Terrestrial versus aquatic carbon fluxes in an agricultural coastal floodplain

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Terrestrial versus aquatic carbon fluxes in an agricultural coastal floodplain

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A thesis submitted in fulfillment of the degree of Doctor of Philosophy
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).

Signed ………………………………………………………… Date …27-5-2017………………
Abstract

There are many agricultural landscapes that have been developed in floodplains, containing an aquatic environment in the form of drainage canals that previous carbon budget analysis have not fully considered. Understanding the contribution of different flux components in ecosystem carbon budgets is crucial for monitoring how the carbon cycle respond to environmental change. Furthermore, our mechanistic understanding aquatic carbon dynamics in drained wetlands is relatively unknown. The aim of this study was to quantify net ecosystem carbon budget (NECB) for an agricultural floodplain by integrating measurements of both terrestrial and aquatic carbon fluxes, and assess the impact of episodic events (floods) and groundwater seepage on aquatic carbon fluxes and hydrology.

During a large flood event, drastic changes in drain CO\textsubscript{2} and CH\textsubscript{4} dynamics were captured by deploying a novel automated technique using air-water equilibrators. Extreme super-saturation of CO\textsubscript{2} (25,480\%) was driven by large groundwater fluxes of up to 325 cm d\textsuperscript{-1} during flood recession periods. This extreme post-flood CO\textsubscript{2} pulse was further accentuated by a unique process where high carbonate alkalinity groundwater was delivered to acidic surface waters (pH ~4). A progressive increase in CH\textsubscript{4} concentrations of up to ~2400 nM day\textsuperscript{-1} occurred as a combination of increased substrate availability delivered by post-flood drainage water and longer residence times. Total DOC, POC, and DIC export was 7.1, 2.6, and 14.4 g C m\textsuperscript{-2} yr\textsuperscript{-1} of catchment area respectively, and gaseous fluxes (diffusive) of CO\textsubscript{2} and CH\textsubscript{4} were 16 and 0.05 g C m\textsuperscript{-2} yr\textsuperscript{-1}, respectively. The total aquatic carbon flux of ~40 g C m\textsuperscript{-2} yr\textsuperscript{-1} was a minor component of the NECB, representing ~4\% of the terrestrial carbon uptake (NEE = -900 g C m\textsuperscript{-2} yr\textsuperscript{-1}). Despite the small contribution found at this site, the annual aquatic carbon loss was within the same order of magnitude compared to a range of other ecosystems (1 to 100 g C m\textsuperscript{-2} yr\textsuperscript{-1}). After taking into account biomass residue (453 g C m\textsuperscript{-2} yr\textsuperscript{-1}) and harvest (1,429 g C m\textsuperscript{-2} yr\textsuperscript{-1}) the final NECB was 100 g C m\textsuperscript{-2} yr\textsuperscript{-1}.

This study provided the first full NECB integrating fluvial fluxes of a subtropical agricultural wetland in the southern hemisphere, and demonstrated an extreme case where the total aquatic carbon flux was a very minor component of the terrestrial carbon uptake. Given the large variability in the aquatic carbon contribution across studies, the role of the fluvial carbon pathway in terrestrial-aquatic systems needs to be reassessed in underrepresented ecosystems.
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Chapter 1 - Introduction
1.1 Conceptual overview
Carbon is stored across the land, marine, and atmospheric reservoirs (Le Quéré et al., 2015). Within these reservoirs, carbon is either transformed, transported, or sequestered by biological and physical processes (Figure 1.1). Exchange of CO$_2$ between the atmosphere and land and ocean ultimately governs the balance of the carbon cycle and controls the Earth’s climate. The capacity of land and ocean reservoirs to absorb atmospheric CO$_2$ determines their sink strength and ability to provide a negative feedback to climate warming. Determining whether an ecosystem is a source or sink of carbon is the focus of many research questions in the face of climate change. Quantifying the difference between carbon inputs and outputs within a defined boundary represents the core concept of defining the carbon budget of ecosystems.

The movement of carbon between the terrestrial and marine biospheres is largely driven by the aquatic continuum (although groundwater remains excluded in present day carbon budgets), which provide a critical interface for transport between these systems (Polsenaere et al., 2013, Figure 1.1). Constraining the movement and fate of carbon transported via the land-ocean aquatic continuum has presented major challenges, which during the past few centuries has been further complicated by anthropogenic disturbances (Regnier et al., 2013). Prior to human intervention, the transfer of carbon between the land, ocean and atmosphere was assumed to be in quasi-steady-state equilibrium at the millennial timescale (Figure 1.1).
Complete ecosystem carbon budgets are few and far between in catchments containing multiple components contributing to the carbon budget. This is largely due to the disciplinary nature of science, where methodological constraints force most studies to focus on specific components of the carbon balance individually (Falkowski et al., 2000). Consequently, the importance of certain carbon processes and pools remains unsubstantiated in discipline-focused ecosystem studies. However, detailed studies on singular components of ecosystem carbon dynamics enabled some of the first large catchment scale integrative carbon budget calculations to be made, as a result of a large amount of research from the same subarctic landscape (Christensen...
et al., 2007). In this work, measurements made across different vegetation types, glaciers, lakes, and rivers were integrated to calculate the carbon budget of the large subarctic catchment. The importance of fully integrated carbon balances has been demonstrated by numerous studies where correct accounting of all ecosystem processes have shifted the source/sink status of systems (Genereux et al., 2013; Chu et al., 2015; Lundin et al., 2016). Such findings often challenge pre-held assumptions of the functioning of certain ecosystems as carbon sinks or sources. The lack of integrated carbon budgets represents a major knowledge gap in understanding ecosystem scale carbon dynamics. Without a complete understanding of how carbon is exchanged and processed between different pools, our ability to predict how the carbon cycle of ecosystems will respond to future disturbances is limited.

Calculating the carbon budget of an ecosystem determines whether the system is a net sink or source of carbon; sink being net accumulation and source being a net loss of carbon. When quantified over a catchment scale this is referred to as the net ecosystem carbon budget (NECB) and is defined as the sum of all carbon inputs and outputs across an ecosystem boundary over a specified time scale (Chapin et al., 2006). The various carbon pathways, the inputs and outputs, that make up the following equation are inclusive of all physical, biological, and anthropogenic processes relevant to the studied system:

\[
\text{NECB} = -\text{NEE} + F_{CH_4} + F_{\text{aquatic}} + F_{PC}
\]

Where \(\text{NEE}\) is the net ecosystem exchange (the net \(\text{CO}_2\) flux from the ecosystem to the atmosphere), \(F_{CH_4}\) is the net \(\text{CH}_4\) flux to the atmosphere, \(F_{\text{aquatic}}\) represents the movement of dissolved and particulate carbon via aquatic flow paths (surface discharge, groundwater, leaching loss), and \(F_{PC}\) is the net lateral transfer of particulate carbon by other processes such as manure addition, root biomass from previous year, sediment deposition, and anthropogenic transport or harvest. All fluxes are represented in the same spatial and temporal integrated units; as a rate (temporal) over the land surface area (spatial) considered. NEE is defined as the difference between ecosystem respiration (ER) and gross primary production (GPP) (ER-GPP), where a negative sign indicates a net uptake of \(\text{CO}_2\) (Lovett et al., 2006). The term net ecosystem production (NEP) is relatable with NEE, the important difference being an opposite sign (i.e. a positive NEP indicates a net uptake of \(\text{CO}_2\)). For all other terms in the NECB a net loss of carbon (flux out of the system) is representative as a negative flux (Chapin et al., 2006).
1 Introduction

The resulting calculation provides a rate of carbon accumulation or loss, often over one year. If an ecosystem is in steady state, then closure of the carbon balance will equate to NECB = 0. Depending on the ecosystem some carbon fluxes may be more important than others, and some may be excluded altogether if deemed not relevant. It is important to note that if the ecosystem contains an aquatic component the evasion of CO$_2$ and CH$_4$ from the surface of the water body be incorporated into the $NEE$ and $F_{CH4}$ terms, respectively. Depending on the method used to calculate aquatic gaseous fluxes, the temporal and spatial scale boundaries of the observations need to be specified to ensure correct accounting of aquatic fluxes. For example, does a flux tower measuring NEE include the stream area within its footprint? The total aquatic carbon export encompasses dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC). These forms of carbon can originate from in situ production and terrestrial sources such as groundwater input of leached DIC root respiration and DOC from decomposed plant matter. This type of terrestrial-aquatic carbon link demonstrates the reason for accounting for such terrestrial carbon subsidies, as the fate of this carbon may be assumed sequestered if left unmeasured (Lovett et al., 2006).

1.2 Role of aquatic systems in the terrestrial carbon cycle

The aquatic carbon flux pathway in the past had been implicitly ignored from global carbon budgets as uncertainties are large and available information is deemed insufficient for annual estimates (Le Quéré et al., 2015). However, the importance of the aquatic pathway is highlighted by the fact that the major fate of terrestrially fixed carbon (over continental scales) is export as riverine DOC (Schlesinger, 1997). The revised concept that inland waters not only transport terrestrial carbon directly to oceans but are “active pipes” that process, store, and evade this transported carbon further demonstrated the potentially important role of these systems in terrestrial carbon cycles (Cole et al., 2007). Since inland waters were acknowledged as active components of the carbon cycle, considerable research efforts have focused on quantifying carbon fluxes along the aquatic continuum.

Fluvial environments are transitional ecosystems that facilitate the exchange of carbon from terrestrial landscapes to the atmospheres and oceans. They are biogeochemical hotspots that often exhibit disproportionately larger fluxes of carbon compared to the surrounding landscape (McClain et al., 2003; Jonsson et al., 2007; Aufdemkampe et al., 2011). The input of terrestrial organic matter into aquatic environments can accelerate decomposition and release large amounts of carbon dioxide (CO$_2$) and methane (CH$_4$), potentially offsetting terrestrial carbon
sinks (Bastviken et al., 2011; Regnier et al., 2013). Millennia-aged organic carbon sourced from the surrounding soil can be metabolised in a matter of weeks once entering the aquatic environment (Cole and Caraco, 2001).

The global estimate of the land carbon sink is $2.6 \pm 1.7$ Pg C yr$^{-1}$ (Denman et al., 2007), however this estimate fails to account for carbon fluxes from inland waters including rivers and streams. Current global estimates of lateral carbon export, CO$_2$, and CH$_4$ evasion amounts to 0.9, 1.8, and 0.075 (0.7 Pg C CO$_2$-eq) Pg C yr$^{-1}$, respectively (Cole et al., 2007; Raymond et al., 2013; Stanley et al., 2016). Combined, the total aquatic flux amounts to ~2.7 Pg C yr$^{-1}$ which is equivalent to the land uptake. Yet these estimates are limited by available data, containing large uncertainties and lack a mechanistic understanding of the controlling processes.

Fluxes of CO$_2$ and CH$_4$ in aquatic systems are highly dynamic in nature due to the sensitivity of production and consumption processes to changes in physical and biogeochemical aspects of fluvial systems. The dissolved CO$_2$ concentration of freshwater ecosystems varies with season and metabolism, yet are supersaturated most of the time and are a generally a source of atmospheric CO$_2$ on an annual basis (Aufdemkampe et al., 2011; Butman et al., 2011). Hydrological flow pathways can increase CO$_2$ concentration in tributaries via inputs of CO$_2$ sourced from soil respiration (Yao et al., 2007) and mobilisation of labile organic substrates (Duarte and Prairie, 2005). A primary control of CO$_2$ evasion from fluvial systems is related to the size and order of the tributary (Butman et al., 2011; Hotchkiss et al., 2013). Smaller streams typically show a strong link to terrestrial sources of CO$_2$, predominately from groundwater and carbonate weathering. In large rivers, drivers of CO$_2$ are mostly related to internal metabolism (Hotchkiss et al., 2013).

Our current understanding of the processes controlling CH$_4$ production and loss are greatly lacking (Stanley et al., 2016). This is largely due to the limited global measurements of CH$_4$ in fluvial environments compared to CO$_2$ (951 vs. 6708, respectively, Stanley et al., 2016), and the fact that CH$_4$ concentrations are highly variable (over two orders of magnitude) at temporal and spatial scales within fluvial networks (Hope et al., 2004; Campeau and Giorgio, 2014). Studies have reported a range of driving variables for CH$_4$, including the availability of organic matter and alternate electron acceptors, temperature, nutrient loading, and sedimentation (Crawford and Stanley, 2016; Schade et al., 2016; Stanley et al., 2016). Hydrology can also exert an important control on the delivery and persistence of CH$_4$ in streams, where a number
of studies have demonstrated an inverse relationship with discharge (Hope et al., 2001; Anthony et al., 2012; Bouillon et al., 2014; Webb et al., 2016a). How the multiple array of processes driving fluvial CO₂ and CH₄ dynamics operate over longer time scales and are quantifiably represented in annual carbon budgets are not well understood (Striegl et al., 2012; Shade et al., 2016). Therefore, there is an intrinsic need to understand the variability and drivers of CO₂ and CH₄ over short and long temporal scales.

Groundwater input can represent a significant source of CO₂ and CH₄ emissions to surface waters (Santos et al., 2012; Atkins et al., 2013; Webb et al., 2016a), however often remains unquantified in aquatic biogeochemical budgets. This is largely due to inherent difficulties in estimating this water flow pathway (Kalbus et al., 2006). Groundwater-surface water interactions can strongly influence carbon cycling in fluvial environments, and can even stimulate organic carbon turnover (Tockner et al., 2000; Hunt et al., 2006; Stegen et al., 2016). Furthermore, the groundwater flow path provides a direct, unhindered conduit for terrestrial carbon transport to fluvial networks, and can exert a major influence on watershed carbon budgets (Genereux et al., 2013). Concentrations of CO₂ in floodplain groundwaters are spatially variable but consistently higher than that of surface waters due to root respiration and organic matter oxidation (Macpherson, 2009). Likewise, the abundance of labile organic carbon can produce low oxygen conditions which generate high CH₄ concentrations (Gooddy and Darling, 2005). The temporal and spatial scale of groundwater-surface water interactions has been greatly modified in landscapes that have experienced artificial drainage for agriculture, such as floodplains and wetlands. Understanding the influence groundwater interaction has on surface water carbon metabolism in these modified coastal floodplains may be critical to constraining unresolved CO₂ and CH₄ fluxes.

1.3 Impact of hydrologic extremes on the carbon cycle

Many studies have demonstrated the important influence hydrology has on the transport and processing of terrestrially-derived carbon in rivers and streams (Meybeck, 1982). Hydrologic processes control the input and mineralisation rate of terrestrial carbon along the land-ocean continuum via erosion, extent of contact with the soil surface, and residence time (Abril et al., 2002; Battin et al., 2008; Bauer et al., 2013). For example, total annual carbon fluxes from dissolved organic carbon (DOC) export often displays a positive relationship with annual discharge between watersheds (Genereux et al., 2013). An important consequence of altered flow regimes on carbon budgets is that episodic high discharge events can be responsible for
43-81% of total annual DOC and particulate organic carbon (POC) exports in river systems (Dalzell et al., 2007; Yoon and Raymond, 2012; Bianchi et al., 2013).

It is hypothesised that increases in precipitation will accelerate the removal of soil carbon to aquatic systems, and consequently increase the remineralisation of organic carbon to CO₂ (Regnier et al., 2013; Raymond et al., 2016). The processes governing this potential perturbation are considered to be primarily driven by hydrologic residence time (Catalan et al., 2016). Carbon export load and remineralisation rate was found to be negatively correlated with hydrologic residence time, where large yet short events caused a greater pulse response in lake carbon dynamics (Zwart et al., 2016).

The potential enhancement of CO₂ and CH₄ fluxes in response to episodic events is currently not factored into quantitative models. Quantifying the impact episodic discharge events and changes in rainfall patterns have on CO₂ and CH₄ fluxes is a crucial aspect in constraining global emissions from fluvial environments. Episodic hydrological events in floodplain river systems have been found to induce disproportionately large carbon fluxes (Bass et al., 2014; Gatland et al., 2014; Ruiz-Halpern et al., 2015; Webb et al., 2016a). Recent studies have demonstrated that fluxes CO₂ and CH₄ can increase by a factor of 2-53 and 6-49 in response to flood events, respectively (Sarma et al., 2011; Gatland et al., 2014; Webb et al., 2016a). However, the timing of minimum and maximum CO₂ concentrations during flood events varies considerably between sites (Yao et al., 2007; Bass et al., 2014). In contrast to lateral carbon fluxes which are generally closely coupled with the flood pulse (Schulte-Wulwer-Leidig and Mollenhauer, 1983; Ward et al., 2012), some studies have shown that the immediate post-flood period may represent peak fluxes of CO₂ and CH₄ (Gatland et al., 2014; Webb et al., 2016a; Ruiz-Halpern et al., 2015). In some of these studies, the extreme post-flood peak in CO₂ fluxes has been attributed to large groundwater input during the receding limb of the event.

1.4 Carbon balance of agricultural ecosystems
The NECB has been assessed in a large number of in agricultural environments, from temperate to tropical croplands, with annual carbon budgets ranging from net carbon sources to sinks (Kutsch et al., 2010; Bhattacharyya et al., 2014; Eichelmann et al 2016). In dryland agricultural sites, the carbon budget is mostly contained within soil and vegetation exchange with the atmosphere, in which case micro-meteorological measurements encompass the majority of NECB measurements where soil leaching represents a minor flux (Smith et al., 2010). However, there are many agricultural landscapes that have been developed in floodplains and
wetlands, containing drainage canals that have not been fully considered as an active component in catchment NECB. Although agricultural wetlands often remain highly productive systems (Gleason et al., 2009), a loss of soil carbon stock is generally observed due to agricultural drainage (Armentano and Menges, 1986; Huang et al., 2009). Given the increasing importance of sustainable agriculture, integrated carbon budgets including aquatic pathways needs to be quantified in agro-ecosystems.

Human land use patterns are substantially changing the hydrology and chemistry of connected tributaries, which influences fluvial carbon exchanges with the land, atmosphere, and coastal ocean (Raymond et al., 2008; Aufdemkampe et al., 2011). It is estimated that human land use activities since 1750 have increased the global flux of carbon to inland waters by as much as 1.0 Pg C yr$^{-1}$, and about 0.4 Pg C yr$^{-1}$ of this additional carbon is lost as CO$_2$ evasion (Regnier et al., 2013). The aquatic flux in agricultural wetlands comes in the form of either leaching loss through soil drainage or lateral transfer from drainage channels. The movement of water drives the fluvial flux of carbon through a landscape, and it is the enhancement of hydrological movement via artificial drains that has exacerbated terrestrial carbon loss from converted peatlands (Holden et al., 2004; Moore et al., 2013; Evans et al., 2016). Disturbance of tropical peatlands due to rice and palm oil production was found to increase the total annual organic carbon flux of draining rivers by 20 to 45% (Moore et al., 2013). Artificial drainage canals have also been found to be a significant source of CO$_2$ and CH$_4$ emissions (Schrier-Uijl et al., 2011; Teh et al., 2011; Jauhiainen and Silvennoinen 2012; Luan and Wu, 2015). This is mostly likely due to their first order connection with the landscape, with canal flux rates of 54-670 mg m$^{-2}$ h$^{-1}$ CO$_2$ and 4-46 mg m$^{-2}$ h$^{-1}$ CH$_4$ similar to the range of 165-1,270 mg m$^{-2}$ h$^{-1}$ CO$_2$ (Koprivnjak et al., 2010; Butman and Raymond, 2011; Crawford et al., 2013) and 0.4-12 mg m$^{-2}$ h$^{-1}$ CH$_4$ (Sebacher et al., 1986; Crawford et al., 2013) reported in first order streams. Given these findings, the aquatic carbon export and emission from converted wetland-agricultural systems could be a potentially important unaccounted carbon loss pathway.

1.5 Rationale
Cross disciplinary linkages and human-environment interactions remains some of the most important challenges in ecosystem science (Carpenter and Turner, 2017). These themes are particularly relevant for terrestrial and aquatic ecosystems, which have closely coupled biogeochemical cycles for which human activities have caused a disturbance in their interacting carbon cycle (Falkowski et al., 2000). Recent research highlights the important role inland
waters have in the global carbon cycle. However, incomplete accounting of the aquatic carbon flux in catchment level ecosystem hinders our understanding of how this pathway is impacted by climatic and land use changes.

Traditional methods, including MODIS and conventional eddy covariance techniques, used for estimating ecosystem carbon budgets cannot accurately estimate the complete carbon balance of terrestrial-aquatic systems. This is eloquently demonstrated in Chapin et al., (2006), which illustrates how within a 3D boundary that defines the NECB, different measurement approaches are only representative of certain carbon fluxes. However, the concept of ecosystem boundary can pose multiple challenges that affect mass balance calculations, such as fluxes originating from outside of the measurement boundary. With a focus on understanding catchment scale carbon flux pathways in linked ecosystems, simplification of ecosystem boundaries is required for managing the complexity. Well constrained catchments with local hydrology present ideal model ecosystems to study such carbon budgets. An integrated approach utilising measurement techniques from different disciplines will address the methodological issues in quantifying all relevant carbon flux pathways in catchment scale carbon budgets.

Much of the uncertainty in regional and global scale estimates of aquatic carbon fluxes originate from the temporal heterogeneity of hydrologic responses and the different functioning of aquatic carbon cycling in anthropogenically disturbed watersheds (Jenerette and Lal, 2005; Crawford and Stanley, 2016; Schade et al., 2016). For example, Alvarez et al., (2012) highlighted how large uncertainties in organic carbon export from most catchments worldwide stem from low temporal resolution sampling that do not capture disturbance events such as floods and snowmelt. Despite an increase in research aimed at understanding event-driven elemental transformations across spatiotemporal scales in fluvial environment’s (Bernhardt et al., 2017), little is known about the effect extreme events have on the annual carbon budget of terrestrial-aquatic ecosystems. Anticipating these impacts remains a research priority.

Anthropogenic changes to terrestrial-aquatic ecosystems has greatly altered the functioning of carbon pathways, sources, and sink (Zhang et al., 2013; Ren et al., 2016; Raymond et al., 2008). As a result, land use alterations have greatly shifted the timing and magnitude of carbon export from land to aquatic ecosystems, and the rate of processing during transport along the aquatic continuum. However, most of our knowledge of land use effects on aquatic carbon cycling has been developed from studies on large rivers, for which the carbon biogeochemistry is a net
result of multiple sources and in situ processing often complicated by a large network of tributaries. In fact, anthropogenic landscapes in general are relatively understudied compared to natural biomes (Martin et al., 2012). Artificially constructed waterways or straightened streams are widespread in low-lying agricultural environments and represent the most direct connection with these impacted landscapes (Blann et al., 2009). First order drainage networks are important transport control points within the landscapes (Bernhardt et al., 2017), and have been shown to contribute disproportionately large CO₂ and CH₄ evasion rates compared to larger downstream waters (Schrier-Uijl et al., 2011; Vermaat et al., 2011; Atkins et al., 2013). To gain a better understanding of how human land use impacts the functioning of the aquatic pathway as transporters and processors of terrestrial carbon, headwaters representing the first point of contact need to be studied.

As has been highlighted earlier, hydrological connections between watercourses and their associated catchments function as important exchange pathways for carbon. Therefore, understanding the hydrology of a catchment is vital for correct accounting of aquatic carbon fluxes and for constraining sources. However, a major misrepresented element in ecosystem carbon studies is the groundwater flow pathway. Groundwater flow paths in floodplain environments are particularly important as they exist in the subsurface zone, facilitating direct exchanges of carbon subsidies between terrestrial and aquatic environments (Shindler and Smitt et al., 2017). A growing number of studies have recognised a link between groundwater discharge and CO₂ supersaturation (Santos et al., 2012; Sadat-Noori et al., 2015a; Jeffrey et al., 2016). However, due to variable results from limited studies, the role of groundwater as a removal pathway for terrestrial fixed carbon and source of CO₂ and CH₄ to surface waters remains unclear.

1.6 Aims and hypothesis
Constraining carbon budgets in ecosystems at the terrestrial-aquatic interface remains an incomplete yet evolving area of research today. Recurrent shortcomings that have been identified mostly stems from the difficulty in linking terrestrial and aquatic measurements together, and capturing important events that drive aquatic carbon fluxes. The overarching hypothesis for this dissertation is that the aquatic carbon pathway will play an important role in the NECB of the system and that large precipitation events will drive most of this annual carbon loss. To address this hypothesis, the study aims to evaluate the fluxes of carbon within and between the terrestrial and aquatic components of a catchment-scale carbon budget, and to
resolve the role and function of the aquatic carbon pathway in a managed floodplain landscape. Therefore, this work will utilise an integrated approach involving an array of measurements and techniques to link terrestrial and aquatic carbon cycling. The following chapters will:

- Assess the performance of an underway technique for making real-time continuous observations of CO₂ and CH₄ concentrations and δ¹³C values in aquatic environments.
- Analyse how the drainage network of a hydrologically altered floodplain functions as a source of CO₂ and CH₄ emissions during flood and non-flood conditions.
- Quantify a detailed water budget capturing the contribution of flood events and groundwater discharge using a groundwater tracer model approach.
- Quantify the annual carbon budget of the agricultural floodplain by measuring land-atmosphere fluxes of CO₂ simultaneously with aquatic carbon export and evasion, and explore the contribution of the aquatic carbon flux across other ecosystems.

1.7 Overview

A brief summary of each data chapter is given below. As of February 2017, three manuscripts have been published, and the remaining will be submitted shortly. Chapters 2-4 are presented in the original text which they were published in.

Chapter 2. *Automated, in situ measurements of dissolved CO₂, CH₄, and δ¹³C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators*

This chapter was published in the journal *Limnology and Oceanography: Methods* in 2016 (Webb et al. 2016, volume 14, issue 5, pages 323-337), and presents an evaluation of the equilibration response time of six air-water equilibrators under simulated step experiments of dissolved CO₂, CH₄, δ¹³C-CO₂ and δ¹³C-CH₄ values using laser absorption spectroscopy. To our knowledge, this was the first paper to estimate the instantaneous response time of both CO₂ and CH₄ concentrations and carbon stable isotope ratios. The effect of water flow rate on equilibration time was also investigated and found to be highly important in controlling gas equilibration times. The ability to measure these gases simultaneously and continuously with their δ¹³C values offers a profound advancement in the way carbon cycling is studied in aquatic systems. This work provides methodological insight into the resolution of air-water equilibration devices for real-time measurements, which can be used to resolve the
sppiotemporal limitations in CO\textsubscript{2} and CH\textsubscript{4} concentration and isotopic measurements across aquatic ecosystems.

**Chapter 3. Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: Post-flood hydrological and biological drivers**

This paper, which was published in *Chemical Geology* in 2016 (Webb et al. 2016, volume 440, pages 313-325), presents a high temporal resolution study of dissolved CO\textsubscript{2}, and CH\textsubscript{4} dynamics using the technique tested in Chapter 2 to capture the impact flood events have on carbon emissions from agricultural drainage networks. Using a natural geochemical tracer for groundwater (radon-222), the contribution of groundwater to total drain fluxes was found to be large for CO\textsubscript{2} yet negligible for CH\textsubscript{4}. Extreme CO\textsubscript{2} supersaturation observed in this study was four to eight-times higher than other recorded post-flood CO\textsubscript{2} responses, and was sustained by large inputs of high carbonate alkalinity groundwater into acidic surface waters. In contrast, drain sediments were the major driver of CH\textsubscript{4} dynamics. Carbon stable isotopes of CH\textsubscript{4} (δ\textsuperscript{13}C-CH\textsubscript{4}) and dissolved oxygen saturation levels revealed a strong diurnal control over post-flood drain CH\textsubscript{4} dynamics. Findings from this study revealed how major drivers in CO\textsubscript{2}, and CH\textsubscript{4} dynamics can operate over different hydrological and biological scales, and how the unique geochemistry of certain coastal floodplains can have a profound influence over post-flood fluvial CO\textsubscript{2}, and CH\textsubscript{4} (diffusive) emissions.

**Chapter 4. Constraining the annual groundwater contribution to the water balance of an agricultural floodplain using radon: The importance of floods**

This chapter was recently published in *Water Resources Research* in 2017 (Webb et al. 2017, early view), and presents findings of a detailed water budget capturing the contribution flood events and groundwater discharge within an extensively drained agricultural floodplain using a radon mass balance. Findings revealed that some of the largest groundwater discharge rates ever recorded occurred during the flood recession period, and that groundwater discharge was amplified by the enhanced drainage network. This paper was the first to directly quantify the extent flood events have on groundwater discharge, and builds on hydrological understanding of groundwater-surface water dynamics within drained floodplains that are widespread worldwide.

**Chapter 5. Importance of aquatic carbon fluxes in catchment carbon budgets**
This chapter details the first complete carbon budget of a floodplain system that is intensively managed for cropland production, and plans to be submitted for publication soon. By combining estimates of NEE with drainage water measurements of carbon exports and CO$_2$ and CH$_4$ evasion (diffusive only), this study was able to reconcile the contribution of aquatic carbon fluxes to annual terrestrial carbon uptake for the first time in a drained agricultural floodplain ecosystem. After accounting for all measured carbon fluxes and biomass exchanges, the floodplain had a relatively neutral NECB of 100 g C m$^{-2}$ yr$^{-1}$ (per catchment area). The contribution of all aquatic carbon fluxes was found to be a minor component of the overall carbon budget, representing only ~4% of terrestrial NEE. These findings are a stark contrast to the integrative carbon budgets of sub artic ecosystems, which report aquatic carbon contributions of 10 to >100%. This chapter explores the factors driving the importance of aquatic carbon fluxes in catchment carbon budgets and reveals how our understanding of this role is limited to certain ecosystem types.
Chapter 2 - Automated, in situ measurements of dissolved CO₂, CH₄, and δ¹³C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

Abstract

Combining air-water equilibrators with a field deployable cavity enhanced laser absorption spectrometer (CELAS) can generate precise, high resolution, measurements of dissolved CO$_2$ and CH$_4$ concentrations and $\delta^{13}$C values in aquatic systems. However, equilibration response times for combined measurements of CO$_2$ and CH$_4$ isotopologues have not been assessed. We performed laboratory step experiments on six different equilibrators to constrain CO$_2$ and CH$_4$ equilibration time constants ($\tau$; high-to-low exponential decay constant). Three equilibrator types were then used in field-based step experiments to determine $\tau$ for the individual isotopologues $^{12}$CO$_2$, $^{13}$CO$_2$, $^{12}$CH$_4$, and $^{13}$CH$_4$. In the laboratory experiments, $\tau$ ranged from 34-124 s for CO$_2$ and 117-2041 s for CH$_4$ among the six equilibrators. The ratio between response times of CO$_2$ and CH$_4$ was substantially lower in the membrane type equilibrators ($\tau$-CH$_4$~5 times > $\tau$-CO$_2$) than in the showerhead and marble types ($\tau$-CH$_4$~15 times > $\tau$-CO$_2$). Individual isotopologue time constants under a water flow rate of ~5.5 L min$^{-1}$ ranged from 33.7-43.1 s for $^{12}$CO$_2$ and $^{13}$CO$_2$, and 177-347 s for $^{12}$CH$_4$, and $^{13}$CH$_4$. The $\tau$ of CO$_2$ isotopologues were within 2 seconds while $\tau$ of CH$_4$ isotopologues were the same. Further investigations into water flow rate revealed an exponential decrease in equilibration time from 1.5-9 L min$^{-1}$ in a marble-type equilibrator. The response time was always longer from high-to-low than low-to-high concentrations. By taking into consideration the equilibration response time, measurements of CO$_2$, CH$_4$, $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-CH$_4$ can be resolved in near real-time using appropriate water-air equilibration devices.

Key words: Cavity ringdown spectroscopy, isotopologues, stable isotope, carbon dioxide, methane, equilibrator, greenhouse gases
2.1 Introduction

The role of aquatic environments in processing carbon is now widely recognised (Cole et al. 2007). However, fluxes of CO₂ and CH₄ from aquatic environments are still poorly represented in the global carbon cycle and have large uncertainties (Bastviken et al. 2011; Borges and Abril 2011; Chen et al. 2013; Raymond et al. 2013). These large uncertainties are in part associated to a lack of understanding of the drivers of CO₂ and CH₄ in inland and coastal waters (Borges and Abril 2011; Chen et al. 2013; Raymond et al. 2013). Carbon stable isotope ratios of CO₂ (δ¹³C-CO₂) and CH₄ (δ¹³C-CH₄) can reveal hydrological and biological processes governing carbon dynamics in complex aquatic systems (Corbett et al. 2013; Gatland et al. 2014; Maher et al. 2015). δ¹³C-CO₂ and δ¹³C-CH₄ in freshwater and marine systems vary as a result from mixing processes and the isotopic fractionation associated with the different source and sink pathways (Sansone et al. 1999; Palmer et al. 2001; Dubois et al. 2010). These processes which influence dissolved δ¹³C-CO₂ and δ¹³C-CH₄ occur over various temporal and spatial scales (Maher et al. 2015). Therefore, high temporal and spatial resolution δ¹³C-CO₂ and δ¹³C-CH₄ measurements can help elucidate the controls and pathways of the aquatic carbon cycle.

The conventional method to determine dissolved δ¹³C-CO₂ and δ¹³C-CH₄ values in aquatic environments involves the collection of discrete samples which are then analysed with Isotope Ratio Mass Spectrometry (IRMS). This method provides high precision observations but may be costly and labour intensive. IRMS samples must be collected in the field, treated, stored and run in a specialised laboratory by trained technicians. Combined, these factors restrict sampling frequency, leading to limitations in data spatial and temporal resolution. High frequency measurements are critical where rapid changes occur in aquatic environments (Gülzow et al. 2011; Maher et al. 2013).

Cavity enhanced laser absorption spectroscopy (CELAS) is emerging as a technique that can make in situ, quasi-continuous measurements of various gases and their stable isotopes in the atmosphere (Crossen 2008; Gupta et al. 2009; Maher et al. 2014, Tait et al., 2015). Because the field deployable instrumentation can maintain its calibration for extended periods, sample conditioning and maintenance costs may be reduced (Gupta et al. 2009; Winderlich et al. 2010; Andrews et al. 2014). For example, in a recent study, an CELAS analyser demonstrated undetectable drift over five years of monitoring atmospheric CO₂ and CH₄ concentrations (Andrews et al. 2014). Various studies have demonstrated that the analyser has a precision and
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accuracy similar to what is obtained by laboratory-based IRMS (Gupta et al. 2009; Berryman et al. 2011; Midwood et al. 2011; Vogel et al. 2013).

In the past few years CELAS analysers have been used for the quasi-continuous measurements of water stable isotopes, δ¹³C-CO₂ and δ¹³C-CH₄ in aquatic environments (Friedrichs et al. 2010; Munksgaard et al. 2011; Becker et al. 2012; Maher et al. 2015). Continuous measurements of δ¹³C-CO₂ and CO₂ using a cavity ringdown spectroscopy (CRDS) analyser combined with air-water equilibrators has been achieved on ship deployments during ocean surveys (Friedrichs et al. 2010; Becker et al. 2012; Bass et al. 2014). Bass et al. (2014) identified processes governing the change in δ¹³C-CO₂ values across the Southern Ocean, including the location of upwelling waters and primary production (Bass et al. 2014). Maher et al. (2013) demonstrated the applicability of CRDS to take continuous isotopic measurements to assess CO₂ and CH₄ dynamics in coastal environments. Whilst the precision and applicability of the CRDS technique for stable isotope measurements in waters has been demonstrated (Maher et al. 2013; Friedrichs et al. 2010; Munksgaard et al. 2011), equilibration times associated with the use of air-water equilibrators for continuous ^12CO₂, ^13CO₂, ^13CH₄ and ^13CH₄ measurement have not been assessed.

One of the main issues when using air-water equilibrators is that there is a delay in the measured response to a change in actual dissolved gas concentrations due to the time taken for the gases to equilibrate between the water and air phase within the equilibration device. Based on the equilibrator design and properties of the gas being sampled equilibration response times can range anywhere between 1 min (Frankignoulle et al. 2001; Rhee et al. 2009) and >8 h (Johnson 1999) (Table 2.1). When taking direct real-time measurements in the field it is critical to know the response time of the equilibrator being used for a particular gas and its isotopologues so that the user is aware of any temporal limitations when analysing the data. Assuming instantaneous equilibration may result in spatial and/or temporal dislocation between actual and assumed measurement location and/or time.

A large range of different air-water equilibrators have been used in the literature. Equilibrators are operationally dissimilar from each other with design modifications and varying water/air flow rates (Table 2.1). There have been some intercomparison studies looking at the performance of different equilibrators for dissolved CO₂ measurements (Körtzinger et al., 2000, Santos et al., 2012), however equilibrator experiments for dissolved CH₄, δ¹³C-CO₂ and δ¹³C-CH₄ measurements have not yet been compared in detail. Here, we compare the
Automated, in situ measurements of dissolved CO₂, CH₄, and δ¹³C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

performance of six different air-water equilibrators coupled to a CELAS analyser for quasi-continuous measurements of CO₂ and CH₄ concentrations and carbon isotopologues (¹²CO₂, ¹³CO₂, ¹²CH₄, and ¹³CH₄) in a laboratory and field setting. Concentration response times first were characterised for each equilibrator in laboratory step experiments, before moving on to field step experiments with three chosen equilibrator types to investigate individual carbon isotopologue (¹²C and ¹³C) response times. Our results are intended to provide guidance to field scientists undertaking in situ measurements of CO₂, CH₄, δ¹³C-CO₂ and δ¹³C-CH₄ using air-water equilibrators coupled to CELAS.

Table 2.1 Comparison of measured response times from other studies for different types of gases and air-water equilibration devices. Values in parenthesis define either the time constant used where τ₁ was calculated from the exponential rise (e-folding time) and τ₂ was calculated from the exponential decay, or the response time given as a percentage of the final value (tₚ).

<table>
<thead>
<tr>
<th>Equilibrator</th>
<th>Gas tested</th>
<th>Response times (minutes)</th>
<th>Flow rate</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Water (L min⁻¹)</td>
<td>Air (mL min⁻¹)</td>
</tr>
<tr>
<td>Marble</td>
<td>CO₂</td>
<td>1.08 (t₉₀%)</td>
<td>3</td>
<td>n.d</td>
</tr>
<tr>
<td>Glass-bed</td>
<td>N₂O</td>
<td>7 (t₉₀%)</td>
<td>1.8</td>
<td>400</td>
</tr>
<tr>
<td>Weiss-type small</td>
<td>N₂O, CO</td>
<td>2.5 (τ₂), 15 (τ₂)</td>
<td>2</td>
<td>235</td>
</tr>
<tr>
<td>Weiss type-small</td>
<td>CH₄</td>
<td>40.8 (τ₂)</td>
<td>3</td>
<td>n.d</td>
</tr>
<tr>
<td>Showerhead-type</td>
<td>CO₂, ²²⁴Rn</td>
<td>8-13 (t₉₀%), 29-53 (t₉₀%)</td>
<td>2.8</td>
<td>1000</td>
</tr>
<tr>
<td>Marble</td>
<td>CO₂, ²²⁴Rn</td>
<td>10-12 (t₉₀%), 21-24 (t₉₀%)</td>
<td>5.4</td>
<td>1000</td>
</tr>
<tr>
<td>Raschig rings counter-flow</td>
<td>O₂</td>
<td>6.5-8 (τ₁)</td>
<td>3</td>
<td>500-1000</td>
</tr>
<tr>
<td>MiniModule membrane</td>
<td>SF₆</td>
<td>9 (τ₁)</td>
<td>2</td>
<td>n.d</td>
</tr>
<tr>
<td>Passive membrane</td>
<td>CO₂</td>
<td>1.2 (τ₁)</td>
<td>N/A</td>
<td>n.d</td>
</tr>
<tr>
<td>Bubble-type</td>
<td>CO₂, CH₄</td>
<td>3.8 (τ₂), 11.3 (τ₂)</td>
<td>0.5 ¹</td>
<td>450</td>
</tr>
<tr>
<td>Showerhead-laminar flow</td>
<td>CO₂</td>
<td>1.25 (τ₁)</td>
<td>0.25-2.5</td>
<td>1000-1200</td>
</tr>
<tr>
<td>Weiss-type large</td>
<td>CH₄, N₂O</td>
<td>20 (τ₁), 1 (τ₁)</td>
<td>24-30</td>
<td>200 mL h⁻¹</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>0.59 (t₆₀%)</td>
<td>33 s (water</td>
<td>n.d</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>residence time</td>
<td></td>
</tr>
<tr>
<td>Weiss-type small</td>
<td>CO₂</td>
<td>6 (t₉₀%)</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Weiss-type large</td>
<td>CO₂, CO</td>
<td>12 (t₉₀%), 504 (t₉₀%)</td>
<td>13-20</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td>N₂O</td>
<td>6.4 (t₉₀%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 Materials and procedure

2.2.1 Laboratory experiments

Step experiments were performed between six different equilibrators using low and high concentration water for carbon dioxide and methane to assess concentration equilibration time constants (τ). Two 200 L reservoirs where filled with tap water. One was maintained at laboratory air equilibrium concentration (CO₂: 430 to 470 ppm; CH₄: 1.7 to 1.94 ppm) by aerating for the preceding 15 hours, and throughout the experiment (Figure 2.1). The second reservoir had higher CO₂ (~ 850 ppm) and CH₄ (~ 25 ppm) concentrations which was achieved by adding between 1.5 L to 3 L of natural pond water to the 200 L reservoir. Duplicate tests for each equilibrator experiment were run, with each experiment consisting of three concentration steps (low→high→low) to allow two response times to be calculated (i.e. low-high and high-low). However, due to difficulties in maintaining a stable concentration in the high concentration reservoir due to evasion and methane oxidation, τ was only calculated for the high-low step, as done in previous studies (Johnson 1999; Gülzow et al, 2011). Water temperature was kept constant at 21°C during all experiments. The same water pump was used for all experiments (i.e., a 12 Volt/4 Amp Rule™ bilge pump, 500 Gallon Per Hour). However, because of equilibrator-specific characteristics, the water flow rate was different for each equilibrator and measured via the outlet water stream.

A commercial CELAS analyser (Picarro, G2201-i cavity ring down spectrometer with factory modification for low-leak, i.e. <0.05 sccm over 12 hours) was used to measure the individual carbon isotopologues (¹²C and ¹³C) of both CO₂ and CH₄ simultaneously. From this data total concentrations were obtained by simply adding the ¹²C and ¹³C together for each gas species. Carbon stable isotope ratios for CO₂ and CH₄ are converted to standard δ¹³C notation by the instrument based on the ratio of sample ¹³C/¹²C to a standard ¹³C/¹²C (referenced to VPDB), and reported in per mille (%). The CELAS analyser uses a laser absorption spectroscopic technique, and measures the decay time of light within a high-finesse optical cavity along an absorption feature specific to the gas species being measured. Due to the high spectral resolution of the analyser (0.0001 cm⁻¹), and the long effective path length (>10 km), sensitivity is extremely high (Pelt, 2008). The analyser has three main operating modes; CO₂ isotope-only mode, CH₄ isotope-only mode, and simultaneous CO₂/CH₄ mode. During this study we used the simultaneous mode, which has an operational range of 100-4000 ppm and 1.8-1000 ppm for CO₂ and CH₄ respectively. For the simultaneous mode (both CO₂ and CH₄ isotope) used here the manufacturer guaranteed δ¹³C precision (1σ, 5 min average) of 0.16‰ and 0.55‰ for
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CO$_2$ and CH$_4$ respectively, while concentration precision (1σ, 30 sec average) is 210 ppb (+0.05% of reading) and 60 ppb (+0.05% of reading).

The water pump delivered water at a constant flow to an air-water equilibrator, which facilitated the exchange of CO$_2$ and CH$_4$ gases between water and air until equilibrium was reached (Figure 2.1). A dual air loop setup between the equilibrator, external air pump (12 Volt DC micro diaphragm pump, Parker T2-05) and analyser was designed so that air circulates at 1000 sccm to and from the equilibrator independently of the analyser, which maintains a slower flow rate of ~25 sccm. The delay caused by the gas volume between the equilibrator to instrument and instrument cavity was measured at 50 s, and was corrected for during step experiments. By accounting for the dead space time delay in the connecting gas lines, any delay observed during experiments should be representative of the physical air-water equilibration process within the specific equilibrator. Raw data points were measured at ~1 Hz. Water vapour in the sample gas stream was maintained at < 0.1% for all experiments with a Drierite desiccant in a 40 mL cartridge. The CELAS analyser measured concentrations in ppm which were converted into a ratio ranging from 0-1, where 0 was the minimum concentration (atmosphere equilibrated reservoir), and 1 was the maximum concentration (high concentration reservoir).

The equilibration response time was assessed by calculating the time constant ($\tau$) of exponential decay during high-to-low equilibration. The time constant for each experiment was calculated using Johnson’s (1999) level one model to a return to equilibrium step response, fitting a least squares exponential of the form:

$$C_e = A + B e^{-t/\tau}$$

where $C_e$ is the gas concentration in the equilibrator, $t$ is time, and A, B, and $\tau$ are constants found for each fit (total of 200 iterations using 1 Hz data). This model assumes that no chemical or biological reactions are taking place during the equilibration process that may alter the concentration of the gas in question, and that no exchange is occurring with the outside air. We adopted this simple model as despite that fact that some of the equilibrators tested are vented to the atmosphere, the expected error for equilibrator measurements of CO$_2$ and CH$_4$ are minor (0.2 and 2% respectively) when compared to disequilibrium associated with pressure differences (Johnson, 1999). Because the system response to a step signal is exponential (eqn.
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1), the fraction of equilibration can be easily calculated, e.g. $\tau \times 3$ corresponds to 95% total equilibration.

**Figure 2.1** Schematic diagram of the laboratory setup of the air-water equilibration system involving a CELAS analyser for dissolved CO$_2$, CH$_4$, δ$^{13}$C-CO$_2$, and δ$^{13}$C-CH$_4$ values during step experiments. Solid arrows indicate liquid flow and dotted arrows indicate gas flow.

### 2.2.2 Air-water equilibration devices

Six air-water equilibrators were tested, including a marble equilibrator, two showerhead “Weiss-type” designs, and three different sized membrane equilibrators. The mechanism of equilibration in the marble and showerhead types is turbulent transfer across the air-water surface, whereas gaseous transfer via permeation occurs in the three membrane equilibrators.

The marble equilibrator consisted of a vertical Plexiglas cylinder (height: 50 cm, diameter: 10 cm) filled with inert glass marbles (Frankignoulle et al. 2001). This equilibrator was initially designed to measure CO$_2$ and CH$_4$ in highly turbid environments at fast response times, which is enhanced by increased surface area, reduced air volume and high flow nozzle for faster flow rate (Frankignoulle et al. 2001; Abril et al. 2006). The water flow to the equilibrator was at a rate of 3.8 L min$^{-1}$, and the gas headspace was ~1.3 L.

The RAD AQUA “Weiss-type” showerhead equilibrator consisted of a vertical acrylic cylinder (height: 25 cm, diameter: 10 cm) fitted with two nozzles that aspirate water into the headspace
before being collected at the bottom in a PVC pipe tray. This equilibrator is commercially available (www.durridge.com) and is widely used for measuring geochemical tracers in water such as radon (Dimova et al. 2009; Santos et al. 2012; Sadat-Noori et al., 2015b). Water flow to the equilibrator was maintained at 2.6 L min$^{-1}$, and the equilibrator has a water volume of ~0.6 L and a gas headspace of ~1.4 L.

The General Oceanics equilibrator is another commercially available showerhead type equilibrator essentially the same design as the original “Weiss-type” but smaller (Pierrot et al. 2009) and is often used in oceanic autonomous underway $p$CO$_2$ measuring systems. It has a similar design to the RAD AQUA showerhead in that it aspirates water coming through a nozzle into an equilibration chamber. However, the General Oceanics has a water jacket surrounding the equilibration chamber to maintain temperature stability, and has a smaller headspace volume. Water flow to the equilibrator was 1.9 L min$^{-1}$, water volume was ~0.5 L and the headspace was ~0.8 L.

Three membrane-type contactors of different sizes were tested (Liqui-Cel contactors, www.liquicel.com; Hales et al. 2004; Loose et al. 2009). Water flows through hydrophobic microporous hollow fibre membranes in one end of the cell and exists at the opposite end. Air is pumped in the opposite direction around the outside of the fibres, with gases in the aqueous stream moving between the gas phase and aqueous phase through the membrane to achieve equilibrium. The small membrane contactor (hereafter referred to a small Liqui-Cel) was 17.8 cm long, had a membrane area of 0.18 m$^2$, and a water flow rate of 1.65 L min$^{-1}$. The medium membrane contactor (hereafter referred to as medium Liqui-Cel) was 26.6 cm long, had a membrane area of 0.99 m$^2$, and a water flow rate of 2.4 L min$^{-1}$. The large membrane contactor (hereafter referred to as large Liqui-Cel) was 28.18 cm long, had a membrane area of 1.4 m$^2$ and a water flow rate of 5.6 L min$^{-1}$.

2.2.3 Field experiments

Three of the equilibrator types (marble, RAD-AQUA showerhead, and large LiquiCel), were assessed under “field” conditions for response times of CO$_2$ and CH$_4$ isotopes. Here, we calculated the time constant for the individual isotopologues $^{12}$CO$_2$, $^{13}$CO$_2$, $^{12}$CH$_4$, and $^{13}$CH$_4$ during triplicate experiments for each equilibrator. Following a similar setup to the laboratory experiments, low-high and high-low step response were performed in a closed loop between different reservoirs. Two submersible pumps were used with one in each reservoir, and water flow into the equilibrator was controlled by an in-line tap. Outflow was maintained at ~5.5 L
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min⁻¹ for the three equilibrators. The low concentration reservoir was a 200 L drum filled with lake water that had been equilibrated with the atmosphere, and the high concentration reservoir was a heterotrophic retention pond containing macrophytes. Any artefact that may arise during switching between the reservoirs was avoided by using a three way valve setup between water pumps. Time constants for carbon stable isotope ratios could not be quantitatively derived when expressed in typical δ¹³C notation (i.e., δ¹³C relates to a ratio of ratios) as it does not satisfy boundary conditions for first-order kinetics. We do however provide examples of the step response seen for δ¹³C-CO₂ and δ¹³C-CH₄ and explain the return to equilibrium response for isotopic composition.

2.2.4 Desiccant experiment

Pre-dried sample gas containing less than 1% H₂O is usually a requirement when measuring aqueous dissolved gases on an equilibrator-CELAS setup. This prevents any condensation within the analyser, and reduces any potential interference between the spectral features of H₂O and the measured gases which may not be adequately accounted for by instrument correction factors (Nara et al., 2012). However, certain types of desiccants can induce memory effects on gases such as CO₂, resulting from absorption equilibria at the surface (e.g. Santos et al. 2012). During our experiments we used two different types of desiccants, Drierite in the laboratory experiments and magnesium perchlorate (Mg(ClO₄)₂) in the field experiments. To determine the extent of potential interference on the response time experiments for CO₂ and CH₄, a second CELAS analyser (same model CRDS; G2201-i Picarro) was connected to the closed loop upstream of the desiccant. A showerhead equilibrator with an approximate flow rate of 8 L min⁻¹ was used for this experiment.

2.3 Assessment and discussion

2.3.1 Desiccant experiment

Figure 2.2 illustrates the response curves relating to desiccant and non-desiccant measurement on two CELAS systems running in series with the one air-water equilibrator (marble), accounting for differences in the gas travel time between the equilibrator and each of the CELAS analysers. The Drierite desiccant had an effect on the CO₂ response during both changes between low and high concentration water source, resulting in a total equilibration delay of ~90 s. Similar to the findings in Santos et al. (2012), no significant ongoing absorption/desorption could be distinguished after steady state conditions had been reached.
No desiccant absorption effect was found for CH$_4$ in both desiccant types, and Mg(ClO$_4$)$_2$ did not induce a delay on CO$_2$ response time.

![Figure 2.2](image)

**Figure 2.2** Step experiments carried out to determine the effect of two desiccants, Drierite (A) and magnesium perchlorate (Mg(ClO$_4$)$_2$) (B), on the response times of CO$_2$ and CH$_4$ through a showerhead equilibrator. A time delay of 1.5 minutes was observed for CO$_2$ concentrations when Drierite was used as a desiccant. Mg(ClO$_4$)$_2$ had no effect on concentration response times and CH$_4$ remained unaffected by both desiccants.

### 2.3.2 Laboratory experiments

The equilibration response time of various air-water equilibrators for several gases have been assessed, including O$_2$, N$_2$, CH$_4$, $^{222}$Rn, SF$_6$, and CO, but mostly for CO$_2$ (Table 2.1). Several types of air-water equilibrators that have been used for continuous CO$_2$ and/or CH$_4$ measurements, including the showerhead type, permeable membranes, bubble-type, and marble-type (Table 2.1). We build on this earlier work by simultaneously comparing CO$_2$ and CH$_4$ equilibration times using six different equilibrators and assess the utility of different air-water equilibrators for field-based measurements of dissolved $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-CH$_4$ values.

Equilibrium of dissolved CO$_2$ and CH$_4$ was achieved in all six air-water equilibrators (Figure 2.3). All step experiments showed the expected trend towards equilibrium (Figure 2.3). The water-headspace disequilibrium decreased exponentially before reaching equilibrium...
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concentration. Equilibration times were fastest going from low to high concentrations, which was also observed in some similar step experiments measuring air-water equilibration times of CH₄, N₂O, CO₂ and radon (²²²Rn) (Gülzow et al. 2011; Santos et al. 2012; Grefe et al. 2014). Gülzow et al. (2011) argued that the effect of the high-low versus low-high mismatch is a result of loss of concentration in the high concentration pool over the time of the step experiment. To avoid this reservoir effect we have only used the high-low step response to calculate τ values, as was also done by Johnson (1999) and Gülzow et al. (2011).

Differences in equilibration times between CO₂ and CH₄ was noticeable over all equilibrators, where CH₄ response times took on average 5 times longer than CO₂ in the membrane types and ~15 times longer in the aspirating equilibrators (Figure 2.3). Similar results were found in the response time between the simultaneous measurement of CO₂ and ²²²Rn using similar equilibrators, where ²²²Rn took 1.8-7.3 (low-high) and 2.0-10.8 (high-low) times longer than CO₂ to reach equilibrium (Santos et al. 2012). CO₂ is 25 times more soluble than CH₄ based on the Bunsen coefficients of 870.5 mL L⁻¹ atm⁻¹ and 34.69 mL L⁻¹ atm⁻¹ for CO₂ and CH₄ respectively at 20 °C in freshwater (Weiss 1974; Yamamoto et al. 1976). Solubility can explain the discrepancies in the equilibration time τ between two gases, as was found in Schneider et al. (2007), where τ was an order of magnitude different between CO₂ and O₂ (corresponding to their solubility coefficients). Clearly the differences in solubility properties played a role in the discrepancies in the equilibration τ between gases. However, if this were purely the case, CH₄ equilibration times would have taken 25 times longer. Factors that define the time constant of gaseous air-water equilibration include the volume of the equilibrator headspace (Ve), flow rate of sample water stream (Qw), the equilibrator specific gas transfer coefficient (ε), and the solubility coefficient (α), as demonstrated in the following equation from Johnson (1999):

\[ \tau_1 = \frac{V_e}{Q_w \varepsilon \alpha} \]

Therefore, variability in the ratio of CO₂ and CH₄ equilibration times between the different equilibrators has also been influenced by differences in equilibrator design (i.e. the mechanism, gas and water phase volume, and transfer velocity of gas exchange between gas and water phases) along with the differing outflow rates of each air-water equilibrator. It is important to note that all variables in equation 2 excluding the solubility coefficient and ε (due to differences in gas specific Schmidt number) are identical for different gases, but variable among different equilibrators. Air-water equilibrators are designed to enhance gas transfer across the air-water
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Interface, however some have specific qualities that further enhance transfer more than others. For example, a reduction in air volume can greatly reduce equilibration times. Arévalo-Martínez et al (2013) reduced τ for N$_2$O and CO to 2.5 and 45 min respectively compared to values of 6.4 min and 216.3 min reported by Johnson (1999), with both studies using a similar Weiss-style equilibrator with the system used by Arévalo-Martínez et al (2013) having a smaller headspace volume.

![Experimental response times of dissolved CO$_2$ and CH$_4$ from six different air-water equilibrators when switching between low-high-low concentrations. Concentrations are normalised to 0 and 1, where 0 is the minimum and 1 is the maximum concentration reached. Time constants (τ) were derived from the decay end of each experiment and are given in seconds. Shaded area indicates the time period the equilibrator was measuring from the high concentration reservoir.](image)

**Figure 2.3** Experimental response times of dissolved CO$_2$ and CH$_4$ from six different air-water equilibrators when switching between low-high-low concentrations. Concentrations are normalised to 0 and 1, where 0 is the minimum and 1 is the maximum concentration reached. Time constants (τ) were derived from the decay end of each experiment and are given in seconds. Shaded area indicates the time period the equilibrator was measuring from the high concentration reservoir.
Liqui-Cel equilibrators achieved notably faster (by at least two-fold) response times for CH$_4$ compared to the three aspirating equilibrators. This is likely due to the very small headspace in combination with a large surface area (0.18 m$^2$, 0.99 m$^2$, and 1.4 m$^2$ for the small, medium, and large Liqui-Cel respectively) available for gas transfer. A small headspace relative to water volume has proven to work well for improving the response time of less soluble gases such as carbon monoxide (CO) and oxygen (O$_2$). Comparing the response times estimated for CO in a Weiss type equilibrator between two studies (Johnson 1999; Arévalo-Martínez et al. 2013), the smaller equilibrator achieved ~4 times faster equilibration (Table 2.1). By reducing a headspace by 100 mL and increasing the water volume in a bubble type equilibrator, the response time of O$_2$ equilibration was reduced to match the resolution of continuous latitudinal $p$CO$_2$ ocean measurements (Schneider et al. 2007).

2.3.3 Isotopologue equilibration from field experiments

The individual isotopologue time constants were calculated using the high to low component of field step experiments, using 1 second time intervals from the raw data. Figures 2.4 and 2.5 show this exponential decay portion of the experiment. CO$_2$ isotopologue time constants were very similar between the three equilibrator types, ranging between 33.7-42.8 s and 34.1-43.1 s in $^{12}$CO$_2$ and $^{13}$CO$_2$ respectively. As was observed in the laboratory experiments, CH$_4$ isotopologue time constants were substantially longer than CO$_2$ isotopologues, this time by about five to tenfold. CO$_2$ required 1.7-2.2 min and CH$_4$ 8.9-17 min under these field conditions at a 5.5 L min$^{-1}$ outflow rate to reach 95% of equilibrium (i.e. 3τ). For each equilibrator, the $^{12}$C and $^{13}$C time constant were practically identical, except for <1 s difference between $^{12}$CO$_2$ and $^{13}$CO$_2$ (discussed below). This finding is expected due to the very small difference in solubility between $^{12}$CO$_2$ and $^{13}$CO$_2$ (~ 0.1%, Vogel et al., 1970) and between $^{12}$CH$_4$ and $^{13}$CH$_4$ (~ 0.05%, Bacsik et al., 2002), as well as the negligible kinetic fractionation factors which under experimental diffusive conditions is between ~ 0.9 and 1.3 ‰ for CO$_2$ (Inoue and Sugimura, 1985; Wanninkhof, 1985) and ~ 0.8‰ for CH$_4$ (Knox et al., 1992). The kinetic fractionation is likely to be much less in the equilibrators tested due to the higher turbulence within the equilibrators compared to the diffusive experiments used to determine kinetic fractionation associated with gas exchange. For example, kinetic fractionation approaches 0 when exchange is via bubble injection (Knox et al., 1992).
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Figure 2.4 Step experiments carried out in field conditions showing the high-low equilibration response time for $^{12}$CO$_2$ and $^{13}$CO$_2$ in the marble, showerhead, and large LiquiCel equilibrators. Response times are reported as the average decay time constant ± standard deviation (seconds) from triplicate trials.
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2.3.4 Isotope mixing effects

Isotopic fractionation accompanies phase changes between water and air for both $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-CH$_4$ values due to the slight differences in the rate of transfer between the light (12C) and heavy (13C) isotope. This was observed in CO$_2$ where the $^{13}$CO$_2$ isotopologue time constant was slightly longer (0.3-0.5 second) than the $^{12}$CO$_2$ isotopologue time constant, resulting in spikes for $\delta^{13}$C-CO$_2$ (Figure 2.6). The same was not observed for CH$_4$ isotopologues, likely due to the smaller differences in solubility between $^{12}$CH$_4$ and $^{13}$CH$_4$ (~0.05%) than $^{12}$CO$_2$ and $^{13}$CO$_2$ (~0.1%) (Vogel et al., 1970, Bacsik et al., 2002). Figure 2.6 illustrates this kinetic fractionation when looking at the response in $\delta^{13}$C-CO$_2$ values during initial low-high and high-low switch. During fractionation 1, the lighter CO$_2$ isotopologue ($^{12}$CO$_2$) in the high concentration water stream transfers out of the liquid into the gas phase more rapidly than $^{13}$CO$_2$, temporally depleting the $\delta^{13}$C-CO$_2$ value in the gas phase. The reverse happens during fractionation 2, where the $^{12}$CO$_2$ isotopologue transfers more rapidly back into the water stream as the gas phase CO$_2$ concentration is now higher than the liquid phase concentration. This

---

**Figure 2.5** Step experiments carried out in field conditions showing the high-low equilibration time for $^{12}$CH$_4$ and $^{13}$CH$_4$ in the marble, showerhead, and large LiquiCel equilibrators. Response times are reported as the average decay time constant ± standard deviation (seconds) from triplicate trials.
leaves proportionally more $^{13}$CO$_2$ in the headspace, resulting in a temporary enrichment of the $\delta^{13}$C-CO$_2$ value. Such switching spikes in the $\delta^{13}$C-CO$_2$ value have also been observed by Friedrich et al. (2010) and should be removed from the dataset.

![Figure 2.6](image.png)

**Figure 2.6** Example of kinetic fractionation of $^{13}$CO$_2$ during the two different stages of equilibration between differing concentration and $\delta^{13}$C-CO$_2$ compositions. Fractionation 1 represents low-high switch and fractionation 2 represents high-low switch as described in the text. Data presented has been smoothed to 30 s averaging interval.

The actual time required for isotopic compositions ($\delta^{13}$CO$_2$ and $\delta^{13}$CH$_4$) to reach complete equilibration can be different compared to the same response times derived from the isotopologues. A pronounced delay is noticed for the high concentration isotopic endmember when returning to the lower concentration endmember in the $\delta^{13}$C-CH$_4$ response curves (Figure 2.7B). This is due to a well-known isotopic mixing effect which relates to the isotope value of a mixture comprised of two different concentrations and isotopic compositions (Faure, 1986; Fry, 2006). The gas concentration in the equilibrator headspace is related to the fraction ($f$) of the low concentration gas versus high concentration gas, along with the corresponding concentrations of the low and high concentration gases:

$$
\text{Conc}_{\text{Sample}} = (\text{Low}_f \times \text{Low}_{\text{conc}}) + (\text{High}_f \times \text{High}_{\text{conc}})
$$

where $\text{Low}_f$ refers to the fraction of low concentration gas to high concentration gas and $\text{High}_f$ is the fraction of high to low concentration, $\text{Low}_{\text{conc}}$ refers to the actual concentration (ppm) of the lower concentration gas and $\text{High}_{\text{conc}}$ the actual concentration of higher concentration gas (ppm). $\text{Conc}_{\text{Sample}}$ is the gas concentration in the equilibrator. The mixing of two different gas compositions should behave conservatively, that is when the fraction of each endmember is 0.5
the concentration of the sample should be intermediate between the compositions of the endmembers.

When applied to isotopic equilibration, the mixing is a function of both concentration and isotopic composition ($\delta$) of the gasses in the two water types:

$$\delta_{\text{Sample}} = \left( (\text{Low}_f \times \text{Low}_{\text{conc}} \times \text{Low}_\delta) + (\text{High}_f \times \text{High}_{\text{conc}} \times \text{High}_\delta) \right) / \text{Conc}_{\text{sample}}$$

As a result the changes isotopic composition during mixing of waters with differing isotope and concentrations is not linear, which in turn affects the equilibration response of $\delta^{13}$C values between high to low and low to high steps (Figure 2.7A). The equilibration time for low-high and high-low transitions will vary based on the difference in concentration of the two components (Kendall & Caldwell, 1998). Figure 2.7A illustrates the isotope mixing concept for $\delta^{13}$C-CH$_4$ time under four simulated scenarios from low-high and high-low equilibration. This model is based on the concentration change within the headspace mixing conservatively (i.e. a linear change in concentration over the equilibration time). In all scenarios, the low concentration sample has a concentration of 2 ppm and $\delta^{13}$C-CH$_4$ of -45‰. The high concentration sample has a $\delta^{13}$C-CH$_4$ of -30‰ and a concentration difference of 0.1, 3, 10 and 100 ppm from the low (i.e. a concentration of 2.1, 5, 12 and 102 ppm) represented by green, blue, black and red symbols respectively on Figure 2.7A. Taking the 102 ppm high concentration example from Figure 2.7A (red symbols), when equilibrating from low-high a shift from 0 to 10% (relative to volume of gas) proportion of the high concentration sample into the headspace results in a change from -45‰ to -32.25‰ which represents 85% of the change towards the final value (-30‰). However when equilibrating from high-low, a 10% input of low concentration into the headspace containing high concentration sample results in a change of only 0.27% (from -30‰ to -30.27‰). Hence, the return of high concentration isotopic endmember back to low concentration isotopic composition will require near complete equilibration (100%) of the concentration first. This concentration effect on isotopic mixing equilibration applies to both $\delta^{13}$C-CO$_2$ and $\delta^{13}$C-CH$_4$ values, yet will be most pronounced for CH$_4$ due to the slower concentration response time.
Automated, in situ measurements of dissolved CO$_2$, CH$_4$, and δ$^{13}$C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

Figure 2.7 A) Model illustrating the isotopic mixing effect on the equilibration of δ$^{13}$C-CH$_4$ values between two water bodies with distinctly different δ$^{13}$C-CH$_4$ composition and different concentrations. The low concentration sample has a fixed concentration of 2 ppm and δ$^{13}$C-CH$_4$ of -45‰, and the high concentration sample has a δ$^{13}$C-CH$_4$ of -30‰ with concentrations 2.1 (green), 5 (blue), 12 (black) and 102 (red) ppm. High$f$ refers to the fraction of the headspace containing the high concentration sample (High$f$ = High$f$/Low$f$ + High$f$), and Low$f$ refers to the fraction of the headspace containing the low concentration sample (Low$f$ = Low$f$/Low$f$ + High$f$). For example a High$f$ value of 0.2 means that the headspace is comprised of 20% high concentration gas and 80% low concentration gas. Each marker along a specific concentration response curve represents an equal unit of time. Response curve of concentration equilibration is modelled as linear. B) Example of the hyperbolas that formed during step response experiments for δ$^{13}$C-CH$_4$ values, demonstrating equilibration delay for δ$^{13}$C-CH$_4$ values when going from high-low concentration. This experiment was carried out with a showerhead equilibrator at a flow rate of 9 L min$^{-1}$ and had a concentration difference of ~660 ppm. Data presented has been smoothed to 30 s averaging interval.

2.3.5 Relationship between flow rates and response times

Variables that define the equilibration time of gas transfer between aqueous and gaseous phases in an equilibrator include surface area, transfer coefficient, pressure, solubility coefficient, volume of gaseous phase, and volume of water phase (Johnson, 1999; Schneider et al. 2007; Gülzow et al. 2011). Environmental factors such as temperature and salinity can also affect the response time by changing solubility, gas diffusivity, and water viscosity (Macintyre et al., 1995). Air-water equilibrators are designed to optimise this transfer, which can most easily be manipulated by changing water flow rates. Increasing the flow rate effectively increases the turbulent transfer. This is due to a rapid rate of water renewal at the air-water interface which
increases the gas transfer velocity (Johnson, et al., 2010). Eventually, $\tau$ will become limited by either the water flow rate or the equilibrator specific gas exchange coefficient (Rafelski et al., 2013). Therefore, manipulating the water flow rate may be an efficient and simple way to shorten the response time (Schubert et al. 2006; Schubert et al. 2012). Equilibrium times ($3 \times \tau, 95\%$) for various flow rates ranging between 1.5-9 L m$^{-1}$ for the marble equilibrator were fitted with an inverse first order polynomial equation (Figure 2.8).

Flow rates clearly influenced equilibration times with equilibration time decreasing with increasing flow rate through the equilibrator (Figure 2.8). The effect of a more rapid air-water gas exchange with increasing water velocity is clear, with a 7.5 L min$^{-1}$ increase in water flow rate decreasing CO$_2$ and CH$_4$ equilibration times by ~5 and ~110 minutes respectively. The fastest equilibration response times for CO$_2$ and CH$_4$ achieved using a maximum flow rate of 9 L min$^{-1}$ were 2 min and 12.4 min respectively. Another study that modelled flow rate effect on response times from experimental results found a threshold after ~13 L min$^{-1}$ for O$_2$ in a showerhead-based equilibrator filled with raschig rings, and an equilibration time of 5.14 minutes extrapolated to an infinite flow rate (Rafelski et al. 2013). Although the fastest possible response time when monitoring gases in aquatic systems is always preferred, the benefit of achieving this by increasing flow rate after 7 L min$^{-1}$ is small, at least for a marble equilibrator of the same design as that used in this study.
Automated, in situ measurements of dissolved CO\textsubscript{2}, CH\textsubscript{4}, and δ\textsuperscript{13}C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

Figure 2.8 Effect of water flow rate on equilibration response time for CO\textsubscript{2}, and CH\textsubscript{4} concentrations from seven step experiments with the marble equilibrator. While our analysis focuses on the high-to-low response times, we also plot the low-to-high response times for completeness. Note that response times here are reported as time taken to reach equilibrium (3 x τ, 95% Δp-relaxation). Results were fitted with an inverse first order polynomial equation t= tf∞+(a/f).

2.4 Comments and recommendations

Our results show that measurements of dissolved CO\textsubscript{2}, CH\textsubscript{4}, δ\textsuperscript{13}C-CO\textsubscript{2} and δ\textsuperscript{13}C-CH\textsubscript{4} can be made using various air-water equilibrators, with equilibration response times suitable for most continuous monitoring applications. To achieve rapid equilibration times of <2 min and <20 min for CO\textsubscript{2} and CH\textsubscript{4} isotopologues respectively in showerhead type equilibrators, a substantial flow rate of at least 5.5 L min\textsuperscript{-1} is required. Methane has a longer equilibration time and therefore this should be considered when designing field experiments. The sub-20 min equilibration time achieved for CH\textsubscript{4} should be adequate for many applications (e.g. Gülzow et al. 2013; Yuhong et al. 2015). The membrane type equilibrators appeared to have the best design for facilitating rapid air-water transfer of the equilibrators tested here, achieving <2 min and <10 min equilibration time for CO\textsubscript{2} and CH\textsubscript{4} respectively. However, caution should be exercised when using membrane equilibrators as the process of permeation brings about certain physical/chemical processes (sorption, diffusion, desorption) that may lead to isotopic fractionation. Generally, it is not recommended to use the LiquiCel type equilibrators in turbid
Automated, in situ measurements of dissolved CO$_2$, CH$_4$, and δ$^{13}$C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

waters and at flow rates above the capacity of the membrane, as these factors can deform the membrane structure, and cause isotopic fractionation of the δ$^{13}$C values (e.g. Wankel et al., 2013) which needs to be adequately characterized to define dissolved δ$^{13}$C values.

The most appropriate air-water equilibrator to use will vary depending on the study goals, gas species being measured, and temporal resolution of measurements required. For high resolution time series and surveys in dynamic waters such as estuaries, eutrophic systems and mangroves we suggest using the Marble equilibrator as it is can achieve fast equilibration of both CO$_2$ and CH$_4$ in turbid waters. However, memory effects of CH$_4$ absorbing onto the marbles and/or Plexiglas surfaces have been observed in the marble type equilibrator after equilibrating from high-low concentration stations, recording 50-70% higher values at <20 µatm (Abril et al. 2006). Despite no memory effects between initial and final low concentrations observed during our experiments, we also recommend limiting the use of the marble and showerhead equilibrators to highly supersaturated waters due to their ability to introduce small amounts of atmospheric air via venting whilst maintaining atmospheric pressure.

Users should be aware of the isotopic mixing effect that occurs when mixing high concentration waters with low concentration water with different isotopic δ$^{13}$C compositions, which creates a longer delay in absolute equilibration time. This mixing effect can be observed in both δ$^{13}$C-CH$_4$ and δ$^{13}$C-CO$_2$, however is greater for CH$_4$ due to its longer equilibration time as a result of its lower solubility. Individual CH$_4$ isotopologue 95% equilibration time constants were <20 mins. However, to reach equilibrium δ$^{13}$C values near complete equilibration is required, extending this response time to ~80 mins for δ$^{13}$C-CH$_4$ when transitioning from high to low concentration waters. This isotope mixing effect however is most pronounced during conditions of 1) equilibration from high-low, and 2) when the concentration difference is high. Because the rate of isotope change is largely driven by the concentration ratio (Figure 2.7), under typical field scenarios where the rate and magnitude of concentration change over a small time period is generally small (i.e. not instantaneous change from high levels of supersaturation to atmospheric equilibrium) isotopic resolution should be similar to concentrations. Results from field campaigns show that the equilibrator-CELAS setup can capture tidal and diurnal changes in concentration and δ$^{13}$C-CH$_4$ at hourly resolutions (Maher; 2013; Gatland et al., 2014; Call et al. 2015; Maher et al. 2015, O’Reilly et al., 2015).

Water flow rate substantially decreases equilibration response time, however the benefit of increasing flow rate decreases substantially after about 7 L min$^{-1}$ for the marble equilibrator
Automated, in situ measurements of dissolved CO₂, CH₄, and δ¹³C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators

The optimum flow rate will vary between different equilibrators that rely on turbulent gas exchange, however the trend will be the same as demonstrated in Figure 2.8. For the membrane based equilibrators increasing flow rate will also increase gas transfer, however gas exchange will eventually become limited by diffusion through the membrane. In fact high water flow rates can decrease gas exchange through the membrane resulting from high hydrostatic pressure deforming the pores (Boulart et al. 2010; Wankel et al. 2013). Since power consumption is often an important consideration when making field measurements, a trade-off needs to be established between an optimum water flow rate, equilibration time, and power requirements of larger pumps.

The review provided here on six commonly used equilibrators for simultaneous measurement of CO₂, CH₄, δ¹³C-CO₂ and δ¹³C-CH₄ highlights the range of response times and therefore the applicability of the various equilibration devices for different applications. The air-water equilibrator-CELAS combination has the ability to perform fast CO₂ and CH₄ and isotopic measurements in aquatic environments at a frequency that cannot be achieved with traditional discrete sampling and laboratory-based stable isotope analysis. This set up can be applied to any aquatic environment using a suitable air-water equilibrator, and can be deployed easily in remote locations with a portable power supply. The ability to capture higher frequency changes at both temporal and spatial scales can provide new insights into the processes governing CO₂ and CH₄ biogeochemical cycles in dynamic aquatic environments.
Chapter 3 - Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: post-flood hydrological and biological drivers

Abstract

Many coastal floodplains have been artificially drained for agriculture, altering hydrological connectivity and the delivery of groundwater-derived solutes including carbon dioxide (CO$_2$) and methane (CH$_4$) to surface waters. Here, we investigated the drivers of CO$_2$ and CH$_4$ within the artificial drains of a coastal floodplain under sugarcane plantation and quantify the contribution of groundwater discharge to CO$_2$ and CH$_4$ dynamics over a flood (290 mm of rainfall). High temporal resolution, in situ observations of dissolved CO$_2$ and CH$_4$, carbon stable isotope for CH$_4$ ($\delta^{13}$C-CH$_4$), and the natural groundwater tracer radon ($^{222}$Rn) allowed us to quantify CO$_2$, CH$_4$ and groundwater dynamics during the rapid recession of a flood over a five day period. Extreme super-saturation of free CO$_2$ ([CO$_2^*$]) up to 2,951 µM (25,480% of atmospheric equilibrium) was driven by large groundwater input into the drains (maximum 87 cm day$^{-1}$), caused by a steep hydraulic head in the adjacent groundwater. Groundwater input sustained between 95-124% of the surface [CO$_2^*$] flux during the flood recession by delivering high carbonate alkalinity groundwater (DIC = 10,533 µM, ~pH = 7.05) to acidic surface water (pH <4), consequently transforming all groundwater-derived DIC to [CO$_2^*$]. In contrast, groundwater was not a major direct driver of CH$_4$ contributing only 14% of total CH$_4$ fluxes. A progressive increase in CH$_4$ concentrations of up to ~2,400 nM day$^{-1}$ occurred as a combination of increased substrate availability delivered by post-flood drainage water and longer residence times, which allowed for a biogenic CH$_4$ signal to develop. The progressive enrichment in $\delta^{13}$C-CH$_4$ values (-70‰ to -48‰) and increase in CH$_4$ concentrations (46-2,460 nM) support coupled production-oxidation, with concentrations and $\delta^{13}$C values remaining higher (-47‰ and 2,798 nM) than pre-flood conditions (-55‰ and 534 nM) three weeks after the flood. Our findings demonstrate how separate processes can drive the aquatic CO$_2$ and CH$_4$ response to a flood event in a drained coastal floodplain, and the key role groundwater had in post-flood [CO$_2^*$] evasion to the atmosphere, but not CH$_4$.

Key words: Wetland, acid sulfate soils, seepage, greenhouse gas, stable isotopes
3.1 Introduction

Floodplain ecosystems play an important role in carbon cycling at the terrestrial-aquatic interface, and have some of the highest global rates of primary production and carbon sequestration. Primary productivity in floodplain wetlands range from 205 to 2,438 g m\(^{-2}\) yr\(^{-1}\) (Mitsch et al., 1991; San-José et al., 2010), and carbon burial rates range from 57 to 921 g m\(^{-2}\) yr\(^{-1}\) (Hopkinson et al., 2012; Marín-Muñiz et al., 2014). However, understanding the processes driving carbon dioxide (CO\(_2\)) and methane (CH\(_4\)) cycling has proven difficult. Floodplains have variable hydrological regimes of discharge and inundation which can produce large carbon exports in the form of CO\(_2\) and CH\(_4\) outgassing and lateral aquatic discharge (Pulliam, 1993; Gatland et al., 2014). Carbon exports are often poorly quantified and not integrated into floodplain carbon budgets. Consequently, only a few estimates exist for carbon loss from floodplains (Pulliam, 1993; Gatland et al., 2014; Batson et al., 2015).

Changes in floodplain hydrology can produce feedback mechanisms in biogeochemical processes such as varying sediment and nutrient loads, alterations to aquatic metabolism, distribution in vegetation (Hamilton, 2010), and can also exert controls over greenhouse gas fluxes (Altor and Mitsch, 2008; Battin et al., 2008; Mitsch et al., 2010). Climate-driven changes in precipitation, conversion of wetlands to crops and intensification of artificial drainage can significantly alter the functioning of floodplain ecosystems (Hamilton, 2010; Schottler et al., 2014). Coastal floodplains in particular have been exposed to significant anthropogenic pressures such as agriculture and urban development. The average rate of wetland conversion to developed land has progressively increased to a current rate of about 1% yr\(^{-1}\) (Davidson, 2014).

The water quality issues associated with the drainage of modified coastal floodplains have been widely documented (Wilson et al., 1999; Johnston et al., 2003; Macdonald et al., 2004; Macdonald et al., 2007). In pyritic coastal floodplains, changes in water table height due to drainage oxidises the underlying sediments which produces extreme acidification and deoxygenation events after floods (Wong et al., 2011). Under these conditions, extremely high post-flood CO\(_2\) supersaturation has been recorded in floodplain drainage waters (Atkins et al., 2013; Gatland et al., 2014; Ruiz-Halpern 2015). These high \(p\)CO\(_2\) values result in particularly high atmospheric fluxes. Climate models predict greater hydrological extremes, including more intense flood events, in regions of Australia where most of these modified coastal floodplains...
exist (Hughes, 2003). Therefore, there is a need to understand the consequences floods may have on fluvial CO₂ and CH₄ losses from these modified landscapes.

An abundance of labile organic matter can produce low oxygen conditions that generate high CO₂ and CH₄ concentrations in shallow floodplain groundwaters. Artificial drains can provide conduits for shallow groundwater to discharge into surface waters, effectively increasing hydrological connectivity (Johnston et al., 2005). Groundwater discharge can be an important source of CO₂ into surface small streams (Borges et al., 2015, Hotchkiss et al., 2015), however due to difficulties in constraining groundwater-surface water interactions, it is a pathway often neglected in aquatic carbon budgets (Macpherson, 2009). In coastal acid sulphate soil (CASS) floodplains, groundwater discharge can significantly alter the chemistry of drainage waters by contributing large quantities of reducible Fe, Mn, and SO₄⁻² minerals, dissolved nutrients, and acid (Johnston et al., 2004; Burton et al., 2006; Santos et al., 2011; Jeffrey et al., 2016). This can affect the redox conditions of the surface water which combined with large quantities of labile organic matter may alter pathways and rates of carbon metabolism (Johnston et al., 2003; Wong et al., 2011). Understanding the influence groundwater discharge has on surface water carbon metabolism in these modified coastal floodplains may be critical for understanding CO₂ and CH₄ dynamics.

High resolution sampling is essential for capturing the temporal changes in carbon dynamics, which can undergo rapid transformations during and after a flood in floodplains. Here, we rely on high resolution observations of dissolved CH₄ concentrations and carbon stable isotope ratios (δ¹³C-CH₄), dissolved CO₂, and radon (²²²Rn, a natural groundwater tracer) following a flood in the drainage canals of an agricultural modified floodplain, to determine the main processes contributing to the post-flood response of CO₂ and CH₄. We attempt to resolve the contribution of floodwaters versus groundwater discharge to CO₂ and CH₄ exports. Our focus on quantifying the processes that enhance CO₂ and CH₄ concentrations after a flood contributes to quantifying the role of inland waters in the terrestrial carbon balance, where episodic events are often unaccounted for. We hypothesise that rapid drainage of flood waters will greatly enhance CO₂ and CH₄ concentrations, and that groundwater discharge will be primarily responsible for post-flood CO₂ and CH₄ dynamics in artificial drains.
3 \textbf{Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: post-flood hydrological and biological drivers}

3.2 \textbf{Material and Methods}

3.2.1 \textbf{Study site}

This study was undertaken in a hydrologically well constrained highly modified floodplain, where discharge, along with surface and groundwater levels are primarily controlled by a mechanical pump. The study site is a 100 ha sub-catchment situated within the low-lying Tweed River floodplain \( (28°17'1.69''\text{S}, 153°30'15.02''\text{E}) \) in Australia (Figure 3.1). The system represents a typical example of a natural wetland drained for agricultural development (in this case sugar cane cultivation). The Tweed floodplain consists of coastal acid sulphate soils containing high levels of iron sulphides (\( \text{FeS}_2 \)) (Naylor et al., 1998). Sugarcane has been the dominant land use in the area for the last \( \sim 40 \) years. Prior to sugar cane cultivation the sub-catchment had been modified wetland pasture since 1930, and was originally a low-lying freshwater wetland comprised of Melaleuca vegetation (Wilson, 1995).

Hydrology within the sub-catchment is greatly modified with a large network of shallow artificial drains \( (\sim 12.9 \text{ km of drains within a 100 km}^2 \text{ catchment}) \), flap floodgates impeding tidal water infiltration, and an electric pump which controls surface and groundwater levels (Green et al., 2006). All drains within the catchment have shallow water depths, with the main drains having depths between 30 cm and 60 cm during baseline conditions. Smaller field drains are about 50 cm deep and usually only contain water after major rainfall. Two tidal creeks border the sub-catchment and a disconnected interception drain separates the site from neighbouring properties (Figure 3.1), making this a hydrologically isolated sub-catchment, except during floods (Smith et al., 2003). Catchment discharge is controlled by the automatic electric pump at the outlet of the sub-catchment (Figure 3.1), where pumping starts as water levels go above \(-453 \text{ mm Australian Height Datum (AHD)}\) and stop when below \(-453 \text{ mm AHD}\) (Green et al., 2006). As a result, groundwater levels are generally maintained at a relatively constant height of \(-0.5 \text{ m AHD}\) (Smith et al., 2003), reducing groundwater seepage, except when significant rainfall events occur.
3 Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: post-flood hydrological and biological drivers

Figure 3.1 Location of study site and sampling points: (A) McLeods Creek sub-catchment located within the Tweed River floodplain (1100 km$^2$), the northern-most coastal region of New South Wales, eastern Australia (from Smith and Melville, 2004); and (B) sub-catchment (0.01 km$^2$) where the time series was carried out. The extensive drainage network and the location of discrete groundwater and surface water samples is shown.

3.2.2 Sampling Strategy

Our experimental approach was to (1) monitor changes in CO$_2$ and CH$_4$ concentrations by undertaking high temporal resolution in situ CO$_2$, CH$_4$, $\delta^{13}$C-CH$_4$, and $^{222}$Rn measurements within drainage waters from flood to return to pre-flood flow (2) construct a mass balance for groundwater using radon as tracer to quantify the contribution of groundwater to CO$_2$ and CH$_4$ dynamics post-flood, (3) constrain the major sources (groundwater and in-drain production)
and sinks (aquatic export and gaseous evasion) of CO$_2$ and CH$_4$ to the surface waters of the catchment.

Firstly, discrete samples of dissolved CO$_2$, CH$_4$, $\delta^{13}$C-CO$_2$, $\delta^{13}$C-CH$_4$, $^{222}$Rn, and water quality parameters were taken within the drain surface waters (Figure 3.1) both before, during, and after continuous monitoring. These discrete samples represent conditions described as pre-flood (1-3 weeks before flood), flood (period of inundation), and post-flood (1-3 weeks after flood recovery) and were taken from three different locations along the main drain (Figure 3.1). Water quality parameters were taken on site using a Hach®, HQ40d for pH, DO, and temperature, and a TROLL 9500 multiparameter sonde for conductivity. Six litre samples for surface water $^{222}$Rn concentrations were collected in specially designed 8 L HDPE plastic bottles, leaving a headspace (Stringer and Burnett, 2004). A submersible Rule iL280 Amazon pump was used to sample water. Samples for dissolved CO$_2$ and CH$_4$ were collected in duplicate 200 mL opaque bottles with the submersible pump by filling the bottles from the bottom and overflowing approximately three times the volume. Samples were then treated with 200 µL of HgCl$_2$ and capped ensuring no headspace.

A 290 mm rain event over five days caused large portions of the floodplain to become inundated (up to 80 cm) between the 20$^{th}$ and 26$^{th}$ January 2015. During this time discrete samples were taken once a day between the 23$^{rd}$ and 25$^{th}$ to characterise concentrations during flood conditions. Field sampling was concentrated to flood waters rather than drains due to inundation of the catchment and carried out via the procedures described above.

High frequency continuous observations took place during the receding phase of the flood from 26$^{th}$ to 31$^{st}$ January 2015. A submersible pump was placed just above the bottom of the main drain, about 90 m upstream of the artificial pump, and delivered a constant stream of water through two showerhead-type gas equilibration devices (General Oceanics, Inc) following procedures described elsewhere (Maher et al., 2013; Webb et al, 2016b). To maintain atmospheric pressure during air-water gas equilibration and avoid contamination with outside air, the first equilibrator was vented to a second equilibrator which was open to the atmosphere. Sample air was pumped from the equilibrators at a rate of 1 L min$^{-1}$ to three gas analysers connected in series. Dissolved CH$_4$ and $\delta^{13}$C-CH$_4$ was measured on a cavity ringdown spectroscopy (CRDS) analyser (Picarro G2201-i). An infrared gas analyser (LI-840, LI-COR, Inc.) was used to measure dissolved CO$_2$ and a radon-in-air monitor (RAD7, Durridge Co., Inc.) for radon. The equilibrated sample air was continuously pumped in a closed air loop setup.
between the equilibration device and gas analyzers using an external air pump (12 V DC micro diaphragm pump). The equilibration times for radon, CO\textsubscript{2} and CH\textsubscript{4} using this experimental setup are about 30 minutes, 5 minutes and 20 minutes respectively (Santos et al., 2012, Webb et al., 2016b).

Physiochemical water quality parameters were monitored during the time series. A calibrated multi-parameter water quality logger (Hydrolab DS5X) was deployed in the drain next to the pump to measure in situ temperature, conductivity, pH, and dissolved oxygen (DO). Depth and velocity measurements were recorded using a Starflow (model 6529 G-512K) ultrasonic Doppler flowmeter 100 m upstream of the artificial pump, positioned at the exit of a 76 cm diameter pipe culvert. Discharge was calculated using the changing cross sectional area as a function of depth within the pipe and the measured velocity (±2% error) at the time. Wind data was obtained from an onsite weather station (R.M Young Wind Sentry Set) located approximately 800 m downstream of the sampling site.

Groundwater samples for total alkalinity and dissolved CO\textsubscript{2} and CH\textsubscript{4} were collected from a total of eight shallow wells. These groundwater locations were sampled both prior to and after flood within the sub-catchment (Figure 3.1). Bores were dug using a hand auger, installed with PVC pipes with 50-cm-long slotted screens, and sample water extracted via syringe after purging the well water volume at least three times. Water table depths varied between 0.3-1.7 m below the surface during each sampling expedition. This allowed us to constrain any heterogeneity in profile depths by obtaining an integrated endmember for the measured groundwater-derived solutes (averages and errors are reported in Table 3.1). Sediments were taken for groundwater radon equilibration experiments from two different soil layers, the oxidised sulfuric zone and unconsolidated sulfidic zone which are typical profiles in the acid sulphate soils of the region (Johnston et al., 2009). In situ water quality parameters, including temperature, pH, dissolved oxygen, and conductivity were taken with a Hach®, HQ40d portable meter and a TROLL 9500 multiparameter sonde (for conductivity).
Table 3.1 Average ± standard error of measured parameters taken as discrete samples outside of continuous monitoring. Pre-flood represents conditions 5-6 weeks before time series deployment, flood is 1-3 days before time series deployment, and post flood is 1-4 weeks after time series deployment. Groundwater samples were taken from 8 sites within the sub-catchment as shown in Figure 3.1.

<table>
<thead>
<tr>
<th></th>
<th>[CO₂*] (µM)</th>
<th>DIC (µM)</th>
<th>δ¹³C-CO₂ (%)</th>
<th>CH₄ (nM)</th>
<th>δ¹³C-CH₄ (%)</th>
<th>²²²Rn (dpm L⁻¹)</th>
<th>pH</th>
<th>Conductivity (µS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-flood</td>
<td>148 ± 31</td>
<td>1,915 ± 442</td>
<td>-9.3 ± 0.8</td>
<td>534 ± 137</td>
<td>-55.2 ± 3.0</td>
<td>7 ± 2</td>
<td>6.75 ± 0.31</td>
<td>43,335 ± 414</td>
</tr>
<tr>
<td>Flood</td>
<td>284 ± 64</td>
<td>536 ± 89</td>
<td>-14.9 ± 1.9</td>
<td>121 ± 53</td>
<td>-53.0 ± 3.2</td>
<td>36 ± 12</td>
<td>4.71 ± 0.24</td>
<td>616 ± 205</td>
</tr>
<tr>
<td>Post-flood</td>
<td>223 ± 60</td>
<td>224 ± 51</td>
<td>-15.2 ± 1.3</td>
<td>2,798 ± 156</td>
<td>-47.1 ± 1.8</td>
<td>10 ± 3</td>
<td>3.38 ± 0.12</td>
<td>6,935 ± 617</td>
</tr>
<tr>
<td>Groundwater</td>
<td>1,693 ± 495</td>
<td>10,533 ± 1,280</td>
<td>-16.5 ± 1.0</td>
<td>548 ± 185</td>
<td>-66.6 ± 4.9</td>
<td>151 ± 50</td>
<td>7.05 ± 0.22</td>
<td>11,233 ± 1,068</td>
</tr>
</tbody>
</table>

3.3 **Analytical methods**

3.3.1 **Total alkalinity and DIC**

Total alkalinity (TA) was determined by performing Gran titrations using a Metrohm Titrando automatic titrator. A Metrohm Electrode Plus was used for measuring pH during the titrations which was calibrated to Oakton National Bureau of Standards (NBS) of 4, 7, and 10. Pre-standardized 0.01 mol L⁻¹ HCl was used as the titrant. Replicates of each sample was run and the average of the two samples was used. The average uncertainty of duplicate TA measurements was 0.43% ± 0.73%. Total dissolved inorganic carbon (DIC) was calculated from the measured TA concentrations and field pH as determined in the Excel macro CO2SYS (version 25) (Pierrot et al., 2006). DIC calculations were run using the NBS pH scale and freshwater constants from Millero (1979) for K1 and K2 of carbonic acid.

3.3.2 **Radon analysis**

Discrete samples for radon analysis were connected to a radon-in-air monitor (RAD7, Durridge Co., Inc.) in a closed loop set-up for >2 h while equilibration was facilitated by continuous bubbling driven by the RAD7 internal air pump (Lee and Kim, 2006). Total volume of the sample in the bottle was ~ 6 L, leaving ~ 2 L of headspace for the equilibration to take place. Each sample volume was measured precisely with a graduated cylinder after analysis. An average was taken of the >10 x 10 minute counting cycles after equilibration was reached between the water and air phase (equilibration time ~40 min, Lee and Kim, 2006) for each analysis. Radon concentrations were determined after accounting for radon lost through decay during the time from sample extraction to analysis. During the continuous measurement
sampling phase, radon was measured in 10 minute cycles via the equilibrator setup described in section 2.2 (Burnett et al., 2001).

The groundwater radon endmember was characterised via six sediment incubations, following the sediment equilibration technique described in Corbett et al. (1998). Briefly, 1 kg sediment samples were obtained from two soil layers below the surface up to 1 m depth. Samples were only taken from this depth as shallow groundwater is the major interacting groundwater source with the surface water due to the presence of a 10 m thick layer of gel-like marine/estuarine clay that exists >1.5 m from the surface. This deeper sediment has a very low hydraulic conductivity (White et al., 2003), and acts as a confining layer between any deeper groundwater aquifers. Known volumes of radium-free tap water equilibrated with the atmosphere was added to the sediments and incubated for 21 days to allow for radon source (\(^{226}\text{Ra}\) decay) and sink (\(^{222}\text{Rn}\) decay) to reach steady state equilibrium. The radon concentration in the water was then measured on a RAD7 using procedures described above. The radon concentrations from each sediment incubation were averaged to provide an integrative groundwater radon endmember. This technique is a widely used approach for estimating the radon endmember in groundwater discharge studies (Burnett et al., 2007; Peterson et al. 2008; Schmidt et al., 2010).

3.3.3 Groundwater discharge estimates

Groundwater discharge was estimated using a radon mass balance approach that estimates minimum possible groundwater discharge. The model is based on a radon mass balance approach developed by Peterson et al. (2010) and modified by Santos and Eyre (2011), using the continuous radon measurements and taking into account \(^{222}\text{Rn}\) sources from diffusion and radium (\(^{226}\text{Ra}\) decay). Firstly, radon excess was calculated to estimate the surface water radon concentrations attributed to groundwater inputs:

\[
^{222}\text{Rn}_{\text{ex}} = ^{222}\text{Rn} - ^{222}\text{Rn}_{\text{min}}
\]

where \(^{222}\text{Rn}_{\text{ex}}\) (dpm m\(^{-3}\)) is the surface water radon concentrations that can be explained by groundwater inputs, \(^{222}\text{Rn}\) (dpm m\(^{-3}\)) is the actual surface water radon concentrations measured during the time series, \(^{222}\text{Rn}_{\text{min}}\) is the minimum \(^{222}\text{Rn}\) concentration in surface water observed when groundwater table is below the drain level (i.e. no groundwater input). This approach has been used previously (Peterson et al., 2008; Schmidt et al., 2010) and estimates maximum diffusion and \(^{226}\text{Ra}\) because it assumes no groundwater discharge when radon reaches its
minimum value. The minimum groundwater discharge was calculated by the proportion of surface water $^{222}\text{Rn}$ excess concentration to the average groundwater $^{222}\text{Rn}$ endmember concentration, multiplied by the discharge ($Q$, m$^3$ min$^{-1}$) when pump was on and the drain volume change ($V_{\text{diff}}$, m$^3$ min$^{-1}$) when pump was off:

$$Q_{\text{gw}}^{\text{Pump on}} = \frac{^{222}\text{Rn}_{\text{ex}}}{^{222}\text{Rn}_{\text{gw}}} \times Q$$

$$Q_{\text{gw}}^{\text{Pump off}} = \frac{^{222}\text{Rn}_{\text{ex}}}{^{222}\text{Rn}_{\text{gw}}} \times V_{\text{diff}}$$

Where $Q_{\text{gw}}$ (m$^3$ min$^{-1}$) is the average groundwater discharge rate, $^{222}\text{Rn}_{\text{gw}}$ (dpm m$^{-3}$) is the radon concentration in the groundwater endmember. Additionally, an upper limit to the groundwater flux can be calculated which takes into account the loss of $^{222}\text{Rn}$ via evasion and $^{222}\text{Rn}$ decay in transit downstream of where groundwater enters the surface water (Santos et al., 2011; Santos et al., 2014). Atmospheric evasion is often the largest form of $^{222}\text{Rn}$ loss from aquatic systems (Atkins et al., 2013; Sadat-Noori et al., 2015b), however incorporating evasion can disproportionately overestimate groundwater flux in streams with high surface area if $^{222}\text{Rn}$ concentrations are sampled at the location of groundwater entry (Peterson et al., 2010). Furthermore, it has been shown that evasion is not a major loss pathway for radon in channelized streams (Burnett et al., 2010). Here we opted for using the conservative minimum groundwater flux model as the similarity between the maximum surface $^{222}\text{Rn}$ concentrations and average groundwater $^{222}\text{Rn}$ concentrations suggested minor evasion and the short residence time of the system means minimal time for decay within the drains. Additional detail on this groundwater discharge model is described in De Weys et al. (2011), Peterson et al. (2010), and Sadat-Noori et al. (2015b).

### 3.3.4 Carbon dioxide and methane analysis and fluxes

Dissolved CO$_2$ and CH$_4$ were prepared for analysis using a headspace technique (Gatland et al., 2014). Briefly, 50 mL of air free of CO$_2$ and CH$_4$ (Coregas “Zero Air”) was added to each inverted bottle while simultaneously extracting 50 mL of sample water. After ~18 h of equilibration at room temperature (21°C) the headspace air was then extracted at the same rate as water was added back into the bottle, and put into gas tight 0.5 L Tedlar® film bags. Samples were diluted with 200 mL of zero air and analysed on a cavity ring down spectroscopy (CRDS) analyser (G2201-i Picarro Inc. Santa Clara, CA, USA) for concentrations and carbon stable isotope ratios. Each bag was run for 5-10 mins by connecting the bag to the inlet line which runs through a desiccant tube of Mg(ClO$_4$)$_2$ before entering the analyser. An average of the
data output was recorded once concentrations stabilized within the analyser. The standard deviation between duplicate samples was on average 10% and 7% for CO$_2$ and CH$_4$ concentrations, and 0.28‰ and 0.61‰ for δ$^{13}$C-CO$_2$ and δ$^{13}$C-CH$_4$ values, respectively.

For the continuous monitoring, CH$_4$ concentrations and δ$^{13}$C-CH$_4$ values were measured at approximately one second intervals (later averaged to one minute) using a CRDS analyser (Picarro G2201-i) on CH$_4$ isotope only mode (operational range 1.8-1500 ppm). The manufacturer guaranteed accuracy for CH$_4$ measured at concentrations >10 ppm is 50 ppb + 0.05% of reading for concentrations and <0.5‰ for δ$^{13}$C-CH$_4$ values. CO$_2$ concentrations and δ$^{13}$C-CO$_2$ values could not be measured on the CRDS as CO$_2$ concentrations exceeded the operating range of the analyser (>4000 ppm). CO$_2$ concentrations were instead measured every minute using an infrared gas analyser (IRGA) (LI-840A, LI-COR, USA) connected in series with the CRDS. Manufacturer accuracy is specified at <1.5% of reading within a measurement range of 0-20,000 ppm. The IRGA analyser was calibrated up to 20,000 ppm before deployment, and corrections were applied to measured CO$_2$ values >20,000 ppm using 20,000, 50,000 and 100,000 ppm standards that were analysed following the time series.

Aqueous CO$_2$ and CH$_4$ concentrations were then determined from Henry’s law, using the measured equilibrated concentration obtained from the CRDS and IRGA (ppm), temperature and conductivity of the sample water, and atmospheric pressure. Concentrations were derived from the headspace fugacity of CO$_2$ and CH$_4$ as calculated according to Pierrot et al. (2009), assuming 100% humidity. Solubility coefficients for CO$_2$ and CH$_4$ were derived from Weiss (1974) and Yamamoto et al., (1976), respectively.

Air-water flux estimates of CO$_2$ and CH$_4$ ($F$, mmol m$^{-2}$ d$^{-1}$) were calculated as follows:

$$F = k \propto (pC_{(water)} - pC_{(air)})$$

where $k$ is the gas transfer velocity (m d$^{-1}$), $\propto$ is the solubility coefficient of the respective gas, $pC_{(water)}$ is the partial pressure of CO$_2$ or CH$_4$ in water, and $pC_{(air)}$ is the partial pressure of CO$_2$ or CH$_4$ in the atmosphere. The $k_{600}$ value was empirically derived from the O’Connor and Dobbins (1957) parameterisation using surface water velocity and depth:

$$k_{600} = 1.539w^{0.5}h^{-0.5}$$
where $k_{600}$ is the gas transfer velocity (cm h$^{-1}$) for a gas with a Schmidt number of 600, $w$ is the water velocity (cm s$^{-1}$) and $h$ is the depth (m). The erratic nature of surface discharge at this site as controlled by the automatic pump meant that certain periods had zero detectable surface water velocity. To account for these periods, we applied a $k_{600}$ value of 0.93 cm h$^{-1}$ derived from Ho et al. (1997) to represent diffusion under zero flow conditions, allowing for the calculated evasion during these stagnant periods when the O'Connor and Dobbins (1958) reaeration equation breaks down due to zero velocity.

A total mass balance for CO$_2$ and CH$_4$ from the drains is balanced by the sum of the following parameters over the study period:

$$C_{\text{total}} = [C_{\text{gw}} + C_{\text{drain}}] - [C_f + C_Q]$$

Where $C_{\text{total}}$ refers to the total flux of CO$_2$ or CH$_4$ generated from the aquatic system over the study period, $C_{\text{gw}}$ is the total groundwater input, $C_{\text{drain}}$ is the total in-drain production of CO$_2$ or CH$_4$, $C_f$ is the total evasion flux from the drains, and $C_Q$ is the total downstream export. Groundwater flux and in-drain production are inputs into the system and evasion and discharge are exports out of the system.

The groundwater discharge rate ($Q_{gw}$) determined by the radon mass balance was used as the final groundwater input in the mass balance. CO$_2$ and CH$_4$ derived groundwater fluxes were calculated by multiplying the average radon-derived groundwater input ($Q_{gw}$) by the CO$_2$ (GW-CO$_2$) or CH$_4$ (GW-CH$_4$) endmember concentration. The error provided for groundwater-derived CO$_2$ and CH$_4$ inputs was propagated using the standard error of both groundwater discharge (Table 3.2) and CO$_2$ and CH$_4$ endmember concentrations (Table 3.1). The minimum concentration was multiplied by the lower groundwater discharge and the maximum concentration was multiplied by the upper groundwater discharge. The difference between the average $C_{gw}$ flux with the lower and upper $C_{gw}$ flux range is the reported error.
Table 3.2 Results of radon mass balance calculations for groundwater flux estimates showing averages with range in parenthesis. Radon diffusion was assumed constant at 2,400 dpm m\(^{-3}\). Total % of discharge is based on the sum of the average groundwater flux between minimum and maximum estimates (± standard error) over total surface water discharge for each phase.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Flood</th>
<th>GW-surplus</th>
<th>Recovery</th>
<th>Baseline</th>
<th>Total (5 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{222})Rn(_{ex}) dpm m(^{-3})</td>
<td>34,400 (26,005-78,147)</td>
<td>131,078 (84,572-147,216)</td>
<td>74,030 (39,714-100,584)</td>
<td>17,127 (57,65,620)</td>
<td>27,210</td>
</tr>
<tr>
<td>Decay dpm m(^{-2}) day(^{-1})</td>
<td>1,348 (70-1,649)</td>
<td>10,925 (5,862-16,586)</td>
<td>8,303 (3,507-11,795)</td>
<td>2,076 (227-7,232)</td>
<td>632</td>
</tr>
<tr>
<td>Atm flux dpm m(^{-2}) day(^{-1})</td>
<td>51 (31-93)</td>
<td>315 (49-531)</td>
<td>169 (59-432)</td>
<td>32 (0.06-205)</td>
<td>6,974</td>
</tr>
<tr>
<td>(Q_{gw-min}) flux m(^{3}) day(^{-1})</td>
<td>1,116 (644-2,033)</td>
<td>4,605 (1,791-8,875)</td>
<td>1,355 (23-4,806)</td>
<td>185 (-1.5-3,824)</td>
<td>10,258</td>
</tr>
<tr>
<td>(Q_{gw-max}) flux m(^{3}) day(^{-1})</td>
<td>6,300 (2,598-7,413)</td>
<td>5,647 (2,611-9,950)</td>
<td>1,809 (299-5,358)</td>
<td>303 (11-4,190)</td>
<td>97.7 ± 19</td>
</tr>
<tr>
<td>Total % of discharge</td>
<td>81.6 ± 55</td>
<td>110.2 ± 11</td>
<td>115.6 ± 17</td>
<td>41 ± 10</td>
<td>97.7 ± 19</td>
</tr>
</tbody>
</table>

Usually the free CO\(_2\) [CO\(_2^*\)] concentration, defined as aqueous CO\(_2\) + H\(_2\)CO\(_3\), in the groundwater is used as the endmember to calculate relative groundwater CO\(_2\) contribution (Atkins et al., 2013). However, in this case we used the groundwater dissolved inorganic carbon (DIC) concentration derived from sampled alkalinity expressed as ‘potential CO\(_2\)’ for the endmember. This was warranted because of the large difference in pH between the drain water (pH 3-4) and groundwater (pH ~7.05) and therefore different speciation of the carbonate system with all DIC being in the form of [CO\(_2^*\)] within the drains. For comparison, both the calculated [CO\(_2^*\)] and DIC-CO\(_2\) (i.e. potential CO\(_2\)) derived groundwater fluxes are shown and discussed in section 4.3.

Total CO\(_2\) and CH\(_4\) evasion (C\(_e\)) was calculated by taking the flux estimates calculated from O’Connor and Dobbins (1958) and Ho et al., (1997) multiplied by the changing drain surface area at each 10 minute interval. The cumulative fluxes were then calculated over the five days. Total aquatic CO\(_2\) and CH\(_4\) downstream export was calculated by the surface water discharge multiplied by dissolved CO\(_2\) and CH\(_4\) surface water concentration. Manufacturer specified instrumental errors were applied to the velocity recordings in the Starflow ultrasonic Doppler flowmeter and the CO\(_2\) and CH\(_4\) concentrations from the CRDS analyser to report final error propagated in export calculations. Having accounted for three of the mass balance terms, the total in-drain input (floodwater, sediment and aquatic metabolism) can be assumed as the ‘missing’ flux. Rearranging equation 6, C\(_{drain}\) can be determined:
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\[ C_{\text{drain}} = [C_f + C_Q] - C_{gw} \]

Using this approach, the contribution of surface water and groundwater inputs feeding into the total drain CO₂ and CH₄ budget can be estimated. All other non-groundwater derived fluxes are assumed to result from production within the drains. Errors were propagated for in-drain calculations.

3.4 Results
A flood event occurred from 20th to 24th of January 2015 leading up to post-flood sampling after a 58 mm and 185 mm rainfall event, respectively (Figure 3.2). A total of 290 mm of rain fell and 9,794 m³ of water discharged via the drains during the flood and sampling period. The oscillating surface water levels resulted from the automatic pump operating since the flood onset, and are not representative of natural drainage. Due to the catchment’s enhanced drainage characteristics, the surface water hydrograph rises and falls rapidly in response to the rain event (Figure 3.2B). Peak discharge was reached 18 hours after the first 58 mm rainfall. The pumping switches off once water levels drop to 80 cm depth below the top of the drain surface. The height difference (cm) of groundwater and surface water suggests a steep hydraulic gradient where the rate of surface water discharge exceeds the rate of shallow groundwater flow throughout the soil (Figure 3.2B). During baseline conditions surface water and groundwater levels were similar. The rapid onset of the flood event followed by enhanced drainage shifted the floodplain hydrology from surface water excess to groundwater excess in a matter of 14 hours (Figure 3.2C). Surface water excess is defined by periods when the groundwater table is below the surface water level, such as during conditions when drains fill with floodwater faster than it takes for the groundwater table to rise. Groundwater excess is the opposite situation where the groundwater table is positioned above the surface water level, which occurs when drain waters are discharged faster than the groundwater discharge.
Figure 3.2 Time series of rainfall and hydrology data in the Tweed Valley sugarcane sub-catchment during January 19-31, 2015. The continuous monitoring period January 26-31, 2015 is shown to the right of the dashed line. (A) daily precipitation (mm); (B) depth from surface in outlet drain (black) and groundwater depth from bore near outlet drain (red); (C) hydraulic head (cm) is defined as the difference between groundwater (GW) and drain surface water (SW) depth, where a positive hydraulic head represents groundwater excess (groundwater height exceeds surface water and negative hydraulic head represents surface water excess (surface water height exceeds groundwater); (D) hourly discharge (m$^3$); (E) cumulative floodplain discharge (black) and rainfall (red) (ML).

During the five day time series deployment, [CO$_2$] and CH$_4$ concentrations remained above equilibrium concentrations (which are ~12.9 µM and ~2.5 nM at in situ temperature, pH, conductivity and pressure) and spanned three orders of magnitude, 72-2,950 µM and 46-2,460 nM respectively (Figure 3.3). During initial flood conditions [CO$_2$] and CH$_4$ concentrations average 284 ± 64 µM and 121 ± 53 nM respectively, similar to pre-flood conditions of ~193 µM and ~536 nM respectively (Table 3.1). The time series data was separated into four distinct phases highlighted in Figure 3.3 as flood (26/01/2015 16:00 to 23:00), groundwater excess
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(26/01/2015 23:00 to 27/01/2015 20:00), recovery (27/01/2015 20:00 to 29/01/2015 10:30), and baseline conditions (29/01/2015 10:30 to 31/01/2015 14:30).

Conductivity ranged from 670-5,015 µS cm\(^{-1}\) throughout the study. A significant increase from 728-3,468 µS cm\(^{-1}\) occurred during the groundwater excess phase before stabilising once the drain depth reached baseline levels. Surface water pH decreased substantially from 4.05-3.35 during the groundwater phase before also stabilising at ~3.2. Surface water temperatures ranged from 20.4 to 34.6°C with diurnal temperature changes spanning a much as 14°C between night and day. Dissolved oxygen saturation was highest during the day and lowest at night, with fluctuations between 15.3% and 98.4% during the first 2.5 days and 31% to 244% during the last 2.5 days.

Once floodwaters had receded and surface water became confined to the drainage canals, a five-fold and seven-fold increase in \(^{222}\)Rn and CO\(_2\) concentrations was observed respectively (Figure 3.3). This rapid increase in \(^{222}\)Rn concentrations marked the start of the groundwater excess phase, where maximum \(^{222}\)Rn concentrations of 150 dpm L\(^{-1}\) similar to the groundwater endmember average 146 ± 27 dpm L\(^{-1}\) of indicated drain water was derived purely from groundwater. In contrast to CO\(_2\), CH\(_4\) concentrations remained on a steady increase until the 30\(^{th}\) January, yet δ\(^{13}\)C-CH\(_4\) values decreased from -60‰ to -70‰ during the groundwater excess phase.

Radon levels remained high (30-100 dpm L\(^{-1}\)) during the recovery phase but decreased in a step wise fashion during the day and plateaued at night. Radon concentrations reached baseline levels of 2-5 dpm L\(^{-1}\) after four days following the flood recession. CO\(_2\) concentrations followed the same trend as \(^{222}\)Rn, decreasing in a step wise fashion each day. Yet CO\(_2\) was not exclusively driven by groundwater as the \(^{222}\)Rn trend may first indicate, but also by photosynthesis during the day and respiration at night. This can be observed from the sharp decrease in [CO\(_2\)] from 2,835 to 1,900 µM in the groundwater surplus phase during the day that is not replicated in \(^{222}\)Rn levels. CH\(_4\) continued to increase throughout the recovery phase before it reached a maximum concentration of 2,459 nM six days post-flood. During the baseline phase this was followed by a decrease from 2,459 to 275 nM. All daily peaks in CH\(_4\) appeared to occur between 9-11am following the minimum daily DO levels which occurred at 7:30-8 am.
Figure 3.3 Time series of continuously measured parameters within the outlet drain following the flood event (January, 26-31, 2015). Left stack (from top): dissolved radon (dpm L⁻¹); dissolved CO₂ (µM); dissolved CH₄ (nM); δ¹³C-CH₄ values (‰); molar ratio CH₄:CO₂; hydraulic head (cm) between groundwater (GW) and surface water (SW). Right stack (from top): temperature (°C); pH; conductivity (µS cm⁻¹); dissolved oxygen (%); drain water depth (cm); and discharge (m³ min⁻¹) controlled by automatic pump. Shaded areas represent dark hours and coloured bars highlight the duration of each phase. Dashed lines represent pre-flood conditions.

Table 3.1 shows the pre-flood baseline conditions, initial flood inundation, and post-flood conditions for dissolved CO₂, CH₄, ²²²Rn and water quality variables. Baseline concentrations of [CO₂] and CH₄ were on average 148 µM and 534 nM, respectively, which is 20- and 5-fold lower than the peak concentrations observed during the flood recovery (Figure 3.3). Pre-flood conditions represented a period following relatively low rainfall (133 mm in 80 days) and was reflected by the high conductivity of drain water (43,335 µS cm⁻¹). The first flush of the flood diluted CO₂, CH₄ and conductivity, increased ²²²Rn to 36 dpm L⁻¹, and decreased pH to 4.71 (Table 3.1). A 5.7‰ depletion in δ¹³C-CO₂ was observed from pre-flood to flood conditions.
(from -9.3‰ to -14.9‰), whereas no significant change occurred in δ\(^{13}\)C-CH\(_4\) values. δ\(^{13}\)C-CH\(_4\) values increased from -53.0‰ to -47.1‰ between flood to post-flood conditions. Average CO\(_2\) and CH\(_4\) concentrations were 223 ± 60 µM and 2,798 ± 156 nM respectively during the post-flood period, which for CH\(_4\) were the highest concentrations observed during the entire study.

Table 3.2 shows the groundwater flux rate for the flood recovery period (continuous monitoring) and the other terms associated with the radon mass balance calculations. The aerial flux rate of groundwater flux, expressed as cm day\(^{-1}\) normalised to the drain area, is also provided. A total of 6,408 ± 1,204 m\(^3\) groundwater was discharged into the drains over the five days of monitoring (uncertainty results from the standard error in the \(^{222}\)Rn endmember concentrations; section 2.3.1). On average the groundwater flux rate for the entire period was 1,272 m\(^3\) day\(^{-1}\), which is equivalent to ~12 cm day\(^{-1}\). The highest groundwater flux rate calculated was 8,138 m\(^3\) day\(^{-1}\) (~ 85 cm day\(^{-1}\)) and occurred during the groundwater excess phase during flood recession. Over the five-day continuous monitoring period groundwater contributed an estimated 71 ± 14% of total surface water drain discharge.

3.5 Discussion

3.5.1 Drivers of CO\(_2\) dynamics

The asynchronous relationship between CO\(_2\) and CH\(_4\) suggests different processes driving their production, consumption, and transport (Figure 3.3). Typically in natural floodplains, high CO\(_2\) supersaturation in streams is sustained by wetland carbon inputs (Borges et al., 2015). In small tributaries groundwater becomes more important as a source of CO\(_2\) (Hotchkiss et al., 2015). The contribution of groundwater may be enhanced in our study site by the lack of wetland coverage and artificial hydrology which creates a steep hydraulic head (Figure 3.3). The extreme CO\(_2\) supersaturation was not sustained when groundwater input was negligible (average \(p\)CO\(_2\) 3,055 µatm) in comparison to other small sub-tropical and tropical floodplain tributaries with wetland coverage sustaining higher \(p\)CO\(_2\) values under non-flood conditions (7,500-12,000 µatm) (Abril et al., 2013; Gatland et al., 2014; Borges et al., 2015,). An important finding of this study is the extreme post-flood response observed for CO\(_2\). The CO\(_2\) concentrations observed in this study are four to eight-times higher than those reported in post-flood waters from other modified coastal floodplains (Atkins et al., 2013; Gatland et al., 2014; Ruiz-Halpern et al., 2015). These differences are likely related to the small catchment and
higher density of drains (12.4 km km\(^{-2}\)) in this study compared to other systems (0.2 to 3 km km\(^{-2}\)).

Although δ\(^{13}\)C-CO\(_2\) values were not recorded during the time series, differences between the δ\(^{13}\)C-CO\(_2\) values from the discrete samples and DIC samples taken during the time series reveal a distinct response to the flood event (Table 3.1). Discrete samples taken 5-6 weeks before time series deployment show that pre-flood δ\(^{13}\)C-CO\(_2\) values (-9.3‰) were near atmospheric equilibrium (-8‰) (Fry, 2006). The flood event reduced CO\(_2\) concentrations due to dilution, and a \(\sim 5.6\)% depletion in δ\(^{13}\)C-CO\(_2\) values was observed (Table 3.1). The more enriched δ\(^{13}\)C-CO\(_2\) values during pre-flood conditions are likely representative of high rates of in situ photosynthesis from aquatic plants within the relatively stagnant drain waters at the time. Additionally, methanogenesis would have contributed enriched δ\(^{13}\)C-CO\(_2\) values to the CO\(_2\) pool as methanogenesis produces an isotope separation factor of 40-60‰ between δ\(^{13}\)C-CO\(_2\) and δ\(^{13}\)C-CH\(_4\) (Whiticar, 1999). Both photosynthesis and methanogenesis are associated with a kinetic isotope effect and discriminate against the \(^{13}\)CO\(_2\), resulting in residual CO\(_2\) that is enriched in \(^{13}\)CO\(_2\) (Whiticar, 1999; Fry, 2006). During flood conditions the main CO\(_2\) source likely shifted to soil respiration, producing a more depleted δ\(^{13}\)C-CO\(_2\) value of -14.9‰. This is similar to the average groundwater δ\(^{13}\)C-CO\(_2\) value of -16.5 ± 1.0‰, where the source of groundwater-derived CO\(_2\) would also have been largely from soil respiration. Furthermore, organic matter decomposition from sugarcane is likely contributing to the CO\(_2\) pool within the floodwater, which also has distinct C\(_4\) plant δ\(^{13}\)C values of -13‰ to -11‰ (Neves et al., 2015), similar to the observed floodwater δ\(^{13}\)C-CO\(_2\) values (Table 3.1).

Groundwater discharge played an important role in contributing to the extreme supersaturation of drain CO\(_2\) losses. When the water table was 20 cm to 65 cm below the soil surface, high \(^{222}\)Rn and CO\(_2\) concentrations were sustained (Figure 3.4), which coincided with the highest average groundwater discharge rate of 5,885 m\(^3\) day\(^{-1}\) (Table 3.2). Under baseline conditions the water table remained at or below the drain surface water level (-70 cm below surface). Figure 3.4 demonstrates how groundwater input traced by radon decreases substantially after the water table reaches 70 cm below the surface. Based on our groundwater samples which had near neutral pH (6.7-7.9), the depth of the unconsolidated sulfidic marine clay layer can be as high as 0.4 m below the surface. Due to the neutral pH of sampled groundwater, the DIC groundwater endmember was mostly in the form of bicarbonate (HCO\(_3^-\)) and not CO\(_2\) (Millero, 1979). However, after large rainfall events the water table rises to the soil surface and
groundwater spans across two distinct soil layers containing different geochemistry. Due to the major pH differences between the reduced and oxidised layer, the groundwater-derived $[\text{CO}_2^*]$ endmember will be significantly higher in the oxidised sulfuric surface layer (pH <4.4). Considering that the fate of all groundwater-derived DIC being discharged is entering into acidic surface waters (pH<4.2), the groundwater-derived input of $[\text{CO}_2^*]$ should be calculated based on the DIC endmember. As a result, the $[\text{CO}_2^*]$ endmember (groundwater DIC = 10,533 µM) was six-fold greater than originally assumed (groundwater $[\text{CO}_2]$ = 1,693 µM). This lead to a more realistic groundwater-derived $[\text{CO}_2^*]$ input which contributes 99% of the total CO$_2$ surface budget during the groundwater excess stage (Figure 3.6), compared to only a 16% contribution assuming the endmember was 1,693 µM (Table 3.3).
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Figure 3.4 Measured dissolved $^{222}$Rn (dpm L$^{-1}$), CO$_2$ (μM), CH$_4$ (nM), and δ$^{13}$C-CH$_4$ values (‰) as a function of water table position below the soil surface (cm) of bore adjacent to the outlet drain during time series (January, 26-31, 2015).

During the recovery and baseline phase, groundwater remained the dominant source of excess CO$_2$ (Figure 3.6), however other processes were starting to drive much of the temporal variability. Drain diurnal metabolism became more pronounced as DO saturation fluctuated from 42% to 240% between night and day (Figure 3.3). This consequently decreased surface water CO$_2$ concentrations substantially during the day. The mass balance calculations also indicated that large CO$_2$ consumption was occurring (~24% of the CO$_2$ inputs were unaccounted for during baseline, Figure 3.6). Shallow agricultural drains can experience extremely high metabolism due to high light and nutrients levels under warm conditions, resulting in large oscillations in DO saturation (Johnston, 2003; Santos and Eyre, 2011). More specifically to acid sulphate soil drains, the combination of low pH and oxygenated waters increases the bioavailability of organically complexed nutrients (Ahern et al., 2006), which are likely to be high after a flood.

3.5.2 Drivers of CH$_4$ dynamics

The factors controlling CH$_4$ dynamics in floodplain surface waters are complex. Several physical and chemical factors including conductivity, sulphate, oxygen, organic matter content, water table position, temperature dependence, and ecosystem primary productivity are commonly found to influence the extent of methanogenesis (Moore and Roulet, 1993; Whiting and Chanton, 1993; Purvaja and Ramesh, 2001; Yvon-Durocher et al., 2014). However, drained wetlands do not necessarily exhibit the same functional relationships between environmental conditions driving CH$_4$ flux in natural wetlands (Turetsky et al., 2014). In acid sulphate soil landscapes, the production of CH$_4$ may be limited by the oxidation/reduction state, availability of labile substrate, and the availability of alternative electron acceptors such as Fe, Mn, and SO$_4^{2-}$ (Ponnamperuma, 1972; Dent, 1986; Jugsujinda et al., 1996). Some unique behaviours in surface CH$_4$ concentrations observed here reflect the apparent differences in the drivers of fluvial CH$_4$ concentrations in drained coastal wetlands.

The initial impact of the flood followed by groundwater excess appeared to reduce CH$_4$ concentrations to pre-flood concentrations rather than increase them. Typically CH$_4$ production is enhanced under high water table conditions (Bubier, 1995) which has been reported in other agricultural catchments with drainage ditches (Luan and Wu, 2015). However, in our study CH$_4$ production within the surface waters appeared to be hindered by higher groundwater levels.
and instead concentrations increased when the water table decreased to below -65 cm (Figure 3.4). When groundwater discharge was high, substantial quantities of $\text{H}_2\text{SO}_4$ and Fe oxides would likely have been released into the surface water (Sammut et al., 1996; Wilson et al., 1999; Burton et al., 2006). It is well known that sulfate reducing microbes compete with methanogens for organic substrates and $\text{H}_2$, preferentially inhibiting methanogenesis (Gauci et al., 2000; Dowrick et al., 2006; Baldwin and Mitchell, 2012). The depleted $\delta^{13}\text{C}\text{-CH}_4$ values (-69‰ to -63‰) during the groundwater excess stage are in the range of the groundwater CH$_4$ endmember (-66.6 ± 4.9‰), suggesting that groundwater may be contributing the majority of surface water CH$_4$. However, mass balance calculations indicate that groundwater contributed 57% of the surface water CH$_4$ budget during this phase (Figure 3.6). Rapid transport of surface water CH$_4$ derived from the floodwater likely explains the other half of the CH$_4$ budget during this stage. The more depleted isotope values are indicative of limited CH$_4$ oxidation, which is likely due to the high water discharge (i.e. short residence time) transporting freshly produced CH$_4$ rapidly out of the system. The $\delta^{13}\text{C}\text{-CH}_4$ values also suggest that the original source of CH$_4$ is produced via the fermentation pathway (between -65‰ to -50‰), which is dominant in freshwater environments (Whiticar and Faber, 1986).

Once the water table gradually lowered and groundwater discharge decreased, CH$_4$ concentrations and $\delta^{13}\text{C}\text{-CH}_4$ values increased simultaneously over four days and a strong diurnal control over CH$_4$ concentration resumed (Figure 3.5). Methane oxidation, a microbial process which consequently enriches the residual CH$_4$ in the heavier isotope (Whiticar, 1999), often increases with higher CH$_4$ concentrations (and consequently production) (Boon and Lee, 1997; Shelley et al., 2014). The drain sediment at the study site, classified as monosulfidic black ooze, likely supports the coupling between methanogens and methanotrophs (Figure 3.5). Redox conditions within the monosulfides at the bottom of drains and the boundary between the sediment-water interface have demonstrated a rapid shift from oxic (Eh 100-150 mV) to anoxic (-50-100 mV) in a matter of ~10 cm (Smith and Melville, 2004). Complex interactions between CH$_4$ and other electron acceptors such as iron oxides and sulfate are likely occurring in near-surface monosulfidic black oozes that are unique to acid sulphate soil drains (Smith and Melville, 2004), and should be investigated in detail in future research.

Physical processes controlled by the decrease in discharge are likely contributing to the overall increase in CH$_4$ concentrations. The increasing water residence time as a result of less frequent pumping (Figure 3.2) could lead to a greater accumulation of CH$_4$ in the water column, while
allowing for CH$_4$ oxidation to influence δ$^{13}$C-CH$_4$ values. Some interesting diel trends in CH$_4$
dynamics can also be observed. Figure 3.5A shows 24 h trends in CH$_4$ concentrations during
the five days of flood recovery. There is a clear trend of increasing CH$_4$ concentrations between
9 pm to 10-12 am, indicating a dominance of production over oxidation, before decreasing
during the light hours of 12 pm to 5-8 pm (Figure 3.5). Such diurnal trends become more
distinct over time until the maximum oscillation in CH$_4$ occurred on day five of the time series
where concentrations dropped from 2,459 nM to 280 nM during the oxidation period (Figure
3.5A). Diel CH$_4$ oscillations seem to be related to the dissolved oxygen levels produced in the
water column, however a time lag exists in the oxygen diffusion into the sediments. Figure
3.5B illustrates the time lag between water column CH$_4$ concentrations in response to DO
saturation within the overlying water through diel hysteresis loops. Cycling between aerobic
methane oxidation during the day and anaerobic methane production during the night has been
shown to drive diurnal oscillations in surface water CH$_4$ concentrations and δ$^{13}$C-CH$_4$ values
(King et al., 1990; Maher et al., 2013; Maher et al., 2015). In this case, the extent of CH$_4$
production and oxidation, the net result of measured concentrations and δ$^{13}$C-CH$_4$ values, is
likely controlled by the surface water residence time which increases as flood waters recede
(Figure 3.2). Drain samples taken the 5-6 weeks after intensive sampling period showed a δ$^{13}$C-
CH$_4$ value of -47.1‰ (Table 3.1), indicating the growing importance of methane oxidation as
water residence time increases. Furthermore, high average CH$_4$ concentrations of 2,798 ± 156
nM indicates that the flood had a sustained effect on CH$_4$ production, likely via increased
substrate availability at the sediment surface (Figure 3.5).
Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: post-flood hydrological and biological drivers

Figure 3.5 Diurnal CH₄ concentration trends in response to: (A) time of day (hour), and (B) dissolved oxygen concentrations in surface water (% saturation); separated into five days over the continuous monitoring period. Each day is displayed over a 24 h period between 12:00 pm to 12:00 pm. In figure 3.5A, the time of day was partitioned into periods where methane oxidation dominates (oxidation zone), methane oxidation shifts to methane production (transition zone), and methane production dominates (production zone). The inset in B shows a hysteresis loop that occurred in days 1, 2, 3, and 4.

3.5.3 Mass balance

The contribution of fluxes from various aquatic pathways were determined and partitioned into the different phases (Table 3.3, Figure 3.6). Evasion remained the largest loss term for both CO₂ and CH₄ during flood to baseline conditions (Figure 3.6). CO₂ and CH₄ evasion spanned 1-2 orders of magnitude greater than export loss via controlled pumping across all phases (Table 3.3). The flood, groundwater excess, and recovery phases contributed 96% of the total CO₂ evasion. The large area occupied by surface water inundation accounted for the largest CO₂ flux during the flood phase, whereas the high partial pressures and shallow conditions contributed to the high evasion rates observed for the remaining phases. In contrast, CH₄ evasion between the flood, recovery and baseline phases remained consistent and contributed
23-40% of total CH$_4$ evasion over the time series, whereas CH$_4$ evasion during the groundwater excess phase contributed only 11% to total evasion (Table 3.3).

Figure 3.6 Conceptual model of the major carbon flux pathways and CO$_2$ and CH$_4$ dynamics during the post-flood period within the artificial drains of a modified floodplain. Each numbered box diagram represents a consecutive phase during the recovery of flood to baseline conditions with; 1) being the flood phase; 2) groundwater excess phase; 3) recovery phase; and 4) the phase where baseline conditions are achieved. Two stacks of box diagrams are provided for CO$_2$ and CH$_4$ individually. Coloured arrows represent the different input and outputs of CO$_2$/CH$_4$ fluxes and their relative contribution (numbers in bold related to the contribution to the total flux during each phase). Yellow represents evasion, red represents export, blue represents groundwater flux, and green the unaccounted for flux which we have terms in-drain flux (i.e. processes occurring within the drains). Shaded area within the soil profile shows the groundwater table position.
Table 3.3 shows the average groundwater flux estimates applied to two different endmember scenarios for CO$_2$ (total DIC and [CO$_2^*$]). The [CO$_2^*$] groundwater endmember flux is the traditional approach used to estimate groundwater derived CO$_2$ fluxes within an aquatic system (Atkins et al., 2013; Perkins et al., 2015). Here using [CO$_2^*$] results in a relatively small groundwater contribution (~16%) to the total surface CO$_2$ budget during the groundwater excess phase. This is a severe underestimation in such a system where the pH difference between the surface water and groundwater easily transforms all DIC into [CO$_2^*$]. The groundwater-DIC concentration was six times higher than [CO$_2^*$], and is a measure of ‘potential CO$_2$’ that accounts for the carbonate equilibrium shift that would be occurring following groundwater seepage into the acidic drains. Using this endmember, groundwater contribution to the total CO$_2$ flux during the groundwater surplus phase becomes 99% (Figure 3.6). This revised [CO$_2^*$] endmember calculation is more in agreement with the seven-fold increase in surface water [CO$_2^*$] concentrations that occurred with a five-fold increase in surface $^{222}$Rn during the groundwater excess phase. This highlights the need to account for carbon transformations as groundwater mixes with surface waters.

In contrast to CO$_2$, groundwater-derived CH$_4$ was a very minor component of the total surface CH$_4$ budget (14%). The largest contribution of groundwater to the surface CH$_4$ budget was
57% during the groundwater excess phase (Figure 3.6), however this phase played a minor role in total CH₄ fluxes over the entire study (~12%). This supports the hypothesis that shallow drain sediments or hyporheic production of CH₄ play an important role in driving the total CH₄ flux to the atmosphere. Groundwater had relatively low CH₄ concentrations of 548 ± 185 nM compared to peak surface water concentrations which were an order of magnitude greater. Groundwater usually has a higher CH₄ concentration than corresponding surface water, however reported concentrations are highly variable (56-53,000 nM) (Cable et al., 1996; Santos et al., 2009; O’Reilly et al., 2015; Sadat-Noori et al., 2015a). High concentrations of reduced metabolites including H₂S and FeS₂ are likely to be present (Rosicky et al., 2004) which may inhibit methanogenesis (Khan and Trottier, 1978).

After quantifying the fluxes and exports of [CO₂*] and CH₄, our results show that the magnitude and variability of [CO₂*] and CH₄ response to flood events can be greatly perturbated within extensively drained coastal floodplains. The most significant changes in [CO₂*] and CH₄ dynamics were caused by groundwater discharge and in-drain metabolism which occurred over approximately 10 hours and could only have been captured using the high resolution continuous instrumentation used in this study. Similar setups have been used to continuously monitor [CO₂*] and CH₄ in aquatic environments, and have revealed distinct changes over short lived timescales caused by processes such as tidal pumping, porewater exchange, and diel metabolic cycles (Maher et al., 2013; Call et al., 2015; Maher et al., 2015; Gatland et al., 2014; Looman et al., 2016). However, the magnitude of change in surface water [CO₂*] concentrations captured in this study, spanning 2,700 µM (71,000 µatm) far exceeds that observed in the reported studies over half-day time scales. Although larger fluctuations have been observed for CH₄ concentrations in other systems (Sadat-Noori et al., 2015a), the CH₄ concentration fluctuations caused by diurnal DO oscillations reported here (2,200 nM) were larger than the typical range reported in other recent studies (Maher et al., 2015). Such findings highlight the profound effect flood events can have on fluvial [CO₂*] and CH₄ emissions from drained coastal floodplains. Considering that the Eastern Australia coastal region is subject to frequent large rainfall events (Alexander and Arblaster, 2009) that flood small catchments, the impact fluvial CO₂ and CH₄ emissions have on ecosystem carbon balances should be further investigated and quantified.
3.6 Conclusion

Through high resolution, continuous monitoring, major shifts in CO$_2$ and CH$_4$ dynamics were captured during a receding flood, revealing important controls in the CO$_2$ and CH$_4$ flood response within artificial coastal floodplain drains. The major drivers of CO$_2$ and CH$_4$ dynamics in the surface water budget operated on different processes and temporal scales. Methane sources were dominated by a combination of physical transport and biological processes in the surface water, and groundwater was a relatively minor source of CH$_4$. Post-flood conditions appeared to enhance large diurnal oscillations in CH$_4$ concentrations by up to ten-fold, despite oxygen enriched surface waters during the day. Groundwater input sustained high surface water [CO$_2^*$] flux by delivering high carbonate alkalinity groundwater to acidic surface water which transformed all groundwater-derived DIC to [CO$_2^*$]. Such findings on the groundwater-surface water CO$_2$ relationship highlights a new paradigm on the quantification of groundwater derived CO$_2$ flux into acidic surface waters. Considering the sensitivity of CO$_2$ to pH, we suggest that groundwater and surface water pH be taken into account when calculating groundwater-derived CO$_2$ input into aquatic systems. Where the pH is profoundly different between the surface water and groundwater, the groundwater DIC pool should be used to provide a more accurate measure of groundwater inputs of [CO$_2^*$] in acidic surface waters.
Chapter 4 - Constraining the annual groundwater contribution to the water balance of an agricultural floodplain using radon: The importance of floods

Abstract
The water balance of drained floodplains is highly dynamic with complex groundwater-surface water interactions operating over varying spatial and temporal scales. Here, we hypothesise that the majority of groundwater discharge will follow flood events in a modified wetland. To test this hypothesis, we developed a detailed water balance that quantifies the contribution of groundwater discharge to the annual water budget of an extensively drained agricultural floodplain. A clear relationship between surface water radon measurements and groundwater level indicated alternating connection-disconnection dynamics between the drains and shallow groundwater. This relationship was used to develop a radon mass balance to quantitatively model groundwater discharge continuously throughout the year. Groundwater discharge varied by four orders of magnitude over the study period, with daily average rates ranging from 0 to 27,200 m$^3$ d$^{-1}$, peaking just a few hours after floods receded. Flood events occurred only 12% of the time yet contributed 72 to 76% of the total groundwater discharge. During flood recession periods, aerial groundwater discharge rates reached up to 325 cm d$^{-1}$ which were some of the highest rates ever estimated. We proposed that the high drainage density of this site (12.4 km constructed drains km$^{-2}$ catchment area) enhanced groundwater discharge during wet periods due to increased connectivity with the soil. Overall, groundwater discharge contributed 30-80% to the total surface water discharge. This study offers insight into the dynamic behaviour of groundwater within an extensively drained floodplain, and the importance of capturing flood events to quantify total groundwater contribution to floodplain water balances.

Key words: drainage density, water budget, flood pulse, groundwater-surface water, connectivity, radon, artificial drains, groundwater exchange
4 Constraining the annual groundwater contribution to the water balance of an agricultural floodplain using radon: The importance of floods

4.1 Introduction

Hydrological interactions between streams and the land provide important feedbacks to land surface hydrologic, biogeochemical, and ecosystem dynamics (Shen et al., 2016). Hydrological flow regimes in floodplains are characterised by baseflow, flow pulse (below bankfull), and flood pulse (above bankfull), which can result from different water sources including tributary inflow, overland flow, and groundwater discharge (Tockner et al., 2000). All of these water sources are ultimately driven by precipitation, geomorphology, and aquifer properties. Groundwater-surface water (GW-SW) exchange is particularly important in floodplains and wetlands as water tables are generally near the surface in these depressional landscapes (Jeffrey et al., 2016; Ludwig and Hession, 2015). Specifically, GW-SW connectivity often controls surface discharge within floodplains along with the duration of inundation (Mitsch and Gosselink, 2000). A relatively unconfined groundwater flow often develops in these systems and is referred to as ‘interactive’ groundwater due to active exchanges with surface water (Harvey et al., 2006). Groundwater-surface water interactions can strongly influence benthic productivity in wetland streams, habitat heterogeneity, and surface water biogeochemistry, and can even stimulate organic carbon turnover (Tockner et al., 2000; Hunt et al., 2006; Stegen et al., 2016).

Most detailed studies of groundwater-surface water interactions focus on timescales ranging from hours to months. Short term studies can provide high spatial and temporal resolution of groundwater-surface water interactions (Burnett et al., 2003; Santos et al., 2011; Sadat-Noori et al., 2015b; Luo et al., 2016), and reveal any groundwater driven interactions between hydrologic dynamics and biogeochemical processes (Fleckenstein et al., 2010; Atkins et al., 2013; Makings et al., 2014). However, short term studies are limited in their ability to quantify the contribution of groundwater to the total water balance because of hydrological time lags and temporal bias in sampling. Long term groundwater studies ranging over annual to decadal time scales (Harvey et al., 2006, Wilcox et al., 2006; Wolksi and Savenije, 2006; Krause et al., 2007a) offer insights into the composition of old and new groundwater, residence times, and provide a whole-of-system picture of groundwater contribution to the water balance. However, such long term studies may lack detailed information on temporal groundwater responses to rain events and therefore provide a more generalized view of groundwater discharge.

The temporal and spatial behaviour of groundwater discharge in floodplains is tightly controlled by pressure head gradients and mediated by physical soil and sediment
characteristics governing hydraulic conductivity (Bencala, 1993; Stanford and Ward, 1993). These properties can vary widely over small spatial scales, leading to large uncertainties in hydraulic conductivity that make mechanistic estimates of groundwater-surface water fluxes difficult to constrain (Kalbus et al., 2006; Johnston et al., 2009). Furthermore, groundwater discharge is subject to both temporal and spatial variability which may not be captured by point measurements of groundwater seepage (Peterson et al., 2010; Wilson and Rocha, 2016). Geochemical tracers integrate complex and variable groundwater discharge pathways as they reflect the net groundwater discharge averaged over the reach length (Schmidt and Schubert, 2007; Cook, 2013; Atkinson et al., 2015).

The advent of new automated analytical techniques has allowed the use of chemical tracers to estimate groundwater-surface water exchange over seasonal time scales. For example, radon has been used as a tracer to quantitatively assess groundwater flux in river/stream systems (Genereux and Hemon, 1990; Santos et al., 2008; Peterson et al., 2010). Radon is present in high concentrations in groundwater due to the continuous decay of uranium in soils, making it ideal for estimates of groundwater input. The conservative and inert nature of radon gives it some advantage over other geochemical groundwater tracers commonly used such as conductivity, alkalinity, methane (CH\textsubscript{4}), and stable isotopes of lead, strontium, and carbon, which can be affected by biological and chemical transformations (Bullen and Kendall, 1998; Kalbus et al., 2006; Santos et al., 2008). Chloride (Cl) is one of the most widely used conservative tracers for estimating groundwater discharge. Chloride can be used when groundwater and surface water have contrasting concentrations, but may be a less useful tracer coastal systems subject to salt deposition (Cook, 2013). The stable isotopes of water (δ\textsuperscript{2}H and δ\textsuperscript{18}O), which are indicators of “new” and “old” water (Kendall and Caldwell, 1998), are another commonly used conservative tracer. However, the ability of these tracers to differentiate between groundwater flows and fresh surface water flows is limited by the degree of difference in isotopic composition between the two components (Buttle, 1994), which may be similar for shallow groundwater in floodplain landscapes (i.e. recharges with “new” water from surface water and precipitation). The short lived nature of radon relative to other radioactive isotope tracers (e.g., tritium) means that radon is sensitive to rapid exchanges between surface and groundwater. This makes it an ideal tracer for characterising GW-SW exchange, which can rapidly switch direction during flood events.
The role of flood events in wetland and floodplain groundwater dynamics is poorly understood. However, a number of short term studies have highlighted notable increases in groundwater discharge following flood events (De Weys et al., 2011; Gilfedder et al., 2015), and this is consistent with theory. Flood-stimulated groundwater pulses may have important implications to the overall water balance of wetlands and floodplains. Enhanced groundwater discharge of solutes has also been linked to severe acidification, deoxygenation, and high carbon dioxide in some rivers post-flood (Santos et al., 2011; Atkins et al., 2013).

Studies that integrate both the quantitative and qualitative advantage of assessing groundwater dynamics over different timescales are limited (Wilson et al., 2015). Here, we model a detailed time-series of surface water radon concentrations to quantify groundwater discharge and its contribution to the water budget of an artificially drained agricultural floodplain. Through modelling of radon concentrations, we estimate groundwater discharge to the surface waters at high temporal resolution over an annual cycle. We aim to capture periods of high groundwater discharge that may be overlooked in annual time scales due to limited temporal resolution or not captured during short term studies. We hypothesise that the majority of groundwater discharge will follow flood events and occur over short periods.

4.2 Methods

4.2.1 Study area and sampling approach

The study site is a sub-catchment of the McLeods Creek catchment (28°16´50´´S, 153°30´12´´E) which is situated in the Tweed Valley floodplain in northern New South Wales, Australia (Figure 4.1). McLeods Creek generally floods annually, however the frequency, intensity, and duration of floods vary between years. The site receives on average 1,600 mm rainfall annually and experiences a subtropical climate with monthly mean minimum and maximum temperatures of 8.6 and 29.5°C, respectively (Bureau of Meteorology, 2016). Rainfall persists year round with ~830 mm of rainfall occurring during the hottest months of December-March when large isolated rainfall events are most frequent.

The sub-catchment is a typical Australian coastal lowland that contains unconsolidated estuarine sediments originating from the Holocene period, which due to extensive drainage has developed oxidised acid sulfate soils (White et al., 1997). The site is positioned at a low elevation of ~0.15 m AHD (Australian Height Datum, where 0 m AHD approximates mean sea level). Three soil horizons exist at the site; an organic topsoil (0 to 0.25 m), the oxidised sulfuric
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horizon (0.25 to 0.9 m), and an unconsolidated sulfidic estuarine clay layer (>1 m) comprising of pyrite deposits from the Holocene period (Lin et al., 1998; Smith et al., 2003). Hydraulic conductivity has been measured between 0.74 and 5.54 m day\(^{-1}\) in the upper soil horizon (0 to 1.5 m) (White et al., 1993; Johnston et al., 2009). Large releases of sulfuric acid and dissolved metals including aluminum, iron, zinc and manganese have been observed in surface water discharge after flood events at this site, and was speculated to be related to groundwater discharge (Wilson et al., 1999; Green et al., 2006; Macdonald et al., 2007). However, groundwater discharge has not been quantified.

The floodplain consists of an extensive artificial drainage network and has been used for sugarcane production for the past 40 years (Smith et al., 2003). The drainage network consists of main drains which have widths ranging between 1.0 to 3.5 m and depths of 0.6 to 1.2 m, and are the main conduit for surface water discharge out of the sub-catchment (Figure 4.1). Smaller field drains have a width of 1.5 m and depth of 0.5 m, and are only connected to the main drains during periods of major rainfall. An automatic pump at the catchment outlet (Figure 4.1) controls drain discharge from the site which expels water into the Tweed River. This is triggered when surface water levels go above -0.45 m AHD (0.57 m drain depth). Surface water infiltration from the Tweed River and bordering creeks are blocked by permanent flood gates and levees, allowing for water levels within the site to be maintained below sea level. The main sources of water feeding the drains are rainfall and groundwater. A small amount of tidal creek water is allowed to inflow through McLeods Creek floodgate to the main drain to buffer acidification during dry periods. Surface water actively flows within the drains only after major rainfall, and remains stagnant with intermittent discharge pulses between periods of rainfall.

The sub-catchment is hydrologically isolated from adjacent land and Tweed River by natural levees, artificial bund walls and bordering tributaries (Green et al., 2006). Local groundwater flow is shallow, as is typical of these coastal lowlands (White et al., 2003), and contained within the sub-catchment area that defines the water balance boundary in this study. The estuarine clay layer that exists at 1 m (-0.4 m AHD) below the surface and extends for a further 10 m has an hydraulic conductivity of 0.03 m d\(^{-1}\), which effectively impedes any rainfall transmitted through the upper soil horizons, and infiltration of seawater into the drains (White et al., 1993). Groundwater levels are typically maintained at -0.5 m AHD by artificial pumping of drainage water.
Figure 4.1 Map showing location of the sub-catchment within the Tweed Valley floodplain (modified from Smith and Melville, 2004) and schematic of drainage network within the study site.

The sampling approach consisted of a combination of continuous and discrete measurements of various hydrological parameters over the course of 11 months (336 days). Continuous
measurements for drain surface depth and velocity, groundwater depth, evapotranspiration and precipitation were taken using a series of data loggers (see below). Surface water radon concentrations were measured approximately every two weeks from the outlet drain during individual field campaigns. Samples were obtained using specially designed eight liter bottles (Stringer and Burnett, 2004), and analysed using a radon-in-air closed loop method (Lee and Kim, 2006). During one major flood event in late January 2015, a time series of continuous radon measurements was taken over a period of six days (Webb et al., 2016a). Radon concentrations from this sampling period are included in this paper along with bi-weekly discrete radon samples to help constrain the flood response of radon in surface waters. The groundwater radon endmember was characterised by incubating six 1 kg samples of sediment from the two distinct soil layers below the surface (0.5 m and 1 m) for 21 days to obtain the “sediment equilibrated” radon concentration (Corbett et al., 1998). This approach has been used previously to estimate radon endmembers (Schmidt et al., 2010; Peterson et al., 2010). The analytical uncertainty for radon samples ranged from 2-35% for surface water depending on concentration and 5-9% for groundwater endmember concentrations. Endmember error from natural variability was calculated from the standard error of the six sediment incubation measurements.

4.2.2 Precipitation and evapotranspiration

Daily precipitation and evapotranspiration were measured directly at a meteorological tower located onsite. Rain was measured using a Rimco tipping bucket rain gauge (RIM7499, Campbell Scientific Inc.) with a 20.3 cm diameter collecting funnel and 0.2 mm tip. Gaps in on site precipitation data due to instrument issues made up 16% of the total study period, and were filled from the Murwillumbah Bureau of Meteorology measurement site located ~10 km. Evapotranspiration was measured using an eddy covariance system to measure fluxes of water vapour. Three-dimensional wind speed (CSAT3 sonic anemometer, Campbell Scientific Inc.) and moisture density in air (LI-7500 open path CO\textsubscript{2}/H\textsubscript{2}O analyser, Licor Inc.) were sampled at 10 Hz and then computed to 30 min mean fluxes of latent heat (W m\textsuperscript{-2}). Half-hourly logger computed fluxes were processed following standard OzFlux QA/QC procedures (Eamus et al., 2013), including Webb-Pearman-Leuning (WPL) density correction for latent heat fluxes (Webb et al., 1980) and removal of erroneous data (range test, spike removal, u* filtering). Gaps in latent heat flux data amounted to 24% following QA/QC procedures and were filled using a self-organising linear output (SOLO) artificial neural network model (Eamus et al., 2013). Final gap-filled, corrected latent heat fluxes (energy flux, W m\textsuperscript{-2}) were then converted...
to evapotranspiration rates (water flux) as mm d\(^{-1}\). Water loss from ET and rainfall were upscaled to the total area of the catchment (\(\sim 1,000,000 \text{ m}^2\)). The instrument uncertainty associated with the precipitation and ET measurements were 1% and 5%, respectively.

### 4.2.3 Surface Discharge

Surface flow velocity and depth were measured in a pipe culvert positioned 100 m upstream of the pump using a Starflow ultrasonic Doppler flowmeter. Manufacturer reported accuracy for this instrument is \(\pm 2\%\). Average depth and velocity were recorded over 30 minute intervals. The cross sectional area of the flooded portion of the pipe was calculated from the dimensions of the pipe culvert. Half hourly surface discharge was then calculated by multiplying the cross sectional area by velocity. Significant decreases in surface water depth between intervals determined when the pump was on and when surface discharge was calculated. A two month data gap in flowmeter data was filled from a second depth logger located in a drain 700 m upstream from the catchment outlet. Average velocity for water depth increments of 0.1 m was used to gap fill the velocity data gap. The model fit of predicted total discharge using this gap filling method to actual discharge measurements was within 5%.

### 4.2.4 Drain volume and surface area

Cross sectional drain profiles were measured for each drain within the study site. A total of 40 measurements were taken across the length of 26 individual drains. Drains were grouped into two categories, main drains which generally remain connected for the entire year, and field drains which are only connected after high rainfall (Figure 4.1). Small field drains were grouped into five sections relating to their position within the property. Channel cross sectional area was calculated as a function of (depth – varying) drain width and water height below the surface. For the large drains which had multiple profile measurements, depth along each measured width interval was averaged. A best fit second or third order polynomial equation was used to calculate changing width as a function of changing height. The maximum cross sectional area when the drains were full was then given by the antiderivative of the polynomial equation for width to determine the area under the curve.

Surface water depth data was obtained from one of two depth loggers in the drains, depending on which one was closer. Surface water depths of main drains was taken from one of the two closest depth loggers deployed in the field, and corrected for depth difference between a nearby drain containing a logger. Drain volumes were calculated individually for each large drain by multiplying the drain-specific cross sectional area equation by total drain length. Volumes for
the small field drains were calculated by taking the average cross sectional area equation for a section, and multiplying by the sum of drain lengths within that section.

### 4.2.5 Hydraulic head

Hydraulic head was calculated as the vertical difference in depth between the groundwater level and drain surface water level. Surface water depth was measured in the outlet drain from a Starflow ultrasonic Doppler flowmeter, which was placed in the invert of a drainage pipe located directly upstream. Water depth was converted to AHD from the knowledge that baseline water levels are maintained to at -0.453 m AHD within the drains (Green et al., 2006). This is equivalent to a controlled surface water depth of 0.575 m above the invert of the pipe. Groundwater depth was measured from a CTD diver deployed 1.6 m below the surface inside a perforated PVC pipe which recorded water pressure. The relative accuracy of depth measurements based on manufacturer specifications was ±0.5%. Once corrected for atmospheric pressure (measured at the flux tower), groundwater depth was referenced to surface water depth by accounting for the difference in peak flood depths and converted to AHD.

### 4.2.6 Groundwater storage

Groundwater storage to a depth of 1 m over the annual cycle was calculated as the difference between groundwater depth between the start and end of time series. The following equation was used to calculate total storage:

\[
S_{GW} = (\Delta D \times P \times v/v) \times A
\]

Where \(S_{GW}\) is the storage term in m\(^3\), \(\Delta D\) is the difference in groundwater depth, \(P\) is the soil porosity, and \(A\) is the catchment area excluding drains and roads (assumed impermeable surface). Soil porosity was estimated from the soil moisture content (v/v) at saturation measured by five soil water content reflectometers (CS655, Campbell Scientific) connected to the onsite meteorology tower at depths ranging from 5 cm to 50 cm below surface. The natural variability in soil porosity was found to be ~14%, which was calculated as the standard deviation of three measurements made from the same depth. On a volume per volume basis, the maximum soil moisture content is equal to the porosity of the soil at saturation (Vomocil, 1965).
4.2.7 Radon mass balance

The flux of groundwater discharge was calculated using a radon mass balance technique. Two estimates of groundwater discharge were calculated to represent the minimum \(Q_{GW-min}\) and maximum \(Q_{GW-max}\) range based on two sets of extreme conditions (Peterson et al., 2010; Santos and Eyre, 2011). The minimum and maximum approaches used here accounts for the likely heterogeneity of groundwater input along the drain stretch and provide a range of possible groundwater discharge. An absolute estimate of the real groundwater discharge is not quantifiable using this approach as the exact amount of radon losses from decay and evasion is unknown. Instead, we report final groundwater discharge as a range using the minimum and maximum estimates, between which the real estimate lies (Peterson et al., 2010).

The minimum estimate was derived from the assumption that groundwater input enters directly at the point of measurement in the stream. In this case, any losses of groundwater-derived radon during surface water transit (i.e. decay and evasion), are neglected from the mass balance. Non-groundwater derived sources of radon are also accounted for in the mass balance and include radium (\(^{226}\text{Ra}\)) decay, sediment diffusion, and hyporheic exchange. We first estimate radon excess (\(Rn_{ex}\)) by removing sources of radon other than groundwater from the observed surface water concentrations. In order to achieve that, the minimum radon concentration observed during the year was assumed to represent all radon sources other than groundwater discharge.

The minimum groundwater input was then derived from the ratio of surface water radon concentration (\(Rn_{ex}\)) to the groundwater endmember concentration (\(Rn_{GW}\)) multiplied by the total surface water volume (\(Q_{TOTAL}\)) fluxed out of the system (Burnett et al., 2010):

\[
Q_{GW-min} (m^3 d^{-1}) = \left( \frac{Rn_{ex} (dpm m^{-3})}{Rn_{GW} (dpm m^{-3})} \right) \times Q_{TOTAL} (m^3 d^{-1})
\]

The maximum groundwater discharge estimate takes into account radon losses from the system that would occur if groundwater input was located at the most upstream section of the catchment relative to the sampling point. These losses include atmospheric evasion (\(F_{Rn}\)) and radon decay (\(\lambda\)) and results in higher groundwater discharge required to sustain the measured surface water radon concentration:

\[
Q_{GW-max} (m^3 d^{-1}) = \left( \frac{(Rn_{ex} (dpm m^{-3}) \times Q_{TOTAL} (m^3 d^{-1})) + F_{Rn} (dpm d^{-1}) + \lambda (dpm d^{-1})}{Rn_{GW} (dpm m^{-3})} \right)
\]
Air-water flux estimates of radon \( F, \text{dpm m}^{-2} \text{d}^{-1} \) were calculated as follows:

\[
F = k \propto (C_w - C_a)
\]

where \( k \) is the gas transfer velocity \((\text{m d}^{-1})\), \( \propto \) is the Ostwald solubility coefficient of radon, \( C_w \) is the radon in water concentration \( (\text{dpm m}^{-3}) \), and \( C_a \) is the radon in air concentration \( (\text{dpm m}^{-3}) \). Due to the dynamic nature of surface hydrology in this system, two sets of \( k \) values were used based on the varying conditions of surface water discharge. During stagnant conditions (no drain discharge and surface inundation during floods), a transfer coefficient derived from Ongori et al., (2015) for radon transfer at the water-air surface under very low turbulence conditions was used. This represents a diffusive radon loss to the atmosphere that is primarily driven by the concentration gradient. Radon evasion during active periods of surface discharge (only when surface waters were constrained within the drains) was calculated from the \( k \) parameterisation of O’Connor and Dobbins (1957) using surface water velocity and depth as driving factors for turbulence.

4.2.8 Model uncertainties

Uncertainties in our groundwater discharge model originate from each component of the radon mass balance. The largest degree of uncertainty stems from the assumptions associated with the radon mass balance, where the exact location of groundwater entry points along the drain length is unknown. Because residence time of groundwater discharged to the drains are unknown, we cannot quantify the exact amount of atmospheric loss groundwater-derived radon is exposed to before measurement at the outlet of the catchment. This is a limitation associated with this approach, and consequently makes reporting a singular groundwater discharge value difficult. Our approach relying on extreme assumptions (Peterson et al., 2010) provides a realistic range for possible groundwater discharge. To account for model and endmember uncertainties, we applied lower and upper limits for both the minimum and maximum groundwater scenarios. The lower and upper limits were defined as the mean \((\mu)\) – one standard deviation \((\sigma)\) and mean \(+\) one standard deviation, respectively. Error from the model was derived from the standard error of the equation coefficients and constants and the endmember error was based on the natural variability in radon concentrations between samples. The error of the two terms were then propagated to achieve a combined lower and upper error for minimum and maximum scenarios.
A sensitivity analysis was carried out on the effect of different radon evasion scenarios from a range of empirically derived $k$ models. This included estimates combining the wind speed driven $k$ parameterisation of Raymond and Cole (2001) with depth and current velocity from O’Connor and Dobbin’s (1957), applying current velocity and depth only (O’Connor and Dobbins, 1957), diffusive radon evasion driven by the concentration gradient characterised by the coefficient derived from Ongori et al., (2015), and an extreme case of no evasion (assuming loss by decay only). Final estimates of annual groundwater discharge for each evasion scenario were compared with annual surface discharge to constrain realistic estimates of the maximum groundwater range estimate, but not the minimum groundwater discharge estimate that is not influenced by evasion.

4.3 Results

The floodplain displayed highly dynamic hydrology throughout the year. Direct rainfall was the only source of water into this floodplain and caused large fluctuations in surface and subsurface hydrology. Total annual rainfall was recorded at 1,740 mm which is greater than the mean annual rainfall of 1,600 mm for this region (Bureau of Meteorology, 2016). Large episodic rainfall events between 40 and 220 mm over 48 hours were recorded eight times throughout the year, and caused inundation of the land surface (Figure 4.2). Approximately 70% of total annual rainfall fell during these eight events.

Evapotranspiration (ET) was highly seasonal and reflected the growing stage of sugarcane, with peak biomass growth occurring during the wetter warm months of January to April and reduced evapotranspiration during the cooler months of July to September (Figure 4.2). During flood events ET reduced significantly to $<1.5$ mm d$^{-1}$, which was then followed by a sharp increase shortly after the peak of the flood to some of the highest ET levels observed in the study ($6.1$ mm d$^{-1}$).

The effect of enhanced surface drainage through the extensive network of artificial drains and intermittent pumping could be seen through the highly erratic nature of surface and subsurface hydrology during rain events (Figure 4.2). Surface water depth was temporally variable and reached peak height five-six hours following significant rainfall. Changes in groundwater levels were also responsive to rainfall, and spanned over 1.5 m. Groundwater levels typically increased at the same rate as surface water levels during flood events with minimal delay, implying a connected shallow aquifer. However, water table recession occurred at a slower rate compared to surface water levels (Figure 4.2). Steep vertical hydraulic heads developed during
these recession phases. As a result, the depth difference between groundwater and surface water became positive, ranging from 0.1-0.53 m during flood recession periods (Figure 4.2).

**Figure 4.2** Time series of hydrological parameters measured from 26 November 2014 to 26 October 2015. Shaded areas highlight flood events which caused surface inundation.

Variation in surface radon concentrations spanned an order of magnitude and demonstrated a direct relationship with the position of the water table (Figure 4.3). Radon concentrations increased rapidly between 0.3 to 0 m AHD and decreased back to baseline radon levels of ~4.8 dpm L⁻¹ between 0 to -0.2 m AHD water table position. Based on the change in observed radon concentrations, the model predicted surface water disconnection with the groundwater between groundwater positions < -0.35 m AHD during non-flood conditions and >0.42 m AHD.
during floods. The highest measured surface radon concentrations of 149 dpm L\(^{-1}\) occurred at a receding groundwater position of 0.01 m AHD, and was in the same range to the average groundwater radon concentration of 146 ± 31 dpm L\(^{-1}\).

![Figure 4.3](image)

**Figure 4.3** The relationship between measured surface water radon concentrations and groundwater depth relative to surface water depth. Data was fitted with a four parameter Gaussian curve equation which was applied to continuous groundwater depth measurements to model surface water radon concentrations over the annual cycle.

Surface water radon simulations indicated 13 occasions when radon concentrations exceeded 100 dpm L\(^{-1}\) (Figure 4.4A), approaching the groundwater endmember. Daily volumetric groundwater discharge varied over five orders of magnitude throughout the hydrological year, with discharge during baseline conditions between 0-10 m\(^3\) d\(^{-1}\) and discharge during receding flood periods between 100-20,000 m\(^3\) d\(^{-1}\) (Figure 4.4B). Average baseline groundwater discharge remained elevated at around 35 m\(^3\) day\(^{-1}\) during January to February when the water table was relatively higher. Throughout the study period, minimum aerial groundwater discharge rates ranged from 0 to 180 cm d\(^{-1}\) and maximum rates from 0.3 to 320 cm d\(^{-1}\) (Figure 4.4D).
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**Figure 4.4** Groundwater discharge modelling results, showing: (A) predicted surface water radon concentrations modelled from equation derived in Figure 4.3; (B) the average minimum (blue) and maximum (red) groundwater discharge rates confined by the upper and lower limit (bold lines) for both extreme scenario’s (note the log scale on the y-axis); (C) the minimum and maximum groundwater discharge rates as a percentage of surface discharge; (D) the average minimum and maximum vertical flux of groundwater (note the log scale on the y-axis).

Figure 4.5 demonstrates the cumulative trend in all water balance components over the year as a function of cumulative annual rainfall. The total outputs trend represents the sum of all quantified water loss terms which explained 78% of total annual rainfall. Generally, the contribution of the different water budget terms remained similar because episodic events control hydrology. All water balance components repeat the same response to rainfall illustrated by a stepwise trend, where large increases in cumulative rainfall are followed by sudden increase in water outputs (Figure 4.5). Evapotranspiration represented the largest loss
for rainfall (46%), followed by total surface discharge (28%). As more rainfall cumulates over time, the discrepancy between total water outputs and the unaccounted for flux increases. For the first half of total rainfall, surface discharge remains similar to evapotranspiration, where the contribution of surface discharge to water loss becomes equal when annual rainfall increases to 0.25 (Figure 4.5). The difference then widens with each major rain increase, analogous with the increasing discrepancy in the unaccounted for flux.

![Figure 4.5 Summary of cumulative output water budget terms expressed as a fraction of total annual rainfall against cumulative annual rainfall (input term) over the hydrological year (2014–2015). The total surface discharge represents contributions from both surface and groundwater flows.](image)

4.4 Discussion

4.4.1 Hydrology time series observations

Both surface water and groundwater were highly responsive to rainfall, demonstrating the effective connectivity of the drainage network with the floodplain. A more rapid response in land surface hydrology including shorter lag times is often associated with extensively drained floodplains (Blann et al., 2009; Levavasseur et al., 2012; Shen et al., 2016). This effect may also influence near surface groundwater hydrology, where any recharge following rain appears to be offset by groundwater discharge. The residence time of surface water in this floodplain varied greatly, with long residence times between periods of rain when the water was stagnant to extremely short residence times during flooding. Such a wide variability is typical of
floodplain landscapes which naturally experience periods of disconnection and connection between channel, floodplain surface and groundwater (Tockner et al., 2000; Karim et al., 2016). For example, simulations of a floodplain river segment found that residence time decreased exponentially from 55 to 10 days as surface discharge increased (Helton et al., 2014). By taking into account the average discharge rate when the automatic pump is in continuous operation, it would take approximately 21 hours to replace all water held within all drains when at capacity. Residence time of floodwaters following inundation and back to baseline levels was approximately 3.4 days. These short residence times during flood events are similar to floodwater residence times estimated from another agriculturally impacted floodplain which varied between eight hours to several days during a flood event (Karim et al., 2013).

4.4.2 Radon-derived groundwater discharge estimates

Measured radon concentrations of up to 149 dpm L\(^{-1}\) in surface waters (similar to the measured groundwater endmember of 146 ± 31) suggest that when the groundwater table is -0.1 to 0.1 m AHD elevation groundwater discharge accounts for nearly 100% of surface waters. At 0 m AHD elevation the groundwater level is equivalent to ~20 cm below surface level (top of the drains). This finding that maximum surface radon concentrations coincide with periods of highest groundwater table elevation within the drains confirm that the groundwater-surface water connectivity is maximised due to the lateral drain surface area. The fact that radon concentrations decrease to levels indicative of non-groundwater radon sources once water levels decrease to ~0.35 m AHD (equivalent to where baseline surface water levels sit) supports evidence for shallow lateral groundwater flow as the main source of groundwater in this system, and not upwelling from deeper aquifers. Although this relationship between radon and groundwater table position has not been demonstrated before, such a trend supports evidence for the transmissivity feedback mechanism, which is often revealed by strong correlations between groundwater table levels and stream discharge (Laudon et al., 2004).

The resulting relationship between surface water \(^{222}\text{Rn}\) concentrations and groundwater table position provide a theoretical basis for modelling groundwater discharge. However, the direction of this relationship should be viewed only from high groundwater levels returning to baseline levels (as indicated by the arrows). This is because the rising limb of the groundwater level occurs with a simultaneous rise in surface water levels and no hydraulic head develops. Therefore, the relationship predicting radon concentrations with depth is only applied during the receding phase of the hydrograph. A default concentration equivalent to dilution
concentrations were applied during the rising limb. Applying the equation derived from Figure 4.3, our biweekly surface water radon observations were used to estimate daily concentrations. By simulating continuous surface radon concentrations throughout the year, a detailed radon mass balance was constructed to estimate groundwater discharge into the drains (Figure 4.3).

For the radon mass balance calculations, the surface water radon concentration supported by non-groundwater source (sediment diffusion, $^{226}$Ra decay, and hyporheic exchange) was estimated at 1,962 dpm m$^{-3}$, which is the average concentration of the three lowest discrete radon measurements. The same assumption has been applied to other studies where the lowest values are used as an indicator of “background” radon/radium activity (Peterson et al., 2008; Schmidt et al., 2010). This approach was supported by the known lower groundwater depth relative to surface water depth in the drains during the times of these low concentration measurements, and significantly higher radon concentrations observed with higher groundwater depths.

The modelled groundwater discharge rates produced by the relationship between measured radon concentrations and groundwater depth provides a detailed analysis of groundwater discharge dynamics over an entire year at a resolution often only achieved in short term tracer time series (Figure 4.4). The results from the groundwater model confirm our hypothesis that flood events drive a large portion of the groundwater flux into surface water. Variations in rainfall events significant enough to increase water table height triggered significant variation in groundwater discharge by over five orders of magnitude (Figure 4.4). The largest variation observed was during the floods of January and June, when the groundwater discharge rate ranged from 0-15 m$^3$ day$^{-1}$ pre flood to 1,000-27,200 m$^3$ day$^{-1}$ immediately post-flood (Figure 4.4B). During peak groundwater discharge after these flood events, the groundwater aerial flux ranged from 185-325 cm d$^{-1}$, which given the high hydraulic conductivity of 545 ± 275 cm d$^{-1}$ of surface layers at this site (Johnston et al., 2009) suggests the groundwater flux is maximised within the limits of flow through the soil. Although measurements of hydraulic conductivity are highly heterogeneous, this finding gives confidence in our model derived groundwater aerial flux estimates. This also highlights the usefulness of geochemical tracers to estimate groundwater discharge in systems with heterogeneous hydraulic conductivities due to cracks and macropores.

The rate of groundwater flux varies seasonally in many natural floodplains and wetlands, as factors such as sustained groundwater storage after rainfall and evapotranspiration generally...
control GW-SW interactions (Ramberg et al., 2006; Krause et al., 2007a; Saha et al., 2012; Ludwig et al., 2015). The distinct pulses of groundwater discharge observed at this site highlight the responsiveness of groundwater to individual rainfall events, which prevents the development of a clear seasonal pattern. The rapid return of groundwater levels to baseline conditions due to forced pumping ensures that there is no groundwater storage in the top profile of the soil, and hence no sustained groundwater input after rainfall in contrast to more natural drainage conditions (Saha et al., 2012).

Many other studies have reported noticeable increases in groundwater discharge during wetter periods, usually based on one or two surveys over contrasting conditions (Peterson et al., 2010; Santos and Eyre, 2011; Santos et al., 2011; Atkins et al., 2013; Sadat-Noori et al., 2015b; Jeffrey et al., 2016). The amplitude of variation between baseline and flood groundwater discharge rates in the aforementioned studies ranged between 2 and 145-fold. In our continuous study, the average groundwater discharge rates of 1,600 and 4,900 m$^3$ d$^{-1}$ during periods of flooding (within 5-10 days after floods) were 136 to 230-fold greater than the average baseline rates (7 and 36 m$^3$ d$^{-1}$), making groundwater discharge in the present study the most sensitive yet to rainfall input. Such an extreme groundwater-rainfall response appears to be most pronounced in areas where localised shallow groundwater dominates subsurface flow into relatively small tributaries or drains. High groundwater discharge rates following rainfall in this study is likely enhanced due to two major hydrological alterations to floodplain drainage: (1) forced pumping of surface water against natural flood levels creating a steep hydraulic head (up to 0.55 m), and (2); an extensive and dense network of drainage canals which expand the surface area of groundwater discharge.

### Uncertainties and challenges

The ratio between groundwater discharge and surface water discharge (Figure 4.4C) provides a quality control measure and reality check of our minimum and maximum range groundwater flux model. By definition, plausible groundwater discharge rates should not exceed surface discharge. Throughout the study period, minimum groundwater discharge estimates exceeded surface discharge by on average 5% during periods of peak groundwater flow (Figure 4.4C). In contrast, the average maximum groundwater discharge exceeded surface discharge by ~60% (excluding >200% periods) during these peak groundwater flow periods. These relatively minor occurrences of numerical instability are similar to the 2% uncertainty in discharge measurements and 21% error in the endmember concentrations. Since the highest surface water
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radon concentrations observed is equivalent to average groundwater radon concentrations makes the maximum groundwater model more likely to reach (and exceed) 100% of surface water discharge when these conditions occur. This also suggests that groundwater input likely occurs throughout the entire drainage area rather than at the most upstream site, resulting in a higher probability that the maximum estimate overestimates groundwater discharge in this system. The highest rates of estimated groundwater discharge (provided by the maximum range) exceeded surface water discharge by 200-380% during short periods, suggesting unrealistic groundwater discharge values estimated from our model. Such numerical instability is an artefact of the maximum mass balance model, which can occur because the groundwater flux is being solved by linearizing the first order derivative of the radon mass balance equation (Frei and Gilfedder, 2015). However, the frequency of this occurrence was only 4% over the year, and occurred when rates of surface discharge was reduced during pumping of flood water at high water tables (highly unstable surface water hydrology). The coinciding rates of maximum groundwater discharge during these exceedance periods were in the range of 830-31,175 m$^3$ d$^{-1}$, which are realistic values compared the maximum surface discharge recorded at 35,336 m$^3$ d$^{-1}$ during the study period.

The three main sources of error that were applied to the final groundwater discharge estimates include error from the radon simulations (model), error from the variability in the groundwater radon concentrations (endmember), and assumptions within the radon mass balance calculation (section 2.7). Uncertainty estimates of final groundwater discharge are complicated by the fact that model and endmember error are based on observational data whereas uncertainty associated with the radon mass balance technique is reported in the form of an upper (maximum) and lower range (minimum) in possible groundwater discharge. Therefore, an absolute value for final groundwater discharge is difficult to report when using the minimum and maximum approach. Since model and endmember errors are proportional to the magnitude of the groundwater flux, these errors were applied to both the minimum and maximum model. Results from the uncertainty analysis provided in Table 4.1 demonstrates how the model and endmember error are minor relative to the difference between minimum and maximum estimates. The upper and lower ranges in model, endmember and combined error vary by a factor of 1.4 to 1.8, 1.5, and 1.7 to 2.1 respectively, and the minimum and maximum range vary by a factor of 2.5 to 3.1. The resolution provided by the difference in the minimum and maximum range (factor of ~3) is comparable to groundwater discharge estimates based on short term high-frequency radon time series (Peterson et al., 2008; Peterson et al., 2010; De Weys et
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Over longer time scales (annual) groundwater discharge estimates from studies using water balance approaches have reported ranges anywhere from a factor of 2 to 24 (Laczniak et al., 2001; Zhu et al., 2007).

Table 4.1 Results of uncertainty analysis from model, endmember, and combined error on the annual estimate of groundwater discharge (m$^3$) for the minimum and maximum radon mass balance scenarios. Differences between the lower ($\mu - \sigma$) and upper ($\mu + \sigma$) one standard deviation from the mean ($\sigma$) for each scenario in model and endmember were propagated to a combined error estimation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Model error</th>
<th>Endmember error</th>
<th>Combined error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIN$_m$</td>
<td>MAX$_m$</td>
<td>MIN$_e$</td>
</tr>
<tr>
<td>$\mu - \sigma$</td>
<td>123,006</td>
<td>302,743</td>
<td>182,299</td>
</tr>
<tr>
<td>$\mu$</td>
<td>148,055</td>
<td>423,968</td>
<td>148,055</td>
</tr>
<tr>
<td>$\mu + \sigma$</td>
<td>176,183</td>
<td>552,016</td>
<td>124,642</td>
</tr>
<tr>
<td>Difference $\mu - (\mu - \sigma)$</td>
<td>17%</td>
<td>29%</td>
<td>23%</td>
</tr>
<tr>
<td>Difference $(\mu + \sigma) - \mu$</td>
<td>19%</td>
<td>30%</td>
<td>16%</td>
</tr>
</tbody>
</table>

Another source of uncertainty within the radon mass balance calculations is assigning the correct $k$ value to estimate radon evasion. A sensitivity analysis was carried out on different transfer velocity ($k$) models for radon to determine the variation in maximum groundwater discharge and constrain realistic values (Table 4.1). The $k$ value for the first scenario one was empirically derived from the combined parameterisation of Raymond and Cole (2001) and O’Connor and Dobbins (1957) as a function of wind speed ($w$, at 10 m), current velocity ($c$), and depth ($d$). This yielded the highest flux estimate for radon evasion and resulted in annual groundwater discharge estimate exceeding total surface discharge by 311%, which is clearly unrealistic. Wind speed was discounted in the second scenario (current velocity and depth only), which reduced annual groundwater discharge by a factor of 3.6 and provided a more realistic calculation of 87% of total surface discharge (Table 4.2). The reasoning behind excluding wind is based on the sheltered site characteristics of the drains. This has been demonstrated in other similar canal sites where the high banks caused low evasion of radon from the surface nearly equivalent to diffusion (Burnett et al., 2010). Wind speed was measured above the canopy of the vegetation and walls of the drains and is likely not representative of wind speeds (if any) surface waters were exposed to. The effect of current velocity, although intermittent, is likely an important component of our evasion calculations at our site due to the narrow and shallow nature of the drains. Hence, radon evasion driven by a diffusive concentration gradient only was used between periods of surface water discharge.
Table 4.2 Different radon evasion scenario’s for the calculation of maximum groundwater discharge ($Q_{GW\text{-MAX}}$) and the impact on annual $Q_{GW\text{-MAX}}$. Final $Q_{GW}$ reports the range in acceptable annual groundwater discharge estimates derived from $Q_{GW\text{-MIN}}$ and $Q_{GW\text{-MAX}}$.

<table>
<thead>
<tr>
<th>Evasion method</th>
<th>Average $k$ (m d$^{-1}$)</th>
<th>Average evasion (dpm m$^{-2}$ d$^{-1}$)</th>
<th>Average $Q_{GW}$ flux (m$^3$ d$^{-1}$)</th>
<th>Annual $Q_{GW}$ flux (m$^3$)</th>
<th>$Q_{GW}/Q_{SF}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{GW\text{-MAX}}$ – w+c+d</td>
<td>0.83 (0.36-6.21)</td>
<td>26,889</td>
<td>4,477</td>
<td>1,509,176</td>
<td>311</td>
</tr>
<tr>
<td>$Q_{GW\text{-MAX}}$ – c+d</td>
<td>0.39 (0.12-5.56)</td>
<td>16,626</td>
<td>1,258</td>
<td>423,968</td>
<td>87</td>
</tr>
<tr>
<td>$Q_{GW\text{-MAX}}$ Diffusive,</td>
<td>0.12 ± 0.02</td>
<td>2,527</td>
<td>864</td>
<td>291,400</td>
<td>60</td>
</tr>
<tr>
<td>$Q_{GW\text{-MAX}}$ No evasion</td>
<td>0</td>
<td>0</td>
<td>555</td>
<td>187,243</td>
<td>47</td>
</tr>
<tr>
<td>$Q_{GW\text{-MIN}}$</td>
<td>0</td>
<td>0</td>
<td>439</td>
<td>148,055</td>
<td>31</td>
</tr>
</tbody>
</table>

$w =$ wind, $c =$ current velocity, $d =$ depth

4.4.4 Impact of drainage density on water balance

Increased hydrological connectivity due to extension of the drainage network via artificial drains is widespread in agricultural and urban landscapes (Levavasseur et al., 2012; Kaushal et al., 2014). An increase in drainage density can impact catchment water budgets by altering the rates and pathways of water movement through the landscape (Blann et al., 2009). Such extensions of the natural drainage network typically increase peak surface discharge rates, accelerate surface runoff, and reduce surface storage (Krause et al., 2007b; Blann et al., 2009; Schottler et al., 2014). In these hydrologically modified systems, flood events are generally more intense and return to baseline conditions rapidly, consistent with the surface hydrology results found in this study.

The effect of drainage density on groundwater discharge rates has seldom been discussed before. Model simulations of groundwater dynamics in a lowland-floodplain have predicted that higher drainage density increases surface water-groundwater interactions and reduces groundwater recharge (Krause et al., 2007b). When aerial groundwater discharge rates from the current study were compared with other inland aquatic landscapes, two patterns were revealed; 1) groundwater input is greater under wet conditions, and 2) sites with the largest reported groundwater fluxes also have the highest drainage density (Table 4.3). Here, we compare with a limited number of studies that have used the radon mass balance technique to compute groundwater fluxes reported as a normalised aerial flux (cm d$^{-1}$), and focused on lowland aquatic landscapes such as wetlands, floodplains, and estuaries rather than streams with steep topographic relief. Groundwater discharge is highly variable between sites as it is strongly governed by localised catchment properties, including soil transmissivity and surface
water flow dynamics (Krause and Bronstert, 2007). However, drainage density may be an important underlying factor defining lowland groundwater dynamics (Table 4.3).

Unique to our study is the substantial increase in drainage density from 2.1 to 12.4 during flood conditions, when an increase in hydrologic connectivity facilitates comparatively larger groundwater input (Table 4.3). This drainage density is much larger than previous studies and may explain the higher groundwater discharge rates. A conceptual model of surface water and groundwater flood response was developed to illustrate how increased drainage modifies the surface water and groundwater flows (Figure 4.6). The shortened yet amplified hydrograph of surface water discharge followed by rapid recovery is consistent with the understanding that expanded drainage generates “flashier” hydrographs in watersheds than natural drainage (Levavasseur et al., 2012; Kaushal et al., 2014). As a consequence, increased drainage results in a shorter floodwater residence time, whereas most natural floodplains with smaller drainage density often remain inundated for prolonged periods (up to a month) after a flood event (Ludwig et al., 2015; Karim et al., 2016).
Table 4.3 Aerial groundwater flux and associated drainage density (drainage length km/catchment area km$^2$) of other studies using a radon mass balance approach.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Drainage density (km km$^{-2}$)</th>
<th>Qgw (cm day$^{-1}$)</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Baseflow</td>
<td>Wet conditions</td>
</tr>
<tr>
<td>Coastal plain wetland, Australia</td>
<td>n/a</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gilfedder et al., (2015)</td>
<td></td>
</tr>
<tr>
<td>Coastal lake, Australia</td>
<td>n/a</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Perkins et al., (2015)</td>
<td></td>
</tr>
<tr>
<td>Estuary, Australia</td>
<td></td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wong et al., (2013)</td>
<td></td>
</tr>
<tr>
<td>River, Australia</td>
<td>0.04</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cook et al., (2006)</td>
<td></td>
</tr>
<tr>
<td>Tidal creek, Australia</td>
<td>0.28</td>
<td>35 ± 12</td>
<td>56 ± 13</td>
</tr>
<tr>
<td>Remediated coastal wetland, Australia</td>
<td>0.7-0.9</td>
<td>1.3 ± 0.3</td>
<td>51.4 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jeffrey et al., (2016)</td>
<td></td>
</tr>
<tr>
<td>Altered coastal floodplain, Australia</td>
<td>1</td>
<td>0.58 ± 14.2</td>
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<td></td>
<td>Atkins et al., (2013)</td>
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<tr>
<td>Tidal river, Australia</td>
<td>1.7</td>
<td>26.8</td>
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<td>Makings et al., (2014)</td>
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<tr>
<td>Drained agricultural swamp, Australia</td>
<td>2.75</td>
<td>2.8-129</td>
<td>11.4-328</td>
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<td></td>
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<td>De Weys et al. (2011)</td>
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<tr>
<td>Drained tidal creeks, Florida</td>
<td>4-8</td>
<td>84-125</td>
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<td>Peterson et al. (2010)</td>
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<tr>
<td>Altered coastal floodplain, Australia</td>
<td>2.1-12.4</td>
<td>0-35</td>
<td>185-325</td>
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<tr>
<td></td>
<td></td>
<td>This study</td>
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n/a means there is no drainage density as the area is mostly covered by an expanse of water

Terrestrial versus aquatic carbon fluxes in an agricultural coastal floodplain
The groundwater discharge response from an artificially drained floodplain illustrated in Figure 4.6 represents the simplified discharge patterns observed at the study site during flood events. We suggest that there are a number of important differences in the response of groundwater discharge to floods in floodplain catchments with different drainage density. Firstly, there is a small increase in groundwater discharge from artificially drained floodplains which represents the “first flush” of groundwater during the rising limb of the hydrograph. This is due to the close hydraulic relation of groundwater with surface dynamics specific to this floodplain (Figure 4.2), although a rapid response in groundwater levels to a pulse event has been noted in a few studies on drained landscapes (Wilcox et al., 2006; Kaushal et al., 2014). The mobilization of groundwater following rain events has also been reported in unmodified watersheds using the isotopic hydrograph separation technique and multiple tracers (Sklash et al., 1986; Brown et al., 1999; Burns et al., 2001). However, these observations are primarily reported in small, steep catchments that don’t experience flooding and where stored groundwater is displaced by slope water table development (McDonnel, 1990). In our simplified representation of a natural drainage floodplain we assume that this effect is dampened in flat landscapes with slower surface discharge. Secondly, the duration for which groundwater discharge is impeded by floodwater inundation is shorter for the artificially drained floodplain. This phenomenon happens in both floodplains when the surface water levels are above the surface as there is no positive vertical hydraulic head to drive groundwater discharge into surface water. This type of reduction in groundwater discharge may occur daily on a smaller scale in estuaries during flood tide or storm surges (Wong et al., 2013; Johnston et al., 2005). Thirdly, groundwater discharge is greatly amplified during flood recession compared to the natural floodplain, as drainage of surface water exceeds groundwater discharge creating a steep hydraulic head. Lastly, the rapid return to negligible groundwater discharge post-flood is an important aspect on the effect artificial drainage has on the groundwater dynamics in this system, as groundwater is quickly disconnected from surface water. In more natural systems, the recession limb extends over a longer period and groundwater input into surface water is sustained, which can contribute significantly to surface flow during drier periods (Sophocleous, 2002; Brannen et al., 2015).

The impact of drainage density on groundwater recharge has implications for management of irrigated land in areas where groundwater management is a challenge, either due to salinization associated with rising water tables (Hatton and Nulsen, 1999) or falling groundwater tables.
affecting water resource availability or the health of groundwater-dependent ecosystems (Boulton and Hancock, 2006).

**Figure 4.6** Conceptual model demonstrating the effect of hydrological connectivity on the hydrograph trends of surface water and groundwater discharge during a flood event. Blue represents the response from the studied catchment with extensive artificial drainage and green represents a floodplain catchment retaining natural drainage. The dark shaded grey bar signifies the duration of floodplain inundation after a rain event for artificial drainage and lighter grey the inundation duration in a natural floodplain. Graph not to scale.

### 4.4.5 Water balance

With continuous measurements of water balance components, our data provided insight into the interplay between water transport pathways that would not be realized in static water balance calculations. The radon modelling approach gives insight into groundwater discharge that is often a small component that is difficult to be quantified by difference in the other terms of the water balance. Consequently, total groundwater contribution to the water balance was represented over an annual cycle while providing ranges to highlight radon mass balance model uncertainties.

The total annual water balance amounted to 1,745,000 m$^3$ of total water inputs and 1,301,574 m$^3$ of total water outputs, leaving a surplus of 443,121 m$^3$ or around 25% unaccounted for
Constraining the annual groundwater contribution to the water balance of an agricultural floodplain using radon: The importance of floods

(Figure 4.7A). Propagating all the errors from the loss terms resulted in an estimated uncertainty of 45,000 m$^3$, therefore the unaccounted for water is not represented by cumulated water balance errors.

Given the distinct shifts in surface water and groundwater hydrology driven by floods throughout the year, the total water balance was further divided into dry periods (daily rainfall <10 mm) that represented 253 days (Figure 4.7B) and flood events that represented 83 days (inclusive of flood and recovery to baseline conditions) of the study period (Figure 4.7C). The unaccounted for water surplus calculated during the flood periods clearly indicates that the total annual water surplus originated from these extreme hydrological events. Subsurface storage may have accounted for a portion of this unaccounted flux, however this is unlikely as total storage levels would recover back to baseline levels (Figure 4.2). The remainder of the discrepancy is likely attributed to overbank flow during surface inundation, as floodgates and levees fail to isolate the sub-catchment from adjacent creeks during large flood events.

Most of the annual discharge (75%) occurred during the flood events (Figure 4.7). Streamflow dominated by episodic rainfall events is a common feature of river systems in Australia, with wet seasons contributing >90% of stream flow in some catchments (Karim et al., 2016). Groundwater discharge was found to represent between 31 and 87% of the total surface water discharge, which is a substantial fraction of the surface water budget considering global estimates of 0.01 to 30% of river discharge (Zektser and Loaiciga, 1993). Overall, groundwater discharge made up 9-24% of the total water balance (Figure 4.7), which is within the range of 2 to 30% reported from other watershed budgets (Santos et al., 2008; Saha et al., 2012). Importantly, groundwater discharge dominated the water balance (i.e., >50% of the total flows) during 6-12% of the time.

The importance of quantifying groundwater discharge continuously over an annual cycle is demonstrated in the final water balance. If annual groundwater estimates were based on samples from normal surface flow conditions with minor rainfall, total groundwater discharge would be underestimated by 72 to 76%. Short term flood events had an occurrence frequency of only 1:9 days of the year yet contributed ~74% of the total groundwater discharge (Figure 4.7). Although many short term studies have found that flood events drive large groundwater discharge rates that are significantly higher than baseflow conditions (Table 4.3), this has been the first attempt made to upscale the contribution of these events to annual groundwater discharge.
Figure 4.7 Water balance diagrams for the whole hydrological year (a) including the water budget partitioned into non-flood (b) and flood (c) events. $S$ refers to the discrepancy in the water balance where a positive value indicates a surplus of water input and negative a deficit in water input. $P$=precipitation, $ET$=evapotranspiration from vegetation, $D$=discharge, $GW$=groundwater discharge, $L$=leakage from surrounding creek.

4.5 Conclusions
In this paper, we have calculated surface water-groundwater exchanges on an annual timescale using continuous radon and groundwater level measurements. This approach is less-labour intensive and, provides additional detail compared to previous methods based on discrete
samples only. Groundwater discharge rates varied over five orders of magnitude during our study, demonstrating that high temporal resolution is required to accurately estimate water balances or identify processes controlling groundwater discharge in hydrologically modified floodplains.

Drained floodplains are a common feature in agricultural landscapes and accelerate not only surface water flows, but also groundwater discharge. Groundwater discharge was driven by precipitation events that caused elevation of the water table and stimulated rapid drainage of surface waters. Peak groundwater discharge rates as high as 325 cm d\(^{-1}\) were observed, and were comparatively higher than other lowland groundwater studies during flood events. Groundwater discharge displayed large variability, fluctuating between 0-100% contributions to surface discharge following rain events. Our finding that 72 to 76% of the groundwater discharged over an annual cycle occurred after flood events and was enhanced by artificial drainage provides valuable information for improving management of groundwater in hydrologically modified floodplains.
Chapter 5 - Importance of aquatic carbon fluxes in catchment carbon budgets
Abstract
Carbon losses from aquatic ecosystems may partially offset the terrestrial carbon sink, yet remain poorly understood. Here, we present findings on the complete annual carbon budget of a subtropical agricultural floodplain, and explore the contribution of aquatic carbon flux to net ecosystem exchange (NEE). An integrated approach to measuring all relevant carbon flux pathways is required to provide a comprehensive evaluation of the net ecosystem carbon budget (NECB). Carbon fluxes measured included: land-atmosphere CO$_2$ exchange (NEE), aquatic CO$_2$ and CH$_4$ evasion from drainage canals, and export of DOC, POC, and DIC via discharge. The floodplain remained a large atmospheric CO$_2$ sink throughout the study, with an annual NEE of -900 g C m$^{-2}$ yr$^{-1}$ per catchment area. Accounting for total aquatic carbon exports and biomass input and removal, the system had a relatively neutral NECB of 100 g C m$^{-2}$ yr$^{-1}$. Total aquatic carbon fluxes were estimated at 24, 16, and 0.05 g C m$^{-2}$ yr$^{-1}$ for lateral export, CO$_2$ and CH$_4$ evasion, respectively. This was found to represent a very minor component of the NECB, offsetting only ~4% of terrestrial NEE. A cross-ecosystem analysis of integrative carbon budgets revealed that the importance of aquatic carbon flux in catchments is proportional to the magnitude of terrestrial NEE, which varies by an order of magnitude greater than the aquatic component between ecosystems. We show that the importance of the aquatic carbon flux pathway is not well represented in the carbon budget of highly productive ecosystems in the sub-tropical to tropical climatic regions. To improve our mechanistic understanding of the role of the aquatic carbon flux pathway in terrestrial ecosystem carbon budgets, more site-specific integrative studies need to be undertaken across a broader range of climatic regions and ecosystem types.
5.1 Introduction
Understanding the contribution of different flux components in ecosystem carbon budgets is crucial for monitoring how ecosystem carbon cycle dynamics respond to environmental change. In terrestrial ecosystems that contain an aquatic interface, traditional means of evaluating the carbon budget are confounded by carbon lost via the aquatic continuum. Up until recently aquatic systems have not been included in terrestrial carbon budgets (Cole et al., 2007; Battin et al., 2009). However, recent re-evaluations on the amount of carbon received, transported and lost via atmospheric evasion along the aquatic continuum suggest that aquatic fluxes are of similar magnitude to the terrestrial carbon fixed in their watersheds through net primary production (NPP) (Aufdenkampe et al., 2011; Yu, 2012; Butman et al., 2016).

A great deal of literature has been produced on the land-atmosphere carbon exchange across various ecosystems. Currently, there are 253 eddy covariance (EC) towers globally providing net ecosystem exchange measurements in an effort to monitor the terrestrial carbon budget (FLUXNET, http://www.fluxdata.org/sitepages/aboutfluxnet.aspx). In addition, the number of studies quantifying carbon fluxes across the aquatic continuum, including lateral export and gaseous efflux, is continuing to expand. A number of new global estimates on different forms of aquatic carbon fluxes have been produced (Cole et al., 2007; Bastviken et al., 2011; Raymond et al., 2013), further revealing the potentially important role these systems may have in terrestrial carbon budgets. Due to the revelation that aquatic systems not only transport terrestrially derived carbon out of ecosystems yet can also release substantial quantities of carbon dioxide (CO₂) and methane (CH₄) to the atmosphere (Cole et al., 2007; Stanley et al., 2016), it has become clear that these fluxes need to be integrated into ecosystem carbon budgets to provide a more accurate measure of net carbon accumulation. Despite an increasing number of studies reporting both terrestrial and aquatic carbon fluxes to quantify ecosystem carbon budgets, the importance of aquatic carbon fluxes remains uncertain.

Such uncertainty stems from a lack of parallel measurements for both land and aquatic carbon fluxes, or an incomplete representation of aquatic carbon fluxes. The importance of aquatic environments in terrestrial carbon budgets is confounded by these inconsistencies, and needs to be properly assessed. Given the prevalence of net heterotrophy in inland waters, aquatic CO₂ and CH₄ evasion should be quantified in landscape carbon budgets. A recent review by Ciais et al (2008) suggests that >70% of terrestrially derived carbon is mineralised and lost to the atmosphere in the form of CO₂ and CH₄ while transported in rivers. The inclusion of CO₂ evasion
has been found to increase the total aquatic carbon flux by ~100% in stream systems compared to lateral carbon exports (Wallin et al., 2013). Complete ecosystem carbon budget studies are also underrepresented spatially, as most studies that have integrated the aquatic carbon flux in ecosystem carbon budgets have focused on boreal peatlands. Based on a review on the net ecosystem carbon budget NECB of these systems, aquatic carbon exports (DOC only) were found to offset terrestrial carbon uptake by on average 24.7% and CH$_4$ fluxes 7.1% (Yu, 2012). This is a relatively significant contribution to the NECB, however boreal peatlands have a small median NEE (terrestrial C uptake) value of 40 g C m$^{-2}$ yr$^{-1}$ per catchment area (Frolking et al., 2011) which is within the same order of magnitude as aquatic DOC export from wetlands (~ 16 g C m$^{-2}$ yr$^{-1}$) (Fraser et al., 2001).

Estimating the complete carbon budget of terrestrial-aquatic ecosystems is difficult due to the multiple array of carbon transport processes in these often highly heterogeneous landscapes. As a consequence, some carbon fluxes may be neglected altogether, or certain carbon fluxes may be scaled in a generalised manner such that the impact of certain ecological processes is not fully realised. Such uncertainties are often a limitation of measurement techniques or lack thereof. For example, caution must be taken to not overestimate the NEE of an ecosystem if the canopy structure and terrain present induces horizontal advection of nocturnal CO$_2$ that is removed from the flux tower footprint (van Gorsel et al., 2009; McHugh et al., 2016). Additionally, ensuring that NEE measurements are representative of inhomogeneous surface areas including vegetation cover are important in ecosystem carbon budget interpretations (Griebel et al., 2016).

There are also inherent difficulties in estimating aquatic carbon fluxes within a defined catchment area, including hydrological flow paths that are difficult to quantify. Ephemeral streams can comprise up to 50% of total catchment drainage length yet carbon fluxes are often neglected due to their intermittent nature (Hansen, 2001; Looman et al., 2016). The influence of upland regional groundwater flows into lowland ecosystems can have a profound impact on the carbon budget of the receiving watershed, as this groundwater input supports the carbon export and evasion estimated from the stream (Genereux et al., 2013). All these uncertainties complicate the role of aquatic systems in catchment carbon budgets.

In order to quantify an ecosystem scale carbon budget, comprehensive and long term measurements are required of all carbon pathways relevant to the site. In this study, we quantify the complete annual carbon budget of an agricultural floodplain by measuring land-atmosphere fluxes of CO$_2$ simultaneously with aquatic carbon export and evasion over one year. The chosen
site represents a well constrained “model catchment”, with distinct surface and groundwater flow paths originating within the catchment boundary (Webb et al., 2016c), and a relatively controlled terrestrial carbon uptake pathway by one vegetation type (sugarcane crop). The key features of this study site include strong regulation of water levels via artificial drainage and controlled discharge, and distinct soil characteristics including a deep impermeable pyritic sediment layer overlain by oxidized acid sulfate soil. Such features are common throughout the eastern coast of Australia and parts South East Asia where coastal floodplains underlain with pyrite have been drained and are used for various farming practices (Tulau, 1999). On a regional scale, an estimated 50% of sugarcane farms in NSW are located on acid sulfate soil floodplains (Keene et al., 2003). To minimize flooding most of these types of catchments have artificial drainage networks with controlled input and release of surface water through floodgates and weirs (Johnston et al., 2004). We further explore the contribution of the aquatic carbon flux to terrestrial carbon uptake by presenting the first cross-ecosystem analysis from studies having measured both terrestrial NEE and aquatic carbon flux in transient ecosystems.

5.2 Methods
The present study was undertaken in an agricultural wetland used for sugarcane production, situated in the sub-tropical coastal region of eastern Australia (28°17’1.69″S, 153°30’15.02″E). The site was originally a freshwater tidal wetland connected to the Tweed River estuary, which has been converted to sugarcane production for the past 40 years through drainage construction and implementation of floodgates (see previous Chapters for description of study site). The subcatchment is 1,000,000 m² and contains a high drainage density of 2.1 km km⁻² and average drainage area of 3,000 m² during baseflow conditions. The site frequently experiences large rainfall events that can increase the drainage density to 12.4 km km⁻² (Webb et al., 2016c). The net ecosystem carbon budget (NECB) was calculated by summing all measured carbon components and accounting for biomass inputs (i.e. the previous year’s residue) and outputs (i.e. biomass harvested).

5.2.1 Aquatic carbon export
Measurements of carbon species including dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC) were obtained biweekly throughout the year from the drain network. Additional samples were collected during a six day time series following a flood event in late January 2015, and are included in the annual study.
DOC samples were filtered through pre-combusted (450°C for 4 h) 25 µm GF/F filters using a syringe into 40 mL borosilicate VOC vials and treated with HgCl₂. Samples were sealed with a Teflon rubber septa and stored frozen until analysis. Leftover filters were carefully placed into sterile polycarbonate cases and stored frozen until analysis. DOC was analyzed on an OI Aurora 1030W analyzer (St-Jean, 2003; Maher and Eyre, 2011). POC filters were oven dried and acidified with 8% saturation HCl2 acid vapor in a chamber overnight. Samples were then compacted into silver capsules for POC analysis on a flash elemental analyser (EA). DIC was calculated from total alkalinity (TA) samples and field pH as determined in CO2SYS (version 25) (Pierrot et al., 2006). TA samples were filtered through a disposable 0.7 µm GF/F Whatman filter into an air-tight container with no headspace. TA was determined by performing Gran titrations using a Metrohm Titrandos automatic titrator. A Metrohm Electrode Plus was used for measuring pH during the titrations which was calibrated to Oakton National Bureau of Standards (NBS) of 4, 7, and 10. Pre-standardized 0.01 mol L⁻¹ HCl was used as the titrant. The average uncertainty of duplicate TA measurements was 1.8% ± 3.7%. In cases where TA was undetectable due to low pH sample waters (i.e. pH <4), DIC was assumed equivalent to measured CO₂ concentrations (detailed below). A calibrated handheld Hach® probe (HQ40d) and TROLL 9500 multi-parameter sonde was used to determine drain water physiochemical parameters (temperature, DO%, pH, and salinity). Uncertainty associated with the concentrations of DOC, DIC and POC was determined from the average %CV of replicated measurements (4%, 2%, and 7% respectively). Concentration error and total discharge error (combined error of measured drain discharge and runoff estimates, ±10%) were then propagated accordingly.

Lateral export of dissolved organic, particulate, and dissolved inorganic carbon were estimated using mean monthly concentrations and total monthly discharge. A total of 72, 61, and 77 samples were collected for DOC, POC, and DIC respectively over the year. Discharge measurements were made using a Starflow ultrasonic Doppler flowmeter positioned in a pipe culvert and calculated in 30 min time stamps as described in Webb et al., (2016c). Although the 1 km² catchment is well constrained hydrologically with all discharge being directed to the pump outlet, multiple flood events caused discrepancy in the water balance which was likely attributed to overbank flow. Based on the discrepancy between monthly precipitation, evapotranspiration, and surface discharge, overland flow was included in the calculation of monthly aquatic carbon exports. The total annual runoff (discharge + overland flow) was 1,093 mm y⁻¹. Total annual estimates for carbon export was calculated by summing all monthly
Importance of aquatic carbon fluxes in catchment carbon budgets

5.2.2 Aquatic CO\textsubscript{2} and CH\textsubscript{4} fluxes

Samples for dissolved CO\textsubscript{2} and CH\textsubscript{4} concentrations were measured biweekly throughout the year and intensively during the six day time series in January (Webb et al., 2016a). Duplicate samples were collected in 200 mL opaque bottles using a 12 volt submersible inline pump with controlled flow by filling from the bottom of the bottle and allowing overflow until approximately three times the bottle volume had been flushed. Samples were treated immediately with 200 µL of HgCl\textsubscript{2} and sealed with Teflon-lined caps until analysis preparation within two to eight hours.

Dissolved CO\textsubscript{2} and CH\textsubscript{4} concentrations and stable isotope ratios (δ\textsuperscript{13}C-CO\textsubscript{2} and δ\textsuperscript{13}C-CH\textsubscript{4}) were prepared for analysis using the headspace technique (Hope et al 1995). Briefly, 50 mL synthetic CO\textsubscript{2} and CH\textsubscript{4}-free air (Coregas “Zero Air”) was added to each inverted bottle while simultaneously extracting an equal volume of sample water. After ~18 h of equilibration at room temperature (21°C), the headspace air was extracted using 60 mL syringes fitted with a three-way luer-lock valve (Cole-Parmer) and injected (40 mL) into Tedlar gas bags with 200 mL of CO\textsubscript{2} and CH\textsubscript{4}-free air. Equilibrated air samples were analysed immediately by a cavity ring down spectrometer (G2201-i Picarro Inc. Santa Clara, CA, USA) for CO\textsubscript{2} and CH\textsubscript{4} concentrations and δ\textsuperscript{13}C-CO\textsubscript{2} and δ\textsuperscript{13}C-CH\textsubscript{4} values. The accuracy of duplicate samples was on average 11%, 8%, 3%, and 1% for CO\textsubscript{2}, CH\textsubscript{4}, δ\textsuperscript{13}C-CO\textsubscript{2}, and δ\textsuperscript{13}C-CH\textsubscript{4} respectively.

Headspace concentrations of CO\textsubscript{2} and CH\textsubscript{4} obtained from the dry air sample analysis were corrected for in situ partial pressure (pCO\textsubscript{2} and pCH\textsubscript{4}) according to Pierrot et al. (2009). Solubility coefficients for CO\textsubscript{2} and CH\textsubscript{4} were derived from Weiss (1974) and Yamamoto et al., (1976), respectively. The CO\textsubscript{2} and CH\textsubscript{4} atmospheric exchange across the air-water interface was estimated using the following equation:

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

Where \(k\) is the gas transfer coefficient of CO\textsubscript{2} or CH\textsubscript{4} (cm h\textsuperscript{-1}), \(\alpha\) is the solubility coefficient of CO\textsubscript{2} (Weiss, 1974) and CH\textsubscript{4} (Yamamoto et al., 1976), \(C_{water}\) is the concentration of the gas in the water phase (µatm), and \(C_{air}\) is the concentration of the gas in the air phase (µatm). \(C_{air}\) concentrations were assumed to be constant at an average of 400 and 1.8 µatm for CO\textsubscript{2} and CH\textsubscript{4}, respectively. The \(k\) value was calculated from two empirical calculations based on the...
erratic conditions of the surface water flow regime (Webb et al., 2016a; Webb et al. 2016c). This included an empirical equation by O’Connor and Dobbins (1957) when surface discharge was active (pump on), which calculates transfer velocity as a function of current velocity and depth. During stagnant periods (pump off), the transfer velocity was estimated from the transfer coefficient obtained from SF$_6$ evasion experiments replicating low turbulence conditions (Ho et al., 1997). Gas transfer velocities were corrected for CO$_2$ and CH$_4$ using the calculated Schmidt numbers reported by Wanninkhof (1992) and Wanninkhof et al., (1990) for CO$_2$ and CH$_4$, respectively.

Total CO$_2$ and CH$_4$ fluxes were estimated by scaling the mean concentrations for each month with continuous half-hourly measurements of surface velocity, depth, and modelled drain area$^{18}$. Total annual estimates for carbon evasion were then calculated by summing all half-hour estimates. Uncertainties for drain CO$_2$ and CH$_4$ evasion estimates was quantified by propagating the errors associated with concentration measurements (derived from duplicate samples), instrumental error of velocity and depth, and the error of the low turbulence transfer velocity reported in Ho et al., (1997).

5.2.3 Micrometeorological and soil measurements

Atmospheric exchanges of CO$_2$ was measured from the flux tower using the eddy covariance technique (Baldocchi, 2003). Using this technique captures high frequency fluctuations of CO$_2$ fluxes between the land and atmosphere by combining very fast sampling of CO$_2$ density in air with the covariance of vertical wind velocity measurements. Primary instrumentation consisted of a three-dimensional (3-D) sonic anemometer (CSAT-3, Campbell Scientific Inc., Logan, UT, USA) for measurement of wind velocity components, and an open path infra-red gas analyser (IRGA, LI-7500, Li-COR Biosciences, Lincoln, NE) for measurement of CO$_2$ and water vapor densities. Raw measurements from the sonic anemometer and LI-7500 were sampled at a frequency of 10 Hz with 30 min block averaging and were recorded onto a CR3000 (Campbell Scientific Inc., Logan, UT, USA) data logger. Radiation, air temperature, relative humidity, wind speed and direction, precipitation, soil heat flux, and soil moisture, temperature and conductivity (at 5 cm, 25 cm, and 50 cm below the surface) was also measured at the tower site.

Data quality control (QC) and assurance (QA) was carried out based on pre-established criteria following standard Ozflux procedures (OzFluxQCv2.7.1, https://github.com/OzFlux/OzFluxQC) using Python (Isaac et al., 2016). The data processing
Importance of aquatic carbon fluxes in catchment carbon budgets

The IRGA diagnostic signal strength for CO₂ and H₂O of <40% was used to reject periods when water droplets were present on the optical path.

Stable atmospheric conditions often occur at night due to thermal stratification, suppressing the turbulent flux and systematically underestimating eddy covariance measurements. A u* filter, which determines when the friction velocity falls below a threshold value, is applied to eliminate data from these periods (Goulden et al., 1996; Isaac et al., 2016). Here, the u* threshold (u*ₜₘ) was objectively determined using change point detection (CPD) from the relationship between NEE and u* following Barr et al., (2013). The procedure was repeated 1000 times using the bootstrap technique to obtain the uncertainty in the u*ₜₘ value, expressed as the 95% lower and upper confidence intervals of the frequency distribution. Annual u*ₜₘ determined was 0.26 ± 0.16 m s⁻¹.

5.2.3.1 Gap filling and Flux partitioning

Gaps in the meteorological data were filled using statistical relations with alternate data sourced from ERAI and AWS data sets over 90 day windows (Isaac et al., 2016). The correlation coefficient between measured and alternate data ranged from 0.65 to 0.97 for training variables used in the gap filling of fluxes. Overall, 1-14% of gaps in meteorological data required filling Data gaps in CO₂ fluxes amounted to 43% after QC/QA processing steps and u*ₜₘ filtering. Gaps were filled in 10-day moving windows using a self-organising linear output (SOLO) artificial neural network model (ANN). Training variables used to predict CO₂ fluxes included soil water content, enhanced vegetation index (EVI), ground heat flux, air temperature, soil temperature (5 cm), specific humidity deficit, and net radiation. Model performance was assessed using the regression coefficient, root mean square error (RMSE), and bias error between the modelled and measured fluxes, calculated as 0.95, 3.47 µmol CO₂ m⁻² s⁻¹, -0.007 µmol CO₂ m⁻² s⁻¹, respectively (Appendix 1). Half-hourly NEE measurements were further partitioned into GPP and ER using a nocturnal modelling approach for estimating ER (Isaac et al., 2016). First, u*-filtering was applied to nocturnal CO₂ fluxes and the ANN was trained on the remaining observations (8%). Nocturnal conditions were determined by the down-welling short wave radiation value, defined here as <10 W m⁻², where it was assumed that photosynthesis had ceased and therefore all NEE represent ER. Half hourly nocturnal fluxes were then modelled using SOLO with predictor variables specific humidity, EVI, air...
temperature, and soil temperature (RMSE = 3.389 µmol CO₂ m⁻² s⁻¹) over the entire time series to produce an annual estimate. GPP was calculated as the difference between NEE and ER.

5.2.3.2 Uncertainty
Errors that arise from eddy covariance measurements are minimised during the QC/QA process (Finkelstein and Sims, 2001). The three major sources of uncertainty in NEE measurements include flux measurement variance (random error), uncertainty due to gap filling (model error), and systematic error regarding nocturnal flux underestimation (u* threshold error). Here, we quantify error’s associated with random and model gap filling, and also assess the effect of error in the u* threshold on annual NEE calculations. Random error was calculated using a paired observation technique (Hollinger and Richardson, 2005), where half-hourly fluxes (separated by 24 hours) under a defined set of environmental conditions are compared. Model error was calculated as the difference between observed and model-generated data by random draws made in a 10-day moving window. Cumulative random and model uncertainty were propagated by the sum in quadrature, and calculated from the normal distribution limits (95% confidence intervals) of annual NEE estimates from 10⁴ randomised runs of replacement and gap filling procedure (McHugh et al., 2016). Error associated with the u* filtering technique was calculated by applying the upper (u*upper = 0.42) and lower (u*lower = 0.10) 95% confidence intervals of the estimated u*Th.

5.2.4 Biomass
Carbon contained within the harvested biomass and residue biomass was calculated based on the carbon content and dry mass weight of sugarcane reported in the literature. The carbon content of dry matter was assumed to be 44 ± 2% based on literature ranges of 42-46% (Kiatkittipong et al., 2009; Denmead et al., 2010; Fortes et al., 2012). The dry weight of biomass was calculated assuming an average water content of 65 ± 5% following the reported ranges of 60-70% in Vallis et al., (1996). Trash residue retained on the site from the preceding harvest was assumed 2.9 t ha⁻¹ based on measurements determined from Wang et al., (2008). Root biomass was estimated as 18 ± 1% of the total above ground biomass from the preceding harvest based on figures reported in Chapman et al., (1994).

5.2.5 Net ecosystem carbon budget (NECB)
All carbon mass balance terms follow the definitions provide by Chaplin et al., (2006). The net ecosystem carbon budget (NECB) equation for this agricultural site was adapted to account for cropland practices:
\[ \text{NECB} = -\text{NEE} + F_{\text{Export}} + F_{\text{CH}_4} + F_{\text{Biomass}} - F_{\text{Residue}} \]

Where NEE represents the net CO\(_2\) exchange between the land surface and atmosphere inclusive of canopy, soil, and drain CO\(_2\) flux, \(F_{\text{Export}}\) is the sum of DOC, DIC, and POC lateral export via the drains, \(F_{\text{CH}_4}\) is the evasion of CH\(_4\) from the drain surface, \(F_{\text{Biomass}}\) is the carbon export in the harvested biomass, and \(F_{\text{Residue}}\) is the addition of carbon from harvest residue and root biomass remaining from the preceding harvest. This conceptual model of carbon cycling in crops with residues has been used previously as in Bhattacharyya et al., (2013). Atmospheric DOC inputs and groundwater import of carbon from outside of the catchment area are assumed negligible. Units of all terms are in g m\(^{-2}\) yr\(^{-1}\) spatially averaged to the catchment area. For the \(F\)-terms in this equation, negative values represent a loss and positive a carbon addition (Chapin et al., 2006).

5.3 Results and Discussion

5.3.1 Study site carbon budget

The daily averaged net CO\(_2\) and daily integrated carbon flux displayed large variability throughout the year, and reflected a distinct seasonal trend associated with the biomass growth (Figure 5.1 and 5.2). Several studies that have measured NEE from croplands show a strong seasonal trend in NEE over the growing period (Chi et al., 2016; Vuichard et al., 2016; Waldo et al., 2016). This is often related to changes in leaf area index and reflects the development of the vegetation canopy, which is clearly shown in this study. Average peak daytime CO\(_2\) uptake rates of -40 µmol m\(^{-2}\) s\(^{-1}\) (maximum -58 µmol m\(^{-2}\) s\(^{-1}\)) occurred during the months of February and March 2015, which is equivalent to the highest rates of CO\(_2\) assimilation observed for C4 plants (Yin and Struik, 2009). Over these two months the cumulative carbon uptake was -394 g C m\(^{-2}\) which represents 44% of total NEE over the growing season. During the month of November 2014, daily NEE values were mostly positive ranging from -0.67 to 2.83 g C m\(^{-2}\) yr\(^{-1}\) due to the lack of canopy establishment and dominance of soil respiration. Maximum daily NEE for the present study ranged from -13 to -8 g C m\(^{-2}\) d\(^{-1}\) during the peak growth period, which is similar to the -20 to -4 g C m\(^{-2}\) d\(^{-1}\) estimated by eddy covariance at some tropical mangrove, subtropical forested wetland and urban marsh sites (Barr et al., 2010; Schafer et al., 2014; Shoemaker et al., 2015). Once the biomass growth stabilised from June onwards, maximum daily NEE reduced to -4 to -2 g C m\(^{-2}\) d\(^{-1}\) (Figure 5.2).
Figure 5.1 Diurnal trend of CO$_2$ fluxes for each month. Black line represents the monthly average for each hour and filled areas indicate the range of average ± 1 standard deviation.

Figure 5.2 Annual course of A) daily average CO$_2$ fluxes and B) NEE, GPP, and ER.
5.3.2 Aquatic carbon

Total annual rainfall was 1,740 mm, of which 1,093 mm y\(^{-1}\) was lost as runoff (Appendix 2). Total DOC, POC, and DIC export was 7.1 \(\pm\) 0.8, 2.6 \(\pm\) 0.3, and 14.4 \(\pm\) 1.5 g C m\(^{-2}\) yr\(^{-1}\) respectively, of which 70-77% was lost during flood events which occurred only 12% of the time. This can be noticed in the total monthly exports of December through to February (5 to 14 g C m\(^{-2}\) month\(^{-1}\)) which all experienced flood events (Figure 5.3). The eight floods that occurred during the study represented small floods that occur regularly in the area, as none of the individual rainfall events exceeded the 5 year rainfall average reoccurrence interval of 291 mm over 36 h (Wallace et al., 2009). Dominance of episodic discharge events in controlling annual carbon export has been investigated only in a few locations. Stormflow exports of total carbon has been found to contribute up to 18 to 42 g C m\(^{-2}\) yr\(^{-1}\) from forested watersheds, representing 70-76% of annual carbon export (Waterloo et al., 2006; Dhillon and Inamdar, 2013; Zhou et al., 2013). A limited number of studies have also demonstrated that fluvial emissions of CO\(_2\) and CH\(_4\) can increase by a factor of 2-53 and 6-49 in response to flood events, respectively (Sarma et al., 2011; Gatland et al., 2014; Webb et al., 2016a). Based on our mean monthly concentrations (Table 5.1), total CO\(_2\) and CH\(_4\) evasion during flood periods were 14.9 g C m\(^{-2}\) and 0.04 g C m\(^{-2}\) (94% and 91%), respectively, largely due to increase in water surface area during catchment inundation. However, incorporation of these “hot moments” for aquatic CO\(_2\) and CH\(_4\) evasion are yet to be temporally scaled into annual carbon balances and global estimates.

DIC export and CO\(_2\) evasion remained the dominant aquatic carbon flux for all months except March and April, with monthly contributions ranging from 27-89% (0.01-11.5 g C m\(^{-2}\) month\(^{-1}\)) collectively (Figure 5.3). In contrast to CO\(_2\) evasion, the aquatic CH\(_4\) flux was consistently a minor carbon loss pathway, ranging between 0.03-0.6% (0.1-27 mg C m\(^{-2}\) month\(^{-1}\)) of total aquatic carbon loss. This small relative contribution is consistent with other studies that have reported aquatic CH\(_4\) flux contributions ranging from <1 to 4% (Striegl et al., 2012; Gatland et al., 2014; Stanley et al., 2015; Atkins et al., 2016).

Drains were consistently a source of CO\(_2\) and CH\(_4\) to the atmosphere, with highly variable daily emission rates ranging between 7-5,483 mg m\(^{-2}\) h\(^{-1}\) and 6-5,972 \(\mu\)g m\(^{-2}\) h\(^{-1}\) respectively (Appendix 3). In other artificial drainage networks, CO\(_2\) and CH\(_4\) fluxes ranged from 37 to 1,800 mg m\(^{-2}\) h\(^{-1}\) and 125 to >500,000 \(\mu\)g m\(^{-2}\) h\(^{-1}\), respectively (Schrier-Uijl et al., 2011; Teh et al., 2011; Jauhiainen and Silvennoinen 2012; Gatland et al., 2014; Luan and Wu, 2015).
On average, drain CO₂ and CH₄ emissions were 217 mg m⁻² h⁻¹ and 265 µg m⁻² h⁻¹ integrated over the year, which are in the lower range of reported average fluxes from the aforementioned studies which range from 129-733 mg m⁻² h⁻¹ and 870-44,708 µg m⁻² h⁻¹ for CO₂ and CH₄, respectively. The impact of these large fluxes from drainage systems on offsetting terrestrial carbon uptake varies between sites and is largely attributed to their spatial scale within the catchment. After taking into account the small area (0.3 % of the catchment) occupied by the drains in the present study, aquatic annual CO₂ and CH₄ fluxes equated to 15.9 g C m⁻² yr⁻¹ and 0.047 g C m⁻² yr⁻¹ of catchment area respectively, which was minor compared to the NEE flux.

![Figure 5.3](image-url) Total monthly discharge (black line) and aquatic carbon flux (red line) with bars partitioned into different lateral export and evasion components.

<table>
<thead>
<tr>
<th></th>
<th>DOC (µM)</th>
<th>δ¹³C-DOC</th>
<th>DIC (µM)</th>
<th>POC (µM)</th>
<th>δ¹³C-POC</th>
<th>CO₂ (µM)</th>
<th>δ¹³C-CO₂</th>
<th>CH₄ (µM)</th>
<th>δ¹³C-CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov-14</td>
<td>49 ± 27</td>
<td>0.08 ± 0.04</td>
<td>1310</td>
<td>193 ± 15</td>
<td>-23.07 ± 0.13</td>
<td>179 ± 98</td>
<td>-9.32 ± 0.59</td>
<td>0.59 ± 85.3</td>
<td>-57.70 ± 7.85</td>
</tr>
<tr>
<td>Dec-14</td>
<td>758 ± 233</td>
<td>-21.13 ± 1.52</td>
<td>298 ± 15</td>
<td>193 ± 104</td>
<td>-21.97 ± 3.23</td>
<td>673 ± 67</td>
<td>-13.75 ± 0.42</td>
<td>0.42 ± 7.74</td>
<td>-58.21 ± 7.85</td>
</tr>
<tr>
<td>Jan-15</td>
<td>692 ± 216</td>
<td>-19.67 ± 1.58</td>
<td>1338 ± 104</td>
<td>139 ± 104</td>
<td>-21.97 ± 3.23</td>
<td>673 ± 67</td>
<td>-13.75 ± 0.42</td>
<td>0.42 ± 7.74</td>
<td>-58.21 ± 7.85</td>
</tr>
<tr>
<td>Feb-15</td>
<td>197 ± 156</td>
<td>-21.60 ± 0.71</td>
<td>309 ± 84</td>
<td>106 ± 13</td>
<td>27.10 ± 1.11</td>
<td>219 ± 67</td>
<td>-15.24 ± 3.21</td>
<td>2.86 ± 3.14</td>
<td>-47.06 ± 3.14</td>
</tr>
<tr>
<td>Apr-15</td>
<td>554 ± 182</td>
<td>-18.66 ± 0.66</td>
<td>147 ± 45</td>
<td>308 ± 13</td>
<td>-23.29 ± 1.44</td>
<td>147 ± 45</td>
<td>-14.46 ± 3.21</td>
<td>1.99 ± 3.14</td>
<td>-45.35 ± 3.14</td>
</tr>
<tr>
<td>May-15</td>
<td>667 ± 182</td>
<td>-21.17 ± 0.66</td>
<td>259 ± 45</td>
<td>86 ± 13</td>
<td>-25.55 ± 4.44</td>
<td>130 ± 36</td>
<td>-13.86 ± 4.33</td>
<td>0.50 ± 2.56</td>
<td>-43.42 ± 2.56</td>
</tr>
</tbody>
</table>
Importance of aquatic carbon fluxes in catchment carbon budgets

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>341 ± 160</td>
<td>307 ± 76 0.76</td>
<td>437 ± 153</td>
<td>1025 ± 633</td>
<td>1346 ± 1225</td>
</tr>
<tr>
<td></td>
<td>-22.46 ± 0.62</td>
<td>-23.61 ± 0.76 0.76</td>
<td>-22.18 ± 1.80</td>
<td>-20.51 ± 2.2</td>
<td>-21.86 ± 1.20</td>
</tr>
<tr>
<td></td>
<td>1332 ± 1547</td>
<td>1445 ± 2033</td>
<td>590 ± 509</td>
<td>1077 ± 854</td>
<td>1881 ± 854</td>
</tr>
<tr>
<td></td>
<td>64 ± 27</td>
<td>75 ± 26</td>
<td>109 ± 42</td>
<td>82 ± 12</td>
<td>191 ± 43</td>
</tr>
<tr>
<td></td>
<td>-25.77 ± 1.69</td>
<td>-27.67 ± 1.69 1.69</td>
<td>-25.66 ± 2.2</td>
<td>-23.83 ± 2.2</td>
<td>-24.42 ± 2.47</td>
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<tr>
<td></td>
<td>308 ± 259</td>
<td>493 ± 732</td>
<td>110 ± 66</td>
<td>81 ± 40</td>
<td>175 ± 1.63</td>
</tr>
<tr>
<td></td>
<td>-12.81 ± 3.31</td>
<td>-11.56 ± 3.31 3.31</td>
<td>-5.45 ± 2.63</td>
<td>-14.19 ± 2.63</td>
<td>-14.48 ± 3.26</td>
</tr>
<tr>
<td></td>
<td>0.63 ± 0.63</td>
<td>0.45 ± 0.45 0.45</td>
<td>0.49 ± 0.21</td>
<td>0.67 ± 0.21</td>
<td>2.21 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>-49.23 ± 6.55</td>
<td>-43.61 ± 3.88 3.88</td>
<td>-48.63 ± 6.02</td>
<td>-46.67 ± 6.02</td>
<td>-47.52 ± 5.86</td>
</tr>
<tr>
<td></td>
<td>194 ± 215</td>
<td>259 ± 302</td>
<td>172 ± 44</td>
<td>180 ± 28</td>
<td>350 ± 1.63</td>
</tr>
<tr>
<td></td>
<td>22.46 ± 0.99</td>
<td>22.46 ± 1.14 1.14</td>
<td>22.46 ± 0.62</td>
<td>22.46 ± 0.62</td>
<td>22.46 ± 1.14</td>
</tr>
<tr>
<td></td>
<td>0.62 ± 0.62</td>
<td>0.62 ± 0.62 0.62</td>
<td>0.62 ± 0.62</td>
<td>0.62 ± 0.62</td>
<td>0.62 ± 0.62</td>
</tr>
<tr>
<td></td>
<td>0.36 ± 0.43</td>
<td>0.36 ± 0.43 0.43</td>
<td>0.36 ± 0.43</td>
<td>0.36 ± 0.43</td>
<td>0.36 ± 0.43</td>
</tr>
<tr>
<td></td>
<td>113 ± 160</td>
<td>113 ± 160</td>
<td>113 ± 160</td>
<td>113 ± 160</td>
<td>113 ± 160</td>
</tr>
</tbody>
</table>

5.3.3 Final carbon budget

Integrating the measured fluxes over the study period, the terrestrial component was found to be a sizable sink of atmospheric CO$_2$, with a cumulative NEE of -900 g C m$^{-2}$ yr$^{-1}$ (Table 5.2). Compared to annual estimates of NEE across all flux tower networks, this site represents the higher range of atmospheric carbon assimilation across all ecosystems (mean = -156 ± 284) (Baldocchi, 2014). The total aquatic carbon loss of ~40 g C m$^{-2}$ yr$^{-1}$ integrated over the catchment area had a minor impact on the NECB, representing only ~4% of terrestrial NEE. Carbon export from this study was estimated at 24 g C m$^{-2}$ yr$^{-1}$ which is similar to the global carbon export from streams and rivers of 18 g C m$^{-2}$ yr$^{-1}$ (Battin et al., 2009; Cole et al., 2007; Raymond et al., 2013). Based on the global NEE estimate for the land biosphere (-17.4 g C m$^{-2}$ yr$^{-1}$, Koffi et al., 2012), the global contribution of the aquatic carbon flux (18 g C m$^{-2}$ yr$^{-1}$) is much larger (~100%) than our site specific comparison of aquatic versus terrestrial fluxes (~4%). This difference demonstrates the potential importance of ecosystem-specific NEE in driving the contribution of the aquatic component in catchment scale carbon budgets.

When total biomass inputs and removal pathways were taken into account, the NECB was 100 g C m$^{-2}$ yr$^{-1}$ (error range -175 to 272, Table 5.2), indicating that the site was close to carbon neutral during the measurement period. Our NECB estimates are in the range of average NECB estimated for cropland ecosystems in Europe, which report a small net carbon loss of 95 ± 87 g C m$^{-2}$ yr$^{-1}$ (Kutsch et al., 2010). The error range in final NECB represents 13-20% of the total carbon cycled through the system (total inputs 1,353 g C m$^{-2}$ yr$^{-1}$), demonstrating the insignificance of the aquatic component in this agroecosystem.

The higher carbon pool in the harvested biomass compared to the NEE measured demonstrates that heterotrophic respiration made up a significant component of ecosystem respiration during the study period (Table 5.2). Because all biomass produced during the year represents NPP, a term that defines the net carbon captured by primary producers (GPP - autotrophic respiration), NEE can diverge from total biomass production when decomposition of accumulated organic
matter by other processes are prevalent (Smith et al., 2010). By determining the difference between NPP (~1,800 g C m\(^{-2}\) yr\(^{-1}\)) and NEE (-1,119 to -840 g C m\(^{-2}\) yr\(^{-1}\)), the contribution of heterotrophic respiration can be estimated to be between 680 and 960. This excess respiration is of similar magnitude to the harvest residue and root biomass left over from the previous season (~500 g C m\(^{-2}\) yr\(^{-1}\)), demonstrating that these assumed carbon "stores" are likely an active component of the current NECB.

Table 5.2 Carbon budget of the agricultural floodplain. All components of the carbon budget are from the measurement period 2014-2015, except for harvest and root residue which were left on site from the previous year’s harvest.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Compartment specific (g C m(^{-2}) yr(^{-1}))</th>
<th>Catchment area specific (g C m(^{-2}) yr(^{-1}))</th>
<th>Minimum (g C m(^{-2}) yr(^{-1}))</th>
<th>Maximum (g C m(^{-2}) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NEE</td>
<td>-900 ± 60</td>
<td>-900</td>
<td>-1,064*</td>
<td>-840</td>
</tr>
<tr>
<td>Harvest residue</td>
<td>-126 ± 7</td>
<td>-114</td>
<td>-120</td>
<td>-108</td>
</tr>
<tr>
<td>Root residue</td>
<td>-373 ± 20</td>
<td>-339</td>
<td>-357</td>
<td>-320</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquatic export</td>
<td>483 ± 202</td>
<td>24</td>
<td>14</td>
<td>34</td>
</tr>
<tr>
<td>Aquatic CO(_2) evasion</td>
<td>242 ± 192</td>
<td>16</td>
<td>6</td>
<td>26</td>
</tr>
<tr>
<td>Aquatic CH(_4) evasion</td>
<td>0.89 ± 596</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>Biomass harvest</td>
<td>1,575 ± 85</td>
<td>1,429</td>
<td>1,352</td>
<td>1,506</td>
</tr>
<tr>
<td><strong>Total NECB</strong></td>
<td>100</td>
<td>-175</td>
<td>272</td>
<td></td>
</tr>
</tbody>
</table>

Summary of components of the carbon budget and final net ecosystem carbon budget (NECB). Negative values indicate a carbon sink (input) and positive values indicate a carbon source (loss). Note that aquatic CO\(_2\) evasion is captured in the NEE estimate so was not included in the final NECB calculation. The minimum and maximum estimates represent the mean ± error of the individual compartments, while the minimum and maximum range in the final NECB represents estimates calculated from error propagation. Catchment area specific values are normalized to the total catchment area of 1,000,000 m\(^2\).

* Minimum NEE calculation includes propagation of u\(\ast\)Th, model, and random error (Appendix 1). Maximum NEE calculation includes model and random error only.

5.3.4 Aquatic carbon leakage of terrestrial carbon

In an attempt to elucidate the role of aquatic systems in terrestrial carbon budgets, we compiled data from a range of ecosystems where studies had reported both the terrestrial NEE and aquatic carbon flux in the form of lateral export and/or CO\(_2\) and CH\(_4\) evasion (Appendix 4). For ease of visual representation, all NEE values are plotted with a positive sign although are all a negative flux (carbon uptake). Here, we focused only on ecosystems containing a fluvial aquatic loss and a negative NEE, excluding lakes and soil leaching to groundwater from our analysis.

The contribution of aquatic carbon flux appears proportional to the NEE on land. NEE varies by 100 to 1,000 g C m\(^{-2}\) yr\(^{-1}\) across ecosystems which is an order of magnitude greater than the cross-ecosystem variability in aquatic carbon fluxes (1-100 g C m\(^{-2}\) yr\(^{-1}\)) (Figure 5.4). Contrary
to some belief, terrestrial carbon uptake does not modulate the magnitude of aquatic carbon export in this cross-ecosystem analysis, as no direct relationship could be found when comparing annual total NEE with aquatic carbon flux (Appendix 4). Ecosystems with annual NEE estimates ranging from 200-1,170 g C m\(^{-2}\) yr\(^{-1}\) had minor aquatic carbon contributions of 2-25% (average 7%) while ecosystems with annual NEE <100 g C m\(^{-2}\) yr\(^{-1}\) had mostly larger aquatic carbon contributions of 5-223% (average 44%). A multi-annual study on NEE and aquatic carbon export from a boreal forest also find that the contribution of aquatic carbon (DOC and DIC export only) was anti-correlated to NEE, and varied between 4-28% (Oquist et al., 2014). The study concluded that the relationship was sensitive to changes in annual precipitation, where an increase in precipitation would increase (less uptake) NEE by up to 88 g C m\(^{-2}\) yr\(^{-1}\), while changes in export were relatively minor (up to 14.5 g C m\(^{-2}\) yr\(^{-1}\)). Some studies in tropical forests have found the opposite relationship where NEE reduces (more uptake) with higher precipitation (Fischer et al., 2014). Whatever the control the water balance has on ecosystem carbon balances, it is clear that relative importance of the aquatic carbon flux is mostly dependent on the proportional change in terrestrial NEE.

Our analysis identifies the need to reassess the importance of aquatic carbon flux to the terrestrial carbon budget. Global reviews on the terrestrial aquatic interface have demonstrated how the aquatic carbon flux can potentially have a profound impact on offsetting the terrestrial carbon budget (Cole et al., 2007; Raymond et al., 2013; Regnier et al., 2013), however acknowledge that the representativeness of these estimates are limited by the spatially available datasets (e.g. Lauerwald et al., 2015). Observations from catchment-scale studies that have quantified integrative carbon budgets in terrestrial-aquatic ecosystems, although limited, demonstrate that the relative importance of the aquatic carbon pathway varies from minor to major (Figure 5.4). Our understanding of the aquatic carbon flux contribution has largely developed from Northern hemisphere sub artic peatland ecosystems, which were the focus of pioneering integrative carbon budget studies (Billet et al., 2004; Oquist et al., 2014). Based on our recent review of the published literature, aquatic carbon fluxes in these systems contribute on average 42% of the NEE, which is slightly greater than Yu (2012) review of 32% (based on DOC and CH\(_4\) only), perhaps due to the inclusion of other carbon fluxes in more recent studies. However, the total fluvial carbon export and evasion from sub artic peatlands (3 to 20 g C m\(^{-2}\) yr\(^{-1}\), Appendix 4) are not considerably larger than ecosystems which had a minor (<5%) aquatic carbon contribution to the terrestrial carbon uptake, such as our study for example (~40 g C m\(^{-2}\) yr\(^{-1}\)). Integrative carbon monitoring efforts should focus on under-represented ecosystems
such as sub-tropical to tropical wetlands, particularly those that are facing recent disturbance through agriculture (drained tropical peatlands) and hydrological variability (coastal wetlands).

The findings in Figure 5.4 evoke the question; if the magnitude of NEE variation determines the relative importance of the aquatic carbon flux contribution in ecosystem carbon budgets, what factors control the magnitude of ecosystem carbon loss through the fluvial system? Many factors, including discharge, wetland/peatland coverage, land cover, groundwater input, topography, and catchment area have been identified as controlling drivers of aquatic carbon exports at the catchment scale (Raymond et al., 2008; Genereux et al., 2013; Li et al., 2015; Wit et al., 2015). Many of these factors ultimately influence hydrology, and after analysing a subset of published literature values it is clear that annual discharge ultimately controls the extent of carbon loss through the fluvial network. Total annual aquatic exports spatially scaled to catchment area ranged from 0.02 to 105 g C m$^{-2}$ yr$^{-1}$, and displayed a positive relationship with spatially scaled discharge (Figure 5.5). Some inter-annual carbon budget studies have shown that although both annual NEE and aquatic carbon export can vary by up to a factor of 4-5, the main driver of aquatic carbon export was found to be precipitation which is directly related to discharge variability (Oquist et al., 2014; Leach et al., 2016). Although the impact of increased carbon export on the NECB likely does not exceed the factors controlling annual

**Figure 5.4** Relative annual contribution of the aquatic carbon loss (including DOC, DIC, POC export and CO$_2$ and CH$_4$ evasion if reported) as a function of annual NEE across a variety of ecosystems.
Importance of aquatic carbon fluxes in catchment carbon budgets

NEE variability (Figure 5.5), some wetlands dominated by large hydrologic flows have demonstrated large variability in annual carbon export that ultimately determined the carbon budget (Waletzko et al., 2013; Chu et al., 2015). The impact of increased precipitation on aquatic carbon losses offsetting ecosystem carbon budgets may be significant if terrestrial productivity suffers in response (Oquist et al., 2014).

Figure 5.5 Annual aquatic carbon export as a function of annual discharge reported from other studies and the measured carbon species. Carbon fluxes and discharge are spatially scaled to catchment or region area. Regression lines indicate a significant (p<0.05) relationship.

Although there is a large body of empirical research on fluvial carbon exports, the majority studies have focused only on DOC, neglecting POC and DIC from the calculation (Appendix 5). Furthermore, even fewer studies report all three carbon exports and CO₂ evasion simultaneously for extended periods of time (Argerich et al., 2016). We show that inclusion of other carbon species can provide an important contribution to the total aquatic flux. Studies that quantified all lateral carbon exports had distinctly larger total aquatic carbon flux compared to studies that had only quantified DOC export. Interestingly, only the export estimates that included DIC (DOC+DIC and DOC+POC+DIC) displayed a significant regression relationship with annual discharge (Figure 5.5). The large variability in the carbon export-discharge relationship exists due to catchment-specific factors that control the concentration of dissolved and particulate carbon, which in this analysis varied by ± 120% based on annual flow-weighted
concentration. This variation can affect total export by $\pm 2.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ for every 0.1 m discharge.

5.4 Conclusion
Our current knowledge on the contribution of aquatic carbon fluxes in ecosystem carbon budgets is greatly confined to northern hemisphere subartic peatlands. To our knowledge, this study provided the first full ecosystem carbon budget integrating fluvial fluxes of a subtropical agricultural wetland in the southern hemisphere. The contribution of fluvial carbon fluxes to offsetting terrestrial carbon uptake was demonstrated to be highly variable across different ecosystems at the terrestrial-aquatic interface, highlighting the poorly understood role of aquatic systems in the terrestrial carbon cycle. A cross-ecosystem analysis revealed that annual discharge may be a globally consistent driver of annual carbon exports in most fluvial aquatic systems, where catchments with greater annual runoff generally experience large lateral aquatic carbon losses. To improve knowledge on this potentially important role, there is a critical need to measure integrative carbon budgets of underrepresented ecosystems including coastal wetlands, agro-ecosystems, low land floodplains, and disturbed landscapes across all climatic regions, specifically sub-tropical to tropical. Incorporating terrestrial and aquatic component fluxes from a diversity of ecosystem types will help to resolve the role of the aquatic pathway in the global terrestrial carbon budget. Given that the contribution of the aquatic carbon flux appears to be proportional to the magnitude of terrestrial carbon uptake, we conclude that the role of fluvial carbon pathway in terrestrial-aquatic systems needs to be reassessed in highly productive ecosystems.
Chapter 6 - Summary and conclusions
6 Summary and conclusions

6.1 Synthesis of objectives and findings
This chapter provides a summary of the advances made in this thesis and the broader scale impact. A conceptual model of the agricultural floodplain illustrating the findings of the study is also presented (Figure 6.1). A synthesis of the conclusions are provided for each research objective outlined below:

Chapter 2: Assess the performance of an underway technique for making real-time continuous observations of CO₂ and CH₄ concentrations and δ¹³C values in aquatic environments

The performance of six underway water-air equilibrators was assessed for real-time measurement of CO₂ and CH₄ concentrations and carbon stable isotopes in aquatic systems. With the development of field deployable cavity ringdown spectrometers (CRDS), equilibrators now offer opportunity to provide continuous δ¹³C measurements in natural waters. The detailed assessment revealed important limitations of the method which should be considered when undertaking real-time measurements at fine spatial and temporal scales. The equilibration response time was found to vary greatly between equilibrator designs, where CH₄ concentrations and δ¹³C-CH₄ values were most strongly affected by having response times of 5 to 15 times longer than CO₂. The benefit of increasing water flow rate through the equilibrator was found to be of great importance in offsetting the measurement response time to better reflect real-time observations of these gases in the water. The spatial and temporal ranges of dissolved CO₂ and CH₄ concentrations and isotope values varies widely in inland waters, which this assessment catered for by measuring the response time for both low-to-high and high-to-low concentrations and isotope values. The direction of concentration change was particularly important for measuring δ¹³C-CH₄ values, which can experience an extended delay in equilibration time from high-to-low concentrations.

In the coming years, the use of these commercially available air-water equilibrators with new field deployable greenhouse gas analysers capable of carbon isotope measurement will likely become widely adopted by aquatic scientists in the fields of limnology and oceanography. This work therefore provides an important benchmark for the application of this technique to reveal complex carbon transformation and emission processes over aquatic environments. Further, reporting on the methodological constraints of a new technique is required to ensure that data is not misinterpreted. Using this method to undertake detailed field observations will provide
a process-level understanding on the interaction and response of CO$_2$ and CH$_4$ processes at the terrestrial-aquatic interface.

**Chapter 3: Analyse how the drainage network of a hydrologically altered floodplain functions as a source of CO$_2$ and CH$_4$ emissions during flood and non-flood conditions.**

The method assessed in chapter 2 was put into practice to reveal the temporal scale changes in the flood CO$_2$ and CH$_4$ response in the drainage waters for the first time in such a hydrologically modified floodplain. This research demonstrated the sensitivity of greenhouse gas dynamics to extremes in precipitation in this system (Figure 6.1). During the immediate post-flood period, fluctuations of CO$_2$ and CH$_4$ varied by a factor of 10 and 50 respectively, over the course of 24 h. A unique process driving extreme $p$CO$_2$ saturation levels was revealed for the first time as large inputs of high carbonate alkalinity groundwater into acidic surface waters. The large difference in pH between groundwater and surface water had a profound impact on budgeting the source of CO$_2$, and highlights the importance of accounting for these pH differences in aquatic CO$_2$ studies. Carbon stable isotope measurements helped to reveal the primary source of CH$_4$ as drain sediments and not groundwater in contrast to CO$_2$.

Overall, the CO$_2$ and CH$_4$ dynamics in the agricultural drainage waters where highly responsive to the hydrologic disturbance that rapidly expanded and disconnected the drainage network from the floodplain. The drains were an extreme source of CO$_2$ for a short period following the flood and remained a modest source of CH$_4$ for up to three weeks. These finding contributes to our understanding of how the carbon balance of impacted floodplains may respond to future climatic changes. Hydrology and soil geochemistry proved to be key factors in flood CO$_2$ and CH$_4$ dynamics.

**Chapter 4: Quantify a detailed water budget capturing the contribution of flood events and groundwater discharge using a groundwater tracer model approach.**

Chapter 4 resolved the annual water budget of the drained floodplain, focusing on the under-represented pathway of groundwater discharge. Observations of surface water radon concentrations revealed a distinct relationship with water table height throughout the year within the floodplain, which indicated a clear groundwater link. Although radon is often used as a quantitative tracer for groundwater, such a relationship with the water table had not been
demonstrated before, yet makes sense from a hydrology perspective. The link between water table depth and surface radon concentrations enabled the development of a groundwater model using the radon mass balance technique extrapolated over an annual time frame. Findings revealed that the amount of groundwater discharge changed rapidly over the year, from periods of no groundwater discharge to some of the highest rates ever recorded. These peak inputs of groundwater into the drainage canals would occur immediately after flood events, revealing an important point in time that groundwater discharge is at its greatest. Of the total rain input, evapotranspiration made up 51%, direct surface discharge made up 12%, and 16% was transported via groundwater discharge.

In order to resolve carbon cycling in terrestrial-aquatic systems, the catchment hydrology must first be understood as hydrologic flow pathways act as a primary transport mechanism for terrestrial-aquatic subsidies. This study advanced a method often used for making detailed groundwater observations over short time scales, by applying a simple model to calculate groundwater over longer timescales. The success of this method to reliably calculate groundwater opens up opportunities to better constrain elemental fluxes via the groundwater pathway in managed catchments. Integrating detailed groundwater studies with aquatic carbon measurements represents a timely opportunity to enhance our understanding of aquatic carbon linkages in landscapes.

Chapter 5: Quantify the annual carbon budget of the agricultural floodplain by measuring land-atmosphere fluxes of CO₂ simultaneously with aquatic carbon export and evasion, and explore the contribution of the aquatic carbon flux across other ecosystems.

Chapter 5 brings together the annual measurements of aquatic carbon, hydrology, and NEE with other onsite farm carbon exports to determine the net ecosystem carbon budget of the agricultural floodplain (Figure 6.1). Findings from this study showed that the NEE of the agricultural floodplain was in the highest range of annual NEE estimates from ecosystems, and that total carbon loss from the drainage system did not offset the land atmosphere carbon uptake. In contrast to most NECB studies, the total aquatic carbon flux represented a very minor component of the overall carbon budget (~4% of terrestrial carbon uptake). A detailed review of the literature, revealed that the role of the aquatic pathway is highly variable across ecosystems. Much of our understanding is limited to subarctic catchments, which had aquatic carbon fluxes offsetting between 3 to 223% of terrestrial NEE, or an
average of 30%. A key agent in the driver determining the role of the aquatic carbon pathway in terrestrial carbon budgets was the magnitude of the terrestrial uptake (NEE). Consequently, the agricultural floodplain had minor aquatic carbon contribution as annual NEE was 900 g C m$^{-2}$ yr$^{-1}$ as opposed to subarctic catchments which have an average NEE of 70 g C m$^{-2}$ yr$^{-1}$ across studies. The total aquatic carbon flux did not vary as largely as NEE, being ~40 g C m$^{-2}$ yr$^{-1}$ and ~12 g C m$^{-2}$ yr$^{-1}$ for the study and subarctic catchments respectively.

Using a set of novel techniques to integrate both terrestrial and aquatic carbon components, this study provided a baseline model for monitoring carbon fluxes at the catchment scale. This approach enabled a wide, comprehensive view of the carbon cycle, and revealed new insights into the drivers of carbon retention and loss in drained floodplains.
Figure 6.1  Conceptual model summarising the main findings of the thesis, including the components of the net ecosystem carbon budget (NECB) illustrating the fate of carbon within the agricultural floodplain. Black arrows represent the flux of a carbon pathway with all values in the form of g C m⁻² yr⁻¹ scaled to catchment area (100 ha), except for the soil carbon pool (SC) which represents the carbon store in g C m⁻² (to 30 cm).
All terms are consistent with the definitions in Chapin et al., (2006), where negative values indicate a carbon input and positive a carbon output. In addition to the NECB, numbered insets (red) for certain carbon flux pathways provide further detail of the main findings, which include: 1) the role of groundwater as a dominant source of CO$_2$ to the drainage waters following floods, and the role of flood deposits as a dominant CH$_4$ driver; 2) the proportion of dissolved, particulate and gaseous carbon fluxes that made up the total aquatic carbon export (TC$_{exp}$), showing CO$_2$ evasion to be a dominant component of the aquatic carbon flux; 3) the contribution of eight flood events to the total annual flux of each aquatic carbon species; 4) the distinct change in CO$_2$ uptake that was observed from the sugarcane vegetation during the growing season that lead to such a large negative NEE; and 5) conceptual plot illustrating the responsive nature surface and groundwater runoff in the agricultural floodplain during hydrologic pulse event. Overall, both groundwater and surface water flows intimately links terrestrial and aquatic carbon processes in this floodplain, yet the relatively large land-atmosphere carbon flux devalues the importance of these processes in the NECB.
6.2 Future challenges
This research on the NECB of a subtropical agricultural floodplain represented one of the few NECB studies conducted in the southern hemisphere. It became apparent through the literature review analysis that NECB studies are highly biased towards the northern hemisphere subartic zone. Such a bias hinders our understanding of carbon fluxes in terrestrial-aquatic ecosystems. Ecosystems including tropical peatlands, natural floodplains, agricultural wetlands, marshes, and mangroves across all climatic zones are currently underrepresented in NECB studies. Tropical ecosystems and mangroves in particular are large players in terrestrial-aquatic carbon cycling as they have proven to have fluxes of carbon as large as 2,142 g C m$^{-2}$ yr$^{-1}$ for NEP and 144 g C m$^{-2}$ yr$^{-1}$ for export (Alongi et al., 2011; Zhou et al., 2013). The need to study these underrepresented systems is further exemplified by the anthropogenic and climatic impacts these systems are currently experiencing and may experience in the future, including for example the 50% larger export of fluvial organic carbon fluxes from deforested tropical peatlands compared to intact peatlands (Moore et al., 2013).

Another gap in data that arose from the literature review in Chapter 5 was that often times not all components of the aquatic carbon flux were included in export and evasion calculations. This included measurements of DOC, DIC, POC, and gaseous carbon forms CO$_2$ and CH$_4$. Although more recent studies are including all carbon species in annual aquatic carbon flux calculations, most of the data spanning over three decades is inclusive of DOC only and is severely lacking in simultaneous CO$_2$ and CH$_4$ measurements. Out of the comparable carbon budget studies, only four out of the 55 studies were inclusive of all five aquatic carbon fluxes. With recent technological advances facilitating more widespread measurement of these gases in aquatic environments, this data gap should greatly improve over time.

An uncertainty that arose from Chapter 3 was that very little research has focused on the temporal scale drivers of event-driven CO$_2$ and CH$_4$ dynamics in fluvial environments. It was shown that flood events can cause a disproportionate flux of CO$_2$ and CH$_4$ to the atmosphere in agricultural drainage waters, yet it is unsure whether this effect is consistent with other fluvial environments. Incorporating the temporal response of CO$_2$ and CH$_4$ to hydrological disturbance events in annual aquatic carbon estimates may prove quantifiably important to the carbon budget. Capturing these hot moments will likely result in a modest increase in total CO$_2$ and CH$_4$ fluxes compared to annual estimates scaled from “average” hydrological conditions.
Developing models to extrapolate this biogeochemical response will be the next challenge to overcome, and at present requires a larger cohort of flood response studies to better define the factors driving the magnitude of this response.

The challenge of decoupling the feedbacks between carbon cycling on the land and water in terrestrial-aquatic ecosystems remains complex and intricate, and further research on the drivers of these feedbacks will improve model predictions. How these feedbacks and processes between terrestrial and aquatic interfaces operate under different hydrological regimes needs to be further explored. This will allow better predictions of how changes in rainfall patterns due to climate change will impact both the carbon uptake and loss in these systems.

This research resolved some of the uncertainties in our mechanistic understanding of the aquatic pathway in terrestrial carbon budgets, highlighting how our understanding may be greatly improved if other ecosystems types are included in catchment carbon budget analysis. In order to better constrain estimates of the global carbon cycle, integrative studies of the carbon budget must be done at catchments scales to understand the processes that govern the movement of carbon between the land, water and atmosphere.
Reference list


References


References


Carbon Dioxide, Methane, δ13C-CO2 and δ13C-CH4 in a Proposed Australian Coal Seam Gas Field.

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dynamics in a coral reef lagoon driven by pore water exchange: Insights from automated high


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Krause, S., J. Jacobs, and A. Bronstert (2007b), Modelling the impacts of land-use and drainage density on the water balance of a lowland–floodplain landscape in northeast Germany, Ecological Modelling, 200(3-4), 475-492, doi: http://dx.doi.org/10.1016/j.ecolmodel.2006.08.015.


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References


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Wilson, B.P., (1995). Soil and Hydrological relations to drainage from sugarcane on acid sulphate soils, University of New South Wales.


Zhr, Z. C. (2012). Northern peatland carbon stocks and dynamics: a review. Biogeosciences 9(10); 4071-4085.


Appendices
Appendix 1

Summary of errors and calculated uncertainty associated with the gap filling technique and effect of \( u^* \) on annual NEE estimates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average ± Standard Deviation</th>
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</thead>
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<td>Bias error (( \mu \text{mol CO}_2 \text{ m}^2 \text{s}^{-1} ))</td>
<td>-0.007 ± 0.012</td>
</tr>
<tr>
<td>RMSE (( \mu \text{mol CO}_2 \text{ m}^2 \text{s}^{-1} ))</td>
<td>3.472 ± 1.052</td>
</tr>
<tr>
<td>( u^* ) threshold (m s(^{-1}))</td>
<td>0.26 ± 0.16</td>
</tr>
<tr>
<td>Random error (g C m(^{-2}) yr(^{-1}))</td>
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<td>Annual NEE ( u^*)upper (( \mu + 2\sigma ))</td>
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<td>Annual NEE ( u^*)mean (( \mu ))</td>
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<td>Combined error (g C m(^{-2}) yr(^{-1}))</td>
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Appendix 2

Summary of seasonal and annual totals environmental variables measured during the study period

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<th>Parameter</th>
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<th>Winter</th>
<th>Spring</th>
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<td>Evapotranspiration (mm)</td>
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<td>142</td>
<td>172</td>
<td>824</td>
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<td>Soil** temperature (°C)</td>
<td>25.6 ± 1.0</td>
<td>21.3 ± 2.5</td>
<td>16.2 ± 1.2</td>
<td>17.7 ± 7.9</td>
<td>20.3 ± 5.5</td>
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<tr>
<td>Air temperature (°C)</td>
<td>24.6 ± 3.9</td>
<td>20.4 ± 6.2</td>
<td>14.6 ± 6.1</td>
<td>20.5 ± 6.3</td>
<td>20.0 ± 6.7</td>
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<tr>
<td>Soil** moisture content (v/v)</td>
<td>0.414 ± 0.061</td>
<td>0.430 ± 0.026</td>
<td>0.434 ± 0.016</td>
<td>0.387 ± 0.022</td>
<td>0.418 ± 0.040</td>
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* Discharge includes measured drain discharge and overland flow during floods (estimated from monthly water balance discrepancy).

** Soil within 25-50 cm depth range below surface.
Appendix 3

Drain CO₂ and CH₄ evasion rates showing average, minimum, and maximum ranges for each month of the sampling period.

<table>
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<tr>
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<th>CO₂ (mg m⁻² h⁻¹)</th>
<th>CH₄ (ug m⁻² h⁻¹)</th>
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<td>Average</td>
<td>Minimum</td>
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<td>Nov-14</td>
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<td>Dec-14</td>
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<td>61.79</td>
</tr>
<tr>
<td>Jan-15</td>
<td>819.36</td>
<td>170.33</td>
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<tr>
<td>Feb-15</td>
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</tr>
<tr>
<td>Mar-15</td>
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<tr>
<td>Apr-15</td>
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<td>Jun-15</td>
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<td>Jul-15</td>
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Appendix 4

Annual precipitation, net ecosystem carbon budget (NECB), net ecosystem production (NEP), lateral carbon export, aquatic CO₂ and CH₄ evasion, and contribution of the total aquatic carbon flux (lateral and evasion when measured) to NEP from the literature. Some data is presented in Figure 5.4 of the main text.
## Appendix

### Terrestrial versus aquatic carbon fluxes in an agricultural coastal floodplain

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>Climatic region</th>
<th>Annual precipitation (mm yr(^{-1}))</th>
<th>NECB(a) (g C m(^{-2}) yr(^{-1}))</th>
<th>NEP(b) (g C m(^{-2}) yr(^{-1}))</th>
<th>Carbon export (g C m(^{-2}) yr(^{-1}))</th>
<th>CO(_2) evasion (g C m(^{-2}) yr(^{-1}))</th>
<th>CH(_4) evasion (g C m(^{-2}) yr(^{-1}))</th>
<th>Carbon export/NEP (%)</th>
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<td>Global</td>
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<td>17.4</td>
<td>6</td>
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### Appendices

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Terrestrial versus aquatic carbon fluxes in an agricultural coastal floodplain
## Appendices

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*The NECB represents values reported either in the text, which may include site specific carbon flux components other than aquatic exports and evasion, or calculated based on the data available.

*All NEP estimates are from eddy covariance measurements unless otherwise stated.

*NEP estimates from Peichl et al., (2014)

*NEP estimated from the difference in NPP and soil respiration, measured by MODIS and chambers respectively.

*Carbon exports estimated from difference in NEP and NECB.

*DOC export only

*NEP estimated empirically from chamber measurements.

*DIC export not included.

*Carbon export taken from catchment outlet.

*NEP estimated from radio carbon dating peat cores

*POC export not included


*NEP average of 3 years (range -800 to 5 g C m$^{-2}$ yr$^{-1}$)
Appendix 5

Total annual discharge or runoff, annual carbon export (lateral C flux), and CO₂ evasion (vertical C flux) from different watersheds. All fluxes are spatially scaled to catchment or region area.

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Andrews Experimental Forest, Oregon 1.391 11.4 15.6 DOC, POC, DIC Argerich et al., (2016).
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## Appendices

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*a Discharge from Barry et al., (2014)
*b Average of three years
*c Discharge from Striegl et al., (2007)
*d Runoff calculated from average discharge range