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Tidal variability in methane and nitrous oxide emissions along a subtropical estuarine gradient

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ABSTRACT

This study investigates the tidal variability in methane (CH_4) and nitrous oxide (N_2O) emissions along a gradient of the subtropical Brisbane River estuary. Sampling was conducted at the upper, middle and lower reaches over two tidal cycles in 2013 and 2014. Methane and N_2O emissions varied significantly over tidal cycles at all sites. Methane and N_2O emissions measured at all locations and in both campaigns varied substantially in time, with the maximum to minimum flux ratio in a cycle varying between 2.5 - 9 and 1.7–4.7 times, respectively. Methane emissions peaked just before or at slack tides. In comparison, no clear patterns were observed between the N_2O emissions and the tidal cycle despite there being large variations in N_2O emissions in some cases. Methane concentrations were elevated during low tides whereas N_2O concentrations showed no clear pattern over the tidal cycle. Surface water concentrations and tidal currents played important roles in CH_4 and N_2O emissions, but wind did not. Our findings show that measurements at a single point in time and site would result in significant errors in CH_4 and N_2O emission estimates. An adequate and careful sampling scheme is required to capture spatial and temporal variations of CH_4 and N_2O emissions and surface water concentrations which should cover at least one tidal cycle in different estuarine sections.

1. Introduction

Methane (CH_4) and nitrous oxide (N_2O) are powerful greenhouse gases (GHGs) influencing the Earth's climate with global warming potentials being 34 and 298 times that of carbon dioxide respectively, when calculated on a 100-yr time horizon (Myhre et al., 2013). Coastal areas account for up to 75% (Bange et al., 1994) and 60% (Bange et al., 1996; Seitzinger et al., 2000) of the global oceanic CH_4 and N_2O emissions, respectively. However, global CH_4 and N_2O emission estimates as well as estuary concentration levels show high spatial and temporal variability and data are limited (Law et al., 1992; Middelburg et al., 2002; Abril and Borges, 2005). The lack of data is especially pronounced in estuaries located in subtropical regions, particularly in the Southern Hemisphere (Ortiz-Llorente and Alvarez-Cobelas, 2012), including Australia. These systems are likely an important component for Australian GHG budgets as they occupy a relatively large surface area, over 38,000 km^2 in Australia (Geoscience Australia, 2014).

Methane in estuarine environments is mainly formed by microbial methanogenesis under anoxic conditions (Canfield et al., 2005), e.g. as found in marine sediments. However, CH_4 oxidation, which can occur under aerobic as well as anaerobic conditions in the water column and/or sediments, conversely functions as a major CH_4 sink (Bange, 2006). Nitrous oxide in estuarine environments can be produced under oxic conditions as a byproduct of nitrification, or at oxic-anoxic boundaries as an intermediate of denitrification. Denitrifying organisms can also consume N_2O by reducing N_2O to nitrogen gas (Ward, 1996; Codispoti et al., 2001). Levels of N_2O production during nitrification and denitrification, or consumption during denitrification, can depend on the dissolved oxygen, nitrate or carbon levels occurring in the water column or sediments (Wrage et al., 2001; De Bie et al., 2002; Bange, 2006).

Currently, CH_4 and N_2O emissions in estuarine systems can be directly measured with floating chambers where the gas accumulation over time is used to calculate emission rates (Silvennoinen et al., 2008; Beaulieu et al., 2010). These emissions as well as CH_4 and N_2O surface water concentrations in estuarine systems are typically measured at a fixed time, often in combination with

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spatial surveys at different estuary reaches (i.e. lower, middle, upper) and possibly repeated over seasons (Beaulieu et al., 2010; Musenze et al., 2014). While this sampling scheme may be adequate to capture spatial variations along estuaries at a fixed point in time and general seasonal patterns, it fails to capture diurnal and tidal cycle variability of CH_4 and N_2O emissions or concentrations. Investigations considering diurnal and tidal dynamics are rare, however, variations in these short term periods can be significant due to a combination of mechanisms that occur e.g. physically such as wind or water level changes, biologically such as productivity or respiration, hydrologically such as riverine and oceanic water mixing or anthropogenically such as ship traffic generated waves (Allen et al., 2007; Ferron et al., 2007; Tong et al., 2013; Maeck et al., 2014; Maher et al., 2015). These significant variations are important and need to be considered especially for estimating estuarine GHG budgets of CH_4 and N_2O.

The main objective of our study was to investigate the tidal variability in CH_4 and N_2O emissions along a gradient of the Brisbane River estuary. For this, three sites were chosen, these being located in the lower, middle and upper reaches of the estuary (Fig. 1). Sampling campaigns were conducted during tidal cycles at all three sites in 2014 and at the lower and middle reaches in 2013. The measured CH_4 and N_2O emissions were interpreted and analysed using measured CH_4 and N_2O surface water concentrations, wind speed and current speed. Our study highlights the importance of considering the temporal and spatial variations of emissions in sampling designs for estuaries. Dynamics in CH_4 and N_2O surface water concentrations also need to be considered if these are to be used to interpret CH_4 and N_2O emissions.

2. Materials and methods

2.1. Site description

The Brisbane River estuary, in subtropical South East Queensland, Australia, discharges into Moreton Bay and has confluences with the Bremer River, the Oxley Creek (Fig. 1) and some other smaller creeks (not illustrated in Fig. 1). The surface area of the estuary is 19 km^2 and the catchment area is 13,643 km^2. The estuary has undergone major channel modifications (Eyre et al., 1998) including extensive channel deepening (>10 m), straightening and hardening for the purposes of improved ship navigation and port development (Hossain et al., 2004). These modifications led to an increase in the natural tidal limit of 16 km upstream from the estuary mouth (Holland et al., 2001) to today's 86 km (Davie et al., 1990; Holland et al., 2001). The estuary mouth depth is maintained by dredging to a depth of approximately 13 m, this is followed by a 20 km long channel maintained at 9 m, and the remaining estuary channel has an average depth between 4 and 8 m (Eyre et al., 1998). The estuary experiences semi-diurnal tides with a tidal range at the estuary mouth of approximately 0.7–2.7 m (mean neap tidal range 1.0 m, mean spring tidal range 1.8 m) (Chanson et al., 2014) and an average travel time of the tide, from the estuary mouth to the estuary's confluence with the Bremer River, is approximately 3 h (Bureau of Meteorology, 2014d). The Brisbane River estuary has relatively high water temperatures (ranging between 16 and 29 °C among seasons (EHMP, 2014)) and can experience distinct, seasonal rainfall patterns due to the subtropical location.

Temporal and spatial differences in CH_4 and N_2O emissions were investigated during two sampling campaigns, conducted in the same winter month (August) of two consecutive years (2013 and 2014). In both sampling campaigns, CH_4 and N_2O emissions were measured using floating chambers. In 2013, tidal cycle measurements of CH_4 and N_2O emissions were conducted in the lower reach one day, and then at the middle reach on the following day (Fig. 1, Estuary classification: Department of Environment and Heritage Protection (2014)). In 2014, measurements were conducted at the three sampling sites in the lower, middle and upper reaches on the same day and over the same tidal cycles. A time shift of 1 h between the site in the lower and middle reaches and between the middle and upper reaches ensured our samples were captured on the same

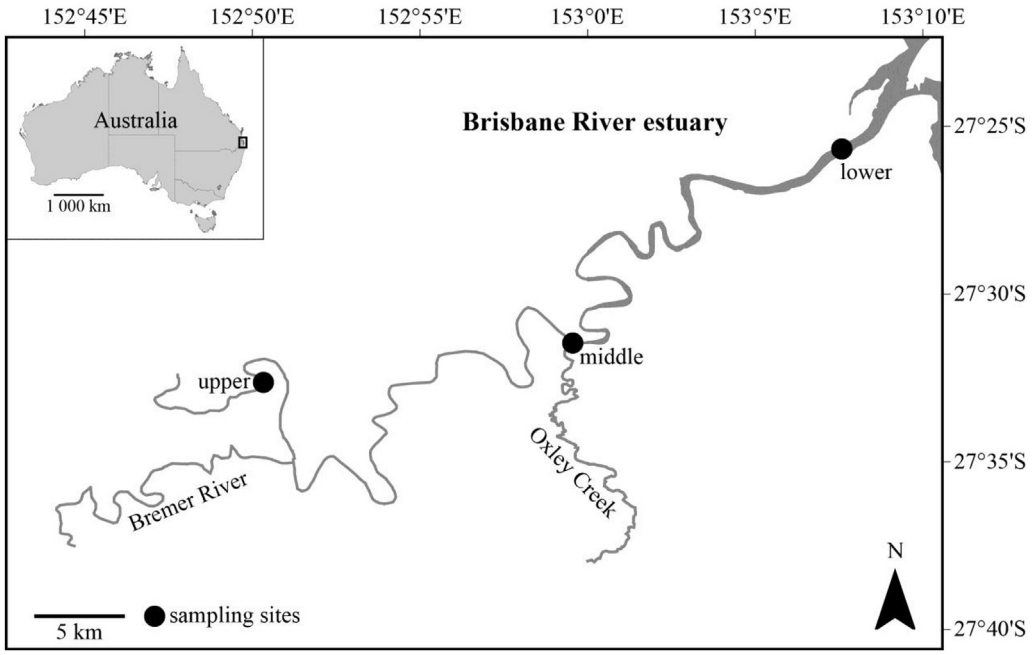

Fig. 1. Locations of sites for the field sampling in the Brisbane River estuary, South East Queensland, Australia. The sampling was conducted at three sites located in the lower, middle and upper reaches. Distances from the estuary mouth were 6 km for the site in the lower reach, 29 km for the site in the middle reach and 82 km for the site in the upper reach.