Estuarine, Coastal and Shelf Science 208 (2018) 83–95

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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

The spatial and temporal drivers of pCO_2, pCH_4 and gas transfer velocity within a subtropical estuary.

Luke C. Jeffrey[a,b,*], Damien T. Maher[a,b], Isaac R. Santos[a], Mitchell Call[a], Michael J. Reading[a,b], Ceylena Holloway[a], Douglas R. Tait[a,b]

[a] National Marine Science Centre, Southern Cross University, PO Box 4321, Coffs Harbour, NSW, 2450, Australia
[b] Southern Cross Geoscience, Southern Cross University, PO Box 157, Lismore, NSW, 2480, Australia

ARTICLE INFO

Keywords:
Groundwater
Methane
Carbon dioxide
Chemical enhancement
Piston velocity
Greenhouse gasses

ABSTRACT

Large uncertainties remain in global estuarine CO_2 and CH_4 emissions estimates due to spatial heterogeneity, differences in methodologies and insufficient data at key locations. This study utilised novel techniques to integrate high-resolution temporal measurements of dissolved CO_2 and CH_4 and gas transfer velocity, within an urbanised subtropical estuary (Coffs Creek, Australia). An intensive four-station 25hr moving time series approach accounted for diurnal, tidal and spatial trends along an estuarine salinity gradient. Using 185 floating chamber measurements, results revealed major differences in emission rates over short distances. Average CO_2 emission rates ranged from 16.7 to 84.4 mmol m^{-2} day^{-1} from lower to upper estuary respectively (averaged 49.0 mmol m^{-2} day^{-1}). The CH_4 emissions ranged from 38.8 to 193.4 μmol m^{-2} day^{-1} (averaged 115.0 μmol m^{-2} day^{-1}), equating to 2.4% of the average CO_2 emissions, when converted to global warming potential CO_2 equivalent (over 100 years). Conservative mixing plots revealed a mid-estuary source of groundwater and porewater exchange that corresponded with a source of pCO_2 and pCH_4 in the mangrove lined portion of the estuary. Between the mouth and upper-estuary, a 230-fold change in gas transfer velocity (k_{600}) (0.1–25.9 cm hr^{-1}), 130-fold change in CO_2 fluxes (1.6–202.6 mmol m^{-2} day^{-1}) and 260-fold change of CH_4 fluxes were observed (2.6–671.1 μmol m^{-2} day^{-1}). Current velocity was the most important driver of k_{600} in the lower estuary ($r^2 = 0.37$, $p < 0.001$) and a significant driver across the whole estuary ($r^2 = 0.77$, $p < 0.001$). A comparison of measured emissions to existing empirical k models indicated empirical models were less effective at characterising emissions within different ecotypes because of changing physical drivers along the estuary. The k_{CO2} chemical enhancement may be significant, especially in low k settings such as upper estuaries. This study highlights the importance of characterizing distinct estuarine zones and accounting for spatio-temporal variability to reduce uncertainties of emissions estimates.

1. Introduction

Estuaries are important biogeochemical reactors linking the land to the ocean. They also provide a variety of natural ecosystem services such as nutrient and pollutant processing, habitat and nurseries for offshore fisheries, carbon storage and sediment deposition zones (Canuel et al., 2012). At a global scale, the anthropogenic inputs and modifications to many estuarine biomes are extensive with more than a quarter of Earth's human population living within 100 km of the coastline (Kummu et al., 2016). As such, estuaries are now considered one of the most altered and vulnerable ecosystems on Earth (Canuel et al., 2012).

Due to large inputs of allochthonous carbon from upstream rivers, groundwater inputs, tidal pumping of porewater and runoff from wetlands, estuarine waters are generally supersaturated in CO_2. As a result, estuaries are largely net sources of CO_2 to the atmosphere. Global estimates of estuarine CO_2 degassing ranging from 0.1 to 0.25 Gt C $year^{-1}$, are comparable to the entire continental shelf CO_2 uptake of 0.25–0.40 Gt C $year^{-1}$, though the more recent estimates tend towards lower global degassing rates and higher shelf uptake rates (Chen et al., 2013; Laruelle et al., 2013; Borges, 2005; Cai, 2011). In addition to CO_2, estuaries are also sources of methane (CH_4) to the atmosphere. A review of estuarine studies (Borges and Abril, 2011) estimated a wide range in CH_4 emissions from different estuary types and zones. The highest CH_4 fluxes came from Fjords (1490 μmol m^{-2} day^{-1}), followed by small deltas and estuaries (868 μmol m^{-2} day^{-1}), lagoons

* Corresponding author. Southern Cross Geoscience, Southern Cross University, PO Box 157, Lismore, NSW, 2480, Australia.
E-mail addresses: l.jeffrey.10@student.scu.edu.au (L.C. Jeffrey), damien.maher@scu.edu.au (D.T. Maher), Isaac.Santos@scu.edu.au (I.R. Santos), m.call.10@student.scu.edu.au (M. Call), m.reading.10@student.scu.edu.au (M.J. Reading), Ceylena.Holloway@scu.edu.au (C. Holloway), douglas.tait@scu.edu.au (D.R. Tait).

https://doi.org/10.1016/j.ecss.2018.04.022
Received 12 December 2017; Received in revised form 29 March 2018; Accepted 18 April 2018
Available online 26 April 2018

(762 μmol m^{-2} day^{-1}) and tidal systems and embayments (666 μmol m^{-2} day^{-1}). The current global CH_4 estuarine flux estimate is between 1 and 7 Tg CH_4 $year^{-1}$ (Bange et al., 1994; Borges and Abril, 2011; Middelburg et al., 2002; Upstill-Goddard et al., 2000). Historically, marine CH_4 emissions were considered to be significantly lower than freshwater CH_4 emissions due to sulphate reduction outcompeting methanogenesis (Martens and Berner, 1974; Burdige, 2012). Furthermore, sulphate reduction is linked to anaerobic oxidation of methane (AOM) (Knittel and Boetius, 2009), which is estimated to consume approximately 90% of all biogenic methane within marine and coastal environments (Hamdan and Wickland, 2016). This view has recently been challenged, as coastal waters receiving high inputs of organic matter were shown to emit much higher CH_4 than previously thought (Borges et al., 2016, 2017). As CH_4 has a ~28 times higher global warming potential than CO_2 over a 100 year time scale (GWP_{100}) (IPCC, 2014), even moderate emissions of CH_4 should still be considered when assessing coastal carbon budgets.

Many uncertainties still remain in quantifying the sources and sinks of both CO_2 and CH_4, due to the heterogeneity and complexity of these dynamic systems, insufficient data coverage in both space and time, and also the variety of gas transfer velocity (k) models utilised to estimate air-sea emissions (Kirschke et al., 2013; Raymond and Cole, 2001; Laruelle et al., 2010; Crosswell et al., 2017). In productive estuarine systems, significant diurnal variability can occur as daytime productivity and night time respiration influence partial pressure CO_2 (pCO_2) (Cotovicz et al., 2015; Dai et al., 2009). Similarly, tidal variability can be significant as the mixing of oceanic and freshwater end-members alter carbonate chemistry as well as sulphate (and other) terminal electron acceptor supply, influencing both pCO_2 and partial pressure CH_4 (pCH_4) (Bouillon et al., 2007; Call et al., 2015). Further, Maher et al. (2015) highlighted that uncertainty in estuarine CO_2 and CH_4 emissions can be extremely high due to differences in methodology, showing that a diurnal spatial survey approach calculated a 70% lower CO_2 flux than utilising a multiple diurnal time series station approach in the same estuary.

The greatest uncertainty in calculating CO_2 and CH_4 air-sea emissions usually lies within parameterization of k. For sparingly soluble gasses like CO_2 and CH_4, k is determined by waterside turbulence (Jähne et al., 1987). Many previous studies have estimated estuarine air-sea carbon emissions using empirical models for k (Raymond et al., 1997; Wang and Cai, 2004; Borges et al., 2005; Guo et al., 2009; Laruelle et al., 2015). Within estuaries the main drivers of k utilised within these models, are wind speed, and/or current velocity, and/or water column depth. These parameters influence turbulence (and therefore k) at the air-water interface, in shallow flowing systems such as estuaries (Zappa et al., 2003; Borges et al., 2004a). Some commonly used models are based on experimental work in oceanic environments, where wind is the dominant driver of turbulence at the water-air interface (Wanninkhof, 1992; Ho et al., 2006). Others have been developed from studies in rivers and only take into account wind speed (Raymond and Cole, 2001), whilst others that are specifically developed for shallow and potentially turbulent estuaries take into account a combination of drivers such as changes in wind, depth and current speed (Borges et al., 2004a; Ho et al., 2014; Rosentreter et al., 2017). For large scale estimates, utilising an empirical k model may be the only logistically viable approach, however this results in data with high uncertainties. For accurate and site specific emissions measurements, in situ k measurements are required.

Due to the dynamic nature and changing morphology within estuaries and flowing waters, both temporal and spatial variability of k is often high (Abril et al., 2009; Lorke et al., 2015). For example, spatial sampling of k can account for changes in estuarine hydrology and morphology influencing the rate of k (i.e. changes in current, depth, wind and fetch) however this approach can exclude tidal and diurnal dynamics which are often highly variable within estuaries (Frankignoulle et al., 1996; Liu et al., 2016). Alternatively, temporal sampling accounts for the high temporal variability in k, however it lacks spatial variability (Abril et al., 2009). Whilst many studies have reduced uncertainties by measuring k in situ, uncertainties can still occur depending on the spatial and temporal sampling strategy employed as there are often compromises made between time and effort, data accuracy and site suitability. Although logistically challenging, combining both spatial and temporal sampling during field campaigns has been shown to reduce uncertainties whilst providing insight into the drivers along the estuarine salinity gradient (Borges et al., 2004b).

Aside from k, atmospheric flux rates of CH_4 and CO_2 are also related to water column CH_4 and CO_2 concentrations, which in turn are controlled by numerous drivers. Estuarine pCO_2 is driven by the complex interaction between in situ respiration and/or production, allochtonous inputs of carbon, nitrification, carbonate precipitation/dissolution, and mixing and/or buffering capacity (Hopkinson and Smith, 2005; Cole et al., 2007; Maher and Eyre, 2012; Staehr et al., 2012; Maher et al., 2015). Within estuaries, CH_4 production generally occurs under anoxic conditions within sediments and is controlled by changes in redox conditions, the availability of electron acceptors, sulphate reduction, AOM, sedimentation rates and lability of carbon source, with the atmospheric flux also influenced by the presence of vegetation, water column oxidation and changes in hydrostatic pressure (Martens et al., 1998; Martens and Berner, 1974; Knittel and Boetius, 2009; Hamdan and Wickland, 2016; Borges and Abril, 2011; Burdige, 2012).

Groundwater and porewater exchange exerts a significant control over estuarine pCO_2 and pCH_4 (Borges et al., 2003; Bouillon et al., 2007; Kim and Hwang, 2002; Santos et al., 2015; Jeffrey et al., 2016; Tait et al., 2017). Natural groundwater tracers such as radon (^{222}Rn) can provide an effective means to both qualitatively and quantitatively explain the role of porewater exchange in estuarine systems. As ^{222}Rn is a soluble noble gas continually produced within the sediments, is non-reactive and has a short half-life of 3.8 days, ^{222}Rn is an ideal tracer in estuarine environments (Burnett et al., 2001; Santos et al., 2012a). Its use has allowed several studies to identify porewater exchange as a major source of surface water CO_2 and CH_4 (Atkins et al., 2013; Maher et al., 2015; Sadat-Noori et al., 2015). Porewater exchange is especially important during low/ebb tidal cycles as the porewater seepage with high concentration dissolved inorganic carbon (DIC) and CH_4 can be released to the water column (Bouillon et al., 2007; O'Reilly et al., 2015). The overall influence of porewater exchange on estuarine surface water chemistry will be a function of the concentration of the constituents in the porewater, the porewater exchange rate, and also the volume or mean depth of the estuary. As such, estuarine pCO_2 and pCH_4 are likely to be more strongly influenced by porewater exchange in smaller, shallower systems with high porewater exchange rates.

This study aims to capture high resolution spatio-temporal CO_2 and CH_4 evasion rates and transfer velocity, whilst determining the drivers of pCO_2 and pCH_4 within an urbanised subtropical estuary. We combine direct measurements of gas emissions with empirical modelling and hypothesise there will be distinct differences in k and emissions rates, in the different hydrological and biogeochemical zones along the estuarine salinity gradient.

1.1. Study area

Field experiments were performed within the Coffs Creek estuary (30.30 °S, 153.10 °E) on the mid-coast of New South Wales, Australia (Fig. 1). The subtropical region receives a mean annual rainfall of ~1650 mm, with ~26% occurring in February and March (Bureau of Meteorology, 2017). The catchment drains an area of 24.5 km^2 with upper reaches descending 490 m to a coastal floodplain. Coffs Creek is classified as a wave dominated estuary at a mature evolutionary stage due to high rates of sediment infilling (Roy et al., 2001). The site was once classified as an intermittently closed and open lagoon system (ICOLL), however in 1987 a training wall was constructed on the northern side of the estuary. This modification increased the discharge