Ambiente & Água - An Interdisciplinary Journal of Applied Science
ISSN 1980-993X – doi:10.4136/1980-993X
www.ambi-agua.net
E-mail: ambi.agua@gmail.com

CO_2 fluxes at the water-atmosphere interface in fluvial environments: an overview of studies in Brazilian rivers

ARTICLES doi:10.4136/ambi-agua.2921

Received: 10 Mar. 2023; Accepted: 17 Jul. 2023

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ABSTRACT

Recent advances in Brazilian scientific production on CO_2 fluxes at the water-atmosphere interface in rivers were reviewed, including estimates of CO_2 partial pressure and fluxes. A total of 17 studies were reviewed. We compiled information regarding the location studied, the methodology used by each author, and the values of CO_2 partial pressure (pCO_2), CO_2 fluxes (FCO_2), and gas exchange coefficient (k) found in each region. The results were spatialized and synthesized. The important role of fluxes in CO_2 degassing and their influence on climate change, as well as the global lack of data on these environments, were the main motivations for this study. The information was scarce, and most studies are focused on the Amazon Basin. However, high-resolution mapping of CO_2 fluxes, at the scale of micro basins and streams, proved to be scarce. We emphasize, therefore, the importance of further studies in the country including other hydrographic regions, and in high resolution. These studies would add to our knowledge of how natural and anthropic processes influence CO_2 flux, in addition to providing better estimates in tropical river systems.

Keywords: climate change, CO_2 emission, CO_2 partial pressure.

Fluxos de CO_2 na interface água - atmosfera em ambientes fluviais: um panorama sobre os estudos nos rios brasileiros

RESUMO

Foram revisados os avanços recentes da produção científica brasileira sobre os fluxos de CO_2 na interface água-atmosfera em ambientes fluviais, incluindo as estimativas de pressão parcial de CO_2 e fluxos de CO_2. Um total de 17 estudos foram revisados. Copilamos informações sobre a localização, a metodologia utilizada por cada autor e os valores da pressão parcial de CO_2 (pCO_2), fluxos de CO_2 (FCO_2) e coeficiente de troca gasosa (k) encontrados em cada região. Os resultados foram espacializados e sintetizados. O importante papel dos rios na desgasseificação de CO_2 e sua influência nas mudanças climáticas, somado à escassez global de dados sobre esses ambientes, foram as principais motivações para a realização desta pesquisa. Foi possível demonstrar a baixa produtividade brasileira e a concentração de estudos na Bacia Amazônica. No entanto, mapeamentos dos fluxos de CO_2 em alta resolução, em escala de microbacias e córregos, se mostraram escassos. Ressaltamos, portanto, a importância de mais estudos no país incluindo outras regiões hidrográficas, e em alta resolução. Estes estudos elucidariam o conhecimento de como os processos naturais e antrópicos influenciam no fluxo de CO2, além de melhores estimativas em sistemas fluviais tropicais.

Palavras-chave: emissão de CO_2, mudanças climáticas, pressão parcial de CO_2.

1. INTRODUCTION

The structure of the Planetary Boundaries (PB) (Rockström *et al.*, 2009) has aroused great interest not only in science but also in politics and has been observed for years. Recent works have shown that climate change has already exceeded safe operation limits and entered a zone of uncertainty (increasing risks) (Persson *et al.*, 2022; Steffen *et al.*, 2015). Carbon dioxide (CO_2) has been identified as one of the most important greenhouse gases responsible for global warming, and emission rates are increasing every year (IPCC, 2022). Therefore, studies have been conducted worldwide to identify potential sources and sinks of CO_2, improve flux estimates, and better understand climate change.

Aquatic ecosystems are important environments for CO_2 gas exchange between the water surface and the atmosphere and play an important role in the carbon cycle (Keller *et al.*, 2020). Global estimates suggest that river systems emit between 112 and 209 Tg C per month into the atmosphere (Liu *et al.*, 2022). According to Gómez-Gener *et al.* (2021), small rivers and streams are critical points in flux estimates in river environments. They account for about 85% of estimated CO_2 emissions in inland waters, even though they represent less than 20% of the freshwater area. This occurs because, once there is a source of carbon input (whether natural or anthropogenic), the hydraulic parameters (such as depth and slope of the channel) and the dynamics of small rivers, influence and amplify the turbulence of the channel, intensifying the processes responsible for gas exchange (Horgby *et al.*, 2019).

Land use and urban impacts on watersheds have also been studied as emission intensifiers in river environments, primarily due to high concentrations of organic matter (OM) (Cheng *et al.*, 2020; Herreid *et al.*, 2021; Tang *et al.*, 2023). Another hypothesis is that tropical regions contribute most of the freshwater CO_2 fluxes (Wen *et al.*, 2021). Liu *et al.* (2022), show that tropical rivers have higher CO_2 fluxes (3,220 g C m^{-2} y^{-1}) than Arctic (1,750 g C m^{-2} y^{-1}) and temperate (2,280 g C m^{-2} y^{-1}) rivers. Thus, rivers have become extremely relevant ecosystems, specifically with respect to CO_2 fluxes and their contribution to climate change. However, estimates of CO_2 fluxes still have great uncertainties (Zhang *et al.*, 2020). Thus, recently, rivers are being seen as important ecosystems in CO_2 fluxes, although their estimates still have large uncertainties (Zhang *et al.*, 2020). In addition, studies on spatial and temporal variations, mainly in small river basins, have gained prominence since CO_2 emissions vary considerably in space and time due to hydrodynamics, which strongly influences biogeochemistry and seasonal variations (Barefoot *et al.*, 2019; Zimmer and McGlynn, 2018).

Despite the great importance, studies of CO_2 fluxes at the water-atmosphere interface, focusing on river environments, are still rare and sparse in Brazil. This is partly due to the cost of analyses and the lack of research infrastructure and support, common in developing countries. However, a critical knowledge gap, especially in the Amazon River Basin, remains the importance of rivers and streams as atmospheric sources of CO_2. According to Richey *et al.* (2002), although the Amazon River systems have high fluxes, they may not significantly contribute to the global carbon balance since estimates suggest that their CO_2 emissions are nearly equal to the amount of carbon sequestered. In this manner, the overall balance tends to nullify.

This study demonstrates the recent status of Brazilian scientific production on CO_2 fluxes in river systems. The main methods currently used were evaluated and discussed, and the variables related to degassing were synthesized to provide estimations of the CO_2 fluxes found in Brazilian rivers. From the analysis of the studies found, knowledge gaps on the subject in the Brazilian territory were identified.

2. MATERIAL AND METHODS

Table 1 shows the workflow of this study. The literature review was based on the methodology described by Clark *et al.* (2020). The research was conducted on the Scopus, Scielo, and Periódicos CAPES platforms. The keywords used in the bibliographic search were defined using tools such as Systematic Review Accelerator (SRA) using Word Frequency Analyzer and VOSviewer. The most frequently found words were “dissolved inorganic carbon”, “carbon dioxide”, “CO_2 partial pressure”, “CO_2 emission” and “CO_2 flow”. These keywords were used together with the transversal word “water” and the Boolean operator “AND”. At the end of the searches, a total of 803 studies were cataloged.

Shared citations between research platforms (duplicates) were checked and removed using Mendeley and SRA – Duplicator. Since the objective of the research is to demonstrate the recent status of scientific advances in Brazil, a period of approximately 20 years was defined for analysis. Therefore, studies written before 2000 and research not conducted in Brazilian aquatic environments (uncontained), were also excluded using the SRA-Helper and Mendeley tools. After filtering, the database consisted of 105 studies published between 2000 and 2022 in aquatic environments on Brazilian territory.

The publications included in the database were classified into different types of aquatic environments based on the title, abstract, and keyword, such as coastal-marine environments (28 studies), reservoirs (26 studies), lagoon environments (27 studies), and river environments (24 studies). Only the river environments were evaluated and reviewed in the study. Of the 24 studies of the river, only 17 contained pCO_2 and/or FCO_2, which were analyzed (Table S1 in Supplementary Material).

Table 1. Summary of workflow and results obtained. * Total of deleted files = duplicates + uncontained. SRA = Systematic Review Accelerator.

Workflow	Taks	Tool used	Number
Systematic Research	Number of databases searched	Scopus, Scielo and Periódicos CAPES	3
	Number of keywords used	Frequency Analyzer and VOSviewer	6
	Number of files found	-	803
File sorting	Number of duplicate files	SRA – Duplicator and Mendeley	235
	Total of deleted files*	SRA-Helper and Mendeley	698
Database Formation	Number of studies qualitatively synthesized	SRA-Helper and Mendeley	105
	Number of full-text articles meta-analyzed	Mendeley	24
Analysis	Number of full-text articles extracted	Mendeley	17

3. RESULTS AND DISCUSSION

3.1. Bibliographic research

Figure 1 shows the spatial distribution of the study and the number of publications per year. In the last 20 years, the number of annual publications on CO_2 fluxes in the river has not exceeded four articles per year, which explains the deficit of studies in river environments in Brazil. According to the research conducted in this work, the majority of the 12 Brazilian Hydrographic Regions have not presented any data on CO_2 fluxes. Of the works found, most were in the Amazon Basin, mainly in the central region of the basin in the state of Amazon (AM).

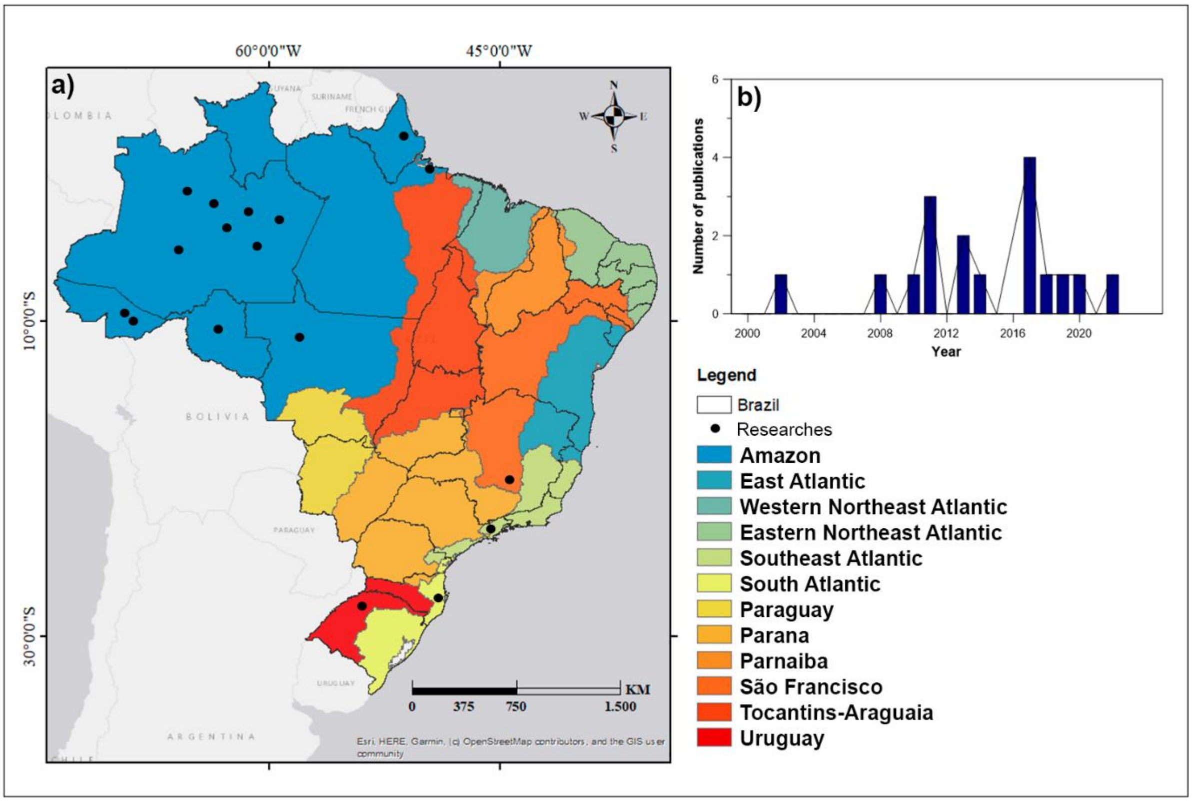

Figure 1. Distribution of research and publications number over the last 20 years in Brazil. a) hydrographic regions of Brazil with the location of the studies found and b) number of publications over the years.

3.2. Analytical methods

Different techniques are available for both direct and indirect measurements of pCO_2 and FCO_2. Currently, there is no consensus on the different methods used in river environments. Table 2 shows the methods used in the analyzed studies.

The partial pressure of CO_2 corresponds to the saturation degree between a water sample and gaseous CO_2 (Dickson, 2010). Direct methods involve two analytical steps: (i) headspace and (ii) gas-phase analysis. The headspace technique concerns the equilibrium relationship between the liquid and gas phases, which in turn follows Henry's Law. The equilibrium can be obtained by an equilibrator (without limitation of water volume) or even by glass vials or syringes (with limitation of water volume). After the equilibration time, the gaseous phase is measured in a gas analyzer. Indirect measurements, in turn, are performed from the thermodynamic equilibrium using the dissolution constants and at least some variables that make up the carbonate system, such as pH, total alkalinity (TA), and dissolved inorganic carbon (DIC).

Table 2. Description and comparison of the methods used. pCO_2 = CO_2 partial pressure and FCO_2 = CO_2 fluxes at the water-atmosphere interface. * = value obtained with floating chambers ** = average value obtained for the Amazon with floating chambers; – no data and ^{a} = not specified.

Reference	**River**	**Basin**	**Region**	**pCO_2**	**FCO_2**	**k_{600}**
(Abril *et al.*, 2014)	Amazon Central River	Amazon	AM	Headspace and infrared gas analyzer	Theoretical diffusion model	**
(Alin *et al.*, 2011)	Amazon River	Amazon	AM	Headspace and infrared gas analysis	Floating Chamber	*
(Almeida *et al.*, 2017)	Madeira River	Amazon	AM	pH - DIC	Theoretical diffusion model	Equation 1 and Equation 9
(Amaral *et al.*, 2019)	Negro and Solimões River	Amazon	AM	Headspace and infrared gas analyzer	Theoretical diffusion model	Equation 1
(Andrade *et al.*, 2011)	8 Streams (Indaiá watershed)	Southeast Atlantic	SP	pH - DIC	-	-
(Lopes Da Silva *et al.*, 2007)	15 watershed Florianópolis Island	South Atlantic	SC	pH - DIC	-	-
(Machado *et al.*, 2022)	Bule watershed	San Francisco	MG	pH - TA	Theoretical diffusion model	Equation 3
(Neu *et al.*, 2011)	Amazon River	Amazon	MT	Headspace and gas chromatography	Floating Chamber	-
(Rasera *et al.*, 2008)	Ji-Paraná River	Amazon	RO	-	Floating Chamber	-
(Rasera *et al.*, 2013)	Amazon River	Amazon	AM	Headspace and gas chromatography / pH - TA	Floating Chambers / Theoretical diffusion model	*
(Richey *et al.*, 2002)	Amazonia Central River	Amazon	AM	-	Floating Chamber	*
(Rosa *et al.*, 2017)	Cumaru, São João, and Pachibá Streams	Amazon	PA	Headspace and gas chromatography	Floating Chamber	-
(Salimon *et al.*, 2013)	Purus River	Amazon	AC	Headspace and infrared gas analyzer	Theoretical diffusion model	Alin *et al*. 2011^a
(Sawakuchi *et al.*, 2017)	Amazon Low, Xingu and Tapajos River	Amazon	AP	Headspace and infrared gas analyzer	Floating Chamber	*
(Scofield *et al.*, 2016)	Negro River	Amazon	AM	Headspace and infrared gas analyzer	Theoretical diffusion model	Equation 1
(Sorribas *et al.*, 2017)	Taboão Creek Basin	Uruguay	RS	pH - DIC	Theoretical diffusion model	Equation 5, 7, 8 and 9
(Sousa *et al.*, 2011)	Acre River	Amazon	AC	pH - DIC	-	-

One of the most important studies discussing indirect pCO_2 is that of Abril *et al.* (2015), in which it was shown that environments with low pH (<6.0) and high concentrations of organic matter can interfere with modeling from the carbonate system and produce an overestimation of pCO_2 and consequently atmospheric emissions. On the other hand, headspace techniques are sometimes costly, and difficult-to-access environments can make studies using this methodology infeasible. Moreover, it is still necessary to use the equipment to measure gas samples. Therefore, indirect calculation of pCO_2 is still considered a useful tool for flux estimation and is used and accepted by several authors, since its prudent use and understanding of its limitations allows the assessment of the orders of magnitude in which fluxes fit.

The magnitude and direction of CO_2 fluxes are proportional to the difference in CO_2 gas concentration between the water-atmosphere interface and the gas exchange coefficient (k). Direct flux measurements can be made using, for example, (i) a floating chamber (Frankignoulle *et al.*, 1998); (ii) the correlation of turbulent eddies (McGillis *et al.*, 2001); (iii) the flow gradient (Zappa *et al.*, 2003) or (iv) volatile tracers (Raymond *et al.*, 2012; Richey *et al.*, 2002). The correlation of turbulent eddies and the flow gradient methods are more appropriate and used for coastal and marine environments, not being methodologies commonly used in river systems. The floating chamber has been most commonly used in river systems due to its low cost, ability to measure in a short time, and simplicity. The main criticisms and discussions of this method are the possible interference of the floating chamber in surface turbulence and consequently in the values of k (Kokic *et al.*, 2018; Lorke *et al.,* 2015; Raymond and Cole, 2001). However, Kremer *et al.* (2003), obtained consistent values using this method. In Brazil, this technique is widely used.

The indirect method of FCO_2 is based on the theoretical diffusion model, which is based on the difference between CO_2 concentrations in water and air and the gas exchange coefficient (k) (Liss and Slater, 1974). The gas exchange coefficient (k) corresponds to the gas transfer rate and can be determined using empirical equations. Currently, there is a debate about the importance of a good measurement of k in rivers. A common application is to parameterize k to k_{600} by normalizing with the Schmidt number (Sc), which, in turn, corresponds to the ratio between the viscosity of the liquid and the diffusion constant of the CO_2 gas at a given temperature and salinity (Jähne *et al.*, 1987). The Schmidt number for carbon dioxide (Sc_{CO2}) in freshwater and at a temperature of 20°C is equal to 600 (Sc_{CO2} (20°C) = 600). Different equations for calculating k in fluvial environments are discussed in the literature (Raymond *et al.*, 2012).

In rivers, k values are strongly influenced by water turbulence, which in turn can be influenced by flow rate and flow velocity, channel slope as well as friction generated on the surface due to wind speed, for example (Butman and Raymond, 2011). In a large hydrographic watershed, the wind has a large influence on the value of k. However, in small rivers and streams, wind velocity becomes less important and can be neglected, and the effect of water friction on the river bottom and current velocity predominate in the values of k (Alin *et al.*, 2011). Thus, the hydraulic and geomorphological parameters become more important. The shallower the depth of a river, the greater the friction from the bottom, and the greater the values of k (Raymond *et al.*, 2012). The slope of the channel also becomes a relevant factor because the greater the slope, the greater the flow velocity, which increases the values of k.

Several equations for the calculation of k_{600} can be found in the literature. Table 3 shows a compilation of the main equations currently found in the literature. Among the studies using k_{600}, the equation by Alin *et al.* (2011) based on wind velocity was the most used, followed by the equations by Raymond *et al.* (2012) using slope and flow velocity. Studies comparing the values of k_{600} using different methods are extremely scarce, although there is evidence that the hydraulic parameters are extremely important factors in the correct estimation of k_{600}, as shown by Raymond *et al.* (2012). Another important discussion is the fact that many studies use static values of k_{600} for the entire watershed. Alin *et al.* (2011) conclude in their study on the Amazon River that small rivers have a large variability in the value of k_{600}, highlighting the importance of hydraulic parameters. Ulseth *et al.* (2019) demonstrate the relevance of slope in small rivers, especially in mountainous areas, and conclude that increasing slope increases the rate of energy dissipation, which in turn increases flow. Thus, many rivers may have been underestimated by using a k_{600} for the entire length of the watershed. Therefore, the importance of further investigation of the k_{600} and comparative studies on the methods is emphasized.

Table 3. Main k_{600} measurement methods. Average wind speed at 10 m above the surface ($\bar{u}_{10}$, m s^{-1}); water current velocity (V, m s^{-1}), water depth (D, m), discharge (Q, m^3 s^{-1}), stream slope (S, m m^{-1}), Froude number ($Fr = V/(gD)^{0,5}$) and energy dissipation rate ($eD = gSv$, m^2 s^{-3} where g = acceleration due to gravity (9.81 m s^{-1}); $^{a}eD < 0.02$ and $^{b}eD > 0.02$).

	Equation	References
1.	$k_{600} = 4.46 + 7.11\ \bar{u}_{10}$	(Alin *et al.*, 2011)
2.	$k_{600} = 25.12 + 2.77\ \bar{u}_{10}$	(Alin *et al.*, 2011)
3.	$k_{600} = 13.82 + 35\ V$	(Alin *et al.*, 2011)
4.	$k_{600} = 7.98 + 5.84\ \bar{u}_{10} + 36\ V$	(Alin *et al.*, 2011)
5.	$k_{600} = (VS)^{0.89}\ D^{0.54}\ 5037$	(Raymond *et al.*, 2012)
6.	$k_{600} = 5937\ (1 - 2.54\ Fr^2)\ (VS^{0.89})\ D^{0.58}$	(Raymond *et al.*, 2012)
7.	$k_{600} = 1162 \times S^{0.77}\ V^{0.85}$	(Raymond *et al.*, 2012)
8.	$k_{600} = (VS)^{0.76}\ 951.5$	(Raymond *et al.*, 2012)
9.	$k_{600} = VS\ 2841 + 2.02$	(Raymond *et al.*, 2012)
10.	$k_{600} = 929\ (VS)^{0.75}\ Q^{0.011}$	(Raymond *et al.*, 2012)
11.	$k_{600} = 4725\ (VS)^{0.86}\ Q^{-0.14}\ D^{0.66}$	(Raymond *et al.*, 2012)
12.	$\ln[k_{600}] = 3.10 + 0.35\ \ln[eD]^{a}$	(Ulseth *et al.*, 2019)
13.	$\ln[k_{600}\ ] = 6.43 + 1.18\ \ln[eD]^{b}$	(Ulseth *et al.*, 2019)

3.3. CO_2 fluxes in rivers in Brazilian territory

Table 4 summarizes the values reported in the Brazilian area. Many studies have shown that rivers are environments that are supersaturated with CO_2 compared to the atmosphere (Wen *et al.*, 2021). In the studies examined, the variation of pCO_2 ranged from 141 – 26,975 µatm. Despite methodological differences, flow velocity was cited as one of the most important factors influencing the magnitude, with high flow episodes generally showing higher pCO_2. Channel slope (Sorribas *et al.*, 2017), lithology (Machado *et al.*, 2022), vegetation, flooded areas, DO concentration, and water temperature (Amaral *et al.*, 2019) were also identified as important factors influencing pCO_2. The anthropogenic impact was studied by (Andrade *et al.*, 2011; Lopes Da Silva *et al.*, 2007), and they found that rivers that drain urban areas have high values compared to non-urban areas, showing the impact of organic matter as an influencing factor on the increase of pCO_2. The high variability in pCO_2 values supports the hypothesis that in fluvial environments, hydro-geomorphological changes along the river channel lead to changes in pCO_2 values, supporting the idea that general estimates for a large watershed may lead to underestimates of pCO_2 given the importance of small rivers and streams (Ward *et al.*, 2017).

Table 4. Values comparison found in studies. pCO_2 = CO_2 partial pressure and FCO_2 = CO_2 fluxes at the water-atmosphere interface. – no data. a = 210 T C y^{-1}; b = 641 – 12,553 (mg m^{-2} d^{-1}); c = 0.44 g C m^{-2} y^{-1}; d = 1.2 Mg C ha^{-1} y^{-1} (470 Tg C y^{-1}).

Reference	**River**	**Basin**	**Region**	**pCO_2**	**FCO_2**	**K_{600}**
				µatm	mmol m^{-2} d^{-1}	cm h^{-1}
(Abril *et al.*, 2014)	Amazon Central River	Amazon	AM	413 - 12,092	a	15 - 30
(Alin *et al.*, 2011)	Amazon River	Amazon	AM	141 –12,616	3.5 - 1,229	1.0 - 71.1
(Almeida *et al.*, 2017)	Madeira River	Amazon	AM	835 - 9,694	b	10.9 - 14.4
(Amaral *et al.*, 2019)	Negro and Solimões River	Amazon	AM	307 - 7,527	-9.3 - 1,128	4.5 - 38.2
(Andrade *et al.*, 2011)	8 Streams (Indaiá watershed)	Southeast Atlantic	SP	492 - 5,073	-	-
(Lopes da Silva *et al.*, 2007)	15 watershed Florianópolis Island	South Atlantic	SC	377 - 2,145	-	-
(Machado *et al.*, 2022)	Bule Stream	San Francisco	MG	738 – 5,568	43.4 - 683.4	12.9 - 13.3
(Neu *et al.*, 2011)	Amazon River	Amazon	MT	6,491 - 14,976	c	-
(Rasera *et al.*, 2008)	Ji-Paraná River	Amazon	RO	-	51.8 - 1,091	-
(Rasera *et al.*, 2013)	Amazon River	Amazon	AM	259 - 7,808	-17.28 - 1,056	1.8 - 38.3
(Richey *et al.*, 2002)	Amazonia Central River	Amazon	AM	4,350 - 5,000	d	5.0 - 9.6
(Rosa *et al.*, 2017)	Cumaru, São João, and Pachibá Streams	Amazon	PA	2,265 - 26,974	293 - 6,510	-
(Salimon *et al.*, 2013)	Purus River	Amazon	AC	780 - 4,029	15.55 - 686	-
(Sawakuchi *et al.*, 2017)	Amazon Low, Xingu and Tapajos River	Amazon	AP	449 - 6,148	65.66 - 1,492	15.8 - 54.3
(Scofield *et al.*, 2016)	Negro River	Amazon	AM	710 - 3,275	96 - 253	15.2
(Sorribas *et al.*, 2017)	Taboão Creek basin	Uruguay	RS	385 - 3,962	1,555	145
(Souza *et al.*, 2011)	Acre River	Amazon	AC	2,494 - 6,493	-	-

The estimated global variation of k_{600} in the river is calculated to be 8-33 cm h^{-1}, and for large tropical and temperate rivers, it is 5-31 cm h^{-1} (Li *et al.*, 2019). The values reported in the studies were extremely wide, sometimes lower or higher than the global estimates. The magnitude of k_{600} has generated much debate, but it is known that this parameter is influenced by several physical variables, which increases its variation along the channel. Hilly terrain, high flow velocities, channel bottom roughness, and water depth are extremely influential factors on k_{600} values, especially in small rivers and streams where shallow water increases turbulence due to high channel bottom shear. On this basis, Ward *et al.* (2017) report that the probability that current global CO_2 flux budgets are underestimated due to a lack of budgets and a poor understaning of the role of small rivers is due to the high variability of k_{600} in smaller rivers (< 100 meters).

In the Amazon Basin, where most of the studies dealt with in Brazil, not all studies have considered k_{600} variations along the river channel. In 2013, studies in the central region of the basin included small rivers in their estimates (Rasera *et al.*, 2013). Another factor in the Amazon Basin is the inclusion of the lower Amazon River, which according to Sawakuchi *et al.* (2017), had higher fluxes than previous estimates for the entire basin (Richey *et al.*, 2002).

For the other regions of the country, there are isolated and specific studies that make a broader and deeper interpretation impossible and show the existing gap in Brazil. However, the common fact observed in this review is the high pCO_2 values, indicating C supersaturation in the observed fluvial environments. It is worth emphasizing the importance of small and large scales studies, including temporal assessment to visualize the flux variations with hydrography, and spatial assessment to obtain a deeper understanding of the variables affecting the dynamics of CO_2 fluxes.

4. CONCLUSIONS

The literature search showed a scarcity of studies on CO_2 fluxes along the numerous hydrographic basins of the Brazilian territory, highlighting the need for further studies, especially in small rivers and streams. The analysed river systems exhibited significant variation in FCO_2. Among the studies utilizing the theoretical diffusion model, a scant number employed hydraulic parameters to calculate the k_{600}, with only two studies employing different equations in their estimations. Direct methods for measuring fluxes, the floating chamber were widely utilized. Few studies were identified concerning small rivers and streams, and in some cases, solely reporting pCO_2 values.

Although most studies are conducted in the Amazon River Basin, this does not mean that there is a large number of research works in the region. The Amazon Basin is known worldwide, and knowledge and accurate estimation of its fluxes are extremely important in the context of global climate change. However, the results presented in this study show that knowledge and estimates of fluxes in other regions of the country need to be expanded. In addition, due to the variability of k values along the channel, the importance of high-resolution studies, on a scale of small rivers and streams is emphasized to better understand how natural and anthropic factors, such as different biomes, zones climatic conditions and changes in land use, can influence the behavior of CO_2 fluxes.

Thus, based on this bibliographic survey, two major gaps in knowledge about CO_2 fluxes in Brazilian river systems are highlighted (i) the carrying out of studies that cover other Brazilian basins besides the Amazon Basin and (ii) the inclusion of an estimation of fluxes using high-resolution mapping, that is, on a scale of small and micro basins. This study aimed to contribute not only to the identification of these gaps but also to highlight the importance of small rivers and streams in the dynamics of CO_2 fluxes in continental environments.

5. ACKNOWLEDGEMENTS

This study was funded by institutions Carlos Chagas Foundation Son of Research Support of the State of Rio de Janeiro (FAPERJ) – E-26/200.695/2021 (262375).

6. REFERENCES

ABRIL, G.; BOUILLON, S.; DARCHAMBEAU, F.; TEODORU, C. R.; MARWICK, T. R.; TAMOOH, F. *et al.* Technical note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters. **Biogeosciences**, v. 12, n. 1, p. 67–78, 2015. https://doi.org/10.5194/bg-12-67-2015

ABRIL, G.; MARTINEZ, J.-M.; ARTIGAS, L. F.; MOREIRA-TURCQ, P.; BENEDETTI, M. F.; VIDAL, L. *et al.* Amazon River carbon dioxide outgassing fuelled by wetlands. **Nature**, v. 505, n. 7483, p. 395–398, 2014. https://doi.org/10.1038/nature12797

ALIN, S. R.; RASERA, M. D. F. F. L.; SALIMON, C. I.; RICHEY, J. E.; HOLTGRIEVE, G. W.; KRUSCHE, A. V. *et al.* Physical controls on carbon dioxide transfer velocity and flux in low-gradient river systems and implications for regional carbon budgets. **Journal of Geophysical Research: Biogeosciences**, v. 116, n. 1, 2011. https://doi.org/10.1029/2010JG001398

ALMEIDA, R. M.; PACHECO, F. S.; BARROS, N.; ROSI, E.; ROLAND, F. Extreme floods increase CO2 outgassing from a large Amazonian river. **Limnology and Oceanography**, v. 62, n. 3, p. 989–999, 2017. https://doi.org/10.1002/lno.10480

AMARAL, J. H. F.; FARJALLA, V. F.; MELACK, J. M.; KASPER, D.; SCOFIELD, V.; BARBOSA, P. M. *et al.* Seasonal and spatial variability of CO2 in aquatic environments of the central lowland Amazon basin. **Biogeochemistry**, v. 143, n. 1, p. 133–149, 2019. https://doi.org/10.1007/s10533-019-00554-9

ANDRADE, T. M. B.; CAMARGO, P. B.; SILVA, D. M. L.; PICCOLO, M. C.; VIEIRA, S. A.; ALVES, L. F. *et al.* Dynamics of dissolved forms of carbon and inorganic nitrogen in small watersheds of the coastal Atlantic forest in southeast Brazil. **Water, Air, and Soil Pollution**, v. 214, n. 1–4, p. 393–408, 2011. https://doi.org/10.1007/s11270-010-0431-z

BAREFOOT, E.; PAVELSKY, T. M.; ALLEN, G. H.; ZIMMER, M. A.; MCGLYNN, B. L. Temporally variable stream width and surface area distributions in a headwater Catchment. **Water Resources Research**, v. 55, n. 8, p. 7166–7181, 2019. https://doi.org/10.1029/2018WR023877

BUTMAN, D.; RAYMOND, P. Significant efflux of carbon dioxide from streams and rivers in the United States. **Nature Geoscience**, v. 4, p. 839–842, 2011. https://doi.org/10.1038/ngeo1294

CHENG, G.; WANG, M.; CHEN, Y.; GAO, W. Source apportionment of water pollutants in the upstream of Yangtze River using APCS–MLR. **Environmental Geochemistry and Health**, v. 42, n. 11, p. 3795–3810, 2020. https://doi.org/10.1007/s10653-020-00641-z

CLARK, J.; GLASZIOU, P.; DEL MAR, C.; BANNACH-BROWN, A.; STEHLIK, P.; SCOTT, A. M. A full systematic review was completed in 2 weeks using automation tools: a case study. **Journal of Clinical Epidemiology**, v. 121, p. 81–90, 2020. https://doi.org/10.1016/j.jclinepi.2020.01.008

DICKSON, A. G. The carbon dioxide system in seawater: equilibrium chemistry and measurements. *In:* GATTUSO, Jean-Pierre *et al.* **Guide to best practices for ocean acidification research and data reporting.** Publications Office of the European Union, 2010.

FRANKIGNOULLE, M.; ABRIL, G.; BORGES, A.; BOURGE, I.; CANON, C.; DELILLE, B. *et al.* Carbon Dioxide Emission from European Estuaries. **Science**, v. 282, n. 5388, p. 434–436, 1998. https://doi.org/10.1126/science.282.5388.434

GÓMEZ-GENER, L.; ROCHER-ROS, G.; BATTIN, T.; COHEN, M. J.; DALMAGRO, H. J.; DINSMORE, K. J. *et al.* Global carbon dioxide efflux from rivers enhanced by high nocturnal emissions. **Nature Geoscience**, v. 14, n. 5, p. 289–294, 2021. https://doi.org/10.1038/s41561-021-00722-3

HERREID, A. M.; WYMORE, A. S.; VARNER, R. K.; POTTER, J. D.; MCDOWELL, W. H. Divergent Controls on Stream Greenhouse Gas Concentrations Across a Land-Use Gradient. **Ecosystems**, v. 24, n. 6, p. 1299–1316, 2021. https://doi.org/10.1007/s10021-020-00584-7

HORGBY, Å.; BOIX CANADELL, M.; ULSETH, A. J.; VENNEMANN, T. W.; BATTIN, T. J. High-Resolution Spatial Sampling Identifies Groundwater as Driver of CO2 Dynamics in an Alpine Stream Network. **Journal of Geophysical Research: Biogeosciences,** v. 124, n. 7, p. 1961–1976, 2019. https://doi.org/10.1029/2019JG005047

IPCC. **Climate Change 2022**: Mitigation of Climate Change - Working Group III Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. 2022. 1991 p. Available at: https://www.ipcc.ch/report/ar6/wg3/downloads/report/IPCC_AR6_WGIII_FullReport.pdf Access: 23 jan. 2023.

JÄHNE, B. *et al.* On the parameters influencing air-water gas exchange. **Journal of Geophysical Research,** v. 92, n. C2, p. 1937–1949, 1987. https://doi.org/10.1029/JC092iC02p01937

KELLER, P. S.; CATALÁN, N.; VON SCHILLER, D.; GROSSART, H. P.; KOSCHORRECK, M.; OBRADOR, B. *et al.* Global CO2 emissions from dry inland waters share common drivers across ecosystems. **Nature Communications**, v. 11, n. 1, 2020. https://doi.org/10.1038/s41467-020-15929-y

KOKIC, J.; SAHLÉE, E.; SOBEK, S.; VACHON, D.; WALLIN, M. High spatial variability of gas transfer velocity in streams revealed by turbulence measurements. **Inland Waters**, 2018. https://dx.doi.org/10.1080/20442041.2018.1500228

KREMER, J. N.; NIXON, S. W.; BUCKLEY, B.; ROQUES, P. Technical Note: Conditions for Using the Floating Chamber Method to Estimate Air-Water Gas Exchange. **Estuaries**, v. 26, n. 4A, 2003.

LI, S.; MAO, R.; MA, Y.; SARMA, V. V. S. S. Gas transfer velocities of CO2 in subtropical monsoonal climate streams and small rivers. **Biogeosciences**, v. 16, n. 3, p. 681–693, 2019. https://doi.org/10.5194/bg-16-681-2019

LISS, P.; SLATER, P. Flux of Gases across the Air-Sea Interface. **Nature**, v. 247, p. 181–184, 1974. https://doi.org/10.1038/247181a0

LIU, S.; KUHN, C.; AMATULLI, G.; AHO, K.; BUTMAN, D. E.; ALLEN, G. H. *et al.* The importance of hydrology in routing terrestrial carbon to the atmosphere via global streams and rivers. **Earth, Atmospheric, and Planetary Sciences**, v. 119, n. 11, 2022. https://doi.org/10.1073/pnas.2106322119

LOPES DA SILVA, D. M.; OMETTO, J. P. H. B.; LOBO, G. A.; LIMA, W. P.; SCARANELLO, M. A. *et al.* Can Land Use Changes Alter Carbon, Nitrogen and Major Ion Transport In Subtropical Brazilian Streams? **Scientia Agricola**, v. 64, n. 4, 2007. https://doi.org/10.1590/S0103-90162007000400002

LORKE, A.; BODMER, P.; NOSS, C.; ALSHBOUL, Z.; KOSCHORRECK, M.; SOMLAI-HAASE, C. *et al.* Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters. **Biogeosciences**, v. 12, p. 7013–7024, 2015. https://doi.org/10.5194/bg-12-7013-2015

MACHADO, D. V.; ALMEIDA, G. S.; MARQUES, E. D.; SILVA-FILHO, E. V. Carbon fluxes in a carbonate rock dominated micro basin of the Quadrilátero Ferrífero, Brazil. **Environmental Science and Pollution Research**, v. 29, n. 50, p. 76177–76191, 2022. https://doi.org/10.1007/s11356-022-21155-4

MCGILLIS, W. R.; EDSON, J. B.; HARE, J. E.; FAIRALL, C. W. Direct covariance air-sea CO_2 fluxes. **Journal of Geophysical Research: Oceans**, v. 106, n. C8, p. 16729–16745, 2001. https://doi.org/10.1029/2000JC000506

NEU, V.; NEILL, C.; KRUSCHE, A. V. Gaseous and fluvial carbon export from an Amazon forest watershed. **Biogeochemistry**, v. 105, n. 1, p. 133–147, 2011. https://doi.org/10.1007/s10533-011-9581-3

PERSSON, L.; CARNEY ALMROTH, B. M.; COLLINS, C. D.; CORNELL, S.; DE WIT, C. A.; DIAMOND, M. L. et al. Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. **Environmental Science and Technology**, v. 56, n. 3, p. 1510–1521, 2022. https://doi.org/10.1021/acs.est.1c04158

RASERA, M. F. F. L.; BALLESTER, M. V. R.; KRUSCHE, A. V.; SALIMON, C.; MONTEBELO, L. A. *et al.* Estimating the surface area of small rivers in the southwestern amazon and their role in CO2 outgassing. **Earth Interactions**, v. 12, n. 6, 2008. https://doi.org/10.1175/2008EI257.1

RASERA, M. DE F. F. L.; KRUSCHE, A. V.; RICHEY, J. E.; BALLESTER, M. V. R.; VICTÓRIA, R. L. Spatial and temporal variability of pCO2 and CO2 efflux in seven Amazonian Rivers. **Biogeochemistry**, n. 116, n. 1–3, p. 241–259, 2013. https://doi.org/10.1007/s10533-013-9854-0

RAYMOND, P. A.; COLE, J. J. Technical Notes and Comments Gas Exchange in Rivers and Estuaries: Choosing a Gas Transfer Velocity. **Estuaries**, v. 24, n. 2, 2001.

RAYMOND, P. A.; ZAPPA, C. J.; BUTMAN, D.; BOTT, T. L.; POTTER, J.; MULHOLLAND, P. *et al.* Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. **Limnology and Oceanography: Fluids and Environments**, v. 2, n. 1, p. 41–53, 2012. https://doi.org/10.1215/21573689-1597669

RICHEY, J. E.; MELACK, J. M.; AUFDENKAMPE, A. K.; BALLESTER, V. M.; HESS, L. L. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO2. **Nature,** v. 416, n. 6881, p. 617–620, 2002. https://doi.org/10.1038/416617a

ROCKSTRÖM, J.; STEFFEN, W.; NOONE, K.; PERSSON, Å.; CHAPIN, F. S.; LAMBIN, E. F. *et al.* A safe operating space for humanity. **Nature,** v. 461, n. 7263, p. 472–475, 2009. https://doi.org/10.1038/461472a

ROSA, M. B. S. DA; FIGUEIREDO, R. D. O.; MARKEWITZ, D.; KRUSCHE, A. V.; COSTA, F. F.; GERHARD, P. Evasion of CO2 and dissolved carbon in river waters of three small catchments in an area occupied by small family farms in the eastern Amazon. **Revista Ambi & Agua**, v. 12, n. 4, p. 556, 2017. https://doi.org/10.4136/ambi-agua.2040

SALIMON, C.; DOS SANTOS SOUSA, E.; ALIN, S. R.; KRUSCHE, A. V.; BALLESTER, M. V. Seasonal variation in dissolved carbon concentrations and fluxes in the upper Purus River, southwestern Amazon. **Biogeochemistry,** v. 114, n. 1–3, p. 245–254, 2013. https://doi.org/10.1007/s10533-012-9806-0

SAWAKUCHI, H. O.; NEU, V.; WARD, N. D.; BARROS, M. DE L. C.; VALERIO, A. M.; GAGNE-MAYNARD, W. e tal. Carbon Dioxide Emissions along the Lower Amazon River. **Frontiers in Marine Science**, v. 4, 2017. https://doi.org/10.3389/fmars.2017.00076

SCOFIELD, V.; MELACK, J. M.; BARBOSA, P. M.; AMARAL, J. H. F.; FORSBERG, B. R.; FARJALLA, V. F. Carbon dioxide outgassing from Amazonian aquatic ecosystems in the Negro River basin. **Biogeochemistry,** v. 129, n. 1–2, p. 77–91, 2016. https://doi.org/10.1007/s10533-016-0220-x

SORRIBAS, M. V.; DA MOTTA MARQUES, D.; CASTRO, N. M. DOS R.; FAN, F. M. Fluvial carbon export and CO2 efflux in representative nested headwater catchments of the eastern La Plata River Basin. **Hydrological Processes,** v. 31, n. 5, p. 995–1006, 2017. https://doi.org/10.1002/hyp.11076

SOUSA, E.; SALIMON, C. I.; DE OLIVEIRA FIGUEIREDO, R.; KRUSCHE, A. V. Dissolved carbon in an urban area of a river in the Brazilian Amazon. **Biogeochemistry**, v. 105, n. 1–3, p. 159–170, 2011. https://doi.org/10.1007/s10533-011-9613-z

STEFFEN, W.; RICHARDSON, K.; ROCKSTRÖM, J.; CORNELL, S. E.; FETZER, I.; BENNETT, E. M. *et al.* Planetary boundaries: Guiding human development on a changing planet. **Science**, v. 347, n. 6223, 2015. https://doi.org/10.1126/science.1259855

TANG, W.; XU, Y. J.; NI, M.; LI, S. Land use and hydrological factors control concentrations and diffusive fluxes of riverine dissolved carbon dioxide and methane in low-order streams. **Water Research**, v. 231, n. 119615, 2023. https://doi.org/10.1016/j.watres.2023.119615

ULSETH, A. J.; HALL, R. O.; BOIX CANADELL, M.; MADINGER, H. L.; NIAYIFAR, A.; BATTIN, T. J. Distinct air–water gas exchange regimes in low- and high-energy streams. **Nature Geoscience**, v. 12, n. 4, p. 259–263, 2019. https://doi.org/10.1038/s41561-019-0324-8

WARD, N. D.; BIANCHI, T. S.; MEDEIROS, P. M.; SEIDEL, M.; RICHEY, J. E.; KEIL, R. G. *et al.* Where carbon goes when water flows: Carbon cycling across the aquatic continuum. **Frontiers in Marine Science,** v. 4, 2017. https://doi.org/10.3389/fmars.2017.00007

WEN, Z.; SHANG, Y.; LYU, L.; LI, S.; TAO, H.; SONG, K. A review of quantifying pco2 in inland waters with a global perspective: Challenges and prospects of implementing remote sensing technology. **Remote Sensing**, v. 13, n. 13, 2021. https://doi.org/10.3390/rs13234916

ZAPPA, C. J.; RAYMOND, P. A.; TERRAY, E. A.; MCGILLIS, W. R. Variation in Surface Turbulence and the Gas Transfer Velocity over a Tidal Cycle in a Macro-tidal Estuary. **Estuaries,** v. 26, n. 6, 2003. https://doi.org/10.1007/BF02803649

ZHANG, T.; LI, J.; PU, J.; MARTIN, J. B.; WANG, S.; YUAN, D. Rainfall possibly disturbs the diurnal pattern of CO2 degassing in the Lijiang River, SW China. **Journal of Hydrology**, v. 590, 2020. https://doi.org/10.1016/j.jhydrol.2020.125540

ZIMMER, M. A.; MCGLYNN, B. L. Lateral, Vertical, and Longitudinal Source Area Connectivity Drive Runoff and Carbon Export Across Watershed Scales. **Water Resources Research,** v. 54, n. 3, p. 1576–1598, 2018. https://doi.org/10.1002/2017WR021718

Supplementary Material

Table S1. Studies analyzed and used in the review.
x = data present in the article.

Reference	Region	pCO_2	FCO_2
Abril, *et al.* 2014	AM	x	x
Allin, *et al.* 2011	AM	x	x
Almeida, *et al.* 2017	AM	x	x
Amaral, *et al.* 2019	AM	x	x
Andrade, et al 2010	SP	x	-
Lopes, et al 2020	SC	x	-
Machado, et al 2022	MG	x	x
Neu, et al 2011	MT	x	x
Rasera, et al 2008	RO	-	x
Rasera, et al 2013	AM	x	x
Rickey, et al 2002	AM	x	x
Rosa, et al 2017	PA	x	x
Salimon, *et al.* 2013	AC	x	x
Sawakuch, *et al.* 2017	AP	x	x
Scofield, *et al.* 2016	AM	x	x
Sorribas, *et al.* 2017	RS	x	x
Souza, *et al.* 2011	AC	x	-

Equation 1:

$$FCO_2 = k\,KH\,\Delta pCO_2 \tag{1}$$

Where:

FCO_2 = flux water-air (mmol m^{-2} d^{-1});

k = CO_2 gas transfer rate (m d^{-1});

KH = CO_2 solubility (mmol m^{-3} μatm^{-1});

ΔpCO_2 = pCO_2 water – pCO_2 atmosphere (µatm)

The CO_2 solubility is calculated by Equation 2, where T = temperature in Kelvin.

$$\mathrm{KH} = \mathrm{EXP}\,(-58{,}0931 + 90{,}5069(100/\mathrm{T}) + 22{,}2940 \ln(\mathrm{T}/100)) \quad (2)$$

CO_2 gas transfer rate (k) and the Schmidt number (Sc) (Equations 3, 4, 5, 6, 7 and 8):

$$\mathrm{Sc} = \mathrm{v}/\mathrm{D} \quad (3)$$

$$k = Sc^{-n} \quad (4)$$

$$k_1/k_2 = (Sc_1/Sc_2)^{-n} \quad (5)$$

$$k = k_{600}\,(Sc_{CO2}/600)^{-0.5} \quad (6)$$

$$Sc = A + BT + CT^2 + CT^3 \quad (7)$$

$$Sc_{CO2} = 1911.1 - 118.11\,T + 3.4527\,T^2 - 0.04132\,T^3 \quad (8)$$

Where:

Sc = Schmidt number

v = water viscosity

D = molecular coefficient of the gas

n = exponent of Schmidt number. Depending on the water surface, where 0.5 beings are used for the river system.