Factors influencing CO_2 and CH_4 fluxes in Tomago wetland

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David Safari, MSc-Environmental Science & Policy (Clark University)

Department of Environmental Sciences

Faculty of Science and Engineering

Macquarie University

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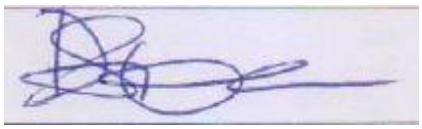
Declaration

I hereby declare that this thesis has not been previously submitted to any other institution or university for a higher degree. Except where otherwise acknowledged, this thesis is comprised entirely of my own work.



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Abstract

The Tomago wetland, Newcastle, is undergoing wetland rehabilitation by restoring tidal inundation to a previously leveed floodplain. It was hypothesised that the restoration of tidal inundation would convert a methane source into a sink as a consequence of soil salinization. A one year experimental design study was instituted to measure the impact of tidal reinstatement on CO_2 and CH_4 fluxes. Prior to tidal reinstatement, eddy covariance towers were installed to measure CO_2 and CH_4 fluxes. Micrometeorological energy balance and environmental variables such as soil water salinity and inundation regime, were undertaken. The highest average diurnal emissions were 2.54 μg m^{-2} s^{-1} CH_4 during the day and 0.45 mg m^{-2} s^{-1} CO_2 at night. Monthly average fluxes peaked in February (0.365 μg m^{-2} s^{-1} CH_4 and 0.137 mg m^{-2} s^{-1} CO_2).There was a significant negative relationship between CO_2 flux and water level ($p < 0.001$), tidal height ($p = 0.02$) and positive relationship with water temperature ($p = 0.002$). CH_4 flux showed positive correlation with water level and negative correlation with EC although not statistically significant. Although tidal flooding did not demonstrate clearly carbon sequestration before and after tidal reinstatement, freshwater events (rainfall) were seen to influence the wetland carbon balance.

Chapter 1: Introduction

Australia contributes approximately 33% of the planet's tidal marsh area although the size (13,765 km^2) of tidal marshes has been reducing since European settlement due to wetland transformation into farmland and coastal developments such as urbanization (Peter I. Macreadie et al., 2017). Studies have revealed that estuarine wetlands, to a greater extent have high carbon sequestration capacity per unit area than other wetland ecosystems especially in undisturbed conditions (Bridgham et al., 2006). Conversion of wetlands into agricultural zones, such as pasture lands, and urban development can reduce carbon storage capacity of the wetland. In many parts of the world including the US, studies indicate that wetland reclamation into pasture lands and crop farms can substantially reduce carbon storage within in the first decade of land use change (Armentano & Menges, 1986). Similar studies that were conducted in Australia also demonstrate that about 50% of the wetlands that were converted into other land use practices, such as pasture land (Streever, 1997), have been affected due to modifications by tidal flows (Howe et al., 2009).

Saltmarshes and mangroves are the most efficient ecosystems in the world for carbon sequestration (Donato et al., 2011; Pidgeon, 2009), placing them as highly influential ecosystems for policy formulation. This is because saltwater intrusion into these environments has a dramatic effect on microbial communities, which play a key role in formation of GHGs (Poffenbarger et al., 2011). In a related study, Weston et al., (2011) stated that salt-water intrusion has a long term effect on microbial cycling of carbon in wetlands due to increase in sulphate ion concentration, causing sulphate ion reduction as a terminal carbon mineralisation process instead of anaerobic methanogenesis. For coastal wetlands, such as Tomago in the Hunter estuary of New Castle, NSW, salt water intrusion was effected by tidal flow restoration after a period of blocking tidal water, leading to drying up of the wetland.

Tidal flow can be managed through construction of flood mitigation drains with modified flood gates (Smart Gates). On the other hand, tidal restriction can cause acidification of coastal wetlands, which is a significant environmental, economic and social problem in many parts of Australia (Indraratna et al., 1999), including the Hunter estuary of New South Wales. Acidification resulted into the formation of acid sulphate soils (ASS) due to pyrite as a dominant iron sulphide formed during the last major interglacial in coastal NSW (Indraratna et al., 2005), and this is one of the major problems that affected Tomago wetland, and thus, lowering its ecosystem productivity.

Prior to construction of the drainage system, Tomago wetland was an important habitat and source of food for fish. The site is a seasonally flooded saltmarsh, with mangrove vegetation on the other side. Tidal flow restriction and drainage system lowered the ground water table, leading to oxidation of sulphides, and thus soil acidification (DPI, 2008). Because of the above effects on water quality and ecosystem functions in the wetland, tidal flow re-instatement was implemented as a long term objective for the rehabilitation of the area by the Hunter-Central Rivers Catchment Management Authority. Further work on re-instatement of tidal flow was effected in November 2015 to improve ecosystem functioning and productivity in the wetland.

In 2011 and 2012, an integrated innovative approach was employed to restore connectivity and tidal flushing to the area neighbouring the National Park. The major works that were performed included: First, hydraulic modelling to calculate the optimal volume of water required to rehabilitate the area through wetland inundation. Secondly, inventing, fabricating and installing a new design of auto tidal floodgates with the ability to withstand large hydraulic stresses, and re-establish water movement through natural drainage channels without exacerbating acidic problems. Thirdly, protecting neighbouring private farmland from inundation (Russel et al., 2012).

Tidal flow restoration allows flushing water to decrease acidity, increase dissolved oxygen, remove exotic freshwater weeds, enhance runoff during wet periods and create healthy fish breeding grounds (Dick & Osunkoya, 2000; Glamore, 2003; Indraratna et al., 2002). Studies on coastal saltmarshes in Australia have concentrated mainly on assessing carbon storage and accretion, geochemistry of acid sulphate soils and GHGs production. This research project sought to investigate diurnal and monthly patterns of CO_2 and CH_4 fluxes, and the influence of environmental factors before and after tidal flow reinstatement in order to assess the effect salt water intrusion (in addition to environmental factors stated below) on GHG fluxes. A study was instituted to investigate the driving environmental factors (specifically, electrical conductivity, rainfall, water level, air and water temperature) for CO_2 and CH_4 fluxes, and assess diurnal and monthly variations of these fluxes before and after tidal flow reinstatement at Tomago wetland.

1.1 Aims and objectives

The study aimed at investigating the influence of environmental factors such as tidal water height, water temperature, precipitation, and electrical conductivity (EC) on the fluxes of greenhouse gases (CH_4 and CO_2) at Tomago saltmarsh in New South Wales. The specific objectives of the study were:

1. Measure, the fluxes of CH_4 and CO_2 using open path eddy covariance method over a one year period.
2. Investigate controlling mechanisms for CO_2 and CH_4 air-surface exchange.
3. Evaluate diel and monthly patterns of CH_4 and CO_2 fluxes, before and after tidal flow re-instatement of the wetland.
4. Assess the impact of rainfall, water temperature, electrical conductivity (EC), water level and tidal height on CH_4 and CO_2 emissions.

1.2 Significance of the study

There is limited information about greenhouse gas air-surface exchange in coastal salt marshes and mangroves in Australia. This study has generated information regarding fluxes of methane and carbon dioxide, and the results will aide environmental management departments and researchers for planning purposes, and scientific literature documentation. The study gives an insight on interventions to reduce greenhouse gas emissions from saltmarshes. Therefore, the findings demonstrate specific recommendations to reduce the effects climate change and global warming by limiting emissions of GHGs from the coastal saltmarsh. The study outcomes are essential in understanding the carbon cycling functions of coastal wetlands, and the role they play in GHG emissions and climate change as a whole. While as the results from this research project will give a strong argument for protection and restoration of degraded saltmarsh ecosystems in NSW and other coastal areas in Australia, the research findings are relevant to enrichment of the scientific understanding of the processes that can control GHG emissions due to tidal inundation.

Chapter 2: Literature review

This chapter shows how different factors affect carbon storage and emission from wetlands. The chapter gathers different ideas and demonstrations on how methane and carbon dioxide fluxes are influenced by physical, geochemical and microbial factors, within coastal saltmarsh and mangrove ecosystems vulnerable to flooding by rainfall and tidal flow in Australia and other continents.

2.1 Dynamics of carbon dioxide in wetlands

While wetlands function as sinks in the carbon cycling process through storing carbon in the vegetation and soil, they can also function as atmospheric sources of carbon dioxide and methane (Mitsch et al., 2013). Through the process of photosynthesis, carbon dioxide is absorbed by green plants to form organic carbon by green plants, as well as autotrophic bacteria (Olsson et al., 2015). The absorbed carbon dioxide eventually gets released back into the atmosphere through decomposition of organic matter under aerobic and anaerobic processes. Tidal marshes are considered to be among the most efficient carbon sinks, with capacity to accumulate and store carbon at rates which are 55-times faster on millennial timescales, compared to tropical rainforests (Mcleod et al., 2011). In Australia and other parts of the world, the capacity to store carbon by tidal marshes has been significantly affected by human activities such as land reclamation (Bu et al., 2015), chemical and physical disturbances (Macreadie et al., 2013), as well as eutrophication (Deegan et al., 2012).

Higher emissions of carbon dioxide are usually released into the atmosphere under aerobic decomposition compared to anaerobic decomposition. The former process mainly produces carbon dioxide as the end product, while the latter produces methane, in addition to carbon dioxide as the end product (Kayranli et al., 2010; Olsson et al., 2015). Carbon dioxide fluxes depend on the available photosynthetically active vegetation, and also on respiration capacity of the entire ecosystem. Increased tidal flow of saltwater into freshwater ecosystems is closely linked to high levels in soil respiration which in turn leads to high emissions of carbon dioxide (Chambers et al., 2011; Weston et al., 2011).

2.2 Methane formation process

The process of methane formation is enhanced under anoxic conditions in sediments (Xiao et al., 2013) by communities of methane producing archaea, also known as methanogens. Most methanogenic communities cannot tolerate high oxygen levels due to their enzymatic instability, and these methanogens are classified according to their energy and carbon sources (Venkiteswaran & Schiff, 2005). Carbon sources include; acetate, methanol, formate, methylamines, carbon monoxide, other secondary alcohols, and hydrogen/carbon dioxide (Borrel et al., 2011; Shoemaker & Schrag, 2010). For instance, the formation of methane can be achieved either by fermentation of acetate or reduction of carbon dioxide (Shoemaker & Schrag, 2010).

$CH_3COOH \rightarrow CO_2 + CH_4$ (Acetoclastic methanogenesis) 25-35‰

$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$ (Hydrogenotrophic methanogenesis) $\geq$ 55‰

In addition, other research findings about the metabolic pathways for methane formation, suggest methylotrophic methanogenesis, in which the methyl group undergoes reduction in methyl-coenzyme M, and finally reduced to methane (Borrel et al., 2011).

Although most findings about methane production are focussed on anaerobic microbial pathways, further work about aerobic methane formation suggests that decomposition of organic phosphorus compounds in marine ecosystems with low nutrient levels can liberate methane as a by-product (Bridgham et al., 2013; Damm et al., 2010). (Bridgham et al., 2013; Keppler et al., 2006). Methanogenesis is closely linked to plant productivity and research shows that CH_4 production is influenced by organic products of photosynthesis in form of root exudates in the rhizosphere (Dorodnikov et al., 2011). More studies indicate that plant root exudates have a stimulating effect on decomposition of soil organic matter (Basiliko et al., 2012; Guenet et al., 2010).

Methane production rate depends on factors including oxygen concentrations, content and quality of organic matter, and temperature. These factors impact the surrounding microbial communities directly or indirectly in the wetland ecosystems (Jacinthe et al., 2012; Xiao et al., 2013). During methanogenesis, methanogens metabolise lighter carbon (carbon-12) in preference to the heavier one (carbon-13) through kinetic isotope fractionation, and as a result, the methane produced is depleted of carbon-13 (^{13}C) by 20-60‰ in relation to the source of organic carbon while the resulting carbon dioxide becomes enriched by the same amount (Shoemaker & Schrag, 2010). The isotopic signature techniques are therefore important in identifying the source of CH_4, whether it is biogenic or thermogenic.

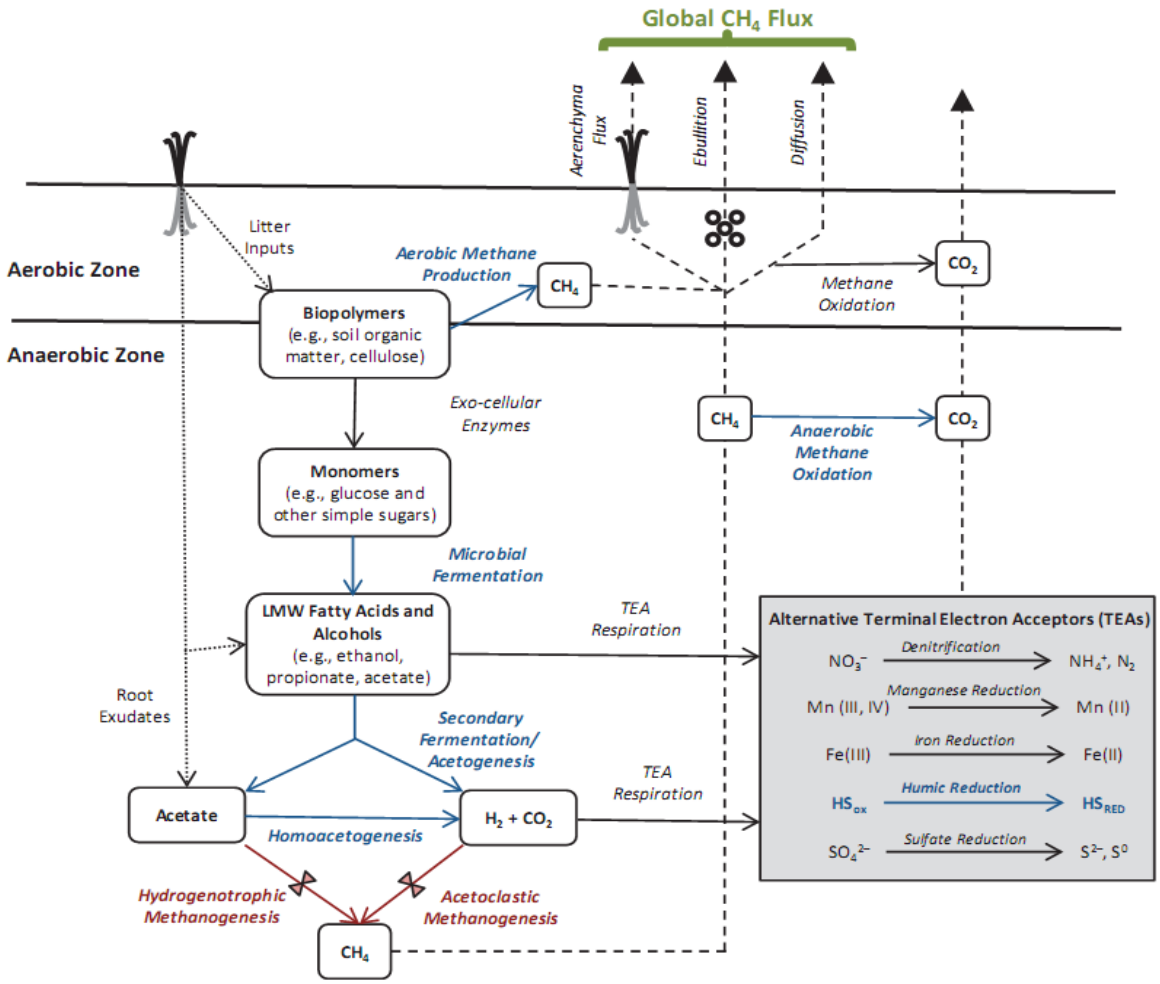


Figure 1: Shows summary of CH_4 cycling in wetland ecosystems. The boxes indicate pools of carbon and solid arrows show mineralisation of carbon sources by specific microbial processes. Dotted lines show carbon inputs from plants and dashed lines illustrate the flux of gaseous end products (CH_4 and CO_2) of the processes to the atmosphere.

Source: Bridgham et al.,(2013)

2.3 Methane transport mechanisms

There are three major modes of transport of methane; diffusion through soil and water, plant mediated transport, and ebullition (Segers, 1998; Shoemaker & Schrag, 2010). One of the major drivers of methane dynamics in wetland ecosystems is vegetation because the absence or presence of plant cover in aquatic ecosystems heavily impacts the transport of methane from sediments to the atmosphere (Bellisario et al., 1999; Kao-Kniffin., 2010).

Kao-Kniffin et al.(2010) found that the removal of sedges from arctic wet meadow caused a reduction in methane emissions and increased the accumulation of methane in flooded soils due to lack of plants through which methane would have been transported . In a related study, Van der Nat & Middelburg (2000) stated that "over 85% of the net methane emissions from the *Scirpus* and *Phragmites* wetland was a result of methane venting to the atmosphere through the root-shoot system". Vegetation structure enhances transport of gases between the sediments and the

atmosphere while plant composition influences the differences in methane flux across plant communities, due to different biogeochemical mechanisms regulating methane production, consumption and transport (Kao-Kniffin et al., 2010).

Methane can diffuse from the sediments through the water column and to the air. Although this process lends itself to a greater percentage can be oxidized by methanotrophs, to form carbon dioxide, if there is oxygen in the water column (DelSontro et al., 2016). A high percentage of methane diffusing from the oxygen-deficient aquatic sediments may be oxidised before crossing the water-air boundary due to high methane oxidation rates in the oxic water columns.

Ebullition is another pathways for releasing methane into the atmosphere without undergoing aerobic oxidation, and it occurs sporadically when supersaturation of pore water with methane occurs (Bridgham et al., 2013; Tokida et al., 2007). It is one mechanism of transport in which methane escapes from the wetland into the atmosphere without oxidation (Tokida et al., 2007). There are many studies linked to the release of significant amounts of methane by ebullition. For instance, in shallow water bodies the majority of CH_4 in bubbles is transported directly from sediments to the atmosphere (DelSontro et al., 2015; DelSontro et al., 2010; Tokida et al., 2007). This pathway is influenced by physical environmental factors such as hydrostatic pressure due to changes in water levels, climatic fluctuations (Varadharajan & Hemond, 2012; Wik et al., 2013) and disturbances of the sediments that are wind related (Tonya DelSontro et al., 2016). Although many studies have classified ebullition to be episodic in nature and occurring under the influence of physical factors, Goodrich et al. (2011) suggested that ebullition occurs regularly like any other transport pathway of methane such as diffusion and plant transport.

2.4 Oxidation of methane

In presence of oxygen in the sediment layer or pore water (water column), methane can be oxidised by bacteria (methanotrophs), and under this process, two oxygen molecules are consumed for every carbon dioxide molecule formed $(CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O)$. The oxidation of methane plays a vital role in influencing the flux of methane in aquatic ecosystems, and biological oxidation of methane depends on physico-chemical parameters and the mode of methane transport (Borrel et al., 2011; Venkiteswaran & Schiff, 2005). The oxidation of methane is a sink activity for methane and contributes significantly towards reduction of the flux of methane in the atmosphere (Venkiteswaran & Schiff, 2005; Whiticar, 1993). Therefore, the amount of methane emitted from wetlands is largely dependent upon the rates of methanogenesis and methane oxidation (Duc, Crill, & Bastviken, 2010; Xiao et al., 2013).

Other studies have shown that methane oxidation can occur in absence of oxygen as long as there is sufficient concentration of other electron acceptors, such as sulphates. In marine ecosystems this process is thought to consume > 90% of the total methane produced (Bridgham et al., 2013; Caldwell et al., 2008; Knittel & Boetius, 2009; Poffenbarger et al., 2011). Although it is believed that anaerobic methane oxidation is possible in freshwater ecosystems, there is scanty information supporting this argument compared to marine ecosystems. Caldwell et al., (2008) suggested that freshwater environments are characterised with low concentrations of sulphates, and thus have limited electron acceptors to drive anaerobic oxidation process of methane.

In line with what other investigators have suggested, (Borrel et al., 2011) noted that other electron acceptors including sulphate and iron (III) can enhance anaerobic methane oxidation in freshwater environments. In a related study, Smemo & Yavitt (2007), showed that a high degree of anaerobic oxidation of methane can occur consuming large quantities of methane produced in freshwater peatland soils, although the electron acceptors were not clearly identified.

In other studies, the existing scientific evidence shows that water table has control over methane oxidation. Studies indicate a decline in the net methane flux caused by lowering water table (Meijide et al., 2011; Moore et al., 2011). In the same way, there is convincing evidence that oxidation of methane can also occur in the rhizosphere, and consumes almost 100% of the gross methane production (Fritz et al., 2011).

2.5 Impact of tidal flow on GHG fluxes

Previous global mangrove wetland carbon budget research has been suggested to have used limited data and underestimated their role as a carbon sinks, resulting in 50% of their net primary productivity (NPP, 112-160 Tg C yr^{-1}) remained unaccounted for (Bouillon et al., 2008). Other findings show that high salt concentration impact significantly on microbial organisms in upland and paddy soils, by reducing microbial biomass which in turn decreases microbial respiration and the rate of methanogenesis (Chambers et al., 2011; Pattnaik et al., 2000). It has been revealed that the underestimated carbon is linked to sediment- air carbon dioxide fluxes (Call et al., 2015). For instance, the carbon that results from underground respiration has been underestimated and this carbon is exported as dissolved inorganic carbon (as CO_2) between the interstitial pore water and surface water by tidal flow (Alongi, 2014; Call et al., 2015).

Unlike the freshwater wetlands and permanently flooded saltmarshes, the semidiurnal movement of the tide can cause the intertidal estuarine marshes to have two different periods of exposed soil surfaces and tidal water inundation over the course of the day, with short term fluctuations in their abiotic environments, and this affects carbon and nutrient fluxes (Daniel M Alongi, 1998).

Emissions of GHGs intertidal estuarine marsh ecosystems are likely to be affected by tidal inundation (Tong et al., 2013). Aquatic organisms such as crabs create burrows in the majority of the mangrove forests, and this serves as a suitable mechanism for increasing sediment-water interface. In addition, nutrients derived from decomposed organic matter in the subsurface layers of mangrove ecosystems are continuously deposited into sediments by tidal pumping (Call et al., 2015).

Tidal pumping has been emphasised in the recent research work as a potential mechanism of concentrating solutes (especially carbon) in mangrove waters due to high dissolved inorganic carbon (DIC) and total alkalinity in mangrove creek waters (Call et al., 2015; Gleeson et al., 2013). According to Linto et al., (2014), the partial pressures of CO_2 and CH_4, total alkalinity and dissolved inorganic carbon concentrations are negatively correlated with tidal height and thus, cannot be linked to tidal pumping of CH_4 and CO_2 in creek waters. However, through the use of natural radioisotope tracers such as Radon-222 (^{222}Rn), nutrients can infiltrate sediments and drain back to the surface creek waters, depending on the strength of the tidal pump (Gleeson et al., 2013). This implies that dissolved inorganic and organic carbon may find its way from deeper sediments into surface waters and atmosphere by tidal pumping mechanism.

Further, climate change is predicted to cause sea level rise that enhances salt-water intrusion in freshwater marshes and coastal estuaries. The resulting saline conditions impact tidal freshwater ecosystems significantly, by lowering primary production and deposition of organic matter by the inhabiting plant communities (Spalding & Hester, 2007). Moreover, salt-water intrusion has a long term effect on microbial cycling of carbon in wetlands due to increase in sulphate ion concentration, causing sulphate ion reduction as a terminal carbon mineralisation process instead of the anaerobic methanogenesis. Previous studies indicate that there is a high concentration of sulphate ions (20-30 mmol L^{-1}) (Chambers et al., 2011) in seawater compared to freshwater wetlands (< 0.1 mmol L^{-1}) (Weston et al., 2011). This piece of work concurs with others studies that emphasize the occurrence of methane oxidation, in the presence of a threshold level of sulphate ions in saltmarsh wetlands under anaerobic conditions.

2.6 Drivers of carbon accumulation and emission in wetlands

2.6.1 Quality and quantity of organic matter

Substrate availability largely determines methane production rates. Seasonal loading of fresh organic carbon into upper sediment layers in aquatic ecosystems trigger methane formation process by microbial communities (Schwarz et al., 2008). This theory also applies in deeper sediments that receive more labile organic matter molecules by diffusion. The rate of methanogenesis is positively

correlated with proportions and quality of organic matter used as substrate by methanogens. In submerged soils, the intensity of microbially mediated redox processes depends on the content and type of organic matter, the capacity of microorganisms to decompose the organic matter, and the number and availability of electron acceptors. Rice field soil studies indicated a positive correlation between methanogenesis and organic matter content only non-saline soils, and no significant relationship was observed in saline soils (Le Mer & Roger, 2001). This relationship between organic matter and salinity of the soils was explained by the inhibition of methanogenesis by salinity.

Freshwater sediments with low C: N ratio (< 10) have greater methane production rates compared to those with high C:N ratio (> 10) (Nguyen, Crill, & Bastviken, 2010), and the presence of alternative electron acceptors such as Mn^{4+}, Fe^{3+}, NO_3^- and SO_4^{2-} reduces methane formation rates due to their competitive inhibition role in methanogenesis (Duc et al., 2010). More to this, addition of different organic materials such as crop residues significantly influences CH_4 oxidation in different ways, depending on the C: N ratios. If the C: N ratio is low (high nitrogen content), there will be a decrease in CH_4 oxidation. Presence of elevated NH_4^+ increases NH_4^+ oxidation, thus inhibiting CH_4 oxidation. On the other hand, release of residues with high C: N ratio has no significant effect on CH_4 oxidation rates (Wendlandt et al., 2010).

In wet peat soil studies, CH_4 production was dependent on organic matter particle size, and results demonstrated that large particles of the magnitude > 2.0 mm indicated a significant contribution to the total CH_4 production capacity. Additionally, CH_4 production capacity reduced significantly with increase in depth, and a positive relationship was observed within a layer of 0 – 5 cm, showing that the major substrates suitable for methanogenesis are the recent plant residues (Van den Pol-van Dasselaar & Oenema, 1999).

2.6.2 Temperature

According to Borrel et al.(2011), temperature has direct and indirect effects on methane production rates in freshwater aquatic ecosystem sediments. Sediment temperatures significantly influence methane production rates, and the numbers of methanogenic bacteria. Leaving rates of methane formation are correlated with elevated sediment temperatures (Kankaala et al., 2004; Westermann, 1993; Xiao et al., 2013). Previous research findings show that there is an optimum range of temperature (20 - 30 ^oC) below which methanogenesis is substantially reduced, but this depends on the methanogenic community available (Olsson et al., 2015).

Temperature also has an indirect effect on production of methanogenic substrates especially during hydrogenotrophic methanogenesis (Borrel et al., 2011). Through laboratory analysis of arctic thaw

pond samples, research results demonstrate that CH_4 and CO_2 production rates increased with temperature (4 ^oC to 9 ^oC), but at different rates (Negandhi et al., 2016). Erhagen et al (2013), and Olefeldt & Roule (2012) noted that CH_4 production has a higher temperature sensitivity (high Q_{10} values) than CO_2 production (respiration) and CO_2 consumption by photosynthesis in aquatic ecosystems assuming the availability of appropriate substrates. Therefore, methanogenesis has the potential to be more temperature sensitive than photosynthesis.

Increased CO_2 concentration and high temperatures increase methanogenesis and decrease methane oxidation in rice paddies (Das & Adhya, 2012). Studies show that CH_4 emissions from these soils increase with increasing concentrations of carbon dioxide in the atmosphere and temperature due to global warming (Das & Adhya, 2012). This effect is connected to a decrease in soil redox potential and an increase in carbon substrates such as acetate, and hence favouring methanogens. In addition, populations of methanotrophic bacteria decrease as redox potentials decrease in a carbon dioxide rich environments in short term laboratory conditions with highly controlled conditions ((Das & Adhya, 2012)

2.6.3 Water table and oxygen availability

The level of water table plays an important role in influencing methane emissions since high water tables limit the amount of oxygen available in the water columns, and therefore, reducing the redox potentials, which in the end, favour methanogenesis in aquatic wetland soils (Olsson et al., 2015). Low water table is related to high oxygen concentration that favours oxidation of methane by methanotrophic communities, and oxidation is the most important process in for CH_4 consumption in the soil. For example, Couwenberg et al.(2011), demonstrated that water tables below 20 cm showed no methane emissions at all in peatlands while sites where the water table was above 20 cm showed a noticeable range of methane emissions (> 0 to 500 kg CH_4 $ha^{-1}yr^{-1}$).

Zhu et al., (2014) found out that decrease in water table due to little precipitation and high evapotranspiration in herbaceous peatlands and gley marshes, low CH_4 emissions were registered compared to the times when the water table was high. Low water table not only favours aerobic methanotrophy but also aerobic breakdown of organic matter, and these two processes lead to emission of carbon dioxide (Olsson et al., 2015). Therefore, this can lead to the production of more carbon dioxide compared to methane.

2.6.4 Vegetation

Vegetation cover is a good parameter used to predict the fluxes of greenhouse gases because its quality and structure depict other prevailing factors such as nutrient availability, soil pH and history of the site and these factors can be correlated to greenhouse gas fluxes. Furthermore, vegetation is

related to long term water level conditions that demonstrate the average GHG fluxes annually (Couwenberg et al., 2011). The presence of vegetation can increase CO_2 fluxes mainly through photosynthesis and total ecosystem respiration (Han et al., 2013) by increasing the amount of organic matter which can undergo decomposition.

CH_4 emissions can also be influenced by the vegetation in a number of ways; the oxygen that is released from the roots form aerobic microsites in the rhizosphere, and this allows CH_4 produced to be oxidised by methanotrophs (Grünfeld & Brix, 1999). Whiting & Chanton (1996) stated that CH_4 concentration in lacunal air of *Peltandra virginica* fluctuates over the course of the day indicating that a bigger fraction of CH_4 is oxidised during transport through plant tissues in the day hours compared to night time. In addition, high primary productivity also increases the availability of carbon substrates for methanogenic activity through biomass decomposition and secretion of root exudates and this can lead to increased CH_4 emissions (Van der Nat & Middelburg, 2000). The process of photosynthesis in plants provides a source for carbohydrates which can be released through plant tissues such as roots along with carbon dioxide from respiration, and all these plant products are used as substrates by microorganisms (Long et al., 2010).

The structure of plants significantly influences the mechanism of transport of the greenhouse gas, and this in turn determines the rate and concentration of the emitted gas into the atmosphere. For example, CH_4 is transported through the aerenchyma tissues (Long et al., 2010) of rice and *Phragmites australis*. Wetland vegetation which has internal air spaces usually provide an alternative transport pathway in addition to diffusion and ebullition from the water sediments (Henneberg., 2012). CH_4 produced from the soil and transported through aerenchyma can easily bypass the water column and reach the atmosphere without being oxidised (Whalen, 2005). Therefore, the type of vegetation available in the wetland may increase or decrease CO_2 and CH_4 fluxes depending on the existing environmental conditions.

2.7 Diurnal and seasonal variations of CH_4 and CO_2 fluxes

Diel variations of CH_4 and CO_2 fluxes demonstrate which biochemical processes occur relatively rapidly in natural aquatic environments, and these variations play an important role in natural water ecosystems (Nimick et al., 2011). The diel variations of methane are widely correlated with both biotic and abiotic components of ecosystems, including temperature, irradiance, plant biomass, and gas transport mechanisms (Whiting & Chanton, 1996; Zhang & Ding, 2011).

During the day, CH_4 emissions are higher than night emissions because the higher the soil temperature in the day, the higher would be CH_4 produced (Tong et al., 2013). This finding however is in contradiction with what King et al. (1990) stated that oxygen levels in water column

and also associated with root inputs can often be higher during the day, thus reducing CH_4 production. The emission of CO_2 from the soil entirely depends on root respiration and decomposition of organic matter. These processes are active biochemical in nature and are dependent upon temperature (Davidson & Janssens, 2006). Temperature has a strong effect on the rate of decomposition of organic matter in wetland soils, and therefore increase in CO_2 and CH_4 emissions tends to increase with an increase in soil temperature (Herbst et al., 2011; Inglett et al., 2012). Studies have shown that diurnal variation of CH_4 emissions with temperature in aquatic fields indicated a positive correlation with distinct diurnal trends (Sass et al., 1994). Daily variations of CH_4 with temperature demonstrated a consistent pattern, with the highest CH_4 fluxes noted in early afternoon and lowest fluxes in early morning.

Diurnal variation patterns of CH_4 fluxes can also be affected by oxygen concentration. For example, the variations showed emission peaks at night due to a low activity of methanotrophic bacteria because of no photosynthesis occurring, otherwise, aerobic oxidation would occur leading to low CH_4 emissions (Andales et al., 1994). Changes in abundance and species composition of microbial populations can significantly determine CH_4 fluxes in natural ecosystems. The abundance and activities of individual species of microorganisms vary greatly with variations in seasons with different environmental conditions (Turetsky et al., 2008).

CH_4 dissolved in soil water can be absorbed into aerenchyma tissue in plants and released into the atmosphere by transpiration, and this contributes to diurnal variation in CH_4 flux from wetland ecosystems (Nisbet et al., 2009). The ability of plants to have an influence on CH_4 flux into the atmosphere therefore is a strong indicator that seasonal variation in the growth and development of plants has a relationship with seasonal variation in methane fluxes. Also, the higher the rate of primary productivity, the more the changes in carbon source-sink potential of the wetland ecosystem (Chambers et al., 2011). In related research, Hirota et al (2007) found out that water level and water temperature fluctuations influenced GHG fluxes in a salt marsh ecosystem. In summers, the high humid climatic conditions support high productivity and influences inputs of organic carbon into the soil while in winter the rate of decomposition of organic carbon is relatively low due to cold conditions (Zhao et al., 2010).

Chapter 3: Materials and methods

A number of field methods were employed (from August 2015-July 2016) to measure turbulent heat and gas fluxes, specifically, sensible and latent heat fluxes (W m^{-2}), CO_2 flux (mg m^{-2} s^{-1}), CH_4 flux (µg m^{-2} s^{-1}) and momentum transfer, U* (m s^{-1}) by using eddy covariance technique. In addition, other instruments were installed to measure environmental factors, and these included electrical conductivity, EC (µS cm^{-1}), soil and water temperature (^oC), rainfall (mm) and water level (m). Meteorological parameters such as air temperature, pressure, and wind speed and direction were also obtained in situ or from a nearby BOM weather station. Details for these measurements are given below.

3.1 Study site

Measurements were carried out in Tomago wetlands in Hunter estuary, NSW, Australia (32º51'52"S, 151º42'15"E), and fluxes were recorded for 1 year. In its natural state, Tomago wetland was an estuarine wetland mainly covered by saltmarsh and mangroves. There was construction of levee and a drainage system between 1913 and 1928, and this led to dominance of grasses for grazing animals, in addition to weeds which were initially less adapted to flooded aquatic environment. Further expansion of the drainage system was done between 1968 and 1980 with the construction of flood gates by the NSW works department to; promote agriculture in the wetland, direct water from smaller floods downstream and provide a flood detention basin in a bid to protect New Castle from heavy floods.

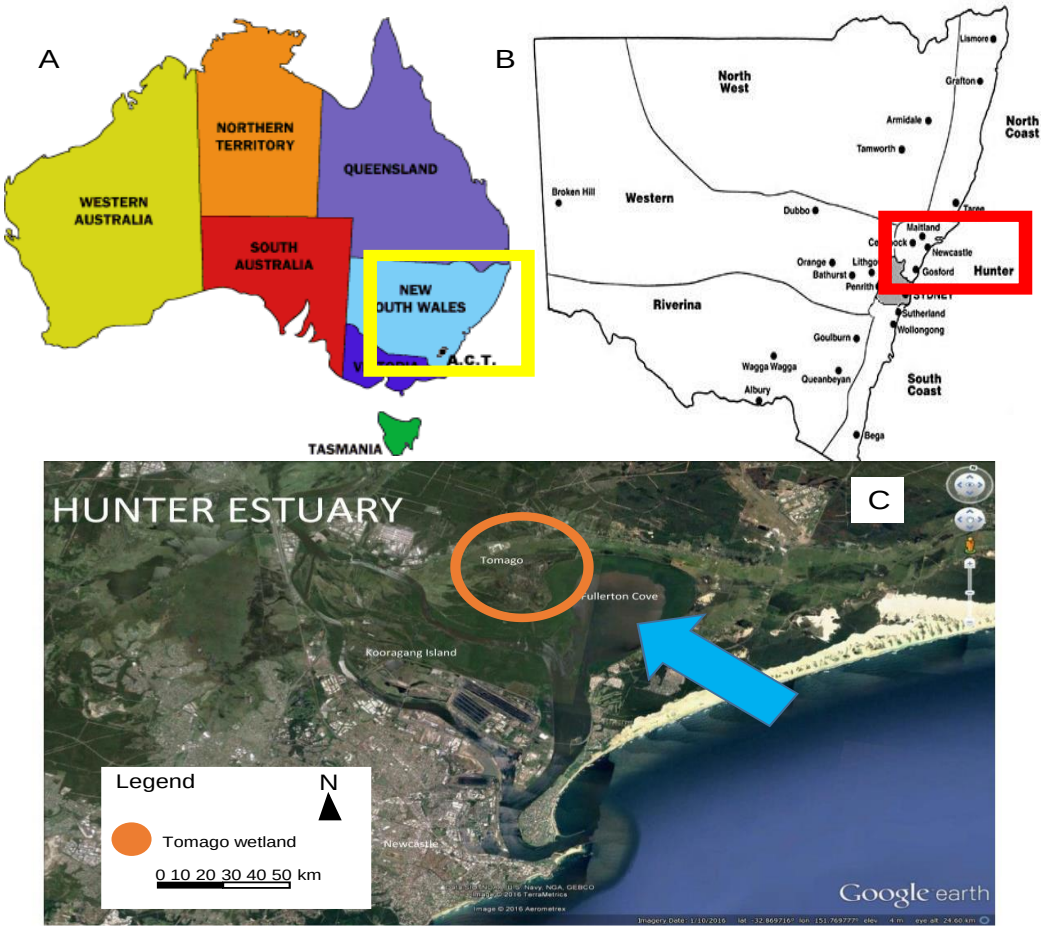


Figure 2: Shows the study area. A-Map of Australia showing New South Wales, in which the study area is located. B-Map of New South Wales showing neighbouring urban centres to the study site. C-Google map of the Hunter estuary in which Tomago (study site) is located

3.2 Gas flux measurement

The eddy covariance (EC) was used, and the system comprised of: the LI-7700 CH_4 open-path gas analyser (LI-COR Biosciences, Lincoln, NE, USA), a Gill WindMaster 3D sonic anemometer (Gill Instruments Limited Lymington Hampshire, UK) and the LI-COR 7500 CO_2/H_2O open-path gas analyser (LI-COR Biosciences). Eddy covariance data were logged through the LI-COR 7550 and smart flux system producing high resolution (i.e., tenth of a second data for all parameters) and half hour fluxes. The major advantage of using the open path analysers is that the instruments have lower power consumption, and therefore were considered suitable to run on solar powered batteries in a remote area, such as Tomago. However, open path gas analysers are prone to interference by any phenomena that interrupts the sensor path such as birds, insects and precipitation. The measuring height was 3.5 m above the ground, and the system recorded data after every 30 minutes. Instruments were installed in August 2015 before flooding, and data was collected up to July 2016.

3.2.1 Eddy covariance

A B

Figure 3: Shows A-Components of open gas analyser system for CH_4 (LI-770), CO_2/H_20 (LI-7500A) and Sonic anemometer (CSAT3). B- Similar equipment (as in A) that was used at the Tomago wetland study site, with a big portion of the site inundated during December 2015.

The eddy covariance (EC) method was used to provide direct measurement of the turbulent flux of methane and carbon dioxide. The Tomago site offered an ideal setting for the application of the EC method (Foken, 2008; Pattey et al., 2006). The eddy turbulent flux was computed basing on the following assumptions among others; terrain was horizontal and uniform, steady environmental conditions (Pattey et al., 2006), and detection of small changes at very high frequency.

Mathematically, in turbulent flow, vertical flux can be expressed as,

$$F = \bar{\rho}\,\overline{w's'}$$

Where $F$is the flux equal to a mean product of air density (ρ), vertical wind speed (w) and the dry mole fraction (s) of the gas of interest in the air.

3.3 Measurement of environmental variables

Soil water temperature and radiation parameters were recorded onto a CR3000 data logger (CR3000; Campbell Scientific). Electrical conductivity (µS cm^{-1}) data were logged by the HOBO instrument that was placed below the water table. This type of data logger was selected to be used because of the larger dynamic range that could be faced in the experiment. The loggers have a USB interface that allows for data offload in the field, even during wet conditions. With long-life lithium battery and operating range as low as 28°F, these loggers withstand extended deployment in rough conditions. The EC logger was placed in a perforated pipe to allow entry of water so that the logger sensor was submerged in water within the pipe. It was then held in suspense within the pipe by using a string tied at the upper end of the pipe. The pipe was placed at a depth of 90 cm in the soil

under water at the inundated area. Data was downloaded by using the installed HOBO software onto the computer at the study site, after every one month for a period of one year.

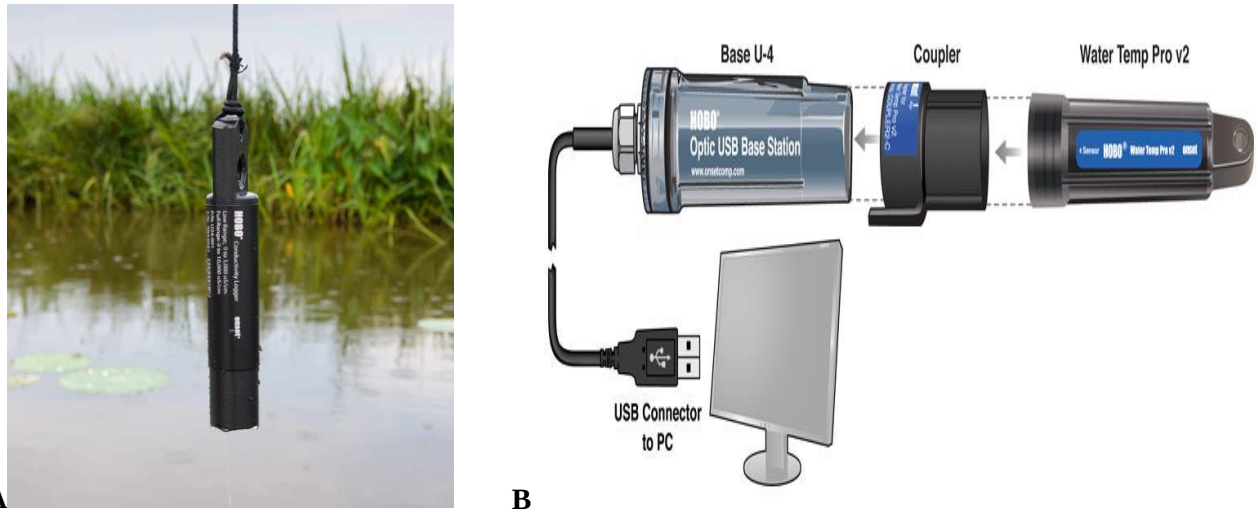


Figure 4: A-Demonstrates innovative ways of deploying a HOBO data logger in flooded environments. B-How the HOBO data logger connects to a computer while downloading data which in most cases is carried out in the field.

Water level was measured using the HOBO U20L-004 research-grade water level data logger which has a 0.1 % level of accuracy in measurement. It is covered by a polypropylene housing that makes it fit to be used in both freshwater and salt water environments, and its non-vented design allows easy deployment in aquatic ecosystems. The logger was fixed flat on the ground surface and then any water depth above it was recorded as a positive water depth value and the negative value was returned whenever there was no water over the logger. All the values (negative and positive) of water depths were recorded in meters. The HOBO U20L-004 was chosen because the HOBOware Pro software allows easy conversion to obtain accurate water level reading with compensation for barometric pressure, temperature and water density.

Rainfall data (mm) from August 2015 to May 2016 was obtained from Williamtown station, Bureau of Meteorology (BOM), NSW, and it was measured using a tipping bucket rain gauge. http://www.bom.gov.au/places/nsw/williamtown/

Data about tidal times and heights for Newcastle-NSW were downloaded from the Bureau of meteorology website: http://www.bom.gov.au/ntc/IDO59001/IDO59001_2016_NSW_TP002.pdf. The corresponding flux data was selected basing on the time for the occurrence of the tide.

3.4 Data capture, processing and QA/QC

The eddy covariance flux data at a frequency of 10 Hz was processed from the LI-COR smart flux system and EddyPro® software (available through LI_COR Biosciences). Foken level 2 QA/QC criteria were applied to all the EC data.

Quality assurance (QA) and quality control (QC) were applied to the data sets. CH_4 and CO_2 flux values associated with spikes resulting from signal loss or instrument malfunctions were removed. Data gaps in some dates of the months were due to maintenance and cleaning of instruments or due to power failure. In addition, high fluctuations in turbulence, especially at night due to low winds, resulted into poor quality data and such data was also filtered out.

The installed LI-7700 has two diagnostic outputs which were used to filter half-hourly values where the instrument was performing poorly. It has the received signal strength indicator (RSSI), which indicates the cleanliness of the mirrors, and a coded value that represents one or more pieces of diagnostic information. Low RSSI values do not always lead to outliers or spikes, but need to be combined with diagnostic code values to properly filter instances of the instrument malfunction from the data. There are also occasions when the mirrors are clean but the diagnostic value records malfunctions (Dengel et al., 2011). For the case of this study, data with signal strength above 20 for CH_4 was considered while the signal strength for CO_2 sensor was set at 80.

Sensible heat flux data was also used to perform quality assurance and quality control the data for outliers. This was achieved by considering fluxes that were in the range of -50 – 500 W m^{-2}. All the values that were outside this range were deleted before computing diurnal sensible heat fluxes. A filter of three times the standard deviation was applied to remove spikes that were not attributable to non-optimal instrument operation. The daily averages of sensible heat flux (W m^{-2}) were used to calculate the day-night transition to determine day and night time hours for CH_4 and CO_2 fluxes. If the sensible heat flux value was greater than 10 W m^{-2}, then the point was considered to be day while values less than 10 W m^{-2} were labelled night (Figure 5, below).

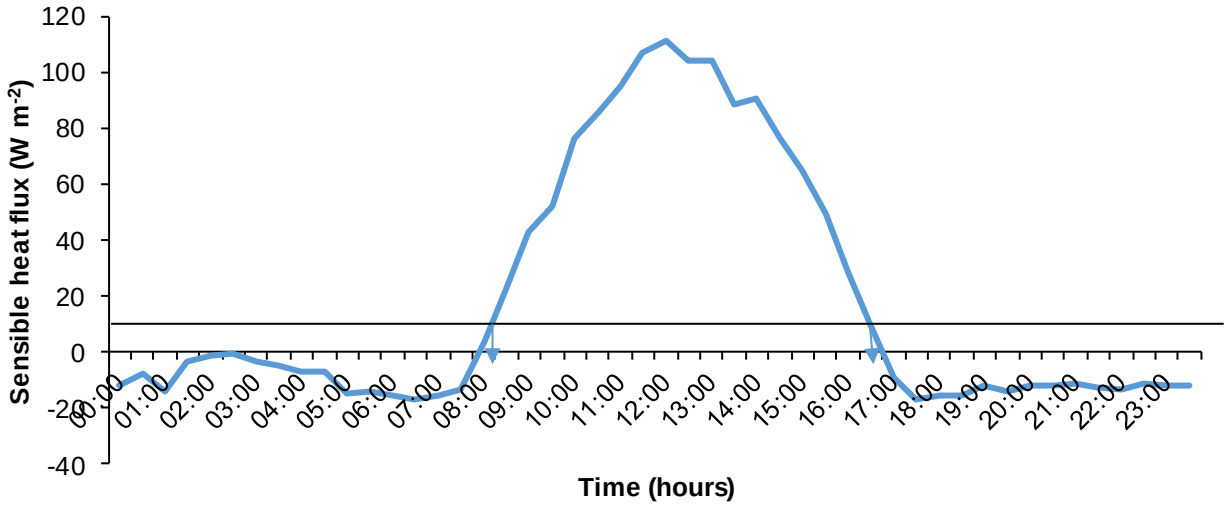


Figure 5: Shows how diurnal variation of sensible heat is used to estimate day and night hours for the month of August 2015

The morning solar energy heats up the soil air molecules to rise into the atmosphere. However, the minimum amount energy absorbed by the soil surface to cause vertical movement of air molecules is 10 W m^{-2}. As the sun sets, the warmed up air moves downwards losing out its energy and heat is absorbed by the soil. Therefore, from figure 5 above, day time fluxes started to occur at 8:30 while night time fluxes occurred at 17:00. The same procedure was followed to identify day and night hours for the rest of the months during data analysis (Figure 28).

3.5 Statistical analysis

Raw processed data was entered into excel sheets and analysed by computing the averages, standard deviations, and standard errors of CH_4 and CO_2 monthly and daily fluxes. In order to investigate diurnal variations of CH_4 and CO_2 fluxes, averages values of fluxes for every 30 minutes interval were calculated for every month. Data was then presented in form of Line graphs in addition to bar graphs for easy interpretation in explain diurnal and monthly variations of methane and carbon dioxide flux patterns and trends. The relationships between environmental factors (soil-water temperature, rainfall, water level, tidal height and electrical conductivity) and GHG fluxes were explored using line and bar graphs, and linear regression with associated correlations at 95% confidence interval. The relationships between different electrical conductivity, rainfall and water temperature were studied using line graphs on a monthly scale.

Chapter 4: Results

4.1 Diurnal variations of CO_2 and CH_4 fluxes, and with environmental factors

4.1.1 Diurnal variations of CO_2 and CH_4 fluxes

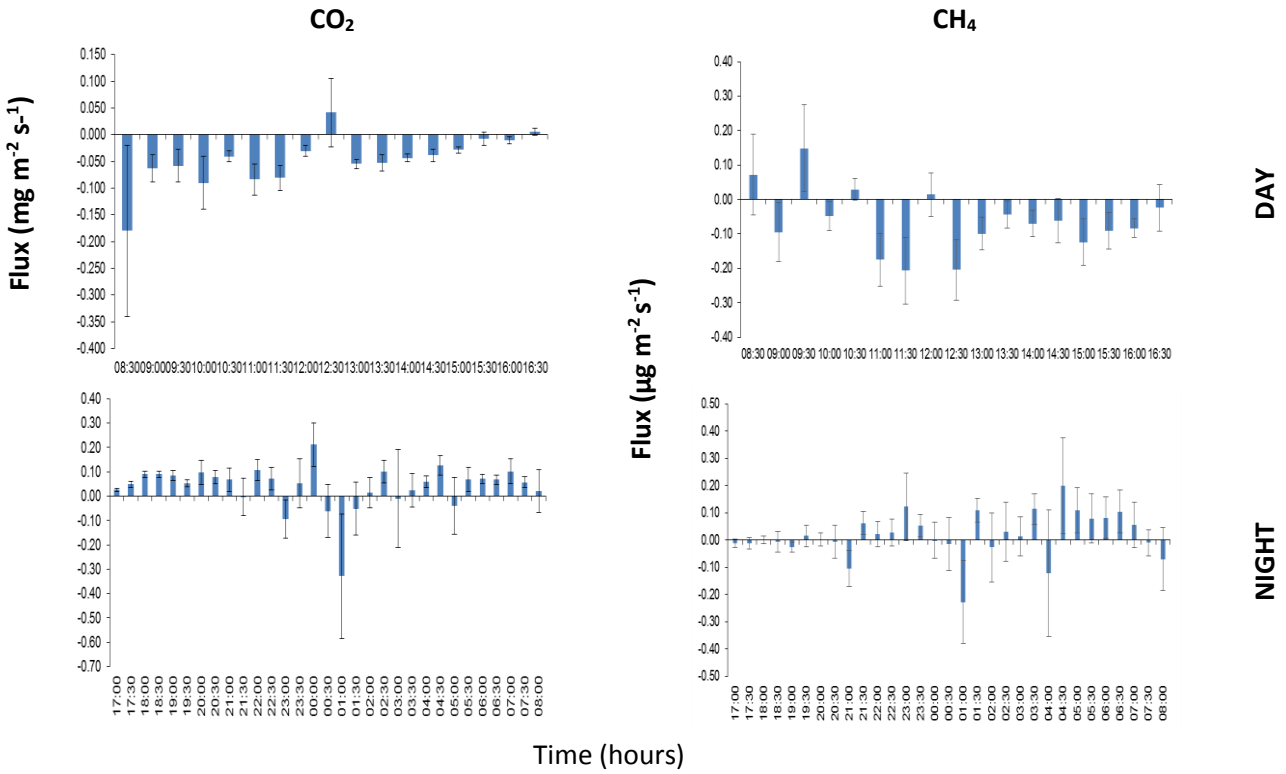


Figure 6: Diurnal variation of CO_2 and CH_4 fluxes in August 2015

August 2015: There was a high rate of CO_2 uptake in the morning and early afternoon day hours during August. The highest rate of CO_2 uptake (-0.18 mg m^{-2} s^{-1}) from the marsh was attained at 08:30 hours followed by -0.09 mg m^{-2} s^{-1} at 10:00 hours and then -0.08 mg m^{-2} s^{-1} at 11:00 and 11:30 hours. The lowest diurnal CO_2 absorption rate was -0.008 mg m^{-2} s^{-1} at 15:30 hours. The maximum CO_2 uptake in the morning is 22 fold the lowest CO_2 uptake which occurred in the evening. CO_2 emissions dominated over CO_2 uptake during nocturnal hours in August 2015. The highest CO_2 emission from the marsh to the atmosphere occurred at 00:30 hours with an emission rate of 0.39 mg m^{-2} s^{-1} followed by 0.21 mg m^{-2} s^{-1} at 0:00 hours. The average CO_2 flux during the day was -0.05 mg m^{-2} s^{-1} while the night time average flux was 0.04 mg m^{-2} s^{-1}.

Results show high CH_4 uptake occurred mainly between the mid-morning hours and early afternoon hours (09:00 – 14:30). The highest CH_4 consumption from the marsh occurred at 01:00 hours with an uptake rate of 0.23 µg m^{-2} s^{-1}. Results indicate the lowest CH_4 consumption rate (0.0007 µg m^{-2} s^{-1}) at 00:00 hours. Although the study shows possible CH_4 emissions during the day, it only

occurred in morning hours between 8:30 and 12:00. The average CH_4 flux was -0.06 µg m^{-2} s^{-1} in the daytime and 0.02 µg m^{-2} s^{-1} during the night.

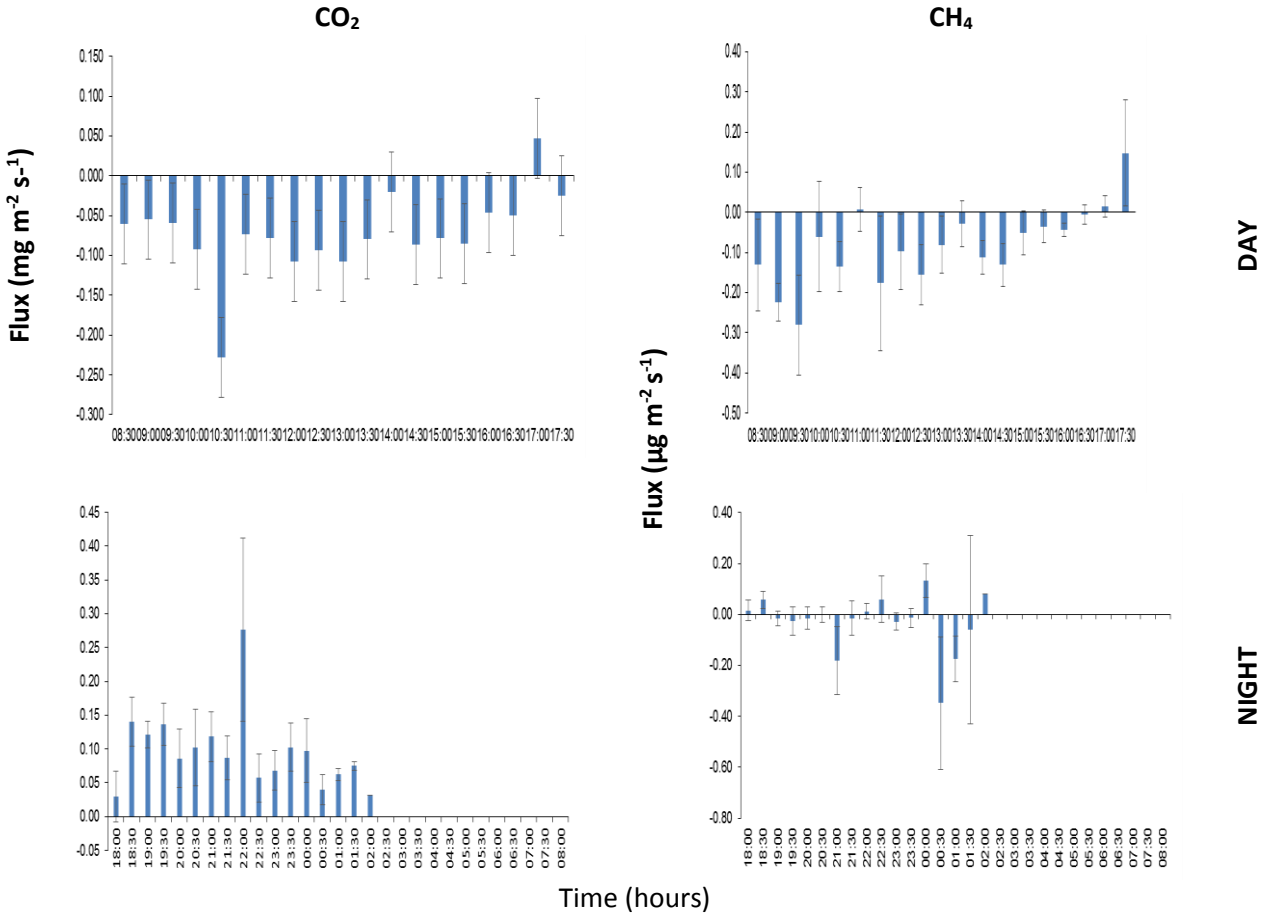


Figure 7: Diurnal variation of CO_2 and CH_4 fluxes during September 2015

September 2015: Results reveal high CO_2 uptake during the day, peaking at -0.23 µg m^{-2} s^{-1} at 10:30 hours followed by -0.108 mg m^{-2} s^{-1} at 1:00 hours. Early morning and evening hours indicated low CO_2 uptake rates during the day throughout the month. Nocturnal hours were characterised by CO_2 emissions only, with no occurrence of CO_2 uptake. The average CO_2 flux during the day was -0.07 mg m^{-2} s^{-1} while night time fluxes averaged at 0.10 mg m^{-2} s^{-1}. There were no CO_2 fluxes recorded between 02:30 and 08:00 hours.

Results show CH_4 consumption for most hours during the day (8:30 – 15:00 hours) with the highest CH_4 uptake (-0.28 µg m^{-2} s^{-1}) at 09:30 hours. For most day time hours, CH_4 consumption rates were more than twice as high as CH_4 emission rates during the night in September. The maximum CH_4 uptake into the marsh at night was -0.23 µg m^{-2} s^{-1} at 00:30 hours. The average CH_4 flux recorded at night was -0.03 µg m^{-2} s^{-1} while day time hours registered -0.08 µg m^{-2} s^{-1}.

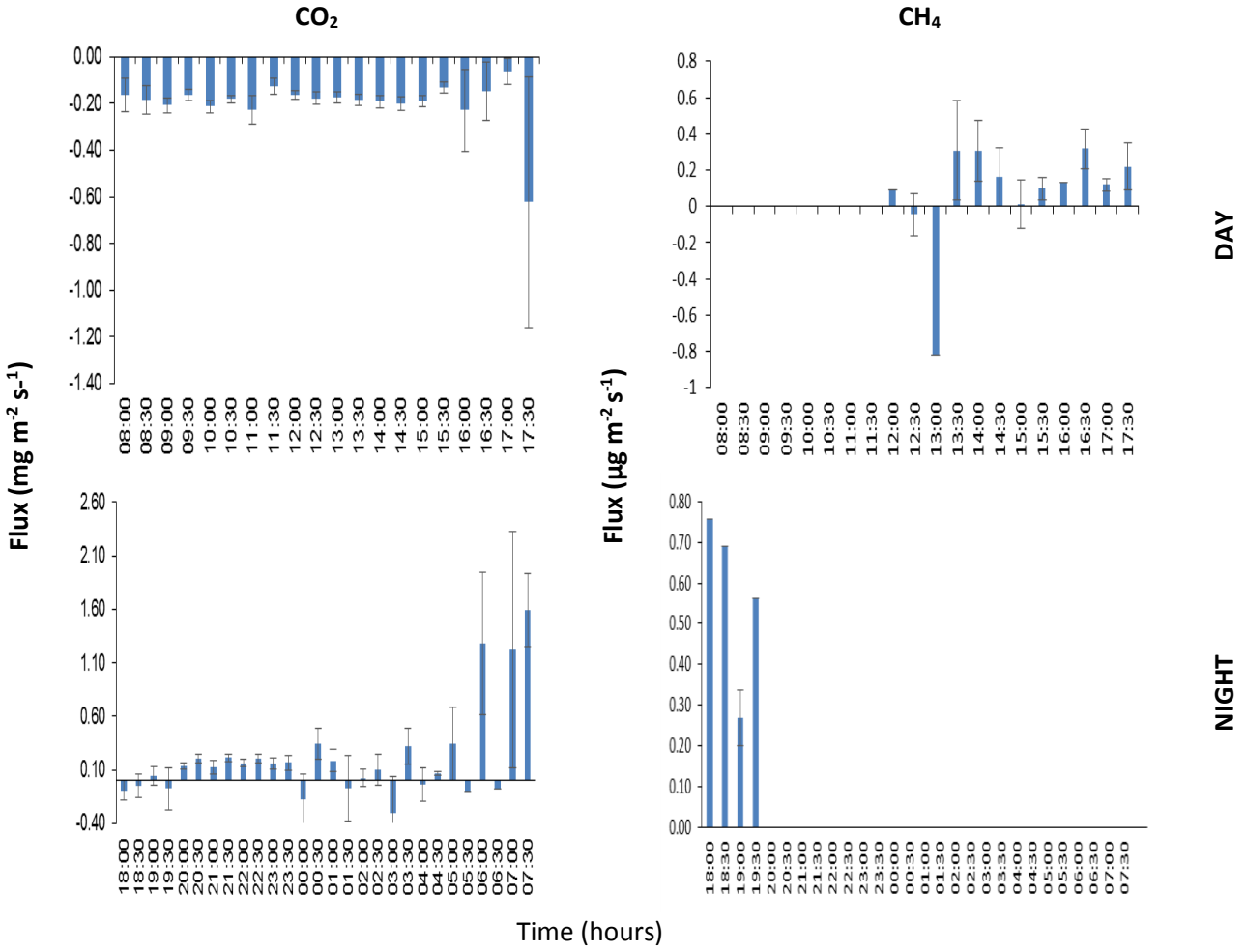


Figure 8: Diurnal variation of CO_2 and CH_4 fluxes in October 2015

October 2015: During the day, CO_2 fluxes ranged from -0.06 to -0.62 mg m^{-2} s^{-1}. The maximum CO_2 uptake (-0.62 mg m^{-2} s^{-1}) was noted during the day at 17:30 hours. There were no average CO_2 emission rates registered during the day throughout October. The majority of night emissions were low CO_2 fluxes (0.02 – 0.35 mg m^{-2} s^{-1}) between 19:00 – 05:00 hours. This was followed by an increase in CO_2 fluxes with a peak (1.59 g m^{-2} s^{-1}) at 07:30 hours. The average CO_2 flux during day time was -0.2 mg m^{-2} s^{-1} and average CO_2 flux for nocturnal hours was 0.21 mg m^{-2} s^{-1}.

Limited data about CH_4 flux during this month was recorded due to instrument maintenance. However, available results show CH_4 emissions dominating over CH_4 uptake during the day and night with flux of 0.32 µg m^{-2} s^{-1} and 0.76 µg m^{-2} s^{-1} at 16:30 and 18:00 hours respectively. The average CH_4 flux recorded during the day was 0.08 µg m^{-2} s^{-1} while at night; an average of 0.57 µg m^{-2} s^{-1} was noted.

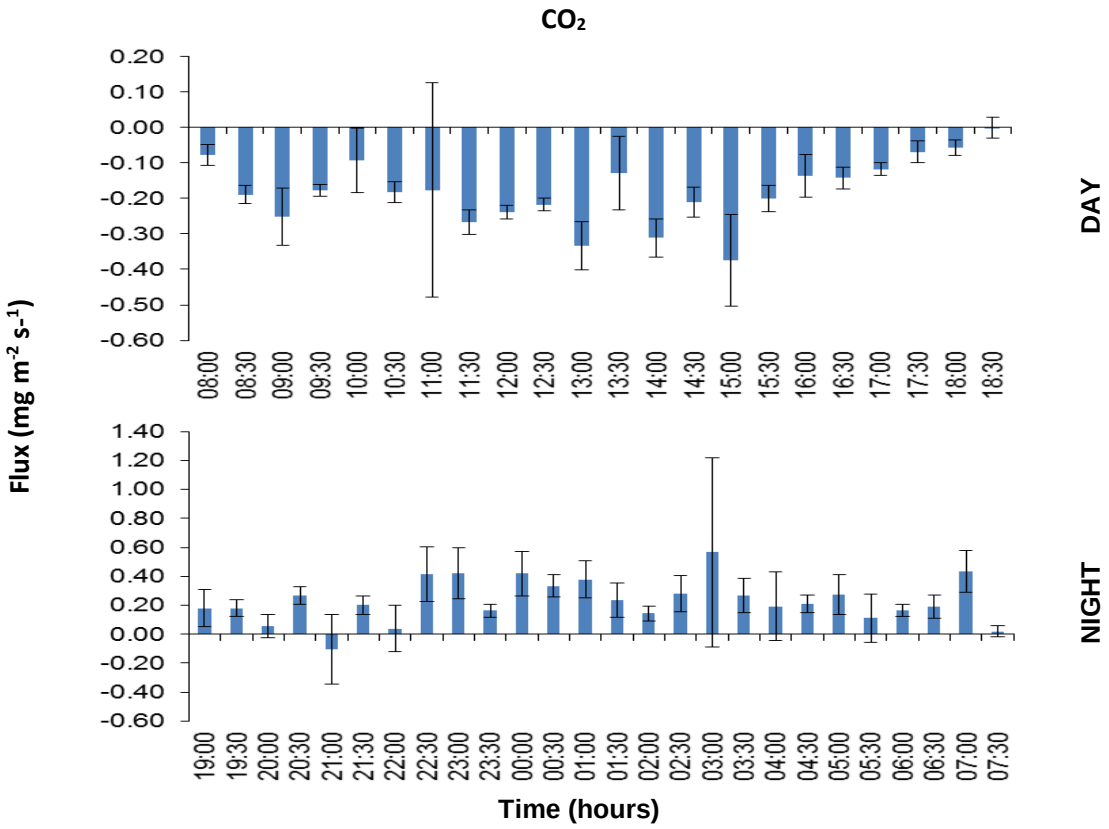


Figure 9: Diurnal variation of CO_2 flux in November 2015

November 2015: In November, CO_2 fluxes ranged from -0.37 to 0.57 mg m^{-2} s^{-1}, with an average CO_2 flux of -0.18 mg m^{-2} s^{-1} in the day time and 0.23 mg m^{-2} s^{-1} at night. Diurnal variation of CO_2 flux demonstrated a markedly clear pattern, with all the day time average fluxes showing uptake of CO_2 and all night hours indicating emissions of CO_2 except at 21:00 hours where the average CO_2 uptake (-0.10 mg m^{-2} s^{-1}) occurred. Results reveal that high uptake of CO_2 in November occurred during early afternoon and some morning hours. It is also shown that the lowest CO_2 uptake occurred in the morning and evening hours. In general, high fluxes of CO_2 emissions were observed in the middle of the night (between 22:30 – 3:00 hours) while high rates of CO_2 uptake occurred in the afternoon hours during the day. There was no data of CH_4 flux collected during November.

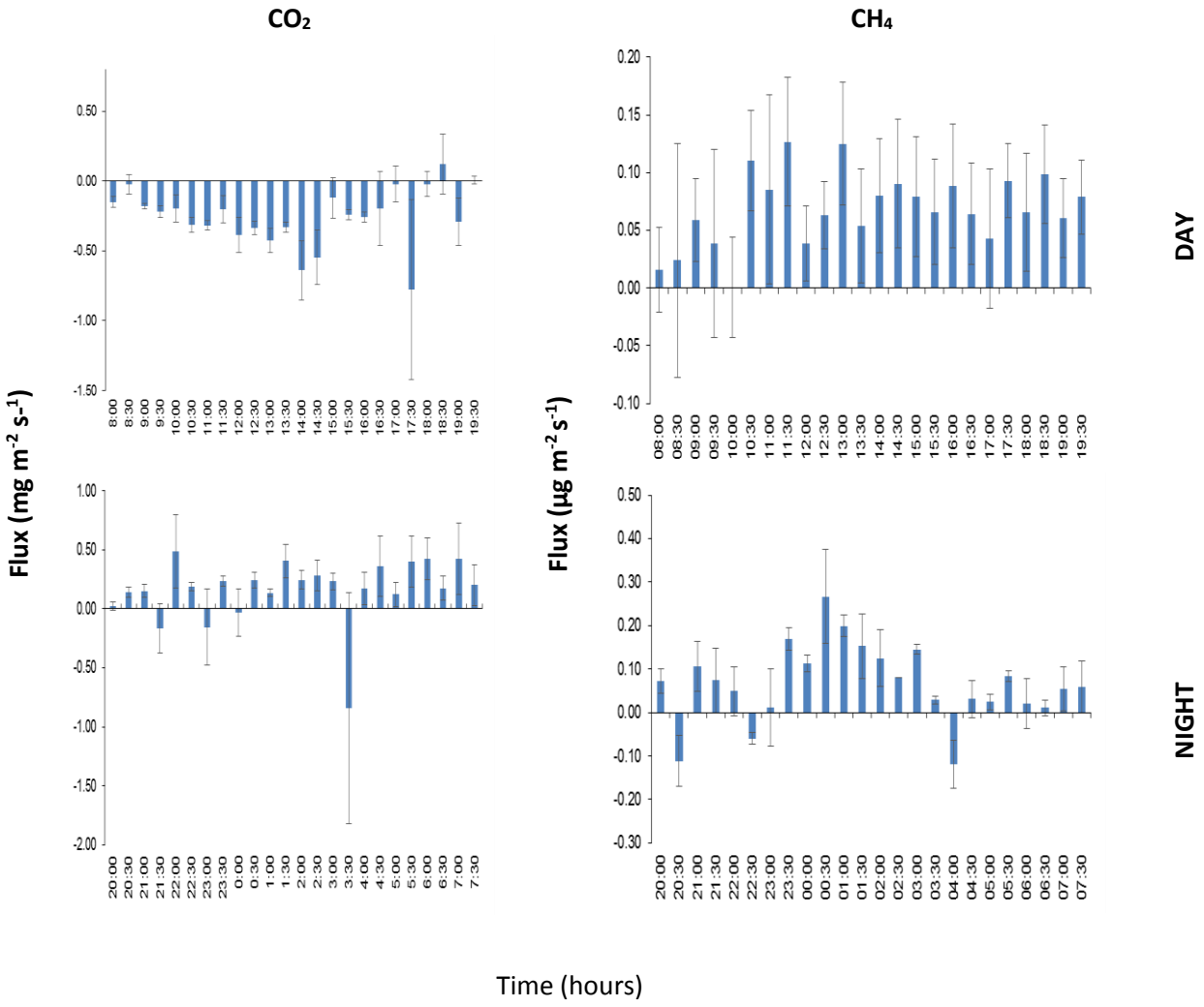


Figure 10: Diurnal variation of CO_2 and CH_4 fluxes in December 2015

December 2015: During the night time, the tidal marsh behaved majorly as CO_2 source with the highest CO_2 flux (0.48 mg m^{-2} s^{-1}) occurred during the night at 22:00 hours while the lowest CO_2 efflux (0.02 mg m^{-2} s^{-1}) was registered at 20:00 hours. However, there were fluctuating CO_2 flux patterns with emissions and uptake occurring during the night. The maximum CO_2 uptake in the day time was -0.78 mg m^{-2} s^{-1} while CO_2 uptake peak was -0.84 mg m^{-2} s^{-1} at night. The average CO_2 flux in the day time was -0.25 mg m^{-2} s^{-1} while nocturnal average of CO_2 flux was 0.16 mg m^{-2} s^{-1}.

In December, there was an obvious CH_4 emission peak value (0.13 µg m^{-2} s^{-1}) by the marsh at 11:30 and 13:00 hours in the day time. The minimum CH_4 emission recorded during the day was 3.64 x 10^{-4} µg m^{-2} s^{-1} at 10:00 hours, which was more than 30 times lower than the minimum CH_4 flux (0.011 µg m^{-2} s^{-1}) recorded at 06:30 hours night time. The average CH_4 flux noted during the day in December was 0.07 µg m^{-2} s^{-1}. There was no average CH_4 uptake recorded in the day hours throughout the month. The maximum CH_4 emission during the night was 0.27 µg m^{-2} s^{-1}, and this occurred at 00:30 hours, and was more than twice as high as the maximum CH_4 flux recorded in the

day time. The maximum CH_4 uptake at night was -0.12 µg m^{-2} s^{-1} at 04:00 hours, and the average CH_4 flux at night was 0.073 µg m^{-2} s^{-1}.

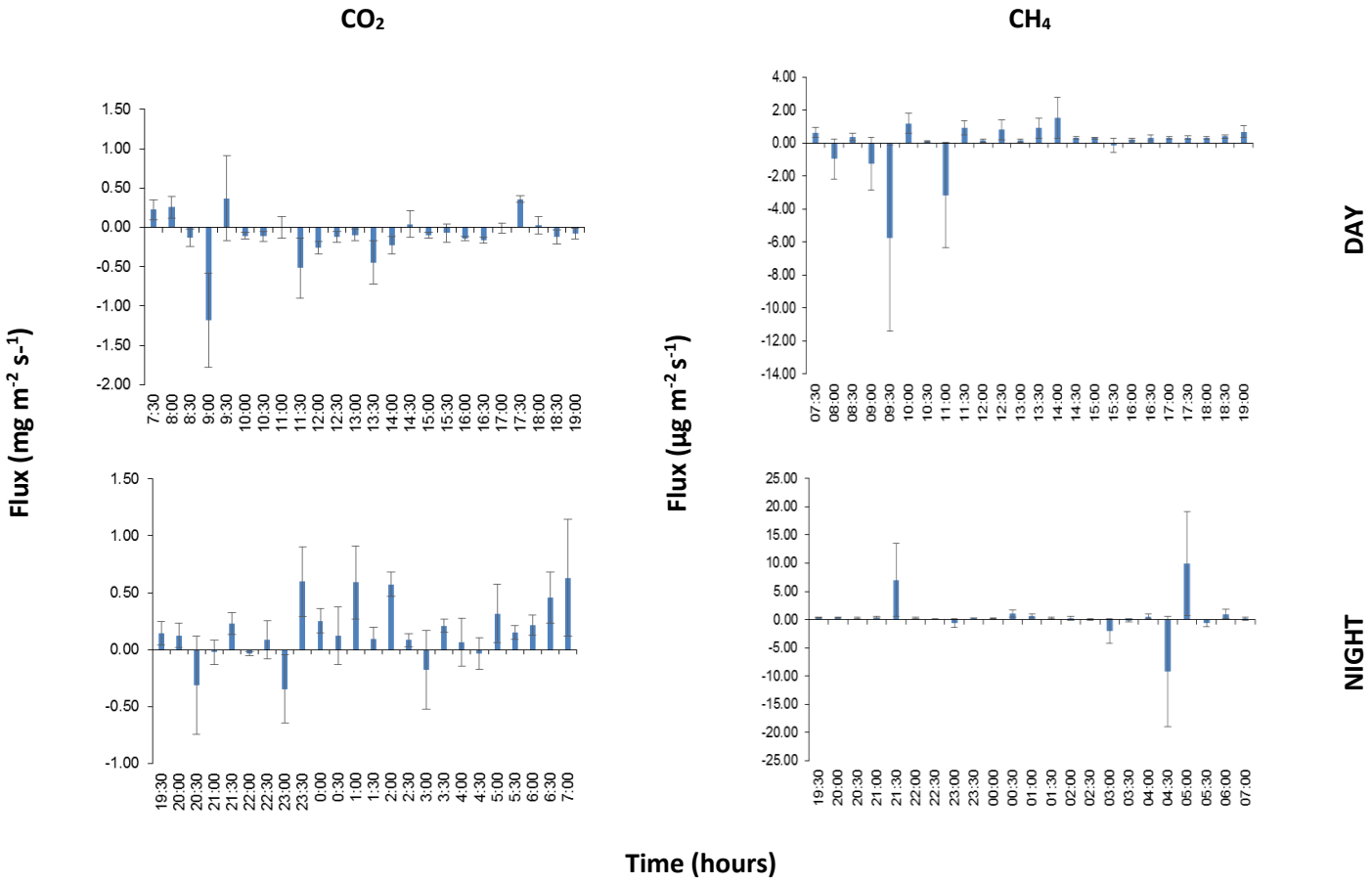


Figure 11: Diurnal variation of CO_2 and CH_4 fluxes during January 2016

January 2016: Diurnal variations of CO_2 flux January showed a fluctuation in pattern ranging from CO_2 uptake peaking at -1.19 mg m^{-2} s^{-1} to CO_2 emission (maximum 0.37 mg m^{-2} s^{-1}) at 9:00 and 9:30 hours respectively during the day. The highest CO_2 flux at night (0.63 mg m^{-2} s^{-1}) was at 7:00 hours followed by 0.60 mg m^{-2} s^{-1} and then 0.59 mg m^{-2} s^{-1} at 23:30 and 1:00 hours respectively, with average of 0.17 mg m^{-2} s^{-1} at night hours.

Generally, CH_4 positive fluxes occurred more frequently during the day compared to night hours, and the highest CH_4 flux (1.51µg m^{-2} s^{-1}) occurred at 14:00 hours. However, CH_4 absorption occurred in the morning during day time, with maximum flux (-5.99 µg m^{-2} s^{-1}) recorded at 09:30 hours. CH_4 fluxes at night fluctuated greatly with both emissions and uptake at different time intervals, and the maximum emission (9.91µg m^{-2} s^{-1}) at 05:00 hours and maximum negative flux (-

9.23 µg m^{-2} s^{-1}) at 04:30 hours occurred. Overall, the average CH_4 flux in the day hours was -0.06 µg m^{-2} s^{-1} while at night, the average CH_4 flux was 0.45 µg m^{-2} s^{-1}.

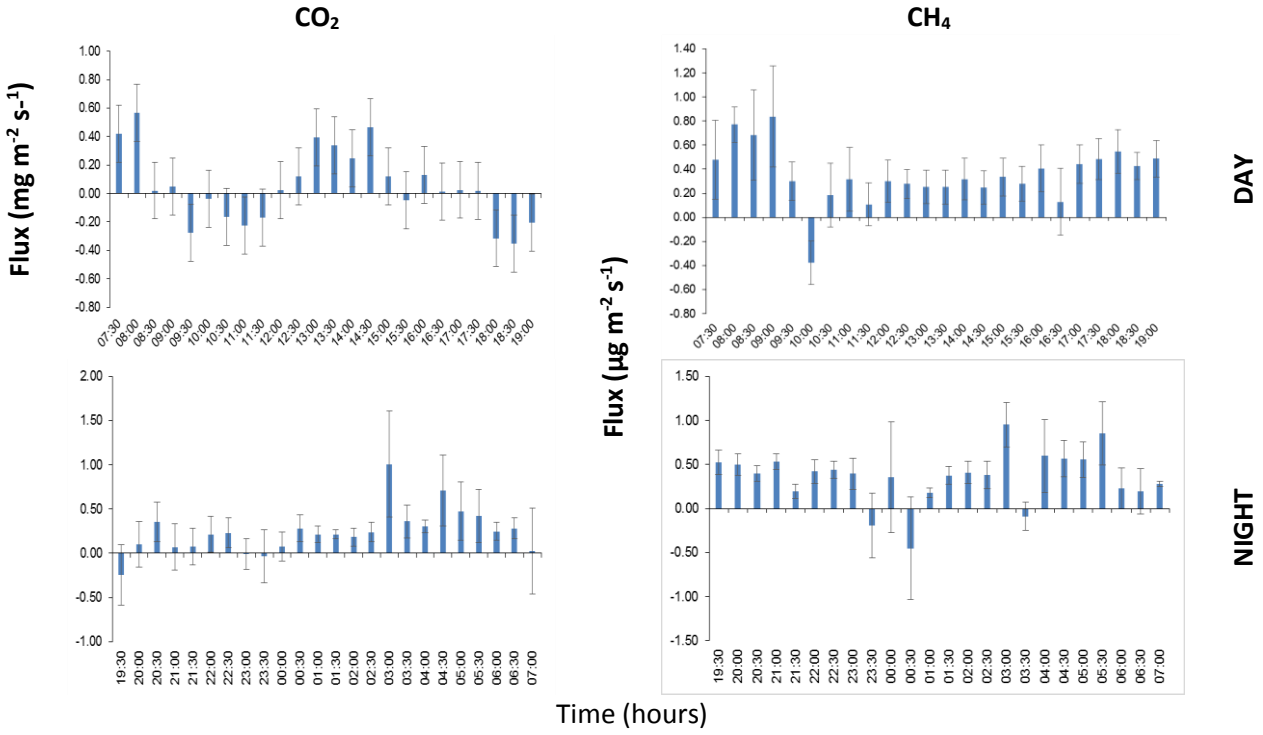


Figure 12: Diurnal variation of CO_2 and CH_4 flux during February 2016

February 2016: There is no consistence in the relationship between CO_2 fluxes and time of the day, and variation fluctuated between CO_2 uptake and emission. The maximum CO_2 emission rate in the day time was 0.57 mg m^{-2} s^{-1} followed by 0.47 mg m^{-2} s^{-1} at 08:00 and 14:30 hours respectively while CO_2 uptake peak was -0.35 mg m^{-2} s^{-1}. The average CO_2 flux during the day time hours was noted to be 0.05 mg m^{-2} s^{-1}. The trend of CO_2 fluxes at night hours generally indicated high and frequent CO_2 emissions than CO_2 uptake, with the maximum CO_2 efflux (1.01 mg m^{-2} s^{-1}) at 03:00 hours, and overall average CO_2 flux at night was 0.24 mg m^{-2} s^{-1}.

CH_4 flux demonstrated distinct emissions during the day and night time, with the highest flux of 0.84 µg m^{-2} s^{-1} followed by 0.77 µg m^{-2} s^{-1} at 08:00 and 09:00 hours respectively in the day time. On the other hand, the maximum flux of CH_4 during the night was 0.95 µg m^{-2} s^{-1} and occurred at 03:00 hour. The average CH_4 flux during the day was 0.35 µg m^{-2} s^{-1} while the average flux of CH_4 at night was noted as 0.36 µg m^{-2} s^{-1}.

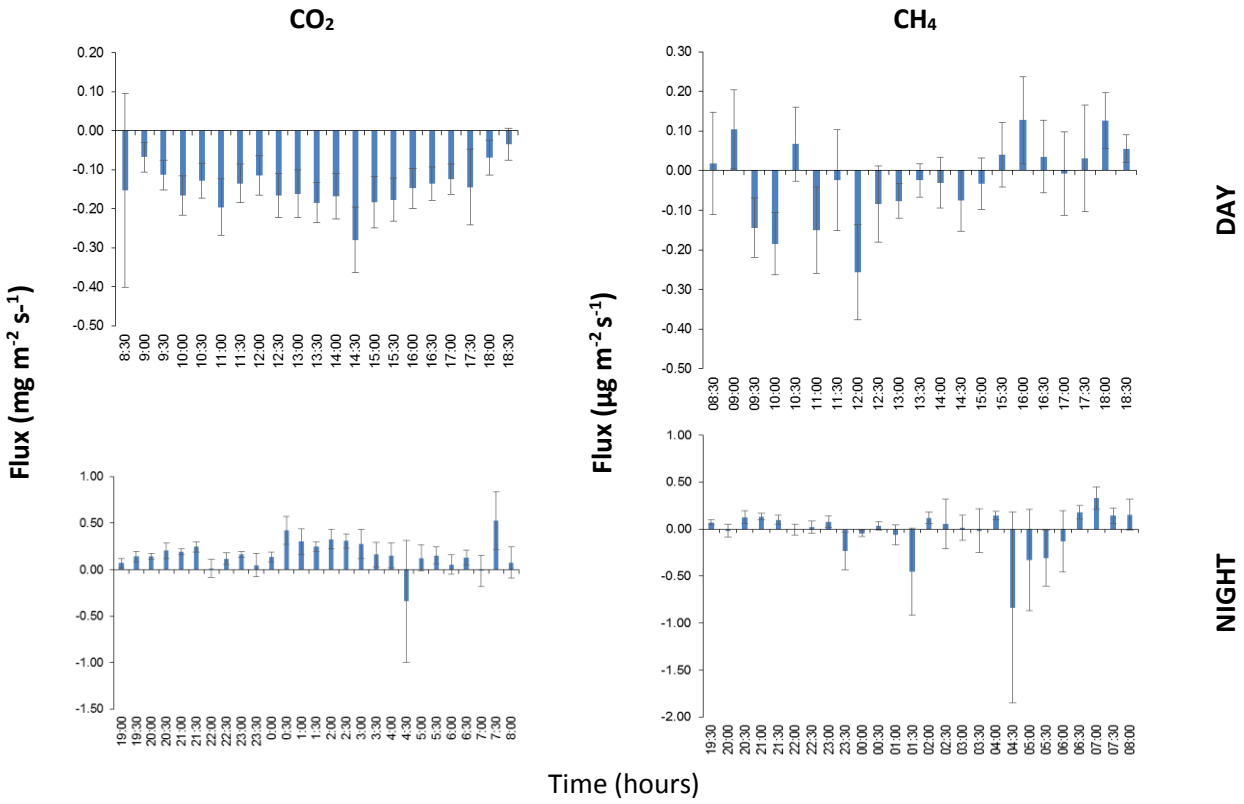


Figure 13: Diurnal variation of CO_2 and CH_4 flux in March 2016

March 2016: The diurnal variation in CO_2 fluxes showed distinct patterns with uptake of CO_2 during the day hours (from 08:30 to 18:30 hours), and emissions dominating during nocturnal hours (19:00 to 08:00). The highest CO_2 uptake rate (-0.28 mg m^{-2} s^{-1}) at 14:30 hours was 7-fold the lowest CO_2 uptake rate (-0.04 mg m^{-2} s^{-1}) which occurred at 18:30 hours during the day. Nocturnal variations in CO_2 efflux showed a gradual increase (with small fluctuations) in fluxes from 19:00 – 07:30 hours. The average CO_2 flux in the day time was -0.15 mg m^{-2} s^{-1}, and the average CO_2 flux at night was 0.16 mg m^{-2} s^{-1}.

CH_4 flux did not indicate a well-defined diurnal trend with distinguishable patterns. The variations ranged from influx to efflux between -0.84 µg m^{-2} s^{-1} and 0.33 µg m^{-2} s^{-1} at 04:30 and 7:00 hours respectively. The average CH_4 flux during the day time was -0.02 µg m^{-2} s^{-1} while the nocturnal average flux was -0.03 µg m^{-2} s^{-1}.

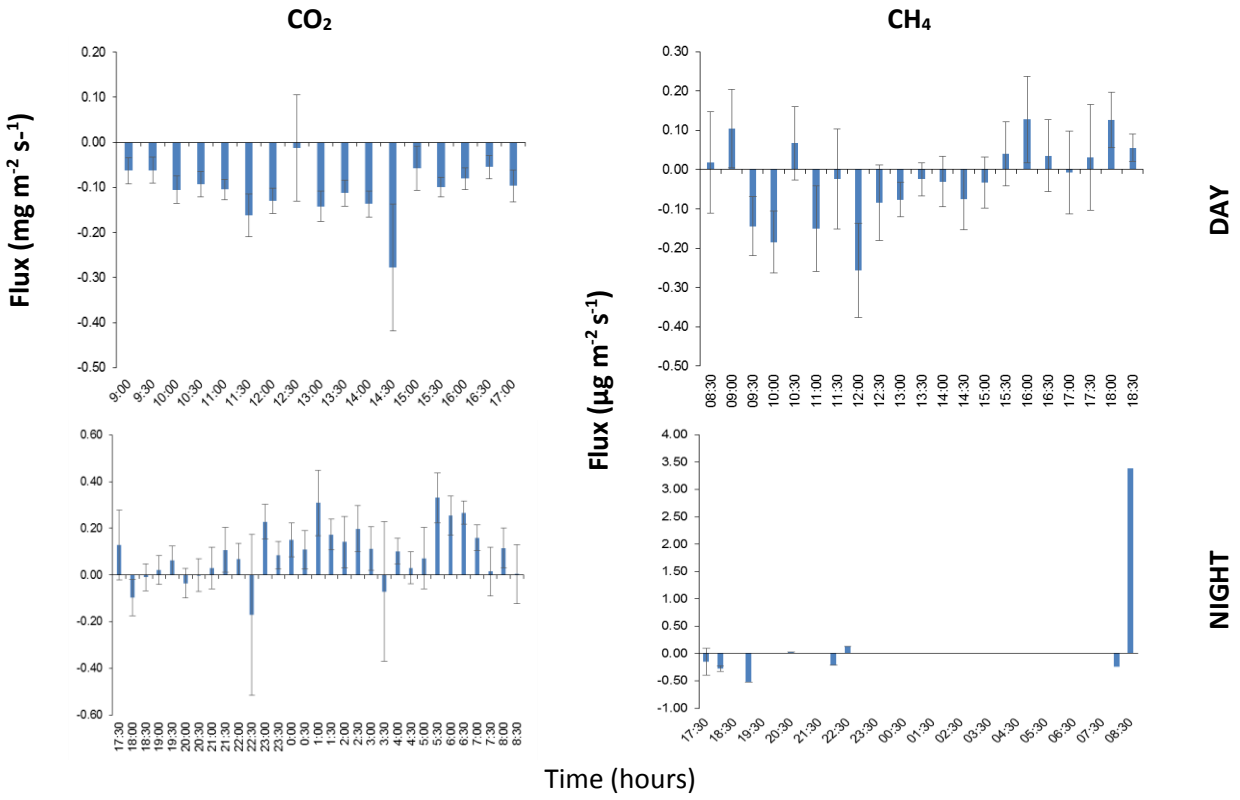


Figure 14: Diurnal variation of CO_2 and CH_4 flux in April 2016

April 2016: Diurnal CO_2 fluxes ranged from -0.28 mg m^{-2} s^{-1} to 0.33 mg m^{-2} s^{-1}, with the highest CO_2 emission rate (0.33 mg m^{-2} s^{-1}) at 05:30 hours during the night. Results indicate uptake of CO_2 from 09:00 to 17:00 hours with no CO_2 emissions throughout the day time. The average CO_2 flux noted during the day time was -0.11 mg m^{-2} s^{-1} and 5 x 10^{-4} mg m^{-2} s^{-1} at night.

Although there was limited CH_4 flux data during this month, results indicate that CH_4 uptake dominated over CH_4 emissions during the day, with highest average CH_4 influx (-1.30 µg m^{-2} s^{-1}) at 11:00 hours. The average CH_4 fluxes during the day and night times were -0.26 µg m^{-2} s^{-1} and 0.27 µg m^{-2} s^{-1} respectively.

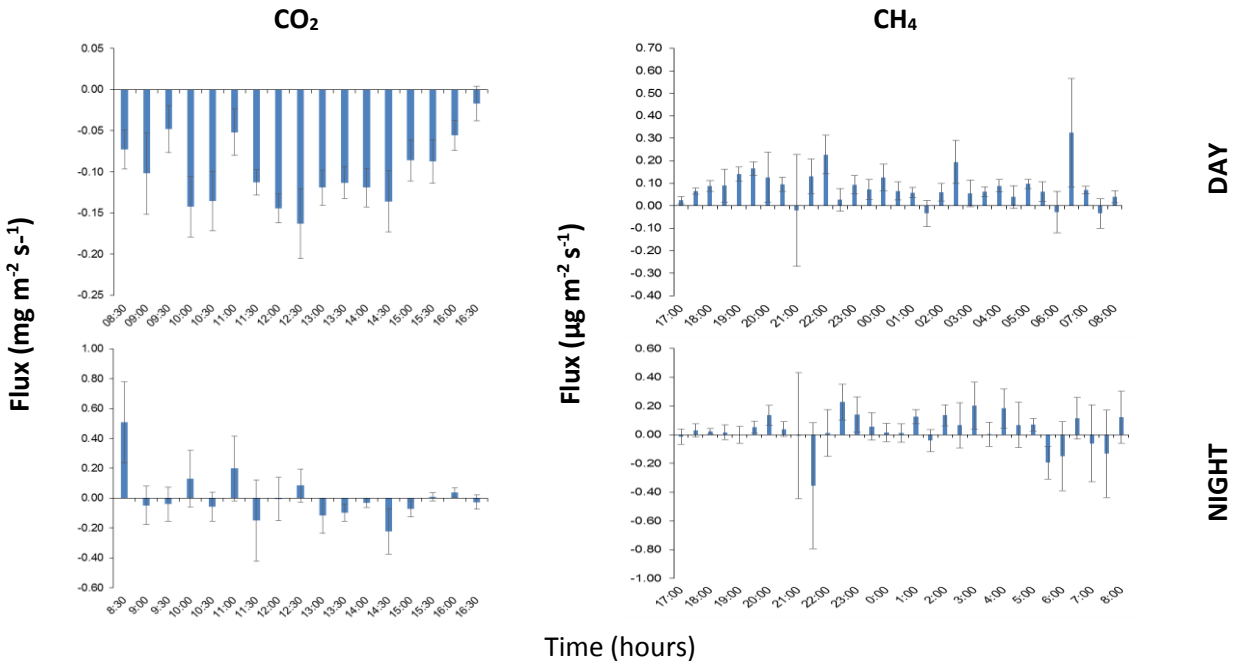


Figure 15: Diurnal variation of CO_2 and CH_4 fluxes in May 2016

May 2016: The study revealed high uptake of CO_2 between 10:00 – 14:30 hours, peaking at 12:30 hours, with an uptake of -0.16 mg m^{-2} s^{-1} from the saltmarsh. The lowest uptake occurred at 16:30 hours, with an influx of -0.02 mg m^{-2} s^{-1} and the average CO_2 flux during day time was noted to be -0.10 mg m^{-2} s^{-1}. Nocturnal CO_2 fluxes in May demonstrated minimal fluctuation in pattern, with emissions from the wetland occurring more frequently than uptake. The highest CO_2 efflux (0.33 mg m^{-2} s^{-1}) was 11-fold the highest CO_2 consumption rate (-0.03 mg m^{-2} s^{-1}) at night, and the overall nocturnal average of CO_2 flux was 0.08 mg m^{-2} s^{-1}.

Diurnal variation in CH_4 flux showed no distinct pattern between day and night time. There were emissions and uptake of CH_4 during the day and at night, and CH_4 flux ranged from -0.36 µg m^{-2} s^{-1} to 0.51 µg m^{-2} s^{-1}. The average CH_4 flux during the day was 0.01 µg m^{-2} s^{-1} while at night; 0.03 mg m^{-2} s^{-1} was noted as the average.

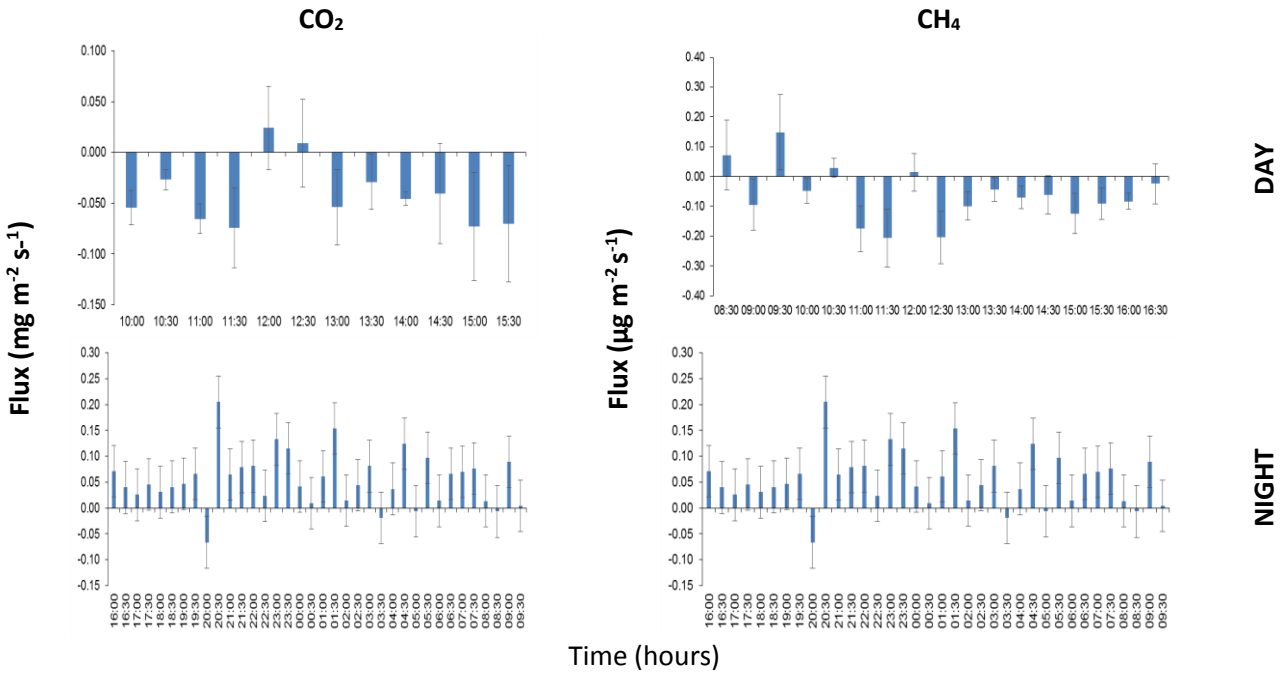


Figure 16: Diurnal variation of CO_2 and CH_4 flux in June 2016

June 2016: Diurnal variation of CO_2 flux demonstrated a clear pattern in which CO_2 uptake occurred more frequently during the daytime while CO_2 emission occurred during the night. The maximum CO_2 uptake was -0.075 mg m^{-2} s^{-1} at 11:30 hours while the maximum CO_2 efflux was 0.20 mg m^{-2} s^{-1} at 20:30 hours. Results indicated the average CO_2 flux during the day to be -0.04 mg m^{-2} s^{-1} and the average CO_2 flux at night time was 0.05 mg m^{-2} s^{-1}.

There was no consistence in diurnal variation of average CH_4 fluxes during June, and flux variation pattern showed CH_4 emission and uptake occurring during the day and night. CH_4 fluxes ranged from -0.12 µg m^{-2} s^{-1} to 0.14 µg m^{-2} s^{-1}, and the average CH_4 flux (0.01 µg m^{-2} s^{-1}) during the day time was the same as nocturnal CH_4 average.

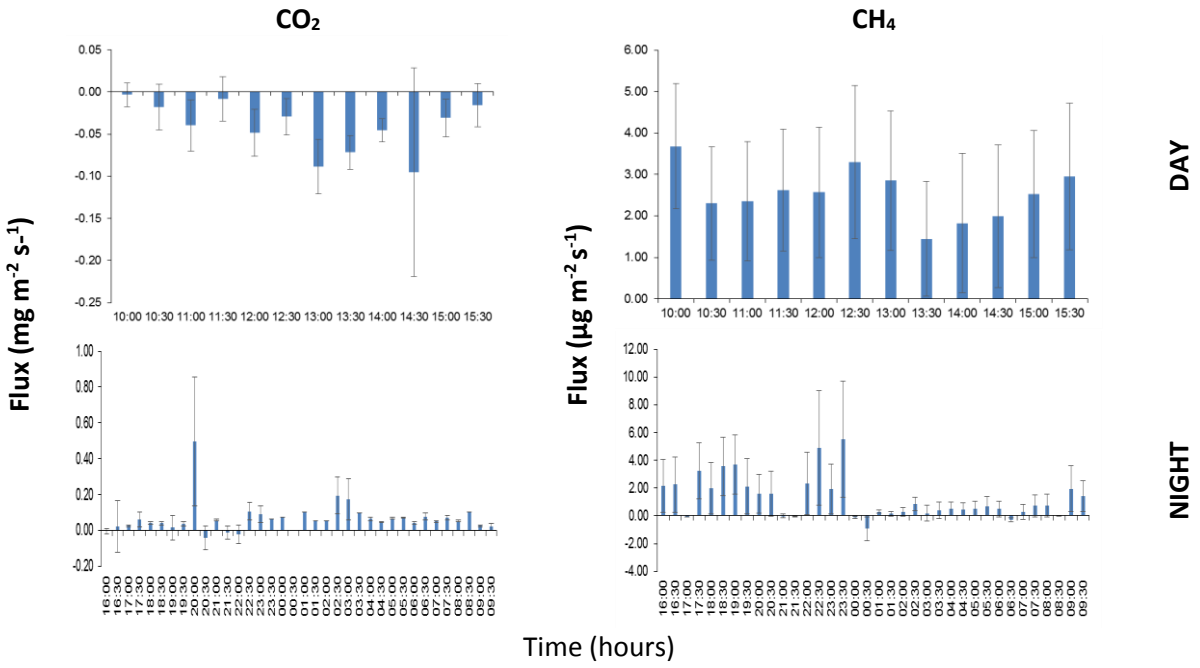


Figure 17: Diurnal variation of CO_2 and CH_4 fluxes in July 2016

July 2016: Diurnal variation of CO_2 flux followed a normal trend in which CO_2 uptake occurred during the day and CO_2 emissions at night, with few anomalies. High CO_2 consumption rates occurred between 12:00 and 14:30 hours with the highest CO_2 flux (-0.1 mg m^{-2} s^{-1}) at 14:30 hours. Low consumption rates of CO_2 occurred mainly in the morning and evening hours. Emissions of CO_2 were dominant during the night, with the highest recorded flux (0.50 mg m^{-2} s^{-1}) at 20:00 hours. The average CO_2 flux during the day was -0.04 mg m^{-2} s^{-1} while the average CO_2 flux at night was 0.07 mg m^{-2} s^{-1}.

There was no distinct diurnal variation pattern of CH_4 flux between day and night times. CH_4 flux showed emissions of CH_4 from the saltmarsh during the day, peaking at 10:00 hours with emission of 3.88 µg m^{-2} s^{-1}. The maximum CH_4 efflux during the night time was 5.51 µg m^{-2} s^{-1} at 23:30 hours, and the average CH_4 flux in the day time was 2.54 µg m^{-2} s^{-1} while the average CH_4 flux in the night was 1.26 mg m^{-2} s^{-1}.

4.1.2 Diurnal variation of CH_4 and CO_2 fluxes with water level

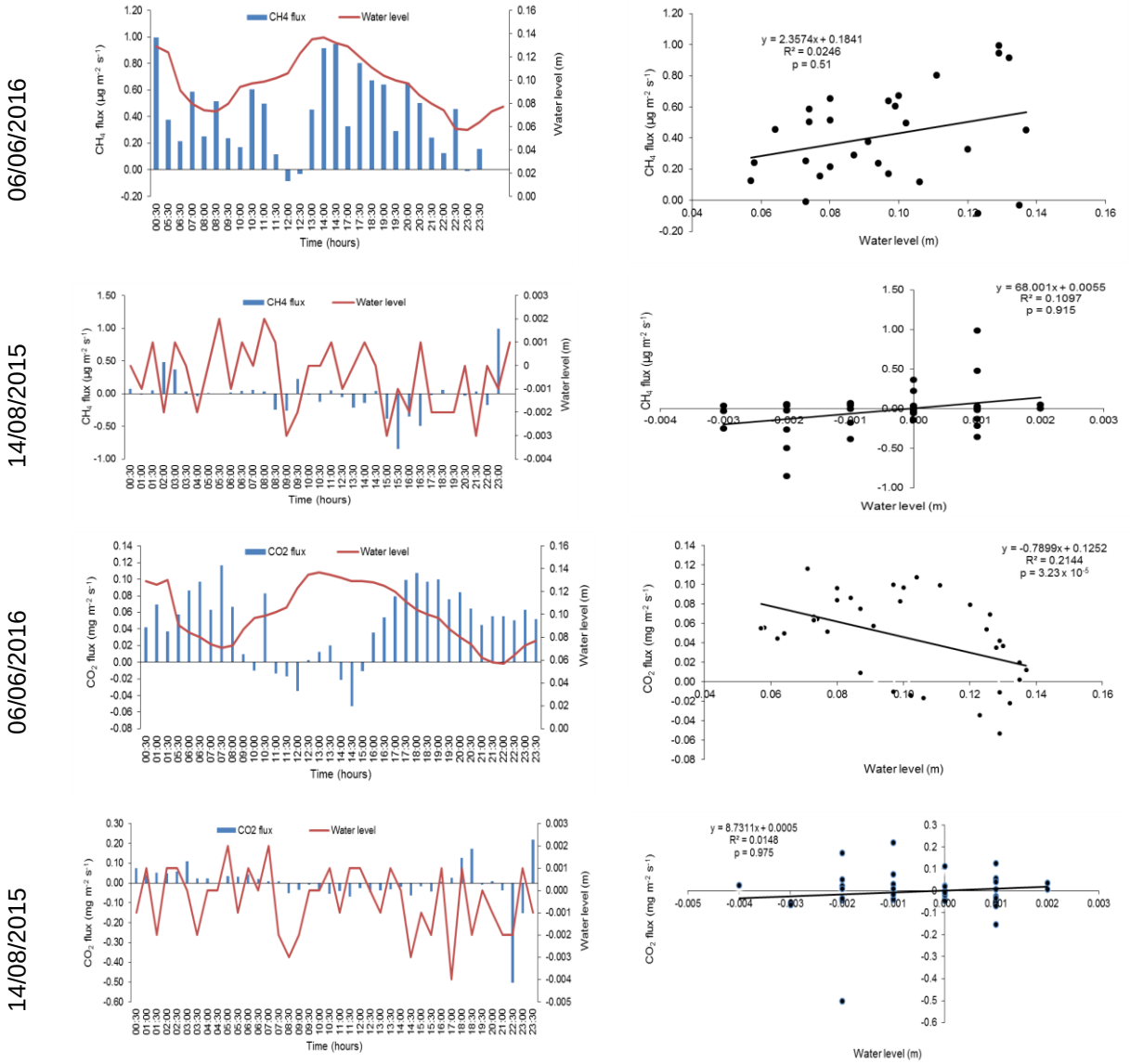


Figure 18: Diurnal variation of CO_2 and CH_4 fluxes with water level during tidal inundation (6th June 2016) and with exposed soil surface stage (14th August 2015)

The diurnal variation of CH_4 flux on 06th June (during tidal inundation) demonstrated a distinct pattern with low emissions during the night time and high emissions in the day time, and uptake of CH_4 around mid-day. CH_4 flux showed positive correlation with water level on a diurnal scale although the relationship was not statistically significant ($p = 0.51$). On the other hand, CO_2 fluxes indicated a significant negative correlation with water level ($p < 0.001$).

On 14th August, there were fluctuations in diurnal variations, with no distinct trends for both CH_4 and CO_2 fluxes, and water level. However, CH_4 and CO_2 fluxes indicated a positive relationship with water level which was not statistically significant.

4.1.3 Diurnal variations of CH_4 with EC and water temperature

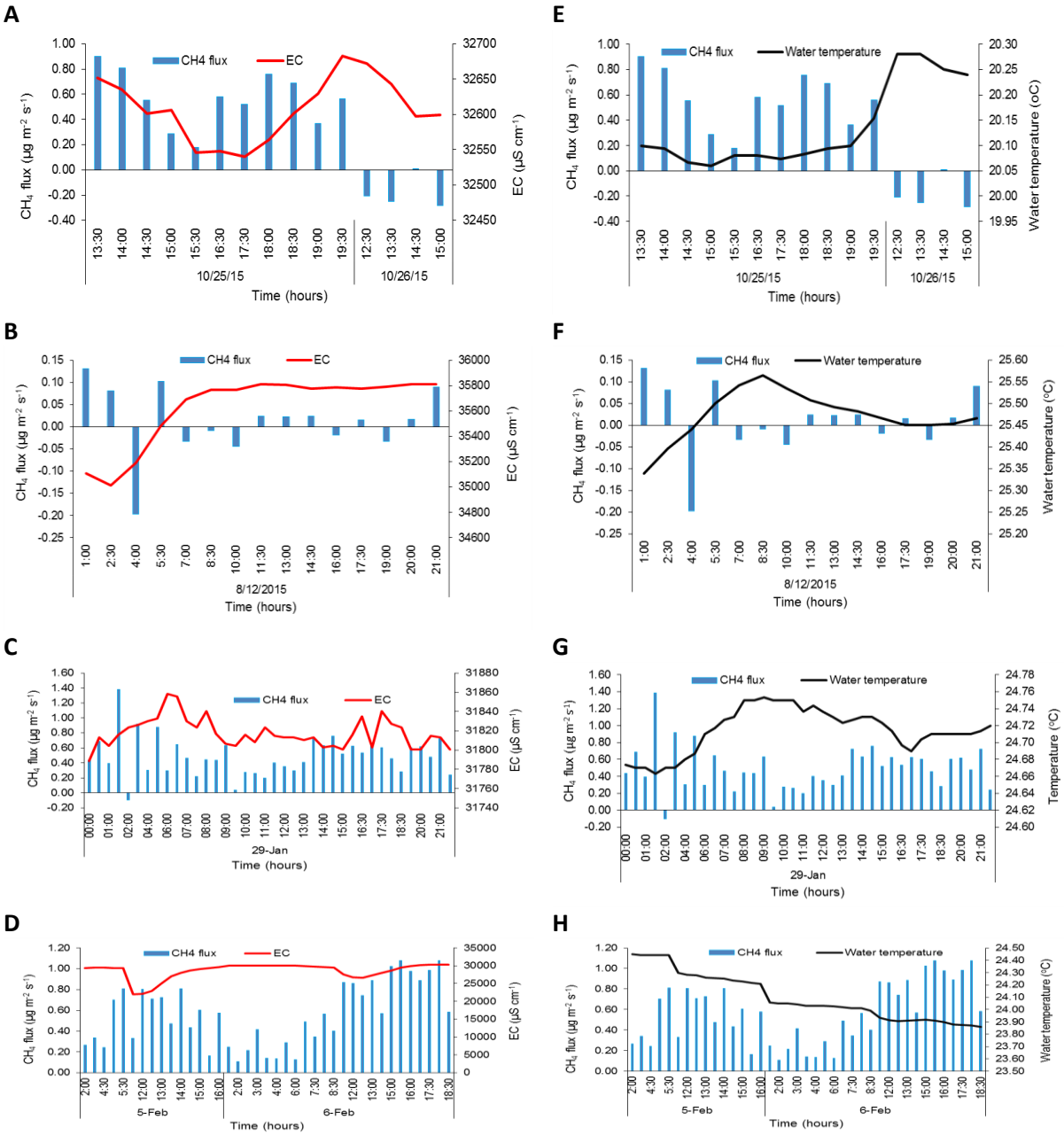


Figure 19: Diurnal variation of CH_4 fluxes with electrical conductivity (EC) and water temperature before tidal inundation-October 2015 (A&E), and after tidal inundation- December 2015 (B&F), January 2016 (C&G) and February 2016 (D&H).

Generally, CH_4 fluxes showed a diurnal variation which was less correlated with EC and water temperature for the dates indicated in the figure above. There was a very low negative correlation (r = -0.17) in October, very low negative correlation (r = -0.09) in December, very low negative correlation (r = -0.01) in January and low negative correlation (r = -0.20) in February. Although results in all these case studies for diurnal variations in EC and CH_4 fluxes indicated a negative correlation, the relationships were not statistically significant. Water temperature was also negatively correlated with CH_4 fluxes (r = -0.80, r = -0.31, r = -0.35 and r = -0.32 for October, December, January and February respectively) but all these relationships were not statistically

significant. Water temperature was positively correlated with EC except during February (r = -0.29), and the highest positive correlation (r = +0.93) was identified in January 2016. From Figure 19 indicated above, the diurnal variations of CH_4 flux with soil water temperature and electrical conductivity before and after tidal inundation were more or less the same in the respective months (October, December, January, and February) that were considered as case studies.

4.1.4 Diurnal variations of CO_2 with EC and water temperature

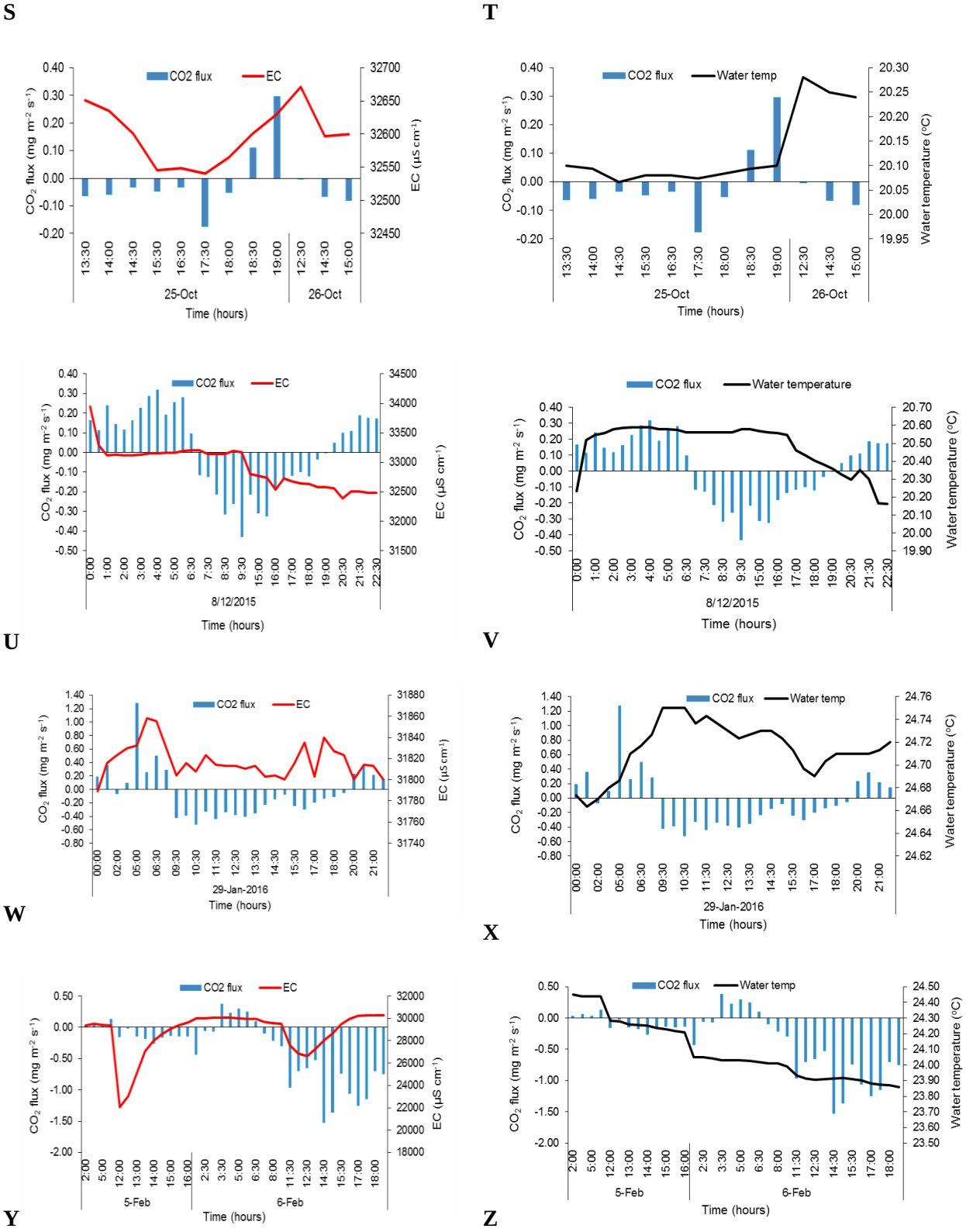


Figure 20: Diurnal variation of EC and water temperature with CO_2 fluxes before tidal inundation-October 2015 (S&T), and after tidal inundation- December 2015 (U&V), January 2016 W&X) and February 2016 (Y&Z).

The diurnal variation of CO_2 flux with electrical conductivity indicated low positive correlation before and after tidal flooding and all these relationships were not statistically significant at 95% level of confidence except for January (r = 0.36, p = 0.25 for October, r = 0.15, p = 0.38 for

December, $r = 0.32$, $p = 0.03$ for January and $r = 0.009$, $p = 0.74$ for February). The relationship between CO_2 flux and EC was not statistically significant before (October) and after (December, January and February) rainwater and tidal flooding. Water temperature appeared to be negatively correlated with CO_2 ($r = -0.077$ for October, $r = -0.214$ for December, $r = -0.55$, $p = 0.002$ for January) except in February ($r = 0.62$, $p < 0.001$) which indicated a high positive correlation. The relationship between CO_2 flux and water temperature was statistically significant for diurnal variations in January and February 2016, and this occurred after tidal flooding.

4.1.5 Diurnal variation of CH_4 and CO_2 with tidal height

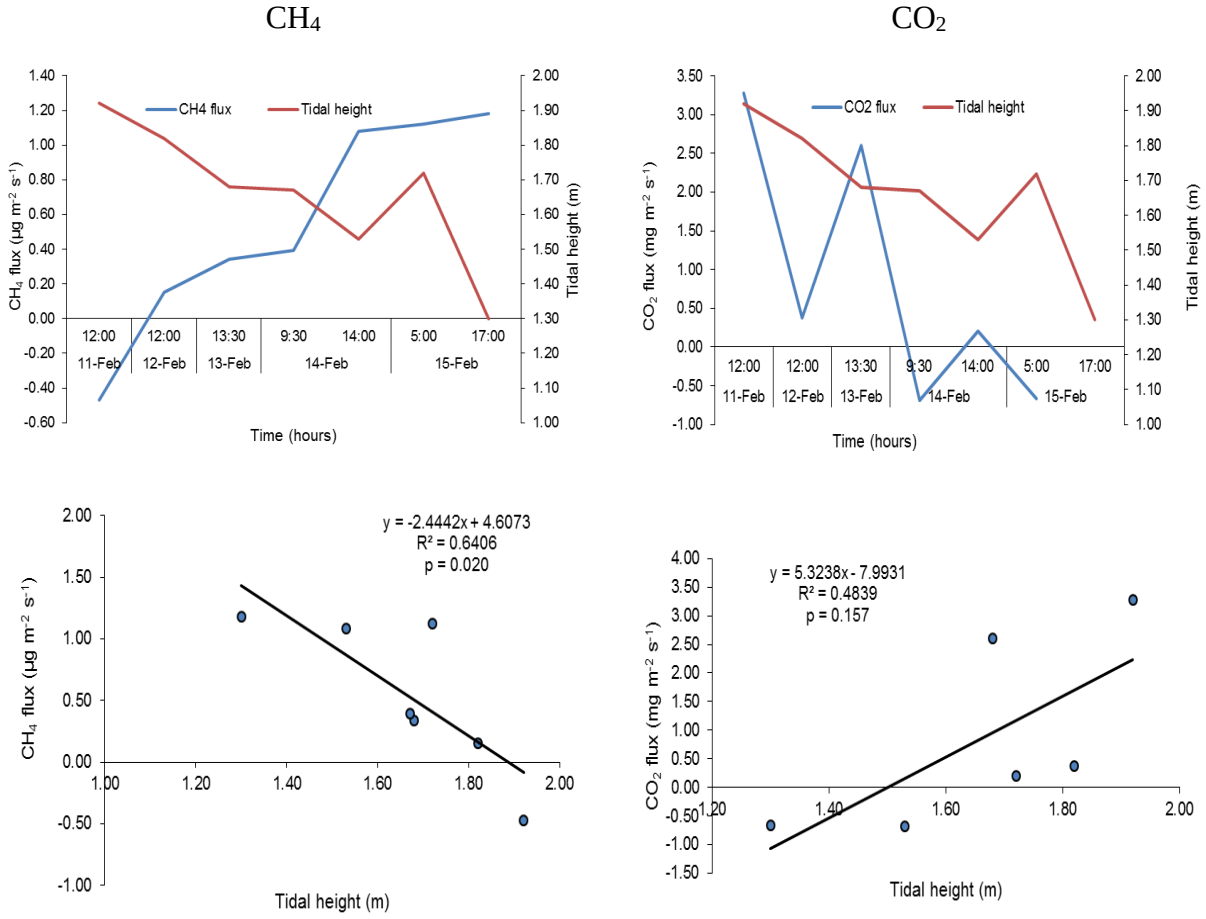


Figure 21: Linear relationship between CH_4 and CO_2 fluxes at the water-air interface and tidal water height in February 2016

Analysis of CH_4 flux data for four days (11th, 12th 13th, and 15th February 2016) from the tidal marsh, indicated a significant negative correlation with tidal height (r = -0.80, p = 0.020) while CO_2 flux during the same period indicated a positive correlation with tidal height (r = 0.69, p = 0.157).

4.2 Seasonal variation of CH_4 and CO_2 fluxes with environmental factors

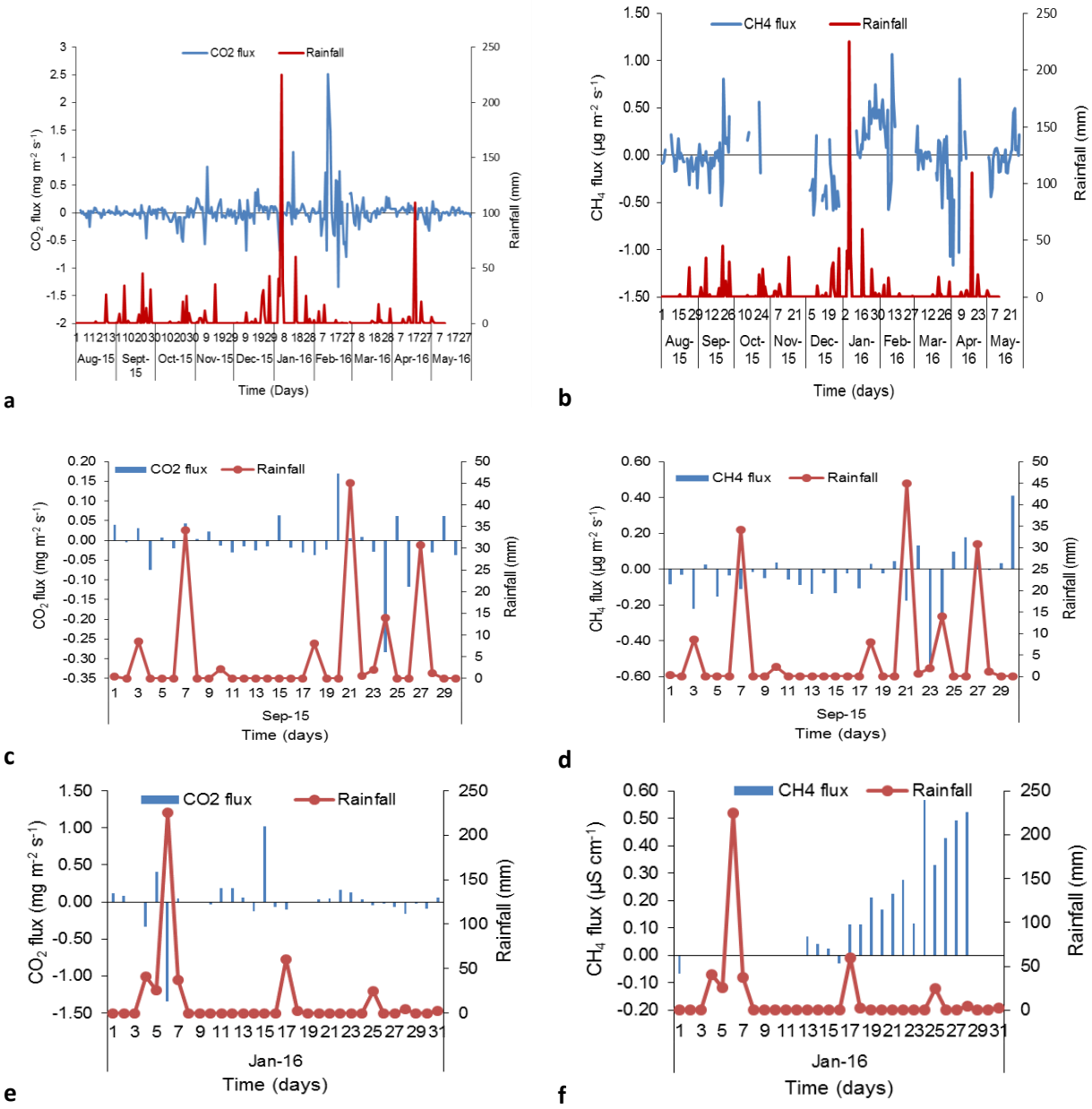


Figure 22: Monthly relationship between CH_4 and CO_2 fluxes with rainfall, for two months used as case studies before flooding (September 2015) and after flooding (January 2016).

Generally, CO_2 and CH_4 fluxes showed a weak positive association with rainfall received at different periods of the months (figures 22 a & b). Increase in rainfall resulted into an increase in CO_2 and CH_4 fluxes except in September 2016 during which an increase in CH_4 fluxes was associated with a decrease in rainfall. The diurnal variations between rainfall and CO_2 and CH_4 fluxes demonstrated irregular patterns on September, 2015 and January, 2016. Rainfall was

irregular except for September, December, January and April which received rainfall almost throughout the months.

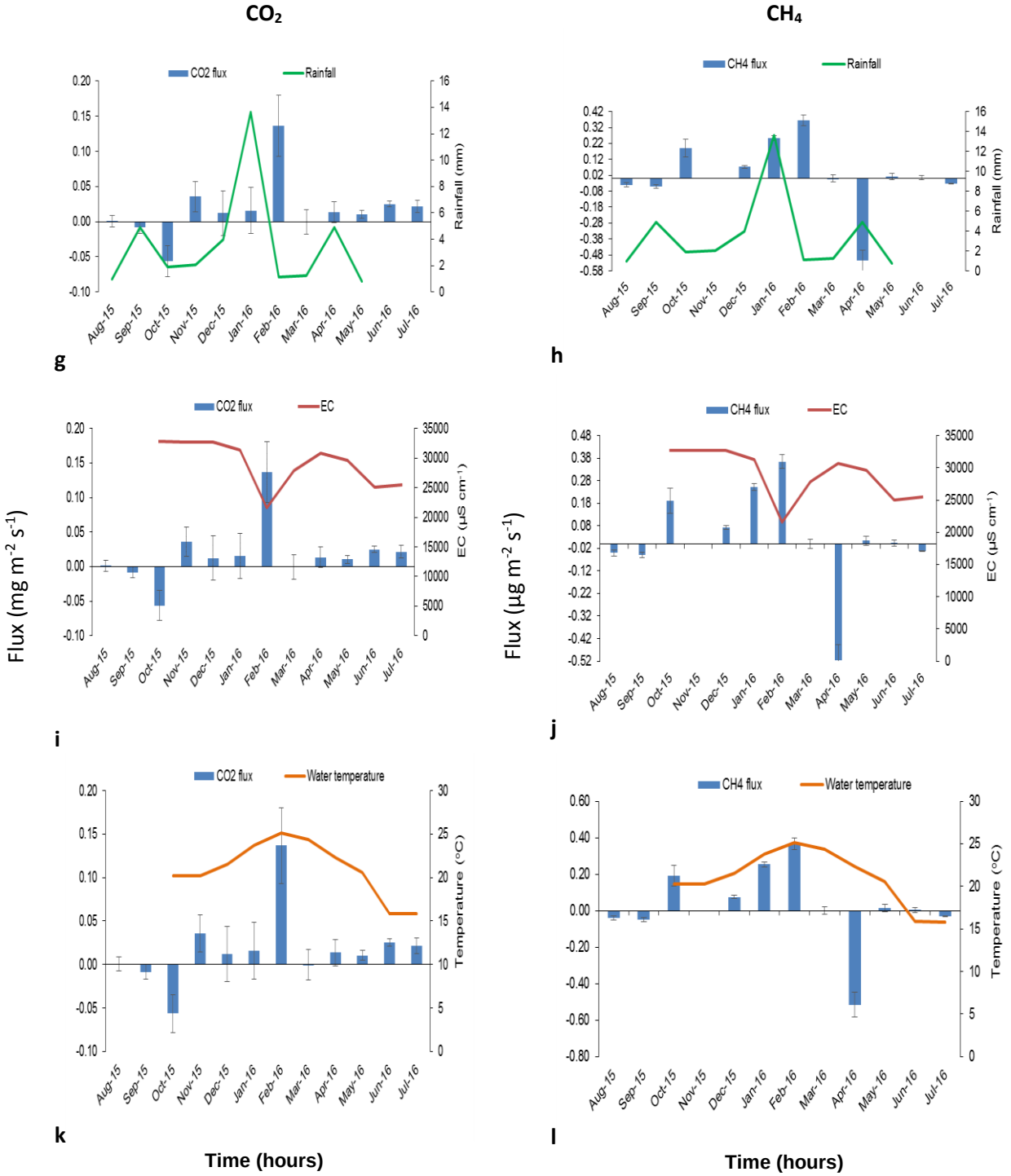


Figure 23: Seasonal variation of rainfall, electrical conductivity (EC), and water temperature with CO_2 and CH_4 fluxes in a period of one year (from August 2015 to July 2016). Water temperature and EC measurements started in October 2015, and also there was no rainfall data for June and July due to technical challenges.

Results indicate that high CO_2 uptake occurred from August to October, with the highest consumption rate of -0.06 mg m^{-2} s^{-1} in October. During this time a small rainfall event occurred, but it was before tidal reinstatement occurred for the wetland. Emissions of CO_2 increased from (0.016 mg m^{-2} s^{-1} in January to a maximum of 0.137 mg m^{-2} s^{-1} in February, and this increase in average monthly CO_2 flux was noted after receiving heavy rainfall in January (monthly average of 13.62 mm). Generally, CH_4 fluxes increased with increase in the monthly rainfall although the relationship was not consistent throughout the study period. Results indicate that the highest monthly average CH_4 emissions (0.37 µg m^{-2} s^{-1}) occurred in February after receiving heavy rainfall in January.

The highest CH_4 emissions (0.37 µg m^{-2} s^{-1}) and CO_2 emissions (0.14 mg m^{-2} s^{-1}) were obtained at the same time in February when soil water indicated the highest average water temperature (25.15ºC). During the same month however, the lowest average EC (21586.35 µS cm^{-1}) was recorded. Results indicated a high consumption of CH_4 at relatively lower temperatures compared to the temperatures at which high CH_4 emission rates were registered. Figure 23(l) shows that -0.52 µg m^{-2} s^{-1} of CH_4 at 22.28 ºC during April were consumed compared to 0.25 µg m^{-2} s^{-1} of CH_4 at 23.74 ºC and 0.37 µg m^{-2} s^{-1}at 25.15 ºC of CH_4 that was emitted during January and February respectively.

There was a reduction in monthly average emissions of CH_4 in May, June, and July. This reduction was attained at the time when water temperature was low (20.59, 15.86 and 15.84 ºC respectively).

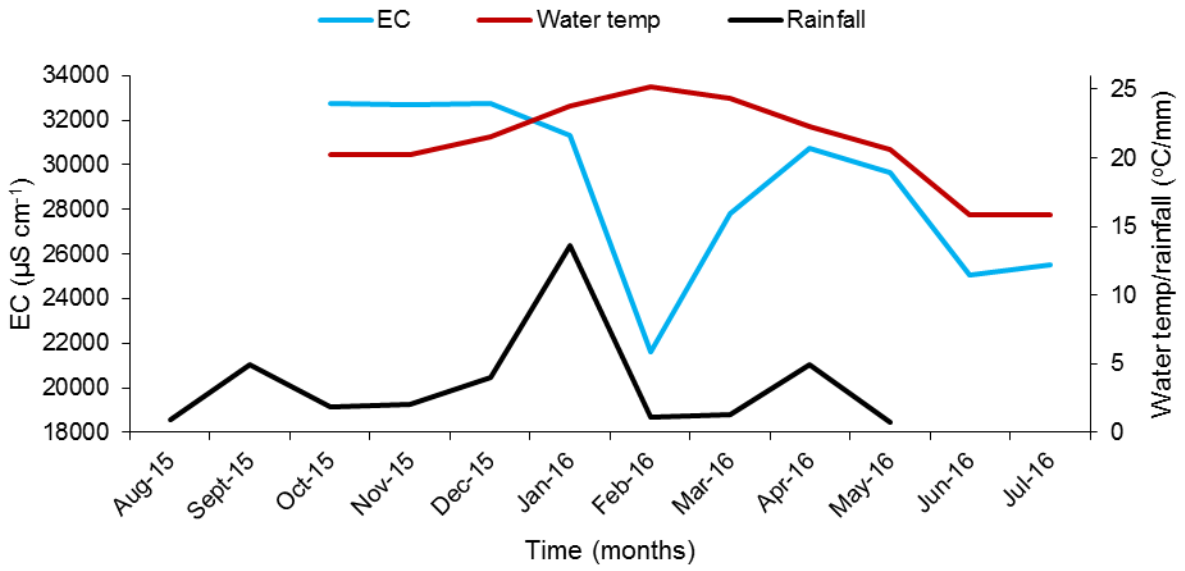


Figure 24: Seasonal variation of electrical conductivity (EC), water temperature and rainfall during the study period (August 2015 to December 2016).

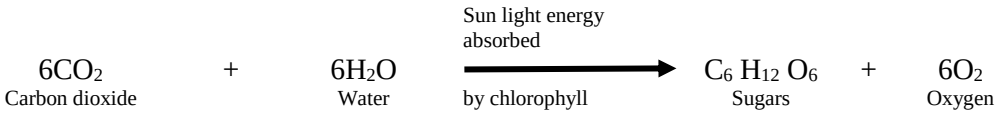
January recorded the highest amount of average rainfall (13.62 mm) during the period of the study. This period was followed by a sudden drop in average rainfall (1.12 mm) that was received during the month of February. A slight increase in rainfall from October to December (1.89 – 3.97 mm) was followed by a gentle decline in electrical conductivity during the same period (32748.85 – 32726.40 µS cm^{-1}). However, after December, the exponential increase in rainfall from December to January (3.97 – 13.63 mm) was followed by sharp decline in electrical conductivity (32726.40 – 21586.36 µS cm^{-1}) up to February during which the lowest EC (21586.36 µS cm^{-1}) was recorded. A slight increase in rainfall from February to March was accompanied by a sharp increase in EC (1.117 – 1.127 mm). Results show that an increase in rainfall from March to April (1.127 - 4.93 mm) was followed by an increase in EC (27818.88 – 30749.94 µS cm^{-1}) and thereafter, EC decreased. Initially, water temperature increased (from 20.25 to 23.74 ^{o}C) with an increase in rainfall (1.89 – 13.63 mm) from October up to January, and continued to increase as rainfall dropped, and attained a peak (25.15 ^{o}C) in February. Thereafter, water temperature dropped gradually (from 22.28 to 15.84 ^{o}C) with a decrease in EC (from 30749.94 to 25499.31µS cm^{-1}) after attaining a maximum value. EC was highly negatively correlated (r = -0.82) with water temperature during the period of rainfall (October to February) and the relationship showed positive correlation (r = +0.75) after flooding (March to July).

Chapter 5. Discussion

5.1 Diurnal variation of CH_4 and CO_2 fluxes

5.1.1 CO_2 flux

Generally, there was significant uptake of CO_2 during the day and emission during the night. During the day, in presence of photosynthetically active light, CO_2 was absorbed by green plants to manufacture food, and this accounts for negative CO_2 fluxes during the day.



The rates of CO_2 uptake on a diurnal scale greatly varied between summer (December through February) and winter (May through July). The maximum CO_2 uptake recorded during the summer was -1.19 mg m^{-2} s^{-1} (January at 9:00 hours), which was more than 7 times higher than the maximum CO_2 uptake during winter, -0.16 mg m^{-2} s^{-1} (May at 12:30 hours). This can be explained by the high soil water temperatures during the summer that have a direct influence on the metabolic reactions such as photosynthesis in plants.

Throughout the entire period of study, high rates of CO_2 uptake were registered between late mornings and early afternoons (9:00 – 14:00 hours). Results demonstrate that CO_2 uptake in Tomago wetland during spring (August through November) was relatively higher than CO_2 uptake during the winter. The noted daily maximum CO_2 uptake (-0.62 mg m^{-2} s^{-1}) in October at 17:30 hours, was approximately 4 times higher than CO_2 uptake (-0.16 mg m^{-2} s^{-1}) in May at 12:30 hours during winter season. Spring seasons are warmer than winter, thus high temperatures enhanced primary productivity in plants which were recovering from the cold winter season.

The significant rates of CO_2 emissions at night hours were mainly due to respiration and decomposition of organic matter. The study results show that there were high CO_2 fluxes during the summer and spring seasons compared to winter season. Increased summer temperatures were suspected have had an influence on microbial activities that increase the rate of respiration in soil and water. This observation is consistent with the previous findings by Wang et al. (2016) in which increased soil respiration was related to high temperatures in a tidal mangrove wetland in China. High uptake of CO_2 during the day indicates the level of productivity for Tomago wetland which is a habitat of many species of vascularised and non-vascularised plants.

During the day time in August and September 2015, CO_2 uptake was attributed to the presence of photosynthetic plants that fix CO_2 during the process of photosynthesis. The high uptake during

morning hours compared to evening hours indicated an elevated rate of photosynthesis because of the availability of limiting factors such as sunlight energy and water. Increased CO_2 emissions during night showed that CO_2 was produced from respiring organisms in the ecosystem, and also decomposing organic matter in the soil sediments and litter on the soil surface. The study suggests that the low rate of respiration at night was the cause of low CO_2 flux at night.

5.1.2 CH_4 flux

Results indicated CH_4 uptake during the day compared to night hours in August and September 2015. This occurrence was as a results of high CH_4 oxidation during the day than in night hours probably by aerobic oxidation. August and September were characterised by low water level in the wetland soil, and thus easy circulation of oxygen, which might have caused aerobic oxidation of methane. During this period of time there was flooding in the wetland because of little rainfall, and also, tidal flow reinstatement had not commenced. The findings about diurnal trends of CH_4 fluxes during this period were contrary to some previous research studies in tidal marshes. For instance, CH_4 fluxes were higher during the day than night hours, and the average CH_4 fluxes (at the exposed soil stage) in the day time were also higher than the average CH_4 fluxes during the night (Tong et al., 2013). Dengel et al.,(2011) also found out that CH_4 fluxes showed a distinct diurnal pattern, with highest emissions occurring during the day and with afternoon emissions substantially exceeding those in the morning. In our study, it is suggested that aerobic oxidation of CH_4 might have been the possible cause for the uptake of CH_4 during the day time in August and September 2015. During this period, there was no flooding and thus the ability for oxygen to circulate into the soil pore space.

Diurnal variation of CH_4 flux during flooding (specifically for December 2015, January, February, and May, 2016) indicated a regular pattern of high CH_4 fluxes during the day than night time. This finding is consistent with previous work by Tong et al., (2013) who noted greater CH_4 emissions from a tidal marsh during the day than at night. Some of the possible reasons for this observation may include: First, the higher soil temperature in the day time may have increased CH_4 production. Second, an increase in light during the day can cause a change in the plant mediated CH_4 transport pathways to change from diffusive mechanism during the night to a convective mechanism during the day and a convective transport rate is much higher than diffusive one (Whiting & Chanton, 1996) , and the amount of labile organic carbon substrates from root exudates can be stimulated by high temperatures (Inglett et al., 2012). Although there was not much plant cover especially after tidal inundation, small patches plant habits were available around the flooded area. Plant mediated CH_4 transport is regulated by the intensity of light which in turn regulates stomatal movement, and conductance (Tong et al., 2013). Third, diurnal variability in wind speed and associated evasion rate

greatly influence diurnal variations in CH_4 (Maher et al., 2015). However, in this particular study, the influence in wind variability was not investigated.

5.2 Diurnal variations of CH_4 and CO_2 fluxes with environmental factors

A decrease in CO_2 flux with an increase in the water level on a diurnal scale could have been due to lowered rate of CO_2 production by aerobic respiration and enhances the rate of CH_4 production by anaerobic methanogenesis. High water levels might have resulted into saturation of the soils with water, thus reducing the ability of oxygen to diffuse from the atmosphere into the soils. On the other hand, low water levels enable oxygen to diffuse from the atmosphere into the soil leading to aerobic CO_2 production but limiting CH_4 production. Figure 18 shows that CO_2 flux decreased as water level increased while CH_4 flux increased with water level on 06th June 2016. These relationships clearly demonstrated the water-saturated soil conditions favourable for CH_4-producing microbial communities after tidal flow inundation and rainfall during the summer season. The diurnal variations of CH_4 and CO_2 on 14th August 2016 showed a very low positive correlation with water level because the tidal flow re-instatement had not been effected. The diurnal change in water level during this time was insignificant and therefore, had less or none influence on CH_4 and CO_2 fluxes.

The negative correlation between the tidal height and methane fluxes may imply that low methane emissions could have occurred during tidal submergence. When the saltmarsh soils are flooded with inflowing water, it's likely that gas diffusion from soil air spaces may be interfered with, and also the inflowing water may dilute CH_4 gas dissolved in the pore water and hence reducing the amount of CH_4 emitted from the saltmarsh (Yamamoto et al., 2009). The decrease in the amount of CH_4 may also be attributed to certain proportions of CH_4 diffusing into the tidal water may get oxidised in the water column before it has reached the water-air interface.

The negative diurnal relationship between electrical conductivity and CH_4 flux from Figure 18 probably indicated inhibition of methanogenesis due to presence of certain ionic species such as Sulphates in the soil sediments. In presence of sulphate ions, the sulphate reducing bacteria outcompete methanogens for the appropriate substrates available such as acetate and hydrogen (D'Angelo & Reddy, 1999). The negative diurnal correlations between CH_4 flux and temperature was not consistent with most research findings, and this demonstrated that temperature was not a driving factor for CH_4 fluxes.

The positive correlation between diurnal CO_2 flux and electrical conductivity was found to be contradictory to some research studies in which EC (linked to salinity) was negatively correlated with CO_2 flux due to high CO_2 absorbing capacity of alkaline wetland soils (Xie., 2009). The increase in EC in Tomago can be linked to the ionisation of acid salts while the increase in CO_2 was

caused by high decomposition rates of organic matter in addition to high respiratory capacity of the ecosystem. Tomago is known to be one of the wetlands in the hunter estuary which was faced with the problem of formation acid sulphate soils (Rogers et al., 2014) before tidal reinstatement. EC was not the controlling factor for CO_2 flux during January. In February, the diurnal water temperature was relatively high compared to the rest of the months, and this could have stimulated microbial activities in soil sediments, allowing decomposition of organic matter to form CO_2. In addition, plant tissue respiration is thought to have been high during summer season leading to increased CO_2 output. This concurs with the findings of most research studies that link CO_2 fluxes to high temperatures due to oxidative breakdown of organic matter, and root and shoot respiration (Herbst et al., 2011; Inglett et al., 2012; Wang et al., 2016)

During tidal inundation period, the marsh showed uptake of CO_2 in the day and at certain time intervals during the night, and this is explained by the solubility driven diffusion of CO_2 into the inflowing tidal water.

5.3 Seasonal variation of environmental factors and, CH_4 and CO_2 fluxes

Rainfall diluted wetland water solutes causing a reduction in electrical conductivity, EC. EC is linked to salinity, which refers to the total soluble salts in water. Results indicate that the highest average rainfall received in January led to a dramatic decrease in EC (Figure 24). Rain water dissolves salts and infiltrates and carries salts from the subsurface layers to deeper soil layers and thus reduces their concentrations in surface waters (Nachshon et al., 2014)

Changes in precipitation patterns influenced the amount of soil water, and also the level of water above the ground level. The rain pulse that occurred during January resulted into increased flooding which in turn influenced CH_4 emissions in February due to favourable conditions for anaerobic microbial communities to perform their biochemical activities. Oxidation of methane decreases when soil water content is high, and this could be attributed to the low solubility and diffusion of oxygen and CH_4 as well in the soil water (Del Grosso et al., 2000). At high moisture content levels, methanogenesis is highly favoured due to low diffusion and solubility rates of oxygen. In areas with water saturated soils, net oxidation has been reported due to the presence of anaerobic CH_4 oxidation (Khalil & Baggs, 2005), and this indicates the importance of flooding water in wetland soils in relation to methane production and oxidation.

The formation of methane depends on the quantity and composition of the methanogenic population present in a wetland ecosystem. High water salinity inhibited methanogenesis probably due to competition from sulphate reducing bacteria (Le Mer & Roger, 2001). Because of the low levels of salinity during February; there was high emission of CH_4 (0.37 $\mu g\ m^{-2}\ s^{-1}$). Electrical conductivity,

EC of water is linked to salinity, and the lower the conductivity, the lower will be the salt ion concentration in water, and hence low salinity levels. The results therefore conquer with previous work by Chambers et al., (2011) who stated that high salt concentration reduces microbial populations in wetlands, by lowering microbial respiration, and hence the rate of methanogenesis. The high emissions of carbon dioxide during the same period (January – February) can be explained by the ability of microbial populations to decompose organic matter, and the availability of organic matter in the sediments, in addition to CO_2 that resulted from respiration of plants and animals. From October to January, the average CO_2 fluxes ranged between -0.056 to 0.016 mg m^{-2} s^{-1} with EC ranging from 31321.09 to 32748.86 µS cm^{-1}. Although the reduction in EC was followed by a slight increase in carbon dioxide production rate, EC might have more of an indirect influence on CO_2 since the reduction in EC was as a result of dilution due to rainfall. Therefore, results rather indicated a close association between rainfall and carbon dioxide flux after flooding (Oct – Nov) when enough rainfall was present to impact the EC (Figures 23 and 24).

High temperatures in summer are favourable for physiological processes in soil microbial processes, and plant respiration. This effect of temperature is supported with the research by Pulliam (1993) and Wang et al., (2016), from which they found that high temperatures promote the oxidative breakdown of organic matter and plant tissue (root and shoot) respiration. In a related study, it was found out that wetlands act as sources of carbon dioxide if climate, hydrologic conditions and soil temperatures enhance oxidation of organic matter and root respiration (Altor & Mitsch, 2008).

Chapter 6. Conclusion and recommendations

6.1 Key findings and conclusions

CH_4 and CO_2 fluxes showed distinct diurnal variation patterns, with low CH_4 emissions during the night and high CH_4 emissions in the daytime, diurnal variation patterns demonstrated a relationship with water level and tidal heights. Almost all the diurnal patterns of CO_2 flux indicated CO_2 uptake during the day and CO_2 emissions at night with the exception of January, February and May when heavy rainfalls occurred. CH_4 fluxes were linked to changes in electrical conductivity and water level although this relationship was not statistically significant while CO_2 flux was found to be driven by rainfall and water level. There was no definitive impact on carbon sequestration by the measurements that were carried out before and after tidal flow reinstatement although results demonstrate that freshwater events were seen to influence the carbon balance in the tidal marsh.

CH_4 uptake during the day and some hours in the night for the soil exposed stage (August, September, 2016), suggests a biogeochemical activity consuming CH_4 after its production. This research suggests that there might have been a possibility of aerobic microbial oxidation of CH_4, causing its uptake during August and September 2015, basing on the fact that during this period, there was no flooding in the wetland and the soil was virtually exposed to air. Although, there are limited studies about the geochemistry of Tomago saltmarsh, other forms of CH_4 oxidation could have occurred in the marsh. For instance, the presence of other electron acceptors such as sulphates in marine ecosystems can lead to oxidation of CH_4 even in the absence of oxygen. These findings were confirmed by Caldwell et al.,(2008) and Bridgham et al.,(2013) in marine environments in which oxidation of CH_4 was possible in presence of sulphate ions, and the process consumed more than 90% of the total CH_4 produced. Therefore anaerobic oxidation of CH_4 could have been present after flooding when the surface was covered with water.

The effect of reducing electrical conductivity (EC) of the water in the marsh by rainfall between December and February was not a normal seasonal event. A lot of rainfall (225 mm) on 6th January was received and this contributed significantly towards flooding of the tidal marsh, leading to dilution of the tidal flooding water. Consequently, the electrical conductivity of water reduced tremendously from 31321.09 $\mu S\ cm^{-1}$ in January to 21586.36 $\mu S\ cm^{-1}$ in February. Results indicated that after this rainfall event, EC started to increase from June through December 2016 as the inflow of tidal water continued. The effect of rainfall was noted to have changed the behaviour of the tidal marsh system in relation to other environmental factors. For instance, there was no relationship between water temperature and EC not until after the December to February rainfall events that water temperature showed a positive relative relationship with electrical conductivity.

There was a very weak relationship between CH_4 flux and CO_2 flux (R^2 = 0.101, p = 0.33) which was not statistically significant. It is therefore likely that CH_4 flux might have had negligible influence on CO_2 flux during the time when study was carried out. High CO_2 fluxes that occurred (maximum 0.14 mg m^{-2} s^{-1} in February) were mainly from respiration and decomposition of organic matter. Decomposition of organic matter occurs during aerobic and anaerobic processes although the former are more efficient and mainly produce CO_2 while the latter is much slower and can produce CH_4 in addition to CO_2 (Olsson et al., 2015).

6.2 Recommendations for future

A further study carried out for a period more than two years would allow better investigation into seasonal wetland behaviour in relation to GHG fluxes. The measurement of CO_2 and CH_4 fluxes alone for a period of one year (August 2015 to July 2016) did not demonstrate clearly the effect of environmental factors on geochemistry of carbon, and thus CH_4 and CO_2 fluxes.

Detailed tidal influence assessment on a seasonal scale would give an insight of better tidal flow wetland management plan and scientific literature documentation. Such a study would put into consideration, among other things, the chemical ion analysis of the soil samples for the key electron acceptors such as sulphates, nitrates, iron (III), manganese (IV) in addition to determination of soil redox potentials and pH of the water. Tomago is a vulnerable wetland because of its being close to the industrial park in Newcastle, NSW and it plays a big role in the recycling of carbon and nitrogen.

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Appendix 1

	CO_2 flux (mg m^{-2} s^{-1})		CH_4 flux (µg m^{-2} s^{-1})	
Time	**Day**	**Night**	**Day**	**Night**
Aug-15	-0.05	0.04	-0.06	0.02
Sep-15	-0.07	0.10	-0.08	-0.03
Oct-15	-0.19	0.22	0.08	0.57
Nov-15	-0.18	0.23		
Dec-15	-0.25	0.16	0.07	0.07
Jan-16	-0.11	0.45	-0.06	0.45
Feb-16	0.05	0.17	0.35	0.36
Marc-16	-0.15	0.16	-0.02	-0.03
April-16	-0.11	0.00	-0.26	0.27
May-16	-0.10	0.08	0.01	0.03
June-16	-0.04	0.05	0.01	0.01
July-16	-0.04	0.07	2.54	1.26

Table 1: Diurnal CH_4 and CO_2 fluxes for day and night hours on a monthly scale.

Time	**CO_2 flux (mg m^{-2} s^{-1})**	**Stdev**	**N**	**Std error**	**Median**	**Maximum**	**Minimum**
Aug-15	0.001	0.227	776	0.008	0.004	1.569	-2.016
Sep-15	-0.008	0.215	691	0.008	-0.026	1.427	-2.602
Oct-15	-0.056	0.620	800	0.020	-0.054	2.780	-11.610
Nov-15	0.036	0.711	1128	0.021	-0.027	13.439	-5.406
Dec-15	-0.001	1.060	916	0.040	0.043	8.100	-21.750
Jan-16	0.016	1.071	1071	0.033	0.017	14.008	-9.997
Feb-16	0.137	1.459	1120	0.044	0.091	12.255	-7.747
Mar-16	-0.001	0.604	1177	0.018	0.031	2.076	-14.353
April-16	0.014	0.497	1079	0.015	-0.001	3.558	-6.696
May-16	0.014	0.543	740	0.020	0.021	3.301	-5.310
June-16	0.025	0.131	967	0.004	0.020	0.811	-0.761
July-16	0.021	0.104	140	0.009	0.029	0.464	-0.347

Table 2: Monthly mean fluxes of CO_2

Time	CH_4 flux (µg m^{-2} s^{-1})	Stdev	N	Std error	Median	Maximum	Minimum
Aug-15	-0.040	0.300	522	0.013	-0.013	1.737	-1.964
Sep-15	-0.050	0.268	513	0.012	-0.016	1.253	-1.368
Oct-15	0.192	0.340	36	0.057	0.160	0.900	-0.820
Nov-15							
Dec-15	0.074	0.166	338	0.009	0.048	0.670	-0.479
Jan-16	0.253	0.364	587	0.015	0.201	1.810	-1.586
Feb-16	0.365	0.580	336	0.032	0.331	2.570	-1.881
Mar-16	-9.15E-05	0.522	606	0.021	0.036	1.316	-7.386
April-16	-0.516	0.651	93	0.068	-0.382	0.872	-2.978
May-16	0.011	0.195	1132	0.006	0.012	1.051	-1.709
June-16	0.004	0.259	678	0.013	-0.006	1.891	-1.364
July-16	-0.033	0.429	283	-0.002	-0.006	3.185	-4.766

Table 3: Monthly mean fluxes of CH_4

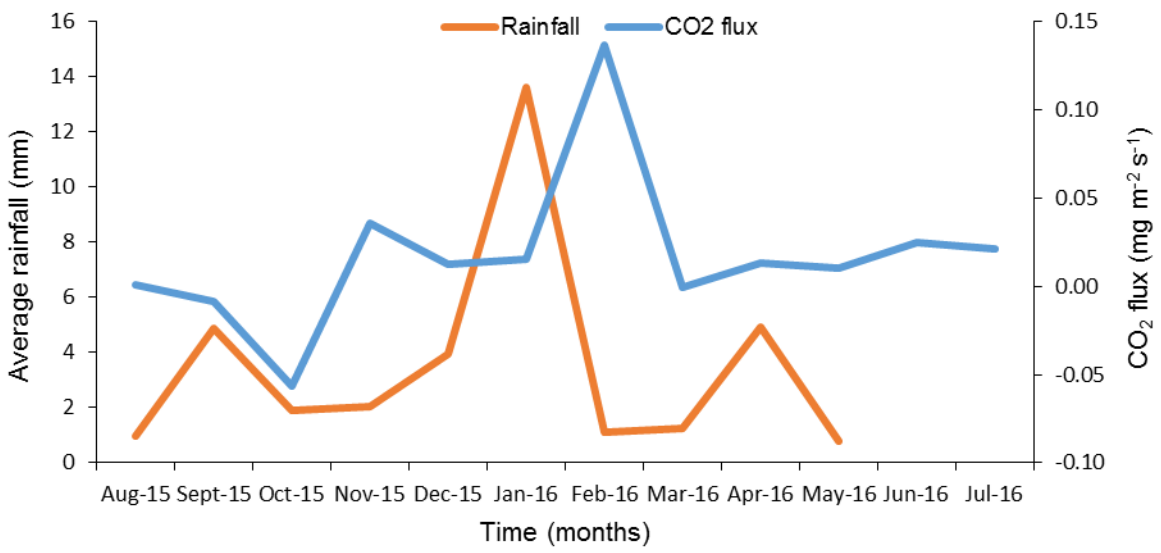

Figure 25: Monthly variation of CO_2 flux with rainfall

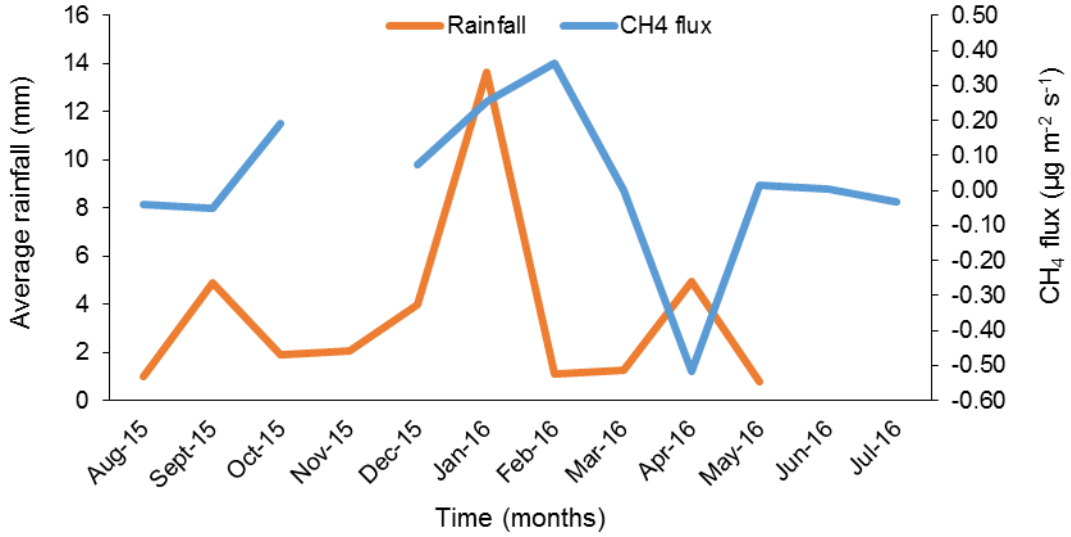

Figure 26: Monthly variation of CH_4 flux with rainfall

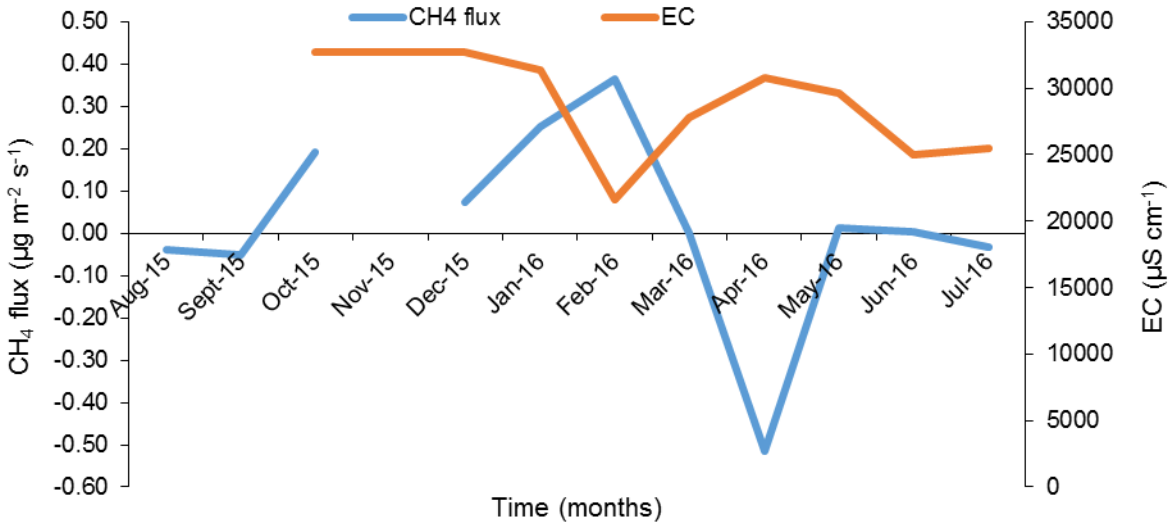

Figure 27: Monthly variation of CH_4 flux and electrical conductivity (EC)

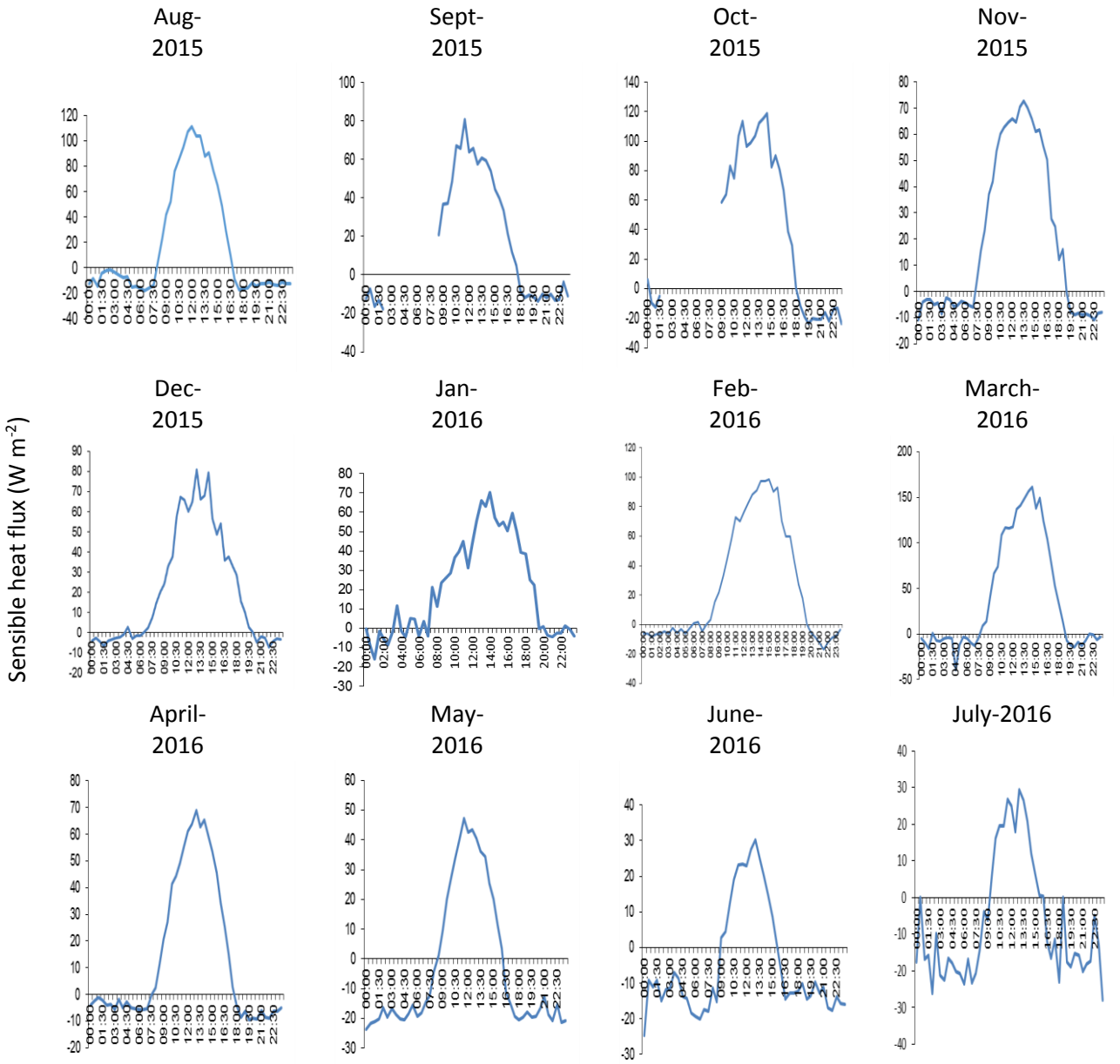

Figure 28: Diurnal variation of sensible heat flux for the entire period of study (from August 2015 to July 2016).