Methane emissions and soil carbon in floodplain wetlands of the Macquarie Marshes

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Saadu Umar Wali

MSc Geography (UDU Sokoto)

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Department of Environmental Sciences

Macquarie University

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Declaration

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

Saadu Umar Wali

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Abstract

Methane (CH_4) emission in wetlands is critical because CH_4 has 25 times the global warming potential of carbon dioxide (CO_2), and wetlands play a critical role in global carbon cycling. Using flux chambers this research investigated CH_4 emissions in three wetland zones in the Macquarie Marshes: reed bed, dry floodplain and dryland. Methane emissions were highly heterogeneous and CH_4 production only occurred in the reed bed (1.73E+01 kg ha^{-1} d^{-1}). In contrast, CH_4 was oxidised in the dry floodplain (-1.03E-03 kg ha^{-1} d^{-1}) and there was no production or oxidation of CH_4 in the dryland zone. Methane flux was strongly correlated with *in situ* moisture content. The median isotopic signature of CH_4 ($\delta^{13}C$; -56.3±2.36 ‰) agrees with wetlands globally and can be used in regional mixing models. The reed bed (809.5 ha) has the potential to release 4.97E-03 Tg yr^{-1} of CH_4 and an equivalent area of dry floodplain could oxidise -2.97E-07 Tg yr^{-1}, yielding a net CH_4 flux of 4.97E-03 Tg yr^{-1}. These results demonstrate for the first time that freshwater floodplain wetlands in dry landscapes can both sequester and emit CH_4, and that where freshwater floodplain wetlands emit CH_4 the rate is comparable to coastal mangroves.

Chapter 1 Introduction

1.1 Introduction

Soil carbon content and emissions of greenhouse gasses (GHGs) including carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) vary between soil types, vegetation communities, landscape units (e.g. rivers, wetlands, drylands), land use types, and climate zones. Understanding biophysical and chemical controls on soil carbon and GHG flux processes is critical for environmental management, particularly for wetlands in drylands (WIDS) that act as hotspots of ecosystem services. This research aims to determine the controls on GHG emissions and soil carbon in the Macquarie Marshes, New South Wales (NSW), Australia, by comparing soil moisture and organic matter content with CH_4 flux and isotopic composition in a wet central reed bed, on the adjacent dry floodplain, and on the surrounding dryland soils. The fundamental research question is "what controls the flux and isotopic signature of CH_4 emissions from an Australian inland wetland?". The research also considers how environmental factors such as soil temperature, pH and electrical conductivity (EC) vary within and between wetland zones, and how these factors affect CH_4 flux, thereby investigating the provenance and characteristics of GHG emissions in different wetland zones with distinctive environmental conditions. While GHG fluxes are highly variable in the landscape, controls on soil carbon and GHG emissions are still debated and there are few datasets to draw conclusions from, especially in relation to WIDS. The rates and characteristics of GHG emissions from WIDS have implications for the global atmospheric GHG budget and may be affected by future changes in rainfall and temperature patterns associated with climate change, ecological productivity, and human land-use.

Despite the importance of wetland vegetation in carbon sequestration, key controls and drivers of wetland GHG fluxes are yet to be fully understood (Mitsch and Gosselink, 2007). While inundation, for instance, can result in bursts of biomass production, the contributions of specific landscape surfaces such as rivers and wetlands to global atmospheric GHGs concentrations vary with landscape types, inundation frequency and other biophysical and geochemical processes (Hall et al., 2016). For example, recent studies revealed that the historical increases in global CH_4 emissions are due largely to the activities of microbes in wetlands, rice paddies, and the guts of ruminants (Nisbet et al., 2016). Net fluxes of GHGs change after inundation, for instance, when inundated soils are drained, the uptake of CO_2 by vegetation increases, but for N_2O and CH_4 fluxes, soil moisture is the major control (VonArnold et al., 2005). Similarly, the rate at which oxygen is depleted depends on the ambient temperature, the availability of organic substrates for microbial respiration, and sometimes the chemical oxygen demand from reductants such as ferrous iron (Mitsch and Gosselink, 2007). Rates of organic decomposition are most rapid in the presence of oxygen and slower for

electron receptors such as nitrates and sulphates. Nitrogen is often the most limiting nutrient in flooded soils (Mitsch and Gosselink, 2007). Therefore, oxidation seemed to be the controlling subscale process for the high CH_4 emissions from wetlands common soils (Langevelda et al., 1997).

Australian research has shown the importance of incorporating knowledge from geographical and environmental science for remediation planning for rivers and wetlands that have been impacted by human activities over long periods (Finlayson et al., 2011). Many conservation strategies for floodplain wetlands, such as the Macquarie Marshes in central NSW, tend to prioritise water distribution and response by ecological communities to flooding (Ralph et al., 2016) instead of critical biophysical controls of organic carbon and GHG fluxes in fluvial systems that produce, store, transform and emit GHGs. In response to water regulation and new conservation policies, the extent of inundation and responses by vegetation communities have been well documented in systems like the Macquarie Marshes (Wang et al., 2015), but the amount of soil carbon produced as a result of inundation as well as the GHG flux characteristics of the wetlands remains unknown.

Therefore, the knowledge gap for GHG flux changes driven by changes in inundation frequency must be addressed. We need to better understand how inundation regimes affect soil carbon production, carbon sequestration by vegetation and CH_4 emissions, as well as CO_2 fluxes affected by seasonal soil moisture removal from wetlands and floodplains (Morin et al., 2014). It is critical, therefore, to understand the links between soil carbon and GHG flux from wetlands in an Australian and global context, as well as the environmental factors (including soil moisture, soil temperature, above ground biomass, soil temperature, pH and conductivity) that can act as major controls on soil carbon and GHG flux. The ability to extend our knowledge of the controls of soil carbon and GHG flux from WIDS, that are likely to affect the global atmospheric GHG budget, is critical for future global warming mitigation and WIDS management.

1.2 GHG flux research for wetlands in drylands

Greenhouse gas flux research has been carried out in many types of landscape units, including: rivers (Battin et al., 2008; Galy et al., 2015; Hall et al., 2016; Hotchkiss et al., 2015; Liikanen et al., 2006; Spencer et al., 2012; von Schiller et al., 2014; Young et al., 2008), wetlands (Anna Joabsson, 1999; Crawford et al., 2014; David Hamilton, 1994; Michael and and Sabmine, 2000; Shoemaker et al., 2012; Song et al., 2012; Ström and Christensen, 2007), drylands (von Schiller et al., 2014); soils (Batson et al., 2015; Jackie Batson1, 2014), groundwater systems (Gleeson et al., 2013; Jungkunst et al., 2008) and vegetation (Chen et al., 2004; Frank et al., 2012; Ibell et al., 2010; Langevelda et al., 1997; Yao et al., 2016). Despite the previous research, GHG emissions from wetlands in drylands are still not well studied. Many wetland ecosystems are recognised as important carbon sinks; however,

the capacity of different wetlands to sequester, transform and emit GHGs is thought to be highly variable. Therefore, wetlands in drylands cannot necessarily be assumed to act as carbon sinks and further research is required into CH_4 flux.

Wetlands in drylands may be permanent, seasonal or ephemeral and may support large, deep, shallow water bodies, or overlay a very rich groundwater aquifer. Methane flux from dry water courses can be substantial, comparable to that from rivers, wetlands and vegetation (von Schiller et al., 2014). Although drained soils may have shallow groundwater tables, their annual CO_2 release, nearly doubled compared to deep groundwater levels (VonArnold et al., 2005), and the average annual CH_4 emissions is about 10 times greater than from deep subsoils. Further, the seasonal pattern in the depth-integrated CH_4 production rates is strongly influenced by temperature (Shoemaker et al., 2012). While anaerobic decomposition continuously produces CH_4 emissions (Jungkunst et al., 2008), soil carbon of drier patches will decompose more rapidly, there by producing more CO_2 effluxes. The three main GHGs, CO_2, CH_4 and N_2O, are stored in wetlands and as such have different global warming potentials (Jungkunst et al., 2008).

In Australia, WIDS are usually sites of high biodiversity that depend on flows from streams, rivers or groundwater, although land use changes (including dams, diversions and river management) have reduced the volume of water reaching many wetlands (Kinsford, 2000), thus, altering the composition of both aquatic and terrestrial ecosystems. In fact, the ecological character of many wetlands across Australia have been changed by drying up of water courses feeding these wetlands (Finlayson et al., 2011), due to increased water regulation, demand by agriculture and industry.

GHG flux from landscapes depends on the type of GHG source, effects associated with producing organisms, and cellular GHG budgets (Hayes, 1993). Similarly, the potential of a particular wetland to sequester, transform and emit GHGs changes with soil moisture regime, vegetation and soil types, as well as time due to environmental conditions and ecological composition (Kai, 2013; Tiunov, 2007). GHG emission models can be used to simulate the global atmospheric GHG emissions. These models are typically based on a broad spatial scale with relatively large uncertainties in bottom up and top down flux characteristics of GHGs. Therefore, site specific studies of GHG flux are advantageous as they enable identification of specific sources of particular GHGs, quantification of emission rates, and greater understanding of how a particular type of GHG flux pattern varies with landscape type and other environmental factors such as soil moisture, soil temperature, vegetation and soil type. Understanding the rates of efflux from a particular landscape and the biophysical and geochemical processes in operation, which accelerate the transformation and emissions of GHGs over

distinct landscapes, creates the ability to address and limit the challenges and uncertainties in GHG flux behaviour by comparing independent results obtained from different landscapes.

Some of the uncertainties and challenges associated with GHG flux research include: effects of environmental change (rainfall and temperature) on GHG flux character (Bunn and Arthington, 2002; Davidson et al., 1998; Leifeld and Fuhrer, 2005; Morin et al., 2014), effects of landscapes types - wetlands and drylands (Langevelda et al., 1997; Ojanen et al., 2010), effects of surface-groundwater interactions (Furukawa et al., 2005; Jungkunst et al., 2008), effects of other environmental factors – soil moisture, temperature, vegetation types (Battin et al., 2008; Morin et al., 2014), and changes in land use (Ibell et al., 2010). In addition, employing site specific GHG flux analysis can allow for comparison of GHG flux characteristics of different wetlands and drylands, resulting in more accurate and robust records of GHG flux pattern from different environments.

Understanding the spatial variability of GHG flux, soil carbon and soil moisture from wetlands particularly in arid and semi-arid regions in Australia is becoming increasingly important in the context of global climate change and the associated projected changes in rainfall and temperature. This research will contribute to the scientific basis of understanding CH_4 emissions from WIDS and has implications for similar WIDS and their management in many parts of the world (e.g. sub-Saharan Africa, Asia and America). The findings of this study will have important implications for our understanding of controls on CH_4 flux and soil carbon in landscapes with distinctive environmental conditions (including soil moisture regimes, vegetation and soil types) in a wetland system with reed beds, creeks and swamps that have a long history of human occupation and use.

1.3 The Macquarie Marshes

The Macquarie Marshes are located on the lower reaches of the Macquarie River in NSW, Australia, and are among the largest multi-channelled floodplain wetlands in the Murray-Darling Basin (Ren et al., 2010). The Marshes are situated between Warren and Carinda, and the alluvial plain where the marshes occur is semiarid and is characterized by irregular local rainfall (Ralph et al., 2016). The floodplain wetlands receive flows from the Macquarie River, which sources its runoff from the middle and upper Macquarie catchment. The geomorphology of the Macquarie Marshes indicate long history of fluvial change linked to climate and hydrology (Ralph and Hesse, 2010). While water regulation has affected the wetlands by causing changes in ecosystem composition in the Marshes, the impacts of these changes on biogeophysical and chemical processes that control soil carbon and CH_4 flux are yet to be investigated and for the first time this is will be addressed by this study. Understanding the processes that control CH_4 flux and soil carbon in the Macquarie Marshes over different wetland zones is critical for WIDS management.

1.4 Aims and Research Question

This research aims to assess the controls on and relationships between CH_4 flux, soil moisture and soil carbon in the Macquarie Marshes by investigating key sites in a core reed bed, the dry floodplain and in the surrounding dryland soils. Therefore, the fundamental research question is "what controls the flux and isotopic signature of CH_4 emissions from an Australian inland wetland?". To answer this question, the following specific objectives have been addressed.

1.4.1 Objectives

i. Define the relationships between soil moisture and CH_4 flux in three wetland zones of the Macquarie Marshes.

ii. Determine whether soil carbon and environmental factors such as soil temperature, soil pH and soil EC vary within the wetland zones, and how this variability affects CH_4 flux, thereby assessing controls on soil carbon and CH_4 emissions in wetland zones with distinctive environmental conditions.

1.4.2 Research hypotheses

To achieve these outcomes, this study tests the following specific hypotheses:

H_1 Soil moisture, soil carbon and CH_4 flux will vary between the three wetland zones, with the regularly inundated reed bed being a major hotspot of organic carbon and CH_4 release;

H_2 Methane isotopic signatures in the wetlands will correspond to CH_4 values reported elsewhere;

H_3 Methane flux will correlate with greater soil moisture, soil organic matter, aboveground biomass, and soil temperature;

H_4 Soil carbon stock in the wetland zones will be determined by aboveground biomass and inundation regime.

This study will provide the first estimates of CH_4 flux in a reed bed, in the dry floodplain and surrounding dryland soils of the Macquarie Marshes, as well as describing the links between CH_4 flux, soil moisture and soil carbon, which could be used for estimation of GHG emissions within the broader Macquarie Marshes and for other wetlands in the Murray-Darling Basin, Australia.

1.5 Thesis Structure

This chapter presented an overview of the importance of GHG and particularly CH_4 research, and highlighted the need to advance the spatial and temporal extents of soil carbon and GHG flux knowledge from wetlands in dry landscapes. It outlined the objectives and hypotheses addressed by this research, and introduced the study area – the Macquarie Marshes.

Chapter 2 is a brief review of relevant literature on dynamics of GHGs, with emphasis on wetlands in drylands. The review addresses research knowledge gaps for Australian wetlands and the need to extend our understanding of environmental controls and drivers of GHG flux from WIDS.

Chapter 3 is the main body of the thesis, and comprises a full draft manuscript of a paper intended for the journal *Biogeosciences*. This paper, titled 'Quantification of flux and isotopic signature of methane emissions from floodplain wetlands of the Macquarie Marshes, Australia' introduces the topic and describes the study sites, methods, and results of the research, as well as discussing the merits of the findings and the broader implications in the context of previous research.

Chapter 4 presents a summary of the major research findings and explains how these relate to the stated objectives and hypotheses.

Chapter 2 Review of methane emissions and soil carbon in wetlands in dry landscapes

2.1 Introduction

This chapter reviews and synthesises literature addressing soil carbon and GHG flux research for wetlands in drylands (WIDS) such as the Macquarie Marshes, Australia. The chapter highlights the existing gaps in knowledge of the environmental controls and drivers of soil carbon and GHG flux from Australian wetlands. However, the effects of auxiliary environmental factors such as soil moisture, soil temperature, and aboveground biomass on soil carbon and GHG flux from wetlands is addressed.

2.2 The relevance of soil carbon and GHG flux research in wetlands

Investigating the controls of soil carbon and GHG flux from WIDS extends the frontiers of knowledge related to spatial and temporal patterns of global GHG emissions. It may also help to identify sources of carbon production and/or sequestration related to GHG flux in wetlands, and to determine whether GHG emissions are controlled by environmental factors such as soil carbon, soil moisture, soil temperature, and aboveground biomass. This creates the ability to assess the extent to which WIDS contribute to the global GHG budget. GHG emission research also increases our ability to predict how the future atmospheric GHG budgets may change, and how environmental changes may affect global biogeochemical cycles and the resultant consequences on the environment and for human wellbeing.

2.3 Research knowledge gaps

The global GHG budget is strongly influenced by ecosystem carbon production, storage, biophysical and geochemical processes that transform and emit GHGs from different landscape surfaces (Bui et al., 2009). While dissolved organic matter (DOM) from wetlands represents a fundamental layer in the global carbon budget (Spencer et al., 2012), CO_2 flux from wetlands, streams and rivers constitutes a major component of global carbon cycle (Crawford et al., 2014). Although wetlands are typically sinks of CO_2 (Morin et al., 2014), wetlands are also dominant sources of global atmospheric CH_4 (Crawford et al., 2014). Therefore, it is quite difficult to understand the role of wetlands in the global atmospheric GHG budget, because of large disparities found in bottom-up and top-down estimates of GHG fluxes. This is particularly the case for WIDS, where inundation, soil moisture and other environmental variables such as annual rainfall and temperature are highly variable.

Soil carbon production, transformation and GHG emission in rivers of Australia indicates that riparian sources dominate carbon pools in streams and catchments, while floodplain sediments represent a substantial sink of riverine particulate organic carbon (POC) (Robertson, 1999). This study acknowledges the interactions between geomorphology, surface flow and river regulation as well as the temporal and climatic influence on POC production. However, the study did not explain how DOC is transformed and emitted from floodplain wetlands. Although, the characteristics of soil carbon in Australian wetlands, like in many regions of the world, vary with rainfall distribution, continental vegetation, soil moisture and temperature patterns (Bui et al., 2009), how these variabilities affect GHGs flux from fluvial systems remain largely unknown particularly in Australian inland wetlands.

The status and knowledge of Australia's wetlands has increased in recent years with greater understanding of their distribution and extent, biota and ecological conditions (Finlayson et al., 2011). While considerable amounts of research were undertaken in Australian inlands freshwater wetlands including (Bui et al., 2009; Kinsford, 2000; Thomas et al., 2011). Most of these studies focussed particularly on inundation extents and response by ecological communities, instead of critical biophysical and geochemical processes that act in conjunction with inundation (or soil moisture) to affect soil carbon (SOM) and GHG flux in fluvial network systems. Generally, in Australia, there has been little input of scientific principles into investigating GHG flux characteristics from typical Australian fresh water wetlands.

The ecological character of many WIDS in Australia has deteriorated in recent decades as a consequence of water regulation (Finlayson et al., 2011). This in addition to changes in annual rainfall, result in fluctuations of standing water level. Falls in groundwater table and drying up of surface water bodies in WIDS contribute greatly to increased CO_2 fluctuations, even though CH_4 fluxes can be slightly reduced (Furukawa et al., 2005). There is no doubt that groundwater levels in Australia, are heavily impacted by changes in annual rainfall and landuse (Giambastiani and Kelly, 2010), but how these changes might affect soil carbon and GHG flux, is largely un investigated from Australia's inland wetlands systems located in drylands. This poses a great challenge that need to be adressed, as shall be attempted in this study.

2.4 Overview of methane emission from different wetlands around the world

Atmospheric CH_4 concentrations have increased since pre-industrial times. From 1750 to 2011 the atmospheric concentration of CO_2 increased by 40%, from 278 ppm to 390.5 ppm (Ciais et al., 2013). During this same period, the atmospheric concentration of CH_4 increased by 150%, from 0.722 ppm to 1.803 ppm (Ciais et al., 2013). Global atmospheric CH_4 concentrations and estimates

of atmospheric lifetime limit total CH_4 emissions between 500 to 600 Tg yr^{-1}. Estimates of global CH_4 emissions from wetlands range from 80 to 280 Tg yr^{-1} (Bridgham et al., 2013). After a decade of stability in atmospheric CH_4 concentrations, atmospheric measurements indicate that since 2007 there has been renewed annual increase in the concentration of CH_4 in the atmosphere. The drivers of this renewed growth are still debated (Ciais et al., 2013). Atmospheric CH_4 budget between 2000-2009 is summarised in Table 2.1. During this period natural wetlands, agriculture and waste dominated emissions.

Table 2.1 Overview of global methane budget for the decade 2000 to 2009. After (Ciais et al., 2013).

Methane source	**Methane flux (Tg yr^{-1})**
Natural wetlands (bottom-up estimates)	177 – 284
Agriculture and waste (rice, animals and waste)	85 – 105
Fossil fuel related emissions	61 - 200
Other natural emissions (geological, termites and freshwater)	32 - 39
Biomass and biofuel burning	-

Wetlands constitutes small portion of global land area (5 to 8 %), but they are the largest natural source of atmospheric CH_4, with median emissions of ~164 Tg yr^{-1}, which constitutes about one third of global emissions (Bridgham et al., 2013). Emissions from northern high altitude wetlands (Zhu et al., 2013) showed that between 1990 to 2009, ~48.7 Tg yr^{-1} is being released. While global wetlands emit large quantities of CH_4, methane emissions from wetlands in both dry and wet climates show a large temporal and spatial variation, which can partly be described by correlations with environmental variables (Sari, 2004). Methane emission from landscapes surfaces have extensively being studied (Table 2.2), with most studies focusing on wet and peatlands.

However, there is disagreement if wetlands are actually carbon sources or sinks (Kayranli et al., 2009). In addition, there is also disagreement in the interpretation of internal drivers of carbon sequestrations and emissions in wetlands (Table 2.3). Further, the environmental conditions in wetlands are also dependent on other external forces, like climate. For instance, Fest et al (2017) compared CH_4 flux from dry and wet forests. Their study revealed that, variation in CH_4 uptake in both dry and wet conditions was strongly controlled by soil moisture. This study agrees with Boeckx, et al., (1996) and Gatland et al (2014). Table 2.3 provides an overview of GHG fluxes and their environmental controls and drivers.

Table 2.2 Overview of methane studies from different ecosystems around the world.

Country	Site name	Ecosystem type	Methane flux (g CH_4 m^{-2} d^{-1})	Citation
Australia	Richmond Catchment	Coastal floodplain	1.04	Atkins et al. (2017)
Australia	Mary River Catchment	Tropical floodplain	25.3E-06	Bass et al. (2014)
Australia	North-eastern NSW	Forested wetlands	1.029	Akumu et al. (2010)
Australia	North-eastern NSW	Costal upland water bodies	0.015	Akumu et al. (2010)
Canada	Haliburton Forest	Temperate Forest	39.33	Wang et al. (2013)
Canada	Boreas fen site	Bog	7.61	Rask et al. (2002)
China	Sichun	Peatland	71.04	Ding et al. (2004)
China	Zoege Plateau	Wetlands	58.8	Chen et al. (2010)
Denmark	-	Fresh water wetland	0.08-0.345	Rask et al. (2002)
England-UK	Tadham Moor	Wetland meadow	-0.066	Zhu et al. (2013)
Finland	Boreal Forest	Peatlands	12.72-588.00	Ojanen et al. (2010)
India	Mooringanag Creek	-	0.64	Call et al. (2015)
Malaysia		Fresh water wetland	16.25	Rask et al. (2002)
Mongolia	Inner Plateau	Riparian Mires	234.30	Wang et al. (2005)
Netherland	R.O.C. Zegveld	Peat soils	0.27-0.43	Langeveld et al. (1997)
Poland	Lodz	Inhabited (city)	0.66-0.24	Pawlak and Fortuniak (2016)
Sweden	Stordalen, Abisko	Sub-arctic wetland	2681.2	Strom and Christensen (2007)
Tanzania	Ras Dege	Coastal wetland	0.160-1.12	Call et al. (2015)
Thailand	Thai Rice Paddies	Freshwater wetland	2.84-8.05	Rask et al (2002)
USA	Prudhoe Bay, Alaska	Wet coastal tundra	0.166-0.203	Zhu et al. (2013)
USA	Barrow Alaska	Wet/moist coastal tundra	0.01-0.17	Zhu et al. (2013)

Table 2.3 Overview of environmental controls and drivers of GHG flux from wetlands.

GHG flux	Controls and drivers	Methods used	Examples/citation
1. High CH_4 flux from forested wetlands compared to open wetlands	Productivity factor, wetland area, precipitation ratio.	A process-based model (Landsat ETM+) + chambers	North-eastern NSW, Australia (Akumu et al., 2010)
2. CO_2 evasion contributed to wetland C loss, CH_4 evasion contributed to CO_2 emissions	Deoxygenation and acidification in waters	Micrometeorological techniques	Richmond River Catchment, Australia (Gatland et al., 2014)
3. Seasonal CH_4 flux correlate strongly with soil temperature and organic acid concentrations	Temperature and microbial substrate availability	Static chambers (squared, 10 – 3-litres)	North-western Eurasian and Greenlandic North, Greenland (Christensen et al., 2003)
4. High correlation between moisture content and reduction of CH_4 uptake rate.	Soil moisture content and temperature	Diffusion chambers (H = 600mm, D = 150mm)	Landfill, Schoten-Antwerp, Belgium (Boeckx et al., 1996)
5. Variability in GHG flux attributable to contrasting dry matter liability and soil physical properties	Soil water depth and soil properties	Drilling-based technique (Lysimetre)	Orke and Majne-gaden, Sweden (Berglund and Berglund, 2011)
Variation of CH_4 flux correlate to seasonal variation of temperature and precipitation.	Temperature and precipitation	Open-ended static chambers	Sanjian Mire, Sanjiang Plain, Hongyuan county, China(Ding et al., 2004)
6. CH_4 fluxes are 30 times higher from ponds compared to adjacent vegetated area.	Underlying peat and N_2 fixing cyanobacteria	Micrometeorological techniques	Boreal and Sub-arctic, USA (David Hamilton, 1994)
CH_4 flux rates varies with planting date, straw addition. Diel variation of CH_4 flux correlates strongly with temperature.	Solar radiation, temperature and straw incorporation	Static chamber technique	Rice fields, Texas, USA(Sass et al., 1991)
7. Large hourly variation in CH_4 fluxes, no systematic diurnal variation in CH_4 fluxes. CH_4 flux was exponential to peat and temperature	Peat depth and annual temperature	Eddy covariance technique	Boreal fen, Finland (Janne et al., 2017)

However, CH_4 production and consumption in both wet and dry ecosystems is a microbiological process, controlled by the energy sources required for methane producing and oxidising bacteria and archaea. There are now many extensive studies on CH_4 emissions in different landscape setting (Table 2.1). However, the controls and drivers of CH_4 emission from wetland are still debated, as it is not clear which environmental factor is the most influential when they all operate simultaneously. Methane flux is highly variable in both wetlands and drylands, because CH_4 fluxes tend to be characteristic of ecosystem types and the prevailing environmental conditions (Table 2.2). Michael and Sabmine (2000) studied groundwater levels and redox potentials of common wetland

soils in a temperate-humid climate, Germany. Their study revealed high emissions of CH_4, fluxes ranged from 5-73 g m^{-2} yr^{-1} which increased with inundation of wetland soils. This finding concurs with Gatland et al. (2014). Their study on CH_4 emissions in coastal wetland, showed high CH_4 fluxes occurred during inundation period. Morin et al. (2014) concluded that CH_4 emissions in wetlands increased as a result of rising water level and atmospheric temperature. Diel variation of CH_4 strongly correlated with temperature, atmospheric pressure and the height of the atmospheric boundary layer (Xu et al., 2017)

2.4.1 Isotopic composition of methane from wetlands

The development of stable isotope techniques is one of the major breakthrough of the last century (Jochen, 2015). The technique is increasingly being used to solve biogeochemical problems in ecosystem (Peterson and Fry, 2016). For carbon stable isotope ratios $\delta^{13}C$ (‰), the calculation is defined as $\delta^{13}C = (R_s / R_{std} - 1) \times 1000$ (Thompson et al., 2016). Where R_s is the isotopic ratio $^{13}C/^{12}C$ of the sample and R_{std} the carbon stable isotope standard. Atmospheric CH_4 has a mean $\delta^{13}C$ value of around -47 ‰ (Jochen, 2015). Measurements of spatial and temporal variation in global $\delta^{13}C$, showed a slight enrichment in southern hemisphere (-47.2 ‰) relative to northern hemisphere (-47.4 ‰). However, CH_4 derived from air bubbles in polar ice, up to 350 years in age, has a ^{13}C value which is 2 ‰ lower than at present. This suggests that anthropogenic burning of fossil fuels and biomass may be the fundamental driver of the present ^{13}C enrichment in methane (Jochen, 2015). Table 2.4 summarizes global estimates of CH_4 from wetlands.

Table 2.4 Overview of global $\delta^{13}C$ CH_4 isotopic signature (‰) from wetlands. After (Ginty, 2016).

Wetland type	**$\delta^{13}C$ CH_4 isotopic signature (‰)**	**Citation**
Rice paddies	-54 to -64	Whiticar, (1999)
Bogs and Tundra	-58	Mikalof Fletcher et al., (2004)
Natural wetlands	-58.3	Whiticar, (1999)
Swamps	-58	Mikalof Fletcher et al, (2004)
Wetland - alaska tundra	-73 to -55	Quay et al., (1988)
Wetland - Peat Bog	-86 to -50	Quay et al., (1988)
Wetlands	-59	Monteil et al., (2011)
Wetlands	-86 to -31	Quay et al., (1991)
Rice paddies	-63	Whiticar, (1990)

Schweitzer et al.'s (2016) review of global fossil fuel CH_4 emissions based on isotope database indicates that CH_4 emissions from natural gas, oil and coal production and their usage are 20 – 60 % greater than the reported estimates by past studies. However, CH_4 production by natural sources have stabilized between 1999 to 2007 before the renewed emissions.

Historical records of $\delta^{13}C$-based source attribution for different periods, showed upward trend of emissions from fossil fuel, industries and geological sources between 0-1700 and 1985-2002 (Schwietzke et al., 2016). From 2003 to 2013, there were declines in CH_4 emissions from these sources. However, biomass and microbial sources showed consistent upward production from 0-1700, through 1985-2002 and from 2003-2013. In addition, two separate studies of $\delta^{13}C$ CH_4 isotopic trends for 1990-2005 arrived at different conclusions. Continuous fossil fuel emission and decreasing microbial emissions in the Northern Hemisphere were first inferred (Schwietzke et al., 2016). In contrast, Kirchke et al (2013) concludes that $\delta^{13}C$ CH_4 isotopic trends were driven by decreasing rice paddies (Kirschke et al., 2013; Zhang et al., 2017).

Many recent studies (Atkins et al., 2017; France, 2016; Holmes et al., 2015; Marushchak et al., 2016; Thompson et al., 2016; Vaughn et al., 2016) have used stable isotope analysis to measure CH_4 flux in wetlands. Isotopic signatures in Richmond River Catchment, for instance, were characteristic of temporal variability rather than spatial trend. The DIC compositions were driven by changes in groundwater flows and rainfall events (Atkins et al., 2017). During warmer months DIC pools is decreased by aquatic photosynthesis, there by enriching $\delta^{13}C$-DIC by preferentially removing the $^{12}CO_2$ isotopologue. During cooler months, $\delta^{13}C$-DIC was lower indicating that groundwater flows outweighed aquatic photosynthesis as the predominant control of the DIC pool during the drier seasons (Atkins et al., 2017). However, combined atmospheric modelling environment and inventory analysis by France et al. (2016) indicates air mass in the planetary boundary layer over Russia and Barents Sea, with wetlands being the likely dominant source of CH_4 in that region. Holmes et al.'s (2015) analysis of factors influencing CH_4 and CO_2 production and oxidation pathways from 58 wetlands, showed a combination of environmental factors including soil pH, vegetation type, soil EC and latitude correlate to the dominant methanogenic pathway. However, their analysis indicates that tropical wetlands do not correlate with these factors in the same way as northern wetlands do, suggesting the effects climate change as responsible for different correlations.

However, plant mediated diffusion through aerenchyma, a process that discriminates ^{13}C CH_4, dominates CH_4 emission pathways from wetlands to the atmosphere (Marushchak et al., 2016). The CH_4 emitted in the atmosphere from wetlands in subarctic tundra, was found to be lighter compared to that of surface pore water, and $\delta^{13}C$ in the emitted CH_4 correlated negatively with vascular plant cover (Marushchak et al., 2016). In the same vein, Thompson et al.'s (2016) analysis of $\delta^{13}C$ and $\delta^{2}H$ of CH_4 showed higher concentrations of CH_4 in the hypoxic deep water coincided with decreasing dissolved CO_2 concentrations. While most depleted values of $\delta^{13}C$ and ^{2}H isotopic values occurred in profundal sediments, and methanotrophic oxidation dominated in epilimnion based upon decreasing concentrations and increasing values of $\delta^{13}C$ CH_4 and $\delta^{2}H$ CH_4(Thompson et al., 2016).

Their comparison of $\delta^{13}C$ and $\delta^{2}H$ observations of CH_4, showed acetate fermentation was likely the dominant production pathway throughout the system. This finding concurs with Vaughn et al. (2016). Their study also found that stable isotope signatures of CH_4 and DIC were dominated by acetate cleavage for CH_4 production in low-centred polygons of arctic polygon tundra.

2.5 Environmental drivers of soil carbon in wetlands

A range of environmental drivers affects soil carbon and CH_4 flux from wetlands. These include groundwater levels, inundation pattern, soil temperature, vegetation types, soil EC and soil pH. Fluctuating water table levels for instance, may hinder the effective production of CH_4 by thwarting the microbial methanogenic consortium through the introduction of oxygen. Soil temperature is also widely considered a highly influential variable on CH_4 level, likely owing to the stimulation of the metabolic tolls of microbial methanogenic consortium in the soil (Morin et al., 2014). While oxygen level affects the relative rate of CH_4 generation and oxidation, both processes are controlled by increased soil temperature (Morin et al., 2014).

Battin, et al. (2009) studied the biophysical controls on organic carbon fluxes in fluvial networks. The study indicates large downstream trend of declining in-stream storage volumes and storage times of dissolved organic carbon (DOC) with increasing river or streams discharge. Because discharge shapes the channel geomorphology and bed topography through fluvial networks and is thus, likely to control rich-scale DOC storage dynamics in floodplain wetlands. For instance, flow over morphological features controls surface and sub-surface fluxes, whereas sediment characteristics control the resistance to exchange. High gradient streambeds create opportunities for subsurface retention and storage of DOC under flow conditions. In contrasts, low-gradient streams and rivers are generally depositional environments during low flows. Fine-grained sediments accumulate, clog interstitial spaces and reduce bed roughness, all of which reduce the potential for surface-subsurface fluxes, storage and retention of DOC in floodplain wetlands.

Mitsch et al.'s (2013) wetland carbon and climate change study showed that while wetlands provide an optimum natural environment for the sequestration of atmospheric CO_2, yet they are large emitters of CH_4. The study further illustrates that when carbon sequestration is compared to CH_4 fluxes; do not have 25 times more CO_2 sequestration than CH_4 emissions. They further illustrate (using dynamic modelling) that carbon flux from temperate and tropical wetlands, that CH_4 emissions from wetlands may become unimportant within 300 years when compared to carbon sequestration in wetlands. However, within that period, most wetlands may become both net atmospheric CH_4 sources and sinks. This study concurs with Birol et al (2009), who showed that wetlands can be both sources

and sinks of carbon, depending on their age, operation and the environmental boundary conditions (e.g. climate and latitude).

2.5.1 Effects of groundwater levels on GHG fluxes

Fluvial water courses in drylands (often connected to groundwater) have the ability to process carbon during downstream transport and emit considerable amount of CO_2 (von Schiller et al., 2014). In floodplain soils, the groundwater level is thought to be the most important control of methane emissions (Michael and and Sabmine, 2000), because the depth of wet soils controls both the depth of methane production zones as well as the thickness of the oxidation zone. In the same vein, deep groundwater levels correspond to a greater vertical extension of the zone of oxidation and subsequently lead to lower emission (Michael and and Sabmine, 2000). At very deep water levels, no significant relationship exists between emissions and the groundwater levels. Groundwater table levels may be seen at as important but it is not positively correlated to higher methane emissions (Michael and and Sabmine, 2000). Variability in GHG emissions from soils are also attributable to contrasting dry matter liability and soil physical properties, which regulate the water table, and while well drained soils can be CH_4 sinks, significant emissions of CH_4 have been reported from drained peatlands (Berglund and Berglund, 2011).

The ecological character of many wetlands across Australia has deteriorated in recent decades as a consequence of water regulation (Finlayson et al., 2011). In addition to changes in annual rainfall, this might account for the observed fluctuations in standing water level. Falls in groundwater table and drying up of surface water bodies in WIDS contribute greatly to increased CO_2 fluctuations, even though CH_4 fluxes can be slightly reduced (Furukawa et al., 2005). There is no doubt that groundwater levels in Australia are heavily impacted by changes in annual rainfall and landuse, but how these changes might affect soil carbon and GHG flux, is largely uninvestigated.

2.5 The importance of inundation in floodplain wetlands

Understanding the response of a wetland ecosystem to inundation over longer timeframes is essential to evaluate how changes in surface flows can affect soil carbon control and GHG flux from wetlands. Thomas et al. (2011) demonstrated the extreme variability of inundation in the Macquarie Marshes by investigating spatio-temporal patterns of radiosynthetically active radiation absorbed by the vegettaion canopy. However the study does not explain how inundation relates to vegetation or biomass, nor how inundation drives critical biophysical processes controlling organic carbon production and GHG flux in the wetlands. However we know that wetland vegetation plays a central role in carbon and nutrient dynamics (Mitsch et al., 2012), and wetland vegetation growth is dependent on floodplain inundation frequncy. While CH_4 emissions from vegetated surfaces has been

extensively studied (Rietl et al., 2017), there are few reports on CO_2 and CH_4 emissions from freshwater wetlands even though the latter correlates with inundation (David Hamilton, 1994; Gatland et al., 2014). It is also important to note that many studies are focused on flood-vegetation response modelling, which does not explain how flood-vegetation responses can be extended to understand soil carbon and GHG fluxes in wetlands.

Wetlands are also highly sensitive to climate fluctuations and associated changes in rainfall and temperature which play a dominant role in an ecosytem primary productivity. While ecosystem productivity is dependent on climate and inflow, the controls of soil carbon and GHG flux is largely a product of biogeophysical and chemical activities within a ecoystem, which can in turn be impacted by changes in temperature and soil moisture regimes. As a result of varying inudation regimes and other external controls and intrinsic processes, many wetlands are highly heterogeneous, which may translate into variability of soil carbon and GHG flux characteristics. The heterogeneous compositions of aquatic species in wetlands have evolved life history strategies primarily in response to the natural flow, and the invasion and success of exotic and introduced species in wetlands is facilitated by changes of flow regimes (Bunn and Arthington, 2002). Ecosystem composition changes in wetlands, is normally associated with changes in biophysical and chemical processes. Establishing these relationships and at the same time quantifying soil carbon and GHG flux in relation to biomass production has become a complex issue in environmental science, because of the difficulties and uncertainties involved in investigating and understanding the controls of soil carbon from landscapes surfaces in relation to atmospheric chemistry (Olsson et al., 2015).

GHG fluxes from wetlands are also highly variable both spatially and temporally. However, the presence of vascular plants has been recognised as one of the key factors controlling the scale of GHG fluxes in wetlands because it affects the biogeochemical processes that act jointly together to produce, transport, and emit GHGs (Anna Joabsson, 1999). However, changes in GHG flux derived from changes in wetland vegetation alone could be inadequate to draw conclusions regarding wetland GHG flux. Because, GHG flux can be affected by grazing animals, changes in inundation as well as temperature, which act to control the biophysical and chemical processes controlling greenhouse flux from wetlands.

2.6 Conclusion

The literature highlights the importance of understanding of environmental controls on GHG production and oxidation from different landscapes. It is clear from the literature that the general links between inundation, soil moisture, vegetation response, soil bacteria, soil carbon and GHG flux are broadly understood. However, more research is required to refine our understanding of when, where and how CH_4 will be produced or oxidised in inland terminal wetlands systems.

Chapter 3 Methane emissions and soil carbon in the Macquarie Marshes

Purpose: This chapter presents original research that has been carried out for this MRes. The chapter introduces the topic, provides an overview of the study area, details of methods and results, and a discussion related to CH_4 flux, soil carbon and environmental conditions in floodplain wetlands of the Macquarie Marshes. The findings presented in this chapter are fundamental to this thesis and build upon the information in the chapters 1 and 2 by applying environmental measurements and gas flux approaches to investigate soil carbon and CH_4 flux in wetlands. Further, the chapter addresses objectives i and ii highlighted in chapter 1, integrating soil carbon and GHG flux techniques.

Format: In line with the Macquarie University policy for higher degree research thesis by publication[1], this chapter has been drafted for submission to a peer-reviewed journal (*Biogeosciences*). Duplication and any referencing and technical inconsistencies have been minimised to simplify the thesis examination process. Supplementary material and references cited in the paper are provided in the reference list and appendices at the end of the thesis, and are intended to be integral reference and supplementary material included in the published version of this paper.

Author contributions: The following contributions have been made by authors of this paper.

Saadu Umar Wali helped to design and develop the study, conducted field sampling and soil analysis, analysed all forms of data, drafted figures, tables and appendices, wrote and edited the paper.

Tim Ralph designed and developed the study with S.U.W., B.K. and T.K., analysed some soil and statistical data, drafted Figure 2, helped to edit the paper, and supervised S.U.W. in the research.

Tsuyoshi Kobayashi designed and developed the study with S.U.W., T.R. and B.K., analysed some statistical data, provided comments on the paper, and co-supervised S.U.W. in the research.

Charlotte Iverach measured the CH_4 concentration and isotopic composition of all air samples.

Bryce Kelly designed and developed the study with S.U.W., T.R. and T.K., oversaw CH_4 flux measurements, analysed the CH_4 data and drafted some figures, provided comments on the paper, and co-supervised S.U.W. in the research.

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1 Macquarie University policy states that a thesis by publication may include relevant papers that have been published, accepted, submitted or prepared for publication for which at least half of the research has been undertaken during enrolment. The paper (or papers for a PhD thesis) should form a coherent and integrated body of work, which form one part of the thesis, rather than separate components (or appendixes). Papers may be single author or co-authored. The candidate must specify his/her specific contribution and contribution of others to the preparation of the thesis or to individual parts of the thesis should be specified in the thesis acknowledgments and/or in relevant footnotes/endnotes. Where a paper has multiple authors, the candidate would usually be the principal author and evidence of this should appear in the appropriate manner for the discipline.MQ Policy: http://www.mq.edu.au/policy/docs/hdr_thesis/guideline_by_publication.html

Quantification of flux and isotopic signature of methane emissions from floodplain wetlands of the Macquarie Marshes, Australia

Saadu Umar Wali[1], Timothy J. Ralph[1], Tsuyoshi Kobayashi[2], Charlotte P. Iverach[3] and Bryce F.J. Kelly[3]

[1]Department of Environmental Sciences, Macquarie University, NSW 2109, Australia.
[2]Science Division, Office of Environment and Heritage NSW, Sydney South, NSW 1232, Australia.
[3]Connected Waters Initiative Research Centre, School of Biological, Earth and Environmental Sciences, UNSW Sydney, NSW 2052, Australia.

3.1 Abstract

Methane (CH_4) emission in wetlands is critical because CH_4 has 25 times the global warming potential of carbon dioxide (CO_2), and wetlands play a critical role in global carbon cycling. Using flux chambers this research investigated CH_4 emissions in three wetland zones in the Macquarie Marshes: reed bed, dry floodplain and dryland. Methane emissions were highly heterogeneous and CH_4 production only occurred in the reed bed (1.73E+01 kg ha^{-1} d^{-1}). In contrast, CH_4 was oxidised in the dry floodplain (-1.03E-03 kg ha^{-1} d^{-1}) and there was no production or oxidation of CH_4 in the dryland zone. Methane flux was strongly correlated with *in situ* moisture content. The median isotopic signature of CH_4 ($\delta^{13}C$; -56.3±2.36 ‰) agrees with wetlands globally and can be used in regional mixing models. The reed bed (809.5 ha) has the potential to release 4.97E-03 Tg yr^{-1} of CH_4 and an equivalent area of dry floodplain could oxidise -2.97E-07 Tg yr^{-1}, yielding a net CH_4 flux of 4.97E-03 Tg yr^{-1}. These results demonstrate for the first time that freshwater floodplain wetlands in dry landscapes can both sequester and emit CH_4, and that where freshwater floodplain wetlands emit CH_4 the rate is comparable to coastal mangroves.

Keywords: Greenhouse gas, methane flux, methane isotopic signature, organic carbon, wetlands in drylands, wetland inundation

3.2 Introduction

Emissions of greenhouse gasses (GHGs) including carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) vary between soil types, vegetation communities, landscape units (e.g. rivers, wetlands, drylands), land use types, and climate zones (Ghosh et al., 2015; Martins et al., 2016). Understanding biophysical and chemical controls of soil carbon and GHG flux processes is critical for environmental management, particularly for wetlands that act as hotspots of ecosystem services (Turetsky et al., 2014; Yao et al., 2016). It has been previously estimated that wetlands contribute one third of atmospheric CH_4 emissions (Frasier et al. 2011), but there is considerable uncertainty in this estimate. Methane is particularly important because it is a potent GHG and has a global warming potential 25 times greater than CO_2 on a 100-year horizon (Musenze et al., 2014). From 2007 to 2013, the average global proportion of CH_4 in the atmosphere increased by 5.7±1.2 ppb yr^{-1} (Nisbet et al., 2016). At the same time, the isotopic signature of $\delta^{13}C$ (a measure of the $^{13}C/^{12}C$ isotope ratio) in CH_4 has shifted to significantly more negative values (Nisbet et al., 2016). Schaefer et al. (2016) attribute these changes in CH_4 flux and isotopic composition to increases in biogenic activities outside the Arctic and, suggests that the values are more consistent with emissions from agriculture and wetlands. Nisbet et al. (2016) attributed post 2007 changes to increased tropical wetland and tropical agricultural CH_4 emissions. They attribute this change to a period of higher than average rainfall in these regions. Although, most CH_4 sources and sinks are well-known, there is uncertainty surrounding their relative contributions to atmospheric CH_4 concentrations (Schwietzke et al., 2016). As a result, the factors responsible for atmospheric CH_4 stabilisation from 1999 to 2006 and the subsequent renewed emissions in 2007 are still unclear. Schwietzke et al. (2016) attribute this to decreasing-to-stable fossil fuel emissions, and stable-to-increasing microbial emissions.

It is clear that the global CH_4 budget is poorly constrained due to a lack of measurement data worldwide. In Australia, for example, there is just one site at Cape Grim from which we can derive a multi-decadal record of CH_4 emissions (Figure 1) (NIR, 2016). In 2015, the global average value for $\delta^{13}CH4$ was -47.38 ‰ (Schaefer et al. 2016), while for Cape Grim the reading was -47.16 ‰ (NAOO Earth System Research Laboratory, Global Monitoring Division, flask data).

To determine the total anthropogenic contribution to greenhouse gas emissions Australia uses a combination of country specific and Intergovernmental Panel on Climate Change (IPCC) methodologies that are in line with IPCC 2006, and agree with global practice. In general, Australia's National Greenhouse Accounts uses a mix of tier 2 and tier 3 estimation techniques, which employ facility-specific emission estimation processes, characterisations of the capital and technology types at the point of emission, dynamic relations that link current emissions outcomes with the activity levels of past years, and assessment of spatial differences across Australia (NIR, 2016). However,

there is no annual reporting in Australia of methane emissions from natural sources, like wetlands, since this is a voluntary reporting category.

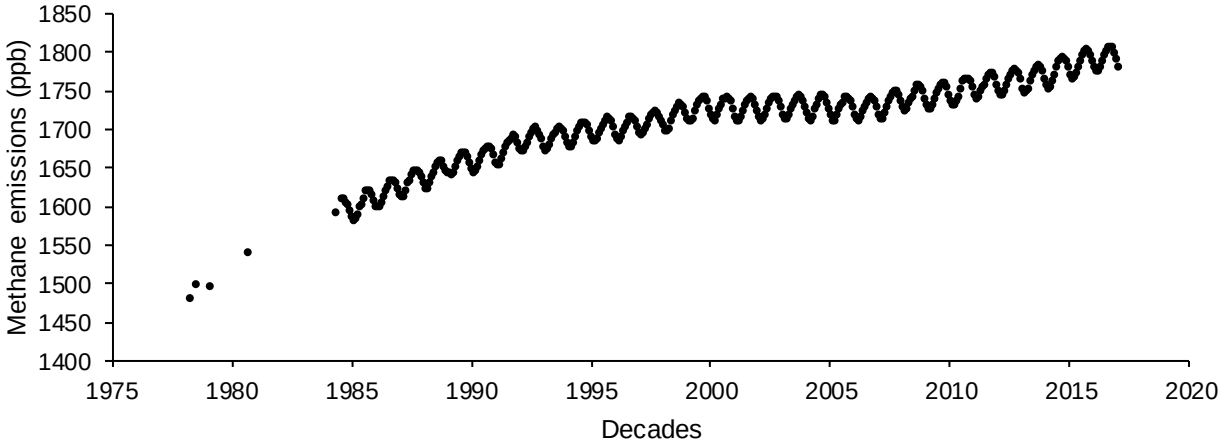

Figure 1. Record of methane emissions at Cape Grim (Data source: NIR, 2016).

Methane emissions in Australia like in other parts of the world is on the rise (Figure 1) and estimates showed CH_4 emissions is highly variable. Natural sources are the dominant source of atmospheric CH_4 (8.86 – 10.38 Tg yr^{-1}) and nearly doubled anthropogenic emissions (4.96 – 5.75 Tg yr^{-1}) (Fraser et al., 2011). Deutscher et al. (2010) estimated that wetlands in northern Australia produced 1 Tg of CH4 per year, and Bloom et al. (2010) estimated that the wetland systems across southern Australia contribute an additional 1 Tg y^{-1}. Fraser et al. (2011) estimated that wetlands contributed 0.2 to 0.6 Tg yr^{-1} of Australia's emissions and they noted that wetland emissions vary substantially from year to year due to Australia's highly variable climate and rainfall distribution.

Methane emissions from wetlands in Australia are mainly focused on coastal wetlands (Atkins et al., 2017; Gatland et al., 2014; Olsson et al., 2015; Peterson and Fry, 2016). There has been no work on measuring CH_4 flux or isotopic composition from Australia's inland wetlands in the Murray-Darling Basin; these being wetlands in drylands (WIDS). Measuring the isotopic composition of sources of CH_4 in WIDS can help with determining proportional contributions from these systems to regional atmospheric measurements. Also, while GHG fluxes are highly variable in the landscape, controls on GHG emissions and soil carbon stores are still debated (Peterson and Fry, 2016) and there are few datasets to draw conclusions from, especially in relation to WIDS. The rates and characteristics of GHG emissions from wetlands have implications for the global atmospheric GHG budget.

The main aim of this paper is to assess the variability of and controls on CH_4 emissions and soil carbon in the Macquarie Marshes, NSW, Australia, by comparing soil moisture, soil character and organic matter with CH_4 flux and isotopic composition in a wet central reed bed, on the adjacent

dry floodplain, and on the surrounding dryland soils. The fundamental research question is "what controls the flux and isotopic signature of CH_4 emissions from an Australian inland wetland?". The research also considers how environmental factors such as soil temperature, pH and soil electrical conductivity (EC) vary between the three wetland zones, and how these factors affect CH_4 flux, thereby investigating the provenance and characteristics of CH_4 emissions in different wetland zones with distinctive environmental conditions. We upscale this work to demonstrate that some zones within the Macquarie Marshes are significant sources of CH_4, while other zones are sinks of CH_4.

3.3 Study site

3.3.1 Geographical setting

The Macquarie Marshes are located on the lower reaches of the Macquarie River in central New South Wales (Figure 2A). The Macquarie River has its source at the confluence of the Fish and Campbell Rivers and flows through a gradually widening, partly confined valley from Wellington to Dubbo, before spreading onto an unconfined alluvial plain at Narromine and Warren. Average annual rainfall is highly variable in the Macquarie catchment, ranging from 200 mm to over 1200 mm (Ren et al., 2010), and average evaporation increases to ~2000 mm in the lower part of the catchment. As a result, the majority of flow is sourced from the sub-humid headwaters of the catchment, and discharge in the river declines significantly downstream (Ralph and Hesse, 2010). Various regulatory structures that were built along the river (e.g. dams, weirs, levees and diversion channels) have affected flow in the river and have reduced the frequency and volume of floods reaching the Macquarie Marshes (Fu et al., 2015). River regulation has nearly eliminated periods of very low to zero flow and has reduced the variability of flows into the wetlands (Wen et al., 2013). Base flows in the river and wetlands are thought to have accelerated the deepening of river channels by erosion, consequently reducing the volume of overbank flows onto the floodplain (Ralph et al., 2016).

The Macquarie Marshes are one of the largest example of a diverse, multi-channelled floodplain wetland system in the Murray-Darling Basin (Ralph et al., 2016). The Marshes consist of ~40,000 ha of permanent and seasonal wetlands, lying on a relatively large flat ~300,000 ha floodplain that can be inundated by large flood events (Figure 2B). The core areas of wetlands in the southern, northern and eastern parts of the Marshes are made up of extensive reed beds, grass plains, woodlands, and forest that rely on overbank and overland flooding from many small anastomosing and distributary channels (Ralph and Hesse, 2010). In places, the wetlands are impacted by human activities, however, they provide abundant habitat for a wide range of aquatic, floodplain and woodland biota. River red gum (*Eucalyptus camaldulensis*), river cooba (*Acacia stenophylla*),

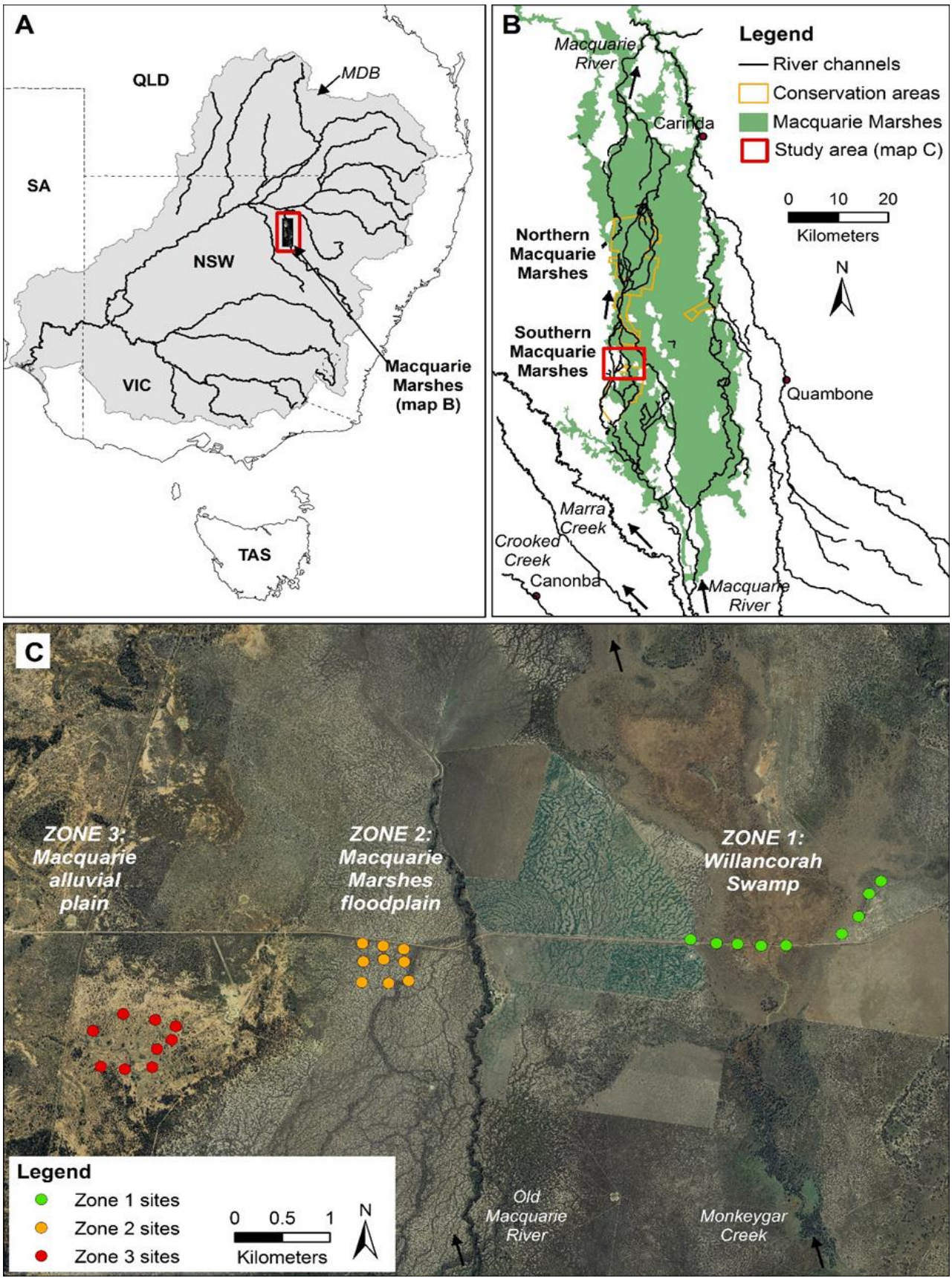

Figure 2. (A) Location of the Macquarie Marshes in NSW, Australia; (B) Willancorah Swamp in the Macquarie Marshes; (C) Wetland zones in and around Willancorah Swamp sampled in this study.

common reed (*Phragmatis australis*), lignum (*Muehlenbeckia florulenta*) and water couch (*Paspalum distichum*) constitute the major vegetation species in the Marshes (Fu et al., 2015). Previous assessment of vegetation in the Macquarie Marshes indicates that the extent and condition of vegetation species have declined due to changes in inundation over time (Fu et al., 2015).

3.3.2 Southern Macquarie Marshes

The southern Macquarie Marshes occur where the Macquarie River enters the core area of wetlands. The main channel of the Macquarie River breaks into smaller distributary channels in this region, forming Monkeygar Creek, which runs parallel to the Old Macquarie River and flows into Willancorah Swamp (Figure 2C). This research focuses on three wetland zones that are easily differentiated near Willancorah Swamp, but that occur more broadly throughout the Macquarie Marshes. Zone 1 is a regularly inundated and densely vegetated reed bed (i,e. Willancorah Swamp), which is the largest of its kind in the southern Macquarie Marshes (Figure 3A). Inundation mapping shows that zone 1 has a very high spring flood frequency, meaning that much of the zone has been inundated annually for the period of inundation mapping (1979-2006) (Thomas et al., 2011).

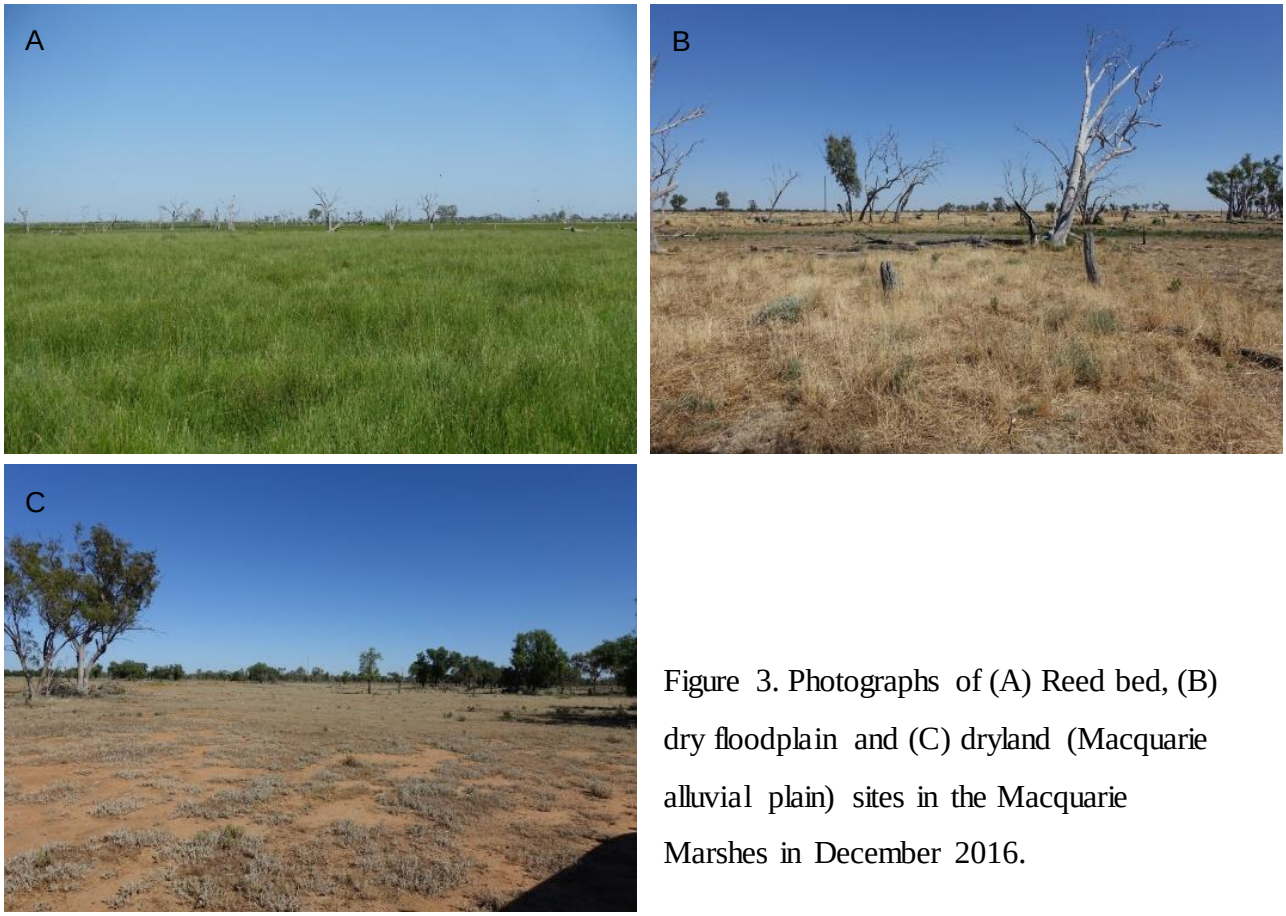

Figure 3. Photographs of (A) Reed bed, (B) dry floodplain and (C) dryland (Macquarie alluvial plain) sites in the Macquarie Marshes in December 2016.

A transition occurs over a distance of ~300 m from zone 1 to zone 2, on both the eastern and western margins of Willancorah Swamp. Zone 2 is a much less frequently inundated floodplain with sparse grassland and some woodland vegetation (i.e. dry floodplain; Figure 3B). The inundation frequency in zone 2 is much lower than zone 1, being flooded only once or twice in 28 years in some places, and having zero flooding in other places (Thomas et al., 2011). Zone 3 occurs on the periphery of the Macquarie Marshes floodplain and is characterised by dry grassland and woodland vegetation (i.e. dryland, actually part of the broader Macquarie alluvial plain; Figure 3C). This zone has a uniform inundation frequency of zero from 1979-2006, but may have been flooded during the largest events in the past 100 years (e.g. 1950s floods). Since we have a poor understanding of CH_4 emissions and isotopic composition from freshwater inland wetlands in Australia, and nothing is known about CH_4 emissions in the Macquarie Marshes, we have investigated CH_4 emissions, isotopic signatures and soil carbon in these three wetland zones for the first time.

3.4 Methods

3.4.1 Static chambers and gas collection

Fieldwork was conducted from 25 November to 3 December 2016. In each of the three wetland zones, nine representative sites were sampled for CH_4 flux and associated soil moisture, soil carbon and other environmental conditions. To measure the CH_4 flux, and collect samples for isotopic analysis, we used a static-chamber method described by Parkin et al. (2010), Sander and Wassmann, (2014), and Winton and Richardson (2015). In preparation for gas sampling, chambers were constructed using 220 L food grade plastic drums (Figure 4A). Each chamber had two vent tubes through which gas samples were collected. One of the tubes extended about 40 cm down into the chamber so that the effects of air extraction and pressure changes during headspace air sampling were minimised (Rochette and Eriksen-Hamel, 2008). Within each chamber there were two fans to ensure a proper mixing and circulation of air to inhibit stratification. Gas samples were collected by inserting a polypropylene syringe into the chamber vents (Figure 4B), which were only opened during gas collection and closed immediately after taking each gas sample. Gas samples were bagged in 4 L flex foil bags, carefully sealed and labelled, stored and transported for laboratory analysis. Gas samples were collected at regular time intervals at every site: 0 minutes, 10 minutes, 20 minutes 30 minutes and 60 minutes. This was done in order to facilitate flux calculations, because using more than three point reduces the uncertainty in flux calculations (Parkin and Venterea 2003). With nine chambers deployed in each wetland zone and five gas samples collected from each of the nine study sites, 45 gas samples were collected from the reed bed, 45 from the dry floodplain and 45 from the dryland plain.

3.4.2 Determination of concentration and isotopic composition of methane

Gas analysis was carried out using PICARRO G2201-i CRDS analyser for isotopic carbon in CO_2 and CH_4. We ran gas samples in the machine for at least 15 minutes before the concentration and isotopic composition were recorded. The G2201-*i* operates in one of the three modes: CO_2 only mode; CH_4 only mode; and combined CO_2/CH_4 mode. We employed a combined mode to measure CO_2 and CH_4 concentrations. The analyser's combined precisions is <0.16 ‰ for $\delta^{13}C$ CO_2 and <1.15 ‰ $\delta^{13}C$ CH_4. Gas concentrations of $^{12}CH_4$ (ppm), $^{13}CH_4$ (ppm), total [CH_4] (ppm) and $\delta^{13}CH_4$ were measured on all the 135 gas samples. Machine drift was checked and corrected by measuring calibrated southern ocean air samples at the beginning of each day, between every other set of site samples and at the end of each day. The standard air was calibrated by CSIRO's Global Atmospheric Sampling Laboratory in Aspendale, Victoria, Australia.

3.4.3 Flux calculations

Gas flux was calculated following the method described by Denmead (2008) and Parkin et al. (2012). Methane flux was calculated from the rate of change of the concentration of the analyte in the chamber. Since the rate of change of headspace trace gas concentration is not constant, we initially calculated slopes of time (seconds) versus [CH_4] using linear regression. The slope is only determined for the linear portion of the graph, usually the first 3 to 4 points. Gas flux was calculated thus:

$$F_g = \frac{V}{A} . \frac{C}{t} \qquad \text{Eq.1}$$

where F_g, is the gas flux (kg m^{-2} s^{-1}), V is the volume the chamber (m^3), A C is the gas concentration *(kg m^{-3})*, and t is time *(s)*.

The CH_4 flux (kg ha^{-1} d^{-1}) is then determined from;

$$Kg_{CH4} = F_g * 10000 * 86400. \qquad \text{Eq.2}$$

Figure 4. (A) Chamber used to measure the flux/concentrations of CH_4 over time; (B) Gas samples from each chamber were injected into flex foil bags; (C) PVC pipe and pit used to obtain the soil cores; and (D) Probes used to measure in situ soil moisture, soil temperature, air temperature, humidity, sunlight intensity and wind speed from the Macquarie Marshes. Photographs by Bradley Graves.

3.4.4 Keeling plot analysis

We used Keeling plots analysis to calculate the $\delta^{13}C$ CH_4 value for each site, using the 5 samples collected at each site. The basis for Keeling plot analysis is conservation of mass during the exchange of carbon between two reservoirs (Kohler et al., 2006). One of the most important considerations in constructing Keeling plot is which regression formulation to use (e.g. ordinary least-squares or OLS vs. reduced major axis, or RMA) (Pataki et al., 2003). The OSL model assumes that the independent variable has no errors associated with it (Vardag et al., 2016), or that these errors are at the experimenter's control. The isotopic composition of a sample consists of a source ($[CH_{4(s)}]$; $\delta^{13}C_{CH4(s)}$) mixed with background air ($[CH_{4(B)}]$; $\delta^{13}C_{CH4(B)}$), is determined from:

$$\delta^{13}C_{CH4\,(A)} = [CH_{4\,(B)}](\delta^{13}C_{CH4\,(B)} - \delta^{13}C_{CH4\,(S)})\left(\frac{1}{[CH_{4\,(A)}]}\right) + \delta^{13}C_{CH4\,(S)}, \qquad \text{Eq.3}$$

where $[CH_{4\,(A)}]$ and $\delta^{13}C_{CH4\,(A)}$ are the concentration and isotopic values measured in the ambient air sample, respectively. Equation 3 was fitted to the data using Mathematica Version 11. The y-axis, intercept is the isotopic signature of the source. The 95 % confidence intervals for the mean of the regression were determined using the Mathematica function Nonlinear Model Fit and the call on the output ("MeanPredictionBands", ConfidenceLevel -> 0.95). These data may also be analysed using the method suggested by Miller and Tans (2003), however Vardag et al. (2016) compared the two methods and found no significant difference between results determined via either the Keeling and Miller-Tans methods.

3.4.5 Soil carbon and ancillary measurements

A 30 cm deep soil core was extracted intact at each site based on IPCC (2007) recommendations for soil carbon analysis, as described by Heywood and Turpin (2003). A total of nine soil cores were collected from each of the three wetland zones using PVC pipes (Figure 4D). The PVC pipes were manually hammered into the soil to 30 cm depth. A spade was then used to dig out the cores. Soil cores were carefully sealed, labelled, stored and transported for further analysis. In preparation for loss on ignition (LOI) and soil moisture analysis, soil cores were sub-sampled into three section (0-10 cm, 10-20 cm, 20-30 cm) following the method described by Heywood and Turpin (2013).

Soil moisture content was determined following the method described by Reeb and Millota (1999). In preparation for soil moisture analysis, the sub-samples were weighed before and after oven drying at 105 ºC for 24 hours. We calculated the percentage of soil moisture thus:

$$SM_{(m)} = \frac{W_{ii} - W_{iii}}{W_{iii} - W_i} x\ 100 \qquad \text{Eq.4}$$

where *Wi* is weight of the sample container (g); *Wiii* is weight of moist soil plus the sample container (g) and *Wii* is weight of dried soil plus the sample container.

We determined soil organic carbon following the total organic matter loss-on-ignition (LOI) method described by Heywood and Tupin (2003). From each 10 cm section of the cores ~20 g sub-samples were taken. We oven-dried sub-samples at 105 ºC for 24 hours to ensure that all moisture was removed before dry sub-samples were weighed to determine the initial weight before ashing. Sub-samples were placed in crucibles and combusted in a Linderberg furnace at 550 ºC for 4 hours. After ashing, the sub-samples were placed into a desiccator to cool for 1 hour. Sub-samples were then re-weighed to obtain an estimate of organic matter content. We calculated LOI thus:

$$W_{LOI} = \frac{W_d - W_c}{W_a - W_d} x\ 100 \qquad \text{Eq.5}$$

where; W_a = mass of empty crucibles (g), W_c = mass of crucible after furnace (g), W_{LOI} = loss on ignition (%).

We calculated total soil organic carbon stock for each sample, thus;

$$\mathrm{SOC}_s = \mathrm{LOI}_{\%} \text{ x } \mathrm{DBD}_s \text{ x V} \qquad \text{Eq.6}$$

where $LOI_{\%}$ is as defined in equation 8, DBD_s is the dry bulk density of the soil samples and V is volume of core segment.

Aboveground biomass sampling was carried out following method described by Picek et al. (2007) and Oliveira et al. (2017). One representative quadrat (1x1 metre) was selected at each of the nine sites in zones 1, 2 and 3 respectively. Biomass analysis was conducted following methods described by (Sileshi, 2014; Verwijst and Telenius, 1999). Biomass samples were first dried at 105 ^{o}C for 24 hours to ensure all moisture was removed. Samples were crushed and dried again at 105 ^{o}C for 24 hours, then reweighed both before and after ashing in a Linderberg furnace at 550 ^{o}C for 4 hours. We calculated aboveground biomass thus:

$$OM_{bm} = \frac{W_{wb} - W_{db}}{W_{bf} - W_{ba}} x\ 100 \qquad \text{Eq.7}$$

where *Wwb* is weight of biomass before oven, *Wbd* is weight of biomass after oven, *Wbf* is weight of sub-samples before furnace and *Wba* is weight of sub-samples after furnace.

In addition, in situ soil moisture was measured at each field site during the CH_4 flux sampling period using a moisture probe (MP406). Soil moisture was recorded at regular time intervals: 0 minutes, 30 minutes and 60 minutes. Soil temperature was measured simultaneously using a Precision Hydrometer (HT-3027SD). The accuracy of this machine after calibration is ±3 % for humidity and ±0.8 ^{o}C for soil temperature. Soil pH and EC were determined flowing the method described by Lim et al. (2017). Soil pH and EC were measured using standard probes in a 1:5 ratio solution of soil and deionised water in 20 ml vials.

3.5 Results

3.5.1 Methane emission from the wetland zones

Methane flux (median) in zone 1 (reed bed) was 1.73E+03 kg ha^{-1} d^{-} (Table 1). In zone 2 (dry floodplain), median CH_4 flux was -1.03E-03 kg ha^{-1} d^{-1}. In zone 3 (dryland plain), median CH_4 flux was 0 kg ha^{-1} d^{-1}. These measurements show that CH_4 is produced almost exclusively in the reed bed and that CH_4 oxidation occurs in the dry floodplain (Figure 5A). In the dryland, there was neither production nor oxidation of CH_4 (Table 1).

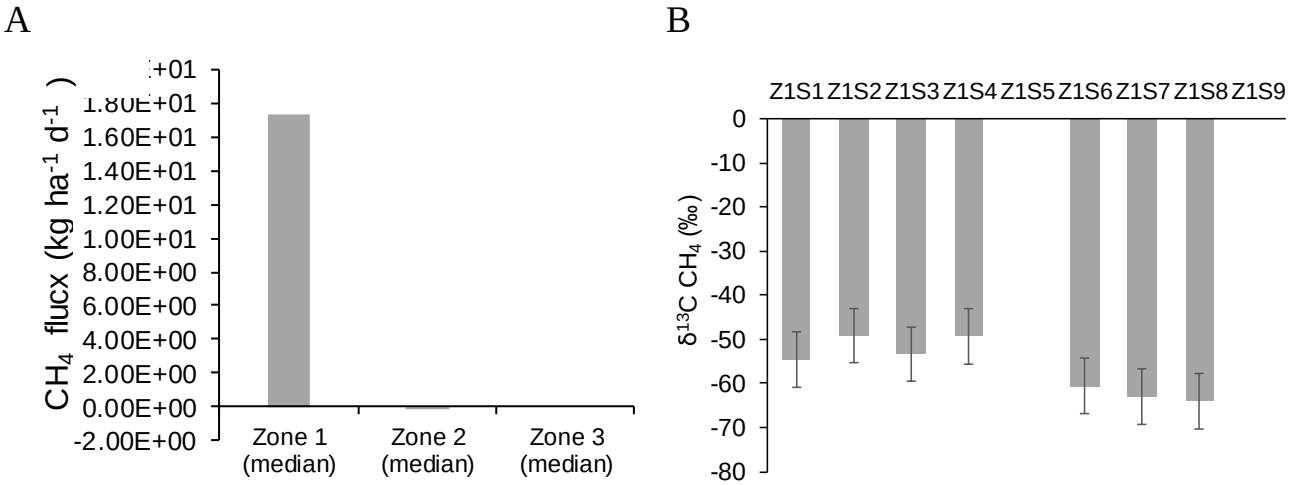

Figure 5. (A) Variability of methane emission between the three-wetland zones. (B) Isotopic composition of methane by site in zone 1.

The median isotopic signature of CH_4 ($\delta^{13}C$) was -56.3 ‰ and ranged from -64.6 to -49.2 ‰ (Figure 5B and Figure 6). In Z1S5 and Z1S9, have a 95% confidence interval of greater than ±15 ‰. In addition, measurements obtained from the dry floodplain and dryland zones (Table 1), are similar to ZIS5 and Z1S9. They all have a 95% confidence interval of greater than ± 15 ‰ (Appendix II).

Table 1. Methane flux and isotopic composition in the three-wetland zones from the Macquarie Marshes.

Study sites		CH_4 flux (kg ha^{-1} d^{-1})	$\delta^{13}C$ CH_4 (‰)	Cl: 95%	Use in flux scatterplots	Comment	Summary	
Zone 1	Site 1	NFC	-54.6	-59.1 to -50.1	No	No rise or fall, no gradient	**Zone 1**	
	Site 2	4.81E+04	-49.2	-51.5 to -46.8	Yes	Production: Flux determined from t = 0 and 10 mins slope	**Units (median)**	**CH_4 flux**
	Site 3	1.38E+01	-53.4	-55.7 to -51.1	No	Production: Flux determined from t = 0,10,20 mins slope	kg ha^{-1} d^{-1}	1.73E+03
	Site 4	3.44E+01	-49.3	-51.6 to -47.0	Yes	Production: Flux determined from t = 0,10,20 mins slope	kg ha^{-1} yr^{-1}	6.31E+05
	Site 5	3.44E-02	**	**	Yes	Production: Flux determined from t = 0,10,20,30 and 60 mins slope	kg ha^{-1} $yr^{-1}$for zone 1	1.40E+06
	Site 6	5.50E-02	-60.6	-74.6 to -46.6	Yes	Production: Flux determined from t = 0,10,20,30 and 60 mins slope	g ha^{-1} y^{-1} for zone 1	1.40E+03
	Site 7	1.38E-01	-63	-69.3 to -56.7	Yes	Production: Flux determined from t = 0,10,20,30 and 60 mins slope	Tg yr^{-1} for zone 1	4.97E-03
	Site 8	-6.88E-02	-64	-74.1 to -53.9	No	High starting concentration, but then slight oxidation, followed by an increase at t = 60 mins. Mixed message result, not used.	$\delta^{13}C$ CH_4 (‰)	-56.3
	Site 9	2.75E+04	**	**	Yes	Production: Flux determined from t = 0 and 10 mins slope		
Zone 2	Site 1	-2.75E-03	**	**	Yes	Oxidation: Flux determined from t = 0,10,20,30 and 60 mins slope	**Zone 2**	
	Site 2	-3.44E-03	**	**	Yes	Oxidation: Flux determined from t = 0,10,20,30 and 60 mins slope	**Units (median)**	**CH_4 flux**
	Site 3	NFC	**	**	Yes	Background air readings, flux set to zero	kg ha^{-1} d^{-1}	-1.03E-03
	Site 4	3.46E-03	**	**	Yes	Low Production: Flux determined from t = 0,10,20,30 and 60 mins slope	kg ha^{-1} yr^{-1}	-3.76E+05
	Site 5	NFC	**	**	No	Mixed reading, mostly background air with one high reading at t = 30. Not used	g ha^{-1} yr^{-1} for zone 2	-3.04E+08
	Site 6	NFC	**	**	Yes	Background air readings, flux set to zero	g ha^{-1} y^{-1} for zone 2	-3.04E+05

	Site 7	NFC	**	**	Yes	Background air readings, flux set to zero	Tg yr^{-1} for zone 2	-2.97E-07
	Site 8	-6.88E-03	**	**	Yes	Low oxidation: Flux determined from t = 0,10, and 20 mins slope	$\delta^{13}C$ CH_4 (‰)	No data
	Site 9	-2.06E-03	**	**	Yes	Low oxidation: Flux determined from t = 0,10, 20, 30 and 60 mins slope.		
Zone 3	Site 1	NFC	**	**	Yes	Background air readings, flux set to zero	**Zone 3**	
	Site 2	NFC	**	**	Yes	Background air readings, flux set to zero	**Units (median)**	**CH_4 flux**
	Site 3	NFC	**	**	Yes	Background air readings, flux set to zero	kg ha^{-1} d^{-1}	0.00E+00
	Site 4	NFC	**	**	No	Mixed reading, mostly background air with one high reading at t = 10. Not used	kg ha^{-1} yr^{-1}	0.00E+00
	Site 5	NFC	**	**	Yes	Background air readings, flux set to zero	kg ha^{-1} yr^{-1} for zone 3	0.00E+00
	Site 6	1.38E-02	**	**	Yes	Low production: Flux determined from t = 0,10, 20, 30 and 60 mins slope.	g ha^{-1} y^{-1} for zone 3	0.00E+00
	Site 7	NFC	**	**	Yes	Background air readings, flux set to zero	Tg yr^{-1} for zone 3	0.00E+00
	Site 8	-3.44E-03	**	**	Yes	Low oxidation: Flux determined from t = 0,10, and 20 mins slope.	$\delta^{13}C$ CH_4 (‰)	No data
	Site 9	-3.44E-03	**	**	Yes	Low oxidation: Flux determined from t = 0 and 10 mins slope..		

Note: NFC = No flux calculation, as the data were not suitable; **= Confidence interval too large, data set not suitable for Keeling Plot analysis.

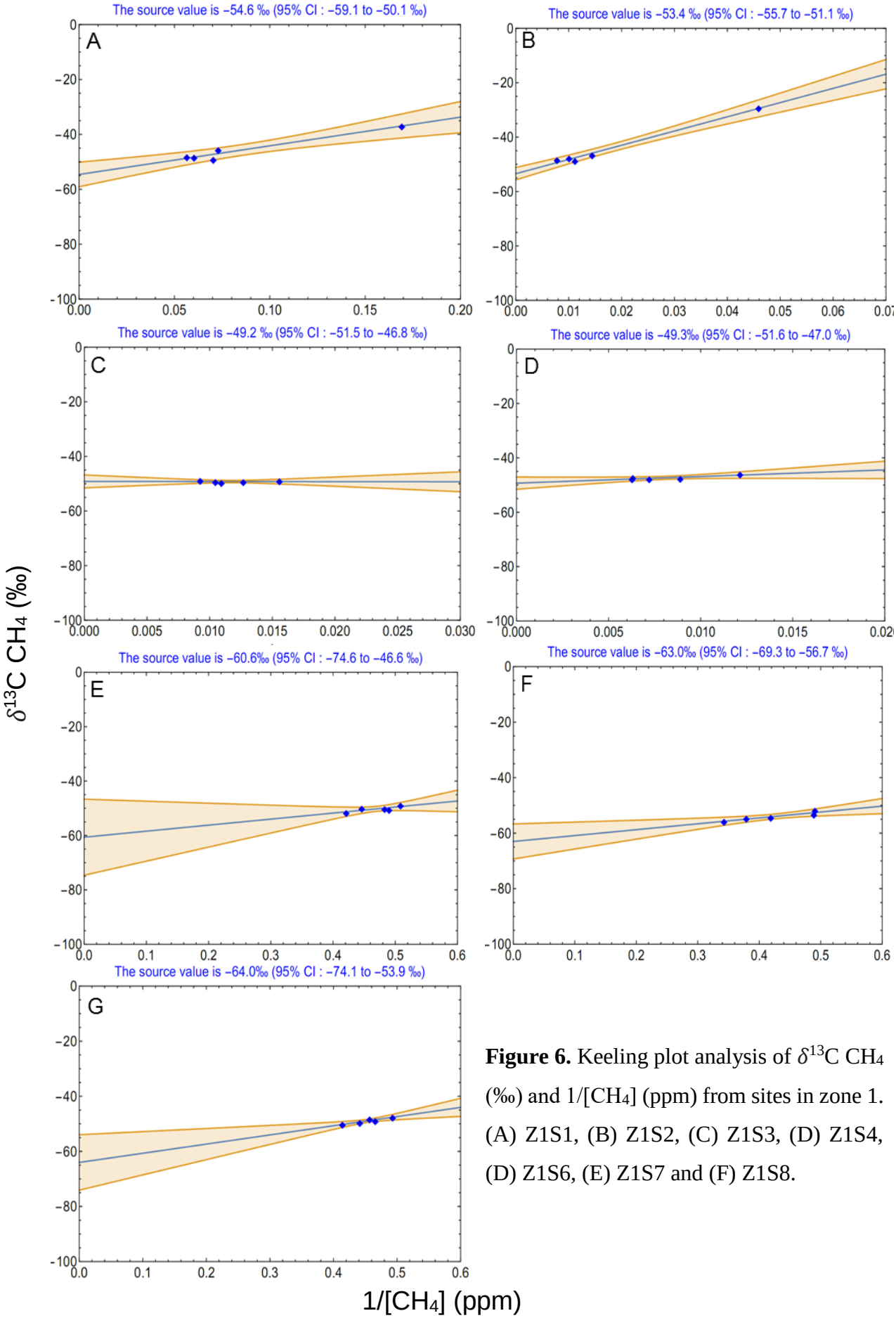

Figure 6. Keeling plot analysis of δ^{13}C CH_4 (‰) and 1/[CH_4] (ppm) from sites in zone 1. (A) Z1S1, (B) Z1S2, (C) Z1S3, (D) Z1S4, (D) Z1S6, (E) Z1S7 and (F) Z1S8.

3.5.2 Soil carbon, aboveground biomass and environmental conditions

Soil organic carbon content derived from LOI varied slightly with depth of soil profile, in all the three-wetland zones (Figure 7). Soil organic carbon was highest in the reed bed and lower in dry floodplain and dryland zones (Figure 8A and Appendix III). Soil organic carbon (mean ± standard error) was 6.62±0.73 % and ranged from 5.09 to 12.13 % in the reed bed. In the dry floodplain, mean soil organic carbon was 4.59±0.36 % and ranged from 2.87 to 6.27 %. In the dryland, mean soil organic carbon was 3.79±0.43 % and ranged from 2.51 to 3.79 %. A Kruskal-Wallis test showed a significant difference (H=11.86, p=0.002) of LOI between the three wetland zones and a *post hoc* Mann-Whitney test showed that the main differences were between zone 1 and zones 2 and 3 (Appendix I). Soil carbon decreases with increased core depths in zone 1. In zone 2 soil carbon was higher in 20 cm soil profile and in zone 3 there was increased soil carbon down profile (Figure 7).

Soil organic carbon stock was higher in the reed bed and lower in dry floodplain and dryland zones (Figure 8B). Soil organic carbon stock (mean ± standard error) was 39±4 t ha^{-1} and ranged from 29 to 68 t ha^{-1} in the reed bed. In the dry floodplain, mean soil organic carbon stock was 24±2 t ha^{-1} and ranged from 16 to 36 t ha^{-1}. In the dryland, mean soil organic carbon stock was 23±3 t ha^{-1} and ranged from 14 to 23 t ha^{-1}. The Kruskal-Wallis non-parametric test showed significant difference (H=10.89, p=0.005) between wetland zones. In addition, a *post hoc* Mann-Whitney pairwise test also indicates that major differences were between zone 1, and zone 2 and 3, not between zones 2 and 3 (Appendix I).

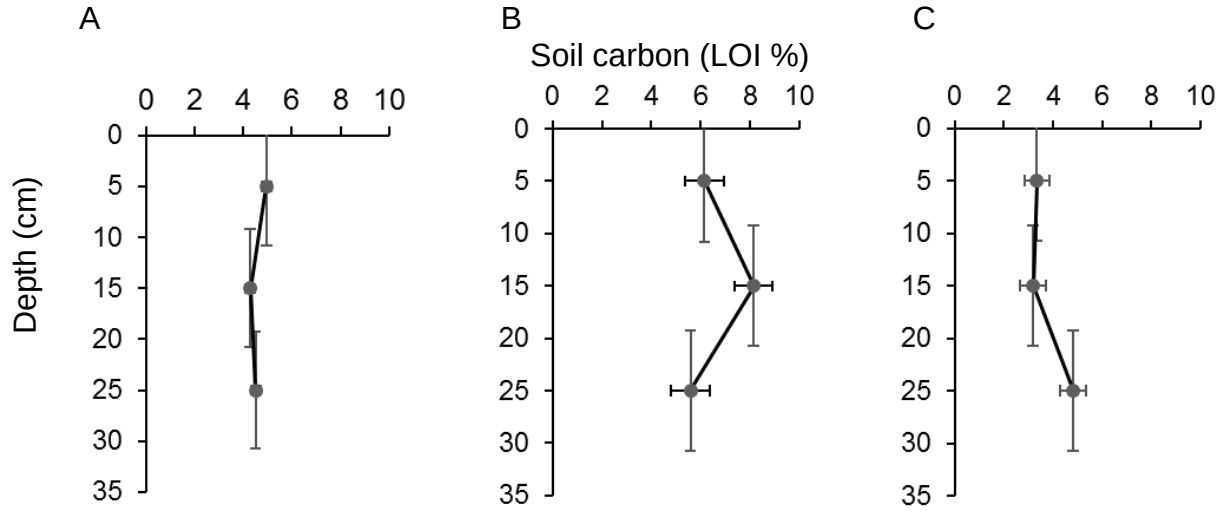

Figure 7. Comparison of soil organic carbon profiles for (A) zone 1, the reed bed, (B) zone 2, the dry floodplain and (C) zone 3, the dryland plain.

Aboveground biomass did not follow a similar pattern with soil organic carbon, and although it was variable, it had a consistent mean value across all three zones (Figure 8C). In zone 1,

aboveground biomass (mean ± standard error) was 10.85±1.00 % and ranged from 5.68 to 14.65 % in the reed bed. In the dry floodplain, mean biomass was 9.64±1.79 % and ranged from 3.83 to 16 %. In the dryland, mean biomass was 8.14±0.61 % and ranged from 1.34 to 5.47 % (see Appendix III). The Kruskal-Wallis non-parametric test indicates a significant difference (H=4.87 p=0.005) in biomass between wetland zones. Results of *post hoc* Mann-Whitney pairwise test were in agreement with Kruskal-Wallis test. Major difference was between zone 1 and zone 2 (Appendix I).

Soil moisture was higher in the reed bed and lowest in dryland (Figure 8D). Soil moisture (mean ± standard error) was 16.50±1.33 % and ranged from 9.81 to 21.56 % in the reed bed (Figure 8D). In the dry floodplain, mean soil moisture was 12.40±3.49 % and ranged from 4.55 to 36.68 %. In the dryland, mean soil moisture was 4.69±0.91 % and ranged from 1.83 to 10.10 %. However, Kruskal-Wallis non-parametric test showed significant difference (H=15.88, p=<0.001) exist between Zones 1, 2 and 3. However, result of a *post hoc* Mann-Whitney pairwise test showed major difference was between zone 1, 2 and 3 (Appendix I). The soil moisture pattern between wetland zones was similar to soil organic matter (LOI) and soil organic carbon stock (Figure 4D).

Soil pH (mean ± standard error) was highest in the reed bed, with a mean of 7.10±0.17 and a range from 6.36 to 8.00 (slightly alkaline, Figure 4E). In the dry floodplain, mean soil pH was 6.83±0.18 and ranged from 6.15 to 8.09 (neutral or slightly acidic). In the dryland, mean soil pH was 6.33±0.10 and ranged from 5.90 to 6.93 (slightly acidic; Appendix III). The Kruskal-Wallis non-parametric test indicates a significant difference (H=11.19, p=0.004) between wetland zones. In addition, the *post hoc* Mann-Whitney test showed major difference was between zone 1 and zones 2 and 3 (Appendix I).

Soil EC (mean ± standard error) was greatest in the reed bed, being 415.24±194.37 µS cm^{-1}, and ranged from 114.10 to 1956.00 µS cm^{-1} (Figure 4F). In the dry floodplain, mean EC was 267.42±29.88 µS cm^{-1} and ranged from 89.64 to 103.20 µS cm^{-1}. In the dryland, mean EC was 244.62±50.73 µS cm^{-1} and ranged from 98.80 to 583.00 µS cm^{-1}. However, there was no significant difference (H=1.24, p=0.53) between wetland zones. Results obtained from a *post hoc* Mann-Whitney test also indicates that major difference was between zone 1, 2 and 3 (Appendix I). Soil temperature was higher in the dryland and lower in the reed bed (Figure 4G). Mean soil temperature was 26.11±1.61 ^{o}C and ranged from 21.86 to 37.63 ^{o}C in the reed bed. In the dry floodplain, mean soil temperature was 32.59±1.03 ^{o}C and ranged from 27.96 to 36.93 ^{o}C. In the dryland, mean soil temperature was 34.06±3.35 ^{o}C and ranged from 16.16 to 44.10 ^{o}C. The Kruskal-Wallis non-parametric test indicates significant difference (H=7.27, p=0.026) of soil moisture content between wetland zones. However, a *post-hoc* Mann-Whitney test showed significant differences between reed bed, dry floodplain and dryland (Appendix I).

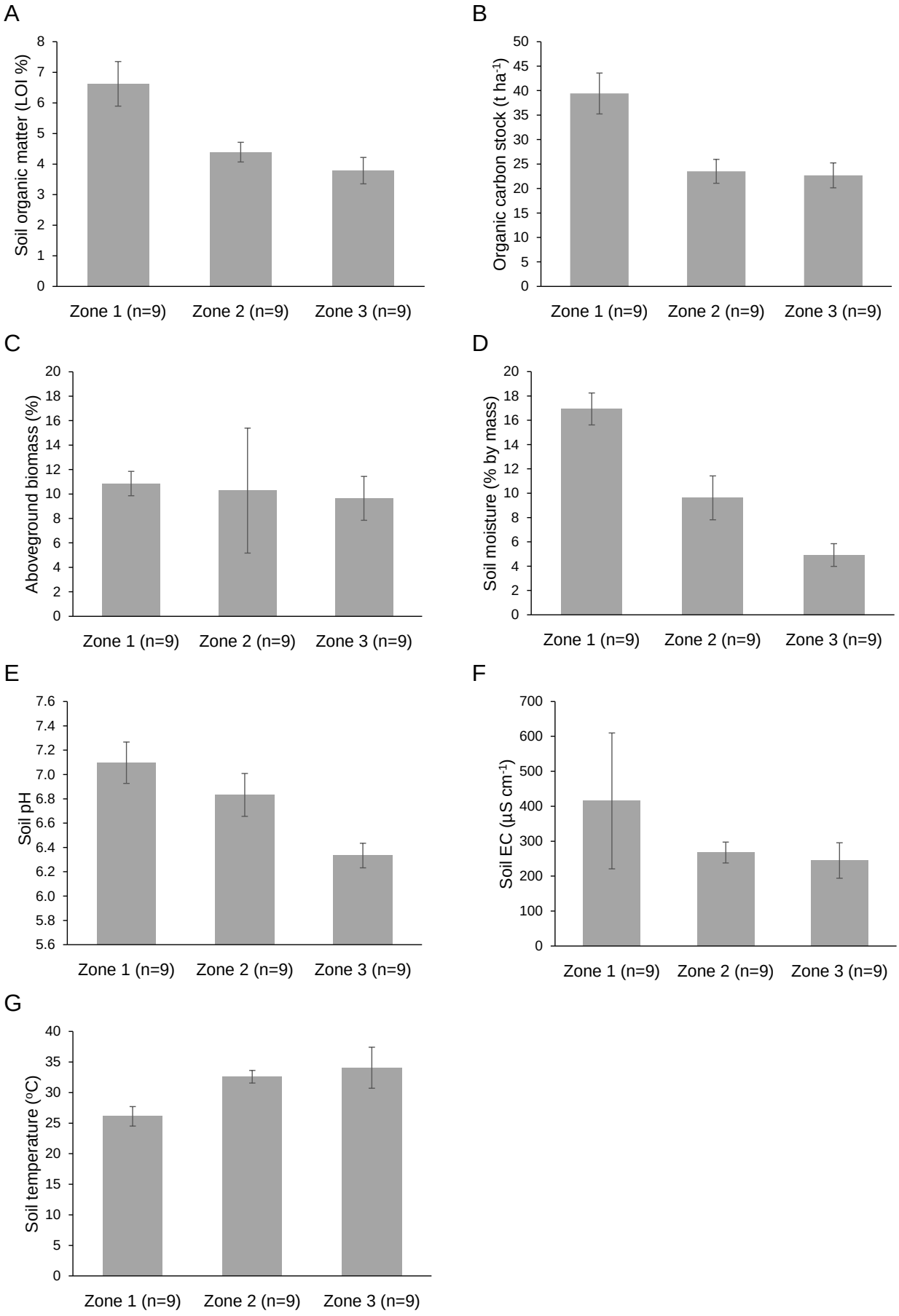

Figure 8. Soil carbon and environmental data. (A) Soil carbon, (B) organic carbon stock, (C) above ground biomass, (D) soil moisture, (E) soil pH, (F) soil EC, and (G) soil temperature.

Overall zone 1 (the reed bed) had greater CH_4 emissions, greater soil carbon stock, greater soil moisture, higher soil EC and higher soil pH than the other two zones (dry floodplain and dryland). In contrast, soil temperature was higher in zone 3 (dryland) where CH_4 flux was balanced, while CH_4 flux was negative in zone 2, and biomass was equivalent in all zones.

3.5.3 Observations of the correlation between methane emission, and physical soil properties

The dependence of CH_4 flux on soil carbon and environmental conditions are summarised in Figures 9, 10 and 11. To enhance the visual trends in the data all flux readings where shifted upwards by 1, and the Log10 value determined. CH_4 flux in Macquarie Marshes is correlated positively with *in situ* soil moisture and to a less extent the soil moisture determined in the laboratory (Figure (9A). The *in situ* soil moisture versus CH_4 flux displays an exponential relationship and this is explored further below.

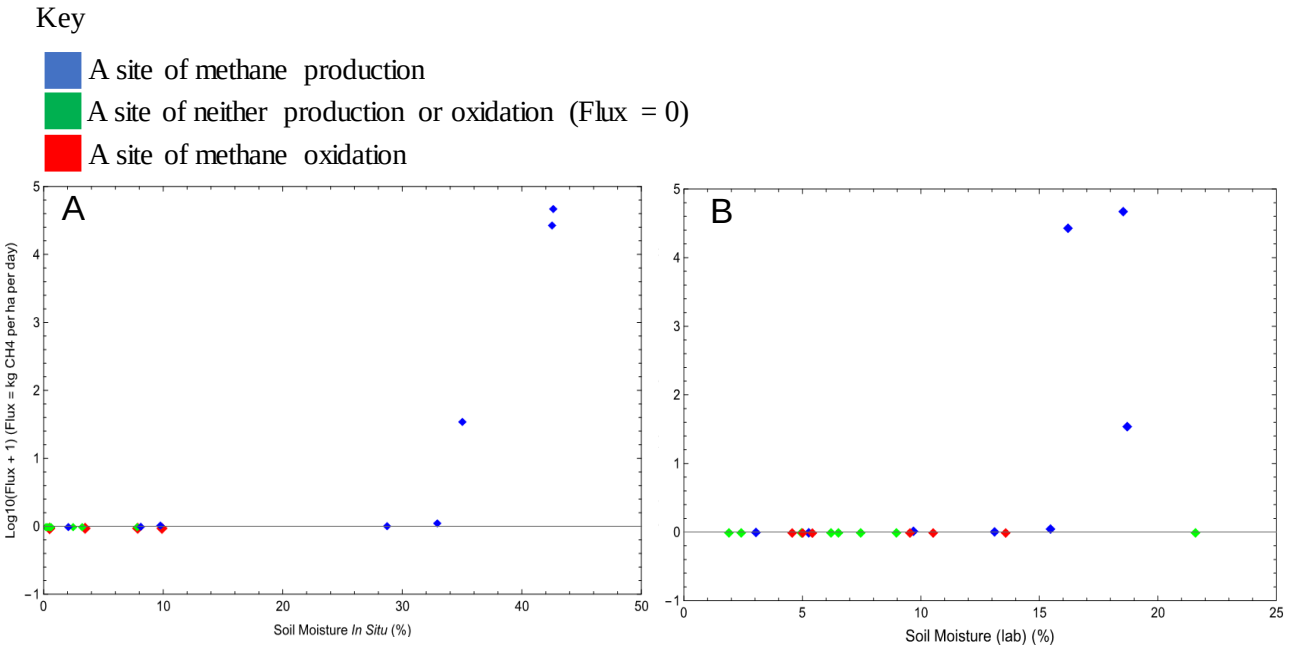

Figure 9. Scatter plots showing correlation between methane flux and soil moisture, (A) in situ soil moisture (%) and (B) soil moisture determined in the laboratory (%).

Figure 10 illustrates the dependence of CH_4 flux for the independent variables soil carbon (F10.A), organic carbon stock (F10.B), soil bulk density (F10.C) and biomass (F10.D), and Figure 11 shows the dependence of CH_4 flux on the independent variables soil pH (F11.A), soil EC (F11.B) and soil temperature (F11.C). Considering all data from zones 1, 2 and 3, there is no visual relationship between CH_4 flux and the independent variables soil carbon, organic carbon, soil bulk density, biomass, soil pH, and soil temperature. The three high flux sites appear as outliers in the graph, and these data would distort any linear regression analyses (least squares regression or principal component analysis). Therefore, such techniques were not applied to these data.

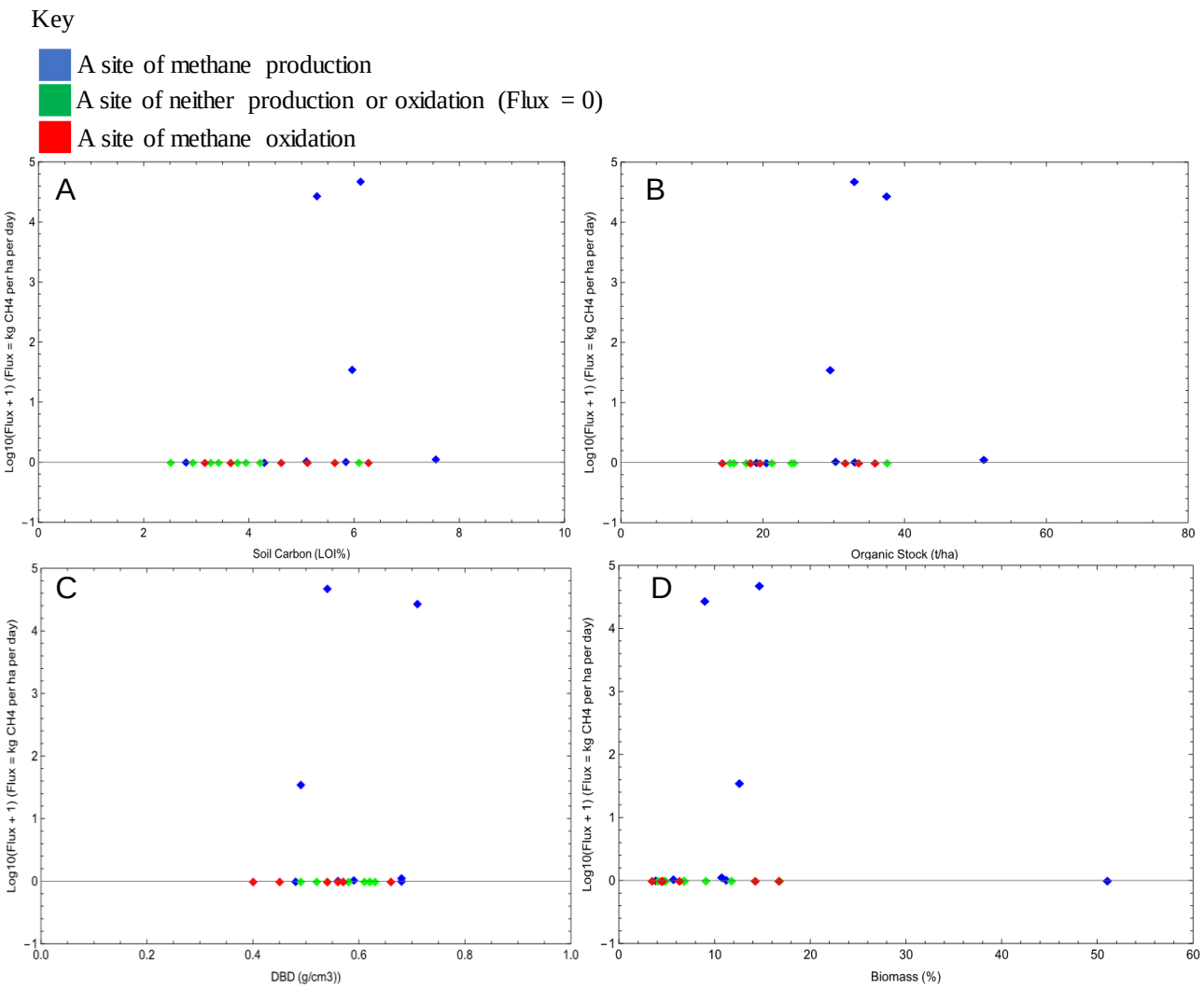

Figure 10. Scatter plots showing correlation between methane flux and (A) soil carbon (LOI), (B) organic carbon stock, (C) soil bulk density, and (D) aboveground biomass.

However, CH_4 flux in the Macquarie Marshes is positively correlated with soil pH, soil EC and soil temperature (Figure 11A, B, and C).

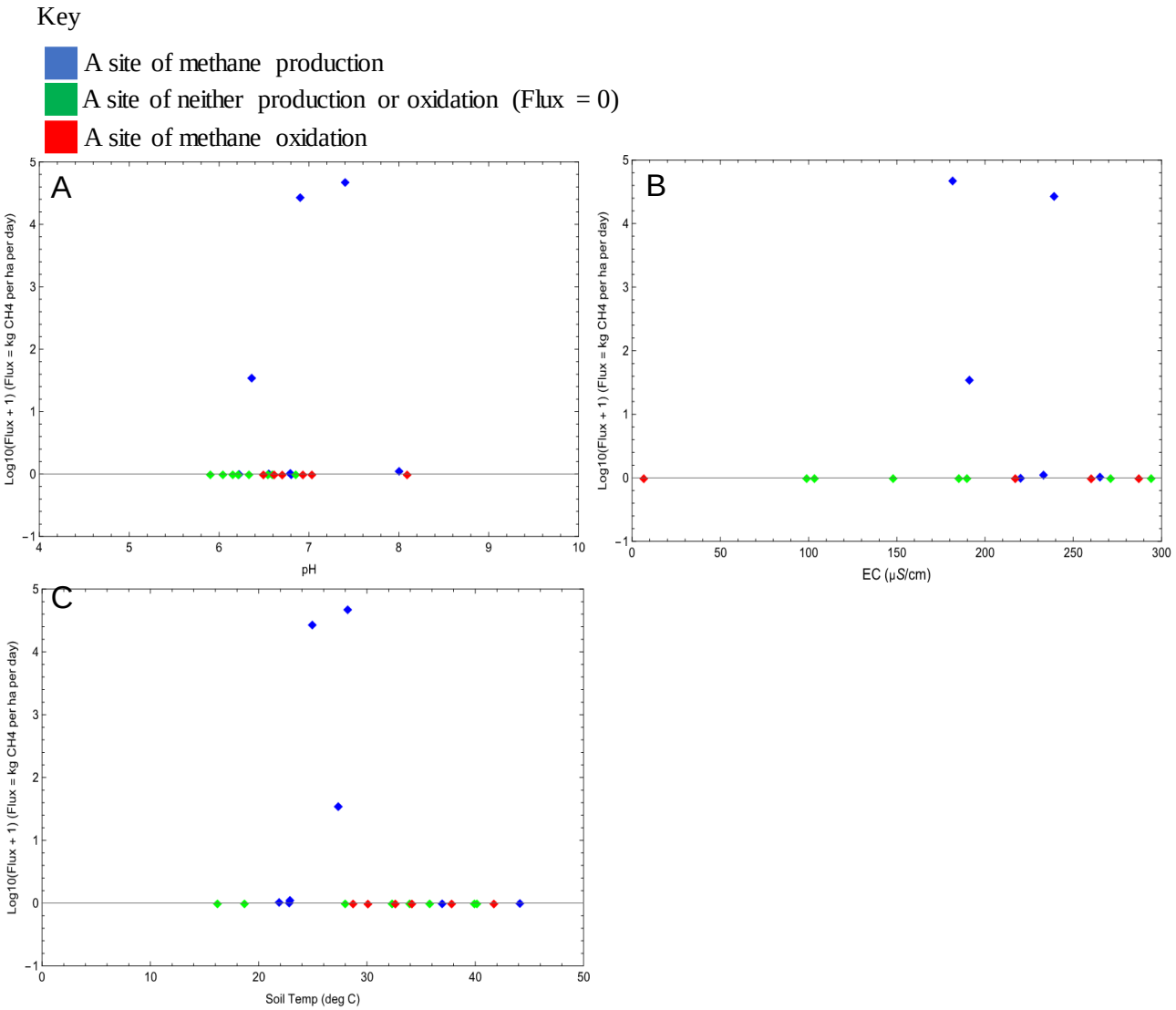

Figure 11. Scatter plots showing correlation between methane flux and; (A) soil pH, (B) soil EC and (C) soil temperature.

3.5.4 Numerical analysis of the relationship between methane flux and in situ moisture content

In Figure 9 it is apparent that CH_4 flux is exponentially dependent on the *in situ* soil moisture. This relationship is further explored by fitting the function $CH4_{flux} = a\,e^{x} + b$ (where *a* and *b* are parameters to be determined, and *x* is the soil moisture*)*. An unconstrained fit of the function results in an unrealistic value for *b* and a biased residual plot. To improve the model fit *b* was set to match the median oxidation rate determined for Zone 2 (-1.03E-03 kg CH_4 / ha^{-1} d^{-1}). This equation was fitted to the data using the NonlinearModelFit function in Mathematica version 11. The best fit model is $-0.00103 + 1.22883\times10^{-14}e^{x}$, with an R^2 of 0.954. The function is displayed fitted to the data in Figure 12, and the residual plot is shown in Figure 13. The t-statistic and p value for the parameter *a* are 20.8766 and 1.58791×10^{-15}, respectively.

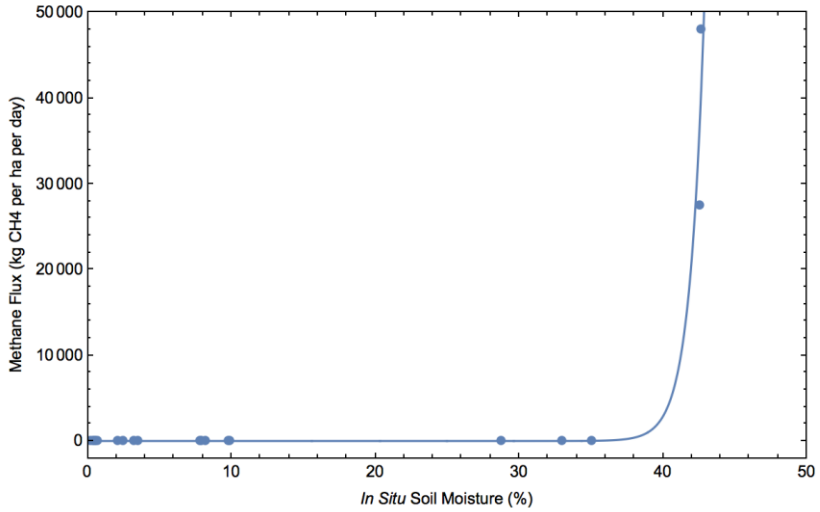

Figure 12. In situ soil moisture versus methane flux.

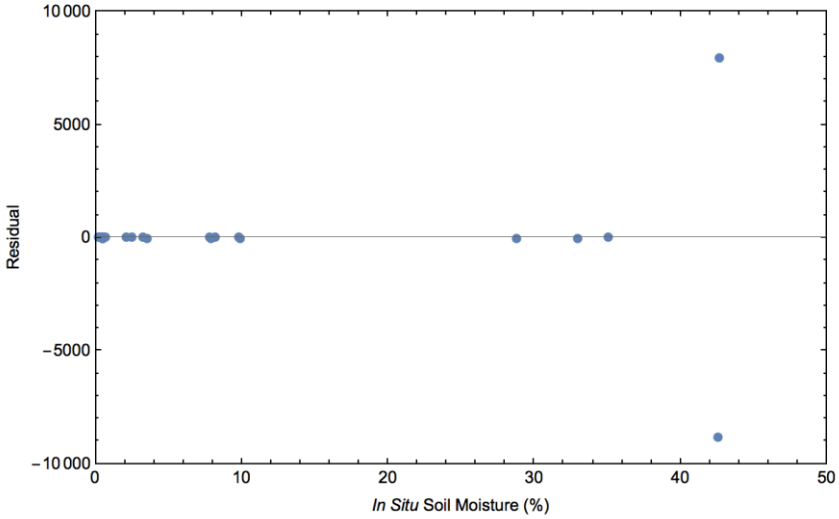

Figure 13. Residual plot of the exponential model fit in Figure 12.

3.6 Discussion

3.6.1 Methane flux and isotopic composition in the Macquarie Marshes

In the southern Macquarie Marshes in the reed bed (zone 1) CH_4 was being produced at a median rate of 1.73E+01 (kg CH_4 ha^{-1} $^{d-1}$). This CH_4 has a median $\delta^{13}C$ signature of -56.3±2.36 ‰. In the dry floodplain (zone 2), CH_4 was being oxidised at a rate of -1.03E-03 (kg CH_4 ha^{-1} d^{-1}). In the dryland plain (zone 3) overall there was neither production or consumption of CH_4. The rate of CH_4 production was strongly dependent on the in situ soil moisture. No correlations were apparent between soil carbon, organic carbon, soil bulk density, biomass, soil pH, or soil temperature and the rate of CH_4 production or consumption. Based on the survey of the literature this was not the expected outcome, and the result is likely due to the small sample size and heterogeneity of soil properties within and between each zone.

Overall, zone 1 in Willancorah Swamp is a location of CH_4 production. Zone 2 in dry floodplain is a location of CH_4 oxidation and in Zone 3, the dryland, neutral condition prevailed, as there was neither production nor oxidation of CH_4. Soil moisture is the major control of CH_4 emission. This makes sense because zone 1 is the reed bed with the highest inundation frequency, zone 2 is the much less frequently inundated floodplain, and zone 3 is the dryland plain on the periphery of Macquarie Marshes floodplain. Therefore, our findings regarding CH_4 production in the marshes and reed bed are also related to the recent inundation regime, although we did not specifically measure inundation in the wetlands.

3.6.2 Comparison with other wetlands in Australia and around the world

The $\delta^{13}C$ CH_4 values obtained from zone 1 (reed bed) are comparable to values reported from wetlands and other ecosystems around the world (Table 2).

Table 2. Reported δ^{13} CH_4 (‰) from wetlands in previous studies.

Location	$\delta^{13}C$ CH_4 (‰)	Citation
Macquarie Marshes, Australia	-64.6 to -49.2 (-56.3)	This study
Marova, Czech Republic	-52.5 to 59.4	(Bednarik et al., 2017)
Ziyang, China	-46.8 to -61.2	(Zhang et al., 2017)
Western Greenland	-66.2 to -55.5	(Thompson et al., 2016)
Kiruna, Sweden	-70.0	(France, 2016)
Arctic Polygon Tundra	-52.3 to -79.7	(Vaughn et al., 2016)
Sub-arctic tundra	-68.2	(Marushchak et al., 2016)
Tropical peatland	-92.32 to -2.83	(Holmes et al., 2015)

The median value of -56.3 ‰ agrees with most global wetland values reported in the literature. The highest value recorded -49.2 ‰ is on the more positive side compared to other wetland settings around the world, while the more negative reading of -64.6 ‰ is very typical for the isotopic composition of wetlands. The median CH_4 flux obtained from reed bed is within the range of CH_4 flux values reported from Australian wetlands (Table 3). The finding from the reed bed (7.19E+04 µg CH_4 m^{-2} h^{1}) compare very well with Akumu et al. (2010), Bass et al. (2014) and Musenze et al. (2014). CH_4 flux in reed bed is comparable to CH_4 values reported in literature (Table 3). However, median CH_4 in dry floodplain is comparable to CH_4 oxidation values reported from agricultural fields in Narrabri, by Fest et al. (2017) and from wet and dry forest in Tasmania and Queensland.

Table 3. Reported methane emissions from wetlands within Australia and around the world.

Location	**Wetland types**	**Study sites**	**Range of CH_4 flux (µg m^{-2} $h^{1)}$**	**Citation**
Semi-arid (Macquarie Marshes)	Freshwater floodplain wetland	1	7.19E+04	This study
Humid-Tropical		3		(Allen et al., 2011)
		1	-68 to -4	(Allen et al., 2011)
		1	-67 to 0 (mean, -32)	(Allen et al., 2011)
	Sugarcane	1	No net flux	(Allen et al., 2011)
		1	-3600	(Allen et al., 2011)
		1	10.8–39.6	(Allen et al., 2011)
Subtropical	Mangrove		20–390	(Allen et al., 2011)
		1	3–17400 (log-normal mean 228)	(Allen et al., 2011)
		4	47–1570 (log-normal mean, 303)	(Allen et al., 2011)
	Sugarcane	1	0.24283 (drains located near cane)	(Allen et al., 2011)
		1		(Allen et al., 2011)
Temperate	Ephemeral wetland	1	4800–36800 (mean, 27200 ± 80)	(Allen et al., 2011)
Subarctic	Undisturbed sites	-	68400	(Turetsky et al., 2014)
Boreal	-	-	36700	(Turetsky et al., 2014)
Temperate	-	-	29900	(Turetsky et al., 2014)
Subtropical	By ecosystem type	-	31000	(Turetsky et al., 2014)
Bog	-	-	25800	(Turetsky et al., 2014)
Poor fen	-	-	51300	(Turetsky et al., 2014)
Rich fen	-	-	44500	(Turetsky et al., 2014)
Swamp	Disturbed sites	-	6100	(Turetsky et al., 2014)
Drying	By type	-	300	(Turetsky et al., 2014)
Wetting	-	-	61100	(Turetsky et al., 2014)

McDaniel et al.'s (2017) measurements of CH_4 emissions in Narrabri, NSW, Australia, showed continued CH_4 oxidation in cultivated fields. Annual CH_4 oxidation estimates from dry floodplain are comparable to their findings (Table 3). This is an indication that many ecosystems in Australia serve as CH_4 sinks.

Methane emission from the reed bed in the Macquarie Marshes also accord to international CH_4 values reported by Olsson et al. (2015) from Liaohe delta in North-east China. Median CH_4 oxidation values obtained from dry floodplain are in agreement with CH_4 values reported by Wang et al. (2013) and Zhu et al. (2013). However, the median CH_4 emission from reed bed is not comparable to Anna and Bo (2001) and Marushchak et al. (2016). In addition, the results are in agreement with values obtained from treeless sub-arctic tundra and Oligotrophic bog in Russia (Zhu et al., 2013). Median CH_4 emission in reed bed is comparable to global CH_4 values reported by Turetsky et al. (2014) (Table 3).

The Macquarie Marshes have ~300,000 ha of floodplain, and within this area, the seasonal and permanent wetlands constitute ~40,000 ha. Estimates of CH_4 emission from this study indicates an annual emission of 4.97E-03 Tg yr^{-1} and annual oxidation of -2.97E-07 Tg yr^{-1}in one reed bed and its adjacent dry floodplain, respectively. Net CH_4 for this small part of the Marshes is estimated at about 4.97E-07 Tg yr^{-1}. This finding is similar to the CH_4 flux estimates and $^{13}C/^{12}C$ isotopic ratio observations made by (Hall et al., 2016; Mikaloff et al., 2004; Paudel et al., 2016). However, CH_4 flux in the Macquarie Marshes may change with inundation. If the dry floodplain received flooding in exceptional circumstances then they may also produce CH_4, since floodplains tend to emit large CH_4 during flood periods (Gatland et al., 2014).

3.6.3 Effects of soil carbon and environmental conditions on methane emission

Soil carbon

Studies on the effects of soil organic matter decomposition on CH_4 emission are not conclusive and show considerable variability depending on the composition of soil organic matter, soil mineral, redox status and soil temperature (Inglett et al., 2012). There was no significant relationship between soil carbon in the upper 30 cm of the soil profile and CH_4 emission in the Macquarie Marshes (Figure 14).

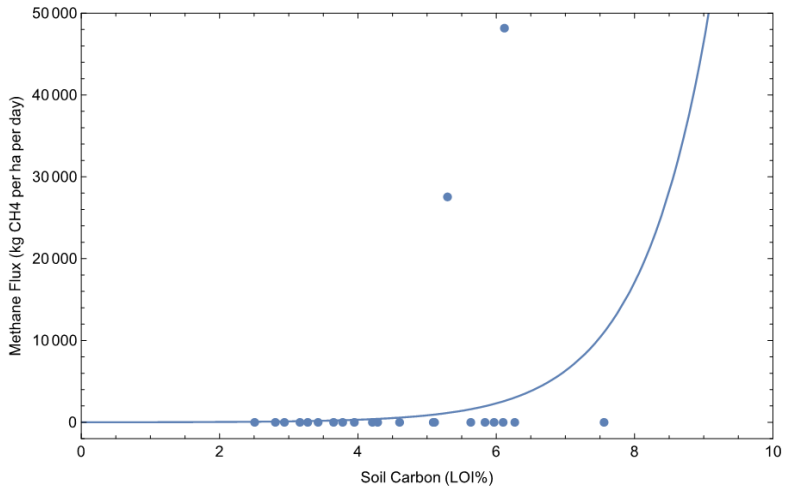

Figure 14. Soil carbon (LOI %) and methane flux

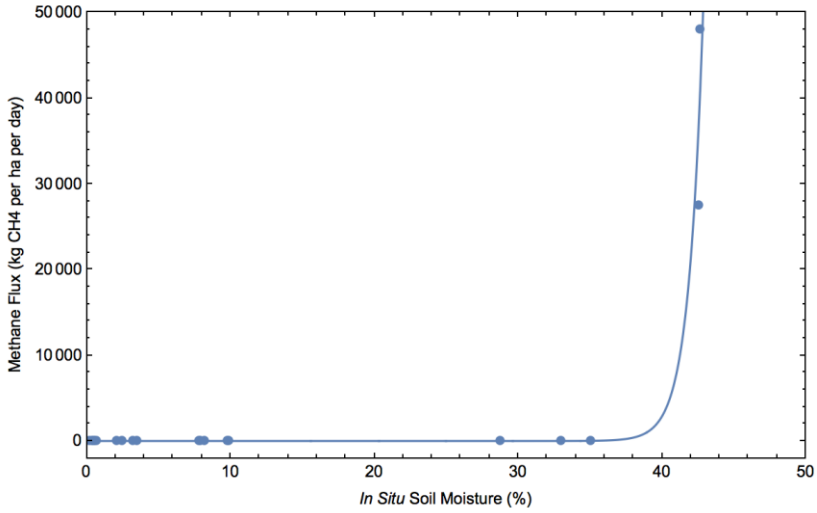

Figure 15. Soil moisture in situ and methane flux

These results disagree with Itoh et al. (2015), Jerman et al. (2017) and Zhong et al. (2017). Christensen et al. (2003) argued that temperature and microbial substrate availability are major controls of CH_4 emission. However, current result disagrees with Das and Adhya (2014) and Pandey et al (2014), their study showed organic matter enriched surface soil horizons (<160 cm) have greater CH_4 production rate. In addition, formation of CH_4 from decomposing ^{14}C-labelled by *Phragmatis australis* was also reported by Sari (2004).

Soil temperature

There was no correlation between soil temperature and CH_4 flux in the Macquarie Marshes. This finding is not comparable to Ingllet et al. (2012) and Maljanen et al. (2017). Their studies indicated that under anaerobic incubations, the proportion of CO_2 and CH_4 lost increases with temperature. Similarly, our results disagrees with (Allen et al., 2011) who observed that sediment

temperature ranging from 18 to 33 ^{o}C are strongly correlated with CH_4 emissions in coastal mangrove swamps and a sub-tropical estuary in Australia. However, CH_4 oxidation in dry floodplain and the lack of significant CH_4 production in dryland may be explained by lack of soil moisture. Current results agrees with Denmead et al. (2010) and Holmes et al. (2015). Their studies showed no dependence of CH_4 emission on soil temperature.

Soil moisture

There was significant exponential relationship between CH_4 flux and *in situ* soil moisture in the Macquarie Marshes (Figure 15). This finding agrees with most studies on CH_4 emissions in wetlands around the world (Call et al., 2015; Fest et al., 2017; Gatland et al., 2014; Wang et al., 2017). However, the observed CH_4 oxidation in dry floodplain may be attributed to lack of soil moisture and/or vegetation (Maher et al., 2015; Rietl et al., 2017). Their study showed that CH_4 oxidation rates increases with decreasing soil moisture levels in wetlands and this relationship explained ~90% of the temporal variability in CH_4 flux. Our finding also agrees with (Atkins et al., 2017; Holmes et al., 2015). Holmes et al.'s (2015) analysis of CO_2 and CH_4 isotopic compositions and production in tropical peatlands found that hydrogenotrophic methanogenesis was the dominant CH_4 production pathway, with up to 100 % of the CH_4 produced via this process. While methane is being oxidised in dry floodplain, this zone could be good emitter of CO_2 (Hotchkiss et al., 2015) because CO_2 flux increases with decreasing soil moisture levels in wetlands (Vardag et al., 2016). Current results disagree with Martins et al. (2015). Their work to identify biotic and abiotic drivers of GHG emission in dryland forest ecosystem found that N_2O and CO_2 were constrained by water availability and CH_4 is constrained by N availability in the soil. Similarly, smaller to negative CH_4 fluxes were reported from dryland wheat and barley on subtropical Vertosols in Australia (Schwenke et al., 2016).

Methane flux in most Australian wetlands is strongly controlled by soil moisture (Fest et al., 2017; Gatland et al., 2014). Methane oxidation in most Australian wetlands increases with continuous declines in soil moisture (Reilly et al., 2015), and this makes it very difficult to draw conclusions regarding the annual CH_4 flux from the drier zones of the Macquarie Marshes, since CH_4 flux character of these zones may be influenced by rainfall and infrequent inundation. In addition, the seasonal drying of soil moisture affects vegetation cover, which consequently may affect CH_4 emission. Seasonal soil moisture and vegetation changes could affect the rate at which atmospheric CO_2 is being stored in living biomass and sediment. When soil moisture levels are elevated the microbial breakdown of organic matter results in the release of CH_4 (Call et al., 2015; Sari, 2004). In most wetlands, soil moisture level is the major regulator of CH_4 flux and since these zones are not permanently dry, their seasonal CH_4 emission can be substantial comparable to the very frequent and nearly permanently inundated sections of reed bed in the Macquarie Marshes. Nevertheless, our

relatively small dataset cannot resolve this and further research is required on the relationship between soil moisture, inundation frequency, and CH_4 flux.

Soil EC and pH

There was no significant correlation between EC and CH_4 emission. This finding agrees with Olsson et al. (2015), who revealed that at high salinity levels CH_4 emissions were always low because methanogens were outcompeted by sulphate-reducing bacteria. Effects of pH on CH_4 oxidation by Scheutz and Kjeldsen (2004) indicates that methanotrophs were optimally adapted to pH. This may explain the lack of significant relationship between pH and CH_4 emission in the Macquarie Marshes. However, results were not in agreement with Yan et al. (2005), who argued that greater CH_4 emission occurs from soils with pH levels between 5.0 and 5.5. In this study, pH levels are >6 in all the three wetland zones. This might explain the weak correlation between CH_4 emission and pH reported by our investigation. However, in reed bed there was a relatively neutral condition (pH~7) in comparison with acidic conditions (pH <7) which prevailed in dry floodplain and dryland zones. Methane is oxidized at pH level ~6.5. Even though, there was no positive correlation between CH_4 flux and soil pH, CH_4 oxidation was observed under acidic conditions (pH <7) in dry floodplain.

Aboveground biomass and vegetation

Variability of vegetation cover may be a factor accounting for variability of CH_4 flux between reed bed, dry floodplain and dryland, since this has been previously documented (Anna and Bo, 2001; Christensen et al., 2003; Hall et al., 2016). Their study showed that vascular plants photosynthetic rate and subsequent allocation of fixed carbon to below ground structures influence both plant CH_4 transport and substrate quality. Phragmites dominated wetlands like the Macquarie Marshes can emit significant amounts of CH_4 because CH_4 produced in deep soil layers are transported through the air-space tissue of the plants to the atmosphere (Olsson et al., 2015). However, the oxidation of CH_4 in dry floodplain may be partly attributed to a lack of vegetation cover. This observation is in agreement with (Bass et al., 2014; Fest et al., 2017; McDaniel et al., 2017; Morin et al., 2014; Olsson et al., 2015). The contrasting vegetation cover in these wetland zones in addition to soil moisture, may account for the observed variability of CH_4 flux, because CH_4 emission tends to be aided by vegetation through the effects of stem clipping (Rietl et al., 2017). However, the balanced situation observed in the dryland may be attributed to patchy vegetation cover, which could not allow for total CH_4 oxidation, even though this wetland zone represents the driest section of the Macquarie Marshes. The effects of vegetation cover on methane emission have been discussed in detail by (Goulding et al., 2017; Itoh et al., 2015; Jones, 2016). Despite the fact that other environmental factors including temperature, soil moisture, soil organic matter and aboveground biomass are known to influence CH_4

emissions from wetlands (Turetsky et al., 2014), it is not clear which of these factors are most significant under field conditions when they all operate simultaneously (Olsson et al., 2015). Further research is needed to determine whether these factors are important in the broader Macquarie Marshes, and in similar floodplain wetlands in Australia.

3.7 Conclusion

Wetlands contribute to global CH_4 emissions (Rietl et al., 2017), and measuring CH_4 emissions from wetlands in drylands is therefore very important when estimating potential wetland carbon losses and global warming impacts (Gatland et al., 2014). Our findings indicate that zonal inundation regimes and soil moisture are the dominant controls of CH_4 emissions from three wetland zones in the Macquarie Marshes. There are very few published studies of $\delta^{13}C$ on CH_4 produced in non-coastal wetlands, and particularly wetlands in drylands. Edward et al. (2000) measured $\delta^{13}C$ CH_4 (-40.7 ‰) in freshwater wetlands and other anaerobic environments. Jeffery (2005) reported $\delta^{13}C$ CH_4 values ranging from -67.3 to -56.6 ‰ from freshwater wetlands, and so our findings are a major contribution to this field.

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3.9 References

See combined list of references at the end of the thesis.

Chapter 4 Conclusion

4.1 Summary of key findings

This research was undertaken primarily to investigate the CH_4 flux in floodplain wetlands of the Macquarie Marshes and to quantify CH_4 flux in relation to soil moisture, soil carbon and other environmental conditions. The findings were discussed within the context of environmental drivers of CH_4 production and consumption in global wetlands. We found that soil moisture controls the flux and isotopic signature of CH_4 emissions from an Australian inland wetland. The major findings from this investigation are summarised below in the context of the main objectives of this thesis:

i. Define the relationships between soil moisture and CH_4 flux wetland zones of the Macquarie Marshes.

This study has defined the relationship between CH_4 flux and soil moisture over different wetland zones in the Macquarie Marshes. The reed bed was the major source of CH_4 and this zone had the highest soil moisture. The dry floodplains of the Marshes which serve as CH_4 sinks and the dryland zone adjacent to the floodplain where balanced conditions prevailed, have less soil moisture.

ii. Determine whether soil carbon and environmental factors such as soil temperature, soil pH and soil EC vary with wetland zones, and how this variability affects CH_4 flux, thereby assessing controls on soil carbon and CH_4 emissions in wetland zones with distinctive environmental conditions.

Methane flux over different wetland zones was characteristic of the prevailing environmental conditions. In reed bed soil moisture, dense vegetation cover and more humid conditions prevail and these account for the observed CH_4 production. In contrast, CH_4 is being oxidised in dry floodplain and this was attributed to dry and acidic conditions in addition to lack of vegetation cover. However, the prevailing neutral conditions in dryland were due to the presence of patchy C4 plants, which helped to keep CH_4 flux to background air conditions. However, soil carbon and soil temperature do not correlate positively with CH_4 fluxes over all the three-wetland zones and there is a need to understand why. Thus, the ability to separate these two situations would allow for improved understanding of the role of soil carbon and soil temperature in CH_4 flux in floodplain wetlands. However, soil pH and soil EC do not correlate with CH_4 emissions. This might have occur given the fact that current investigation was conducted in freshwater floodplain wetland, or the methanogens were outcompeted by sulphate-reducing bacteria. Thus, the ability to link these two explanatory soil parameters to CH_4 emissions in freshwater wetlands will help in understanding the controls and drivers of CH_4 flux in freshwater inland wetland systems.

4.2 Resolving research hypotheses

The major findings are summarised below in the context of the main hypotheses of this thesis:

H_1 *Soil carbon and CH_4 flux will vary between the three-wetland zones, with the regularly inundated reed bed being a major hotspot of soil carbon and CH_4 release.*

There was a significant difference (p=0.002) in soil carbon contents between wetland zones. There was also a significant difference (p=0.005) in organic carbon stock between wetland zones. Importantly, there was a significant difference (p=0.021) in CH_4 emissions between reed bed, dry floodplain and dryland. The reed bed (i.e. zone 1) which is regularly inundated, was the major hotspot of CH_4 emission.

H_2 *Methane isotopic signatures in the wetlands will correspond to CH_4 values reported elsewhere.*

Methane isotopic signatures from reed bed compare very well with isotopic values reported from wetlands around the world. The median $\delta^{13}C$ CH_4 obtained falls within the acceptable range of $\delta^{13}C$ CH_4 used for modelling atmospheric CH_4 concentrations.

H_3 *Methane flux will correlate with greater soil organic matter, soil moisture and soil temperature.*

Soil organic carbon did not correlate positively with CH_4 emission in the Macquarie Marshes. Similarly, there was no significant correlation between soil temperature and CH_4 emissions. In contrast, there was a strong positive exponential relationship between soil moisture and CH_4 emissions.

H_4 *Soil carbon stock in wetland zones will be determined by aboveground biomass and inundation regime.*

There was no significant relationship (p=0.690) between aboveground biomass and LOI %. Also, there was no significant relationship (p=0.511) between soil organic carbon stock and aboveground biomass.

4.3 Direction for future research

This study opens new opportunities for future research, which include:

i. A detailed investigation of CH_4 emission in comparison with CO_2 and N_2O emissions in floodplain wetlands of Macquarie Marshes. This investigation will be important in understanding the proportion of CH_4 efflux relative to CO_2 and N_2O, especially in dry

floodplain where CH_4 is being oxidised owing to seasonal soil moisture removal, which correlates strongly with CO_2 emissions in dry fluvial floodplain wetlands.

ii. Detailed spatial and temporal measurements of GHGs using meteorological techniques such as eddy covariance to determine the long-term flux character of GHGs. This will enable comparison with saline coastal wetlands and facilitates understanding of seasonal and environmental drivers of GHGs flux from inland freshwater wetlands.

iii. A detailed investigation of isotopic composition of GHGs is also important in understanding the differences in isotopic signatures in C3 and C4 plants in dry landscapes like Macquarie Marshes, because sharp natural $\delta^{13}C$ gradients can be found in dry tropics and sub-tropics, where meadows and forest vegetation is strongly represented by C4 and C3 plants.

iv. A comparative measurement of GHGs between Nature Reserve sections of the Macquarie Marshes, which has less recent human interference, and crop fields, in comparison with grazed lands is important. This study will unveil GHGs flux character under different land use patterns which will enable understanding of the major drivers of atmospheric GHGs emissions between natural and anthropogenic process in wetlands.

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Appendices

Appendix IA Determination of chamber trace gas concentrations in Zone 1 – reed bed. Plots without a fitted regression line are not suitable for flux calculation.

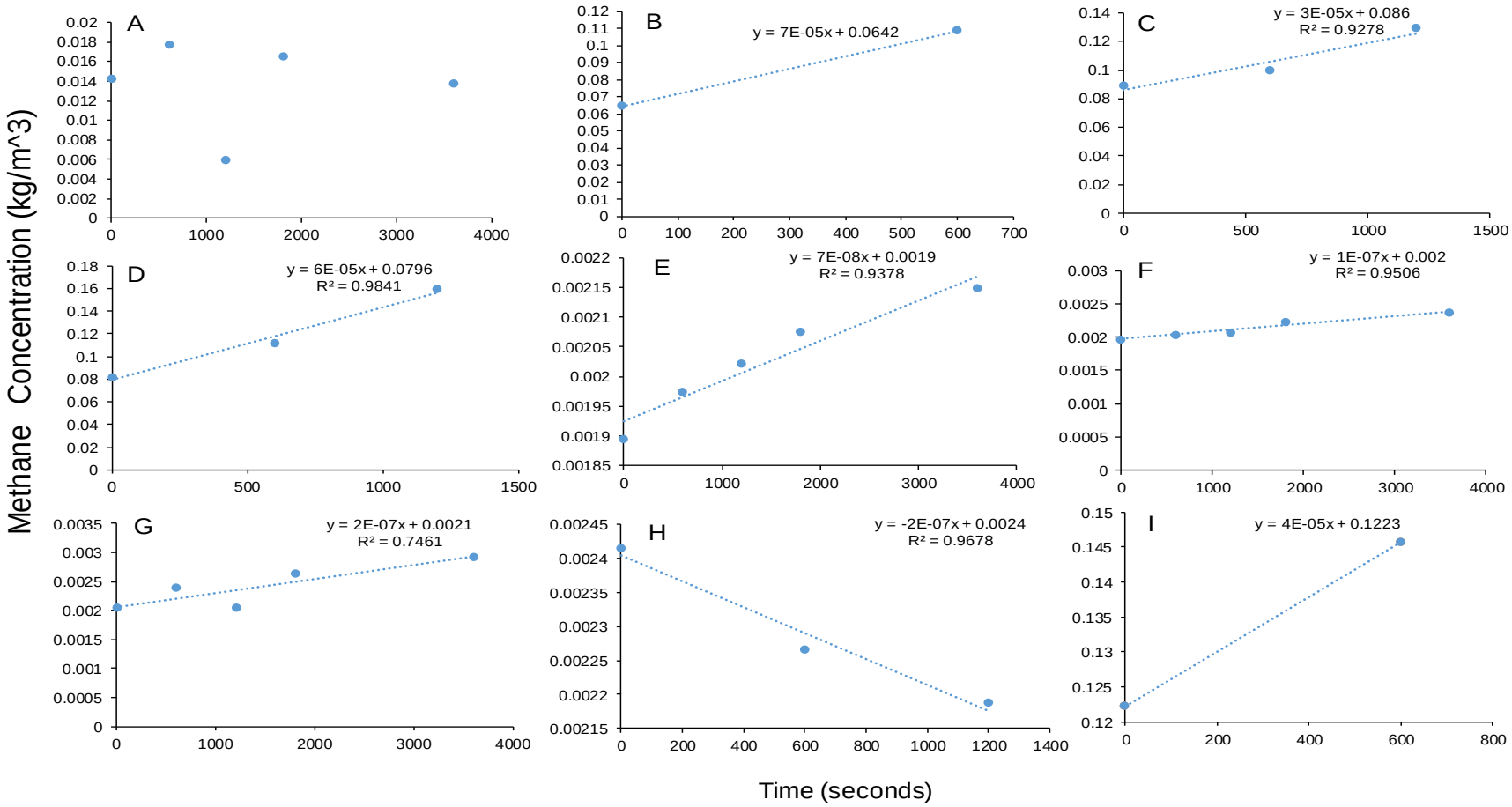


Figure IA Spatial and temporal variability of CH_4 fluxes between landscape units in reed bed; (A) Z1S1, (B) Z1S2, (C) Z1S3, (D) Z1S4, € Z1S5, (F) Z1S6, (G) Z1S7, (H) Z1S8, and (I) Z1S9.

Appendix IB Determination of chamber trace gas concentrations in Zone 2 – dry floodplain. Plots without a fitted regression line are not suitable for flux calculation.

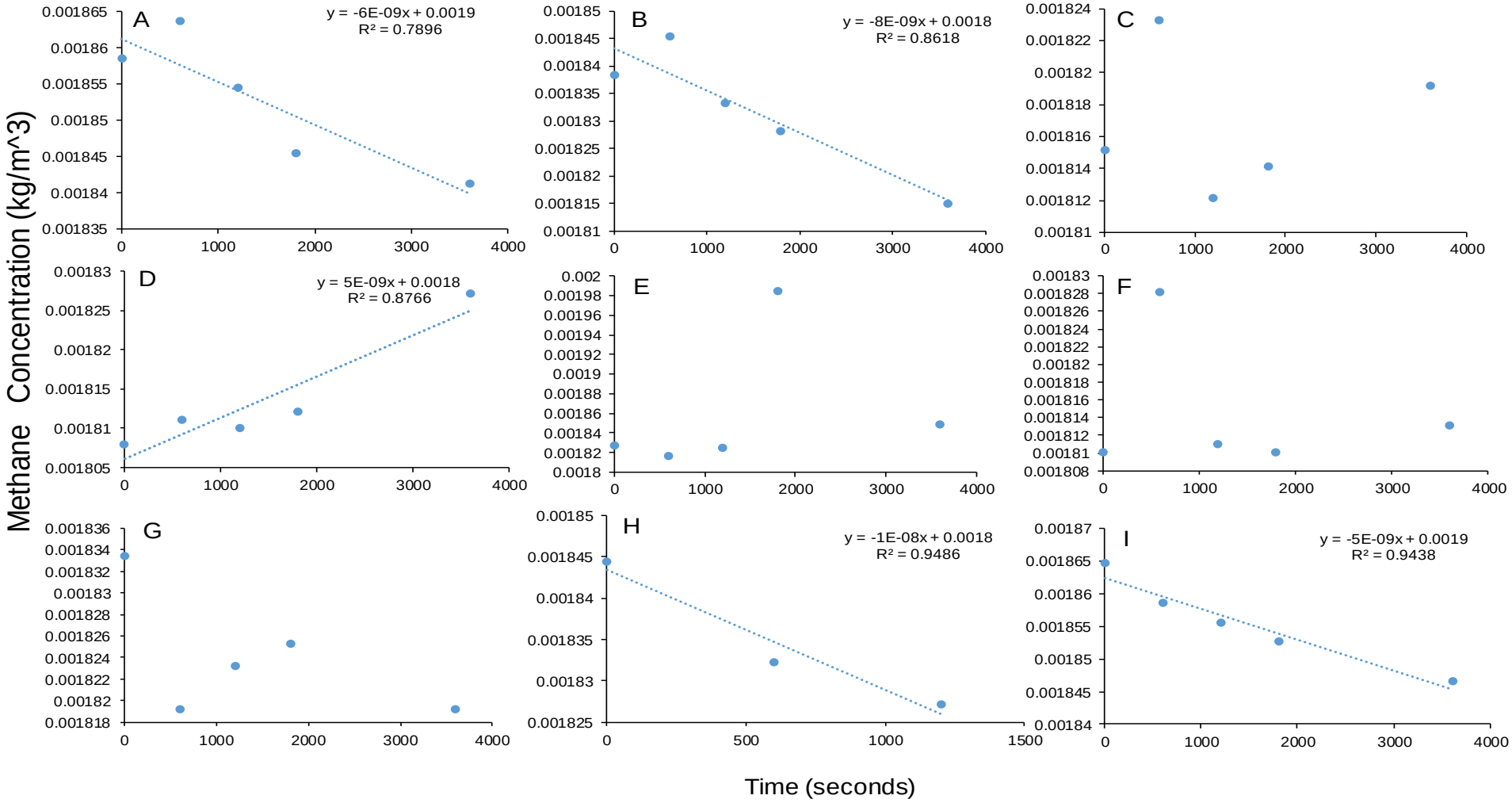


Figure IB Spatial and temporal variability of CH_4 fluxes between landscape units in dry floodplain; (A) Z2S1, (B) Z2S2, (C) Z2S3, (D) Z2S4, (E) Z2S5, (F) Z2S6, (G) Z2S7, (H) Z2S8, and (I) Z2S9

Appendix IC Determination of chamber trace gas concentrations in Zone 3 – drylands. Plots without a fitted regression line are not suitable for flux calculation.

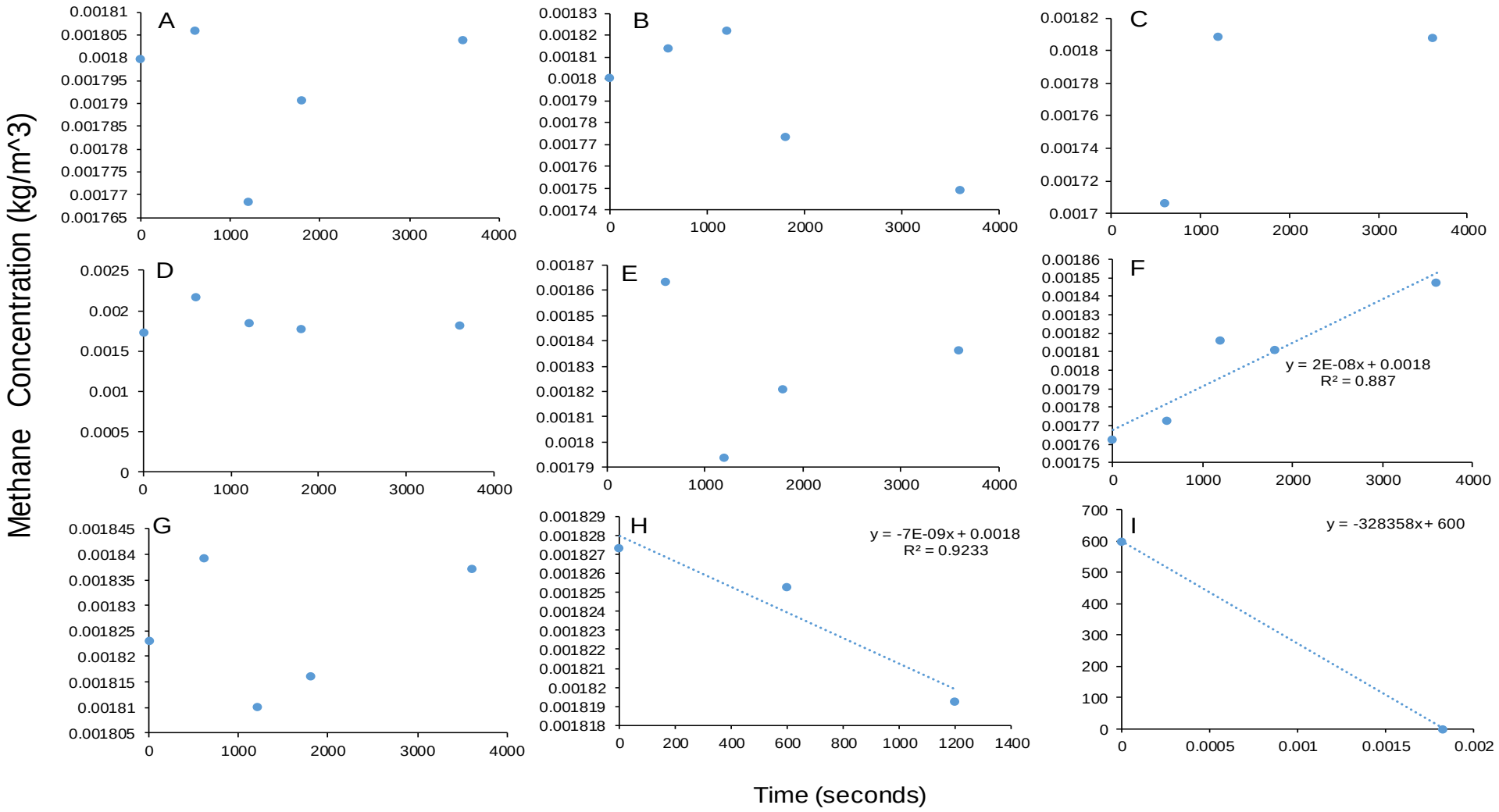
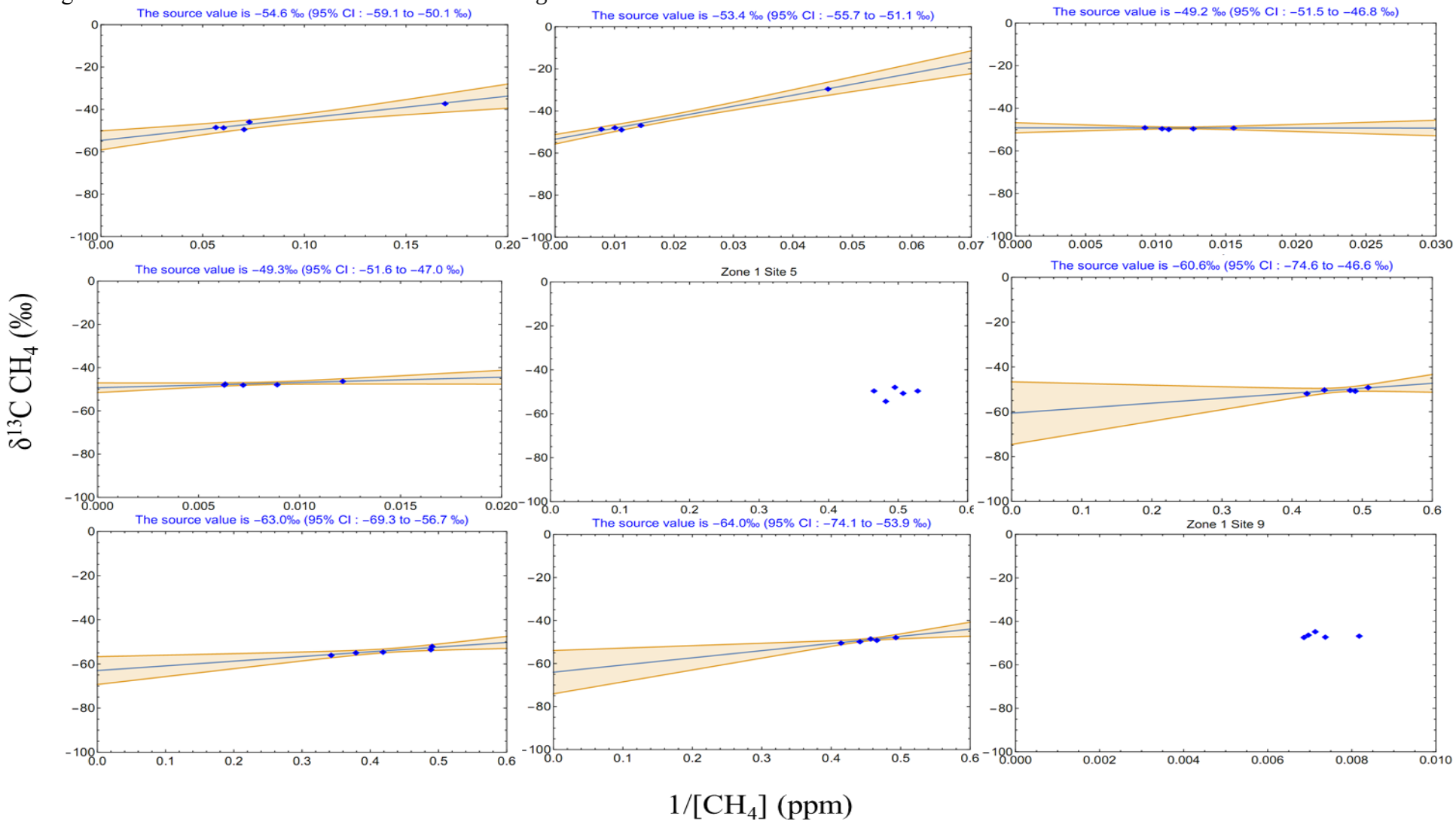
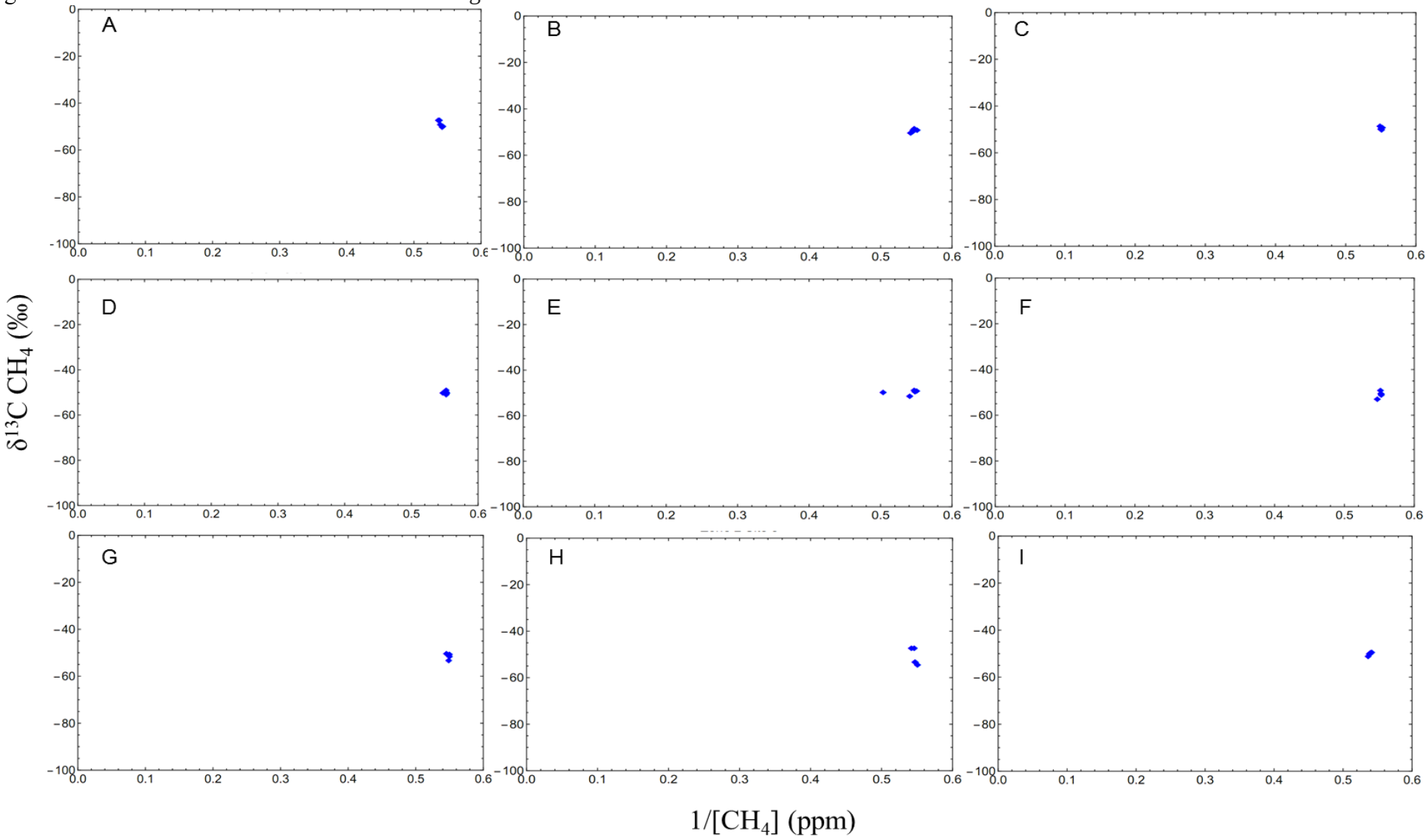


Figure IC Spatial and temporal variability of CH_4 fluxes between landscape units in red soil; (A) Z2S1, (B) Z2S2, (C) Z2S3, (D) Z2S4, (E)(E) Z2S5, (F) Z2S6, (G) Z2S7, (H) Z2S8, and (I) Z2S9.

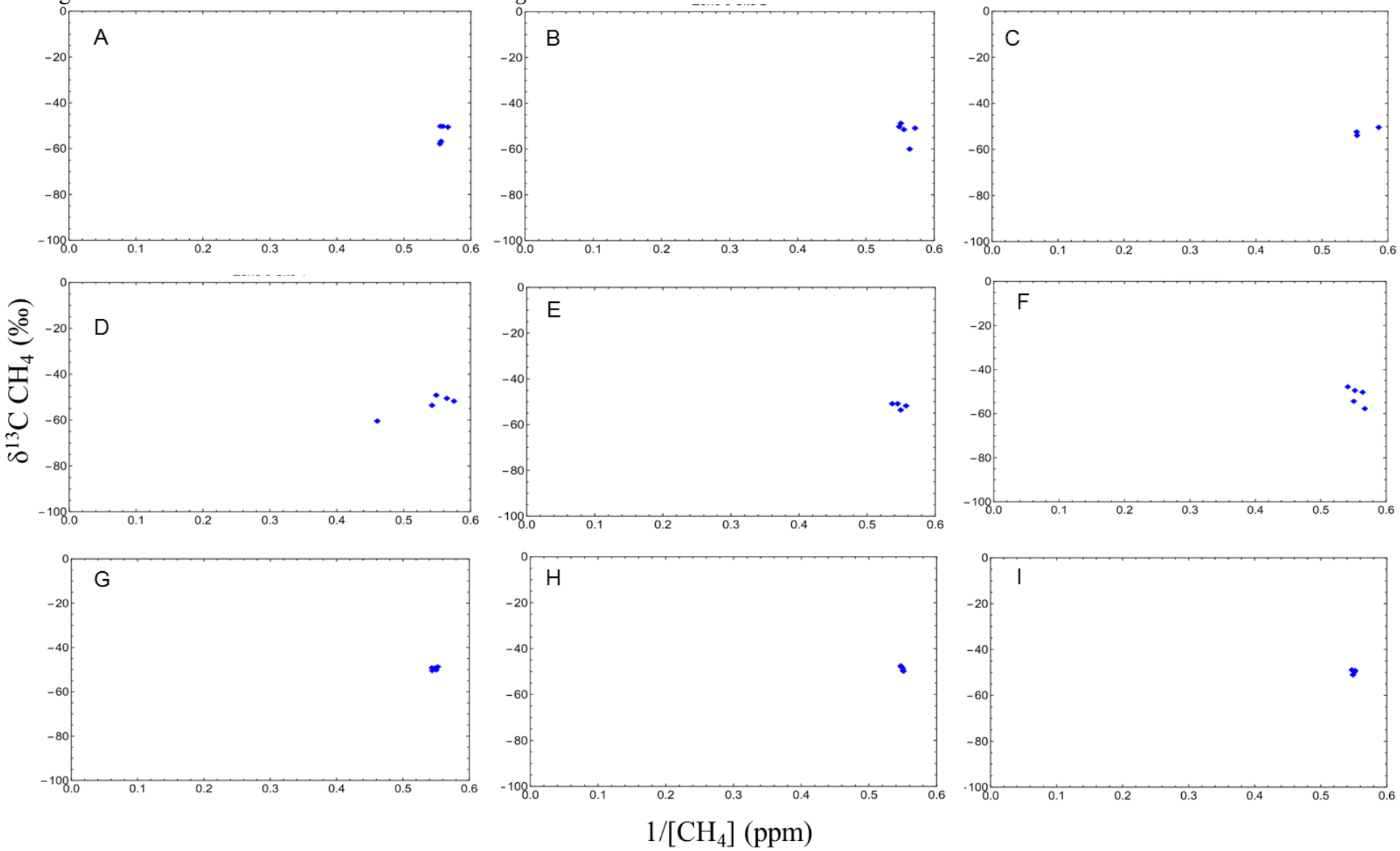
Appendix II A. Keeling plot analysis of $\delta^{13}C$ CH_4 (‰) vs. 1/[CH_4] (ppm) of landscape units in zone 1. (A-I) represent Z1S1 to Z1S9. Plots without fitted regression lines have a 95% confidence interval of greater than +/- 15 ‰.



Appendix II B. Keeling plot analysis of $\delta^{13}C$ CH_4 (‰) vs. 1/[CH_4] (ppm) of landscape units in zone 2. (A-I) represent Z1S1 to Z1S9. Plots without fitted regression lines have a 95% confidence interval of greater than +/- 15 ‰.



Appendix II C. Keeling plot analysis of $\delta^{13}C$ CH_4 (‰) vs. 1/[CH_4] (ppm) of landscape units in zone 3. (A-I) represent Z1S1 to Z1S9. Plots without fitted regression lines have a 95% confidence interval of greater than +/- 15 ‰.



Appendix III. Environmental data

Zone 1 (Reed bed)														
Study sites	Z1S1	Z1S2	Z1S3	Z1S4	Z1S5	Z1S6	Z1S7	Z1S8	Z1S9	Mean	Max	Min	Std Dev	Std Err
Soil carbon (LOI %)	12.13	6.12	6.01	5.96	5.84	5.09	7.55	5.62	5.29	6.62	12.13	5.09	2.18	0.73
Soil moisture % (lab)	18.56	18.53	23.52	18.70	13.10	9.68	15.46	18.59	16.20	16.93	23.52	9.68	3.94	1.31
Soil moisture % (in situ)	33.67	42.63	43.03	35.03	28.73	9.77	32.93	21.00	42.53	32.15	43.03	9.77	11.09	3.70
Soil temp (oC)	23.53	28.20	25.87	27.33	22.80	21.87	22.87	37.63	24.93	26.11	37.63	21.87	4.82	1.61
pH	7.29	7.40	7.08	6.36	6.55	6.79	8.00	7.50	6.90	7.10	8.00	6.36	0.51	0.17
EC (µS/cm)	163.60	181.50	114.10	191.00	394.00	265.00	233.00	1956.00	239.00	415.24	1956.00	114.10	583.11	194.37
Biomass (%)	13.75	14.65	12.74	12.57	11.19	5.68	10.72	7.40	8.95	10.85	14.65	5.68	2.99	1.00
DBD (g/cm3)	0.56	0.54	0.63	0.49	0.56	0.59	0.68	0.61	0.71	0.60	0.71	0.49	0.07	0.02
Organic carbon stock (t/ha)	68.15	32.88	37.93	29.48	32.93	30.24	51.14	34.57	37.43	39.42	68.15	29.48	12.55	4.18
Zone 2 (Dry floodplain)														
Study sites	Z2S1	Z2S2	Z2S3	Z2S4	Z2S5	Z2S6	Z2S7	Z2S8	Z2S9	Mean	Max	Min	Std Dev	Std Err
Soil carbon (LOI %)	5.11	4.61	3.94	4.29	4.96	3.42	3.27	3.65	6.27	4.39	6.27	3.27	0.96	0.32
Soil moisture % (lab)	9.53	4.56	8.96	5.26	11.21	6.51	21.58	5.41	13.57	9.62	21.58	4.56	5.40	1.80
Soil moisture % (in situ)	3.47	9.90	2.47	2.07	0.83	3.23	0.20	0.50	7.87	3.39	9.90	0.20	3.36	1.12
Soil temperature (oC)	32.60	34.13	33.93	36.93	33.20	35.77	27.97	30.07	28.70	32.59	36.93	27.96	3.09	1.03
pH	7.03	8.09	6.85	6.80	6.67	6.59	6.15	6.70	6.61	6.83	8.09	6.15	0.53	0.18

Table 5.3 Continued														
EC (µS/cm)	287.00	379.00	271.00	383.00	317.00	189.60	103.20	260.00	217.00	267.42	383.00	103.20	89.64	29.88
Biomass (%)	4.55	6.30	6.82	51.02	4.35	4.84	6.74	4.43	3.45	10.28	51.02	3.45	15.32	5.11
DBD (g/cm3)	0.66	0.40	0.54	0.48	0.59	0.52	0.49	0.54	0.57	0.53	0.66	0.40	0.07	0.02
Organic carbon stock (t/ha)	33.48	18.24	21.26	20.49	29.22	17.65	15.89	19.57	35.80	23.51	35.80	15.89	7.36	2.45
Zone 3 (Red soil)														
Study sites	Z3S1	Z3S2	Z3S3	Z3S4	Z3S5	Z3S6	Z3S7	Z3S8	Z3S9	Mean	Max	Min	Std Dev	Std Err
Soil carbon (LOI %)	4.21	3.78	2.93	2.96	6.09	2.80	2.51	3.16	5.63	3.79	6.09	2.51	1.29	0.43
Soil moisture % (lab)	7.45	4.95	2.41	2.83	6.20	3.03	1.89	10.51	5.00	4.92	10.51	1.89	2.80	0.93
Soil moisture % (in situ)	0.50	0.63	0.50	1.57	7.83	8.13	0.33	0.50	0.50	2.28	8.13	0.33	3.25	1.08
Soil temperature (oC)	18.67	16.17	39.90	35.80	32.30	44.10	40.13	41.70	37.80	34.06	44.10	16.17	10.05	3.35
pH	6.21	5.90	6.54	6.34	6.04	6.22	6.33	6.93	6.49	6.33	6.93	5.90	0.30	0.10
EC (µS/cm)	98.80	185.00	368.00	178.50	147.80	220.00	294.00	583.00	126.50	244.62	583.00	98.80	152.19	50.73
Biomass (%)	11.74	9.07	4.12	5.54	16.77	3.83	4.78	14.23	16.70	9.64	16.77	3.83	5.38	1.79
DBD (g/cm3)	0.58	0.63	0.62	0.67	0.62	0.68	0.61	0.45	0.56	0.60	0.68	0.45	0.07	0.02
Organic carbon stock (t/ha)	24.36	24.02	18.20	19.76	37.51	19.08	15.36	14.26	31.60	22.68	37.51	14.26	7.67	2.56

Appendix IV Statistical analysis

Appendix IVA. Kruskal-Wallis non-parametric test for methane emission and environmental factors between wetland zones. Values in bold are significantly different.

Variables	Wetland zones	H (chi2):	Hc (tie corrected):	p (same):
Methane (kg CH_4 $ha^{-1}d^{-1}$)	All zones	7.3	7.6	**0.021**
Soil org. matter (LOI %)	All zones	11.86	11.86	**0.002**
Org. carbon stock (t ha^{-1})	All zones	10.89	10.89	**0.005**
Biomass (%)	All zones	4.87	4.87	*0.087*
Soil moisture Lab (%)	All zones	15.88	15.88	**<0.001**
Soil temperature (^oC)	All zones	7.27	2.27	**0.026**
Soil EC (µS/cm)	All zones	1.24	1.24	0.53
pH	All zones	11.19	11.2	**0.004**

Appendix IVB. Post hoc Mann-Whitney Pairwise test for methane emissions and environmental factors between wetland zones. Values in bold are significantly different ($p<0.05$).

Variables	Wetland zones	Reed bed	Dry floodplain	Dryland
CH_4 flux (kg $ha^{-1}d^{-1}$)	Reed bed		**0.021**	**0.020**
	Dry floodplain	14.5		**0.010**
	Dryland	14.5	34	
Soil carbon (LOI %)	Reed bed		**0.005**	**0.002**
	Dry floodplain	8		**<0.001**
	Dryland	9	23	
Organic carbon stock (t ha^{-1})	Reed bed		**0.006**	**0.005**
	Dry floodplain	9		0.812
	Dryland	8	37	
Biomass (%)	Reed bed		**0.013**	0.87
	Dry floodplain	12		**0.028**
	Dryland	34	30	
Soil moisture Lab (%)	Reed bed		**0.010**	**<0.001**
	Dry floodplain	11		**0.030**
	Dryland	1	15	
Soil temperature (^oC)	Reed bed		**0.008**	**0.026**
	Dry floodplain	10		**0.050**
	Dryland	20	25	
Soil EC (µS/cm)	Reed bed		0.57	0.54
	Dry floodplain	33		0.33
	Dryland	33	39	
Soil pH	Reed bed		0.25	**0.002**
	Dry floodplain	27		**0.024**
	Dryland	6		