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Greenhouse gases and submarine groundwater discharge in a Sydney Harbour embayment (Australia)

Mahmood Sadat-Noori [a, b, *], Douglas R. Tait [a, b], Damien T. Maher [b], Ceylena Holloway [a, b], Isaac R. Santos [a, b]

[a] National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, NSW, Australia
[b] School of Environment, Science and Engineering, Southern Cross University, Lismore, NSW, Australia

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ABSTRACT

We investigated whether submarine groundwater discharge (SGD) traced by radon (^{222}Rn, a natural groundwater tracer) may drive carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in surface waters in Chowder Bay, a marine embayment in Sydney Harbour, Australia. A radon mass balance revealed significant groundwater discharge rates into the bay (8.7 ± 5.8 cm d^{-1}). The average CO_2, CH_4, and N_2O concentrations in the subterranean estuary were 3.5, 7.2, and 2.8 times higher than the average surface water concentrations, indicating the possibility of coastal groundwater as a source of greenhouse gases to the bay. SGD-derived fluxes of greenhouse gases were 5.02 ± 2.28 mmol m^{-2} d^{-1}, 5.63 ± 2.55 µmol m^{-2} d^{-1}, and 1.72 ± 0.78 µmol m^{-2} d^{-1} for CO_2, CH_4 and N_2O, respectively. The average CO_2 evasion rate from surface water was 2.29 ± 0.46 mmol m^{-2} d^{-1} while CH_4 and N_2O evasion rates were 12.89 ± 3.05 and 1.23 ± 0.25 µmol m^{-2} d^{-1} respectively. Therefore, groundwater-derived greenhouse gas fluxes accounted for >100% CO_2 and N_2O and ~43% of CH_4 surface water evasion, indicating SGD is likely an important source of greenhouse gases to surface waters. However, this may be due to observations being performed near the SGD source, which may overestimate its contribution to the wider Sydney Harbour. Over a 20-year time frame, the combined emissions of CH_4 and N_2O from surface waters to the atmosphere accounted for 25% of the total CO_2-equivalent emissions. Although this study gives preliminary insight into SGD and greenhouse gas dynamics in Sydney Harbour, more spatial and temporal resolution sampling is required to fully constrain these processes.

1. Introduction

Coastal ecosystems play an important role in the global carbon cycling with most of the world estuaries being a source of the major greenhouse gases [i.e. carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)] to the atmosphere (Borges and Abril, 2011; Bange et al., 1996). Disturbing natural coastal ecosystems and surrounding habitats may lead to significant pollution in waterways and the release of large amounts of buried carbon to the atmosphere (Lovelock et al., 2011; Adame et al., 2013). Previous studies have shown that SGD can deliver significant amounts of nutrients, dissolved carbon and trace metals to coastal waters (Beck et al., 2009; Knee and Paytan, 2011; Porubsky et al., 2014; Lecher et al., 2015). Recently, several studies have suggested that submarine groundwater discharge (SGD) can also deliver large amounts of greenhouse gas into coastal surface waters (O'Reilly et al., 2015; Maher et al., 2015; Sadat-Noori et al., 2016). Solute concentrations, including contaminants, in groundwater are usually higher than in surface marine waters, making groundwater discharge a potentially important driver of surface water chemistry (Santos et al., 2009).

SGD is defined as any water derived by terrestrial and marine forces from the sediment into the surface water column (Moore, 2010). Common drivers of SGD are hydraulic head gradient, tidal pumping, and density-driven convection (Santos et al., 2012). Despite increased awareness, SGD remains poorly understood in several environments such as coastal megacities. For example, SGD studies on two major urbanized Asian megacities revealed that SGD-derived dissolved inorganic nitrogen can account for up to 130 and 46% of the rivers nutrient input, demonstrating that SGD

* Corresponding author. School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia.
E-mail address: mahmood.sadat-noori@scu.edu.au (M. Sadat-Noori).

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should be examined in more detail as an important source of biogeochemically-active elements (Burnett et al., 2007b; Taniguchi et al., 2008).

Over the last two decades there has been significant advances in the techniques used to measure natural geochemical tracers which can quantify SGD (Burnett et al., 2006). Radon (^{222}Rn) is a natural tracer which has proven to be an effective tool in quantitatively investigating groundwater-surface water interactions. The main advantages of ^{222}Rn is its ability to integrate signals related to different groundwater pathways which may be useful in spatially heterogeneous and temporally dynamic systems (Stieglitz et al., 2010; Burnett et al., 2006). Additionally, ^{222}Rn has conservative behaviour, is highly soluble compared to its radioactive parents, occurs naturally, and has higher concentration in groundwater in comparison to surface waters (Burnett et al., 2006). The short half-life of ^{222}Rn (3.84 days) is advantageous as it is on the same time scale as many physical process related to groundwater discharge and physical mixing of coastal waters (Burnett et al., 2010).

The Sydney Harbour Estuary is the centrepiece of Australia's largest city. This iconic waterway has immense social, economic and biological value (Smoothey et al., 2016). The Sydney Harbour catchment accommodates approximately one-fifth of Australia's population (4.8 million residents) (Banks et al., 2016), putting the catchment of the estuary under extensive industrial and coastal development pressure (Johnston et al., 2015; Birch et al., 2015). Although Sydney Harbour Estuary has been studied from the marine, biological and ecological perspectives in detail, the majority of these studies have focused on urban runoff (Stark, 1998), stormwater (Birch et al., 2010) and river inputs (Birch et al., 1996; Banks et al., 2016). Several studies on heavy metals within the Harbour indicated that benthic sediments are highly contaminated with heavy metals, but are much lower in concentration than found in surface waters near the mouth of the estuary (Birch and Taylor, 1999; Hatje et al., 2003; Birch et al., 2015). There are no previous studies addressing SGD and related chemical inputs into Sydney Harbour. Additionally, there is a lack of studies investigating hydrologic process within the Harbour and no time series data sets that identify trends and major drivers of biotic interactions (Johnston et al., 2015).

This study will, for the first time, quantify submarine groundwater discharge and its associated greenhouse gases (GHG) in an embayment of Sydney Harbour. Visible groundwater seeps around Sydney Harbour led us to hypothesize that SGD may be a major source of water and greenhouse gases to the Harbour. We test this hypothesis by conducting high frequency time series measurements of dissolved CO_2, CH_4 and N_2O in Chowder Bay, Sydney Harbour. We use a well-established groundwater tracer approach utilizing a ^{222}Rn mass balance, to quantify groundwater advection rates and compare SGD-derived fluxes of greenhouse gas to fluxes at the surface water-air interface.

2. Material and methods

2.1. Site description

The study was conducted in Chowder Bay, a small cove in Sydney Harbour, Australia. Sydney Harbour is a heavily industrialized waterway surrounded by the city of Sydney (Fig. 1). Sydney Harbour Estuary is ~30 km long, has an average depth of 13 m and is a very productive ecosystem containing a diverse variety of habitats and organisms. The estuary's upper and central sections are comprised of muddy sediment whereas the lower estuary has sandy bottom sediments (Birch et al., 2008). Estuary flushing times can vary from less than a day at the mouth of the estuary to 225 days in the upper parts (Das et al., 2006; Siboni et al., 2016). Chowder Bay is located close to the entrance of Sydney Harbour (33°50′48″S, 151°15′15″E), representing typical marine conditions with some potential influence of urban runoff and inputs from the upper estuary. Although the bay area is protected from dominant south easterly swells it is affected by wind-induced waves and storm swells (Hill et al., 2011). The seafloor is generally sandy with rocky reef outcroppings and gentle slopes (Johnston et al., 2015).

Chowder Bay has an area of about 4300 m^2 and a catchment size of 0.5 km^2. The habitat surrounding Chowder Bay is mainly soft sediments containing some seagrasses (*Zostera capricorni* and *Halophila ovalis*) and shallow fringing rocky reefs (Glasby, 2001). The region receives ~1200 mm of rainfall annually and experiences a mild, warm, temperate climate all year round. Chowder Bay area is located at the low point within its sub-catchment and collects stormwater. The Parramatta River is the main tributary entering Sydney Harbour and has an annual water flux of 473 $\times$ 10^5 m^3 (Hatje et al., 2001). During dry weather conditions fresh-water discharge is low (<0.1 m^3 s^{-1} at all discharge locations). Precipitation, freshwater inflow and evaporation are thought to mostly regulate salinity in Sydney Harbour (Lee et al., 2011). During dry periods, the harbour generally has the same salinity as the ocean (~35) and is well mixed. However, after rainfall the mouth of the Harbour can have salinity of about 30 in the upper 1–2 m (Hedge et al., 2014).

2.2. Surface water GHG and ^{222}Rn time series

A field campaign was carried out from 19th to the 23rd November 2015. We deployed an automatic high frequency time series monitoring station on a jetty 80 m from the shore within Chowder Bay (Fig. 1). The station continually monitored water depth, salinity, temperature, dissolved oxygen, pH, $f$$CO_2$, $p$$CH_4$, N_2O and ^{222}Rn over the duration of the field campaign. Surface water was pumped from 1 m below the surface at a point where the average water depth was ~5 m. An automated ^{222}Rn monitor (RAD7, Durridge Co.) averaged ^{222}Rn concentrations over 30 min cycles for about five days. Two cavity ring-down spectrometers (Picarro G2201-i- and G2308) coupled to a showerhead equilibrator were used to measure dissolved CO_2, CH_4 and N_2O at ~ 1 Hz (Maher et al., 2013) with data averaged over 1 min intervals. Water was pumped at a constant rate of 3 L m^{-1} to an equilibrator chamber where the gas in air and water reaches equilibrium. The equilibrated air is then continuously pumped in a closed-loop from the headspace of the equilibrator chamber through desiccant (Drierite), the RAD7 and the Picarros and then back to the equilibrator. The equilibration time for CO_2, CH_4, and ^{222}Rn using this set up is ~5 min, 20 min, and 30 min respectively (Webb et al., 2016; Santos et al., 2012), with the equilibration time of N_2O assumed to be similar to CO_2 based on their similar solubilities (Arévalo-Martínez et al., 2013). CH_4 and N_2O fugacity were converted to concentrations based on the solubility coefficient calculated as a function of temperature and salinity (Wiesenburg and Guinasso, 1979; Weiss and Price, 1980). The sampling was conducted around neap tide with a tidal range from 0.8 m at the beginning of the campaign and increasing to 1.2 m towards the end (Fig. 2). A calibrated Hydrolab (DX5) automatic logger was used to measure salinity (±0.2), dissolved oxygen (±0.2 mg L^{-1}) and water temperature (±0.10 °C) at 15 min intervals while a depth logger (CTD diver) measured depth (±0.01 m) at 10 min intervals. A high-precision submersible pH sensor (SAMI) was used to measure pH (±0.003 units). Wind speed data (±10%) were obtained from a weather station (Model PH1000) on site.

2.3. Groundwater sampling and analysis

A push point piezometer system was used to collect