

CO₂ efflux from Amazonian headwater streams represents a significant fate for deep soil respiration

Mark S. Johnson,^{1,2} Johannes Lehmann,³ Susan J. Riha,⁴ Alex V. Krusche,⁵ Jeffrey E. Richey,⁶ Jean Pierre H. B. Ometto,^{5,7} and Eduardo Guimarães Couto⁸

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[1] Large Amazonian rivers are known to emit substantial amounts of CO₂ to the atmosphere, while the magnitude of CO₂ degassing from small streams remains a major unknown in regional carbon budgets. We found that 77% of carbon transported by water from the landscape was as terrestrially-respired CO₂ dissolved within soils, over 90% of which evaded to the atmosphere within headwater reaches of streams. Hydrologic transport of dissolved CO₂ was equivalent to nearly half the gaseous CO2 contributions from deep soil (>2 m) to respiration at the soil surface. Dissolved CO₂ in emergent groundwater was isotopically consistent with soil respiration, and demonstrated strong agreement with deep soil CO2 concentrations and seasonal dynamics. During wet seasons, deep soil (2-8 m) CO₂ concentration profiles indicated gaseous diffusion to deeper layers, thereby enhancing CO_2 drainage to streams. Groundwater discharge of CO2 and its subsequent evasion is a significant conduit for terrestrially-respired carbon in tropical headwater catchments. Citation: Johnson, M. S., J. Lehmann, S. J. Riha, A. V. Krusche, J. E. Richey, J. P. H. B. Ometto, and E. G. Couto (2008), CO2 efflux from Amazonian headwater streams represents a significant fate for deep soil respiration, Geophys. Res. Lett., 35, L17401, doi:10.1029/ 2008GL034619.

1. Introduction

[2] CO₂ production within soils is high, with an annual global efflux from soil respiration equivalent to about 10% of atmospheric CO₂ [*Raich and Potter*, 1995]. This estimate is conservative, however, as it does not include aqueous-phase transport of CO₂ from soils to streams. In highly weathered soils where consumption of CO₂ by weathering reactions is low [*van Wambeke*, 1992], this CO₂ pathway may

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be particularly important. Since belowground C allocations are often inferred from vertical processes occurring at the soil surface [*Davidson et al.*, 2002], lateral transfers of soil CO_2 dissolved in percolating water and translocated by hydrologic flowpaths could result in a significant underestimation of soil CO_2 production and an overestimation of C sequestration in soils.

[3] Headwater systems, where hydrologic flowpaths integrate terrestrial biogeochemical processes and join to form springs and 1st order streams, exhibit the highest degree of terrestrial-aquatic connectivity of any spatial scale [*Gomi et al.*, 2002]. While headwater systems drain 70–80% of the landscape [*Gomi et al.*, 2002], the processes and dynamics of C transfers and transformations occurring in tropical headwater systems have been largely overlooked despite their active role in the C cycle [*Cole et al.*, 2007].

[4] Fluxes of CO_2 evading from large Amazonian rivers and wetlands have been shown to be significant to the global carbon cycle [*Richey et al.*, 2002], where evading CO_2 results primarily from the decomposition of terrestriallyderived organic carbon within the water column [*Mayorga et al.*, 2005]. However, it is not known if the C sources, forms and processes in headwater systems are similar to those occurring in higher order Amazonian rivers. Additionally, the magnitude of CO_2 outgassing from small streams remains a "major unknown" in regional C budgets [*Cole et al.*, 2007], as prior studies of CO_2 evasion fluxes are based on samples collected at downstream distances from groundwater emergence ranging from hundreds of meters [*Dawson et al.*, 2002; *Jones and Mulholland*, 1998] to kilometers [*Billett et al.*, 2004].

2. Methods

[5] CO₂ was measured in soils to depths of 8m, in groundwater springs, and in 1st and 2nd order streams for 18 months in four adjacent watersheds in the seasonally dry southern Amazon basin (10°25′S, 58°46′W, 230–250 m asl). Soils in the undisturbed, forested watersheds are a mosaic of Oxisols and Ultisols, the dominant soil formations in the Amazon basin [*van Wambeke*, 1992], and have a subsoil pH generally <4.5 [*Johnson et al.*, 2006a]. The deeply rooted forest vegetation in Amazonian forests is able to access water from depths of more than 8m during the dry season [*Nepstad et al.*, 1994].

[6] The landscape in the study catchments is organized as gently sloping uplands (2-10% slopes) with steeper hillslopes near 1st order streams and wider valley bottoms containing 2nd order and larger streams, typical of the non-Andean portion of the Amazon basin [*Neill et al.*, 2006]. The 1st order streams drain 1-2 ha catchments, while the 2nd

¹Institute for Resources, Environment and Sustainability and Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada.

²Formerly at Department of Crop and Soil Sciences, Cornell University, Ithaca, New York, USA.

³Department of Crop and Soil Sciences, Cornell University, Ithaca, New York, USA.

⁴Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York, USA.

⁵Laboratório de Ecologia Isotópica, CENA, USP, Piracicaba, Brazil.
⁶School of Oceanography, University of Washington, Seattle, Washington, USA.

⁷Also at International Geosphere-Biosphere Programme, CST, INPE, São Jose dos Campos, Brazil.

⁸Department of Soil Science, Universidade Federal de Mato Grosso, Cuiabá Brazil.



Figure 1. Temporal trends in below-canopy throughfall fluxes of water, groundwater table seasonal dynamics and soil CO_2 in primary upland forest ecosystem near Juruena, Mato Grosso, Brazil. For reference, global mean atmospheric CO_2 concentration was about 375 ppmv during the study period.

order stream drains a 600 ha catchment that encompasses the 1st order catchments. Details regarding hydrologic measurements and determinations of pH and electrical conductivity are given by *Johnson et al.* [2006a], with DOC and DIC analysis described by *Johnson et al.* [2006b]. Cations concentrations were determined by ion chromatography.

[7] CO_2 concentrations in the soil atmosphere were determined in the field using a portable infrared gas analyzer (IRGA, Vaisala GMT222, Denmark) biweekly during the rainy season and monthly during the dry season. Soil gas diffusion wells with surface access tubes [Richter et al., 1994] were installed at depths of 0.1, 0.25, 0.5, 1, 2, 4, 6 and 8m in two locations in the forest. At each depth, three 140 mL samples were analyzed after conditioning the IRGA with 140 mL of soil air. The same model IRGA was used in situ to determine dissolved pCO₂ concentrations of springs and 1st and 2nd order streams. When used in situ, the gas bench of the IRGA is deployed in the stream, and dissolved CO₂ diffuses from solution into its headspace [Johnson et al., 2007]. For a portion of the study, the IRGA was deployed in emergent groundwater and powered continuously, with output recorded by data logger. [8] The δ^{13} C composition of soil-respired CO₂ and

[8] The δ^{13} C composition of soil-respired CO₂ and dissolved CO₂ in springs was determined from granular soda lime used to adsorb CO₂. Soil-respired CO₂ was collected using static chambers [*Edwards*, 1982]. We adapted the soil respiration method for use with aqueous samples to allow a direct comparison between these CO₂ fluxes. For aqueous samples, soda lime was exposed to 5 liters of water that was fed from the spring via gravity flow into a container that was flushed with CO₂-free air prior to the introduction of water. The soda lime remained exposed to the water samples for 48 hours, during which time it adsorbed CO₂ evading from water into the headspace and was maintained isolated from atmospheric CO₂. Soda lime was acid-digested in the laboratory, and the resulting CO₂ was analyzed on an isotope ratio mass spectrometer.

and aqueous samples to account for any CO_2 adsorbed during sample handling. The mass and isotopic composition of blanks were used to correct the $\delta^{13}C$ of the samples.

3. CO₂ Evasion Flux Model

[9] We estimated the headwater outgassing CO_2 flux for the non-Andean upland portion of the Amazon basin using a parsimonious model based on the product of groundwater flux and soil pCO₂ converted to mass equivalence using Henry's Law. The spatial distribution of groundwater fluxes was determined using GIS as the difference between longterm averages of annual precipitation [New et al., 1999] and actual evapotranspiration [Tateishi and Ahn, 1996]. The groundwater flux of each 0.1 degree pixel was multiplied by a constant scaling factor such that the GIS-integrated basin-wide water balance was consistent with the 1976-1996 mean annual discharge for the Amazon [Costa and Foley, 1999]. We then excluded from our analysis more than 800,000 km² of large rivers, wetlands and seasonally inundated areas based on remote sensing of high and low water periods [Melack and Hess, 2008]. Interannual variability was estimated from wet and dry year water balances (mean ± 1 SD). Groundwater pCO₂ was computed from soil pH based on equilibrium of CO₂ in solution [McBride, 1994]. Soil pH values were derived based on pH classes for the deepest soil horizon of a digital soils database [Batjes, 2005], and agreed with physical processes [McBride, 1994] and field measurements of deep soil CO₂ [Davidson and Trumbore, 1995; Davidson et al., 2004; this study].

4. Results

[10] Soil CO₂ below 2m depth was consistently in excess of 100 times atmospheric CO₂ concentrations (*ca.* 375 ppm during the study period), and was also highly dynamic, increasing seasonally by as much as 100% (Figure 1). Deep



Figure 2. Dissolved CO_2 as a function of distance downstream from groundwater springs. Data are from four adjacent forested headwater catchments and one forested 2nd order stream in the southern Amazon. The 1st order streams converge into a common 2nd order stream (150 m and 2500 m data points). Data are given as partial pressure of CO_2 in water (vertical axis on the left), and as concentration (vertical axis on the right).

soil CO_2 concentrations indicated a directionality to vertical diffusion that was seasonally dependent: upwards during dry seasons (thus contributing to total soil respiration), but downwards during wet seasons (thus contributing to lateral transport upon equilibration with soil water) (Figure 1).

[11] We found the pCO₂ of groundwater springs to closely reflect the CO₂ concentration in the deep soil: 51900 ± 1600 ppmv CO₂ for emergent groundwater vs. 52700 ± 1400 ppmv CO₂ in the soil profile from 2 to 8 m (means ± 1 SE). Upon emergence, however, rapid outgassing drives off over 90% of the CO₂ transported by groundwater as a result of turbulent mixing in the shallow headwater streams (Figure 2). While diffuse groundwater discharge to streams augments streamflow along the study reaches and is also supersaturated with CO2, it joins stream water that has already substantially degassed. In addition, groundwater inflow as a proportion of total streamflow decreases downstream in the river network as a feature of landscape hydrogeomorphic organization. For comparison, direct groundwater discharge into the mainstem of the Amazon River is estimated at less than 1% of total discharge [Devol et al., 1987].

[12] As nearly 95% of annual stream discharge occurs as groundwater-derived baseflow in the study watersheds

[Johnson et al., 2006a], lateral fluxes of dissolved CO_2 from soils to streams totaled 0.40 Mg C ha⁻¹ yr⁻¹. Comparing this gaseous flux with dissolved and particulate phases of organic and inorganic C [Johnson et al., 2006a, 2006b], we find that 77% of C transported by water from the landscape was by groundwater supersaturated with terrestrially-respired CO_2 dissolved within soils.

[13] Groundwater enters streams with a chemical signature that is representative of deep soil layers in the terrestrial environment: high in dissolved CO₂, and low in both DOC and cations derived from mineral weathering (Table 1). The chemical composition within streams shifts in headwater reaches, with CO2 evasion causing increases in stream water pH and a shift of a portion of the remaining dissolved CO₂ to the chemically-sequestered bicarbonate form, while benthic decomposition of terrestrial litterfall leads to increased concentrations of DOC and cations (Table 1). As a consequence, the ratio of DIC to DOC (DIC:DOC where DIC is the sum of dissolved CO_2 , $HCO_3^$ and CO_3^{2-}) decreases substantially from headwater flowpaths (47) to 1st order (3.0) and 2nd order (1.8) streams, with the latter nearly equivalent to the ratio implied for large Amazonian rivers (1.7) [Richev et al., 2002]. This downstream shift from a headwater system with fluvial C dominated by terrestrial respiration products to a riverine system characterized by in-stream biological and physical processes has also been observed in temperate regions [Dawson et al., 2004].

[14] We found good agreement between the stable isotopic composition of CO₂ in bulk soil respiration at the soil surface and that of CO₂ evading from groundwater springs, which provides further evidence that CO₂ fluxes at the terrestrial-aquatic interface are driven by terrestrial respiration. The δ^{13} C signature of bulk respiration at the soil surface (-25.9‰ ± 0.4, mean ± 1 SE, n = 24) is consistent with the -26.2‰ ± 0.6 (mean ± 1 SE, n = 28) of CO₂ outgassing from emergent groundwater. The δ^{13} C value of emergent groundwater includes adjustment for net fractionation (diffusive enrichment within the soil profile and fractionations during dissolution and evasion) in comparison with soil respiration, and the adjusted value is within the range of measured values for δ^{13} C of primary forest respiration in the Amazon [*Ometto et al.*, 2002].

5. Discussion

[15] Previous work identified the lack of quantification of CO_2 drainage with percolating water as a potential source of underestimation of deep soil CO_2 production, but was not

Table 1. Water Chemistry Parameters for Base Flow in Four Adjacent Headwater Catchments Draining to a 2nd Order Stream in the Southern Amazon Basin^a

	Groundwater Springs	1st Order Streams	2nd Order Stream
pН	4.65 ± 0.03 (142)	6.05 ± 0.03 (296)	6.41 ± 0.06 (60)
EC (μ S cm ⁻¹ at 25°C)	18.7 ± 1.0 (165)	48.8 ± 1.7 (298)	71.9 ± 3.6 (66)
Na (mg L^{-1})	0.98 ± 0.05 (141)	2.42 ± 0.08 (268)	4.53 ± 0.43 (63)
$K (mg L^{-1})$	1.54 ± 0.03 (138)	2.67 ± 0.09 (268)	4.81 ± 0.59 (63)
Mg (mg L^{-1})	0.60 ± 0.02 (139)	1.36 ± 0.04 (268)	2.97 ± 0.29 (63)
$Ca (mg L^{-1})$	0.49 ± 0.04 (138)	2.13 ± 0.08 (268)	4.37 ± 0.32 (57)
DOC (mg C L^{-1})	0.48 ± 0.03 (172)	2.25 ± 0.14 (311)	3.72 ± 0.28 (75)
Dissolved $CO_2 \text{ (mg C L}^{-1}\text{)}$	21.1 ± 0.6 (47)	2.51 ± 0.15 (84)	2.50 ± 0.20 (21)
$HCO_3^- (mg C L^{-1})$	1.47 ± 0.06 (144)	4.13 ± 0.29 (237)	6.00 ± 0.31 (57)

^aValues are means ± 1 SE (number of samples).



Figure 3. Dissolved CO_2 in emergent groundwater. Data are daily means ± 1 SD from continuous *in situ* monitoring during the wet-to-dry season transition in the southern Amazon near Juruena, Brazil.

able to provide an estimate of the magnitude [*Davidson and Trumbore*, 1995]. Applying a soil diffusivity model that does not assume an exponentially increasing CO₂ concentration with depth [*Davidson et al.*, 2004] and is based on soil CO₂ concentrations, moisture contents and physical properties, we calculated the CO₂ flux to the soil surface from deep soil CO₂ production (>2 m) to amount to 94 CO₂-C m⁻² yr⁻¹. Comparing this with the lateral transport of dissolved CO₂ to streams demonstrates that CO₂ drainage is equivalent to almost half the vertical flux of gaseous CO₂ to the soil surface, indicating that plot-based studies focusing on soil respiration have underestimated deep soil CO₂ production.

[16] Total aqueous export of terrestrial respiration products includes CO_2 evaded within headwater catchments plus dissolved CO_2 export and bicarbonate export (Table 1), with the latter described as "hidden soil respiration masquerading as the bicarbonate ion" [*Cole et al.*, 2007]. The low soil pH in the study catchments precludes carbonate weathering; therefore all bicarbonate exported results from silicate weathering, with C originating as carbonic acid derived from terrestrial CO_2 sequestration [*Cole et al.*, 2007]. The sum of CO_2 evasion and export of bicarbonate and dissolved CO_2 from the watersheds amounts to latent terrestrial respiration equivalent to 4% of total soil respiration as estimated by *Chambers et al.* [2004].

[17] The seasonal dynamics of both deep soil CO_2 and dissolved CO_2 at the terrestrial-aquatic interface were consistent with the hypothesis of a dry-season "greeningup" of the Amazon rainforest [Huete et al., 2006]. This is reflected in CO₂ dynamics in the deep soil, resulting from increases in water uptake and root activity at depth at the onset of the dry season, as deeper soil moisture reserves are drawn upon in response to reduced surficial soil moisture availability and seasonal peaks in solar irradiance [Huete et al., 2006]. We found increases in deep soil CO₂ concentrations early in the dry season (e.g. April - May 2005, Figure 1), which subsequently decreased in response to drainage and diffusional losses later in the dry season (June–October 2005, Figure 1). Dissolved CO₂ in emergent groundwater also followed this trend, exhibiting augmented concentrations during the dry season onset and declining again after the peak of the dry season (Figure 3).

[18] We used our findings that headwater outgassing is the result of terrestrially-respired CO₂ degassing from supersaturated emergent groundwater to model the CO_2 evasion flux from non-Andean headwater streams in the Amazon based on basin-wide published spatial datasets of hydrologic variables and soil properties. After excluding open water and low-lying areas potentially subject to seasonal inundation and incorporating considerations of land use change impacts on CO₂ drainage and interannual variability in the water balance, we computed the CO_2 evasion flux from 1st order streams for the upland portion of the Amazon basin as $114 \pm 10 \times 10^{12}$ g CO₂-C yr⁻¹. Total CO₂ evasion from the Amazonian aquatic system including our estimates from headwater streams and previous estimates for large rivers and wetlands [Richey et al., 2002] likely exceeds 580×10^{12} CO₂-C yr⁻¹

[19] The areas with the highest potential CO_2 evasion flux are those where the groundwater flux is highest and soils are acidic, and correspond with those areas with the highest soil CO₂ emissions [Raich and Potter, 1995]. The impact of land use change was incorporated by assuming a 100% increase in stormflow to result from deforestation [Williams et al., 1997]. We also made the simplifying assumption that all stormflow in the perturbed system occurs as overland flow and thus is not available for dissolution and translocation of soil CO₂. These conservative assumptions resulted in a relatively minor reduction of the total headwater outgassing flux by 1.7×10^{12} g CO₂-C yr⁻¹. Since maximum CO₂ 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.

6. Conclusions

[20] Evasion of CO_2 from headwater streams in the Amazon is decoupled from and in addition to CO_2 evasion from larger rivers and wetlands [*Richey et al.*, 2002], and results from different processes. In larger lotic systems, instream processing of allochthonous organic C is the main driver of the CO_2 supersaturation typical of tropical rivers [*Mayorga et al.*, 2005]. In headwater streams, however, CO_2 supersaturation results primarily from groundwater discharge of terrestrially-respired CO_2 dissolved within deep soils. CO_2 drainage and subsequent evasion is an important C pathway in tropical headwater systems where rainfall and groundwater recharge are high, soils are deep and acidic, and vegetation is deeply rooted.

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E. G. Couto, Department of Soil Science, Universidade Federal de Mato Grosso, Cuiabá, MT 78060-900, Brazil.

M. S. Johnson, Institute for Resources, Environment and Sustainability, 440-2202 Main Hall, Vancouver, BC V6T 1Z4, Canada. (mark.johnson@ubc.ca)

J. Lehmann, Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, USA.

A. V. Krusche and J. P. H. B. Ometto, Laboratório de Ecologia Isotópica, CENA, USP, Piracicaba, SP 13400-970, Brazil.

J. E. Richey, School of Oceanography, University of Washington, Seattle, WA 98195, USA.

S. J. Riha, Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, USA.