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Long-term organic carbon sequestration in tidal marsh sediments is dominated by old-aged allochthonous inputs in a macro-tidal estuary

Running head: Carbon sequestration in tidal marsh sediments

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Abstract

Tidal marshes are vegetated coastal ecosystems that are often considered as hotspots of atmospheric CO₂ sequestration. Although large amounts of organic carbon (OC) are indeed being deposited on tidal marshes, there is no direct link between high OC deposition rates and high OC sequestration rates due to two main reasons. First, the deposited OC may become rapidly decomposed once it is buried and, second, a significant part of preserved OC may be allochthonous OC that has been sequestered elsewhere. In this study we aimed to identify the mechanisms controlling long-term OC sequestration in tidal marsh sediments along an estuarine salinity gradient (Scheldt estuary, Belgium and The Netherlands). Analyses of deposited sediments have shown that OC deposited during tidal inundations is up to millennia old. This allochthonous OC is the main component of OC that is effectively preserved in these sediments, as indicated by the low radiocarbon content of buried OC. Furthermore, OC fractionation showed that autochthonous OC is decomposed on a decadal timescale in saltmarsh sediments, while in freshwater marsh sediments locally-produced biomass is more

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efficiently preserved after burial. Our results show that long-term OC sequestration is decoupled from local biomass production in the studied tidal marsh sediments. This implies that OC sequestration rates are greatly overestimated when they are calculated based on short-term OC deposition rates, which are controlled by labile autochthonous OC inputs. Moreover, as allochthonous OC is not sequestered in-situ, it does not contribute to active atmospheric CO₂ sequestration in these ecosystems. A correct assessment of the contribution of allochthonous OC to the total sedimentary OC stock in tidal marsh sediments as well as a correct understanding of the long-term fate of locally-produced OC are both necessary to avoid overestimations of the rate of in-situ atmospheric CO₂ sequestration in tidal marsh sediments.

Introduction

Tidal marshes are vegetated coastal ecosystems that can efficiently adapt to rising sea level by vertical accretion of organic and mineral material and burial of locally produced biomass (Kirwan & Mudd, 2012; Kirwan, Temmerman, Skeehan, Guntenspergen, & Faghe, 2016; Neubauer, 2008). Over the past decades, organic carbon (OC) dynamics in tidal marsh ecosystems have been studied intensively as these coastal zones have been recognized as potential hotspots for atmospheric CO₂ sequestration, often termed 'blue carbon' (Duarte, Losada, Hendriks, Mazarrasa, & Marbà, 2013; Mcleod et al., 2011; Nelleman et al., 2009). As a consequence of their location at the interface between terrestrial, riverine, estuarine and marine ecosystems, tidal marshes do indeed receive considerable OC inputs from different sources. These inputs can be subdivided into (i) OC that is locally produced by macrophytes and microbial communities (autochthonous OC) and (ii) OC that is produced elsewhere, e.g. in terrestrial or marine ecosystems, and subsequently supplied by tidal inundation and deposition at the marsh surface (allochthonous OC).

The contribution of autochthonous and allochthonous sources to the total OC stock in tidal marsh sediments can differ greatly between marshes at different locations. In organogenic tidal marshes, where vertical accretion is dominated by the accumulation of organic material, OC is mostly derived from local biomass, while minerogenic marshes, dominated by mineral sediment accretion, receive a considerable input of sediment-associated OC (Allen, 1990; Bouillon & Boschker, 2006; Middelburg, Nieuwenhuize, Lubberts, & van de Plassche, 1997). However, the relative contribution of autochthonous and allochthonous sources varies strongly among minerogenic marsh sites whereby in some cases autochthonous sources dominate (S. Chen, Torres, & Goñi, 2016; Saintilan, Rogers, Mazumder, & Woodroffe, 2013; Tanner et al., 2010), while the origin of OC is mainly allochthonous in other cases (Boschker, de Brouwer, & Capenberg, 1999; Bouillon & Boschker, 2006; Middelburg et al., 1997).

The rates and mechanisms of OC sequestration do not only vary among saltmarshes, but also along estuarine salinity gradients where marshes vary from salt over brackish to freshwater tidal marshes. Although soil organic carbon (SOC) stocks are generally higher in freshwater tidal marshes as compared to saltmarshes (Craft, 2007; Loomis & Craft, 2010; Van de Broek, Temmerman, Merckx, & Govers, 2016), knowledge on OC sequestration mechanisms in brackish and freshwater tidal marshes is currently limited. Higher SOC stocks in freshwater

tidal marsh sediments, compared to saltmarshes, have been attributed to multiple factors, such as higher rates of primary production of macrophytes (Hansen et al., 2016), higher OC concentrations and/or higher sedimentation rates associated with deposited terrestrial sediments (Hansen et al., 2016; Hayes et al., 2017; Van de Broek et al., 2016), lower extracellular enzyme activity and microbial activity (Morrissey, Gillespie, Morina, & Franklin, 2014) and lower overall decomposition rates of organic matter (Craft, 2007; Loomis & Craft, 2010). Systematic studies of the controls on SOC stocks in tidal marsh sediments along the full salinity gradient of estuaries, including differences in characteristics of OC inputs and preservation mechanisms of OC upon burial, are scarce (Hansen et al., 2016). This lack of information limits our understanding of the mechanisms controlling SOC storage in these ecosystems and hampers constructing reliable projections of the potential of these ecosystems to sequester CO₂ under future climatic and environmental changes.

When considering the potential of tidal marsh sediments to act as a carbon sink on a decadal to centennial timescale, it is important to make a distinction between the terms ‘OC accumulation or deposition’ and ‘OC sequestration’. Organic carbon accumulation or deposition refers to the magnitude of OC inputs to the system, while OC sequestration refers to the long-term removal of carbon from the atmosphere. These terms are, however, often confused, which can lead to misinterpretations of reported data on both variables. For example, reported rates of globally-averaged annual OC accumulation in saltmarsh sediments are 210 - 250 g C m⁻² yr⁻¹ (Chmura, Anisfeld, Cahoon, & Lynch, 2003; Duarte et al., 2013; Ouyang & Lee, 2014), which considerably exceed rates at which OC is sequestered in most terrestrial ecosystems per unit area (McLeod et al., 2011). These OC accumulation rates are calculated by combining sediment deposition rates with topsoil OC densities, thereby neglecting longer-term (decadal – centennial) OC losses through mineralization after burial of organic matter. In these studies, the OC accumulation rates are often equated to the capacity of the tidal marshes for long-term removal of carbon from the atmosphere (the OC sequestration rate). This potentially leads to a substantial overestimation of the long-term OC sink of tidal marsh sediments as (i) substantial losses of OC from the marsh sediments may occur at decadal or centennial timescales and (ii) a significant fraction of the OC that is buried in the marsh sediments may be allochthonous OC that is recycled from other long-term stores and therefore does not contribute to in-situ OC sequestration.

The aim of our study is to assess the controls on OC sequestration in tidal marsh sediments along a temperate, macro-tidal estuary (Scheldt estuary, Belgium and the Netherlands) in order to (i) understand how OC inputs to tidal marshes vary along the full salinity gradient of the estuary and (ii) which factors control OC accumulation as well as long-term sequestration. We performed a systematic analysis of (i) the different inputs of OC to these sediments, both from locally produced biomass and deposited sediments, and (ii) the importance of different physical stabilization mechanisms of OC along a gradient from freshwater- to saltmarsh sediments. Moreover, using the characteristics (OC concentration, $\delta^{13}\text{C}$ and radiocarbon content) of OC from different input sources and the OC preserved in sediments we determined the extent to which OC from different sources contributes to long-

term preservation of OC in these sediments and how this varies along the temperate Scheldt estuary.

Materials and Methods

Study site

The estuary of the Scheldt river is located in northern Belgium and the southwest Netherlands, where it flows into the North Sea (Figure 1). It has a semi-diurnal meso- to macro-tidal regime with a tidal range between 3.8 m at the mouth and 5.2 m upstream of the city of Antwerp (Meire et al., 2005). Tidal marshes are present along the full salinity gradient of the estuary, which can be divided into saltmarshes (salinity > 18), brackish marshes (salinity 5 – 18) and oligohaline/freshwater tidal marshes (salinity 0 – 5), hereafter called freshwater marshes (Figure 1).

For this study, 18 locations on a total of 10 tidal marshes were sampled for the construction of depth profiles of OC characteristics (Figure 1, Table 1). Where possible, both a high-lying and a low-lying area of the tidal marshes were sampled. The high marshes are located at an elevation of about 0.1 – 0.3 m above local mean high water level (MHWL) and are accreting at a rate in equilibrium with local sea level rise (see Temmerman *et al.* (2003, 2004) for detailed studies of the sediment accretion rates at the sampled tidal marshes). The low marshes were located well below local MHWL during the past decades, and have consequently experienced a higher inundation frequency and higher sediment accretion rates compared to the high portions of the same marsh (Temmerman et al., 2003, 2004). As sediment deposition rates at the high portion of the studied tidal marshes are in the order of magnitude of 0.004 – 0.017 m year⁻¹ (Temmerman et al., 2004) and the formation of the low marshes generally started less than a century ago, the time since deposition of the upper meter of the studied sediments is generally less than 100 years (Temmerman et al., 2003, 2004). The collected data was further complemented with similar data from 3 tidal marshes in the Scheldt estuary from which data on OC dynamics is presented in Van de Broek *et al.* (2016). General information about the tidal marshes used in this study is provided in Table 1 and Table S1. The numbers in Table 1 are used to refer to the tidal marshes throughout this paper, in combination with the salinity (s) at which the marshes are located. The description of sample collection and processing applies to all samples collected for this study (Table 1). The SOC depth profiles used from Van de Broek *et al.* (2016) were obtained and processed using identical methods, but one year prior to the samples collected for the present study.

Biomass

The total amount of aboveground biomass was collected at every sampling location for a surface area of 0.25 m² in five replicates. This was done towards the end of August and the beginning of September 2016, when biomass is at its maximum on tidal marshes in western Europe (De Leeuw, Olff, & Bakker, 1990; Groenendijk, 1984). Biomass of *Salix* trees could not be sampled. At locations where *Salix* was present, the mass of *Salix* litter measured at the high marsh at salinity 1.5 (215 g dry weight (DW) m⁻², Van de Broek et al. (2016)) was added to the measured biomass from the local vegetation species. Depth profiles of the total

root biomass were measured by washing the soil samples collected for bulk density measurements, after determination of bulk density, over a 0.7 mm sieve using deionized water and collecting all roots (see next section for depth intervals). Aboveground and belowground biomass was dried at 60 °C before weighing. Weights of aboveground and belowground biomass are reported for a surface area of 1 m².

Soil samples

Undisturbed soil profiles and soil samples for bulk density analyses were collected between July and September 2016 in three replicates at each sampling location using a gouge auger (0.06 m diameter). The undisturbed soil cores were divided into subsamples with 0.03 m depth intervals in the field and transported to the lab in closed ziploc bags. Before analysis, the soil samples were dried at a maximum temperature of 50 °C for 48 hours, crushed to a grainsize < 2 mm and macroscopic vegetation residues were removed manually using tweezers. Samples for bulk density analyses were collected separately by cutting exactly 0.05 m of sediment out of the gouge auger, at depth increments of 0.1 m down to a depth of 0.5 m (0 – 0.05 m; 0.10 – 0.15m etc.) and deeper down the profile at depth increments of 0.2 m (0.50 – 0.55 m; 0.70 – 0.75 m etc.).

Samples for soil bulk density were dried at 105 °C for 24 hours before weighing and calculation of the soil bulk density, using the inside volume of the gouge auger (17.02 cm³ cross section). Sediment grain size was analysed on the samples collected for general soil analyses using a laser diffraction particle size analyser (LTSM 13 320, Beckman Coulter) and classified into clay (< 2 µm), silt (2 – 63 µm) and sand (> 63 µm), after organic matter was removed using hydrogen peroxide (35 %) and aggregates were destroyed using ultrasonic dispersion.

Before analysis of OC characteristics, the soil samples of one of the replicate soil cores at every sampled location were weighed into pre-combusted silver cups and carbonates were removed in situ using a 10 % HCl solution. Organic carbon concentration and stable carbon isotopes ($\delta^{13}\text{C}$) measurements were performed using an Elemental Analyser – isotope ratio mass spectrometer (FlashEA 1112 HT, Thermo Scientific – DELTA V Advantage). The OC concentration of soil samples from the second and third replicate soil cores were determined using mid-infrared (m-IR) spectroscopy, using a calibration dataset which was created by relating the measured OC concentrations of samples from the first replicate soil core to the measured m-IR spectra of these soil samples. The spectra were obtained over a spectral range of 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹, using a PerkinElmer® Forier FT-IR spectrometer which was coupled to a PIKE® XY autosampler. Before the OC concentration was estimated using partial least squares regression (PLSR) with 4 latent variables, the soil spectra were pre-processed using the standard normal variate procedure (SNV, see e.g. Igne et al., 2010; Viscarra Rossel, McBratney, & Minasny, 2010). Total SOC stocks were calculated down to a depth of 0.6 m for each site by combining depth profiles of OC concentration and soil bulk density. This depth was chosen as tidal marsh sediments were present down to this depth at every sampling location, with the exception of the low marshes at salinity 27 and 30.

Soil samples for radiocarbon measurements were prepared the same way as for OC analysis and combusted at 900 °C for 1 hour, after which the produced CO₂ was cryogenically trapped on a vacuum line. Graphitization of CO₂ and ¹⁴C measurements were performed at the Royal Institute for Cultural Heritage in Brussels (Belgium) using a MICADAS (mini carbon dating system). The concentration of ¹⁴C was calculated using the measured ¹⁴C/¹²C ratio relative to 95 % of the oxalic acid standard and corrected for isotopic fractionation using the ¹³C/¹²C ratio (Stuiver & Polach, 1977). Results are expressed as the fraction modern ¹⁴C (F¹⁴C), with values > 1 F¹⁴C indicating the presence of (modern) bomb ¹⁴C, while values < 1 F¹⁴C indicate that the OC has been formed from atmospheric CO₂ before 1950 (Schoor, Druffel, & Trumbore, 2016). The tidal marsh sediments for which radiocarbon analysis was performed are marshes no. 4 (s = 27), 9 (s = 17) and 13 (s = 1.5), which are described in detail in Van de Broek et al. (2016), in addition to both summer and winter deposits at these marshes.

Collection of deposited sediments

In order to determine the characteristics of OC associated with allochthonous inputs, sediments deposited at the surface of tidal marshes along the estuary were collected using sediment traps. These sediment traps consisted of a plastic dish which was fixed at the marsh surface, in which settled suspended sediment was trapped during inundation events. The dishes were covered with a lid which floated on top of the inundation water, allowing sediments to be deposited in the dish, and dropped after the flooding water has receded in order to protect deposited sediments against contamination (Figure S2). As characteristics of OC in the Scheldt estuary are different between summer and winter as a consequence of e.g. phytoplankton growth in summer months (Muylaert, Sabbe, & Vyverman, 2000), sediment traps were installed at three tidal marsh locations in summer 2016 (3 replicates per location), and at 5 locations in winter 2017 (5 replicates per location), as indicated in Table 1, Table S2 and Figure S1. The sediment traps were installed at the high portion of marshes, thus only collecting sediments during spring-tide events. After each spring tide event (4 in summer 2016, 3 in winter 2017), the sediments and water present in the dishes were collected from the traps and the traps were thoroughly cleaned using demineralized water.

In the lab, the collected sediments and water were poured through a 0.7 mm sieve, in order to remove vegetation residues that were present in the dishes. Next, the sediments were rinsed multiple times using demineralized water, in order to remove salt from the solution, and dried at 50 °C. Subsequently, OC concentration and δ¹³C values were measured for all sediment samples according to the procedures explained in the previous section. Radiocarbon contents were determined for one summer and one winter deposit for the tidal marshes at which sediment traps were present during summer 2016. These are the same marshes for which radiocarbon contents were determined for OC present in subsoil sediments.

Physical fractionation of organic carbon

Soil samples for physical OC fractionation were collected at three freshwater tidal marshes, one brackish marsh and three saltmarshes (Table 1 and Figure S1). At every location, both topsoil (0 – 0.05 m) and subsoil sediments were collected using a gouge auger (0.06 m

diameter), in order to analyse SOC fractions of freshly deposited OC (< 5 years old, considering a mean sediment accretion rate of ca. 0.01 m yr⁻¹ (Temmerman et al., 2004)) on the one hand and OC that has been buried for several decades on the other hand (Figure S3). Tidal marsh soils typically exhibit a sharp boundary from silt-size (tidal marsh sediments) to sand-size (former sandflat) sediments with depth. The subsoil samples for OC fractionation were collected as close as possible to the lower boundary of the silt-size sediments. However, if the depth of this boundary was located at > 1 m depth, subsoil sediments were collected between 0.8 – 1 m depth (Figure S3). In total, 27 soil samples were fractionated. When necessary, e.g. in the case of very low bulk density of topsoil sediments, soil material from different soil cores collected next to each other was mixed to obtain enough sediment to perform the fractionation analyses. For three tidal marshes, no. 4 (s = 27), 10 (s = 17) and 14 (s = 1.5), samples from three different locations a couple of meters from each other were analysed to calculate standard deviations on the results (see supplementary data). For the other locations, topsoil and subsoil samples were analysed for only one location.

Soil samples for OC fractionation were dried at 50 °C for 48 hours after sample collection in order to preserve them until fractionation analyses took place. A total of three fractionation steps were performed (Figure 2). Before the first fractionation step the soil samples were re-wetted by putting them in a glass beaker which was subsequently filled with demineralized water, to allow slaking of aggregates. In the first fractionation step the soil samples were separated in three size classes by wet sieving: (i) silt and clay (sc, < 53 µm), (ii) microaggregates, sand and particulate organic matter (POM) (m, 53 – 250 µm) and (iii) macroaggregates and POM (M, > 250 µm). If roots were present, these were removed, oven-dried and weighed. The OC concentration of these root fragments was determined using the elemental analyser as described above. In the second step the M fraction was dispersed using ultrasonic dispersion. Thirty gram of this fraction was suspended in 150 ml demineralised water and subjected to an output energy of 22 J ml⁻¹ (Zimmermann, Leifeld, Schmidt, Smith, & Fuhrer, 2007) and output power of 25 W. The time over which dispersion was performed was calculated at 2 minutes and 18 seconds, based on Poeplau and Don (2014). If less than 30 g of material was available for ultrasonic dispersion, the amount of demineralised water and the output energy were adjusted to achieve the same output energy per unit volume. After ultrasonic dispersion, the material was transferred onto a 53 µm sieve in order to separate the silt and clay fraction (scM, < 53 µm) from the microaggregates sand and POM fraction (mM, > 53 µm). In the last fractionation step, a density separation was applied to the microaggregates, sand and POM fractions obtained after both fractionation step one and two (m and mM) combined, according to De Clercq et al. (2015). These fractions were separated in a sodium polytungstate (Sometu, Berlin, Germany) solution with a density of 1.8 g cm⁻³. The solution containing the sediments was stirred using a spatula after which the heavy fraction was allowed to settle. This resulted in a light fraction (POM) and a heavy fraction (microaggregates and sand, m+S). The fractionation scheme was constructed so that the final fractions can be linked to the different physical mechanisms through which OC is stabilized in the studied sediments: (i) sc and scM is OC that is associated with minerals, (ii) m + S is OC protected mainly by microaggregates and (iii) POM is interpreted as locally produced autochthonous OC that is not fully decomposed. The weight and OC concentration were

determined for the soil fractions obtained after each fractionation step. By combining these data, the contribution of each fraction to the total amount of OC in each soil sample was calculated.

Statistical analysis

Differences in average values of OC stocks down to 0.6 m depth, biomass and deposited OC concentration for the different salinity zones were tested for significance using a one-way analysis of variance (ANOVA) or Kruskal-Wallis test (for non-normal distributed data) using Matlab® software. Homogeneity of variances (Levene's test for normally distributed data, Brown-Forsythe test for non-normal distributed data) and normality (Shapiro-Wilk test) of the data were assessed using Matlab®, at a confidence level of 0.05.

Results

Grain size

The grain size distribution of disaggregated topsoil sediments (0 – 0.03 m depth) of the tidal marshes is dominated by the silt-size fraction and shows no systematic variation along the estuary (Figure 3). The sampled tidal marshes show a limited variation of grain size with depth, with the exception of a sharp increase in sand size particles and a decrease in silt size particles at the boundary between the silt size marsh sediments and sand size former sandflat sediments (supplementary data). Grain size distributions of the soil samples used for fractionation are shown in Figure S4.

Biomass

There is no clear gradient in the amount of both aboveground and root biomass present at the tidal marshes along the estuary (Figure 4). When disregarding the exceptionally large biomass of reed vegetation at marsh no. 13 ($s = 1.5$), the average amount of total biomass was only significantly different between freshwater- ($679 \pm 257 \text{ g DW m}^{-2}$) and brackish marshes ($1751 \pm 449 \text{ g DW m}^{-2}$), while biomass at the saltmarshes ($1438 \pm 405 \text{ g DW m}^{-2}$) was not significantly different from the freshwater- and brackish marshes. A complete description of statistical tests applied to biomass measurement is provided in the supplementary information. Clearly, local variations in vegetation composition have an important effect on local biomass production. The amount of aboveground biomass exceeds root biomass at all tidal marshes except for marshes no. 13 ($s = 1.5$) and no. 3 ($s = 27$), where respectively *P. australis* and *S. anglica* vegetation are present.

Organic carbon characteristics of deposited sediments

Organic carbon concentrations of surface deposits at the sampled tidal marshes differ both temporally, between different seasons, and spatially, along the salinity gradient (Figure 5a). First, sediments deposited during winter consistently contain less OC compared to sediments deposited at the same location in summer. This difference is about 1 – 2 % for the freshwater

and saltmarshes and about 7 % for the brackish marsh. Second, the OC concentration of deposited sediments decreases towards the coast, from 4 – 6 % OC at the freshwater tidal marshes to 2 – 4 % at the saltmarshes, with the exception of summer deposits on the brackish marsh. A description of statistical tests applied to the OC concentration of deposited sediments is provided in the supplementary information.

Also the $\delta^{13}\text{C}$ values of the OC in the deposited sediments show a clear pattern along the estuary. Deposits on freshwater and brackish marshes have a $\delta^{13}\text{C}$ value closely related to that of terrestrial vegetation (-28 ‰), while this value consistently increases from the brackish portion of the estuary towards the coast, with $\delta^{13}\text{C}$ values of about -23 ‰. The variation in $\delta^{13}\text{C}$ values between summer and winter deposits at the same location is limited to 1 ‰.

Soil organic carbon stocks

Combining data on detailed depth profiles of both OC concentration and bulk density (provided in the supplementary data), total OC stocks for the sampled tidal marshes were calculated (Figure 6). There is a clear pattern of decreasing SOC stocks in tidal marsh sediments with increasing salinity. Average OC stocks in the top 0.6 m are $19.4 \pm 1.2 \text{ kg OC m}^{-2}$ in freshwater marsh sediments, $17.3 \pm 0.9 \text{ kg OC m}^{-2}$ in brackish marsh sediments and $12.63 \pm 0.8 \text{ kg OC m}^{-2}$ in saltmarsh sediments. Organic carbon stocks were not significantly different between freshwater- and brackish marshes, but were significantly different between (i) freshwater- and saltmarshes and (ii) brackish- and saltmarshes (see supplementary information). Furthermore, SOC stocks are generally larger for the high marsh locations as compared to low-lying locations of the same tidal marsh.

Radiocarbon content of deposits and SOC

Radiocarbon contents were determined for OC in (i) subsoil sediments in different tidal marshes and (ii) sediments deposited in summer and winter along the estuary (Figure 7). These data show that OC ages were substantially older for winter deposits compared to summer deposits for tidal marshes in all salinity zones, as shown by the lower fraction modern ^{14}C ($F^{14}\text{C}$) in winter deposits compared to summer deposits. The $F^{14}\text{C}$ was < 1 for both summer and winter deposits, indicating that the contribution of carbon fixed from atmospheric CO_2 after 1950 is very low. Furthermore, the $F^{14}\text{C}$ in tidal marsh sediments decreases substantially with depth. As there is a continuous exchange of carbon atoms between SOC and its environment, SOC cannot be regarded as a closed system. It is therefore not straightforward to convert ^{14}C data measured for SOC to calendar years (Schuur et al., 2016). However, for comparison, according to the IntCal13 calibration curve (Reimer et al., 2013), $F^{14}\text{C}$ values of 0.51 and 0.91, which are the lowest and highest values we obtained for OC in subsoil sediments, correspond to calibrated ages of 6230 ± 57 and 694 ± 31 years BP respectively, indicating that a substantial portion of the OC that is preserved at the studied tidal marshes has been fixed from atmospheric CO_2 centuries up to millennia ago. Importantly, this is significantly older than the time since sediment deposition, which is less than a century for the sampled tidal marshes (Temmerman et al., 2004). Furthermore, the $F^{14}\text{C}$ value of topsoil sediments is higher than for subsoil sediments, with the highest and

lowest values resulting in radiocarbon ages of 694 ± 31 and 962 ± 41 calibrated years BP respectively (IntCal, Reimer et al. (2013)), indicating that a substantial portion of fresh OC that is present in topsoil sediments is decomposed after burial.

Organic carbon fractionation

After initial drying of the sediments for OC fractionation, the majority of soil particles was present in macroaggregates ($> 250 \mu\text{m}$) for both topsoil and subsoil sediments (Figure S5). Aggregation was less pronounced for subsoil sediments from saltmarshes, where only about 50% of the soil particles was incorporated in macroaggregates. As macroaggregates were not observed in the field, this suggests that the process of initial sample drying had an effect on the results from the first fractionation step (wet sieving). Therefore, the results from the first fractionation step are not used to derive conclusions about OC stabilization mechanisms in tidal marsh sediments.

During sonication of the macroaggregates (M), this fraction was broken up into silt and clay (scM) on the one hand and microaggregates and POM (mM) on the other hand. The results of this intermediate fractionation step are not described in detailed here but are shown in figure S6. During the last fractionation step, the m and mM fraction were separated into (i) microaggregates and sand (m+S) and (ii) POM (Figure 8, Figure S7). The OC concentration was the largest for the POM fraction and the smallest for the silt and clay fractions (sc and scM) (Figure 8b, d). The microaggregates had an intermediate OC concentration. Roots contained between 4 – 9% of the total amount of OC in the topsoil samples (Figure S8 and supplementary data). In the subsoil samples, a substantial amount of roots was only present in the freshwater marsh no. 14 ($s = 1.5$) (11 % of total OC), while in the other subsoil sediments roots were nearly absent (< 1.1 % of total OC, Figure S9 and supplementary data). For topsoil sediments, the amount of OC present in the m+S fraction was generally larger in freshwater marshes compared to saltmarshes, with the exception of saltmarsh no. 2 ($s = 30$) (Figure 8a). With the exception of the marsh no. 6 ($s = 24$), the amount of POM was relatively constant in topsoils along the estuary. In subsoil sediments, clear patterns could be observed (Figure 8c). First, while in freshwater marsh subsoils about one third of the total OC was present as free POM after the disruption of macroaggregates, POM was nearly absent in the subsoil of saltmarshes (< 0.1 g POM out of 100 g sediments) (Figure 8c and Figure S7). Second, the subsoil m+S fraction stored less OC compared to topsoil samples and showed a strong decrease towards the coast (Figure 8c). As sand generally does not stabilize significant amounts of OC, it can be assumed that the majority of OC in this fraction was stabilized in microaggregates. In the freshwater subsoils, the OC concentration of the m+S fraction was higher (5.0 – 8.0 %) compared to the sc fraction (4.4 – 4.9 %, Figure 8d), suggesting that these aggregates contained a substantial amount of POM. Hence, microaggregates have the potential to protect POM from decomposition in freshwater subsoils (Figure 8d). At the saltmarshes, however, the difference in OC concentration between microaggregates (0.7 – 2.1 %) and the sc fraction (1.0 – 1.3 %) was much smaller, suggesting that the majority of OC in this fraction was associated with silt and clay particles while the amount of POM in these microaggregates was very limited. Third, the OC concentration of the subsoil sc fraction (from 4.4 – 4.9 % at the freshwater marshes to 1.0 – 1.3 % at the saltmarshes) was similar to

the OC concentrations of deposited sediments in winter (Figure 5), from 4.5 ± 0.2 % at the freshwater marshes to 2.3 ± 0.1 % at the saltmarshes.

Discussion

Autochthonous organic carbon inputs along the estuary

Locally produced (autochthonous) biomass is generally considered to contribute significantly to the total OC pool in tidal marsh sediments (Ouyang, Lee, & Connolly, 2017), as tidal marshes are among the most productive ecosystems in the world (Rocha & Goulden, 2009). Along estuaries, biomass is generally larger on freshwater and brackish marshes than on saltmarshes (Dausse et al., 2012; Hansen et al., 2016; Wieski, Guo, Craft, & Pennings, 2010). This is a consequence of the generally larger nutrient availability and lower salinity levels in the former portions of estuaries, in addition to species differences (Whigham, 2009), which pattern is not found in the Scheldt estuary (Figure 4). Moreover, there was no relationship between the SOC stocks down to a depth of 0.6 m and the amount of aboveground-, belowground- and total biomass at the studied tidal marshes, ($r^2 < 0.02$, $n = 16$) (Figure S10). There was, however, a weak relationship between topsoil OC stocks (down to 0.05 m depth) and aboveground biomass ($r^2 = 0.31$), which suggests that local biomass production might have an influence on the amount of topsoil OC and partially controls the spatial pattern OC deposition along the estuary (Figure S11). The lack of a strong relationship between biomass and OC stocks suggests, however, that factors other than local biomass control the long-term sequestration of OC in the studied tidal marsh sediments.

The analysis above only considers macrophyte biomass and does not take into account the potential contribution of edaphic algae to the OC pool of the marsh sediments. The OC produced by algae is generally considered to be very labile and may therefore be expected to be rapidly mineralized in a tidal marsh environment (Chmura & Aharon, 1995). This appears also the case in the Scheldt estuary: Boschker et al. (1999) showed that algal-derived OC was rapidly mineralized on the brackish marsh at salinity 17 as it was the primary source for bacterial growth (Boschker et al., 1999). However, some microbial-derived DOC can potentially be stabilized on mineral surfaces (Ahrens, Braakhekke, Guggenberger, Schrumpf, & Reichstein, 2015).

Allochthonous organic carbon deposits along the estuary

The low radiocarbon contents of deposited OC show that this OC in winter is very old, indicating that a significant fraction of this OC has been fixed from atmospheric CO_2 up to millennia ago (Figure 7). Summer deposits are systematically younger as indicated by a higher F^{14}C , suggesting a contribution of fresh carbon to deposited OC. This contribution is, however, limited: the F^{14}C of summer deposits is still well below 1. Several earlier studies have already shown that the organic matter that is transported within an estuary consists for a substantial fraction of highly processed, stable organic matter (Klap, Boon, Hemminga, & van Soelen, 1996; Raymond & Bauer, 2001), which is being enriched with fresh, more labile

organic matter in summer (De Brabandere et al., 2002; Mariotti, Lancelot, & Billen, 1984; Muylaert et al., 2000).

As the production of riverine and estuarine phytoplankton is generally absent during winter (Hellings, Dehairs, Tackx, Keppens, & Baeyens, 1999; Muylaert et al., 2000), deposited sediments at tidal marshes during this season contain mainly old OC. Also in terrestrial soils, average SOC ages of up to millennia old are regularly reported (He et al., 2016; Martinelli et al., 1996; Rumpel, Kögel-Knabner, & Bruhn, 2002). However, the old SOC in these ecosystems is not necessarily stable, as environmental disturbances can result in a rapid decomposition of old SOC (e.g. Hobbey, Baldock, Hua, & Wilson, 2017). The old OC that is deposited at tidal marshes is, in contrast, likely to be quite stable as it has first been sequestered in terrestrial ecosystems, was then eroded and has travelled through the river system until it was finally deposited on the marsh. The fact that this old OC is not being mineralised is likely to be also related to the fact that suspended sediment in the Scheldt estuary is mainly transported as cohesive organo-mineral aggregates (M. S. Chen, Wartel, Van Eck, & Van Maldegem, 2005), thereby physically protecting the OC.

The concentration of this stable OC in deposited sediments decreases towards the mouth of the estuary, with winter deposits containing 4 – 5 % OC in the freshwater section and 2 – 3 % in the saltwater section (Figure 5). There is also a clear gradient in the source of this stable OC along the estuary. The $\delta^{13}\text{C}$ signal of OC deposited at freshwater marshes, on average $-28 \pm 0.48 \text{ ‰}$ (Figure 5) strongly suggests that this OC has a terrestrial origin (Kohn, 2010). Middelburg and Nieuwenhuize (1998) calculated a value of -26 ‰ for the terrestrial OC present in the estuary. The $\delta^{13}\text{C}$ of the deposited sediment is on average slightly lower than this value, which could indicate that relatively small amounts of fresh material with a lower isotopic signal are also present in the deposits. Winter deposits at saltmarsh no. 4 ($s = 27$) have an average $\delta^{13}\text{C}$ value of $-23.6 \pm 0.46 \text{ ‰}$, which is very similar to $\delta^{13}\text{C}$ values reported for marine sediments in the North Sea in front of the mouth of the Scheldt river (-23.2 to -23.8 ‰ , Salomons and Mook, 1981). This indicates a marine origin of the stable OC that is deposited at the saltmarshes. This is not surprising, as it has been shown that marine sediments are able to efficiently stabilize OC (Keil, Montluçon, Prahl, & Hedges, 1994; Mayer, 1994). The origin of the OC deposited on brackish marshes is a mixture between these terrestrial and marine end-members (Figure 5).

In summer, old OC in deposited sediments is mixed with a substantial amount of fresh, young OC, as indicated by the higher F^{14}C of summer versus winter deposits (Figure 7). Assuming that the concentration of old, stabilized OC in the deposited sediments is constant throughout the year, the importance of labile OC that is deposited in summer can be assessed from the isotopic shift that is observed. At the freshwater marshes, the contribution of labile phytoplankton-derived OC to summer deposits is very limited. Reported $\delta^{13}\text{C}$ values for phytoplankton in the freshwater portion of the estuary are in the range of -29 to -34 ‰ (Hellings et al., 1999; Middelburg & Nieuwenhuize, 1998). A significant contribution of recent OC to summer deposits would therefore result in a significant shift towards lower $\delta^{13}\text{C}$ values, which is not observed. Moreover, the concentration of suspended particulate OC is up to 10 % in this part of the estuary during summer (Abril et al., 2002), while the OC

concentration in deposits is ca. 5.5 %. This suggests that most OC that is produced in the freshwater section of the estuary is not deposited on the freshwater marshes. At the saltmarsh, in contrast, there is a clear contribution of marine phytoplankton-derived OC to summer deposits, as indicated by (i) the doubling in OC concentration in the deposited sediments (Figure 5a), which is (ii) accompanied by a shift in $\delta^{13}\text{C}$ values towards marine values (-18 - -22 ‰, Middelburg and Herman, 2007; Middelburg and Nieuwenhuize, 1998) (Figure 5b) and (iii) the relatively high $F^{14}\text{C}$ of summer deposits (Figure 7). The large inter-annual variation in OC concentration in deposits at the brackish marsh (between 3.7 ± 0.3 % and 11.1 ± 2.2 %) indicates that there is a large amount of labile OC present in summer deposits (Figure 5a), which is confirmed by the higher $F^{14}\text{C}$ in summer deposits (Figure 7). It is not clear why deposition of labile OC is so substantial in this section of the estuary in comparison to the salt and freshwater sections, as phytoplankton blooms are present along the entire estuary (Gypens et al., 2013; Muylaert, Sabbe, & Vyverman, 2009). This additional labile OC is, however, only present in the topsoil layers, below which there is a steep decline in OC concentration with depth (ca. 10 % OC in the topsoil compared to ca. 3 % OC below 0.10 m depth) as well as a clear decrease of $F^{14}\text{C}$ (see supplementary data for depth profiles of OC concentration). Thus, the relatively large input of labile OC in summer has little effect on the long-term SOC storage in these sediments.

Preservation mechanisms of organic carbon in tidal marsh sediments

The $F^{14}\text{C}$ in subsoil tidal marsh sediments suggests that this OC is up to millennia old, while the upper meter of sediments in all studied tidal marshes has been deposited within less than a century (Temmerman et al., 2003, 2004). This can only be explained by the fact that the OC in the studied sediments consists for a significant fraction of old, allochthonous OC. In topsoil sediments of marshes for which the radiocarbon content has been determined, OC is a mixture between this old OC and locally produced biomass, as indicated by the higher $F^{14}\text{C}$ of topsoil sediments.

Depth patterns of the $F^{14}\text{C}$ vary along the estuary. The lack of a decrease in $F^{14}\text{C}$ with depth in the top 0.5 m of freshwater sediments suggests that the contribution of locally produced OC is relatively stable with depth (Figure 7). At the brackish and saltmarsh, in contrast, the steep decrease in OC concentration with depth (see supplementary data) is accompanied by a steep decrease in the $F^{14}\text{C}$, indicating that the majority of fresh OC is rapidly decomposed after burial. Thus, in freshwater sediments a substantial portion of locally produced OC is preserved after burial, while the majority of the fresh OC is rapidly mineralized in brackish and saltmarsh sediments.

Although OC associated with deposited sediments is considered to be an important source of OC for minerogenic tidal marshes (Bouillon & Boschker, 2006; Craft, 2007; Middelburg et al., 1997), stabilization mechanisms of OC in tidal marsh sediments are rarely identified (with the exception of Spohn et al., 2013). From our results it is clear that there are substantial gradients along the estuary with regard to (i) the mechanisms of OC stabilization and (ii) the relative contribution of allochthonous versus autochthonous sources to long-term preserved OC. In our analyses, we interpreted POM as originating from locally produced biomass, a

hypothesis which is supported by the fact that the deposited sediment samples did not contain any visible particulate organic fragments apart from parts of locally produced vegetation, which can be redistributed at the surface of tidal marshes during storm events. While systematic variations of the relative importance of OC fractions in topsoil sediments are limited (Figure 8a), clear patterns along the estuary are present for subsoil sediments (Figure 8c). On the one hand, freshwater marsh sediments preserve a significant amount of locally produced OC (POM) after burial (Figure S7), both as free POM and as POM protected inside microaggregates. The latter is suggested by the observation that the OC concentration of the m + S fraction in freshwater marsh subsoils is substantially larger compared to the silt and clay (sc) fraction, indicating the presence of POM in the microaggregates (Figure 8d). On the other hand, in saltmarsh sediments nearly all POM is decomposed upon burial. These data provide evidence that locally produced biomass is decomposed on a decadal timescale in saltmarsh sediments, while being better preserved and contributing to long-term OC storage in freshwater marsh sediments. Furthermore, the results confirm that the decomposition of OC associated with minerals (sc and scM) upon burial is very limited, as the amount of OC stored in this fraction does not decrease substantially with depth in most tidal marsh sediments (Figure S7). It can be assumed that the majority of OC associated with minerals is allochthonous OC, as all minerals in these tidal marshes have been deposited during inundation events. However, there is a potential exchange of mineral-associated OC through desorption of allochthonous, old OC and adsorption of locally-produced OC (Schrumpf & Kaiser, 2015). This exchange is however likely to be minimal, as suggested by the low $F^{14}C$ values of bulk OC found in the studied sediments.

Based on our data it is not possible to derive an explanation for the rapid decomposition of OC in saltmarsh sediments. Research on the effect of location along an estuary on decomposition of organic matter in tidal marsh sediments has suggested both a positive (Loomis & Craft, 2010) and negative (Mendelssohn et al., 1999) correlation between decomposition and salinity. Experimental studies on the effect of saltwater addition on the decomposition of organic matter formed in freshwater marshes have shown that an increase in salinity generally results in an increase in the decomposition of organic matter (Morrissey et al., 2014; Weston, Dixon, & Joye, 2006; Weston, Vile, Neubauer, & Velinsky, 2011). Results from these studies suggest that sulphate reduction is the preferential decomposition pathway and an increasing availability of extracellular enzymes might be responsible for higher decomposition rates in saltmarsh sediments. However, more research is needed to confirm if these mechanisms can also explain the higher in situ OC loss rates we found in saltmarsh sediments. Another important factor is that rates of mineral sediment deposition at the freshwater marshes are higher compared to the saltmarshes (Temmerman et al., 2004) leading to more rapid advection of deposited OC to deeper soil layers which results in more efficient preservation of OC (Kirwan & Mudd, 2012), as proposed by Van de Broek *et al.* (2016).

In the freshwater subsoils, stable microaggregates store a substantial fraction of total OC, while aggregates in saltwater subsoils were almost completely broken up after sonication (Figure S6). This suggests that aggregates which are formed in freshwater marshes are more

stable and thus more effective at preserving organic matter compared to saltmarshes. To our best knowledge, there are no earlier studies on aggregate stability in tidal marsh sediments along a salinity gradient. The effectiveness of soil aggregates to stabilize organic matter in tidal marsh sediments thus requires further research attention.

The combined results from radiocarbon analysis and OC fractionation quantitatively support the hypothesis that preservation of autochthonous OC is more important in freshwater compared to saltmarsh sediments, while characteristics of OC associated with deposited sediments are a major control on OC stocks along the estuary (Van de Broek et al., 2016). In addition, our results suggest that in minerogenic saltmarshes long-term OC sequestration is decoupled from local primary production, implying that these sediments do not serve as an atmospheric CO₂ sink on a decadal timescale. In contrast, freshwater marsh sediments efficiently store a substantial amount of locally produced OC, thereby actively sequestering atmospheric CO₂ on a decadal to centennial timescale.

These findings have important implications for the assessment of the response of the tidal marsh OC pool to future environmental changes. Studies on the effect of sea level rise on the tidal marsh OC pool generally only consider short-term changes observed in a controlled lab environment (Chambers, Reddy, & Osborne, 2011; Morrissey et al., 2014; Weston et al., 2006, 2011). However, our results show that the response to environmental changes such as a sea level rise over decennial/centennial time scales will be mainly controlled by the supply of allochthonous OC, while the characteristics of in-situ produced biomass and its decomposition are less relevant at this timescale. This stresses the importance of studying OC dynamics in tidal marsh sediments over a period of time (or sediment depth) that is relevant for the change in environmental conditions that is considered.

Consequences for calculated CO₂ sequestration rates

The magnitude of short-term contemporary OC deposition at the studied tidal marshes is controlled by the accumulation of relatively labile OC originating from locally produced biomass, while long-term OC sequestration depends on the supply of stable allochthonous OC from terrestrial and marine origin. This has important consequences for the calculation of OC sequestration rates in coastal sediments, which is generally performed using one of the following methods: (i) using short-term sediment deposition rates in combination with topsoil OC densities (e.g. Chmura, Anisfeld, Cahoon, & Lynch, 2003; Ouyang & Lee, 2014) or (ii) by relating decreasing OC concentrations with depth to time since sediment deposition (e.g. Artigas *et al.*, 2015). However, both approaches generally result in an overestimation of the rate of atmospheric CO₂ sequestration for two reasons, as illustrated in (Figure 9). First, using topsoil OC densities to calculate long-term OC sequestration rates neglects potentially large losses of OC upon burial (Figure 9b, c); the calculated rates should therefore be interpreted as short-term carbon deposition rates. Second, while methods which relate decreasing OC concentrations with depth to the time since sediment deposition account for OC losses through time, they do not account for the fact that a substantial fraction of the OC in coastal sediments can have an allochthonous origin and has not been sequestered at the tidal marsh. As a consequence, this old-aged allochthonous OC does not contribute to active removal of

atmospheric CO₂ by tidal marsh ecosystems (Figure 9c). These considerations are up till now not accounted for in the assessment of rates of blue carbon sequestration in these ecosystems (Chmura et al., 2003; Duarte et al., 2013; Ouyang & Lee, 2014). In order to obtain more reliable estimates of the potential of tidal marsh ecosystems to store atmospheric CO₂, future studies should (i) sample marsh sediments to a sufficient depth so that OC decomposition within the marsh sediments can be accounted for and (ii) identify the contribution of autochthonous and allochthonous OC to total OC storage in marsh sediments.

The results of this study show that the majority of preserved OC in tidal marsh sediments along a temperate estuary is old, allochthonous OC which has not been sequestered in-situ but has a terrestrial or marine origin at freshwater- and saltmarshes respectively. Furthermore, the concentration of stable OC in deposits is substantially higher in freshwater compared to saltwater reaches, contributing to decreasing OC stocks with increasing salinity. Radiocarbon analysis and OC fractionation showed that freshwater tidal marsh sediments effectively preserve locally produced OC, while this is decomposed on a timescale of decades in saltmarsh sediments. As the majority of preserved OC in saltmarsh sediments has not been sequestered in-situ, the contribution of these sediments to atmospheric CO₂ sequestration is very limited on a decadal to centennial timescale. In contrast, freshwater marsh sediments preserve a substantial amount of in-situ produced biomass, thereby actively sequestering atmospheric CO₂.

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Data statement

The data associated with this paper is available at <http://dx.doi.org/10.17632/2nnv9bw3hh.2>.

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Table 1: General characteristics of the sampled tidal marshes and indication of the locations where different analyses are performed (s = summer, w = winter).

Name	Number	Average salinity	Distance from mouth (km)	OC fractionation	Sediment traps	¹⁴ C measurements
Saltmarshes						
Sloehaven low	1	30	6			
Sloehaven high	2	30	6	✓		
Paulina low*	3	27	15			
Paulina high*	4	27	15	✓	✓ (s+w)	✓
Zuidgors low	5	24	24			
Zuidgors high	6	24	24	✓		
Hellegat low	7	22	28			
Hellegat high	8	22	28		✓ (w)	
Brackish marshes						
Waarde low*	9	17	44			✓
Waarde high*	10	17	44	✓	✓ (s+w)	

Kruispolder low	11	15	46		
Kruispolder high	12	15	46		
Freshwater tidal marshes					
Notelaar low*	13	1.5	97		✓
Notelaar high*	14	1.5	97	✓	✓ (s+w)
Mariekerke low	15	0.5	110		
Mariekerke high	16	0.5	110	✓	
Grembergen high	17	0.4	120	✓	
Appels low	18	0.3	127		✓ (w)

* Data and methods for these tidal marshes are presented in Van de Broek *et al.* (2016).

Figure captions

Figure 1: Map of the Scheldt estuary. Black rectangles indicate the locations of the sampled tidal marshes, the numbers refer to the sampling locations as listed in Table 1.

Figure 2: Organic carbon fractionation scheme, with final derived fractions highlighted in blue

Figure 3: Grain size distribution of disaggregated topsoil sediments of tidal marshes along the Scheldt estuary

Figure 4: Total biomass (g DW m⁻²) present at the sampled freshwater (green), brackish (brown) and saltmarshes (blue). Upward pointing bars represent above-ground biomass and downward pointing bars represent belowground biomass, while light colors indicate low marshes and dark colors indicate high marshes. Error bars represent the standard deviation around the average (based on 5 replicate measurements).

Figure 5: Organic carbon concentration and $\delta^{13}\text{C}$ values of sediments deposited at the tidal marsh surface during flooding events. Points represent the average of 4 flooding events in summer (2016) and 3 events in winter (2017), error bars represent the standard deviations.

Figure 6: Total organic carbon stock (kg OC m^{-2}) in the top 0.6 m of tidal marsh sediments along the Scheldt estuary. The dots represent the average values calculated based on three replicate soil cores, error bars represent standard deviations.

Figure 7: Fraction modern ^{14}C ($F^{14}\text{C}$) of deposited sediments at the surface of tidal marshes in summer and winter, and sediments at different depths ('s' in the legend refers to salinity).

Figure 8: Final OC fractions of topsoil (a, b) and subsoil (c, d) tidal marsh sediments along the estuary (see Figure S3 for depths of subsoil samples). a) and c) show the contribution of OC in each fraction to a total soil mass of 100 g, b) and d) show the OC concentration of the different fractions. sc = free silt and clay, scM = silt and clay in macroaggregates, POM = particulate organic matter, m+S = micro aggregates and sand.

Figure 9: Conceptual framework of OC dynamics in tidal saltmarsh sediments and measurements of OC accumulation rates. (a) Topsoil sediments contain large amounts of OC from allochthonous sediments (grey shapes) and both aboveground- and belowground-produced autochthonous biomass (brown and green). Upon burial, however, mainly autochthonous OC is being mineralized. (b) The associated OC depth profile, subdivided into autochthonous- and allochthonous-derived OC. (c) Measured rates of OC accumulation in saltmarsh sediments depend on the timescale considered.











