Aquatic carbon cycling in the tropics: insights into pore-water exchange, outgassing and outwelling

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Aquatic carbon cycling in the tropics: Insights into pore-water exchange, outgassing and outwelling

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Doctor of Philosophy (PhD)

August 2018
Declaration

I certify that the work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for a degree at this or any other university.

I acknowledge that I have read and understood the University's rules, requirements, procedures and policy relating to my higher degree research award and to my thesis. I certify that I have complied with the rules, requirements, procedures and policy of the University (as they may be from time to time).

Name Mitchell Call

Date 30 August 2018

Signature
Acknowledgements

So many people have helped me produce this thesis, however, without my supervisors, Associate Professor Damien Maher (aka “Damo the Gun”) and Professor Isaac Santos, this would never of happened! So thank you very much gents. I am extremely grateful for your mentorship during the 3 years of this PhD and for having the faith to send me to the remote places this PhD has taken me. To list everyone else that has helped me along the way would take far too many pages (as you/they span continents). So to all my colleagues, friends and family that have helped and supported me along the way, thank you so very much. And before I make a special thank you to my mum, I would just like to wish any current or future PhD students whom may read this the best of luck, as only those who have done a PhD will understand the huge amount of time and effort that goes into every word that appears on the pages of this thesis. And finally, thanks mum 😊
Preface

This thesis comprises six chapters, four of which are published in scientific journals. Three chapters of this thesis are based on data captured from three separate study sites located in remote areas of two developing tropical countries. The costs, challenges and risks associated with conducting research in remote tropical locations makes them severely underrepresented in global data set. My work attempts to fill some of the gaps in the cycling of carbon along an aquatic continuum in the tropics. Chapter 1 provides an introduction to the thesis including the aims and objectives for the thesis. Chapter 2 suggests pore-water/groundwater exchange is a relevant source of dissolved CO$_2$ and CH$_4$ to the major tributaries of the central Amazon Basin. Chapter 3 presents large scale implications to global CO$_2$ and CH$_4$ mangrove budgets based on the first estimates of CO$_2$ and CH$_4$ fluxes from a macro-tidal mangrove creek in the 0 ° to 5 ° latitude band. Chapter 4 presents the first carbon exports from two mangroves creeks of differing geomorphologies located in the wet tropics revealing considerable differences in carbon outwelling and emission. Chapter 5 presents a new, novel analytical system to autonomously determine concentrations of dissolved inorganic carbon (DIC) and its carbon stable isotope ratio ($\delta^{13}$C-DIC) at high temporal resolutions. Chapter 6 provides a synthesis of the conclusions.
Papers published and included in the main body of the thesis:


Additional publications that are included in Appendix 2 that represent related significant work undertaken during the course of the thesis:


Statement of contribution

Published and included in the main body of the thesis:


I co-designed the project, performed the field work, analysed and interpreted the data and wrote the original manuscript.


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**Additional publications that represent related significant work undertaken during the course of the thesis:**


I performed field work and edited the original manuscript.


I performed field work and edited the original manuscript.


I performed field work and edited the original manuscript.


I performed field work and edited the original manuscript.


I performed field work and edited the original manuscript.

Principal supervisor name: Associate Professor Damien T. Maher

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Signature and date: 30/08/2018
Abstract

Constraining the global flows of carbon has become a research priority due to the anthropogenic-induced alteration of the global carbon cycle. Carbon budgets are now more detailed, with considerable focus on constraining the flows and partitioning of carbon within ecosystems and quantifying exchanges with the major reservoirs of land, ocean and atmosphere. Tropical rivers, mangroves and the coastal ocean interact between all three reservoirs and are sites of intense carbon processing, playing a disproportionate role in regional and global carbon budgets. The tropics is home to the world’s largest rivers and is where mangroves are most abundant, yet data from systems in this region are lacking in global data sets. This thesis addresses key gaps in the cycling of carbon in the tropics and presents a new sampling methodology to enhance coastal carbon cycling research.

Similarly to rivers globally, constraining the sources driving riverine CO2 and CH4 emissions in the Amazon river system remains a challenge. The relevancy of pore-water/groundwater exchanges as a source of CO2 and CH4 to higher orders rivers in the Amazon basin (and rivers globally) is largely unknown and a difficult pathway to constrain. Longitudinal surveys captured high-resolution surface water pCO2, CH4 and 222Rn (a natural pore-water tracer) data from the major tributaries of the central Amazon basin. Results confirm the heterogeneous nature of pore-water exchange and suggests that pore-water discharge enhanced CO2 supersaturation by 18 to 47 % in receding black and clear waters. A major outcome of my study suggests a direct link between pore-water and riverine CH4, supporting hypotheses that riverine CH4 dynamics appear to be driven in part by hydrology.

Mangroves are now recognised as significant sources of carbon to the coastal ocean and a source of CO2 and CH4 to the atmosphere. I present the first CO2 and CH4 fluxes from a macro-tidal mangrove creek located in the 0 ° to 10 ° latitudinal band, where 30 % of the
world’s mangroves occur. The estimated emissions of CO₂ and CH₄ from the macro-tidal
mangrove creek located in the Amazon region of Brazil (174 ± 129 mmol CO₂ m⁻² d⁻¹ and
855 ± 406 μmol CH₄ m⁻² d⁻¹) are amongst the highest reported for mangrove systems
worldwide. The high temporal resolution measurements over a two week period enabled me
to show how pore-water exchange controls the temporal variability of mangrove water CO₂
and CH₄ over lunar cycles in a macro-tidal system.

Few studies have attempted to estimate the relative contribution of individual carbon
parameters to the total carbon exported from a single mangrove creek. I present the first
carbon exports from two mangroves creeks of differing hydrogeomorphologies located in the
wet tropics. Outwelling rates of POC, DIC and DOC and CO₂ emissions were 33-fold, 27-
fold, 5-fold and 3-fold higher at the estuarine creek than from the mangrove creek fringing
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contributing to total carbon losses at the mangrove creek located within a semi-enclosed bay,
whilst CO₂ emission (61 %) was the major contributor at the mangrove creek located along
the coast and adjacent to fringing reefs. My study demonstrates the considerable
heterogeneity of mangroves creeks that are in close proximity and subject to similar weather
conditions but in differing geomorphological settings.

Finally, I present a new approach to autonomously determine concentrations of
dissolved inorganic carbon (DIC) and its carbon stable isotope ratio (δ¹³C-DIC) at high
temporal resolutions. Coupling two commercially available instruments, the new method
determined DIC and δ¹³C-DIC at sampling resolutions of 16 min⁻¹ with a DIC precision of ±
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Chapter 1 Introduction and aims and objectives

Anthropogenic activities have considerably altered the global carbon cycle (Le Quéré et al. 2015). The subsequent and potential impacts on the climate system and oceanic carbon cycle (e.g. ocean acidification) has provided the impetus for increased research into carbon cycling (Falkowski et al. 2000). As such, global and regional carbon budgets have become more detailed (Canadell et al. 2011; Kirschke et al. 2013; Le Quéré et al. 2015; Saunois et al. 2016) with considerable effort directed toward constraining the flows and partitioning of carbon within ecosystems, and quantifying the magnitude and direction of carbon exchanges with the major reservoirs of land, ocean and atmosphere (Bouillon et al. 2008; Cole et al. 2007). Ecosystems located at the land-aquatic interface, such as rivers, mangroves, and coastal waters, interact between all three reservoirs. Despite covering small areas of the Earth, these systems are becoming increasingly recognised as quantitatively significant in terms of their contributions to regional and global carbon budgets, yet large uncertainties exist (Alongi 2014; Aufdenkampe et al. 2011; Laruelle et al. 2014). This thesis aims to address key gaps in the cycling of carbon along an aquatic continuum (from freshwater rivers to inter-tidal mangroves to the coastal ocean) in the highly productive equatorial region.

The role of rivers (and inland waters in general) in global carbon cycling has evolved considerably. Previously, rivers were seen as “passive pipes” (Figure 1.1), merely a conduit in which terrestrially derived organic and inorganic carbon transits to the world’s oceans (Cole et al. 2007). However, they are now recognised as “highly reactive pipes” that emit globally significant amounts of carbon, potentially offsetting the land sink for anthropogenic CO₂ (Cole et al. 2007; Le Quéré et al. 2015). Estimates of carbon dioxide (CO₂) emission from rivers globally range from 0.6 to 3.9 Pg CO₂ yr⁻¹ (Aufdenkampe et al. 2011; Drake et al. 2017; Lauerwald et al. 2015; Raymond et al. 2013) and estimated efflux of methane (CH₄) from 1.5 Tg C yr⁻¹ to 26.8 Tg C yr⁻¹ (Bastviken et al. 2011; Kirschke et al. 2013; Stanley et al.
The most recent estimates, which are also the largest, are the result of increased data coverage, improved surface area estimates, and revised (i.e. higher) atmospheric exchange rates for CO₂. However, estimates of CO₂ and CH₄ outgassing are still considered conservative, partly due to limited estimates from tropical systems which are the largest contributor of global emissions from rivers (Aufdenkampe et al. 2011; Bastviken et al. 2011; Borges et al. 2015; Drake et al. 2017; Ward et al. 2017).

Figure 1.1 The previous view of rivers as “passive pipes” (top) compared to the current view which recognises rivers as “highly reactive pipes” and a source of atmospheric CO₂ and CH₄ (bottom). Figure amended from Tranvik et al. (2018).

The relative contribution of the sources and processes driving riverine CO₂ are currently unable to be partitioned with any certainty and our understanding of the drivers of CH₄ supersaturation remain limited (Borges et al. 2015; Borges et al. 2018; Raymond et al. 2013; Stanley et al. 2016; Teodoru et al. 2015). Pore-water/groundwater is becoming
increasing recognised as an important source of carbon in estuarine (Call et al. 2015; Macklin et al. 2014; Maher et al. 2015) and floodplain (Webb et al. 2017) environments. For rivers, previous studies have estimated the contribution of this pathway to CO₂ supersaturation based on water flow through rates and soil atmosphere CO₂ (Butman and Raymond 2011; Richey et al. 2002). However, pore-water/groundwater exchanges are spatially and temporally heterogeneous (Cook et al. 2003). The strong correlation between precipitation and riverine CO₂ evasion, suggests (amongst others), higher delivery of soil CO₂ from land to rivers (Butman and Raymond 2011) which may also be the case for CH₄. Thus, where seasonal rainfall results in large oscillations in water stage and areas of inundation (and associated exchanges of interstitial soil water with surface waters), such as in the tropics, pore-water/groundwater exchanges may be more relevant to CO₂ and CH₄ supersaturation in tropical inland waters.

The Amazon River system is the world’s largest. The migration of the Inter-Tropical Convergence Zone (ITCZ) results in large seasonal oscillations in river flow and floodplain inundation across the Amazon basin. Estimates of CO₂ and CH₄ outgassing from Amazon rivers are globally significant and range from 0.5 to 1.4 Pg CO₂ yr⁻¹ (Rasera et al. 2013; Richey et al. 2002; Sawakuchi et al. 2017) and from 0.4 to 0.6 Tg CH₄ yr⁻¹ (Sawakuchi et al. 2014), respectively. Hydrologically, pore-water/groundwater interactions in the Amazon have received attention as synthesised by Miguez-Macho and Fan (2012) and more recently by Pfeffer et al. (2014), yet the role of this pathway in Amazon carbon budgets is largely unknown. Furthermore, it is likely that surface waters that have infiltrated soils during rising waters may progressively return to surface waters during the receding water phase (a process similar to the mangrove tidal pump concept I discuss in Chapter 3). Chapter 2 of this thesis addresses the following question: Is pore-water a relevant source of CO₂ and CH₄ to the major tributaries of the Amazon river system during receding waters? This chapter will
add to the current literature by conducting longitudinal surveys using coupled, high resolution measurements of a natural groundwater tracer and CO₂ and CH₄ to investigate areas of enhanced pore-water to surface water connectivity in three of the major tributaries in the Amazon River system. The sampling methodology is a first for the Amazon and the results provide a basis for future studies quantifying the role of pore-water/groundwater in the Amazonian carbon cycle.

Mangroves are the dominant inter-tidal vegetation in the tropics and recognised as one of the most carbon-rich ecosystems on Earth (Alongi 2014; Donato et al. 2011). They are highly productive systems, with net primary productivity (NPP) rates comparable to humid evergreen forests (Alongi 2009; Alongi 2014; Malhi 2012). Mangroves also have high carbon burial rates (Breithaupt et al. 2012; Jennerjahn and Ittekkot 2002; Twilley et al. 1992), with much of the carbon in mangroves ecosystems stored in sediments (termed “blue carbon”) which are considered an important sink for atmospheric CO₂ (Breithaupt et al. 2012; Donato et al. 2011; Duarte et al. 2013). Whilst mangroves occur from ~ 30 ° N to ~ 40 ° S (Giri et al. 2011), biomass, carbon burial rates, and soil carbon stocks display an increasing trend towards the lower latitudes (Alongi 2014; Sanders et al. 2016; Twilley et al. 1992). Approximately 50 % of mangroves occur in the 0 ° to 10 ° latitudes, yet this region remains underrepresented in global data sets estimating carbon outwelling and water-air emission of CO₂ and CH₄, particularly from mangrove-rich regions such as the Indo-Pacific and North Brazil.

Despite the recent focus on the carbon sequestration potential of mangroves, they have long been known to export carbon to the coastal ocean (Odum et al. 1979; Odum and Heald 1972). The “outwelling” paradigm has shifted from that of particulate carbon to the lateral export of dissolved carbon (organic and inorganic) and the emission of greenhouse gases (Barnes et al. 2006; Bouillon et al. 2008; Maher et al. 2018) driven by the tidally
mediated exchange of interstitial pore-waters with surface waters, a process known as tidal pumping (Stieglitz et al. 2013). The literature shows mangrove waters are generally supersaturated in CO₂ and CH₄ and a significant source of these gases to the atmosphere (Figure 1.2). However, as discussed in Chapter 3 of this thesis, there are large uncertainties in the CO₂ and CH₄ budgets of mangroves. Chapter 3 presents the first CO₂ and CH₄ fluxes from a macro-tidal mangrove creek located in the 0° to 5° latitudinal band. The chapter aims to address the following questions: “are fluxes of CO₂ and CH₄ higher from mangrove systems located nearer the equator?” and “how does hydroperiod (i.e. the frequency and duration of forest inundation) affect CO₂ and CH₄ fluxes over spring-neap cycles in macro-tidal mangrove systems?” This chapter will add to the current literature by presenting the high resolution measurements of surface water CO₂ and CH₄ over a spring-neap cycle from a mangrove creek located in the Southeastern Amazonian Coastal Zone (SACZ). A conceptual model was developed to characterise how hydroperiod effects pore-water to surface water exchanges and controls the temporal variability of mangrove water CO₂ and CH₄ over lunar cycles.

Figure 1.2 The mangrove carbon budget proposed by Bouillon et al. (2008) showing the fate of mangrove net primary production (218 ± 72 Tg C y⁻¹); (a) recent estimates range from 24 to 50 Tg y⁻¹ (Alongi 2014; Rosentreter et al. 2018b); (b) the most recent synthesis of CO₂
efflux suggested $34 \pm 5 \text{Tg C y}^{-1}$ (Rosentreter et al. 2018a). No estimates of CH$_4$ emission were reported by Bouillon et al. (2008).

Much of the recent advances in constraining the various carbon sinks was stimulated by the mangrove carbon budget review by Bouillon et al. (2008) which found that ~ 50% ($112 \pm 85 \text{Tg Cy}^{-1}$) of the net primary production (NPP) of mangroves was unaccounted for (Figure 1.2). DIC appears to be the source of the missing carbon and the major export term (Alongi 2009; Alongi 2014; Bouillon et al. 2008; Maher et al. 2013a), however, both imports and export of DIC from mangrove systems has been reported (Sippo et al. 2016; Taillardat et al. 2018a). Emission of CO$_2$ and CH$_4$ from mangrove waters have been constrained based on revised gas transfer velocities (Ho et al. 2016; Rosentreter et al. 2017) but flux estimates from mangrove-rich biogeographic regions are lacking from global data sets as discussed in Chapter 3 (Rosentreter et al. 2018a; Rosentreter et al. 2018b). Mangroves have also been shown to buffer coastal acidification via exports of total alkalinity but from only two studies based on mangroves located in Australia (Maher et al. 2018; Sippo et al. 2016). Global estimates of DOC and POC exchanges have remained static since the budget review and are still subject to uncertainties of ~ 100% (Alongi 2009; Alongi 2014; Bouillon et al. 2008).

Mangrove carbon budgets are extrapolated from limited studies that are largely based on the quantification of a single carbon species, with only a few studies attempting to estimate the total carbon exported from a single mangrove creek and the relative contribution of DIC, DOC, POC exchanges and CO$_2$ fluxes (Maher et al. 2018; Taillardat et al. 2018a). Furthermore, most studies have been from mangroves located in estuarine complexes, with little to no representation from mangrove creeks that exchange directly with the coastal ocean or adjacent reef systems. Chapter 4 of this thesis hypothesises that the total carbon exported and the contribution of each carbon species is considerably different from mangroves located in a semi-enclosed bay versus a mangroves which are located on the
coast and have greater interconnectivity with the adjacent marine environment (including fringing reefs). This chapter will add to the current literature by presenting the first carbon exports from mangroves located in the wet tropics. Net DIC, DOC, POC and TA exchanges and CO₂ emissions from two tropical mangrove creeks located in different geomorphic settings will be presented.

Stable isotopes are powerful natural tracers of biogeochemical processes (Fry 2006; Fry and Sherr 1989). Paired DIC and carbon stable isotope ratio (δ¹³C-DIC) measurements have been used to help elucidate flows of carbon along the river to ocean aquatic continuum. In the Amazon River and its various tributaries, use of δ¹³C-DIC measurements demonstrate the spatial and temporal variability of the sources of allochthonous (C₃ plants versus C₄ grasses) and autochthonous (i.e. phytoplankton and/or periphyton) carbon fuelling in situ respiration and contributing to CO₂ supersaturation (Ellis et al. 2012; Mayorga et al. 2005; Quay et al. 1992) In mangroves, δ¹³C-DIC data suggests DIC exports are driven by the remineralisation of mangrove litter and estuarine organic matter (e.g. seagrasses) in sediments and exported via the tidally mediated exchange of pore-water (Bouillon et al. 2007c; Maher et al. 2013a). In oceans, δ¹³C-DIC is used to estimate the uptake of anthropogenic CO₂ by the global oceans (Eide et al. 2017; Sonnerup et al. 2000).

As discussed in Chapter 5, current sampling methodologies for δ¹³C-DIC limit sampling frequency and result in low temporal and spatial coverage of coupled DIC and δ¹³C-DIC measurements. This has likely limited the potential utility of δ¹³C-DIC data, particularly where high resolution stable isotope measurements can capture rapid diel (e.g. calcification/dissolution; production/respiration) or tidally driven changes in DIC dynamics. Commercially available instruments are currently used for field-based measurements of CO₂ and its carbon stable isotope value (δ¹³C-CO₂) (Maher et al. 2013b) and the determination of DIC (Friederich et al. 2002; Hiscock and Millero 2005), yet no one has integrated these
instruments to determine coupled measurements of DIC and δ^{13}C-DIC. **Chapter 5** of this thesis addresses the following question: “**Is it possible to integrate two commercially available instruments to autonomously determine concentrations of DIC and δ^{13}C-DIC at high temporal resolutions to provide insights into DIC dynamics?**” I show that coupling two commercially available instruments can achieve precision and accuracy comparable to standard laboratory-based methods and to the standards required to assess long-term anthropogenic-induced changes to oceanic carbon chemistry. The novel approach has the ability to explore potentially complex carbonate system questions as demonstrated in a laboratory based experiment I conducted which provided insights into the drivers of coastal DIC dynamics.
Chapter 2 Radon-traced pore-water as a potential source of CO₂ and CH₄ to receding black and clear water environments in the Amazon Basin


Abstract

Groundwater is a primary source of dissolved CO₂ and CH₄ in Amazonian headwaters, yet in higher order rivers, a groundwater/pore-water source is difficult to constrain due to the high spatial and temporal heterogeneity of pore-water exchange. Here I report coupled, high resolution measurements of pCO₂, CH₄ and ²²²Rn (a natural pore-water and groundwater tracer) during receding waters in the three major water types of the Central Amazon Basin: black (Negro River); clear (Tapajós River); white (Madeira River). Considerable spatial heterogeneity was observed in pCO₂, CH₄, and ²²²Rn concentrations ranging from 460 to 8030 µatm, 7 to 281 nM, and 713 to 8516 dpm m⁻³, respectively. The significant correlations between pCO₂ and CH₄ to ²²²Rn in the black and clear waters suggests that pore-water further enhanced CO₂ supersaturation by 18 – 47 % and is a driver of CH₄ dynamics in these waters.
2.1 Introduction

Our understanding about the role of rivers in global greenhouse gas budgets is evolving. Recent estimates of CO$_2$ efflux from rivers vary in range from 0.6 to 3.9 Pg CO$_2$ yr$^{-1}$ (Aufdenkampe et al. 2011; Drake et al. 2017; Lauerwald et al. 2015; Raymond et al. 2013) and estimated emission of CH$_4$ has recently been revised from 1.5 Tg C yr$^{-1}$ to 26.8 Tg C yr$^{-1}$ (Bastviken et al. 2011; Kirschke et al. 2013; Stanley et al. 2016). The tropics are the largest contributor of global CO$_2$ emissions from rivers, yet the region is under-represented in global data sets and the source of large uncertainties (Borges et al. 2015; Lauerwald et al. 2015). Constraining the relative contribution of the sources driving riverine CO$_2$ and CH$_4$ supersaturation and atmospheric exchange rates remains a challenge and our understanding of the gas dynamics is still evolving (Borges et al. 2015; Borges et al. 2018; Cole et al. 2007; Raymond et al. 2013; Stanley et al. 2016; Teodoru et al. 2015).

The Amazon river system is generally supersaturated in CO$_2$ and CH$_4$, and is estimated to emit globally significant amounts of both gases (Barbosa et al. 2016; Melack et al. 2004; Rasera et al. 2013; Richey et al. 2002; Sawakuchi et al. 2014). The factors contributing to CO$_2$ supersaturation remain unclear and are likely spatially and temporally variable (Richey et al. 2009). Respiration of allochthonous (Mayorga et al. 2005) and autochthonous (Ellis et al. 2012) organic matter (OM), carbonate weathering (Vihermaa et al. 2014), and contributions from wetlands and floodplains (Abril et al. 2014) have all been highlighted as sources of CO$_2$ to Amazonian rivers. Drivers of riverine CH$_4$ dynamics are more ambiguous, with recent studies highlighting hydrological drivers such as seasonal water stage and wetland-river connectivity (Barbosa et al. 2016; Borges et al. 2015; Sawakuchi et al. 2014). Despite these advances, large uncertainties remain in Amazonian CO$_2$ and CH$_4$ budgets (Melack 2016; Richey et al. 2009).
Pore-water and groundwater exchange have been shown to be the primary source of CO₂ and CH₄ in Amazonian headwaters (Johnson et al. 2008; Neu et al. 2011). In higher order Amazonian rivers, pore-water is hypothesised to contribute to CO₂ and CH₄ supersaturation, however, this exchange pathway is difficult to constrain beyond small streams due to high spatial and temporal heterogeneity (Cook et al. 2003). Radon-222 (²²²Rn) is a natural tracer of any water that has been in contact with sediments (pore-water and/or groundwater) and has been used to assess groundwater inputs into river and lakes (Burnett et al. 2010; Cook et al. 2006). More recently, ²²²Rn has revealed how pore-water releases CO₂ and CH₄ to estuarine surface waters (Call et al. 2015; Maher et al. 2015; Sadat-Noori et al. 2016), but no similar investigations have been performed in the Amazon. Here, I define pore-water as the exchange of interstitial water into surface waters (i.e. a combination of meteoric and hyporheic exchange). I investigate whether radon-traced pore-water may be a source of CO₂ and CH₄ to major tributaries of the Amazon river system during receding waters spanning the three major water types (black, clear, white).

2.2 Methods

Longitudinal surveys were conducted in three major tributaries representing the three water types of the central Amazon Basin: black water (Rio Negro ~150 km surveyed); clear water (Tapajós ~ 100 km surveyed); and white water (Madeira ~ 100 km surveyed) (Figure 2.1a, b, c). Each water type has unique chemical characteristics related to the geomorphological properties of their catchments (Junk et al. 2011; Sioli 1968). Briefly, black waters drain large areas of low-lying podzols and contain high levels of dissolved organic material. Clear waters drain Precambrian shields and are low in suspended sediments and organic material. White waters originate in the Andes Mountains and contain high sediment loads and nutrients. Extensive wetlands and floodplains exists in each basin (Hess et al. 2015; Junk et al. 2011), draining into the main river stems via a complex network of fluvial
connections (Mertes et al. 1996). “Igarapés” are forest streams that drain straight to the river channel, or first to floodplain lakes.

Seasonal rainfall and Andes snow melt result in large oscillations in river water levels (Junk et al. 2011) causing the inundation of forests, wetlands and floodplains across the basin (Hess et al. 2015). Surveys were conducted during receding waters during August and September, 2015 (Figure 2.2 for hydrographs for the black, clear and white rivers). The main riverine channel was surveyed for each water type along with two lakes in black waters and one lake in clear waters. At the time of sampling all lakes were connected to the main river channel. Black water lakes were surrounded by flooded forests (large trees, non-herbaceous) as was the clear water lake, however, the western flank was separated from the main channel by a sand bar with a single opening.

Water column $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ were determined by continuously pumping water from a depth of ~ 50 cm at ~ 3 L min$^{-1}$ into two showerhead gas equilibration devices (GED; as described by Pierrot et al. (2009)) aboard a moving vessel that averaged 10.6 ± 3.5 and 5.4 ± 2.9 km h$^{-1}$ during river and lake surveys respectively. Equilibrated headspace air was then pumped through polyethylene lined Bev-A-Line® IV (1/8” ID, 1/4” OD) tubing to a Drierite desiccant and into an Off-Axis Integrated Cavity Output Spectrometer (OA-ICOS, Los Gatos Research) which measured CO$_2$ and CH$_4$ at 1 s intervals with a precision of < 3ppb and < 300ppb for CO$_2$ (0 – 20000 ppm) and CH$_4$ (0 – 10000 ppm) respectively. A separate gas stream from the same GED was pumped to an automated $^{222}\text{Rn}$-in-air analyser which logged data at 10 min intervals. A 30 min moving average of $^{222}\text{Rn}$ data achieved analytical uncertainties of < 10 %. Data points (see Figure 2.1a, b, c) are time stamped according to the data captured by the RAD7. Moving averages of 10 and 30 mins were applied to smooth $p\text{CO}_2$ and CH$_4$ concentrations based on experimentally determined gas equilibration times (Webb et al. 2016). Based on the average velocity of the vessel, each $p\text{CO}_2$ and $^{222}\text{Rn}$ data
point is an integration of the previous 1.8 and 0.9 km travelled in the rivers and lakes respectively (5.3 and 2.7 km for CH₄). Surface water was continuously pumped into a flow-through chamber where a Hydrolab DS5 sonde logged temperature, every 5 min and a BBE Moldaenke Fluoroprobe logged fluorescence every 5 min. All average values reported in results are ± 95% confidence interval. All regression analysis having a p value of < 0.05 were deemed as being significant. No CH₄ data is available from white water due to instrument malfunction.

2.3 Results

2.3.1 Partial pressure of CO₂

Across all water types, $p_{\text{CO}_2}$ displayed considerable spatial variability (Figure 2.1a, b, c). In the black waters, the range in $p_{\text{CO}_2}$ spanned over 4000 µatm, with highest $p_{\text{CO}_2}$ observed where the Igarapé da Freguesia converges with the river at Novo Airão (NA) (Figure 2.1a). Localised areas of elevated riverine $p_{\text{CO}_2}$ were also observed in the vicinity of the adjoining Igarapé Marajá (IM, 7817 µatm) and Igarapé Camará (IC, 7435 µatm), and at the confluence of the floodplain lake, Lago Acajatuba (LA, 7291 µatm). Lowest black water $p_{\text{CO}_2}$ was recorded in Lake 2, however, distinct areas of higher $p_{\text{CO}_2}$ were observed in the southern perimeters of Lake 1 (maximum 7023 µatm) and Lake 2 (maximum 6864 µatm). Overall, average riverine $p_{\text{CO}_2}$ was 26% higher than average lake $p_{\text{CO}_2}$ (Table 2.1).
Figure 2.1 (a) (b) and (c) Spatial survey results for $p$CO$_2$ in the black, clear and white waters respectively. (d) and (e) Spatial survey results for CH$_4$ in black and clear waters respectively. (f) (g) and (h) Spatial survey results for $^{222}$Rn in the black, clear and white waters respectively. Inset Location of study sites in the central Amazon basin. L1 Lake 1, L2 Lake 2, M Manaus, LA Lago Acajatuba, IC Igarapé Camarã, IM Igarapé Marajá, NA Novo Airão, LV Lago Verde, S Santarém, P Pindobal, CB Cajutuba Beach, I Igarapé, H Humaitá. Small black circles represent survey track and data points. White water CH$_4$ data not available. Scale bars are shown in a, b and c. The scale bar for L1 is the same for L2.
Figure 2.2 Hydrographs for the black, clear and white rivers. Water level data was sourced from the Brazilian National Water Agency (http://hidroweb.ana.gov.br) using the gauge stations at Novo Airão, Santarém and Humaitá for the black (Rio Negro), clear (Tapajós) and white (Madeira) rivers, respectively.
Table 2.1 Summary [average ± 95 % confidence interval (n\textsuperscript{a})] of observations during spatial surveys.

<table>
<thead>
<tr>
<th></th>
<th>pCO\textsubscript{2} (µatm)</th>
<th>CH\textsubscript{4} (nM)</th>
<th>\textsuperscript{222}Rn (dpm m\textsuperscript{3})</th>
<th>Chl-a (µg L\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black River</td>
<td>6715 ± 151 (102)</td>
<td>31.30 ± 6.45</td>
<td>2680 ± 199</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>Black Lakes</td>
<td>5336 ± 317 (27)</td>
<td>49.56 ± 17.47</td>
<td>4216 ± 420</td>
<td>8.6 ± 1.4</td>
</tr>
<tr>
<td>Clear River</td>
<td>812 ± 64 (56)</td>
<td>30.30 ± 2.20</td>
<td>3568 ± 493</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td>Clear Lake</td>
<td>1396 ± 138 (30)</td>
<td>190.49 ± 60.08 (9)</td>
<td>5071 ± 643 (31)</td>
<td>15.4 ± 1.5 (20)</td>
</tr>
<tr>
<td>White River</td>
<td>2086 ± 27 (44)</td>
<td>-</td>
<td>4159 ± 224 (45)</td>
<td>5.3 ± 0.2 (45)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} n is the same as pCO\textsubscript{2} for all parameters unless shown

In the clear waters, lowest pCO\textsubscript{2} was observed in the river near Santarem and highest pCO\textsubscript{2} at the north-eastern end of Largo Verde (LV) (Figure 2.1b). Upstream of LV, riverine pCO\textsubscript{2} gradually increased, peaking (1532 µatm) nearby the adjoining igarapé. Other areas of elevated riverine pCO\textsubscript{2} were observed near a small lake at Pindobal (1013 µatm) and in the vicinity of Cajutuba Beach (CB, 1174 µatm). In contrast to black waters, average lake pCO\textsubscript{2} was ~ 72% higher than average riverine pCO\textsubscript{2} in the clear water (Table 2.1). White river pCO\textsubscript{2} spanned only ~ 470 µatm (Figure 2.1c) with average pCO\textsubscript{2} over two-fold higher than the average clear river pCO\textsubscript{2} but less than one third of average black river pCO\textsubscript{2} (Table 2.1). Significant inverse relationships (p<0.05) were observed between pCO\textsubscript{2} and Chl-a in the black river, black lakes, and clear river (Figure 2.3c, f).

2.3.2 CH\textsubscript{4} concentrations

Methane concentrations spanned a range of 274 nM, with lowest concentrations in downstream river locations and maximal concentrations in the lakes (Figure 2.1d, e). Black river CH\textsubscript{4} concentrations were generally < 40 nM, however, concentrations up to 157 nM were observed in the vicinity of NA. Clear river CH\textsubscript{4} ranged from 15 to 41 nM with highest concentrations in the vicinity of CB and the igarapé. Overall, average CH\textsubscript{4} concentrations were higher in the lakes than in the rivers (Table 2.1).
2.3.3 Radon-222

A general trend of higher $^{222}\text{Rn}$ concentrations in upstream locations was evident in all water types (Figure 2.1f, g, h). In black waters, localised areas of elevated concentrations were observed in the river at IC (3423 dpm m$^{-3}$), IM (3389 dpm m$^{-3}$) and NA (4647 dpm m$^{-3}$), and maximum values in the lakes (L1 6159 dpm m$^{-3}$, L2 6506 dpm m$^{-3}$). Clear water concentrations of $^{222}\text{Rn}$ were also highest in the lake, with distinct areas of higher riverine concentrations in the vicinity of CB (4778 dpm m$^{-3}$) and the igarapé (7797 dpm m$^{-3}$). Overall, average lake concentrations of $^{222}\text{Rn}$ were ~ 40% and ~ 60% higher than average riverine concentrations in the clear and black waters respectively. The white river had the lowest range of $^{222}\text{Rn}$ (Figure 2.1h) but the highest average riverine concentration of the three water types (Table 2.1). Significant positive relationships (p<0.05) were observed between $p\text{CO}_2$ and CH$_4$ with $^{222}\text{Rn}$ in the rivers and lakes of the black and clear waters (Figure 2.3a, b, d, e).
Figure 2.3 (a) and (b) Linear regression of $p$CO$_2$ and CH$_4$ with $^{222}$Rn in black river and black lakes. (d) and (e) Linear regression of $p$CO$_2$ and CH$_4$ with $^{222}$Rn in clear river and clear lake. (c) and (f). Linear regression of Chl-a with $p$CO$_2$ in black river and black lakes, and clear river and lake, respectively. No relationships were observed in the White waters.

2.4 Discussion

My study presents concurrent surface water measurements of a natural pore-water tracer ($^{222}$Rn) with $p$CO$_2$ and CH$_4$ concentrations from waters of the central Amazonian basin. I build on an earlier study documenting $^{222}$Rn concentrations in Amazonian rivers (Devol et al. 1987) by reporting high resolution measurements to map potential areas of
increased pore-water to surface water interactions. The significant positive correlations observed between $pCO_2$ and $CH_4$ with $^{222}$Rn suggest pore-water may be a relevant source of $pCO_2$ and $CH_4$ during receding black and clear waters, providing a basis for designing future studies to quantify the influence of pore-water exchange in carbon budgets of Amazon waters.

2.4.1 CO$_2$ and CH$_4$ distribution

Wide ranges of $pCO_2$ have been reported from the diverse aquatic systems in the Amazon Basin (Abril et al. 2014; Melack 2016; Rasera et al. 2013; Richey et al. 2002). Seasonally, $pCO_2$ tracks the hydrograph (Richey et al. 2009; Richey et al. 2002) and the results from this study are in general agreement with published observations in terms of season and water type. The average $pCO_2$ observed in the receding black and clear rivers (i.e. Negro and Tapajós) is higher than those reported by Abril et al. (2014), likely due to my surveys extending further upstream where $pCO_2$ was considerably higher. Receding white river (Madeira) observations are higher than those reported at the mouth (~1300 µatm) by Abril et al. (2014), but lower than the ~ 4100 µatm reported further upstream by Almeida et al. (2017). Clear rivers had the lowest $pCO_2$ of the three water types which is consistent with other studies (Abril et al. 2014; Alin et al. 2011; Rasera et al. 2013). The high spatial resolution data from my study revealed higher $pCO_2$ upstream and close to igarapés confluence with the main channels, suggesting igarapés may be a source of CO$_2$ to the main channels.

Data on Amazonian CH$_4$ concentrations is much sparser than $pCO_2$, with large spatial and temporal variability of concentrations and associated fluxes (Barbosa et al. 2016; Borges et al. 2015; Melack et al. 2004; Sawakuchi et al. 2014). In contrast to the large spatially distributed measurements of previous studies such as Barbosa et al. (2016), which measured
CH₄ at four locations along a 700km transect of the Negro River and in 21 tributaries within the Negro basin, this paper presents smaller scale CH₄ measurements. Methane distribution was characterised by a few localised areas of distinctly higher concentrations in lakes, which are known emitters of CH₄ (Crill et al. 1988; Devol et al. 1988), and where the igarapé joins the black river at NA.

2.4.2 Radon tracing of surface water CO₂ and CH₄ sources

Radon-222 is produced in sediments by the radioactive decay of radium-226 (²²⁶Ra) and has a short half-life of 3.8 days. The noble gas is often highly enriched in groundwater/pore-water and once discharged to surface waters the only losses are radioactive decay and atmospheric evasion (Cook et al. 2008). Radon-222 activities in surface waters integrate the various recent groundwater and pore-water exchange pathways, such as hyporheic exchange or the lateral flow from regional aquifers to the main channels. Whilst it was beyond the scope of this initial study to differentiate between the different radon pathways, these observations imply pore-water-connectivity in the river and lakes during receding waters.

Diffusion of ²²²Rn from sediments can also be a source to surface waters. Based on the average ²²⁶Ra content in sediments from Amazon floodplain lakes (2.09 ± 1.55 dpm g⁻¹; Sanders et al. (2017)) and using the empirical equation to relate ²²⁶Ra activity in sediments with ²²²Rn diffusion (J_diffusion = 495.²²⁶Ra_sed + 18.2; see Burnett et al. (2003)), I estimate a ²²²Rn diffusion rate of 1053 dpm m² d⁻¹ across the sediment interface. Water level data for the black, clear and white rivers (no depth data for lakes) were estimated to be ~ 16 m, ~ 5.5 m and ~ 12 m, respectively (Figure 2.2). Therefore, assuming homogeneous depth, the contribution of ²²²Rn diffusion from sediments can sustain maximum river ²²²Rn concentrations of 365, 1060 and 487 dpm m⁻³, respectively. Whilst the sediment ²²²Ra content
was determined from four sites within the Amazon basin, thus placing considerable uncertainty in my estimates, they indicate that the contribution of diffusion from sediments to surface water $^{222}\text{Rn}$ concentrations were $\sim 14\%$, $\sim 12\%$ and $30\%$ in the black, white and clear rivers, respectively. Therefore, most of the radon observed in the rivers seem to be sourced from advective pore-water or groundwater pathways.

To my knowledge, only one previous study has documented $^{222}\text{Rn}$ concentrations in the Amazon. Devol et al. (1987) reported a similar span in $^{222}\text{Rn}$ values (1400 to 9240 dpm m$^{-3}$) from eight sites along a 1700 km transect of the Amazon River mainstream and at the mouths of seven tributaries during rising waters (February-March). Samples taken at the mouth of the Rio Negro (2050 dpm m$^{-3}$) and Madeira (4450 dpm m$^{-3}$) are within ranges observed in this study, however, the high resolution measurements obtained here illustrate the high spatial variability of $^{222}\text{Rn}$ that can occur at smaller scales, reflecting the heterogeneous nature of pore-water exchange with surface waters. The general trend of higher $^{222}\text{Rn}$ concentrations upstream from river mouths suggests greater pore-water influence on surface water chemistry in these locations which is consistent with other studies in rivers and wetlands (Cook et al. 2003; Santos and Eyre 2011). Whilst evasion could explain the reduced $^{222}\text{Rn}$ concentrations downstream, the observed trend cannot simply be explained by degassing and suggests $^{222}\text{Rn}$ inputs along the rivers sampled (Figure 2.1f, g, h; Figure 2.4). Adjoining lakes appeared to be subject to increased pore-water influences. Furthermore, river segments near igarapés had distinctly higher $^{222}\text{Rn}$, suggesting these channels may drain surrounding soils. The hypothesised enrichment of $^{222}\text{Rn}$ in narrower and steeper-banked igarapés may be due to the larger sediment surface area relative to the overlying water and/or the expected increase in hydrostatic pressure with the surrounding water table during receding waters (i.e. increased pore-water discharge).
Figure 2.4 Example of $^{222}$Rn activities in the black, clear and white rivers. The observed trends cannot simply be explained by degassing and suggests $^{222}$Rn inputs along the river transects sampled.

Whilst pore-water inputs may be small relative to surface water processes, the significant positive relationship observed between $p$CO$_2$ and CH$_4$ with $^{222}$Rn in the rivers and lakes of the black and clear waters suggests a common source (Figure 2.3a, b, d, e). Other studies have used $^{222}$Rn to suggest that groundwater is a significant source of CO$_2$ and CH$_4$ to surface waters (Atkins et al. 2017; Webb et al. 2017). Based on water flow through rates, Richey et al. (2002) estimated that soil atmosphere CO$_2$ exported to streams via the lateral flow of groundwater could account for 25% of evasion from the waters of the central Amazonian basin. Using the y-intercept of the $p$CO$_2$-$^{222}$Rn linear regression in the black river and lakes (Figure 2.3a) and the average $p$CO$_2$ of each (Table 2.1), I find similar values. Average $p$CO$_2$ would be 21% lower than observed in the black river and 23% lower in the black lakes if there were no recent pore-water inputs ($^{222}$Rn approaching zero). In the clear river and lake, average $p$CO$_2$ may be 18% and 47% lower respectively. This implies that
while other sources contribute to CO₂ supersaturation, pore-water may be a relevant source of CO₂ in these receding waters. No significant relationships were observed in the white river which may be due to the limited spatial extent of the river studied. In addition to pore-water, primary production and respiration may also exert a strong control on pCO₂ in the Amazon. The significant inverse relationship observed between pCO₂ and Chl-a in the black river, black lakes, and clear river (Figure 2.3c, f), indicates primary production is an important controller of pCO₂ which is consistent with the recent findings of Amaral et al. (2018). This is particularly evident in black lakes where the concentrations of Chl-a were considerably higher (relative to the black river, Table 2.1) and may explain the lower pCO₂ and weaker (albeit still significant) pCO₂ - ²²²Rn relationship (Figure 2.3a).

Although wetlands are becoming increasingly recognised as an important source of CH₄ to adjoining rivers (Borges et al. 2015; Devol et al. 1990), Sawakuchi et al. (2014) suggested wetland-sourced CH₄ may not be as relevant during their study based on higher CH₄ fluxes during low waters versus high waters in Amazonian Rivers. The observed CH₄-²²²Rn relationship (Figure 2.3b, e) supports the hypothesis that pore-water may be an important mechanism in driving riverine CH₄ dynamics (Stanley et al. 2016) and may explain the de-coupled wetland-river connectivity observed in Sawakuchi et al. (2014). Similarly to the tidal pump concept (Call et al. 2015; Stieglitz et al. 2013), where surface water infiltrates sediments during incoming tides (rising waters) and then returns to surface waters during outgoing tides (receding waters), I hypothesise that such a process may be occurring at seasonal scales (as opposed to diurnal/semi-diurnal tidal pumping) in the black and clear waters sampled during this study. Such a concept would result in a trend of increasing CH₄ concentrations as the water levels transitioned from high to low which was observed in white water rivers and floodplain lakes by Barbosa et al. (2016). Sawakuchi et al. (2014) and Barbosa et al. (2016) suggest that dilution and higher rates of CH₄ oxidation during high
water may also explain higher concentrations during the low water period. Clearly, further seasonal studies on CH₄ concentrations in the Amazon basin are required to determine the main drivers of riverine CH₄ dynamics.

2.5 Conclusion

This study presents coupled, high resolution spatial measurements of pCO₂, CH₄ and ²²⁲Rn of the major tributaries of the central Amazon basin on a scale of ~ 100 km. Relationships suggest that pore-water may be a relevant source of CO₂ and CH₄ to the receding black and clear water tributaries of the central Amazon Basin. Igarapés appear to be sources of dissolved CO₂ and CH₄ to the main channels and I hypothesise that a portion of this CO₂ and CH₄ may be derived from draining surrounding soils. Whilst this initial study cannot quantify pore-water exchange rates, it provides a basis for more extensive, quantitative studies on the role of pore-water in the Amazonian carbon cycle.
Chapter 3 High pore-water derived CO2 and CH4 emissions from a macro-tidal mangrove creek in the Amazon region


Abstract

This paper presents the first CO2 and CH4 flux estimates from a macro-tidal mangrove creek located in the 0° to 5° latitude band, where ~30% of the world’s mangroves occur. High resolution CO2, CH4 and 222Rn (a natural pore-water tracer) concentrations were measured over a spring-neap tidal cycle from a mangrove creek located in North Brazil (~0.8° S). Surface water pCO2, CH4 and 222Rn ranged from 592 to 15,361 μatm, 58 to 1,469 nM, and 585 to 16,583 dpm m⁻³ with considerable temporal variability observed semi diurnally (i.e. hourly) and over the spring-neap cycle (i.e. weekly). Tidally-driven pore-water exchange (tidal pumping) drove surface water pCO2 and CH4, leading to high concentrations at low-tide (semi-diurnal variability). Higher pCO2 and CH4 were also observed after the inundation of the upper inter-tidal flat, with peak concentrations coinciding with the “first flush” of aged pore-waters. I hypothesise that additional pore-water exchanges occur during forest inundation in macro-tidal mangrove systems, controlling mangrove creek water pCO2 and CH4 concentrations over spring-neap cycles. Estimated CO2 and CH4 water-atmosphere flux rates averaged 174 ± 129 mmol m⁻² d⁻¹ and 855 ± 406 μmol m⁻² d⁻¹, respectively. These emissions are amongst the highest reported for mangrove systems worldwide and suggest that the most recent global estimates based mostly on data from higher latitudes may have underestimated the role of mangroves in greenhouse gas emissions.
3.1 Introduction

Mangroves span diverse geomorphic and climatic conditions, occupying an estimated ~ 83,000 to ~ 138,000 km² of the inter-tidal areas from ~ 30 ° N to ~ 40 ° S (Giri et al. 2011; Hamilton and Casey 2016). In spite of the small area, mangroves process globally significant amounts of carbon (Alongi 2014; Bouillon et al. 2008) with mangrove biomass, carbon burial rates, and soil carbon stocks displaying an increasing trend towards the lower latitudes (Alongi 2014; Sanders et al. 2016; Twilley et al. 1992). Contributing up to 15 % (26.1 Tg C) of the total organic carbon buried in marine environments annually (Breithaupt et al. 2012; Jennerjahn and Ittekkot 2002), mangrove sediments are a large repository of organic matter (~ 1000 Tg C globally) and an important sink for atmospheric CO₂, termed “blue carbon” (Donato et al. 2011; Duarte et al. 2013; Nelleman et al. 2008).

Despite growing interest in quantifying the various mangrove carbon sinks (Bouillon et al. 2008; Donato et al. 2011; Maher et al. 2013a), large uncertainties remain in mangrove CO₂ and CH₄ budgets. Mangrove creek waters are generally supersaturated in dissolved CO₂ and CH₄, with estimates of CO₂ emission from mangrove waters estimated (on average) to range from 26 to 50 Tg C y⁻¹ (Alongi 2014; Borges et al. 2003; Bouillon et al. 2008; Rosentreter et al. 2018a). Adjusted to 20-year CO₂ equivalents, global mangrove water CH₄ emissions are highly uncertain, and are estimated to vary over an order of magnitude from ~ 5 to ~ 50 Tg C yr⁻¹ (Alongi 2014; Barnes et al. 2006; Rosentreter et al. 2018b). Rosentreter et al. (2018b) recently suggested that emission of CH₄ from mangrove waters and exposed sediments may offset blue carbon burial rates in mangrove sediments by 20%.

However, no estimates of water-atmosphere CH₄ fluxes exist from mangroves located between 5 ° N and 5 ° S (Rosentreter et al. 2018b), where ~ 30% of the world’s mangroves occur (Giri et al. 2011). This region is also underrepresented in global datasets for water-atmosphere CO₂ flux estimates (Bouillon et al. 2008; Rosentreter et al. 2018a) with only
meso-tidal (tidal amplitude 2 to 4 m) mangrove creeks from Kenya and Papua New Guinea included in global data compilations (Borges et al. 2003; Bouillon et al. 2007a; Bouillon et al. 2007b). There are no estimates from macro-tidal systems (tidal amplitude > 4 m) nor from mangrove-rich countries such as Indonesia or North Brazil, which contain 22 % and 7 % of the world’s mangroves, respectively (Giri et al. 2011). Clearly, more data is required from key regional areas and different tidal regimes to reduce uncertainties, aid latitudinal scaling and constrain regional and global carbon budgets.

Water column greenhouse gas dynamics in mangroves are related to tidally-driven pore-water exchange. Tidal pumping is the tidally mediated exchange of interstitial pore-water (enriched in the by-products of organic matter degradation) with surface waters (Ovalle et al. 1990). Also known as the “mangrove pump” (Stieglitz et al. 2013), tidal pumping in mangroves can filter the entire continental shelf volume on time scales of centuries (Tait et al. 2016). Our understanding of this quantitatively significant hydrologic exchange mechanism and its influence on mangrove carbon cycling and coastal carbon budgets is evolving (Borges et al. 2003; Bouillon et al. 2008; Maher et al. 2013a; Maher et al. 2017; Ovalle et al. 1990). Facilitated by the diurnal/semi-diurnal flushing of crab burrows, tidal pumping is now recognised as a major source of pore-water derived DOC (Dittmar et al. 2006; Dittmar et al. 2001; Sippo et al. 2017), DIC (Bouillon et al. 2007c; Maher et al. 2013a), alkalinity (Sippo et al. 2016), metals (Holloway et al. 2016) and greenhouse gases (Barnes et al. 2006; Call et al. 2015; Kristensen et al. 2008b; Linto et al. 2014) to mangrove waters and adjacent ecosystems. However, the influence of tidal pumping on carbon cycling has generally been determined from semi-diurnal tidal trends observed over 24 hr sampling periods, overlooking the potential influence of varying tidal amplitude over spring-neap tidal cycles. Recently, Taillardat et al. (2018a) and Taillardat et al. (2018b) reported variable carbon dynamics and
exports from separate 24-hr studies conducted over spring neap cycles from a meso-tidal creek in Vietnam (10° N) subject to asymmetrical tidal regimes (i.e. diurnal tidal inequality).

As an extension of the “mangrove pump” concept by Stieglitz et al. (2013), the “lunar mangrove pump” hypothesises a weekly pore-water–surface water exchange process occurs in addition to the daily flushing of crab burrows (Call et al. 2015). Based on high resolution $p$CO$_2$ and CH$_4$ data captured over a spring-neap-spring tidal cycle, Call et al. (2015) suggested that a portion of the tidal water that infiltrates sediments during spring tides is retained within the sediments before progressively seeping back into surface waters as tidal amplitude decreases. The longer residence time enriches pore-water in dissolved CO$_2$ and CH$_4$, leading to highest surface water $p$CO$_2$ and CH$_4$ during neap tides. The “lunar mangrove pump” concept was based on a micro-tidal system (tidal amplitude < 2 m) in which adjacent forests were inundated each tidal cycle, with only the forests in the upper reaches of the basin periodically inundated during spring tides. However, such a concept may not apply to mature macro-tidal mangrove systems, where adjacent forests are only inundated during spring tides.

This paper presents high resolution $p$CO$_2$, CH$_4$ and $^{222}$Rn (a natural pore-water tracer) observations over a spring-neap tidal cycle from a tropical macro-tidal mangrove creek located in North Brazil (~ 0.8° S). I hypothesise that tidal pumping will control mangrove creek water $p$CO$_2$ and CH$_4$ and that there will be considerable temporal variability in mangrove creek water $p$CO$_2$ and CH$_4$ (and associated estimates of atmospheric fluxes) as tidal amplitude and forest inundation change over a spring-neap tidal cycle. Additionally, I propose that the estimated CO$_2$ and CH$_4$ flux rates will be considerably higher than the global averages, based on increasing mangrove production and sediment carbon stocks in the low latitudes (Alongi 2014) and the higher current velocities (and associated gas transfer velocities) expected in macro-tidal mangrove ecosystems.
3.2 Methods

3.2.1 Study site

The study was conducted in “Furo do Meio”, a macro-tidal mangrove creek located within the Caeté Estuary, near Bragança, North Brazil (Figure 3.1). Situated on a low topographic relief peninsula (elevation gradient 1.5 m; see Lara et al. (2010)) within the Southeastern Amazonian Coastal Zone (SACZ), the deep channelled, 4 km long creek receives no upstream freshwater inputs (other than during precipitation events) and has been studied previously to quantify exports of dissolved and particulate organic matter and nutrients (Dittmar et al. 2006; Dittmar and Lara 2001a; Dittmar and Lara 2001b; Dittmar et al. 2001). The sampling location was located approximately mid-way along the well-mixed creek (the same location as used in previous studies) and drains a well-defined catchment of 2.2 km², much of which is only inundated during spring tides. As part of the world’s largest continuous belt of mangroves (7,600 km²) (Souza Filho 2005), the well-developed mangrove forests (maximum tree height > 20 m) of the peninsula contain four mangrove species: *Rhizophora mangle*, *Avicennia germinans*, *Avicennia schaueriana*, and *Laguncularia racemose*. Of the five principal types of mangrove forest described by Mehlig et al. (2010), *Rhizophora* dominated forest (which also contains *A. germinans* as the second most abundant tree with *L. racemose* a minor constituent) is the prevailing forest type on the peninsula (62 % of cover) including the study site catchment. Annual litter production of 13.1 Mg ha⁻¹ y⁻¹ (Mehlig et al. 2010) and sedimentary organic carbon pool of 4500 mol C m⁻² (Koch et al. 2010) have been reported from the study site. Crab burrows are ubiquitous in sediments. The SACZ experience a monsoon-like climate with temperatures averaging 28.6 ± 1.3 °C (range 23.2 to 31.9 °C) annually with an annual precipitation in the coastal area ranging from 2400 to 3300 mm during the wet season (December to May) and negligible rainfall during September to November (Gonçalves et al. 2009) when my sampling was performed.
3.2.2 Surface water sampling

Surface water sampling was conducted over 11 days from 26th September to 7th October, 2017, spanning 21 tidal cycles from neap to spring tides. Water column $p$CO$_2$, CH$_4$ and $^{222}$Rn were determined by continuously pumping water from a depth of ~ 30 cm at ~ 3 L min$^{-1}$ into two showerhead gas equilibration devices (GED) (Pierrot et al. 2009; Santos et al. 2012) aboard a vessel moored in the middle of the creek channel (Figure 3.1). The second equilibrator, which is vented to the atmosphere, is used to replace and gas lost from the main equilibrator with pre-equilibrated headspace gas and prevent pressure changes that create analytical uncertainty (Pierrot et al. 2009). Equilibrated headspace air was then pumped through polyethylene lined Bev-A-Line® IV (1/8” ID, 1/4” OD) tubing to a Drierite desiccant and into an Off-Axis Integrated Cavity Output Spectrometer (OA-ICOS, Los Gatos Research) which measured CO$_2$ (0 – 20000 ppm) and CH$_4$ (0 – 10 %) at 1 s intervals with a
precision of < 300 ppb and < 2 ppb, respectively. A separate gas stream from the same GED was pumped to an automated $^{222}$Rn-in-air analyser (RAD7, Durridge) which logged data at 10 min intervals. A 30 min moving average of $^{222}$Rn data achieved analytical uncertainties of < 10 % for each time step and accounted for instrument response time. One minute averages of $p$CO$_2$ and CH$_4$ data were shifted by 10 and 30 mins respectively, based on the gas equilibration time for the GED (Webb et al. 2016). A Hydrolab DS5 sonde logged temperature, salinity and dissolved oxygen every 5 min. Depth and current velocity were logged every at 5 min intervals using a Unidata Starflow current meter (model 6526). For all physiochemical parameters, interpolated values were used to calculate fluxes at one minute intervals. All regression analysis having a P value of < 0.05 were deemed as being significant. No $^{222}$Rn data was available for the first ~ 4 days due to instrument malfunction, however, based on the robust $^{222}$Rn-$p$CO$_2$ relationship below, data was extrapolated to enable tidal amplitude analysis of $^{222}$Rn.

3.2.3 Flux calculations

CO$_2$ and CH$_4$ water-atmosphere fluxes ($F$) were determined according to:

$$F = k \alpha (p_{\text{water}} - p_{\text{air}})$$  (1)

where $k$ is the gas transfer velocity (cm h$^{-1}$), $\alpha$ is the solubility co-efficient of the respective gas, $p_{\text{water}}$ and $p_{\text{air}}$ are the partial pressures of each gas ($\mu$atm) in the water and atmosphere respectively. Solubility coefficients for CO$_2$ and CH$_4$ were determined according to Weiss (1974) and Yamamoto et al. (1976).

The gas transfer velocity ($k$) was determined using four different empirically derived models based on wind speed, current velocity and depth. Borges et al. (2004) as determined within estuaries:

$$k_{600} = 1.0 + 1.719 v^{0.5} h^{-0.5} + 2.58u$$  (2)
where \( k_{600} \) is the gas transfer velocity (cm hr\(^{-1}\)) normalised to the Schmidt number of 600, \( v \) is the water velocity (cm s\(^{-1}\)), \( h \) is the depth (m) and \( u \) is the wind speed at 10 m (m s\(^{-1}\)).

The combined parameterisations of Ho et al. (2006) and O’Connor and Dobbins (1958) based on the study by Ho et al. (2016) in a mangrove dominated estuary:

\[
k_{600} = (0.77v^{0.5}h^{-0.5}) + (0.266u^2)
\]  

(3)

Rosentreter et al. (2017) as determined for CO\(_2\) and CH\(_4\) within sub-tropical mangrove systems:

\[
k_{600-CO2} = -0.08 + 0.26v + 0.83u + 0.59h
\]  

(4)

\[
k_{600-CH4} = -1.07 + 0.36v + 0.99u + 0.87h
\]  

(5)

The average daily wind speeds were used for each day of the sampling period and were sourced from the nearest Brazilian Institute of Meteorology (INMET) station at Bragança (station code A226) located ~ 20 km from the study site.

3.2.4 Pore-water sampling

Pore-water samples (n=10) were collected from the 7\(^{th}\) to the 11\(^{th}\) October, 2017, at low tide from the creek banks (which were inundated semi-diurnally) and within the forest (which were inundated during spring tides only) adjacent to the sampling location. Bores were dug to a depth of up to ~ 50 cm below the water table and purged two times before sampling (bores at the creek bank penetrated two different substratums: sand and mud). A peristaltic pump and gas-tight high density polyethylene (HDPE) bottles were used to collect samples which were then analysed within 24 hours using the RAD7 and OA-ICOS according to Lee and Kim (2006) but modified to integrate a second closed loop to the OA-ICOS.
3.3 Results

3.3.1 Tidal surface water time series

Depth ranged from 0.85 to 5.58 m (average 2.88 ± 1.36 m, n=3172; Figure 3.2) and tidal amplitude ranged from 2.11 m (neap) to 4.72 m (spring), averaging 3.55 ± 0.9 m (Figure 3.3). Surface waters breached creek banks at ~ 4.9 m depth, inundating forests adjacent to the sampling location. Herein, “pre-inundation” (or “pre”) refers to the period when surface waters were contained within creek banks and “post-inundation” (or “post”) refers to the period when surface waters inundated forests adjacent to, and upstream of, the sampling location. All errors represent the standard deviation of the complete dataset, and therefore encompass the temporal variability of the measured parameters. Average current velocity was twice as high post-inundation (25.8 ± 26.0 cm s⁻¹, range 126 cm s⁻¹) versus pre-inundation (11.3 ± 9.8 cm s⁻¹; range 54.6 cm s⁻¹; Figure 3.4), with peak current velocity occurring during the ebb flow of the spring tide. The duration of flood and ebb tides averaged 5.2 ± 0.6 and 7.3 ± 0.5 hours respectively. Average daily wind speeds ranged from 1.7 to 3.7 m s⁻¹ (average 2.8 ± 1.6 m s⁻¹).

All physiochemical parameters displayed considerable temporal variability (Figure 2). Surface water temperature ranged from 27.0 to 33.5 °C (average 29.0 ± 1.1 °C, n=3118) with average temperatures lower post-inundation (28.8 ± 1.3 °C, n=1290) versus pre-inundation (average 29.2 ± 0.8 °C, n=1828). Salinity ranged from 32.0 to 37.4 (average 34.5 ± 1.0, n=3034; Figure 3.2) and displayed a significant inverse correlation with depth (p<0.001, r²=0.59, n=3005) due to evapotranspiration within the catchment (Dittmar and Lara 2001b). Highest salinity occurred ~ 2 days post inundation (during low-tide; Figure 3.2) as did the largest inter-tidal ranges (Figure 3.3). On average, salinity was highest post-inundation (versus pre-inundation; Figure 3.4).
Figure 3.2 Time series of $^{222}$Rn, $p$CO$_2$, CH$_4$ and physicochemical parameters. Red data points represent data extrapolated from $p$CO$_2$-$^{222}$Rn relationship (see Figure 3.6). Shaded area represents when inundation of forest occurred adjacent to, and upstream of, the study site (i.e. “post-inundation” period). Dashed lines represent neap and spring tides.
Figure 3.3 Intra-tidal range of $^{222}$Rn, $p$CO$_2$ and CH$_4$ for each individual tidal cycle (n=21). Red columns represent data interpolated from the $^{222}$Rn-$p$CO$_2$ relationship (see Figure 3.6). Blue line represents approximate time when inundation of forest occurred at the study site (~4.9 m depth). Dashed lines represent neap and spring tides.
Figure 3.4 Box plots for: the entire dataset (“All”); to compare pre- and post-inundation (“Pre”/”Post”); and to compare flood tides and ebb tides for the entire data set (“Flood”/”Ebb”) and for pre-inundation (“Pre Flood”/”Pre Ebb”) and post-inundation (“Post...”)
Considerable temporal variability was observed for \( pCO_2 \), CH4 and \( ^{222}\text{Rn} \) (Figure 3.2). Methane values ranged from 58 to 1,469 nM (average 525 ± 275 nM, \( n=15,188 \)), \( ^{222}\text{Rn} \) from 585 to 16,583 dpm m\(^{-3} \) (average 5,489 ± 4,141 dpm m\(^{-3} \), \( n=914 \)) and \( pCO_2 \) from 592 to 15,361 μatm (average 4,918 ± 3,559 μatm, \( n=15,659 \)). Each gas displayed a tidal trend with concentrations lowest at high tides and highest at low tides. The intra-tidal range, that is, the difference between the minimum (occurring at high tide) and maximum (occurring at low tide) for \( pCO_2 \), CH4 and \( ^{222}\text{Rn} \) varied for each individual tidal cycle (Figure 3.3). CH4, \( ^{222}\text{Rn} \) and \( pCO_2 \) were, on average, higher during ebb tides than flood tides and the greatest difference between average ebb and average flood \( pCO_2 \), CH4 and \( ^{222}\text{Rn} \) occurred post-inundation (Figure 3.4). Peak \( pCO_2 \), CH4 and \( ^{222}\text{Rn} \) occurred ~ 2 days (~ 3 tidal cycles) post-inundation (the lowest concentrations also occurred post-inundation for each gas).

### 3.3.2 \( CO_2 \) and CH4 emissions

Mangrove creek waters were a source of CO2 and CH4 to the atmosphere during the study (Table 3.1). Depending on the parameterisation used, average flux rates for the study period ranged from 91 ± 77 to 285 ± 231 mmol m\(^{-2} \) d\(^{-1} \) and 413± 249 to 1,288 ± 713 μmol m\(^{-2} \) d\(^{-1} \) for CO2 and CH4, respectively, with Borges et al. (2004) estimating the highest flux rates whilst the combined parameterisation of Ho et al. (2006) and O’Connor and Dobbins (1958) resulted in the lowest (Table 3.1). Irrespective of the \( k \) model used, CO2 and CH4 flux rates were highest post-inundation (versus pre-inundation) and during ebb tides (versus flood).

Table 3.1 Average surface water-atmosphere flux rates for CO2 and CH4 (± SD) based on the parameterisations of B04 Borges et al. (2004); H&O Ho et al. (2006) and O’Connor and Dobbins (1958); and R17 Rosentreter et al. (2017), for the entire study period (“All”), pre-
inundation and post-inundation (“Pre” and “Post”), and for flood tides and ebb tides for the entire data set (“Flood” and “Ebb”) and for pre-inundation (“Pre Flood”/”Pre Ebb”) and post-inundation (“Post Flood”/”Post Ebb”) periods.

<table>
<thead>
<tr>
<th></th>
<th>All</th>
<th>Pre</th>
<th>Post</th>
<th>Flood</th>
<th>Ebb</th>
<th>Pre Flood</th>
<th>Pre Ebb</th>
<th>Flood</th>
<th>Ebb</th>
<th>Pre Flood</th>
<th>Pre Ebb</th>
<th>Post Flood</th>
<th>Post Ebb</th>
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</thead>
<tbody>
<tr>
<td>Average $CO_2$ flux rates (mmol $m^{-2} d^{-1}$)</td>
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</tr>
<tr>
<td>B04</td>
<td>285±231</td>
<td>244±173</td>
<td>340±282</td>
<td>188±183</td>
<td>353±237</td>
<td>206±160</td>
<td>277±177</td>
<td>156±215</td>
<td>437±265</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&amp;O</td>
<td>91±77</td>
<td>75±55</td>
<td>114±95</td>
<td>59±60</td>
<td>114±80</td>
<td>62±50</td>
<td>85±56</td>
<td>53±74</td>
<td>146±90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R17</td>
<td>145±93</td>
<td>123±61</td>
<td>174±117</td>
<td>100±73</td>
<td>176±93</td>
<td>106±61</td>
<td>137±58</td>
<td>91±90</td>
<td>218±106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave</td>
<td>174±129</td>
<td>147±94</td>
<td>209±158</td>
<td>116±103</td>
<td>214±130</td>
<td>125±88</td>
<td>166±95</td>
<td>100±124</td>
<td>267±142</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

| Average $CH_4$ flux rate ($\mu$mol $m^{-2} d^{-1}$) |       |      |      |       |      |           |         |       |      |           |         |             |         |
| B04               | 1,288±713 | 1,196±441 | 1,408±944 | 1,158±654 | 1,379±738 | 1,198±435 | 1,194±446 | 1,090±913 | 1,578±916 |
| H&O               | 413±249 | 366±153 | 474±325 | 365±225 | 447±259 | 362±146 | 370±158 | 371±319 | 529±315 |
| R17               | 865±424 | 812±381 | 934±467 | 875±489 | 858±371 | 837±419 | 790±343 | 942±587 | 930±387 |
| Ave               | 855±406 | 791±281 | 939±514 | 800±419 | 895±391 | 799±289 | 785±274 | 801±580 | 1,012±459 |

### 3.3.3 Pore-water

Pore-water $pCO_2$, $CH_4$ and $^{222}Rn$ showed considerable variability, with ranges spanning 78,769 $\mu$atm, 79,333 nM and 58,016 dpm m$^{-3}$, respectively. On average, all gases were considerably higher in pore-water than surface waters (Table 3.2) with $CH_4$, $^{222}Rn$ and $pCO_2$ ~ 29-fold, ~ 8-fold and ~ 6-fold higher respectively.
Table 3.2 Pore-water $pCO_2$, CH$_4$, $^{222}$Rn, and physicochemical parameters.

<table>
<thead>
<tr>
<th></th>
<th>Temp (°C)</th>
<th>DO (mg L$^{-1}$)</th>
<th>pH</th>
<th>Sal</th>
<th>$^{222}$Rn (dpm m$^{-3}$)</th>
<th>CH$_4$ (nM)</th>
<th>$pCO_2$ (μatm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Creek bank – sand</td>
<td>32.0</td>
<td>1.96</td>
<td>7.2</td>
<td>31.4</td>
<td>42,822</td>
<td>352</td>
<td>7,086</td>
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<tr>
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<td>29.1</td>
<td>3.67</td>
<td>7.3</td>
<td>33.1</td>
<td>24,976</td>
<td>382</td>
<td>5,521</td>
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<tr>
<td>Creek bank – mud</td>
<td>29.9</td>
<td>3.44</td>
<td>7.6</td>
<td>32.2</td>
<td>24,989</td>
<td>25,776</td>
<td>14,492</td>
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<tr>
<td>Creek bank – mud</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
<td>34.7</td>
<td>42,805</td>
<td>8,770</td>
<td>12,757</td>
</tr>
<tr>
<td>Forest</td>
<td>29.0</td>
<td>1.54</td>
<td>6.2</td>
<td>36.2</td>
<td>43,236</td>
<td>1,903</td>
<td>42,662</td>
</tr>
<tr>
<td>Forest</td>
<td>28.9</td>
<td>2.35</td>
<td>6.7</td>
<td>33.4</td>
<td>46,901</td>
<td>365</td>
<td>17,311</td>
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<td>Forest</td>
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<td>0.33</td>
<td>6.5</td>
<td>34.1</td>
<td>33,137</td>
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<tr>
<td>Forest</td>
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<td>1.15</td>
<td>6.0</td>
<td>39.1</td>
<td>57,142</td>
<td>4,563</td>
<td>84,290</td>
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<tr>
<td>Forest</td>
<td>28.1</td>
<td>-</td>
<td>-</td>
<td>26.2</td>
<td>44,589</td>
<td>79,685</td>
<td>26,852</td>
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<tr>
<td><strong>Average</strong></td>
<td><strong>29.4</strong></td>
<td><strong>2.45</strong></td>
<td><strong>6.9</strong></td>
<td><strong>33.3</strong></td>
<td><strong>44,359</strong></td>
<td><strong>15,260</strong></td>
<td><strong>29,459</strong></td>
</tr>
<tr>
<td><strong>SD</strong></td>
<td><strong>1.1</strong></td>
<td><strong>1.56</strong></td>
<td><strong>0.6</strong></td>
<td><strong>3.3</strong></td>
<td><strong>16,817</strong></td>
<td><strong>24,909</strong></td>
<td><strong>24,076</strong></td>
</tr>
</tbody>
</table>

3.4 Discussion

3.4.1 Mangrove creek water CO$_2$ and CH$_4$ emissions

The high resolution measurements demonstrate the considerable temporal variability in surface water $pCO_2$ and CH$_4$ concentrations that can occur over a spring-neap tidal cycle in a tropical macro-tidal mangrove creek. In this system, $pCO_2$ and CH$_4$ spanned ~ 15,000 μatm and ~1,400 nM, respectively, varying at semi-diurnal (i.e. hourly) and weekly scales (Figure 3.2 and 3.3). The continuous sampling over spring-neap cycles revealed $pCO_2$ was, on average ~ 18% higher post-inundation versus pre, whereas CH$_4$ was similar (Figure 3.4). Average $pCO_2$ and CH$_4$ were higher during ebb tides versus flood tides with the difference being largest post-inundation when the average $pCO_2$ for ebb tides (~ 6,800 μatm) was 2-fold higher than the average $pCO_2$ for flood tides (~ 2,700 μatm) and average CH$_4$ was nearly 50% higher (ebb ~ 600 nM versus flood ~ 400 nM; Figure 3.4). The only other study to
measure $p$CO$_2$ and CH$_4$ at high resolution over a spring-neap cycle reported semi-diurnal and weekly temporal variability of surface water $p$CO$_2$ and CH$_4$ but from a sub-tropical micro-tidal mangrove creek, where the ranges of $p$CO$_2$ and CH$_4$ were $\sim$ 9,000 μatm and $\sim$ 200 nM, respectively (Call et al. 2015). Semi-diurnal $p$CO$_2$ variability spanning $\sim$ 7,000 μatm and $\sim$12,000 μatm were observed by Rosentreter et al. (2018a) in sub-tropical macro- and micro-tidal systems ($\sim$ 20 ° S). In the 0 ° to 5 ° latitudinal region, no $p$CO$_2$ time-series data exists with previous studies based on longitudinal surveys of $p$CO$_2$ calculated from pH and total alkalinity (TA) measurements (Borges et al. 2003; Bouillon et al. 2007a; Bouillon et al. 2007b).

The average and maximum $p$CO$_2$ reported here ($\sim$ 5000 and $\sim$15,000 μatm, respectively) are considerably higher than what has been reported from mangrove waters in the 0 ° to 5 ° latitude band. In Kenyan meso-tidal mangrove creeks, Bouillon et al. (2007a) and Bouillon et al. (2007b) reported average $p$CO$_2$ of 2,600 μatm (maximum 5,300 μatm) and $\sim$3900 μatm (maximum 6,400 μatm), respectively, and in Papua New Guinea, Borges et al. (2003) reported $\sim$ 1200 μatm (maximum $\sim$1700 μatm). Only four other studies have reported similar or higher maximum $p$CO$_2$ than this study: Taillardat et al. (2018a) and Taillardat et al. (2018b) $\sim$ 17,000 μatm; Rosentreter et al. (2018a) $\sim$ 13,000 μatm; and Call et al. (2015) $\sim$27,000 μatm; each coinciding with low tide. The Taillardat et al. (2018a) and Taillardat et al. (2018b) studies were conducted in a tropical meso-tidal mangrove creek whilst Rosentreter et al. (2018a) and Call et al. (2015) were conducted in subtropical micro-tidal mangrove creeks, the latter obtained from an upstream creek location and hypothesised to be recently exfiltrated pore-water. Overall, the average surface water $p$CO$_2$ observed in this study is similar to other micro- and meso-tidal systems (Koné and Borges 2008; Rosentreter et al. 2018a; Rosentreter et al. 2017) but considerably higher (2- to 10-fold) than that reported from other macro-tidal systems (Akhand et al. 2016; Rosentreter et al. 2018a).
Notably, our study was conducted in the dry season, however, other studies have reported average $p$CO$_2$ up to 3-fold higher during the wet season than the dry season (Rosentreter et al. 2018a; Taillardat et al. 2018b).

This study is the first to report CH$_4$ concentrations from a mangrove creek located in the 0 to 5° S latitude band and are amongst the highest ever reported from mangrove creek waters (Call et al. 2015; Kristensen et al. 2008b; Linto et al. 2014). Compared to the maximum CH$_4$ concentration here (~ 1500 nM), Rosentreter et al. (2018b) reported CH$_4$ concentrations up to ~ 1100 nM in a macro-tidal mangrove creek, but located at a subtropical latitude (~ 23° S) and observed during the wet season when maximal CH$_4$ concentrations were up to 4-fold higher than dry season maxima potentially due to freshwater inputs (my study was conducted in the dry season). Barnes et al. (2006) observed no significant differences between wet and dry season CH$_4$ concentrations from a micro-tidal mangrove creek in the Andaman Islands (~ 12° N; range 282 to 704 nM) and reported an overall average CH$_4$ concentration of ~ 480 nM, which was slightly lower than ours (~ 520 nM). My data adds to the considerable variability in reported CH$_4$ concentrations from mangrove systems spanning different latitudes, seasons and tidal regimes, however, the high CH$_4$ concentrations in my study may be related to the higher mangrove production and sediment carbon stocks in the low latitudes and the associated climatic conditions (Bouillon et al. 2008; Sanders et al. 2016; Twilley et al. 1992). High export rates of pore-water sourced inorganic nutrients and dissolved organic matter (DOM) have been observed in this creek, suggesting high rates of remineralisation in these tropical sediments (Dittmar and Lara 2001b). We speculate that the high nutrient and DOM production is also related to the high CH$_4$, and indeed $p$CO$_2$.

Estimating the gas transfer velocity ($k$) is the largest source of uncertainty when determining water-atmosphere CO$_2$ and CH$_4$ fluxes (Raymond and Cole 2001; Wanninkhof
et al. 2009; Zappa et al. 2007). Due to the influence of bottom shear generated turbulence when depths are < ~ 5 m (Ho et al. 2011), depth and current velocity can be important drivers of \( k \) in mangroves, therefore, empirical models combining these parameters in addition to wind are the most appropriate predictor of \( k \) (Ho et al. 2016; Rosentreter et al. 2017). The different parameterisations used in this study provide ranges of potential outgassing rates and when averaging all data, results in estimated CO\(_2\) and CH\(_4\) water-atmosphere flux rates of 174 ± 129 mmol m\(^{-2}\) d\(^{-1}\) and 855 ± 406 μmol m\(^{-2}\) d\(^{-1}\), respectively (Table 1). Compared to pre-inundation, post-inundation flux rates for CO\(_2\) and CH\(_4\) were ~ 40 % and ~ 20 % higher, respectively (Table 3.1). Globally, mangrove water-atmosphere flux rates are estimated (on average) to range from 43 to 72 mmol m\(^{-2}\) d\(^{-1}\) for CO\(_2\) (Alongi 2014; Borges et al. 2003; Bouillon et al. 2008; Rosentreter et al. 2018a) and 288 to 409 μmol m\(^{-2}\) d\(^{-1}\) for CH\(_4\) (Barnes et al. 2006; Rosentreter et al. 2018b). The estimated CO\(_2\) and CH\(_4\) flux rates from this tropical macro-tidal system are amongst the highest reported from mangroves and the potential implications for mangrove CO\(_2\) and CH\(_4\) budgets is discussed below.

3.4.2 Macro-tidal versus micro-tidal mangrove creeks and the “first flush” hypothesis

Semi-diurnally, pore-water exchange appears to be a driver of \( pCO_2 \) and CH\(_4\) dynamics in mangrove creeks irrespective of tidal regime (i.e. micro, meso or macro). In this macro-tidal system, \(^{222}\)Rn, \( pCO_2 \) and CH\(_4\) followed a tidal trend, displaying significant inverse correlations with depth (Figure 3.5) which is consistent with previous studies suggesting a pore-water source of surface water \( pCO_2 \) and CH\(_4\) in micro- and meso-tidal systems (Bouillon et al. 2007c; Kristensen et al. 2008b; Linto et al. 2014; Taillardat et al. 2018a; Taillardat et al. 2018b). The significant positive correlation between \(^{222}\)Rn and \( pCO_2 \) and CH\(_4\) (Figure 3.6) suggests a direct link between pore-water exchange and surface water \( pCO_2 \) and CH\(_4\) as found in other micro and macro-tidal mangrove creeks (Call et al. 2015; Rosentreter et al. 2018a; Taillardat et al. 2018b) and other coastal systems (Macklin et al.
2014; Maher et al. 2015). Furthermore, pore-water endmember $p$CO$_2$, and CH$_4$ and $^{222}$Rn concentrations were, on average, 6-fold, 29-fold, and 8-fold higher than average surface water concentrations (Table 3.2) with similar endmember values reported by Call et al. (2015) for $p$CO$_2$ (24,055 μatm, standard error 3,465 μatm) and CH$_4$ (15,462 nM, standard error 9,918 nM) from a micro-tidal system.

Figure 3.5 Correlation of $p$CO$_2$, CH$_4$ and $^{222}$Rn concentrations with depth. Lines represent an inverse first order polynomial ($y = y_0 + a/x$).
At spring-neap time scales, results from this macro-tidal systems contrast with those from the micro-tidal system upon which the “lunar mangrove pump” concept was based. In that system, the average $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ of each tidal cycle (i.e. low to low) displayed a significant inverse correlation with tidal amplitude, with an upward trend of intra-tidal maximal $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ (and respective intra-tidal ranges) observed during the transition from spring to neap tides with peak $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ (and largest intra-tidal ranges) occurring around the neap tide. In contrast, the maximal intra-tidal $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ (and respective ranges) in this macro-tidal system were lowest around the neap tide (when surface waters were confined to creek banks) and trended upwards as the transition to the spring tide commenced (Figures 3.2 and 3.3). Concentrations peaked ~ 2 days after inundation of forests (but prior to the spring tide) with maximal intra-tidal $p\text{CO}_2$, CH$_4$ and
$^{222}\text{Rn}$ (and ranges) declining thereafter (Figures 3.2 and 3.3). Furthermore, the average $p\text{CO}_2$ and $^{222}\text{Rn}$ concentration of each individual tidal cycle displayed a significant positive correlation with tidal amplitude pre-inundation, however, a significant inverse correlation was observed post-inundation (Figure 3.7). This contrasting relationship between pre- and post-inundation periods was also observed for the intra-tidal minimum $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ versus tidal amplitude (inverse correlation pre-inundation but positive correlation post-inundation) and for the intra-tidal maximum $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ versus tidal amplitude (positive correlation pre-inundation but inverse correlation post-inundation; Figure 3.7). Although pore-water exchange is a driver of surface water $p\text{CO}_2$ and CH$_4$ at semi-diurnal scales in both micro and macro-tidal systems, clearly, different processes control the gas dynamics over spring-neap cycles.

![Graph showing correlation of tidal amplitude with $^{222}\text{Rn}$, $p\text{CO}_2$, and CH$_4$](image)

**Figure 3.7** Correlation of tidal amplitude with the average, minimum and maximum $^{222}\text{Rn}$, $p\text{CO}_2$ and CH$_4$ for each individual tidal cycle (low to low). Blue squares and red triangles
represent pre-inundation and post-inundation of mangroves forests adjacent to (and upstream of) the sampling location, respectively. All regressions are p<0.0001 unless shown otherwise.

The “lunar mangrove pump” concept was based on a micro-tidal system (amplitude 1.27 to 1.72 m) in which the forests within the catchment were inundated each tidal cycle, with only forests in the upper reaches of the basin periodically inundated during spring tides (refer to Maher et al. (2013a) for the digital elevation model of the catchment). Conversely, in the macro-tidal system here (amplitude 2.11 to 4.72 m), surface waters were constrained to the creek banks and only inundated forests adjacent to, and upstream of, the sampling location at depths above ~ 4.9 m. The contrast in $p$CO$_2$, CH$_4$ and $^{222}$Rn trends observed over the spring-neap cycle suggests that the “lunar mangrove pump” concept may not apply to macro-tidal systems due to differing hydrogeomorphology between micro- and macro-tidal mangrove systems. Specifically, due to the different frequency and duration of forest inundation (i.e. hydroperiod), I hypothesise a “first flush” concept to explain the temporal variability of $p$CO$_2$ and CH$_4$ observed in this macro-tidal mangrove creek.

I suggest that two pore-water exchange mechanisms occur over different time scales in this macro-tidal mangrove creek. Semi-diurnally (i.e. hourly), the flushing of crab burrows leads to higher $p$CO$_2$ and CH$_4$ at low-tides in both micro- and macro-tidal mangrove systems. However, at spring-neap time scales (i.e. weekly), differing pore-water exchange mechanisms occur. In micro-tidal systems, a portion of tidal water that infiltrated sediments during spring tides remains in the sediments (becoming more enriched in CO$_2$ and CH$_4$) and progressively seeps back into surface waters as tidal amplitude decreases (due to decreasing hydrostatic pressure), leading to higher $p$CO$_2$ and CH$_4$ at neap tides. Whilst this process would still occur in the macro-tidal system, I hypothesise that a portion of the tidal water that infiltrated sediments during spring tides does not seep back into surface waters due to the low topographic relief of the mature forest (Figure 3.8a). When the creek water breaches the steep
channels and inundates the forest (as tidal amplitude increases) this “aged” pore-water is “flushed” back into the creek waters (Fig. 8b). The peak $p$CO$_2$, CH$_4$ and $^{222}$Rn that was observed ~ 2 days post-inundation reflects this “first flush” of the adjacent forest sediments.

The inflexion point of the contrasting positive and inverse regressions lines for the intra-tidal average, intra-tidal minimum, and intra-tidal maximum $p$CO$_2$, CH$_4$ and $^{222}$Rn versus tidal amplitude (Figure 3.7) indicates when the pore-water contribution to the creek surface water would be at its maximum. Although a greater areal extent of forest is inundated with successive higher-amplitude tides prior to the spring-tide, dilution results in the decreasing trend of maximal inter-tidal $p$CO$_2$, CH$_4$ and $^{222}$Rn (Figure 3.2).

Figure 3.8 The “first flush” mangrove pump, a model of the pore-water exchange that operates over a spring-neap tidal cycle in a mature macro-tidal mangrove forest. The flushing of crab burrows (within creek banks) and the seeping of pore-waters to surface waters via burrows in mangrove sediments occurs semi-diurnally (“base-line” pore-water exchange) (a,
b). Due to the deep channelled mangrove creek that cut through the low-relief mangrove forests, creek waters are contained with creek banks during neap tides and a portion of surface waters that infiltrated sediments during previous spring tides is retained in sediments (“aged” pore-water) (a). As tidal amplitude increases, surface waters inundate adjacent forests, “flushing” the “aged” pore-water from forest sediments. This “first flush” of the mangrove sediments and additional pore-water exchange leads to peak surface water $p\text{CO}_2$ and CH$_4$ concentrations occurring post inundation (b).

Using observations from the same macro-tidal mangrove system with an excess of dissolved nutrients and DOM in pore-waters, Dittmar and Lara (2001b) also suggested that tidal range and frequency of forest flooding controls the advective flow of pore-waters and the magnitude of exports of these solutes to adjacent systems. Similarly to my hypothesis, Dittmar and Lara (2001b) proposed two separate pore-water exchange mechanisms: “Highly mobile” pore-waters which flow through sediment macro-pores (i.e. crab burrows); and, “less mobile” pore-water that flows at much slower rates through micro-pores within sediments (i.e. pore-water seepage). This less mobile pore-water would be more enriched in solutes due to the increased residence time in sediments. The high resolution measurements of $p\text{CO}_2$, CH$_4$ and $^{222}\text{Rn}$ support these hypothesis with higher concentrations at low-tides (when semi-diurnal hydraulic gradients are greatest) and higher intra-tidal maximal concentrations as tidal amplitude (and hydraulic gradient) increases. My study extends this understanding by proposing the “first flush” concept to describe the temporal variability observed over the spring-neap cycle in this macro-tidal creek driven by tidal amplitude and frequency of forest inundation. We note that other studies have shown the importance of seasonality as a driver of GHG emissions (i.e. higher fluxes during the wet season) in tropical mangrove systems (Rosentreter et al. 2018a; Taillardat et al. 2018b), therefore, the “first flush” hypotheses, which was based on dry season sampling, requires testing during wet season conditions.
3.4.3 Implications

I suggest that the additional pore-water exchanges during forest inundation in macro-tidal mangrove systems enhance average mangrove creek water $p$CO$_2$ and CH$_4$ concentrations over spring-neap cycles. During neap tides, when surface waters are constrained by creek banks, “base-line” pore-water exchanges are limited to the flushing of crab burrows (located within creek banks) and pore-water seepage via the cracks and fissures in creek bank sediments (Figure 3.8a). As tidal amplitude increases, the creek bank is overtopped and surface water infiltrates the adjacent forests, resulting in additional pore-water exchanges and higher $p$CO$_2$ and CH$_4$ post-inundation (Figure 3.8b). Thus, neglecting temporal variability over the spring-neap cycle during study design may result in over- or under-estimation of $p$CO$_2$ and CH$_4$ concentrations and associated flux estimates.

Furthermore, in a tropical meso-tidal mangrove creek (10° N) with strong diurnal inequality in tidal regime over the lunar month, Taillardat et al. (2018b) reported $p$CO$_2$ ranging from ~600 to ~3,000 μatm during the dry season (~3,000 to 16,000 μatm in the wet season) during 24-hr studies conducted during a spring-neap cycle with tidal frequency (diurnal/semi-diurnal; symmetric/asymmetric) and tidal amplitude suggested to control pore-water inputs and $p$CO$_2$.

Whilst the global data set for CO$_2$ flux estimates from mangrove waters spans a larger latitudinal range than CH$_4$, this study presents the first estimates from a macro-tidal mangrove ecosystem located in the 0 to 5° latitudinal band. Average CO$_2$ flux rates from this region are from meso-tidal systems (only 3 studies) and range from 44 to 71 mmol m$^{-2}$ d$^{-1}$ (Borges et al. 2003; Bouillon et al. 2007a; Bouillon et al. 2007b), considerably lower than the average CO$_2$ flux rate from this macro-tidal system ($174 \pm 129$ mmol m$^{-2}$ d$^{-1}$) determined during pre- and post-inundation periods. Additionally, the average CO$_2$ flux rate here is the highest reported for macro-tidal mangrove systems, with only Rosentreter et al. (2018a)
reporting a similarly high flux rate of ~140 mmol m\(^{-2}\) d\(^{-1}\) from a sub-tropical macro-tidal system (~23° S) in the wet season with lower salinities. The only other studies to report higher average CO\(_2\) fluxes were also determined from high resolution \(p\)CO\(_2\) measurements over spring-neap cycles that captured temporal variations driven by tidal dynamics: ~200 mmol m\(^{-2}\) d\(^{-1}\) from a sub-tropical (~23° S) micro-tidal system (Call et al. 2015); and an average rate of ~240 mmol m\(^{-2}\) d\(^{-1}\) from a tropical (~10° N) meso-tidal system during wet and dry seasons (Taillardat et al. 2018a; Taillardat et al. 2018b).

Globally, mangrove water-atmosphere CO\(_2\) flux rates are estimated (on average) to range from 43 to 72 mmol m\(^{-2}\) d\(^{-1}\) (Alongi 2014; Borges et al. 2003; Bouillon et al. 2008; Rosentreter et al. 2018a). However, no previous estimates have attempted to scale emissions by latitude and tidal regime. The most recent synthesis of CO\(_2\) emissions from mangrove waters proposed an average flux rate of ~57 ± 9 mmol m\(^{-2}\) d\(^{-1}\), corresponding to global CO\(_2\) emissions of 34.1 ± 5.4 Tg C y\(^{-1}\) when scaled to a mangrove area of 137,760 km\(^2\) (Rosentreter et al. 2018a). Based on that data set, if I incorporate the estimates from this study and the recent work of Taillardat et al. (2018a) and Taillardat et al. (2018b), and then scale fluxes by latitudinal region in the same manner as a recent CH\(_4\) synthesis (Rosentreter et al. 2018b) and by tidal regime, global CO\(_2\) emissions equate to 45.5 Tg C y\(^{-1}\) (Table 3.3).
Table 3.3 Latitudinal mangrove area (km²), CH₄ flux rate ± SD (µmol m² d⁻¹), CO₂ flux rate ± SD (mmol m² d⁻¹) and CO₂ efflux (Tg C y⁻¹) for micro-, meso-, and macro-tidal mangroves. CO₂ and CH₄ flux rates were sourced from Table 4 in (Rosentreter et al. 2018a) and Table S2 in (Rosentreter et al. 2018b), respectively (unless stated). Mangrove latitudinal areas are based on (Giri et al. 2011). Global micro-, meso-, and macro-tidal data were sourced from ECDS (https://ecds.se/dataset/global-tide-variables). No CH₄ emissions were calculated due to lack of data.

| Latitude | Micro-tidal Area | CH₄ flux rate | CO₂ flux rate | CO₂ efflux | Meso-tidal Area | CH₄ flux rate | CO₂ flux rate | CO₂ efflux | Macro-tidal Area | CH₄ flux rate | CO₂ flux rate | CO₂ efflux | Total Area | CO₂ efflux |
|----------|------------------|---------------|---------------|------------|----------------|---------------|---------------|------------|----------------|---------------|---------------|------------|------------|------------|------------|
| 0–5°     | 3,124            | 114±29        | 1.6           | 28,908     | 52±7          | 6.6           | 11,968        | 855±7      | 174±107        | 3.3           | 20,000±107  | 9.1        | 44,000     | 17.3       |
| 5–10°    | 3,776            | 114±28        | 1.9           | 19,129     | 35±17         | 2.9           | 7,095         | -          | 107±93         | 3.3           | 30,000±93   | 1.7        | 9,300      | 6.2        |
| 10–15°   | 3,107            | 50±28         | 0.7           | 10,632     | 148±140b      | 6.9           | 9761          | -          | 40±17          | 1.7           | 23,500±17    | 1.7        | 9,300      | 6.2        |
| 15–20°   | 6,872            | 43±31         | 1.3           | 4,218      | 58±46         | 1.1           | 5,410         | -          | 9±2           | 0.2           | 16,500±21    | 0.2        | 9,300      | 6.2        |
| 20–25°   | 7,921            | 69±51         | 2.4           | 6,303      | 115±149       | 3.2           | 4,576         | -          | 33±53          | 0.7           | 18,800±33    | 0.7        | 9,300      | 6.2        |
| 25–30°   | 3,099            | 82±91         | 1.1           | 1,155      | 115±6         | 0.6           | 47            | 573        | 33±0.01        | <0.01         | 4,300±1.7    | 0.1        | 9,300      | 6.2        |
| 30–35°   | 68               | 55±13         | 0.02          | 242        | 115±7.5       | 0.1           | -             | -          | -              | -             | -              | -          | 310        | 0.1        |
| 35–40°   | 1                | <0.01         | 349           | 115±7.5    | 0.2           | -             | -             | -          | -              | -             | -              | -          | 350        | 0.2        |
| Total    | 27,967           | 8.9           | 70,935        | 21.5       | 38,857        | 15            | 137,760       | 45.5       |                |                |                |            |            |            |

a Based on 5-10° micro-tidal CO₂ flux rate. b Includes the average flux rates from (Taillardat et al. 2018a) and (Taillardat et al. 2018b). c Based on 20-25° meso-tidal CO₂ flux rate. d This study. e Average of 0-5° and 10-15° macro-tidal CO₂ flux rates. f Based on 20-25° macro-tidal CO₂ flux rate.
There are obvious uncertainties in this estimate, such as the upscaling of emissions for macro-tidal mangroves in the 0 to 5° latitudinal band (which comprise ~ 30% of mangroves in that latitudinal band and ~9% of mangroves worldwide) based on this single study. There are also large discrepancies in estimates of global mangrove area (Giri et al. 2011; Hamilton and Casey 2016). The use of the global mangrove area of Giri et al. (2011) allows a comparison with the most recent CO₂ and CH₄ budgets (Rosentreter et al. 2018a; Rosentreter et al. 2018b). Additionally, mangroves are highly dynamic, with the ratio of flooded versus air exposed areas constantly changing. Bouillon et al. (2008) extrapolated CO₂ emissions to a whole mangrove surface area due to similar evasion rates from exposed soils and water, which has been replicated in later budgets (Alongi 2014; Rosentreter et al. 2018a). Despite these limitations, this exercise demonstrates the potential influence of tidal regime on global CO₂ budgets and highlights the gaps in the global data set for mangrove CO₂ (and CH₄) emissions, e.g. no data from macro-tidal mangroves in the 5 to 10° latitudinal band (Table 3.3). Future budgets should also consider seasonality since seasonal variations in mangrove water pCO₂ and associated flux have been reported (Rosentreter et al. 2018a; Taillardat et al. 2018b).

This study presents new observations which improves our current understanding of CH₄ latitudinal distribution and budgets. The CH₄ emission rate here is considerably higher than those used in the most recent mangrove CH₄ budget, which was based on data collected from only 9 mangrove creeks spanning 6° to 27° of latitude with average CH₄ flux rates ranging from 35 to 660 μmol m⁻² d⁻¹ (Rosentreter et al. 2018b). Rosentreter et al. (2018b) reported a quadratic relationship in the latitudinal distribution of CH₄ flux rates with highest average CH₄ emissions (sediment and water combined) from the mid-latitudes (20° to 25°). However, the water-atmosphere component of ~ 570 μmol m⁻² d⁻¹ for the 20° to 25° latitudinal region is considerably lower than this study. When estimating the carbon burial
offset of CH₄ emission from mangrove ecosystems (sediment and water combined), Rosentreter et al. (2018b) reported a similar offset of ~ 20 % when determined by latitudinal scaling or as a simple averaging of fluxes to the global mangrove area. However, due to no water-atmosphere CH₄ flux estimates from the 0 to 5 ° latitudinal band, the average water-atmosphere CH₄ flux rate from the next latitudinal zone (5 ° to 10 °; 3 studies) was used which is an order of magnitude lower (80 μmol m⁻² d⁻¹) than the average CH₄ flux rate from this study (855 ± 406 μmol m⁻² d⁻¹).

As the sparseness of data on CH₄ emissions prevents scaling by tidal regime (Table 3.3), if we simply use the flux rate from my results, the estimated global CH₄ emissions (adjusted to 20-year CO₂ equivalents) for the 0 to 5 ° latitudinal band would change from 0.24 Tg yr⁻¹ to ~ 2.5 Tg yr⁻¹, increasing the offset of carbon burial in this latitudinal band from 1.4 % to ~ 15 %. Due to the large area of mangroves in this band (44,000 km² or 32 % of global mangroves), this may potentially double the estimated global CH₄ emission (adjusted to 20-year CO₂ equivalents) to ~ 6 Tg yr⁻¹. Obviously the same limitations previously discussed for CO₂ emissions apply to CH₄. Clearly, more data are required to constrain mangrove CH₄ budgets and identify global trends, but results from this study suggests that the recent (and most extensive) estimate of CH₄ emissions from mangrove waters is conservative.
Chapter 4 Carbon outwelling and emissions from two contrasting mangrove creeks during the monsoon storm season in Palau, Micronesia


Abstract

Mangroves sequester large amounts of carbon in soils but limited information is available on carbon losses from tropical mangrove systems. Here, I quantify carbon outwelling, CO₂ emissions and pore-water exchange rates from two nearby (~ 2 km apart) tropical mangrove creeks located in different geomorphic settings on the island of Palau, Micronesia during the monsoon storm season. On average, POC and pCO₂ were > 100 % higher and DOC, DIC and TA were 62 %, 25 %, 16 % higher, respectively, from Creek 1 (located within a semi-enclosed bay) than from Creek 2 (located along the coast adjacent to fringing reefs). Both creeks were net exporters of DIC, DOC, POC, TA and emitters of CO₂. However, outwelling rates of POC, DIC and DOC and CO₂ emissions were 27-fold, 8-fold, 4-fold and 3-fold higher at Creek 1. DIC outwelling (37 %) and CO₂ emissions (39 %) were the major terms contributing to total carbon losses at Creek 1, whilst CO₂ emission (61 %) was the major contributor at Creek 2. Monsoon storms appeared to explain the organic carbon dynamics whilst tidal pumping appears to drive the inorganic carbon dynamics at both creeks. My data demonstrates the considerable heterogeneity of mangrove creeks that are in close proximity and subject to similar weather conditions but in differing geomorphological settings.
4.1 Introduction

Mangroves are highly productive and recognised as one of the most carbon-rich ecosystems in the world (Alongi 2014; Donato et al. 2011). Occurring in 118 countries from ~ 30 ° N to ~ 40 ° S (Giri et al. 2011), mangroves span a range of climatic and geomorphic settings, inhabiting a wide range of inter-tidal settings from estuarine complexes to the coastlines of oceanic islands. Outwelling can release large amounts of material (particulate, dissolved, organic, inorganic) from mangroves to the coastal ocean. Factors such as seasonal precipitation (e.g. wet, dry), tidal dynamics (i.e. tidal amplitude, regime and symmetry) and terrestrial connectivity (i.e. freshwater inputs) contribute to large inter-site variability in outwelling between mangrove ecosystems and influence the connectivity between mangroves and their adjacent aquatic environments (Boto and Bunt 1981; Kristensen et al. 2017; Odum et al. 1979; Twilley 1985; Twilley 1988) and the atmosphere (Call et al. 2015; Jeffrey et al. 2018).

Considerable research effort has been directed towards constraining mangrove carbon flows since Bouillon et al. (2008) found that ~ 50 % of mangrove NPP (~ 112 ± 85 Tg C yr⁻¹) was unaccounted for by the various sinks. Recent evidence suggests that dissolved inorganic carbon (DIC) outwelling appears to be the major sink of this missing carbon and the predominant export term in mangrove carbon budgets (Alongi 2009; Alongi 2014; Bouillon et al. 2008; Ho et al. 2017; Maher et al. 2018; Maher et al. 2013a; Ray et al. 2018). Mangroves have also been show to potentially buffer costal acidification via exports of total alkalinity (TA) with recent studies by Sippo et al. (2016) and Maher et al. (2018) reporting TA export up to 132 mmol m⁻² d⁻¹, however, these datasets are limited to Australian mangrove systems where only ~ 7 % of global mangrove stocks occur (Giri et al. 2011).

Previous estimates of CO₂ efflux from mangrove waters globally range from 26 to 50 Tg C yr⁻¹ (Alongi 2009; Alongi 2014; Borges et al. 2003; Bouillon et al. 2008). These have
recently been constrained to $34.1 \pm 5.4$ Tg C yr$^{-1}$ (Rosentreter et al. 2018a) based on more data and revised atmospheric exchange rates (Ho et al. 2016; Rosentreter et al. 2017), yet large uncertainties remain, partly due to limited studies from tropical systems. Contrary to DIC exports and water-atmosphere fluxes, estimated global exports of dissolved organic carbon (DOC) and particulate organic carbon (POC) have remained static but are still subject to large uncertainties, ranging from $15$ ($\pm 13$) to $24$ ($\pm 21$) Tg C yr$^{-1}$ and $22$ ($\pm 27$) to $28$ ($\pm 21$) Tg C yr$^{-1}$, respectively (Alongi 2009; Alongi 2014; Alongi and Mukhopadhyay 2015; Bouillon et al. 2008).

Much of the carbon in mangrove forests is stored in the sediments (Donato et al. 2011) where aerobic respiration and sulfate reduction are the dominant remineralisation processes (Alongi 2009; Kristensen et al. 2008a). The tidally mediated exchange of pore-water (i.e. tidal pumping) is a major carbon export mechanism in mangroves (Ovalle et al. 1990; Stieglitz et al. 2013; Tait et al. 2016), transporting the by-products of sub-surface respiration such as DIC (Bouillon et al. 2007c; Maher et al. 2013a), alkalinity (Sippo et al. 2016), greenhouse gases (Barnes et al. 2006; Call et al. 2015; Kristensen et al. 2008b) and DOC (Dittmar et al. 2006; Dittmar et al. 2001; Sippo et al. 2017) to mangrove creeks and adjacent waters. However, estimates of pore-water exchange rates from mangroves are limited (Taillardat et al. 2018a; Tait et al. 2016).

Mangroves located in the $0^\circ$ to $10^\circ$ latitudinal band, where $\sim 50\%$ of mangroves occur (Giri et al. 2011), are underrepresented in global datasets. Furthermore, only a few studies have attempted to estimate the contribution of individual carbon parameters to the total carbon exported from a single mangrove creek (Maher et al. 2018; Taillardat et al. 2018a). This paper presents net DOC, POC, DIC and TA exchanges, CO$_2$ emissions and pore-water discharge rates from two tropical mangrove creeks located in different geomorphic settings on the island of Palau, Micronesia. I predict that there will be
considerable differences between the quantity exchanged and contribution of each carbon parameter to total carbon exports from a mangrove creek located in a semi-enclosed bay that is subject to large sediments loads and longer water residence time (~ 7 days), compared to a mangrove creek located on the coast which is flushed semi-diurnally and has greater interconnectivity with the adjacent marine environment (including fringing coral reefs).

4.2 Methods

4.2.1 Study site

Sampling was conducted in two micro-tidal mangrove creeks located on the volcanic island of Badeldaob, Palau (Figure 4.1). The topography of Badeldaob (maximum elevation 242 m) is characterised by rolling uplands accompanied by steep ridges with abundant streams and rivers that drain directly into the adjacent marine environment or bays (Golbuu et al. 2011). Creek1 (7°21'60"N, 134°34'39"E; length ~ 600 m; width at sampling location 6 m) is situated within the semi-enclosed Airai Bay in which the Ngerikiil River (catchment 28.5 km²) drains (Golbuu et al. 2011). Airai Bay receives large sediments loads via the Ngerikiil Rivers with suspended sediment concentrations exceeding 1500 mg l⁻¹ during river floods (Golbuu et al. 2003). Water residence time in the bay is ~ 7 days and with 98 % of the riverine sediment settling in Airai Bay, the influx of terrigenous sediments (due to anthropogenic activities) has resulted in the burial of corals in the bay and a shift to algal dominance (Golbuu et al. 2003). Creek 2 (7°23'28"N, 134°35'8"E; length ~ 850 m; width at sampling location 5 m) is situated on the eastern coast of the island within a much smaller bay (comparative to Airai Bay) that receives no riverine inputs and opens directly to the adjacent marine environment, with fringing coral reefs ~ 900 m offshore. Creek 2 is situated at the base of steep slopes, whereas the gradient of land adjacent to Creek 1 is comparatively much gentler (Figure 4.1). Most of the mangrove forests that fringe the coastline in Palau (i.e. Creek 2) sit atop former reef flats and coral sands (Kauffman et al. 2011). The mangrove
forests of each catchment were dominated by *Rhizophora apiculata*, *Sonneratia alba* and *Bruguierra gymnorrhiza* and had abundant crab burrows in sediments. Palau is located in the wet tropics (7°22'N, 134°32'E) and has a mean annual rainfall of 3700 mm with the driest month being February (~ 210 mm). Heaviest rains occur from June to August (~ 1200 mm) due to monsoonal storms which was when this study was conducted.
Figure 4.1 Location of Creek 1 and Creek 2 on the island of Badeldaob, Palau. Sampling was conducted near the mouths of each creek as denoted by the red triangles.

4.2.2 Surface water sampling

Time series were conducted over a ~25 h period commencing 24th June 2015 and 26th June 2015 for Creek 1 and Creek 2, respectively. Sampling of both creeks was conducted during the neap phase of the tidal cycle when the maximum tidal range at each creek was ~
0.9 m (during spring tides, tidal amplitude is ~ 2 m). From a small vessel moored in the middle of each creek and close to the mouth, discrete samples for DIC, DOC, POC and TA were collected from a depth of ~ 10 cm every hour (2 hours for POC) using a sample-rinsed polypropylene syringe and filtered through 0.7 μm Whatman GF/F filters. DIC and DOC were collected in pre-combusted 40 mL borosilicate vials containing 100 μL of saturated HgCl₂ solution leaving no headspace or bubbles. TA was collected in 30 mL polypropylene vials and all discrete samples were stored on ice until returning to the laboratory where samples were kept refrigerated (4 °C) until analysis. POC samples were immediately filtered upon collection through pre-combusted GF/F filters and kept frozen until analysis. Radon-222 (²²²Rn; a natural pore-water tracer) was determined every 10 min using an automated ²²²Rn-in-air analyser (RAD7, Durridge) and a showerhead air-water exchanger (Santos et al. 2012). A Hydrolab DS5 sonde logged temperature and salinity every 5 min and a SAMI-pH sensor (Sunburst Sensors; accuracy ± 0.003 pH units) logged pH on the total scale every 15 min. Creek depth and current velocities were measured and averaged over 5 min intervals using a bottom mounted acoustic doppler current profiler (ADCP, SonTek Argonaut; accuracy ± 1 %). Current velocity was set to bin 10 cm vertical averages with the integrated mean reported. Wind speed was logged every minute using a sonic anemometer at a height of ~ 3 m.

4.2.3 Pore-water sampling

Pore-water samples were collected at low-tide within the adjacent forests on the 24th and 26th June 2015 from Creek 1 (n=3) and on the 28th June 2015 from Creek 2 (n=2). Bores were dug to a depth of up to ~ 50 cm below the water table (Maher et al. 2013a; Taillardat et al. 2018a) and purged two times before sampling immediately thereafter from the recharging well. A peristaltic pump and gas-tight high density polyethylene (HDPE) bottles were used to collect samples which were then analysed within 24 hours using the RAD7 according to Lee
and Kim (2006). Samples for DIC, DOC and TA were collected by syringe and treated with HgCl₂ as described earlier.

### 4.2.4 Analytical methods

DIC and DOC were analysed using an organic carbon analyser (TOC-L CSH CSN; Shimadzu Corp., Japan) with a precision of 0.01 mM and 0.02 mM, respectively. TA was measured by Gran titration (Metrohm Titrino 848 Automatic Potentiometric Titrator) with an accuracy better than 10 μM and standardized to Dickson Certified Reference Material (batch 111). POC filters were fumed with concentrated HCl for 24 h then dried at 60 °C for 24 h prior to analysis using a Flash EA coupled to a Thermo Delta V + isotope ratio mass spectrometer via a continuous flow interface with a precision of 0.5%.

### 4.2.5 Water-atmosphere flux calculations

Creek water pCO₂ was determined by TA and pH using the CO2SYS program (Pierrot et al. 2006) with the carbonic acid disassociation constants from Cai and Wang (1998) and the KHSO₄ from Dickson (1990). CO₂ water-atmosphere fluxes (F) were determined according to:

\[
F = k\alpha(p_{\text{water}} - p_{\text{air}})
\]

where \( k \) is the gas transfer velocity (cm h⁻¹), \( \alpha \) is the solubility co-efficient of the respective gas, \( p_{\text{water}} \) and \( p_{\text{air}} \) are the partial pressures of each gas (μatm) in the water and atmosphere respectively. Solubility coefficients for CO₂ were determined according to Weiss (1974). \( k_{600} \) was normalised to in situ \( k \) using (Wanninkhof 2014):

\[
k_{600} = k(600/Sc)^{0.5}
\]
The gas transfer velocity \((k)\) was determined using three different empirically derived models based on wind speed, current velocity and depth. Borges et al. (2004) as determined in estuaries:

\[
k_{600} = 1.0 + 1.719 v^{0.5} h^{-0.5} + 2.58u
\]  

The combined parameterisations of Ho et al. (2006) and O'Connor and Dobbins (1958) based on the study by Ho et al. (2016) in a mangrove-dominated estuary:

\[
k_{600} = (0.77 v^{0.5} h^{-0.5}) + (0.266 u^2)
\]  

Rosentreter et al. (2017) as determined within sub-tropical mangrove systems:

\[
k_{600} = -0.08 + 0.26v + 0.83u + 0.59h
\]

where \(k_{600}\) is the gas transfer velocity (cm hr\(^{-1}\)) normalised to the Schmidt number of 600, \(v\) is the water velocity (cm s\(^{-1}\)), \(h\) is the depth (m) and \(u\) is the wind speed at 10 m (m s\(^{-1}\)). Wind was corrected to a 10 m height using the power law relationship of Amorocho and DeVries (1980).

### 4.2.6 Outwelling estimates

The net exchange of DIC, DOC, POC and TA was estimated using an Eulerian approach:

\[
\int_{t_0}^{t} QC \, dt
\]

where \(Q\) is discharge (m\(^3\) 10 min\(^{-1}\)) calculated as a function of the cross-sectional area and current velocity, assuming a constant velocity across the width of the creek. This approach omits edge effects, however, due to the geometry of the creeks (steep banks, homogenous cross sectional depth) this error is likely small. \(C\) is the concentration of either DIC, DOC,
TA or POC (mmol C l\(^{-1}\)), calculated as the average of two consecutive concentrations measured at hourly intervals. Q and C were integrated (\(t_0\) to \(t\)) throughout the sampling period (two low-high-low tidal cycles) and normalized to the catchment area of each creek estimated using Google Earth. Positive fluxes represent export from the mangrove to adjacent waters, while negative fluxes represent import to the mangroves. Based on low-tide surveying, channels at the sampling location displayed homogeneous depth across both creeks with near vertical banks, thus the cross-sectional area of each creek was treated as a rectangle, with area varying as a function of tidal height. Errors for all export terms and the \(^{222}\text{Rn}\) mass balance (see below) were calculated via standard propagation of error techniques. In addition to instrument precision, cross sectional area and current velocity were each assigned an uncertainty of 25%.

A \(^{222}\text{Rn}\) mass balance model was used to calculate the volume of pore-water exchange similarly to Tait et al. (2016). Based on the temporal observations of \(^{222}\text{Rn}\) concentrations in the creek and accounting for the potential sources of \(^{222}\text{Rn}\) (incoming surface water, \(^{222}\text{Rn}\) diffusion from sediments, and decay of radium-226 to \(^{222}\text{Rn}\)) and potential sinks of \(^{222}\text{Rn}\) (\(^{222}\text{Rn}\) decay, atmospheric evasion, and outgoing creek water), pore-water exchange (PW; m\(^3\) 10 min\(^{-1}\)) was calculated after integrating observations over a full tidal cycle:

\[
PW = \frac{((Rn_W \cdot Q) - R_{Dec} - (Rn_{Diff} \cdot A)) + (J_{atm} \cdot A) + (Rn_W \cdot \lambda \cdot A))}{PW_{end}}
\]  \hspace{1cm} (7)

where at each 10 min time step \(Rn_W\) is the \(^{222}\text{Rn}\) concentration of the water column (dpm m\(^{-3}\)); \(Q\) is the discharge from the creek calculated as a function of cross-sectional area and current velocity and assuming a constant velocity across the width of the creek (m\(^3\)); \(R_{Dec}\) is the \(^{222}\text{Rn}\) concentration produced through the decay of \(^{226}\text{Ra}\) (dpm m\(^{-3}\)); \(Rn_{Diff}\) is the diffusion of \(^{222}\text{Rn}\) from sediments (dpm m\(^{-2}\)); \(A\) is the inundated area (m\(^2\)); \(J_{atm}\) is the atmospheric
evasion of $^{222}$Rn (dpm m$^{-2}$); $\lambda$ is the decay constant of $^{222}$Rn (0.181 day$^{-1}$); and $PW_{end}$ is the average $^{222}$Rn concentration of pore-water samples.

$Ra_{Dec}$ was measured by filtering surface water (34 L) through MnO$_2$ impregnated fibres every two hours which were then analysed for $^{226}$Ra via delayed coincidence counter (Moore and Arnold 1996). $J_{atm}$ was calculated the same as CO$_2$ (i.e. average of the three parameterisations) but corrected for the Schmidt number of $^{222}$Rn at in situ temperature and salinity (Wanninkhof 2014). $Rn_{Diff}$ was calculated independently using a depth-independent approach (Martens et al. 1980):

$$Rn_{Diff} = (\lambda D_s)^{0.5} (PW_{end} - Rn_w)$$  \hspace{1cm} (8)

where $D_s$ is the effective wet bulk sediment diffusion coefficient in sediment (m$^2$ d$^{-1}$) calculated as a function of temperature $D_s = \phi(10^{(980/T)+1.59})$ (Ullman and Aller 1982) with porosity ($\phi$) considered as 0.4 based on sediment grain density (Armstrong 2006).

4.3 Results

4.3.1 Tidal and physico-chemical dynamics

In addition to tidally driven variability, monsoonal storm events began ~ 12 hours after the start of each times series (coinciding with low-tide) at both creeks No precipitation data was measured at the study site, however, 97 mm and 78 mm of precipitation was measured at the Badeldaob Koror Airport, ~ 5 km away from the study sites (https://www.ncdc.noaa.gov/cdo-web/datatools/lcd; station ID WBAN:40310) during the time series of Creek 1 and Creek 2, respectively. Heavy precipitation lasted for ~ 2 hours at the beginning of each storm event with lighter precipitation continuing till the end of each time series, resulting in physico-chemical parameters displaying considerable temporal variability during each time series and between each creek (Figure 4.2). Depth at Creek 1 and Creek 2 ranged from 0.46 to 1.30 m, (average 0.81 ± 0.25 m) and from 0.52 to 1.41 m.
(average 0.95 ± 0.27 m), respectively. Current velocities were highest at Creek 2 (range 2.0 to 21.2 cm s⁻¹; average 7.9 ± 4.9 cm s⁻¹) compared to Creek 1 (range 2.8 to 16.0 cm s⁻¹; 7.5 ± 3.3 cm s⁻¹) with highest velocities at high tide at Creek 1 but at low tide at Creek 2. Wind speeds were, on average higher at Creek 1 (2.4 ± 1.5 m s⁻¹) versus Creek 2 (1.7 ± 1.4 m s⁻¹). Prior to the monsoonal storm, Creek 2 displayed acute, tidally driven changes in salinity (and water temperature), ranging from low salinity water at low tide (salinity 3.1; water temperature ~ 27 °C) but rapidly switching to marine water during the flood tide (salinity 31.0 and water temperature ~ 29 °C at high tide; Figure 4.2). Following the storm, water temperature and salinity at the fringing creek remained at low-tide levels observed prior to the rain event, however, pH rapidly returned to ~ 7.90 during the flood tide (after dropping to 7.20 following the storm; Figure 4.2). At Creek 1, water temperature, salinity and pH spanned lower ranges (i.e. lower variability) than Creek 2 (Figure 4.2) with lowest values occurring post the monsoonal storm.
Figure 4.2 Time series of depth, current speed, discharge (Q), wind speed, surface water temperature, salinity, pH, POC, DOC, DIC, TA, $p$CO$_2$ and $^{222}$Rn over a ~ 25 h period at two mangroves creeks. Negative current velocities indicate flood tidal flows whilst positive indicate ebb flows. Blue lines denote when a significant monsoonal storm event occurred at each creek. Time is local time (LT).

4.3.2 Carbon parameters and radon-222

Carbon parameters displayed considerable temporal variability at each creek (Figure 4.2) with average POC and $p$CO$_2$ > 100 % higher and average DOC, DIC and TA 62 %, 25 %, 16 % higher, respectively, from Creek 1 than from Creek 2 (Table 4.1). POC and DOC displayed no tidal trends at either creek with Creek 1 displaying the largest range in concentrations for both parameters. Following the monsoon storm, POC concentrations were noticeably higher at both creeks whilst DOC concentrations were lower at Creek 1 and more scattered at Creek 2. Contrary to POC and DOC, DIC, TA and $^{222}$Rn displayed tidal trends at both creeks. Pore-water DOC, DIC and TA were, on average, double that of average surface water concentrations in both systems (Table 4.1) and average $^{222}$Rn concentrations were ~ 16- and ~ 6-fold higher than average creek water concentrations in Creek 1 and Creek 2, respectively.
Table 4.1 Summary of surface water and pore-water results from Creek 1 and Creek 2.
Average ± SD. Range in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Surface water</th>
<th></th>
<th>Pore-water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Creek 1</td>
<td>Creek 2</td>
<td>Creek 1</td>
<td>Creek 2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>27.9±0.7</td>
<td>27.3±0.9</td>
<td>28.4±0.3</td>
<td>26.8±0.6</td>
</tr>
<tr>
<td></td>
<td>(26.6-29.5)</td>
<td>(26.6-29.8)</td>
<td>(28.2-28.8)</td>
<td>(26.1-27.3)</td>
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<tr>
<td>Salinity</td>
<td>16.5±4.6</td>
<td>9.1±8.1</td>
<td>9.6±10.2</td>
<td>14.7±8.7</td>
</tr>
<tr>
<td></td>
<td>(7.3-25.5)</td>
<td>(3.2-31.0)</td>
<td>(1.9-21.2)</td>
<td>(6.1-23.5)</td>
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<tr>
<td>pH</td>
<td>7.39±0.17</td>
<td>7.73±0.21</td>
<td>6.60±0.20</td>
<td>6.33±0.22</td>
</tr>
<tr>
<td></td>
<td>(7.13-7.82)</td>
<td>(7.20-7.96)</td>
<td>(6.45-6.83)</td>
<td>(6.08-6.47)</td>
</tr>
<tr>
<td>POC (µM)</td>
<td>91±91</td>
<td>38±13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(18-316)</td>
<td>(23-58)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC (µM)</td>
<td>351±107</td>
<td>217±36</td>
<td>623±161</td>
<td>482±48</td>
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<td></td>
<td>(217-617)</td>
<td>(172-291)</td>
<td>(439-733)</td>
<td>(439-534)</td>
</tr>
<tr>
<td>DIC (µM)</td>
<td>2,100±292</td>
<td>1,681±426</td>
<td>4,834±1,519</td>
<td>3,905±711</td>
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<td>(1,523-2,588)</td>
<td>(1,016-2,136)</td>
<td>(3,720-6,564)</td>
<td>(3,276-4,677)</td>
</tr>
<tr>
<td>TA (µM)</td>
<td>2,026±207</td>
<td>1,745±501</td>
<td>3,917±1,147</td>
<td>2,757±774</td>
</tr>
<tr>
<td></td>
<td>(1,644-2,339)</td>
<td>(972-2,240)</td>
<td>(2,844-5,602)</td>
<td>(1,893-3,387)</td>
</tr>
<tr>
<td>pCO₂ (µatm)</td>
<td>2,549±997</td>
<td>1,013±421</td>
<td>31,218±1,965</td>
<td>38,110±9,530</td>
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<td></td>
<td>(735-4,752)</td>
<td>(484-2,186)</td>
<td>(29,026-32,821)</td>
<td>(27,625-46,245)</td>
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<tr>
<td>²²²Rn (dpm m⁻³)</td>
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<td>3,250±2,001</td>
<td>291,311±92,263</td>
<td>17,738±7,622</td>
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<td>(983-45,761)</td>
<td>(695-7,203)</td>
<td>(192,839-375,760)</td>
<td>(8,893-22,892)</td>
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<tr>
<td>k₆₃₀ (cm hr⁻¹)</td>
<td>1.4±0.6</td>
<td>1.2±0.6</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>(0.8-4.1)</td>
<td>(0.5-4.4)</td>
<td></td>
<td></td>
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</tbody>
</table>
4.3.3 Carbon outwelling and pore-water exchange

Both creeks were net exporters of DIC, DOC, POC and emitters of CO$_2$ however, the export rates and contribution of each parameter to total carbon exports varied considerably between creeks (Figure 4.3). Outwelling rates of POC, DIC and DOC were 27-fold, 8-fold and 4-fold higher at Creek 1 compared to Creek 2, respectively. Depending on the parameterisation used, average CO$_2$ emission rates for Creek 1 and Creek 2 ranged from 50 ± 30 to 145 ± 93 mmol m$^{-2}$ d$^{-1}$ and 18 ± 20 to 49 ± 59 mmol m$^{-2}$ d$^{-1}$, respectively, with Borges et al. (2004) estimating the highest flux rates whilst Rosentreter et al. (2017) resulted in the lowest. Averaging all data for both creeks results in estimated CO$_2$ water-atmosphere flux rates of 83 ± 78 mmol m$^{-2}$ d$^{-1}$ for Creek 1 and 32 ± 47 mmol m$^{-2}$ d$^{-1}$ for Creek 2 (Figure 4.3). DIC export and CO$_2$ emissions were the major terms contributing to total carbon outwelling at Creek 1, whilst CO$_2$ emission was the major contributor at Creek 2. The contribution of DOC export was similar at both creeks whilst POC was the minor term. Outwelling of TA was considerably higher (~ 20-fold) at Creek 1 (48 ± 17 mmol m$^{-2}$ d$^{-1}$) compared to Creek 2 (2 ± 1 mmol m$^{-2}$ d$^{-1}$). Pore-water exchange rates were highest at Creek 2 (6.2 ± 4.8 cm d$^{-1}$) compared to Creek 1 (3.3 ± 3.3 cm d$^{-1}$).
4.4 Discussion

In spite of the two creeks being located within ~ 2 kilometres of each other, and the sampling being undertaken on consecutive days with a similar amount of rain at each creek, the temporal carbon dynamics and lateral carbon export rates varied substantially between the two sites. Here, I discuss the drivers of carbon dynamics and lateral exchange within each creek and compare the systems.

4.4.1 Creek carbon hydrodynamics

The hydrodynamics of the two creeks differed. Creek 2, which is located at the base of steep topography and within a bay that opens directly to the marine environment (Figure 4.1), appears to be heavily influenced by marine and low salinity (i.e. terrestrial) water inputs.
Prior to the storm event, salinity trends (~ 31 at high tide, ~3 at low tide; Figure 2) suggests water in Creek 2 has a short residence time, likely replaced at semi-diurnal scales. Salinity at high tide was slightly below that expected of marine water (i.e. ~ 31 versus ~ 35), suggesting incomplete tidal flushing of water within the small bay in which Creek 2 is located. Following the storm, salinity remained low (~ 6) in Creek 2, regardless of tidal stage, suggesting significant inputs of terrestrial waters to the creek and the adjacent bay, likely due to the adjacent steep topography which may enhance surface water run-off from the adjacent terrestrial environment to the mangroves (we note that no rivers discharge into this bay). In contrast, Creek 1 appears more “buffered” from marine and terrestrial inputs with salinity ranging from 11 to 26 prior to the storm and 7 to 24 following the storm. This is likely due to its location in a semi-enclosed bay which has been reported to have a ~ 7 day water residence time (Golbuu et al. 2003). Overall, the net water discharge rate (normalised to catchment area) was 37 % higher at Creek 2 (24.7 mm d⁻¹) than Creek 1 (18.1 mm d⁻¹).

Whilst observations at both creeks suggest a dilution effect due to increased surface water inputs following the storm events, particularly at the fringing creek. However, the natural groundwater tracer, ²²²Rn, followed a distinct tidal trend in both locations, consistent with tidal pumping (Call et al. 2015). The estimated pore-water discharge rates at both creeks are similar to the average rate (4.9 ± 1.5 cm d⁻¹) reported from a single creek over a lunar cycle in Vietnam (Taillardat et al. 2018a), yet considerably lower than the average (16.3 ± 5.1 cm d⁻¹) reported by Tait et al. (2016), which was determined from a minimum of five tidal cycles from six Australian mangrove creeks (spanning 10-40 ° S). Pore-water discharge at Creek 2 (6.2 ± 4.8 cm d⁻¹) was almost double that observed at Creek 1 (3.3 ± 3.3 cm d⁻¹). The higher rate may be due to the substrates underlying the fringing mangrove creek which are likely former reef flats and coral sands (Kauffman et al. 2011). Furthermore, Creek 1 is located within Airai Bay which is subject to the high sediment yields from the Ngerikiil River
(Golbuu et al. 2003), which may contribute to a less porous substrate than Creek 2. As endmember values are an important source of uncertainty when estimating pore-water discharge rates (Dulaiova et al. 2008), we note the limited number of pore-water samples from Creek 1 (n=3) and Creek 2 (n=2), yet our pore-water discharge rates appear reasonable given the agreement with published rates.

POC and DOC concentrations were > 100 % and 62 % higher at Creek 1 than Creek 2, respectively (Table 4.1), likely related to the high sediments loads (and associated supply of OM) that Creek 1 is subject to. Both parameters displayed no tidal trends at either creek (Figure 4.2) with no clear relationship with depth contrasting with other studies (Bouillon et al. 2007c; Maher et al. 2013a; Sadat-Noori et al. 2016; Taillardat et al. 2018a). Instead, DOC and POC dynamics appeared to be controlled over short-time frames by the storm events. Following the monsoonal storm, POC concentrations increased by up to 17-fold (Figure 4.2) at Creek 1 and up to ~ 3-fold higher at Creek 2, likely due to increased surface run-off and associated mobilisation of particulate matter. A similar trend of sharp increases in POC due to heavy rain was observed by Dittmar and Lara (2001b) in a Brazilian macro-tidal mangrove system where they observed POC concentrations increase ~16-fold from ~ 500 µM to ~ 8000 µM. Conversely, DOC concentrations were generally lower following the storm at Creek 1 with maximum DOC during the ebb tide prior to the storm of ~ 600 µM, but only ~ 400 µM during the ebb tide following the storm, whilst at Creek 2 DOC concentrations were highly variable following the storm. This contrasts with Taillardat et al. (2018a) who suggested increased leaching of soluble organic matter lead to a steady increase in DOC concentrations following rain in a mangrove creek in Vietnam. In Florida, increased DOC concentrations due to rain (Twilley 1985) and seasonal freshwater inputs (Romigh et al. 2006) have also been observed. Given the intensity and regularity of storm events in Palau, it is plausible that it may have a dilution effect on DOC (as observed at Creek 1) or that there is likely not a
build-up of leachable DOC due to the Palau’s high annual rainfall (3700 mm y⁻¹) compared to that reported by the studies conducted in Florida (≈ 1400 mm y⁻¹) or Vietnam (1,600 to 2250 mm y⁻¹). Whilst this study suggests that rainfall can influence DOC and POC dynamics, the longer term influence cannot be assessed based on the timeframe of this study.

In contrast to the organic carbon parameters, the inorganic carbon pool was more closely coupled to tidal dynamics. At Creek 1, DIC, TA and $p$CO₂ displayed a significant inverse correlation with depth and a significant positive relationship with $^{222}$Rn (Figure 4.4 and 4.5) which are often observed in mangrove creeks and consistent with a tidal pumping source (Borges et al. 2003; Bouillon et al. 2007c; Call et al. 2015; Maher et al. 2013a; Sippo et al. 2016). At Creek 2, the inorganic carbon parameters displayed mixed relationships. $p$CO₂ displayed a significant inverse relationship with depth and a significant positive relationship with $^{222}$Rn, similar to Creek 1 and suggesting a pore-water CO₂ source, yet DIC and TA displayed a significant positive correlation with depth and a significant inverse relationship with $^{222}$Rn (Figure 4.4 and 4.5) suggesting mixing rather than pore-water exchange may be more important.
Figure 4.4 Correlation of DIC, TA, $pCO_2$ and $^{222}$Rn with depth at Creek 1 (red) and Creek 2 (blue). P values are < 0.001 unless stated otherwise.
Figure 4.5 Correlation of DIC, TA and $p$CO$_2$ with $^{222}$Rn at Creek 1 (red) and Creek 2 (blue). P values are < 0.001 unless stated otherwise.

The contrasting relationships between DIC and TA with depth and $^{222}$Rn at Creek 1 and Creek 2 may be explained by the covariation between salinity normalised TA ($n$TA) and DIC ($n$DIC). The ratio of $n$DIC to $n$TA provides insights into the biogeochemical drivers of DIC and TA, whereby the slope value indicates the pathway(s) of organic matter mineralisation (Borges et al. 2003; Bouillon et al. 2007b). The slope values varied considerably for each flood and ebb tide at both creeks (Figure 4.6). Slope values at Creek 1 supports the role of sub-surface processes and pore-water exchange as a driver of TA and
DIC. There, the slope of the second ebb tide (which occurred during daylight hours) produced a slope similar to that of sulfate reduction (1.0), which was also observed in other mangroves situated in a delta/estuarine environment (Bouillon et al. 2007a). For the first ebb tide (which occurred during night hours) and for the entire time series (i.e. “All data” in Figure 4.6), slopes with lower values were produced which were similar to that reported by Borges et al. (2003) form an estuarine mangrove creek where aerobic respiration, in addition to sulfate reduction, were suggested to strongly contribute to the TA and DIC dynamics.

At Creek 2, the first flood tide (which occurred during night hours) produced a slope (1.9; Figure 4.6) similar to that of carbonate dissolution (2.0), suggesting processes occurring in the adjacent fringing reefs (that the incoming tidal water traverses) controls DIC and TA dynamics during that flood tide. A “back of the envelope” calculation using the average current velocity measured at Creek 2 (7.9 cm s\(^{-1}\)), suggests it would take approximately ~ 3 hrs (approximately half the time of a semi-diurnal tide) for the water overlying the fringing reefs to transit to the mouth of the creek (~ 900 m). To my knowledge, no other studies have reported a slope of ~ 2.0 from mangroves (Borges et al. 2003; Bouillon et al. 2007a; Linto et al. 2014; Sippo et al. 2016; Zablocki et al. 2011). The slope of the proceeding ebb tide produced a value consistent with sulfate reduction (1.0), suggesting tidal pumping is the dominant controller of DIC and TA dynamics during that ebb tide. The slope of the second flood tide (1.2) that occurred during day-light hours suggests less contribution from carbonate dissolution and may be a function of the tropical storm (i.e. mixing processes) as well as diurnal variability in calcification/dissolution in coral reefs (Cyronak et al. 2018; McMahon et al. 2013; Shaw et al. 2015). The slope of the second ebb tide (0.6) suggests a similar contribution of aerobic respiration and sulfate reduction to creek carbonate dynamics. The steeper slope value for all samples at Creek 1 compared to Creek 2 may be due to
connectivity with the adjacent fringing reefs or that mangroves along the coastline in Palau sit atop former reef flats and coral sands (Kauffman et al. 2011).

Figure 4.6 Salinity normalised TA ($n_{TA}$) versus DIC ($n_{DIC}$) and corresponding slope values for the first flood and ebb tides (“1st flood”, “1st ebb”), the second flood and ebb tides (“2nd flood”, “2nd ebb”) and for all data during each time series (“All data”) at the estuarine and fringing mangrove creeks. Dashed lines correspond to stoichiometric ratios of the processes that can control $n_{TA}$ and $n_{DIC}$: $AR$ aerobic respiration; $SR$ sulfate reduction; and $CD$ calcium carbonate dissolution. DIC and TA were normalised to the average salinity prior to and following the storm events for each creek.

Redox processes and rates of OM mineralisation in mangrove sediments are highly heterogeneous, controlled by a number of factors such as OM input and hydrology (see review by Kristensen et al. (2017). Average $p$CO$_2$, DIC and TA and were considerably higher
at Creek 1 than Creek 2 (> 100 %, 25 % and 16 % higher, respectively) and evidence suggests a tidal pumping (sediment) source of these inorganic parameters. Thus, it appears that the sediments at Creek 1 may have higher remineralisation rates than that of Creek 2, possibly due to increased supply of organic matter inputs, which is plausible given the high sediment load Airai Bay receives. Furthermore, pore-water residence time, which is hypothesised to control mangrove creek $pCO_2$ dynamics (Call et al. 2015), may differ between the creeks. Based on the hydrodynamics (i.e. semi-diurnal flushing; terrestrial water inputs) and higher pore-water exchange rates observed at the Creek 2, this may suggest lower pore-water residence times in sediments and may explain the lower $pCO_2$, DIC and TA.

4.4.2 Carbon outwelling

In a review of mangrove POC and DOC exchanges, Adame and Lovelock (2011) found that ten (of twelve) studies reported POC exports (maximum rate 65 mmol m$^2$ d$^{-1}$) and nine (of fourteen) studies reported DOC exports (maximum rate 32 mmol m$^2$ d$^{-1}$). Of these studies, POC exchange only correlated significantly with mean minimum temperature whilst DOC displayed no significant correlations with any of the environmental factors considered (i.e. latitude, temperature, precipitation, geomorphology, forest area, and mangrove species). Given sampling was conducted on consecutive days, rainfall was similar during both studies and the mangrove species were similar between sites, this study demonstrates the potential role of geomorphology as a driver of POC and DOC exchanges. Export rates for Creek 1 are within previously published ranges (Maher et al. 2018; Maher et al. 2013a; Sippo et al. 2016; Taillardat et al. 2018a) and similar to global averages (Adame and Lovelock 2011; Alongi 2014; Bouillon et al. 2008). However, the POC and DOC export rates at Creek 2 were considerably lower than Creek 1, which were 27-fold and 4-fold higher, respectively (Figure 4.3).
DIC exports have recently been suggested as a major term in carbon budgets but only a few studies have attempted to quantify exports (Bouillon et al. 2008; Maher et al. 2018; Maher et al. 2013a; Ray et al. 2018). The DIC export rate from Creek 1 (79.0 mmol m\(^{-2}\) d\(^{-1}\); Figure 4.3) is similar to the average rate of 59 mmol m\(^{-2}\) d\(^{-1}\) reported by Sippo et al. (2016) from six different sites (including micro-, meso-, and macro-tidal systems) spanning 12 ° to 38 ° S in Australia. But the rate is considerably lower than that reported by Maher et al. (2013a) from a micro-tidal mangrove creek (27 ° S) and the global estimate of Bouillon et al. (2008), both ~ 250 mmol m\(^{-2}\) d\(^{-1}\). More recently, Taillardat et al. (2018a) reported the highest DIC exports rates from a meso-tidal mangrove creek in Vietnam, varying from 350 to ~ 680 mmol m\(^{-2}\) d\(^{-1}\) over a lunar tidal cycle. Apart from DIC imports reported for two mangrove creeks (3 and 97 mmol m\(^{2}\) d\(^{-1}\)) by Sippo et al. (2016), the export rate from the Creek 2 (~ 3 mmol m\(^{-2}\) d\(^{-1}\)) is the lowest reported.

The average CO\(_2\) flux rate at Creek 1 (~ 83 mmol m\(^{-2}\) d\(^{-1}\)) was more than double that at Creek 2 (~ 32 mmol m\(^{2}\) d\(^{-1}\), Figure 4.3), driven largely by the difference in \(p\)CO\(_2\) between the creeks (average temperature and transfer velocity were similar for both creeks, Table 4.1) which was, on average, > 100 % higher at Creek 1 than Creek 2 (Table 4.1). The contribution of CO\(_2\) efflux to total carbon exports was similar to that of DIC (~ 37 % and 39 %, respectively) at Creek 1, yet at Creek 2, CO\(_2\) efflux was the major term (63 %) whilst DIC contributed 20 % (Figure 3). Contribution of DOC exports was the same at both creeks (16 %) and POC was the minor export term (8 % at Creek 1 and 1 % at Creek 2). Taillardat et al. (2018a) reported varying contributions of DIC (69 to 82 %), CO\(_2\) emission (9 to 32 %) and DOC (4 to 8 %) from a tropical meso-tidal mangrove creek in the dry season driven by diurnal inequality in tidal amplitudes and symmetry, however, no POC exports were reported. In a sub-tropical micro-tidal estuarine mangrove creek, Maher et al. (2013a) reported POC
imports and an order of magnitude difference between the export rate of DIC (~ 250 mmol m$^2$ d$^{-1}$) and DOC (~ 25 mmol m$^2$ d$^{-1}$).

Overall, carbon exports and emissions have been shown to vary considerably over lunar cycles (i.e. the transition from spring to neap tides) and between seasons (i.e. wet versus dry) in mangrove creeks (Call et al. 2015; Rosentreter et al. 2018a; Taillardat et al. 2018a; Taillardat et al. 2018b). Whilst this study is limited in that it reports carbon outwelling and CO$_2$ fluxes over a ~ 25 hr period during neap tides and the monsoon storm season, our data demonstrates the considerable heterogeneity of mangroves creeks that are in close proximity and subject to similar weather conditions but in differing geomorphological settings. Results from Creek 1 are in general agreement with the literature, which is likely due to most studies that have estimated the various pathways of the mangrove carbon cycle (and indeed mangrove carbon budgets) have been from mangroves located in estuarine complexes. However, the net exports of DIC, DOC and POC and the emission of CO$_2$ from Creek 2 were considerably lower than Creek 1 and the relative contribution of each parameter differed. Differences appear to be related to the supply of OM, the residence time of pore-waters in sediments and connectivity (and associated flushing) with marine water. We suggest further estimates of combined exports of POC, DOC, DIC and CO$_2$ emissions from mangroves creeks is required to capture the heterogeneity of these systems which may have implications on global mangrove carbon budgets and outwelling estimates from mangrove forests.
Chapter 5 Coupling infrared gas analysis and cavity ring down spectroscopy for autonomous, high temporal resolution measurements of DIC and δ\textsuperscript{13}C-DIC


Abstract

A new approach to autonomously determine concentrations of dissolved inorganic carbon (DIC) and its carbon stable isotope ratio (δ\textsuperscript{13}C-DIC) at high temporal resolution is presented. The simple method requires no customised design. Instead it uses two commercially available instruments currently used in aquatic carbon research. An inorganic carbon analyser utilising non-dispersive infrared detection (NDIR) is coupled to a Cavity Ring-down Spectrometer (CRDS) to determine DIC and δ\textsuperscript{13}C-DIC based on the liberated CO\textsubscript{2} from acidified aliquots of water. Using a small sample volume of 2 ml, the precision and accuracy of the new method was comparable to standard isotope ratio mass spectrometry (IRMS) methods. The system achieved a sampling resolution of 16 mins, with a DIC precision of ± 1.5 to 2 μmol kg\textsuperscript{-1} and δ\textsuperscript{13}C-DIC precision of ± 0.14 ‰ for concentrations spanning 1000 to 3600 μmol kg\textsuperscript{-1}. Accuracy of 0.1 ± 0.06 ‰ for δ\textsuperscript{13}C-DIC based on DIC concentrations ranging from 2000 μmol kg\textsuperscript{-1} to 2230 μmol kg\textsuperscript{-1} was achieved during a laboratory-based algal bloom experiment. The high precision data that can be autonomously obtained by the system should enable complex carbonate system questions to be explored in aquatic sciences using high temporal resolution observations.
5.1 Introduction

Dissolved inorganic carbon (DIC) is an important component of the evolving global carbon cycle, with ~ 26 % of yearly anthropogenic carbon dioxide (CO₂) emissions stored as DIC in the global ocean (Le Quéré et al. 2015). This influx of carbon to the oceans has resulted in increased field-monitoring (Sabine et al. 2010), laboratory-based experiments of how changing seawater carbonate chemistry effects biological process (Gattuso and Hansson 2011), as well as the development of new measurement technologies (Byrne 2014; Martz et al. 2015). Currently, the spatial and temporal coverage of paired DIC and carbon stable isotope ratio (δ¹³C-DIC) measurements is poor (Becker et al. 2016). However, greater interest is being placed on the coupled high-resolution measurement of DIC and δ¹³C-DIC as it can provide insights into the processes controlling DIC concentrations, helping elucidate flows of carbon within and between reservoirs (Bass et al. 2014b).

Whilst a variety of methods to autonomously measure DIC concentrations have been developed (Bandstra et al. 2006; Fassbender et al. 2015; Huang et al. 2015; Liu et al. 2013) the conventional method for determining δ¹³C-DIC requires discrete samples to be collected and stored prior to acidification and analysis in a laboratory by isotope ratio mass spectrometry (IRMS). IRMS analysis offers high precision, however, the collection, handling and preservation of discrete samples may introduce sampling artefacts and reduce accuracy (Li and Liu 2011; Taipale and Sonninen 2009). Furthermore, the laborious process limits sampling frequency, resulting in low temporal and spatial coverage of coupled DIC and δ¹³C-DIC measurements.

High resolution, field-based measurement of CO₂ and its carbon stable isotope value (δ¹³C-CO₂) is now achievable via laser spectroscopy systems such as Cavity Ring-Down Spectrometers (CRDS) (Crosson 2008) and Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) (Baer et al. 2002), with precision and accuracy comparable to laboratory-based
IRMS (Berryman et al. 2011; Midwood and Millard 2011; Vogel et al. 2013). The use of CRDS in the aquatic environment is becoming more prevalent with CRDS successfully coupled to air-water equilibrators for on-site, high-resolution measurement of dissolved CO₂ and its isotopic composition (Becker et al. 2012; Maher et al. 2013b). Recently, Bass et al. (2012) coupled a CRDS to a customised acidification interface utilising expanded polytetrafluoroethylene (ePTFE) tubing to measure in-situ concentrations of DIC and its δ¹³C-DIC. The permeable membrane based equilibration system autonomously measured DIC and δ¹³C-DIC at 15 minute intervals to a precision of ± 10 µmol kg⁻¹ and ± 0.2 ‰ respectively, and has been shown to be sufficient for identifying spatial and short-term temporal variability in DIC concentrations in a variety of aquatic systems (Bass et al. 2014a; Bass et al. 2014b; Bass et al. 2013). However, a precision of ~2 µmol kg⁻¹ or better is required in order to assess other processes such as long-term anthropogenic-induced changes to oceanic carbon chemistry (Newton et al. 2014) or in laboratory-based experiments when trying to detect small changes in DIC.

This paper presents an alternative approach to autonomously determine concentrations of DIC and δ¹³C-DIC. The simple method does not require the need to design or replicate a customised system. Instead, it couples two commercially available instruments, an inorganic carbon analyser utilising non-dispersive infrared detection (NDIR) and a CRDS. The system can be automated, is low maintenance, and achieves a sampling resolution of ~16 mins. Using only a small sample volume (2 ml), the method achieves high precision and accuracy comparable to traditional IRMS techniques.
5.2 Materials and procedures

5.2.1 Approach

Two commercially available instruments, an Autonomous Infra Red Inorganic Carbon Analyser (AIRICA, Marianda Company, Kiel, Germany), and a CRDS (Picarro G2201-i, Picarro Inc., Santa Clara, CA, USA) were coupled to autonomously measure concentrations of DIC and its carbon stable isotope ratio ($\delta^{13}$C-DIC) based on the CO$_2$ extracted from acidified samples (Figure 5.1). These instruments offer high precision and accuracy, and are currently used in aquatic carbon research. To test the response of the method, here-in termed AIRICA-CRDS, laboratory-based experiments on precision were conducted as well as a mesocosm experiment simulating an algal bloom in coastal waters.

Figure 5.1 Schematic of the coupled Autonomous Infra Red Inorganic Carbon Analyser (AIRICA) and Cavity Ring Down Spectrometer (CRDS) set up to autonomously and continuously measure DIC concentrations and $\delta^{13}$C-DIC values. Solid arrows indicate liquid flow and dashed arrows indicate gas flow. SP = syringe pump.
5.2.2 Instrumentation

The AIRICA system determines DIC to within ± 1.5 to 2 μmol kg⁻¹ (0.1 %) based on the NDIR gas analysis method (Goyet and Snover 1993; O’Sullivan and Millero 1998).

Briefly, the AIRICA’s high precision syringe pump draws a sample into a stripper that is pre-loaded with acid, effectively reducing the sample pH below 4.5 and converting all DIC to CO₂. A carrier gas strips the CO₂ from the acidified sample and the gas stream flows through a Peltier-element cooled condenser, followed by a Nafion dryer (both reducing water vapour content) before measurement by a NDIR analyser (LI-COR LI-7000, LI-COR Inc., Lincoln, NE, USA). DIC concentrations are determined by integrating the CO₂ mixing ratio signal in the NDIR analyser over the integration period, with the area versus concentration relationship established by 5-point calibration using in-house standards. The calibration factor was validated against Dickson certified reference materials (CRMs; Batch # 136, DIC 2021.15 μmol kg⁻¹, Sal 33.678). The carrier gas used comprised of instrument air (as opposed to CO₂-free carrier gas), with a background CO₂ mixing ratio of 289 ppm and a δ¹³C-CO₂ of -10.1 ‰. This carrier gas was used as the CRDS requires a gas with a similar composition to air.

Furthermore, as the lower specified concentration range of the CRDS is ~ 380 ppm, to achieve the precision and accuracy obtained by the AIRICA-CRDS from the CO₂ extracted from a small sample (2 ml), the background CO₂ enables accurate measurement of a δ¹³C-CO₂ over a greater proportion of the integration period (discussed below).

The CRDS uses a laser-based spectroscopic technique that measures the individual carbon isotopologues (¹²C and ¹³C) of CO₂ at ~ 1 Hz and converts to standard δ¹³C (‰) notation (referenced to Vienna PeeDee Belemnite). When the instrument is set in the CO₂ isotope only operating mode as used in this experiment (the CRDS can also simultaneously determine the carbon stable isotope ratio of methane), the guaranteed precision of the instrument by the manufacturer is 0.05 % for the CO₂ concentration (ppm) and 0.12 ‰ for
δ^{13}C (1σ, 5 min average) spanning 380 to 2000 ppm. δ^{13}C-DIC was determined using the δ^{13}C values of the extracted CO2 measured during the integration period (see Determination of δ^{13}C-DIC).

The coupling of the two instruments was achieved by simply linking the outlet of the AIRICA’s NDIR analyser with the inlet of the CRDS using polyethylene lined Bev-A-Line® IV (1/8” ID, 1/4” OD) tubing (Figure 5.1). A vent ensured no pressure build up at the inlet of the CRDS or backpressure on the AIRICA as the gas flow rate for the AIRICA varied from 70 to 300 ml min^{-1} (discussed below), while the CRDS has a flow rate of ~ 35 ml min^{-1}. An additional drying agent (magnesium perchlorate) was used to dry the gas stream prior to entering the CRDS to minimise any potential artefacts in isotope values introduced by uncertainties in the manufacturers in-built water vapour corrections (Nara et al. 2012). Magnesium perchlorate was used as it does not induce a delay in CO2 response time as is the case with some other desiccants (e.g. Drierite) (Webb et al. 2016).

To maximise precision and accuracy, DIC and δ^{13}C-DIC were determined from separate injections. The measurement parameters were customised for each analysis such that the integration period for DIC and δ^{13}C-DIC were 100 s and 310 s respectively. Therefore, in order to achieve autonomous measurement of DIC and δ^{13}C-DIC, a computer script using AutoIt (Carvalho 2017) was developed to autonomously modify the AIRICA’s operating parameters at pre-determined time intervals without the need for an operator (the computer script is supplied in Appendix 2). The script was sequenced so that a single measurement cycle consisted of the AIRICA system acidifying three aliquots of sample. The first aliquot was used to flush the system, the second aliquot was to determine DIC concentration, and the third aliquot was to determine δ^{13}C-DIC. The system was flushed with carrier gas between each aliquot to remove the excess CO2 and return to carrier gas concentrations. The cycle was then repeated, achieving a DIC and δ^{13}C-DIC measurement, on average, every ~ 16 minutes.
(refer to Figure 5.2 for a depiction of the typical CRDS output for a single measurement cycle).

![Typical output from the CRDS showing 3 measurements cycles for $^{13}$CO$_2$ (top) and $^{12}$CO$_2$ (bottom). An individual measurement cycle consists of the AIRICA system acidifying 3 aliquots of water. The first is a rinse, the second used to determine DIC concentration, and the third to determine $\delta^{13}$C-DIC.](image)

**Figure 5.2** Typical output from the CRDS showing 3 measurements cycles for $^{13}$CO$_2$ (top) and $^{12}$CO$_2$ (bottom). An individual measurement cycle consists of the AIRICA system acidifying 3 aliquots of water. The first is a rinse, the second used to determine DIC concentration, and the third to determine $\delta^{13}$C-DIC.

### 5.2.3 Procedure

To determine DIC, the AIRICA’s syringe pump was rinsed twice with 2100 µl of sample (filled and emptied at 300 µl s$^{-1}$) with the first rinse going directly to waste and the second rinse wasted via the stripper (Figure 5.1). The syringe pump then drew 2000 µl of
sample at 200 µl s⁻¹ which was then injected at 80 µl s⁻¹ into the stripper to which two drops of 10 % H₃PO₄ had been added. With a carrier gas flow rate through the stripper set a 300 ml min⁻¹, DIC concentrations were determined from integrating the CO₂ mixing ratio signal in the LICOR during an integration period of 100 s. The system was then flushed with carrier gas at 150 ml min⁻¹ to purge the liberated CO₂ from the system and return to carrier gas values prior to δ¹³C-DIC sampling. Sampling volume for δ¹³C-DIC was the same as for DIC, however, to obtain a longer integration period the following AIRICA parameters were adjusted: the rate the sample was injected from the syringe pump to the stripper (i.e. injection rate) was reduced to 15 µl s⁻¹ (from 80 µl s⁻¹); the carrier gas flow rate through the stripper was reduced to 70 ml min⁻¹ (from 300 ml min⁻¹); and the integration period was increased to 310 s (from 100 s). δ¹³C-DIC was determined from the δ¹³C-CO₂ data measured at ~ 1Hz during the integration period (discussed below). After the sampling for δ¹³C-DIC was completed, the cycle was restarted autonomously using the custom AutoIt script.

5.2.4 Determination of δ¹³C-DIC

The δ¹³C-CO₂ of the gas stream is a function of the carrier gas and that of the liberated CO₂ from the acidified sample (Eq. 1):

\[ \delta^{13}C_{\text{total}} = (\delta^{13}C_{\text{carrier}} \times \frac{\text{CO}_2\text{carrier}}{\text{CO}_2\text{total}}) + (\delta^{13}C_{\text{sample}} \times \frac{\text{CO}_2\text{sample}}{\text{CO}_2\text{total}}) \]  

(1)

whereby

\[ \frac{\text{CO}_2\text{carrier}}{\text{CO}_2\text{total}} = \frac{\text{CO}_2\text{carrier}}{\text{CO}_2\text{total}} \]

\[ \frac{\text{CO}_2\text{sample}}{\text{CO}_2\text{total}} = \frac{\text{CO}_2\text{sample}}{\text{CO}_2\text{total}} \]

\[ \text{CO}_2\text{sample} = \text{CO}_2\text{total} - \text{CO}_2\text{carrier} \]

where \( \delta^{13}C_{\text{total}} \) is the \( \delta^{13}C\)-CO₂ of the measured gas stream CO₂ (‰); \( \delta^{13}C_{\text{carrier}} \) is the \( \delta^{13}C\)-CO₂ of the carrier gas CO₂ (‰); \( \text{CO}_2\text{carrier} \) is the \( ^{12+13}\text{CO}_2 \) concentration of the carrier gas (ppm);
\( \delta^{13}C_{\text{sample}} \) is the \( \delta^{13}C\text{-CO}_2 \) of the acidified sample (‰); \( \text{CO}_2\text{sample} \) is the \( ^{12+13}\text{CO}_2 \) concentration of the acidified sample (ppm); and \( \text{CO}_2\text{total} \) is the \( ^{12+13}\text{CO}_2 \) concentration of the measured gas stream (ppm).

The \( \delta^{13}C\text{-CO}_2 \) values of \( \text{CO}_2 \) concentrations less than 400 ppm were excluded due to the guaranteed specifications of the instrument spanning 380 to 2000 ppm. Of the remaining \( \delta^{13}C\text{-CO}_2 \) values, a mass balance was then used (to account for the \( \delta^{13}C \) value of the carrier gas) to determine a sample \( \delta^{13}C\text{-CO}_2 \) (i.e. \( \delta^{13}C_{\text{sample}} \)) value based on each measured \( \text{CO}_2 \) concentration (Eq. 2):

\[
\delta^{13}C_{\text{sample}} = \frac{\left( \delta^{13}C_{\text{total}} \times \text{CO}_2\text{total} \right) - \left( \delta^{13}C_{\text{carrier}} \times \text{CO}_2\text{carrier} \right)}{(\text{CO}_2\text{total} - \text{CO}_2\text{carrier})}
\]

Five iterations of outlier removal were conducted on the ~1 Hz \( \delta^{13}C_{\text{sample}} \) values, with removal of values with an absolute difference (versus the mean of all \( \delta^{13}C_{\text{sample}} \) values for the sample) greater than two times the standard deviation of the sample. The remaining \( \delta^{13}C_{\text{sample}} \) values were then averaged to determine the final \( \delta^{13}C\text{-DIC} \) value of the sample. All analysis was undertaken using Matlab (The Mathworks Inc., Natick, MA, USA) (see supplementary information for script).

5.2.5 Evaluation of precision and accuracy

\( \delta^{13}C\text{-DIC} \) standards were made using \( \text{Na}_2\text{CO}_3 \) for the isotopically heavy standard (-3.2 ± 0.1 ‰) and \( \text{K}_2\text{CO}_3 \) for the depleted standard (-26.8 ± 0.1 ‰) with both solids verified by IRMS using the international reference materials NBS-19 and LSVEC. The \( \text{Na}_2\text{CO}_3 \) solid was used to make a set of five standard solutions ranging from ~500 to ~3600 µmol kg\(^{-1}\) and one standard solution was made using the \( \text{K}_2\text{CO}_3 \) solid (~2000 µmol kg\(^{-1}\)). All standards were made by dissolving carbonate solids in ultra-pure water (18.2 Milli-Q\(^{®}\)). Precision was evaluated based on the standard deviation of at least six replicate measurements for each standard. Accuracy was tested by comparing AIRICA-CRDS \( \delta^{13}C\text{-DIC} \) values to IRMS
measured values from discrete samples collected during the bloom experiment (below). Both
the precision measurements and bloom experiments were undertaken in a temperature-
controlled laboratory with temperature ranging < 2 °C over the course of the experiments.

5.2.6 Algal bloom experiment

An algal bloom experiment was conducted to test the response of the method (Figure 5.1) over an ~ 8 day period. Seawater (salinity 35.69) was collected from a nearby beach
(28°49'22.01"S, 153°36'23.48"E) the morning the experiment commenced (19/01/2016). The
water was enriched with 64 μmol l⁻¹ each of nitrate (NO₃⁻) and orthosilicate (SiO₄³⁻), and 4
μmol l⁻¹ of orthophosphate (PO₄³⁻). In order to counteract the impact of the SiO₄³⁻ addition on
total alkalinity, 128 μmol l⁻¹ of hydrochloric acid (HCl) was added. The mesocosm was
incubated under high pressure sodium bulbs (400W Phillips Son T Agro) at ~ 200 μmol m⁻²
s⁻¹ for 18 hrs per day (12:00 am to 6:00 am). The surface of the incubation vessel was
covered with a transparent sheet of plastic film to inhibit evaporation and CO₂ exchange with
the atmosphere allowing for an interpretation of the results in terms of a closed system.
Macroalgae (Ulva sp.) and an additional dose of nutrients, were added to the sample water on
the 25/1/16 (10:00 am) to further enhance biological activity. To achieve unattended
sampling, incubated water was continuously recirculated through a sealed Schott bottle (250
ml) at ~ 1 l min⁻¹, from where the AIRICA’s high precision syringe pump drew the sample
(Figure 5.1). DIC and δ¹³C-DIC were sampled autonomously according to the procedure
outlined above. In order to evaluate the accuracy of the AIRICA-CRDS method, 19 discrete
samples for δ¹³C-DIC were collected throughout the bloom experiment for IRMS analysis.
The samples were generally collected at the start and end of the light period from the return
line of the recirculating system into 40 ml pre-combusted borosilicate vials, closed without
headspace by Teflon-lined septa screw caps, poisoned with 50 μl of saturated HgCl₂ solution
and stored at ~ 4 °C in the dark until analysis (within a week). The samples were also
analysed for $\delta^{13}$C-DOC to determine the isotopic composition of the carbon pool available for microbial respiration. Samples were analysed using an OI Aurora 1030W TOC analyser interfaced to a Thermo Delta V$^{\text{Plus}}$ Isotope Ratio Mass Spectrometer (IRMS) (Maher and Eyre 2011). Precision of $\delta^{13}$C-DIC and $\delta^{13}$C-DOC IRMS measurements were $\pm 0.1\%$ and $\pm 0.3\%$ respectively. Samples for DOC concentration were analysed using a Shimadzu (TOC-VCPH) analyser. Particulate organic carbon (POC, mostly representing phytoplankton) was sampled at the end of the experiment by filtering 150 ml of the incubated water through pre-combusted GF/F filters and dried ($60^\circ$C) before analysis. Macroalgae was sampled at the end of the experiment, dried ($60^\circ$C) and ground prior to analysis. The $\delta^{13}$C values of the macroalgae and the POC were measured in triplicate samples using a Thermo Flash EA coupled to a Delta V$^{\text{Plus}}$ IRMS ($\pm 0.1\%$). All $\delta^{13}$C values are reported based on the VPDB scale.

5.3 Results and discussion

5.3.1 Precision

The AIRICA-CRDS system exhibited a relatively small but detectable concentration effect on measured $\delta^{13}$C-DIC with an increase of $0.19\%$ observed from 1000 $\mu$mol kg$^{-1}$ to 3600 $\mu$mol kg$^{-1}$ (Figure 5.3a). It is unclear if this effect is an artefact of the system or if it can be explained by ingassing of isotopically lighter atmospheric CO$_2$ (due to the high total alkalinity to DIC ratio of the standards) during the making of standards. CO$_2$ ingassing would have a larger effect on lower concentration standards (making them more depleted) than higher concentration standards, which follows the pattern observed here (Figure 5.3a). Similarly, Bass et al. (2012) reported a concentration effect of $< 0.2\%$ increase from 1000 $\mu$mol kg$^{-1}$ to 2100 $\mu$mol kg$^{-1}$ and did not correct $\delta^{13}$C-DIC values as the observed effect was within the precision of internal calibration standards.
Figure 5.3 a) Concentration effect on $\delta^{13}$C-DIC data produced by the AIRICA-CRDS b) Uncertainty in $\delta^{13}$C-DIC versus DIC concentration.

The AIRICA-CRDS method had decreasing $\delta^{13}$C-DIC uncertainty with higher DIC concentrations (Figure 5.3b). Standard deviations of the isotopically heavy standards decreased from ± 0.17 ‰ at ~ 1000 µmol kg$^{-1}$ (n=6) to ± 0.07 ‰ at ~ 3600 µmol kg$^{-1}$ (n=8), however, below 1000 µmol kg$^{-1}$ standard deviations were relatively high (± 0.63 ‰ at 500 µmol kg$^{-1}$, n=6). For the isotopically lighter standard, the uncertainty was ± 0.17 ‰ at a DIC concentration of ~ 2000 µmol kg$^{-1}$ (Table 5.1). Bass et al. (2012) also reported decreasing uncertainty with increasing concentrations of DIC. Their membrane based equilibration system attained standard deviations < ± 0.2 ‰ for concentrations above 360 µmol kg$^{-1}$ using a sample volume of 350 mL and an equilibration time of 720 s. In comparison, AIRICA-CRDS achieved < ± 0.2 ‰ uncertainty at ~ 1000 µmol kg$^{-1}$ on a sample volume of 2 mL and an integration time of 310 s.
Table 5.1 $\delta^{13}$C values – IRMS (‰)

<table>
<thead>
<tr>
<th>Carbonate Standard 1 (Na$_2$CO$_3$)</th>
<th>$\delta^{13}$C – IRMS (‰)</th>
<th>$\delta^{13}$C DIC – AIRICA-CRDS (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard 1 (~500 µmol)</td>
<td>-3.2 ± 0.1 (n = 3)</td>
<td>-3.47 ± 0.63 (n = 7)</td>
</tr>
<tr>
<td>Standard 1 (~1000 µmol)</td>
<td>-3.77 ± 0.17 (n = 6)</td>
<td></td>
</tr>
<tr>
<td>Standard 1 (~1900 µmol)</td>
<td>-3.68 ± 0.16 (n = 57)</td>
<td></td>
</tr>
<tr>
<td>Standard 1 (~2800 µmol)</td>
<td>-3.60 ± 0.11 (n = 6)</td>
<td></td>
</tr>
<tr>
<td>Standard 1 (~3600 µmol)</td>
<td>-3.58 ± 0.07 (n = 8)</td>
<td></td>
</tr>
<tr>
<td>Carbonate Standard 2 (K$_2$CO$_3$)</td>
<td>-26.8 ± 0.1 (n = 3)</td>
<td>-26.67 ± 0.17 (n = 7)</td>
</tr>
<tr>
<td>Standard 2 (~2000 µmol)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To achieve the manufacturer guaranteed specifications of ± 0.12 ‰ $\delta^{13}$C-CO$_2$, CO$_2$ concentrations in the gas stream, which is a sum of the CO$_2$ in the carrier gas and the liberated CO$_2$ from the acidified sample, should be between 380 to 2000 ppm. The concentration of the liberated CO$_2$ is a function of the sample size, the injection rate, and the gas flow rate, each of which can be independently adjusted by the user through the AIRICA software. For $\delta^{13}$C-DIC measurements, the 2 ml of sample was injected into the stripper at 15 µl s$^{-1}$ and extracted with a carrier gas flow rate of 70 ml min$^{-1}$ (achieving a total measurement time of 310 s), resulting in the AIRICA-CRDS achieving an average precision of 0.14 ± 0.04 ‰ (n = 84) for all standards above 1000 µmol kg$^{-1}$. While I optimised the system for coastal and oceanic DIC concentrations, if sampling low DIC concentrations (i.e. < 1000 µmol kg$^{-1}$), similarly precise $\delta^{13}$C-DIC values may be achievable if, for example, a larger syringe volume is used to increase sample size. This ability for customisation adds to the functionality of the AIRICA-CRDS system. In comparison to the AIRICA-CRDS reported here, a worldwide proficiency test of $\delta^{13}$C-DIC analysis found laboratory precision ranged from 0.1 to 0.5 ‰ depending on different methodologies (Van Geldern et al. 2013). However, the inter-
laboratory results revealed average standard deviations of ± 0.45 ‰ and ± 0.47 ‰ for δ¹³C-DIC values for lake water and seawater measurements respectively.

5.3.2 Accuracy

Accuracy of the AIRICA-CRDS δ¹³C-DIC was determined by direct comparison with IRMS measurements collected simultaneously during the algal bloom experiment (Figure 5.4). The average difference in measured δ¹³C values between methods was 0.1 ± 0.06 ‰ which is similar to the accuracy of the IRMS (0.1 ‰). This robust relationship was based on DIC concentrations ranging from 1986 µmol kg⁻¹ to 2232 µmol kg⁻¹ (average 2129 µmol kg⁻¹) during the dynamic bloom experiment. This demonstrates that the automated AIRICA-CRDS system described here attains similar accuracy to IRMS δ¹³C-DIC measurements at typical coastal and oceanic DIC concentrations.

Figure 5.4 Comparison of ARICA-CRDS δ¹³C-DIC vs IRMS δ¹³C-DIC.

5.3.3 Bloom experiment

The performance of the AIRICA-CRDS to characterise changes in δ¹³C-DIC values and DIC concentrations in the marine environment is demonstrated by the algal bloom experiment (Figure 5.5a). A total of 664 DIC concentrations and 661 δ¹³C-DIC values were
autonomously measured during the ~ 8 day incubation. Concentrations of DIC ranged from 1965 to 2253 μmol kg\(^{-1}\) and \(\delta^{13}\)C-DIC ranged from 0.96 ‰ to -3.61 ‰.

Figure 5.5 a) \(\delta^{13}\)C-DIC values and DIC concentrations measured by the AIRICA-CRDS system during the ~ 8 day laboratory bloom experiment. Blue and red lines are 5 point averages for \(\delta^{13}\)C-DIC and DIC respectively. Black triangles are discrete IRMS \(\delta^{13}\)C-DIC values plotted for comparison. Shaded areas indicate dark incubations. Lower case letters indicate the sections used for Keeling plots (see Figure 5.6). Dotted line is when macroalgae (Ulva sp.) and additional nutrients were added. b) IRMS \(\delta^{13}\)C-DOC values and DOC
concentrations for discrete samples. Inset box displays IRMS δ\(^{13}\)C values for POC and Ulva sp.

The AIRICA-CRDS method captured a temporally inverse relationship between δ\(^{13}\)C-DIC values and DIC concentrations throughout the algal bloom experiment. During the first 3 days respiration was the dominant metabolic process releasing isotopically lighter DIC (originating from organic matter). Respiration increased the pool of DIC from ~ 1995 to ~ 2230 μmol kg\(^{-1}\) and simultaneously lowered δ\(^{13}\)C-DIC from ~ 0.7 ‰ to ~ -2.7 ‰. After 3 days diel cycling (light-dark) of DIC and δ\(^{13}\)C-DIC commenced, likely due to the time lag associated with primary producer biomass increase after the initial addition of nutrients. During daylight hours, photosynthetic production preferentially consumed the isotopically lighter \(^{12}\)CO\(_2\) component of the DIC pool, decreasing DIC concentrations and increasing δ\(^{13}\)C-DIC values. Conversely, during the dark hours, respiration increased DIC concentrations and decreased δ\(^{13}\)C-DIC values. Over the course of days 4, 5 and 6, overall net production drew down the DIC pool. On day 7 no dark incubation occurred resulting in a large photosynthetically-driven decrease in the DIC concentration from 2164 μmol kg\(^{-1}\) to 1965 μmol kg\(^{-1}\) and an increase of δ\(^{13}\)C-DIC from ~ -3.1 ‰ to ~ -1.7 ‰. Similar diel variations were observed for DIC and δ\(^{13}\)C-DIC in a mesocosm coral reef metabolism experiment (Bass et al. 2012).

5.3.4 Insights from high resolution DIC and δ\(^{13}\)C-DIC measurements

The AIRICA-CRDS’s high resolution measurements of δ\(^{13}\)C-DIC can provide insights into drivers of DIC in aquatic environments. To illustrate a potential application of the AIRICA-CRDS approach, Keeling plots are used to interpret carbon sources during a simulated algal bloom experiment. Keeling plots (Keeling 1958) visualize a simple two component mixing model and are commonly used to interpret sources of added carbon in
aquatic, terrestrial and atmospheric sciences (see Pataki et al. (2003) for details on underlying assumptions and types of regression models available). Using a Model II regression (which assumes significant errors in the measurement of both variables), the y-intercept of the regression between the inverse of DIC concentration (1/DIC) and $\delta^{13}$C-DIC estimates the isotopic composition of the carbon source. The approach has been used to determine the isotopic composition of the DIC source in various settings including freshwater lakes (Karlsson et al. 2007), coral reefs (Carvalho et al. 2015), mangroves (Maher et al. 2013a) and groundwaters (Porowska 2015).

The $\delta^{13}$C-DIC source values were estimated by Keeling plots for each linear increase (respiration) in DIC concentrations during the simulated algal bloom based on 5-point averages of measured DIC and $\delta^{13}$C-DIC (Figure 5.6). The uncertainty in the intercept (i.e. the $\delta^{13}$C-DIC source value) is dependent on the rate of change in DIC concentration during the dark incubation period (see Pataki et al. (2003) and references therein for regression formulations). Uncertainty decreased as the absolute change in DIC increased, achieving < 2 ‰ uncertainty when the change in DIC was greater than ~ 40 μmol kg$^{-1}$ (Figure 5.7). It is noted that the intercept uncertainty is much higher than the uncertainty for each $\delta^{13}$C-DIC and DIC value (± 0.14 ‰ and ± 1.5 to 2 μmol kg$^{-1}$ respectively). A Keeling plot based on DIC concentrations during dark incubation periods over the first three days (Figure 5.6a), produced a $\delta^{13}$C-DIC intercept value of -27.8 ± 1.2 ‰ which is similar to that of terrestrial C3 vegetation (Smith and Epstein 1971). In contrast, the $\delta^{13}$C-DIC intercept value for the final dark incubation of -17.4 ± 0.9 ‰ (Figure 5.6b) is similar to that of marine organic matter (OM). Thus, results suggest a distinct shift in the source of DIC during the course of the experiment, from terrestrially derived OM present in the sampled coastal seawater to marine derived OM at the end. This is likely due to a shift towards a dominance of marine
organic matter toward the end of the experiment as a result of the algal bloom and the added macroalgae (added on day 6, Figure 5.5).

Figure 5.6 Regressions of 1/DIC concentration vs. $\delta^{13}$C-DIC values (Keeling plots). Letters correspond with the linear increase in DIC concentrations shown in Figure 5.5a.

Figure 5.7 Relationship between Keeling intercept uncertainty and changes in DIC concentration. Higher changes in DIC resulted in lower uncertainties in Keeling plot interpretations.

The DOC results support my interpretation of a shift in the DIC source. DOC concentrations increased from 88 μmol kg$^{-1}$ at the beginning of the experiment to 364 μmol kg$^{-1}$ at the end. $\delta^{13}$C-DOC values decreased during the first 3 days of the experiment before increasing during the final ~2 days. Keeling plot intercepts based on DOC concentrations for the initial ~3 day period (-31.8 ± 1.5 ‰) and final ~2 day period (-17.6 ± 2 ‰) suggests a
distinct shift in the carbon source contributing to the DOC pool from a terrestrially derived
DOC source to a marine source. This is consistent with the shift observed in the DIC pool.
The IRMS $\delta^{13}$C-POC results for phytoplankton (-25.7 ‰) and macroalgae (i.e. Ulva sp., -
10.1 ‰) suggests a similar contribution of both sources to the final $\delta^{13}$C-DOC intercept value
of -17.6 ‰ and the $\delta^{13}$C-DIC value of -17.4 ‰. The AIRICA-CRDS system could similarly
be used to characterise the importance of various other processes, such as, the relative
importance of organic matter respiration versus carbonate dissolution as a source of DIC
from coastal systems (Carvalho et al. 2015) and the importance of allochthonous versus
autochthonous organic matter for supporting bacterial productivity (Guillemette et al. 2013).

5.4 Comments

The utility of the AIRICA-CRDS method for autonomous, high resolution
measurements of DIC and $\delta^{13}$C-DIC in a laboratory configuration has been demonstrated.
Yet, the simple system also has the capacity for field deployment. Both of the commercially
available instruments (coupled without any modifications to their hardware) have been used
in field-based studies. CRDS have been deployed in a range of environmental settings
including large research vessels (Bass et al. 2014b; Becker et al. 2012), vehicles (Maher et al.
2014), and small boats (Maher et al. 2015). Determination of DIC based on the NDIR gas
analysis method has been used to conduct continuous shipboard measurements (Friederich et
al. 2002; Hiscock and Millero 2005) and the AIRICA system has been deployed on research
vessels to determine concentrations of DIC from discrete samples (Balch et al. 2016; Bates et
al. 2014; Bates et al. 2013). Assuming access to an appropriate power source and suitable
environmental conditions to house the instruments, the AIRICA-CRDS system has potential
to be deployed in the field, however, further testing is required to test this capability.

The AIRICA-CRDS is an alternative system that enables autonomous, high resolution
measurements of DIC and $\delta^{13}$C-DIC with precision and accuracy comparable to traditional
IRMS techniques. In the described configuration, the system achieved a sampling resolution of 16 mins, with a DIC precision of ± 1.5-2 µmol kg\(^{-1}\) and \(\delta^{13}\)C-DIC precision of ± 0.14 ‰ for concentrations spanning 1000 to 3600 µmol kg\(^{-1}\). A change in DIC concentrations of ~ 40 µmol kg\(^{-1}\) was sufficient to obtain a precision of < 2 ‰ in source interpretations based on Keeling plots. Whilst I optimized the system for typical estuarine/marine DIC concentrations, the system has the potential to be optimised for other environments through changes to the syringe size, sample volume and injection speed. This ability for customisation adds to the functionality of the AIRICA-CRDS system, offering the potential to explore complex carbonate systems question across a range of aquatic settings.
Chapter 6 Conclusions and future directions

To synthesise the conclusions from this thesis, the research questions posed in the introduction are discussed below along with recommendations for future work. There are obviously many directions that I could suggest for future studies, particularly in the face of anthropogenic induced phenomena e.g. a warming climate, changing climate system, deforestation (mangroves included). Furthermore, the concepts I propose, such as the “seasonal pore-water pump” (Chapter 2), or the “first flush” hypothesis (Chapter 3) could indeed apply to other aquatic ecosystems located where large oscillations in seasonal rainfall or water stage occur (e.g. river systems subject to snow melt) or in other inter-tidal systems (e.g. salt marshes, inter-tidal mud flats). However, the future directions I suggest relate directly to the outcomes of the question(s) posed and are what I believe to be the next logical step in order to advance these studies.

1. Is pore-water a relevant source of CO2 and CH4 to the major tributaries of the Amazon river system during receding waters?

Chapter 2 showed that using a natural groundwater tracer can provide insights in to the groundwater-surface water connectivity in the central Amazon Basin. Indeed, the results confirm the heterogeneous nature of pore-water exchange that can occur at kilometre scales in rivers, and hundreds of metres in lakes. In rivers, upstream reaches appeared to be areas of increased pore-water exchanges where at the confluence of igarapés and the main channel. The contribution of pore-water exchange to CO2 supersaturation based on the use of $^{222}$Rn agreed well those estimates based on hydraulic conductivity and soil atmosphere CO2, however, my results (18-47% contribution) also reflect the variability of sources contributing to riverine CO2. A major outcome of this chapter is that my results suggest a direct link
between pore-water and riverine CH$_4$, supporting hypotheses that riverine CH$_4$ dynamics appear hydrology related.

The Amazon basin is a heterogeneous mix of aquatic environments that are subject to large seasonal oscillations in precipitation, water stage and connectivity. It is likely that pore-water/groundwater exchanges and its role in aquatic carbon cycling is highly variable, both spatially and temporally, across the Amazon basin and various aquatic systems. Future studies should attempt to quantify pore-water/groundwater to surface water exchanges and the contribution of this pathway to CO$_2$ and CH$_4$ supersaturation and indeed other carbon parameters such as DOC, DIC and TA. As discussed in Chapter 4, endmember values are an important source of uncertainty when estimating pore-water discharge rates and its contribution to surface water carbon dynamics. I regret that such data was not available for Chapter 2, thus future studies must aim to thoroughly characterise pore-water/groundwater endmembers and their composition (i.e. $p$CO$_2$, CH$_4$, DIC, DOC, TA) in order to quantitatively estimate the contribution of this pathway to carbon cycling in the Amazon. As a start, I suggest identifying an igarapé that has a well-defined catchment area, whereby a quantitative assessment of pore-water/groundwater discharge can be undertaken.

Similarly to Chapter 3, which characterises how hydroperiod effects pore-water to surface water exchanges and controls mangrove water CO$_2$ and CH$_4$ over lunar cycles, I suggest hydroperiod may drive CO$_2$ and CH$_4$ dynamics in tropical rivers systems over seasonal scales. The “seasonal pore-water pump” hypothesis can help guide future research efforts. Longitudinal surveys similar to my study could be attempted throughout the whole period of receding waters, from early receding to late receding, and also during the low water phase. Characterisation of the pore-water/groundwater endmembers (as discussed above) should occur concomitantly, to investigate any temporal variability (similar to the future research direction in suggest for Chapter 3 below). Indeed, a times series-approach could also
be employed to log potential seasonal changes in surface water $^{222}$Rn and carbon parameters (the aforementioned igarapé would be an ideal initial sampling location). Furthermore, the seasonal pore-water pump hypothesis should be also be tested in the wetlands and floodplains (which are hypothesised to contribute to riverine CO$_2$ and CH$_4$ supersaturation) that drain into the Amazon river system. Given the magnitude of the Amazon basin and the seasonal oscillations, quantifying the role of pore-water/groundwater exchanges and its contribution is an enormous challenge and I hope this initial study stimulates future research.

2. “Are fluxes of CO$_2$ and CH$_4$ higher from mangrove systems located nearer the equator?” and “how does hydroperiod (i.e. the frequency and duration of forest inundation) affect CO$_2$ and CH$_4$ fluxes over spring-neap cycles in macro-tidal mangrove systems?”

The estimated emissions of CO$_2$ from the macro-tidal mangrove creek located in the Amazon region of Brazil during the dry season (~ 1° S; 174 ± 129 mmol m$^{-2}$ d$^{-1}$) are amongst the highest reported for mangrove systems worldwide. Average CO$_2$ emissions of 200 mmol m$^{-2}$ d$^{-1}$ have been reported from micro-tidal mangroves located 23° south of the equator during the dry season (Call et al. 2015) and 240 mmol m$^{-2}$ d$^{-1}$ from a meso-tidal mangrove system located 10° north of the Equator, respectively (Taillardat et al. 2018b), suggesting no latitudinal trend in CO$_2$ emissions. However, this chapter showed that if the global dataset for mangrove CO$_2$ emissions is scaled by latitudinal region and tidal regime, global emissions would increase from 34.1 to 45.5 Tg C y$^{-1}$, with the 0 to 5° latitudinal band disproportionately contributing 38% to total emissions, despite containing only 30% of the world’s mangroves. No previous mangrove CO$_2$ (or CH$_4$) budget has attempted such an exercise and in doing so, highlighting large gaps in the global data set for mangrove CO$_2$ emissions, e.g. no data from macro-tidal mangroves in the 5 to 10° latitudinal band or micro-tidal mangroves in the 0 to 5° latitudinal band. The limitations of the scaling exercise
provides direction for future studies on mangrove carbon cycling e.g. if CO2 and CH4 budgets are to be constrained, an accurate estimate of the global mangrove area is required, which is a challenge given the ratio of flooded versus air exposed areas are constantly changing. Furthermore, mangroves span wide climatic regions and it became apparent that studies documenting the seasonality of CO2 (and CH4) emissions are few, particularly in the tropics where large seasonal oscillations in rainfall occur and have been shown to lead to higher flux rates during wet seasons.

Similarly to Chapter 2, which presented new data to explain riverine CH4 dynamics, Chapter 3 presents new observations which improves our current understanding of mangrove CH4 latitudinal distribution and budgets. The estimated emission of CH4 from my study (855 ± 406 μmol m−2 d−1) is the highest reported from mangroves globally, suggesting that, in addition to mangrove biomass, carbon burial and soil carbon stocks, CH4 supersaturation and fluxes appear to be higher in the lower latitudes. However, the global dataset for mangrove water-atmosphere CH4 fluxes is limited, preventing scaling of fluxes by tidal regime. There are no estimates from macro-tidal systems located in 5 to 20 ° latitudinal band (comprising 16 % of the global mangrove area), nor from meso-tidal systems in the 0 to 5 ° latitudinal band (comprising 21 % of the global mangrove area). Such areas should be targeted in future studies.

The conceptual model presented in Chapter 3, suggests hydroperiod drives mangrove creek water pCO2 and CH4 dynamics and associated fluxes in macro-tidal systems over spring-neap cycles. This link between the frequency and duration of mangrove forests in macro-tidal systems and enhanced CO2 and CH4 fluxes may also apply to DIC, DOC, TA and POC in such systems, however, no such studies have been attempted to test this hypothesis at the resolution studied here. This is partly due to methodological constraints which I addressed in Chapter 5 of this thesis with the development of a new methodology to autonomously
measure DIC at high resolution scales. Such a methodology could be deployed in future studies investigating DIC dynamics over spring-neap cycles (pending the future research direction I suggest for Chapter 5 below). Furthermore, I believe a time series approach to investigate pore-water compositional changes over spring-neap and seasonal scales in micro-, meso-, and macro-tidal systems would enhance our understanding of tidal pumping on mangrove carbon cycling. Current methods to sample pore-waters is a laborious, time consuming process, thus such a study would require innovative methodological development. Sediment properties (e.g. organic carbon content, accretion/burial rates, porosity, etc.) may influence tidal pumping and the associated exports of subterranean derived carbon to surface waters (as discussed in Chapter 4), thus, concomitant measurements of these components would aid the identification of any potential broad controls.

3. **Does the total carbon exported and the contribution of each carbon species (DIC, DOC, POC and CO2 efflux) vary considerably between mangroves located in differing geomorphological settings?**

In Chapter 4 I present the combined exports of POC, DOC, DIC and CO2 emissions from two mangroves located in the wet tropics. Despite being only ~ 2km apart, POC and $pCO_2$ were, on average, > 100 % higher and DOC, DIC and TA were 62 %, 25 %, 16 % higher, respectively, from Creek 1 (located within a semi-enclosed bay) than from Creek 2 (located along the coast adjacent to fringing reefs). Outwelling rates of POC, DIC and DOC and CO2 emissions were 27-fold, 8-fold, 4-fold and 3-fold higher at the estuarine creek. DIC outwelling (37 %) and CO2 emissions (39 %) were the major terms contributing to total carbon losses at Creek 1, whilst CO2 emission (61 %) was the major contributor at Creek 2. The differences appear to be related to the supply of organic matter (OM), the residence time of pore-waters in sediments, and the connectivity (and associated flushing) with marine water.
Whilst no broad scale trends can be determined based on the timeframe of this study, the contrasting export results between the two mangrove creeks demonstrate the high variability that can occur from systems located in differing geomorphological settings, and clearly demonstrates the heterogeneity of mangroves. This is only the second study to estimate the combined exports of DIC, DOC, POC, TA and emission of $p$CO$_2$ from mangrove ecosystems. If mangrove budgets are to be constrained, and if DIC is to be confirmed as the dominant form of carbon exported from mangroves (which was not observed at Creek 2), more studies estimating the combined exports of POC, DOC, DIC and CO$_2$ emissions from mangroves creeks are required. Similarly to Chapter 3 (as discussed above), I regret not having data on the sediment properties for each creek, thus the suggestion that this parameter be incorporated in future studies applies here also. Based on the spring-neap trends observed in Chapter 3, ideally, future studies would be conducted at those scales, and replicated during the different seasons in micro, meso and macro tidal systems. Such studies would be highly laborious and challenging, so I suggest initially targeting the systems located in the geographic regions (outlined in Table 3.3) e.g. meso-tidal systems in the 0 to 5° latitudinal band. If such in depth studies were conducted in mangroves spanning their wide distribution, potential controls on carbon outwelling may be identified (e.g. latitude, tidal regime, seasonality).

4. “Is it possible to integrate two commercially available instruments to autonomously determine concentrations of dissolved inorganic carbon (DIC) and its carbon stable isotope ratio ($\delta^{13}$C-DIC) at high temporal resolutions to provide insights into DIC dynamics?”

In a novel approach, the AIRICA-CRDS system I present in Chapter 5 enables autonomous, high resolution measurements of DIC and $\delta^{13}$C-DIC with precision and accuracy comparable to traditional IRMS techniques. By coupling two commercially
available instruments, I showed it is possible to autonomously determine DIC and $\delta^{13}$C-DIC at sampling resolutions of 16 min$^{-1}$ with a DIC precision of $\pm$ 1.5 to 2 µmol kg$^{-1}$ and $\delta^{13}$C-DIC precision of $\pm$ 0.14 ‰ (for concentrations spanning 1000 to 3600 µmol kg$^{-1}$) and an accuracy of $0.1 \pm 0.06$ ‰ for $\delta^{13}$C-DIC (based on DIC concentrations ranging from 2000 µmol kg$^{-1}$ to 2230 µmol kg$^{-1}$) which is required in order to assess long-term anthropogenic-induced changes to oceanic carbon chemistry.

The high resolution measurements can provide insights into drivers of DIC in aquatic environments, as shown in the algal bloom experiment. A distinct shift in the source of DIC during the course of the experiment was observed, from terrestrially derived OM present in the sampled coastal seawater to marine derived OM at the end. Previously unavailable, the high resolution capability of the AIRICA-CRDS offers exciting opportunities to explore complex carbonate systems where precise DIC measurements (~2 µmol kg$^{-1}$ or better) are required, for example, in laboratory based ocean acidification-related experiments. The next logical step for the development of this method is to test its capability in field-based experiments, which, if successful presents exciting opportunities to investigate DIC dynamics in a range of coastal and marine settings. Furthermore, the AIRICA-CRDS can be readily customised, offering the potential to be used in freshwater environments (i.e. rivers, wetlands), however, future studies are also required to test this capability with.
Appendix 1 Supplementary information for Chapter 5

Supplementary methods

*AutoIt computer script*

This script is based on timed mouse clicks and keyboard entries.

In order that the script works, the user needs to have a monitor with the same screen resolution as the one used in this case (1366 x 768 pixels).

If not, the parameters passed to the functions regarding positioning of mouse clicks will need to be changed in order that the script works properly.

This script deals entirely with the software controlling the AIRICA by means of automating its operation.

It consists of a large infinite loop (While 1 … WEND) that has two main parts: the first part optimizes sampling and analysis for concentration measurements, while the second part optimizes them for isotopic measurement.

```autoit
opt("Wintitlematchmode",1)

While 1
WinMove("AIRICA measurement","",0,0)
WinActivate("AIRICA measurement")

;************

;Start of first part of the script

;************
```
; clicking on edit sample list
MouseClick("left",50,180)
Sleep(1000)

; adding sample name
MouseClick("left",440,508)
Sleep(1000)
Send("\{BACKSPACE 50\} \{DEL 50\}")
Send("Sample")
Send(@YDAY&@HOUR&@MIN)
Sleep(500)
MouseClick("left",520,508)
Sleep(500)
MouseClick("left",645,508)
Sleep(1000)

; clicking on edit calculation mode
MouseClick("left",200,255)
Sleep(1000)
MouseClick("left",300,265)

Send("{BACKSPACE 5}{DEL 5}"")

Send("2")

Sleep(1000)

MouseClick("left",320,305)

Sleep(1000)

Send("{UP 10}"")

Send("{ENTER}" )

MouseClick("left",475,305)

Sleep(1000)

Send("{ENTER}" )

Sleep(1000)

;clicking on edit extraction parameters

MouseClick("left",175,325)

Sleep(1000)

MouseClick("left",645,175)

Send("{BACKSPACE 5}{DEL 5}"")

Send("210")

Sleep(500)
MouseClick("left",645,200)
Send("{BACKSPACE 5} {DEL 5}"
Send("50")
Sleep(500)
MouseClick("left",645,225)
Send("{BACKSPACE 5} {DEL 5}"
Send("60")
Sleep(500)
MouseClick("left",645,250)
Send("{BACKSPACE 5} {DEL 5}"
Send("0")
Sleep(500)
MouseClick("left",645,370)
Send("{BACKSPACE 5} {DEL 5}"
Send("80")
Sleep(500)
MouseClick("left",645,418)
Send("{BACKSPACE 5} {DEL 5}"
Send("2")
Sleep(500)
MouseClick("left",645,440)
Send("{DOWN 5} {UP}")
Send("{ENTER}")
MouseClick("left",635,535)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
Send("{ENTER}")
Sleep(1000)

;click on set flow parameter
MouseClick("left",910,85)
Sleep(1000)
MouseClick("left",630,325)
Send("{BACKSPACE 5} {DEL 5}")
Send("300")
MouseClick("left",630,388)
Sleep(1000)
Send("{ENTER}")
Sleep(1000)
;click on set blank
MouseClick("left",560,85)
Sleep(1000)
MouseClick("left",500,420)
Send(" {BACKSPACE 10} {DEL 10} ")
Send("2")
MouseClick("left",595,430)
Sleep(1000)

;clicking on sample to start measurement
MouseClick("left",224,134)
Sleep(1000)
MouseClick("left",95,95)
Sleep(1000)
Send(" {ENTER} ")
Sleep(1000)
Send(" {ENTER} ")
Sleep(1000)
; monitoring a pixel in order to deal with different analysis times, if necessary

Sleep(10*1000)

$TargetPixelColor = PixelGetColor(268,63)

While $TargetPixelColor <> 6684444
    Sleep(5000)
    $TargetPixelColor = PixelGetColor(268,63)
WEnd

Sleep(20*1000)

; ************
; Start of second part of the script
; ************

; clicking on edit sample list

WinMove("AIRICA measurement","",0,0)

WinActivate("AIRICA measurement")

MouseClicked("left",50,180)

Sleep(1000)

; adding sample name
MouseClick("left",440,508)
Sleep(1000)
Send("{BACKSPACE 50} {DEL 50}")
Send("Sample")
Send(@YDAY&@HOUR&@MIN)
Sleep(500)
MouseClick("left",520,508)
_sleep(500)
MouseClick("left",645,508)
Sleep(1000)
;clicking on edit calculation mode
MouseClick("left",200,255)
Sleep(1000)
MouseClick("left",300,265)
Send("{BACKSPACE 5} {DEL 5}")
Send("1")
Sleep(1000)
MouseClick("left",320,305)
Sleep(1000)
Send("\{UP 10\}"")
Send("\{ENTER\}"")

MouseClick("left",475,305)
Sleep(1000)
Send("\{ENTER\}"")
Sleep(1000)

;clicking on edit extraction parameters

MouseClick("left",175,325)
Sleep(1000)
MouseClick("left",645,175)
Send("\{BACKSPACE 5\} \{DEL 5\}"")
Send("380")
Sleep(500)
MouseClick("left",645,200)
Send("\{BACKSPACE 5\} \{DEL 5\}"")
Send("25")
Sleep(500)
MouseClick("left",645,225)
Send("\{BACKSPACE 5\} \{DEL 5\}"
Send("45")

Sleep(500)

MouseClick("left",645,250)

Send("{BACKSPACE 5} {DEL 5}")

Send("0")

Sleep(500)

MouseClick("left",645,370)

Send("{BACKSPACE 5} {DEL 5}")

Send("15")

Sleep(500)

MouseClick("left",645,418)

Send("{BACKSPACE 5} {DEL 5}")

Send("1")

Sleep(500)

MouseClick("left",645,440)

Send("{UP 6}")

Send("{ENTER}")

MouseClick("left",635,535)

Sleep(1000)

Send("{ENTER}")
Sleep(1000)

Send("{ENTER}\"")

Sleep(1000)

;click on set flow parameter

MouseClick("left",910,85)

Sleep(1000)

MouseClick("left",630,325)

Send("{BACKSPACE 5}{DEL 5}\")

Send("70")

Sleep(1000)

MouseClick("left",630,388)

Sleep(1000)

Send("{ENTER}\")

Sleep(1000)

;click on set blank

MouseClick("left",560,85)

Sleep(1000)

MouseClick("left",500,420)
Send("\{BACKSPACE 10\} \{DEL 10\}")

Send("200")

Sleep(1000)

MouseClicked("left",595,430)

Sleep(1000)

; clicking on sample to start measurement

MouseClicked("left",224,134)

Sleep(1000)

MouseClicked("left",95,95)

Sleep(1000)

Send("\{ENTER\}")

Sleep(1000)

Send("\{ENTER\}")

Sleep(1000)

Sleep(10*1000)

$TargetPixelColor = PixelGetColor(268,63)

While $TargetPixelColor <> 6684444
    Sleep(5000)
$\text{TargetPixelColor} = \text{PixelGetColor}(268,63)$

WEnd

MouseClick("left",938,124)

Sleep(1000)

MouseClick("left",670,405)

Send("\{BACKSPACE 10\} \{DEL 10\}")

Send("300")

Sleep(8000)

MouseClick("left",765,400)

Sleep(1000)

Sleep(50*1000)

WEnd
Matlab script

%1) Remove headers from PICARRO output csv (see PICARRO_out.csv for details)

%2) Replace comma by space in PICARRO output csv

%3) Remove occasional 'Z' in last line of PICARRO output csv

%4) PICARRO output csv has to start below peak cut-off def., i.e. pCO2 below 400

%5) Remove any prolonged portions above the cut-off def., which

%are not associate to peaks from seawater injections

%(e.g. measurements of laboratory air). Otherwise those parts will be

%identified as peaks and inflate the matrix.

%6) Delta13C_DIC values for the large CRDS injections and

%corresponding times are stored in a matrix called 'FinalOutput'

clear all

close all

fread='PICARRO_out.csv';  %name of PICARRO input csv in same folder as

%this script

%means of carrier gas (instrument air) C12 and C13 concentrations
% and isotopic signature determined from several hours of continuous measurements

carriergas12=285.8;
carriergas13=3.181;
carriergasdelta=-10.09;

% BE CAREFUL WHEN MAKING CHANGES BEYOND THIS POINT

%----------------------------------------------------------

[DATE TIME AMPM FRAC_DAYS_SINCE_JAN1 FRAC_HRS_SINCE_JAN1
JULIAN_DAYS EPOCH_TIME ALARM_STATUS INST_STATUS CavityPressure
CavityTemp WarmBoxTemp EtalonTemp DasTemp MPVPosition solenoid_valves
OutletValve MeasurementMode species HP_12CH4 HP_12CH4_dry HP_13CH4
HR_13CH4 Delta_iCH4_Raw HP_Delta_iCH4_Raw HP_Delta_iCH4_30s
HP_Delta_iCH4_2min HP_Delta_iCH4_5min HR_12CH4 HR_12CH4_dry
HR_Delta_iCH4_Raw HR_Delta_iCH4_30s HR_Delta_iCH4_2min HR_Delta_iCH4_5min
ChemDetect H2O X12CO2 X12CO2_dry X13CO2 Delta_Raw_iCO2 Delta_30s_iCO2
Delta_2min_iCO2 Delta_5min_iCO2 peak87_baseave_spec peak88_baseave peakheight_5
peak0_spec ch4_splinemax peak30_spec peak_30]=textread(fread,'%s %s %s %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %
fclose('all')

%normalize time axis to beginning of experiment on Jan 19th 12:00

time=JULIAN_DAYS-19.5;

%find all 12C data above 400ppm and the start and end point for each peak

pfsa=find(X12CO2>400);

dpfsa=find(diff(pfsa)>10);

%Compiling peak area data in a single matrix each

peaks12=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;

peaks13=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;

deltaC=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;

peakstime=ones(max(diff(dpfsa)),round(length(dpfsa)))*NaN;

peaklength(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=(pfsa(dpfsa(1))-pfsa(1)+1);
peaks12(1:(pfsa(dpfsa(1))-pfsa(1)+1))=X12CO2([pfsa(1):pfsa(dpfsa(1))]);

peaks13(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=X13CO2([pfsa(1):pfsa(dpfsa(1))]);

deltaC(1:(pfsa(dpfsa(1))-pfsa(1)+1),1)=Delta_Raw_iCO2([pfsa(1):pfsa(dpfsa(1))]);

peakstime(1:(pfsa(dpfsa(1))-pfsa(1)+1))=time([pfsa(1):pfsa(dpfsa(1))]);

for i=2:length(dpfsa)

    peaks12(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ... 
        X12CO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);

    peaks13(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ... 
        X13CO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);

    deltaC(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ... 
        Delta_Raw_iCO2([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);

    peakstime(1:(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1),i)= ... 
        time([pfsa(dpfsa(i-1)+1):pfsa(dpfsa(i))]);

    peaklength(i)=(pfsa(dpfsa(i))-pfsa(dpfsa(i-1)+1)+1);

end

deltaC_added=((peaks12+peaks13).*deltaC-(carriergas12+ ... 

carriergas13)* ... 

carriergasdelta)./(peaks12+peaks13-carriergas12- ...
carriergas13);

mean_peaktime=nanmean(peakstime);

%filter for outliers, i.e. off by more than 2 std in comparison to
%mean

deltaC_mean=nanmean(deltaC_added);
deltaC_std=nanstd(deltaC_added);
deltaC_added_it1=deltaC_added;

for i=1:length(dpfsa)
    deltaC_added_it1(find(abs(deltaC_mean(i)-deltaC_added(:,i)) >
    abs(deltaC_std(i).*2)),i)=NaN;
end

deltaC_mean_it1=nanmean(deltaC_added_it1);
deltaC_std_it1=nanstd(deltaC_added_it1);
second iteration

\[ \text{deltaC\_added\_it2} = \text{deltaC\_added\_it1} ; \]

for \( i = 1 : \text{length(dpfsa)} \)

\[ \text{deltaC\_added\_it2}(\text{find}( \text{abs(\text{deltaC\_mean\_it1}(i) - \text{deltaC\_added\_it1(:,i)))} > \text{abs(\text{deltaC\_std\_it1}(i) \times 2)})) , i) = \text{NaN} ; \]

end

\[ \text{deltaC\_mean\_it2} = \text{nanmean(\text{deltaC\_added\_it2})} ; \]
\[ \text{deltaC\_std\_it2} = \text{nanstd(\text{deltaC\_added\_it2})} ; \]

third iteration

\[ \text{deltaC\_added\_it3} = \text{deltaC\_added\_it2} ; \]

for \( i = 1 : \text{length(dpfsa)} \)

\[ \text{deltaC\_added\_it3}(\text{find}( \text{abs(\text{deltaC\_mean\_it2}(i) - \text{deltaC\_added\_it2(:,i)))} > \text{abs(\text{deltaC\_std\_it2}(i) \times 2))}, i) = \text{NaN} ; \]

end
deltaC_mean_it3=nanmean(deltaC_added_it3);
deltaC_std_it3=nanstd(deltaC_added_it3);

%%%%%final iteration

deltaC_added_final=deltaC_added;
deltaC_mean_final=deltaC_mean;
deltaC_std_final=deltaC_std;
for g=1:40
for i=1:length(dpfsa)
    deltaC_added_final(find(abs(deltaC_mean_final(i)-deltaC_added_final(:,i)) > abs(deltaC_std_final(i).*2)),i)=NaN;
end

deltaC_mean_final=nanmean(deltaC_added_final);
deltaC_std_final=nanstd(deltaC_added_final);
end

%distinguish between small peaks for DIC measurements and large for
%d13C_DIC

large = find(peaklength > 170 & peaklength < 450);
small = find(peaklength < 150 & peaklength > 25);

% create matrix with data for large peaks only
C12_pm_large = peaks12(:,large);
delta_pm_large = deltaC(:,large);
time_pm_large = peaktime(:,large);

% final output
% measurement time and isotopic composition
FinalOutput = [mean_peaktime(large) deltaC_mean_final(large)']

% some data visualization

figure
axes('Position',[0.15 0.5 0.8 0.4])

plot(time, X12CO2,'k')
ylabel('
\textsuperscript{12}CO_2 (ppmv)')

xlabel('Time since start of the Experiment')

text(7.695,-400, 'Please note the two small peaks (seawater injections for determination of DIC)')

text(7.695,-490, 'followed by a large peak (injection for determination of carbon isotope signature)')

axis([7.695 7.84 0 1000])

figure

axes('Position',[0.15 0.5 0.8 0.4])

plot(time_pm_large,C12_pm_large)

ylabel('
\textsuperscript{12}CO_2 (ppmv)')

xlabel('Time since start of the Experiment')
Large peaks as identified by the script, resulting from the slow seawater injection, and used for subsequent \( \delta^{13}C_{(Dickson)} \) calculations.'Interpreter','latex')

axis([7.695 7.84 0 1000])

figure

axes('Position',[0.15 0.5 0.8 0.4])

plot(mean_peakstime(large), deltaC_mean_final(large),'ko','MarkerFaceColor','k')

ylabel('\( \delta^{13}C_{(Dickson)} \) (\(^\circ/oo\))','Interpreter','tex')

xlabel('Time since start of the Experiment')

text(7.695,-3.4, 'Calculated \( \delta^{13}C_{(Dickson)} \), using the large peaks','Interpreter','latex')

axis([7.695 7.84 -3 -2])

end
Appendix 2 Co-authored publications

Briefly, the relevancy of the five additional co-authored publications that represent significant work I undertook during the course of my thesis is described below.


This study suggested tidal pumping was an important controller of \( pCO_2 \) and \( CH_4 \) in the mangrove dominated section of an urbanised subtropical estuary. \( CO_2 \) and \( CH_4 \) emissions estimated in-situ using floating chamber techniques found good agreement with emissions estimated using certain modelling approaches that accounted for current velocity, depth and wind.


This is the only study to estimate exports of DIC, DOC, TA and POC, and sources of atmospheric radiative forcing (i.e. emission of \( CO_2 \), \( CH_4 \) and \( N_2O \)) from a sub-tropical mangrove system. Of total carbon outwelling, DIC export to the adjacent coastal ocean was the major term and represents a significant long-term sink (in addition to carbon burial in mangrove sediments) of atmospheric greenhouse gases.

This study revealed that the mechanism of tidal pumping transports century-old sequestered carbon (i.e. blue carbon) from mangrove sediments to mangrove creek waters and beyond (i.e. adjacent aquatic systems) in the form of dissolved inorganic carbon.

Rosentreter, J.A., Maher, D.T., Ho, D.T., Call, M., Barr, J.G. and Eyre, B.D. (2017) Spatial and temporal variability of CO\textsubscript{2} and CH\textsubscript{4} gas transfer velocities and quantification of the CH\textsubscript{4} microbubble flux in mangrove dominated estuaries. Limnology and Oceanography 62, 561-578.

This study presented empirical models for calculating the gas transfer velocity ($k$) of CO\textsubscript{2} and CH\textsubscript{4} based on floating chamber experiments in conducted in six mangrove dominated estuaries. Accounting for current velocity, depth and wind, the models showed good agreement with those based on side-by-side tracer release experiments. The proposed parameterisations were used to estimate water-atmosphere CO\textsubscript{2} and CH\textsubscript{4} fluxes in Chapter 3 and Chapter 4 (CO\textsubscript{2} only) of this thesis.


This study constructed ~ 100 year geochronologies based on sediment cores from a sub-tropical mangrove system. Results suggests anthropogenic influence (i.e. wastewater discharge) and associated import of phosphorus to the mangrove creek may increase organic carbon burial.
References


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Johnson, M. S. and others 2008. CO$_2$ efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. Geophysical Research Letters 35.


Sioli, H. 1968. Hydrochemistry and Geology in the Brazilian Amazon Region.


