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Carbon dioxide and methane emissions across tropical and subtropical inland water ecosystems in Brazil: meta-analysis of general patterns and potential drivers

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ABSTRACT

Carbon dioxide and methane emissions across tropical and subtropical inland water ecosystems in Brazil: meta-analysis of general patterns and potential drivers

Investigations on CO_2 and CH_4 emissions from aquatic systems have increased in the last decades, but most studies focus on high-latitude water bodies, with limited information available for tropical and subtropical zones. Here, we compiled CO_2 and CH_4 emissions by lentic, lotic, and other types of aquatic ecosystems (e.g., floodplains, estuaries, and mangroves) in different biomes in Brazil. We used a literature search of papers published in the last ~30 years to analyze reported emission rates, if they were from the diffusive (DF) and/or ebullitive (EB) pathways, and the most used methods. Most studies were carried out in two biomes (Amazon and Atlantic rainforest). The highest emissions were reported in lentic ecosystems (from 0.05 to 4568 mmol CO_2 m^{-2} day^{-1}, and from 0.19 to 348 mmol CH_4 m^{-2} day^{-1}). The DF pathway was more frequently analyzed, and the floating chamber was the most used measurement method. Our analyses indicated the EB pathway can be significant, especially for CH_4 in shallow waters. There were many missing data for either DF or EB so we used studies that measured both and system depth to estimate the missing values and then used total emissions (DF+EB) to run predictive models. For the CO_2 emissions, pH, water depth, dissolved oxygen, and water temperature were important predictors, whereas the potential drivers for the CH_4 emissions were electrical conductivity and the CO_2 emissions. More data are necessary to more clearly characterize the drivers of the emissions of such gases, further understand the dynamics of their emissions, as well as refine emission inventories on both regional and global scales in tropical regions.

Key words: Brazilian biomes, gas emissions, greenhouse gases, emission pathways, tropical and subtropical aquatic systems

RESUMO

Emissões de dióxido de carbono e metano por ecossistemas aquáticos brasileiros de águas interiores: meta-análise de padrões gerais e fatores intervenientes

Estudos sobre as emissões de CO_2 e CH_4 por ecossistemas aquáticos aumentaram nas últimas décadas, mas a maioria dos estudos enfatizou corpos de água de elevadas latitudes, com informações ainda limitadas disponíveis para zonas tropicais e subtropicais. Neste estudo, compilamos emissões de CO_2 e CH_4 por ambientes lênticos, lóticos e outros tipos de ecossistemas aquáticos (e.g., áreas alagadas, estuários e manguezais) em diferentes biomas no Brasil. Utilizamos uma busca bibliográfica de artigos publicados nos últimos ~30 anos para analisar as taxas de emissão reportadas, se elas foram provenientes das vias difusiva (DF) e/ou ebulitiva (EB), além dos métodos mais comumente utilizados para sua estimativa. A maioria dos estudos foi desenvolvida em dois biomas (Amazônia e Mata Atlântica). As maiores emissões foram reportadas em ambientes lênticos (de 0.05 a 4568 mmol CO_2 m^{-2} dia^{-1}, e de 0.19 a 348 mmol CH_4 m^{-2} dia^{-1}). A via DF foi mais frequentemente analisada e a câmara flutuante foi o método de estimativa mais comumente empregado. Nossas análises indicaram que a via EB pode ser significativa, especialmente para o CH_4 e ambientes mais rasos. Havia muitos dados faltantes ou para DF ou para EB, então utilizamos os estudos que mediram ambas as vias, além da profundidade do ambiente, para estimar os valores faltantes e então *utilizar as emissões totais (DF+EB) para executar modelos preditivos. Para as emissões de CO_2, pH, profundidade da coluna de água, oxigênio dissolvido e temperatura da água foram preditores importantes, enquanto os preditores potenciais para as emissões de CH_4 foram a condutividade elétrica e as próprias emissões de CO_2. Mais dados são necessários para caracterizar mais claramente os fatores intervenientes nas emissões de tais gases, compreender melhor a dinâmica das emissões, assim como refinar os inventários de emissões em escalas regionais e globais em regiões tropicais.*

Palavras chave: *biomas brasileiros, emissão de gases, gases de efeito estufa, vias de emissão, sistemas aquáticos tropicais e subtropicais*

INTRODUCTION

Carbon dioxide (CO_2) and methane (CH_4) are key greenhouse gases (Stanley et al., 2016; Prairie et al., 2018; Keller et al., 2020) that can be emitted by inland water ecosystems (e.g., Schade et al., 2016; Kosten et al., 2018; Santos et al., 2019). According to the Global Monitoring Laboratory from Earth: System Research Laboratories (https://www.esrl.noaa.gov/gmd/ccgg), current (i.e., in January 2022) global atmospheric CO_2 and CH_4 concentrations are approximately 417 ppm and 1901 ppb respectively. CH_4 has a global warming potential 25 times greater per molecule so it is about 10 % as important of a greenhouse gas as CO_2. Several biological processes (e.g., aerobic and anaerobic oxidation of organic matter by aquatic biota, methanogenesis) across different compartments (e.g., water column, sediment, hyporheic zones, and adjacent terrestrial ecosystems such as riparian zones) mediate the occurrence and distribution of CO_2 and CH_4 in lentic (e.g., lakes and reservoirs), lotic (e.g., rivers and streams) and other aquatic ecosystems (e.g., floodplains, estuaries and mangroves) (Hotchkiss et al., 2015; Campos et al., 2016).

Researchers most commonly report CO_2 and CH_4 emissions from inland waters in artic, boreal, alpine, and temperate regions, and thus global estimates could be biased due to the lack of information for tropical and subtropical regions. Tropical and subtropical biomes often occur in developing countries, where the rapid population growth and the changes in land use can increase freshwater CO_2 and CH_4 emissions. In Brazil, emissions from large rivers and artificial reservoirs, which are very common for hydroelectricity generation in the country, are substantial (Fearnside 1995; Demarty & Bastien 2011; Sawakuchi et al., 2014, 2017).

Biological reactions and conversions are important contributors for aquatic CO_2 and CH_4 emissions, but their relative importance is still not fully characterized across contrasting inland water ecosystem types, because they may be controlled by a complex suite of physical and chemical processes (Baker et al., 1999; Hlaváčová et al., 2005). Different environmental conditions, including water properties (e.g., temperature, atmospheric pressure, salinity, dissolved oxygen, pH, alkalinity) as well as morphological, hydrological, and climate characteristics (e.g., width, depth, water velocity, discharge, air temperature, wind velocity) have been used to predict emissions of CO_2 (Nydahl et al., 2020; Keller et al., 2020) and CH_4 (Martinez-Cruz et al., 2017; Ortega et al., 2019).

Deeper and more stagnant aquatic ecosystems can present slow gas transfer velocities at the air-water interface due to the low rates of turbulent mixing. Shallower ecosystems with higher water velocities and wind exposure are usually associated with greater interfacial turbulence and faster gas transfer throughout the water column. Hence, the potential for CO_2 emissions in turbulent aquatic ecosystems can be more relevant than CH_4, since the concentration of dissolved CO_2 is higher than CH_4 due to the contrasting solubility of both gases and the bicarbonate equilibrium which allows CO_2 to assume ionic forms (Abril et al., 2015; Khan et al., 2020). Additionally, turbulence favors more oxic conditions due to the mixing of the water column, and therefore CH_4 production is less likely because higher concentrations of dissolved oxygen interfere with methanogenesis and also promote the oxidation of CH_4 (Robison et al., 2022).

The two main emission pathways for both CO_2 and CH_4 are diffusive (DF) and the ebullitive (EB) fluxes. The diffusive transfer of gases from the water column to the atmosphere is mainly governed by their respective saturation concentrations (Gualtieri & Doria 2008). The DF follows the Fick's Law of Diffusion (Equation 1, Vachon et al., 2010), and encompasses the evasion of the dissolved gases formed in the water column to the atmosphere right from the interface between both compartments (Belger et al., 2011; Xiao et al., 2016; Ortega et al., 2019; Smith & Böhlke 2019).

$$F = k\ Kh\ (pX_{water} - pX_{air}) \quad (1)$$

Where *F* is the gas emission, *k* is the gas exchange velocity, *Kh* is the Henry's coefficient (corrected for salinity, pressure and temperature (ASCE 2007), and pX_{water} and pX_{air} are the gas partial pressures in water and air, respectively. According to Hall and Ulseth (2020), (pX_{water} - pX_{air}) defines the net gas flux in relation to the aquatic ecosystem, being either positive ($pX_{water} > pX_{air}$) with the net gas flux from the water to the atmosphere (i.e., evasion), or negative ($pX_{water} < pX_{air}$) (i.e., influx).

Ebullitive flux in turn occurs when gas supersaturation in the sediments or deeper waters leads to formation of bubbles which rise through the water column and escape to the atmosphere (Belger et al., 2011; Xiao et al., 2016; Ortega et al., 2019; Smith & Böhlke 2019). This process is more common in littoral zones or shallow water bodies because bubbles created in benthic zones of deeper waters can re-dissolve into the water column where methanotrophy can convert the CH_4 to CO_2 before it is released to the atmosphere by DF. While both pathways coexist for CO_2 and CH_4 emissions, DF may be more related to CO_2, because it is less likely to form bubbles given its high solubility in water and the bicarbonate equilibrium.

Researchers have used several methods for direct or indirect estimations of CO_2 and CH_4 emissions (Abril et al., 2015; Lorke et al., 2015; Lesmeister & Koschorreck 2017; Martinsen et al., 2018; Raymond et al., 2012; Vachon & Prairie, 2013). The floating chamber (FC) method uses a chamber floating on the water surface to capture gas as it is released. This method has been applied to different types of aquatic environments and mainly used to estimate the DF pathway of CO_2 or CH_4 (Mannich et al., 2019). The floating chamber and funnel trap (FC+FT) method allows the determination of both DF and EB pathways. The headspace (HD) method, which involves the extraction of gases that are dissolved in water to the gas phase, is simpler than the previous two, as it does not require apparatus deployed on the water surface. The HD estimates potential emissions to the atmosphere via diffusion (Magen et al., 2014; Koschorreck et al., 2020) but misses EB. An even simpler method is the indirect estimation of the emissions using equations (EQ), based on water variables such as stoichiometric and empirical relationships (Butman & Raymond 2011; Abril et al., 2015).

A growing number of studies on CO_2 and CH_4 emissions focus on Brazilian biomes, including the Atlantic rainforest (Noriega & Araujo 2014), Amazon (Almeida et al., 2017), Pantanal (Bergier et al., 2015), Caatinga (Almeida et al., 2016), Pampa (Kosten et al., 2010), and Cerrado (Almeida et al., 2019). Most studies focus on lakes and reservoirs (Kosten et al., 2010), particularly for reservoirs for hydroelectricity production, and most of these studies were conducted at regional or local scales (Sawakuchi et al., 2017; Silva et al., 2018; Kosten et al., 2018). We are aware of no previous publications compiling all the available information in a large tropical/subtropical area to assess general patterns and potential drivers of the emissions. Here, we investigate CO_2 and CH_4 emissions by lentic, lotic, and other types of aquatic ecosystems located in different Brazilian biomes. We analyzed emission rates, most used methods, and potential drivers with a comprehensive literature search of papers published in the last ~30 years. Lastly, we used the drivers and rates to create predictive models of emissions as a starting point to guide a more robust global estimation of such emissions.

MATERIALS AND METHODS

We analyzed published data on inland water ecosystems located in tropical and subtropical regions in major Brazilian biomes (i.e., Atlantic rainforest, Amazon, Pantanal, Caatinga, Pampa, and Cerrado). We searched for scientific publications reporting CO_2 and/or CH_4 emissions from lentic (i.e., lakes and reservoirs), lotic (i.e., rivers and streams, the latter being of 3rd order or lower), or other (i.e., floodplains, estuaries, and mangroves). We selected peer-reviewed papers published in both national and international journals. Conference proceedings, dissertations, theses, books, or book chapters were not considered in this study.

The selection process of the papers was conducted following three steps:

Step 1: Keywords (Table S1, Supporting Information, available at https://www.limnetica.net/en/limnetica) were entered into the Google Scholar search platform between March and April 2020;

Step 2: The results were filtered by years (past ~30 years, from 1988 to 2019) and gases studied (CO_2 and/or CH_4);

Step 3: For each paper, information about the studied sites, types of aquatic ecosystems, biomes, emissions pathways, methods used, as well as physical, chemical, and biological water variables were collected (Table S2.1, Supporting Information available at https://www.limnetica.net/en/limnetica). For 57 selected papers, we identified the biome where each study was carried out and spatially represented the sampling sites in relation to the Brazilian biomes. Further analyses were carried out for a subset of 37 papers in which the authors quantified CO_2 and/or CH_4 emissions (e.g., expressed as mass per area per time) (Table S2.2, Supporting Information available at https://www.limnetica.net/en/limnetica). Emissions with negative values were not considered, because they represent the influx of gases, and not their evasion. When more than one emission estimate was available (e.g., because of temporal variability at a single site), we considered the arithmetic means of the emission values for the data compilation. For our further analysis, we calculated medians due to the possible presence of outliers. All emissions units were standardized to mmol m^{-2} day^{-1} and the raw dataset is fully available as SI (Table S3, Supporting Information available at https://www.limnetica.net/en/limnetica).

According to the Shapiro-Wilk test, most of the dataset had non-normal distribution, so all data were ln-transformed to achieve normal distributions. For an initial screening of the compiled CO_2 and CH_4 emissions, the data were grouped by the representativeness of the Brazilian biomes; by the emission pathways (i.e., DF, DF+EB or not specified); and by the methods used to estimate the emissions (i.e., FC, FC+FT, HD or EQ). We used one-way ANOVA and paired t test to assess significant differences of the CO_2 and CH_4 emissions in relation to the pathways, ecosystem types, and methods used.

We anticipated that the mix of different emission pathways reported by each paper would create bias in our subsequent statistical analyses. Some papers reported only the DF pathway while others reported only the EB. Some did not even specify which pathways were considered in the measurements. To fill these gaps, for the cases with data fully available (i.e., both DF and EB pathways), we calculated the EB/DF ratio for both gases and plotted these ratios against water depth which, as discussed in the introduction, can influence the importance of EB. The regression equation for EB/DF for both gases allowed us to estimate the emission of the respective missing pathway (DF or EB, depending on the case) (SI, Table S4, Supporting Information available at https://www.limnetica.net/en/limnetica). We used multiple linear regression (MLR) models with forward stepwise selection to test relative importance of predictors of total emissions of CO_2 and CH_4, accounting for both DF+EB pathways (either as originally reported by each reference or estimated following the procedure described above). All statistical analyses were performed using the software Statistica 10 (Statsoft, Tulsa, OK, USA).

RESULTS

Among the 57 papers analyzed, 35 %, 16 %, and 49 % reported emissions of CO_2 only, CH_4 only, and both, respectively. There was a diversity of study sites (n = 560), including lakes (30 %), rivers (29 %), reservoirs (17 %), floodplains (14 %), estuaries (5 %), streams (4 %), and mangroves (< 1 %). The sites were located across the major Brazilian biomes (Fig. 1), mainly Amazon (54 %) and Atlantic rainforest (24 %), with other biomes with less than 10 % each (Cerrado, Caatinga, Pantanal, and Pampa).

In the subset of 37 papers with explicit data on CO_2 and/or CH_4 emissions, our dataset had more sites with total emissions available for CO_2 than for CH_4 (n = 184 *versus* n = 68). Data for CO_2 were more common for lotic ecosystems (n = 97), but CH_4 emission rates were more abundant for lentic systems (n = 42). Most papers used a daily frequency measurement strategy with a total temporal extent varying from one month to seven years (SI, Table S2.2).

Most papers for lotic ecosystems did not specify the emission pathways for CO_2 (n = 59, Fig. 2). When such pathways were specified, the DF was most described for all aquatic ecosystems and for both studied gases. The EB was more frequently accounted for lentic ecosystems. Median emissions when only the DF pathway was reported were 107; 583 and 58 mmol m^{-2} day^{-1} for CO_2, and 1.3; 6.1 and 10.8 mmol m^{-2} day^{-1} for CH_4 in lentic, lotic and other ecosystems, respectively. Median DF+EB emissions were generally higher for most ecosystem types, especially for CH_4. For example, considering only paired data (i.e., when both DF and DF+EB were reported in each paper), median CH_4 emissions in lentic ecosystems by the DF+EB pathway was about 3.1 times greater than median DF emissions (n = 17).

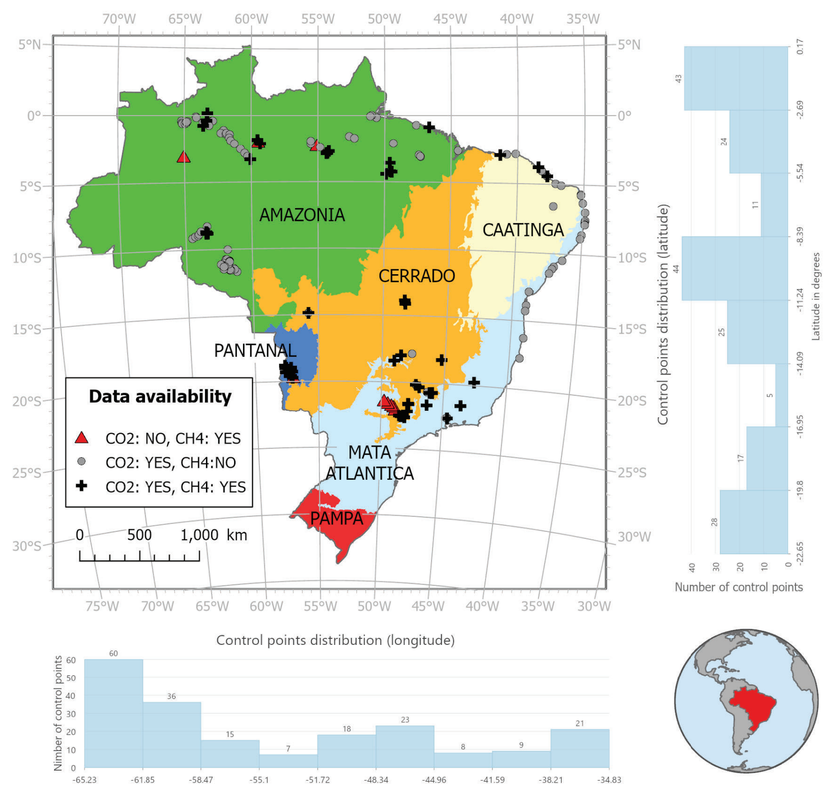

Figure 1. Spatial distribution of the site locations for carbon dioxide (CO_2) and methane (CH_4) resulting from the literature search in different Brazilian inland water ecosystems and the biomes they are in. Sites either had data for just CO_2 (grey circles), just CH_4 (red triangles), or both (black crosses). Histograms indicate latitudinal and longitudinal distributions. *Distribuição espacial dos pontos estudados em relação às emissões de dióxido de carbono (CO_2) e metano (CH_4), resultantes da revisão bibliográfica em diferentes ecossistemas aquáticos brasileiros de águas interiores, além dos biomas nos quais eles estão localizados. Os dados disponíveis se referem apenas ao CO_2 (círculos cinzas), apenas ao CH_4 (triângulos vermelhos) ou a ambos os gases (cruzes pretas). Os histogramas indicam as distribuições de latitudes e longitudes.*

In lentic and lotic ecosystems, the FC method for the quantification of CO_2 (medians of 102 and 237 mmol m^{-2} day^{-1}, respectively) and CH_4 (medians of 1.6 and 9.1 mmol m^{-2} day^{-1}) emissions (Fig. 3) was used most. For other ecosystems, the most common strategy was the use of EQ for CO_2, and the HD method for CH_4. We did not find data on emissions quantified by the FC+FT method in lotic ecosystems. However, the FC+FT method was used in lentic and other ecosystems, with usually higher estimates for both gases when compared to the other methods.

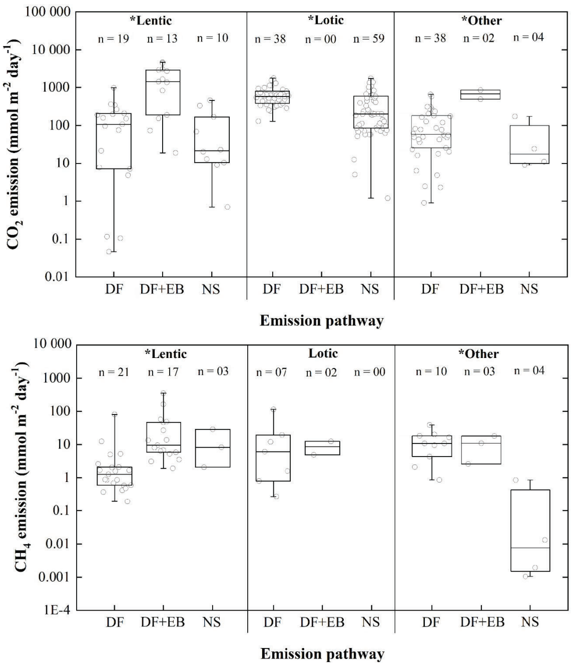

Figure 2. Carbon dioxide (CO_2) and methane (CH_4) emissions reported across different Brazilian inland water ecosystems grouped according to emission pathways: DF (diffusive pathway), DF+EB (diffusive and ebullitive pathways), and NS (not specified pathway). Lentic corresponds to lakes and reservoirs, lotic corresponds to rivers and streams, the latter being of 3rd order or lower, and other corresponds to floodplains, estuaries, and mangroves. The data were compiled from the literature search on published data for Brazil. Significant differences (One-way ANOVA test, $p < 0.05$) in relation to emissions pathways are highlighted by "*". Boxes represent the 25th and 75th percentiles, center lines the median, and the whiskers the maximum and minimum values. The total number of data points available for each emission pathway is also shown above each box (n). *Emissões de dióxido de carbono (CO_2) e metano (CH_4) reportadas para diferentes ecossistemas brasileiros de águas interiores agrupados de acordo com as vias de emissão: DF (via difusiva), DF+EB (vias difusivas e ebulitivas) e NS (via não especificada). Lêntico corresponde a lagos e reservatórios, lótico corresponde a rios e riachos, sendo este último considerados até 3ª ordem, e outros correspondem as planícies de inundação, estuários e manguezais. Os dados foram compilados a partir de uma busca na literatura de dados publicados para o Brasil. Diferenças significativas (Análise de Variância,* p *< 0.05) em relação às vias de emissão foram indicadas por "*". As caixas representam os percentis 25 e 75 %, as linhas centrais a mediana e os extremos os valores máximo e mínimo. O número total de dados disponíveis para cada via de emissão também é mostrado acima de cada caixa (n).*

One-way ANOVAs indicated that CO_2 emissions presented statistically significant variations based on method and habitat. When rates were analyzed by method, EQ, FC, and HD methods gave similar estimates, and FC+FT gave about three times higher emissions. Ecosystem type was also highly significant given the greatest rates from lentic water bodies. Paired t test indicated a highly significant difference between ebullitive and diffusive pathways for CO_2 with diffusive pathways being a mean of more than 10-fold greater than ebullitive (Figs. 2 and 3, Table S5 (Supporting Information available at https://www.limnetica.net/en/limnetica)). The method used for CH_4 was highly significant with HD resulting in the greatest emission rates. Ecosystem type was not significant for total CH_4 after correction for multiple tests, and ebullitive and diffusive pathways were not statistically different for this gas (Table S5 - SI).

We used the relationships between the emissions from both pathways (as the ratio EB/DF) *versus* depth (Fig. 4) to back calculate the emissions for the cases with a missing pathway (either DF or EB), but with water depth available. The equations were significant and had R^2 of 0.39 and 0.37 for CO_2 and CH_4, respectively (Fig. 4). The emissions were then plotted for the pathways DF only and DF+EB, the latter being either as originally reported in the paper or calculated with the equations we obtained (Fig. 4). These data are shown by biome in Fig. 5 and by aquatic ecosystem type in Fig 6.

While the number of cases was low, we argue that Fig. 5 and Fig. 6 more consistently represent the emissions across our study sites and allow a better comparison among biomes, ecosystem types and emission pathways. For CO_2, median DF+EB emissions ranged from 194 (Atlantic Rainforest) to 2176 (Cerrado) mmol m^{-2}

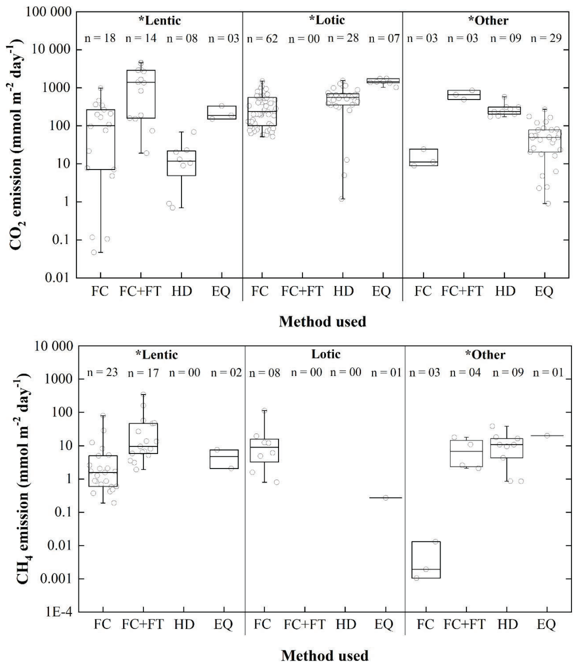

Figure 3. Carbon dioxide (CO_2) and methane (CH_4) emissions reported across different Brazilian inland water ecosystems grouped according to the methods used for their quantification: FC (floating chamber), FC+FT (floating chamber and funnel trap), HD (headspace), and EQ (indirectly/empirically estimated through other water variables). Lentic corresponds to lakes and reservoirs, lotic corresponds to rivers and streams, the latter being of 3rd order or lower, and other corresponds to floodplains, estuaries, and mangroves. The data were compiled from the literature search on published data for Brazil. Significant differences (One-way ANOVA test, $p < 0.05$) in relation to the methods used are highlighted by "*". Boxes represent the 25th and 75th percentiles, center lines the median, and the whiskers the maximum and minimum values. The total number of data points available for each method is also shown above each box (n). *Emissões de dióxido de carbono (CO_2) e metano (CH_4) reportadas para diferentes ecossistemas brasileiros de águas interiores agrupados de acordo com os métodos utilizados para estimativa das emissões: FC (câmara flutuante), FC+FT (câmara flutuante e funil coletor de bolhas), HD (headspace) e EQ (estimado indiretamente/empiricamente por meio de outras variáveis da água). Lêntico corresponde a lagos e reservatórios, lótico corresponde a rios e riachos, sendo este último considerados até 3ª ordem, e outros correspondes as planícies de inundação, estuários e manguezais. Os dados foram compilados a partir de uma busca na literatura de dados publicados para o Brasil. Diferenças significativas (Análise de Variância,* p *< 0.05) em relação aos métodos utilizados foram indicadas por "*". As caixas representam os percentis 25 e 75 %, as linhas centrais a mediana e os extremos os valores máximo e mínimo. O número total de dados disponíveis para cada método também é mostrado acima de cada caixa (n).*

day^{-1}. For CH_4, such emissions varied from 3.1 (Caatinga) to 105.7 (Pantanal) mmol m^{-2} day^{-1}. Interestingly, emissions of CO_2 from the DF pathway were very similar to the sum of pathways (DF+EB), indicating that DF was prevalent. On the other hand, the EB pathway was somewhat (but not significantly) more important for CH_4. The major differences between DF *versus* DF+EB emissions were observed

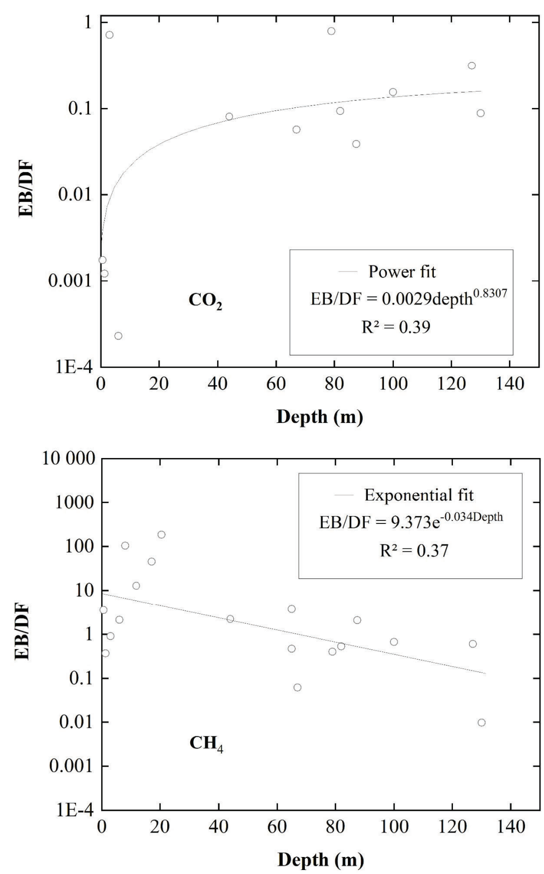

Figure 4. Ratios of the carbon dioxide (CO_2) and methane (CH_4) emissions from the ebullitive/diffusive pathways (EB/DF) plotted against water depth across different Brazilian inland water ecosystems. Only paired data were considered and the respective equations and coefficients of determination (R^2) are shown for each case. *Razões das emissões de dióxido de carbono (CO_2) e metano (CH_4) a partir das vias ebulitiva/difusiva (EB/DF) plotadas em função da profundidade da água para diferentes ecossistemas brasileiros de águas interiores. Apenas dados pareados foram considerados e as respectivas equações e coeficientes de determinação (R^2) são mostrados para cada caso.*

for CH_4 in the Pantanal and Cerrado, with the respective medians up to ~10 and 5 times higher for the DF+EB in comparison to the DF only pathway (Fig. 5). When we considered the emissions divided according to the ecosystem type (Fig. 6), our results suggested that neglecting

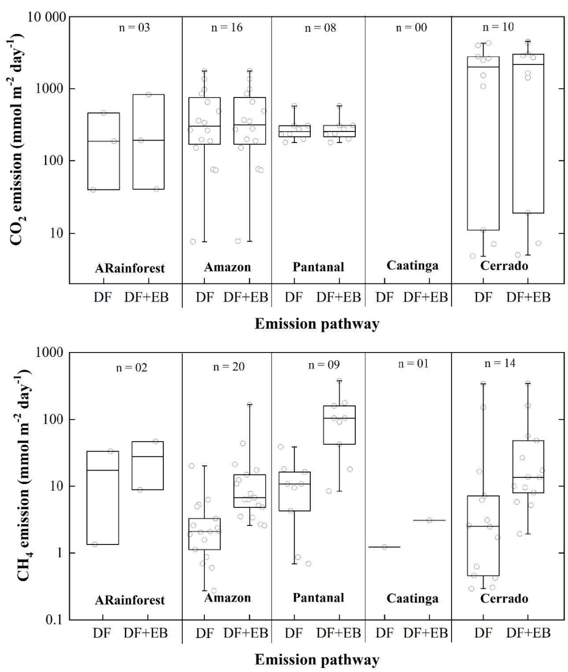

Figure 5. Carbon dioxide (CO_2) and methane (CH_4) corrected emissions across different Brazilian inland water ecosystems at different biomes: Atlantic rainforest (ARainforest), Amazon, Pantanal, Caatinga, and Cerrado. DF (diffusive pathway), DF+EB (diffusive and ebullitive pathways). When either DF or EB was not available, the total emissions (DF+EB) were estimated from the water depth for each case through the equation we obtained on the relationship between water depth and the EB/DF emission ratio. The data were compiled from the literature search on published data for Brazil. Boxes represent the 25th and 75th percentiles, center lines the median, and the whiskers the maximum and minimum values. The total number of data points available for each Brazilian biome is also shown above each box (n). *Emissões corrigidas de dióxido de carbono (CO_2) e metano (CH_4) por diferentes ecossistemas brasileiros de águas interiores localizados em diferentes biomas: Mata Atlântica (ARainforest), Amazônia (Amazon), Pantanal, Caatinga e Cerrado. DF (via difusiva), DF+EB (vias difusivas e ebulitivas). Nos casos em que DF ou EB não estavam disponíveis, as emissões totais (DF+EB) foram estimadas a partir da profundidade de água em cada caso, a partir da equação que obtivemos correlacionando a profundidade da água com a razão das emissões EB/DF. Os dados foram compilados a partir de uma busca na literatura de dados publicados para o Brasil. As caixas representam os percentis 25 e 75 %, as linhas centrais a mediana e os extremos os valores máximo e mínimo. O número total de dados disponíveis para cada bioma brasileiro também é mostrado acima de cada caixa (n).*

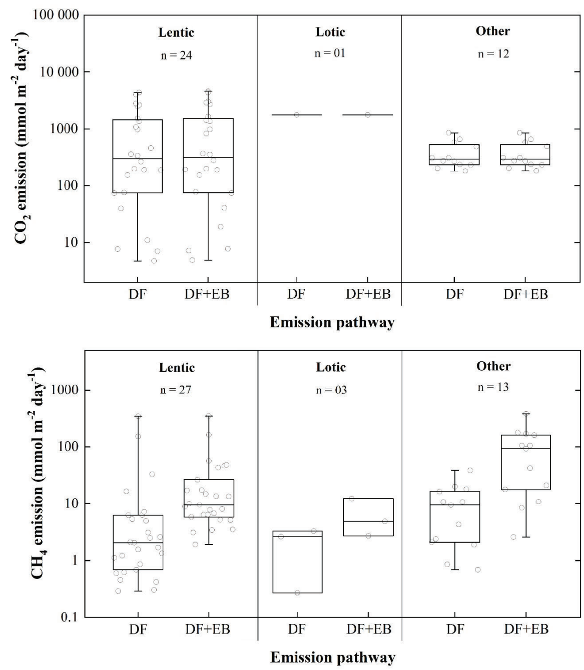

Figure 6. Carbon dioxide (CO_2) and methane (CH_4) corrected emissions across different Brazilian inland water ecosystems: lentic (lakes and reservoirs), lotic (rivers and streams, the latter being of 3rd order or lower), and others (floodplains, estuaries, and mangroves). DF (diffusive pathway), DF+EB (diffusive and ebullitive pathways). When either DF or EB was not available, the total emissions (DF+EB) were estimated from the water depth for each case through the equation we obtained on the relationship between water depth and the EB/DF emission ratio. The data were compiled from the literature search on published data for Brazil. Boxes represent the 25th and 75th percentiles, center lines the median, and the whiskers the maximum and minimum values. The total number of data points available for each aquatic ecosystem type is also shown above each box (n). *Emissões corrigidas de dióxido de carbono (CO_2) e metano (CH_4) por diferentes ecossistemas brasileiros de águas interiores: lênticos (lagos e reservatórios), lóticos (rios e riachos, sendo este último considerado até 3ª ordem), e outros (planícies de inundação, estuários e manguezais). DF (via difusiva), DF+EB (vias difusivas e ebulitivas). Nos casos em que DF ou EB não estavam disponíveis, as emissões totais (DF+EB) foram estimadas a partir da profundidade de água em cada caso, a partir da equação que obtivemos correlacionando a profundidade da água com a razão das emissões EB/DF. Os dados foram compilados a partir de uma busca na literatura de dados publicados para o Brasil. As caixas representam os percentis 25 e 75 %, as linhas centrais a mediana e os extremos os valores máximo e mínimo. O número total de dados disponíveis para cada tipo de ecossistema aquático também é mostrado acima de cada caixa (n).*

Table 1. Best multiple linear regression models for carbon dioxide (CO_2) and methane (CH_4) total emissions (accounting for both diffusive and ebullitive pathways, either originally reported by each reference or estimated through our equation on water depth versus EB/DF ratio). Different variables were tested as predictors. The data were compiled from the literature search on published data for Brazil. B is the slope for the variables. SE is the standard error and R^2 is the coefficient of determination. All effects were significant at $p < 0.05$. *Melhores modelos de regressão linear múltipla para emissões totais de dióxido de carbono (CO_2) e metano (CH_4) (computando-se a soma das vias difusiva e ebulitiva, ou orginalmente reportadas em cada referência ou estimadas de acordo com a nossa equação correlacionado profundidade da água com a razão EB/DF). Diferentes variáveis foram testadas como preditoras. Os dados foram compilados a partir da revisão bibliográfica sobre ambas as emissões em ecossistemas brasileiros de águas interiores. B é o coeficiente angular das variáveis. SE é o erro padrão e R^2 é o coeficiente de determinação. Todos os modelos foram significativos (*p *< 0.05).*

Model	Dependent variable	Independent variable*	B	SE	p-value	Adjusted R^2
A1	CO_2	Intercept	74.81	13.9	1×10^{-3}	0.74
		pH	-33.92	6.80	1×10^{-3}	
A2	CO_2	Intercept	6.97	0.33	1×10^{-6}	0.75
		h	-1.27	0.25	2×10^{-3}	
A3	CO_2	Intercept	13.98	1.43	2×10^{-4}	0.88
		O_2	-5.39	0.77	1×10^{-3}	
A4	CO_2	Intercept	34.05	7.21	5×10^{-4}	0.93
		h	-2.65	0.24	3×10^{-6}	
		Ta	-7.65	2.08	3×10^{-3}	
A5	CO_2	Intercept	-9.21	4.94	9×10^{-2}	0.94
		h	-2.82	0.26	5×10^{-6}	
		pH	8.73	2.53	8×10^{-3}	
B1	CH_4	Intercept	-6.66	3.23	5×10^{-2}	0.40
		EC	2.79	0.86	6×10^{-3}	
B2	CH_4	Intercept	1.11	0.87	2×10^{-1}	0.51
		Total CO_2 emissions	0.60	0.17	7×10^{-3}	

*CO_2 (carbon dioxide emission, mmol m^{-2} day^{-1}), CH_4 (methane emission, mmol m^{-2} day^{-1}), pH (potential of hydrogen), h (water depth, m), O_2 (dissolved oxygen concentration, mg L^{-1}), Ta (water temperature, °C) and EC (electrical conductivity, µS cm^{-1})

the EB component is problematic and can underestimate total emissions for CH_4 for all ecosystem types.

We produced seven MLR models (significant at $p < 0.05$; adjusted R^2 ranging from 0.40 to 0.94), with the models for CO_2 emissions usually with greater R^2. The first set of models (A1 to A5, Table 1) had CO_2 total emissions (i.e., DF+EB) as dependent variable and indicated pH, water depth, dissolved oxygen, and water temperature as potential predictors, most with a negative influence (Table 1). The second set of models suggested that electrical conductivity and CO_2 emissions were relevant predictors of CH_4 total emissions (i.e., DF+EB), both with a positive influence (Table 1). We note that depth could be confounded in this analysis because it was used to fill in missing data, however it was not significant for both gases, suggesting our results are not related to a statistical artifact.

DISCUSSION

Patterns for CO_2 and CH_4 emission pathways and methods used in Brazilian inland water ecosystems

In general, the CO_2 and CH_4 total emissions we compiled for the Brazilian aquatic ecosystems were bracketed by the ranges reported elsewhere in the world (Table 2). Our data were also comparable to the estimates provided by Raymond et al. (2013) in their study on the global CO_2 emissions from inland waters. However, for lentic water bodies, we observed ranges of emissions higher than those published for most other regions (Table 2). For example, maximum CO_2 emissions in Brazilian lakes and reservoirs were 2.5 and 43 times higher in comparison to their counterparts in Polish lakes (Woszczyk & Schubert, 2021) and reservoirs in the United States (Beaulieu et al., 2020), respectively. For CH_4, large discrepancies were also observed (e.g., our maximum emissions were approximately almost 2500 times greater than the estimates for Russian reservoirs by Fedorov et al., 2015).

The CO_2 and CH_4 emissions from our dataset on lotic water bodies were greater than rates reported for rivers in the Sub-Saharan Africa (Borges et al., 2015) and rivers and streams in northwestern Canada (Hutchins et al., 2020), but lower than those from rivers and streams in southwestern Sweden (Natchimuthu et al., 2017) (Table 2). Natchimuthu et al. (2017) attributed their high emissions for both gases to the high gas transfer rates at water-air interface as driven by turbulent mixing in flowing waters. While some Brazilian lotic ecosystems had high gas transfer rates reported as well, our dataset encompassed many study sites from large rivers with less interfacial turbulence (e.g., Amazonas, Solimões, Negro – Fig. 1), probably with lower gas transfer rates relative to smaller rivers and streams. On the other hand, the CO_2 emissions we compiled are within the range reported for Pampean plain streams (Feijoó et al., 2022).

The comparisons above should be viewed with caution because the pathways studied and the methods used in each case in Table 2 were contrasting and we recognize our dataset is limited. Our data compilation suggested that better coupling the methods used for estimating the emissions and the respective tracked pathways is necessary to create more reliable estimates for global models or gas budgets, avoiding either under or overestimations.

In our lentic dataset, our analyses suggested that DF and DF+EB were the most relevant studied pathways for both gases emissions (Fig. 4) in

Table 2. Ranges of carbon dioxide (CO_2) and methane (CH_4) emissions reported for different types of inland water ecosystems across the world, the respective emission pathway considered (DF is diffusive and EB is ebullitive), as well as the methods used (FC is floating chamber, FT is funnel trap, HD is headspace, and EQ is the indirect estimation by water variables). *Variação das emissões de dióxido de carbono (CO_2) e metano (CH_4) reportadas para diferentes tipos de ecossistemas de águas interiores ao redor do mundo, as respectivas vias de emissão consideradas (DF é a difusiva e EB a ebulitiva), bem como os métodos usados (FC é câmara flutuante, FT é o funil coletor de bolhas, HD é headspace e EQ é a estimativa indireta por variáveis de água).*

Type and location of the studied sites	Emission pathway	Methods used	CO_2 emission range (mmol m^{-2} day^{-1})	CH_4 emission range (mmol m^{-2} day^{-1})	Reference
Reservoir (Russia)	DF+EB	HD and FC	21.8 - 62.2	0.02 - 0.14	(Fedorov et al., 2015)
Reservoirs (United States)	DF+EB	FC+FT	<0 - 105	0.04 - 233	(Beaulieu et al., 2020)
Lakes (Poland)	DF	EQ* and HD**	<0 - 1861	0.08 - 8	(Woszczyk & Schubert, 2021)
Lakes and reservoirs (Amazon)	DF	EQ	103	n.a	
Lakes and reservoirs (Caatinga)	DF	EQ	12 - 108	n.a	(Raymond et al., 2013)
Lakes and reservoirs (Cerrado)	DF	EQ	9.4	n.a	
Lakes and reservoirs (Atlantic Rainforest)	DF	EQ	10	n.a	
Lakes and reservoirs (Brazil)	DF+EB and NS	FC, FC+FT, HD and EQ	0.05 - 4568	0.19 - 348	This study
Rivers (Sub-Saharan Africa)	DF* and DF+EB**	FC	186 - 1149	0.5 - 18	(Borges et al., 2015)
Rivers and streams (Sweden)	DF	FC* and HD**	3.3 - 90 300	0.01 - 930	(Natchimuthu et al., 2017)
Rivers and streams (Canada)	DF	HD	0.02 - 1.38	n.a	(Hutchins et al., 2020)
Rivers (China)	DF	HD	<0 - 2070	<0.1 - 16.5	(Xiao et al., 2021)
Rivers and streams (Amazon)	DF	EQ	1599	n.a	
Rivers and streams (Caatinga)	DF	EQ	10-12	n.a	(Raymond et al., 2013)
Rivers and streams (Cerrado)	DF	EQ	9	n.a	
Rivers and streams (Atlantic Rainforest)	DF	EQ	10	n.a	
Rivers and streams (Brazil)	DF+EB and NS	FC, HD and EQ	1.2 - 1759	0.3 - 114	This study
Floodplains (Austria)	NS	FC	<0 - 620	<0 - 0.58	(Machado et al., 2020)
Estuaries (Chile)	NS	HD	5 - 609	0.03 - 0.09	(Daniel et al., 2013)
Estuaries (United States)	DF	HD	<0 - 20.1	n.a	(Crosswell et al., 2017)
Estuaries (China)	DF	EQ	<0 - 228	n.a	(Shen et al., 2020)
Mangroves (United States)	DF	FC	<0 - 570	<0 - 45.4	(Martin et al., 2020)
Floodplains, estuaries and mangroves (Brazil)	DF+EB and NS	FC, FC+FT, HD and EQ	0.9 - 856	0.001 - 39	This study

*for CO_2 emissions; **for CH_4 emissions; n.a is not available data, and NS is not specified pathway. < 0 values indicated influx of the gases, which it is not relevant for our paper.

relation to lotic and other ecosystems. Moreover, the FC and FC+FT measurement methods were the most used for assessing CO_2 and CH_4 lentic emissions. This indicates that such pathways and methods are more frequently reported by the Brazilian studies on both emissions. In addition, while different methods have been used by other studies worldwide (Table 2), the FC method is especially widespread.

For most of our dataset on lotic emissions, the CO_2 emission pathways were not available because they were either not specified by the authors or not possible to differentiate because of the method used (EQ). Moreover, lotic ecosystems had very limited data available on CH_4, making it more complicated to analyze the pathways and methodological issues. This limited lotic CH_4 emissions data suggests that measurements in these habitats can be more complex due to the hydrodynamics and morphology of such systems in comparison to the other types. Recent papers (e.g., Lorke et al. 2015) have provided guidance on how to apply and adapt different methods for estimating gas emissions in running waters.

When the pathway was specified in our dataset, the DF was the most commonly pathway analyzed, similarly to other studies worldwide (Table 2). In shallow ecosystems with low water velocity, it is easier to target the DF pathway relative to deeper or higher water velocity sites. In the former case, emissions from the EB pathway to the atmosphere can be very temporally variable, which makes measurements of the DF pathway more common. However, the use of methods for estimating both DF and EB pathways under turbulent conditions may be unfeasible because establishing a control volume at the air-water interface can be difficult due to disturbances on the water surface (e.g., water waves). Such methodological issues can partially explain the divergence in selecting the most appropriate method for the estimations (see Fig. 3 and Table 2).

Spatial variability of CO_2 and CH_4 total emissions by Brazilian inland water ecosystems

The spatial distribution of the sites with data available on the studied gases indicated that lentic and lotic ecosystems were more represented. For CO_2 emissions, the data on DF *versus* DF+EB (Fig. 6) suggested that the contribution of the EB pathway was not very important, and that the DF pathway was prevalent for this gas. For example, the median values for CO_2 emissions were 304 (DF only) *versus* 318 (DF+EB) mmol m^{-2} day^{-1} in lentic systems and 1759 (DF only) *versus* 1766 (DF+EB) mmol m^{-2} day^{-1} in lotic ecosystems (Fig. 6). However, for CH_4, the EB was more relevant (e.g., medians of 2.1 *versus* 9.6 mmol m^{-2} day^{-1} for DF and DF+EB, respectively, in lentic systems) (Fig. 6), indicating the importance of finding suitable methods for estimating both pathways for this gas to avoid underestimation of total flux rates.

Most studied sites in our data compilation were located in the Amazon biome (Fig. 1), which is responsible for 83.5 % of the total surface freshwater discharge from Brazil (ANA 2019). In this biome, our data compilation after the correction for the total emissions (DF+EB, following Fig. 4 equations) showed CO_2 emissions had a wider range (8 to 1766 mmol m^{-2} day^{-1}, Fig. 5) than reported emissions by Amazon soils, which varied from 178 to 1042 mmol m^{-2} day^{-1} (Garcia-Montiel et al., 2002), potentially influenced by the smaller number of measurements in the latter case. The maximum total CH_4 emissions (DF+EB) for the valid cases we compiled (Fig. 5) was approximately 130 times higher than the maximum emissions (1.25 mmol m^{-2} day^{-1}) observed in the eastern Amazon by Wilson et al. (2020), who reported global estimates summing up contributions of the atmospheric, soil, aquatic and forest compartments. This indicates that due to the large area of the Amazon biome (accounting for about 40 % of the Brazilian territory), significant spatial and temporal heterogeneity of gas emission is expected (see Melack et al., 2004).

In the Atlantic rainforest, we found a very limited number of paired estimates and therefore DF+EB emissions (medians of 194 mmol m^{-2} day^{-1} and 28 mmol m^{-2} day^{-1}, Fig. 5) are probably not representative. Vitória et al. (2020) studied soil emissions in this biome and highlighted that CO_2 evasion was associated to different soil textures, as well as the air humidity and temperature. The Atlantic rainforest originally covered the Brazilian coastal areas, but now the few remnant areas of native vegetation are under pressure from anthropogenic activities (Noriega & Araujo 2014) such as industrial and agricultural expansion.

For the Cerrado biome, natural and human-induced biomass burning is common especially in the dry season, representing an important source of CO_2 to the atmosphere. Maximum CO_2 emissions were 544 mmol m^{-2} day^{-1} in terrestrial Cerrado areas subjected to prescribed fire (Pinto et al., 2002). Some of our data points on total CO_2 emissions in water bodies were even greater (Fig. 5), indicating that aquatic emissions can rival or exceed those from terrestrial compartments. Our data compilation also showed that Cerrado areas had more estimates of CH_4 emissions than most other biomes, probably due to the many hydroelectric reservoirs in this region (Kosten et al., 2018). These are potential sources of CH_4 due to their high depths, anoxic hypolimnion, and high organic matter availability from drowned terrestrial vegetation, which can promote methanogenesis (Beaulieu et al., 2020; McClure et al., 2020).

Potential drivers for CO_2 and CH_4 total emissions by Brazilian inland water ecosystems

Models predicting CO_2 and CH_4 emissions through other environmental variables are necessary for better understanding the global sources of both gases. Our MLR models highlighted pH, water depth, dissolved oxygen, electrical conductivity, and water temperature as potential predictors of CO_2 and CH_4 emissions (Table 1). Similar models across the world were proposed at regional and even global scales (Holgerson & Raymond 2016; Charles et al., 2020), with usually more than one driver influencing their composition (Table 3). Most common predictors include a suite of physical, chemical and biological water variables (Crawford et al., 2014; Smith et al., 2017; McClure et al., 2020; Hutchins et al., 2020; Machado et al., 2020) and also other variables as atmospheric pressure and surface area (Holgerson & Raymond 2016). Our best models (with higher adjusted R^2) indicated two potential drivers for CO_2 emissions (water depth and pH, Table 1, $R^2 = 0.94$), and only one predictor for CH_4 emissions (CO_2 emissions, Table 1, $R^2 = 0.51$). The fact that global models use different variables than our best models for Brazil indicates regional tuning of models to predict gas emissions would lead to more accurate global estimates.

Table 3. Comparison among multiple linear regression (MLR) models for carbon dioxide (CO_2) and methane (CH_4) emissions across the world. R^2 is coefficient of determination. *Comparação entre os modelos de regressão linear múltipla (MLR) para as emissões de dióxido de carbono (CO_2) e metano (CH_4) obtidos ao redor do mundo. R^2 é o coeficiente de determinação.*

Inland water ecosystems	Models	R^2	References
[a]Lakes and streams	$Ln(pCO_2) = -1.56pH + 0.001ANC - 0.07Calcium$	0.86	(Crawford et al., 2014)
	$Ln(pCH_4) = 0.46CO_2 + 0.003ANC - 0.27Calcium$	0.57	
[b]Small ponds	$Ln(CO_2) = 4.44 + 0.008Ln(area) \times latitude - 0.0042latitude^2$	0.36	(Holgerson & Raymond 2016)
	$Ln(CH_4) = 4.25 - 0.278Ln(area) - 0.080$	0.58	
[c]Streams and rivers	$CO_2 = 1.08TDN - 0.22Temperature - 0.46DO + 0.09HIX + 0.11BIX + 0.18\%SWM + 0.32log(DOC:NO_3^-)$	0.78	(Smith et al., 2017)
	$CH_4 = 0.25Temperature - 0.27DO - 0.15HIX - 0.16\%IC + 0.16\%SWM + 0.55log(DOC:NO_3^-)$	0.50	
[d]Streams	$CO_2 = 0.55PeakT + 0.37PeakC$	0.46	(Machado et al., 2020)
	$CH_4 = 0.63PeakA + 0.15Nitrite$	0.46	
[e]Rivers and floodplains	$Log(CO_2) = 0.00418NPP - 0.181Log(area) - 0.286$	0.56	(Hutchins et al., 2020)
[f]Reservoirs	$Ln(diffCH_4) = 1.11 + 0.26(AR1) + 0.38(phytoplankton)$	0.25	(McClure et al., 2020)
	$Ln(ebuCH_4) = -5.11 + 0.37(AR1) + 0.30(SWItemp) + 1.14 (Wind speed) - 0.53(\Delta Press)$	0.86	
[g]Lakes, reservoirs, rivers, streams, floodplains, estuaries and mangroves	$Ln(CO_2 + 1) = -9.21 - 2.82Ln(h + 1) + 8.73Ln(pH + 1)$	0.94	This study
	$Ln(CH_4 + 1) = 1.11 + 0.6Ln (CO_2 + 1)$	0.51	

[a]pCO_2 is carbon dioxide partial pressure (µatm), pH is hydrogen potential, ANC is acid neutralizing capacity, Calcium is the calcium concentration, pCH_4 is methane partial pressure (µatm) and CO_2 is the carbon dioxide flux (mol m^{-2} day^{-1}). [b]CO_2 is carbon dioxide concentration (µmol L^{-1}), area is the aquatic ecosystem superficial area (ha), latitude is latitude geoposition of the aquatic ecosystems (decimal degrees) and CH_4 is methane concentration (µmol L^{-1}). [c]CO_2 is carbon dioxide concentration (µM), TDN is total dissolved nitrogen (mg L^{-1}), temperature is the water temperature (°C), DO is dissolved oxygen concentration (mg L^{-1}), HIX is humification index, BIX is autochthonous productivity index, SWM is watershed drained by stormwater best management practices, DOC is dissolved organic carbon concentration (mg L^{-1}), NO_3^- is nitrate concentration (mg L^{-1}), CH_4 is methane concentration (µM) and IC is inorganic carbon (mg L^{-1}). [d]CO_2 is carbon dioxide emission (mg C m^{-2} h^{-1}), PeakT is fluorescence peak of protein like fraction (Ex/Em = 270-280 nm/320-350 nm), PeakC is fluorescence peak humic degraded material (Ex/Em = 330-350 nm/420-480 nm), CH_4 is methane emission (µg C m^{-2} h^{-1}), PeakA is fluorescence peak humic degraded material (Ex/Em = 250-260 nm/380-480 nm) and Nitrite is soil/sediment nitrite concentration (µg g^{-1}). [e]CO_2 is carbon dioxide concentration (mg C L^{-1}), NPP is net primary production (g C m^{-2} $year^{-1}$) and area is watershed area (km^2). [f]$diffCH_4$ is methane diffusive emission (mg m^{-2} day^{-1}), AR1 is null autoregressive, phytoplankton is phytoplankton biomass (µg L^{-1}), $ebuCH_4$ is methane ebullitive emission (mg CH_4 m^{-2} day^{-1}), SWItemp is the water temperature (°C), Wind speed is the wind speed (m s^{-1}) and ΔPress is the difference of mean weekly atmospheric pressure measured at surface reservoir (kPa). [g]CO_2 is carbon dioxide total emissions (mmol m^{-2} day^{-1}), h is water depth (m), pH is hydrogen potential and CH_4 is methane total emission (mmol m^{-2} day^{-1}).

In our study, the models suggested CO_2 emissions were lower in deeper systems. In both studies from Verspagen et al. (2014) and Zagarese et al. (2021), the relationship between depth (h) and carbon dioxide emissions was generally positive. Conversely, the results obtained by Sun et al. (2021) showed a negative correlation between *h* and CO_2 emissions in a Chinese lake. Greater depths can create more anoxic conditions and larger aphotic zones, favoring the methanogenic process (Bergier et al., 2015; Stanley et al., 2016). Also, tropical and subtropical water bodies are more likely to be permanently stratified (Van De Waal et al., 2010), so the development of anoxia in the hypolimnion is more likely than in temperate systems (Fernández et al., 2014; Fukushima et al., 2017). Anoxia favors less efficient carbon processing and CO_2 generation relative to aerobic respiration. The negative correlation between O_2 and CO_2 emissions reinforced such influence of the aquatic metabolism (Hotchkiss et al., 2015) and its interactions with trophic state (Halbedel & Koschorreck, 2013).

The effect of pH on CO_2 emissions was unclear as it had a negative and positive influence in different models (Table 1). Extreme values of pH can cause imbalances in chemical reactions in the water column, affecting the aquatic metabolism (Khan et al., 2020) and methanogenesis (Ye et al., 2012). The relationships between pH and CO_2 are likely complex because both respiration and photosynthesis can change pH so it is difficult to separate cause and effect from CO_2 emissions (Kragh & Sand-Jensen, 2018).

The positive relationship of CH_4 and CO_2 emission was similar to that found by Crawford et al. (2014) who found CO_2 emission was a significant positive predictor for CH_4 emission, but CH_4 emission in turn did not predict CO_2 emission. In addition, if the methods used and pathways analyzed are not paired, there may be divergence among the data. In our models, we only included the emissions from the sum of DF+EB pathways as the independent variables, but sill our CH_4 emissions did not predict CO_2 emissions.

CONCLUSIONS

Our literature review indicated that most studied sites for the emissions of CO_2 and CH_4 were located in the Amazon and Atlantic rainforest biomes. DF was the most analyzed pathway and FC was the most frequently used method. Moreover, the compiled emissions from tropical and subtropical water bodies had a significant variation and were generally bracketed by the ranges reported for temperate waters. In general, our study highlighted that a clearer definition of which emission pathways are measured is fundamental to define appropriate methods for the estimation of CO_2 and CH_4 emissions. Many studies in our compilation did not inform the reported emission pathway or only included a single pathway (usually DF). This lack of information is problematic, particularly for CH_4, for which emissions from the EB pathway should not be neglected.

After back-correcting the emissions as an attempt to estimate total emissions (DF+EB) where data were missing, different water variables were correlated with CO_2 and CH_4 emissions. While our dataset was limited and our equations for back correcting the emissions had modest R^2 values, our models indicated a coupling between the gases studied (i.e., CO_2 emissions predicted CH_4 emissions) and the potential influence of pH, water depth, dissolved oxygen, electrical conductivity, and water temperature. As we did not directly assess the anthropogenic influences on emissions of both gases, we reinforce the need for further studies of such interactions. In addition, the improvement of methods to estimate emissions is needed to assess development of more robust predictive models to improve the quality and consistency of the CO_2 and CH_4 budgets in tropical and subtropical zones. The heterogeneity of rates observed in the Brazilian studies indicate that global models with even finer spatial resolution are warranted to estimate global rates of CO_2 and CH_4 emissions from freshwaters.

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