Radon-traced pore-water as a potential source of CO\textsubscript{2} and CH\textsubscript{4} to receding black and clear water environments in the Amazon Basin

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**Scientific Significance Statement**

Rivers are generally supersaturated in CO\textsubscript{2} and CH\textsubscript{4}, and in some rivers, such as the headwaters of the Amazon River system, groundwater and pore-water exchange have been shown to be the primary source of these dissolved gases. However, it is not clear whether groundwater or pore-water is an important source of these gases in higher order parts of the Amazon River system that are much more heterogeneous. Using Radon-222, a natural tracer, we show that pore-water exchange may be a relevant source of dissolved CO\textsubscript{2} and CH\textsubscript{4} to major black and clear water tributaries of the central Amazon Basin during receding waters.

**Abstract**

Groundwater is a primary source of dissolved CO\textsubscript{2} and CH\textsubscript{4} in Amazonian headwaters, yet in higher order rivers, a groundwater/pore-water source is difficult to constrain due to the high spatial and temporal heterogeneity of pore-water exchange. Here, we report coupled, high resolution measurements of \(p\text{CO}_2\), CH\textsubscript{4}, and \(^{222}\text{Rn}\) (a natural pore-water and groundwater tracer) during receding waters in the three major water types of the Central Amazon Basin: black (Negro River); clear (Tapajós River); white (Madeira River). Considerable spatial heterogeneity was observed in \(p\text{CO}_2\), CH\textsubscript{4}, and \(^{222}\text{Rn}\) concentrations ranging from 460 μatm to 8030 μatm, 7 nM to 281 nM, and 713 dpm m\textsuperscript{-3} to 8516 dpm m\textsuperscript{-3}, respectively. The significant correlations between \(p\text{CO}_2\) and CH\textsubscript{4} to \(^{222}\text{Rn}\) in the black and clear waters suggests that pore-water further enhanced CO\textsubscript{2} supersaturation by 18–47% and is a driver of CH\textsubscript{4} dynamics in these waters.

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Our understanding about the role of rivers in global greenhouse gas budgets is evolving. Recent estimates of CO$_2$ flux from rivers vary in magnitude from 0.6 Pg CO$_2$ yr$^{-1}$ to 3.9 Pg CO$_2$ yr$^{-1}$ (Aufdenkampe et al. 2011; Raymond et al. 2013; Lauerwald et al. 2015; Drake et al. 2018) and estimated emission of CH$_4$ has recently been revised from 1.5 Tg C yr$^{-1}$ to 26.8 Tg C yr$^{-1}$ (Bastviken et al. 2011; Stanley et al. 2016; see also Kirschke et al. 2013). The tropics are the largest contributor of global CO$_2$ emissions from rivers, yet the region is underrepresented in global data sets and the source of large uncertainties (Borges et al. 2015; Lauerwald et al. 2015). Constraining the relative contribution of the sources driving riverine CO$_2$ and CH$_4$ supersaturation and atmospheric exchange rates remains a challenge (Cole et al. 2007; Raymond et al. 2013; Borges et al. 2015, 2018; Teodoru et al. 2015; Stanley et al. 2016).

The Amazon river system is generally supersaturated in CO$_2$ and CH$_4$, and is estimated to emit globally significant amounts of both gases (Richey et al. 2002; Melack et al. 2004; Rasera et al. 2013; Sawakuchi et al. 2014; Barbosa et al. 2016). The factors contributing to CO$_2$ supersaturation remain unclear and are likely spatially and temporally variable (Richey et al. 2009). Respiration of allochthonous (Mayorga et al. 2005) and autochthonous (Ellis et al. 2012) organic matter, carbonate weathering (Vihervaara et al. 2014), and contributions from wetlands and floodplains (Abril et al. 2014) have all been highlighted as sources of CO$_2$ to Amazonian rivers. Drivers of riverine CH$_4$ dynamics are more ambiguous, with recent studies highlighting hydrological drivers such as seasonal water stage and wetland-river connectivity (Sawakuchi et al. 2014; Borges et al. 2015; Barbosa et al. 2016). Despite these advances, large uncertainties remain in Amazonian CO$_2$ and CH$_4$ budgets (Richey et al. 2009; Melack 2016).

Pore-water and groundwater exchange have been shown to be the primary source of CO$_2$ and CH$_4$ in Amazonian headwaters (Johnson et al. 2008; Neu et al. 2011). In higher order Amazonian rivers, pore-water is hypothesized to contribute to CO$_2$ and CH$_4$ supersaturation, however, this exchange pathway is difficult to constrain beyond small streams due to high spatial and temporal heterogeneity (Cook et al. 2003). Radon-222 (222Rn) is a natural tracer of any water that has been in contact with sediments (pore-water and/or groundwater) and has been used to assess groundwater inputs into river and lakes (Cook et al. 2006; Burnett et al. 2010). More recently, 222Rn has revealed how pore-water releases CO$_2$ and CH$_4$ to estuarine surface waters (Call et al. 2015; Maher et al. 2015; Sadat-Noori et al. 2016), but no similar investigations have been performed in the Amazon. Here, we define pore-water as the exchange of interstitial water into surface waters (i.e., a combination of meteoric and hyporheic exchange). We investigate whether radon-traced pore-water may be a source of CO$_2$ and CH$_4$ to major tributaries of the Amazon river system during receding waters spanning the three major water types (black, clear, white).

**Methods**

Longitudinal surveys were conducted in three major tributaries representing the three water types of the central Amazon Basin: black water (Rio Negro ~ 150 km surveyed); clear water (Tapajós ~ 100 km surveyed); and white water (Madeira ~ 100 km surveyed) (Fig. 1a–c). Each water type has unique chemical characteristics related to the geomorphological properties of their catchments (Sioli 1968; Junk et al. 2011). Briefly, black waters drain large areas of low-lying podzols and contain high levels of dissolved organic material. Clear waters drain Precambrian shields and are low in suspended sediments and organic material. White waters originate in the Andes Mountains and contain high sediment loads and nutrients. Extensive wetlands and floodplains exist in each basin (Junk et al. 2011; Hess et al. 2015), draining into the main river stems via a complex network of fluvial connections (Mertes et al. 1996). “Igarapés” are forest streams that drain straight to the river channel, or first to floodplain lakes.

Seasonal rainfall and Andes snow melt result in large oscillations in river water levels (Junk et al. 2011) causing the inundation of forests, wetlands, and floodplains across the basin (Hess et al. 2015). Surveys were conducted during receding waters during August 2015 and September 2015 (see Supporting Information for hydrographs for the black, clear, and white rivers). The main riverine channel was surveyed for each water type along with two lakes in black waters and one lake in clear waters. At the time of sampling, all lakes were connected to the main river channel. Black water lakes were surrounded by flooded forests (large trees, non-herbaceous) as was the clear water lake, however, the western flank was separated from the main channel by a sand bar with a single opening.

Water column pCO$_2$, CH$_4$, and 222Rn were determined by continuously pumping water from a depth of ~ 50 cm into two showerhead gas equilibration devices (GED) aboard a moving vessel that averaged 10.6 ± 3.5 km h$^{-1}$ and 5.4 ± 2.9 km h$^{-1}$ during river and lake surveys, respectively. Equilibrated headspace air was then pumped into an Off-Axis Integrated Cavity Output Spectrometer which measured CO$_2$ and CH$_4$ at 1 s intervals. A separate gas stream from the same GED was pumped to an automated 222Rn-in-air analyzer which logged data at 10 min intervals. Moving averages of 10 min and 30 min were applied to smooth pCO$_2$ and CH$_4$ concentrations based on experimentally determined gas equilibration times (Webb et al. 2016). A Hydrolab DS5 sonde logged temperature, every 5 min and a BBE Mola daenke Fluoroprobe logged fluorescence every 5 min. All
average values reported in results are ± 95% confidence interval. All regression analyses having a $p$ value of < 0.05 were deemed as being significant. No CH$_4$ data is available from white water due to instrument malfunction. Detailed descriptions of longitudinal surveys are provided as Supporting Information.
Partial pressure of CO₂

Across all water types, pCO₂ displayed considerable spatial variability (Fig. 1a–c). In the black waters, the range in pCO₂ spanned over 4000 μatm, with highest pCO₂ observed where the Igapó da Freguesia converges with the river at Novo Airão (NA) (Fig. 1a). Localized areas of elevated riverine pCO₂ were also observed in the vicinity of the adjoining Igapó Marajá (IM, 7817 μatm) and Igapó Camará (IC, 7435 μatm), and at the confluence of the floodplain lake, Lago Acajatuba (LA, 7291 μatm). Lowest black water pCO₂ was recorded in Lake 2, however, distinct areas of higher pCO₂ were observed in the southern perimeters of Lake 1 (max 7023 μatm) and Lake 2 (max 6864 μatm). Overall, average riverine pCO₂ was 26% higher than average lake pCO₂ (Table 1).

In the clear waters, lowest pCO₂ was observed in the river near Santarem and highest pCO₂ at the north-eastern end of Largo Verde (LV) (Fig. 1b). Upstream of LV, riverine pCO₂ gradually increased, peaking (1532 μatm) at the Igapó Marajá (IM, 1013 μatm) and at the confluence of the floodplain lake, Lago Acajatuba (LA, 7291 μatm). Lowest black water pCO₂ was recorded in Lake 2, however, distinct areas of higher pCO₂ were observed in the southern perimeters of Lake 1 (max 7023 μatm) and Lake 2 (max 6864 μatm). Overall, average riverine pCO₂ was 26% higher than average lake pCO₂ (Table 1).

In the vicinity of CB and the igarapé da Freguesia converges with the river at Novo Airão (NA) (Fig. 1a). Localized areas of elevated riverine pCO₂ were also observed in the vicinity of the adjoining Igapó Marajá (IM, 7817 μatm) and Igapó Camará (IC, 7435 μatm), and at the confluence of the floodplain lake, Lago Acajatuba (LA, 7291 μatm). Overall, average riverine pCO₂ was 26% higher than average lake pCO₂ (Table 1).

CH₄ concentrations

Methane concentrations spanned a range of 274 nM, with lowest concentrations in downstream river locations and maximal concentrations in the lakes (Fig. 1d,e). Black river CH₄ concentrations were generally <40 nM, however, concentrations up to 157 nM were observed in the vicinity of NA. Clear river CH₄ ranged from 15 nM to 41 nM with highest concentrations in the vicinity of CB and the igarapé. Overall, average CH₄ concentrations were higher in the lakes than in the rivers (Table 1).

Radon-222

A general trend of higher ²²²Rn concentrations in upstream locations was evident in all water types (Fig. 1f–h). In black waters, localized areas of elevated concentrations were observed in the river at IC (3423 dpm m⁻³), IM (3389 dpm m⁻³), and NA (4647 dpm m⁻³), and maximum values in the lakes (L1: 6159 dpm m⁻³, L2: 6506 dpm m⁻³). Clear water concentrations of ²²²Rn were also highest in the lake, with distinct areas of higher riverine concentrations in the vicinity of CB (4778 dpm m⁻³) and the igapó (7797 dpm m⁻³). Overall, average lake concentrations of ²²²Rn were ~40% and ~60% higher than average riverine concentrations in the clear and black waters, respectively. The white river had the lowest range of ²²²Rn (Fig. 1h) but the highest average riverine concentration of the three water types (Table 1). Significant positive relationships (p<0.05) were observed between pCO₂ and CH₄ with ²²²Rn in the rivers and lakes of the black and clear waters (Fig. 2a,b,d,e).

Discussion

Our study presents concurrent surface-water measurements of a natural pore-water tracer (²²²Rn) with pCO₂ and CH₄ concentrations from waters of the central Amazonian basin. We build on an earlier study documenting ²²²Rn concentrations in Amazonian rivers (Devol et al. 1987) by reporting high resolution measurements to map potential areas of increased pore-water to surface-water interactions. The significant positive correlations observed between pCO₂ and CH₄ with ²²²Rn suggest pore-water may be a relevant source of pCO₂ and CH₄ during receding black and clear waters, providing a basis for designing future studies to quantify the influence of pore-water exchange in carbon budgets of Amazon waters.

CO₂ and CH₄ distribution

Wide ranges of pCO₂ have been reported from the diverse aquatic systems in the Amazon Basin (Richey et al. 2002; Rasera et al. 2013; Abril et al. 2014; Melack 2016). Seasonally, pCO₂ tracks the hydrograph (Richey et al. 2002, 2009) and the results from this study are in general agreement with published observations in terms of season and water type. The average pCO₂ observed in the receding black and clear rivers (i.e., Negro and Tapajós) is higher than those
reported by Abril et al. (2014), likely due to our surveys extending further upstream where $p$CO$_2$ was considerably higher. Receding white river (Madeira) observations are higher than those reported at the mouth ($pCO_2$ 1300 atm) by Abril et al. (2014), but lower than the $pCO_2$ 4100 atm reported further upstream by Almeida et al. (2017). Clear rivers had the lowest $p$CO$_2$ of the three water types which is consistent with other studies (Alin et al. 2011; Rasera et al. 2013; Abril et al. 2014). The high-spatial resolution data from our study revealed higher $p$CO$_2$ upstream and close to igarapés confluence with the main channels, suggesting igarapés may be a source of CO$_2$ to the main channels.

Data on Amazonian CH$_4$ concentrations are much sparser than $p$CO$_2$, with large spatial and temporal variability of concentrations and associated fluxes (Melack et al. 2004; Sawakuchi et al. 2014; Borges et al. 2015; Barbosa et al. 2016). In contrast to the large spatially distributed measurements of previous studies such as Barbosa et al. (2016),

\[ \text{Fig. 2. (a, b) Linear regression of } pCO_2 \text{ and } CH_4 \text{ with } ^{222}\text{Rn in black river and black lakes. (d, e) Linear regression of } pCO_2 \text{ and } CH_4 \text{ with } ^{222}\text{Rn in clear river and clear lake. (c, f) Linear regression of Chl a with } pCO_2 \text{ in black river and black lakes, and clear river and lake, respectively. No relationships were observed in the white waters.} \]
which measured \( \text{CH}_4 \) at four locations along a 700 km transect of the Negro River and in 21 tributaries within the Negro basin, this article presents smaller scale \( \text{CH}_4 \) measurements. Methane distribution was characterized by a few localized areas of distinctly higher concentrations in lakes, which are known emitters of \( \text{CH}_4 \) (Crill et al. 1988; Devol et al. 1988), and where the igarapé joins the black river at NA.

Radon tracing of surface water \( \text{CO}_2 \) and \( \text{CH}_4 \) sources

Radon-222 is produced in sediments by the radioactive decay of radium-226 (\( ^{226}\text{Ra} \)) and has a short half-life of 3.8 d. The noble gas is often highly enriched in groundwater/pore-water and once discharged to surface waters the only losses are radioactive decay and atmospheric evasion (Cook et al. 2008). Radon-222 activities in surface waters integrate the various recent groundwater and pore-water exchange pathways, such as hyporheic exchange or the lateral flow from regional aquifers to the main channels. While it was beyond the scope of this initial study to differentiate between the different radon pathways, our observations imply pore-water connectivity in the river and lakes during receding waters.

Diffusion of \( ^{222}\text{Rn} \) from sediments can also be a source to surface waters. Based on the average \( ^{226}\text{Ra} \) content in sediments from Amazon floodplain lakes (2.09 ± 1.55 dpm g\(^{-1}\); Sanders et al. 2017) and using the empirical equation to relate \( ^{226}\text{Ra} \) activity in sediments with \( ^{222}\text{Rn} \) diffusion (\( J_{\text{diffusion}} = 495.2^{226}\text{Ra}_{\text{sed}} + 18.2; \) see Burnett et al. 2003), we estimate a \( ^{222}\text{Rn} \) diffusion rate of 1053 dpm m\(^2\) d\(^{-1}\) across the sediment interface. Water level data for the black, clear, and white rivers (no depth data for lakes) were estimated to be \( \sim 16 \text{ m}, \sim 5.5 \text{ m}, \text{ and } \sim 12 \text{ m} \), respectively (Supporting Information Fig. S2). Therefore, assuming homogeneous depth, the contribution of \( ^{222}\text{Rn} \) diffusion from sediments can sustain maximum river \( ^{222}\text{Rn} \) concentrations of 365 dpm m\(^{-3}\), 1060 dpm m\(^{-3}\), and 487 dpm m\(^{-3}\), respectively. While the sediment \( ^{226}\text{Ra} \) content was determined from four sites within the Amazon basin, thus placing considerable uncertainty in our estimates, they indicate that the contribution of diffusion from sediments to surface water \( ^{222}\text{Rn} \) concentrations were \( \sim 14\% \), \( \sim 12\% \), and \( \sim 30\% \) in the black, white, and clear rivers, respectively. Therefore, most of the radon observed in the rivers seems to be sourced from advective pore-water or groundwater pathways.

To our knowledge, only one previous study has documented \( ^{222}\text{Rn} \) concentrations in the Amazon. Devol et al. (1987) reported a similar span in \( ^{222}\text{Rn} \) values (1400–9240 dpm m\(^{-3}\)) from eight sites along a 1700 km transect of the Amazon River mainstream and at the mouths of seven tributaries during rising waters (February–March). Samples taken at the mouth of the Rio Negro (2050 dpm m\(^{-3}\)) and Madeira (4450 dpm m\(^{-3}\)) are within ranges observed in this study, however, the high-resolution measurements obtained here illustrate the high-spatial variability of \( ^{222}\text{Rn} \) that can occur at smaller scales, reflecting the heterogeneous nature of pore-water exchange with surface waters. The general trend of higher \( ^{222}\text{Rn} \) concentrations upstream from river mouths suggests greater pore-water influence on surface-water chemistry in these locations which is consistent with other studies in rivers and wetlands (Cook et al. 2003; Santos and Eyre 2011). While evasion could explain the reduced \( ^{222}\text{Rn} \) concentrations downstream, the observed trend cannot simply be explained by degassing and suggests \( ^{222}\text{Rn} \) inputs along the rivers sampled (Fig. 1f–h; Supporting Information Fig. S3). Adjoining lakes appeared to be subject to increased pore-water influences. Furthermore, river segments near igarapés had distinctly higher \( ^{222}\text{Rn} \), suggesting these channels may drain surrounding soils. The hypothesized enrichment of \( ^{222}\text{Rn} \) in narrower and steeper-banked igarapés may be due to the larger sediment surface area relative to the overlying water and/or the expected increase in hydrostatic pressure with the surrounding water table during receding waters (i.e., increased pore-water discharge).

While pore-water inputs may be small relative to surface-water processes, the significant positive relationship observed between \( p\text{CO}_2 \) and \( \text{CH}_4 \) with \( ^{222}\text{Rn} \) in the rivers and lakes of the black and clear waters suggests a common source (Fig. 2a,b,d,e). Other studies have used \( ^{222}\text{Rn} \) to suggest that groundwater is a significant source of \( \text{CO}_2 \) and \( \text{CH}_4 \) to surface waters (Atkins et al. 2017; Webb et al. 2017). Based on water flow through rates, Richey et al. (2002) estimated that \( \text{CO}_2 \) derived from soil respiration is exported to streams via the lateral flow of groundwater and could account for 25% of evasion from the waters of the central Amazonian basin. Using the \( y \)-intercept of the \( p\text{CO}_2-^{222}\text{Rn} \) linear regression in the black river and lakes (Fig. 2a) and the average \( p\text{CO}_2 \) of each (Table 1), we find similar values. Average \( p\text{CO}_2 \) would be 21% lower than observed in the black river and 23% lower in the black lakes if there were no recent pore-water inputs (\( ^{222}\text{Rn} \) approaching zero). In the clear river and lake, average \( p\text{CO}_2 \) may be 18% and 47% lower, respectively. This implies that while other sources contribute to \( \text{CO}_2 \) supersaturation, pore-water may be a relevant source of \( \text{CO}_2 \) in these receding waters. No significant relationships were observed in the white river which may be due to the limited spatial extent of the river studied. In addition to pore-water, primary production and respiration may also exert a strong control on \( p\text{CO}_2 \) in the Amazon. The significant inverse relationship observed between \( p\text{CO}_2 \) and Chl \( a \) in the black river, black lakes, and clear river (Fig. 2c,f), indicates primary production is an important controller of \( p\text{CO}_2 \) which is consistent with the recent findings of Amaral et al. (2018). This is particularly evident in black lakes where the concentrations of Chl \( a \) were considerably higher (relative to the black river, Table 1) and may explain the lower \( p\text{CO}_2 \) and weaker (albeit still significant) \( p\text{CO}_2-^{222}\text{Rn} \) relationship (Fig. 2a).
Although wetlands are becoming increasingly recognized as an important source of CH₄ to adjoining rivers (Devol et al. 1990; Borges et al. 2015), Sawakuchi et al. (2014) suggested wetland-sourced CH₄ may not be as relevant during their study based on higher CH₄ fluxes during low waters vs. high waters in Amazonian Rivers. The observed CH₄-222Rn relationship (Fig. 2b,e) supports the hypothesis that pore-water may be an important mechanism in driving riverine CH₄ dynamics (see review by Stanley et al. 2016) and may explain the decoupled wetland-river connectivity observed in Sawakuchi et al. 2014. Similarly to the tidal pump concept (see Stieglitz et al. 2013; Call et al. 2015), where surface water infiltrates sediments during incoming tides (rising waters) and then returns to surface waters during outgoing tides (receding waters), we hypothesize that such a process may be occurring at seasonal scales (as opposed to diurnal/semi-diurnal tidal pumping) in the black and clear waters sampled during this study. Such a concept would result in a trend of increasing CH₄ concentrations as the water levels transitioned from high to low which was observed in white water rivers and floodplain lakes by Barbosa et al. (2016). Sawakuchi et al. (2014) and Barbosa et al. (2016) suggest that dilution and higher rates of CH₄ oxidation during high water may also explain higher concentrations during the low water period. Clearly, further seasonal studies on CH₄ concentrations in the Amazon basin are required to determine the main drivers of riverine CH₄ dynamics.

**Conclusion**

This study presents coupled, high resolution spatial measurements of ρCO₂, CH₄, and 222Rn of the major tributaries of the central Amazon basin on a scale of ~100 km. Relationships suggest that pore-water may be a relevant source of CO₂ and CH₄ to the receding black and clear water tributaries of the central Amazon Basin. Igapóes appear to be sources of dissolved CO₂ and CH₄ to the main channels and we hypothesize that a portion of this CO₂ and CH₄ may be derived from draining surrounding soils. While this initial study cannot quantify pore-water exchange rates, it provides a basis for more extensive, quantitative studies on the role of pore-water in the Amazonian carbon cycle.

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