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TOWARDS A BETTER UNDERSTANDING OF RESERVOIR CARBON CYCLING: DRAWDOWN EMISSIONS AND SEQUESTRATION IN SEDIMENTS OF CHAPÉU D'UVAS RESERVOIR

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Dissertação apresentada ao Programa de Pós-Graduação em Ecologia da Universidade Federal de Juiz de Fora, como parte dos requisitos necessários para obter o título de Mestre em Ecologia Aplicada ao Manejo e Conservação de Recursos Naturais.

Orientqadora: Prof. Dra. Raquel Fernandes Mendonça

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Towards a better understanding of reservoir carbon cycling: drawdown emissions and sequestration in sediments of Chapéu D'Uvas reservoir

Contents

Abstract

Man-made reservoirs are environments of intense organic carbon (OC) processing. The trapping of high fluvial sediment loads combined to often anoxic bottom waters lead to an efficient preservation of OC in reservoir sediments. At the same time that reservoirs bury large amounts of OC they are significant sources of the greenhouse gases CO_2 or CH_4 to the atmosphere. Accurate measurements of OC burial in reservoirs are still very scarce, as well as measurement of some emission pathways, for example, the carbon release from sediment periodically exposed to the atmosphere (drawdown zones emission). Moreover, many of the current estimates available lack spatial and temporal resolution. In this study we aimed to evaluate the OC burial in the sediment and the CO_2 emissions in the drawdown area of the tropical reservoir of Chapéu D'Uvas (CDU), located in southeastern Brazil. The approaches adopted here include both spatial and temporal variability. The variation in sediment accumulation in the CDU reservoir (from zero to 2.8 cm y^{-1}) explained 70% or the variability in OC burial rate. Average spatially-resolved OC burial rate since reservoir flooding was 35 g C m^{-2} y^{-1}, which is similar to the rates found for other tropical reservoirs. Our results suggest that soil erosion in the catchment contribute with a high share of the reservoir sediment load. The CO_2 emissions in the drawdown area of CDU were higher in dry periods (mean = 1163 mg C m^{-2} y^{-1}) compared to rainy periods (526 mg C m^{-2} y^{-1}). In addition, dry exposed sediments had higher emissions (1316 mg C m^{-2} y^{-1}) then wet sediments (685 mg C m^{-2} y^{-1}), although sediment re-wetting by rain events was shown to cause increase in emissions. Drawdown emissions were also significantly higher at night than during the day, implying that usual day measurements may underestimate the actual emissions. We finish the study by presenting a carbon balance for the CDU reservoir, which combines the fluxes measured in this study with values from the literature of water surface diffusive and ebullitive emissions. The burial of organic carbon in the CDU reservoir represented ~30% of the total emissions (436 t C yr^{-1}) or, only 17% of total emissions in CO_2-equivalent, i.e. considering the global warming potential of CH_4.

Resumo

Reservatórios artificiais são ambientes de intenso processamento de carbono orgânico (CO). O aprisionamento de altas cargas de sedimentos fluviais combinados com as águas do fundo frequentemente anóxicas, leva a uma preservação eficiente de CO em sedimentos de reservatórios. Ao mesmo tempo em que os reservatórios enterram grandes quantidades de CO, eles são fontes significativas dos gases de efeito estufa dióxido de carbono (CO_2) e (CH_4) para a atmosfera. As medições precisas do enterro de CO nos reservatórios ainda são muito escassas, bem como a medição de algumas vias de emissão, como por exemplo a emissão de carbono de sedimentos periodicamente expostos paras a atmosfera (emissão pela zonas de deplecionamento). Além disso, muitas das estimativas atuais disponíveis carecem de resolução espacial e temporal. Neste estudo, objetivamos avaliar o enterro de CO nos sedimentos e as emissões de CO_2 na área de deplecionamento do reservatório de Chapéu D´Uvas (CDU), localizado no sudeste do Brasil. As abordagens adotadas aqui incluem alta resolução espacial e temporal. A variação no acúmulo de sedimentos no reservatório da CDU (de 0 a 2,8 cm ano^{-1}) explicou 70% da variabilidade na taxa de enterro de CO. A taxa média de enterro de CO desde a inundação do reservatório foi de 35 g C m^{-2} ano^{-1}, o que é semelhante às taxas encontradas para outros reservatórios tropicais. Nossos resultados sugerem que a erosão do solo na bacia hidrográfica contribui com uma alta parcela da carga de sedimentos do reservatório. As emissões de CO_2 na área de deplecionamento do reservatório de CDU foram maiores nos períodos secos (média = 1163 mg C m^{-2} ano^{-1}) em comparação aos períodos chuvosos (526 mg C m^{-2} ano^{-1}). Além disso, os sedimentos secos da área de deplecionamento apresentaram maiores emissões (1316 mg C m^{-2} ano^{-1}) do que os sedimentos úmidos (685 mg C m^{-2} ano^{-1}), embora tenhamos demonstrado que o re-umedecimento de sedimentos por eventos de chuva causa aumento nas emissões. As emissões na área de deplecionamento também foram significativamente maiores à noite do que durante o dia, indicando que medições feitas apenas durante o dia podem subestimar as emissões reais. Concluímos o estudo apresentando um balanço de carbono para o reservatório de CDU, que combina os fluxos medidos neste estudo com os valores da literatura de emissões difusivas e ebulitivas da superfície da água. O enterro de CO no reservatório da CDU representou ~ 30% do total de emissões pelo reservatório (436 t C ano^{-1}) ou apenas 17% do total de emissões equivalentes de CO_2, ou seja, considerando o potencial de aquecimento global do CH_4.

1. GENERAL INTRODUCTION

The damming of rivers causes deep changes in watersheds scales. Geographic isolation of aquatic and terrestrial species, as well as changes in water and soil biogeochemistry, temperature, and stratification of the water column are examples of these changes (Friedl e Wüest, 2002). A reservoir construction floods a vast land area, which before, in most cases, was covered by vegetation in contact with atmospheric air, and after the dam is covered by water (**Figure 1**). Flooding of terrestrial areas causes the death or migration of the local fauna, as well as death of all the vegetation in the flooded area. Not only it reduces the carbon fixation by photosynthesis in the watershed, but much of this dead biomass is decomposed by microorganisms and transformed into greenhouse gases (GHG), mainly carbon dioxide (CO_2) and methane (CH_4). It has been estimated that the highest decomposition rates and consequent GHG emissions in a newly built reservoir occur during its first 20 years (Abril *et al.*, 2005; Barros *et al.*, 2011). On the other hand, reservoirs are fundamental for human development, as they store large volumes of water that can be used for consumption, power generation, irrigation, flood control, aquaculture, navigation, recreation and others. As a result of the increasing demand for such services, reservoirs are increasing in number year after year and so has the interest of the scientific community in understanding their environmental impacts (Nilsson *et al.*, 2005).

Figure 1: Modification of the ecosystem during and after the construction of the São Miguel Hydroelectric Plant on the Teles Pires River, located on the border of the states of Mato Grosso and Pará, Brazil. The figure shows three satellite images (Google Earth) before, during and after the construction of the dam. (2009): before damming. (2014): during the construction of the dam. (2016): after damming, showing the flooding of a vast region.

Reservoirs play a dualistic role in relation to the global carbon cycle. They store organic carbon in their sediments at the same time that they emit large amounts of GHG, especially CH_4, due to the intense mineralization of organic matter under anoxic conditions (Deemer *et al.*, 2016). Naturally, i.e. in watersheds without dams, the organic matter that enters water bodies from effluents or erosive processes on the river banks flows through the rivers towards the ocean. This organic matter have three basic destinations: (i) it is stored in the sediments, (ii) it is mineralized in the course, or (iii) it reaches the ocean (Cole *et al.*, 2007). It has been estimated that 48% of the terrestrial organic and inorganic carbon entering inland waters reaches the oceans, 12% is stocked in sediments and the remaining 40% are mineralized along the way (Cole *et al.*, 2007). Once a watercourse is interrupted, all catchment hydrology is changed. For example, the water residence time increases, favoring sedimentation of the terrestrial suspended material to the bottom of the reservoir. As consequence, an increase in sedimentation rates is observed. Increased sedimentation rate leads to an increase in organic carbon (OC) burial rate (Mendonça *et al.*, 2016). In addition, the high transparency of water due to the sedimentation of suspended material, coupled with abundant nutrient availability, favors primary production and the reservoir becomes a source of autochthonous organic matter (Friedl e Wüest, 2002; Rangel *et al.*, 2012). High sedimentation rates create a physical barrier in sediment layers as they prevent oxygen penetration into deeper layers, significantly decreasing the efficiency of organic carbon mineralization (Sobek *et al.*, 2009). Therefore, non-mineralized organic carbon of both terrestrial and autochthonous sources is stored in the sediment for unknown timescales, depending on the fate of the dam.

Reservoirs are also important sources of carbon to the atmosphere (Raymond *et al.*, 2013; Deemer *et al.*, 2016). In tropical regions, where carbon burial efficiency tends to be lower (Alin e Johnson, 2007) due to the positive effect of temperature on mineralization (Cardoso *et al.*, 2014), emission rates are expected to be higher than burial. On a global scale, reservoirs are responsible for emitting about 0.8 Pg of carbon equivalent to the atmosphere (Deemer *et al.*, 2016). Reservoir GHG emissions vary greatly in space and time, and their drivers are still poorly understood.

There are 4 main CO_2 and CH_4 emission pathways in reservoir: diffusion, ebullition, degassing and drawdown emissions. The diffusion of gases in water is explained by the difference between the concentrations of this gas in water and in the air and by the velocity of gas exchanges (k) (Cole e Caraco, 1998; Abril *et al.*, 2005; Sobek *et al.*, 2005). In other words, when water is

supersaturated with a gas, for example CO_2, the CO_2 molecule tends to escape to the atmosphere in order to achieve a balance between the concentrations of gases in water and air. Diffusion is the main pathway of CO_2 emissions in aquatic environments, representing 90% of the total CO_2 emitted (Deemer *et al.*, 2016). In terms of CH_4 emissions from reservoirs, approximately 40% is emitted through diffusion, the remaining 60% being released to the atmosphere through ebullition (Deemer *et al.*, 2016). CH_4 is produced under anoxic conditions at the bottom of the reservoir. When the concentration of CH_4 in the upper layer of the sediment exceeds the solubility of CH_4 in water, added to the hydrostatic pressure of the water column, bubbles are formed. Changes in hydrostatic pressure or the influence of organism's bioturbation such as benthic) fish (Oliveira Junior *et al.*, 2019), for example, can release these bubbles, which reach the atmosphere after passing through the water column. Degassing is a process of dissolved gases emission in water that happens instantly, after the passage of water through the turbines of a hydroelectric or in a spillway. In general, the bottom of the reservoirs is anoxic, containing high concentrations of CO_2 (dissolved) and CH_4 (bubbles). When the water passes through the floodgates or the turbines, the reservoir faces a rapid depressurization, the result is the instantaneous emission of gases that were dissolved in the water. Man-made reservoirs are subject to periodic variations in water levels. Emissions in the drawdown (i.e. periodically flooded) areas occur when the reservoir's water level drops, exposing a vast area of sediment, previously covered by water, to atmospheric air. The exposure of the sediment to atmospheric air provides oxygen for the microbial community persisting in the sediment. Consequently, an increase in the metabolic activity of these microorganisms occurs, leading to an increase in CO_2 emissions.

Emissions from drawdown zones (Deshmukh *et al.*, 2018) have been neglected in the calculations of freshwater global carbon budgets, which only take into account emissions from the water surface. Only in the last decade, more attention has been paid to GHG emissions in sediments periodically exposed to the atmosphere and the studies have been showing that these fluxes are quantitatively very important (Catalán *et al.*, 2014; Von Schiller *et al.*, 2014; Jin *et al.*, 2016; Obrador *et al.*, 2018; Marcé *et al.*, 2019). For example, a recent study showed that exposed sediment accounts for ~ 10% of global carbon emission in terms of CO_2-equivalent from continental waters (Marcé *et al.*, 2019).

Better understanding of the carbon dynamics in reservoirs is critical for improving our understanding of the effect of anthropogenic alterations in freshwater systems (e.g. by building dams) on the global carbon cycle. This knowledge is particularly relevant for tropical countries where catchments potential to building dams are still high (Kumar A *et al.*, 2011) and where carbon processing tends to be more intense (Tranvik *et al.*, 2009). This master dissertation used the reservoir of Chapéu D'Uvas (CDU), a water supply reservoir located close to the Federal University of Juiz de Fora (UFJF), as a study model. The CDU reservoir has been intensely studied by limnologists at UFJF, especially over the past ~7 years, when extensive efforts have been made to estimate its carbon footprint. However, two very important carbon processing pathways remain largely unknown, not only for the CDU reservoir, but for artificial reservoirs in general – OC burial in sediments and carbon emission from drawdown zones. The two main objectives of this study were, then, related to these two carbon processing routes. The first was to determine the carbon burial rate in the sediment of the CDU reservoir with a highly spatially resolve approach. The second was to evaluate the carbon emissions from the drawdown area of the CDU reservoir with refines spatial and temporal (daily and seasonal) resolution.

2. CHAPTER 1: Organic carbon burial in a tropical oligotrophic reservoir

2.1. Introduction

Inland waters play an important role in the global carbon cycle, with (Cole *et al.*, 2007; Tranvik *et al.*, 2009) lakes and reservoirs sequestering organic carbon (OC) at higher rates than the ocean and terrestrial environments (Schlesinger, 1990; Stallard, 1998; Cole *et al.*, 2007). There are several causes for the high OC sink in freshwater sediments. Firstly, lakes and reservoirs receive large amounts of sediment from the river basins containing terrestrial carbon, and this input is increased with anthropogenic activities, for example those that increase erosion. Secondly, these environments are highly productive generating autochthonous organic matter (Downing, 2008). Finally, they usually present low oxygen concentrations (Wachenfeldt *et al.*, 2008), causing the sediment deposited at the bottom of these freshwater systems to decompose less efficiently than if it would be deposited in the ocean (Sobek *et al.*, 2009; Isidorova *et al.*, 2019a). When compared

to natural lakes, human-made reservoirs are efficient in sequestering OC - they bury OC at ~6 times higher rates (Mendonca *et al.*, 2017). This happens because reservoirs are usually built at the end of large watersheds, receiving large amounts of terrestrial sediments from riverine inputs but also because reservoirs more often present stratification of the water column, making the bottom anoxic and, favoring sediment OC preservation (Sobek *et al.*, 2009).

Despite its importance to the regional and global carbon cycle, OC burial in reservoirs is largely understudied (Mendonca *et al.*, 2017). One of the reasons for the lack of good estimates of OC burial in reservoirs is methodological difficulties – OC burial varies largely in space as reservoirs are often very heterogeneous in terms of morphology and hydrology (Mendonça *et al.*, 2014; Wang *et al.*, 2019). Also, OC burial is often overlooked in carbon balance assessments as it is not clear to which extent reservoir OC burial is a new anthropogenic carbon sink and if OC in reservoir sediment is effectively buried or prone to degradation (Mendonca *et al.*, 2012; Prairie *et al.*, 2018). However, recent evidences suggested that even the terrestrial share of the OC buried in reservoir partly represents a new anthropogenic carbon sink as OC would not be buried as efficiently in any depositional environment in the absence of the dam (Isidorova *et al.*, 2019a). Moreover, an experiment on OC degradation showed that sediments older than 6-12 years can be considered as effectively buried (Isidorova *et al.*, 2019b). It should be regarded, though, that in terms of greenhouse gas effect, the high OC burial in reservoir is not simply positive, since it fuels the production of large amounts of methane (Sobek *et al.*, 2012; Maeck *et al.*, 2013), a gas with 32 times higher warming potential than CO2 (IPCC, 2013). Accessing the carbon footprint of reservoirs is of increasing importance as the number of dams has increased worldwide in recent years (Wehrli, 2011). Especially in the tropics, there is a growing demand for new dams for hydroelectricity, irrigation, water supply etc. Even though OC burial efficiency in tropical systems tends to be lower than in temperate ones due to the positive effect of temperature on OC mineralization (Gudasz *et al.*, 2010; Cardoso *et al.*, 2014), evidences have been showing that also in tropical reservoirs OC burial represents an important carbon sink (Kunz *et al.*, 2011; Mendonça *et al.*, 2014). The aim of this study was to determine, through a spatially resolved approach, the OC burial rate in the sediment of a tropical reservoir and to investigate the drivers of its spatial variability. We also evaluated the relative importance of OC burial when compared to emissions from the reservoir. Our hypothesis was that OC burial in the CDU reservoir would be low when

compared to other tropical reservoir, as it has a relatively small catchment area (low terrestrial OC load) and is oligotrophic (low autochthonous OC production).

2.2 Methods

Study area

The study was carried out in Chapéu D'uvas (21º 33'S, 43º 35'W), an oligotrophic reservoir (average of total nitrogen and total phosphorus: 452 µg L^{-1} and 12 µg L^{-1}, respectively, Paranaíba et al. 2018) located in the Atlantic Forest biome, that supplies with water the city of Juiz de Fora (~600,000 inhabitants), at southeastern Brazil. The reservoir was filled in 1994 by damming the Paraibuna River, flooding an area of 12 km^2. It has an average depth of 19 m and a maximum depth of 41m. The land use in Chapéu D'Uvas' catchment is characterized by the presence of grassland (~ 66.0% of the total area), forest (~ 30.0%) and Eucalyptus plantation (~ 4.0%)(Machado, 2012).

Sediment sampling

The sediment sampling was performed in three different campaigns between March and April 2018. A sediment sampler equipped with a hammer system (UWITEC, Mondsee, Austria) was used to sample 149 sediment cores, covering the entire reservoir extent (**Figure 2**). Sampling was mainly performed in the deeper parts of transects transversal to the main river stem (114 cores) but some cores (total of 35) about evenly distributed along the reservoir were sampled near the margins. Cores measuring 120 or 60 cm of length and 6 cm of internal diameter were hammered into the sediment in order to retrieve the entire post-flooding sediment layer and part of the pre-flooding soil (Mendonça *et al.*, 2014). The transition between pre-flooding soil and post-flooding sediment was visually identified in the field in all sampled cores. Immediately after sampling, the thickness of the post-flooding sediment layer was measured and the water column depth was determined using a portable depth sounder (HONDEX PS-7).

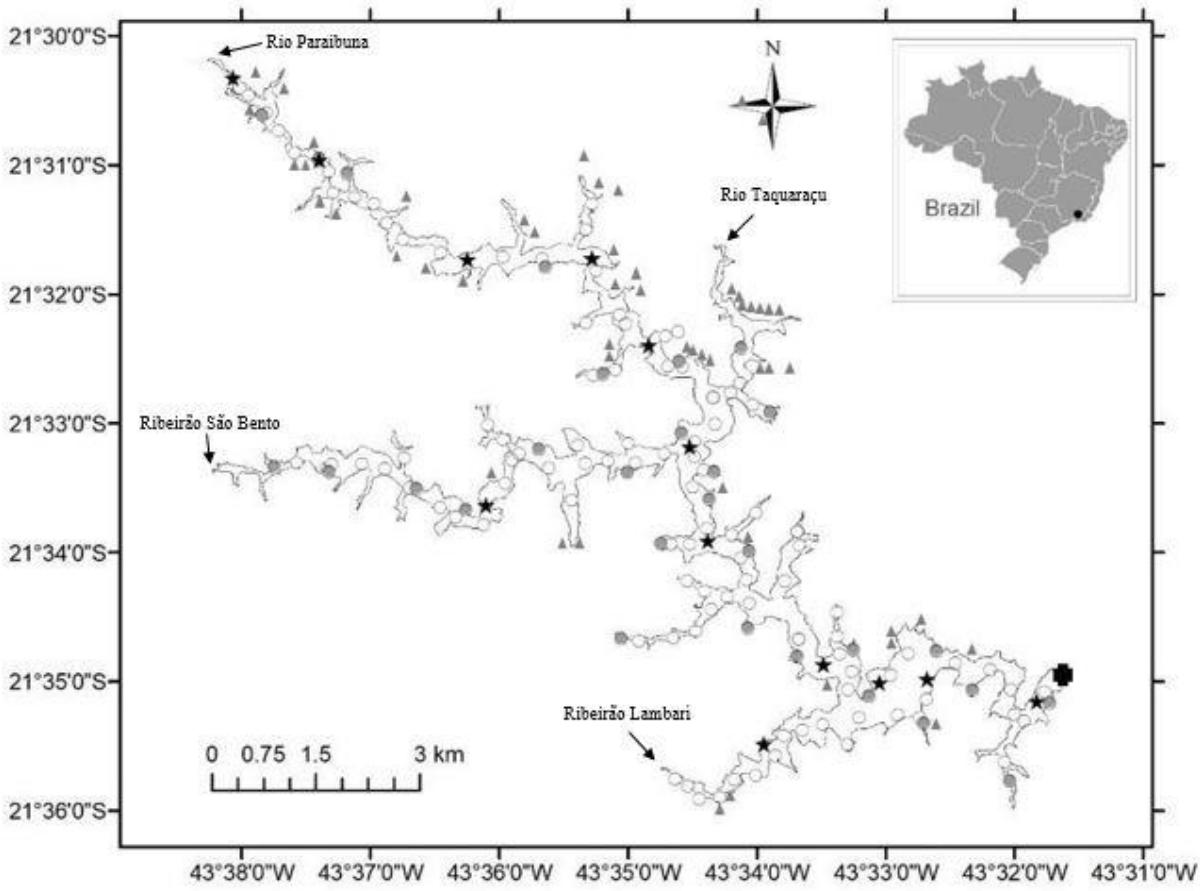

Figure 2. Reservoir location, in Southeast Brazil, and sediment sampling points. Gray circles indicate points located close to the margins (n=35); white circles and black stars indicate points in the deepest part of transects transversal to the reservoir water flow (n=114); black stars also indicate pelagic points from which the sediment was analyzed at the laboratory (13); black cross indicates the location of the dam; all points were sampled for sediment thickness (n=149).

A total of 13 cores evenly distributed along the reservoir were taken to the laboratory and sliced in 2 cm thick subsamples which were stored at ~5°C for further analysis.

Sediment analysis

At the laboratory, the water and the organic matter contents of each sediment slice was measured gravimetrically, based on the weight of the wet sediment, of the dry sediment, and of the sediment after ignition at 550ºC for 4 h. The carbon content was analyzed on the 2 top slices, on the penultimate slice and on one slice every 10 cm along the rest of the core, using a carbon

analyzer (SSM 5000-A, Shimadzu). The OC concentration in the non-analyzed slices were estimated by assuming linear variation along the core depth.

Erosion spots, farms, houses, and river entrances identification

Possible sources of sedimentary OC, i.e. erosion areas, farms, houses and river entrances, were identified along the reservoir area in order to evaluate its effect on the spatial distribution of OC burial. The identification of the erosion spots along the reservoir shore was done by visually analyzing satellite images on Google Earth (**Figure 3**). Each identified spot was marked with a polygon and its area was later measured using the software QGIS 2.18.26. In addition to the erosion spots, we counted the settlements around the reservoir shoreline, including farms, isolated houses and small villages and the tributary rivers/streams connected directly to the reservoir. The identification of the settlements and tributaries was also done by using Google Earth software.

Figure 3: Example of erosion area by the margin of the CDU reservoir (Satellite image from Google Earth).

Data analysis and calculations

The sediment accumulation rate (SAR, cm y^{-1}) was calculated as the ratio of the total accumulated post-flooding sediment thickness at each sampling site (cm) and the reservoir age (24 years).

$$SAR = \frac{Sediment\ thikness}{reservoir\ age}$$

We analyzed the OC burial rate for the 13 cores brought for analysis in the laboratory. The mass of OC (g C) in each slice of sediment was obtained through the content of OC (g C g^{-1}) multiplied by the mass of dry sediment (g). To obtain the total mass of OC (g C) in each core, we summed the masses of OC in all the post-flooding sediment slices. Then, we calculated the average OC burial rate (g C m^{-2} y^{-1}) for each of the 13 cores from the total mass of OC (in all slices), the surface area of the core (2.8 x 10^{-3} m^2), and the age of the reservoir (24 years).

$$OCB = \frac{OC\ in\ sediment}{core\ area\ X\ reservoir\ age}$$

The relationship between SAR and OC burial rate in the 13 cores (see Results; $R^2 = 0.70$, $p<0.0001$; **Figure 4**) was used to estimate the OC burial rate (g C m^{-2} yr^{-1}) for the remaining 136 cores for which OC content was not analyzed.

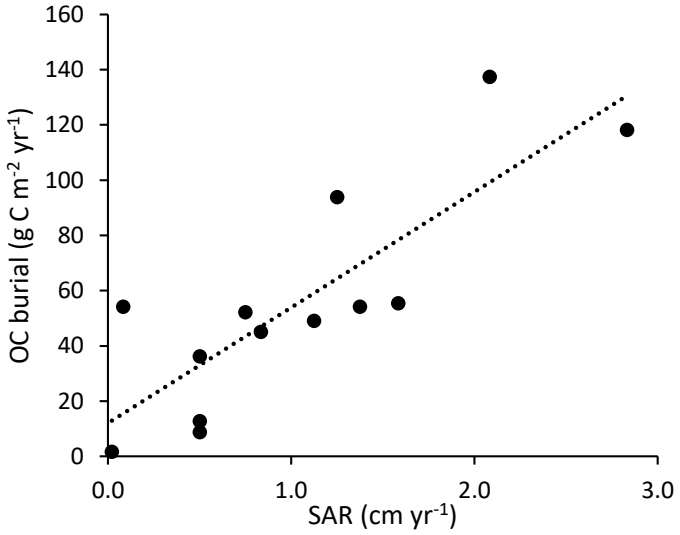

Figure 4: Regression model of sediment accumulation rate (SAR; cm yr^{-1}) and OC burial rate (g C m^{-2} yr^{-1}), with $y = 41.8x + 12.1$, $R^2 = 0.70$, $p<0.0001$.

In order to estimate the average spatially-resolved SAR and OC burial rates, the data from the 149 coring sites were interpolated to the reservoir area using the Inverse Distance Weighted algorithm (IDW, cell size of approximately 22 m x 22 m). The interpolation shown in the maps and used to relate the spatial variability in OC burial to the reservoir characteristics was done excluding the sites sampled in the margins, to prevent interference of the low sediment deposition at the margins. The interpolations and the maps were done using the software ArcGIS 10.6.1 (ESRI).

2.3 Results

The SAR in the cores varied from 0.02 to 2.83 cm yr^{-1} (n=114) for those located at the deeper parts of transversal transects along the reservoir and from 0.01 to 0.38 cm y^{-1} for those located along the margins (n=35, **Table 1**). The average SAR for all sediment cores was 0.56 cm y^{-1} (SD of 0.55), which was very similar to the average SAR as calculated from the interpolation of the sampling cores to the whole reservoir (0.58 cm y^{-1}). The regression analysis indicated that SAR explains 70% of the variability in OC burial in the 13 cores analyzed for OC content (OC burial = 41.8 SAR - 12.1; $R^2 = 0.70$, $p<0.0001$; **Figure 2**) and therefore the regression's equation

was used to estimate OC burial in the remaining cores. OC burial rates varied from 11.8 a 131.1 g C m^{-2} y^{-1}, with an average of 35.5 g C m^{-2} y^{-1}. Spatially resolved OC burial rate was again similar to the core average – 36.3 g C m^{-2} y^{-1}.

Table 1: Comparison of Sediment accumulation rate from margin and from the center of the river channel.

	Min (cm)	*Max (cm)*	*Average (cm)*
Margin	0.3	0.9	3.25
center of the channel	0.5	68.0	16.58

A total of 92 erosion sites were marked around the reservoir, with a total area of 19.000 m^2. We also counted 50 houses or farms and 5 main rivers flowing into the reservoir (**Figure 6**). There was no direct relationship between the spatial distribution of erosion sites or settlements and the sites of higher OC burial. Areas of higher OC burial rates occurred in some of the river inflow areas but also in parts of the main reservoir body. There was no trend of decreasing OC burial from the river inflow areas towards the dam (R^2 = 0.02) but OC burial increased significantly with increasing water column depth in the different parts of the reservoir **(Figure 7).**

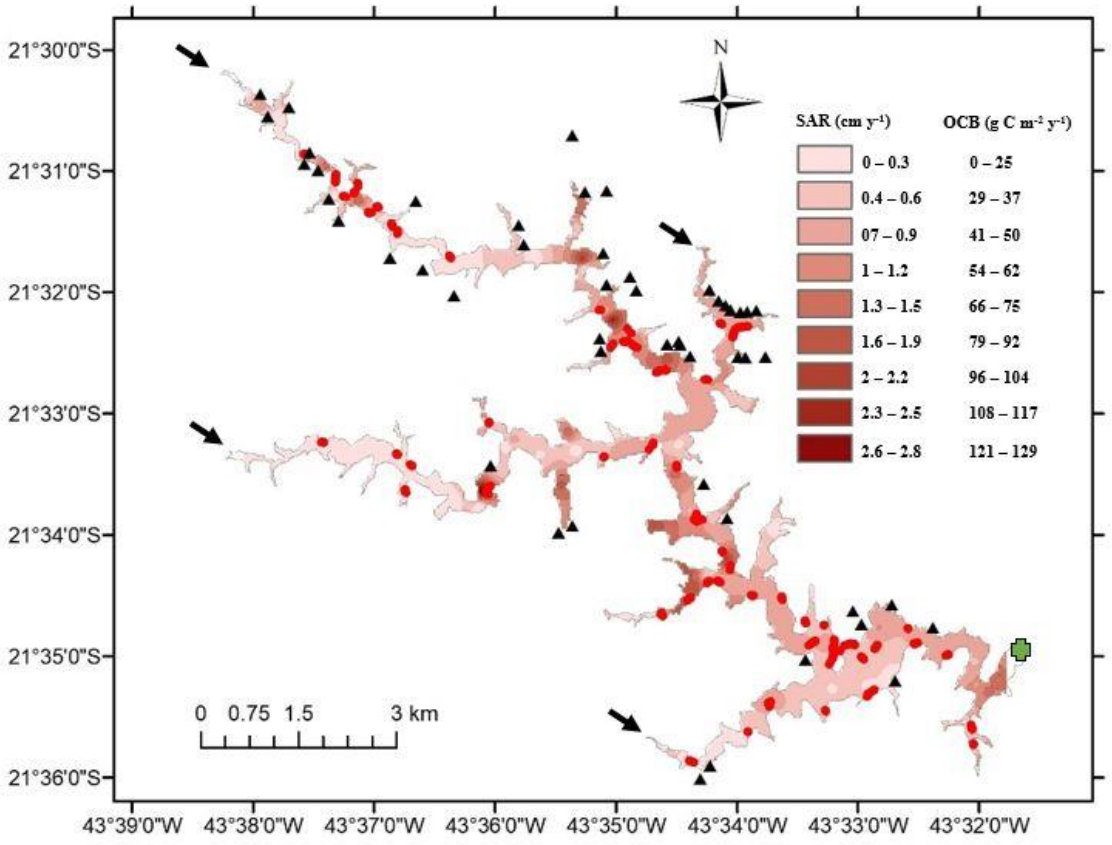

Figure 6: Mapping of the erosion areas (red marks) and the settlements (black triangles) along the margins of Chapéu D'Uvas reservoir. Green cross indicates the location of the dam.

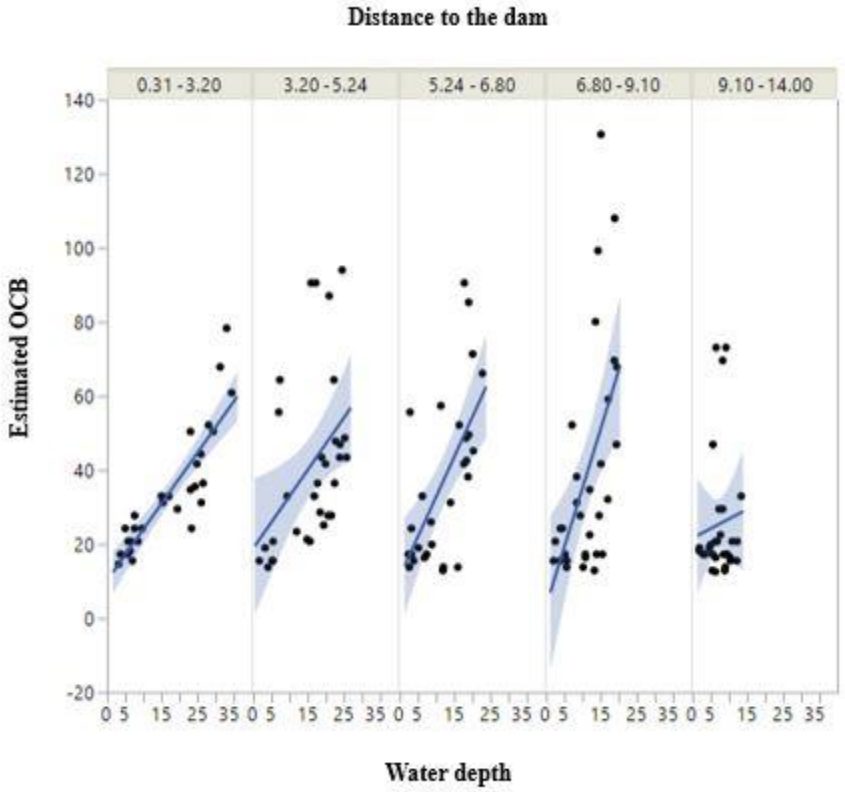

Figure 7: Relationship between OCB and distance of each core sampled to the dam. The closer to the dam the clear the relationship. this is probably because the further away locations are more heterogeneous (composed of different arms of the reservoir).

2.4 Discussion

The spatially resolved average SAR and OC burial rate in the CDU reservoir (0.56 cm y^{-1} and 35 g C m^{-2} y^{-1}, respectively) were within the range of values reported to other tropical reservoirs, even though this is an oligotrophic reservoir located in a small watershed in comparison to the others. For instance, Mendonça (2014) measured the OCB rate in a large hydroelectric reservoir in southeast Brazil and found that on average 42.2 g C m^{-2} y^{-1} was buried in that reservoir with a SAR of 0.51 cm^{-2} y^{-1}. Kunz and others (2011), shows that the oligotrophic Kariba lake in Africa presented a OCB of 23 g C m^{-2} y^{-1}. The effect of low productivity and small catchment area in CDU, which should imply in low inputs of both terrestrial and aquatic OC to the sediment, may have been compensated by the likely high erosion in the catchment. OC burial in CDU was also

in the same order of magnitude of values found for some temperate and boreal reservoirs (63 and 100 g C m^{-2} yr^{-1} in Huairou and Shisanling reservoirs, respectively (Luo et al., 2016); 33 g C m^{-2} yr^{-1} in Eastmain-1 (Teodoru et al., 2012), even though the efficiency of organic carbon burying tends to be lower in tropical regions, as temperature has a strong positive effect on carbon mineralization (Gudasz *et al.*, 2010; Cardoso *et al.*, 2014).

When compared to the most recent estimate of OC burial in global reservoirs (mean:144 g C m^{-2} y^{-1} (Mendonça, 2017), OC burial in CDU is much lower. However, global values may be overestimated since data on carbon burial measurements in the world are scarce and unevenly distributed, with a disproportionally large number of studies in small eutrophic ponds (e.g. Downing et al. 2008).

On average, areas close to margins accumulated 5 times less sediment and, thus, less OC, than the deeper parts of the reservoir (**Table 1***)*. Indeed, sediment accumulation tends to decrease from the main river channel towards the margins (Mendonça *et al.*, 2014) due to a process known as 'sediment focusing' (Davis e Ford, 1982; Blais e Kalff, 1995). Sediment focusing is the tendency of sediment to be moved from the steeper to flatter bottoms due to downwards gravitational transport or from shallower to deeper areas due to the resuspension in shallow waters. Resuspension in shallow waters is caused by higher water turbulence near the sediment. The higher OC burial in deeper areas reflected in strong relationship between OC burial and water column depth when the reservoir is split into zones according to the distance to the dam (in order to reduce the effect of the spatiality, **Figure 7**).

Sediment accumulation and OC burial were also higher in some sites near river inflow areas than close to the dam, as previously described for a hydroelectric reservoir (Mendonça et al 2014). Riverine water inflow brings with it sediments containing terrestrial organic matter from the drainage basin and effluents from human activities, which tend to be deposited when the water residence time decreases in the reservoir body. However, because some tributaries did not contribute with high sediment load and areas of higher accumulation also occurred in some spots along the reservoir body, there was no strong tendency of decreasing in OC burial with increasing the distance to the dam (R^2 = 0.02, only the pelagic sites included). River inflow into reservoirs usually bring high loads of nutrients, causing primary production (and consequent deposition of autochthone OC) to increase towards the dam, as the deposition of terrestrial OC decreases (De

Junet *et al.*, 2009). It leads to a decrease in the efficiency of carbon burial towards the dam (Mendonça *et al.*, 2016). This effect river-dam patterns might have been diminished due to the fact that the tributaries of the CDU reservoir have very small catchment areas - even the main tributary, the Paraibuna river, is borne only a ~ 36km away from the reservoir. Moreover, none of the inflowing rivers pass through populous cities, not capturing large quantities of anthropic effluents. It is also important to consider that OC burial might have been underestimated in the upper reach of the main tributary (Paraibuna river, upper arrow in Figure 2) because the fluvial sediment deposited in this area is probably very similar to the pre-flooding riverine sediment. It is likely, then, that only the most organic top sediment in this area was accounted as post-flooding material. It is difficult to estimate based on our data if it occurred in other tributaries as well and by how much this has affected our OC burial estimate. This possible underestimation of OC burial in river inflow areas makes of our reservoir-wide OC burial rate estimate a conservative one and is likely to have occurred in other estimates of OC burial in reservoirs as well.

Considering that the fluvial sediment load to the reservoir tends to be relatively low, the high soil erosion in the reservoir catchment, especially along the reservoir shoreline, is likely to cause the relatively high OC burial registered in CDU, with no clear river-dam pattern. The high frequency of erosion areas at the reservoir shoreline stands out when navigating through the CDU reservoir (see **Figure 6** for an example). We counted 92 erosion spots along the reservoir shoreline, which covers a total area of ~19.000 m^2 and a summed extension of ~4 km of reservoir shore. Erosive processes can have many causes and most of them are linked to human activities. For example, the advance of agriculture has changed much of the earth's surface as for planting it is necessary to remove the vegetation cover (Matthews, 1983). The removal of the vegetation cover puts the rainwater in direct contact with the land which results in the loss of fine soil and consequently, the erosive process starts. We also identified 50 settlements close to the reservoir, among isolated houses and small farms. Agricultural practices, farming or building constructions can substantially increase the erosion process around the reservoir. Meade (1990), argues that agricultural practices can accelerate the erosion process by up to 100-fold. Thus, agriculture and other practices that cause intensive soil change increase sedimentation rates in the water body. The catchment draining to the CDU reservoir is comprised of 66% grassland, 30% of Atlantic forest remnants and 4% of eucalyptus plantation. It means that 70% of the vegetation around the reservoir was removed in the past for coffee plantation and most of it is now used for cattle grazing

(Machado, 2012). Certainly, the erosive processes, added to the presence of houses, villages and small farms substantially increase the entry of terrestrial sediments containing organic matter into the reservoir. However, our analysis showed no spatial correlation between the erosion and settlement spots and the areas of higher OC burial rates. It indicates that once inside the reservoir, the sediments are transported and further deposited in accumulation areas defined by the system's morphology and hydrology.

The total sink of OC in the sediment of CDU reservoir was a significant component of the reservoir carbon balance, being higher than the total carbon emission through water-atmosphere diffusion. We estimate that the CDU reservoir is responsible for burying a total of 436 tons of OC in its sediment annually. A study previously carried out in the same reservoir showed that the average spatially resolved diffusive CO_2 and CH_4 emissions from the water surface was 336 t C y^{-1} (252 as CO_2 and 84 as CH_4, Paranaíba et al. 2018). If the carbon emission from the reservoir's drawdown area is also considered, the total emission from CDU increases by ~1100 t C (Almeida *et al.*, 2019), and burial becomes equivalent to 30% of the reservoir's emission. However, total carbon emission from water surface should increase substantially when CH_4 ebullition, a major pathway of emission in reservoirs (Deemer *et al.*, 2016), is included. Indeed, a recent study in one bay of the CDU reservoir indicated that ebullition from the reservoir can be high (Linkhorst *et al.*, 2020), although there is no estimative available for the whole reservoir area. The relative importance of OC burial in reservoirs is further reduced if we consider the Global Warming Potential of CH_4, which is 34 times higher than that of CO_2 for a time span of 100 years (IPCC 2013). If the fluxes are calculated in terms of CO_2 equivalents, carbon emission from diffusion alone is ~7 times larger than OC burial. A complete carbon budget of the CDU reservoir, however, should consider other pathways of carbon emission, e.g. degassing at the turbines, downstream emission and emission from the drawdown area.

2.5 Conclusion

In warmer regions, the temperature favors the mineralization of the organic matter available in the reservoir, transformed into CO_2 that will be diffused through the water column until it reaches the atmosphere. Thus, carbon burial in these environments is low compared to reservoirs in tropical regions. In addition, the CDU reservoir is considered to be oligotrophic,

which means that autochthonous organic matter production is also low. The spatial distribution of carbon burial in the CDU reservoir appears to be driven by variables such as erosive processes in the catchment area, the presence of settlements, small farms, river inlets and hydrology. In fact, these variables are reported in the literature as factors that substantially increase the entry of organic carbon into the reservoir. However, our analyzes did not show a strong correlation between these factors and the spatial distribution of the buried organic carbon. Finally, the CDU reservoir buried 30% of the emitted CO_2. However, when we transform CH_4 into carbon equivalent, the input now represents 17% of emissions. For a better carbon balance in the CDU reservoir, it is essential that more accurate estimates of ebullition emissions are considered, since ebullition is an important emission route in continental waters. In addition, it is important to consider emissions downstream (degassing), in order to cover all the main emission pathways in reservoirs, contributing to a better estimate of the carbon balance.

3. CHAPTER 2: Year-round CO_2 emissions from the drawdown area of a tropical reservoir: strong seasonal, diel and spatial variation

3.1 Introduction

The number of dams in rivers has been rising worldwide to meet the increasing human demand for hydropower, water supply, and flood control. In addition to affecting river hydrology, dams alter the physicochemical and biological characteristics of watercourses (Nilsson *et al.*, 2005). Alterations include an increase in water residence time, changes in temperature causing thermal stratification of the water column, decreased turbidity, increased autochthonous primary production (Friedl e Wüest, 2002), and increased organic matter burial in the sediment (Mendonça *et al.*, 2014; 2016; 2017). In addition, man-made reservoirs are important sources of the greenhouse gases (GHG) carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) to the atmosphere (St. Louis *et al.*, 2000; Deemer *et al.*, 2016). Globally, reservoir water surfaces are estimated to emit 0.8 Pg CO_2 equivalent per year, representing 1.5% of the total anthropogenic GHG emissions (Deemer *et al.*, 2016).

GHG emissions in reservoirs may vary widely over space (Roland *et al.*, 2010; Teodoru *et al.*, 2012; Paranaíba *et al.*, 2018) and time (Teodoru *et al.*, 2012; Linkhorst *et al.*, 2020). But the mechanisms governing spatial and particularly temporal heterogeneity in emissions remain poorly known. This is especially true for areas subject to seasonal drying and re-flooding, typically referred to as drawdown areas. Most estimates of carbon balance in inland waters disregard emissions from drawdown areas (St. Louis *et al.*, 2000; Barros *et al.*, 2011; Bastviken *et al.*, 2011; Raymond *et al.*, 2013; Li e Zhang, 2014; Holgerson e Raymond, 2016). In reservoirs, drawdown areas are covered with water during rainy periods or when the reservoir floodgate is closed. However, reservoir water level drops during droughts or when the floodgates are open, exposing marginal sediments to direct contact with the atmosphere. Exposure of sediment to air induces the activity of microorganisms, which mineralize the available organic matter, leading to increased CO_2 emissions (Jin *et al.*, 2016; Weise *et al.*, 2016). Recent evidence indicate that the drawdown areas of reservoirs are important sources of CO_2 to the atmosphere, emitting CO_2 at rates that are about one order of magnitude higher than the fluxes from adjacent water surfaces (Deshmukh *et al.*, 2018; Almeida *et al.*, 2019; Marcé *et al.*, 2019; Keller *et al.*, 2020). Most assessments of CH_4 emissions from reservoir drawdown areas have reported low fluxes, representing a small fraction of total reservoir GHG emission (Yang *et al.*, 2013; Yang *et al.*, 2014; Serça *et al.*, 2016), even in tropical areas (Almeida *et al.*, 2019; Amorim *et al.*, 2019). In a recent study, for example, emissions of CH_4 from the deepest part of a reservoir in China have been shown to be 300 times higher them the emissions from the drawdown area (Yang *et al.*, 2014). For this reason, our paper will focus only in CO_2 emissions.

The magnitude of CO_2 emissions from drawdown areas has been shown to be controlled by sediment moisture (Gómez-Gener *et al.*, 2016; Jin *et al.*, 2016; Almeida *et al.*, 2019; Keller *et al.*, 2020), temperature (Jin *et al.*, 2016; Keller *et al.*, 2020) and the surrounding land cover (Almeida *et al.*, 2019). When the sediment begins to dry, there is an increase in the availability of oxygen in the sediment, which increases enzymatic activity and decomposition of organic matter, thereby increasing CO_2 emissions (Fromin *et al.*, 2010). A recent study showed that temperature controls emissions in dry sediment beds and upland soils (Gómez-Gener *et al.*, 2016), since temperature is positively related to microbial activity. In addition, periodically flooded areas surrounded by forest tend to present higher CO_2 emission than areas not adjacent to forests (Catalán *et al.*, 2014; Bolpagni *et al.*, 2016; Obrador *et al.*, 2018), which is likely explained by a

relatively higher load of organic matter from forested areas to marginal sediments (Almeida *et al.*, 2019).

The inclusion of drawdown fluxes on freshwater GHG emission assessments is limited to a few recently published studies (Lu *et al.*, 2011; Yang *et al.*, 2012; Yang *et al.*, 2014; Jin *et al.*, 2016; Li *et al.*, 2016; Serça *et al.*, 2016; Deshmukh *et al.*, 2018; Kosten *et al.*, 2018; Almeida *et al.*, 2019; Amorim *et al.*, 2019). Despite the rapid advance towards quantifying and understanding the drivers of spatial variability in drawdown CO2 emissions (Keller, *et al*., 2020), very little is known about the temporal variability in these fluxes. To our knowledge, only one system has been studied with seasonal resolution (Three Gorges Reservoir, in China; Yang et al., 2012, Li et al. 2016) and none has been studied with daily resolution. Evidences from soil respiration studies indicate that mainly due to the effect of temperature, both seasonal and daily variations in CO2 fluxes should be taken into account in soil emission estimates (Davidson *et al.*, 1998; Law *et al.*, 1999; Sotta *et al.*, 2004; Liu *et al.*, 2006). It is likely, however unknown, that the same is valid for drawdown sediments. Here we accessed the CO2 emission rates in the drawdown zone of a tropical reservoir considering the spatial and temporal (seasonal and daily) variability. We also estimated the relative contribution of the drawdown zone to the total reservoir's year-round CO2 emission. Moreover, we investigated the potential drivers of variability in drawdown CO2 emission and performed a simple experiment to understand the effect of rain events on emissions.

3.2 Methods

Study area

Our study was carried out in Chapéu D'Uvas (CDU; 21º33'S, 43º35'W), an oligotrophic reservoir (average concentration of total nitrogen and total phosphorus: 452 µg L^{-1} and 12 µg L^{-1}, respectively) (Paranaíba *et al.*, 2018) located in the municipality of Ewbank da Câmara, southeastern Brazil. This reservoir serves as a major supply of water to the city of Juiz de Fora (~600,000 inhabitants). Although the construction of the reservoir began in the 1950s, damming the Paraibuna River, the project was completed only in 1994, flooding an area of approximately 12 km^2 in the Atlantic Forest biome (Ibge, 2012). The average depth of the reservoir is 19 m, with

a maximum depth of 40 m near the dam. The main land use in the reservoir watershed is grassland used for cattle grazing (66%), followed by remnants of natural forest (30%) and Eucalyptus plantations (4%) (Machado, 2012).

3.2.1 Sampling strategy

Variability at annual timescale

To assess the seasonal variation and the influence of surrounding land cover on CO_2 emission from the drawdown areas, measurements were performed monthly between August 2018 and July 2019, except for September 2018, February and May 2019. We distinguished 4 hydrological periods during the sampling year, which we refer to as "late dry season" (2 sampling campaigns between July – October 2018), "early rainy season" (3 sampling campaigns between November 2018 – January 2019), "late rainy season" (2 sampling campaigns between February – April 2019), and "early dry season" (2 sampling campaigns between May – July 2019We selected 8 sampling sites in the major surrounding land cover types: 4 sampling sites surrounded by grassland, and 4 sampling sites surrounded by forestlands (**Figure 7**). As Eucalyptus plantations represent only a small fraction of the reservoir watershed land cover, it was not included in the sampling scheme. At each sampling site, triplicate measurements were performed at each of 3 different zones: (i) underwater shoreline (UW), which is characterized by 1 to 3 cm of water overlying the marginal sediments; (ii) wet sediments (WS), which are those marginal sediments that were only recently exposed to the atmosphere; and (iii) dry sediments (DS), which had been exposed to the atmosphere for longer times and were visually dry (**Figure 8**). In the field, we were able to visually distinguish wet and dry sediment based on sediment color (**Figure 8**). This visual distinction was later confirmed by moisture content analysis in the laboratory.

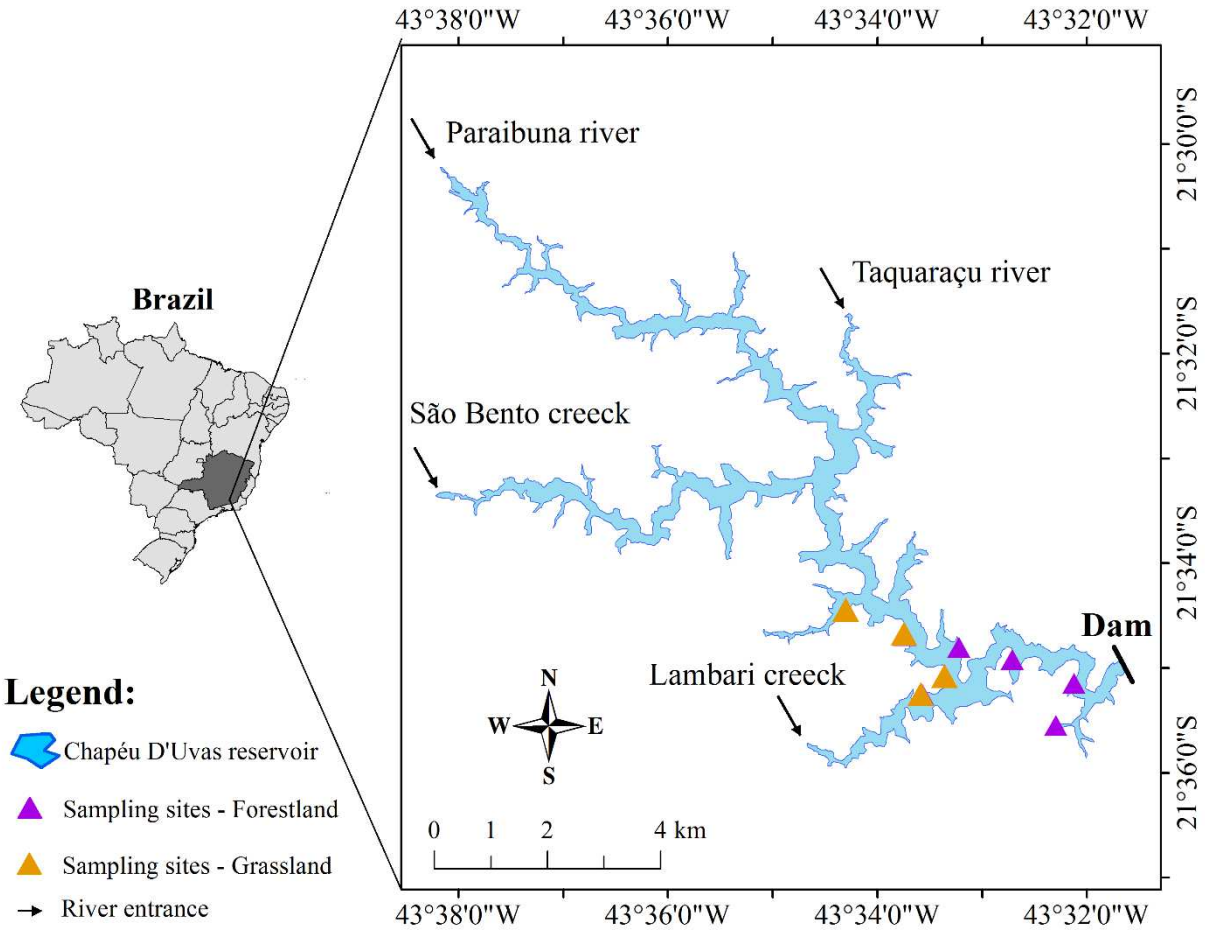

Fig. 7: Chapéu D'Uvas reservoir (CDU) and the location of the sampling sites.

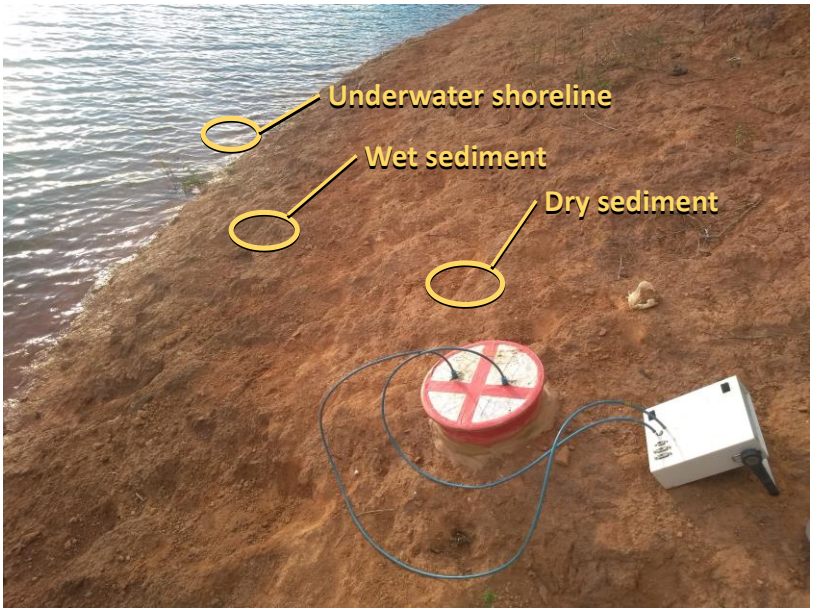

Fig. 8: Drawdown zone of Chapéu D'Uvas reservoir (CDU) showing the three zones from which the fluxes were measured. Also shown is a static chamber connected to the portable gas analyzer.

3.2.2 Measurements of CO_2 fluxes

At each sampling site, measurements of CO_2 fluxes were performed using a static opaque chamber (cylindrical, 6.24 L of volume, and 0.07 m^2 of surface area) connected to an infrared gas analyzer (IRGA, EGM-4 PP Systems). Changes in CO_2 partial pressure inside the chamber were monitored over 5 minutes, and the CO_2 fluxes (mg C m^{-2} d^{-1}) were calculated following the equation below:

$$F_{CO_2} = \left(\frac{dpCO_2}{dt}\right) * \left(\frac{V}{R*T*S}\right)$$

where $dpCO_2$ is the slope of the pCO_2 changes (µatm) over time, V is the volume of the chamber (m^3), S is the surface area covered by the chamber (m^2), T is the air temperature (K), and R is the gas law constant (8.3141 atm K^{-1} mol^{-1}).

Triplicate chambers were deployed 2 m apart from each other to capture spatial variability within each sampling zone. For measurements made over the exposed sediments (WS and DS), the chambers were placed on the sediment and sealed with pottery clay (Lesmeister e Koschorreck, 2017) to avoid disturbance and gas leakage during the measurements.

Variability at short timescale

To assess the diel variation of CO_2 flux in drawdown zones adjacent to the different land cover types, we conducted four 24-hour-measurement campaigns. Two diel campaigns were performed at sampling sites near grassland (March and July 2019) and two at sites near forestland (April and July 2019). CO_2 flux rates were assessed every 3 hours using the same methodology as in the annual timescale.

We also conducted an experiment to investigate how CO_2 fluxes from the drawdown zone of CDU reservoir change after a rain event. The experiment was conducted in two sampling sites (one near forest and one near grassland) and in two zones (WS and DS), totaling four rain simulation events. In each of these events, we mimicked 2.5 mm of rainfall by gently pouring 5 liters of water over an area of 2 m^2 with a bucket for 15 minutes. The CO_2 fluxes were measured in triplicates before and 30 minutes after the rain simulation using the same methodology as in the annual timescale.

3.2.3 Environmental variables and sediment properties

Daily rainfall data from August 2018 to July 2019 were obtained from the closest meteorological station, located ~40 Km from the CDU reservoir (INMET - station A518, S -21.769965°; W -43.364329°; http://www.inmet.gov.br/portal/). After each chamber deployment, air temperature, atmospheric pressure, and wind speed were measured using a portable

anemometer (Skymaster Speedtech SM-28, accuracy: 3%). Soil temperature, and conductivity were also measured in situ using a conductivity meter (Akrom KR31). For analysis of moisture, pH and organic matter content, sediment samples were collected at the location of the previous chamber measurements, placed in plastic bags and stored in cool boxes (~10º C) until further laboratory analysis. In the laboratory, 10 g of fresh sediments were placed in glass bottles and mixed with 25 mL of distilled water. After 1 hour standing, the pH of the suspended solution was measured with a conventional pH electrode (HANNA – HI8424). The laboratory analysis of moisture confirmed that WS were wetter than DS. To quantify the moisture content of the exposed sediment samples, 10 g of fresh sediments were placed in ceramic vessels and dried at 105 °C until reaching a constant weight. The moisture percentage was calculated by weight loss after drying. The organic matter content was measured after the moisture analysis, using the same samples. The vessels containing the samples from moisture analysis were placed in an oven under 450°C for 4 h, and the organic matter percentage was calculated by weight loss after ignition after the samples reached constant weight.

3.2.4 Calculations and data analysis

In order to estimate the contribution of the drawdown zone to the combined emissions from the water surface and the drawdown zone, hereafter referred to as total CO_2 emission from the CDU reservoir (kg C d^{-1}), we multiplied the CO_2 emission rates from the drawdown area, the underwater shoreline and the open water by their respective surface areas (m^2). As the water level varied, these areas were dynamic and calculated on a daily basis (see below). The drawdown emissions were calculated based on the average dry and wet sediment fluxes (as we had no information on the share of dry and wet sediment we assumed an equal areal extent) for each measurement site/time. Next, a single drawdown CO_2 flux was estimated for each sampling campaign by calculating the weighted average of the fluxes from forest and grassland sites normalized. The weight was determined by the percentage of reservoir bordering forest and grassland. We estimated the drawdown area for each day by subtracting the open water area from the maximum reservoir surface water area (10.6 km^2, from Almeida et al. 2019). The daily open water area was calculated from historical water level (Cesama, 2019), using the following equation

from Almeida et al. (2019): open water area (km^2) = 0.41 * water level (m) - 293.7. The average CO_2 emission rates from the underwater shoreline area determined for each campaign were linearly interpolated to estimate year-round daily emissions rates. The underwater shoreline area in each day was calculated by multiplying the reservoir perimeter by 0.3 m (diameter of the gas chamber). Reservoir perimeter data was available for four dates. The area for the intermediated dates was approximated through linear interpolation. Open water diffusive CO_2 fluxes from four different hydrological seasons, between 2015-2016, were obtained from Paranaíba et al. (under review), assuming that the between-seasonal variability of diffusive CO2 emission is larger than the between-year variability.

Statistical analyses were performed using the software JMP® (version 14.3.0). To meet normality and homoscedasticity requirements, we log-transformed the CO_2 flux data. To test for possible differences in CO_2 fluxes between land use types and moisture zones we used a two-way ANOVA. To assess potential day and night differences in CO_2 emissions we used a t-test. We also performed a paired *t*-test to verify if there is statistical difference between CO_2 fluxes before and after the rain simulation event. A principal component analysis (PCA) was used to visualize the relationships of CO_2 fluxes between continuous variables measured in the field (air and soil temperature, temperature difference between air and soil, conductivity, wind speed, pressure,) and in the laboratory (moisture, pH, and organic matter contents). A multiple linear regression model was applied using the most important predictors identified in the PCA to assess which variables significantly influence CO_2 emissions in the drawdown areas.

3.3 Results

Variability at annual timescale

The CO_2 fluxes measured in the drawdown zone of CDU reservoir varied from 21 to 10,116 mg C m^{-2} d^{-1}. Emissions were higher in areas near forest than near grassland, regardless of the sampling zone (t-Ratio = 3.43; p = 0.0007. Only for the dry sediment zone there was no statistical difference between areas near forest and grassland although there was a tendency of higher values in the first one (**Figure 9**). When comparing inundated, wet and dry zones, the dry sediments had

the highest CO_2 fluxes, regardless of the land cover type (F-Ratio = 30.94; $p < 0.0001$) (**Figure 9**). The CO_2 fluxes from wet sediments were consistently higher than the fluxes from the underwater shoreline zone, although there was no statistical difference between them for both forest and grassland sites ($p = 0.0591$) (**Figure 9**).

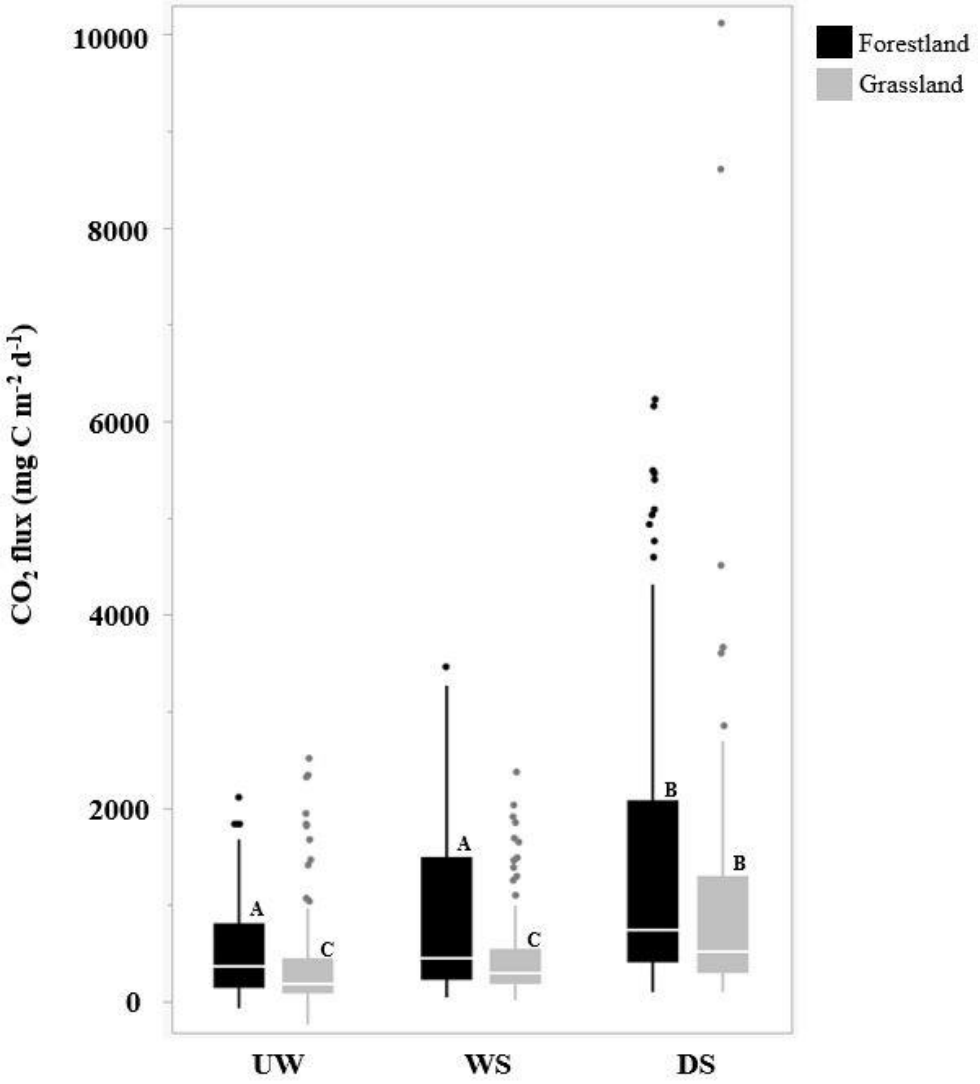

Fig. 9: CO_2 emissions by zone and land use. UW: under water shoreline sediment; WS: wet sediment; DS: dry sediment. Statistically different emissions assessed by a two-way ANOVA are indicated with different capital letters. Each box plot received a letter (A, B, and C). The same letter in different boxplots means that there was no statistical difference between periods. Black boxes represent zones nearby forestland, grey boxes represent zones nearby grassland. The lines within the boxes indicate the median, the boxes delimit the 25th and 75th percentiles, and the whiskers delimit the 5th and 95th percentiles.

The weighted average (i.e., area-weighted fluxes from grassland and forestland) monthly CO_2 emission rates from the whole drawdown area of the CDU reservoir measured over the course of one year varied from 145 mg C m^{-2} d^{-1} in June 2019 (early dry season) to 3021 mg C m^{-2} d^{-1} in August 2018 (late dry season) (**Figure 10.a**). The total monthly fluxes from drawdown areas varied from 730 kg C d^{-1} in March 2019 (late rainy season) to 5110 kg C d^{-1} in August 2018 (late dry season). The highest drawdown CO_2 emission rates occurred in the dry period, with no statistical difference between early (mean = 1133 mg C m^{-2} d^{-1}) and late dry season (mean = 1617 mg C m^{-2} d^{-1}) (**Figure 10.b**). The lowest areal CO_2 emissions were registered in the rainy season, with significantly lower fluxes at its end (mean = 351 mg C m^{-2} d^{-1}) than at its beginning (mean = 932 mg C m^{-2} d^{-1}) (t-Ratio = 13.8; $p < 0.0001$).

The annual amount of CO_2 emitted from the drawdown area derived from our monthly field campaigns was 644 tons C, representing 80% of the total CO_2 emissions from CDU when also accounting for water surface emissions (**Figure 11**). Total CO_2 emissions from the CDU reservoir (drawdown + water surface) were temporally variable, with lowest values in March 2019 (late rainy season, 1210 kg C d^{-1}) and highest values in August 2018 (late dry season, 5616 kg C d^{-1}). The relative contribution of drawdown areas to the total reservoir emission also varied over time, with a larger contribution of open water emissions in June 2019 (early dry season, 56% of total reservoir emission) and smaller in December 2018 (early rainy season, 6% of total reservoir emission) (**Figure 11**).

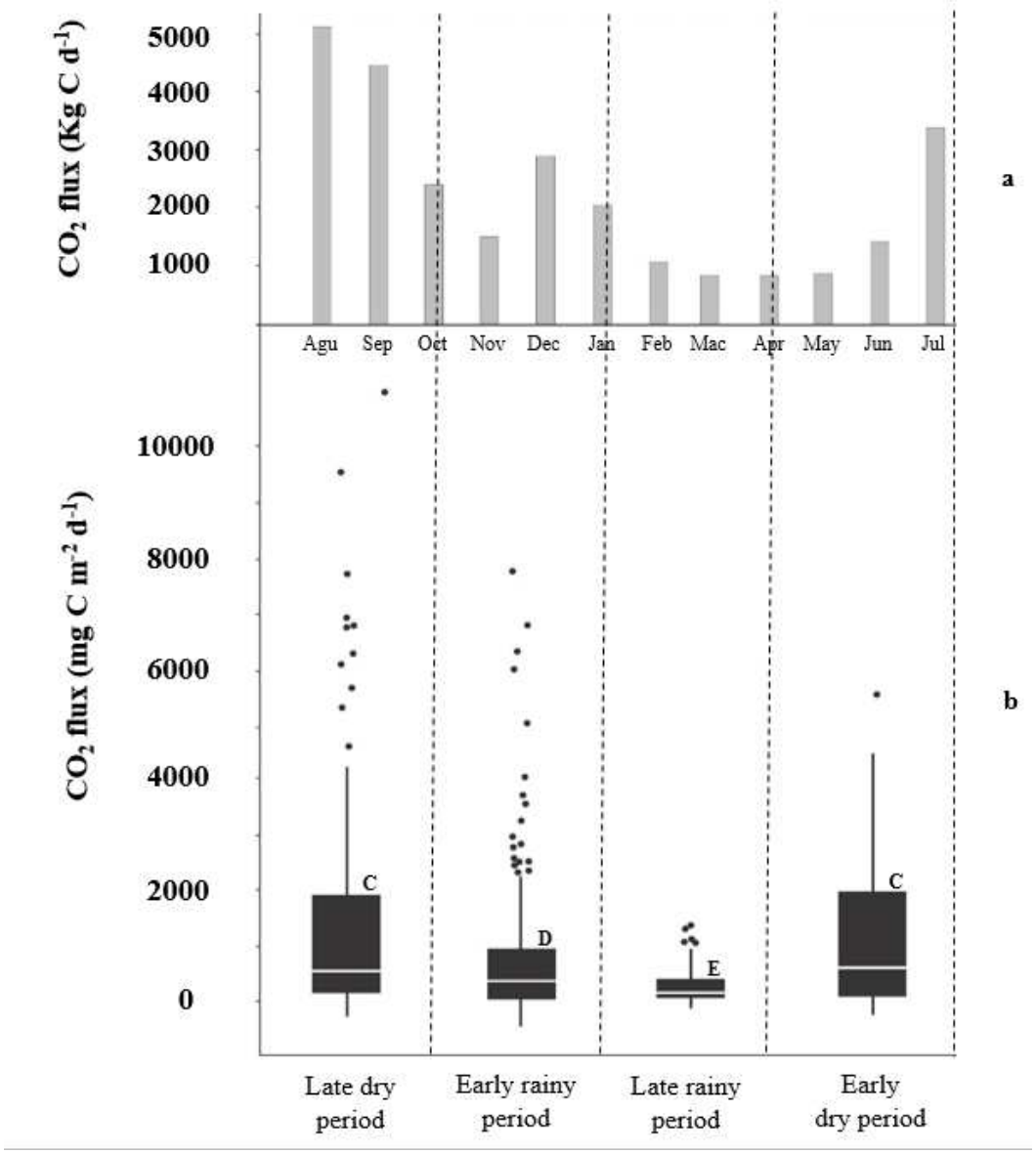

Fig. 10: (10.a): Total CO_2 flux per month from the entire drawdown zone (wet and dry sediments) of Chapéu D'Uvas reservoir. (**10.b)**: CO_2 fluxes from drawdown areas in Chapéu D'Uvas reservoir separated by seasons according to the rain distribution throughout the year. Statistically different emissions assessed by a two-way ANOVA are indicated with different capital letters. Each box plot received a letter (C, D, and E). The same letter in different boxplots means that there was no statistical difference between

periods. The lines within the boxes indicate the median, the boxes delimit the 25th and 75th percentiles, and the whiskers delimit the 5th and 95th percentiles.

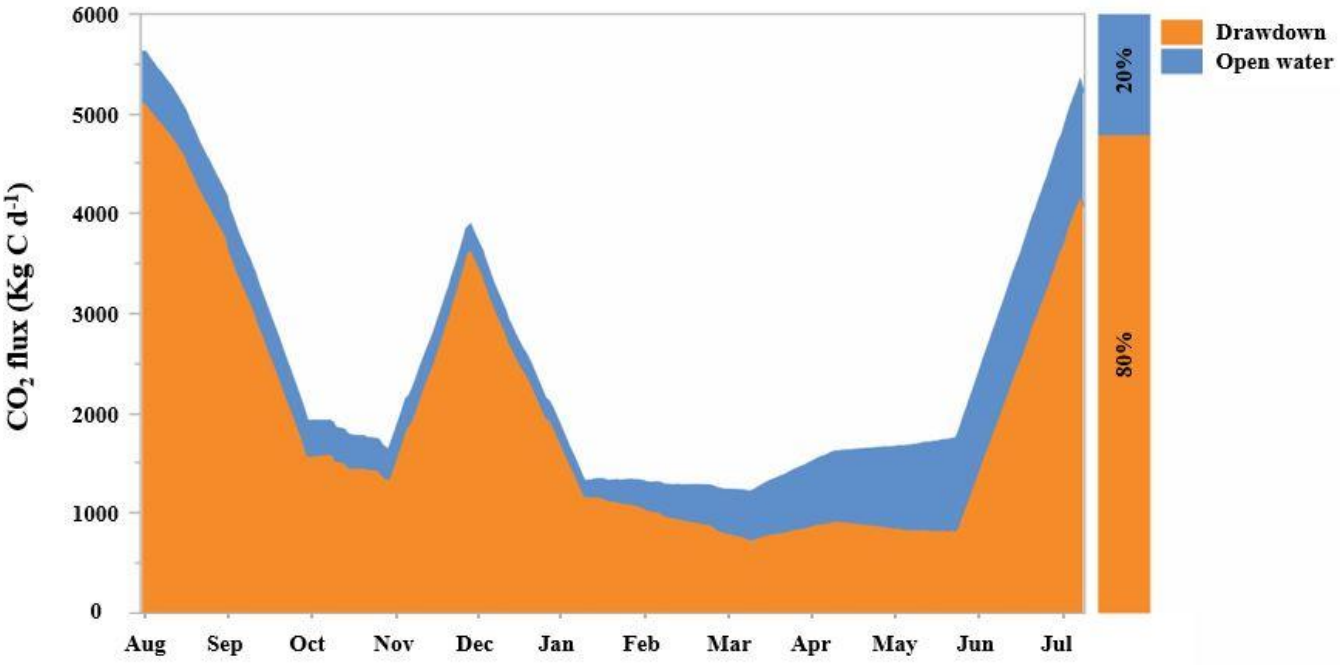

Fig. 11: Contribution of each zone of the Chapéu D'Uvas reservoir (CDU; open water, drawdown) to the total CO_2 emission. The bar on the right represents the average contribution of each zone during the entire period. See methods section for details on data sources and calculations.

Variability at short timescale - Diel measurements

Fluxes were on average 57% higher at night than during the day (**Figure 12**). The average day-time emission was 274 mg C m^{-2} d^{-1} (SD = 214 mg C m^{-2} d^{-1}) whereas the night-time average was 453 mg C m^{-2} d^{-1} (SD = 565 mg C m^{-2} d^{-1}). The diel measurements conducted in July 2019 in both grasslands and forestland did not reveal a significant difference in emissions between land use types ($p = 0.1022$). Considering the individual campaigns, only in March 2019 and April 2019 we found statistical difference between day and night emissions (t-Ratio = 2.032; $p = 0.0482$ and t-Ratio = 4.196; $p = 0.0003$, respectively).

The only variable that may explain the higher emission at night is the temperature difference between soil and air. At some sites, this temperature difference was higher than 5 °C

during the nighttime (**Figure 12**). We also found that an emission pick occurs at night when the temperature difference is between 0.5 and 1.5 °C (**Figure SP1**).

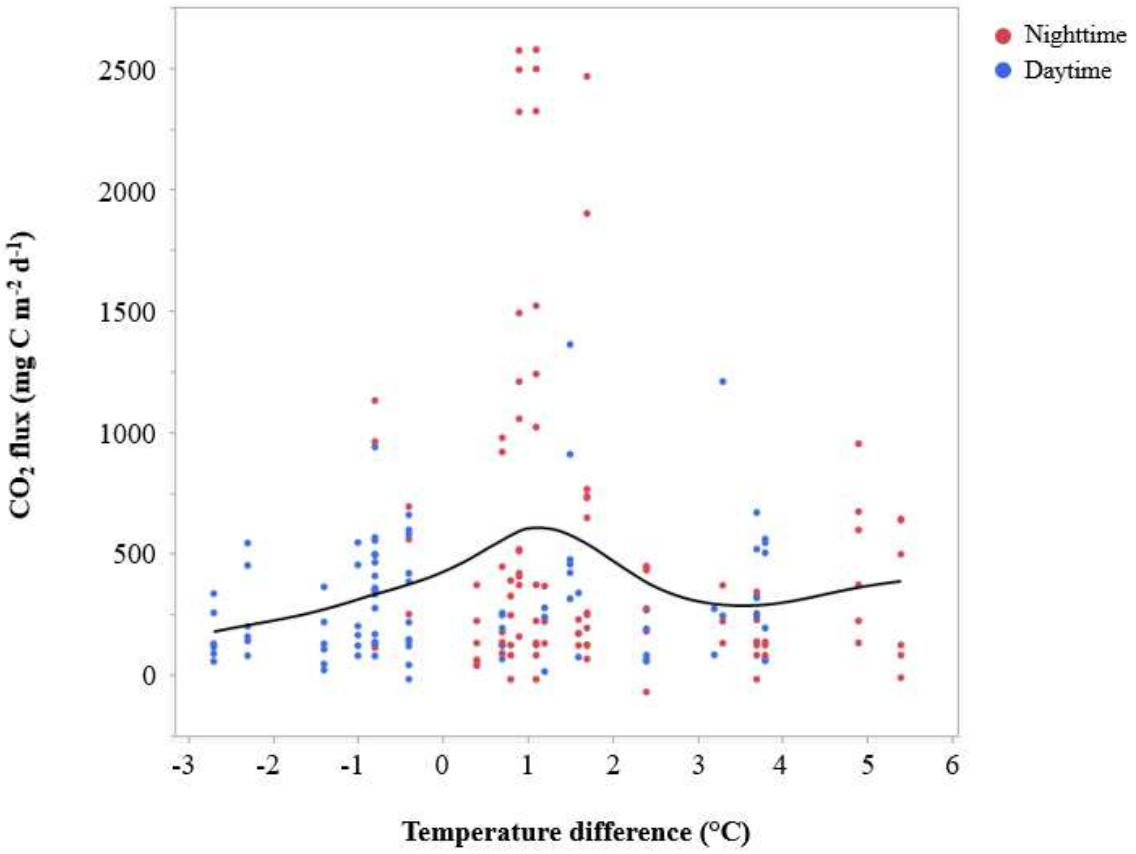

Fig. SP1: CO_2 flux by temperature difference between soil and air showing a pick emission at night when the temperature difference is around 0.5 and 1.5 °C.

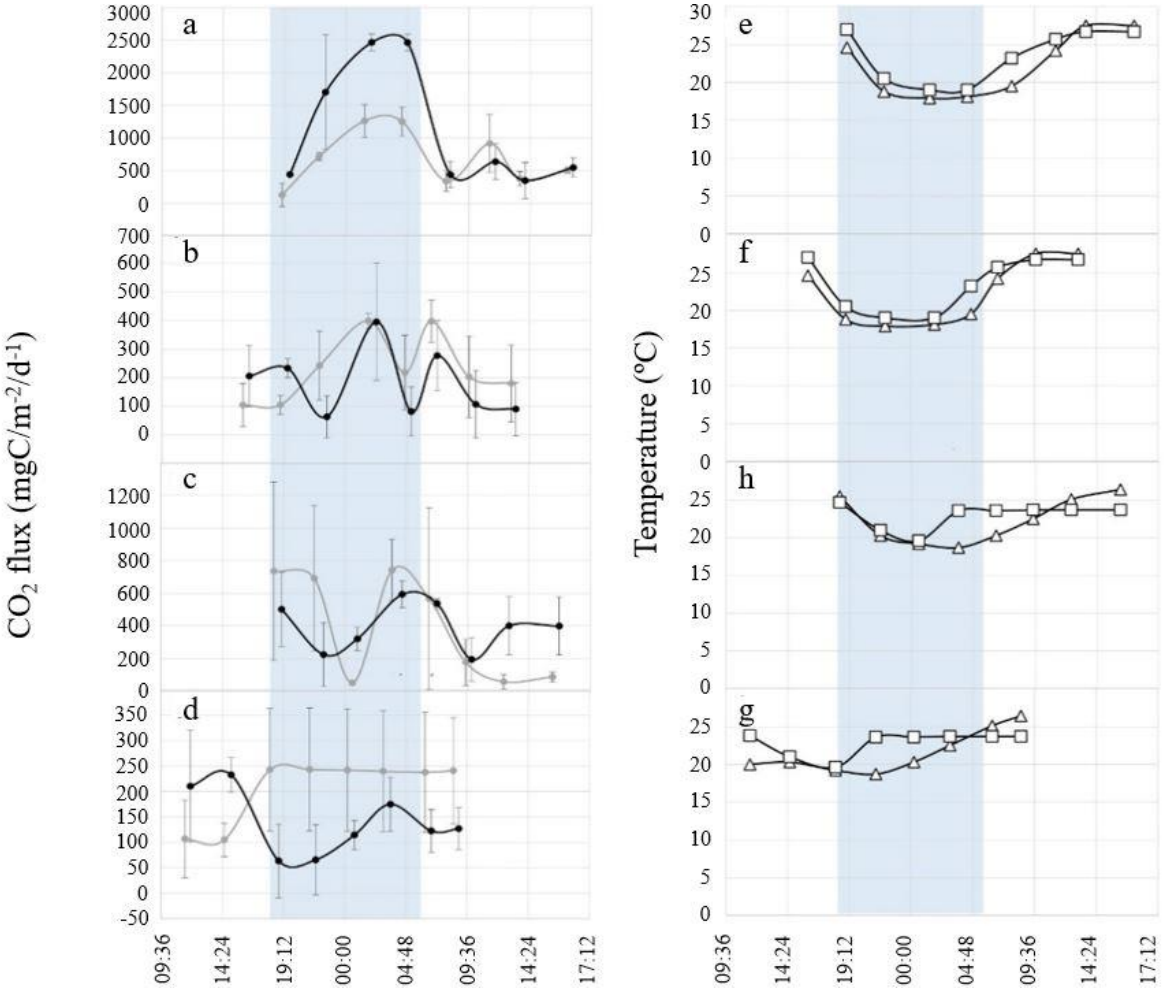

Fig. 12: Diel variability of CO_2 fluxes (a-d) and temperature (e-f). The gray areas correspond to the night period. (a, b, c, d): Diel CO_2 flux in different campaigns. Gray line: wet sediment; black line: dry sediment. (e, f, g, h): Temperature variation over a 24-hour period. Triangles represent air temperature; squares represent soil temperature.

Variability at short timescale - Effect of rain simulation

The rain simulation experiment showed a significant increase in CO_2 fluxes 30 minutes after a rain event (**Figure 13**). The average CO_2 emissions before and after the rain events were 241 mg C m^{-2} d^{-1} and 293 mg C m^{-2} d^{-1} respectively. We also found higher CO_2 emissions in areas surrounded by forestland than by grassland before (average = 282 and 200 mg C m^{-2} d^{-1} respectively) and after the rain simulation (average = 330 and 255 mg C m^{-2} d^{-1} respectively).

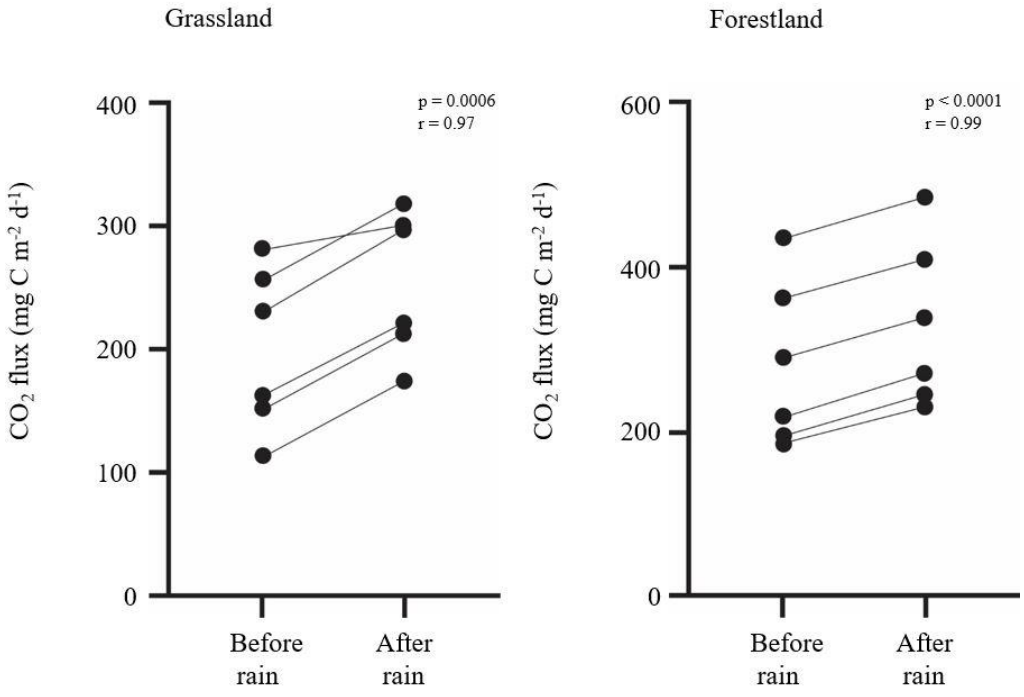

Fig. 13: CO_2 fluxes before and 30 minutes after the rain simulation event (paired t-test).

Drivers of CO_2 emissions

The PCA showed that the CO_2 fluxes were positively related to temperature difference between soil and air. Conversely, negative relationships with moisture, soil conductivity, pH, atmospheric pressure and soil temperature were observed (**Figure 14**). The organic matter content was higher in forestlands compared to grasslands **(Table 2 and Figure 15**, t = -6.9; p <0.0001). Evaluating the variables mentioned above, using a multiple linear regression model, we observed that only moisture (p <0.0001), organic matter (p <0.0010), and atmospheric pressure (p <0.0001) had significant effects on CO_2 flux.

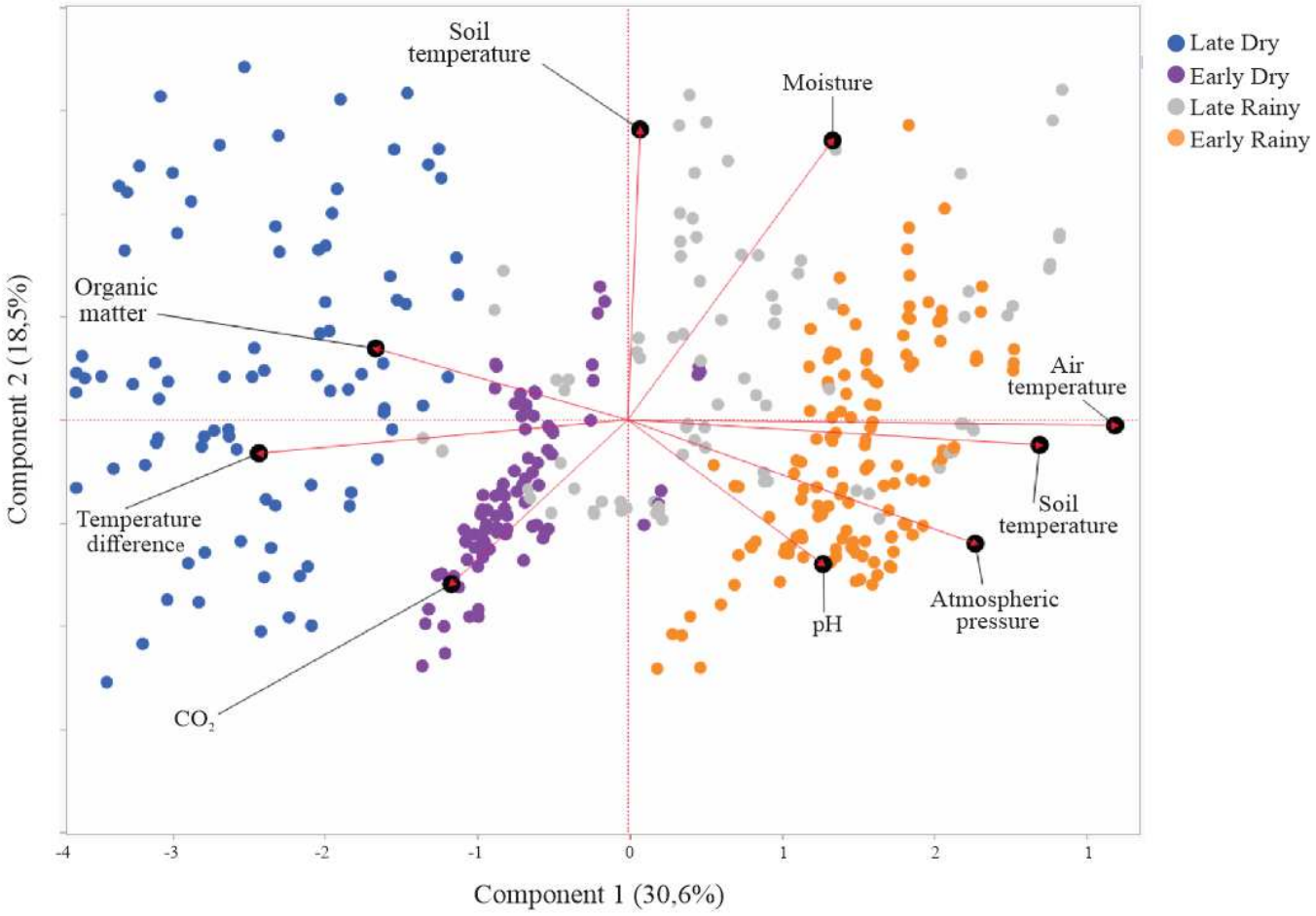

Fig. 14: Principal component analysis (PCA) plot showing the different variables measured at different locations of the drawdown area of the Chapéu D'Uvas reservoir (CDU) over the year. Vectors indicate the direction and strength of each variable to the overall distribution. Colors mean different rainy seasons.

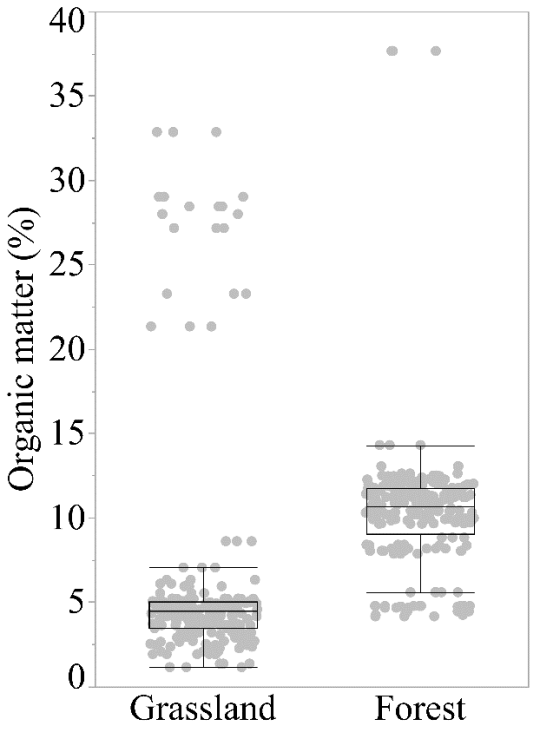

Fig. 15: Percentage of organic matter in different types of land use. Drawdown areas surrounded by forestlands had higher organic matter content in the sediment compared to grassland areas (t-Ratio = -6.9; $p < 0.0001$).

Table 2: Mean flux of CO_2, moisture and organic matter content, conductivity, and pH between different types of land use and chamber zone in the drawdown areas of Chapéu D'Uvas reservoir (CDU). UW: Under water shoreline sediment; WS: Wet sediments; DS: Dry sediment.

Land use	*Chamber zone*	*CO2 emissions (mg C m^{-2} d^{-1})*	*Moisture (%)*	*Orgânic matter (%)*	*Conductivity, average ± SD, (µS cm^{-1})*	*pH, average ± SD*
Grassland	*UW*	*406*	*-*	*-*	*19 ± 22*	*6.5 ± 0.9*
	WS	*498*	*9.2*	*5.3*		
	DS	*1073*	*2.9*	*7.6*		
Forestland	*UW*	*527*	*-*	*-*	*12 ± 21*	*6.9 ± 0.8*
	WS	*877*	*10.0*	*10.8*		
	DS	*1466*	*2.9*	*9.9*		

3.4 Discussion

Our data shows that CO_2 emissions from the drawdown zone of CDU reservoir varied by a factor of 10 over the year, with higher emissions occurring in the drier months (August and September 2018 and from April to July 2019), which confirms our hypothesis. Also as hypothesized, simulated rain events enhanced emissions. Contrary to our expectations, however, we did not find a clear pattern of daily variation in CO_2 emission, with slightly higher values during the night than during the day in one sampling occasion.

Variability in drawdown CO_2 emissions over the year

Drawdown CO_2 emissions from the CDU reservoir varied by one order of magnitude over the sampling months (from 287 to 2417 mg C m^{-2} d^{-1}; **Figure 10b)**, indicating that seasonality is an important factor to be considered in emission assessments. It contradicts a previous study in the subtropical Nam Theun 2 reservoir, which suggested that temporal variability in drawdown CO_2 emissions should be negligible based on a lack of spatial variation in relation to temperature and humidity (Deshmukh et al. 2018). In the case of CDU reservoir, temperature and humidity did drive spatial and temporal variability in CO2 emissions (Figure 8). Our study is the first that we

know of to measure drawdown CO2 emission with time-resolution, so it does not allow us to make extrapolations to other systems. However, the large variability we found implies that measurements performed during short time spans can overestimate/underestimate the actual annual fluxes in certain reservoirs. In the case of the CDU reservoir, this error would be of up to ~60%.

The emission rates were significantly higher in drier periods (late and early dry season, **Figure 10b and Figure 11**). Sediment desiccation increases bacterial activity and modifies the bacterial community composition (Weise *et al.*, 2016). These microorganisms produce enzymes capable of breaking down organic matter (Fenner e Freeman, 2011). A study in 26 ponds in UK showed higher CO_2 fluxes from drier ponds compared to flooded ones (Gilbert *et al.*, 2017). Furthermore, as the sediment becomes drier due to the absence of rainfall, emissions tend to continue increasing up to a critical low moisture content after which microorganisms become water limited (Jin *et al.*, 2016). Oxygen limitation, on the other hand, may reduce microbial CO_2 production in waterlogged sediment (Zehnder e Svensson, 1986; Mclatchey e Reddy, 1998).

The effect of water and oxygen on sediment biogeochemistry may explain why CO_2 emission increases as we move from under water shoreline to wet exposed sediment and then to a dry exposed sediment (**Table 2 and Figure 9**). This has been shown previously in different studies where the CO_2 fluxes were substantially higher in sediment periodically exposed than in the water column of reservoirs (Jin *et al.*, 2016; Almeida *et al.*, 2019) and nearby water courses (Von Schiller *et al.*, 2014; Gómez-Gener *et al.*, 2015). Indeed, we observed a tendency of increase in CO_2 emissions with decreasing water content of exposed sediments, ($R^2 = 0.17$, $p < 0.0001$, **Figure SP2 b**). Other factors such as temperature and sediment quality may also be important. The interplay between different variables affecting CO_2 fluxes from exposed sediment in continental waters imply that predictions of CO_2 emissions based on a limited set of variables comes with large uncertainties. In this case, we used a multiple linear regression model to assess which variables or interplay between them had significant effects on the CO_2 flux. However, only moisture, organic matter, and atmospheric pressure presented significant effects and the model explained only 17% of the variability in CO_2 fluxes (**Figure SP2)**

It is important to highlight that the characterization of the dry period here does not necessarily mean that at the time of sampling the sediment was completely dry. As shown in **Figure SP3**, for some of the campaigns it rained at the day or the day before fieldwork.

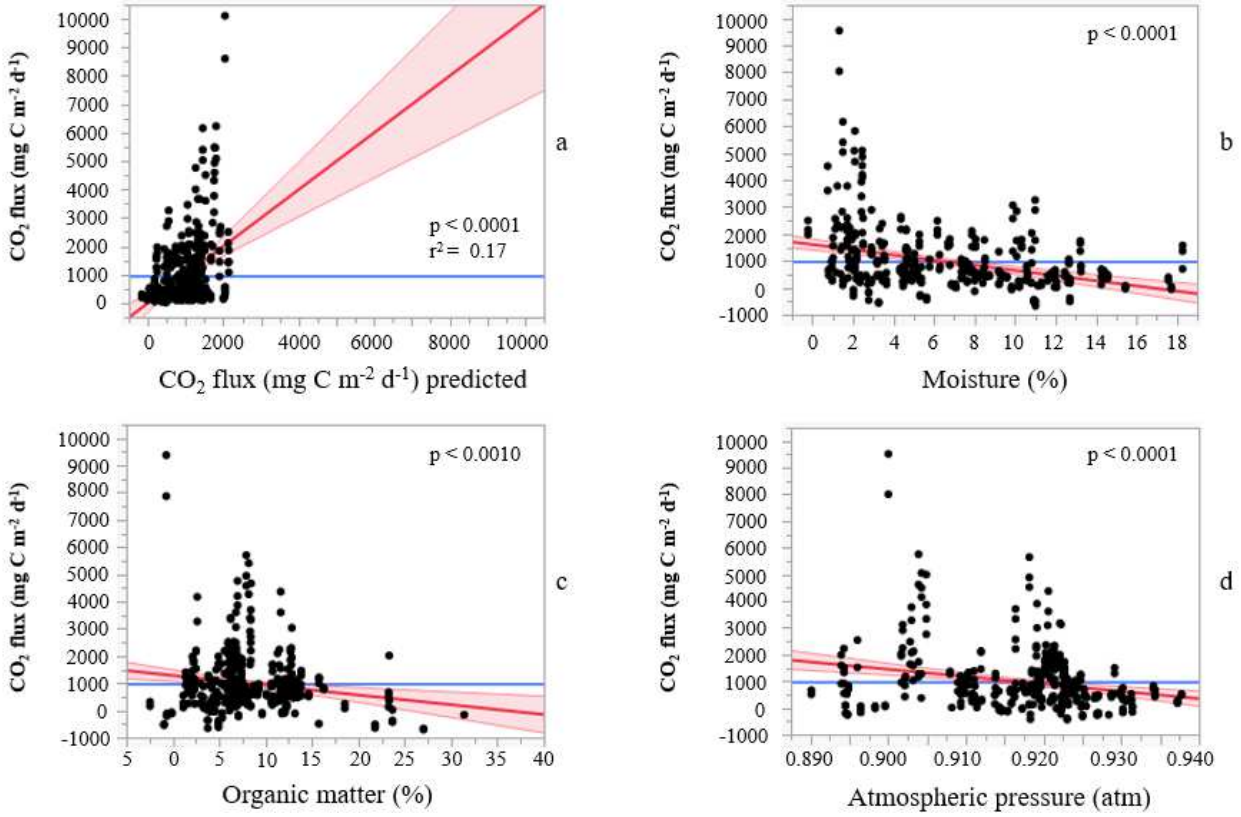

Fig. SP2: Multiple linear regression model using the most important predictors identified in the PCA which had a significant effect on the CO_2 flux. (a): Whole model. (b,c,d): CO_2 flux plotted against moisture, organic matter, and atmospheric pressure respectively with a negative and significant effect on the CO_2 flux. Black dots represent the mean of the data, the blue line represents the mean and the red line represents the trend of the data.

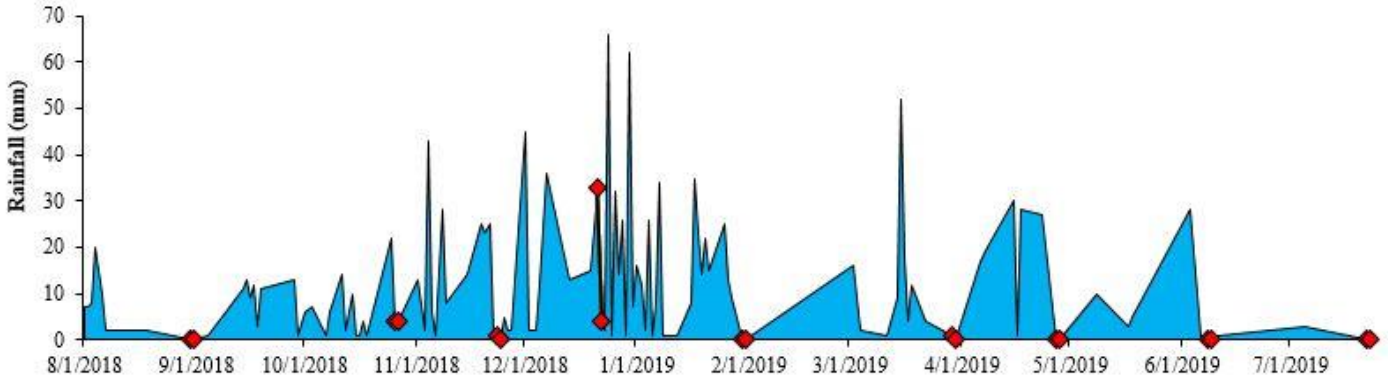

Fig. SP3: Rainfall (blue area) and sampling days (red diamonds) in the Chapéu D'Uvas reservoirs between 30 August 2018 and 23 July 2019.

Another variable that may be related to enhancing CO_2 emissions from exposed sediments in continental waters is the presence of vegetation in the sediment. The marginal sediments of water bodies may quickly be colonized by microalgae and vascular plants as they are exposed to the atmosphere. Some studies have indicated a strong relationship between high CO_2 emissions rates from exposed sediments colonized by autotrophic organisms (Catalán *et al.*, 2014; Bolpagni *et al.*, 2016; Obrador *et al.*, 2018). First, vegetation-covered sediments can have a high CO_2 flux due to the respiration of plant roots. Second, root growth increases soil porosity, which favors gas diffusion (Luo e Zhou, 2006; Cable *et al.*, 2008). In the case of the CDU reservoir, the drawdown area was most often free of plants and when plants were present the chamber was not placed on them. However, microphytobenthos could be present in the sediment, which was not checked in this work.

Sediment organic matter content has also been reported as an important driver of CO_2 emissions (Gallo *et al.*, 2014; Bolpagni *et al.*, 2016; Gómez-Gener *et al.*, 2016; Deshmukh *et al.*, 2018; Almeida *et al.*, 2019; Keller *et al.*, 2020). The drawdown area of a reservoir is considered to be a transition region between the terrestrial and aquatic environments. In this way, this region of the reservoir receives a large share of the organic matter coming from surrounding terrestrial environments. The higher organic matter content in the sediment can fuel microbial activity and thereby CO_2 emissions. The PCA showed a weak relationship between organic matter content and CO_2 emissions (**Figure 12**), although the higher organic matter content in sites adjacent to forest

(**Figure 13**) might explain the higher CO_2 fluxes from these locations in comparison to the sites close to grassland (**Figure 9**).

Finally, temperature may also be related to CO_2 emissions in exposed sediment. A study by Gómez-Gener *et al.* (2016) showed that in addition to the content of water, texture and the organic matter quantity, temperature was one of the variables that were most related to CO_2 emissions. On the other hand, Gallo *et al.* (2014) found the opposite: temperature was not related to emissions but to moisture. Our results reveal that despite the air temperature, soil and the temperature difference (soil - air) showed a positive relationship with CO_2 emissions, this relationship was not significant.

Our results confirmed a previous study showing that CO_2 emissions from exposed sediments may be linked to surrounding land cover (Almeida *et al.*, 2019); importantly, we show that this pattern is consistent throughout the year. As drawdown areas surrounded by forestland receive more organic matter than grassland areas (**Figure 15**; t-Ratio = -6.9; $p < 0.0001$), it is plausible to infer that CO_2 emissions will be higher in areas with higher organic matter content.

Despite the results obtained in the annual timescale campaigns, we only sampled during the daylight, which may lead to an underestimation of the data obtained. Our diel campaigns suggest that nighttime emission rates are on average about 60% higher than daytime emissions (see discussion session '*Diel variation in drawdown CO_2 emissions*'). Thus, we can conclude that if both daytime and nighttime emissions are taken into account in the total balance, CO_2 emissions could be even higher.

Rain events increase emissions

Some studies indicate, and our experiment corroborates that immediately after a rain event a peak of CO_2 emission occurs (Denef *et al.*, 2001; Fierer e Schimel, 2002; 2003; Austin *et al.*, 2004; Jarvis *et al.*, 2007; Inglima *et al.*, 2009; Kosten *et al.*, 2018; Paranaíba *et al.*, 2020), which is explained by a phenomenon known as the Birch Effect, where there is a rapid mineralization of microbial biomass, present in the sediment, in response to water availability (Birch, 1964). Although analysis of our annual data indicates that wet sediments tend to emit less CO_2 than dry sediments, our rain simulation experiment indicated that CO_2 emissions increase immediately (30

minutes) after a rain event (Figure 7). Therefore, the CO_2 emission rates reported in our monthly campaigns may have been influenced by rain events that occurred immediately before the samplings. Several studies show an increase in soil microbial activities and a consequent increase in CO_2 emissions after a re-wetting process (Denef *et al.*, 2001; Fierer e Schimel, 2002; 2003; Austin *et al.*, 2004; Jarvis *et al.*, 2007; Inglima *et al.*, 2009; Kosten *et al.*, 2018). Laboratory experiments following the development of emissions upon drying and rewetting indicates that the CO_2 emissions peak immediately after sediment rewetting (Kosten *et al.*, 2018; Paranaíba *et al.*, 2020). Even though our experiment did not evaluate the development of emissions with time after re-wetting, it shows that rain events can cause short-term increases in emissions, which may play an important, although still unknown, overall effect on annual CO_2 emissions from drawdown zones.

Diel variation in drawdown CO_2 emissions

We evaluated the diel variation in drawdown CO_2 emissions by measuring the fluxes over 24-hour periods in two different sites (neighbored by forest and grassland areas) and two different occasions. In all measurement occasions we found strong diel variations in emissions from both wet and dry sediments, with CO_2 fluxes being on average 57% higher at night (averages of 274 and 475 mg C m^{-2} d^{-1} during day and night, respectively), although the diel variability did not follow a consistent and clear pattern **(Figure 12**). Studies conducted in terrestrial ecosystems generally report the opposite: diel variation in soil CO_2 efflux is positively correlated with temperature and therefore the fluxes are usually higher during the day (Davidson *et al.*, 1998; Law *et al.*, 1999; Sotta *et al.*, 2004; Liu *et al.*, 2006). The concentration of CO_2 in soils depends on biotic and abiotic factors, including autotrophic and heterotrophic respiration, and CO_2 diffusivity (Riveros-Iregui *et al.*, 2007). In forests, autotrophic respiration, which is driven by photosynthetically active radiation, positively affects soil respiration throughout diel cycles, with highest CO_2 production occurring during the day (Tang *et al.*, 2005; Riveros-Iregui *et al.*, 2007). However, when the effect of sunlight on soil CO_2 production is absent due to lack of autotrophs, as is the case of the drawdown areas of CDU reservoir, the occurrence of higher CO_2 efflux during the day may be suppressed (Riveros-Iregui *et al.*, 2007), and possibly replaced by higher efflux of CO_2 during the night (Gaumont-Guay *et al.*, 2006). This occurs because the time lag between

maximum temperature and maximum soil respiration is longer for heterotrophic respiration than for autotrophic respiration, since autotrophic soil respiration responds mainly to sunlight and air temperature, while the heterotrophic respiration of the soil responds mainly to the temperature of the soil (Riveros-Iregui *et al.*, 2007), which in turn lags behind air temperature due to the delayed propagation through the soil. Indeed, in CDU the air cools down at night but the sediment remains relatively warmer (**Figure 12**), which possibly increases the thermal diffusivity and causes accumulated soil CO_2 to evade more rapidly. Even though the exact factors or processes causing higher nighttime emissions are not yet well defined and if we assume that diel cycles are representative of diel CO_2 emission cycles over the year and across land cover types and sediment wetness, it is clear that disregarding nocturnal fluxes in emissions estimates may lead to underestimating the actual emissions. Still, most studies are conducted during the day.

Contribution of drawdown area to total reservoir CO_2 emission

The CO_2 emitted by the drawdown area of CDU represented 80% of the total CO_2 emission from the reservoir, or four times more than the CO_2 emissions from the water surface (**Figure 11**). This value is even more striking when we consider the proportions of the areas - the drawdown area of CDU was on average 4 times smaller than its open water area. A few recent studies have also shown that periodically exposed sediments emit more CO_2 than adjacent flooded areas (Von Schiller *et al.*, 2014; Jin *et al.*, 2016; Gilbert *et al.*, 2017; Almeida *et al.*, 2019). This pattern seems to occur globally, and in other types of freshwater systems, like lakes and ponds, as well (Keller et al. 2020). Furthermore, taking into account climate change scenarios that predict increase of extreme drought events (IPCC, 2013) and the consequent exposure of larger areas of freshwater sediments to the atmosphere, emissions from dry reservoir sediments may become more important. However, it is important to notice, that if CH4 fluxes are also counted, the relative importance of GHG emission from the drawdown area might decrease, as CH4 emissions from the water column of reservoirs tend to be high, especially through ebullition (reference), while drawdown CH4 emissions tend to be low (reference).

Importantly, it is likely that most of the CO_2 emission from drawdown areas of artificial reservoirs can be accounted as an anthropogenic GHG source. The drawdown areas of reservoirs used for water supply or for the production of electricity tend to be larger than that from other freshwater systems due to the opening and closing of the spillways in addition to the natural water level fluctuation. The spillways management may also lead to drying and re-wetting cycles more frequent than the natural seasonal variability, also triggering higher emissions.

3.5 Conclusion

This study showed that there is a great variability in CO_2 emissions in the drawdown areas of the CDU reservoir over a year. Thus, measures taken at certain times of the year may underestimate or overestimate the emissions on this system. We therefore suggest that if the number of sampling has to be limited to a low amount (e.g. two per year), they should be preferably performed in the extremes of dry and wet seasons. Moreover, it seems that measurements during the day only underestimate the real daily emissions. Additional measurements of CO_2 fluxes over 24h, preferably in systems of contrasting characteristics, could help defining a correction factor for measurements performed during the day. Even though questions still remain, our sampling effort is unprecedented and it certainly contributed with reducing uncertainties regarding this important source of GHG from reservoirs.

4. GENERAL DISCUSSION

The dynamics of carbon in reservoirs, which considers the different emission pathways and also the burial of organic carbon to the sediment, has been extensively explored in recent decades, in order to contribute to the increasingly accurate calculation of the carbon balance in continental water systems.

Our study showed that the CDU reservoir buried 436 t of OC over a year. This result is similar to that found in studies carried out in tropical regions. On the other hand, reservoirs located in temperate regions may have significantly higher rates of carbon burial. Burial rates of organic carbon in aquatic systems located in temperate climates tend to be higher due to the strong relationship that the mineralization of organic matter has with temperature (Gudasz *et al.*, 2010; Cardoso *et al.*, 2014). Temperature regulates the metabolism of organisms (Yvon-Durocher e Allen, 2012), which has a direct consequence on mineralization rates. In other words, higher temperatures lead to high mineralization rates and, consequently, less carbon burial (Gudasz *et al.*, 2010).

Regarding the different GHG emissions pathways in reservoirs, in this work we focus only on CO_2 emissions in the drawdown areas. We found that, in the driest months of the year, CO_2 emissions were 54% higher than emissions in rainy seasons. Additionally, we found that the exposed sediments that were dry at the time of the measurements emitted 47% more than the emissions in wet exposed sediments. In several parts of the world it is already possible to observe extreme drought events linked to climate change (IPCC, 2014). In addition, the 2014 Intergovernmental Panel on Climate Change report, projects that the water surface will be reduced in most of the dry subtropical regions of the world (IPCC, 2014). In this perspective, the reduction of the aquatic surface will lead to an exposure of huge amounts of sediment present in different aquatic systems such as rivers, lakes, reservoirs, riverine and others. Consequently, there will be a significant increase in greenhouse gas emissions in these environments, mainly CO_2. When the sediment dries, the microbial metabolism increases significantly due to the increase in the activity of enzymes such as phenol oxidase and hydrolases in contact with oxygen (Jin *et al.*, 2016; Weise *et al.*, 2016). A global estimate points out that CO_2 emissions in exposed sediments represent ~ 10% of global emissions (Marcé *et al.*, 2019). Another important result found in this work was in relation to nocturnal CO_2 emissions, mainly driven by temperature difference (soil - air). Measurement campaigns over 24h periods have shown that there is a peak emission during the night. We found that nighttime emissions were 26% higher than daytime emissions. This occurs because at night the soil is slightly warmer than the air temperature, due to the greater specific heat of the soil. Thus, the heterotrophic organisms existing in the soil contribute to this peak of emission during the night, since their respiration depends only on the temperature of the soil. On the other hand, the absence of plants in these places suppresses the influence that solar radiation has on the

production of CO_2 in autotrophs organisms during the day (Riveros-Iregui *et al.*, 2007). Thus, measurements that take into account only emissions during the day may be underestimating the total CO_2 emission. The rain simulation experiment showed that CO_2 emissions were 17% higher after the simulation. Although our experiment did not take into account measurement frequencies, which may underestimate the results (Gallo *et al.*, 2014; Kosten *et al.*, 2018), our finding confirmed previous studies where there was an increase in CO_2 emissions after sediment rewetting. For instance, the sediment core incubation experiment by Kosten et al. (2018) found that CO_2 emissions was 5 times higher in sediments that have been rewetting compared to emissions in consistently wet sediments and similar to emissions in dry sediments. Another example was a study by Yu et al. (2014) that showed that GHG emissions may be higher during and after drought and rewetting events.

With respect to the carbon balance, the CDU reservoir was responsible for burying 436 t C y^{-1}. In contrast, a recent study pointed out that the diffusion of GHG (CO_2 and CH_4) in CDU through the water/atmosphere interface emitted 700 t C y^{-1} (Paranaiba, in preparation). Another recent study in one of the CDU reservoir bays, estimated for the entire reservoir that boiling CH_4 emissions represented an increase of 33 t C y^{-1} (disregarding the global warming potential) in the annual contribution to the atmosphere (Linkhorst *et al.*, 2020). Finally, in this study, we show that the drawdown area of the CDU reservoir contributed to an increase of 716 t C y^{-1} to the atmosphere. Thus, the total carbon balance in the CDU Reservoir combines the sum of the emissions through the diffusive pathways, minus the carbon buried to the reservoir sediment. Total emissions amounted to 1449 t C y^{-1} (drawdown + water surface + ebullition) against 436 t C y^{-1} buried for the sediment. This means that 30% of the carbon emitted was buried by the sediment. However, if we consider the global warming potential of the methane molecule (GWP = 34, IPCC, 2013) the scenario changes substantially, making the pathways of GHG emissions to be 5 times greater in the amount of carbon emitted compared to the carbon buried for the sediment.

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