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Methane and carbon dioxide dynamics in a subtropical estuary over a diel cycle: Insights from automated in situ radioactive and stable isotope measurements

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ABSTRACT

Estuaries have high rates of primary production and respiration and can be hotspots for carbon dioxide and methane enriched submarine groundwater discharge. Here, we report high resolution $p\mathrm{CO_2}$, $\mathrm{CH_4}$, $\delta^{13}\mathrm{C–CO_2}$, $\delta^{13}\mathrm{C–CH_4}$ and radon ($^{222}\mathrm{Rn}$, a natural groundwater tracer) observations along North Creek estuary, Australia (S28°48′, E153°34′) during four spatial surveys over a diurnal cycle in January 2013 (summer). There were distinct tidal and diurnal differences in estuarine $p\mathrm{CO_2}$ and $\mathrm{CH_4}$, which lead to tidal differences of 3.6 fold and 5 fold in the estimated $\mathrm{CO_2}$ and $\mathrm{CH_4}$ diffusive water to air fluxes respectively, and up to a 2.4 fold difference in diurnal flux estimates of $\mathrm{CH_4}$. Carbon stable isotopes revealed tidal and diurnal differences in the source $\delta^{13}\mathrm{C}$ value of $\mathrm{CO_2}$ and $\mathrm{CH_4}$, and minor $\mathrm{CH_4}$ oxidation within the estuary. The $\mathrm{CO_2}$ outgassing rates based on the spatial surveys were different than the outgassing derived from three fixed time series stations along the estuary. There was agreement between the methods in the lower and upper estuary where $p\mathrm{CO_2}$ had a relatively low range over the study (~600 μatm and 3000 μatm respectively). However, in the mangrove surrounded mid estuary where $p\mathrm{CO_2}$ ranged from ~1450 to 11,000 μatm over a tidal cycle, fluxes estimated by the survey method were ~30% of the time series estimates. This study highlights the importance of considering tidal and diurnal variability when estimating the flux of $\mathrm{CO_2}$ and $\mathrm{CH_4}$ from estuaries, and discusses how a combination of diurnal (productivity/respiration) and tidal (groundwater/mixing) processes may drive surface water $p\mathrm{CO_2}$ and $\mathrm{CH_4}$ over short-term time scales.

1. Introduction

Atmospheric concentrations of $\mathrm{CO_2}$ have increased by approximately 40% since the industrial revolution and, concurrently, atmospheric $\mathrm{CH_4}$ concentrations have more than doubled since pre-industrial times (IPCC, 2007). There is still a paucity of data from a number of biomes to adequately constrain the global $\mathrm{CO_2}$ and $\mathrm{CH_4}$ cycles. Despite the relatively small surface area, global estuarine $\mathrm{CO_2}$ degassing is estimated to be as large as the $\mathrm{CO_2}$ uptake by the continental shelf (Borges, 2005; Borges et al., 2005; Cai, 2011), but large uncertainties remain in estimates of the global estuarine $\mathrm{CO_2}$ flux (Laruelle et al., 2010; Borges and Abril, 2011; Cai, 2011; Maher and Eyre, 2012). Even fewer estimates are available on the global estuarine $\mathrm{CH_4}$ flux (Borges and Abril, 2011; Oritz-Llorente and Alvarez-Cobelas, 2012). Difficulties in calculating global emissions of $\mathrm{CO_2}$ and $\mathrm{CH_4}$ from estuaries include the lack of empirical data on controlling factors, the high degree of spatial and temporal variability in these systems, and the lack of data in subtropical and tropical systems.

Previous studies have found high temporal and spatial variability in $p\mathrm{CO_2}$ and $\mathrm{CH_4}$ concentrations within estuarine systems (Sansone et al., 1999; Middelburg et al., 2002; Chen et al., 2008; Macklin et al.,2014). However it has generally been observed that estuarine systems are net sources of $\mathrm{CO_2}$ and $\mathrm{CH_4}$ to the atmosphere. Typically $p\mathrm{CO_2}$ and dissolved $\mathrm{CH_4}$ concentrations are measured during a spatial survey or at fixed time series stations, however these sampling strategies may not adequately measure the high degree of both spatial and temporal variability often found in estuarine systems. Fixed time series measurements using automated instrumentation (e.g. Atkins et al., 2013) capture temporal variability extremely well, with the resolution of measurements typically at the scale of minutes. However the measurements are restricted to a single location, preventing assessment of spatial variation. Survey methods using continuous underway measurements or discrete sampling offer the advantage of determining spatial variation, and are therefore the most commonly utilized method for estimating estuary-wide fluxes. However single surveys do not capture variability induced by diel and tidal cycles, which may be significant. For example

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CO_2 and CH_4 concentrations in mangrove creeks and marshes can vary by up to an order of magnitude over a tidal cycle (e.g. Borges et al., 2003; Wang and Cai, 2004; Bouillon et al., 2007; Gatland et al., 2014), and significant diel variability in pCO_2 and CH_4 concentrations driven by photosynthesis and respiration has been observed in estuarine macrophyte beds (Maher et al., 2013b; Saderne et al., 2013). Therefore, careful consideration of diel and tidal effects upon pCO_2 and CH_4 concentrations need to be assessed when calculating whole system fluxes.

A combination of factors may drive the diurnal and tidal variation of CO_2 and CH_4 fluxes in estuaries. Estuaries can have high productivity and respiration rates (Kemp et al., 1997; McGlathery et al., 2001; Middelburg and Herman, 2007; Maher and Eyre, 2012) which influence pCO_2 on diurnal scales through the uptake (photosynthesis) and release (respiration) of CO_2 during day and night periods, respectively. Diel cycles may also influence surface water CH_4 concentrations, with previous studies finding light-induced inhibition of CH_4 oxidation rates in freshwater lakes (Murase and Sugimoto, 2005; Tang et al., 2014). In addition, productivity and respiration driven cycles of sediment oxygen dynamics may lead to oscillation in aerobic methane oxidation and methane production rates (King et al., 1990; Maher et al., 2013b), and methylated substrates produced by phytoplankton have been shown to sustain aerobic CH_4 production in the ocean (Karl et al., 2008).

The actions of tides can deliver groundwater enriched in solutes through tidal pumping, directly influencing surface water pCO_2 and CH_4 (Borges et al., 2003; Dulaiova et al., 2006; Bouillon et al., 2007; Kristensen et al., 2008; Dorsett et al., 2011; Atkins et al., 2013). In addition, groundwater can deliver dissolved organic matter (Santos et al., 2008; Bauer and Bianchi, 2011) and nutrients (Gleeson et al., 2013; Charbonnier et al., 2013; Santos et al., 2013; Makings et al., 2014) to surface waters, which may indirectly influence pCO_2 through enhanced autotrophic and/or heterotrophic metabolism. Therefore calculations of estuarine air–water CO_2 and CH_4 fluxes determined by surveys of surface water pCO_2 and CH_4 that do not capture tidal and diurnal variability may produce inaccurate estimates.

Determining the major drivers of estuarine surface water pCO_2 and CH_4 involves disentangling the various tidal and diel processes. Recent development of cavity ring-down spectroscopy (CRDS) for high resolution in situ measurements of $\delta^{13}C–CO_2$ and $\delta^{13}C–CH_4$ may help constrain the source $\delta^{13}C$ value of the dissolved CO_2 and CH_4 pools (Bass et al., 2013; Maher et al., 2013b; Gatland et al., 2014), thereby giving insights into the processes controlling surface water pCO_2 and CH_4 concentrations. For example, respiration will produce CO_2 with a similar $\delta^{13}C$ to the organic matter source (Lin and Ehleringer, 1997), and the dominant CH_4 production pathways produce CH_4 with differing $\delta^{13}C$ values (Whiticar et al., 1986). In addition, development of high precision continuous measurement of in situ ^{222}Rn (a natural groundwater tracer with a half-life of 3.84 days) now enables qualitative and quantitative assessment of groundwater input to estuaries (Dulaiova et al., 2005; Peterson et al., 2010). By combining simultaneous measurements of surface water ^{222}Rn, pCO_2, CH_4, and $\delta^{13}C–CO_2$ and $\delta^{13}C–CH_4$ insights into the contribution of biological (e.g. primary production/respiration) versus hydrological (e.g. groundwater and surface runoff) drivers of surface water CO_2 and CH_4 concentrations can be gained.

We hypothesize that estimates of CO_2 and CH_4 fluxes from estuaries will vary significantly over diurnal and tidal cycles, due to tidal pumping and ecosystem metabolism. We tested this hypothesis by undertaking four surveys over a 24 hour period along a small shallow estuary making continuous underway measurements of ^{222}Rn, pCO_2, pCH_4, $\delta^{13}C–CO_2$ and $\delta^{13}C–CH_4$ along with other physico-chemical parameters (wind speed, temperature, dissolved oxygen, chromophoric dissolved organic matter, chlorophyll a, and alkalinity). In addition three fixed time series stations were simultaneously deployed along the length of the estuary measuring pCO_2 and ^{222}Rn to compare water to air flux estimates and temporal variability in concentrations between the survey and the fixed time series method.

2. Methods

2.1. Study site

North Creek is a small subtropical estuary located on the North Coast of New South Wales, Australia (Fig. 1). The estuary is shallow (average depth ~2 m) and well mixed with a tidal range of ~2 m. The region has a mean annual rainfall of 1863 mm with the wetter months occurring over summer and autumn. Intense rain events associated with tropical low-pressure systems contribute a majority of this rain to the catchment (Eyre and Pont, 2003). The hydrology of North Creek has been modified significantly in the last 100 years, through extensive drainage of wetland areas, which have been converted to agricultural land. An extensive drainage network including floodgates was constructed to facilitate drainage and prevent tidal inundation (King, 2003). Groundwater has been found to account for up to ~76% of surface waters of the upper reaches of North Creek (Atkins et al., 2013), but earlier investigations did not assess the mid and lower estuarine sections.

For the purposes of this study, the estuary was divided into three zones (Fig. 1). The first zone, the lower estuary, comprises of large marine influenced tidal flats. Land usage is largely residential, with the city of Ballina (population ~8000) surrounding the lower estuary. Riparian vegetation is largely absent however there are small patches of remnant mangrove, salt marsh and river-flat forest communities. The mid-reaches (hereafter termed mid-estuary) is located within Ballina Nature Reserve, with an intact riparian zone of mangrove and swamp sclerophyll forests (King, 2003). The upper reach (hereafter termed upper estuary) is highly modified. It has been straightened to provide drainage for agriculture (predominantly sugar cane cultivation) and is generally devoid of riparian vegetation.

2.2. Spatial survey

Four spatial surveys were conducted over two consecutive tidal cycles starting on the 15th of January 2013. A boat was driven at 5–6 $km\ h^{-1}$ along North Creek with surveys starting during the two low (pre-dusk and pre-dawn) and two high tides (~midday and ~midnight) to investigate tidal and diurnal influences on pCO_2 and CH_4 concentrations. Water was pumped continuously from a depth of ~0.5 m at a flow rate of ~3 $L\ min^{-1}$ using a Rule™ bilge pump to a showerhead equilibrator, and ^{222}Rn, CO_2 and CH_4 were measured in a dried closed gas loop using the system described in Santos et al. (2012). ^{222}Rn was measured at 10 minute intervals using a RAD7 radon detector. The RAD7 uses a silicon semi-conductor to count the positively charged ^{218}Po and ^{214}Po daughters. Dissolved ^{222}Rn concentrations were then calculated using the temperature and salinity function of solubility (Schubert et al., 2012). pCO_2, pCH_4, $\delta^{13}C–CO_2$ and $\delta^{13}C–CH_4$ were measured from the same gas stream using a cavity ring down spectrometer (CRDS, Picarro G2201-*i*) at ~1 second intervals and then averaged over 1 minute intervals (Maher et al., 2013b). The xCO_2 and xCH_4 (i.e. dry CO_2 and CH_4 concentrations measured by the CRDS) were converted to in situ pCO_2 and CH_4 using standards equations (Pierrot et al., 2009) with pCH_4 converted to concentrations using the solubility coefficients of Yamamoto et al. (1976).

Four calibration gases (two CO_2 and two CH_4) were analyzed prior to each survey. CO_2 standards had a concentration of 306 ppm ($\delta^{13}C–CO_2 = -14.4‰$) and 2017 ppm ($\delta^{13}C–CO_2 = -17.1‰$) with the $\delta^{13}C$ values referenced using an Isotope Ratio Mass Spectrometer (IRMS) which was referenced to NIST certified standards. CH_4 standards had a concentration of 3 ppm ($\delta^{13}C–CH_4 = -45.9‰$) and 200 ppm ($\delta^{13}C–CH_4 = -40.1‰$). The $\delta^{13}C–CH_4$ values of the standards were obtained by running the standards through a factory calibrated CRDS, and were later referenced against certified standards obtained from Isometric