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Organic chemistry insights for the exceptional soil carbon storage of the seagrass *Posidonia australis*

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ABSTRACT

The high organic carbon (OC) stores in seagrass meadows have led to their recognition as significant Blue Carbon sinks, though the diagenetic conditions that enable OC retention in seagrass soils remain poorly understood. In this study, seagrass soils were sampled from a *Posidonia australis* meadow in Oyster Harbour (Albany; south-western Australia) to investigate the preservation of sedimentary OC. We analysed soil characteristics (colour, grain size and redox potential), radiocarbon age, and characterised the soil organic matter (OM) using solid state CP/MAS ^{13}C NMR spectroscopy to examine the preservation of OM down the soil profile. There was minimal change in organic composition over 1,700 years of accumulation, indicating long-term OM preservation. Primarily, this preservation appears to be driven by the recalcitrance of seagrass detritus buried in anoxic soils. The majority (70–83%) of total sedimentary OM comprised components directly attributable to seagrass origins (lignin, carbohydrate and black carbon-like matter), while the remainder consisted mostly of protein, some of which may have been present in seagrass biomass, along with likely contributions from algae and microbes. Although black carbon originates from organic matter combustion, here we provide evidence that the ^{13}C NMR signal identified as black carbon-like matter in our soils is possibly associated with seagrass-derived organic matter consisting of degraded lignin products or other non-pyrogenic aromatics. The increase in the relative abundance of this black carbon-like matter with aging suggests its selective preservation. The relative abundances of carbohydrates significantly decreased with age down core (i.e. they appeared to be selectively decomposed), while lignin and protein did not show any quantitative changes in relative abundance (non-selective preservation). These findings demonstrate the exceptional preservation of *P. australis* derived OC, which contributes to our understanding of the higher OC storage capacity of *Posidonia* compared to other seagrass species.

1. Introduction

The organic carbon (OC) sequestration capacity of seagrass meadows has led to their recognition as important 'Blue Carbon' sinks, and their restoration is being considered as a strategy for climate change mitigation and adaptation (Nellemann et al., 2009; Duarte et al., 2013a, b). Sequestration of soil OC in seagrass meadows results from a combination of factors, including the high productivity of seagrasses (Cebrian and Duarte 1995), the large supply of seagrass detritus coupled with its low degradation rate (Harrison, 1989), and the capacity of seagrass canopies to trap and retain organic particles (Hendriks et al., 2010; Peralta et al., 2008). Soil OC stocks in seagrass meadows can be as high as 115–829 Mg OC ha^{-1}, significantly broader than the range of 150–200 Mg OC ha^{-1} reported for soils of terrestrial forests (Fourqurean et al., 2012a). A major factor contributing to the high OC sequestration in seagrass meadows is the high degree of organic matter (OM) preservation in anoxic conditions (Pedersen et al., 2011). However, the biogeochemical processes in seagrass soils that lead to large OC stores remain poorly understood.

The concentration of OM in seagrass soils is a function of physical, biological and chemical factors (Serrano et al., 2016a; Mazarrasa et al., 2018). Physical factors primarily relate to the geomorphology of the

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environment in which seagrass meadows occur. Seagrasses typically inhabit sheltered areas (Carruthers et al., 2007) whose depositional nature is conducive for the retention and burial of both autochthonously produced OM and imported allochthonous OM (Kennedy et al., 2010). Furthermore, the predominance of fine sediments reduces oxygen exchange and results in low redox potentials within the top 15 mm of the soil (Dauwe et al., 2001). Anoxic conditions generally enhance long-term OM preservation (Wakeham and Canuel, 2006; Burdige, 2007), although for early diagenesis of labile compounds, rates of OM decomposition can be similar under aerobic and anaerobic conditions (Kristensen et al., 1995). Biological factors influence the amount and type of OM that is available for burial. Seagrasses are generally highly productive (Mateo et al., 2006), though meadow cover and the compartmentalisation of the productivity to below-ground organs vary (Duarte, 1991). This suggests that there may be differences in the quantity and quality of OM supplied for burial among seagrass meadows. Previous studies reported differences in seagrass carbon quality across tissue types and taxa (Trevathan-Tackett et al., 2017), however, little is known about diagenetic changes during burial that contribute to strong OM preservation potential in seagrass meadows (Kaal et al., 2016). There are also variations in the proportions of seagrass-derived and non-seagrass-derived OM buried in the soil, with *Posidonia* spp. contributing to larger amounts of OM into the soil OC pool compared to relatively smaller seagrass species (Kennedy et al., 2010). This may be important to OM preservation because seagrasses contain relatively high amounts of degradation-resistant organic compounds in their tissues (Mateo et al., 2006; Trevathan-Tackett et al., 2015), often referred to as lignic components (e.g. Klap et al., 2000; Torbatinejad et al., 2007), compared to other potential OM sources. Species of *Posidonia* have relatively high tissue concentrations of lignic compounds while *Zostera marina* contains cutans and tannins, which have similar preservation potential to lignin (Kaal et al., 2016; Tegelaar et al., 1989). Indeed, a portion of the seagrass below-ground biomass is buried in the sediment and will mostly undergo anaerobic diagenesis after senescence, which may enhance its preservation (Kristensen et al., 1995). In contrast, non-seagrass-derived OM, consisting of seston and algae deposited in seagrass soils contains more labile biomolecules that undergo more rapid microbial cycling and remineralisation during early diagenesis (Laursen et al., 1996; Säwström et al., 2016).

Conformational biochemical changes occur after OM deposition and burial due to a number of diagenetic processes in marine sediments. OM in the sediment surface is usually more reactive than OM in deeper sediments due to greater exposure to physical processes and microbial degradation, which leads to high decomposition rates (Henrichs, 1992). However, a fraction of the OM escapes early diagenesis due to its recalcitrant nature or rapid burial (Burdige, 2007). Upon deeper sediment burial, decomposition under anoxic conditions may occur but is limited by slow rates of microbial activity (Wakeham and Canuel, 2006). The OM that overcomes early diagenesis can be further preserved through processes such as vulcanization, condensation and/or geopolymerization with or without bacterial influence (Tegelaar et al., 1989; Hedges et al., 2000). For detrital matter originating from recalcitrant plant matter, selective preservation and mineral shielding are thought to be the major processes leading to OM preservation (Hedges et al., 2001). These diagenetic processes may also work synergistically rather than as distinct processes (Burdige, 2007). As such, considerable difficulty arises in elucidating individual processes responsible for OM preservation.

Identifying changes in the biochemical forms of OM through millenary sedimentary deposits in seagrass soils may help elucidate diagenetic mechanisms responsible for its preservation. However, structural elucidation of buried OM is made difficult by the heterogeneity of its biochemical constituents. At present, there are no direct or standardised approaches to characterise the molecular biochemical components of buried OM (Burdige, 2007). Characterisation is further hampered because the resolution provided through conventional analysis (such as hydrolysis, solvent extraction or chromatographic methods) is insufficient to decipher intricate bonding linkages of the various compounds that occur within the OM matrix (Burdige, 2007). In addition, conventional analytical methods do not provide quantitative detection of all OM naturally present in samples and can suffer from the synthesis of artefacts during procedural steps (Nelson and Baldock, 2005). These conventional methods are more applicable as biomarker techniques that identify specific compounds or components to a high degree of resolution, rather than for bulk sediment characterisation (Kögel-Knabner, 2000). On the other hand, methods have been developed employing solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy for biochemical characterisation of OM from fresh plant matter and marine sediments, providing insights on the stability and sources of persistent forms of OM in marine sediments (Baldock et al., 2004; Nelson and Baldock, 2005). Therefore, ^{13}C NMR has potential to characterise and apportion macromolecular composition in seagrass focussed studies contributing to understand its implications for long-term carbon sequestration (Trevathan-Tackett et al., 2017).

Seagrass meadows formed by *Posidonia* species contain the largest OC sinks (ranging from 150 to 1,760 Mg OC ha^{-1} in 2 m-thick deposits; Serrano et al., 2016b) among seagrasses worldwide (Fourqurean et al., 2012a). Bulk characterisation of living and detrital *P. australis* tissues confirmed the presence of recalcitrant OM (i.e. lignic matter; Kuo, 1978; Kuo and Cambridge, 1978; Torbatinejad et al., 2007; Kaal et al., 2018). However, such characterisation has not been carried out on *P. australis* sediments, which accumulate over millennia. Occurrences of buried fibre-like detrital matter in the seagrass meadows of Oyster Harbour (southern Western Australia) have been reported to soil depths of 2 m aged ~3,000 Cal. yr BP (Rozaimi et al., 2016). However, the biochemical structural composition of the OM, and the extent of changes through depth/aging after burial (i.e. the preservation mechanisms) remains unknown.

In this paper, we investigate the extent of OM preservation in a *P. australis* meadow by studying the characteristics and changes with aging of the OM stored in seagrass soils at Oyster Harbour. In this regard, we studied the link between the chronostratigraphic profile and soil biogeochemical attributes. This approach can provide new insights into the pathway for OM preservation beneath seagrass meadows that triggers the accumulation of Blue Carbon in these ecosystems.

2. Materials and methods

2.1. Study site and coring

Oyster Harbour is a naturally protected estuary with freshwater inputs from the Kalgan and King Rivers in the north and marine exchange through a narrow channel in the south (D'Adamo, 1991, Fig. 1). The sediments are medium-coarse to fine grained silty sands together with biogenic carbonates (McKenzie, 1962). In winter months, fine sediments enter the estuary from the rivers following heavy rain. The estuary has had a continuous presence of *P. australis* meadows since the last millennia (Rozaimi et al., 2016).

A soil core was taken from a large mono-specific *P. australis* meadow located on the eastern margin of the estuary (S 34°58′58.0″, E 117°58′29.9″) at 2 m water depth in 2012. A pre-drilled PVC pipe (80 mm inner diameter) with 10 transverse sampling ports (after Fourqurean et al., 2012b) along the coring barrel was hammered manually into the seafloor. The ports were sealed with PVC tape both on the inner and outer walls to prevent sample loss and alteration of soil integrity during coring and core extraction. The core barrel was sharpened at the distal end to assist with penetration. Within 10 min of core retrieval, the PVC tape covering each sampling port was removed sequentially from the top to the distal core end to measure redox potential by inserting a platinum electrode (WTW SenTix ORP) into each sampling port. Following that, a 50 ml tube (inner diameter of 30 mm) was inserted into the ports to sample the soil.

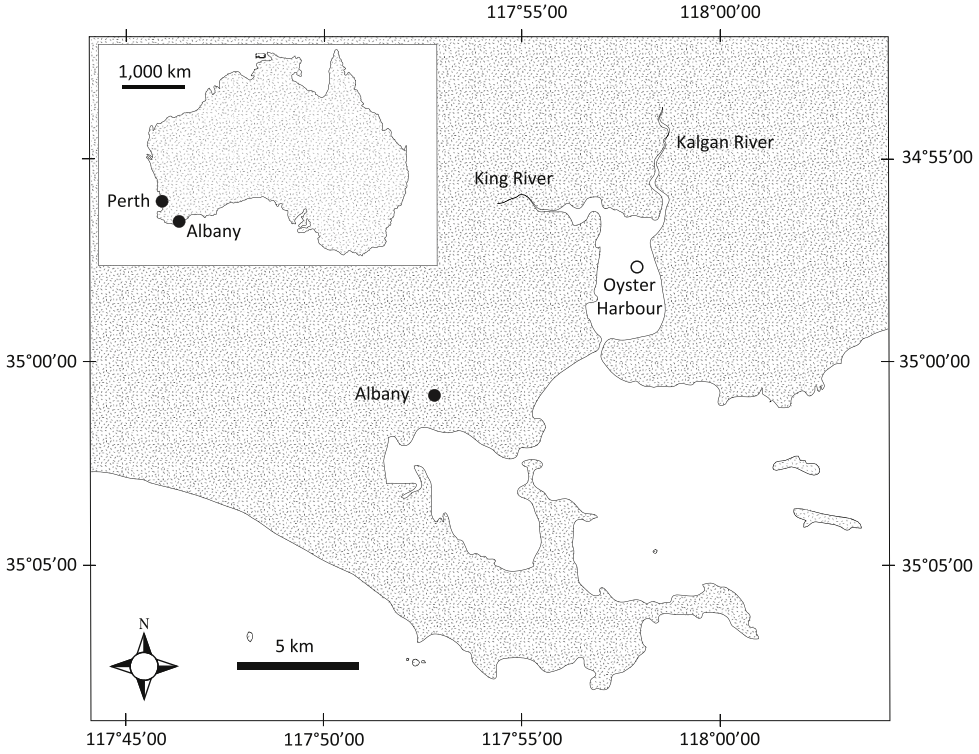


Fig. 1. Location of the study site at Oyster Harbour (Albany, south-western Australia). The open circle denotes the sampling site within the estuary.

Compression of unconsolidated soil during coring is an inevitable phenomenon and resulted in the recovery of a 100 cm core out of the 150 cm core barrel used (33% compression). By linear proportions, the core was decompressed to occupy the length of the core barrel embedded within the sampling point and thus providing the corrected core length. The 10 sampling ports corresponded to the following corrected depths for the sampled soil layers: 2–4 cm, 7–9 cm, 12–14 cm, 17–19 cm, 22–24 cm, 28–30 cm, 34–36 cm, 51–53 cm, 91–93 cm, and 131–133 cm. All variables relating to the stratigraphy of the soil core were plotted against these corrected core lengths.

In the laboratory, the bulk sediment samples were oven-dried at 60 °C until constant weight and divided by quartering for subsequent analyses. Two sets of sub-samples were used for soil grain size and ^{14}C analysis. The other sets were ground to a fine powder and used for the analysis of bulk soil organic characteristics (i.e. OM, OC and N contents, $\delta^{13}C$ signatures and NMR spectroscopy).

2.2. Age-depth model

Plant fibres (i.e. *Posidonia* sheaths) were identified and isolated from the 22–24 cm, 51–53 cm and 131–133 cm soil layers for dating by ^{14}C accelerator mass spectrometry (AMS). These samples were rinsed in ultrapure MilliQ water, placed in a sonic bath (5 min) to dislodge any attached soil particles and inspected under a microscope to ensure minimal presence of extraneous particulate contaminants in the samples. The cleaned samples were then sent to DirectAMS (Seattle; USA) for a further acid-base-acid treatment prior to ^{14}C analysis (Brock et al., 2010). An age-depth model was built using the ^{14}C dates and the year the core was collected was added as the age of the soil-water interface with an error of ±5 years. This age-depth model was generated using a Bayesian approach with the software Bacon 2.2 (Blaauw and Christen, 2011), assuming a DeltaR of 71 ± 22 yr (Ulm, 2006), and indicates that the *P. australis* soil core encompassed the last ~1,700 Cal. yr BP (Fig. 2).

2.3. Biogeochemical analyses

For soil grain size analysis, bulk soil subsamples were digested with 10% hydrogen peroxide, dried, subjected to ultrasonic agitation in a sodium polyphosphate solution as a dispersing agent and subsequently introduced to a Mastersizer particle analyser (Malvern) at the Centro de Estudios Avanzados de Blanes (Centre for Advanced Studies of Blanes). Results are provided as the proportion of particle size fractions (%) across five category ranges (<63 μm, 63–250 μm, 125–250 μm, 250–500 μm, 500–2000 μm, and >2000 μm fractions). The sediment colour was determined using the Munsell Colour Chart classifications (Munsell, 2000).

For OM content estimates, ground subsamples were combusted in a muffle furnace at 550 °C for 4 h to obtain the weight loss on ignition (Heiri et al., 2001; Rozaimi et al., 2017). Another sub-sample was used for OC and N content, and $\delta^{13}C$ analysis. To remove all inorganic carbon, 1 g of ground sample was acidified in 1 M hydrochloric acid. When effervescence ceased, after 12 h, the mixture was centrifuged (3,400 rpm for 5 min) and the supernatant removed by pipette. Deionised water (10 mL) was added to wash the sample of residual acid, the mixture centrifuged and the supernatant removed by pipette. Each acidified sample was then oven-dried until constant weight. Then, ~10 mg of acidified sample was encapsulated in a tin capsule and combusted in a continuous flow isotope ratio mass spectrometer analyser (PDZ Europa: Sercon) at the University of California Davis Stable Isotope Facility. The OC and N contents were corrected for the pre-acidified bulk weight. $\delta^{13}C$ values are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard. ~5 g of bulk soil samples were inspected under the stereoscope and large organic particles (>0.2 mm) were collected to determine whether they corresponded to seagrass debris or charcoal (i.e. black carbon).

2.4. ^{13}C NMR spectroscopy

Prior to NMR analysis, the soil samples were pre-treated based on a

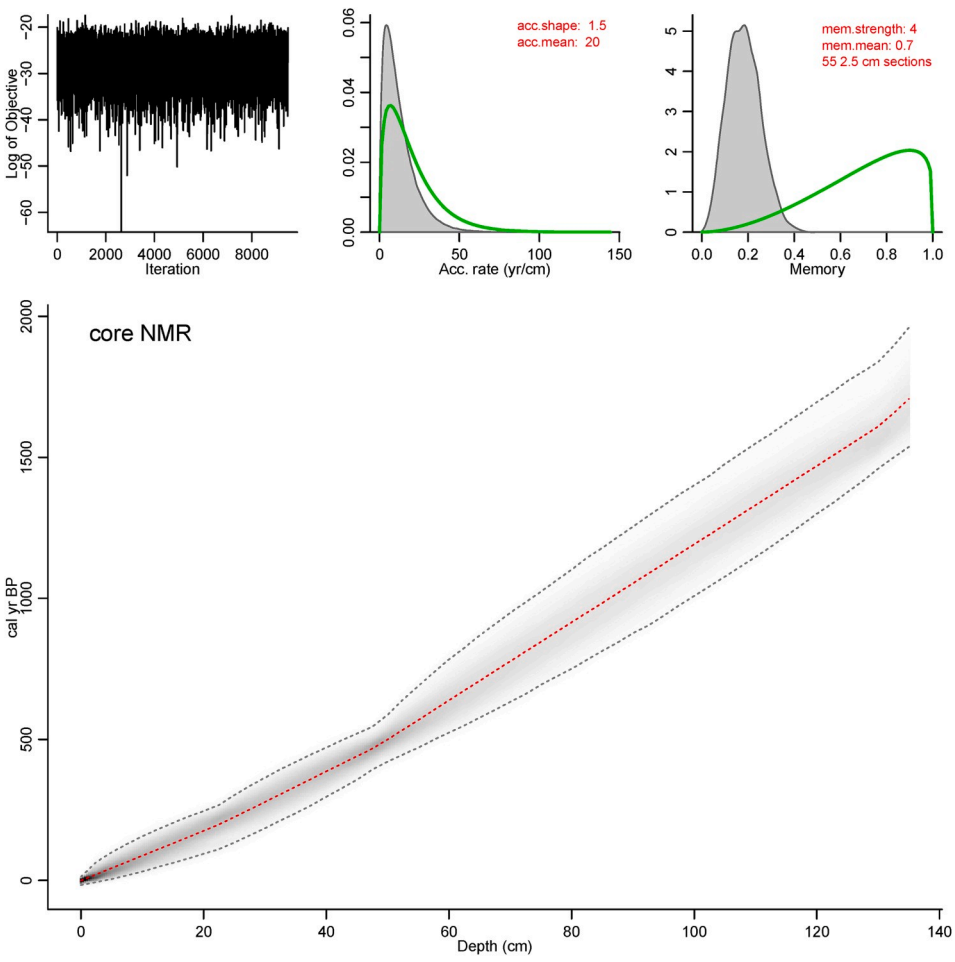


Fig. 2. Chronostratigraphic framework for the *Posidonia australis* core sampled at Oyster Harbour constructed using Bacon 2.2 software. Upper left: Markov Chain Monte Carlo iterations showing a stationary distribution with little structure among iterations. Upper middle: prior (green curve) and posterior (filled grey curve) distribution of accumulation rates. The average accumulation rate was set to 20 yr cm^{-1}. Upper right: prior and posterior probability distributions for memory (i.e. autocorrelation strength). The solid line represents a best fit (smooth-spline model) using three radiocarbon dates calibrated and corrected for the reservoir effect. The age-depth relationship is consistent with an average ± SE sediment accretion rate of 0.076 ± 0.012 cm yr^{-1} (i.e. each cm of sediment represents 13.8 ± 2.11 yr cm^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

modification of methods outlined by Skjemstad et al. (1994) and Schmidt et al. (1997). The pre-treatment aimed to digest the mineral fraction and concentrate the OM fraction, thereby improving NMR sensitivity (Skjemstad et al., 1994). In addition, the pre-treatment removed sedimentary paramagnetic constituents, which would otherwise decrease signal intensity and peak resolution (Skjemstad et al., 1994; Smernik and Oades 1999, 2000). Ground sediment samples (5 g) were placed in centrifuge tubes and 50 ml of 10% (v/v) hydrofluoric acid was added. This mixture was shaken end over end for 5 h. After standing for a further 12 h, samples were centrifuged (2,000 rpm for 20 min). The supernatant was discarded through a Millipore 5 μm Durapore membrane filter that retained any light sediment fraction. Another cycle of this pre-treatment step was performed with the residue subsequently washed three times with 50 ml of Milli-Q water. Washed samples were combined with any light fraction obtained through the membrane filter and dried at 75 °C.

Solid-state ^{13}C NMR spectra were acquired with cross polarization and magic angle spinning at a ^{13}C frequency of 50.33 MHz on a Bruker 200 Avance spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps, and spun at 5 kHz. Spectra were acquired using a ramped-amplitude cross polarization (CP-ramp) pulse sequence, in which the ^{1}H spin lock power was varied linearly during the contact time. A 1-ms contact time and a 1-s recycle delay were used and 4,000–20,000 transients were collected for each spectrum. All spectra were processed with a 50 Hz Lorentzian line broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm (i.e. the spectrum of hexamethylbenzene was acquired separately). All spectral processing was completed using Bruker TopSpin 3 software. Empty rotor background signals were subtracted and the resultant spectra were integrated across the following chemical shift limits to provide estimates of broad carbon types after Baldock and Smernik (2002), i.e. amide/-carbonyl (210–165 ppm), O-aryl (165–145 ppm), aryl (145–110 ppm), di-O-alkyl (110–95 ppm), O-alkyl (95–60 ppm), N-alkyl/methoxyl (60–45 ppm), and alkyl (45–10 ppm). The proportional detections of each region (%) were then used in a molecular mixing model from eight equations to assign the detections into six components of organic biochemical families (i.e. % of carbohydrate, lignin, protein, lipid, carbonyl and black carbon; Baldock et al., 2004; Nelson and Baldock, 2005).

2.5. Statistical analyses

Stable isotope mixing models were run to estimate the proportion of seagrass, algae, terrestrial OM and black carbon to the seagrass soil OM pool using $\delta^{13}C$ and N/C ratios of the samples. These endmember values were used to estimate the proportion of relative OM contribution to soil OC stocks in each core layer using Stable Isotope Mixing Models in R ('simmr' and 'rjags' packages; Parnell et al., 2010). Endmember $\delta^{13}C$ values and N/C ratios (calculated as the reciprocal of C/N values) were sourced from published work (Supplementary Information 1). Model convergence was confirmed using diagnostic plots and upper confidence intervals, while no overlap between source $\delta^{13}C$ signature averages ± SD were observed.

A principal component analysis (PCA) was carried out in order to provide insights into relationships among the various analyses carried out. Parameters included in the PCA were biochemical components derived from ^{13}C NMR analysis (carbohydrate, lipid, black carbon,

carbonyl, protein and lignin) and soil characteristics (%OC, %N, redox potential, colour, $\delta^{13}C$ and the percentage of particles in the size ranges 0.063–0.25 mm and 0.25–0.5 mm). Data were transformed to Z-scores; calculated as: $[X_i - X_{avg}]/SD$, were X_i is the percentage of a given type in a given sample, X_{avg} is the average of the population and SD is the standard deviation, to avoid the scaling effect and obtain average-centred distributions. The numerical procedures were performed using the SPSS statistical software package.

3. Results and discussion

3.1. Physical attributes and chronostratigraphy of P. australis soils

The *P. australis* soil core studied encompassed ~1,700 Cal. yr BP of accumulation (Table 1 and Fig. 2), and the presence of coarse seagrass debris along the record indicates that seagrass meadows have been present in the area over the period reconstructed (Rozaimi et al., 2016). The top 14 cm of the soil had live *P. australis* below-ground organs (i.e. roots, leaf sheaths, and rhizome tissues), while an agglomeration of below-ground seagrass detritus (i.e. rhizome, sheaths and roots) and biogenic carbonates embedded within a siliciclastic sediment matrix (i.e. seagrass mat; Boudouresque and Meinesz, 1982) was present along the 1.5 m long core. The chronostratigraphic relationship did not vary markedly along the core sequence, indicating stability in soil accretion rates over the last millennia (average ± SE, 0.076 ± 0.012 cm yr^{-1}; Fig. 2).

The soil colour within the 24 cm depth-layer was greyish-brown (Gley1 4/N), but progressively changed from lighter brown (10 YR 6/3) to a consistent brown (10 YR 6/4) towards the bottom of the core (Munsell, 2000, Table 2). The colour of the seagrass mat (i.e. greyish-brown to consistent brown) indicates the presence of reduced iron (Giosan et al., 2002), and thus the presence of a reducing environment that is favourable for OM preservation (Burdige, 2007). The diffuse changes in soil colour across core stratigraphy rather than distinct laminations indicates the stability of the seagrass meadow over the last 1,700 Cal. yr BP.

The mineral matrix within the mat sequence had a predominance of sediment particles <250 μm (average ± SE, 42.9 ± 2.86%; Table 2). McKenzie (1962) reported that the sediment of the estuary was a composite of terrigenous and organogenic components – the former transported from the catchment into Oyster Harbour as fine inorganic matter. The prevalence of silt and clay, and fine sands is consistent with the sheltered nature of the estuarine environment and with the high retention capacity of fine-grained particles by seagrasses, enhancing soil stabilisation while reducing erosion, and increasing sedimentation (Hendriks et al., 2010; Peralta et al., 2008). Fine sediments (<63 μm) reduce oxygenation and are conducive to negative redox potentials below the soil surface (Burdige, 2007), as found throughout the *P. australis* soil sequence (Table 2). Samples within the top 9 cm were less reducing (−25 to −100 mV) than samples at greater soil depth (ranging from −230 to −500 mV; Table 2). Anaerobic processes begin to occur in moderately reducing conditions around +300 mV and are especially pronounced in highly reducing conditions below −200 mV (Delaune and Reddy, 2005). In the *P. australis* mat, burial below the top 10 cm layer would promote OM preservation, further enhanced at greater depths by the highly reducing environment.

Table 1
Radiocarbon (^{14}C) dating results of the *P. australis* sheath samples along the core.

Study site	Soil depth (cm)	# lab ID	Material	Raw age (year BP)	Age error (+/−)
Oyster Harbour (*P. australis*)	22.5	[a]D-AMS 005957	seagrass sheaths	383	24
	52.5	[a]D-AMS 005958	seagrass sheaths	887	26
	132.5	[a]D-AMS 005959	seagrass sheaths	2025	26

3.2. Soil organic content and origin

Soil OM content in the *P. australis* mat ranged from 8.6% to 22.3%, while OC content ranged from 3.0% to 6.8% (Fig. 3). The highest OC content was recorded near the soil surface (6.8% OC at 2–4 cm), and averaged 4.0 ± 0.3% OC downcore. The total soil OC stocks under the *P. australis* meadows at Oyster Harbour (19.9 kg m^{-2} in the top meter) were higher than global estimates (14 kg m^{-2}; Fourqurean et al., 2012a), while OC accumulation rates (17.2 g OC m^{-2} yr^{-1} in the top meter) were lower than global estimates (58 g OC m^{-2} yr^{-1}; Duarte et al., 2013b). There was no significant correlation between age and either OM or OC contents ($P > 0.05$ and $R^2 = 0.001$ in both cases). The OC/OM ratios ranged between 2.8 and 3.3 indicating similar OC richness of the OM with soil depth and ageing (Fig. 3). Surficial soil may contain larger amounts of labile OM compared to deeper sediments, owing to the rapid remineralisation of the more labile OM compounds during early diagenesis under less reducing conditions (Henrichs, 1992, Table 2). The small variation in OC/OM ratio downcore suggests that after initial decomposition of the labile OM (after ca. 200 Cal. yr BP), the remainder is preserved with no major degradation with aging, which would otherwise have decreased the OM content and increased the OC content of the OM (e.g. Emerson and Hedges, 1988). In some seagrass soils, the OM and OC contents decrease with depth and aging but in others they remain stable, resulting in high soil OC stores (Fourqurean et al., 2012a). This highlights differences in OM preservation with ageing among different seagrass meadows, and supports the hypothesis of relatively higher OC storage capacity of *Posidonia* meadows compared to other seagrass habitats (Fourqurean et al., 2012a; Serrano et al., 2016b).

The organic characteristics (i.e. %OC, N/C ratios and $\delta^{13}C$ signatures) of bulk seagrass soils provide information on the possible source and preservation of the buried OM. *P. australis* has high productivity (Marba and Walker, 1999) resulting in carbon-rich but nitrogen-poor tissues (Duarte, 1990). Across the core sequence, nitrogen (N) content was comparatively low (<0.3% N) compared to OC content (3.0%–6.8% OC; Fig. 3). The resultant N/C ratios in the soil (ranging from 0.038 to 0.050; the corresponding range of reciprocal values for C/N ratios is 16–26) resemble the N/C ratios in seagrass tissues, since C/N ratios < 18 indicate a contribution of seston- and algal-derived OM (Meyers, 1994; Ashikin et al., 2020, Fig. 4). In addition, the $\delta^{13}C$ values of the bulk soil OM (ranging from −8.9‰ to −13.1‰; Fig. 3) resemble those of fresh *P. australis* tissues (−9.9‰ to −11.9‰; Hindell et al., 2004; Hyndes and Lavery, 2005; Hemminga and Mateo, 1996), and differ from those of seston, algae or terrestrial OM (ranging from −13‰ to −29‰; Loneragan et al., 1997; Smit et al., 2005). The results of the stable isotope mixing models showed that seagrass OM contributed 54 ± 3% (average ± SD) to the soil OC pool, while algae and terrestrial OM contributed 34 ± 1% and 12 ± 2%, respectively. The lack of significant changes with age/soil depth of $\delta^{13}C$ values of bulk soil OM ($P > 0.05$; $R^2 = 0.11$) and the stable isotope mixing model results (Figs. 3 and 5) suggests OM stability with ageing, while the $\delta^{13}C$ values and C/N ratios (Fig. 4) suggests that *P. australis* was a major contributor to the soil OM pool at Oyster Harbour.

3.3. ^{13}C NMR spectroscopy

The ^{13}C NMR spectra of the 10 samples analysed along the *P. australis* core are remarkably similar, indicating low variation in the quality of the OM with depth and ageing (Fig. 5). Quantitative analyses of the spectra, via integration across seven broad chemical shift regions that can be assigned primarily to broad OC-types, confirms this similarity (see Table 3 for NMR integral data). The majority of the NMR signal was detected in the aryl (145–110 ppm; 21–26%) and O-alkyl (95–60 ppm; 27–38%) regions, indicative of the prevalence of lignin and

Table 2
Sediment physical characteristics (colour, redox potential and grain size fraction) and nitrogen content. Ages marked with (*) correspond to samples dated by AMS 14C; all other sample ages are estimates modelled through Clam.R software (Blaauw, 2010). The codes in parentheses refer to the corresponding Munsell Colour Chart classifications (Munsell, 2000).

Study site	Soil depth (cm)	Age (Cal. yr BP)	Soil colour	Redox (mV)	Grain size fraction (%)				
					Silt & clay (<63 μm)	Fine sand (>63<250 μm)	Medium sand (>250<500 μm)	Coarse sand (>500<2000 μm)	Gravel (>2000 μm)
Oyster Harbour (*P. australis*)	0-5	21	Greyish-brown (Gley1 4/N)	-25	5.7	50.3	17.5	13.5	13.0
	5-10	65	Greyish-brown (Gley1 4/N)	-100	4.6	47.7	16.2	9.6	21.9
	10-15	109	Greyish-brown (Gley1 4/N)	-228	3.6	34.4	23.3	18.8	20.0
	15-20	153	Greyish-brown (Gley1 4/N)	-336	6.9	42.7	18.0	11.3	21.2
	20-25	198	Greyish-brown (Gley1 4/N)	-378	4.5	38.1	19.7	14.8	22.9
	25-30	251	Lighter brown (10YR 6/3)	-426	1.8	23.4	18.2	21.1	35.5
	30-35	305	Lighter brown (10YR 6/3)	-522	7.1	35.9	22.6	20.0	14.4
	50-55	534	Consistent brown (10 YR 6/4)	-572	4.1	41.9	28.4	18.6	6.9
	85-90	1018	Consistent brown (10 YR 6/4)	-505	3.2	30.8	22.1	16.5	27.8
	130-135	1656	Consistent brown (10 YR 6/4)	-520	3.6	39.5	25.9	19.5	11.5

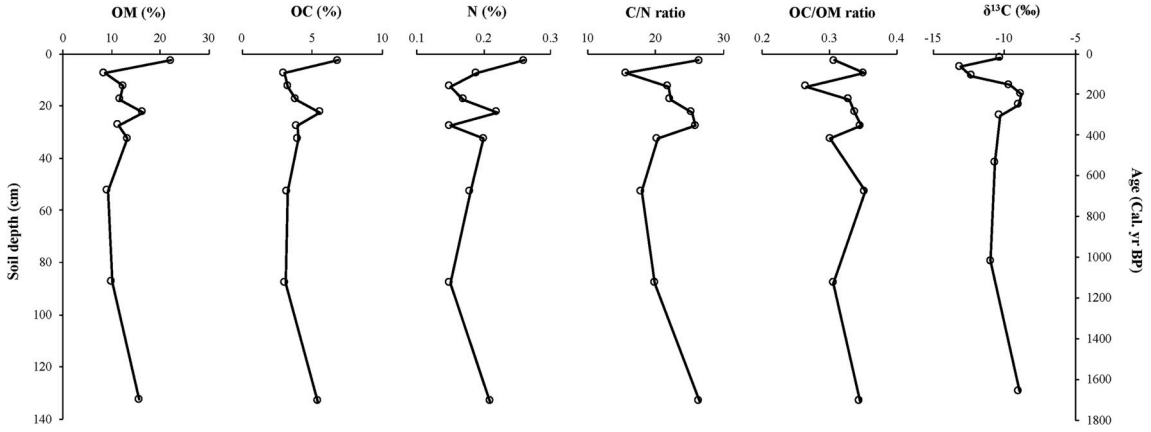


Fig. 3. Chronostratigraphic profile of organic matter (OM) characteristics in the *P. australis* core sampled at Oyster Harbour: organic matter (OM) content, organic carbon (OC) content, nitrogen (N) content, C/N ratio, OC/OM ratio and $\delta^{13}C$ isotope values of bulk soil OM.

carbohydrate in the OM, respectively (Fig. 5). The molecular mixing model approach of Nelson and Baldock (2005) was used to convert these NMR spectral regions into estimates of broad biochemical classes. As Nelson and Baldock (2005) note, there are limitations to this approach. In particular, since protein is the only N-containing component in the mixing model, all N is identified as protein. Any chitin present, for example, would be identified as a mixture of protein and carbohydrate. Nonetheless, the mixing model facilitates interpretation of ^{13}C NMR data by converting a distribution of carbon assigned to NMR-specific groupings (i.e. amide/carbonyl, O-aryl, aryl, di-O-alkyl, O-alkyl, N-alkyl/methoxyl and alkyl) into a distribution of more widely understood biochemical groupings (carbohydrate, lignin, protein, lipid, carbonyl and black carbon) consistent with the acquired ^{13}C NMR data.

Based on the molecular mixing model of Nelson and Baldock (2005), the contents of lignin (17–25%), protein (9–19%), lipid (3–11%) and carbonyl carbon (<2%) remained relatively constant with ageing ($P < 0.05$), but carbohydrate content (21–40%) decreased exponentially with age ($R^2 = 0.87$) and black carbon (19–28%) increased linearly with age ($R^2 = 0.71$; Fig. 6). The higher reactivity of carbohydrates (de Leeuw and Largeau, 1993; Tegelaar et al., 1989) likely explains its degradation with ageing. In common with land plants, much of the biomass of seagrasses is comprised of cellulose-rich cell walls, so presumably the majority of carbohydrate present in these samples is cellulose, although minor quantities of hemicellulose will also be present (Torbatinejad et al., 2007). Degradation of cellulose proceeds in anoxic soils, likely due to the activities of anaerobic micro-organisms working synergistically, but not as efficiently as it occurs in aerobic systems (Leschine, 1995). The low rates of decomposition in anoxic conditions found in seagrass soils resulted in the persistence of carbohydrate in the soil (20–30%) even after millennia of diagenesis, a process also observed in terrestrial peat (Bourdon et al., 2000). Burial in anoxic conditions likely enhanced the longevity of cellulose and lignin (e.g. lignocellulose complex; Derenne and Largeau, 2001). However, lignin is one of the most recalcitrant biomolecules in plant tissues (Lewis and Yamamoto, 1990) and the results obtained suggest that upon burial of seagrass detritus at our study site, there is an uncoupling of the degradation of carbohydrates and lignin that likely began in the living seagrass as a lignocellulose complex.

The predominance of carbohydrate and lignin indicates a prevalence of plant matter within the soil OM. While carbohydrates are present in both plant and non-plant OM (Richmond, 1991), lignin occurs uniquely in vascular plant tissues and it is generally associated with cellulose and hemicellulose (Burdige, 2007). The presence of lignin in soils usually indicates a dominant contribution by terrestrial-based angiosperms (Baldock et al., 2004), but seagrasses are also vascular plants and represent a unique exception to the rule that lignin indicates a terrestrial origin of soil OM. The tissues of *P. australis* contain large amounts of lignin and carbohydrate (20 and 50%, respectively; Torbatinejad et al., 2007; Kaal et al., 2018), and the similarity of the N/C ratios and $\delta^{13}C$ values of bulk soil OM with those of *P. australis* suggests that a large portion of the soil OM, including lignin and carbohydrates, originated from seagrasses rather than terrestrial plants (Figs. 4 and 7).

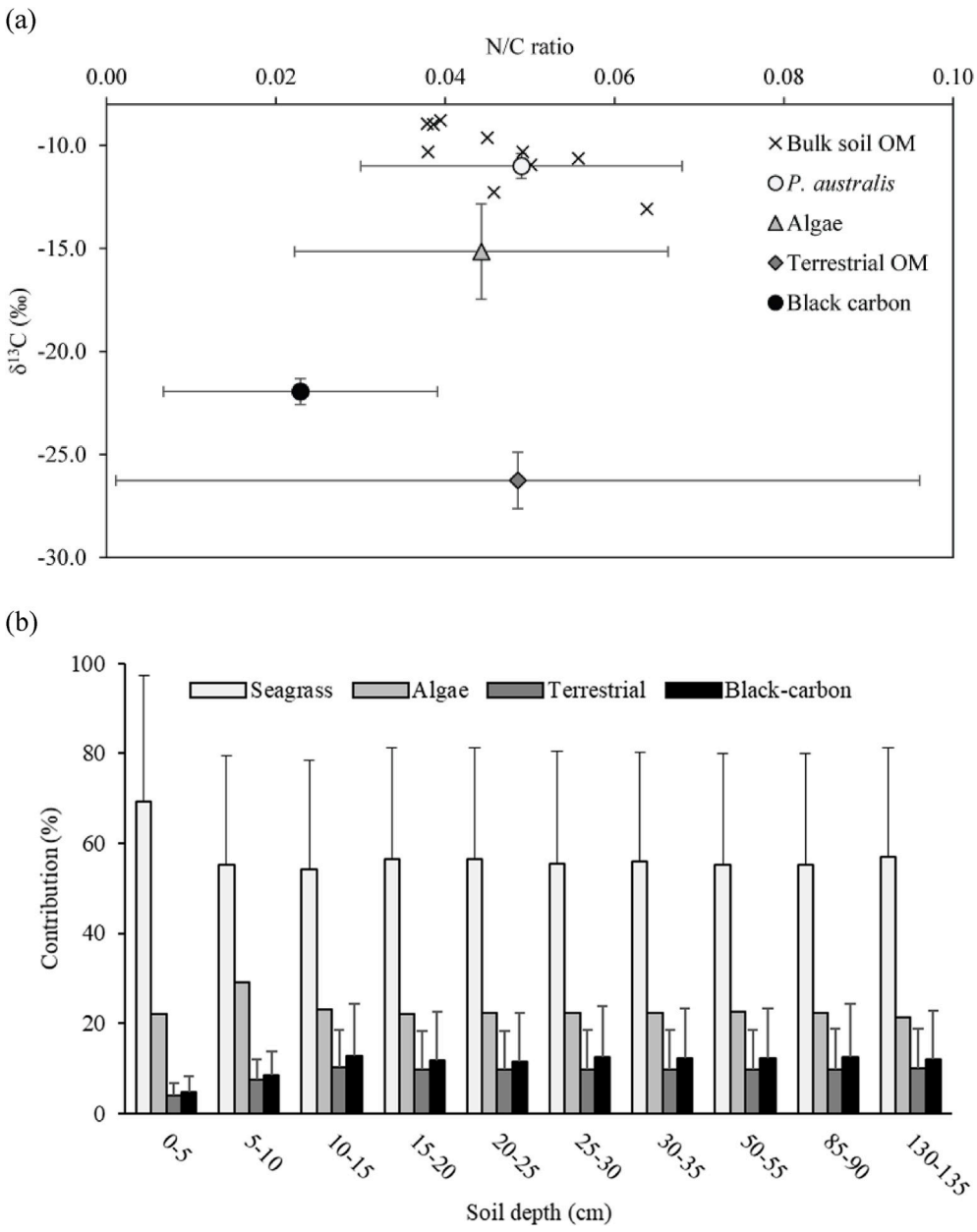


Fig. 4. Endmember values and their estimated contributions (%) to soil organic matter in the *P. australis* core sampled at Oyster Harbour. (a) Scatterplot of N/C ratio against $\delta^{13}C$ endmember values (average ± SD) and $\delta^{13}C$ values of bulk soil organic matter (crosses) from the *P. australis* core. (b) Bar graph showing the results of the isotopic mixing model ('simmr' and 'rjags' packages; Parnell et al., 2010). The four-source mixing model was used to determine the contribution of seagrass, algae, terrestrial organic matter and black carbon to the soil organic carbon pool (average ± SD).

Although results from the molecular mixing model analysis of the NMR data (Fig. 6) indicate significant amounts of black carbon in the *P. australis* mat, there is some uncertainty regarding this interpretation. Old seagrass roots and rhizomes can have a texture similar to char (Babcock et al., 2007), and the rhizomes in soils older than 500 Cal. yr BP at Oyster Harbour were a dark shade of brown-black (5 YR 2/2 to 5 YR 2/1) with a brittle texture that disintegrated easily. Although the occurrence of black carbon in seagrass soils has only been reported once (Chew and Gallagher, 2018), it seems likely that charcoal can be transported to coastal areas via run-off (de la Rosa et al., 2011) and accumulate in seagrass soils. In particular, this phenomenon could be of relevance in Australia owing to the high occurrence of wild fires. Black carbon is composed of diverse OM types but always originates from incomplete combustion (e.g. Coppola et al., 2014). A plot of N/C ratios against $\delta^{13}C$ values highlights similarities in these parameters between soil samples and *P. australis* tissues, but not black carbon samples (Fig. 4). In addition, particles with morphology consistent with that previously reported for black carbon particles were not observed under the stereoscope in our seagrass soils, suggesting that the component determined in the mixing model as black carbon was, in fact, unlikely to be black carbon (i.e. char, as commonly identified in terrestrial ecosystems).

Previous studies have reported that black carbon can be overestimated or mis-identified using a variety of black carbon quantification approaches (Glaser and Knorr, 2008; Simpson and Hatcher, 2004). In the case of the molecular mixing model used here, there are some plausible explanations for overestimation of black carbon. First, the majority of signal for both lignin and black carbon occur in a similar region of the NMR spectrum, i.e. in the 145–110 ppm aromatic region (Fig. 5). Lignin produces signals centred at 130 and 150 ppm (as well as at 55 ppm) while black carbon produces a broad signal at approximately 130 ppm and thus there can be uncertainty in attributing aromatic signal to black carbon or to lignin and other non-pyrogenic aromatics (Simpson and Hatcher, 2004). Degradation of lignin that results in the loss of the methoxyl group, as demonstrated by Simpson and Hatcher (2004), is likely to result in identification of this degraded lignin as black carbon. Alternatively, there may be a diagenetic process that produces OM with black carbon-like character from the buried detrital matter, as has been

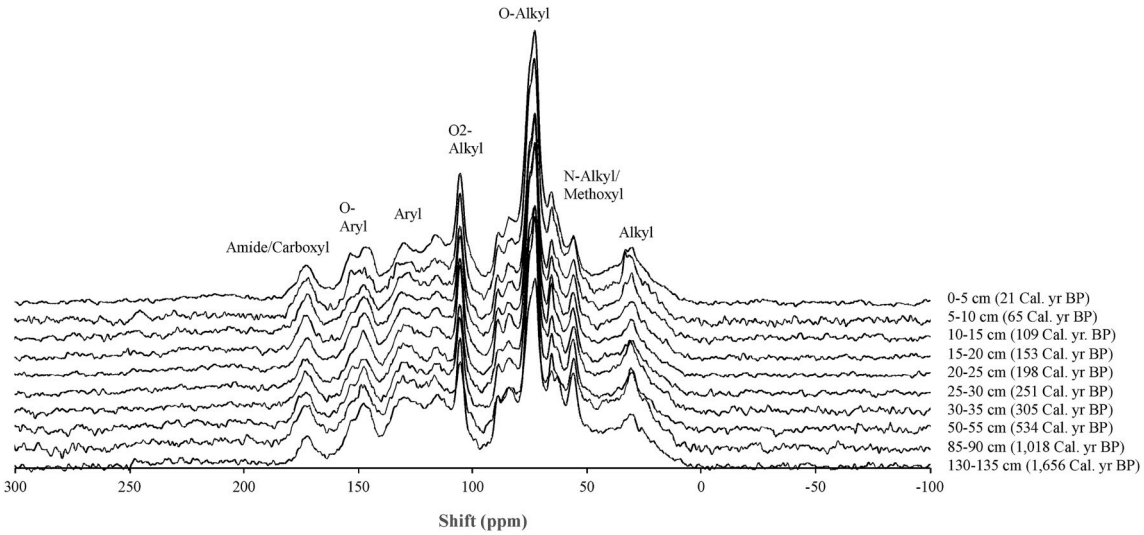


Fig. 5. Solid-state ^{13}C nuclear magnetic resonance (NMR) with cross polarization/magic angle spinning spectra of the 10 soil samples along the *P. australis* core. Numbers in the right side of the figure indicate the sampled depth layers (cm) and the estimated radiocarbon age in calendar years before present (Cal. yr BP).

Table 3
Proportion of the chemical shift limits used to provide estimates of broad carbon types after Baldock and Smernik (2002). *Average spectral intensities of main ^{13}C NMR functional groups of *P. australis* tissues (leaf, sheath, rhizome and root) reported by Trevathan-Tackett et al. (2017).

Study site	Soil depth (cm)	Proportion of biochemical component (%)						
		Amide/Carboxyl (210-165 ppm)	O-Aryl (165-145 ppm)	Aryl (145-110 ppm)	O_2-Alkyl (110-95 ppm)	O-Alkyl (95-60 ppm)	N-Alkyl/Methoxyl (60-45 ppm)	Alkyl (45-10 ppm)
Oyster Harbour (*P. australis* bulk soils)	0-5	7.3	8.1	20.9	9.9	37.8	6.2	9.8
	5-10	7.6	7.7	21.4	9.0	36.5	7.5	10.4
	10-15	9.6	9.5	23.3	8.4	31.8	6.9	10.4
	15-20	8.6	9.1	24.1	8.9	32.8	7.2	9.4
	20-25	8.4	9.3	24.7	8.6	32.3	7.4	9.3
	25-30	8.0	8.4	24.1	8.6	33.6	7.5	9.8
	30-35	8.6	8.4	23.1	8.0	31.2	8.0	12.7
	50-55	8.0	9.1	24.9	8.5	31.7	7.9	9.9
	70-75	8.6	9.3	26.0	7.3	26.8	8.5	13.6
	130-135	5.6	8.4	24.9	8.6	34.5	8.2	9.9
Average ± SD		8.0 ± 1.1	8.7 ± 0.6	23.7 ± 1.6	8.6 ± 0.7	32.9 ± 3.0	7.5 ± 0.7	10.5 ± 1.4
**P. australis* tissues		8.9	6.3	13.3	11.4	46.9	4.5	8.8

reported in terrestrial systems (Glaser and Knorr, 2008). A more definitive characterisation of this black carbon-like biochemical component and identification of the processes leading to its formation are beyond the scope of this study. However, it can be concluded that this OM component is non-pyrogenic, but condensed and aromatic in nature (after Glaser and Knorr, 2008) and that it probably originates mainly from *P. australis* detritus since visual observations showed large amounts of seagrass detritus along the core. The high contribution of seagrass OM (up to 69%) and the low contribution of terrestrial OM (4–13%) in the soil OC pool (Fig. 4), together with the similarities between ^{13}C NMR signatures of *P. australis* tissues reported by Trevathan-Tackett et al. (2017) and the *P. australis* bulk soils analysed in this study supports this hypothesis.

Based on the molecular mixing model of Nelson and Baldock (2005), proteins comprised 9–19% of soil OM with little variation with age and persisted over 1,700 yr (Fig. 6). The presence of proteinaceous substances in marine sediments is usually attributed to planktonic and algae inputs (Hedges et al., 1997; Kennedy et al., 2010), though protein from terrestrial sources have also been identified in seagrass soils (i.e. glomalin; López-Merino et al., 2015). Seagrasses are generally N poor (1–3%; Duarte, 1990) and may thus supply relatively small quantities of protein to the soils. Owing to the contribution of algae in the soil OC pool (~34%), it seems plausible that phytoplankton, micro- and macroalgae contributed to the accumulation of proteins in seagrass soils. Indeed, up to 8% of soil OC in *Posidonia* soils can be bacterial biomass (Danovaro et al., 1994) and therefore, the protein content may reflect both microbial biomass and proteinaceous by-products of microbial diagenesis. Notwithstanding the protein source, nitrogenous compounds may rapidly degrade during early diagenesis in oxic conditions, although reducing conditions deeper in the soil may promote its preservation due to microbial polymerisation and condensation, forming refractory proteinaceous matter (Derenne and Largeau, 2001; Wakeham and Canuel, 2006; Burdige, 2007). Further preservation may then be initiated by mineral shielding but *in situ* formation of these new compounds further complicates the identification of the protein source (Burdige, 2007). Without further characterisation, the nature of the protein in *Posidonia* soils cannot be definitively described.

3.4. Organic carbon preservation in seagrass soils

Multiple factors appear to have worked in concert to create a favourable setting for OM preservation in the Oyster Harbour *P. australis* meadow over at least 1,700 years (Fig. 7). Two principal components (PC1 and PC2) explained 63% of the total variance. The first principal component (PC1) accounts for 39% of the explained variance and is linked to high loadings of carbohydrates, lipids, black carbon-like material, redox, %OC, N, colour and particles >0.063 < 0.25 mm and >0.25 < 0.5 mm (Fig. 7). The second principal component (PC2)

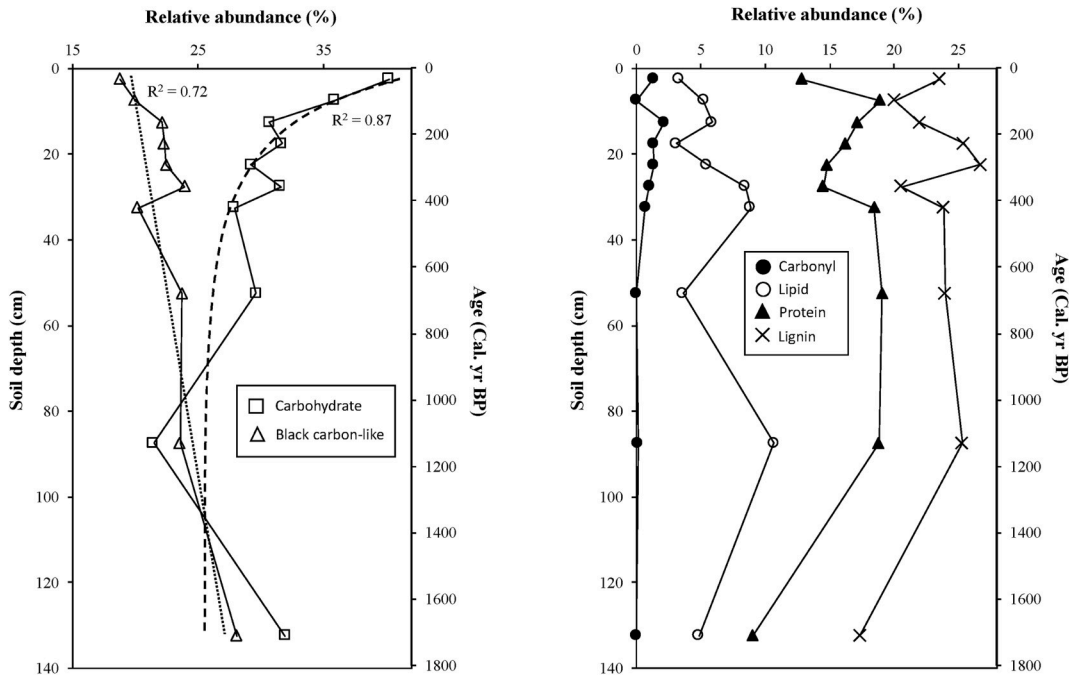
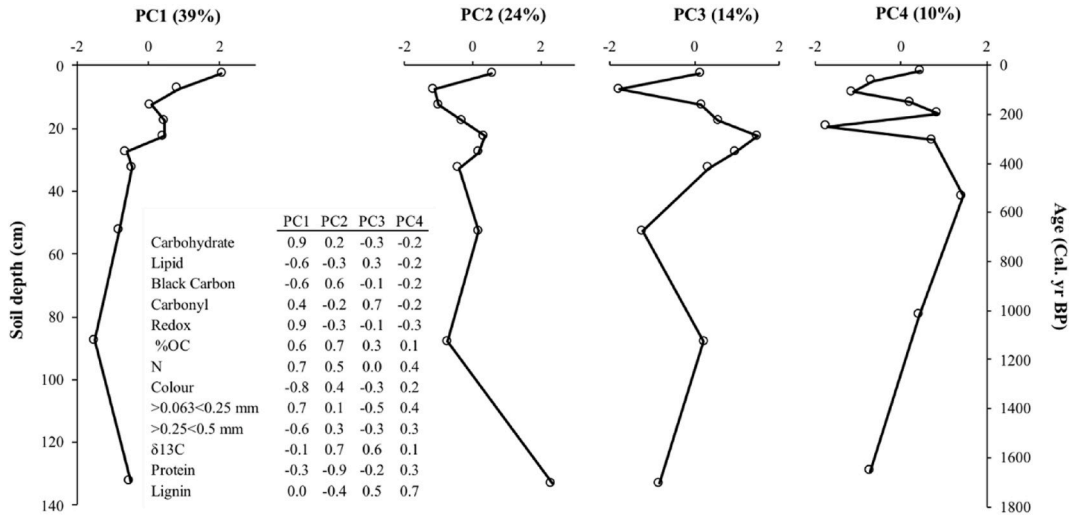


Fig. 6. Chronostratigraphic trends of the relative abundances of the six biochemical components along the *P. australis* core (estimated from NMR spectra using the molecular mixing model of Nelson and Baldock, 2005). Left: R^2 values shown for carbohydrate (exponential regression) and black carbon-like matter (linear regression) proportions, as a function of age. Right: trends of carbonyl, lipid, protein and lignin as a function of age.



	PC1	PC2	PC3	PC4
Carbohydrate	0.9	0.2	-0.3	-0.2
Lipid	-0.6	-0.3	0.3	-0.2
Black Carbon	-0.6	0.6	-0.1	-0.2
Carbonyl	0.4	-0.2	0.7	-0.2
Redox	0.9	-0.3	-0.1	-0.3
%OC	0.6	0.7	0.3	0.1
N	0.7	0.5	0.0	0.4
Colour	-0.8	0.4	-0.3	0.2
>0.063<0.25 mm	0.7	0.1	-0.5	0.4
>0.25<0.5 mm	-0.6	0.3	-0.3	0.3
δ13C	-0.1	0.7	0.6	0.1
Protein	-0.3	-0.9	-0.2	0.3
Lignin	0.0	-0.4	0.5	0.7

Fig. 7. Variations of principal components (PC1, PC2, PC3 and PC4) against soil depth (cm) and age (Cal. yr BP) in the *Posidonia australis* core and correlation scores of the variables and their association with the four components.

explains 24% of total variance and is dominated by high loadings of black carbon-like material, %OC, $\delta^{13}C$ and protein. The third and fourth principal components (explaining 14% and 10% of total variance, respectively) are dominated by carbonyl carbon and $\delta^{13}C$, and lignin, respectively. The PC1 results suggest that carbohydrate content decreased with ageing, and lipid and black carbon-like material contents increased downcore linked to a decrease in C/N and particles >0.063 < 0.25 mm, a shift in soil colour from greyish brown to consistent brown, and a downcore shift from oxic to anoxic conditions. The PC2 results suggest that ~50 years after burial, black carbon-like content increased with ageing linked to higher $\delta^{13}C$ and %OC values, while protein content decreased suggesting an increase in seagrass matter with soil depth/ageing (see below).

Cumulative contents of lignin, carbohydrate and black carbon-like matter (having a total relative abundance of 70–83%), taken in concert with bulk OM characteristics (i.e. N/C ratios and $\delta^{13}C$) suggested that *P. australis* organic matter was a major contributor to the sedimentary OM pool at Oyster Harbour. This contrasts with previous studies from non-seagrass marine sediments from US and Mexico coasts showing that terrestrial- and planktonic-derived OM constituted the bulk of the OC (Dickens et al., 2006). In addition, higher proportions of lipid, protein and carbohydrate with negligible detection of lignin and black carbon were reported for estuarine sediments bereft of seagrasses in South Australia (Krull et al., 2009). In other parts of that estuary, lignin that was detected was taken as evidence that the site was once vegetated by the macrophyte *Ruppia megacarpa* (Krull et al., 2009).

The soil OC stocks (19.9 kg OC m^{-2} in the top meter) at Oyster Harbour rank among the highest reported to date for seagrass meadows

(Fourqurean et al., 2012a). Apart from the surficial soil layer of 0–5 cm, the contribution by *P. australis*-derived OM to the soil OM pool at Oyster Harbour (54–57%; Fig. 4) is similar to the estimates in other seagrass meadows worldwide (50%; Kennedy et al., 2010). Only established meadows of certain seagrass species (e.g. *Posidonia*), which partition a comparatively high amount of production to large, below-ground organs, located in relatively sheltered areas tend to form organic-rich mats (Serrano et al., 2016b). As such, the carbon sequestration potential, and likely preservation processes described in this study may not necessarily be representative of all seagrass meadows.

The preservation of seagrass detritus over millennial time scales may occur in a number of ways. One process often associated with the preservation of recalcitrant plant matter is selective preservation, which refers to the tendency for biomacromolecules that are intrinsically non-soluble, non-hydrolysable, and resistant to biological degradation to comprise increasing proportions of OM with increasing diagenetic maturity (Burdige, 2007; Tegelaar et al., 1989). The black carbon-like matter was the only OM component that exhibited an increase in relative abundance with soil depth (Fig. 6), consistent with selective preservation. The NMR results showed that the chronostratigraphic trends of lignin, protein and lipid show little or no shift with ageing (Figs. 6 and 7), suggesting that these components were possibly subject to physical protection, also termed non-selective preservation (after Hedges et al., 2001). Non-selective preservation is defined as OM that should have undergone remineralisation but was not degraded due to protection by organic or inorganic matrices resulting in longer post-burial residence times than their chemistries would predict (Hedges et al., 2001).

In this study, it is concluded that two different processes of OM preservation within *P. australis* soils lead to the sequestration and long-term retention of OC: non-selective preservation of lignin, lipid, carbohydrates and protein, and selective preservation of black carbon-like matter. While OC sequestration in seagrass soils is inherently complex when considered in terms of OM input, accumulation and remineralisation, this study provides some biogeochemical basis for understanding the persistence of soil OM with ageing. The findings are consistent with accepted processes of OC sequestration, whereby multiple diagenetic processes work in concert with physical, chemical and biological factors, resulting in OM storage and preservation. It is likely that other diagenetic mechanisms may also contribute to OM sequestration and warrant further investigations in other seagrass habitats. The findings demonstrate the exceptional preservation of *P. australis*-derived OC, thereby providing new insights explaining the higher OC storage capacity of *Posidonia* compared to other seagrass species. Further studies are required to elucidate differences in OM quality and diagenesis across seagrass species and geomorphological settings, contributing to understand the factors driving differences in OC sequestration among seagrass habitats.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Oscar Serrano: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. **Mohammad Rozaimi:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. **Paul S. Lavery:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Ronald J. Smernik:** Methodology, Software, Validation, Formal analysis, Resources, Data curation, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecss.2020.106662.

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