Assessing coastal carbon variability in two Delaware tidal marshes

Kari A. St. Laurent[1,2] · Daniel J. Hribar[3] · Annette J. Carlson[4] · Calyn M. Crawford[5] · Drexel Siok[1]

Abstract

Coastal wetlands provide numerous ecosystem services, including the ability to sequester and store carbon. Recent initiatives, such as the U.S. Climate Alliance's National Working Lands Challenge, have sought to better understand and quantify this 'blue carbon' storage as a land management approach to maintain, or potentially offset, atmospheric carbon emissions. To build on this effort locally, loss on ignition and elemental analyses were used to assess sediment organic matter, dry bulk density, and carbon density variability within the root zone of a mesohaline and oligohaline tidal marsh in Delaware. Additionally, we assessed sediment carbon variability at depth greater than one meter and quantified the black carbon fraction in the mesohaline tidal marsh. Organic matter concentrations ranged between $11.85 \pm 1.19\%$ and $23.12 \pm 6.15\%$ and sediment carbon density ranged from 0.03 ± 0.01 g cm^{-3} to 0.06 ± 0.02 g cm^{-3} with both found to significantly differ between the mesohaline and oligohaline tidal marsh systems. Significant differences between dominant vegetation types were also found. We used these data to further estimate and valuate the carbon stock at the mesohaline tidal marsh to be 350 ± 310 metric tons of soil carbon accumulation per year with a social carbon value of $\$40,000 \pm \$35,000$. This work improves our knowledge of Delaware-specific carbon stocks, and it may further facilitate broad estimates of carbon storage in under-sampled areas, and thereby enable better quantification of economic and natural benefits of tidal wetland systems by land managers.

Introduction

Tidal wetlands provide a multitude of ecosystem services including, but not limited to, nutrient retention, wave attenuation,

✉ Kari A. St. Laurent
  kari.stlaurent@delaware.gov

[1] Delaware Department of Natural Resources and Environmental Control, Division of Climate, Coastal and Energy, Dover, DE 19901, USA

[2] Delaware Department of Natural Resources and Environmental Control, Delaware National Estuarine Research Reserve, Dover, DE 19901, USA

[3] School of Environment and Natural Resources, Ohio State University, Columbus, OH 43210, USA

[4] College of Natural Resources & Sciences, Department of Oceanography, Humboldt State University, Arcata, CA 95521, USA

[5] School of the Earth, Ocean, and Environment, University of South Carolina, Columbia, SC 2920, USA

nursery habitat, and carbon storage (Barbier et al. 2011; Daily et al. 1997; DeGroot et al. 2002; Gedan et al. 2009). Understanding the role of tidal wetlands in global carbon sequestration and storage processes, termed 'blue carbon,' is vital for discussions related to carbon mitigation pathways and emissions reductions scenarios. Globally, salt marsh ecosystems bury an estimated 4.8 to 87.2 Tg C yr^{-1} and have an estimated mean global carbon stock of 570 to 10,360 million Mg of carbon (Chmura et al. 2003; Duarte et al. 2005; Howard et al. 2017; Mcleod et al. 2011) This potential for long-term carbon storage demonstrates that tidal wetlands are an important carbon sink and provide key opportunities for the mitigation of carbon dioxide emissions when they are created or restored.

Blue carbon ecosystems (salt marshes, mangrove forests, and submerged aquatic vegetation beds) have a greater potential carbon stock per unit area relative to most terrestrial ecosystems due to the high carbon concentration found within their sediments (Murray et al. 2011). Global studies suggest between 50% and 90% of the carbon stored in tidal wetlands is within the soil (Howard et al. 2017; Pendleton et al. 2012). Other synthesis studies have estimated >95% of the carbon stored in salt marsh ecosystems is contained within the soils while, in comparison, tropical forests store approximately

75% of carbon within living biomass stocks and only a quarter within soils (Murray et al. 2011). Carbon-rich sediments of tidal wetlands have been measured up to 6–8 m deep (Chmura et al. 2003; Chmura 2009). Consequently, coastal wetlands are believed to be responsible for 1–2% of the United States' total annual carbon sink despite comprising only ~0.3% (6.4 million acres) of the conterminous United States by area (Chmura et al. 2003; Dahl and Stedman 2013). This demonstrates that tidal wetlands disproportionately store large quantities of carbon relative to their current spatial extent in the United States.

Observations of tidal wetlands vertically accreting due to inorganic mineral deposition and organic matter accumulation may help these habitats keep pace with elevation changes in response to sea level rise and land subsidence (Neubauer 2008; Nyman et al. 2006; Orson et al. 1998; Turner et al. 2002). Tidal marsh sediments become anoxic with depth, which causes the rate of organic carbon remineralization to slow as microbial activity is comparatively decreased as a result of less energy efficient catabolic pathways (Chmura 2011; Macreadie et al. 2011). Tidal marsh sediments are also denoted as long-term carbon sinks that can store fixed atmospheric carbon on the order of centuries to millennia (Mcleod et al. 2011; Nellemann et al. 2009). This allows tidal wetlands to store immense amounts of sediment organic carbon long-term and accumulate additional carbon stocks each year.

Despite their value per capita, tidal wetlands are increasingly at-risk and have been drastically reduced or degraded due to a suite of growing pressures, such as land use changes, coastal development, and sea level rise (Kirwan and Megonigal 2013). Between 2004 and 2009, the observed wetland area along the U.S. Atlantic seaboard decreased by 0.7% in coastal watersheds, and prior wetland loss was estimated at 60,000 acres/year from 1998 to 2004 (Dahl and Stedman 2013). Presently, salt marshes are estimated to have an annual global loss rate of 1–2% (Culbertson et al. 2009).

In Delaware alone, 238 acres of estuarine emergent wetlands were lost between 1992 to 2007 and up to 54% of all wetlands have been functionally lost since the 1780's (Tiner et al. 2011). The removal of tidal wetlands, or the prevention of inland wetland migration due to the 'coastal squeeze effect' (Pontee 2013), can greatly reduce or even reverse carbon storage and sequestration processes (Mcleod et al. 2011; Nellemann et al. 2009). As these wetlands are degraded, the ability of their sediments to store carbon is negated and previously sequestered organic carbon may be freed through remineralization, outputting carbon dioxide. Short-term changes in salinity may further affect the output of methane and carbon dioxide gas, as higher salinities have been shown to reduce methane production but increase organic matter mineralization rates (Chambers et al. 2011; Neubauer 2013).

Delaware has the lowest mean elevation in the United States, making it particularly vulnerable to rising sea levels.

The current sea level rise rate of 3.53 mm per year from the Lewes, Delaware tide station (Station ID: 8557380) is projected to accelerate over the next few decades in response to climatic processes, land use changes, and other pressures (Callahan et al. 2017). Coastal land subsidence, which is occurring at an estimated rate of 1.7 mm per year in Delaware, further compounds issues associated with salt intrusion and wetland loss (Engelhart et al. 2009).

Blue carbon accounting has gained global awareness as a potential carbon financing opportunity for tidal wetland restoration projects (Wylie et al. 2016). In the United States, tidal wetland restoration and protection projects are increasingly being considered as a potential pathway for states to meet their greenhouse gas emissions reductions goals. Delaware established the goal to reduce greenhouse gas emissions by 30% by 2030 from a 2008 baseline in 2013 under Executive Order 41: *Preparing Delaware for Emerging Climate Impacts and Seizing Economic Opportunities from Reducing Emissions*. Delaware's current Governor John Carney has also committed to the United States Climate Alliance, which has been created as a voluntary program to support states seeking to address climate change through the goals outlined in the Paris Agreement. Various working groups, such as the Natural and Working Lands Challenge, have also been formed and supported by the United States Climate Alliance to enhance the creation, protection, and/or optimization of carbon sequestration benefits of forests, croplands, and tidal wetlands.

While numerous blue carbon studies have been conducted in coastal habitats, the availability of site-specific data is imperative to best understand the role tidal wetlands play in local carbon cycles. Coastal carbon stocks average 0.039 ± 0.003 g cm^{-3} globally (Chmura et al. 2003), but these may vary widely in response to environmental factors such as temperature, in-situ production, hydroperiod, and nutrient inputs (Mcleod et al. 2011). Quantifying blue carbon densities in new areas will increase knowledge of coastal carbon stock variability, provide data for optimizing regional soil carbon models, and inform strategic initiatives for the utilization of tidal wetlands in carbon emissions reduction schemes.

Establishing a baseline of the variability and range of carbon densities within two representative Mid-Atlantic tidal marshes is the first step in understanding the role tidal wetlands could play in helping maintain, or potentially reduce, current levels of greenhouse gas emissions. Local data are needed to better estimate carbon storage changes with wetland loss, decide whether wetland creation or restoration is advantageous, and advance quantifiable metrics for tidal wetland carbon accounting.

The goal and purpose of this work is to enhance the global and national inventory of coastal carbon densities through the collection and analysis of marsh sediments in two Delaware tidal wetlands. More specifically, the study aims to 1) assess carbon density variability, 2) investigate the relationships

between organic matter and organic carbon concentration at depth and across different vegetation types, 3) evaluate wetland carbon to nitrogen ratios, 4) determine the fraction of organic carbon apportioned as soot-like black carbon, and 5) estimate carbon storage values in Delaware wetlands. This analysis will allow broad implications to be made of the carbon storage capacity of the state's coastal marshes and the potential of these systems as a pathway to mitigate or reduce greenhouse gas emissions.

Methods

Study area

Data for this study were collected from two tidal wetlands at the Delaware National Estuarine Research Reserve (DNERR) located approximately 50 km apart: The St. Jones Reserve and the Blackbird Creek Reserve (Fig. 1). The St. Jones Reserve is a mesohaline salt marsh located in Dover, Delaware with an elevation range, relative to the National Vertical Reference Datum of 1988, between −1.34 and 3.74 m and a mean elevation of 0.60 ± 0.26 m (McKenna et al. 2018). The average salinity, calculated from the Scotton Landing water quality station (1995–2020), is 10.8 ± 6.9 ppt with a large range spanning from 0.1 to 29.9 ppt. The predominant tidal marsh vegetation type is *Spartina alterniflora* with *Spartina patens*, *Spatina cyanosuriodes*, *Distichlis spicata*, and *Phragmites australis* all visually present. The St. Jones watershed is a fairly developed system with classified land-use based on NOAA's Coastal Change Analysis Program (C-CAP) of 50% agriculture, 26% forested/wetland, and 21% urban ("St. Jones River", (St. Jones River 2020)).

The Blackbird Creek Reserve is an oligohaline system located in Townsend, Delaware with an elevation range of −0.40 and 4.48 m and a mean of 0.48 ± 0.24 m (McKenna et al. 2018). The average salinity, determined from the Blackbird Landing water quality sonde (1995–2020), is 1.9 ± 2.1 ppt with a range of 0–9.4 ppt. The vegetation type varies along the salinity gradient, including mixes of *S. alterniflora* with more tidal freshwater species such as *Pontederia cordata*, *Persicaria punctate*, *Amaranthus cannabinus*, *Peltandra virginica, and Zizania aquatica*. The Blackbird Creek watershed is less developed, with 50% of the watershed denoted as forest/wetland, 44% agriculture, and 3% as urban classified by C-CAP ("Blackbird Creek", (Blackbird Creek 2020)).

Sample collection

Shallow sediment cores ($n = 50$; 20–30 cm depth) and deep sediment cores ($n = 6$; 122–137 cm depth; 10 cm diameter)
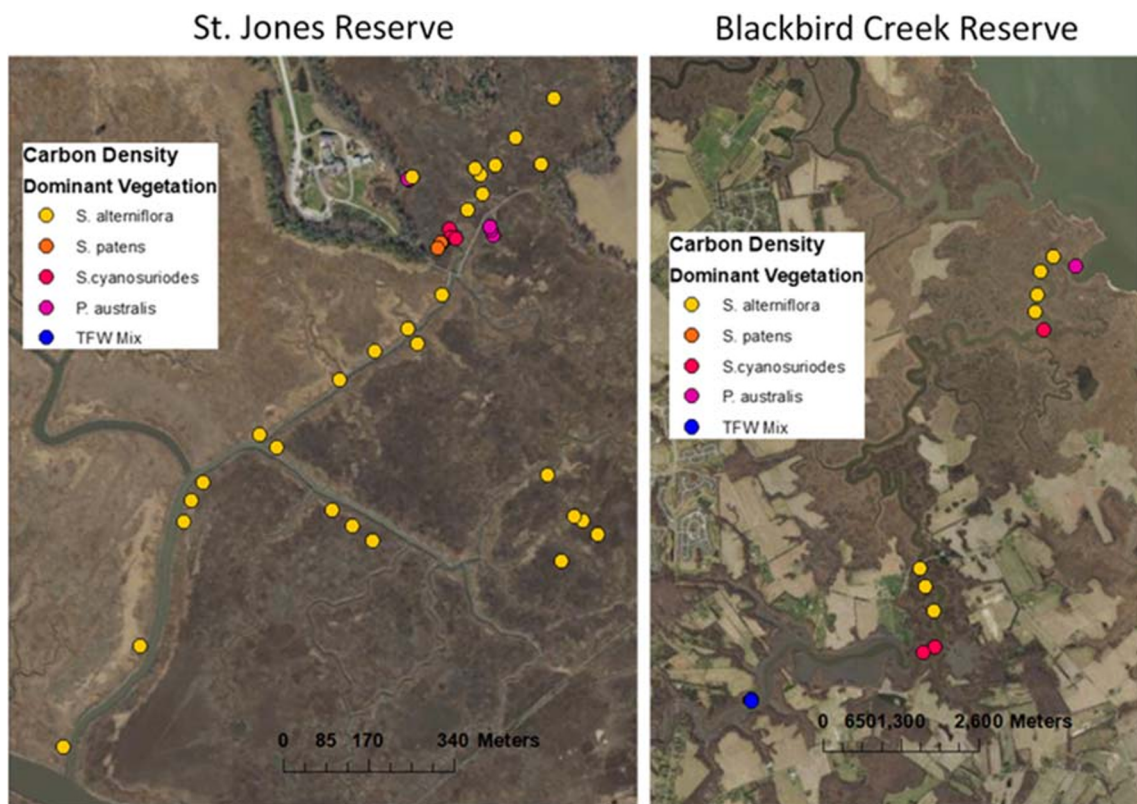

Fig. 1 Aerial map of the sediment cores collected from the St. Jones Reserve and Blackbird Creek Reserve denoted by dominate vegetation

were collected by driving a PVC tube into the marsh surface. Deep cores were collected in June 2018 at the St. Jones Reserve and shallow sediment cores were collected between June and July in both 2017 (5 cm diameter) and 2019 (7.6 cm diameter) at both the St. Jones Reserve ($n = 36$) and the Blackbird Creek Reserve ($n = 14$). Sample sites from 2017 and 2019 were selected using the Create Random Points function in the Data Management toolbox using ArcMap (version 10.6 and below). Sample sites for the deep cores were collected using the Generate Points Along Lines function in ArcMap's Data Management toolbox to create 6 equidistant points along the main tidal gut within St. Jones Reserve. A GPS point was taken at each core using a Garmin handheld GPSMAP 64-series unit.

At each core collection site, the vegetation composition was measured within a 1 m^2 quadrat through visual estimates in 5% intervals, including both bare ground and wrack categories following the National Estuarine Research Reserve System's emergent tidal vegetation monitoring protocol (Moore 2013). We note that the samples collected in 2019 were designed to randomly collect 10 shallow cores from *S. alterniflora* and 3 cores each from *S. patens*, *S. cyanosuriodes*, and *P. australis* to increase the diversity of sub-sampled vegetation types. Dominant vegetation types were assigned to each core site as defined by whichever species had the highest percent coverage. In most cases, percent vegetative coverage was dominated by a single species with varying degrees of bare ground (see supplemental materials). Porewater salinity was measured during sample collection in 2017 and 2018 using a porewater sipper and a refractometer.

Collected sediment cores were immediately segmented after collection and kept refrigerated (35 °C) during processing and analysis. Shallow sediments were removed from collection tubes using an extruder and segmented into halves (2017) and quarters (2019). Deep cores were first cross-sectioned, described using a Munsel color book, and sectioned into a 'root zone' (0–32 cm) further divided into 10 cm segments. Observationally, the top ~30 cm represented the depth of the active root zone and represents a previously used sediment depth for estimating carbon stocks (Ewers Lewis et al. 2018).

Carbon assessment

Organic matter (OM) concentrations were measured in triplicate using a loss on ignition (LOI) methodology similar to Heiri et al. (2001). Samples were dried at 50 °C for 24–48 h and homogenized using a mortar and pestle. Homogenized sediments were passed through a 1 mm sieve to extract large root fragments; root fragments less than 1 mm were considered as part of the sediment matrix.

Sediments were heated at 550 °C in a muffle furnace for 4 h for the 2017 sediment cores and 8 h for the 2018 and 2019 sediment cores and weighed using an analytical balance. An LOI method development test found that the OM concentration did not significantly vary between 4 and 8 h at 550 °C; thus we felt confident that the OM would be comparable between the different temperature treatments (see SI for more details). Sediments were kept in a desiccator after removal from the muffle furnace before weight measurement.

The OM concentration, as a percentage, was calculated as follows:

$$LOI_{550} = \left(\frac{DW_{50} - DW_{550}}{DW_{50}} \right) * 100 \qquad (1)$$

where DW represents the dried and homogenized sediment weight denoted at 50 °C and 550 °C.

The OM concentration was empirically converted to a sediment carbon concentration using the following equation from Holmquist et al. (2018), which was established using tidal wetland sediment samples from around the United States:

$$Sediment\ Carbon = 0.074 \pm 0.014(OM)^2 + 0.421$$
$$\pm 0.012(OM) - 0.0080 \pm 0.0021 \qquad (2)$$

A subset of samples (64%) were additionally measured in triplicate for elemental carbon, nitrogen, sulfur, and hydrogen on an Elementar Cube (Vario microcube) by the Advanced Materials Characterization Laboratory (AMCL) at the University of Delaware.

Sediments from the 2019 *S. alterniflora*-dominated shallow cores were additionally measured for soot-like black carbon using a chemothermal oxidation at 375 °C (Gustafsson et al. 2001; Gustafsson and Gschwend 1998). Briefly, sediments were acidified with 10% of 1 M hydrochloric acid then combusted in a muffle furnace equipped with a filtered air pump at 375 °C for 2 h. The air pump continuously input ambient oxygen into the furnace which has been shown to combust the thermally labile organic matter but retain the thermally recalcitrant organic carbon, hereby termed black carbon (Elmquist et al. 2004; Gelinas et al. 2001; Gustafsson and Gschwend 1998). Combusted samples were sent to the AMCL for analysis.

Dry bulk density (DBD) was assessed using volume-calibrated crucibles to determine the mass per volume of homogenized sediments in triplicate from each sediment core site. The DBD was used to convert sediment carbon concentrations to carbon densities.

Statistical analysis

Triplicate measurements were taken for organic matter, elemental analysis, and black carbon for each sample. In the shallow sediment cores that were subdivided into a top and bottom (2017 and 2019), data were combined to create one 'surface' data point which represented the top 20 to 30 cm.

Some samples did not have enough homogenized sediment volume to take triplicate DBD measurements; in such cases, the mean DBD was used to impute the missing data. All statistical analyses were done in R version 3.6.1.

Organic matter, sediment carbon, and dry bulk density values were assessed for differences in the mean between the St. Jones and Blackbird Creek Reserves using an unpaired two-sample Mann-Whitney U test and denoted as significantly different if the p value was <0.05. We elected to use a non-parametric approach due to the unequal sample sizes between groups. This approach was verified by applying a Shapiro-Wilk test for normality. A Tukey's honest significant difference (HSD) test was applied in R (agricolae package) to assess differences between the dominant vegetation species within each site (De Mendiburu 2020). The package multcompView was used to check the p value correlations of the Tukey HSD test (Grave et al. 2019).

Best linear fits were assessed using an Akaike information criteria (AIC) and Pearson's product-moment correlation was applied to obtain a correlation coefficient. Kernel density plots were additionally used to assess differences in the distribution of carbon density data by each vegetation species. A Shapiro-Wilks test for normality was first applied and density plots were considered to be from a different distribution if an Anderson-Darling test (R package kSamples) was found to have a p value <0.05 (Fritz and Scholz 2019).

Sediment carbon data from the St. Jones Reserve was spatially interpolated using a Kriging analysis from the Interpolation toolbox in the ArcGIS (version 10.6) spatial analyst tool. A new polygon of the tidal wetland area managed by DNERR was created in ArcMap by a point and click method using internal wetland delineation aerial expertise. Small tidal tributaries were not removed and *Phragmites australis* stands were considered wetland. This new polygon of DNERR managed lands was used to clip the Kriging interpolation.

St. Jones Reserve sediment accretion estimates

Vertical marsh accretion was determined using feldspar clay markers from 3 sites within the St. Jones Reserve and 4 sites at Blackbird Creek Reserve (Table 1).

All sites are located within *S.alterniflora*, with the exception of "BBLR" which is within *Scirpus americus*. All feldspar clay marker sites are denoted as mesohaline to polyhaline. Feldspar clay markers are laid in triplicate at surface elevation table sites, installed as described by Cahoon et al. (2002). A fourth feldspar location was available for the St. Jones Reserve but was excluded from this analysis due to the accretion rates being almost 5 times higher than the mean of the other three. This site has high fiddler crab burrowing activity that we believe to be artificially increasing the

Table 1 Locations and date of placement for the feldspar clay markers used to derive accretion. Not that 'SJ' and "BB" denote the St. Jones and Blackbird Creek Reserves

Site	Coordinate Location	Date of Installation
SJBW	39.08807, −75.43750	2004-06-22
SJRD	39.08688, −75.43333	2013-06-06
SJTR	39.08353, −75.43836	2013-06-06
BBEN	39.39721, −75.61931	2004-12-16
BBDL	39.39439, −75.59839	2005-02-15
BBLR	39.38743, −75.63652	2004-12-14
BBBV	39.40034, −75.62407	2005-02-15

sediment accretion rates observed, which does not reflect that of the broader St. Jones Reserve marsh.

Methane estimates

The carbon dioxide sequestered by tidal wetlands could be negated by methane emissions. Lower pore-water salinities have been correlated to increased methane output due to a decrease availability of sulfate and other ions with decreased salinity (Poffenbarger et al. 2011; Sutton-Grier et al. 2011; Weston et al. 2006). With the collected salinity data, methane emissions were approximated using the following empirical equation developed by Poffenbarger et al. (2011):

$$loglog\ CH_4 = -0.056*S + 1.38 \qquad (3)$$

where CH_4 is the estimated methane gas emission and S is the porewater salinity measured during core sampling.

Results

Organic matter and dry bulk density

Surface sediment organic matter (OM) concentrations were highly variable (Table 2) with an average of $20.85 \pm 10.21\%$ for the St. Jones Reserve (range 6.87 to 52.97%) and $15.01 \pm 5.12\%$ for the Blackbird Creek Reserve (range 8.63 to 32.20%). Organic matter concentrations were significantly higher at the St. Jones Reserve compared to the less saline Blackbird Creek Reserve ($p < 0.05$). We note that the St. Jones Reserve sample size ($n = 283$) was more than double that for Blackbird Creek Reserve ($n = 103$). The OM concentrations also varied by year, likely due to differences in the bulk core processing and sample size, with 2019 sediments being the most variable at $24.17 \pm 11.38\%$.

A Tukey post-hoc test showed significant differences of OM between different dominant vegetation species (Fig. 2). Within the St. Jones Reserve, *S.alterniflora* ($n = 217$) and

Table 2 Summary of dry bulk density (DBD), organic matter (OM), organic carbon (OC), and carbon density (Converted from OM) for surface sediments (top 30–40 cm) collected from the St. Jones (SJ) and Blackbird Creek (BB) Reserves

Site	Dominant Vegetation	DBD (g/cm³)	OM (%)	C (%)	C Density (g/cm³)
BB	*S. alterniflora*	0.65± 0.08	13.72± 4.05	5.13± 1.82	0.03± 0.01
BB	*S. cyanosuriodes*	0.68± 0.05	11.85± 1.19	4.30± 0.52	0.03± 0.00
BB	*P. australis*	0.70± 0.03	14.49± 1.99	5.46± 0.88	0.04± 0.00
BB	*Tidal Freshwater Mix*	0.47± 0.08	20.73± 5.59	8.27± 2.54	0.04± 0.01
SJ	*S. alterniflora*	0.66± 0.11	22.18± 10.69	8.99± 4.97	0.06± 0.02
SJ	*S. patens*	0.64± 0.07	23.12± 6.15	9.35± 2.80	0.06± 0.01
SJ	*S. cyanosuriodes*	0.82± 0.03	13.80± 0.78	5.15± 0.34	0.04± 0.00
SJ	*P. australis*	0.86± 0.13	14.29± 7.35	5.40± 3.35	0.04± 0.02

S. patens ($n = 18$) were both significantly different compared to *S. cyanosuriodes* ($n = 18$) and *P. australis* ($n = 30$). The Blackbird Creek Reserve included a mix of tidal freshwater vegetation ($n = 25$; TFW mix) which was found to be significantly different compared to *S.alterniflora* ($n = 47$), *S. cyanosuriodes* ($n = 24$), and *P. australis* ($n = 7$).

Dry bulk density (DBD) differed between the St. Jones and Blackbird Creek Reserves ($p < 0.05$; Table 2), with an average density of 0.69 ± 0.14 g/cm³ for the former (range 0.32 to 1.09 g/cm³) and 0.62 ± 0.11 g/cm³ for the latter (range 0.37 to 0.76 g/cm³). The DBD of each core was used to convert organic carbon values to organic carbon density to normalize the data and allow for better comparison between sediment cores and sites.

Sediment carbon concentrations

Sediment carbon was determined by both an elemental analysis on a subset of the sediment samples (hereafter denoted as C_{ea}) and by using Eq. (2) to algorithmically convert OM to sediment carbon (Holmquist et al. 2018). Since elemental analysis was conducted on a subset of samples, we elected to use the OM-converted sediment carbon values for the carbon density calculations (below). Carbon density hereafter refers to the OM-converted sediment carbon values. This implies that the same significant differences (i.e. between site and vegetation types) will also exist for the sediment carbon since it is a poly-linear conversion. As a result, converted OC concentrations were significantly higher at the St. Jones Reserve ($8.38 \pm 4.74\%$) compared to Blackbird Creek Reserve ($5.71 \pm 2.30\%$).

We compared the relationship between DBD and sediment organic matter using both a linear relationship and a local regression (loess) filter (Fig. 3). An Akaike information criteria (AIC) was used to determine the linear model with the best fit and an optimal α and degree for the loess was determined using the R "paleoMAS" package (Correa-Metrio et al. 2015). A polylinear equation with a degree of 2 had the best fit (AIC = 2052) and had a correlation significantly different than 0 using a Pearson's product-moment
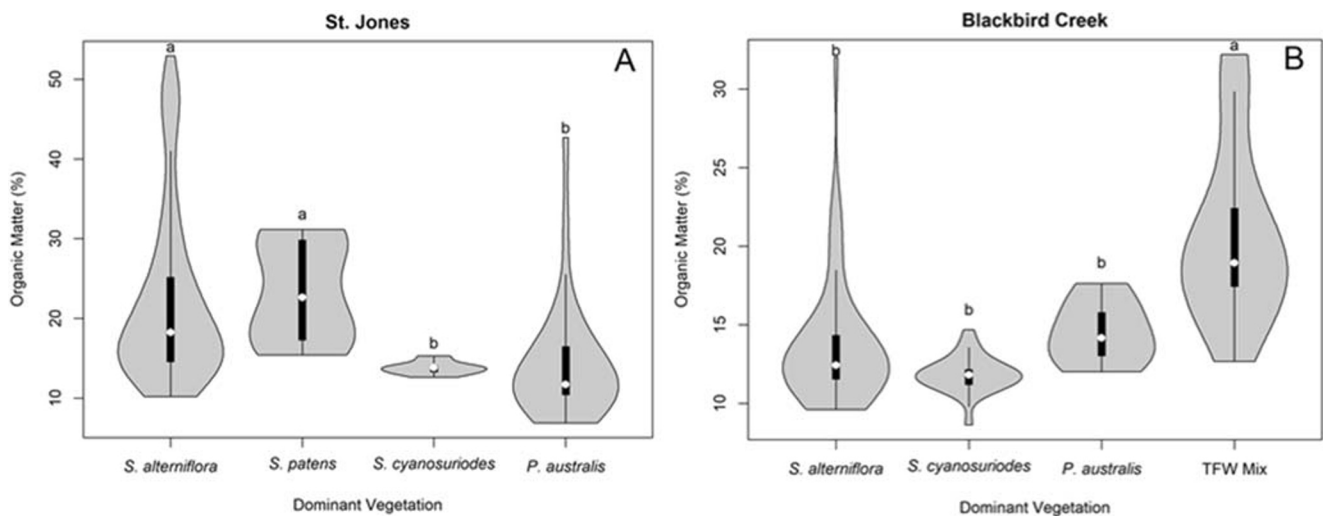

Fig. 2 Violin plots of sediment organic matter separated by the dominant vegetation type for (**a**) St. Jones and (**b**) Blackbird Creek Reserves. Compressed letter displays show grouped datasets via a Tukey post-hoc test

correlation ($r^2 = -0.35$). The loess filter has an optimal span (α) of 0.150 and a degree of 2 (AIC = 1303), indicating a significant inverse relationship between the soil DBD and sediment carbon content. The majority of the spread derived from the *S. alterniflora* DBD variability at the St. Jones Reserve.

A subset of samples (64%) was also measured for carbon via elemental analysis. Carbon content between the OM-converted sediment values and those processed by elemental analysis had a strong linear correlation ($R^2 = 0.90$). We did not evaluate or remove any outliers but note that there were a handful of points that greatly deviated from the 1:1 line. However, this strong relationship shows confidence in our method to convert OM to sediment carbon. Because the converted sediment carbon values only differ from the OM values by a scaler, the trend and linear fit between loss on ignition (OM) and elemental analysis of carbon is identical to the OM-converted vs elemental analysis plot ($R^2 = 0.90$). Thus, we believe that the use of loss on ignition was a reasonable approach to increase our sample size. Previous efforts have found OM to have a polylinear (degree = 2) best fit; however, we observed a linear (degree = 1) best fit (AIC = 726). A larger sample size of elemental carbon values could help improve this fit.

Sample sizes for the elemental analysis were lower than the OM (via LOI) analyses and primarily represented *S. alterniflora* dominated communities ($n = 21$ for Blackbird Creek Reserve; $n = 93$ for St. Jones Reserve) while *S. cyanosuriodes* (St. Jones Reserve) and the tidal freshwater mix (Blackbird Creek Reserve) each had an $n = 9$ and

P. australis for both sites had an $n = 3$. Carbon content showed the highest distribution spread in the *S. alterniflora* community ($5.41 \pm 2.21\%$ and $9.03 \pm 4.83\%$ for Blackbird Creek Reserve and St. Jones Reserve, respectively), likely due to the larger sample size. The greatest overall values were found in the tidal freshwater vegetation mix ($9.42 \pm 1.92\%$) from Blackbird Creek Reserve.

Elemental analysis

Nitrogen and sulfur were also measured alongside carbon in the elemental analysis (Table 3). We note again that sample size was much greater for *S. alterniflora* (83% of data). Nitrogen content was variable, ranging from 0.89 ± 0.24 mg cm^{-3} in *P. austalis* at the St. Jones Reserve ($n = 3$) up to 6.28 ± 0.50 mg cm^{-3} in *P. austalis* at Blackbird Creek Reserve (n = 3). Sulfur was also variable ranging from 2.08 ± 0.34 mg cm^{-3} in *P. austalis* (n = 3) up to 13.11 ± 16.86 mg cm^{-3} in *S. cyanosuriodes* both at Blackbird Creek Reserve (n = 3). Nitrogen and sulfur densities of *S. alterniflora* were not significantly different between the St. Jones and Blackbird Creek Reserves. However, nitrogen and sulfur densities independent of vegetation type were found to be significantly different between the two sites. Nitrogen and sulfur densities at the St. Jones Reserve were 4.6 ± 4.5 mg cm^{-3} and 8.1 ± 3.9 mg cm^{-3} while for Blackbird Creek Reserve, these values were 4.8 ± 1.6 mg cm^{-3} and 7.3 ± 9.1 mg cm^{-3}, respectively. Carbon to nitrogen ratios also varied greatly and were significantly different between the St. Jones (14.2 ± 4.3) and Blackbird Creek (8.7 ± 5.2) Reserves.

Carbon density

Carbon density was found to be significantly different between the St. Jones (0.054 ± 0.022 g cm^{-3}) and Blackbird Creek (0.033 ± 0.001 g cm^{-3}) Reserves. At St. Jones Reserve, the median and modal values were 0.047 and 0.041/0.042 (bimodal) g cm^{-3} while at Blackbird Creek Reserve, these values were 0.031 and 0.029 g cm^{-3}, respectively. Kernel density plots (Fig. 4) further show the longer right-end tail for the vegetation types of *S. alterniflora* and *P. australis* as well as the apparent, but small, bimodal distribution for *S. cyanosuriodes*, *S. patens*, and the tidal freshwater mix.

Sediment carbon densities from both sites were pooled by dominant vegetation type and plotted using a Kernel density to assess and compare frequency distribution (Fig. 4). An Anderson-Darling test and a Mann-Whitney U test were applied to compare the carbon density distributions and means since carbon density by vegetation was found to be non-normally distributed. All carbon densities, parsed by vegetation, were found to have significantly different density
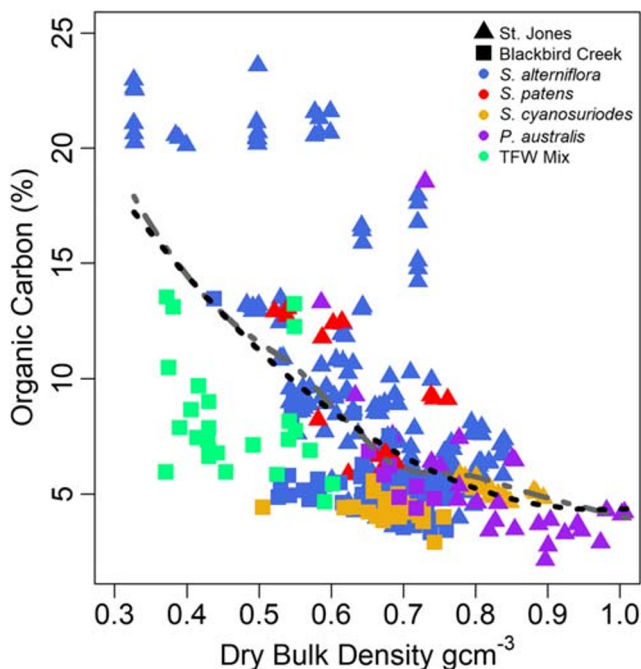

Fig. 3 Plot of calculated organic carbon (OC) vs dry bulk density (DBD) by site and dominant vegetation type

Table 3   CNS analysis and c/n ratio by site and dominant veg type

Dominant Vegetation	Site	C_{ea} Density (g/cm^3)	N Density (mg/cm^3)	S Density (mg/cm^3)	C/N
S. alterniflora	BB	0.03± 0.01	4.38± 1.89	6.85± 5.59	9.92± 6.40
S. cyanosuriodes	BB	0.03± 0.01	4.92± 1.76	13.11± 16.86	7.68± 5.23
P. australis	BB	0.04± 0.00	6.28± 0.50	2.08± 0.34	6.11± 0.17
TFW Mix	BB	0.04± 0.00	5.20± 0.35	4.12± 0.99	7.70± 0.93
S. alterniflora	SJ	0.05± 0.02	4.77± 4.55	8.27± 3.91	13.72± 3.15
P. australis	SJ	0.03± 0.00	0.89± 0.24	3.29± 0.70	30.11± 4.21

distributions and means except for the tidal freshwater mix compared to both *S. cyanosuriodes* and *P. australis* ($p < 0.05$ for Anderson-Darling and Mann-Whitney U tests).

Kernel densities were also plotted for vegetation by site (Supplementary Information). Data were found to be non-normally distributed for all vegetative carbon density data sets with the exception of *S. cyanosuriodes* (St. Jones and Blackbird Creek Reserves) and *P. australis* (Blackbird Creek Reserve). All mean and density distributions pooled by dominant vegetation were found to be significantly different except for the following at the St. Jones Reserve: *S. patens* and *S. alterniflora* (mean); *S. cyanosuriodes* and *P. australis* (mean); and the Blackbird Creek Reserve: *S. alterniflora* and *S. cyanosuriodes* (mean and distribution); *P. austalis* and the tidal freshwater mix (mean and distribution).

The collected sediment data were also organized by the dominant vegetation species for carbon density (Fig. 5a, b). A post-hoc Tukey test revealed the mean values for *S. alterniflora* and *P. australis* at St. Jones Reserve differed significantly, while the mean value of the tidal freshwater mix at Blackbird Creek Reserve differed significantly from means

Fig. 4 Kernel density plots by dominant vegetation for all carbon densities measured in this study

for both *S. alterniflora* and *S. cyanosuriodes*. We note a much greater sample size for sediments from *S. alterniflora* dominated marsh ($n = 38$ cores).

Black carbon ratios

Black carbon (BC) was measured in 10 sediment cores dominated by *S. alterniflora* (Table 4). Sediment concentrations were variable and heterogenous with observed values ranging from 10.56 ± 1.6 g BC kgsed^{-1} to 50.63 ± 7.76 g BC kgsed^{-1}. The overall mean value for black carbon content was 30.12 ± 10.6 g BC kgsed^{-1}. The fraction of BC that composed the total sediment organic carbon (C_{ea}) was $27.5 \pm 3.9\%$ and ranged from 26 to 30%. Black nitrogen had a mean value of 4.92 ± 2.9 g N kgsed^{-1}.

Sediment accumulation

An average sediment accumulation rate was calculated as the average from three feldspar clay markers from the St. Jones Reserve and four from the Blackbird Creek Reserve (Table 1). For the St. Jones Reserve, accretion rates between the plots are variable at 7.0 ± 6.0 mm yr^{-1} (SJBW), 3.4 ± 1.8 mm yr^{-1} (SJRD), and 4.2 ± 2.5 mm yr^{-1} (SJTR), with an overall site mean of 5.9 ± 5.3 mm yr^{-1}. Sediment accumulation rates are higher at the Blackbird Creek at 13.9 ± 11.2 mm yr^{-1} (BBBV), 19.1 ± 15.2 mm yr^{-1} (BBDL), 29.6 ± 30.1 mm yr^{-1} (BBEN), and 10.6 ± 7.2 mm yr^{-1} (BBLR), with a site mean of 18.6 ± 20.0 mm yr^{-1}.

Discussion

Carbon variability across salinity regime

Carbon density, organic matter concentration, and dry bulk density were significantly different between the St. Jones and Blackbird Creek Reserves, suggesting that there were different carbon storage quantities between these two tidal wetlands. While we do note more core samples were taken at St. Jones Reserve ($n = 42$) as compared to the Blackbird
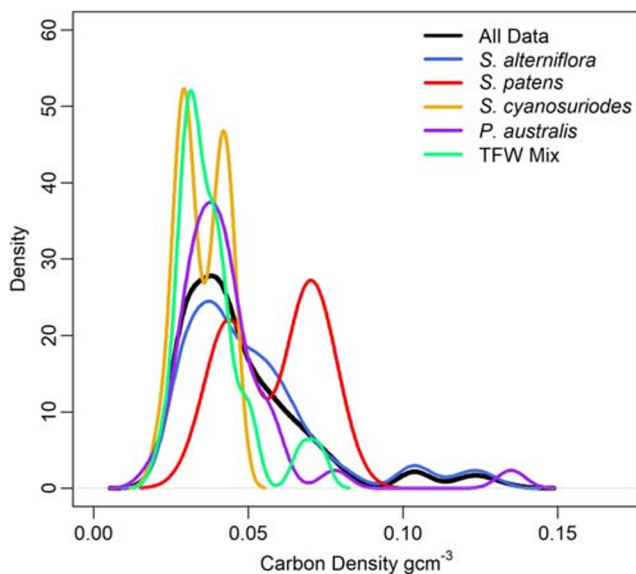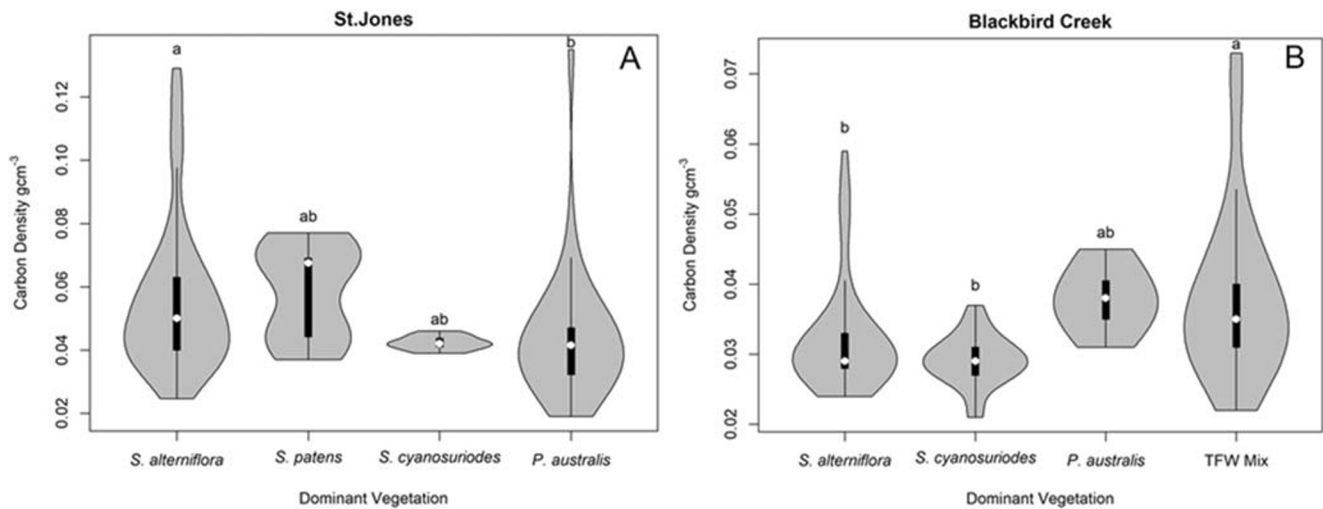
Fig. 5 Violin plots showing the distribution of carbon density (gcm^{-3}) by dominate emergent tidal vegetation species at (**a**) St. Jones and (**b**) Blackbird Creek Reserves. Note that TFW is a mix tidal freshwater vegetation species

Creek Reserve ($n = 14$), our data shows that 'blue carbon' quantities from the Blackbird Creek Reserve were generally lower compared to the St. Jones Reserve. Mean carbon density values measured in *S. alterniflora* dominated areas at the St. Jones Reserve (0.06 gcm^{-3}; $n = 217$) were double those measured at Blackbird Creek Reserve (0.03 gcm^{-3}; $n = 47$). Relative to the global average carbon stock value of 0.039 ± 0.003 g cm^{-3} (Chmura et al. 2003), the St. Jones Reserve demonstrated elevated carbon densities. The range of organic matter concentrations was also greater at St. Jones (10.21 to 52.97%) compared to Blackbird Creek (9.62 to 32.03%) Reserve.

Blackbird Creek Reserve is a tidal freshwater marsh (oligohaline) with a mean salinity of 1.9 ± 2.1 ppt, while the St. Jones Reserve is a more mesohaline saltmarsh with a mean salinity of 10.8 ± 6.9 ppt. The finding of lower carbon density values at the Blackbird Creek Reserve was unexpected as

higher saline waters generally allow for more sulfate reduction, which can turnover organic matter at a faster rate compared to metabolic pathways such as methanogenesis (Sutton-Grier et al. 2011; Weston et al. 2006). For example, soil organic carbon concentrations were nearly 4.5 times greater in a tidal freshwater marsh compared to a saltmarsh in the Scheldt Estuary (Van De Broek et al. 2016). In this European study, regions of the estuary with reduced salinity exhibited higher rates of carbon burial and the depositing allochthonous terrestrial matter was a more stable carbon form.

In general, most tidal wetland studies have shown that soil organic carbon stocks typically decrease with an increasing salinity (Baustian et al. 2017; Christopher Craft 2007; Hansen et al. 2017). A previous tidal wetland study in Delaware found a greater carbon stock in tidal freshwater wetlands compared to oligohaline and mesohaline systems (Weston et al. 2014). Low salinity tidal marshes have demonstrated suppressed decomposition, likely due to limitations in the availability of sulfate and reduced rate of root decomposition (Craft 2007). In the current study, the higher carbon stocks at the St. Jones Reserve could be due to several contributing factors, including differences in sediment accumulation rates, organic matter decomposition rates, and the stability of the organic matter. While we did not measure organic matter decomposition, we are able to use feldspar clay marker horizons to suggest that sediment accretion rates are nearly 4 times greater at the Blackbird Creek Reserve (18.6 ± 20.0 mm yr^{-1}) compared to the St. Jones Reserve (5.9 ± 5.3 mm yr^{-1}). There has also been evidence that tidal freshwater marshes can be extraordinarily sensitive to pulses of brackish water, resulting in rapid soil respiration increases up to 112% due to increases in sulfate and bioavailable nitrogen (Chambers et al. 2013) and significant decreases in soil carbon (Weston et al. 2011).

Table 4 Black carbon (BC) and black nitrogen (BN) sediment weight percentages and ratios with total organic nitrogen (TON) and total organic carbon (TOC)

Core #	BC (%)	BN (%)	BC/BN	BN/TON	BC/TOC
1	4.81 ± 1.17	0.83 ± 0.26	5.91 ± 0.43	1.47 ± 0.10	0.29 ± 0.01
2	2.28 ± 0.08	0.35 ± 0.05	6.55 ± 0.69	1.70 ± 0.13	0.26 ± 0.01
3	2.03 ± 0.15	0.29 ± 0.02	7.06 ± 0.27	1.77 ± 0.13	0.26 ± 0.01
4	1.56 ± 0.16	0.24 ± 0.01	6.48 ± 0.60	1.88 ± 0.11	0.26 ± 0.03
5	2.46 ± 0.59	0.41 ± 0.13	6.19 ± 0.53	2.80 ± 1.41	0.25 ± 0.01
6	4.69 ± 2.29	0.63 ± 0.35	7.83 ± 0.77	1.60 ± 0.35	0.30 ± 0.04
7	5.63 ± 0.77	1.01 ± 0.25	5.69 ± 0.67	4.45 ± 3.74	0.28 ± 0.05
8	1.78 ± 0.15	0.25 ± 0.04	7.33 ± 1.76	1.71 ± 0.12	0.29 ± 0.06
9	3.12 ± 0.37	0.47 ± 0.03	6.67 ± 0.45	3.88 ± 2.77	0.27 ± 0.04
10	2.87 ± 0.57	0.46 ± 0.10	6.25 ± 0.12	1.69 ± 0.36	0.28 ± 0.06

A change point was detected at a salinity of 14 ppt for the carbon density variance for all data (not parsed by site or vegetation) using the ChangePoint package in R with the method "at most one change" (Killick et al. 2016). When the salinity was >14 ppt, an F-test found that carbon density variance was significantly lower (6.87×10^{-5} gC cm^{-3}) compared to when the salinity was <14 ppt (9.67×10^{-4} gC cm^{-3}). Thus, lower salinity values corresponded with greater carbon density variance. We hypothesize that this could be attributed to the more dynamic range of microbial metabolic pathways caused by changes in salinity as well as a ramped-up respiration effect when lower salinity soils are exposed to short pulses of higher saline waters (Chambers et al. 2013). The oligohaline systems could have more frequent periodic changes from sulfate reduction to methanogenesis, causing the rate of carbon turnover and accumulation to change drastically. This relates to the finding by Poffenbarger et al. that methane output decreased significantly at salinities lower than 18 ppt, presumably due to the abundance of sulfate (Poffenbarger et al. 2011).

Soil carbon stocks can also be affected by the dominant vegetation type due to influences on the production and accumulation of labile organic matter (Shao et al. 2015), elevation position denoted by high and low marsh area in part due to marsh age (Choi et al. 2001), and the presence of macropores such as crab burrows that can alter biogeochemical cycles (Guimond et al. 2020). In this study, we cannot assess why the Blackbird Creek Reserve had lower carbon densities compared to the St. Jones Reserve or whether the differences are a result of natural variation between two different watersheds. Large-scale soil carbon mapping efforts such as Holmquist et al. have found carbon density variation is not well-predicted by factors such as salinity or vegetation type, demonstrating local studies are valuable to understand small scale variability (Holmquist et al. 2018). Future studies should consider assessments of carbon stability, decomposition rates, organic matter sources, biotic-causes biogeochemistry and other natural and anthropogenic variability.

Broad generalities

Using organic matter as a carbon proxy

This study shows loss on ignition was a significantly comparable approach to elemental analysis and is a reasonable proxy to measuring sediment carbon in tidal marsh sediments. Global organic matter (loss on ignition) to organic carbon (elemental analysis) syntheses have established this strong relationship and devised best fit algorithms to convert organic matter data to a sediment carbon value (Craft et al. 1991; Holmquist et al. 2018). Our data in two Delaware tidal wetlands supports the use of this relationship at the local level.

We opted to use the algorithm (Eq. 2) established by Holmquist et al. that is a global approximation since only 64% of our sediments were analyzed via elemental analysis (Holmquist et al. 2018). However, we did apply an AIC to establish a local relationship between loss on ignition (organic matter) and sediment carbon that could be applied in the future. These relationships will become more robust as more tidal wetland data are collected in Delaware and the Mid-Atlantic. AIC showed that both a linear (Eq. 4; AIC = 499; $r^2 = 0.89$) and a polylinear to the second degree (Eq. 5; AIC = 497; $r^2 = 0.90$) were significant fits.

$$OC_1 = 0.415(OM) - 0.565 \qquad (4)$$

$$OC_2 = 0.002(OM^2) + 0.293(OM) + 0.820 \qquad (5)$$

The use of these established relationships between organic matter and sediment carbon will increase sampling and analysis capacity. Loss on ignition is an easy and readily accessible technique that can be more widely applied by environmental research groups lacking access to advanced instrumentation. Sample processing and analysis via an elemental analysis laboratory can average $10–$20 per sample depending on the required level of sediment preparation, while loss on ignition can be done 'in-house' with access to simple equipment such as a muffle furnace and analytical balance. In other words, the cost of a project can drastically decrease if organic matter is measured in lieu of sediment carbon. Thus, this study has shown that loss of ignition is an acceptable method to efficiently obtain a large quantity of organic matter soil values that can accurately be converted to organic carbon. While there can be problems with the operational nature of loss on ignition (e.g. salt volatilization, moisture absorption, incomplete combustion, etc.), it is a suitable method for studying blue carbon.

Consistent carbon densities in top meter

Most sediment cores collected in this study were within the active root zone (top 30 cm). However, studies such as Hinson et al. have recommended using the top 1 m for conservation-focused tidal wetland efforts since projects including the U.S. National Greenhouse Gas Inventory use 1 m as the default soil depth (Hinson et al. 2017). Thus, the question arises whether shallow surface sediment carbon is reflective of the carbon densities down to 1 m or if carbon values vary with depth. Downcore variability was found in a previous U.S. study where dry bulk density increased with depth while the organic matter content decreased with depth, resulting in a stable carbon density downcore in the top 1 m (Holmquist et al. 2018).

To investigate this, we collected six >1 m sediment cores from the St. Jones Reserve at equidistant intervals along the main tidal gut which feeds the St. Jones Reserve marsh area. All sediment cores displayed varying downcore patterns

between dry bulk density, organic carbon percentage, and carbon density. A Mann-Kendall test was applied and found that carbon densities had a significant downcore trend in four of the six cores. The general directionality of those downcore trends were negative in two cores and positive in four cores (Fig. 6). In general, the organic carbon concentration had the same downcore pattern and directionality as the carbon density. We also performed a change point analysis using the changepoint R package (Killick et al. 2016) as visually, many of the downcore carbon density trends appear to be constant until a certain depth. The 'at most one change' point was 107 cm, 37 cm, 57 cm, 87 cm, 117 cm, and 87 cm sequentially by cores 1 through 6 (Fig. 6).

The variability in downcore carbon density suggests that using the top meter of sediment as an approximation for 'surface' carbon stocks is broadly reasonable, but far from perfect. As our sediment accumulation rates are also drastically different between our two study sites, collecting sediments to the same depth likely represents differently aged sediments, as noted in Van de Van De Broek et al. (2016). We do caution

that there are changes in carbon density within the first meter due to factors such as the presence of live roots, organic matter decomposition, and changes in dry bulk density. For example, in Core 5, we found a large *P. australis* root below 120 cm (Fig. 6). Even though we removed large root mass from the sediment analyses, we expect that the sediments were enriched in organic matter from the actively growing root mass. We suggest that taking a few deeper (>30 cm) cores is helpful to understand downcore carbon density variability and whether scaling studies to a particular sediment depth is reasonable.

Methane estimates by salinity

While organic matter accumulation into tidal wetland sediments is a CO_2 sink, the output of methane gas could negate some of these carbon sequestration benefits. Methane is a potent greenhouse gas that has a 100-year global warming potential 28 times greater than CO_2 (Myhre et al. 2013). It has been proposed that methane and CO_2 emissions could

Fig. 6 Carbon density plotted downcore at the six sampled sites. The horizontal solid line represented the changepoint
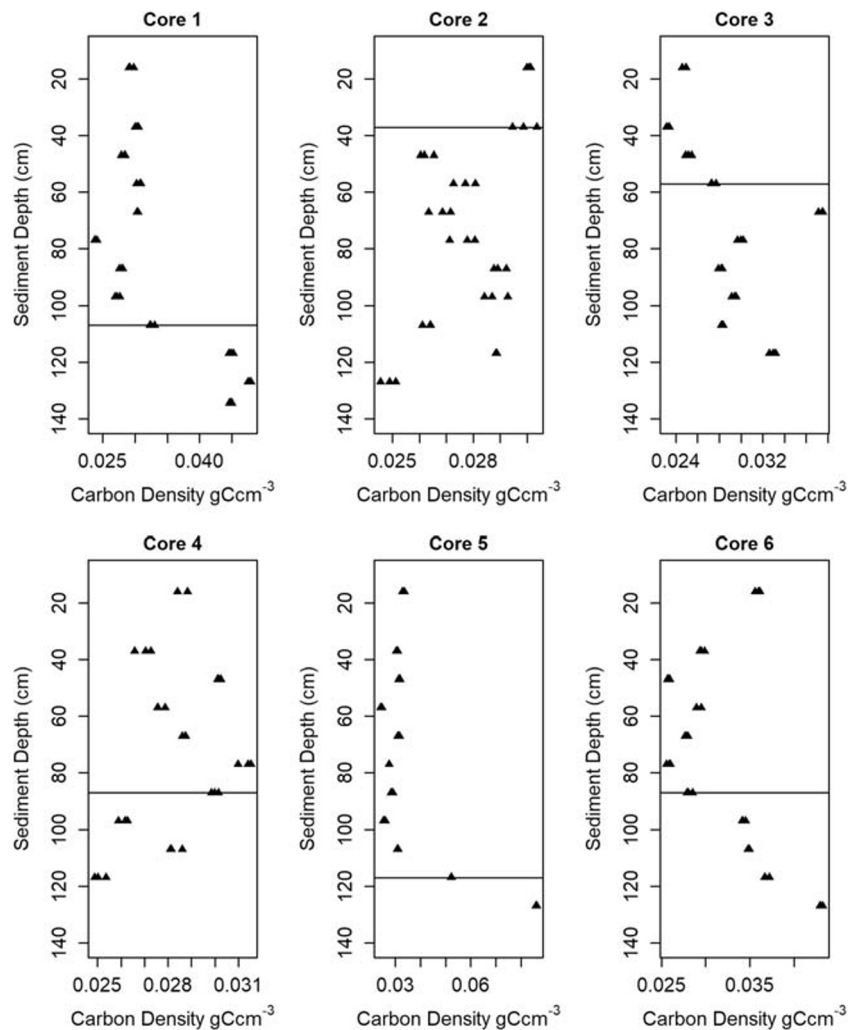
be substantially reduced by restoring saline tidal flow to impaired and tidally restricted wetlands such as impoundments (Kroeger et al. 2017). Furthermore, polyhaline tidal marshes with salinities >18 ppt have been found to have significantly lower methane emissions than oligohaline tidal marshes (Poffenbarger et al. 2011). This observation is primarily due to the tendency for methanogenesis to be a dominant metabolic pathway in lower saline waters due to the lower availability of sulfate (Sutton-Grier et al. 2011; Weston et al. 2006, 2014). Broadly, the lower the salinity, the higher probability to have high methane outputs.

This link between porewater salinity and methane flux has been used to create a direct logarithmic relationship (see Eq. 3 from Poffenbarger et al. 2011). While we did not measure methane gas flux, we were able to collect porewater salinity in our 2017 and 2018 sediment cores to estimate the annual methane emissions at our two test sites. Calculated annual methane fluxes were higher at the Blackbird Creek Reserve (15.3 ± 3.4 gCH$_4$ m^{-2} yr^{-1}) compared to the St. Jones Reserve (3.0 ± 2.4 gCH$_4$ m^{-2} yr^{-1}) which was expected based on the characteristic salinities of each site. For comparison, a previous study from the Delaware River estuary measured methane flux to the atmosphere at ~22 gCH$_4$ m^{-2} yr^{-1} (Weston et al. 2014) demonstrating our calculated methane emission rates to be reasonable. Estimated annual methane emissions parsed by dominant vegetation type are also as expected, following the pattern of vegetation species which can tolerate higher and more variable salinities. S.alterniflora (2.4 ± 1.7 gCH$_4$ m^{-2} yr^{-1}) has lower estimated methane fluxes compared to P.australis (7.8 ± 2.0 gCH$_4$ m^{-2} yr^{-1}) at the St. Jones Reserve while at the Blackbird Creek Reserve, the tidal freshwater mix (21.1 gCH$_4$ m^{-2} yr^{-1}) had the greatest methane flux flowed by P.austalis (14.3 gCH$_4$ m^{-2} yr^{-1}), S.cyanosuriodes (13.7 ± 0.9 gCH$_4$ m^{-2} yr^{-1}), and S.alterniflora (13.3 ± 1.3 gCH$_4$ m^{-2} yr^{-1}).

At both our study sites, the annual carbon accumulation exceeded the CO$_2$-equivalent methane emissions. The annual CO$_2$ accumulation into sediments at the St. Jones and Blackbird Creek Reserves is 1160 ± 480 gCO$_2$ m^{-2} yr^{-1} and 2272 ± 594 gCO$_2$ m^{-2} yr^{-1}, respectively using the average sediment accumulation rates and carbon densities by site. Calculated methane emissions were compared to accumulated carbon using a CO$_2$-equivalent (CO$_2$-e) of 28 for methane (Myhre et al. 2013). Annual mean methane emissions between sites are 83 ± 67 gCO$_2$-e m^{-2} yr^{-1} for the St. Jones Reserve and 429 ± 96 gCO$_2$-e m^{-2} yr^{-1} for the Blackbird Creek Reserve. While this estimated carbon calculation does not account for CO$_2$ losses from respiration or nitrous oxide emissions, etc., it demonstrates that both the St. Jones and Blackbird Creek Reserves are likely carbon sinks. The Blackbird Creek Reserve's higher methane emissions are offset in our simple calculation by the high sediment accumulation rate and thus, high annual sediment carbon accumulation.

The production of methane in tidal wetlands could change in the future due to pressures including sea level rise, increased atmospheric CO$_2$, and the expansion of invasive species such as P.austalis. Saltwater intrusion into freshwater tidal marshes has been measured to increase and prolong sulfate reduction, increase methane emissions, stimulate microbial decomposition, and subsequently decrease soil organic carbon content (Weston et al. 2011). This is a concern since sea level rise and migrating salt gradients up tidal tributaries could mean a lower rate of carbon accumulation (Baustian et al. 2017) and temporary increases in methane emissions (Weston et al. 2011) but could lead to overall lower methane emissions for long-term higher salinity exposure (Neubauer et al. 2013). Likewise, the ubiquitous invasive wetland reed P.australis has been measured to produce more methane compared to native Phragmites sp. and methane production increased under an increased CO$_2$ and nutrient scenario (Mozdzer and Megonigal 2013). While polyhaline marshes were consistently a carbon sink, tidal freshwater marshes alternate between a carbon sink and source across years (Weston et al. 2014). Sediment carbon, methane emissions, and other biogeochemistry parameters should be routinely evaluated in tidal marshes to assess and document changes in the carbon sequestration ecosystem service as climate change progresses. These measurements are particularly important in any impaired or degraded tidal wetlands that may be candidates for wetland restoration such as tidal reconnection or that may be influenced by local controlling factors, including hydroperiod, geomorphology, vegetation, and total suspended solids, among others. While we expect our study sites to be carbon sinks, a complete carbon balance needs to be collected to understand the spatially integrated and temporally variable carbon dynamics.

Black carbon ratios

Black carbon represents a continuum of incompletely combusted organic materials that can represent different chemical species and organic matter stabilities (Masiello 2004). The analytical method applied can denote drastically different combusted carbonaceous products ranging from charcoal to the highly condensed soot (Pohl et al. 2014). The method applied here is a chemothermal oxidation at 375 °C which isolates the thermally recalcitrant, soot-like fraction of organic matter (Gustafsson and Gschwend 1998). This soot-like black carbon thus could be a longer sink for fixed organic carbon (Kuhlbusch and Crutzen 1995). Previous studies have found black carbon to compose 15–30% of the total organic matter in marine sediments (Middelburg et al. 1999), however fewer studies have assessed the contribution of soot-like black carbon to tidal wetland sediments. Allochthonous by definition, soot-like black carbon can be deposited onto the tidal

marsh platform through atmospheric deposition or by sediment accretion from tidally transported particles.

To our knowledge, very few studies have applied a chemothermal oxidation to assess soot-like black carbon concentrations in a salt marsh; however, the application of biochar as a potential soil conditioner in tidal wetland sediments has gained experimental interest (Gilmour et al. 2018) and tidal exchanges has been hypothesized to be a major carrier of dissolved black carbon (Dittmar et al. 2012). The St. Jones Reserve is within a highly urbanized airshed near the Dover Air Force Base, and in a region with agricultural burning activities. Thus, we sought to apply the chemothermal oxidation at 375 °C methodology to better understand the presence of black carbon in coastal wetland sediments. Our analysis found that soot-like black carbon composed $27.5 \pm 3.9\%$ of the total sediment organic carbon (C_{ea}). We note that C_{ea} was significantly correlated ($R^2 = 0.92$) to the black carbon, which could suggest either a steady input of black carbon relative to organic matter or a methodological bias. Defined operationally by the CTO-375 method, black carbon compromised over a quarter of the organic carbon at the St. Jones Reserve. We feel that, given the high productivity of tidal wetland ecosystems, our fraction of black carbon to sedimentary organic carbon appears high. A potential problem with the chemothermal oxidation at 375 °C methodology is charring, or when you create black carbon during the combustion process to isolate black carbon (Gustafsson et al. 2001). Continued work is needed to resolve soot-like black carbon measurements and methodologies in high organic matter systems.

Approximating the value of local tidal marshes

Tidal marshes have generated increased interest due to their ability to sequester and store carbon. A previous Delaware Estuary scale effort valued the present-day net carbon sequestration of tidal wetlands to be $3.66 billion, demonstrating the immense monetary value of Mid-Atlantic tidal wetlands (Carr et al. 2018). This ecosystem service of carbon sequestration and storage has the potential to help states such as Delaware better meet their greenhouse gas emissions reductions goals. Initiatives such as the Natural and Working Lands Challenge through the U.S. Climate Alliance have sought to quantify carbon sequestration by agricultural lands, forests, and tidal wetlands as well as methods to increase that sequestration benefit. Tidal wetlands have not been as simplistic to incorporate into state planning efforts due to the lack of an easy to apply quantification tool, the inherent variability of carbon sequestration, and the difficulty of collecting samples. The suggested 'pathway' for tidal wetlands that has been largely discussed by the U.S. Climate Alliance involves the tidal reconnection of managed freshwater impoundments to reduce methane emissions (Kroeger et al. 2017).

While this restoration approach has a high potential to reduce greenhouse gas emission sources, it is not largely applicable in Delaware as the avian habitat and recreational value of impounded freshwater ponds is high. For example, avian species diversity in New Jersey was found to be greater in a managed coastal impoundment compared to a natural tidal marsh (Burger et al. 1982). Here we propose an alternative tidal wetland 'pathway' for consideration: avoided conversion of tidal wetlands. While avoiding loss would not enhance carbon sequestration or add to the state's progress in emissions reductions, it would prevent against unaccounted for carbon sequestration loss. Delaware's collective tidal wetlands are passively sequestering carbon as part of their baseline. Here we argue that the loss of additional salt marsh moves that baseline further back. From 1992 to 2007, Delaware's emergent estuarine marshes observed a net loss of about 15 acres per year (Tiner et al. 2011), and the Delaware estuary as a whole has observed a tidal wetland loss of 43.5 km^2 to open water since 1975 (Carr et al. 2018). This loss rate of estuarine wetlands is equivalent to roughly 6% of our St. Jones study areas each year. Thus, the loss of tidal wetlands is a loss of both an active carbon sequestering habitat and a potential source of carbon through the mobilization and remineralization of stored organic carbon (Pendleton et al. 2012).

Here, we applied a simple envelope calculation to approximate the monetary value of the carbon already stored in the top 1 m of the St. Jones Reserve tidal marsh area managed by the Delaware National Estuarine Research Reserve (DNERR) and estimated the annual added carbon through sediment accretion using feldspar clay markers.

$$Area_{SJ} \times Soil\ Depth_{SJ} \times Cden_{SJ} \times 3.667 \times Carbon \quad (6)$$

Area refers to the tidal wetland area managed by DNERR which is approximately 270 acres or 1.09 km^2. A soil depth of 1 m was assumed and the carbon density applied was the St. Jones Reserve average of 0.054 ± 0.022 g cm^{-3}. Soil carbon was stoichiometrically converted to carbon dioxide ($44gCO_2/12gC$) to estimate the CO_2 equivalency of the stored soil carbon. We elected to use a social cost of carbon of $30.78/tCO2 but note that estimates of social carbon costs drastically range across studies from -$13.36/tCO$_2$ to $2386.91/tCO$_2$ (Wang et al. 2019). This approximation yields that $\sim 5.9 \times 10^4$ metric tons of carbon are presently stored in the top 1 m of the tidal marsh managed by the St. Jones Reserve, which is roughly equivalent to $6.6 million U.S. dollars in terms of social carbon.

Three feldspar clay markers were used to estimate the annual accretion of new material in the St. Jones Reserve managed area which had an overall site mean of 5.9 ± 5.3 mm yr^{-1}. This computes an average carbon accumulation for the St. Jones Reserve of 317 ± 285 g m^{-2} yr^{-1}. This is higher than

the global average carbon accumulation rate for salt marshes of $244.7\,g\,m^{-2}\,yr^{-1}$ (Ouyang and Lee 2014). Scaling up for the average carbon density and area of this parcel, that translates to 350 ± 310 metric tons of soil carbon accumulation ($1300 \pm 1100\,tCO_2$) each year or $\sim\$40,000 \pm \$35,000$ per year based on the social cost of carbon. While this value may not be substantial and includes inherent uncertainty, it demonstrates the value of even a small tidal wetland parcel. The current loss rate of emergent estuarine wetlands in Delaware is 15 acres per year, corresponding to $-3200tC\,yr^{-1}$ ($12,000tCO_2\,yr^{-1}$) being lost annually.

Conclusions

This study contributed to the growing inventory of tidal wetland carbon concentrations and densities and demonstrated that, while broad generalities may be applied (i.e. ecosystem-wide means), there is still considerable variability and subsequent importance in analyzing carbon stocks from local tidal marshes of interest to better understand the site-specific carbon storage values. Carbon densities at our two study sites showed Delaware salt marshes presently store considerable amounts of carbon and that the more saline tidal marsh has greater carbon densities, despite having lower sediment accumulation rates and presumably greater rates of decomposition. Carbon values were also found to be more variable at salinities <14 ppt and had distinct patterns by different dominant vegetation types. Similar to other studies, we also found organic matter had a strong polylinear correlation to the sediment carbon content, justifying the use of cheaper analytical methods such as loss on ignition which can greatly increase sample processing. Recalcitrant 'soot-like' carbon was found to compose over a quarter of the sediment carbon, representing a potential sink of thermally stable carbon. Finally, the St. Jones Reserve tidal marsh area was estimated to have a higher than global average sediment accumulation rate with a social carbon estimate of $\$40,000 \pm \$35,000$ of new carbon accumulated each year. Therefore, tidal wetland protection should be considered as an approach to reduce carbon emissions as to not reverse natural land processes of carbon sequestration. This work demonstrates that site-specific analyses beneficial for state management provide unique insights while still complementing broader scale efforts.

Data availability All data collected in this study is available as a table in either the main body of supplemental information of this paper. All data as a .csv or .xls file are available upon request to the corresponding author.

Compliance with ethical standards

Conflicts of interest/competing interests There are no conflicts of interest or competing interests.

Code availability Not applicable.

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