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Variations of methane emissions within and between three hydroelectric reservoirs in Brazil

Variationen av metanemissioner inom och mellan tre hydroelektriska vattendammar

Karin Grandin

ABSTRACT

Variations of CH_4 emissions within and between three hydroelectric reservoirs in Brazil

Karin Grandin

Hydroelectricity is an energy resource which for a long time has been considered environmentally neutral regarding greenhouse gas emission. During the last years this view has changed. Studies have shown that reservoirs connected to hydroelectric power plants emit methane (CH_4) and other greenhouse gases to the atmosphere, especially in the tropical regions where the emission level of CH_4 is the highest. The purpose of this thesis was to investigate the variations of CH_4 emissions in Funil reservoir, Santo Antônio reservoir and Três Marias reservoir and to identify variables that increase the CH_4 emissions.

The CH_4 emissions were measured by floating static chambers positioned on the surface at several locations within each reservoir. A gas sample was collected after 10, 20 and 30 minutes from each chamber. The samples were analyzed through gas chromatography to obtain the concentration of CH_4 in each sample. Calculations of the change in CH_4 concentration over time were used to establish the flux of CH_4 at each location.

The obtained result from Funil reservoir showed CH_4 fluxes in the range of -0.04 to 13.16 mmol/m^2/day with significantly different fluxes between sites ($p < 0.05$). The CH_4 fluxes in Santo Antonio reservoir were within the range of -0.33 to 72.21 mmol/m^2/day. In this reservoir fluxes were not significantly different between sites ($p < 0.05$). The results obtained from Três Marias showed CH_4 fluxes in the range of -0.31 to 0.56 mmol/m^2/day with significantly different fluxes between sites ($p < 0.05$). The highest fluxes were found in Santo Antônio which were significantly different from the CH_4 fluxes in Três Marias ($p < 0.05$). The CH_4 flux was positively correlated with CO_2 and dissolved organic carbon (DOC) and negatively correlated with O_2 and depth in Santo Antônio. The same correlations were evident for the whole data set. In total the measured fluxes from the three reservoirs ranged from -0.33 to 72. 21 mmol/m^2/day and the mean flux was 2.31 mmol/$m^{2/}$day. These fluxes are low compared to earlier results. The variation in CH_4 flux within and between the reservoirs was significantly different in a major part of the comparisons. Even though the majority of the fluxes were different, variables that increase the CH_4 emission rate were illuminated. A low depth and low O_2 concentration increase the CH_4 emission rate. A high concentration of DOC and CO_2 indicates that a high amount of organic carbon was available for the production of CH_4, leading to an increased CH_4 emission rate.

Keywords: CH_4 emissions, tropical reservoirs, hydroelectricity, flooded vegetation

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REFERAT

Variationen av metanemissioner inom och mellan tre hydroelektriska vattendammar i Brasilien

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Vattenkraft är en energikälla som länge har ansetts vara klimatneutral gällande växthusgaser, men under de senaste åren har denna bild förändrats. Studier har visat att hydroelektriska vattendammar avger metan (CH_4) och andra växthusgaser till atmosfären och att CH_4 emissionerna från dessa dammar är störst i tropiskt klimat. Syftet med detta projekt var att undersöka variationerna av CH_4 emissioner i de hydroelektriska vattendammarna Funil, Santo Antônio och Três Marias i Brasilien, och att bedöma vilka variabler som påverkar avgången av CH_4 i dessa vattendammar.

För att mäta avgångarna av metan placerades statiska flytkammare på vattenytan på ett antal platser inom varje vattendamm. Ett gasprov togs efter 10, 20 och 30 minuter från varje kammare. Gasproverna analyserades genom gaskromatografi och därmed erhölls koncentrationen av metan i varje prov. Beräkningar av förändringen i koncentration från början till slutet av mättiden gav metanflödet.

Resultaten från Funil visade signifikant skilda CH_4 flöden mellan mätplatser från -0,04 till 13,16 mmol/m^2/dag. I Santo Antônio var det lägsta flödet -0,33 mmol/m^2/dag och det högsta 72,21 mmol/m^2/dag, och här var flödena mellan mätplatserna ej signifikant skilda. Funil visade också signifikant skilda flöden mellan mätplatser från -0,31 till 0,56 mmol/m^2/dag. De högsta CH_4 flödena erhölls i Santo Antônio, och dessa flöden var signifikant skilda från flödena i Três Marias. CH_4 flödet var positivt korrelerat med CO_2 och DOC och negativt korrelerat med O_2 och djup i Santo Antônio. Samma korrelationer gällde för hela datamängden från de tre vattendammarna tillsammans.

De uppmätta flödena av CH_4 från de tre dammarna varierade från -0,33 till 72,21 mmol/m^2/dag och medelflödet var 2,31 mmol/m^2/dag. Dessa flöden var låga i jämförelse med tidigare resultat. Trots att variationen i CH_4 flödena var stor inom och mellan vattendammarna kunde variabler som ökar CH_4 emissionerna identifieras. En hög koncentration av CO_2 och DOC indikerade att det fanns stor tillgång på organiskt kol som kunde användas till produktionen av CH_4, vilket ökade emissionerna av CH_4. Variablerna O_2 och djup hade också påverkan på CH_4 flödet, där ett litet djup och låg O_2 koncentration ökade emissionerna av CH_4.

Nyckelord: metanemissioner, tropiska vattendammar, vattenkraft, översvämmad vegetation

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PREFACE

This master's thesis is the last part of the Master of Science program in Aquatic and Environmental Engineering of 30 ECTS at Uppsala University. It was performed in the spring semester 2012 and the major part of the thesis was carried out during two months in Brazil. The thesis was made in cooperation with the Laboratory of Aquatic Ecology at the Federal University of Juiz de Fora in Minas Gerais, Brazil.

The supervisors of the thesis were Eva Podgrajsek at the Department of Earth Sciences at Uppsala University and Luciana de Oliveira Vidal at the Laboratory of Aquatic Ecology at the Federal University of Juiz de Fora in Minas Gerais, Brazil. The subject reviewer was Gesa Weyhenmeyer at the Department of Ecology and Evolution at Uppsala University.

Sida (the Swedish International Development Agency) together with the Brazilian project BALCAR were financing this thesis. BALCAR is a project sponsored by Electrobrás, the Brazilian hydropower agency owned by the government. This thesis would have been impossible to compass without the financial support from Sida and Electrobrás. In order to evaluate the obtained results from the performed measurements complementary data were needed. This data were supplied by several people at the Aquatic Ecology Laboratory in Juiz de Fora. The results in this study would have been limited without this resource.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Vattenkraften är en ständigt växande energikälla som används i hög utsträckning världen över. I dagsläget har 17 % av de potentiella platserna för vattenkraft utnyttjats. Detta innebär att det finns mycket utrymme för vattenkraftens framfart. Samtidigt som nya områden exploateras ökar medvetenheten om de negativa effekterna denna energikälla har på naturen och klimatet. Vattenkraft anses vara en förnyelsebar energikälla eftersom energin ej kommer från fossila bränslen utan från naturliga förnyelsebara processer. Hydroelektriska vattendammar avger trots den förnyelsebara karaktären växthusgaserna koldioxid, metan och kväveoxid till atmosfären. Dessa gaser avges även vid förbränning av olja, naturgas och kol. Syftet med den studie som denna rapport baseras på var att se hur utsläppen av metan varierar inom och mellan tre hydroelektriska vattendammar i Brasilien och vilka faktorer som påverkar utsläppen.

Metan är en växthusgas som bildas i sedimentet på botten av vattendammar som restprodukt när bakterier bryter ner organsikt kol. Från att ha tillverkats i sedimentet kan metangasen antingen stiga upp genom vattnet och avges till atmosfären eller ombildas till koldioxid. Om vattnet är syrerikt är chansen stor att ombildning till koldioxid sker, medan en låg syrehalt gynnar utsläpp av metan till atmosfären. Det som främst styr vilken växthusgas som avges är alltså mängden tillgängligt syre i vattnet, medan produktionen av metan främst styrs av tillgången på organsikt kol. Utsläppen av metan beror även på ytterligare faktorer som exempelvis latitud, temperatur, ålder på vattendammen, djup i vattendammen och vattenflöde. Många av de studier som genomförts har påvisat att de största utsläppen av metan sker i tropiska områden i jämförelse med tempererade och boreala områden. Detta beror på att dessa områden påverkas av variabler som är relaterade till höga metanutsläpp i större utsträckning än områden längre från ekvatorn.

I Brasilien kommer 85 % av energiproduktionen från vattenkraft. En majoritet av vattenkraftverken är lokaliserad i sydöstra delen av landet vilken är den del där befolkningen och den industriella verksamheten är som störst. I denna del är taket nått för hur mycket vattenkraft som får utvinnas. Brasilien är ett land som just nu genomgår en stor ekonomisk och industriell expansion, vilket medför att energibehovet ökar i samma takt. För att tillfredsställa den växande energikonsumtionen sker en stor utbyggnad av vattenkraften, främst i och omkring Amazonas, i den nordöstra delen av landet där 50 % av den totala vattenkraftspotentialen finns.

För att se hur metanutsläppen varierar och vilka faktorer som påverkar variationen genomfördes mätningar av metanutsläppen från de tre tropiska vattendammarna Funil, Santo Antônio och Três Marias i Brasilien. Funil är lokaliserad i sydöstra Brasilien i närheten av Rio de Janeiro. Denna vattendam har höga halter av näringsämnen eftersom tillrinningsområdet är tätbefolkat och innehar många industrier. Vattnet är grönt vilket har orsakats av en hög koncentration av alger. Dessa algerna har producerats på grund av den stora tillförseln av

näringsämnen. Santo Antônio ligger i Amazonas vid utkanten av staden Porto Velho. Denna vattendam är nyligen konstruerad i anslutning till två vattenkraftverk; Santo Antônio och Jirua som ska börja generera energi 2014. Till följd av byggnationen av vattendammen har stora landområden med mycket vegetation översvämmats. Três Marias är placerad i mitten av Brasilien, strax norr om staden Belo Horizonte. Denna vattendamm har klart blått vatten och en area av 1000 km^2.

Mätningarna gjordes genom statiska flytkammare som placerades på vattenytan i vattendammarna. Tre flytkammare användes på 7 till 13 mätplatser inom varje damm och från dessa kammare togs luftprover var tionde minut under en halvtimme. De uppmätta proverna analyserades sedan genom gaskromatografi för att koncentrationen av metan i varje prov skulle erhållas. När koncentrationen i varje prov var känd kunde metanflödet beräknas genom hur koncentrationen förändrades med tiden.

Mätningar av metanutsläppen från de tre vattendammarna visade att Santo Antônio hade de högsta utsläppen av metan och den största spridningen (-0,33–72,21 mmol/m^2/dag) följd av Funil (-0,04–13,15 mmol/$m^{2/}$dag). I Três Marias var utsläppen av metan lägst och spridningen minst (-0,31–0,56 mmol/m^2/dag). I Santo Antonio var utsläppen störst från de områden som nyligen har översvämmats eftersom det finns en stor tillgång på lättnedbrytbart organsikt material på dessa platser. Utsläpp av metan skedde även genom vattenväxter. Då transporterades metan från sedimentet, genom stjälkarna i växterna och upp till atmosfären. På dessa platser var även syrehalten låg. Funil hade högre metanutsläpp än Três Marias, vilket troligen berodde på en högre tillgång på organsikt materia och en lägre syrehalt i vattnet. I Três Marias var metanutsläppen lägst eftersom tillgången på organsikt material var begränsad, samtidigt som syrehalten var hög.

Det var stor skillnad i metanutsläpp mellan Três Marias och Funil, men också mellan Três Marias och Santo Antônio. Likheterna i flöde var störst mellan Funil och Santo Antônio. Trots att metanutsläppen hade stor spridning, kunde variabler som ökade utsläppen identifieras. En hög koncentration av löst organiskt kol, tillsammans med grunt vatten och låg syrekoncentration gjorde att utsläppen av metan till atmosfären ökade.

WORDLIST

Allochthonous carbon	external carbon that enters an aquatic system
Anoxic	low concentrations of O_2 in the water
Aquatic boundary layer	the water layer closest to the surface
Boreal ecosystem	located in the sub Antarctic and sub-Arctic regions
DOC	Dissolved Organic Carbon
Epilimnion	the surface layer of water in a thermally stratified freshwater basin
GHG	Green House Gas
Hypolimnion	the colder water mass located at the lake floor in a thermally stratified freshwater basin
Hypoxia	to low O_2 concentration for the occurrence of oxidation
Lentic	areas with still water, like the water in lakes and ponds
Littoral zone	the part of a water basin located closest to the shore
Lotic	areas with fast moving water, like the water in rivers
Macrophyte	a large plant in water vegetation
Monomictic	a lake that is entirely mixed once a year
Organic carbon sink	where organic carbon is stored, for example in trees
Organic carbon sources	where organic carbon is released, for example reservoirs
Oxic	high concentration of O_2 in the water
Riverine zone	the zone closest to the inlet of the reservoir which establishes river–like characteristics
Temperate ecosystem	next to the temperate zone and closer to the equator
TotN	Total Nitrogen
TotP	Total Phosphorus
Transition zone	the zone in a reservoir where the river turns into a lake
Turbidity	the cloudiness in the water
Vareza	a special kind of rainforest in the Amazon region which is seasonally flooded
Water column	a column of water from the lake floor to surface

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1 INTRODUCTION

Methane, (CH_4) is a greenhouse gas with a 23 times higher global warming potential than CO_2. This gas is estimated to be responsible for 20 % of the increased greenhouse effect observed since the mid 1700s (Bastviken 2009). The amount of CH_4 has increased as a consequence of anthropogenic activities, mainly human waste treatment, cattle ranching and agriculture, but also by hydroelectric power generation.

Hydroelectric reservoirs contribute to the increased greenhouse effect by emitting CH_4 and other greenhouse gases (GHG) to the atmosphere. The level of emissions can be significant at a global scale. The emissions, particularly in the tropics, can in some cases be comparable to the emissions from fossil–fuel power plants considering GHG emissions per megawatt produced (Santos *et al.* 2006). At the moment 17 % of the potential hydroelectric sites are used globally (Pircher 1993). A major part of the new constructed hydroelectric reservoirs are built in the tropics, but most of the existing data on GHG emissions are based on measurements in temperate areas (Roland *et al*. 2010). Due to this there is a lack of information regarding the CH_4 emissions in the areas currently most exploited, which also are the areas with highest known GHG emission rate (Louis *et al.* 2000).

In Brazil, approximately 85 % of the energy supply is generated from hydroelectricity and most of the hydropower plants are located in the south eastern part of the country. This is the area where the demand of electricity is the highest due to high population density and intense industrial activity (Soares *et al.*2008). In this area the exploitation of hydropower plants has reached the limit. Further on most of the new constructed hydropower plants are planned to be situated in the tropic Amazon region (IAEA n.d).

It is important to further investigate the processes that occur within the reservoirs where CH_4 is involved, especially in the tropics. Thereby more knowledge will be achieved on how to locate and construct future hydropower plants and reservoirs in order to minimize the CH_4 emission rates. By doing so, hydropower will continue to be considered an environmentally friendly energy resource.

1.1 PROJECT BACKGROUND

This study was made in cooperation with the Laboratory of Aquatic Ecology at the Federal University of Juiz de Fora, Minas Gerais, Brazil. At this laboratory a research group is working with the project BALCAR (Balanço de Carbono) where they perform a large–scale field study of the carbon budget in 11 hydro power reservoirs in Brazil. The purpose with the BALCAR project is to investigate how man–made hydropower reservoirs affect the carbon cycle in the prescribed ecosystem, especially the quantity of greenhouse gas emissions. The main goals within the BALCAR project are:

- To determine the emissions of greenhouse gases: carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), from the reservoirs.
- To identify the pathways of the carbon cycle in these reservoirs, as well as the environmental factors involved in it.
- To evaluate the influence of morphological, morphometric, biogeochemical and operational variables on the greenhouse gas emissions.
- To establish the previous pattern of greenhouse gas emission, prior to the flooding of the reservoirs.
- To develop a spatial and temporal model of the greenhouse gas emissions in reservoirs that flood Cerrado environments (Cimbleris 2007).

Electrobrás, the Brazilian hydropower agency owned by the government, is financing the BALCAR project through their three underlying companies FURNAS, ELECTRONORTE and CHESF. The project was established in order to follow the Brazilian law 9.991/2000. This law implies that energy producing companies have to make a minimum annual investment of 1% of their net annual revenue in development and research.

The BALCAR project is also performed as a part of the obligations Brazil has as a participant in the United Framework Convention on Climate Change. The framework convention is an attempt to handle the problems connected to the increased greenhouse effect, where the aim is to restrict the concentrations of gases in the atmosphere (Rosa *et al.* 2002). Brazil thereby made a commitment when signing this framework to develop and maintain updated information about the sources and sinks of greenhouse gas emissions, mainly carbon dioxide, CH_4 and nitrous oxide (Cimbleris 2007).

1.2 PURPOSE

The purpose of the thesis was to investigate the variation of CH_4 emissions in three different reservoirs in Brazil and to illuminate the variables that increase the CH_4 emission rate. This was done by comparing the emissions within and between the reservoirs but also by comparing CH_4 emissions with measured variables.

1.3 LIMITATIONS

Several limitations emerged during the project, most of them connected to the short time available in Brazil, but also limitations regarding the equipment needed to make the measurements. By spending nine weeks in Brazil, the time used for measurements at the three reservoirs was relatively short. Therefore, the number of locations used for measurements

within each reservoir was few in relation to the size of the reservoirs. At every reservoir groups of people were making measurements at the same time. Thereby compromises were done regarding how to perform the measurements. Also the time to do the analyses of the measured samples in the lab was limited, and due to this the number of analyzed samples was restricted. The available equipment was limited which also gave rise to limitations.

2. BACKGROUND

2.1 CH_4 IN HYDROELECTRIC RESERVOIRS

2.1.1 Characteristics of CH_4

CH_4 is one of the most abundant organic compounds on earth. The gas is colorless and odorless, melting at -182.5 ^{0} C and boiling at -161.5 ^{0} C. The Henry´s law constant for CH_4 at 25^0 C is $1.29 \cdot 10^{-3}$ M atm^{-1} and this feature gives CH_4 low water solubility. CH_4 is the main element in biogas, natural gas and marsh gas and is combustible when 5–15 % of the air constitutes of CH_4 (Bastviken 2009). CH_4 is emitted to the atmosphere by a variety of anthropogenic and natural sources and the concentration of CH_4 in the atmosphere is 1700 parts per billion (ppb) (SLCF 2011). At the same time as CH_4 is emitted to the atmosphere the gas is also degraded there by photo oxidative and hydroxyl radical related processes. The residence time for CH_4 in the atmosphere is 8–12 years, a short residence time in comparison to CO_2, which has a residence time of 30–95 year (Jacobson 2005). Due to the short residence time, a steady–state increase of CH_4 to the atmosphere requires a high amount of constant emissions from different sources (Bastviken 2009).

2.1.2 How CH_4 is created

In hydroelectric reservoirs and other freshwater ecosystems, CH_4 is produced in the anoxic sediment and then released to the water column. Here the gas either gets oxidized or transported to the water surface where it is emitted to the atmosphere. CH_4 is produced in the sediment from decomposed organic material through methanogenesis, a process performed by methanogenic achaebacteria. The methanogenesis strictly depends on anoxic conditions and on a limited number of substrates with low molecular weight. The methanogenesis occurs mainly through two different pathways; acetotrophic methanogenesis (acetat dependent) and hydrogenotrophic methanogenesis (H_2 dependent). During acetotrofic methanogenesis CH_4 is created by dividing acetate (CH_3COO) into CH_4 and CO_2. In the hydrogenotrophic methanogenesis a reaction takes place between CO_2 and H_2 resulting in two components; CH_4 and H_2O. The most important substrates regarding the methanogenesis are considered to be acetate, H_2 and CO_2. Other substrates like formate, methanol, dimethyl sulfide, tri–, di–, and monomethylamines and ethylamine can also be used in the process. The acetotropic and hydrogenotrophic methanogenesis most often occur simultaneously. Each process contributes between 20–80% to the overall CH_4 production that occures in the sediment.

The performance of methanogenesis depends on a long chain of reactions where organic matter is the main component eventually liberating the needed substrates. Different bacterial processes occur in parallel to the methanogenesis and due to this a competition about the substrate might appear. Depending on current circumstances the methanogenic bacterias can be concurred out by more efficient substrate uptake systems. These circumstances are affected

by different variables, for example pH, Methanogenesis can occur in other parts of the inland water systems, but the sediment is the main location. This is because this part of the water systems most often establishes anoxic conditions and also carries large amounts of substrate (Bastviken 2009).

2.1.3 How CH_4 is produced, transported and emitted to the atmosphere

When CH_4 is produced in the sediment, it can either get trapped there, or escape towards the water surface. If CH_4 escapes the sediment, it either reaches the water surface and then diffuses to the atmosphere, or it gets transformed by methano–oxidizing–bacteria (MOB) through oxidation. Oxidation is an energy releasing process performed by methano–oxidizing–bacteria (MOB) with the purpose to make energy available for the bacteria. To enable oxidation, O_2 or another potent oxidant must be available. The MOB can be divided into three groups with different aims and characteristics, but mutually they all sequentially oxidize CH_4. First into methanol, formaldehyde, format and then finally CO_2. The oxidation rate is the greatest in connection to the oxic–anoxic boundary layer where both O_2 and CH_4 are accessible. This boundary zone exists either in the water column, surface sediment or in the deeper sediments next to roots liberating O_2. The zone where the oxidation arises is commonly a few millimeters thick if it appears in the sediment. If the oxidation takes place in the water column the zone is most often thicker, more on a decimeter–meter scale. The location of the oxidation zone is controlled by the spatial and temporal variation in O_2.

The presence of CH_4 highly depends on the oxygen level in the water column. If the water column is oxic, the main part of CH_4 will be oxidized by MOB. If the water column is anoxic the possibility for CH_4 to reach the water surface is high (Bastviken 2009).

CH_4 that evades oxidation will escape from the freshwater ecosystem to the atmosphere. This can happen through three different pathways:

1. **Ebullition bubbles** that escape from the sediment and quickly transports through the water column. No oxidation takes place even if the water column is oxic due to the rapid transportation velocity. The hydrostatic pressure, thereby depth, and the formation rate of CH_4 are main factors that control the amount of CH_4 released by ebullition. It is more common that ebullition bubbles occur at shallow depths due to the low hydrostatic pressure at these places. Also weather conditions highly affect the hydrostatical pressure. It has been shown that storms and frontal passages increase the amount of escaping ebullition bubbles because the air pressure gets lower (Abril *et al.* 2005).

2. **Diffusive flux** between the air and surface water. The transportation is caused by processes of turbulent enhanced diffusion. Due to the low speed of the diffusive released CH_4, oxidation can occur especially in oxic water layers or sediments.

Thereby the amount of CH_4 released through diffusion highly depends on the oxygen level in the water column. Since CH_4 has a low solubility in water most freshwater systems are oversaturated in CH_4. This means that the diffusive flux, mainly driven by concentration differences and turbulence, most often will emit CH_4 to the atmosphere because of the oversaturation (Rosa *et al.* 2004).

3. **Flux through macrophytes.** Aquatic plants can emit CH_4 to the atmosphere from their leaves. CH_4 is transported from the sediment to the leaves through the stems of the plant by using the transportation system that normally transports O_2. This process can be passive or driven by pressure differences depending of the species of the macrophytes (Bastviken 2009).

In reservoirs two additional pathways exist due to the man−made artificial influence on the ecosystem.

4. **Degassing downstream** the reservoir. Due to the turbulence the turbines cause on the water transported downstream the reservoir, extended amounts of CH_4 can be emitted to the atmosphere straight after the dam (UNESCO/IHA 2009).

5. **Increased diffusive** flux along the river downstream. Further downstream the same kind of diffusive flux will occur as the diffusive flux upstream. The downstream flux will be higher because of the turbulence that still appears in the water.Theese emissions can occur 10 meters to 50 km downstream (UNESCO/IHA 2009).

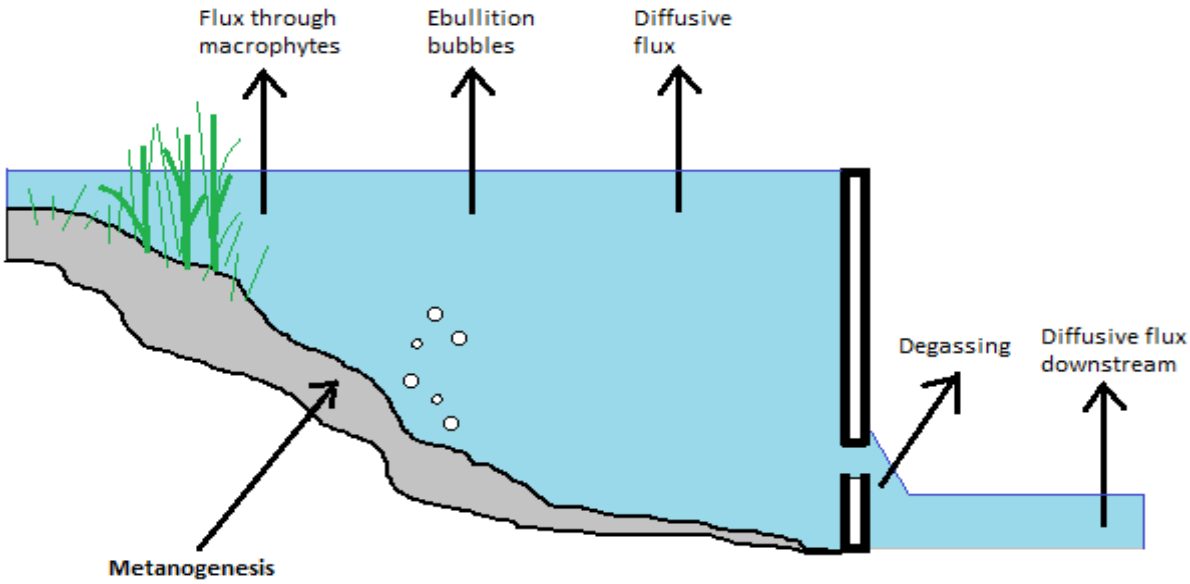

Figure 1 The different pathways of CH_4 emissions connected to hydroelectric reservoirs.

The major part of the open water CH_4 emissions come from plants and ebullition bubbles, where approximately 50 % is caused by ebullition. This number should be considered together with the fact that ebullition is the pathway most difficult to quantify. The probability that these emissions are underestimated is high due to lack of measured data (Bastviken 2009).

The CH_4 emissions highly depend on the characteristics of a reservoir. Reservoirs have limnological properties representative for both rivers and lakes (Thornton 1990). There is a common longitudal pattern observed in many reservoirs where the upper part of the reservoir has characteristics similar to a river, while the lower part is more comparable with a lake (De Freitas Terra *et al.* 2010). A longitudal pattern can appear in reservoirs caused by lotic influences, and lead to a creation of three distinct zones defined by their biological, chemical and physical characteristics.

The riverine zone, which is the zone closest to the river, is defined by a high inflow of nutrients where the primary production is low because of the high turbidity. The transition zone appears afterwards when the water moves further into the reservoir. In this zone the sedimentation rate and light availability increase and as a consequence the primary production gets higher. The lentic zone is at the end of the reservoir, close to the dam. The high sedimentation rate in this area limits the primary production.

Several features affect the size and borders between these zones, like water retention time, morphometric, thermal stratification and latitude. The variable that affects the zonation the most is the retention time. If the retention time is short, a great part of the reservoir comprises the riverine zone (Soares *et al.* 2008).

2.2 VARIABLES DETERMINIG CH_4 EMISSIONS

The processes of producing, transporting and emitting CH_4 rely on many different variables. These variables altogether determine the rate of CH_4 production, rate of oxidation and also the present pathways. The opinions about which variables that affect the CH_4 emissions the most vary. Many articles are pointing at the importance of latitude, climate, dissolved organic carbon and age of reservoir in connection to the CH_4 emissions (Barros *et al.* 2011; Rosa *et al.* 2002).The most important variables are described below.

Depth

The depth is an important variable regarding whether CH_4 in the sediment will be released or not since CH_4 emissions are controlled by the hydrostatical pressure. The hydrostatic pressure is often low in shallow parts of a reservoir. It is thereby easier for CH_4 gas to overcome the hydrostatical pressure in these areas compared to deeper areas, resulting in ebullition release.

Dissolved oxygen
The amount of oxygen in the water has a great influence on whether CH_4 will be transported to the surface or if it will go through oxidation on its way up. The limiting level where a water body is considered to establish hypoxic condition is at the oxygen concentration of 2–3 mg/L (Kalff 2002).

Turbulence, turbidity and retention time
The direction and speed of the water flow within a reservoir affects the processes where CH_4 is involved. A short retention time is a result of high water speed and this occurrence obstruct the sedimentation of incoming organic material. This results in a loss of substrate that could have been used in the methanogenesis process. The water speed and direction also affect the oxidation process. A high turbulence increases the mixing of the water, and this can generate a more oxic water body. But the mixing can also ease the release of CH_4 to the atmosphere by moving water, with a high concentration of CH_4 located close to the sediment, upwards. Turbulence also exposes a larger surface area to the atmosphere which enables an increase in the flux of CH_4 (Bastviken 2009). The CH_4 emissions that are released downstream the dam are highly affected by the turbulence. It is thereby difficult to conclude whether turbulence increases or decreases the CH_4 emissions, because it varies depending on the current circumstances. Turbulence most often occurs as a consequence of certain weather conditions such as wind and rain, or in connection to the dam and the turbines.

Dissolved organic carbon
Organic carbon has an important role regarding the production of CH_4. However, the composition of the available organic carbon is more important than the quantity. Unstable organic carbon, like litter and leaves decompose quickly, while older, more stable organic carbon, such as soil and peat, decompose slowly. When a reservoir is constructed flooded organic material is transferred into the reservoir and a big part of the organic carbon is easily decomposable organic carbon (Louis *et al.* 2000). In younger reservoirs, less than 15 year old, the flooded biomass stands for the major part of the organic carbon source (Barros *et al.* 2011). Tree boles need very long time to decompose when they are found in flooded areas because the lignin that is decomposed by fungal cannot be decomposed due to the surrounding water (Louis *et al.* 2000). The amount of allochthonous organic carbon transferred into the reservoir also affects the emission rate (Louis *et al.* 2000). Climate type and surrounding vegetation thereby have great impact on the CH_4 emissions since type and quality of the allochthonous organic carbon transferred into the reservoir affect the CH_4 emission rates.

Age of reservoir
The age is an important variable that affect the emissions. Because of differences in decomposable organic carbon access, younger reservoirs emit more CH_4 than older reservoirs. When a reservoir starts to get older the emission rate first decrease exponentially and then slows down with time (Barros *et al.* 2011).

Concentration total phosphorus and total nitrogen
The concentration of total phosphorus (total P) and total nitrogen (total N) affect CH_4 emission since the primary production, controlled by these nutrients, is the source of organic material in the sediment. The primary production rate depends on the available amount of these nutrients, and more organic material is created if great loads of phosphorus and nitrogen are present. Thereby more organic material is transferred to the sediment ready to be decomposed which will increase the produced amount of CH_4.

Temperature
The decomposition of organic carbon is high in the tropics due to the high annual mean temperature in the water (Louis *et al.* 2000). The optimal temperature for methanogenesis is around 30 °C in the sediment (Jones *et al.* 1982) and if the temperature increases with 10^0C the potential production rate of CH_4 is increasing fourfold (Conrad 2002). CH_4 oxidation rates seem to be less sensitive to temperature changes than methanogenesis, but high light intensity, which can be coupled to temperature, inhibits the CH_4 oxidation (Bastviken 2009).

Latitude
Latitude is assumed to affect the amount of emissions due to differences in climate type and temperature (Rosa *et al.* 2002). The temperature brings energy to the whole ecosystem, which determines the rates of the processes within the system. The climate type determines the load of allochthonous organic material that enters the reservoir.

pH
When the pH level in a lake is within a normal pH interval this variable does not seem to affect the methanogenesis. But a small change in pH within the normal interval might affect the composition of substances available for the process. Thereby the methanogenesis is affected indirectly. The optimal pH for the methanogenesis process is 5–6 (Zinder 1993). When the pH is low acetotropic methanogenesis seems to be the dominant one and when pH is high the hydrogenotrophic methanogenesis is favored. No clear pattern has been observed between pH and the CH_4 oxidation rates. A reason for this might be the ability the microbal communities locally adapt to various pH intervals (Bastviken 2009).

Dam construction

The ways of operating a hydropower plant highly affect the CH_4 emissions from the reservoir. The energy generation occurs when water passes the turbines, and depending on the placement of the water outlet and the position of the turbines the amount of emissions downstream varies. If the outlet is located at a great depth there is a high risk that the water will bring CH_4 through the outlet which will cause degassing emissions (UNESCO/IHA 2009). Also the difference in water level caused by the energy generation affects the emissions. If the water level is low for a long time, new vegetation will grow along the shore. When the water level raises this vegetation will be flooded and transferred into a part of the load of organic easily decomposed material in the reservoir. The hydrostatical pressure in the reservoir is affected when there is a change in water level, which may lead to releases of ebullition bubbles (Louis *et al.* 2000).

2.3 BRAZIL

2.3.1 The Brazilian climate

CH_4 emissions from reservoirs highly depend on the climate, because the climate affects a number of other variables that are connected to the CH_4 processes. Major parts of Brazil are located on– or close to the equator and this placement cause a tropical climate and high atmospheric humidity. The Amazon lowland and surrounding areas receive more than 2000 mm of rain annually. The annual rainfall in the rest of Brazil is approximately 1000–1500 mm. Brazil represents several different biomass, but the ones that covers most of the land are the semi–arid "Sertão", the rain forest "Foresta", the low and bushy shrubs called "Caatinga" and the savanna and grassland called "Cerrado". The Sertão exist in the inner north–eastern part and frequently suffers from droughts. The Foresta is found in the surrounding of the Amazon basin, and the Cerrado is the biome in great parts of the south and south–east of Brazil. The Caatiga is situated in the inner north–east. There are three major river systems in Brazil; The Amazon in the north, the São Francisco in the east and the Parana–paraguay–Plata in the south. The Amazon is the second longest river in the world (6440 km) and the major river in South America (IAEA n.d). Most hydro power plants and reservoirs in Brazil are situated in the south–east region. The biome in this area mostly consists of Cerrado and the climate is categorized as humid–tropic. The three reservoirs used for this study are located in different biomass and different river systems. Funil reservoir is located in the Cerrado and is a part of the Parana–Paraguay–Plata River system, Santo Antônio is situated in the Foresta in the Amazon basin and Três Marias is situated in the Cerrado and the São Francisco River system. All three reservoirs are situated in the tropic region.

2.2.2. Hydroelectricity in Brazil

Brazil is the fifth greatest country in the world in area and has one of the largest hydroelectric potential worldwide. Most of the potential has not yet been exploited but the hydroelectric resources in the south, south–east and north–east have already been thoroughly used. To feed the growing need of energy the north and central west regions, where the Amazon is situated are starting to get exploited (IAEA n.d). About 50% of the hydroelectric potential of Brazil is located in the Amazon basin (Braga *et al.* 1998).

At the moment Brazil is going through a great expansion period regarding hydropower. In the late 90s the energy department of the Brazilian government compiled a program called "plan 2015" where a decision were made about constructing 424 new hydroelectric dams during the period 2000–2015. In 2009, 50 of these had been constructed and at that time 70 more was projected. So far about 2200 large dams have been constructed in Brazil (120 in Sweden) and more than 3.5 million hectare has been flooded (Naturskyddsföreningen 2009).

2.4 PREVIOUS RESULTS REGARDING CH_4 EMISSIONS IN THE TROPICS

Studies of the CH_4 emissions in tropical flooded areas started in the eighties, and the Amazonian area and the African forest were the first regions that were surveyed (Rosa *et al.* 2002). Many studies have been focusing on this topic since then. Here are some examples and the obtained results of the CH_4 fluxes in the studies.

Batlett *et al.* (1993) studied flooded vegetation, both with and without floating vegetation. The measurements varied between 0.47 mmol/m^2/day and 60.27 mmol/m^2/day and the mean flux was 12.47 mmol/m^2/day.

Hamilton *et al.* (1995) investigated the Pantanal wetland of Brazil. 540 samples were taken in this savanna floodplain region, where the sampling areas constituted of sheet flooding, marsh streams and the major river in the area. The calculated mean diffusive CH_4 flux in the air–water interphase was 14.65 mmol/m^2/day.

Galy–Lacaux *et al.* (1997) analyzed the CH_4 flux rate in the Petit Saut reservoir, located on the Sinnamary River in French Guinea, South America. The mean fluxes of diffusion during the study ranged from 7.5 mmol/m^2/day to 202 mmol/m^2/day. The measurements occurred over a two year period, between 1994 – 1995 and the measurements started when the reservoir was filled with water and 300 km^2 were flooded. During the 2 years, 10% of the carbon stored in the reservoir was released to the atmosphere as CH_4.

3 METHOD

3.1 STUDY SITES

The three sites where measurements were made are Funil reservoir (FU), Santo Antônio reservoir (SA) and Três Marias reservoir (TM) (Figure 2). The reservoirs are described further down and the most important variables are summarized in table 1. The measurements were made in February 2012, during the Brazilian summer which also is the wet season.

Figure 2 Locations of the study sites source: (Wikipedia).

3.1.1 Funil reservoir

Funil reservoir was constructed in 1969 and is the largest impoundment in the Rio the Janeiro state, southeastern Brazil (Terra *et al.* 2010). The reservoir is drained by the Paraiba do Sul River which is one of the most heavily used riverine systems in Brazil since the river is located in connection to a major industrial and urban areas of the country (Pinto *et al.* 2006).The river starts in the Sao Paulo state and passes through large industrial areas before it continues to Funil reservoir. The water in Paraiba do Sul is used for hydroelectric power production, irrigation, industrial self–supply systems, aquaculture, and also as public and domestic drinking water. Approximately 14 million people are estimated to receive drinking water from this river (Branco *et al.* 2002). As a consequence of these anthropogenic influences the Paraiba do Sul River is carrying a heavy load of nutrients and due to this Funil reservoir is very eutrophic (Soares *et al.* 2008). A freshwater system is classified as moderately eutrophic when the median total P concentration is between 10−30 µg/l (Khan & Ansari 2005). In Funil reservoir the mean concentration is 96 µg/l (Soares *et al.* 2008). The phytoplankton biomass is also very high in Funil reservoir with median chlorophyll–a concentration of 10.0 µg/L (Soares *et al.* 2008) and intense cyanobacterial blooms occurs frequently (Klapper 1998; Branco *et al.* 2002; Rocha *et al.* 2002). Although there is a high level of nutrients anoxic conditions rarely occur in Funil (Soares *et al.* 2008) most likely due to the high level of mixing through the year. The high amount of algae in the surface water, which produce O_2 are also contributing to the high O_2 concentration (Nathan Barros, personal communication).

Funil reservoir is located in the Brazilian Cerrado biome (savannah) and the general climate is humid–tropic. The soil in the Cerrado biome is poor and overlies the pre–cambrium rock (Roland *et al.* 2010).

There is a limited amount of vegetation in the area surrounding the reservoir as a result of previous agriculture used for coffee plantations and pasture (Terra *et al.* 2010). A major part of this vegetation consists of planted eucalyptus trees. The company supplying the energy, Electrobras Furnas, has settled a reforestation program in the area surrounding the reservoir with the purpose to restore the forest (Terra *et al.* 2010). The operation water level ranges from 444 m.a.s.l. to 465.5 m.a.s.l. during the year, which means that the water level varies about 15 m. This water fluctuation cause no further erosion or sedimentation in the reservoir (Terra *et al.* 2010).

Figure 3 The green water in Funil reservoir.

Funil reservoir has a long and wide section in the middle of the reservoir where the origin is the Paraiba do Sul River. This part is connected to two branches; one from the Santana tributary and the other one from the Lajes tributary (Branco *et al.* 2002). The reservoir basin follows the typical spatial zonation described above (riverine–transitional–lentic), where variation in light availability and nutrients in the sediment is the reason for the zonation (Soares *et al.* 2008). In the riverine zone the predominant substrate is clay and the average depth is 4 m. In the transition zone the substrate is mostly consisting of stones and rocks and the average depth is 11 m. The depth in the lentic zone is about 20 m and the sediment consists of sand (Terra *et al.* 2010).

The Secchi depth is low in the whole reservoir, but lowest in the riverine zone and highest in the transitional– and the lentic zones. The lower value in the riverine zone appears due to the turbidity and inflow of suspended material. The transparency increases in the transition– and lentic zone because of the decreased turbidity and inflow of suspended material (Branco *et al.* 2002; Terra *et al.* 2010).

3.1.2 Santo Antônio reservoir

Santo Antonio reservoir is located in the Amazon region in the northwestern part of Brazil next to the city of Porto Velho (Figure 2). The reservoir is mainly a part of the Madeira River, but also the tributaries Jaci–paraná and Jatuarana and the reservoir has more riverine characteristics than lake characteristics. There are two hydroelectric power plants in this part of the river; the Santo Antonio dam and the Jirau dam. At the moment these hydroelectric

power stations are under construction but are planned to be ready to generate energy in 2014 (Odebrecht). The two power plants will together produce 6.450 megawatt (MW) of electricity, and thereby become the third largest hydropower complex in the country (Leite *et al*. 2011). In order to minimize the flooded area, a "run of river" system is constructed, where low head bulb turbines will rotate by the natural speed and flow of the river. This system does not need a large fall height of water to generate energy, which result in a minimized flooded area. 44 low–head bulb turbines will be used at each of the two power plants (Santo Antônio Energia 2009). The purpose of building these two power stations is to support the southern parts of Brazil with energy resulting in a 2500 km long transmission corridor (Switker & Bonilha 2008).

Areas next to the shore of the Madeira River, Jaci–paraná and Jatuarana have been flooded during the construction of the power stations. Part of this flooding is natural and varies depending on season but the flooding is to a certain extent man–made. The Madeira River was half the size before the reservoir was constructed. In Jatuarana the width of the tributary has increased from approximately 10 m to about 100 m since it became a part of the reservoir (Rafael Almeida, personal communication)(Figure 4).Some of the flooded areas are deforested while several others are covered with vegetation. On many places this vegetation has not been removed before the flooding, therefore large amounts of organic material have been transported into the reservoir. The water is very dark in those flooded areas where no deforestation has occurred, due to the high amount of flooded organic material and also because of the material the drainage area brings into the flooded parts (Castillo *et al.* 2004). Gas bubbles are visible at many places in the tributaries (Figure 5).

The Madeira River is a so called white river which means that the river has a white color caused by the high amount of suspended material transported by the water. The origin of the water and the suspended material is the sedimentary and morphometric rocks in the Andes (Stallard & Edmond 1983; Lyons & Bird 1995) and in the pre–Cambrian and Cenozoic sediments that is present in the catchment area (Junk *et al.* 2011). This geologic structure together with seismic phenomenon in the Andes, soils vulnerable to erosion, a river with

Figure 4 Flooded road in Jatuarana.

Figure 4 Bubbles in a tributary in Santo Antônio.

unstable sandbanks and heavy rainfall contribute to the great load of suspended material (Carvalho *et al*. 2011). The Madeira River is carrying nearly half the load of the sediments and nutrients transported from the Amazon region into the Atlantic Ocean (Latrubesse *et al.* 2005). This makes Madeira River the principal contributor to the life and diversity of the Amazon (Switker & Bonilha 2008). The Secchi depth is very low in the river as a consequence of the high amount of suspended material in the water (about 10 cm), both downstream and in the reservoir. This result in a low ability for the sunlight to penetrate the water and thereby almost no cyanobacteria can be found in the river. The few existing phytoplankton are quickly transported downstream due to the short retention time in the river and tributaries (Rafael Almeida, personal communication). The suspended material is deposited in *várzeas*, a local name for large floodplains. These areas are highly productive and covered with aquatic and terrestrial plants and floodplain forests (Junk *et al.* 2011). Madeira River is draining geologically recently formed terrains and the high amount of suspended material transported in the Madeira River is a consequence of that (Rafael Almeida, personal communication).

3.1.3 Três Marias Reservoir

Três Marias reservoir is located in the northern part of the state of Minas Gerais (Figure 2) and is mainly drainage by the São Fransico River, but also the tributaries S. Vicente, Paraopeba, Extrema, Sucurúi, Ribeirão do Boi, Borrachudo and Indaiá (Fonseca *et al.* 2007). The purpose of building the dam was flood control, flow regulation and hydro power generation and the construction work ended in 1960. Since then this reservoir is one of the largest artificial lakes in Brazil (Arantes *et al.* 2011). The reservoir is oligotrophic and monomictic where the mixing event takes place in July in the dry season due to a high wind speed. It is stratified when the temperature difference between the hypolimnion and epilimnion is greater than 3 degrees and this occurs during the wet season between November and February (Carolsfeld *et al.* 2003). Mixing events can also appear in the wet season because of rain, but the reservoir is most often stratified (Felipe Pacheco, personal communication). The dry winter and the rainy summer cause a high intensity of soil and rock weathering and this enables soluble elements to leach into the drainage basin, most commonly happening between October and April (Fonseca *et al.* 2007).

Figure 5 The blue-green water in Três Marias reservoir.

Três Marias reservoir is set in the *Cerrado*, the Brazilian savannah, and this area has been a subject to deforestation during the

last decades. Native species have been replaced by eucalyptus and large cattle ranches and over–erosion of soil has become a problem within the reservoir and tributaries (Sampaio & Lopez 2003 in Brito *et al.* 2011). The soluble elements and the eroded soil turn into suspended material and when this material is transported to the outlet of the reservoir it gets trapped behind the dam. The accumulated sediment load causes major environmental and technical problems such as filling the reservoir and thereby changing the characteristics. The tributaries Borrachudo and Indaiá are the main contributors to the high sediment load (Fonseca *et al.* 2007). The water level in the reservoir varies 2 – 5 meters within a year and the water level is the lowest between October– November. This is because water is released through the dam during this time period to enable water to flow in when the wet season starts in December. Water is dammed during the wet season to enable energy generation during the dry season (Felipe Pacheco, personal communication).

Table 1 The characteristics of Funil, Santo Antônio and Três Marias.

Reservoir	Funil reservoir	Santo Antonio reservoir	Tres Marias reservoir
Altitude (m.a.s.l.)	440	180	584
Longitude	22°30'S	8^0 48'06" S	180^0 12' 262 S
Latitute	44°45'W	63^0 57' 03" W	45^0 15' 321 W
Biome	Cerrado/savanna	Cerrado/savanna	Rain forest
Main river	Paraíba do Sul	Madeira	São Francisco
Year of impoundment	1969 [a]	2014 [d]	1960 [l]
Energy generation (MW)	180 [b]	3150 [k]	396 [l]
Area (km^2)	40 [c]	271 [e]	1040 [l]
Volume (m^3)	890 x 10^6 [c]	xxx	15.27 x 10^9 [l]
Maximum depth (m)	45 [b]	50 [j]	75 [l]
Mean depth (m)	20 [b]	10– 22 [j]	12 [l]
Retention time (days)	10–50 [c]	2–10 river,30 tributaries [f]	120 [l]
Watershed area (km^2)	16800 [a]	954000 [g]	634000 [n]
Watershed discharge (m^3/s)	220 [a]	32000 [h]	700 [l]
Annual precipitation (mm)	1337 [b]	1950 [i]	1250 [m]
Average air temperature (^0C)	18.40 [b]	25.10 [e]	22.24 [e]
Nutrient status	Eutrophic [c]	Meso–oligotrophic	Oligotrophic
Numbers of stations in reservoir	12	7	13
Macrophytes	NO	YES	YES
Annual difference in water level (m)	15 [a]	10–15 [f]	2–5
Color of water	green	beige/white	blue/green

a Terra *et al.* (2010)
b Roland *et al.* (2010)
c Soares *et al.* (2008)
d Odebrecht
e Wikipedia
f Rafael Almeida, Personal communication
g Leite *et al.* (2011)
h Latrubesse *et al.* (2005)
i Guyot *et al.* (2006)
j Rhibra project
k SantoAntônio Energia (2009)
l Brito *et al.* (2011)
m Fonseca *et al.* (2007)
n Carvalho *et al.* (2011)

3.2 THE FLOATING CHAMBER METHOD

3.2.1 Measurements

The method that was used to measure the CH_4 emissions from the water surface to the atmosphere was the floating chambers method. This method is further described in the UNESCO/IHA measurement specification guidance for evaluating the GHG status of man–made freshwater reservoirs (UNESCO/IHA 2009). The measurements were done by the use of three floating chambers placed on the water surface at every measurement location. Initial gas samples were taken with syringes from the air and water in the surrounding of the chambers. A syringe was connected to a hose on top of each chamber and gas was collected after 10, 20 and 30 minutes from every chamber. Each gas sample was transferred from the syringe to a vial. The samples in the vials were then analyzed by the use of gas chromatography (GC) to obtain the concentration of CH_4 in each gas sample. The concentrations of CH_4 in the initial samples and in the samples from the chambers were used to calculate the flux of CH_4 emissions to the atmosphere. A more detailed description regarding how the measurements were performed is available in appendix A.

The spatial measurements in Funil were distributed in 12 stations located to make the best possible representation of the whole reservoir. The water level was very low when the measurements took place and reddish clay was exposed in the littoral zone due to the low water level. The water in the whole reservoir was very green (Figure 3), and the color was most evident at the stations close to the inlet of the reservoir. Also a lot of visible garbage was floating around in the reservoir, mostly close to the inlet, so it is clearly understandable that the reservoir receives much material that affects the ecosystem within the reservoir. The measurements were made during the rainy season in the summer and normally this time of the year a thermal stratification appear in this reservoir (Soares *et al.* 2008). No macrophytes were observed.

The measurements in Santo Antônio reservoir were made at 7 different stations in the reservoir. Three stations were situated in the river while the other four were situated in the tributaries. One tributary station where used to measure emissions from macrophytes. Measurements were also made downstream at three different places, two in the river and one in a small bay. The water level differs 12 meters during the year and the level was high when the measurement took place (approx. 3 m below the highest level) but the water level would increase until March and then decrease. Erosion was visible almost everywhere next to the shore downstream and could easily be seen. Macrophytes occurred at many places both upstream and downstream the reservoir.

Measurements were made at 13 stations in the Três Marias reservoir. Also temporal measurements were made close to the shore to measure how the amount of CH_4 increased during 36 hours. The water level was high because the measurements were taken in the wet season. Phytoplankton and zooplankton can easily be seen in the water all over the reservoir

and thereby the color of the water is green–blue (Figure 6). Macrophytes also exist at numerous places in the reservoir.

3.2.2 Data Analysis

The concentrations of CH_4 in the samples obtained from the gas chromatography were used to calculate the fluxes of CH_4 at every station. The fluxes were calculated by a linear approximation and a non–linear function (described further down), and the fluxes that were used for the continued analyzes were based on the non–linear function. These analyzed fluxes were obtained from the three chambers at each station after 30 minutes deployment time. The fluxes obtained after 10 and 20 minutes deployment time were not used in the analysis because they were unreliable. Therefore 36 fluxes were used in the results from Funil (12 station · 3 chamber) and 39 (13 stations · 3 chambers) from Três Marias. In Santo Antonio 19 measurements were used (6 stations · 3 chamber + 1). The additional single flux came from the control chamber at station 7 with the macrophytes.

The differences in CH4 fluxes within and between the reservoirs were statistically calculated with the Wilcoxon Rank Sum Test. This test compares the median value between two populations of data and calculates whether the data is significantly different or not. The test is based on the null hypothesis "means are equal" were the significance limit is 0.05. The populations are considered equal when the significance (P) is above 0.05 (the null hypothesis cannot be rejected, H=0), and significantly different when the significance (P) is below 0.05 (the null hypothesis can be rejected, H=1). The obtained flux data did not have a normal distribution and this is why this test was used.

A principal component analysis (PCA) was performed in Matlab to detect the combined effect of variables on CH_4. The central idea of PCA is to reduce the number of dimension in a dataset, where related variables form one dimension. The method creates a reduced set of variables, where each new variable is a linear combination of the original variables. The new variables are so called principal components (Mathworks 2012). The PCA displays the variables in a coordinate system and how they are related to each other. Variables that are situated close to each other are related. If variables are situated in the diagonal opposite quadrant they affect the system in a different direction. Variables that are located in quadrants next to each other do not have any strong relationship. The result from a PCA can also be displayed in a table.

The PCA was made by loading 15 chosen variables (CH_4 flux, CH_4 concentration in chamber samples, depth, concentration of dissolved O_2 in the water, concentration of CO_2 in the water, air temperature, concentration of DOC, water temperature, wind speed, total N concentrations, total P concentration, chlorophyll–a concentration, pH) into the workspace as a matrix. The variables in the matrix were log–transformed to put them in a normal

distribution. The matrix was also standardized in order to pay regard to the different units among the variables. The used command was `stdr`. The principal components were then found by the command `primcomp`. A m–file was created with the code to generate a plot of the PCA with the 1st component on the x–axis and the 2nd component on the y–axis which displayed the scores and the loadings. An additional plot of the explanation in the variance for each component was generated. One PCA was constructed for the whole dataset representing the three reservoirs, and one PCA for each reservoir. The outliers were included in the dataset when the PCA were performed. The stations with missing data were excluded in the analysis.

The strongest relationships between CH_4 flux and the variables in the PCA were analyzed by correlation analyses in Matlab. The correlation analysis displayed positive correlations, negative correlation and no correlation between CH_4 and the different variables based on the significance (P) and explanation degree (R). A value of P below 0.05 and a value of R close to 1 indicated a positive correlation, while a value of P below 0.05 and value of R close to -1 indicated a negative correlation.

3.3 CALCULATIONS

The flux of CH_4 was calculated by two different methods; a linear approximation and a non–linear function for diffusive flux (David Bastviken, personal communication).

3.3.1 Calculating the concentration of CH_4 in initial water samples

To be able to calculate the CH_4 flux by the non–linear function, the concentration of CH_4 in the initial water sample was calculated by the ideal gas law together with measurements from the gas chromatography (GC). In order to calculate the initial concentration of CH_4 in the water the amount of CH_4 compound in the initial air sample (n) and in the initial water sample (n_{tot}) was determined.

In the air sample the amount of compound was calculated by

$$n = \frac{P \cdot V}{R \cdot T} \quad (1)$$

where:
n = amount of compound in air sample (moles)
V = volume of air, 0.060 L
R = gas constant = 0,082056 (L atm K^{-1} $moles^{-1}$)
T = temperature of air (K)
P = partial pressure of CH_4 in air sample (atm)

and

$$P = P_{tot} \cdot ppm_{sample} \cdot 10^{-6} \quad (2)$$

where
$ppm_{aamples}$= concentration (ppm) of CH_4 in air sample obtained from the GC
P_{tot} = total atmospheric air pressure (atm).

The total atmospheric air pressure, P_{tot} varies depending on the altitude. P_{tot} at a certain altitude can be calculated by

$$p_{tot} = 101325 \cdot (1 - 2.25577 \cdot 10^{-5} \cdot h) \cdot 5.25588 \quad (3)$$

where
h = altitude above sea level (m).

In the water sample the amount of compound was divided into two parts; gas headspace (n_g) and water headspace (n_{H2O}), which together equals the amount of CH_4 compound in the water sample (n_{tot}).

The amount of compound in the gas phase (n_g) was calculated by equation 1 and 2 where

n = amount of compound in headspace gas of water sample (moles)
V = volume of gas in headspace, 0.020 L
T= temperature of water (K)
P= partial pressure of CH_4 in gas phase (atm)
ppm_{sample}= concentration (ppm) of CH_4 in gas headspace in water sample obtained from GC.

Henry´s law was used to calculate the amount of compound in the water headspace

$$C_{H2O} = P_{H2Ohead} \cdot K_h \quad (4)$$

where
C_{H2O}= concentration of CH_4 in water (M)
$P_{H2Ohead=}$ partial pressure of CH_4 in water headspace (atm)
K_h= Henry´s law constant (M atm^{-1}).

P_{H2O} was calculated by equation 2 where the concentration (ppm) of CH_4 in the gas phase in the water sample were obtained from the GC.

The amount of compound in the water phase was calculated by

$$n_{H2O} = C_{H2O} \cdot V_{H2O} = P_{H2Ohead} \cdot K_h \cdot V_{H2O} \quad (5)$$

where
n_{H2O} = amount of compound in headspace water of water sample (moles)
V_{H2O} = volume of water in headspace, 0.040 L.

The total amount of compound in the water sample was given by

$$n_{tot} = n_g + n_{H2O} \quad (6)$$

and the initial concentration of CH_4 in the water was calculated by

$$C_{H2O} = \frac{n_{tot} - n_{air}}{V_{H2O}} \quad (7)$$

3.3 2 Calculating the flux of CH_4

The flux of CH_4 can be calculated in a simplified way by the use of a linear approximation. It can also be calculated by a non–linear function, which imitates the flux of CH_4 in a chamber better than the linear approximation. CH_4 can only be emitted until the air in the chamber is saturated in CH_4, since the chamber limits the area where the diffused CH_4 can occur. The non–linear function takes into account the decrease in flux over time that occurs when the diffusion is getting closer towards equilibrium. Since the flux decreases with time a linear approximation will underestimate the flux of CH_4. Therefore the non–linear function gives a more accurate result than the linear approximation when measurements are done over a longer time.

Linear approximation

The linear approximation of the flux was obtained by using the initial CH_4 concentration in the air and the end CH_4 concentration in the chamber together with the ideal gas law.

The initial partial pressure of CH_4 was approximated by the partial pressure of CH_4 in the initial air sample calculated by equation 2. The partial pressure of CH_4 in the chamber sample at the end of the deployment time was also calculated by equation 2.

The formula for the flux was transformed together with equation 1

$$F = \frac{n_{end} - n_{init}}{(A \cdot (t_{end} - t_{init}))} \quad \rightarrow \quad F = \frac{(ppm_{end} - ppm_{init}) \cdot \frac{1}{10^6} \cdot \frac{V}{R \cdot T}}{A \cdot (t_{end} - t_{init})} \qquad (8)$$

where
F= flux (moles m^{-2} d^{-1})
A= bottom area of chamber (m^2)
V= chamber volume (L)
T= air temperature (K)
t_{end}-t_{init}= the deployment time (days)
n_{init} = initial amount of compound during deployment time
n_{end} = end amount of compound during deployment time.

Non–linear diffusive flux

When calculating the non–linear diffusive flux the following equation was used

$$F = k \cdot (C_{H2O} - C_{eq}) \qquad (9)$$

where
k= gas transfer velocity (m d^{-1})

C_{eq}= the CH_4 concentration in the water given equilibrium with the CH_4 partial pressure in the floating chamber (M).

To calculate the instantaneous flux, *k* is needed. To calculate *k*, equation 9 was rewritten as

$$\frac{(P_t - P_0)\cdot V}{R\cdot T\cdot A} = k \cdot (P_{H2O} \cdot K_h - P_0 \cdot K_h) \quad (10)$$

where
P_t = partial pressure of CH_4 in the chamber at time t (atm)
P_0 = partial pressure of CH_4 in the chamber at time 0 (atm)
P_{H2O}= the partial pressure of CH_4 in the chamber at equilibrium with C_{H2O} (atm).

The derivative of the partial pressure was used to find *k* from K.

$$\frac{dP}{dt} = K \cdot (P_{H2O} - P) \quad (11)$$

The gas transfer velocity, *k* is described by

$$K = k \cdot \frac{K_h \cdot R \cdot T \cdot A}{V} \quad (12)$$

The solution for equation 11 is

$$(P_{H2O} - P) = B \cdot e^{-Kt} \quad (13)$$

By setting t = 0 the value of B was obtained, and thereby K was the only unknown variable in equation 11.

$$K = \frac{1}{t} \cdot \ln\left(\frac{P_{H2O} - P}{B}\right) \quad (14)$$

4 RESULTS

4.1 VARIATION IN CH_4 FLUXES

The CH_4 fluxes displayed on the maps constitute mean values taken from the three chambers at each station after 30 minutes deployment time. The fluxes in Funil ranged from 0.01 mmol/m^2/day to 0.65 mmol/m^2/day, except from station 7 (5.75 mmol/m^2/day) and station 9 (9.97 mmol/m^2/day)

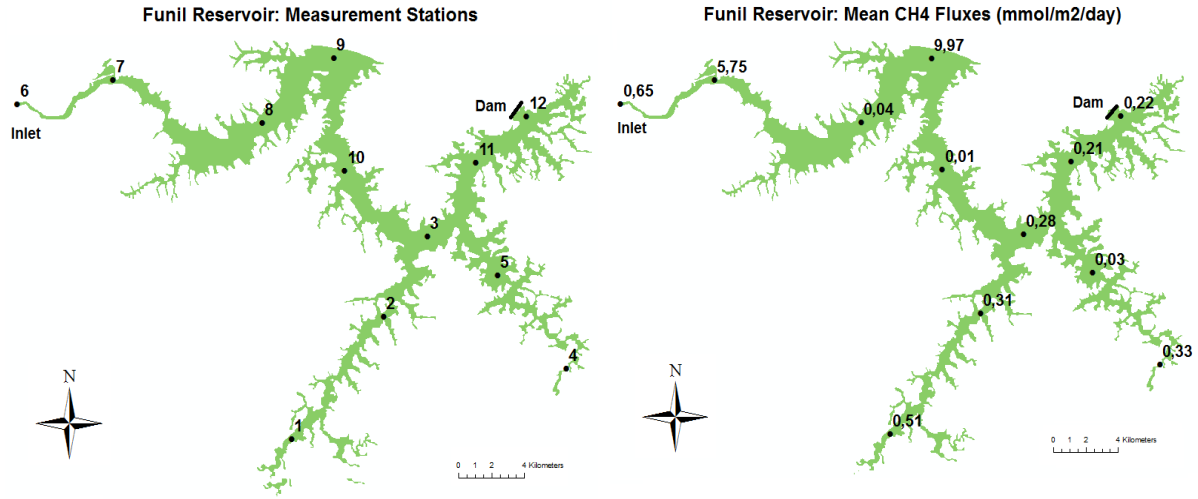

Figure 7 Funil reservoir: measurement stations and their mean CH_4 fluxes after 30 minutes deployment time.

The highest mean CH_4 fluxes in Santo Antônio were found at station 2 (39.6 mmol/m^2/day), 5 (16.13 mmol/m^2/day) and 7 (36.44/7.56 mmol/m^2/day). Station 7 showed higher flux from macrophytes (36.44 mmol/m^2/day) than from the control chamber (7.56 mmol/m^2/day). The remaining mean fluxes were within the range -0.27 mmol/m^2/day – 0.42 mmol/m^2/day.

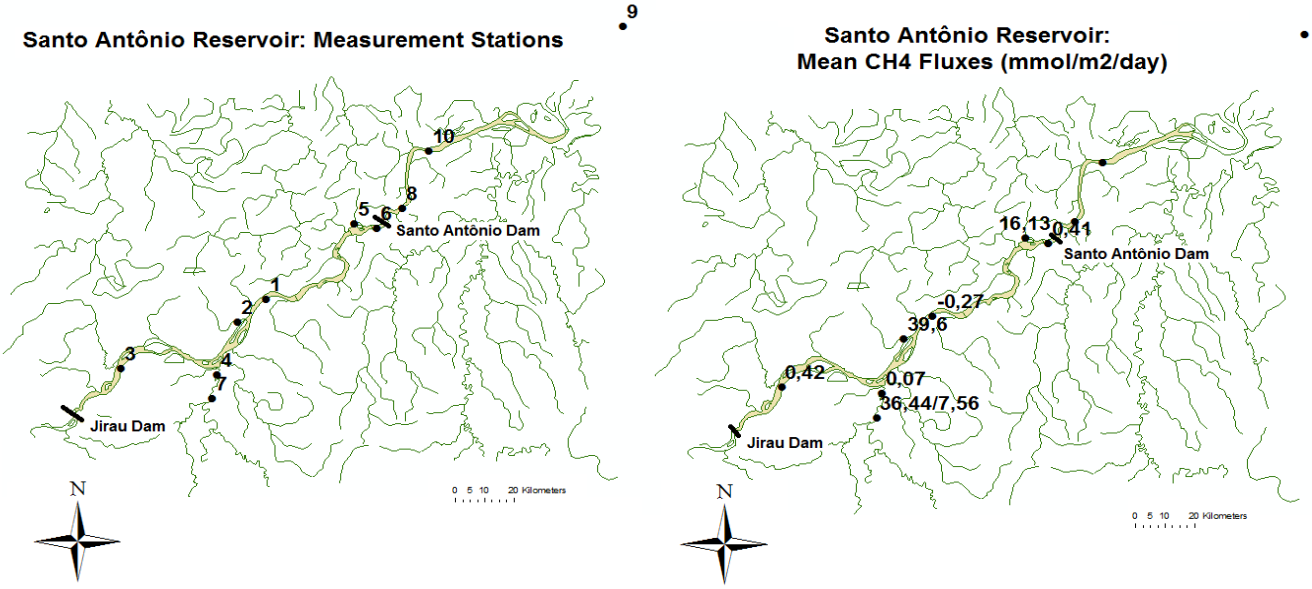

Figure 8 Santo Antônio reservoir: measurement stations and their mean CH_4 fluxes after 30 minutes deployment time.

The results of the mean CH_4 fluxes in Três Marias reservoir were within the range -0.09 – 0.48 mmol/m^2/day.

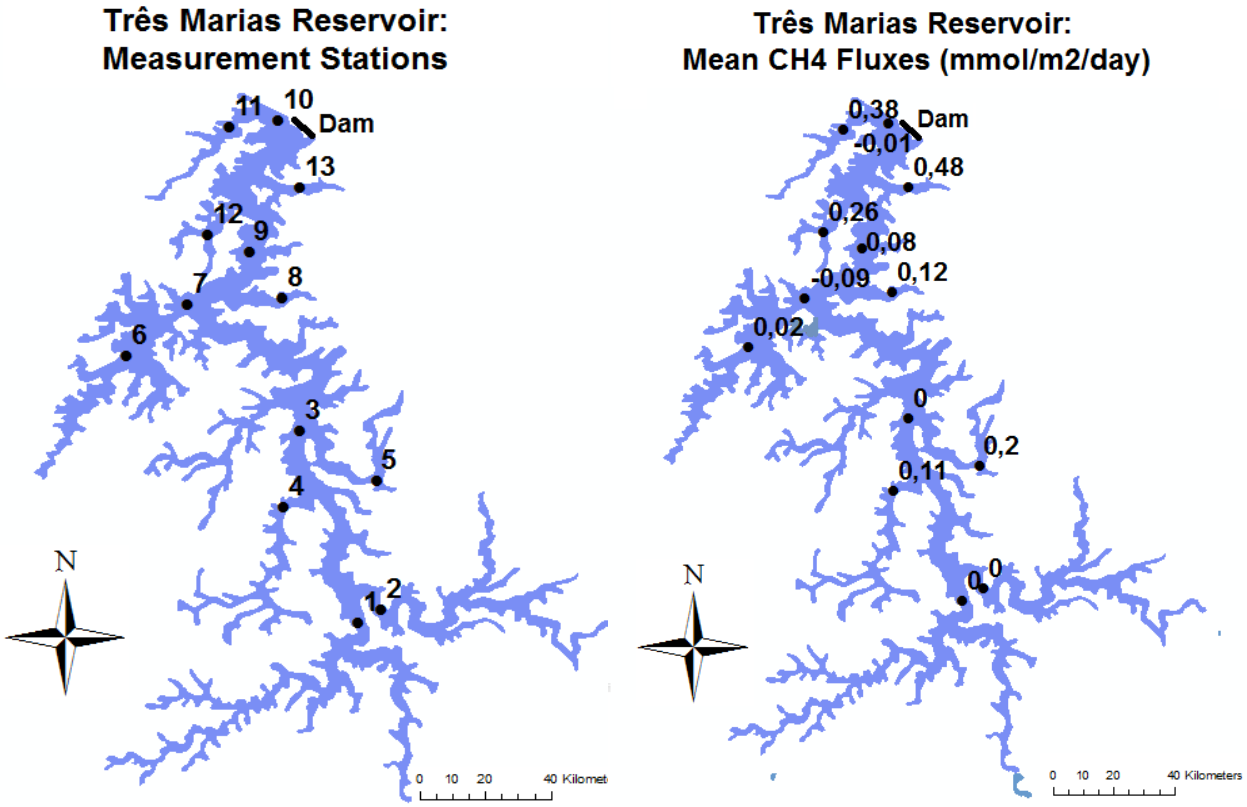

Figure 9 Três Marias reservoir: measurement stations and their mean CH_4 fluxes after 30 minutes deployment time.

Table 2 Summarized data of the mean CH_4 flux after 30 minutes deployment time at all stations in each reservoir

Station	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Flux Funil (mmol/m^2/day)	0.51	0.31	0.28	0.33	0.025	0.65	5.75	0.04	9.97	0.01	0.21	0.22	x
Flux Santo Antônio (mmol/m^2/day)	-0.27	39.6	0.42	0.07	16.13	0.41	36.44/ 7.56	x	x	x	x	x	x
Flux Três Marias (mmol/m^2/day)	0.00	-0.00	0.00	0.11	0.20	0.02	-0.09	0.12	0.08	-0.01	0.38	0.26	0.48

The CH_4 fluxes in Santo Antônio had the highest maximum, median, mean, standard deviation and variance (Table 3). The CH_4 fluxes in Funil had a higher maximum, median, mean, standard deviation and variance than Três Marias. Santo Antônio had a wide range regarding the variability in flux with 25% of the measurements within an approximate range of range 0 – 15 mmol/m^2/day and one major outlier (Figure 10). Funil had a more narrow range of CH_4 fluxes, but three outliers are observed in the boxplot. The fluxes in Três Marias were concentrated in a small range and no outliers were found. These results were based on the CH_4 fluxes obtained at 30 minutes deployment time from *all* chambers at each station in every reservoir (Table 3, Figure 10). This is why the min and max differ from the earlier mentioned results (Figure 7, 8 , 9, Table 2).

Table 3 The CH_4 flux variability within each reservoir. regarding min, max, median, mean, standard deviation, variance and number of samples. Data based on the CH_4 fluxes measured in all chambers at 30 minutes deployment time.

Reservoir	Min	Max	Median	Mean	STD	Var	n
Flux Funil (mmol/m^2/day)	-0.04	13.15	0.27	0.99	2.68	7.20	36
Flux Santo Antônio (mmol/m^2/day)	-0.33	72.21	0.46	9.30	17.68	312.5	19
Flux Três Marias (mmol/m^2/day)	-0.31	0.56	0.08	0.12	0.20	0.04	36
Flux All (mmol/m^2/day)	-0.33	72.21	0.21	2.31	8.71	75.88	91

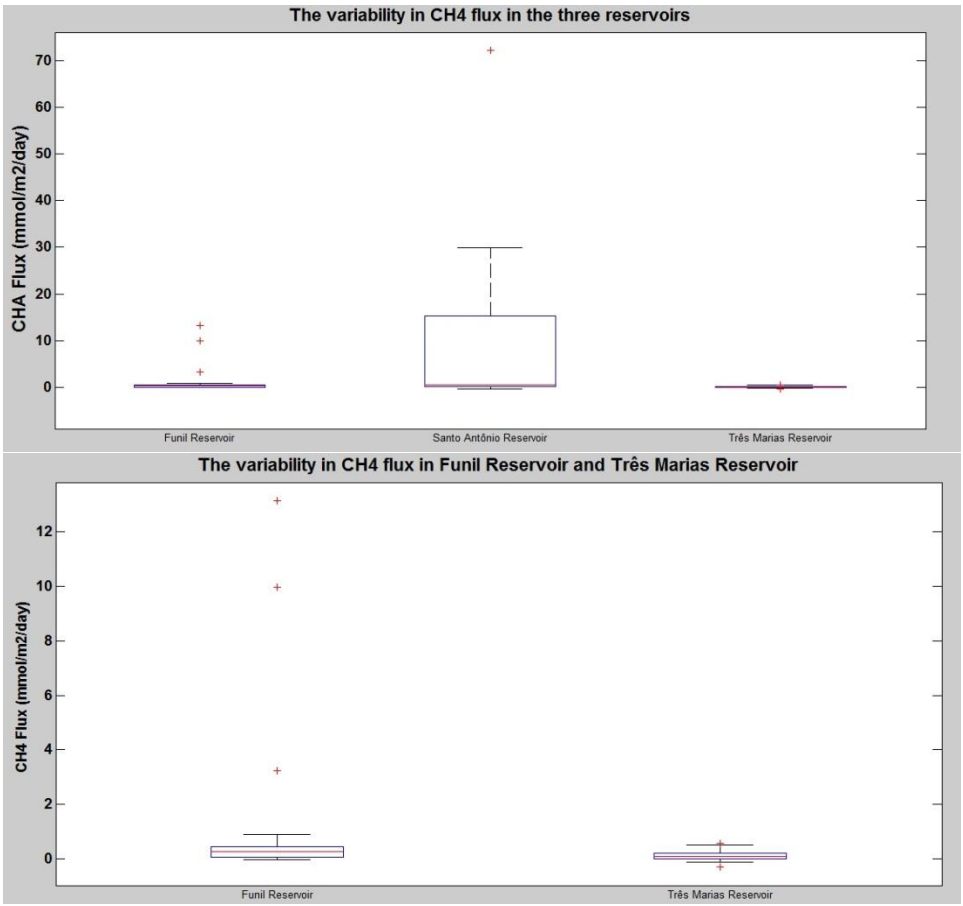

Figure 10 The boxplots display the variability in CH_4 flux within the reservoirs with all chamber measurements obtained at 30 minutes deployment time.

4.1.1 Wilcoxon Rank Sum test – Between and within the reservoirs

Três Marias reservoir and Funil reservoir had significantly different CH_4 fluxes ($P < 0.05$) (Table 4). There was also a significant difference between Santo Antônio and Três Marias ($P < 0.05$). Funil and Santo Antônio had the most similar distributions of CH_4 fluxes according to the Wilcoxon Rank Sum test ($P > 0.05$). The dataset from Funil and Três Marias had comparable median values which further explain the relationship (Figure 10, Table 3). The CH_4 fluxes were significantly different within Funil and within Três Marias, while the CH_4 fluxes in Santo Antônio not were significantly different according to the Wilcoxon Rank Sum Test (Table 4).

Table 4 Wicoxon Rank Sum Test of the CH_4 fluxes between and within the reservoirs, all chamber measurements after 30 minutes deployment time. FU–Funil, SA–Santo Antônio, TM–Três Marias.

Wilcoxon Rank Sum Test **between** the reservoirs (significance level 0.05)			Wilcoxon Rank Sum Test **within** the reservoirs (significance level 0.05)		
Reservoirs	P	H	Reservoir	P	H
TM–FU	$4.9461 \cdot 10^{-4}$	1	FU	$8.9352 \cdot 10^{-11}$	1
FU–SA	0.1701	0	SA	0.1695	0
SA–TM	0.0066	1	TM	$3.0198 \cdot 10^{-14}$	1

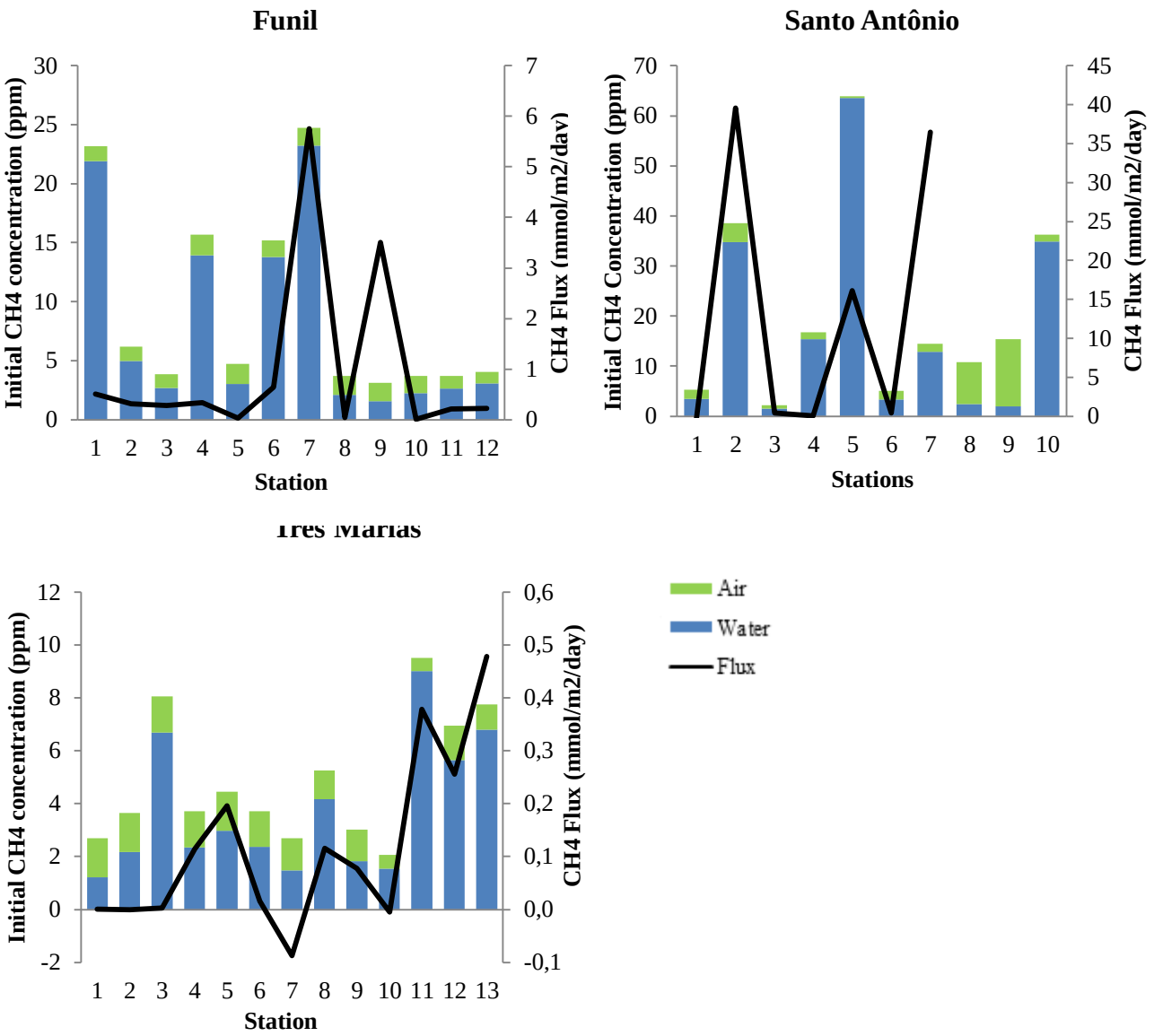

Figure 11 The concentration of CH_4 in initial water and air samples in Funil, Santo Antônio and Três Marias.

There was a much greater concentration of CH_4 in the initial water sample (blue), than in the initial air sample (green) at most stations (Figure 11). Two exceptions where the initial air sample had a higher concentration were station 8 and 9 in Santo Antônio. These stations were situated downstream the reservoir. The mean CH_4 flux (black line) was generally high at stations where the concentration of CH_4 in the water was high. The greatest exception was station 9 in Funil. The flux at this station was very high even though there was a low concentration of CH_4 in the water. The graph of Santo Antônio shows no flux at station 8, 9 and 10. The water at these stations was very turbulent and chamber measurements could not be done due to this and thereby no fluxes were obtained.

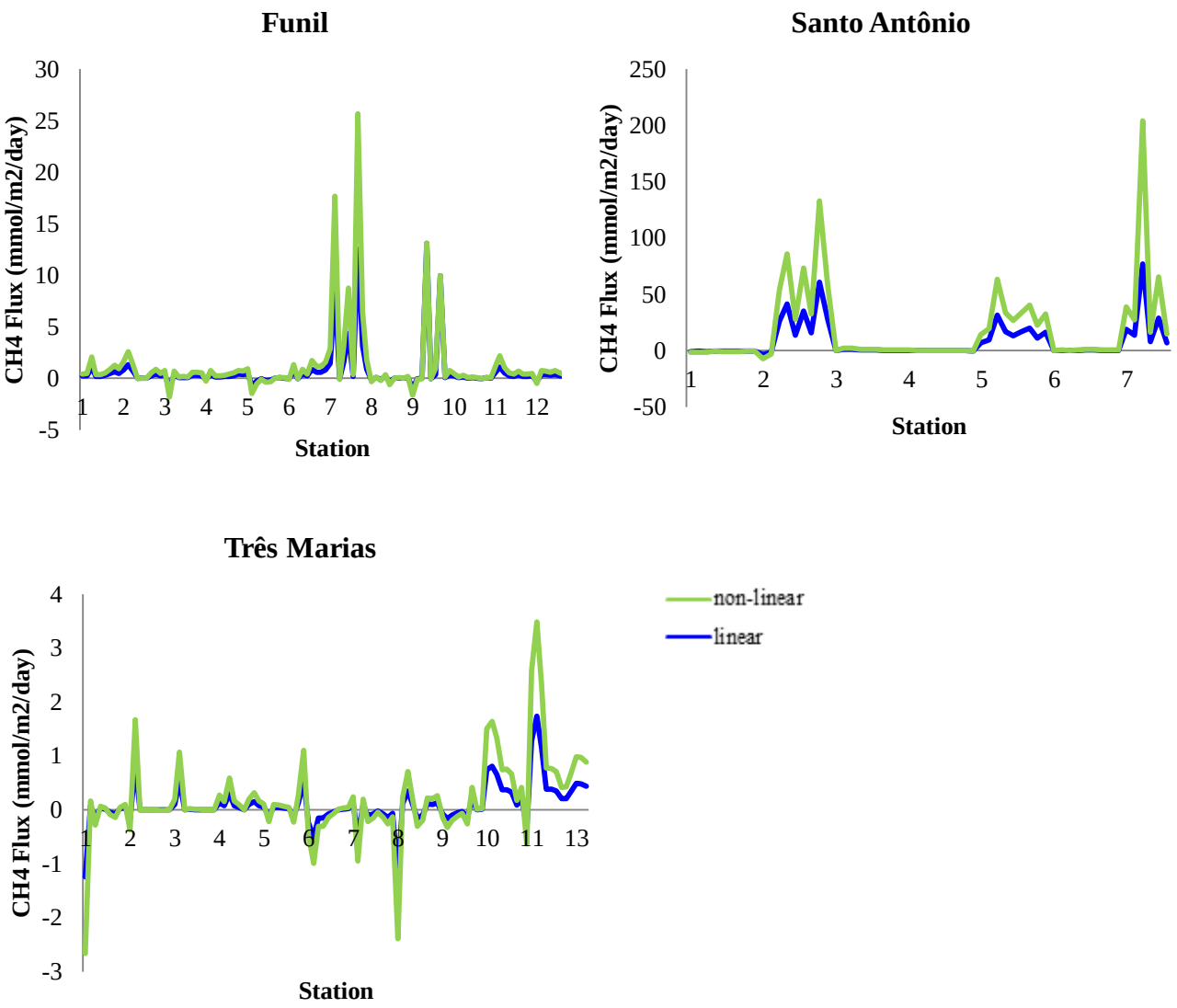

Figure 12 Linear and non-linear calculations of the CH_4 flux in Funil, Santo Antônio and Três Marias.

The CH_4 mean fluxes after 30 minutes deployment time calculated by the linear approximation (blue) and by the diffusive non–linear calculations (green) gave slightly different results (Figure 12). The results showed that the linear and non–linear flux curves most often fit very well with each other, especially where the fluxes were close to zero. The curves differed more at stations with higher flux, where the non–linear equations generally gave a higher flux. The fluxes displayed in the results were without exceptions based on the non–linear calculations which better describe the CH_4 emissions in a chamber.

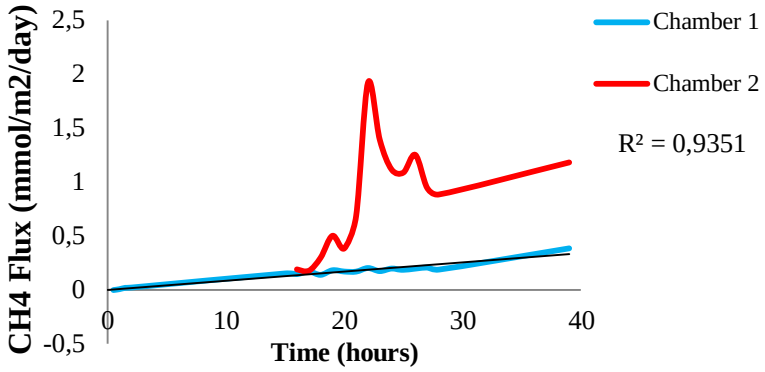

Figure 13 Temporal measurements of CH_4 flux in Três Marias during 36 hours deployment time from two chambers next to each other.

The fluxes from the temporal measurements in Três Marias showed a linear regression (R^2=0.94) regarding the CH_4 flux in chamber 1 (Figure 13). Chamber 2 had an increase in CH_4 flux during the first 7 hours deployment time, followed by a decrease and a small increase. There was a big difference regarding the change in flux in chamber 1 and 2. Chamber 1 was deployed in the water at 4 pm, and chamber 2 at 7 am the next morning, 15 hours later.

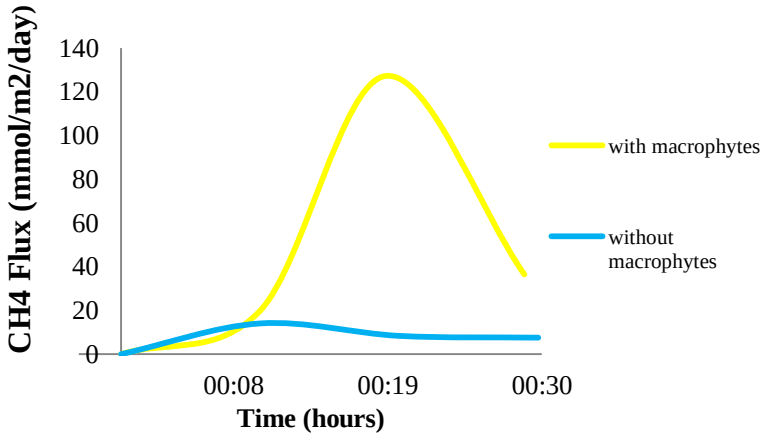

Figure 14 The CH_4 flux obtained from macrophytes and a control chamber in Santo Antônio at station 7.

The fluxes from the macrophyte– measurements at station 7 in Santo Antônio showed a higher CH_4 flux in the chamber placed on top of the macrophytes (yellow) compared to the control chamber (blue, Figure 14).

4.2 VARIABLES

Table 5a and b CH_4 flux after 30 minutes deployment time and measured variables at each station and reservoir. The displayed concentrations show the concentrations in the water at each station.

Station	CH_4 flux (mol/m2/day)	Depth (m)	CO_2 (ppm)	Dissolved O_2(mg/L)	Wind speed (m/s):	Air temp (^oC)
Funil						
1	0.51	8.7	1005	5.59	2.2	24.45
2	0.31	26	271	6.5	1.5	24.45
3	0.28	31	515	7.56	4.6	24.00
4	0.33	3.9	1433	6.53	0.5	23.00
5	0.03	36	1433	7.12	1	23.37
6	0.65	7.9	366	6.31	2.5	22.26
7	5.75	11	348	6.08	3.1	21.86
8	0.04	11	330	4.63	1.2	22.02
9	9.97	34	544	5.25	3.2	21.49
10	0.01	39	758	7.36	1.5	24.91
11	0.21	42	553	5.8	2.1	24.90
12	0.22	56	591	4.86	2.1	27.15
Mean	1.53	26	679	6.13	2.13	23.66
Santo Antônio						
1	-0.27	29	1239	6.28	0.5	27.9
2	39.60	5.32	2098	3.69	0.5	28.5
3	0.42	29	1287	6.6	0.7	31.3
4	0.07	9	2520	3.69	0	41.8
5	16.13	7	3640	1.57	0.6	30.7
6	0.41	28	1678	6.06	1.3	35.8
7	36.44/ 7.56	10	2423	6.58	0.25	34.8
Mean	13.26	16.8	2127	4.92	0.55	32.97
Três Marias						
1	0.00	23.4	316	7.5	0.4	25.6
2	0.00	14.9	316	7.09	0	26.8
3	0.00	29.1	434	7.01	0	26.3
4	0.11	25.4	434	7.28	1.5	27.4
5	0.20	16.7	391	7.29	1.3	27.3
6	0.02	28.9	357	7.4	0.4	30
7	-0.09	39	342	7.37	0.2	30.1
8	0.12	6.3	324	7.48	X	30.5
9	0.08	49.3	365	7.49	X	29.1
10	-0.01	49.3	287	7.96	1.5	26.7
11	0.38	41	300	7.68	4.5	25
12	0.26	10	401	7.47	2.9	27.1
13	0.48	40	388	7.99	2.1	30
Mean	0.12	28.7	358	7.46	1.35	27.84

Station	Watertemp (°C)	pH	Chl– A (µg/L)	Tot N (µg/L)	Tot P (µg/L)	Turbidity (NTU)	DOC (mg C/L)
Funil							
1	27.64	7.61	3.40	1301	26	4.68	4.96
2	27.20	8.75	1.25	1767	24	8.22	3.88
3	26.71	9.36	4.3	1988	117	17.8	4.61
4	27.32	8.12	2.9	1759	45	6.46	4.18
5	26.85	9.3	1.2	1465	23	9.01	4.07
6	22.39	7.49	1.15	1973	88	56	6.36
7	22.29	7.33	X	X	X	X	X
8	26.44	7.31	X	X	248	36.2	5.31
9	26.66	7.29	28.6	4033	170	34	5.57
10	27.42	9.23	2.8	1745	26	26.9	5.09
11	26.00	8.33	1.9	1474	35	11.3	4.41
12	22.18	7.68	0.9	1514	35	0	4.36
Mean	25.76	8.15	4.84	1902	76	19	4.80
Santo Antônio							
1	27.63	6.47	1.28	1014	670	567	5.66
2	28.8	5.9	2.52	1167	34	5	10.99
3	27.73	5.92	1.48	1253	463	596	7.80
4	28.42	5.68	2.57	817	37	18.9	6.14
5	29.37	5.92	0.54	1133	28	8.1	8.11
6	27.6	6.83	2.64	1122	528	583	6.68
7	26.47	5.3	1.58	1037	46	20.4	6.07
Mean	28.00	6.00	1.80	1078	258	257	7.35
Três Marias							
1	28.25	7.6	4	536	26	8	3.78
2	28.54	7.34	2.85	1048	27	24.6	3.79
3	27.41	7.26	3.85	490	22	6.9	3.52
4	28.43	7.25	2.3	541	26	6.6	3.56
5	28.31	7.51	2.35	650	35	2.5	3.61
6	29.8	7.63	0.55	771	23	1.7	3.66
7	30.4	7.94	2.85	772	20	2.4	4.54
8	29.5	7.76	1.8	732	19	12.4	4.13
9	29.33	7.86	3.7	749	20	2.2	3.75
10	28.07	7.85	2.4	399	17	2.3	11.69
11	28.02	8.07	0.8	361	40	5.5	3.55
12	28.07	7.57	0.65	435	12	1.1	3.77
13	28.5	8.22	3.8	698	20	2.6	3.50
Mean	28.66	7.68	2.45	629	24	6	4.37

4.2.1 Principial component analysis

A principial component analysis (PCA) was constructed where the following variables were used as input variables:

CH_4 concentration (ppm)	Wind speed (m/s)	Tot N (µg/L)
CH_4 flux (mmol/m^2/day)	Water temperature (^{0}C)	Turbidity (NTU)
Dissolved O_2 (mg/L)	Air temperature (^{0}C)	DOC (µg/L)
O_2 saturation (%)	pH	Chlorophyll–a (µg/L)
Depth (m)	Tot P (µg/L)	CO_2 (ppm)

The CH_4 concentration is the concentration in each sample from the chambers. The dissolved O_2, CO_2 and DOC are the concentrations in the water.

The variables CH_4 flux, CH_4 concentration, CO_2 and DOC were related in the PCA of the whole dataset. A relationship was also visible between dissolved O_2, O_2 saturation, pH and depth. CH_4, DOC and CO_2 were located far away from O_2, pH and depth. 50 % of the variation in the dataset was explained in the PCA by component 1 and 2.

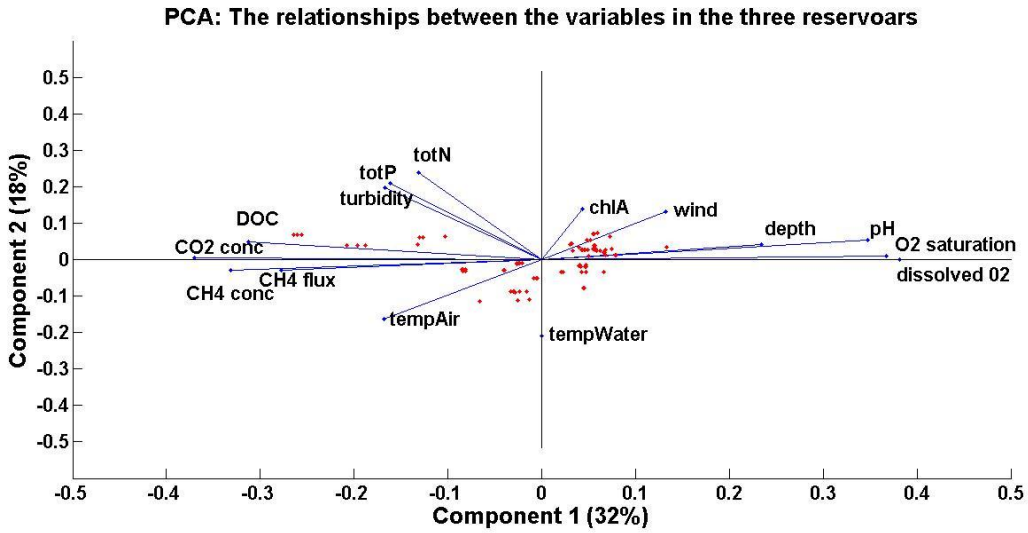

Figure 15 PCA of the whole data set with 15 variables.

The CH_4 flux in Funil was related to the wind speed. A relationship was also visible between dissolved O_2, O_2 saturation, pH, CO_2 concentration and water temperature. This cluster and the CH_4 flux and wind speed were located in opposite quadrants which indicate a negative relationship between them. 56 % of the variation in the dataset was explained in the PCA by component 1 and 2.

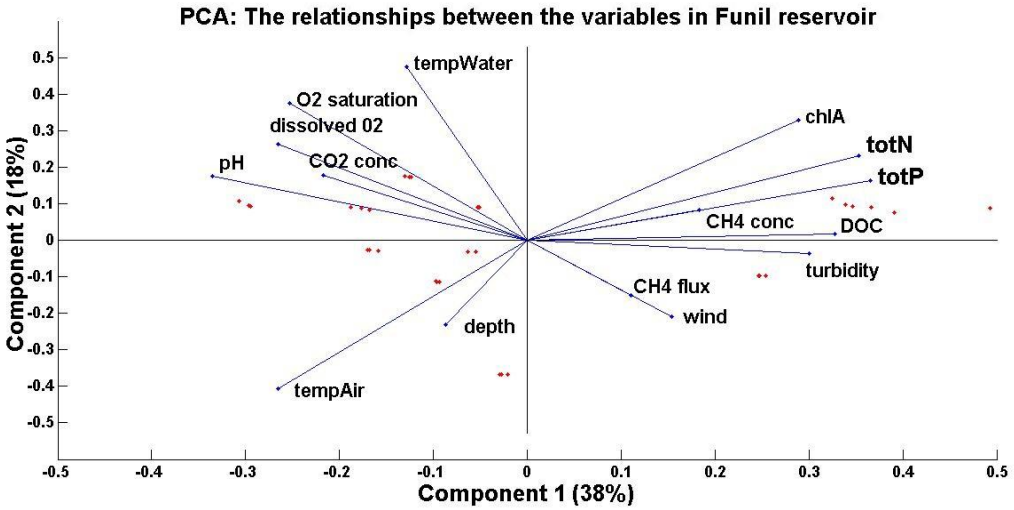

Figure 16 PCA of Funil with 15 variables.

A relationship between CH_4 flux, CH_4 concentration and DOC was visible in Santo Antônio. The dissolved O_2, O_2 saturation, depth, pH, total P and turbidity were also related. These two clusters were located far away from each other. 72 % of the variation in the dataset was explained in the PCA by component 1 and 2.

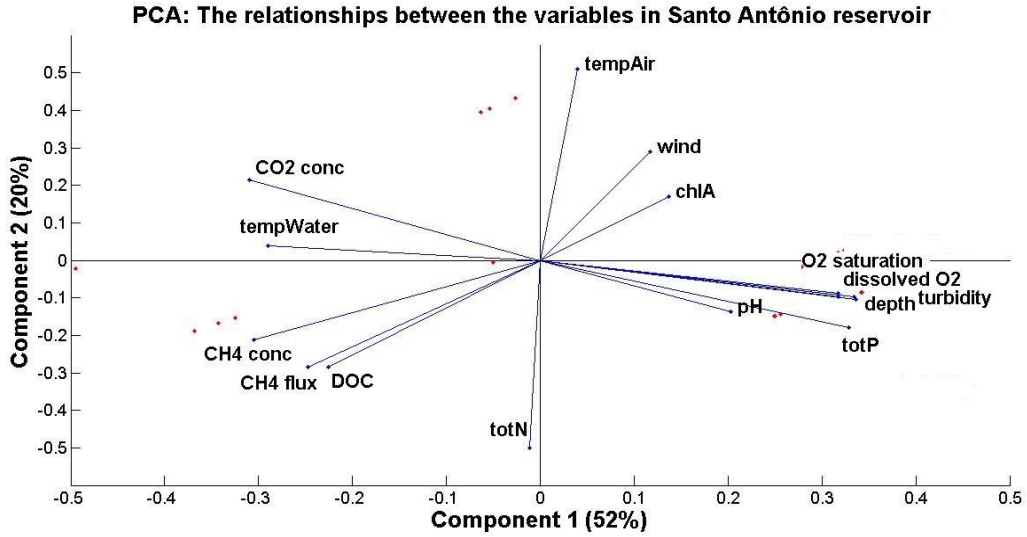

Figure 17 PCA of Santo Antônio with 15 variables.

In Três Marias the CH_4 flux is related to the dissolved O_2 saturation. A relationship was seen between water and air temperature. 54 % of the variation in the dataset was explained in the PCA by component 1 and 2.

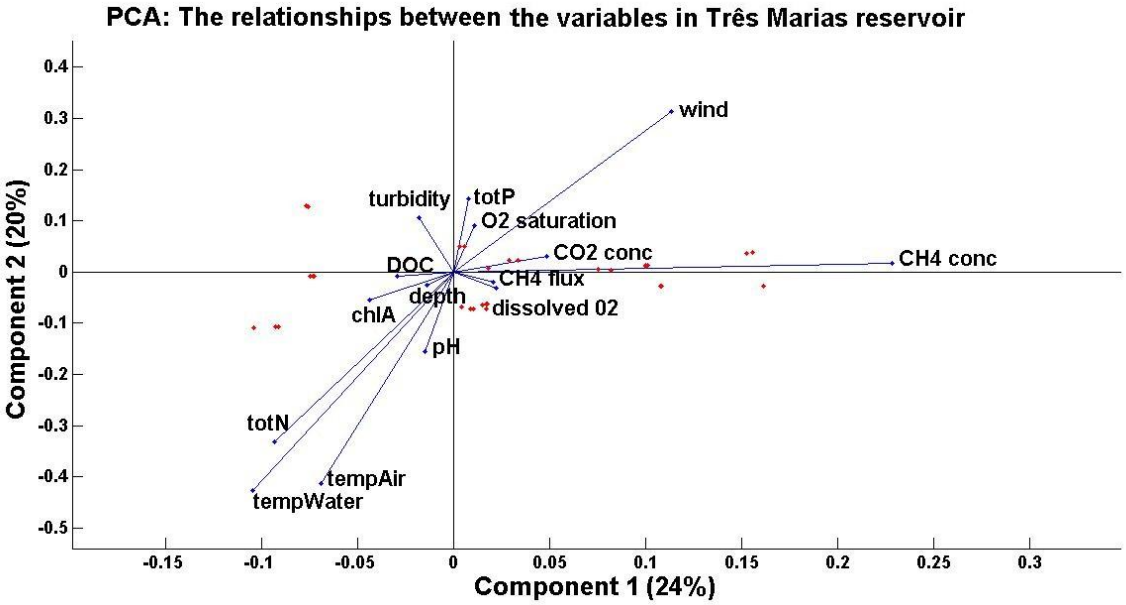

Figure 18 PCA of Três Marias with 15 variables.

4.2.2 Correlation analysis

Four variables (DOC,O_2, CO_2 and depth) commonly related to CH_4 flux in the PCA analyses were further analyzed regarding their impact on CH_4 fluxes. In the Funil reservoir none of the four variables showed a significant correlation to the CH_4 flux. In Santo Antônio a positive correlation existed between CH_4 flux – DOC and CH_4 flux – CO, and a negative correlation between CH_4– O_2 and CH_4–depth. The same correlations were evident for the whole data set. In Três Marias a positive correlation was found between CH_4 – O_2.

Table 6 Correlations between CH_4 and DOC, O_2, CO_2 and depth at each site within the reservoirs. P is the significance level and R is the correlation coefficient.

Reservoir	DOC (µg/L)		O_2 (mg/L)		CO_2 (ppm)		Depth(m)	
	P	R	P	R	P	R	P	R
Flux Funil	0.37	0.16	0.64	-0.08	0.43	-0.14	0.24	-0.21
Flux Santo Antônio	**0.00**	**0.79**	**0.01**	**-0.56**	**0.03**	**0.51**	**0.00**	**-0.68**
Flux Três Marias	0.30	0.17	**0.00**	**0.70**	0.72	-0.06	0.73	0.06
Flux All reservoirs	**0.00**	**0.55**	**0.00**	**-0.51**	**0.00**	**0.49**	**0.00**	**-0.33**

5 DISCUSSION

5.1 FUNIL RESERVOIR.

The 12 stations in Funil reservoir showed CH_4 fluxes within the range of -0.04 and 13.15 mmol/m^2/day. The mean flux was 0.99 mmol/m^2/day (Table 3). Most of the fluxes were within a range of 0–1 mmol/m^2/day and three fluxes were above this range, located at station 7 and 9 (Table 5a, appendix C).

By considering the water color, together with previous knowledge about the water quality in Funil, it can be assumed that a great load of nutrients is transported into this reservoir. Funil had the highest mean concentrations regarding chlorophyll−a and total N, and the second highest mean regarding the concentration of total P and DOC (Table 5b). The primary production increases when nutrients like dissolved organic carbon, phosphorus and nitrogen are available, which brings more organic material to the reservoir and the sediment. When nutrients are available, a large CH_4 production in the sediment could be assumed. The range of CH_4 fluxes in Funil is slightly higher than the range in Três Marias, but lower than earlier results (Hamilton *et al*. 1995; Batlett *et al*. 1993; Galy–Lacaux *et al*. 1997) . The oxygen level in Funil enables methanotroph bacteria to perform oxidation which is the process that probably keeps down the CH_4 emission level in Funil.

The initial water samples at all stations showed a higher concentration of CH_4 compared to the initial air sample. This is an expected result due to the oversaturation of CH_4 in the water that normally occurs in freshwater lakes (Jones & Mulholland 1998). At station 1, 4, 6 and 7 the concentration of CH_4 in the initial water sample was the highest. At these stations a slightly higher flux of CH_4 was present compared to the other stations (Figure 11).

Station 7 and 9 had higher fluxes than the rest of the stations in Funil. Station 7 was located in the riverine zone of the reservoir, where a higher water flux was present. To avoid drifting too much, the boat used for the measurement were tied to a concrete block while the measurements were performed. Earlier studies have shown a higher diffusive flux rate when the chamber does not drift along with the water (UNESCO/IHA 2009). This could be a reason for the high flux at this station. Because of the attachment, artificial turbulence might have been created, leading to an increased CH_4 emission rate. The high flux of CH_4 in all three chambers strengthens this theory and discourages an ebullition bubble to have caused the high flux. Thus, the results from this station cannot be considered to reflect a natural flux. The initial water sample at station 7 had a high concentration of CH_4. This shows that great amounts of CH_4 are available which makes the high flux at this station reliable, and also dismiss the theory of an ebullition bubble.

Station 9 had a very high flux of CH_4 in one of the chambers. This might be a result of an ebullition bubble. This station had the highest levels of phosphorus, chlorophyll−a and total N

within the reservoir, which probates the creation of CH_4 (Table 5b). The oxygen level in the water does not affect ebullition bubbles, since they ascend fast and thereby avoid oxidation. Another evidence that reinforce the high flux to be an ebullition bubble is the low flux of CH_4 in the other two chambers and low concentration of CH_4 in the water (Figure 11). Earlier results from 13 Swedish lakes, 11 North American lakes and literature values from 49 lakes have shown that less than 10% of chamber measurements generally consist of ebullition bubbles (Bastviken *et al.* 2004). In Funil one chamber at station 9 contains a probable ebullition bubble. The rate in Funil was thereby 3%. One reason for the low level of ebullition bubbles could be the limited number of measurements.

5.2 SANTO ANTÔNIO RESERVOIR

The CH_4 fluxes in Santo Antônio ranged between -0.33 mmol/m^2/day and 72.21 mmol/m^2/day and the mean CH_4 flux was 9.30 mmol/m^2/day. The variance was 312,5 mmol/m^2/day which indicates that there is a great variability in the data within the reservoir (Table 3, appendix C). Very high fluxes of CH_4 were observed at station 2, 5 and 7 and lower fluxes at the other four stations (Table 2). These three stations are situated in the flooded tributaries Jatuarana (station 5) and Jaci–Paraná (station 7) and the smaller Ceará Creek (station 2). Both Ceará and Jatuarana have black water, caused by the high amount of organic material that is transported into the tributary both from the catchment area and the flooded surrounding vegetation (Castillo *et al*. 2004). Station 2 and 5 were located in the middle of the flooded tributaries where trees and other vegetation overtopped the water surface since no deforestation had occurred before the flooding. This vegetation could especially be seen at station 5, where the measurement station was surrounded by flooded palm trees. Flooded trees and other vegetation were not visible to the same extent at station 2, but at this station gas bubble were observed at the water surface. These bubbles were probably a result of ebullition. This station was chosen by recommendations from people working with the environmental monitoring in the area because of the high amount of bubbles and the black water characteristics. Before the flooding this area was a Vareza but since the construction of the reservoir it has turned into a bay. The chambers were placed straight above the bubbles when the measurements were made. The depths at these two stations were shallow (5 and 7 meters) and the amount of oxygen was the lowest within the reservoir (3.69 mg/l and 1.57 mg/l). These features, together with the concentration of dissolved organic carbon (DOC 10.99 mg C/L and 8.11 mg C/L) were factors that contributed to the high level of CH_4 emissions at these two stations (Table 5a and 5b). Station 7 was located in the tributary Jaci–Paraná next to– and above macrophytes. The water color in Jaci–Paraná is somewhere between black and beige which indicates a lower organic carbon content than in the earlier mentioned tributaries (Castillo *et al.* 2004). At this location one chamber was placed above macrophytes and one control chamber was placed in the water next to the macrophytes. The chamber placed on top of the macrophytes showed a much higher flux of CH_4 compared to the control chamber in the water (Figure 14, Table 2). The control chamber had high CH_4 flux, but not as high as at station 2

and 5. The depth (10 m) and the oxygen level (6.58 mg/l) at this station was greater than at station 2 and 5 and the DOC (6.07 mg C/L) was lower. This contributes to the explanation why the control chamber had lower fluxes than these stations (Table 5a, 5b and 6). The reason why the chamber on top of the macrophytes had a higher flux is because CH_4 is transported from the sediments straight to the atmosphere through the stems of the plants. If the transportation would have occurred in the water column instead, the CH_4 would partly have been oxidized into CO_2 due to the oxygen in the water. The control chamber had a lower CH_4 flux due to this oxidation process. In total, four stations were located in the tributaries, but the fourth station showed lower CH_4 concentrations than the other three (station 4). This station was also situated in a flooded part of the tributary Jaci–Paraná, but in this area deforestation had occurred before the flooding. Because of the deforestation, less organic material was available for decomposition. This could be the reason why less CH_4 were produced, even though the depth (9 m) and oxygen level (3.69 mg/l) was low. The DOC concentration in the water was 6.14 mg C/l which is lower than at station 2 and 5 with further strengthens the reasoning.

In addition from the four stations located in the tributaries, three stations in the riverine zone of the reservoir were used for measurements. None of these stations showed a flux of CH_4 comparable to the fluxes in the tributaries, which probably is a consequence of the high speed of the water, high oxygen level and great depth in this part of the reservoir (Table 5a). The riverine zone has white water which carries large amounts of nutrients, like phosphorus. The white water has a low Secchi depth which, together with the water speed, limits the primary production. Thereby small amounts of organic material reach the sediment resulting in a restricted methanogenesis activity. The high level of phosphorus and the low level of chlorophyll–a at the riverine stations (station 1, station 3 and station 6) in Santo Antônio further support the explanation of the low CH_4 flux (Table 5b). Station 6 was located close to the dam and the boat was anchored to avoid drifting at this location. The CH_4 flux at this station was slightly higher than the flux at the other stations in the river (Table 5a). The initial samples showed a generally higher concentration of CH_4 in the water at the station with a high flux rate. Station 4 had a comparably high concentration of CH_4 in the water, but a low flux (Figure 11).

Initial measurements taken from the air and the water downstream the reservoir at station 8 and 9 showed a much higher concentration of CH_4 in the air samples compared to the water samples. This might be a result of the degassing that occurs in the outlet of the dam, when CH_4 is released to the atmosphere due to the turbulence in the turbines and the outlet. This cause a higher concentration of CH_4 in the air downstream the reservoir, compared to the air upstream. The influence of degassing can occur 10 m to 50 km downstream the dam (UNESCO/IHA 2009). Station 9 was located furthest away from the dam at a distance of 40 km. Station 10 downstream showed a different result in the initial samples of air and water.

The location of this station was a small flooded bay which was not influenced by the dam and the river to the same extent as station 8 and 9.

5.3 TRÊS MARIAS RESERVOIR

The results obtained in Três Marias showed a CH_4 flux within the range of -0.31 mmol/m^2/day and 0.56 mmol/m^2/day The mean CH_4 flux was 0.12 mmol/m^2/day and the variation is 0.04 mmol/m^2/day (Table 3). The fluxes in Três Marias were significantly lower than the fluxes in Funil and Santo Antônio (Table 4) and the variance within the reservoir was very low. The concentration of CH_4 in the initial water samples was lower at all stations compared to Funil and Santo Antônio and this indicates that a small amount of CH_4 is available to generate diffusive emissions to the atmosphere. None of the chambers in Três Marias showed an extraordinary result pointing at any occurrence of ebullition bubbles. Even though the fluxes were within a narrow range, a relation could be seen between the initial concentration of CH_4 in the water and the CH_4 fluxes. Station 5, 8, 11, 12 and 13 had the highest CH_4 fluxes and these stations also had the highest concentrations of CH_4 in the water compared to the other stations. The chambers at station 5 were surrounded by macrophytes, which might explain the relatively higher flux. The measurements at station 1 and 2 were done after a long heavy rain. Normally these kind of weather conditions increase the amount of CH_4 that is emitted (Guerin *et al.* 2007), but the result did not show the highest flux of CH_4 at these stations. The CH_4 fluxes at all stations were very low, compared to Funil, Santo Antônio and earlier studies (Hamilton *et al.* 1995; Batlett *et al.* 1993; Galy–Lacaux *et al.* 1997), even though some of the stations emitted more CH_4 than the others. This low flux is probably a result of a low organic carbon inflow in combination with a water body with a high level of oxygen.

Temporal measurements were made in Três Marias during a 36 hours deployment time where two chambers were placed next to the shore. These measurements where done in order to investigate whether the increasing flux in the chambers followed a linear or exponential pattern. The first chamber was placed in the water in the evening and the second chamber was placed next to the first chamber in the morning, 15 hours later. The results from these measurements (Figure 13) did not show any clear pattern, except from an increase in flux of CH_4 through time. The first chamber showed a linear increase (R^2=0.94) in the flux during the deployment time. Samples were taken every 30 minutes in the beginning of the deployment time of the first chamber, but after 2 hours a heavy rain disturbed the measuring process. The sampling stopped and continued when the deployment time had reached 15 hours. Thereby no samples were made between the 2nd and 15th hour of deployment time in the first chamber. The second chamber showed more of an exponential curve in the beginning of the deployment time, followed by a decrease in flux with a small peak after about 26 hours. The structure of the flux curve from the second chamber was more uneven than the curve from the first chamber. These results indicate that equilibrium had not been established inside any of

the two chambers, which probably is a result of a too short deployment time and also because of external disturbance. It is also difficult to conclude whether an increased flux in general follows a linear or exponential pattern from these results, since the flux from each chamber differed a lot. To be able to make better conclusions further temporal measurements need to be done over a longer time period with more than one chamber at each measuring event. A control chamber that was measure and repositioned every hour would be a good complement to the other chambers.

5.4 COMPARISION OF CH_4 EMISSIONS

The Wilcoxon Rank Sum Test (significance level 0.05) showed a significant difference in CH_4 flux between Funil and Três Marias ($p < 0.05$) and also between Três Marias and Santo Antonio ($p < 0.05$). The fluxes in Santo Antônio and Funil were not significantly different ($p > 0.05$) (Table 4). Both Funil and Três Marias had mean fluxes close to each other which also were lower than the fluxes in Santo Antônio. This indicates that there is a similarity between Funil and Três Marias. But the Wilcoxon Rank Sum test compares the variation between data sets rather than similarities. Both Santo Antônio and Funil had outliers that cause a variation in the flux. Funil had one station (station 9) and Santo Antônio 3 stations (2,5 and 7) with probable ebullition bubbles, while Três Marias had no chamber with an outlying flux. The cause of this might be that ebullition bubbles are produced in the sediment in Funil and Santo Antônio, but not in Três Marias because a higher amount of organic material are available in Funil and Santo Antônio.

The CH_4 fluxes within the reservoirs were significantly different in Três Marias ($p < 0.05$) and Funil ($p < 0.05$). The CH_4 fluxes within Santo Antônio ($p < 0.05$) were not significantly different, according to the same test (Table 4). Wilcoxon test evaluates if the variation among the fluxes are similar and the overall variation does not say anything about that. This is why the fluxes in Santo Antônio were not significantly different, even though the variation among the data was the highest.

5.5 PRINCIPAL COMPONENT ANALYSIS (PCA)

Four Principal component analyzes were done; one for the whole dataset from all three reservoirs and one for each reservoir.

In the PCA analysis for the whole dataset (Figure 15), the variables CH_4 flux, CH_4 concentration, DOC and CO_2 were related. This relationship is probably based on the methanogenesis and the respiration processes, where organic material is consumed and CH_4 and CO_2 are produced. Thus, a high concentration of DOC gives a high concentration of CH_4 and CO_2. The concentration of dissolved O_2, O_2 saturation, pH and depth were also related. The CH_4, DOC and CO_2 are located in opposite direction from O_2, pH and depth which means

that these clusters of variables affect the ecosystem in the reservoirs in different directions. This indicates that a high emission rate of CH_4 occurs when the oxygen level is low and when there is a shallow depth.

The PCA of Funil (Figure 16) showed a positive relationship between CH_4 flux and wind speed. A relationship was also visible between the dissolved O_2, O_2 saturation, pH and CO_2 concentration. The relationship between CH_4 and wind speed was probably caused by an increase in exposure area of the water towards the atmosphere due to the wind generated waves, leading to an increased flux. The placement of CH_4 in the opposite quadrant to the cluster indicates that they affect the system in different directions. Since CO_2 is related to O_2 it can be assumed that this relationship is caused by the oxidation process. The concentration of CO_2 in the water is high when there is a high oxidation rate, since CO_2 is produced in this process. A high oxidation rate occurs when the O_2 level is high.

The PCA of Santo Antônio (Figure 17) showed a very different result compared to Funil. There was a relation between the CH_4 flux, CH_4 concentration and DOC. The production of CH_4 relies on organic carbon, and the DOC is related to the available concentration of organic carbon in the sediment, which explains this relationship. CH_4 and DOC were located far away from a cluster with the variables dissolved O_2, O_2 saturation, depth, total P and turbidity. Low O_2 concentrations, low depth and low turbidity are evident at the stations in the tributaries where the CH_4 fluxes are high, while the fluxes in the riverine zone are low together with a high O_2 concentration, depth and turbidity. The reason why total P is a part of this cluster is that a lot of phosphorus is transported in the riverine zone. The explanation degree in component 1 and 2 was 72 % and this degree of explanation was the highest among the PCA plots.

The PCA performed in Três Marias (Figure 19) showed a relationship between CH_4 flux and dissolved O_2. This relationship implies that a high O_2 concentration gives a high CH_4 flux, but this is not how the reality works, since a high level of O_2 benefit CH_4 oxidation. This relationship is probably a consequence of the low range in flux within the reservoir, caused by chance. No other relationships were visible.

When comparing the four PCA:s, it can be seen that the results differed regarding the related variables. The great variation is a result of three ecosystems with similar attributes, but also different variables that affect the CH_4 emissions to different extents. Another reason could be the small amount of available data from each reservoir in combination with the high variability among the data. Measurements were done during a limited time resulting in a low amount of data with a high variability. If measurements were done during a longer period of time with a wider spatial distribution, a more representative picture about the variables would be obtained. Since the first PCA contains the whole dataset and thereby the highest amount of data this PCA should be the most representative one regarding the connections between the variable.

5.6 EXPLAINING VARIABLES

According to the PCA:s, Table 5a, 5b and 6, the variables CO_2, DOC, depth and O_2 had the strongest relationships to the CH_4 fluxes.

Depth

There was a negative correlation between the CH_4 concentration and the depth at the sampling locations in Santo Antônio and among the three reservoirs together (Table 6). An explanation for this relationship can be found in the hydrostatical pressure. When the water depth is small the hydrostatical pressure is low. It is thereby easier for produced CH_4 to overcome this pressure and escape toward the atmosphere at shallow depths than in deeper areas. The pathway of these emissions is through ebullition (Bastviken 2009). No correlation was seen in Funil and Três Marias, probably due to the greather depths in these reservoirs compared to Santo Antônio.

Concentration of CO_2 in the water

There was a positive correlation between the CH_4 flux and CO_2 concentration in Santo Antônio and among the three reservoirs together (Table 6).The highest CO_2 concentration in the water existed in the tributaries in Santo Antônio where the CH_4 fluxes also were the highest, especially station 2, 5 and 7 (Table 5a). Because of the high amount of available organic carbon at these stations, both the production of CO_2 and CH_4 are favored, since CO_2 and CH_4 production rely on organic carbon. The main process that releases CO_2 is the respiration, and this process consumes O_2. The O_2 levels at these stations are generally low and this indicates that respiration is the process that releases the CO_2. There was no significant correlation between the CO_2 concentration and CH_4 flux in Funil and Três Marias, but it can be seen that the mean CO_2 concentration was higher in Funil than in Três Marias (Table 5a). The greater concentration of CO_2 in Funil could be a product of a higher rate of CH_4 oxidation which further indicates that the production rate of CH_4 is higher in Funil than in Três Marias (Bastviken 2009). The higher concentration of CO_2 in Funil can also be caused by a higher respiration rate in Funil compared to Três Marias. The major reason why the concentration of CO_2 differed within and between the reservoirs is probably because of differences in available organic matter and oxidation.

Dissolved O_2

A negative correlation was observed between the dissolved O_2 and the CH_4 flux in Santo Antônio and among the three reservoirs (Table 6). The dissolved oxygen concentration in Santo Antonio was high in the main river and low in the tributaries at station 2 and 5. The high flux of CH_4 at station 2 and 5 can be explained by the low concentrations of dissolved oxygen causing a limited oxidation of CH_4. At station 7 the concentration of both CH_4 and oxygen was high, but the reason for the high CH_4 flux was the macrophytes present at this

station. No negative correlation was observed in Funil and Três Marias, but a positive correlation was observed between CH_4 and O_2 in Três Marias. This correlation was probably a result of a very low CH_4 flux which by chance was correlated with O_2. Três Marias had the highest O_2 concentration in the water which partly could be an explanation why the flux of CH_4 was low in this reservoir. Funil reservoir had a lower mean concentration of O_2 but still enough for oxidation to be performed (Soares *et al.* 2008). The oxidation rate might be greater in Três Marias than in Funil due to the difference in dissolved O_2.This could be the reason for the higher flux of CH_4 in Funil. The level where the concentration of O_2 is considered to cause a hypoxic environment is at a concentration of 2–3 mg/l (Kalff 2002) and there was only one station (station 5 in Santo Antônio) who had an oxygen level below this concentration.

Dissolved organic carbon, DOC

There was a positive correlation between CH_4 and DOC in Santo Antônio and among the three reservoirs together (Table 6). The highest concentration of dissolved organic carbon was found in Santo Antônio at station 2 and 5 which also had high fluxes of CH_4. Since organic material is required for the methanogenesis process locations with high organic carbon content in the sediment produce the largest amount of methane. A high concentration of dissolved organic carbon in the water is related to the carbon content in the sediment. No correlations were seen in Funil and Três Marias.

Other measured variables

No clear pattern between CH_4 flux and the variables wind speed, temperature, pH, turbidity, total N, total P and chlorophyll−a was observed. One reason why no relationship between wind speed and the CH_4 fluxes were visible is because there is no major difference in wind between the stations and reservoirs. The wind does not directly affect the diffusive emissions since the emissions are controlled by the aquatic boundary layer (McGillis *et al.* 2001), but the aquatic boundary layer is affected by the wind. If greater differences were evident in wind speed a higher CH_4 flux would be expected at locations with low wind speed (Sharpe *et al.* 2002). No clear pattern was seen between the air- and water temperature and the flux of CH_4 in any of the reservoirs. Earlier results have suggested that the temperature affect the CH_4 emissions because the methanogenesis process rate increase with temperature (Conrad 2002). Since the measurements were done at one occasion in every reservoir the connections between temperature and CH_4 emissions could not be observed. If measurements would have continued during the year the effect of this variable on the CH_4 emissions would probably be different. The turbidity in not related to the CH_4 emissions in general in the study, but the turbidity in Santo Antônio was high where the fluxes were low. This variable would probably have a stronger connection to CH_4 emissions in a larger study, where a high turbidity would exists at locations with a low flux. The total N concentration, total P concentration and

Chlorophyll–a did not have a clear connection to the CH_4 emissions, but these variables are influencing the amount of organic carbon within a reservoir. In the long run these variables are important in the processes related to CH_4, but this could not be visible in this study.

Age of reservoir

Another factor that affects the CH_4 flux is the age of the reservoir. Santo Antônio is a newly constructed reservoir and thereby large areas in the tributaries are flooded. When this happens, newly constructed organic material is decomposed and turned into CH_4. Funil reservoir and Três Marias reservoir were constructed in 1960 and therefore no easily decomposed organic material originated from the time of construction is left in this reservoir. This could be another reason why the CH_4 fluxes in Santo Antônio were so much higher than the fluxes in Funil and Três Marias (Barros *et al.* 2011).

5.7 LINEAR AND NON–LINEAR CALCULATIONS OF FLUX

The calculations of the CH_4 flux can be done in two different ways; with a linear approximation and with a non–linear function (Figure 12). When the increasing flux in a chamber follows a pattern that has more of an exponential character than linear, the non–linear function gives a better result. This is why the greatest differences in flux obtained from the two methods were found where the fluxes are the highest. Since the non–linear flux takes into account the decrease in flux during time, the result from the non–linear calculations can be considered to reflect the reality in the chamber better than the linear approximation. The results obtained from the different method showed a higher flux when the non–linear method was used compared to the linear. These differences were visible at the stations with the highest flux. The linear approximation does not follow the non–linear function because the high emissions are non–linear, while lower fluxes have more of a linear behavior. The temporal measurements in Três Marias (Figure 13) showed a linear pattern in the first chamber and more of an exponential pattern in the second chamber. The fluxes in both chambers were calculated by the non–linear functions. It is difficult to decide whether the increased flux of CH_4 follows a linear or an exponential pattern in the chamber from these results. Chamber 1 was placed in the water in the afternoon while chamber 2 was placed in the water in the morning, and this difference in time might affect the CH_4 fluxes because of differences in light, temperature and the activity in the surrounding water. The chambers were located next to each other, which mean that they should be in touch with the same concentration of CH_4 in the water. The difference in CH_4 flux in the two chambers is big and there is no clear explanation to this.

5.8 EVALUATING THE METHOD

The floating chamber method has been used worldwide in many different constellations, both for CO_2 measurements and CH_4 measurements. It is a very easy and cheap method to use and the theory behind the method is easy to understand. There were many situations in the field where the reliability regarding the method was discussed, due to the errors that can occur in connection to the measurements. Also during the analysis with the GC many questions appeared regarding the credibility in the results. The GC showed uneven results and the standard curve differed a lot through the days of analyses. The method has been dismissed by several researchers mainly because the floating chamber method is said to increase the turbulence at the water surface which enables more CH_4 to diffuse to the air (Raymond & Cole 2001). By constructing chambers with wall that extends into the water, this turbulence can be avoided (Matthews *et al.* 2003). The chambers also isolate the water surface from the impact of wind. However, studies show that the exchange of gas is controlled by the turbulence in the aquatic boundary layer and therefore the wind does not have a great influence on the emissions (McGillis *et al.* 2001). Guerin *et al*. (2007) investigated this method further and also compared it with the eddy covariance technique. The conclusion was that the floating chamber method is a reliable method. The main thing to keep in mind, except from the extended chamber walls, is to leave the chambers drifting while the measurements are made. The results from the two stations where the boat was fixed are unreliable according to this.

5.9 ERRORS

The errors that possibly occurred in the field and in the lab were mostly connected to the chamber construction or the sampling method. The three chambers that were used were a bit bigger than most used chambers, which might give a different flux. The UNESCO/IHA measurement specification (UNESCO/IHA 2009) suggest a chamber with the volume 20 dm^3 and an area of 0.2 m^2 and the volume of the three chambers used in this study was 35.75 dm^3 and an area was 16.58 dm^2 and 16.66 dm^2. No optimal extension of the chamber walls into the water was considered; therefore the buoys were attached without any defined height above the water surface. If the walls extend to far into the water, the turbulence in the boundary layer might get affected.

Another possible error is the deployment time. There was a lack of certainty regarding the optimal deployment time of the chambers, since there was no time to try out the best time interval and length of measurements. The 3 x 10 minute time interval was decided from previous studies and also because this timespan suited with the other groups who shared the boat in the field. Because of this important moments regarding the CH_4 flux behavior might have been left out in the measurements. The obtained fluxes from the first 10 and 20 minutes were not used in the results because of their insecurity. Also the limited numbers of measurement taken at each reservoir could give rise to results that not correspond to the

values that reflect the concentrations and fluxes in the whole reservoir. Another error was the unequal hour of sampling during the day at all stations. The light and temperature differs depending on the hour and this might affect the CH_4 emissions. Therefore a comparison between the CH_4 fluxes might not be reliable since the fluxes represent different time span. The GC gave rise to possible errors. The integrated area that was used to calculate the CH_4 concentration could be integrated very differently depending on where the baseline was drawn. This lead to an uncertain standard curve in many cases, and a big difference among the constructed standard curves. If more time were available the samples could have been analyzed by the GC more than one time, which would have given more secure results.

5.10 SUMMARY OF THE RESULTS

- The CH_4 fluxes in Funil Reservoir were within the range of -0.04 to 13.16 mmol/m^2/day, and the emissions within the reservoir were significantly different.

- The CH_4 fluxes in Santo Antônio Reservoir were within the range of -0.33 to 72.21 mmol/m^2/day, and the emissions within the reservoir were significantly similar.

- The CH_4 fluxes in Três Marias Reservoir were within the range of -0.31 to 0.56 mmol/m^2/day, and the emissions within the reservoir were significantly different.

- Santo Antônio and Três Marias had significantly different CH_4 fluxes. So did Funil and Três Marias. Funil and Santo Antônio had significantly similar CH_4 fluxes.

- The CH_4 flux was positively correlated with CO_2 and DOC and negatively correlated with O_2 and depth in Santo Antônio. The same correlations were evident for the whole data set.

6 CONCLUSION

The measured fluxes in the three reservoirs ranged from -0.33 to 72.21 mmol/m^2/day and the mean flux was 2.31 mmol/$m^{2/}$day. These fluxes are low compared to earlier results. The variation in CH_4 flux within and between the reservoirs was significantly different in a major part of the comparisons. Variables that increase the CH_4 emission rate were illuminated, even though most fluxes were significantly different. A low depth and low O_2 concentration increase the CH_4 emission rate. A high concentration of DOC and CO_2 indicates that a high amount of organic carbon is available for the production of CH_4, leading to an increased CH_4 emission rate.

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APPENDIX A

A.1 THE FLOATIONG CHAMBER METHOD

A.1.1 Preparation

Three chambers were constructed for the measurements. Each chamber consisted of a plastic bucket. Two of them had the same shape and the third one was slightly different. The outside walls of the buckets were covered with metallic aluminum tape with the purpose to reflect the sunlight from the chambers.

A hole was drilled on top of each chamber and another hole was drilled through three rubber stoppers. Each rubber stopper was connected to the hole in one chamber and a hose was attached through the rubber stoppers. A small part of the hose reached inside the chambers while the rest was located outside. To avoid undesired exchange of air each hole with rubber stopper was sealed with silicon, both inside and outside the chambers. A three stop was fastened at the end of each hose. The three stops were serving as locks between the air inside the chambers and the air outside. When the three stops were opened, air could pass freely in each hose. When the three stops were closed no external air could reach inside the chambers through each hose.

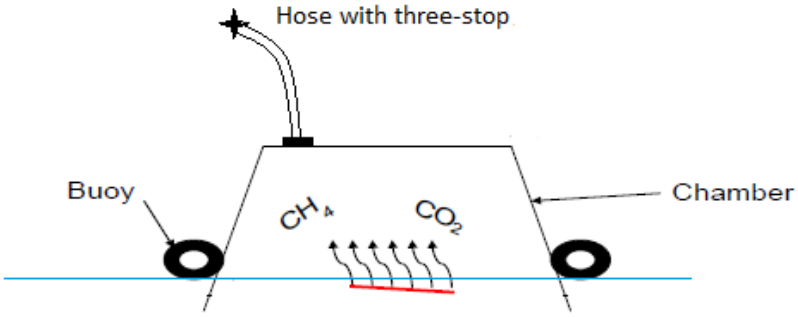

Figure A1 The view of a constructed chamber.

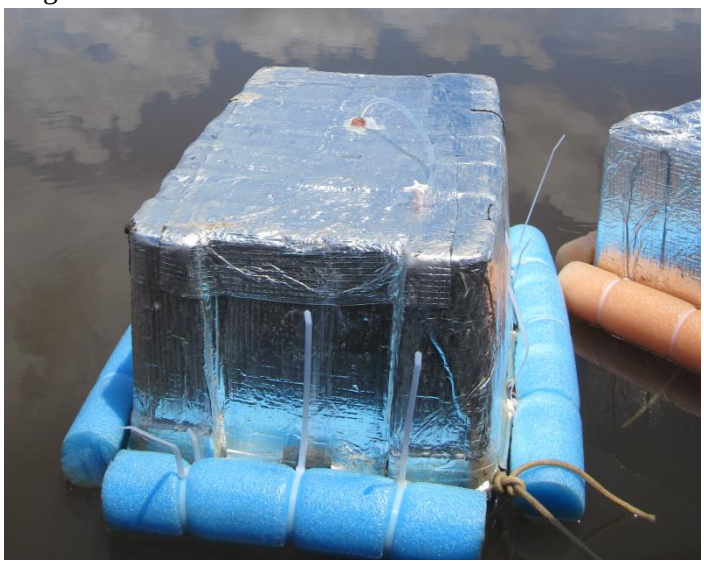

Figure A2 The view of a chamber in the water.

A rope was then fixed on each chamber with aluminum tape. The placement of the rope was approximately 10 cm above the opened area that faced the water. Cylindric buoys were placed on top of the rope on each side of every chamber. On the long side the buoys were 49 cm long and on the short sides 33 cm long. To firm them next to the chambers a flat surface area along one side on each buoy were cut out. A notch was cut in the middle of the flat

surface to make them even more stable. This notch was attached on top of the rope on the chambers. The buoys were tied to the rope by cable ties. The ends of each fixed rope were tied together and ca 2 m of the rope was left with the purpose to fix each chamber to the boat while making measurements. The buoys were blue, yellow and orange giving each chamber one of these color.

The chambers were tested in a pond after the construction to make sure they were floating in a stable way (Figure A2). The three stops attached to the hoses where opened when the chambers were placed in the water. The purpose was to ease the process of stabilizing the pressure within the chamber with the atmospheric pressure. The chambers were a bit unstable at the start, but got stabilized after a short time in the water. To further regulate the buoyancy of the chambers the buoys were moved up and down. The movements enabled the chambers to get into a straight position in the water. The chambers were moved around while testing them to make sure they resisted rain and waves and other weather conditions. The high placement level of the buoys gave chamber–walls that extended about 10 cm below the surface water level. By having chamber–walls underneath the water surface, influences caused by weather conditions could be minimized (UNESCO/IHA 2009). When testing the chambers it could clearly be visible that this way of placing the buoys made the chambers more stable. The reason for choosing three chambers was because replicates were required to ensure more secure results and also to enable ebullition bubbles to be captured.

To be able to calculate the flux of CH_4, the volume of the chambers above the water surface were measured and also the water–facing area of the chambers. First the water level in relation to the floating chambers needed to be established. This was done in the pond by marking each chamber where the water level was located. The volume was measured by turning the chambers upside down and then filling it with water to the marked level. Each chamber had a volume of 35.75 liters. The water facing areae was calculated by scales. The area of the blue and yellow chamber was 16.58 dm^2 and the area of the orange was 16.66 dm^2.

The vials that were used to store the samples were filled with a saturated salt solution before the measurements were done. Water and salt were mixed until the salt was dissolved and the solution was saturated. At 20^0C the concentration of saturation is approximately 300 g salt/liter water (UNESCO 2009). The vials were placed in the salt solution until they were completely filled and a rubber stopper was used to enclose each vial. A small needle connected to a syringe was attached through the rubber stopper before the enclosing process. This enabled overspill water to escapes through the needle and syringe which made the vial close properly. Each vial was visually inspected to make sure that no bubbles occurred in the vial. If no bubbles were visible the syringe with needle were pulled out from the rubber stopper. The vial was sealed with a metal lid on top of the rubber stopper to make sure no external air entered the vial. The 385 vials used for the study went through the same procedure. It is important to make sure that no air bubbles occur in the vials straight after they

are closed with the rubber stopper because external air bubbles might affect the CH_4 gas. Bubbles might occur later due to differences in temperature or pressure compared to present temperature and pressure when preparing the vials. Bubbles that occur later consist of vacuum and will thus not affect the result of the measurements. The salt solution was replaced by the air sample in the field. By using the salt solution no disturbing gas occurred in the vial when the sample was transferred into it and thereby no other gas can affect the sampled gas.

A.1.2 In the field

The measurements were made with three chambers at every measurement station in each reservoir and a boat was used to reach these stations. The chambers were placed in the water next to each other with the three stops opened. The three stops were closed after a while when the chambers were stabilized in the water. The time of this occurrence was written down in a protocol. An initial air sample was collected with a 60 ml syringe with three stop straight above the chambers. The three stop attached to the syringe was closed and the time of sampling was written down in the protocol. Then an initial 60 ml water sample was collected from the surface water next to the three chambers with a 60 ml syringe connected to a three stop. 20 ml of water was then pressed out of the syringe and replaced by air and then the three stop were closed. After this procedure the syringe contained 40 ml of water and 20 ml of air. The time for the sampling was written down in the protocol and then the syringe was shaken for 1 minute. Equilibrium was achieved between the gas in the gas phase and the gas in the water phase by shaking the syringe. The gas phase was transferred to another syringe when 1 minute had passed (Figure A3). It was very important that no water went with the gas into the new syringe.

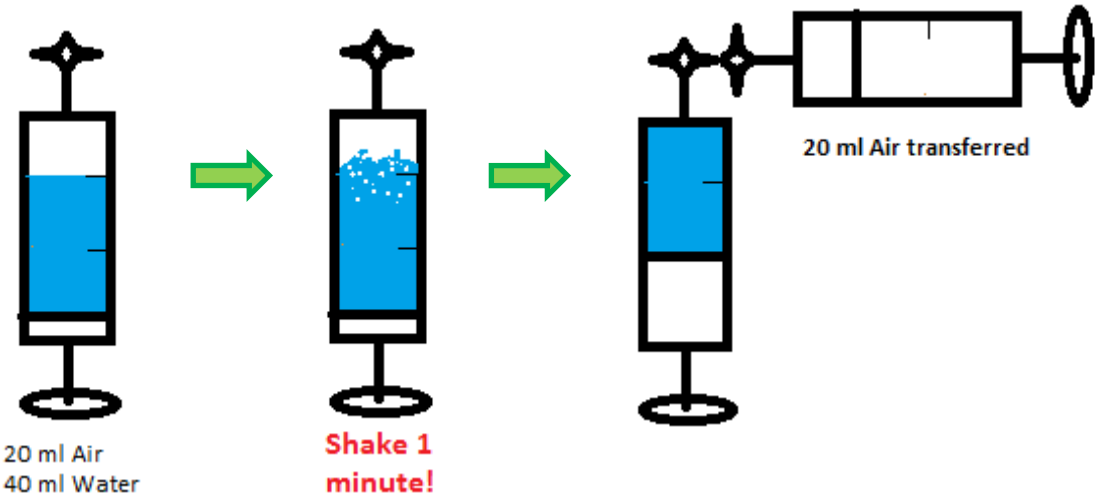

Figure A3 The procedure of taking the initial water sample.

When 10 minutes had passed, an air sample of 60 ml was collected from each chamber through a syringe with a three stop. The three stop on the syringe were connected to the three stop on the chamber and both three stops were opened. Air from the chamber was drawn into the syringe and then pushed back three times to mix the air inside the chamber. The sample was collected after the mixing and both three stops were closed. Air samples were collected again in the same way when 10 minutes had passed. After another 10 minutes the last samples were collected. In total, samples from the three chambers were taken after 10, 20 and 30 minutes. Thereby one initial air sample, one initial water sample and nine chamber samples were collected at each measurement station.

The collected samples stored in syringes were transferred into the prepared vials during the time between the sampling events. Each sample was stored in one vial. The first step in the transferring process was to push a needle halfway through the rubber stopper which seals the vial. Then a needle was attached to the syringe with the sample and pushed through the rubber stopper the whole way. The three stop attached to the syringe was then unclosed at the same time as the earlier attached needle was push in the whole way. The air in the syringe was pressed towards the vial with a constant pressure. The vial was held upside down (the rubber stopper facing the ground) during the process. Due to this, the salt solution in the vial run out through the sole needle and got replaced by the gas sample. The two needles were removed from the rubber stopper when about ¾ of the vial was filled with the gas sample. It is very important to leave some salt solution in the vial when taking out the needle and the syringe to make sure overpressure exist and thereby no external air can get drawn into the vial trough the needle (Figure A4).

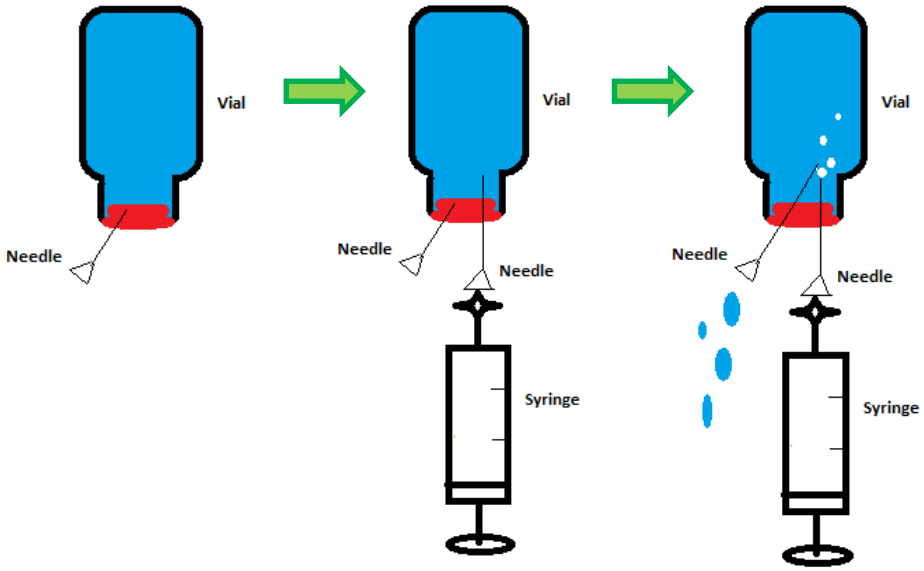

Figure A4 How a gas sample was transferred into a vial.

All air samples taken in the field were transferred to a vial in the same way. Except from the gas samples the air temperature, water temperature and wind speed were measured to enable the calculations regarding the flux of CH_4. The air– and water temperature were obtained from a thermometer and the wind speed from an anemometer. The air pressure was also required to fulfill the calculation. The air pressure at each reservoir was calculated from the altitude. Several other variables connected to the CH_4 emissions were measured. A multiparameter sonde (Yellow spring 6920) was used to determine the conductivity, the concentration of dissolved oxygen, the oxygen saturation, the pH and the turbidity in the water at each station. A GPS was used to establish the coordinates for each station and a depth sounder in the boat gave information of the depth. The partial pressure for CO_2 was measured by an Infrared Gas Analyzer (IRGA). The partial pressure of CO_2 was measured at most places, but the machine did not work properly at some locations. Gas chromatography was used to determine the partial pressure of CO_2 at the stations where data were missing.

Chlorophyll–a, the concentrations of NO_3, NO_2, NH_4, inorganic dissolved nitrogen, total organic nitrogen, total N, SiO_3, PO_4 and total P were measured by another part of the research group, and these data have been available in the thesis for comparisons with CH_4 emissions.

Three chambers were used for measurements during half an hour at all chamber stations in all reservoirs, except from station 7, 8, 9 and 10 in Santo Antônio. Emissions from macrophytes were measured at station 7 by using two chambers. One chamber above macrophytes and one control chamber in the water net to the macrophyte. Initial air– and water samples were collected at station 8, 9 and 10 but the water at these stations was to turbulent for chamber measurements. In total, the flux were measured at 7 stations in Santo Antônio. 12 stations were used for measurements in Funil and 13 stations were used for measurements in Três Marias. Temporal measurements were also done in Três Marias with two chambers for a 36 hours deployment time. Chamber 1 was deployed in the water at 4.00 pm, while chamber 2 was deployed in the water 15 hours after.

A.1.3 Analysis in the lab

The CH_4 concentrations in the collected gas samples were determined by gas chromatography (GC) further described by Poole (2003). This analysis method separates different substances in the collected samples due to their differences in velocity in a colon. The colon in the chromatograph holds a mobile phase consisting of a gas (H_2, He or N_2) and a stationary phase most often consisting of silicon polymer. The components in the analyzed sample are separated between the stationary phase and the mobile phase in the colon. The components that are situated in the mobile phase moves forward, while the component in the stationary phase stands still. The components pass true the colon with different velocities depending on chemical and physical characteristics like boiling point, vapor pressure, molecular mass and

polarity. The substances are getting detected and identified electronically when they reach the end of the colon.

In the gas chromatograph a Flame Ionization Detector (FID) is used to detect CO_2 and CH_4. FID first detects the CH_4 in the gas and then CO_2 because CH_4 is transported much faster in the colon than CO_2 due to less weight. Normally CH_4 and CO_2 are analyzed individually. The FID detector can be programmed to analyze both CO_2 and CH_4 at the same time but that takes a long time. To make an analysis 10 ml of gas was transferred into a small syringe. The gas in the syringe was then injected into the gas chromatograph through an opening close to the FID. As soon as the gas enters the FID the analysis starts and the gas continues to the metallic round formed colon. Here the gas is heated to 150 ^{0}C which enable the separation of the components. It took about 6 minutes to analyze the concentration of CH_4 in a gas. The result obtained after an analysis is a curve that has a peak after a certain amount of time, known as the peak of CH_4. The integrated area of the peak corresponds to the detected concentration of CH_4.

To be able to calculate the concentration of CH_4 in the gas sample a standard curve was created. The standard curve consisted of three standard gas samples with known CH_4 concentrations but unknown integrated area. Each standard gas was injected by the 10 ml syringe into the FID in the gas chromatograph. For each gas an area of the CH_4 peak was obtained. The standard curve was constructed by a regression line represented by the three standards. The curve was created with the measured areas on the x–axis and the known concentrations on the y–axis. Every standard were injected two to three times to make sure the obtained integrated areas corresponded to each other. If the correspondence for each standard is high, a reliable standard curve can be created.

When the standard curve was obtained the measured gas samples were injected by the 10 ml syringe into the FID. The gas was collected with the syringe from each vial. For each sample an area representing the CH_4 concentration appeared. By placing this area on the constructed standard curve the concentration of CH_4 in each sample could be found. The concentrations of CH_4 in 370 out of the 385 samples were determined through this analyze method. The first five samples were analyzed two times to make sure the results were alike. The remaining samples were analyzed once each due to lack of time. The time was running out in end of the analysis, therefore 15 samples in Três Marias were not analyzed. A standard curve was created three times during each day of analyses to make sure the gas chromatograph works properly and gave correct results. One standard curve was created in the morning at the start, one at midday and one in the evening before the analyses were finished.

When the CH_4 concentrations in the samples were established, CO_2 analyses took place for stations where the partial pressure of CO_2 was missing. The same procedure as for CH_4 was used during the analysis. The only difference was that the injected gas had to go through a methanizer which transferred CO_2 into the lighter CH_4. It is easier for the gas chromatograph

to analyze CH_4 than CO_2 and this is why CO_2 is transferred into CH_4. The obtained graphs were showing the CH_4 content this time as well, but now representing the concentration of CO_2. This way of measuring CO_2 is not as accurate as the IRGA, since CO_2 can leak out from the vials between the time of sampling and analyzing. CO_2 can also leak out when samples are taken from the vials for the CH_4 analysis.

APPENDIX B

B.1 MATLAB CODE FOR THE PCA ANALYSIS

```
stdr = std(TOTall);    %Standardize the data because the variables have
different units
sr = TOTall./repmat(stdr,285,1);

[coefs,scores,variances,t2] = princomp(sr); %the PCA is preformed resulting
infour outputs

percent_explained = 100*variances/sum(variances) %calculate var explained
by each princ comp

figure
pareto(percent_explained)   %screenplot of variability
xlabel('Principal Component')
ylabel('Variance Explained (%)')

figure
biplot(coefs(:,1:2), 'scores',scores(:,1:2),...
'varlabels',VAR);
axis([-.5 .5 -.6 .6]);
```

APPENDIX C

C.3 DATA

Station	FU	SA	TM
1	0.438827	-0.32809	-0.07076
1	0.635736	-0.24514	0.023414
1	0.45041	-0.23836	0.048456
2	0.263912	16.59589	-0.00157
2	0.435567	72.212	-0.00166
2	0.237137	29.99214	0.00084
3	0.296694	0.472462	0.002118
3	0.286746	0.445257	0.004504
3	0.265044	0.344056	0.00206
4	0.262501	0.089831	0.102375
4	0.382213	0.179481	0.158729
4	0.352291	-0.06011	0.0815
5	0.006574	20.34974	-0.11494
5	0.039421	11.53069	0.141276
5	0.031521	16.51137	0.560918
6	0.587912	0.316161	0.006969
6	0.563868	0.466036	0.017611
6	0.789109	0.460742	0.022224
7	13.15461	7.557262	-0.07062
7	3.212265		-0.12916
7	0.881387		-0.06377
8	0.031835		0.109027
8	0.004125		0.103679
8	0.078801		0.135686
9	9.97		0.213802
9	0.055562		0.008091
9	0.50738		0.010867
10	-0.03894		0.088431
10	0.039333		0.209068
10	0.01729		-0.31334
11	0.203723		0.390886
11	0.192103		0.387434
11	0.240775		0.357964
12	0.184424		0.210791
12	0.194944		0.212665
12	0.282427		0.34257
13			0.496954
13			0.489506
13			0.448451