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Comparison of CO_2 flux in an Amazonian natural lake and hydroelectric reservoir

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Bachelor thesis, 15 credits,
in Physical Geography and Ecosystem Science

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Abstract

Due to global demand for alternative energy sources, the industry of hydropower is continuing to thrive. Not only are there already thousands of dams worldwide, but many more developments are planned for the future. This has increased attention towards the topic of reservoirs, and more specifically their potential to act as a source of greenhouse gases. Despite tropical locations being known as ‘hydro hot spots’, there is still a surprising scarcity of studies existing in these areas. Furthermore, lakes and reservoirs are often grouped together as a singular entity, with response to phenomena such as seasonal dynamics being believed to be the same. The focus of this thesis was therefore to explore CO_2 exchange from water bodies in the Amazon. This involved comparison of flux from a hydroelectric reservoir to that of an adjacent natural lake. Data was compiled from previous studies, with necessary additional information also being sourced. The ‘Thin Boundary Layer’ method was used to calculate and quantify fluxes, before then employing statistical methods to aid further analysis. Results revealed that both sites were CO_2 emitters continuously throughout the year. Response to seasonal changes was also observed, linking to the influence of the ‘Amazonian flood pulse’. Although both sites experienced greatest flux during ‘low’ phase, different explanations are offered. The natural lake appeared more dependent on hydrological factors such as riverine inputs, whilst changes seen at the reservoir showed stronger links with morphological variables. Data availability, methodological constraints and neglect of other potentially influential factors are however pointed out. Future works in this field are therefore recommended in order to further expand upon these findings.

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1 Introduction

Throughout recent history the construction of hydroelectric dams has become increasingly more frequent. With growing global populations and rising energy demands, the capabilities of hydropower to provide and supply energy are being recognised. This has generated a global ‘boom’ in development (Barros et al. 2011; Zarfl et al. 2015). Currently, over 50,000 dams exist in the world (Lehner et al. 2011), with at least 3,700 major projects being either already underway or planned for the near future (Zarfl et al. 2015). Inevitably, this expansion of developments has in turn resulted in the creation and abundance of reservoirs. At present it is estimated that reservoirs cover an area of 400,000 km^2 worldwide (Cole et al. 2007), therefore making up a substantial share of inland waters (Raymond et al. 2013).

Recent research regarding reservoirs is currently stirring up global debate. Although previously considered as an environmentally ‘clean’ energy source, outlooks are now shifting towards the view that hydropower may actually not be as green as once thought (Fearnside 1995; St. Louis et al. 2000; Fearnside 2002; Richey et al. 2002; Kemenes et al. 2020). This is due to the growing pool of evidence demonstrating that emissions cause them to be a source of greenhouse gas to the atmosphere, rather than carbon neutral (Barros et al. 2011; Deemer et al. 2016; Prairie et al. 2018). In a study conducted by Barros et al. (2011) 88% of a total of 85 reservoirs analysed were found to be sources of CO_2 to the atmosphere. In addition, in many cases outgassing has been seen to such a degree that benefits gained from reducing fossil fuel usage were completely counteracted (Barros et al. 2011). However, despite these discoveries, no consensus has yet been reached (Barros et al. 2011; Lehner et al. 2011). The importance of conducting reservoir studies has therefore come to light (Duchemin et al. 2000; St. Louis et al. 2000; Prairie et al. 2018). Many investigations highlighting carbon dynamics have already been carried out and have helped to improve understanding of these systems. For example; Bergström et al. (2004), Deemer et al. (2016), Duchemin et al. (2000), Fearnside (1995), Fearnside (2002). With this being said, some discrepancies in the state of current research can be pointed out.

Firstly, many studies have been based on the assumption that reservoir behaviour reflects that of other large terrestrial water bodies (Raymond et al. 2013). This contradicts the knowledge that artificial reservoirs are distinct from natural systems in many key aspects (Deemer et al. 2016; Hayes et al. 2017). Fundamental differences in morphological and hydrological features are well known, with many scientific papers highlighting these contrasts (Wakjira and Mengistou 2015; Hayes et al. 2017). Anthropogenic control and flooding regimes are also known to vary between the two. Despite this, few studies have detailed comparisons (Åberg et al. 2004), thus potentially failing to distinguish possible differences.

Locational bias is another element evident in current work. The majority of studies take place in boreal and temperate regions, with a comparatively scarce amount of data being produced for tropical zones (Almeida et al. 2016; Hayes et al. 2017). Considering the fact that latitudinal influence on reservoir emissions is well known (Duchemin et al. 2000; Barros et al. 2011), it is even more essential that these areas receive adequate attention (St. Louis et al. 2000). Expectations reveal that tropical reservoirs may release more than 3 times the amount of CO_2 than from boreal or temperate zones (Duchemin et al. 2000). They are also estimated to be responsible for approximately 70% of global reservoir fluxes (St. Louis et al. 2000). The thriving nature of hydro projects in these regions of the world, and plans for future developments also add to this argument (Zarfl et al. 2015). This rings particularly true for Amazonian areas, where more than 190 dams are already standing, with 246 in planning or under construction (de Sousa Lobo et al. 2018).

Another overlooked area in need of further exploration is the topic of seasonality. More specifically, this should be directed towards tropical regions where seasonal variations of water body characteristics are especially prevalent (Kolding and van Zwieten 2012). This is due to the ‘flood pulse’ dynamic which predictability occurs every year, modifying both inundation levels and organic carbon (OC) (Hess et al. 2003). Works such as Rudorff et al. (2011) and Devol et al. (1990) have already suggested ideas on the effect of temporal patterns. But refined analysis and additional investigation of fluxes are still needed for uncertainties to be resolved (Novo et al. 2006; Barros et al. 2011; Deemer et al. 2016).

1.1 Aim

Considering the information presented above, the importance of expanding knowledge regarding behaviour of fluxes from tropical hydroelectric reservoirs becomes apparent. This thesis therefore aims to continue investigation in this field.

This will take the form of a comparison study, where atmospheric CO_2 exchange in an Amazonian natural lake and adjacent hydroelectric reservoir will be examined. Particular attention will be given towards the seasonal element, with analysis being focused around intra-annual variation and flood pulse dynamics. CO_2 flux from the water bodies will first be quantified. Seasonal patterns will then be determined, before also exploring comparisons between the two sites.

2. Background

2.1 Outline of surface exchange

Ultimately, the exchange of CO_2 across surface waters is governed by its concentration relative to the atmosphere. When surface waters are supersaturated the gas is emitted, acting as a source. The converse is true when waters are undersaturated (Cole and Prairie 2009). In the freshwater waterbodies of the tropics, one of the main processes controlling the amount of CO_2 available in the Dissolved Inorganic Carbon (DIC) pool is in-situ degradation of Organic Matter (OM) (Prairie et al. 2018).

OM may be in the form of either Dissolved Organic Carbon (DOC) or Particulate Organic Carbon (POC), and can arrive by both autochthonous and allochthonous inputs. Allochthonous inputs include those brought into the system from elsewhere, for example by terrestrial and riparian sources. Submerged vegetation and drowned soils that have resulted from impoundment also act as an OM source in reservoirs (Gruca-Rokosz et al. 2017; Prairie et al. 2018). On the other hand, autochthonous inputs are those generated within the system itself. This refers to the biomass yielded from primary productivity as well as exudation from macrophytes (Linkhorst 2019). It must be noted however, that primary productivity also consumes CO_2 via uptake during photosynthesis (Abril et al. 2014).

Throughout the water column, OM is degraded through microbial respiration (Abril et al. 2014). Photolysis can also transform OM into CO_2. As well as this, some suspended particles may undergo sedimentation where they descend to the benthic zone and become bound in sediments. Here, particles can be trapped and endure long term storage (Linkhorst 2019). However, they may also be mineralised in sediments, again by microbial respiration (Abril et al. 2014). Furthermore, in anoxic conditions the process of methanogenesis may occur and produce methane (CH4). This can either be emitted at the surface directly, or may alternatively undergo oxidation by methanotrophic bacteria, resulting in an addition of CO_2 to the DIC pool (Tranvik et al. 2009; Prairie et al. 2018). A visual representation of these processes can be seen in *Figure 1.*

In terms of surface release, gases can be emitted by either diffusion or ebullition. Due to its high solubility, diffusion is the major pathway for CO_2 emissions, with ebullitive emissions being considered as negligible (Dos Santos et al. 2005; Therrien et al. 2005). This is shown by Casper et al. (2000), who estimated that 99% of CO_2 loss was due to diffusion across the air-water interface. Dos Santos et al. (2005) also state that 99.9% reaches the atmosphere via this pathway.

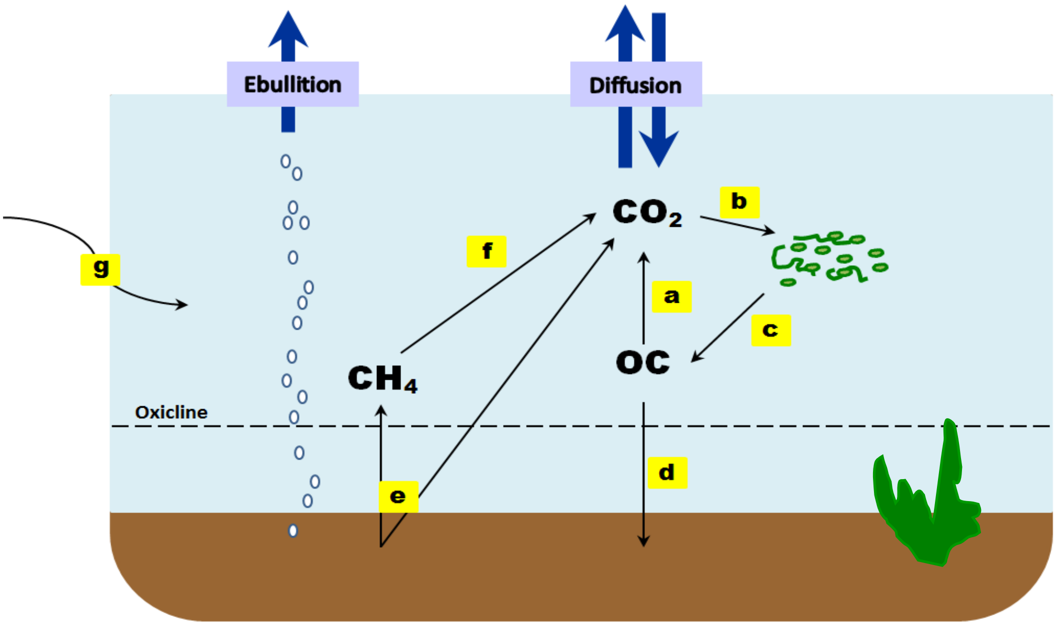

Figure 1. Illustrative diagram of carbon dynamics in lakes and reservoirs.
Fundamental processes and pathways relating to CO2 are shown – a. Mineralisation; b. Photosynthesis; c. Microbial respiration; d. Sedimentation and burial; e. Methanogenesis; f. Oxidation of methane; g. Allochthonous input

2.2 Amazonian flood pulse

The flood pulse concept is a theory initially presented by Junk et al. (1989), describing the seasonal phenomenon of river inflow dynamics. In Amazonia, this is demonstrated by the highly variable water levels seen in floodplains and lakes. These occur as a result of regional precipitation patterns, which show pronounced rainy and dry seasons. Large watersheds reflect these patterns producing a unimodal arrangement with one distinct peak per year (de Sousa Lobo et al. 2018). This fluctuation is known to be predictable, therefore differing from typically erratic pulses observed in temperate zones (Junk et al. 1989; Hess et al. 2003; de Sousa Lobo et al. 2018).

It is proposed with this concept that seasonal water level changes are the main driving force controlling hydrological, ecological and biogeochemical processes (de Sousa Lobo et al. 2018). This is due to the fact that the flood pulse regulates water body properties that are intrinsically linked to energy and nutrient exchanges with the river system. For example; flooded area, flood duration, lake connectivity and water residence times (Casali et al. 2011). Inflowing waters supply and replenish nutrient pools, having a large impact on floodplains. As these waters recede, processes once again become less dependent and more subject to local conditions (Junk et al. 1989).

3 Methods

3.1 Study sites

Two study sites are investigated in this thesis - a natural lake *(Lago Grande de Curuai)* and a hydroelectric reservoir *(Balbina Reservoir)*. Both are located in the Central Amazonian Basin, lying along similar latitudes and distanced by approximately 470km. *Figure 2* outlines their locations. Both sites have previously been the subject of studies analysing CO2 emissions (Kemenes et al. 2011; Rudorff et al. 2011). However comparative analysis of seasonality has not yet been a topic of focus.

3.1.1 Lago Grande de Curuai

Lago Grande de Curuai is a complex floodplain system lying near the city of Obidos in the Brazilian state of Para (*Figure 2)*. In its entirety, the network comprises 30 interconnected lakes which cumulatively flood an area of 2274km² (Rudorff et al. 2011). Several links to the Amazon river are present, with two of the channels, 'Foz Sul' and 'Foz Norde', representing permanent ties (Moreira-Turcq et al. 2013). These links are responsible for controlling the characteristic highly variable water levels. Throughout the year distinct stages are seen, each synchronising with the annual Amazonian flood pulse (Moreira-Turcq et al. 2005; Alcântara et al. 2009). In total 77% of inflow originates from the Amazon river, with the remaining being accounted for by runoff (10%), rainfall (9%) and seepage (4%) (Bonnet et al. 2008). This creates 4 distinct hydrological phases as follows; rising (February-April), high (May-July), receding (August-October) and low (November-January) (Novo et al. 2006; Barbosa et al. 2010; Moreira-Turcq et al. 2013). In addition to this seasonal water level variation, extreme drought and flood years are also known to occur. These are caused by El Niňo and La Niňa Oscillations, which produce weather phenomena and altered precipitation patterns (Silva et al. 2019). In terms of water properties, weak vertical stratification is observed in the column due to mixed waves and free convection at night (Moreira-Turcq et al. 2013). Residence time is 3±0.2 months (Bonnet et al. 2008) and the lake can be characterised as 'white water' (Sobrinho et al. 2016). This relates to high concentration of suspended sediments that are mainly composed of nutrient rich clay and silt (Sanders et al. 2016). These sediments tend to accumulate during the influx of the rising season, but reduce in low season due to exportation (Alcântara et al. 2009).

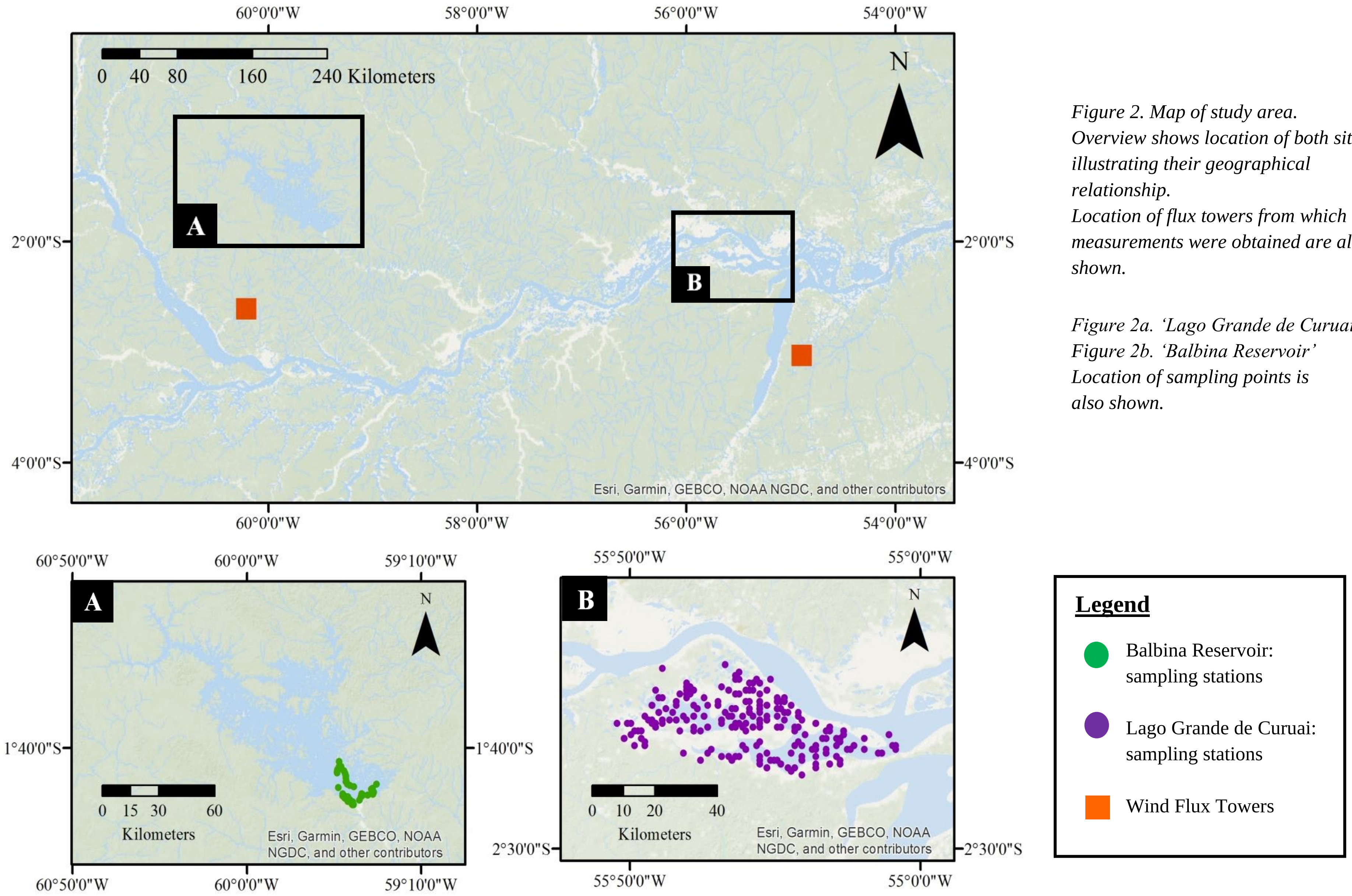

Figure 2. Map of study area.
Overview shows location of both sites, illustrating their geographical relationship.
Location of flux towers from which wind measurements were obtained are also shown.

Figure 2a. 'Lago Grande de Curuai'
Figure 2b. 'Balbina Reservoir'
Location of sampling points is also shown.

3.1.2 Balbina Reservoir

Balbina Reservoir, which spans an area of 2360km² (Fearnside 1989), is one of the largest reservoirs in tropical South America and the second largest in the Amazonian basin (Kemenes et al. 2011). More specifically, location is 146km northeast of the city of Manaus in the state of Amazonas, Brazil (*Figure 2).* Formation occurred in 1987 when the newly built 'Balbina dam' underwent initial impoundment. None of the forested area was cleared prior to flooding, instead being left to decompose beneath the surface. The development was closed in 1989 and is no longer operational. Although equipped with generators holding a production potential of 250MW, only 112.2MW were ever produced. This makes Balbina highly controversial in the world of hydropower, being often referred to as 'notorious' due to its many shortcomings (Fearnside 1989). One of the reasons accounting for this is the flat topography that underlies the area. This creates a huge and shallow reservoir, branded with a high surface area to volume ratio and minimal energy yield. This morphometry also promotes the growth of rooted aquatic vegetation and aids creation of acidic and anoxic bottom waters (Fearnside 1989; Kemenes et al. 2011). Strong thermal stratification is also present for the majority of the year, with the exception of slight weakness seen in March-May during the rainy season (Kasper et al. 2014). Residence time is also exceptionally long, averaging 11.7 months with many stagnant areas potentially taking several years to turn over (Fearnside 1989). Inputs to the reservoir come from the 'Uatuma river', a northern tributary of the Amazon (Kasper et al. 2014). Water level variations therefore occur in coordination with the flood pulse, but with some control still being administered by the dam (Kasper et al. 2014). Uatuma is a black water river (de Sousa Lobo et al. 2018), meaning that Balbina concurrently low concentrations of sediment and poor nutrient richness (Alcântara et al. 2009). The drainage area is unusually small for a hydroelectric project, being just 8 times the size of the reservoir itself (Fearnside 1989).

3.2 Data collection and treatment

3.2.1 Surface water CO_2 concentrations

Measurements of surface water partial pressures were sourced from datasets produced by previous studies. These were accessed through 'NASA Earthdata Search', an online platform from which data is available to be both viewed and downloaded (NASA 2019). Both datasets used were obtained as part of projects within the Large Scale Bio-Atmosphere Experiment (LBA). The LBA is an ongoing initiative started in January 1999, which focuses on understanding the ecological functioning of the region with particular emphasis on the carbon cycle (Avissar and Nobre 2002).

For the *Lago Grande de Curuai* site, surface water CO_2 concentrations were derived from the dataset '*LBA-ECO LC-07 Water Quality, CO_2, Chlorophyll, Lago Curuai, Para, Brazil: 2003-2004*' (Barbosa et al. 2012). Samples within this dataset were gathered by four campaigns, with each one taking place during a specific seasonal phase; (September 2003, receding. November 2003, low. February 2004, rising. June 2004, high.). Timings of these phases were determined by analysis of 10 year water level data (Barbosa et al. 2010). Each campaign spanned a total 10-16 days, with collection occurring between the hours of 10.00-14.00. Samples were gathered following a dispersed pattern from approximately 70 stations throughout the lake at a depth of 0.4-0.5m below the surface (Rudorff et al. 2011). Location of sampling points can be seen in *Figure 2*. At each station, conductivity and pH were measured routinely. DIC was also determined. This then allowed for the estimation of surface water dissolved CO_2 concentrations. A comprehensive description of these methods can be found in (Barbosa et al. 2010) and (Rudorff et al. 2011).

At *Balbina Reservoir,* data was sourced from the dataset '*LBA-ECO LC-07 Methane and carbon emissions from Balbina Reservoir*' (Kemenes 2013). The reservoir portion of this campaign was conducted between April 2005 to February 2006, at an area located in the main impoundment near the dam (*Figure 2).* Data was collected at approximately monthly intervals between April-November 2005, before then resuming in February 2006 (Kemenes 2013). For the purpose of this thesis, samples were divided into 4 seasonal phases, each consisting of 10-14 points. Timings of these were defined in correspondence with the hydrological phases of the input river (Kasper et al. 2014). At each station, surface water samples were obtained directly with a syringe. Concentrations of CO_2 were then found with a dual column gas chromatograph. Further detail of measurement acquisition can be found in Kemenes et al. (2011).

3.2.2 Atmospheric CO_2 concentrations

Atmospheric CO_2 concentrations were used for the purpose of representing concentration of dissolved CO_2 in equilibrium with the atmosphere. These were acquired from global values and sourced from the Earth System Research Laboratory (ESRL). This provided a continuous record of daily atmospheric CO_2 concentrations at the site of Mauna Loa Observatory, Hawaii. Although this provided comprehensive measurements, three dates were reported as 'NoData' (14.06.2004, 19.06.04, 11.06.2004). In these cases an average of the surrounding ±1-3 days was therefore taken.

3.2.3 Wind measurements

In the case of both *Lago Grande de Curuai* and *Balbina Reservoir*, it was not possible to obtain on-site wind measurements. Values from nearby flux towers were therefore used instead. The location of these towers is shown in *Figure 2*. Conversion of these measurements to 10m height was also required.

For *Lago Grande de Curuai*, the dataset from '*LBA-ECO CD-03 Flux-Meteorological Data, km 77 Pasture Site, Para, Brazil: 2000-2005*' (Fitzjarrald and Sakai 2010) was used. This provided hourly readings from a pasture site, at heights of 2.7m, 7.2m, 8.3m and 12m. Due to the fact that velocities were given as horizontal and vertical components, they first had to be transformed into a singular value by using Pythagorean Theorem. The TREND function from Microsoft excel (Microsoft 2010) was then used to fit a function relating height and velocity. From this, it was possible to extract an estimate for 10m. In occasional cases where limited height measurements were given, an average of the 7.2m and 12m values was taken.

For *Balbina Reservoir*, readings were derived from '*LBA-ECO CD-32 Flux Tower Network Data Compilation, Brazilian Amazon: 1999-2006*' (Saleska 2013). In this case, values were given for a forest site at a height of 50m. 10m estimates were therefore extrapolated by using a wind power profile based on the power law assumption (Peterson and Jr. 1978; Sisterson et al. 1983). This is shown in *Equation 1*. For the two dates with 'NoData', the value of the nearest recorded day was used instead.

$$u_1 = (\frac{z}{z_1})^p$$

Equation 1. Power Law
Where u is mean velocity (m/s) at height z (m), and u_1 is the velocity (m/s) at height z_1 (m). Value p is 1/7 (Sisterson et al. 1983).

3.2.4 Seasonal parameters

The seasonal parameters of depth, flooded area and surface temperature were each derived from different sources. Depth measurements for *Lago Grande de Curuai*, and flooded area values for both sites were found from literature; Rudorff et al. (2011) and Kemenes et al. (2011). These gave singular values for phase averages. Surface temperatures on the other hand were acquired from the datasets '*LBA-ECO LC-07 Water Quality, CO_2, Chlorophyll, Lago Curuai, Para, Brazil: 2003-2004*' and '*LBA-ECO LC-07 Methane and carbon emissions from Balbina Reservoir*', therefore corresponding to the sample locations of surface CO_2 concentration. This was also true for *Balbina Reservoir*, where depth values were gained from the same dataset and averaged to gain a singular value.

3.3 Calculation of flux

3.3.1 Flux values

CO_2 flux was calculated using the Thin Boundary Layer Method (TBL) (Barrette and Laprise 2005). The TBL method is based on the rate of exchange being dependent on two main factors; concentration gradient between water and air, and a transfer coefficient (Raymond et al. 1997). The form used in this thesis is displayed in *Equation 2.* Details of the individual terms are given in the following text. Furthermore, after calculation a selection of resulting values were cross checked against directly measured fluxes from the dataset '*LBA-ECO LC-07 Methane and carbon emissions from Balbina Reservoir*', in order to assure accuracy.

$$F = k \, * \, \frac{p_w - p_{eq}}{RT}$$

Equation 2. Thin Boundary Layer Method
Where F is flux across the air-water interface (mol/cm²/hr), k is piston velocity (cm/hr), $p_w - p_{eq}$ *is the partial pressure gradient between surface water and atmospheric equilibrium (atm), R is the ideal gas constant and T is temperature (Kelvin).*

Piston velocity 'k', also referred to as gas transfer velocity, is known to be a function of complex boundary layer processes. These include turbulence, kinematic viscosity of the water and the diffusion coefficient of the gas. In practice however, it is frequently parameterised as a function of wind speed (Wanninkhof 1992, 2014). For this investigation, piston velocities were found by using two different formulas resulting in minimum and maximum values. This was done in order to account for the fact that formulas have been derived from studies of differing scales. Creating a range was therefore considered a more appropriate approach (Hélie and Hillaire-Marcel 2005). *Equation 3* shows the calculation produced by McGillis et al. (2001) for ocean environments, whilst *Equation 4* shows that for small lakes as created by Cole and Caraco (1998). The final flux values gained were an average of those produced by use of these two 'k' values.

$$k = \ 3.3 \ + 0.026 \, * \, u_{10}^3 \qquad (McGillis\ et\ al. 2001)$$
$$k = \ 2.07 + 0.215 \, * \, u_{10}^3 \qquad (Cole\ and\ Caraco. 1998)$$

Equations 3&4. Piston Velocity
Where k is piston velocity (cm/hr) and u_{10} *is wind speed at 10 metre height (m/s).*

In order to convert surface water CO_2 concentrations to partial pressures, Henry's law was used. This law describes the relationship between the solubility of a gas and its partial pressure above a liquid. Various forms of this equation exist, all requiring the use of Henry's Constant (H). The form used in this study is shown in *Equation 5.* (Coker 2007; Smith and Harvey 2007; Leng et al. 2015).

$$p = C * H$$

Equation 5. Henry's law
Where p is partial pressure (atm), C is concentration (mol fraction) and H is Henry's Constant (atm/mol fraction).

Dissolved surface water CO_2 concentrations were first converted to units of mol fractions, in order to prepare the term for use in the equation. It was also necessary to calculate Henry's Constant. This is dependent on solute as well as temperature (Coker 2007), so was therefore computed individually for each sampling point using surface water temperatures. *Equation 6* depicts the equations used for this calculation.

$$log_{10}H = A + BT + Clog_{10}T + DT$$

Equation 6. Henry's law constant
Where H is Henry's constant (atm/mol fraction). A, B, C and D are regression coefficients for gas, and T is temperature (Kelvin).

3.3.2 Estimation of total exchange

To gain an estimate of total exchange, flooded area was multiplied with flux (*Equation 7).* This was done using averaged measurements from each season. An annual average was also calculated.

$$Total\ exchange\ = flux * flooded\ area$$

Equation 7. Total exchange
Where flux is given in mmol/m²/hr, flooded area is given in m², and the resulting total exchange is given in mmol/hr

3.4 Statistical analysis

Statistical analysis was implemented using R software (RStudio 2019). Firstly, a summary of some general descriptive statistics was found. This included measures of central tendency (mean and median), measures of variation (range, interquartile range, standard deviation), as well as reliability of the sample mean (standard error)(Philip Wheather and Cook 2000). Data distribution was then investigated further. This was done using graphical visualisation, Shapiro Wilks test for normality ($P=0.05$) (Shapiro and Wilk 1965), and skewness testing (Philip Wheather and Cook 2000). Results from this indicated a normal distribution for all hydraulic phases at *Balbina Reservoir*, whilst *Lago Grande de Curuai* exhibited a positive skew (skewness>1) and non-normal distribution.

Once informed of distributions, appropriate significance tests could then be chosen. The nonparametric ‘Wilcoxon Mann Whitney’ test was conducted to allow for comparison of the median of differences between sites (Philip Wheather and Cook 2000; RStudio 2019). The null hypothesis was stated as there being a difference between samples, with significance level being either $P<0.05$ or $P<0.01$. One-way ‘ANOVA (Analysis of Variance)’ tests were then used to investigate phase differences within each site. This type of test compares the two main sources of variation - both explained and inherent. An assumption of ‘ANOVA’ is that samples have a normal distribution (Philip Wheather and Cook 2000). Therefore a logarithmic transformation (Philip Wheather and Cook 2000) was performed on the dataset of *Lago Grande de Curuai* prior to carrying this out. Application of this test reveals overall significance, but fails to identify where these differences lie. Hence, a post-hoc ‘Tukey Honest Significant Difference’ test was applied to the variance model. This enabled a multiple comparison, showing significance between all possible pairs of the sample.(Philip Wheather and Cook 2000; RStudio 2019).

As a final step, the relationship between flux and seasonal parameters was assessed. The nonparametric ‘Spearman’s’ rank test was employed for this task. This gave the coefficient r_s, representing both the strength and direction of the correlation (Philip Wheather and Cook 2000). A simple linear regression model was then applied. This produced a coefficient of determination r^2, a measure that describes the proportion of variation in one variable that can be explained by the other (Philip Wheather and Cook 2000). A P-value denoting the significance of the relationship was also produced, being considered to a confidence level of 95% ($P<0.05$).

4 Results

4.1 Lago Grande de Curuai

Figure 3 outlines the results of fluxes seen at *Lago Grande de Curuai* during each of the four hydrological seasons. By inspecting this figure, the largest flux (Median=33.05 mmol/m²/hr) is experienced during the low phase, occurring between November-January. This is followed by the rising phase of February-April. Subsequently, the two smallest fluxes are shown to occur during high and receding phases, taking place from May-July and August-October respectively. If then looking to *Table 1*, the significance of differences between these seasons becomes evident. All differences experienced are to an accuracy level of 99% (ANOVA, $P<0.01$). However, no significant difference is seen between fluxes of the low and rising phases, as well as between those of high and receding. Interquartile range is greatest during high phase (IQR=40.38), but with every phase experiencing outliers. These extreme values all positively exceed the 3rd quartile, linking to the positive skew of the data (skewness=1.83).

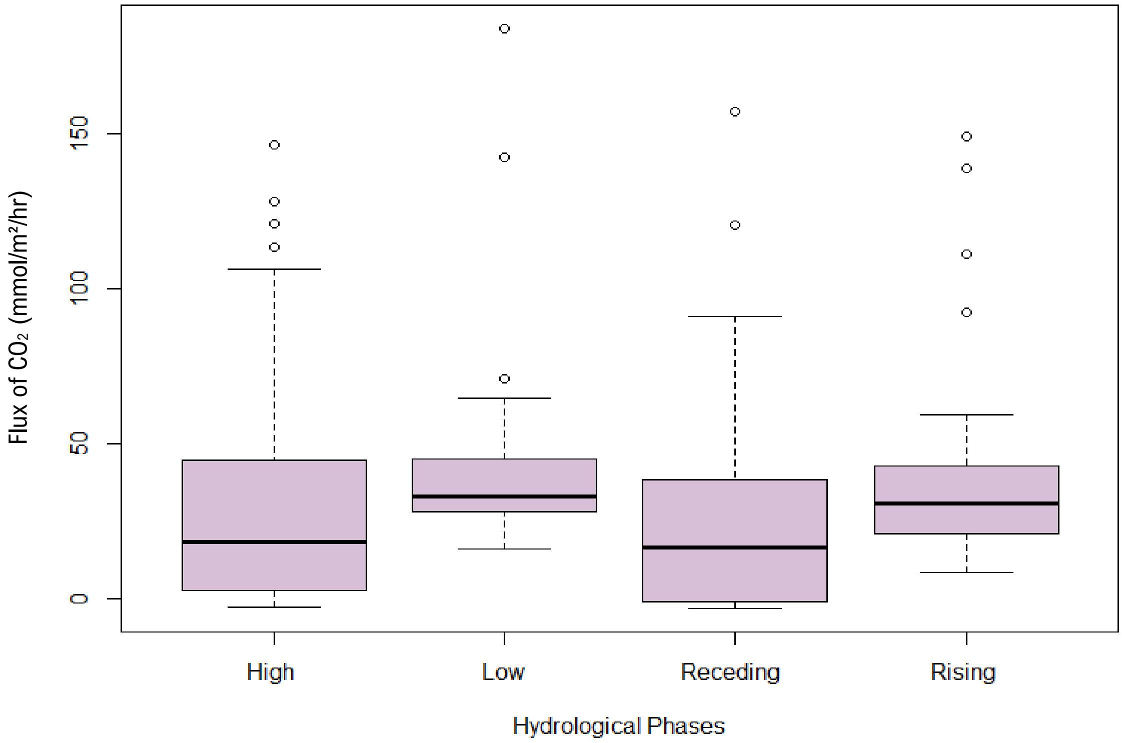

Figure 3. Flux at different hydrological phases at Lago Grande de Curuai.
Box plot visualises descriptive statistics of flux at the site of 'Lago Grande de Curuai' during the 4 hydrological phases (rising, high, receding and low). Central lines are median values Range is illustrated by whiskers, whilst interquartile ranges are depicted by box limits. Extreme outlying values are also indicated.

Table 1. Results of 'Tukey Honest Significant Difference' test between all hydrological phases at 'Lago Grande de Curuai'. Level of significance is indicated by both symbols and P values. P values are to 1 s.f. ✔✔= 99% significance (P<0.01), ✔= 95% significance (P<0.05), ✖= statistically insignificant (P>0.05).

	Rising	High	Receding	Low
Rising		✔✔	✔✔	✖
High	0.001		✖	✔✔
Receding	0.000007	0.5		✔✔
Low	0.8	0.00003	0.0000001	

4.2 Balbina Reservoir

As seen at *Lago Grande de Curuai*, the phase demonstrating the largest flux is also low at *Balbina Reservoir* (*Figure 4)*. Here, the median value is 29.11 mmol/m²/hr. The following order of phases is however altered. In *Balbina Reservoir's* case, low phase flux values are succeeded by receding, high and rising phases respectively. Interquartile range is greatest during the receding phase (IQR=15.90 mmol/m²/hr) and smallest in high (IQR=7.04 mmol/m²/hr). The only extreme value also occurs in the high phase, with no other phases showing outliers. *Table 2* then provides an insight into significance between the phases at *Balbina Reservoir*. This shows that the low season displays significant differences against all others. This however is to varying degrees of accuracy (ANOVA: Low-Rising P<0.01, Low-High P<0.05, Low-Receding P<0.05). No significant differences between other phases were observed in this dataset.

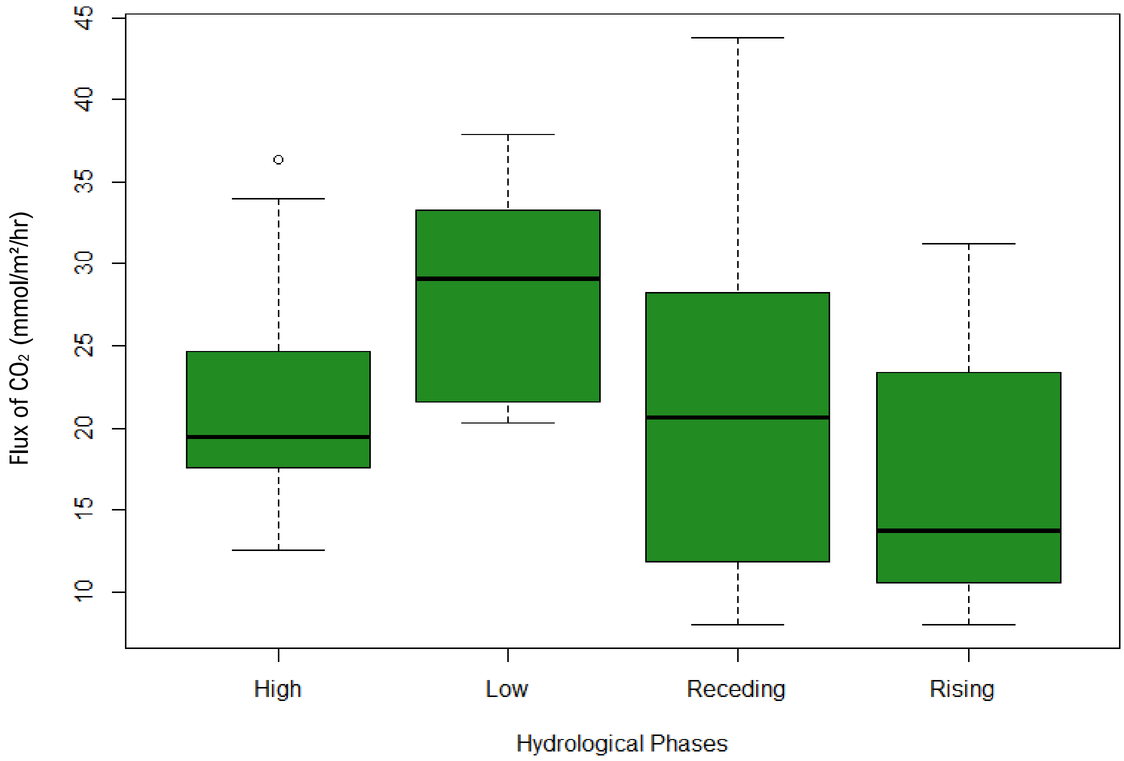

Figure 4. Flux at different hydrological phases at 'Balbina Reservoir'.
Box plot visualises descriptive statistics of flux at the site of 'Balbina Reservoir' during the 4 hydrological phases (rising, high, receding and low). Central lines are median values Range is illustrated by whiskers, whilst interquartile ranges are depicted by box limits. Extreme outlying values are also indicated.

Table 2. Results of 'Tukey Honest Significant Difference' test between all hydrological phases at 'Balbina Reservoir'. Level of significance is indicated by both symbols and P values. P values are to 1 s.f.
✔✔= 99% significance ($P<0.01$), ✔= 95% significance ($P<0.05$), ✖= statistically insignificant ($P>0.05$).

	Rising	**High**	**Receding**	**Low**
Rising		✖	✖	✔✔
High	0.2		✖	✔
Receding	0.3	0.1		✔
Low	0.0004	0.049	0.04	

4.3 Comparison between sites

In *Table 3*, descriptive statistics of both sites throughout all phases are presented. From this, it is observed that mean values of flux at all seasons are greater at *Lago Grande de Curuai.* This however is not the case if turning to medians. These show that fluxes experienced during the low and rising phases are greater at *Lago Grande de Curuai*, whilst high and receding phases are larger at *Balbina Reservoir*. *Figure 5* demonstrates this more clearly. This aligns with the fact that skewness was exhibited by both datasets, suggesting median as a more appropriate measure of central tendency. Standard error values must also be considered when comparing medians between the two sites, as overlap can then be revealed. In general *Balbina Reservoir* shows smaller standard errors (*Table 3*), indicating that the reliability of the sample mean is greater at this site, despite the sample size being much smaller (n=14-23).

Overall, the annual magnitude of flux was shown to be significantly higher at *Lago Grande de Curuai* (Wilcoxon Mann Whitney test, $P<0.01$). However, this was not the case for individual seasons, as seen by the results displayed in *Figure 5.* Here, it is seen that no significant differences were found between the sites during high and receding phases. These also happen to correspond to the two phases at which *Balbina Reservoir's* median flux values were higher. Significance ($P<0.05$) was found however between low and rising, where *Lago Grande de Curuai* was significantly higher.

In terms of spread of values, *Lago Grande de Curuai* experiences a much wider range of flux (*Table 3).* This can be seen by range values being up to an order of magnitude 4 times greater than *Balbina Reservoir*. It must be noted however that interquartile ranges are substantially reduced in comparison, highlighting the occurrence of extreme values in both cases. Contrasts between patterns of ranges and interquartile ranges are also exhibited between different seasons. Both sites experience greatest range in the receding phase, whilst this is no longer apparent in interquartile range values. Measures of spread can also be distinguished by standard deviation values, which once again are larger at the site of *Lago Grande de Curuai*.

Another note regarding spread is that some minimum values experienced at *Lago Grande de Curuai* delve into negative numbers (*Table 3*). In fact, an annual total of 34 sampling points were calculated to have a negative flux; 14 occurring during high season and 20 during receding. These negative values indicate an uptake of CO_2 by surface water. This is never experienced in values at *Balbina Reservoir.*

Table 3. Descriptive statistics of flux
Shows statistical values regarding measures of central tendency and variation and description. Both 'Lago Grande de Curuai' and 'Balbina Reservoir' are shown, with values for all hydrological phases. Appropriate number of significant figures varies for each statistic.

	Lago Grande de Curuai				**Balbina Reservoir**			
	Rising	High	Receding	Low	Rising	High	Receding	Low
Mean	36.3	30.6	24.3	39.9	16.2	21.7	21.3	28.7
Median	30.9	18.4	16.8	33.1	13.8	19.4	20.7	29.1
Min	8.8	-2.4	-3.0	16	8.1	13	8.1	20.3
Max	149	147	157	184	31.4	36.4	43.8	37.9
Range	141	149	160	168	23.2	23.9	35.7	17.6
Interquartile range	22	40	39	17	12	7.0	16	11
Standard deviation	25	37	31	25	7.3	6.1	10.5	6.3
Standard error	3.0	4.2	3.7	2.9	1.9	1.3	2.4	1.7

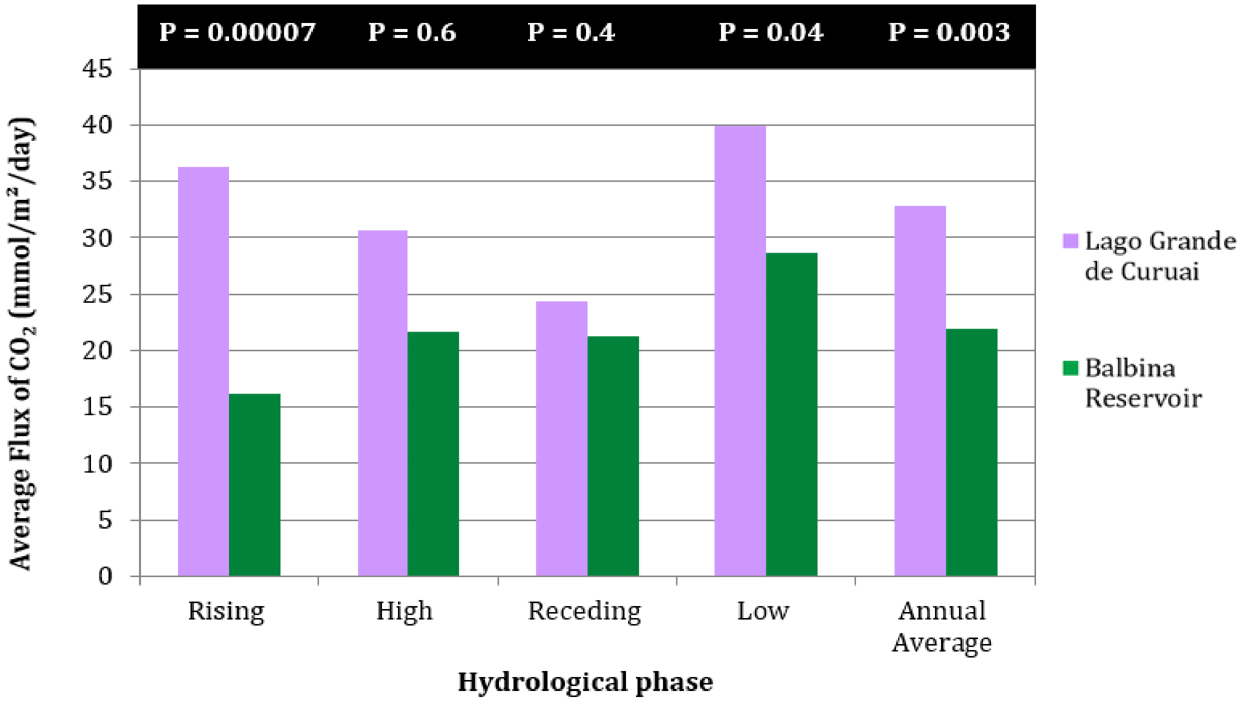

Figure 5. Comparison flux between sites.
Bars are indicative of average flux at 'Lago Grande de Curuai' and 'Balbina Reservoir' throughout corresponding phases. P values display results of Mann Whitney significance testing. These are considered at accuracy levels of 99% (P<0.01) and 95% (P<0.05).

4.4 Seasonal parameters

Surface water temperature values remained similar throughout the year at both sites. Variation between average seasonal values was within ±3 Kelvin (*Table 4*). Both sites showed a slight negative correlation coefficient of -0.15 between flux magnitude and surface water temperatures. However this relationship was only significant at *Lago Grande de Curuai* ($P<0.001$). r^2 was still low in this case, being just 0.03.

On the other hand, the series of depth values demonstrates a large difference between sites (*Table 4). Balbina Reservoir* is 3 times deeper than *Lago Grande de Curuai* in all 4 hydrological phases. In the low season this difference reaches more than 10m. An unexpected value is seen at *Balbina Reservoir,* as greatest depth readings are reported during the low season. Similar degrees of annual variation are seen at both sites however. Curuai's annual range is 2.4m, whilst Balbina is 3.23m. In terms of correlation and regression, relationships to flux are shown to be insignificant in both cases.

The correlation between flux and flooded area was found to be negative. Although this relationship was only significant ($P<0.05$) at *Lago Grande de Curuai* where $r_s=-0.24$. High phase exhibits similar maximum extents for both water bodies. *Lago Grande de Curuai* experiences a much more substantial reduction in area during low season in comparison. At this phase, *Balbina Reservoir* becomes just 68% of its maximum extent, whilst *Lago Grande de Curuai* is reduced to just 37% (*Table 4).*

Table 4. Values for seasonal parameters.
Flooded area, depth and surface temperature for both 'Lago Grande de Curuai' and 'Balbina Reservoir', during all hydrological phases. Average values are indicated in the uppermost right corner, with individual seasonal averages displayed below. Values are given to an appropriate degree of decimal places.

Site	**Flooded area (km^2)**	**Depth (m)**	**Surface temperature (Kelvin)**
Lago de Grande Curuai	Annual Average: 1789 Rising: 2015 High: 2274 Receding: 2015 Low: 850	Annual Average: 1.8 Rising: 1.6 High: 3.2 Receding: 1.6 Low: 0.6	Annual Average: 304.1 Rising: 303.4 High: 303.0 Receding: 305.6 Low: 304.5
Balbina Reservoir	Annual Average: 1918 Rising:1900 High: 2286 Receding: 1923 Low: 1563	Annual Average: 10.6 Rising: 10.0 High: 11.2 Receding: 9.2 Low: 12.4	Annual Average: 304p.0 Rising: 303.9 High: 303.3 Receding: 304.8 Low: 304.2

4.5 Estimation of total exchange

Average estimates of total exchange from flooded areas indicate that *Balbina Reservoir* evades a larger volume of CO_2 to the atmosphere in 3 out of the 4 phases. The exception to this is the rising phase, where *Lago Grande de Curuai* emits more than double that of *Balbina Reservoir.* An average total for the year also points to *Lago Grande de Curuai* being a larger source overall. All results are provided in *Table 5.*

Table 5. Total exchange of CO_2 from flooded areas.
Estimates are given for both 'Lago Grande de Curuai' and 'Balbina Reservoir', for all hydrological phases as well as an annual average. All values are given to 2 significant figures.

	Lago Grande de Curuai (mmol/hr)	**Balbina Reservoir (mmol/hr)**
Rising	62,000,000	26,000,000
High	42,000,000	44,000,000
Receding	34,000,000	40,000,000
Low	28,000,000	45,000,000
Average	41,000,000	39,000,000

5 Discussion

5.1 Discussion of findings

As seen in the results, annual average fluxes of 24.76 mmol/m²/day and 20.74 mmol/m²/day were obtained for *Lago Grande de Curuai* and *Balbina Reservoir* respectively. Compared to estimates previously acquired at these sites, the values obtained in this thesis are distinctly lower (Kemenes et al. 2011; Rudorff et al. 2011). This augmentation is also true when comparing to the majority of other tropically located studies. In 2002, St. Louis et al. (2000) estimated diffusive emissions from Brazilian reservoirs to be between 65-90 mmol/m²/day. Similarly, Duchemin et al. (2000), Lima et al. (2002) and Barros et al. (2011) all experience heightened values. An exception however can be seen by Paranaíba et al. (2018), whose study of 3 tropical reservoirs acquired an average flux value of 6.5 mmol/m²/day. Results also align with mean worldwide reservoir emissions calculated by Deemer et al. (2016) of 27.47 mmol/m²/day. Furthermore, it is worth noting that although lower than may be expected, results still exhibit values higher than those gained at temperate and boreal locations (Cole and Caraco 1998; Bergström et al. 2004).

If then comparing between sites, the significant difference of flux contrasts results seen in boreal regions (Bergström et al. 2004; Åberg et al. 2004). In these areas fluxes in natural lakes and reservoirs were found to be similar. This however is not the case here. Characteristics can help to explain this difference and the higher flux generally seen at *Lago Grande de Curuai*. Firstly, *Lago Grande de Curuai* has a weaker stratification than that of the strong pattern of *Balbina Reservoir* (Kasper et al. 2014). This is generated by the depth disparity between the two. The water column of *Lago Grande de Curuai* therefore experiences greater thermal mixing, bringing elevated CO_2 concentrations to surface waters (Rudorff et al. 2011). Preference to the sedimentation and bottom storage ability of *Balbina Reservoir* is also indicated by its greater depth. When waters are shallow, more sediment becomes in contact with the upper layers, meaning burial is likely to be suppressed in favour of mineralisation. The converse is true for deeper zones (Tranvik et al. 2009; Linkhorst 2019). Furthermore, quality and quantity of sediments also support this flux observation. The high load and nutrient rich white waters of *Lago Grande de Curuai* offer superior inputs to those of black water *Balbina Reservoir* (Abril et al. 2014). This promotes primary production which thereby supplies autochthonous inputs and spurs microbial respiration (Abril et al. 2014).

In terms of seasonal magnitude, the fact that the low season exhibited the largest emissions offers different explanations for each site. At *Lago Grande de Curuai*, shallow waters allow for wind driven turbidity. This stirs up bottom sediments, increasing the amount of particulate material suspended in the water (Alcântara et al. 2009). Given the fact that bottom sediments are high in OC (Gruca-Rokosz et al. 2017), the introduction of POC to the water column can lead to greater mineralisation and production of CO_2. Turbidity has also been shown to reduce sunlight penetration, therefore hindering photosynthesis which uptakes CO_2 (Hess et al. 2003; Barbosa et al. 2010). However, in Amazonian lake, rate of photosynthesis is considered to be less influential to carbon balance. This due to substantial respiration rates, which outweigh the photosynthetic process (Almeida et al. 2016).

The occurrence of high flux during low phase at *Balbina Reservoir*, could be attributed to the reduction of flooded area. This decreases water dilution, therefore concentrating nutrients and OM and allowing for greater evasion per unit area (Tremblay et al. 2005). Depth adjustments also change volume of water and dilution, but these are unexpectedly high during this phase at *Balbina Reservoir*. This could potentially be due to the location of measurement points being near to the dam, which often represent the deepest zones (Wakjira and Mengistou 2015; Chanudet et al. 2020). In this case therefore, areal extent can be thought of as the main morphological controlling factor. Lack of allochthonous input during this high flux phase also points to the fact that external input is not a major control.

The order of subsequent flux rates from phases showed alternate patterns between the two sites. At *Lago Grande de Curuai*, an influx of OM during the rising phase could account for the occurrence of the second largest flux. OM is imported to the floodplain from the Amazon river mainly during rising water, therefore increasing the amount available for degradation (Kolding and van Zwieten 2012; Moreira-Turcq et al. 2013). In contrast, the receding phase demonstrated the second highest rate at *Balbina Reservoir*. During this phase, allochthonous inputs are lessened (Kolding and van Zwieten 2012). Having said this, residence time is substantially longer at this site (Fearnside 1989), increasing the chance of a more complete decay of OM within the water (Rudorff et al. 2011; Prairie et al. 2018). Influence of influx is therefore not as dominant within this system, allowing for higher flux despite lack of inputs. Submerged vegetation may also add to this reduced reliance. Moreover, *Balbina Reservoir* records its shallowest depths at this phase. This in turn lowers the thermocline and increases the likelihood of OC enriched bottom layer sediments being brought to the upper layers (Kolding and van Zwieten 2012; Kasper et al. 2014).

The seasonal difference significance indicates that flux tends to be separated biannually, rather than by the 4 hydrologic phases. At *Balbina Reservoir*, only the low season is recognisably different, once again suggesting the influence of flooded area extent. On the other hand, at *Lago Grande de Curuai* the split is seen with low and rising being distinct from high and receding. During high and receding, *Lago Grande de Curuai* also demonstrates capacity to be a carbon sink. As well as the reasons already mentioned, it can be said that reduced autochthonous inputs during these phases could further explain this pattern (Casali et al. 2011). This is due to lessened primary production, caused by limitation of nutrients and radiation in the water column (Casali et al. 2011; Rudorff et al. 2011; Barbosa et al. 2012). Having said this, the highest surface water temperatures are also measured during the rising phase at both sites. Although commonly known to enhance primary productivity, temperature is rarely a limiting factor in the tropics (Barbosa et al. 2010; Gruca-Rokosz et al. 2017). This idea is supported by the low r^2 value of the temperature relationship.

Adding to this, higher dependence on allochthonous inputs at *Lago Grande de Curuai* is suggested by seasonal differences between sites. During receding and high seasons, when there is diminished inflow (Moreira-Turcq et al. 2013), flux is significantly similar. However, at low and rising phases when OM inputs are re-established (Moreira-Turcq et al. 2013), *Lago de Grande Curuai* experiences significantly higher flux than *Balbina Reservoir*. Additional responsible parameters potentially include the number of input channels, river type as well as distance from influx zone (Linkhorst 2019). These are outlined by the fact that *Balbina Reservoir* has only one blackwater input channel (Fearnside 1989), with measurement point location being distanced from this source.

Spatial distribution should also be mentioned with reference to outliers at *Lago de Grande Curuai.* Upon further inspection, it appears that these values tend to be located in littoral regions, lying along the peripheries of the lake. This links to an increased availability of OM (Chanudet et al. 2020), therefore explaining the extreme positive values. The singular outlier at *Balbina Reservoir* could not be attributed to any such pattern, and is instead thought of as a result of unique conditions or measurement discrepancy.

A final note is directed toward the greater annual variation of both flux and flooded area seen at *Lago Grande de Curuai*. Influence of this becomes apparent in total exchange estimates. Despite *Lago Grande de Curuai's* larger flux during all seasons, as a total system *Balbina Reservoir* emits a greater volume of CO_2 for the majority of the year (receding, low and high phases). This is caused by smaller seasonal changes in flooded area at *Balbina Reservoir,* which could potentially be attributed to the anthropogenic control of the dam (Fearnside 1989) (de Sousa Lobo et al. 2018). The significance of a negative correlation between area and flux at *Lago Grande de Curuai* also supports this idea, illustrating the fluctuations of a natural system (Hess et al. 2003). This once again emphasises the impact of morphological factors on open water emissions from *Balbina reservoir.* A vital note however, is that these estimates do not take into account emissions from the surrounding floodplain, which could have a substantial role (Abril et al. 2014; Sobrinho et al. 2016). The strikingly high amount of emissions at *Lago Grande de Curuai* during the rising phase also cause the total annual release of CO_2 to be greatest at this site.

5.2 Evaluation of methodology

When evaluating results, it is also important to consider potential inaccuracies that may be caused by methodological practices. In this case, a possible source is the method used for flux calculations. In comparison to more reliable 'floating chamber' techniques, flux values obtained are usually much lower (Lambert and Fréchette 2005). However, given the fact that *Balbina reservoir* data was cross validated with estimates from these techniques, inaccuracies from this are presumed to be small. Another potential source of error is that calculation of CO_2 concentrations often shows imperfect agreement with direct measures (Cole et al. 1994; Raymond et al. 1997). In practice, this is often decided by practical constraints (St. Louis et al. 2000).

In addition, the use of a wind-based model for piston velocity ‘k’ may also cause inaccuracies, as this does not account for other influencing factors (Wanninkhof 1992; Abril et al. 2014). Additional drivers such as turbulence, convection and stability are all known as regulators, but are not necessarily intrinsically linked to wind speed (Wanninkhof 1992; Read et al. 2012). Predictions may therefore be flawed. When looking to studies obtaining similar fluxes, influence of ‘k’ becomes evident. Those showing similar flux values also obtain ‘k’ values within the range seen here (Paranaíba et al. 2018). Studies with larger fluxes however, also report higher ‘k’ values (Kemenes et al. 2011). Having said this, there is still some debate regarding the affect of wind on flux. Lambert and Fréchette (2005) states this to be the major influencing factor, whilst Raymond et al. (1997) argues that seasonal changes in concentration are more important.

Continuing with wind measurement errors, attention must also be drawn to the fact that measurements were not taken directly from the sites. They are therefore unlikely to represent site specific patterns (Paranaíba et al. 2018). This is highlighted by measurements obtained by Rudorff et al. (2011) for *Lago Grande de Curuai* during the same time period, which show an average velocity roughly 3.5m/s faster than those acquired here. In addition, extrapolation techniques cannot be fully relied upon to accurately describe a complete wind profile (Sisterson et al. 1983). Atmospheric CO_2 concentrations were derived from average global values, again potentially being unrepresentative of site conditions. This is a limitation of data availability.

Quality of datasets was also constraining. Sampling was not conducted with the original intention of satisfying this investigation's specific aims. This therefore led to elements of dataset weakness (Alin and Johnson 2007). For example; sample size, location of samples, as well as measurement period inconsistencies both within and between sites.

5.3 Other considerations and future perspectives

The omission of ebullitive flux in this study was decided by findings of past studies, as well as data constraints. Ebullitive emissions are considered to be negligible with regard to CO_2 emissions in waters (Therrien et al. 2005), however rate of gas ebullition is known to vary with the key seasonal parameter of depth (Casper et al. 2000). It could also potentially become an important pathway at reservoir sites where turbines are active. Results from whole system studies at *Balbina Reservoir* indicate that 48% of CO_2 which passed through turbines was immediately lost through this pathway (Kemenes et al. 2011). Downstream flux from outflowing rivers is also thought to be significant in system entirety estimates (Barros et al. 2011; Prairie et al. 2018), but have not been considered in this study.

Ebullition is also more dominant in the emission of other greenhouse gases such as methane. Methane's potential to absorb outgoing long radiation is approximately 20 times that of CO_2. It's role in the global warming effect can therefore not be ignored. It's emission has also been shown to demonstrate seasonal cycles (Devol et al. 1990). The likelihood of *Balbina Reservoir* to emit methane is particularly large due to the conducive anoxic bottom water conditions (Dos Santos et al. 2005; Kasper et al. 2014). Lack of methane measurement inclusion may therefore lead to results not being fully indicative of climate change contribution.

Additionally, results of this study must be approached with caution when applying findings to other areas. This is due to the fact seasonality at these particular sites is induced by the distinct phenomenon of the Amazonian flood pulse. Furthermore, *Balbina Reservoir* possesses unique characteristics that may not relate to other typical reservoirs. For example, it has an extremely long residence time, an unusually small drainage basin and is incredibly shallow (Wakjira and Mengistou 2015; Hayes et al. 2017). It is also a relatively old reservoir, which is known to decrease gas flux (Therrien et al. 2005). Furthermore specific conditions during measurement years have been noted at both sites. The area experienced a drought in 2005 (Silva et al. 2019), *with Lago Grade de Curuai* also demonstrating supereutrophic characteristics during the hydrological year of 2003-2004 (Affonso et al. 2011). Eutrophication promotes high rates of mineralisation and burial (Almeida et al. 2016; Deemer et al. 2016), whilst droughts tend to reduce water levels and extent (Silva et al. 2019). Open water emissions may therefore be restricted.

A final note must be extended to both temporal timescales and spatial distributions. Variability through inter-annual timescales are not able to be captured in the timeframe of a one-year study (Rudorff et al. 2011). Shorter periods such as diel variability were also not included here. Further investigation as to how these behave is therefore needed. Additionally spatial variation should not be disregarded. In fact, Almeida et al. (2016) states that this could result in up to a 25% error in total system fluxes. To obtain an adequate representation for a whole water body, it therefore is important to include samples from all different areas present (Lambert and Fréchette 2005). Future research should therefore be conducted with thought given to both spatial and temporal resolutions.

6 Conclusion

In conclusion, both sites were shown to act as a source of CO_2 to the atmosphere throughout the entire annual cycle. Despite being much lower than previous estimates, results still indicate that emissions from tropical sites are greater than those of temperate regions. Seasonal behaviours also appear prominent, with the two locations sharing some similarities but also displaying differences.

In terms of influence on dynamics, classical characteristic features still appear to play an underlying role. But response to flood pulse does seem to vary between the two water bodies. Whilst the natural lake expressed a greater inclination towards influx and water quality controls, the hydroelectric reservoir appeared to be primarily driven by morphological changes. A greater stability of emission rates was also observed in the reservoir, with the lake showing more variability.

For future research, it is suggested that continued effort and resources are put towards this field. Drawbacks of this study can also not be ignored, and limitations regarding data availability as well as methodology and discrepancies have been outlined. Further investigations at additional sites, over longer timescales and coupled with focused data collection should therefore be conducted. This would allow more detailed insights into the mechanisms at play and offer the opportunity for more conclusive outcomes to be drawn.

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