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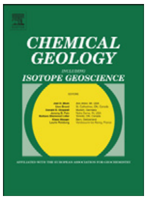

Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: Post-flood hydrological and biological drivers

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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 event (290 mm of rainfall). High temporal resolution, in situ observations of dissolved CO_2 and CH_4, carbon stable isotopes of 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 water table. Groundwater input sustained between 95 and 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 ~2400 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 (46–2460 nM) support coupled production-oxidation, with concentrations and $\delta^{13}C$ values remaining higher (2,798 nM and -47‰) than pre-flood conditions (534 nM and -55‰) 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.

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 2438 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

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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 the present 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, 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 et al., 2015). These high pCO_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 CO_2 and CH_4 losses from these modified landscapes.

An abundance of labile organic matter can produce low oxygen conditions that generate high CO_2 and CH_4 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 CO_2 into 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 SO_4^{-2} minerals, dissolved nutrients, and acid (Johnston et al., 2004; Burton et al., 2006; Santos and Eyre, 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 CO_2 and CH_4 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 CH_4 concentrations and carbon stable isotope ratios ($\delta^{13}C-CH_4$), dissolved CO_2, and radon (^{222}Rn, 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 CO_2 and CH_4. We attempt to resolve the contribution of floodwaters versus groundwater discharge to CO_2 and CH_4 exports. Our focus on quantifying the processes that enhance CO_2 and CH_4 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 CO_2 and CH_4 concentrations, and that groundwater discharge will be primarily responsible for post-flood CO_2 and CH_4 dynamics in artificial drains.

2. Material and methods

2.1. 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″S, 153°30′15.02″E) in Australia (Fig. 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 (FeS_2) (Naylor et al., 1998). Sugarcane has been the dominant land use in the area for the last ~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 (~12.9 km of drains within a 100 km^2 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 water 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 (Fig. 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 (Fig. 1), where pumping starts as water levels go above −453 mm Australian Height Datum (AHD) and stop when below −453 mm AHD (Green et al., 2006). As a result, groundwater levels are generally maintained at a relatively constant height of −0.5 m AHD (Smith et al., 2003), reducing groundwater seepage, except when significant rainfall events occur.

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 a 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 (Fig. 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 (Fig. 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 were collected for surface water ^{222}Rn analysis 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 20th and 26th January 2015. During this time, discrete samples were taken once a day between the 23rd and 25th to characterise concentrations during flood conditions. Field sampling was conducted in 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 26th to 31st January 2015. A submersible pump was placed just above the bottom of the main drain, about 90 m