Journal of Hydrology 493 (2013) 30–42

Contents lists available at SciVerse ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Carbon dioxide dynamics driven by groundwater discharge in a coastal floodplain creek

Marnie L. Atkins, Isaac R. Santos *, Sergio Ruiz-Halpern, Damien T. Maher

Centre for Coastal Biogeochemistry, School of Environment, Science and Engineering, Southern Cross University, Lismore, New South Wales, Australia

ARTICLE INFO

Article history:
Received 28 October 2012
Received in revised form 19 March 2013
Accepted 5 April 2013
Available online 18 April 2013
This manuscript was handled by Corrado Corradini, Editor-in-Chief, with the assistance of Michel Bakalowicz, Associate Editor

Keywords:
Submarine groundwater discharge
Subterranean estuary
Geochemical tracers
Saltmarsh
Greenhouse gases
Permeable sediments

SUMMARY

Dissolved carbon dioxide (CO_2) may be highly enriched in groundwater. However, the contribution of groundwater discharge as a source of CO_2 to rivers, estuaries and coastal waters is poorly understood. We performed high resolution measurements of radon (^{222}Rn, a natural groundwater tracer) and the partial pressure of CO_2 (pCO_2) in a highly modified tidal creek and estuary (North Creek, Richmond River, New South Wales, Australia) to assess whether CO_2 in surface waters was driven by groundwater discharge. A spatial survey revealed increasing ^{222}Rn activities (up to 17.3 dpm L^{-1}) and pCO_2 (up to 11,151 μatm) in the upstream direction. The enrichment occurred in a drained coastal acid sulphate soil wetland upstream of a mangrove forest. Time series experiments (24-h) were performed at two stations upstream and downstream of the pCO_2 enrichment area. Upstream measurements demonstrated a significant correlation between pCO_2 and ^{222}Rn while downstream values resulted in a significant inverse relationship between pCO_2 and dissolved oxygen apparently as a result of respiration in nearby mangroves. Measurements taken 2 days after a 245 mm precipitation event revealed the highest recorded ^{222}Rn activities (up to 86.1 dpm L^{-1}) and high pCO_2 (up to 11,217 μatm), showing a strong groundwater influence after flooding. These observations imply that groundwater discharge drove CO_2 dynamics at the upstream station while multiple complex processes drove CO_2 at the downstream station. A ^{222}Rn mass balance model demonstrated that groundwater discharge accounted for about 76% of surface water in this floodplain creek. The CO_2 evasion rates (799 ± 225 mmol m^{-2} d^{-1}) were driven primarily by currents rather than wind. Groundwater-derived CO_2 fluxes into the creek averaged 1622 mmol m^{-2} d^{-1}, a value twice as high as atmospheric CO_2 evasion and consistent with carbon uptake within the creek and downstream exports. These results demonstrate that groundwater seepage was a major factor driving CO_2 evasion to the atmosphere from the creek. Groundwater discharge should be accounted for in CO_2 budgets in coastal systems.

1. Introduction

While dissolved CO_2 may be highly enriched in groundwater (Macpherson, 2009), carbon budgets usually ignore groundwater discharge as a potential driver of CO_2 in surface waters. High pCO_2 detected within coastal wetlands indicate that groundwater discharge from aquifers to the estuarine and coastal zone may be a significant source of atmospheric CO_2 (Cai et al., 2003). Previous investigations have suggested estuaries may be groundwater discharge hotspots (Schwartz, 2003). However, the contribution of groundwater discharge as a source of CO_2 to freshwater ecosystems, estuaries and coastal waters is poorly understood (Cole et al., 2007; Maher et al., 2013).

Highly dynamic estuarine ecosystems are one of the most productive environments globally, providing the major pathway for carbon and nutrients travelling across the land–ocean interface (Meybeck, 1982). Most riverine and estuarine systems are net heterotrophic (Gattuso et al., 1998), where respiration exceeds primary production resulting in an overall increase in pCO_2 within the water column (Abril et al., 2000; Chen et al., 2012). When pCO_2 increases above atmospheric values (i.e., ~390 μatm), the concentration gradient between the water-phase and air-phase creates a water-to-air CO_2 flux. Therefore, most rivers and estuaries act as sources of CO_2 to the atmosphere (Abril et al., 2000; Borges et al., 2003; Jiang et al., 2008; Zhai et al., 2005). Despite the relatively small area of rivers and estuaries, these ecosystems are considered a significant component of the global carbon cycle due to high CO_2 fluxes to the atmosphere (Borges et al., 2005; Cai and Wang, 1998; Frankignoulle et al., 1998).

The major processes contributing to CO_2 enrichments within aquatic systems are in situ respiration driven by natural and anthropogenic organic matter inputs (Cole and Caraco, 2001; Richey et al., 1988), groundwater discharge (Jiang et al., 2008; Maher

* Corresponding author. Tel.: +61 2 66203494; fax: +61 2 66212669.
E-mail address: isaac.santos@scu.edu.au (I.R. Santos).

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http://dx.doi.org/10.1016/j.jhydrol.2013.04.008

et al., 2013), terrestrial surface water runoff (Raymond et al., 2000) and precipitation of carbonate or silicate minerals (Hagedorn and Cartwright, 2010). Of these processes, organic matter decomposition is often considered the major driver of estuarine CO_2. The magnitude of estuarine CO_2 fluxes are often thought to be mainly derived from the balance between photosynthetic CO_2 uptake and the subsequent release via respiration (Ahad et al., 2008; Chen et al., 2012; Maher and Eyre, 2012).

Upper estuaries are usually narrow with strong currents causing bottom sediment resuspension resulting in high turbidity and limited primary productivity (Chen et al., 2012; Zhai et al., 2005). This process, along with CO_2 enriched groundwater discharge, organic matter degradation and lateral input of CO_2 enriched waters derived from intertidal vegetation combine to contribute to the overall CO_2 enrichment (Chen et al., 2012). Hence upper estuaries may emit more CO_2 on an aerial basis than wider lower to mid estuaries where a combination of slower moving waters, alkalinity buffering, smaller CO_2 contributions from wetlands and enhanced photosynthesis result in lower pCO_2 (Chen et al., 2012).

General global patterns of CO_2 fluxes within estuarine zones are still not well understood due to a lack of data (Cai, 2011; Chen et al., 2012; Maher and Eyre, 2012). Currently, estuarine pCO_2 data is spatially biased with most studies conducted within the Northern Hemisphere. In addition, limited data on coastal subtropical and tropical estuarine environments (Kone and Borges, 2008) and limited data on CO_2 evasion over tidal cycles adds to the large uncertainty. CO_2 flux variability may be extreme over small spatial and short temporal scales with considerable differences within the same estuary (Abril et al., 2000; Frankignoulle et al., 1998; Maher and Eyre, 2012). The global CO_2 estuarine flux estimate will be better constrained with further investigations incorporating seasonal and tidal variations across a wide range of regional estuarine zones.

Groundwater has been recognised as a significant source of dissolved nutrients, trace metals, and organic and inorganic carbon to adjacent estuarine and coastal environments (Moore, 2010; Sanders et al., 2012; Slomp and Van Cappellen, 2004). Groundwater often contains much higher concentrations of dissolved species than surface waters, thus even small amounts discharging into surface water bodies can have important implications on aquatic biogeochemical cycles. Groundwater physico-chemical characteristics are highly dependent on the chemical composition of the surrounding rock and sediment, and the interactions between penetrating surface water and soil in the unsaturated zone. Thus, groundwater can become enriched in CO_2 due to soil respiration (Savoy et al., 2011).

^{222}Rn is an excellent natural groundwater tracer since it is often enriched in groundwater relative to surface waters by 2–4 orders of magnitude (Burnett et al., 2001; Dulaiova et al., 2005; Santos et al., 2011). ^{222}Rn is a noble gas and part of the uranium decay chain. Hence, any water in contact with sediments will acquire a ^{222}Rn signal because uranium is present in most sediments. Its decay rate ($t_{1/2}$ = 3.8 days) is comparable to many physical processes in surface waters (Swarzenski et al., 2006). Therefore, ^{222}Rn activities are not only higher at the groundwater discharge point but also detectable a short distance from the source (Cook et al., 2006; Schmidt et al., 2010). Traditional ^{222}Rn analytical methods relying on grab samples may be time consuming and limit sampling resolution. Advances in technology have produced automated ^{222}Rn-in-water monitoring systems that can be easily used in the field, allowing for continuous, precise and rapid ^{222}Rn-in-water assessments (Burnett et al., 2010; Dulaiova et al., 2005). By utilising a mass balance approach based on ^{222}Rn fluxes, total groundwater flux into adjacent surface waters can be estimated (Cook et al., 2008; de Weys et al., 2011).

In this paper, we hypothesise that CO_2 dynamics within a coastal floodplain creek is driven by groundwater discharge. Groundwater discharge was estimated by conducting ^{222}Rn time series measurements at two fixed stations. CO_2, current velocities and wind speeds were also measured over full tidal cycles enabling quantification of CO_2 evasion from the floodplain creek into the atmosphere. Previous studies have used ^{222}Rn and CO_2 to assess the recharge dynamics of karst aquifers (Savoy et al., 2011) and have estimated groundwater-derived dissolved inorganic carbon fluxes to coastal waters (Cai et al., 2003; Liu et al., 2012; Maher et al., 2013; Santos et al., 2012a). This study advances previous investigations by quantifying how groundwater discharge may contribute to CO_2 evasion from surface waters.

2. Material and methods

2.1. Study site

A series of field experiments were conducted in North Creek on the north coast of New South Wales, Australia (Fig. 1). North Creek

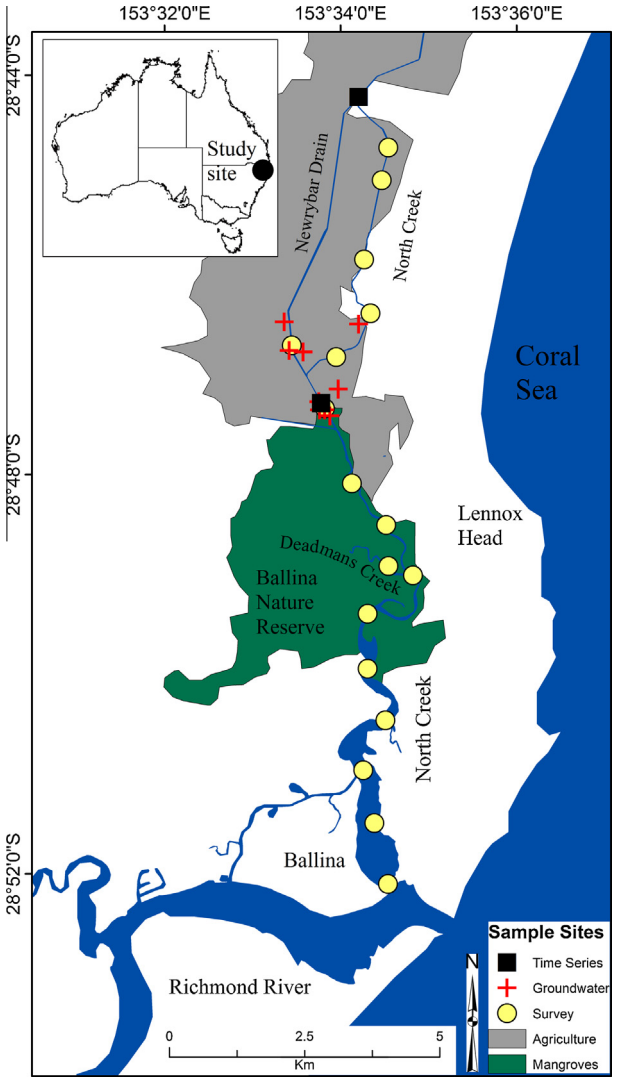

Fig. 1. Map of North Creek, northern New South Wales, Australia. The lower urbanised zone, the middle Ballina Nature Reserve and the upper agricultural fields are present. The yellow circles represent the survey sites, commencing at the creek mouth and ceasing in the upper reaches. The black squares represent the time series locations and the red crosses indicate groundwater sample sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)