Mangrove outwelling is a significant source of oceanic exchangeable organic carbon

James Z. Sippo,¹,²* Damien T. Maher,¹,² Douglas R. Tait,¹,² Sergio Ruiz-Halpern,¹ Christian J. Sanders,¹,² Isaac R. Santos¹,²

¹School of Environment, Science and Engineering, Southern Cross University, Lismore, 2480 Australia; ²National Marine Science Centre, Southern Cross University, Coffs Harbour, New South Wales 2450, Australia

Exchangeable dissolved organic carbon (EDOC) consists of volatile and semi volatile organic compounds which are globally ubiquitous carbon species and play an important role in atmospheric chemistry. However, no studies have quantified EDOC outwelling from mangrove forests, in spite of these systems contributing >10% of the terrestrially derived dissolved organic carbon (DOC) to the ocean. By measuring EDOC and DOC outwelling from a mangrove tidal creek and concentrations in mangrove forests over a large latitudinal gradient (26°), we found that EDOC makes up ~13% of the DOC pool, and that mangroves may export 3.1 Tg C yr⁻¹ of EDOC to the coastal ocean. These results highlight that outwelling from mangroves may be a major, yet previously overlooked source of EDOC to the ocean.
for atmospheric hydroxyl radicals, and a major source of secondary organic aerosols to the atmosphere (Gantt et al. 2009; Carpenter et al. 2012).

The exchange of VOCs and SOCs occurs between oceans and atmosphere where the ocean can act as both a source and as sink of anthropogenic and biogenic VOC and SOC compounds (Dachs et al. 2005; Ruiz-Halpern et al. 2010; Gonzalez-Gaya et al. 2016). The estimated VOC evasion from the ocean surface to the atmosphere is 4.9–5 Tg C a⁻¹ (Guenther et al. 1995; Ehhalt 2001). However, these estimates are based largely on the exchange of major compounds and may not account for a significant fraction of VOCs and SOCs present in the atmosphere or ocean (Goldstein and Galbally 2003; Exton et al. 2015). However, there are no studies examining the lateral exchange of EDOC at the land-ocean interface.

Mangrove forests are recognized as the largest store of carbon in the coastal zone and are amongst the most productive ecosystems on earth (Bouillon 2011; Breithaupt et al. 2012). Mangrove forests contribute >10% of terrestrially derived DOC flux to the ocean (Dittmar et al. 2006). This contribution does not include EDOC because the analytical methods used to measure DOC normally acidify samples and purge inorganic carbon prior to measurement of DOC. This procedure also removes VOCs and SOCs from water samples. As a result, previous DOC exchange estimates in mangroves (e.g., Bouillon et al. 2007; Maher et al. 2013) have not taken into account the contribution of EDOC.

Here, we report EDOC and DOC observations in six pristine mangrove tidal creeks along a latitudinal gradient to assess whether mangrove forests export EDOC to the coastal ocean, and whether VOCs make a significant contribution to the mangrove DOC pool. We also investigate whether pore-water exchange is a major source of EDOC to surface mangrove waters.

**Methods**

**Study sites**

The study was undertaken in six pristine mangrove tidal creeks on the northern, eastern, and southern Australian coastlines over a latitudinal range from 12°S to 38°S (Table 1; Table 1. Site description identifying the predominant mangrove species at the six study sites in Australia.

| Site                  | Description                                                                 | Latitude | Longitude | Mangrove species                                                                 | Dominant species                                                                 |
|-----------------------|------------------------------------------------------------------------------|----------|-----------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Darwin                | Sadgroves Creek within Darwin Harbour, Northern Territory                     | −12.441°| 130.860°  | 36                                                                              | Avicennia marina, Aegiceras corniculatum, Bruguiera gymnorrhiza and Centopras australis |
| Hinchinbrook Island   | Coral Creek on Hinchinbrook Island, Great Barrier Reef (GBR), Queensland     | −18.244°| 146.228°  | 29                                                                              | Rhizophora stylosa                                                              |
| Seventeen Seventy     | Tom’s Creek near Seventeen Seventy, Queensland                               | −24.190°| 151.876°  | 13                                                                              | A. marina and R. stylosa                                                       |
| Jacobs Well           | Unnamed tidal creek in southern Moreton Bay, Queensland                      | −27.783°| 153.375°  | 7                                                                               | A. marina, A. corniculatum, B. gymnorrhiza and R. stylosa.                      |
| Newcastle             | Dunns Creek near Newcastle, New South Wales                                  | −32.850°| 151.767°  | 3                                                                               | A. marina                                                                      |
| Barwon Heads          | An unnamed tidal creek on Barwon River, south west Melbourne, Victoria       | −38.262°| 144.496°  | 1                                                                               | A. marina                                                                      |
Fig. 1. The six study sites were in tidal creeks of pristine mangrove forests over a 26° latitudinal gradient in Australia. Site characteristics are included where Temp is average annual air temperature (°C), Rainfall is average annual rainfall (mm), Area is catchment area of tidal creeks (ha) and Tide is tidal range (m).

Fig. 1). All study sites had low lying topography with maximum elevations below 5.5 m Australian Height Datum and no obvious source of riverine input. Therefore, the creeks received no apparent freshwater input other than direct rainfall and it is assumed that any changes in water chemistry are related to processes occurring within the mangrove intertidal flat rather than influences from upstream freshwater inputs. This study builds on recent investigations at the same sites focusing on pore-water exchange (Tait et al. 2016), alkalinity and dissolved inorganic carbon exchange (Sippo et al. 2016), nitrous oxide fluxes (Maher et al. 2016), trace metal fluxes (Holloway et al. 2016), and system scale carbon stock estimates (Sanders et al. 2016).

**Sampling and analysis**

Surface-water EDOC and DOC concentrations, were measured at hourly intervals over 25 h periods (i.e., two tidal cycles) near the mouth of the tidal creek at all sites. At the Moreton Bay site, a more intensive sampling campaign was conducted to quantify exchange with the coastal ocean and air water fluxes. EDOC, GOC, and DOC concentrations were measured hourly over three 25-h periods for the duration of a spring-neap-spring cycle (~15 days). All six sites were sampled during their respective dry season in 2014, i.e., during the winter for the three low latitude sites and during the summer for the three high latitude sites.

VOC is operationally defined as EDOC in the water phase and as GOC in the air phase (Dachs et al. 2005). EDOC concentrations were measured from 1 L of water added to an acid cleaned bottle following Dachs et al. (2005) and Ruiz-Halpern et al. (2010). Briefly, water samples were purged by recirculating air in the dead volume of the sample bottle and Teflon tubing. The gas stream containing the exchangeable VOC was redissolved in duplicate precombusted 40 mL borosilicate vials containing acidified (pH < 2 to ensure no inorganic carbon adsorption) milliQ water. The air stream returned to the sampling bottle in a closed loop. Exchange of EDOC from the water sample was enhanced through continuous bubbling via a glass frit in the sample bottle. Samples were then stored in the dark at 4°C until analyses.

GOC concentrations were measured as GOC H⁻¹ (that is the equilibrium concentration of GOC), therefore, avoiding the need to calculate the Henry’s law constant (H) for each compound, which are unknown (see Dachs et al. 2005 and Ruiz-Halpern et al. 2010 for a detailed explanation). At the Moreton Bay Site, samples were taken at 3–4 h intervals and interpolated to hourly intervals near the mouth of the tidal creek. No GOC H⁻¹ data was available for the other five sites. GOC H⁻¹ concentrations were measured by equilibrating acidified milliQ with the atmosphere. Atmospheric air was pumped through duplicate precombusted 40 mL borosilicate vials containing acidified milliQ water for 25 min using an oil-free diaphragm pump. DOC samples were collected with a 40-mL sample rinsed polypropylene syringe, and filtered through GFF filters into precombusted borosilicate vials.

The samples were kept cool and in the dark until analysis using a TOC analyser (TOC-VCPH; Shimadzu). The vials were analyzed as for DOC (NPOC method, Spyres et al. 2000) but with the purging step eliminated. Following this analysis, the same samples were analyzed for DOC and TIC to check for contamination. If DOC and/or inorganic carbon
contamination was detected, it was subtracted from the VOC measurement. DOC reference standards (2 μmol L$^{-1}$ and 44 μmol L$^{-1}$; Hansell Lab, University of Miami) were run throughout each analysis (CV = 1.5%). Methods for measuring estuarine water depth, water temperature, wind speed, salinity, and current velocity methods and data are reported in a companion paper (Sippo et al. 2016).

Pore-water samples were collected from ~12 sites within the catchment of each tidal creek. Samples were taken by digging bores with a hand auger to a depth of ~30 cm below the water table. Water within the bore was purged three times using a peristaltic pump. EDOC and DOC samples were then taken from the bottom of the bore into 1 L Schott bottles (EDOC), or by using a syringe with the sample filtered through GFF filters into precombusted 40 mL borosilicate vials (DOC). Samples were treated and analyzed as described earlier for surface-water samples.

### Atmospheric evasion

Air-water VOC flux values were calculated according to:

$$F = k(EDOC - GOC) H^{-1}$$

(1)

where $F$ is the flux value (mmol m$^{-2}$ d$^{-1}$), $k$ is the gas transfer velocity (m d$^{-1}$), EDOC and GOC H$^{-1}$ are the exchangeable organic carbon concentration in the water, and the atmospheric equilibrium concentration, respectively. Positive values indicate a flux from water to the atmosphere while negative values indicate a flux from the atmosphere to water.

The gas transfer velocity ($k$) was calculated using a combination of empirically derived $k$ models which integrate wind speed, current velocity, and depth, which was developed in tidal mangrove forests using a deliberate gas tracer experiment (Ho et al. 2014) and used in several recent mangrove gas flux papers (Call et al. 2015; Maher et al. 2016; Sippo et al. 2016, Rosentreter et al. 2016). The equation merges the reaeration coefficient determined by O’Connor and Dobbs (1958) using depth and current velocity, with the wind-driven $k$ parameterization of Raymond and Cole (2001):

$$k_{600} = (1.58 e^{-3u}) + (1.539 v^{0.5} h^{-0.5})$$

(2)

where $k_{600}$ is the gas transfer velocity (cm h$^{-1}$) normalized to a Schmidt number of 600, $u$ is the wind speed at a height of 10 m (m s$^{-1}$), $v$ is the water velocity (cm s$^{-1}$), and $h$ is water depth (m). $k_{600}$ values were corrected to the in situ Schmidt number assuming a molecular weight of VOC of 120 g mol$^{-1}$ (see Dachs et al. 2005 for further details). Evasion was calculated only for the Moreton Bay system because atmospheric VOC H$^{-1}$ data were unavailable for the other five mangrove creeks.

### Outwelling estimates

Oceanic exchange rates were calculated in mmol m$^{-2}$ day$^{-1}$ at Moreton Bay where atmospheric evasion rates were also available. A digital elevation model (DEM) of the creek catchment was constructed with LiDAR data (1 m resolution ± 0.2 m elevation accuracy). Change of water volume within the catchment was calculated using the DEM and ARC GIS Hydrology toolbox (Maher et al. 2013). Concentrations of EDOC and DOC were multiplied by the change in water volume over the hourly sampling interval, integrated over two tidal cycles and normalized to catchment area and the duration of the study to give an export rate in mmol m$^{-2}$ (catchment area) d$^{-1}$.

### Results and discussion

#### Drivers of EDOC concentrations

Surface-water EDOC concentrations averaged 34 μM (range = 14–82 μM) across the six sites, with the highest concentrations occurring at lower latitude sites (Fig. 2). Pore-water EDOC concentrations were similar to surface waters, averaging 35 (range = 11–154) μM across the six sites, decreasing at higher latitudes. These average concentrations are similar to EDOC concentrations observed in the open ocean (30 ± 6 μM in spring and ~36 μM in fall) (Dachs et al. 2005), although with much higher variability. The mean surface-water DOC concentration was 279 μM (range = 84–478 μM) across the sites while the mean DOC concentration in pore water was 1155 μM (range = 332–3430 μM) and were 2- to 13-fold higher than those in respective surface waters at the six sites (Fig. 2). No clear tidal trends were observed at five out of the six sites, so average concentrations only are reported in Fig. 2.

We anticipated that pore-water inputs would be a major driver of mangrove EDOC exports, similar to DOC and DIC (Bouillon et al. 2007, Maher et al. 2013), and alkalinity exports (Sippo et al. 2016). Despite significant pore-water exchange reported at the sites (2.1–35.5 cm d$^{-1}$, Tait et al. 2016) and consistent inverse relationships between water depth and EDOC concentrations (Fig. 4), mean pore-water EDOC concentrations were lower than surface waters at five of the six sites (Fig. 2). Therefore, pore-water exchange is unlikely to be a major source of surface-water EDOC in mangroves.

Temperature and light have been identified as environmental controls of biogenic hydrocarbon emissions from plant leaves (Guenther et al. 1995; Fuentes et al. 2000; Laothawornkitkul et al. 2009). However, temperature did not follow a clear trend with latitude due to the seasonality of the study (i.e., the three low latitude sites were sampled in the winter and the three high latitude sites were sampled in the summer), explaining the weak correlation between temperature and EDOC (Fig. 3). Although this is the first estimate of EDOC dynamics in mangroves, clearly the lack of
seasonal data must be considered when interpreting these findings. However, mean temperatures range 29–16°C over the 26° latitude, which is a much greater difference than the variability of mean annual minimum and maximum temperatures at each site (Fig. 1).

Above ground plant biomass had the highest positive correlation to EDOC ($r^2 = 0.91$) and offers the best explanation to the latitudinal trend in EDOC concentrations (Fig. 3). Average annual temperatures also strongly correlated with EDOC concentrations ($r^2 = 0.89$), yet this is likely because

Fig. 2. Box plots of surface-water EDOC and DOC in surface waters and pore waters of six Australian mangrove dominated tidal creeks, ordered from low latitude on the left to high latitude on the right. The central horizontal line represents the median, the box represents the upper and lower quartiles, and the whiskers represent the maximum and minimum values excluding outliers, i.e., black dots. Sample size > 25 at each site.

Fig. 3. Correlations of mean EDOC concentrations (n > 25 at each site) at the six study sites vs. (a) degrees latitude, (b) above ground plant biomass* (c) mean water temperature, (d) mean annual air temperature, and (e) DOC concentrations (n > 25 at each site). *Above ground plant biomass data is sourced from Sanders et al. (2016). Error bars indicate standard error (SE).
temperature is a significant driver of plant biomass (Hutchison et al. 2014; Sanders et al. 2016). Vegetation is the largest source of VOCs to the atmosphere (Guenther et al. 1995; Ehhalt et al. 2001) and VOCs are emitted from all parts of a plant (Laothawornkitkul et al. 2009). We suggest that leaching of EDOC primarily through mangrove roots and submerged pneumatophores is the major source of EDOC to creek waters, and, therefore, water column concentrations and exchange rates are coupled to biomass. However, while mangrove biomass does not vary over seasons, the specific mechanism of EDOC release has not been constrained and may be seasonal, e.g., due to seasonal variability in productivity and respiration. Further, processes not considered by this study such as EDOC production by phytoplankton or benthic microalgae may also be controlling EDOC concentrations in mangrove creek waters.

**EDOC exchange with the coastal ocean and atmosphere**

At Moreton Bay where atmospheric GOC concentrations were available, the EDOC flux between water and air averaged 0.6 mmol m\(^{-2}\) d\(^{-1}\). The creek ranged from a sink of atmospheric EDOC at mid tide (−4.0 mmol m\(^{-2}\) d\(^{-1}\)) to a source at neap tide (5.3 mmol m\(^{-2}\) d\(^{-1}\)). Overall, the net exchange of EDOC between mangrove water and air was a small source to the atmosphere (0.6 ± 4.7 mmol m\(^{-2}\) d\(^{-1}\)). However, there was an oscillation between the source and sink of EDOC to the atmosphere over individual tidal cycles and over the spring neap cycle (Fig. 4). Water depth was correlated to EDOC concentrations during spring tide (\(r^2 = 0.74\)), mid tide (\(r^2 = 0.39\)), and neap tide (\(r^2 = 0.42\)), where low tides had the highest flux from water to air throughout the study. Observations in a subarctic fjord, a Mediterranean bay and the Antarctic were similar in both magnitude and direction, with EDOC flux oscillating between production and uptake (Ruiz-Halpern et al. 2014a, b).

Our study provides a first estimate of EDOC exchange between pristine mangrove forests and the coastal ocean and atmosphere. Mean lateral EDOC export to the coastal ocean was 4.7 ± 1.9 mmol m\(^{-2}\) d\(^{-1}\), equivalent to 11.6% ± 6.1% of the calculated DOC exports (Table 2) and ~6% of DIC exports (83 mmol m\(^{-2}\) d\(^{-1}\) calculated from the same creek by Sippo et al. (2016). Our estimates of DOC exports (average 42.1 ± 6.7 mmol m\(^{-2}\) d\(^{-1}\)) were at the high end of previous estimates for mangroves (e.g., see Adame and Lovelock, 2011). The ratio of EDOC to DOC concentrations observed across the six sites showed low variability (EDOC = 13% ± 4% of DOC) with a trend of increasing ratio with decreasing latitude.

**Table 2.** Carbon exchange between mangrove tidal creek waters and the atmosphere and coastal ocean over spring to neap tidal cycles at Moreton Bay.

| Tide  | Air-water EDOC flux (mmol m\(^{-2}\) d\(^{-1}\)) | Tidal EDOC exchange (mmol m\(^{-2}\) d\(^{-1}\)) | Net EDOC exchange (mmol m\(^{-2}\) d\(^{-1}\)) | DOC exchange (mmol m\(^{-2}\) d\(^{-1}\)) | EDOC % of DOC exchange |
|-------|----------------------------------------|----------------------------------|----------------------------------|----------------------------------|--------------------------|
| Spring | 0.5                                    | 6.8                              | 7.3                              | 37.0                             | 18.4                     |
| Mid   | −4.0                                   | 3.2                              | −0.8                             | 49.7                             | 6.4                      |
| Neap  | 5.3                                    | 4.0                              | 9.3                              | 39.8                             | 10.1                     |
| Average | **0.6 ± 4.7**                          | **4.7 ± 1.9**                    | **5.3 ± 5.3**                    | **42.2 ± 6.7**                   | **11.6 ± 6.1**           |

Net EDOC exchange is calculated as the sum of air-water EDOC flux and tidal EDOC exchange. So the sum of columns 1 and 2 = column 3. The last column, EDOC % of DOC, is calculated as tidal EDOC exchange/DOC exchange × 100.
There was no significant relationship between the spring-neap cycle and EDOC exports. However, the largest net export of EDOC from mangrove forests occurred during the neap tide (Table 2). This is similar to the results of a study by Call et al. (2015) at the same study site, who found that pore water enriched in CO₂ and CH₄ preferentially seeps into surface waters at neap tides. Further, water volumes are lowest in the creek at neap tides which would increase the influence that autochthonous EDOC production has on surface water concentrations.

Global implications

Global mangrove forests may export 24 ± 21 Tg C of DOC to the ocean annually (Bouillon et al. 2008). The methods used to measure DOC and estimate these exports generally exclude VOC. Our results indicate that EDOC contributes 13% ± 4% of the DOC pool within mangrove waters. If our results are representative of mangroves globally, an upscaling based on the EDOC to DOC ratio reveals that EDOC may account for an additional outwelling of 3.1 ± 1.0 Tg C yr⁻¹ from mangroves. This value is equivalent to ~60% of the global VOC flux from the open ocean to the atmosphere (Guenther et al. 1995; Ehhalt 2001) and ~2% of the modeled atmospheric EDOC deposition to the ocean (Jurado et al. 2008). If mangrove outwelling accounts for 10% of terrestrial DOC in the ocean as suggested by Dittmar et al. (2006), our estimated mangrove EDOC exports could account for 1.3–2.5% of the total terrestrial DOC input to the ocean. This brings the total DOC exports from mangroves (including EDOC) to 11.3–12.5% of the terrestrially-derived DOC inputs to the ocean.

Our investigation further supports the increasing evidence on the disproportionally large role that mangroves play in the exchange of carbon between land and ocean. We conclude that (1) mangrove biomass is a major control of EDOC concentrations over a latitudinal gradient, (2) EDOC accounts for 13% ± 4% of DOC in mangroves, (3) pore-water exchange is not a major source of EDOC to mangrove creeks, and (4) outwelling from mangroves may be a significant, but previously overlooked source of EDOC to the ocean. Seasonality of EDOC production and exchange was not investigated in this study. Further research on the seasonal variability of EDOC within mangroves is required to further constrain our initial estimates.

References

Adame, M. F., & Lovelock, C. E. 2011. Carbon and nutrient exchange of mangrove forests with the coastal ocean. Hydrobiologia, 663: 23–50. doi:10.1007/s10750-010-0554-7

Barr, J.G., J.D. Fuentes, N. Wang, Y. Edmonds, J.C. Zieman, B.P. Hayden, D.L. Childers. 2003. Red mangroves emit hydrocarbons. Southeast. Nat. 2: 499–510.

Bouillon, S. 2011. Carbon Cycle: Storage beneath mangroves. Nat. Geosci, 4: 282–283. doi:10.1038/ngeo1130

Bouillon, S. and others 2008. Mangrove production and carbon sinks: A revision of global budget estimates. Global Biogeochem. Cycles 22. doi:10.1029/2007gb003052

Bouillon, S., Dehairs, F., Velimirov, B., Abril, G., & Borges, A. V. 2007. Dynamics of organic and inorganic carbon across contiguous mangrove and seagrass systems (Gazi Bay, Kenya). J. Geophys. Res.; Biogeosci. 112: doi:10.1029/2006JG000325

Breithaupt, J. L., Smoak, J. M., Smith, T. J., Sanders, C. J., & Hoare, A. 2012. Organic carbon burial rates in mangrove sediments: Strengthening the global budget. Global Biogeochem. Cycles, 26: 475–488. doi:10.1029/2012GB004375

Call, M. and others 2015. Spatial and temporal variability of carbon dioxide and methane fluxes over semi-diurnal and spring-neap-spring timescales in a mangrove creek. Geochim. Cosmochim. Acta, 150: 211–225. doi:10.1016/j.gca.2014.11.023

Carpenter, L. J., Archer, S. D., & Beale, R. 2012. Ocean-atmosphere trace gas exchange. Chem. Soc. Rev. 41: 6473–6506. doi:10.1039/C2CS35121H

Dachs, J., Calleja, M. L., Duarte, C. M., del Vento, S., Turpin, B., Polidori, A., G. J. Herndl., Agustí, S. 2005. High atmosphere-ocean exchange of organic carbon in the NE subtropical Atlantic. Geophys. Res. Lett. 32: doi:10.1029/2005GL023799

Dittmar, T., Hertkorn, N., Kattner, G., & Lara, R. J. 2006. Mangroves, a major source of dissolved organic carbon to the oceans. Global Biogeochem. Cycles 20: doi:10.1029/2005GB002570

Ehhalt D., and others. 2001. Atmospheric chemistry and greenhouse gases, p. 881. In J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C. A. Johnson [eds.], Climate change 2001: The scientific basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press.

Exton, D. A., McGenity, T. J., Steinke, M., Kamykowski, D. 2009. A new physically-based quantification of marine isoprene and other biogenic hydrocarbons. Southeast. Nat.

Fuentes, J. D. and others 2000. Biogenic Hydrocarbons in the Earth’s Atmosphere. Environ. Sci. Technol. 34: 1537:BHITAB

Gantt, B., Meskhidze, N., & Kamykowski, D. 2009. A new physically-based quantification of marine isoprene and primary organic aerosol emissions. Atmos.Chem. Phys. 9: 4915–4927. doi:10.5194/acp-9-4915-2009

Goldstein, A. H., & Galbally, I. E. 2007. Known and Unexplored Organic Constituents in the Earth’s Atmosphere. Environ. Sci. Technol. 41: 1514–1521. doi:10.1021/es072476p
Gonzalez-Gaya, B. and others 2016. High atmosphere-ocean exchange of semivolatile aromatic hydrocarbons. Nat. Geosci. 9: 438–442. doi:10.1038/ngeo2714

Guenther, A. and others 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res.: Atmos. 100: 8873–8892. doi:10.1029/94JD02950

Ho, D. T., Ferrón, S., Engel, V. C., Larsen, L. G., & Barr, J. G. 2014. Air-water gas exchange and CO2 flux in a mangrove-dominated estuary. Geophys. Res. Lett. 41: 2013GL058785. doi:10.1002/2013GL058785

Holloway, C. J. and others 2016. Manganese and iron release from mangrove porewaters: A significant component of oceanic budgets? Mar. Chem. 184: 43–52. doi:10.1016/j.marchem.2016.05.013

Hutchinson, J., Manica, A., Swetnam, R., Balmford, A., & Spalding, M. 2014. Predicting Global Patterns in Mangrove Forest Biomass. Conserv. Lett. 7: 233–240. doi:10.1111/conl.12060

Jurado, E., Dachs, J., Duarte, C. M., & Simó, R. 2008. Atmospheric deposition of organic and black carbon to the global oceans. Atmos. Environ. 42: 7931–7939. doi:10.1016/j.atmosenv.2008.07.029

Laethawornkitkul, J., Taylor, J. E., Paul, N. D., & Hewitt, C. N. 2009. Biogenic volatile organic compounds in the Earth system. New Phytol. 183: 27–51. doi:10.1111/j.1469-8137.2009.02989.x

Mackenzie, F.T., Lerman, A., Ver, L.M.B., 1998. Role of continental margin in the global carbon balance during the past three centuries. Geology. 26: 423–426. doi:10.1130/0091-7678(1998)26<423:ROCMIT>2.3.CO;2

Maher, D., Santos, I., Golsby-Smith, L., Gleeson, J., & Eyre, B. 2013. Groundwater-derived dissolved inorganic and organic carbon exports from a mangrove tidal creek: The missing mangrove carbon sink? Limnol. Oceanogr. 58: 475–488. doi:10.4319/lo.2013.58.2.0475

Maher, D. T., Sippo, J. Z., Tait, D. R., Holloway, C., & Santos, I. R. 2016. Pristine mangrove creek waters are a sink of nitrous oxide. Sci. Rep. 6: 25701. doi:10.1038/srep25701

O’Connor, D. J., & Dobbins, W. E. 1958. Mechanism of reaeration in natural streams. Trans. Am. Soc. Civ. Eng. 123: 641–666.

Park, J.-H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karl, J., & Holzinger, R. 2013. Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds. Science. 341: 643–647. doi:10.1126/science.1235053

Raymond, P., & Cole, J. 2001. Gas exchange in rivers and estuaries: Choosing a gas transfer velocity. Estuaries, 24: 312–317. doi:10.2307/1352954

Rosentreter, J. A., D. T. Maher, D. T. Ho, M. Call, J. G. Barr, and B. D. Eyre. 2016. Spatial and temporal variability of CO2 and CH4 gas transfer velocities and quantification of the CH4 microbubble flux in mangrove dominated estuaries. Limnol. Oceanogr. doi: 10.1002/ino.10444

Ruiz-Halpern, S., Sejr, M. K., Duarte, C. M., Krause-Jensen, D., Dalsgaard, T., Dachs, J., & Rysgaard, S. 2010. Air-water exchange and vertical profiles of organic carbon in a sub-arctic fjord. Limnol. Oceanogr. 55: 1733–1740. doi: 10.4319/lo.2010.55.4.1733

Ruiz-Halpern, S., Calleja, M. L., Dachs, J., Del Vento, S., Pastor, M., Palmer, M., Agusti, S. and Duarte, C. M. 2014a. Ocean–atmosphere exchange of organic carbon and CO2 surrounding the Antarctic Peninsula. Biogeosciences. 11: 2755–2770. doi:10.5194/bg-11-2755-2014

Ruiz-Halpern, S., Vaquer-Sunyer, R., & Duarte, C. M. 2014b. Annual benthic metabolism and organic carbon fluxes in a semi-enclosed Mediterranean bay dominated by the macroalgae Caulerpa prolifera. Front. Mar. Sci. 1: 2296–7745. doi:10.3389/fmars.2014.00067

Sanders, C. J., D. T. Maher, D. R. Tait, D. Williams, C. Holloway, J. Z. Sippo, and I. R. Santos 2016. Are global mangrove carbon stocks driven by rainfall?, J. Geophys. Res.: Biogeosci.. 121: 2600–2609, doi:10.1002/2016JD025510

Sippo, J. Z., Maher, D. T., Tait, D. R., Holloway, C., & Santos, I. R. 2016. Are mangroves drivers or buffers of coastal acidification? Insights from alkalinity and dissolved inorganic carbon export estimates across a latitudinal transect. Global Biogeochem. Cycles. 30: 753–766. doi:10.1002/2015GB005324

Spyres, G., Ninmo, M., Worsfold, P. J., Achterberg, E. P., and Miller, A. E. J. 2000. Determination of dissolved organic carbon in seawater using high temperature catalytic oxidation techniques. Trends Analyt. Chem. 19: 498–506. doi: 10.1016/S0165-9936(00)00022-4

Tait, D. R., Maher, D. T., Macklin, P. A., & Santos, I. R. 2016. Mangrove pore water exchange across a latitudinal gradient. Geophys. Res. Lett. 43: 3334–3341. doi:10.1002/2016GL068289

Walsh, J.J., 1991. Importance of continental margins in the Earth system. New Phytol. 11: 285–307. doi. 10.1111/j.1469-8137.1991.tb04182.x

We would like to thank Ceylena Holloway, Paul Macklin, Darren Williams, and a number of members from the Centre for Coastal Biogeochemistry for data collection at Moreton Bay. James Z. Sippo acknowledges support from an AINSE Postgraduate Research Award. This project was funded through an AINSE Postgraduate Research Award. This project was funded through an AINSE Postgraduate Research Award. This project was funded through an AINSE Postgraduate Research Award. This project was funded through an AINSE Postgraduate Research Award. This project was funded through an AINSE Postgraduate Research Award.

Submitted 07 July 2016
Revised 25 October 2016
Accepted 22 November 2016