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Large variability in organic carbon and $CaCO_3$ burial in seagrass meadows: a case study from three Australian estuaries

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ABSTRACT: Blue carbon refers to the carbon accumulation capacity of vegetated coastal habitats, including salt marshes, mangroves forests and seagrass meadows. Here we present estimates of organic carbon (C_{org}) and calcium carbonate ($CaCO_3$) burial rates from 4 seagrass species (*Halophila ovalis*, *Posidonia australis*, *Ruppia megacarpa*, *Zostera muelleri*) in 3 temperate estuaries on the east coast of Australia. The C_{org} burial rates (mean ± SE) varied by an order of magnitude across the seagrass communities (16 ± 3 to 130 ± 40 g m^{-2} yr^{-1}). The $\delta^{13}C_{org}$ and C_{org}:N ratios suggest that the seagrass communities buried variable mixtures of seagrass, algal and mangrove/terrestrial material. $CaCO_3$ burial rates ranged from 15 ± 11 to 188 ± 122 g m^{-2} yr^{-1}, which, if precipitated by calcifying organisms in these or nearby habitats, may offset up to 89% of the C_{org} burial across the 8 seagrass communities. Our results highlight a large range in both C_{org} and $CaCO_3$ burial rates, and the provenance of the carbon sequestered in seagrasses, factors that need to be considered when assessing the role of seagrasses in blue carbon and climate change mitigation strategies.

KEY WORDS: Seagrass · Carbon content · Accumulation · Sedimentation · Blue carbon

1. INTRODUCTION

There is growing interest in the capacity of coastal vegetated systems, particularly mangroves, saltmarshes and seagrass meadows, to sequester and store atmospheric carbon, termed 'blue carbon'. Seagrasses are highly productive angiosperms that grow in estuaries and coastal areas along the coasts of all continents, except Antarctica. Australia has the largest area of seagrass meadows worldwide (~20% of global area of seagrass), and contains more than half of the world's species, with a vast geographic distribution across tropical, subtropical and temperate regions (Mount et al. 2008, Lavery et al. 2013, Coles et al. 2015, York et al. 2017). As a result, Australia is one of the world's richest regions in seagrass blue carbon. However, there is currently limited information on the carbon burial rates from a range of species and different estuaries (Lavery et al. 2013).

Carbon burial rates may differ among species, as a result of size and turnover rates for example, as well as estuarine characteristics, such as geomorphology and hydrology (Mazarrasa et al. 2018). Carbon buried in seagrass communities may come from

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*Corresponding author: christian.sanders@scu.edu.au the seagrass as well as other sources (Kennedy et al. 2010, Oreska et al. 2018). For example, allochthonous organic carbon (C_{org}) can make up large portions of the organic material input to seagrass communities (Kennedy et al. 2010, Oakes & Eyre 2014). Furthermore, seagrass communities are areas of calcium carbonate ($CaCO_3$) accumulation due to the calcifying organisms that live in these habitats and potentially in nearby ecosystems (Mazarrasa et al. 2015, Howard et al. 2018, Saderne et al. 2019). Quantifying $CaCO_3$ burial is important because the process of $CaCO_3$ precipitation could influence the emission of CO_2, which may partially offset the atmospheric CO_2 removed through C_{org} burial (Macreadie et al. 2017, Howard et al. 2018).

We hypothesize that the seagrass meadows on the southeastern coast of Australia bury only low amounts of $CaCO_3$ as a component of the total seagrass carbon burial. This hypothesis is based on the local geology of these catchments which suggests few geogenic $CaCO_3$ sources and no apparent external source such as coral reefs. The hypothesis was tested by measuring the total carbon (C_{org} and $CaCO_3$) burial rates along with proxies to estimate source ($\delta^{13}C$ and C_{org}:N molar ratios) in 4 different seagrass species within 1 estuary, in 3 seagrass species in another nearby estuary, and in the same species (*Halophila ovalis*) in 3 different estuaries. The 3 estuaries were selected as they are in close geographic proximity (within 100 km) and therefore have a similar climate, while being geomorphologically and hydrologically different. The selected estuaries and have been previously studied to examine whole ecosystem scale carbon and nitrogen budgets (Maher & Eyre 2012).

2. MATERIALS AND METHODS

The 3 studied estuaries are located on the southeast coast of Australia and represent a range of estuary types at different stages of maturity (amount of infill) (Roy et al. 2001) (Table 1). Wallis Lake is the largest and most immature of the 3 estuaries with an open water area of 90 km^2 and the lowest freshwater inflow. Camden Haven has a shallower central basin as a result of infill, and the Hastings River estuary is a river-dominated system with no central mud basin due to complete infilling. The seagrass coverage in these estuaries ranges from ~10 to 37 % (Table 1). All 3 estuaries are net autotrophic, with a net ecosystem metabolism average of 105 g C m^{-2} yr^{-1} (Maher & Eyre 2012).

Eight sediment cores were collected in November 2013 within the major seagrass species of this region. The details on each study site are shown in Table 1 and detailed maps are presented in Fig. S1 in the Supplement at www.int-res.com/articles/suppl/m616p211_supp.pdf. Water depths at each of the study sites were less than 1 m at low tide. For each core a PVC pipe (50 cm length, 5 cm inner diameter) was gently inserted within seagrass meadows through percussion and rotation to a depth of up to 30 cm. No apparent compaction was observed and therefore corrections were not undertaken. A rubber plug was used to create a vacuum seal before the core was removed and capped on both ends, to prevent compaction while the sediment was extruded. The sediment cores were sectioned on-site at 4 cm intervals. Sample intervals (4–5 intervals per sediment core) were bagged, placed on ice and returned to the lab-

Table 1. Characterization of the 3 estuaries in this study: Hastings River, Camden Haven, and Wallis Lake. Based on Eyre & Maher (2010) and Maher & Eyre (2012). GPP: gross primary production; NP: net primary production. Seagrass area is also given as a percentage of water area (values in brackets). tC: tons of carbon. The values in brackets in the last 3 rows are the errors based on calculation in Maher & Eyre (2012)

Property	Hastings River	Camden Haven	Wallis Lake
Catchment area (km^2)	3595	440	1420
Water area (km^2)	19	30	90
Seagrass area (km^2)	2 (10 %)	11 (37 %)	33 (37 %)
Mean water residence time (d)	10	45	>60
Freshwater inflow (Ml)	482 009	229 932	146 368
Salinity averages	5	22	20
Tidal or river dominant	River	Tidal	Tidal
Seagrass production (tC)	1665	8936	28 091
Seagrass respiration (tC)	1412	6460	25 040
Estuary annual GPP (mol C m^{-2} yr^{-1})	25 (5.7)	10.5 (1.5)	15 (2.3)
Estuary annual respiration (mol C m^{-2} yr^{-1})	14.9 (2.4)	8.7 (1.0)	11 (2.3)
Estuary annual NP (mol C m^{-2} yr^{-1})	10.2 (6.5)	1.8 (1.9)	4.0 (3.6)

oratory. Plant material, including leaves and roots, was removed before analysis.

For grain size analysis, organic matter was removed with a 10 % hydrogen peroxide solution and disaggregation was achieved with 4 % sodium hexametaphosphate. Sediment intervals were analysed for sand, silt, and clay content using a CILAS 1064 diffraction laser unit. The dry bulk density was determined as the dry sediment weight over the initial sediment volume (g cm^{-3}). One sub-sample of each core fraction was acidified to remove carbonate material, then dried and ground to powder. A separate subsample was ground to powder without removing carbonate material. These specific subsamples were analyzed for C_{org}, N, $\delta^{15}N$ and $\delta^{13}C_{org}$ using a Flash Elemental Analyser coupled to a Thermo Fisher Delta V isotope ratio mass spectrometer (Thermo Flash EA 1112). The carbon fractions measured were total carbon and C_{org}, and the inorganic carbon was determined as the difference between total C and $C_{org.}$ Analytical precision was as follows: C = 0.1 %, N = 0.1 %, $\delta^{13}C$ = 0.1 ‰, and $\delta^{15}N$ = 0.15 ‰. Working standards were used (glucose, 10.7 ‰ and urea, −41.3 ‰) to calibrate for $\delta^{13}C$. A pair of standards were measured with every 20 samples. These standards were calibrated initially against international absolute standards LSVEC and NIST8542.

The ^{210}Pb activities in each sediment core interval were determined by the direct measurement of 46.5 KeV gamma peaks. Identical geometry was used for all samples and sample dry weights were between 20 and 50 g. Each of the intervals were sealed in 70 ml petri-dishes for at least 3 weeks to establish secular equilibrium between ^{226}Ra and its daughter products ^{214}Pb and ^{214}Bi. The ^{226}Ra activity was calculated by averaging its daughters' peaks, ^{214}Pb and ^{214}Bi (295.2 KeV, 351.9 KeV, 609.3 KeV) (Moore 1984). Activities were calculated by multiplying the counts per minute by a correction factor that includes the gamma ray intensity and detector efficiency determined from standard calibrations. The ^{210}Pb self-absorption corrections were calculated following the method of Cutshall et al. (1983). Excess ^{210}Pb ($^{210}Pb_{ex}$) activity was calculated by subtracting the supported ^{210}Pb (i.e. ^{226}Ra) from the total ^{210}Pb activity. The sediment accumulation rate (SAR) was calculated according to the constant initial concentration method (Appleby & Oldfield 1992).

Burial rates of C_{org} and $CaCO_3$ were calculated by multiplying their respective contents by the mass accumulation rates. Ternary mixing diagrams and $\delta^{13}C_{org}$ and N:C_{org} molar ratio endmember values (Eyre et al. 2013), were used to determine the relative contribution of algae, seagrass, and mangrove organic matter to the sedimentary organic material.

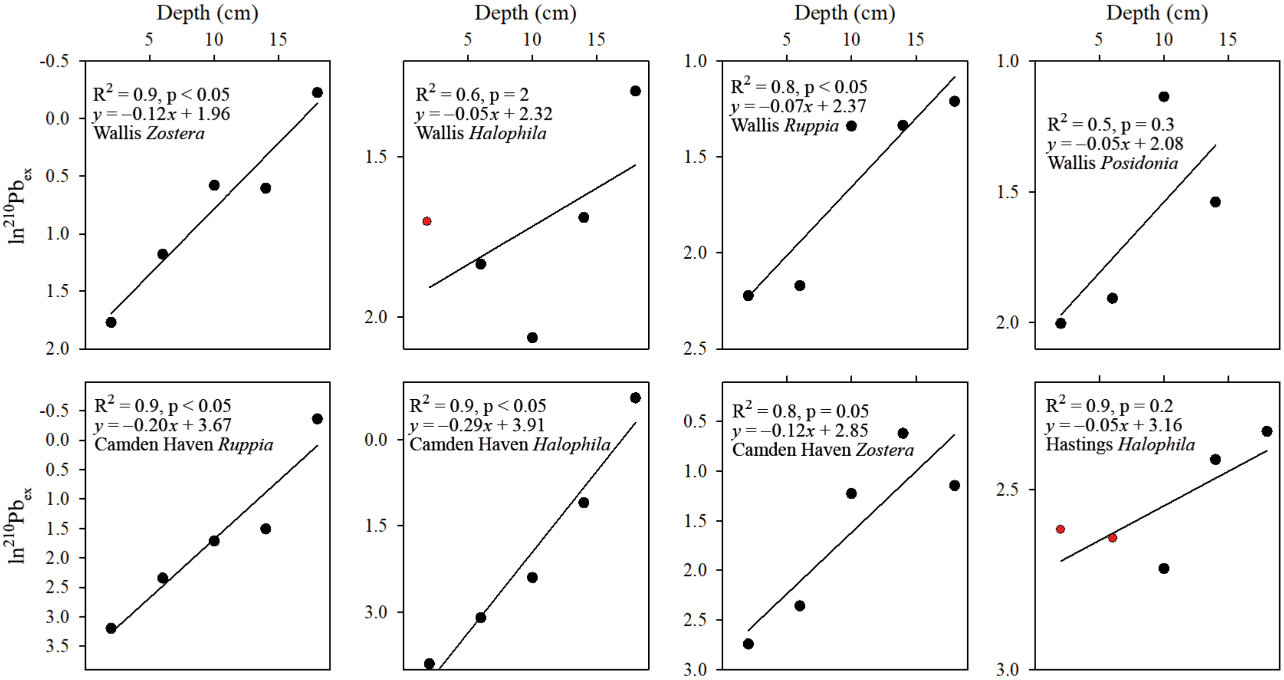

Fig. 1. Logarithmic excess ^{210}Pb ($ln^{210}Pb_{ex}$) distribution against depth as used for the sediment accretion rate estimates from the 8 sediment cores in this work. Red symbols: mixed layers, likely due to bioturbation and physical reworking (excluded when calculating SAR)

Table 2. Sediment core interval averages ± SE from the 8 cores studied in this work. The number of sediment core intervals (SCI), sediment accumulation rates (SAR), dry bulk densities (DBD), $\delta^{13}C_{org}$, $\%C_{org}$, $\%CaCO_3$, and C_{org}:N molar ratios are shown for each sediment core

Seagrass species	SCI	SAR (mm yr^{-1})	DBD (g cm^{-3})	C_{org} (g m^{-2} yr^{-1})	$CaCO_3$ (g m^{-2} yr^{-1})	$\delta^{13}C_{org}$	$\%C_{org}$	$\%CaCO_3$	C_{org}:N	% Sand
Wallis Lake										
Posidonia australis	4	5.7 ± 2.3	1.2 ± 0.1	66 ± 35	188 ± 122	−16.0 ± 0.2	1.0 ± 0.3	2.7 ± 1.4	15.0 ± 1.8	85 ± 4
Ruppia megacarpa	5	4.3 ± 0.9	0.6 ± 0.1	114 ± 37	96 ± 42	−16.1 ± 0.4	4.9 ± 0.6	3.7 ± 1.3	16.5 ± 1.2	29 ± 8
Halophila ovalis	5	6.2 ± 2.2	1.4 ± 0.1	34 ± 15	113 ± 60	−17.3 ± 0.2	0.4 ± 0.1	1.3 ± 0.5	12.9 ± 2.0	93 ± 2
Zostera capricorni	5	2.6 ± 0.4	0.7 ± 0.1	57 ± 13	63 ± 27	−15.4 ± 0.3	3.2 ± 0.3	3.4 ± 1.3	17.2 ± 0.6	33 ± 7
Camden Haven										
R. megacarpa	5	1.6 ± 0.2	0.8 ± 0.1	27 ± 6	15 ± 11	−21.4 ± 0.8	2.2 ± 0.3	1.2 ± 0.8	18.0 ± 1.9	43 ± 7
Z. muelleri	5	2.5 ± 2.1	0.6 ± 0.1	34 ± 28	31 ± 25	−20.2 ± 0.6	2.2 ± 0.2	1.9 ± 0.3	15.2 ± 0.4	42 ± 7
H. ovalis	5	1.1 ± 0.1	0.6 ± 0.1	16 ± 3	129 ± 24	−19.9 ± 0.8	2.3 ± 0.3	18.9 ± 0.9	15.3 ± 0.5	44 ± 9
Hastings River										
H. ovalis	5	6.5 ± 1.7	1.1 ± 0.1	130 ± 40	44 ± 94	−25.7 ± 0.3	1.9 ± 0.2	0.6 ± 1.3	18.9 ± 0.5	35 ± 2

3. RESULTS

All 8 cores provided usable $^{210}Pb_{ex}$ profiles (Fig. 1). However, the $^{210}Pb_{ex}$ profiles indicate that *Halophila ovalis* meadows in Hastings River and Wallis Lake had lower activities in the surface intervals (upper 4 cm) (Sanders et al. 2010), consistent with mixing or scatter, which could lead to an overestimation of mean SAR (Arias-Ortiz et al. 2018). Considering the large uncertainties in some profiles, the SAR (mean ± SE) varied from 1.1 ± 0.1 to 6.5 ± 1.7 mm yr^{-1}. The highest and the lowest rates of accretion were found in *H. ovalis* meadows in the Hastings River and Camden Haven estuaries, respectively. The dry bulk densities ranged from 0.6 ± 0.1 to 1.4 ± 0.1 g cm^{-3}, with both extremes found in Wallis Lake meadows. The C_{org} content ranged between 0.4 ± 0.1 and 4.9 ± 0.6% with the highest values found in the Wallis Lake *Ruppia megacarpa* meadows (Table 2). The $CaCO_3$ content ranged from 0.6 ± 1.3 to 18.9 ± 0.9% with the highest values found in the Camden Haven *H. ovalis* site (Table 2).

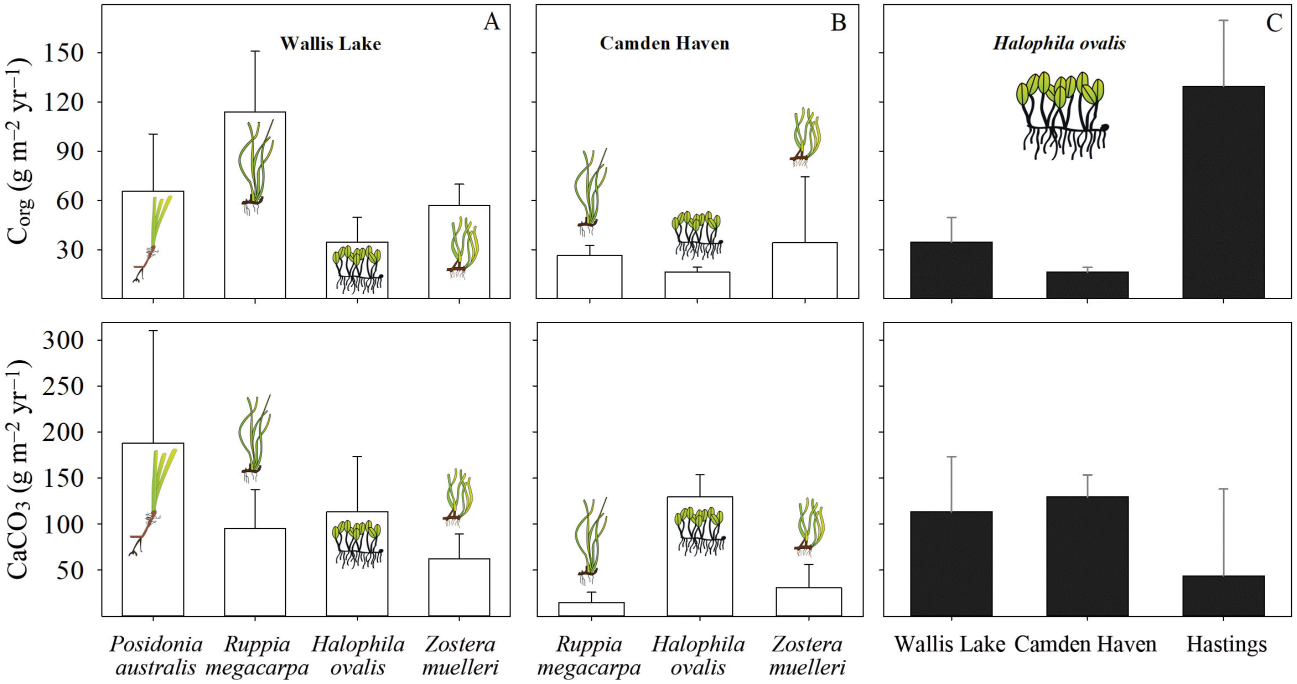

Fig. 2. C_{org} and $CaCO_3$ burial of (A) 4 different species in the same estuary (Wallis Lake), (B) 3 different species in the same estuary (Camden Haven), and (C) for the same species in different estuaries (Hastings River, Camden Haven, Wallis Lake). Error bars indicate flux uncertainties based on SE between sediment core intervals

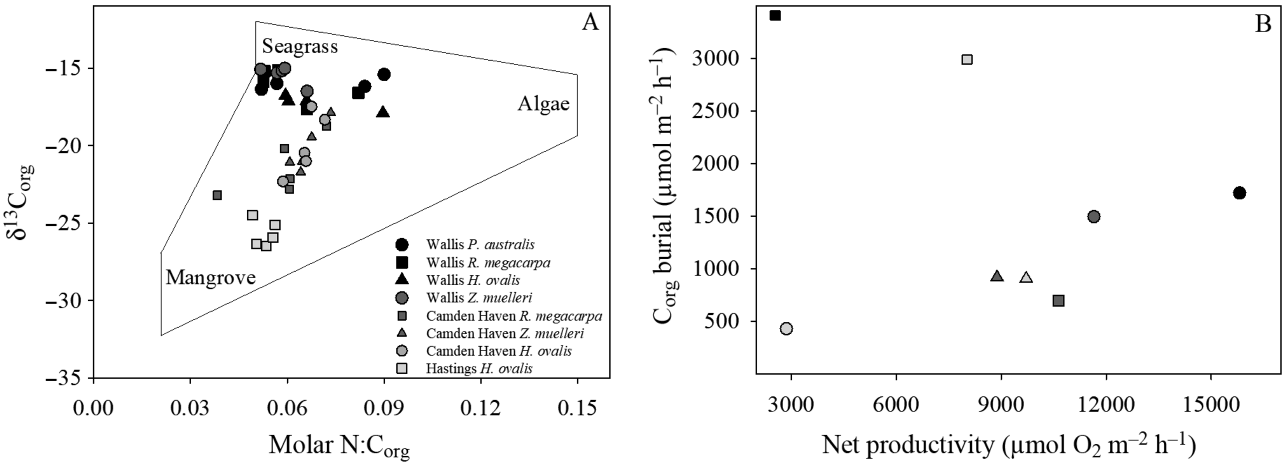

Fig. 3. Contributions to seagrass carbon burial. (A) Ternary mixing diagram demonstrating the relative contribution of algae, seagrass, and terrestrial/mangrove organic matter, based on $\delta^{13}C$ vs. molar $N{:}C_{org}$ proxies, from each sediment core interval of the 8 sediment cores in this work (endmember data from Eyre et al. 2013). Endmember values are incorporated as the boundary of ranges of this panel. $N{:}C_{org}$ ratios are shown here for comparative purposes, i.e. $C_{org}{:}N$ ratio of 6.6 = $N{:}C_{org}$ ratio of 0.15 and $C_{org}{:}N$ ratio of 50 = $N{:}C_{org}$ ratio of 0.02. (B) C_{org} burial rates (µmol m^{-2} h^{-1}) as a function of the annual average net primary production (µmol O_2 m^{-2} h^{-1}) of the seagrass community (Maher & Eyre 2011)

C_{org} burial rates varied from 16 ± 3 to 130 ± 40 g m^{-2} yr^{-1} with the highest rates found in the *H. ovalis* meadows of the Hastings River estuary (Fig. 2). The $CaCO_3$ burial rates varied from 15 ± 11 in *R. megacarpa* to 188 ± 122 g m^{-2} yr^{-1} in the *Posidonia australis* meadows of the Wallis Lake estuary (Fig. 2). A two-tailed Student *t*-test indicated that both C_{org} and $CaCO_3$ burial were not significantly different ($p > 0.05$) between estuaries (Wallis Lake and Camden Haven, excluding *P. australis* from Wallis Lake as this species was not measured in Camden Haven). However, the same seagrass species, *H. ovalis*, had significantly greater C_{org} in the river dominated estuary, Hastings River, as compared to the tidal dominated Wallis Lake and Camden Haven estuaries.

$\delta^{13}C_{org}$ values and $N{:}C_{org}$ molar ratios of each of the sediment core intervals are shown in Fig. 3A. These ratios indicate the possible contribution of specific organic material sources, i.e. seagrass, mangrove and marine algae. $\delta^{13}C$ values and molar $N{:}C_{org}$ ratio show low variability along the sediment column.

4. DISCUSSION

The range of seagrass C_{org} burial rates in the 3 studied estuaries (16 to 130 g m^{-2} yr^{-1}) were generally lower than the global range (45 to 190 g C_{org} m^{-2} yr^{-1}; McLeod et al. 2011). The average C_{org} burial rate (60 ± 74 g m^{-2} yr^{-1}) was also substantially lower than the global average (138 ± 38 m^{-2} yr^{-1}; McLeod et al. 2011). One explanation for these lower rates is that the global dataset is dominated by meadows from the tropical regions of the North America and Asia as well as Southern Europe (Kennedy et al. 2010), while the 3 estuaries in this study are warm temperate systems. Tropical regions are associated with greater primary production than temperate regions, likely contributing to the lower C_{org} burial rates found in the present study and in other temperate seagrass habitats (Jankowska et al. 2016). However, the small and fast-growing seagrass species *Halophila ovalis* in the Hastings River estuary was found to have high C_{org} burial rates, directly related to the high SAR (Table 1) towards the higher extremes of the global averages. It should be noted that the high SAR in both of the *Halophila ovalis* meadows in Hastings River and Wallis Lake may be the result of an overestimation as indicated by the mixed upper layers, likely due to bioturbation and physical reworking, as revealed by the $\ln^{210}Pb_{ex}$ profiles. This is particularly the case where the value of $\ln^{210}Pb_{ex}$ fitting is > 0.05 (Arias-Ortiz et al. 2018).

The studied seagrass meadows are areas of high $CaCO_3$ burial, probably influenced by the calcifying organisms that live in these habitats (Fig. 2). While $CaCO_3$ could be sourced from other carbonate producing ecosystems nearby (Mazarrasa et al. 2015), there is no obvious source except for possible input from the ocean. *Posidonia australis* in the Wallis Lake estuary had the highest $CaCO_3$ burial rate, likely because this estuary has the lowest freshwater inflow and high concentrations of sand, indicating a more dominant marine source (Sanders et al. 2012) (Table 1). Even though areas with the highest $CaCO_3$ burial had generally higher sand concentrations, indicative of more oceanic influence, no significant relation was found between grain size and C_{org} or $CaCO_3$ burial. Some of the variability in C_{org} and $CaCO_3$ burial rates between the different seagrasses meadows in this region may come from production, such as autochthonous seagrass leaves and roots, microphytobenthos, and *in situ* calcifying organisms. For instance, even though seagrass plants do not calcify, they provide a habitat for calcifying organisms such as calcified algae and foraminifera (Mazarrasa et al. 2015). The $CaCO_3$ produced from these organisms may then accumulate in the seagrass soils. Alternatively, sources of carbon in the sediments may also include allochthonous material derived from calcifying organisms imported from the coastal ocean (Mazarrasa et al. 2015).

Along the study sites the net primary production of the seagrass communities (Maher & Eyre 2011) were directly related to C_{org} burial in most of the meadows (Fig. 3B). Excluding two outlier sites, a significant correlation may be found between the remaining seagrass primary production and C_{org} burial rates ($y = 0.004x + 0.84$, n = 6, $R^2 = 0.76$, $p < 0.05$). The 2 seagrass sites excluded were *H. ovalis* in Hastings River, which was found here to have a large input of mangrove material (see next paragraph), and *R. megacarpa* in Wallis Lake, which had a large accumulation of seagrass wrack (C. J. Sanders pers. obs.). These factors most likely resulted in higher burial rates for a given net primary productivity at both sites. The sources of carbon in the seagrass sediments may also include allochthonous sources including photosynthetic CO_2 fixation within the estuary and nearby coastal wetland runoff (Oreska et al. 2018). Kennedy et al. (2010) found that over 50% of C_{org} burial in seagrass beds originates from non-seagrass sources.

Wallis Lake *P. australis*, *R. megacarpa* and *H. ovalis* sediments were found to have a mixture of mostly seagrass and algal material (Fig. 3A). All 3 seagrass species in Camden Haven had a mixture of seagrass, algal and terrestrially derived C3 material. C3 terrestrial C_{org} (most likely stemming from mangroves) dominated the *H. ovalis* seagrass community in Hastings River, the site with the highest C_{org} burial rates. This site had high concentrations of mud, and a C_{org} burial rate of 91 g m^{-2} yr^{-1} which was previously measured in a non-seagrass area in this estuary (Maher & Eyre 2012). Algal material would also be derived from the *in situ* production of epiphytes and benthic microalgae (Jankowska et al. 2016, Oreska et al. 2018). The $\delta^{13}C$ and molar $N:C_{org}$ values varied little with depth (see Table 2 and Fig. 3A) which indicates that these seagrass communities have likely persisted in these sites during the previous century.

The relative importance of terrestrial versus autochthonous material follows the estuarine evolution gradient and estuarine geomorphology (Roy et al. 2001), with higher autochthonous inputs to the immature Wallis Lake, intermediate autochthonous inputs to the more mature Camden Haven, and the lowest autochthonous input and highest allochthonous input to the mature river-dominated Hastings River estuary. This trend also follows water residence times which range from ~10 d in the Hastings River estuary, 45 d in the Camden Haven and >60 d in Wallis Lake, suggesting that estuarine geomorphology and hydrology plays a major role in the provenance of C_{org} being sequestered in estuarine seagrass meadows (Table 1).

It is important to differentiate between geogenic and biogenic calcium carbonates within blue carbon soil assessments in order to properly assess the role of $CaCO_3$ cycling in blue carbon accounting (Macreadie et al. 2017, Saderne et al. 2019). Because the local geology of these catchments suggests little geogenic $CaCO_3$ in the sediment matrix (www.ga.gov.au/metadata-gateway/metadata/record/74371/), we therefore assume that the $CaCO_3$ present in seagrass soils is biogenic. In terms of blue carbon research, $CaCO_3$ precipitation is important as it may represent a source of CO_2 to the atmosphere. This is because calcification produces CO_2, with a ratio of approximately 0.63 moles of CO_2 emitted per mole of $CaCO_3$ precipitated (Saderne et al. 2019). Therefore, the large $CaCO_3$ precipitation and burial in the seagrass found in this work may partially offset CO_2 sequestration associated with C_{org} burial if precipitated within the meadows (Macreadie et al. 2017, Howard et al. 2018). If $CaCO_3$ was formed within the seagrass meadows, then based on these ratios and the total average, we estimate that the $CaCO_3$ precipitation and burial could offset almost 89% of the C_{org} burial across the 8 seagrass meadows studied. Considering these assumptions, the $CaCO_3$ offset could be near 54 g m^{-2} yr^{-1}, resulting in a net C_{org} burial sink average for seagrass communities in the 3 estuaries of approximately 6 g C_{org} m^{-2} yr^{-1}. However, if a portion of the $CaCO_3$ buried in seagrass sediments originates from allochthonous sources rather than being produced within the habitat, then this offset would be smaller.

In summary, this work reports both C_{org} and $CaCO_3$ burial rates in 3 estuaries that range in stages of

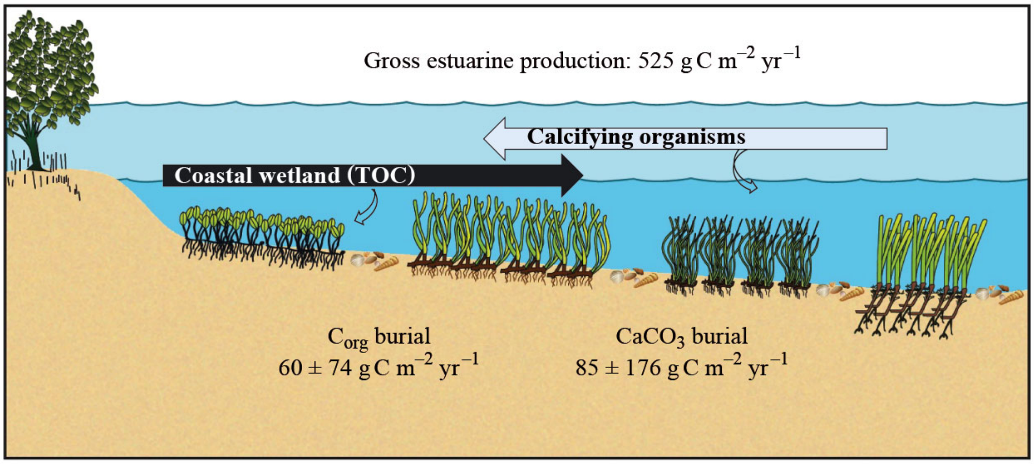

Fig. 4. Conceptual model showing the seagrass C_{org} and $CaCO_3$ burial rate averages (± SE) and likely sources. TOC: total organic carbon

maturity (Fig. 4). The seagrasses burial rates appeared to be related to the estuarine evolution, geomorphology and water residence times. The C_{org} burial rates were found to be likely influenced by the net primary production of the seagrass meadows and organic matter input from nearby coastal wetland vegetation. However, no clear trends were noted in terms of seagrass species. It could also not be determined if the $CaCO_3$ is autochthonous, which would partially offset the carbon sequestration capacity of the seagrass meadows in this region. Therefore this study outlines the large range of variables that may contribute to C_{org} and $CaCO_3$ burial within geographically similar estuaries with differing characteristics, including marine and freshwaters sources. These are factors that need to be considered when assessing the role of seagrasses in blue carbon research.

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