (POC) enters rivers



**Figure 1.** Schematic illustration of the major reservoirs and pathways in fluvial systems. Inputs from land occur directly or pass through the riparian zone. Streams coalesce to form larger rivers that exchange with their floodplain. Rivers can pass directly to the coastal zone or be restrained behind dams. Dotted lines indicate exchange with the atmosphere, grounded areas indicate sinks, arrows within boxes indicate internal transformations (adapted from the work of *Richey* [2004]). Copyright 2004 Scientific Committee on Problems of the Environment. Reproduced by permission of Island Press, Washington, DC.



**Figure 2.** Grid-based view of land surface processes transferring water and its dissolved and particulate load to streams, where these constituents are subsequently processed and routed downstream.

from the erosion of soils (typically older materials) and as leaf litter (typically newly produced). Dissolved organic carbon (DOC) is produced through soil organic carbon being rendered soluble and entering streams via groundwater, surface runoff, and subsurface stormflow. Both POC and DOC also come from autochthonous production in rivers and associated floodplain environments. Atmospheric CO<sub>2</sub> fixed through photosynthesis and released into soils via microbial and root respiration is dissolved in soil water. This process sequesters atmospheric CO<sub>2</sub> via weathering of carbonate and silicate rocks, establishes the alkalinity, and influences the pH of water, which governs the subsequent partitioning of DIC between pCO<sub>2</sub>, bicarbonate, and carbonate ions. The dynamics of carbon in fluvial systems are not defined solely by the export fluxes of bulk carbon. Rather, they are defined as a complex interplay of multiple carbon fractions; each exhibits distinct dynamics and compositional traits that hold over broad ranges of geological, hydrological, and climatic conditions [Hedges et al., 1994].

### 3. PATHWAYS OF RIVER CARBON THROUGH THE AMAZON

#### 3.1. Small Springs and Seeps

A major unknown is what happens in small streams and seeps. How does terrestrial production via litterfall get transported into stream discharge? *McClain et al.* [1997] estimated that for terra firme streams near Manaus, 20% to 40% (in Oxisols and Spodosols, respectively) of the dissolved organic matter (DOM) could derive from a combination of wetland seepage and in-channel leaching of POC. *Remington*

*et al.* [2007] evaluated processes across a toposequence responsible for partitioning of DOC produced from litter between particles and what is available for export to streams. DOC was sorbed more rapidly on the plateau and slope than in the valley bottom, as a function of both soil organic carbon content and mineral surface area.

*Johnson et al.* [2006] examined the forms and quantities of organic carbon fluxes at the soil surface, and organic carbon exports from four small (1–2 ha) headwater catchments in the Jurueña watershed, in the upper Rio Tapajós watershed. Litterfall carbon at the soil surface was 43 times greater than the DOC flux in throughfall, with the highest rates of carbon deposition during the dry season. For watershed exports, however, the form and timing of organic carbon was reversed, where DOC comprised 59% of the annual TOC export, and exports were greatest during the 4-month rainy season (63% of total annual exports). As is seen in larger rivers, fine particulate organic carbon (FPOC) in stream water represented a substantially larger flux than coarse particulate organic carbon (CPOC), with 37% and 4% of total annual organic carbon exports, respectively, and with POC mobilized primarily in the rainy season and strongly connected to storm events. In the rainy season, over 90% of FPOC exports were transported by stormflow, while only 32% of DOC exports were exported by stormflow. Stream water DOC concentrations were found to increase linearly with increasing terrestrial litterfall during the dry season, indicating that in-stream processing of allochthonous litterfall is an important source of DOC during the dry season.

*Waterloo et al.* [2006] examined organic carbon export dynamics in the blackwater Igarapé Asu rainforest catchment of the Rio Negro. They found that DOC concentrations in rainfall, 1–2 mg L<sup>-1</sup>, were similar to those measured in rainfall elsewhere in the Amazon basin, producing annual atmospheric DOC deposition estimates of 2–5 g m<sup>-2</sup> a<sup>-1</sup>. Daily average DOC concentrations in runoff ranged from 8 mg L<sup>-1</sup> under low flow conditions to 27 mg L<sup>-1</sup> during large quick flow events. POC (>10 μm) averaged 28% of OC, with a median concentration of 4.1 mg L<sup>-1</sup>. Exports associated with large storms were much higher than average daily export. Export of carbon during the wet seasons amounted to 70% of the total. Annual exports in river water were different between the years because of differences in runoff, from 26 g C m<sup>-2</sup> in 2002 (transported by 1362 mm of runoff) to 11.7 g C m<sup>-2</sup> in 2003 (transported by 780 mm of runoff). Organic carbon exports were dominated by DOC, with exports in sediment constituting 6–8% of the total. Organic carbon export in stream water varied from 23 to 9 g m<sup>-2</sup> of watershed area in 2002 and 2003, respectively. The annual average organic carbon export of 19 g m<sup>-2</sup> a<sup>-1</sup>, as the sum of dissolved and particulate fractions over the 2 years of the study, was about

5–6% of the rainforest net primary production of 300–400 g m<sup>-2</sup> a<sup>-1</sup>, estimated from eddy covariance measurements [see *Tomasella et al.*, this volume].

Neither of these studies included *p*CO<sub>2</sub> in their evaluations. *Krusche et al.* [2009] found concentrations ranging from 5000 μatm to over 20,000 μatm in blackwater streams not far from Igarapé Asu. While these concentrations are roughly that of DOC in these streams, they are 10–100 times supersaturated relative to the atmosphere. *Johnson et al.* [2008] found that 77% of carbon transported by water from the landscape was as terrestrially respired CO<sub>2</sub> dissolved within soils, over 90% of which evaded to the atmosphere within headwater reaches via turbulent mixing due to streambed roughness. Hydrologic transport of *p*CO<sub>2</sub> was equivalent to nearly half the gaseous CO<sub>2</sub> contributions from deep soil (>2 m) to respiration at the soil surface. The *p*CO<sub>2</sub> in emergent groundwater was isotopically consistent with soil respiration and demonstrated agreement with deep soil CO<sub>2</sub> concentrations and seasonal dynamics. Deep soil (2–8 m) CO<sub>2</sub> concentration profiles during wet seasons indicated gaseous diffusion to deeper layers, thereby enhancing CO<sub>2</sub> drainage to streams. Hence, groundwater discharge of CO<sub>2</sub> and its subsequent evasion is a significant conduit for terrestrially respired carbon in tropical headwater catchments. This subsurface transport of soil CO<sub>2</sub> to tropical headwater streams was an order of magnitude greater than for temperate headwater catchments. Hence, tropical headwaters comprise a zone of rapid biogeochemical transformation, where emergent groundwater fuel base flow with water having a ratio of DIC to DOC nearly 30 times greater than the ratio for large Amazonian rivers.

Following development of a method for real-time direct in situ measurement of *p*CO<sub>2</sub> in surface water and emergent groundwater [*Johnson et al.*, 2009], several previously unobserved features of carbon cycling in headwater catchments became apparent. The CO<sub>2</sub> concentration of hydrological flow paths were evaluated, and their relative contributions during base flow and storm events were explored empirically [*Johnson et al.*, 2006] and through hydrograph separation of event water [*Johnson et al.*, 2007]. Base flow continually delivers groundwater discharge to streams that is highly supersaturated in CO<sub>2</sub>. The excess CO<sub>2</sub> results from equilibration of soil water with the high CO<sub>2</sub> concentrations of the soil atmosphere derived from autotrophic and heterotrophic respiration within soils. Groundwater discharge occurs in both focused and diffusive forms, where the former represents groundwater emergence in springs and seeps, and the latter occurs via groundwater discharge across the streambed along the length of stream reaches that gain in discharge. The *p*CO<sub>2</sub> concentration in focused groundwater discharge, prior to interactions with the atmosphere, was



generally above 50,000  $\mu\text{atm}$  ( $\sim 20 \text{ mg CO}_2\text{-C L}^{-1}$ ) [Johnson *et al.*, 2008]. Diffusive groundwater discharge contributes to maintaining stream  $p\text{CO}_2$  well above equilibrium, even as excess  $\text{CO}_2$  evades from the stream surface due to turbulent mixing in the headwater channels.

During storm events, the pre-event component of stormflow (e.g., water that is stored in catchments prior to precipitation events and released to streams during storms) was found to dominate total stormflow, although quick flow derived from direct precipitation and surface runoff contributes water that is at or near atmospheric concentration for  $\text{CO}_2$  [Johnson *et al.*, 2007]. Modeling of the hydrologic flow paths via hydrograph separation found that a slower event-water flow path (e.g., subsurface stormflow) contributes “pre-event  $\text{CO}_2$ ” via event-water peak, while a faster event-water flow path delivers low  $\text{CO}_2$  water to streams. That is, water entering streams via surface runoff and direct precipitation is low in  $\text{CO}_2$ , while water newly input to soils during a storm event dissolves and translocates soil  $\text{CO}_2$  to streams. As the subsurface stormflow event-flow path is later-arriving than quicker flow paths (direct precipitation and surface runoff), the subsurface stormflow results in a pulse of  $\text{CO}_2$  observed on the falling limb of storm hydrographs. The event-water  $\text{CO}_2$  concentration peaks during the  $\text{CO}_2$  pulse, and its concentration ( $\sim 25,000 \text{ ppm}$ ) is consistent with that of soil  $\text{CO}_2$  in the upper 50 cm of soil [Johnson *et al.*, 2008], although it is only about half the concentration of  $\text{CO}_2$  in emergent groundwater [Johnson *et al.*, 2006].

The mechanism of equilibration of soil water with soil  $\text{CO}_2$  during percolation and subsequent transport of terrestrial respiration products to streams allowed Johnson *et al.* [2008] to model potential headwater  $\text{CO}_2$  evasion based on basin-wide published spatial data sets of hydrologic variables and soil properties. In this approach, groundwater concentrations of dissolved  $\text{CO}_2$  were estimated based on carbonate equilibrium reactions for  $\text{CO}_2$  in soil solution in relation to subsoil pH for the simplest case of pure water in equilibrium with soil  $\text{CO}_2$  [McBride, 1994], which is valid for soils without exposure to strong acid inputs such as from acid rain [McBride, 1994]. Thus, soil pH determines the minimum  $p\text{CO}_2$  of soil solution and groundwater, although the  $p\text{CO}_2$  of soil air can increase significantly due to biological activity. However, in order to provide a minimum (e.g., conservative) estimate of dissolved  $\text{CO}_2$  delivered to streams via  $\text{CO}_2$ -supersaturated groundwater flow paths, the model was structured to only consider equilibration reactions based on basin-wide spatial data sets. Soil pH was derived from the lower soil horizon (30–100 cm) of a global soils database [Batjes, 2005], which reports soil reaction class based upon the predominant soils of each pixel. Johnson *et al.* [2008] assigned soil pH values for each class (Table 1). In a very few cases (less than

**Table 1.** Soil Reaction Classes and pH Ranges From Digital Soils Database, and Soil pH Used for Computing Soil  $p\text{CO}_2$ <sup>a</sup>

Soil Reaction Class	Soil pH Range	pH Used	Modeled Soil $p\text{CO}_2$ , %
1	pH < 5.5	4.5	5.13
2	5.5 < pH < 6.5	6.0	0.04
3	6.5 < pH < 7.5	7.0	0.04
4	7.5 < pH < 8.5	8.0	0.04
5	pH > 8.5 (complex)	9.0	0.04
6	pH < 6.5 (complex)	5.0	0.51
7	5.5 < pH < 8.5 (complex)	7.0	0.04
8	pH > 7.5 (complex)	8.0	0.04

<sup>a</sup>See Batjes [2005]. Atmospheric  $\text{CO}_2$  concentration (0.04%) was used as a minimum condition when resulting  $p\text{CO}_2$  values were less than atmospheric.

20 pixels), classes were reassigned due to missing data in the underlying database, which led to skewed soil pH values and isolated pixels of differing soil pH relative to soil carbonate contents from the same database [Batjes, 2005].

Previous estimates of DIC fluxes into groundwater using soil pH utilized a pH value of 4.0 for the most strongly acidic class of soils [Kessler and Harvey, 2001]. Johnson *et al.* [2008] used a more conservative pH value of 4.5 together with an updated soil database with additional soil reaction classes compared to the earlier version [Kessler and Harvey, 2001]. This approach yielded modeled values of soil  $p\text{CO}_2$  (Table 2) that agreed with, or were conservative relative to, theoretical [Brady and Weil, 1999; McBride, 1994] and observed values for eastern Amazonia for forest and pasture soils at 8 m [Davidson and Trumbore, 1995], for forested soils at 8 m in southern Amazonia [Johnson *et al.*, 2008] and for central Amazonian forest soils at 11 m under normal and drought conditions [Davidson *et al.*, 2004].

The spatial distribution of groundwater fluxes was determined by Johnson *et al.* [2008] as the difference between long-term averages of annual precipitation [New *et al.*, 1999] and actual evapotranspiration [Ahn and Tateishi, 1994], which was scaled to the 1976–1996 mean annual discharge for the Amazon [Costa and Foley, 1999] to determine the water balance for each  $0.1^\circ$  pixel for average years. One standard deviation from the 1976–1996 mean annual water balance [Costa and Foley, 1999] was used to calculate wet and dry year water balances. The groundwater flux was set to zero for pixels where evapotranspiration exceeded precipitation. Johnson *et al.* [2008] excluded more than 300,000  $\text{km}^2$  of large rivers, wetlands, and seasonally inundated areas in central Amazonia, and an additional 500,000  $\text{km}^2$  of permanently or seasonally inundated areas in other regions

**Table 2.** Measured and Modeled Soil  $p\text{CO}_2$  for Amazonian Soils<sup>a</sup>

Location	Station ID <sup>b</sup>	Deepest Layer Reported, m	Measured Soil $p\text{CO}_2$ of Deepest Layer (Site Description)	Modeled $p\text{CO}_2$ , %	Reference
Eastern Amazon 2°59'S 47°31'W	1	8	6.9% (forest) 6.3% (pasture)	5.13	<i>Davidson and Trumbore</i> [1995]
Southern Amazon 10°25'S 58°46'W	2	8	4.9% (forest)	5.13	<i>Johnson et al.</i> [2008]
Central Amazon 2.897°S 54.952°W	3	11	5.5% (control) 6.4% (throughfall exclusion)	5.13	<i>Davidson et al.</i> [2004]

<sup>a</sup>Measured values are means of data that include both dry season and wet season measurements for the deepest layer reported.

<sup>b</sup>Station ID corresponds to the numbering of locations in Plate 1.

of the Amazon basin based on remote sensing of high and low water periods [Melack and Hess, 2009]. The resulting mean annual groundwater discharge to headwater streams, 833 mm  $\text{a}^{-1}$ , was significantly less than published estimates of groundwater drainage fluxes for the Amazon basin (1250 mm  $\text{a}^{-1}$ ) [Richey et al., 2002], but near estimates for headwater contributions to river network discharge in the Amazon [McClain and Elsenbeer, 2001].

The potential headwater  $\text{CO}_2$  outgassing flux for the terra firme portion of the Amazon basin was then calculated as the product of the groundwater flux and soil  $p\text{CO}_2$ . The resulting  $\text{CO}_2$  evasion flux from first-order streams for the terra firme portion of the Amazon basin was estimated as  $114 (\pm 10) \times 10^{12}$  g C  $\text{a}^{-1}$  [Johnson et al., 2008] (Plate 1). The areas with the highest potential  $\text{CO}_2$  evasion flux are those where the water flux (as precipitation minus evapotranspiration) is highest, and soils are acidic. These areas exhibit close correspondence with those areas with the highest soil  $\text{CO}_2$  emissions [Raich and Potter, 1995], which provides an independent check of the headwater  $\text{CO}_2$  evasion flux model, as the soil respiration data of Raich and Potter [1995] were not used to drive the model.

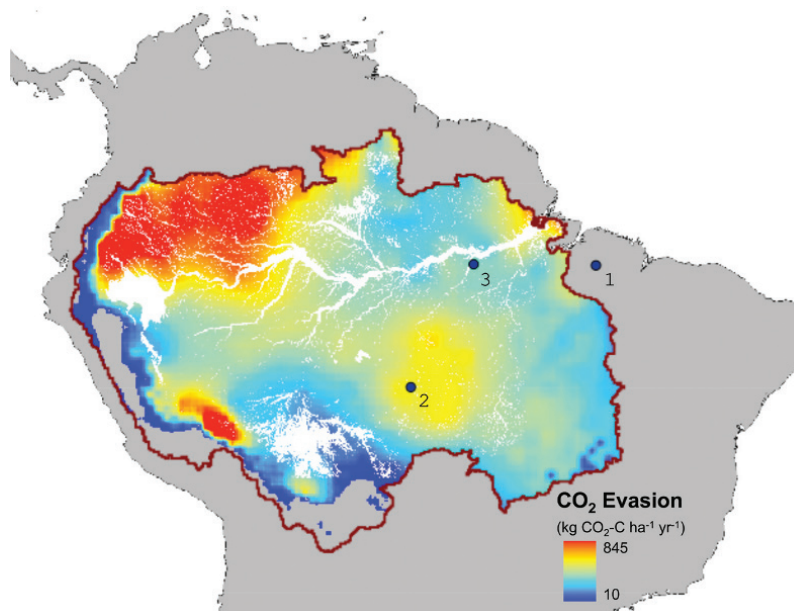
Variability in the annual water balance for 1976 through 1996 [Costa and Foley, 1999] translates to a wet-year augmentation of the headwater outgassing flux by  $1.0 \times 10^{13}$  g C  $\text{a}^{-1}$  for a wet year and an equivalent decrease for a dry year. The influence of land use change on this flux is more difficult to ascertain. Deforestation in the Brazilian component of the Amazon basin through 2004 has resulted in conversion of 16% of the original forest to other uses [Ometto et al., 2005]. However, since maximum  $\text{CO}_2$  concentrations in deep (>2 m) soil have not been shown to differ significantly between Amazonian forests and pastures [Davidson and Trumbore, 1995], the main influence on the headwater outgassing flux

is likely due to factors affecting the water balance following forest conversion. Although reduced evapotranspiration could increase the  $\text{CO}_2$  drainage flux, this term of the water balance is complicated by large uncertainties [Williams et al., 1997]. In order to maintain a conservative estimate of the headwater  $\text{CO}_2$  outgassing flux, Johnson et al. [2008] confined their analysis to reduced infiltration following land use conversion. Their simplifying assumptions that (1) stormflow increases by 100% following forest conversion [Williams et al., 1997], and (2) all stormflow in the perturbed system occurs as overland flow and does not transport soil  $\text{CO}_2$ , resulted in a reduction of the total headwater outgassing flux by  $1.7 \times 10^{12}$  g C  $\text{a}^{-1}$ .

Overall, groundwater discharge is the predominant hydrologic flow path contributing inorganic carbon to headwater streams, while base flow and quick flow contribute approximately equivalent organic carbon fluxes. Total fluvial carbon fluxes in the headwaters are dominated by  $\text{CO}_2$  derived from terrestrial soil respiration, which is largely lost within the headwater reaches via gaseous evasion to the atmosphere. Quick flow delivers the majority of bioavailable DOC and POC to streams [Johnson et al., 2006], and while DOC and POC are biogeochemically and ecologically significant to downstream fluvial network, they are a lesser component of the carbon mass balance of headwater catchments compared to  $\text{CO}_2$  evasion.

### 3.2. Mesoscale Distributions of River Carbon Fractions

The first problem in understanding fluvial carbon dynamics at scales larger than relatively easily measured discrete streams is determining the spatial and temporal distributions across a range of environments. Because of the vast and remote nature of the Amazon basin, the logistics of establish-



**Plate 1.** Potential headwater CO<sub>2</sub> evasion flux for the Amazon basin modeled using available spatial data sets for hydrologic variables and soil *p*CO<sub>2</sub> calculated from carbonate equilibrium reactions (adapted from the work of *Johnson et al.* [2008]). Gray areas within the basin correspond to pixels where precipitation is less than evapotranspiration and do not contribute to the evasion flux. White areas within the basin represent more than 800,000 km<sup>2</sup> of rivers, wetlands, and seasonally inundated areas that were excluded from headwater evasion calculations. The basin-wide headwater CO<sub>2</sub> evasion flux was estimated as  $1.14 \times 10^{14}$  g C a<sup>-1</sup> after excluding permanently and seasonally inundated areas and accounting for land use change impacts, with a mean modeled CO<sub>2</sub> efflux from headwater streams of 195 kg C ha<sup>-1</sup> a<sup>-1</sup>. The numbered symbols refer to study locations of deep soil CO<sub>2</sub>: 1, *Davidson and Trumbore* [1995], 2, *Johnson et al.* [2008], and 3, *Davidson et al.* [2004], respectively. Additional study location details are presented in Table 2.

ing a comprehensive and representative sampling network are considerable. It is simply not feasible to send out a team from a central university or laboratory and expect it to collect data with sufficient resolution in space and time. Accordingly, a sampling (and education and training) network was established, the “Rede Beija Rio,” wherein each node is occupied by a researcher or a team of researchers from that site (Figure 3).

An initial analysis of the data shows a series of provocative trends, demonstrating a high degree of spatial and temporal coherence in the distributions of carbon fractions across mesoscale rivers of the Amazon basin (*J. Richey and A. Krusche*, unpublished data, 2009). As illustrated in Figure 4, the dominant feature across all scales was a clear relation between discharge and biogeochemical concentrations, with systematic variance among sites. For example, *p*CO<sub>2</sub> is positively correlated with discharge and tracks the hydrograph at all sites. The *p*CO<sub>2</sub> at low water ranges from 500 μatm in the Rio Araguaia and Rio Ji-Paraná to 1000 μatm in the Rio Solimões, to 2000 μatm in the Rio Negro. High water concentrations exhibit a broader range and higher magnitude,

from 3000 μatm (Rio Pimento Bueno) to 5000 μatm in the Rio Solimões and 7000 μatm in the lower Rio Negro. Interestingly, *p*CO<sub>2</sub> in the far upper Rio Negro, where pH is in the 3.5 range, had lower concentrations than at the mouth. The highest observed values were 20,000 μatm in Campinas, a blackwater tributary of the Rio Negro. The pH is inversely associated with the hydrograph and with *p*CO<sub>2</sub>. Rivers draining most directly from the Andes have considerable ranges in pH, such as the Rio Purús (7–8.4), Rio Madeira (6.3–7.5), and Rio Solimões (6.3–7.5). Rivers of more lowland origin averaged ~5 to 7, with low levels (to pH 3) in the blackwaters of the Rio Negro. DOC is strongly and positively correlated with the stage of the hydrograph, tracking *p*CO<sub>2</sub> [cf. *Moreira-Turcq et al.*, 2003]. The lowest increases in DOC concentrations of 3 to 6 mg L<sup>-1</sup> were seen along the Rio Solimões and Rio Madeira, whereas broader increases were observed in the Rio Negro and its tributaries to the blackwater rivers of the Rio Negro. The Rio Teles Pires and Rio Araguaia showed lower increases, ranging from 2 to 6 mg L<sup>-1</sup>. These general patterns are reflected in major and minor ions, nutrients, sediments and sediment composition.

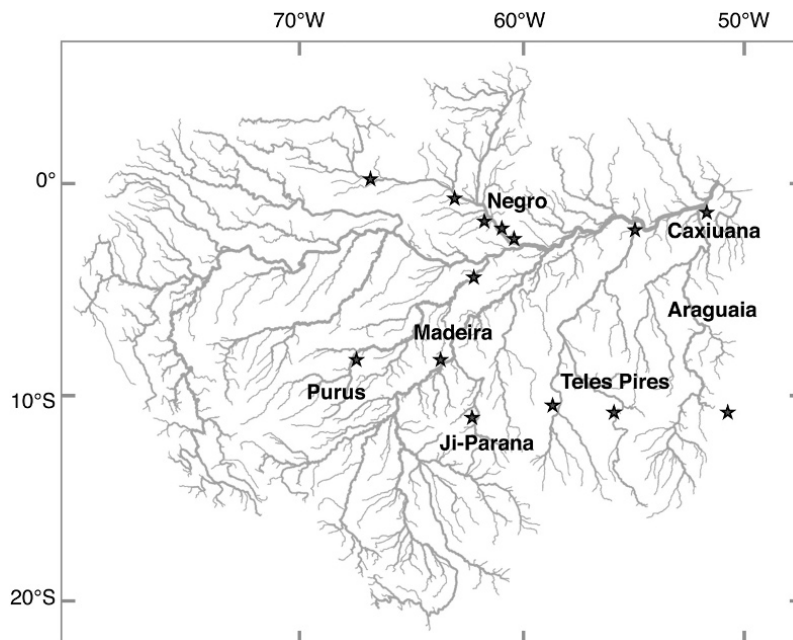


Figure 3. Sites of the Rede Beija Rio sampling network.

Overall, the relations between hydrograph and chemical species are consistent among sites. Concentrations of chemical species are maintained from smaller tributaries to large rivers, which suggest a constancy of processes at work. The next step will be to analyze some of the key processes maintaining these patterns.

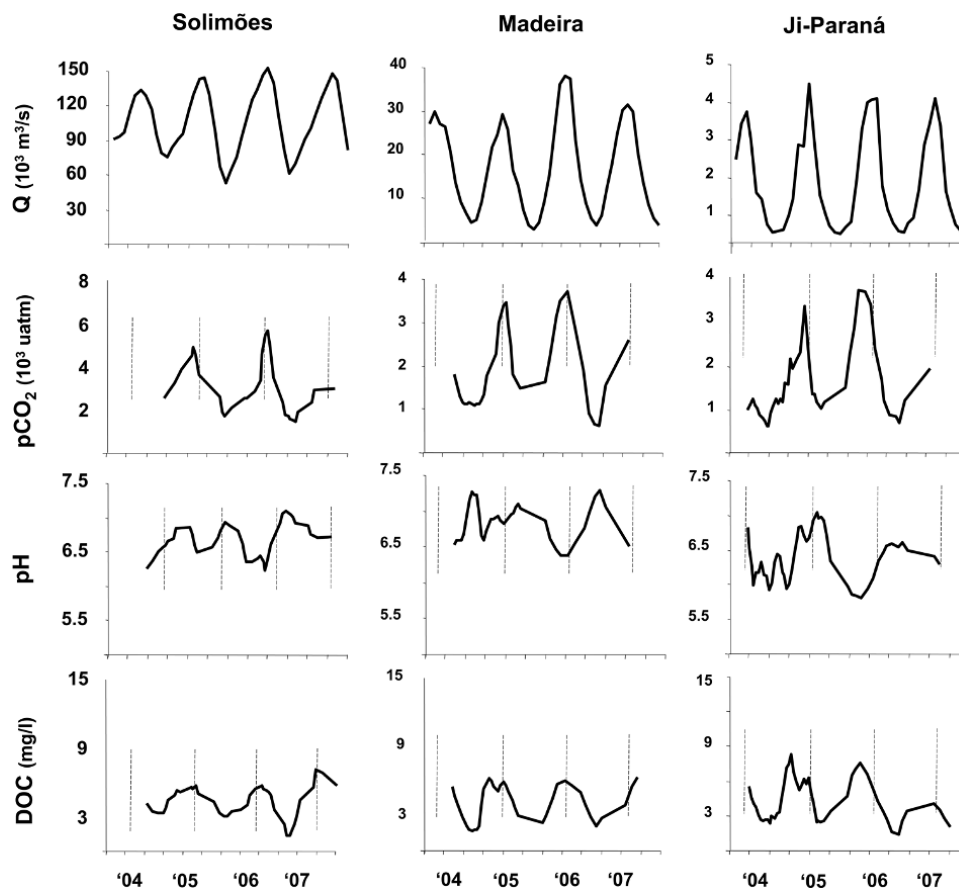
### 3.3. Gas Exchange

In considering gas exchange between the hydrosphere and the atmosphere, it is first necessary to understand the physical processes controlling the exchange of gases between water and air. Because  $\text{CO}_2$  is often supersaturated in the waters of the Amazon relative to the atmosphere, there is an outgassing. The question then is, how much, and what controls it? Quantifying gas exchange correctly is a critical and difficult element in defining the overall carbon balance in fluvial systems. Gas exchange between water surfaces and the atmosphere is controlled by microscale water-side turbulence [Banerjee and MacIntyre, 2004], and can be described by the simple equation,  $F_{\text{CO}_2} = k s (\Delta p\text{CO}_2)$ , where  $k$  is the gas transfer velocity,  $s$  is  $\text{CO}_2$  solubility, and  $\Delta p\text{CO}_2$  represents the air-water  $\text{CO}_2$  concentration gradient. In the fast-flowing river environments of Amazonia, the turbulence controlling the parameter  $k$  is induced by a dynamic combination of river currents, wind, and rainfall. The parameter  $k$  is difficult to measure accurately and has been the subject

of different techniques. Eddy covariance has been utilized in marine systems and sparsely tested on large rivers (e.g., S. Miller, on the Amazon, unpublished data, 2004). However, it is not possible to deploy the open-air eddy covariance method in smaller-scale aquatic environments because of the contribution of the terrestrial environment to the gas flux signal. Injection of dual tracers has commonly been utilized on small streams, but the approach is not realistic across a spectrum of larger rivers.

S. R. Alin et al. (Environmental controls on carbon dioxide flux, transfer velocity, and partial pressure in the Amazon and Mekong river basins (Brazil, Southeast Asia), manuscript in preparation, 2009) used the eddy accumulation approach, using floating chambers attached to a portable  $\text{CO}_2$  analyzer. Although this technique has been criticized [e.g., Belanger and Korzum, 1991], they have been found by numerous authors to provide consistent results under certain conditions, namely, low to moderate wind ( $<8\text{--}10 \text{ m s}^{-1}$ ) and wave conditions and when the air-water  $\Delta p\text{CO}_2$  is  $>300 \mu\text{atm}$  [Kremer et al., 2003; Borges et al., 2004]. These conditions are routinely met in Amazonian rivers, as winds rarely exceed  $5 \text{ m s}^{-1}$ , and air-water  $p\text{CO}_2$  gradients are generally much steeper than  $300 \mu\text{atm}$ , frequently exhibiting gradients on the order of thousands of microatmospheres. Guerin et al. [2007] got comparable results between the chambers and eddy covariance in lake environments, where both techniques could be simultaneously applied. Further, the floating





**Figure 4.** The 2004–2007 discharge hydrographs ( $Q$ ) and chemical hydrographs for  $p\text{CO}_2$ , pH, and DOC, from the Rede Beija Rio sampling network, illustrated for the main stem (Solimões at Manacapurú), the Rio Madeira at Porto Velho (tributary to the Amazon main stem), and the Ji-Paraná (tributary to the Madeira). Vertical dashed lines indicate hydrograph peak, for comparison to chemistry.

chamber approach can be consistently applied across a wide range of environments, whereas other approaches are more restricted.

Bin-averaged data for lake, stream, and river environments show clear differences among these broad environment types, which correspond to significant differences in water turbulence regimes (Alin et al., manuscript in preparation, 2009). Gas transfer velocities measured in streams and rivers are higher than lake and bay values due to the effects of water velocity and bed friction on turbulence. In the Amazon and Mekong rivers, water velocities are frequently in the range of 100–300  $\text{cm s}^{-1}$ , suggesting that observations of elevated  $k$  values may be explained by the greater contribution of water current velocity to the turbulence controlling gas transfer.

A consideration of equal importance to the exchange coefficient for regional evaluation of outgassing is the river sur-

face area exposed. Analyses to date [e.g., Richey et al., 2002] used satellite observations to define the river network, but that technology is applicable only to channels greater than 100 m in width. Considering that 92% of the Amazon River network [Mayorga et al., 2005] is composed of rivers with channels less than 100 m wide, these areas, although still not well-mapped, must play an important role as  $\text{CO}_2$  sources to the atmosphere. The surface area extent of small to medium size tropical rivers can have large variations through the hydrological cycle, affecting the size of the air-water interface and therefore gas evasion. Rasera et al. [2008] used a geographic information systems-based method to calculate the extent of river water for the Ji-Paraná basin, a mesoscale river (75,400  $\text{km}^2$ ) located in western Amazonia, then computed outgassing from these areas couple with local measurements of gas fluxes.  $\text{CO}_2$  outgassing was the main carbon export pathway from the Ji-Paraná, totaling 289  $\text{Gg C a}^{-1}$ ,

about 2.4 times the amount of carbon exported as DIC and 1.6 times the dissolved organic carbon export. Applying this model to the entire Amazon River network of channels less than 100 m wide (third to fifth order), *Rasera et al.* [2008] calculated that the surface area of small rivers is  $0.3 \pm 0.05$  million km<sup>2</sup>, and it is potentially evading to the atmosphere  $170 \pm 42$  Tg C a<sup>-1</sup> as CO<sub>2</sub>. Therefore, these ecosystems play an important role in the regional carbon balance.

CO<sub>2</sub> is not the only form of gaseous carbon present in the rivers of Amazonia. Throughout the basin, redox conditions favor the existence of methane [*Devol et al.*, 1988; *Bartlett et al.*, 1990]. *Melack et al.* [2004] estimated that methane emissions accounted for another 6.8 Tg C a<sup>-1</sup> ( $\pm 1.3$  Tg C a<sup>-1</sup>) for the same quadrant of central Amazonia analyzed by *Richey et al.* [2002]. When extrapolated to the whole basin area below the 500 m contour, this results in emissions of approximately 22 Tg C a<sup>-1</sup>. It should be noted that, although these figures might be modest for the carbon balance of Amazonia, the photochemical properties of methane make it a far more potent greenhouse gas, with roughly 20 times the greenhouse warming potential of CO<sub>2</sub>.

#### 3.4. Composite Tracers of Landscape and in Situ Processes

A significant challenge is how to deconvolve signals of external sources from internal processes. Beyond its concentration, a molecule found in a parcel of water bears the imprint, or signature, of its history. If that signature can be interpreted, important insight can be gained as to the biogeochemical factors that influenced that molecule. Using an extensive survey of carbon isotopes in organic and inorganic fractions throughout mountain and lowland rivers of the Amazon basin, *Mayorga et al.* [2005] showed that the primary source of respired CO<sub>2</sub> in the lowlands was <5 years old on average and that *p*CO<sub>2</sub> was commonly isotopically distinct from coincident organic carbon fractions (DOC, FPOC, and CPOC). Measured organic carbon fractions range in age from a decade to thousands of years and are everywhere depleted in <sup>13</sup>C relative to *p*CO<sub>2</sub>. The isotopic composition of outgassed CO<sub>2</sub> may not reflect in situ respiration sources everywhere and varies significantly among regions, with progressive evolution of carbon isotopic values downstream, as aged *p*CO<sub>2</sub> from upstream weathering sources is outgassed. Elemental, isotopic, and biochemical compositions of riverine organic matter evolve from Andean source waters to large lowland rivers, providing further evidence for upstream to downstream changes in composition, supporting the importance of sorptive processes implicated in previous experimental studies in natural systems [*Aufdenkampe et al.*, 2001, 2007]. Regional heterogeneity is observed in the isotopic composition of *p*CO<sub>2</sub> exported from upland soils to streams. Sandy,

forested Rio Negro soils export contemporary <sup>13</sup>C-depleted CO<sub>2</sub> to streams, which strongly resembles the <sup>13</sup>C signature of C3 plants. In contrast, human-impacted pasture streams in Rondônia export young but highly <sup>13</sup>C-enriched CO<sub>2</sub>, resembling C4 vegetation. Finally, lowland watersheds in western Amazonia appear to include significant carbonate outcrops, leading to substantial exports of <sup>14</sup>C-depleted and <sup>13</sup>C-enriched DIC from carbonate dissolution. While bulk dissolved and POC appear to be isotopically decoupled from CO<sub>2</sub> in Amazonian rivers, they remain key components of river ecosystems and exports to the ocean. They are actively processed in the river system, albeit at slower rates.

#### 3.5. Factors Controlling Aquatic Respiration and Its Role in Fueling CO<sub>2</sub> Outgassing

A distinguishing feature of Amazonian waters is the elevated concentration of *p*CO<sub>2</sub> relative to the atmosphere. The central ecological question is what maintains *p*CO<sub>2</sub> supersaturation in these waters? In situ respiration of organic matter derived from adjacent upland ecosystems [see *Trumbore et al.*, this volume] and flushed into rivers is thought to be the primary source of CO<sub>2</sub> saturation [*Mayorga et al.*, 2005]. Total basin-wide inputs of DOC, FPOC, and CPOC are inadequate to support in situ oxidation occurring on the Amazon main stem by at least a factor of two, suggesting that an unmeasured pool of labile organic matter exists that is rapidly consumed [*Richey et al.*, 1990]. As a contribution to our knowledge of how metabolism varies both spatially and temporally across water types and of factors driving metabolism, E. E. Ellis et al. (Factors controlling aquatic respiration and its role in fueling CO<sub>2</sub> gas evasion in rivers of the central and southwestern Amazon Basin, submitted to *Limnology and Oceanography*, 2009) analyzed the spatial and temporal extent and the dynamics of in situ water-column metabolism, in rivers and streams of the central and southwestern Amazon basin.

Using O<sub>2</sub> consumption for measuring respiration and the stable oxygen isotopes ratios of dissolved oxygen to estimate the ratio of gross primary production (GPP) to respiratory uptake of dissolved oxygen (P:R) (following *Quay et al.* [1995]), Ellis et al. (submitted manuscript, 2009) found that respiration rates spanned three orders of magnitude, with values from 0.034 to 1.78 μmol O<sub>2</sub> L<sup>-1</sup> h<sup>-1</sup>.

Oxygen isotopes indicated that some sites are net heterotrophic, while gross photosynthesis exceeds respiration at other sites. Minimum and maximum values of δ<sup>18</sup>O values ranged from 20.8‰ (in a small tributary of the Rio Acre) to 27.6‰ (in the main stem Rio Solimões), with a fraction of dissolved oxygen saturation of 1.00 and 0.54, respectively. The ratio of gross photosynthesis:respiration

(P:R) ranged from 0.38 in the Solimões River to 1.1 in the Rio Purús in the state of Acre. GPP ranged from 0.02 to  $1.5 \mu\text{mol O}_2 \text{ L}^{-1} \text{ h}^{-1}$ . These ratios (P:R) are higher than those reported previously, which ranged from 0.26 to 0.67 and were primarily collected along the Amazon main stem and in the mouths of major tributaries [Quay *et al.*, 1995].

What leads to such variations? In a dual isotope study ( $\delta^{13}\text{C}$  and the  $\Delta^{14}\text{C}$ ), Mayorga *et al.* [2005] suggested that a young (less than 5 years old), isotopically enriched pool of OC is fueling respiration in lowland Amazonian rivers, compared to the bulk size fractions. Ellis *et al.* (submitted manuscript, 2009) investigated the relationship between water-column respiration rates and environmental variables. Out of the bulk size fractions studied, respiration rates were most positively correlated with FPOC. In terms of size fractions of carbon, respiration rates were also correlated with the percentage (but not the concentration) of low molecular weight (LMW) DOC (<5 kDa). They were not correlated with the concentration of DOC or CPOC. The lability of FPOC is consistent with the decrease in the  $^{13}\text{C}$  composition of the FPOC from the Andes (where most sediment originates), to the lowlands, where it is identical to that of lowland-derived OM [Mayorga *et al.*, 2005; Quay *et al.*, 1995]. This indicates almost complete remineralization of Andean-derived FPOC and replacement with lowland-derived organic carbon, likely through preferential sorption of fresh organic matter [Aufdenkampe *et al.*, 2001].

Respiration is not controlled solely by the bioavailability of FPOC. Ellis *et al.* (submitted manuscript, 2009) found that pH was highly correlated with respiration, with pH ranging from 4.6 to 8.6 across the rivers studied. pH may indirectly affect respiration rates by controlling bacterial abundance. Bacterial abundance alone explained 78% of the variation in respiration rates, but the relationship between respiration rates and abundance was no longer significant once the effects of pH had been controlled for. Furthermore, the relationship between respiration rates and LMW DOC was no longer significant after accounting for pH.

While phytoplankton production is well documented in floodplain waters [e.g., Novo *et al.*, 2006], its role as a carbon source is generally considered to be minimal in rivers of the Amazon basin. However, Ellis *et al.* (submitted manuscript, 2009) found that in situ photosynthetic production calculated from the  $\delta^{18}\text{O}$  of dissolved oxygen at sites with pH >7 during low water contributed to the high respiration rates. These sites were more saturated with dissolved oxygen and had a significantly greater ratio of P:R than low pH sites or measurements reported by Quay *et al.* [1995] along the Amazon main stem and in the mouths of major tributaries [Quay *et al.*, 1995]. The reason for the increased productivity of these high pH rivers is that they were all

tributaries of the Rio Purús that were sampled at low water during the study period. Because the average depth was only 1.3 m, these rivers were likely not limited by light, enabling planktonic autochthonous production to occur. These results demonstrate that autochthonous material can be a significant source of labile carbon during the low-water period in upstream tributaries. Thus, algal material is a labile substrate that contributes to the high respiration rates observed in some rivers. The question then remains how far downstream an algal signal might persist.

The organic matter sources available to fuel microbial respiration throughout the basin consist of material ultimately derived from C3 plants, C4 macrophytes, and algae. Ellis *et al.* (submitted manuscript, 2009) examined the  $\delta^{13}\text{C}$  of respired  $\text{CO}_2$  to determine the mix of sources being oxidized at any one time and place. They found that respiration-derived  $\text{CO}_2$  in the Rio Negro and two small, shaded, streams in Acre were consistent with carbon originating from C3 plants ( $\delta^{13}\text{C}$  of respired  $\text{CO}_2$  ranged between  $-28.3\text{‰}$  and  $-30.1\text{‰}$ ). The  $\delta^{13}\text{C}$  of respired  $\text{CO}_2$  in shallow Purús tributaries (with high P:R ratios) were consistent with the oxidation of both algal and C3 plant sources: the  $\delta^{13}\text{C}$  was  $-33.2\text{‰}$  and  $-31.2\text{‰}$ , in the Acre and Purús rivers, respectively. Downstream, the Solimões main stem demonstrates considerable temporal variability in the organic source fueling respiration. During early falling water, organic matter with a  $\delta^{13}\text{C}$  of  $-32.6\text{‰}$  is fueling respiration. This suggests that tissues derived from both C3 plant material and algae are respired at this site. Because the oxygen isotope data from the Solimões provides little evidence of autochthonous production, algal material produced in fringing floodplains and upstream tributaries (which were at low water) likely contributes to respiration. However, during early rising water, the material being respired was  $-22.9\text{‰}$ , consistent with the results of Quay *et al.* [1995] during the low/early rising water stage. These results are consistent with 34–40% of the respiration fueled by C4 aquatic macrophytes and the remainder coming from C3 plants.

Given that riverine respiration has been hypothesized to be the primary source of  $\text{CO}_2$  saturation in freshwater, how much of the  $\text{CO}_2$  evasion flux can be accounted for by water-column respiration? Depending on the size of the river and the water type (e.g., black- versus whitewater rivers), Ellis *et al.* (submitted manuscript, 2009) suggest that depth-integrated respiration rates account for less than 1% to as much as 100% of the outgassing flux. The outgassing flux is largely supported by sources other than water-column respiration in small streams (the depth-integrated respiration rate is less than 4% of the outgassing flux for all streams), most likely benthic respiration. The contribution of water-column respiration to outgassing appears to be affected by water type

in the large, lowland rivers of Amazonia. Between 66% and 128% of outgassing CO<sub>2</sub> is accounted for by water-column respiration in large white-water rivers (Amazon, Madeira, and Solimões), whose gas evasion fluxes ranged from 0.8 to 3.7 g C m<sup>-2</sup> d<sup>-1</sup>. In the Rio Negro, the areal respiration flux accounted for only between 15% and 34% of the outgassing flux. Additional sources of CO<sub>2</sub> production in blackwater rivers could be due to photomineralization (the complete oxidation of organic carbon to CO<sub>2</sub> by light). *Remington* [2008] estimated that photomineralization was on the order of 7–8%, but cautioned that this percentage is likely too low due to methodological reasons.

The Amazon River has been proposed to be in a “dynamic equilibrium,” or quasi-steady state, with respect to CO<sub>2</sub> and O<sub>2</sub> [*Devol et al.*, 1988; *Quay et al.*, 1995], based on evidence that inputs of CO<sub>2</sub> via respiration are balanced by the rate of outgassing CO<sub>2</sub> [*Devol et al.*, 1988]. Furthermore, a dynamic equilibrium with respect to δ<sup>13</sup>C has been hypothesized as the δ<sup>13</sup>C of respired CO<sub>2</sub>, has been shown to equal the δ<sup>13</sup>C of outgassing CO<sub>2</sub> of the Amazon River [*Quay et al.*, 1995]. Consequently, other studies have assumed that the <sup>13</sup>C of CO<sub>2</sub> gas in solution in carbonate-free lowlands is equal to that of respired CO<sub>2</sub> without measuring the δ<sup>13</sup>C of respired CO<sub>2</sub> [*Mayorga et al.*, 2005]. However, *Ellis et al.* (submitted manuscript, 2009) found that the δ<sup>13</sup>C of respired CO<sub>2</sub> was not equal to that of dissolved free CO<sub>2</sub> at some of the sites. Potential explanations for this discrepancy vary between sites, but it is generally due to the long equilibration time for δ<sup>13</sup>C, long turnover times of DIC by respiration, gas exchange, and alternative sources of CO<sub>2</sub> production. Overall, it would seem that these isotopic signals measured to date are likely reflective of the transition to a steady state value of –28‰ starting from the isotopic signature set in the Andes and modified by respiration of organic matter derived from C3 vegetation, with C4 vegetation becoming more important in the lowlands at certain stages of the hydrograph.

Overall, *Ellis et al.* (submitted manuscript, 2009) demonstrate that no single organic matter source consistently fuels respiration; instead, the δ<sup>13</sup>C of respiration-derived CO<sub>2</sub> varies with time and space. In most cases, the respired carbon is isotopically similar to the bulk carbon, contrary to that reported by *Mayorga et al.* [2005]. The respiration of organic matter from adjacent terrestrial ecosystems is hypothesized to be the primary source sustaining CO<sub>2</sub> saturation in Amazonia [*Richey et al.*, 2002]. However, this research has provided evidence that, in some cases, C4 macrophytes and algae are being respired in addition to terrestrially derived C3 sources. The role of macrophytes in fueling respiration changes seasonally and photosynthetic production occurs in shallow whitewater rivers during low water. Therefore, it is necessary to measure both temporal and spatial changes

of sources of organic matter that are fueling respiration in Amazonia and further identify alternative sources of CO<sub>2</sub> production in order to accurately resolve the terrestrial carbon budget of Amazonia.

### 3.6. Photooxidation

Net ecosystem production is typically thought of as representing the net (biological) fluxes of O<sub>2</sub> and pCO<sub>2</sub>. However, another process may also contribute under certain conditions: photooxidation and its metabolites or breakdown products [*Amon and Benner*, 1996]. As past research suggests that bulk organic carbon in these large rivers is largely unavailable for bacterial consumption during transport [*Ertel et al.*, 1986; *Hedges et al.*, 1986, 1994], a small, rapidly turning-over, pool may be responsible [*Richey et al.*, 1990]. Low molecular weight organic acids (LMWOAs) are a rapidly cycling, little-studied pool of biologically labile organic compounds [*Kaplan and Newbold*, 2003] and are produced by photochemical degradation of aquatic humic substances [*Miller and Moran*, 1997]. To examine the possible role of photooxidation in producing these compounds, *Remington* [2008] measured photochemical production rates of DIC and two LMWOAs (acetic and formic acid) from DOM in the Solimões and Negro rivers. Depth-integrated photochemical DIC flux was 25% of the measured CO<sub>2</sub> flux (*Alin et al.*, manuscript in preparation, 2009) in the Rio Negro, whereas the combined acetic and formic acid production rate was 4% of the CO<sub>2</sub> flux. It should be noted that this rate is for depth integration (50 m); volumetric surface rates were much higher and could be considered as more representative of shallower rivers. There was no statistically significant production of any of these compounds from DOM in the Rio Solimões. Based on these data, *Remington* [2008] hypothesized that photolytic production of DIC, acetic and formic acids, and other biologically labile compounds are significant CO<sub>2</sub> sources to river channels with humic-rich and clear, low-sediment waters of the Amazon basin. Photochemical production of these and other biolabile compounds may become even more significant at smaller scales with open canopies and shallower water.

## 4. EFFECTS OF ANTHROPOGENIC DISTURBANCE ON RIVER CARBON FLUXES

The clearest evidence of the consequences of land cover and land use changes in the biogeochemistry of carbon in the rivers of Amazonia come from studies conducted in small basins (<100 km<sup>2</sup>). In streams of the Nova Vida Farm, in central Rondônia, conversion of forests into pastures altered the functioning of these systems [see *Tomasella et al.*, this



volume; *Thomas et al.*, 2004; *Neill et al.*, 2006]. The absence of forest canopy cover for the pasture watershed allowed extensive growth of naturally occurring *Paspallum* grasses on the margins and inside stream channels. The resulting increase in organic matter loading promoted higher respiration rates, resulting in increased CO<sub>2</sub> evasion and a shift of the oxic conditions observed in the forest streams to almost anoxia in the pasture ones [*Neill et al.*, 2006]. The isotopic composition ( $\delta^{13}\text{C}$ ) of both particulate and dissolved organic fractions in the forest and pasture streams reflected the predominance of C<sub>3</sub> and C<sub>4</sub> plants as sources for the riverine carbon in forest and pasture catchments, respectively. However, downstream from the confluence of these first-order streams that have only one vegetation type (e.g., forest or pasture), and where the larger watershed presents patches of forest within the predominant pasture cover, these isotopic signatures resemble again those of the forest stream. In the larger Rio Ji-Paraná, where the tributaries Rolim de Moura and Urupá have more than 50% of their basins covered with pastures [*Ballester et al.*, 2003], a similar pattern is found, and both particulate and dissolved forms of carbon resemble the isotopic signature of soils, which carry a C<sub>3</sub> signal [*Bernardes et al.*, 2004].

Other evidence of the consequences of forest to pasture conversion was obtained in a detailed study of flow paths and elemental fluxes in zero-order streams in Rondônia (Rancho Grande). At this scale, a small fraction of total precipitation appears in stream flow (0.8% in the forest and 17% in the pasture), but most of the increased flow in the pasture appears as overland flow (60% of total sources), whereas in the forest, this flow path was negligible [*Chaves et al.*, 2009]. Mainly as a result of this increased overland flow, pasture streams exported on an annual basis almost 20 times more dissolved organic carbon than forests (from 4.23 to 72.61 kg ha<sup>-1</sup>). The analysis of rain events at this site, occurring from the beginning to the middle of the rainy season, showed that the forest retains most of the DOC entering the system from precipitation. In the pasture, however, net losses of carbon to the streams occurred throughout the year with the exception of the beginning of the rainy season [*Gouveia-Neto*, 2006].

At the larger scale, i.e., the Ji-Paraná river basin, higher DOC concentrations were related to higher values of total suspended sediments (TSS) during the wet season [*Ballester et al.*, 2003]. TSS originated in pasture areas, where soil compaction led to less infiltration and higher surface runoff, promoting leaching of soil superficial layers carrying more DOC to the stream, while areas covered by forest had higher infiltration deeper into the soils. The percentage of the basin area covered by pasture was a good predictor for DOC concentrations during the wet season.

## 5. RELATION OF RIVER FLUXES TO REGIONAL CARBON BALANCES

The *Richey et al.* [2002] estimate of outgassing of  $1.2 \pm 0.3 \text{ Mg C ha}^{-1} \text{ a}^{-1}$  from Amazonian rivers and wetlands offered arguments to complement early and intriguing results of the LBA experiment, suggesting that forests were large sinks of carbon [*Malhi and Grace*, 2000]. Since there was no evidences of carbon accumulation in the basin to support uptake rates of that magnitude, the export in riverine systems would comprise an unknown (at the time) but significant pathway of the regional carbon cycle, as a source to the atmosphere equivalent to lower estimates of forest sequestration. At the same time, this would imply large transfers of carbon from land to water, with outgassing over 10 times the fluvial export of organic carbon to the ocean. Our understanding since then has increased.

First, how accurate are the numbers? The *Richey et al.* [2002] estimate was based primarily on data from the Amazon main stem and floodplain, and mouths of major tributaries. Data collected since then allows us to re-evaluate this number. As reported by Alin et al. (manuscript in preparation, 2009), more extensive measurements of gas exchange showed that for the large rivers, fluxes were comparable to the *Richey et al.* [2002] results, but gas transfer velocities measured in rivers less than 100 m wide were considerably higher. *Rasera et al.* [2008] computed that outgassing from rivers <100 m was more than twice that reported by *Richey et al.* [2002]. *Johnson et al.* [2008] estimated that CO<sub>2</sub> outgassing of terrestrially respired carbon from headwater streams represents a carbon flux to the atmosphere of more than 100 Tg C a<sup>-1</sup> for the Amazon basin, which is decoupled from and in addition to CO<sub>2</sub> evasion from larger rivers and wetlands. We now believe that CO<sub>2</sub> outgassing from the hydrosphere to the atmosphere varies locally with current velocity, water depth, and time of day. Cumulatively, CO<sub>2</sub> evasion terms exceed the value of  $1.2 \text{ Mg C ha}^{-1} \text{ a}^{-1}$  and represent a land-water-atmosphere transfer comparable to that of terrestrial sequestration.

The heterotrophic nature (R > P) of the waters of the Amazon basin and the areal extent of flooding making these systems a significant source of carbon to the atmosphere raises critical ecological questions, such as where does the carbon come from that ultimately is evaded, and how are carbon sources affected by land use change and climatic variability? From estimates of potential source strengths, we hypothesized that evasion is driven primarily by in-stream respiration of organic carbon fixed originally on land and to a lesser extent along river margins and mobilized into flowing waters and not just by dissolved CO<sub>2</sub> in groundwater. This presents us with a problem. Despite negligible measured downstream gradients in dissolved and particulate organic

matter and constituent biochemicals that appear, in general, quite refractory, measured respiration rates in Amazonian waters are sufficiently large to recycle essentially all organic matter in a parcel of river water well before it reaches the ocean [Richey *et al.*, 1990; Hedges *et al.*, 2000].

The magnitude of and physical controls on gas transfer velocity appear to operate similarly across river basins, but to vary substantially with physical scale. Important transitions in the environmental controls on gas exchange appear to occur with the physical scale of the river channel, as well as between standing and running water environments. Furthermore, the large variability seen in the small rivers highlights the critical importance of collecting numerous spatially distributed measurements of gas exchange variables rather than going to great effort to hone values at a few study sites that may or may not represent the drainage network as a whole.

An argument against the interpretation of the outgassing as a “separate” flux is that the outgassing is detected by the eddy covariance towers and hence was already included in the respiration term of the forest. The use of eddy covariance measurements to evaluate net ecosystem exchange of CO<sub>2</sub> and ecosystem respiration in the tall-stature, tropical forest is more problematic than originally thought, and is a topic of active research [see Saleska *et al.*, this volume, 2005; Acevedo *et al.*, 2007; Hutrya *et al.*, 2007; Malhi and Aragão, 2007]. It is most likely that these towers do not detect any of the fluvial signals, including those of smaller streams and seeps. The fluvial fluxes, while small relative to photosynthesis and ecosystem respiration, are large relative to the magnitude of net ecosystem exchange ascribed to the forest using eddy covariance measurements. Hence carbon processing through the fluvial systems of the Amazon basin indicates the strength of land-water coupling and, ultimately, the importance of fluvial systems in the regional carbon budget of the tropics.

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