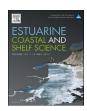
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# CO<sub>2</sub> emissions from a temperate drowned river valley estuary adjacent to an emerging megacity (Sydney Harbour)



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#### ABSTRACT

The Sydney Harbour Estuary is a large drowned river valley adjacent to Sydney, a large urban metropolis on track to become a megacity; estimated to reach a population of 10 million by 2100. Monthly underway surveys of surface water pCO<sub>2</sub> were undertaken along the main channel and tributaries, from January to December 2013. pCO<sub>2</sub> showed substantial spatio-temporal variability in the narrow high residence time upper and mid sections of the estuary, with values reaching a maximum of 5650 µatm in the upper reaches and as low as 173 µatm in the mid estuary section, dominated by respiration and photosynthesis respectively. The large lower estuary displayed less variability in pCO2 with values ranging from 343 to 544 µatm controlled mainly by tidal pumping and temperature. Air-water CO<sub>2</sub> emissions reached a maximum of 181 mmol C  $m^{-2}$   $d^{-1}$  during spring in the eutrophic upper estuary. After a summer high rainfall event nutrient-stimulated biological pumping promoted a large uptake of CO2 transitioning the Sydney Harbour Estuary into a CO<sub>2</sub> sink with a maximum uptake of rate of -10.6 mmol C m<sup>-2</sup> d<sup>-1</sup> in the mid-section of the estuary. Annually the Sydney Harbour Estuary was heterotrophic and a weak source of  $CO_2$  with an air-water emission rate of 1.2–5 mmol C m<sup>-2</sup> d<sup>-1</sup> (0.4–1.8 mol C m<sup>-2</sup> y<sup>-1</sup>) resulting in a total carbon emission of around 930 tonnes per annum. CO<sub>2</sub> emissions (weighted m<sup>3</sup> s<sup>-1</sup> of discharge per km<sup>2</sup> of estuary surface area) from Sydney Harbour were an order of magnitude lower than other temperate large tectonic deltas, lagoons and engineered systems of China, India, Taiwan and Europe but were similar to other natural drowned river valley systems in the USA. Discharge per unit area appears to be a good predictor of CO<sub>2</sub> emissions from estuaries of a similar climate and geomorphic class.

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#### 1. Introduction

Estuaries link the land and ocean water carbon cycles creating a highly reactive zone where organic matter is rapidly processed, resulting in high air-water carbon dioxide (CO<sub>2</sub>) emissions (Cai, 2011). The importance of air-water CO<sub>2</sub> emissions from estuaries was convincingly demonstrated with a large European data-set by Frankingnoulle et al. (1998). More recently it has been highlighted that estuarine emissions of CO<sub>2</sub> to the atmosphere are significant compared to other components of the global carbon cycle (Borges et al., 2005; Borges and Abril, 2011). Air-water CO<sub>2</sub> emissions from estuaries are highly variable due to differences in the processing of carbon in individual estuaries, as well as in distinct sections of the estuary. A review 165 estuaries found that upper

estuaries with salinities of less than two were a strong source of  $CO_2$  (39 ± 56 mol C m<sup>-2</sup> y<sup>-1</sup>), with mid estuaries a moderate source  $(17.5 \pm 34 \text{ mol C m}^{-2} \text{ y}^{-1})$  and lower estuaries with salinities of more than 25 a weak source of  $CO_2$  (8.4  $\pm$  14 mol C m<sup>-2</sup> y<sup>-1</sup>; Chen et al., 2013). The total annual emission of CO<sub>2</sub> from the world's estuaries from several recent syntheses (Regnier et al., 2013; Chen et al., 2013; Cai, 2011; Bauer et al., 2013) was estimated to be 0.10 to  $0.25 \text{ Pg C y}^{-1}$ . However,  $CO_2$  data are too sparse and unevenly distributed to provide good global coverage and large uncertainties remain (Laruelle et al., 2014). These estimates are generally biased by measurements from highly engineered and polluted estuaries of the Northern Hemisphere, poor representation from the Southern Hemisphere and no Australian estuaries have been included. In addition, of the 165 estuaries in the budget of Chen et al., 2013, 10% of the data are classified as minor estuary types (lagoons, ponds, creeks and streams) and 5% from high latitude fjords. With the major focus of previous studies having been on small scale riverdominated estuaries (Joesoef et al., 2015) there has been less

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research on CO<sub>2</sub> dynamics in large estuaries and bay systems (Dinauer and Mucci, 2017) including the larger geomorphic estuary classes of tectonic and drowned river valley systems, the most common type of estuary in temperate climates (Pritchard, 1967). The air-water CO<sub>2</sub> emissions from only three estuaries adjacent to megacities have been included in global estuarine CO<sub>2</sub> emissions, the Pearl (Guangzhou), Yangtze (Shanghai) and Hudson River (New York), with the Hudson being the only temperate, drowned river valley system adjacent to a megacity. In addition, when comparing the magnitude of emissions between estuaries globally large discrepancies can emerge depending on the gas transfer model used (Borges et al., 2004; Macklin et al., 2014). Properly constraining the gas transfer velocity in estuaries is important, as this is the largest source of error in the computation of air-sea CO<sub>2</sub> emissions (Raymond and Cole, 2001) but this is difficult due to their hydrodynamic and geomorphic complexity (Abril et al., 2000).

Very little is known about  $CO_2$  emissions from Australian estuaries (Gillanders et al., 2011). There was a small net uptake of -0.4 to -2.0 mmol m<sup>-2</sup> d<sup>-1</sup> of  $CO_2$  in three warm temperate east Australian estuaries driven by net autotrophic production (Maher and Eyre, 2012). In contrast, there was a very high water column  $pCO_2$  (19,801  $\mu$ atm) and a large emission of  $CO_2$  (up to 252.1 mmol m<sup>-2</sup> d<sup>-1</sup>) from a river dominated estuary draining an acidic wetland (Ruiz-Halpern et al., 2015). A hypersaline bay with restricted circulation in Western Australia was a weak emitter of  $CO_2$  (2.0 mmol m<sup>-2</sup> d<sup>-1</sup>; Smith and Atkinson, 1983) as was a subtropical estuary in South East Queensland (0.2 mmol m<sup>-2</sup>d<sup>-1</sup>; Adiyanti et al., 2016). Clearly, there is a large spatial variability in  $CO_2$  emissions from different types of Australian estuaries, and little is known about the large drowned river valley systems.

Sydney Harbour estuary is located in the Southern Hemisphere adjacent to Australia's most populated city and is one of the world's largest natural harbours. The temperate climate of the region is highly variable and subject to episodic high rainfall events. The estuary has the classic funnel shape geomorphology of a large drowned river valley system. It has long been known as a sheltered harbour with weaker wind speeds throughout the narrow upper reaches due to complex topographic sheltering and stronger winds developing over the wider well-flushed lower estuary (Spark and Connor, 2004). The three upper estuaries (Parramatta River, Lane Cove River and Middle Harbour) are narrow and irregular with several branching tributaries (Roy, 1984). These narrow channels emerge into the much larger seawater end known as Port Jackson that deepens and widens toward the mouth forming a characteristic triangular funnel shape with an exponential increase of the cross-section seaward (Pritchard, 1967) that amplifies tidal flushing with water from the coastal zone (Fig. 1).

With a small catchment to estuary surface area ratio (10:1) and no permanent rivers entering the system under normal moderate to low rainfall conditions a large percentage of the nutrients carried in freshwater runoff from the urbanised areas is discharged and retained in the narrow channels of the upper estuary sections promoting eutrophication (Jeffries et al., 2016). Excess nutrients delivered to estuaries from urban run-off can either enhance CO<sub>2</sub> emissions (Frankingnoulle et al., 1998; Sarma et al., 2012) or CO<sub>2</sub> uptake (Gypens et al., 2009; Cotovicz et al., 2015). There have been no previous studies of surface water  $pCO_2$  or  $CO_2$  emissions in Sydney Harbour.

High resolution surveys of surface water  $pCO_2$ , chlorophyll-a (Chl-a), dissolved oxygen, pH, salinity, temperature and wind speed were undertaken in the Sydney Harbour Estuary.  $CO_2$  airwater emissions from the were also quantified and compared with other large temperate estuaries using appropriate gas model equations. Our hypotheses were that (1) the Sydney Harbour Estuary would be a small net source of  $CO_2$  due to low river inflows,

weak wind speeds, high primary production and classic funnel shaped drowned river valley geomorphology (2) CO<sub>2</sub> emissions in the Sydney Harbour Estuary would be enhanced by organic enrichment in runoff after high rainfalls due to enhance water column respiration (3) the highest CO<sub>2</sub> emissions would be in the upper estuary sections due to the influence of urbanisation and (4) that discharge per unit catchment area would be a good predictor of CO<sub>2</sub> emissions from estuaries.

#### 2. Material and methods

#### 2.1. Study site

The Sydney Harbour Estuary is on the south-eastern Australian coast extending across the largest metropolitan and most densely populated region of the country, which is predicted to reach 10 million people by 2100 (5 million currently)(Fig. 1). The estuary is a semi-diurnal microtidal system with generally low freshwater inputs as no large rivers enter the system (Lee et al., 2011; Das et al., 2000). The rainfall regime is characterised by mainly dry conditions punctuated by infrequent, high-rainfall events (>50 mm/day). Development has altered the Sydney catchment dramatically with 86% urbanised (Lee et al., 2011), which creates extensive impervious surfaces. Together with wide-ranging sewerage and stormwater drains the area of low or zero soil infiltration capacity has increased leading to the acceleration of water transmission to river channels and increased incidence of sewer overflows and stormwater contamination (Hose et al., 2006). The catchment comprises extensive areas of parkland in the Lane Cove River Valley and Garigal National park in Middle Harbour. The Sydney Harbour Estuary study area has a low catchment to water surface area ratio (10:1) draining a combined catchment area of only 500 km<sup>2</sup> into a water surface area of over 50 km<sup>2</sup>. Notably 70% of the freshwater flow is discharged into the very narrow channels of the upper estuary sections that cover an area of only 2 km<sup>2</sup> (4%) of the total estuary surface area.

#### 2.2. Field surveys

A total of 12 monthly field excursions were completed along the waterways of the Sydney Harbour Estuary and its tributaries during 2013 with supplementary sampling undertaken in August and October 2015 due to instrument failure during these months in 2013. Rainfall and runoff was similar in August and October in 2013 and 2015. Sampling was conducted underway with instrumentation deployed from a 5.7 m, centre console research vessel that was driven at a steady 4–6 km/h along the longitudinal axis of the estuary and up each of the main tributaries to the weir barrier or tidal limits.

Sampling started from the outer harbour in the morning and then travelled up the more restricted channels of the tributaries. The vessel location and other parameters were logged continuously while underway using a hand held Garmin GPS (extrex) and a YSI (Yellow Springs Instruments, Model 6600 V2) multiparameter sonde in a flow-thru cell. The YSI was the primary instrument used for sampling temperature (temp), salinity (sal), chlorophyll-a (Chla), dissolved oxygen saturation (OSat)(%) and pH (National Bureau Standard, NBS scale), with the sampling interval set to 10 s. The YSI probes were calibrated in accordance with the manufacturer's specifications (www.ysi.com) before each sampling operation. At 12 sampling locations along the harbour vertical profiles of temperature, salinity, pH, OSat, Chl-a and turbidity were also measured using a YSI 6600 multiparameter sonde. These stations were used to cross check the underway data. Additional discrete samples of Chl-a were taken for spectrophotometric analysis, which were used

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