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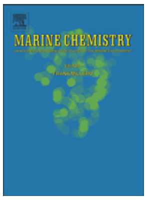

Manganese and iron release from mangrove porewaters: A significant component of oceanic budgets?

Ceylena J. Holloway [a,*], Isaac R. Santos [a,b], Douglas R. Tait [a,b], Christian J. Sanders [a], Andrew L. Rose [b,c], Bernhard Schnetger [d], Hans-Jürgen Brumsack [d], Paul A. Macklin [a,b], James Z. Sippo [a,b], Damien T. Maher [b]

[a] National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, PO Box 4321, Coffs Harbour, NSW 2450, Australia
[b] School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia
[c] Southern Cross GeoScience, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia
[d] Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl-von-Ossietzky University Oldenburg, D-26111 Oldenburg, Germany

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ABSTRACT

Mangrove porewater can be highly enriched in dissolved manganese (Mn), iron (Fe), and other trace metals. As a result, porewater exchange may release dissolved metals to surface waters. This study assessed dissolved Mn exchange with the coastal ocean in four mangroves ecosystems, and whether porewater exchange represents a major driver of the oceanic exchange along a latitudinal gradient in Australia (from 28° S to 12° S). Dissolved Fe was also determined but concentrations were below detection in most surface water samples, preventing any flux estimates. Average concentrations of Mn in porewater were approximately an order of magnitude greater than surface waters at all sites, resulting in average porewater-derived Mn fluxes of 441 kmol km^{-2} $year^{-1}$ at the four sites. Time series surface water observations indicate that average Mn concentrations decrease at lower latitudes. The average dissolved Mn export rate from the four mangrove systems to the coastal ocean was 88 kmol km^{-2} $year^{-1}$. Porewater-derived Mn inputs were greater than surface water exports, which may be explained by dissolved Mn precipitation, oxidation or flocculation at the sediment water interface. While the removal of Mn at the sediment-water interface brings about uncertainties in the estimated porewater fluxes, it has no impact on estimated surface water exports to the coastal ocean. If our surface water export estimates are representative of the global mangrove area (140,000 km^2), mangroves may deliver 12 Gmol $year^{-1}$ of dissolved Mn to the coastal ocean. These fluxes are greater than the estimated flux from global riverine (5.4 Gmol $year^{-1}$) and atmospheric (11 Gmol $year^{-1}$) sources, demonstrating that mangroves may be a major player in the oceanic cycle of Mn.

1. Introduction

Manganese (Mn) is an essential micronutrient for marine organisms and is central component in photosynthetic processes. Iron (Fe) is considered a vital biological requirement for all marine organisms (Sunda, 2002). Exports of dissolved Fe and Mn from mangroves may play an important role in oceanic trace metal budgets, but the magnitude of these fluxes remain largely unknown (Sanders et al., 2012). Alternatively, mangroves can be efficient sinks of essential trace metals (Bayen, 2012; Lewis et al., 2011; Machado et al., 2002). Biogeochemical processes such as adsorption, oxidation, reduction and precipitation often determine whether mangrove systems are a net sink or source of metals (Bayen, 2012; Hatje et al., 2003b; Machado et al., 2002). Due to biogeochemical and hydrological processes, mangroves can release accumulated Fe and Mn into adjacent surface waters (Alongi et al., 2001; Bayen, 2012; Lewis et al., 2011; Sanders et al., 2012). For example, studies in Malaysia have shown that a mangrove estuary is capable of exporting large amounts of dissolved Mn to the coastal ocean (Alongi et al., 1998).

Fe and Mn are important redox reactive elements at the sediment-water interface of mangroves. In the upper oxic region, Mn is normally present as solid phase oxides and oxyhydroxides. In the deeper anoxic sediments, Mn can be reduced to a soluble form. Rapid reoxidation can occur during transport and re-exposure to oxygen (Atkinson et al., 2007; Martynova, 2013). Mn cycling in estuarine and coastal waters is complicated due to the interconnectivity of numerous biogeochemical, hydrological and physicochemical processes that determine its behaviour (Feng et al., 2015). The redox conditions are often connected to the quality and quantity of the organic matter deposited at the sediment-water interface and its decomposition rate (Marchand et al., 2011b; Martynova, 2014). In estuarine and coastal systems, trace metals

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[*] Corresponding author.
E-mail address: ceylena.holloway@scu.edu.au (C.J. Holloway).

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present at the sediment-water interface may be cycled and/or released to the overlying surface waters via diffusion, porewater exchange, sediment resuspension and submarine groundwater discharge (SGD) (Charette and Sholkovitz, 2006).

SGD and porewater exchange are potentially large, yet poorly quantified sources of trace metals to the coastal ocean (Beck et al., 2010; Windom et al., 2006). SGD has been reported to be the major source of dissolved Fe into South Atlantic coastal waters (Windom et al., 2006). In the Wadden Sea, Germany, tidally driven porewater exchange was found to be a significant source of Mn to surface waters (Dellwig et al., 2007; Kowalski et al., 2012; Moore et al., 2011). Mn and Fe in mangrove groundwater can be highly dynamic and SGD fluxes of these metals may be 2–3 orders of magnitude greater than local river inputs as estimated for a mangrove system in Brazil (Sanders et al., 2012). Heavy metal transformations in coastal groundwater and porewater prior to the seepage zone often determine porewater fluxes to the ocean (Charette and Sholkovitz, 2002; O'Connor et al., 2015; Roy et al., 2012).

Most previous research on the dynamics of dissolved trace metals dynamics in mangroves has focused on highly impacted systems or major estuarine systems (Gurumurthy et al., 2014), and diffusive fluxes at the sediment-water interface (Alongi et al., 1998). Generally, these studies indicate that metal exchange is controlled by freshwater discharge and biogeochemical processes affecting redox reactions and pH mediated adsorption/desorption reactions (Klinkhammer and McManus, 2001; Machado et al., 2002; Shynu et al., 2012). The lack of studies in pristine mangroves may lead to a misinterpretation of Fe and Mn exchange from mangrove systems (Gurumurthy et al., 2014).

This study investigates dissolved Fe and Mn exchange with the coastal ocean in four mangrove ecosystems, and assesses whether porewater exchange represents a major driver of the oceanic Fe and Mn exchange along a latitudinal gradient from 28° S to 12° S in Australia. We initially hypothesised that the mobilisation of Fe and Mn from mangrove sediments is driven by tidal pumping and biogeochemical conditions (i.e., oxygen concentration, pH, organic matter concentration, and salinity) of porewater and surface water. We quantified the total surface water exports of Mn via detailed time series observations, and the relative contribution of porewater exchange using radon (^{222}Rn) as a porewater tracer. This paper builds on the literature by (1) focusing on the contribution of the mangrove intertidal forest rather than nearby estuaries, (2) presenting an estimate of global Mn exports from mangroves to the ocean, and (3) estimating radon-derived porewater advection rather than diffusive sediment fluxes. Because surface water Fe samples were below detection limits in several samples, this paper focuses on Mn while reporting the more limited Fe dataset. The radon-derived porewater exchange estimates are reported in a companion paper (Tait et al., 2016).

2. Material and methods

2.1. Study sites

Four mangrove creeks were selected across a latitudinal gradient in Australia (Fig. 1, Table 1). All sites had (1) low-lying surrounding topography to ensure surface drainage in the area was minimal; (2) limited or no freshwater inputs to prevent estuarine processes from masking processes taking place within the mangroves; and (3) minimal anthropogenic disturbance to gain insight into how pristine mangroves may compare to the more widely studied impacted mangrove systems. The field sites chosen were: (1) Jacobs Well, Moreton Bay Queensland; (2) Tom's Creek, Seventeen Seventy, Queensland; (3) Coral Creek, Hinchinbrook Island, Queensland; and (4) Sadgroves Creek, Darwin, Northern Territory. Specific site characteristics are summarised in Table 1.

The Moreton Bay site has previously been studied in a porewater exchange and carbon cycle context (Maher et al., 2013). The creek is vertically well mixed and receives no upstream freshwater inputs. Moreton Bay is a subtropical estuary characterised by a semi diurnal tidal regime with spring and neap tidal ranges between 1 and 2 m. Moreton Bay is known to receive significant SGD inputs (Stewart et al., 2015). The prominent mangrove species within the system were *Avicennia marina*, *Aegiceras corniculatum*, *Bruguiera gymnorrhiza*, *Rhizophora stylosa*, *Ceriops australis*, *Excoecaria agallocha*, and *Lumnitzera racemos.*

The Seventeen Seventy site (Tom's Creek) is a tidal mangrove creek, located in southeast Queensland. The region has a sub-tropical, maritime climate influenced by the southeast trade winds (BOM, 2015). The tidal regime is semidiurnal with minimal variation between spring and neap tide ranges (3 to 3.5 m). The mangroves at Tom's Creek exhibit distinct banding from seaward to land, with areas of salt flats inland. Common mangrove species included *Avicennia marina* and *Rhizophora stylosa.*

The Hinchinbrook Island site (Coral Creek) is a tidal creek located in Missionary Bay on the western side of the island. The area is dominated by densely vegetated mangrove swamps in pristine condition. Coral Creek is a relatively flat bottom creek with steep banks reaching 4 to 6 m (Wolanski et al., 1980). A previous radon and radium isotope investigation at this site revealed significant porewater exchange rates (Stieglitz et al., 2013). At the time of this study the mangroves on the western bank of Coral Creek were recovering from a tropical cyclone. *Rhizophora stylosa* was the dominant mangrove species noted at this

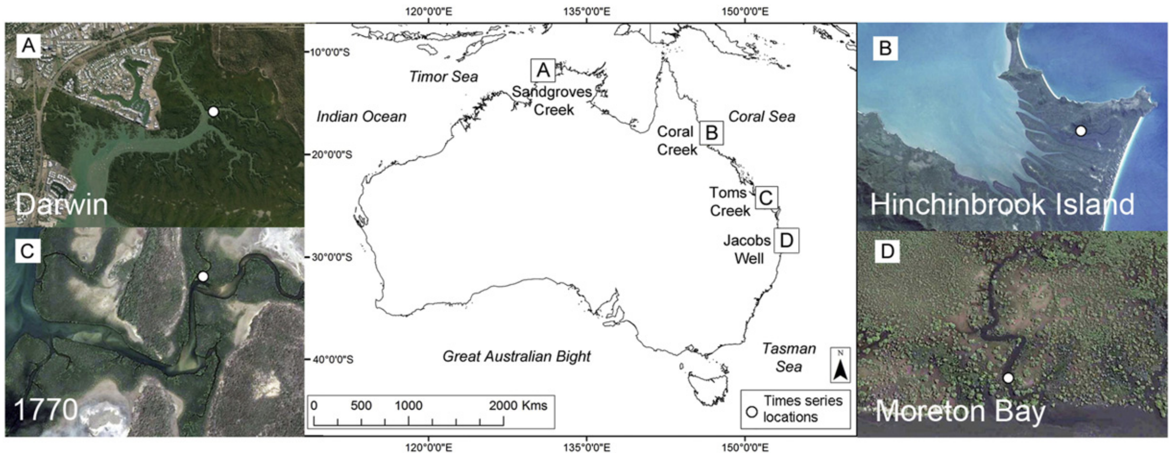

Fig. 1. Site map, indicating the four study sites in Australia: (A) Darwin, (B) Hinchinbrook Island, (C) Seventeen Seventy, and (D) Jacobs Well.