A re-evaluation of wetland carbon sink concepts and measurements: A diagenetic solution down sediments

John Barry Gallagher[1], Ke Zhang[2], Chee Hoe Chuan[3]

[1]Institute for Marine and Antarctic Studies, University of Tasmania, Australia, 7000
Orcid ID: 0000-0002-2622-0912.
johnbarry.gallagher@utas.edu.au & johnbarrygallagher@icloud.com.

[2]State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, PR China, 210008
Orcid ID 0000-0002-1841-9016.

[3]Borneo Marine Research Institute, Universiti Malaysia Sabah, Jalan UMS, Kota Kinabalu, Sabah, Malaysia, 88400.
Orcid ID 0000-0003-4715-5387

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Abstract

Aquatic canopy ecosystems' ability to mitigate greenhouse gases (*GHG*) is currently based on the rate of sedimentary organic carbon accumulation (*CA*) and the protection of vulnerable stocks from remineralisation. However, remineralisation of allochthonous inputs constrains *CA* as sequestration, assessments neglect remineralisation over climatic scales, and often fail to account for recalcitrant material. The article clarifies the meaning of stock and sequestration as mitigation services through their net ecosystem production (*NEP)* and addresses the concerns through a series of hypothetical evolving ecosystems. A diagenetic solution is proposed that accounts for continuous remineralisation of *CA* and the remineralised fraction of labile allochthonous inputs to estimate the *NEP*. The solution was applied and tested for a seagrass and mangrove ecosystem. Uncorrected and corrected average *CA* was greater than the *cal. NEP* values by a factor of two for the seagrass and 30 for the mangrove. Nevertheless, the *NEP* values fell within reported ranges i.e., 27.6 g C m^{-2} yr^{-1} (mangrove) and 7.2 g C m^{-2} yr^{-1} (seagrass). The overestimate was largely maintained after including vulnerable stocks in the total carbon accreditation calculus. However, with the inclusion of *CA*, the total average carbon mitigation rates converged to 1 124 (seagrass) and 1 783 g C m^{-2} yr^{-1} (mangroves), when argued, in some circumstances, as a vulnerable stock concept after hindcasting to their original time of annual deposition. Mitigation concepts and measurements require re-evaluation and will assure that carbon credits are not overvalued, which would otherwise permit *GHG* emissions above the capacity of the ecosystem.

Keywords: Blue carbon · Teal carbon · Black carbon · Net ecosystem production · Carbon accumulation · Allochthonous recalcitrants

Introduction

Anthropogenic greenhouse gas (*GHG*) emissions are responsible for global heating and will likely disrupt both society and global ecosystems (Hoegh-Guldberg et al. 2018). This has led to a call to mitigate those emissions (UNFCCC 2015). However, along with altruism, incentives have to be provided for successful mitigation, such as through carbon trading or allocation schemes. Engineered or artificial approaches rely on investments into energy efficiency, recycling, and forced sequestration of emissions, in conjunction with a switch away from carbon-based fossil fuels (Lal 2008). In contrast, an ecosystem approach involves the restoration of lost natural carbon sinks, their preservation or enhancement of those sinks. This has led to extensive replanting and protection of terrestrial forests (Mackey et al. 2008). Indeed, a well-managed healthy ecosystem has the necessary vigour, resilience, and self-organization to sustain itself (Costanza & Mageau 1999; de Paoli et al. 2017).

While valuable, forests support a relatively low carbon production density (Lal 2008) and are vulnerable to fire. These constraints are not as apparent for freshwater and coastal canopy wetlands, namely, mangroves, seagrass, and saltmarsh (Duarte et al. 2010). These two ecosystem niches are now commonly referred to as teal and blue carbon ecosystems respectively (Zinke 2020). Freshwater wetlands occupy an area between 2% to 5% of the land and store between 20% and 30% of organic carbon of the terrigenous landscape (Kayranli et al. 2010). Similarly, coastal canopy systems occupy < 2% of the marine seascape. Together, these coastal systems have been estimated to contribute around 50% of the ocean's organic carbon storage, largely within an accreting soil–sediment column (Duarte et al. 2005). Although the magnitude of this claim has been disputed (Johannessen and Macdonald, 2016). We also contend that misunderstandings and errors have arisen in the definition and measurement of carbon sequestration and storage. First, there is an implicit and untested assumption that total sedimentary organic carbon accumulation is a proxy for carbon sequestration. Second, the majority of carbon sink assessments still fail to subtract intrinsically recalcitrant allochthonous or autochthonous carbon from stocks and sequestration estimates (Gallagher et al. 2021; Rillig 2018). Third, the traditional conceptual model does not account for remineralisation of its sedimentary organic carbon over climatic time scales (Chuan et al. 2020; Maher et al. 2017). Fourth, a large number of blue and teal carbon researchers still equate the ecosystems' total organic carbon balance, in isolation, as a mitigation service.

Aims

The article aims to review the measurement of carbon stock and sequestration concepts and clarify the additional constraints needed to qualify as a mitigation service. The currently-favoured methods for stock and sequestration are outlined; constraints and methods discussed, and sequestration misconceptions addressed for different circumstances for systems closed and open to allochthonous inputs. We then demonstrate what would be required to measure true sequestration and stock variability over climatic time scales from the sedimentary record, and argue the necessity for an additional sediment stock concept. Finally, these concepts are implemented and evaluated using two disparate examples, namely, a submerged seagrass meadow and an intertidal mangrove wetland both open to different forms of allochthonous organic carbon. We acknowledge but do not address the uncertain fate of organic carbon export and its downstream impacts not currently recognised in policy frameworks; the uncertain roles of biogenic and geogenic calcium carbonate formation and dissolution; biogenic production and emissions of other greenhouse gases other than CO_2 (Howard et al. 2018; Mitsch et al. 2013); the role of UV exposure on detritus; and net inputs of any dissolved inorganic carbon (DIC) from adjacent rivers (Chapin et al. 2006), possibly coastal upwelling, on net atmospheric exchange and biological assimilation.

The role of sediment carbon stocks in mitigation

Organic carbon stocks as a mitigation service are best understood as that fraction vulnerable to remineralisation after the disturbance (Jennerjahn 2020). The extent of sediment disturbance is commonly set to 1 m deep and the fraction remineralised > 25 % (Pendleton et al. 2012). The fate of the canopy, however, is not as clear, for example, a mangrove may be stored as a product or burnt for charcoal (Eong 1993). Once the stock has been estimated (g C m^{-2}), the values are then transformed to a vector quantity (g C m^{-2} yr^{-1}) for dimensional integrity with carbon sequestration, in the time it takes for the vulnerable fraction to be remineralised (IPCC 2014). As a mitigation service, however, this estimate cannot be understood in isolation. Ultimately, mitigation is relative to the carbon sink of a likely replacement (Siikamäki et al. 2013). For example, the value of a mangrove's vulnerable stock becomes relative to the final state of its aquaculture pond replacement (Järviö et al. 2018). Alternatively, the loss of a natural seagrass wetland could directly progress to a rocky barren ground state with no remaining stocks (Wilson 1949). For an existing anthropogenic state, such as reservoirs, mitigation services are related to the valley ecosystem it replaced, and ultimately relative to the state at the end of the reservoirs life (Prairie et al. 2018). Indeed, the latter could be equally applied to natural systems. For example, mangroves that have encroached onto saltmarsh during sea-level rise (Rogers et al. 2005) become the balance between the saltmarsh, mangrove a likely disturbed non-vegetated state.

Measuring carbon stocks.

The attraction of focusing only on standing stock measurements comes from their relative simplicity. This is an important attribute to capture the inherent variability for some systems (Hu et al, 2021). For example, there is a simplicity in that estimates of tree biomass can be made using accessible allometric width, carbon content, bulk density parameters. Except for intermediate and faster-growing R-strategist macrophytes, the timing for both biomass assessments is usually not that critical. Even over decades, stationary climate cycles can produce stationery trends in biomass and productivity for the slowest of seagrass species (e.g. Marba & Duarte 1997). Although the response may well change with climate in the coming decades. For sediments, stocks can take decades to centuries to accumulate (Wilkinson et al. 2018) and are likely to change significantly between years. Furthermore, once the sediment samples are dried, the analysis can be handled through more specialised laboratory services. This service can be readily extended to the analysis of organic stable isotope signatures to estimate the fractions of different sources (Gonneea et al. 2004). Alternatively, a less resource-intensive approach uses organic carbon proxies. These can be dry bulk density (Callaway et al. 2012), gravimetric losses after combustion, chemical oxidation and titration (Byers et al. 1978; Heiri et al. 2001), or infrared reflectance (Bellon-Maurel & McBratney 2011). Except for chemical titration, the above proxies to some degree require a global (Fourqurean et al. 2012) or preferably regional (Craft et al. 1991) calibration with standard methods, remembering to include regression variance in the final estimate (Gallagher et al. 2021).

Limitations and misunderstandings of the stock concept

Intrinsically recalcitrant organic carbon produced within or outside the ecosystem is not vulnerable to remineralisation after disturbance. However, removing them from the stock calculus has not yet been adopted in the majority of blue and teal carbon assessments, despite recognition by the IPCC (Bindoff et al. 2019). Arguably the most ubiquitous of the intrinsic recalcitrants is black carbon (BC). For which, there is very little impediment to quantifying this component. The carbon content can be estimated after thermal or chemical isolation within a sedimentary matrix using standard laboratory equipment (Chew & Gallagher 2018). Carbon and N isotopic signatures can then be used to assist in identifying their allochthonous or autochthonous nature (Gallagher et al. 2021; Leorri et al. 2018). Nevertheless, BC estimates across coastal wetland ecosystems remain globally under sampled. This is despite contributing substantial fractions to the sediments' TOC (means between 3-38%) (data from Chew and Gallagher 2018; Gallagher et al. 2021; Gallagher et al. 2019). Estimates across freshwater wetlands, however, are scarce but may still be significant. Sediment and soil BC fractions between 35.9% and 41% of its TOC have been reported within an industrial setting for ponds and paddies (Song et al. 2002).

Along with BC, other intrinsically recalcitrant forms may require evaluation. These are kerogens, geologically old organic materials washed in from catchment shales, and microplastics. Unfortunately, wetland measurements of sedimentary kerogens are restricted to a shallow pond and paddy field located within an industrial region (reportedly 24% and 30.8% of TOC respectively; Song et al. 2002). Similarly, the importance of microplastics to the carbon budget within soils can be substantial but for wetland sediments, no data is available (Rillig 2018). Along with intrinsically recalcitrant material, labile material can become effectively recalcitrant from physical protection. This can occur within a sedimentary clay matrix, estimated to be less than 5% of the TOC (Needelman et al. 2018). Although, it is not clear whether such associations remain recalcitrant after disturbance when subject to continuous resuspension (Cathalot et al. 2013). Physical protection is also manifest from occluded carbon contained within the glassy structures of plant phytoliths. Within non-alkaline soils, phytolith-occluded carbon can represent most of the remains of organic matter (Parr & Sullivan 2005). However, for aquatic systems, data is limited to two tropical river-estuarine systems as biogenic silica fractions within the water column or non-vegetated surface sediments, (Cary et al. 2005; Zang et al. 2016).

Carbon sequestration through sedimentation

Sequestration happens when the rate of ecosystem CO_2 fixation exceeds that of the communities respiration. When the biomass is at a steady-state then the excess carbon is locked in as organic matter largely accumulating down the sediments. The balance is referred to as the net ecosystem production (*NEP*). Shallow canopy systems can stabilise and preserve the remains within the sediments that make these systems so valuable. Like stocks, the amount sequestered is compared to its anthropogenic replacement (Eq. 1). Unlike stocks, traditional estimates of sequestration have been aggregated down the sediment column for temporal trends and variance, once below a diagenetically active surface layer (Cebrian 1999).

$$Cmit\ = (NEP + \frac{\theta}{\varphi_1} Cstock) - (NEPRr + \frac{\theta}{\varphi_2} Crstock) \qquad (1)$$

Eq. 1 Where *Cmit* is the *GHG* carbon mitigation service and *NEP* the annual atmospheric carbon dioxide sequestration rate, positive for uptake; *Cstock* represents biomass and sedimentary organic carbon stocks that have accounted for BC, with θ the vulnerable fraction likely to be remineralised over a time φ to attain an equilibrium should the ecosystem be degraded or destroyed; *NEPRr* is the atmospheric carbon dioxide sequestration rate of the replacement ecosystem, and *Crstock* the organic carbon stock of the replacement ecosystem that has accounted for *BC*, with θ is the fraction vulnerable to remineralisation after destruction or disturbance, over time φ for each circumstance.

As the above equation stands, there is no information on what determines the extent of the balance, other than the net productivity of the plant. The carbon use or consumption will depend on the innate digestibility of the plant (Cebrian 2002) and any allochthonous material along with its rate of supply. Whereas, for the sediment deposits, the innate digestibility is constrained by the 'aging' of the organic mix within the sediments, and physical protection associated with the clay fractions (Burdige 2007). Clearly, unlike stocks, sequestration is more valuable for an ecosystem capable of both directing CO_2 towards the production of autochthonous recalcitrants and the protection of labile fractions. Although it should be noted that gaseous emissions in the production of autochthonous BC would constrain its mitigation service (Santín et al. 2015). As in the case of stocks, allochthonous recalcitrants continue to play no role in the sequestration calculus; and to include them would amount to double-accounting across ecosystems.

Measuring sequestration

Direct measurements of *NEP* are resource and knowledge-intensive. Carbon sink assessment programs require either numerous spatial and seasonal diurnal deployments of benthic chambers or measurements of the water columns' metabolic gases (Maher & Eyre 2012; Gruber et al. 2011). Alternatively, continuous eddy covariance deployments on single benthic frames or atmospheric towers have been deployed (Lu et al. 2017; Rodil et al. 2019). The eddy covariance footprint can be more than 200 m long, but changes with wind direction require statistical imputation methods to effect a contiguous time series. However, while valuable, these approaches do not function on the time scale needed for estimating variance and trends over climatic scales. Furthermore, across intertidal systems fluxes immediately above the macrophyte assemblage fail to account for the lateral loss of CO_2 from the deeper parts of the sediment column (Fig. 1c) (Maher et al. 2018).

In place of direct measurements, annual sedimentary organic carbon accumulation has been touted as a measure of sequestration. Unlike direct measurements, it reduces the need for specialised equipment, variability can be estimated down the sediment column over decades, and it accounts for any lateral losses of CO_2 from sediment columns during tidal exchange, Furthermore, evidence suggests a single sedimentation rate can closely represent the mean for the region (Callaway et al. 2012). The method employs the product of the carbon concentration and its sediment accumulation rate. Accumulation rates are usually calculated using global geochronological models from the supply and decay of the natural radioisotope ^{210}Pb over the last 100 to 150 years, widely accessible as a service within specialized laboratories (Lavelle et al. 1986). These concepts and means are pervasive across the field (e.g., Carnell et al. 2018; Chmura 2013; Forbrich et al. 2018; Mitsch et al. 2013; Murray et al. 2011; Murray & Vegh 2012; Troxler 2013; Villa & Bernal 2018; Weston et al. 2014).

Limitations and misunderstandings of sequestration down the sedimentary record

Sequestration calculations using the product of the sediment accumulation rate and organic concentration appear to solve the issues associated with direct measurements of sequestration as their *NEP*. Indeed, the equivalency of carbon accumulation and sequestration is pervasive across the science (e.g., Carnell et al. 2018; Chmura 2013; Forbrich et al. 2018; Mitsch et al. 2013; Murray et al. 2011; Murray & Vegh 2012; Troxler 2013; Villa & Bernal 2018; Weston et al. 2014). Some articles do so without explicitly stating an equivalency with *NEP*. Nevertheless, equivalency is often implied when comparisons are made with carbon accumulation or used to constrain lateral exchange of CO_2 from vertical *NEP* measurements from the canopy community or atmospheric exchange (Forbrich et al. 2018; Mitsch et al. 2013; Troxler 2013; Weston et al. 201). However, this application is erroneous from three standpoints. First, total sedimentary organic carbon accumulation cannot be equivalent to *NEP* as sequestration in open systems (Prairie et al. 2018). This is manifested when considering that most teal and some blue carbon ecosystems are net heterotrophic from the consumption of allochthonous subsidies (Duarte & Prairie 2005), yet continue to accumulate organic carbon to the sediment column. Second, remineralisation of deposited allochthonous and autochthonous organic carbon is not confined to the first year of deposition but continues to be remineralized over the century (Gälman et al. 2008; Maher et al. 2017; Zimmerman & Canuel 2002). Consequently, the respiration component of the annual *NEP* continues over the ensuing century. It would seem then that concentration terms used to address carbon accumulation need to be normalised for remineralisation at centennial climatic scales to be a mitigation service (Chuan et al. 2020). Third, there are considerations of applying best practices to determine accurate sedimentation rates. Natural ^{210}Pb geochronological models have several built-in assumptions that are not always or sufficiently addressed within blue carbon research. For example, overestimates can arise from neglecting the effects of surface mixing/bioturbation of older deposits (Johannessen & Macdonald 2016), when the ^{210}Pb inventory of the deep mixed layer is > 15% of the total (Lu & Matsumoto 2005). The assumptions of sedimentation and ^{210}Pb supply variance used in standard mapping models are not always tested from the convergence of one or more independent markers (Abril 2004). Although, more recently evaluation has been replaced by applying by eye, an approximately *ln*-linear portion of the decay profile as representing the average accretion rate (Arias-Ortiz et al. 2018). Whether that scenario analysis is justified, the averaged sediment accumulation rate cannot capture variability and trends.

Sequestration and carbon accumulation

The issues of sequestration and carbon accumulation equivalency and continued reminerilsation are expanded and formalised with the use of three hypothetical scenarios **(**Fig. 1). Case I, II, and III develop from a simple closed immature system to a more complex mature open system. Whereupon use the use of uncorrected carbon accumulation becomes increasingly divergent from *NEP*. A means is then discussed on how to obtain the required additional information contained within the sedimentary record with a robust decomposition model.

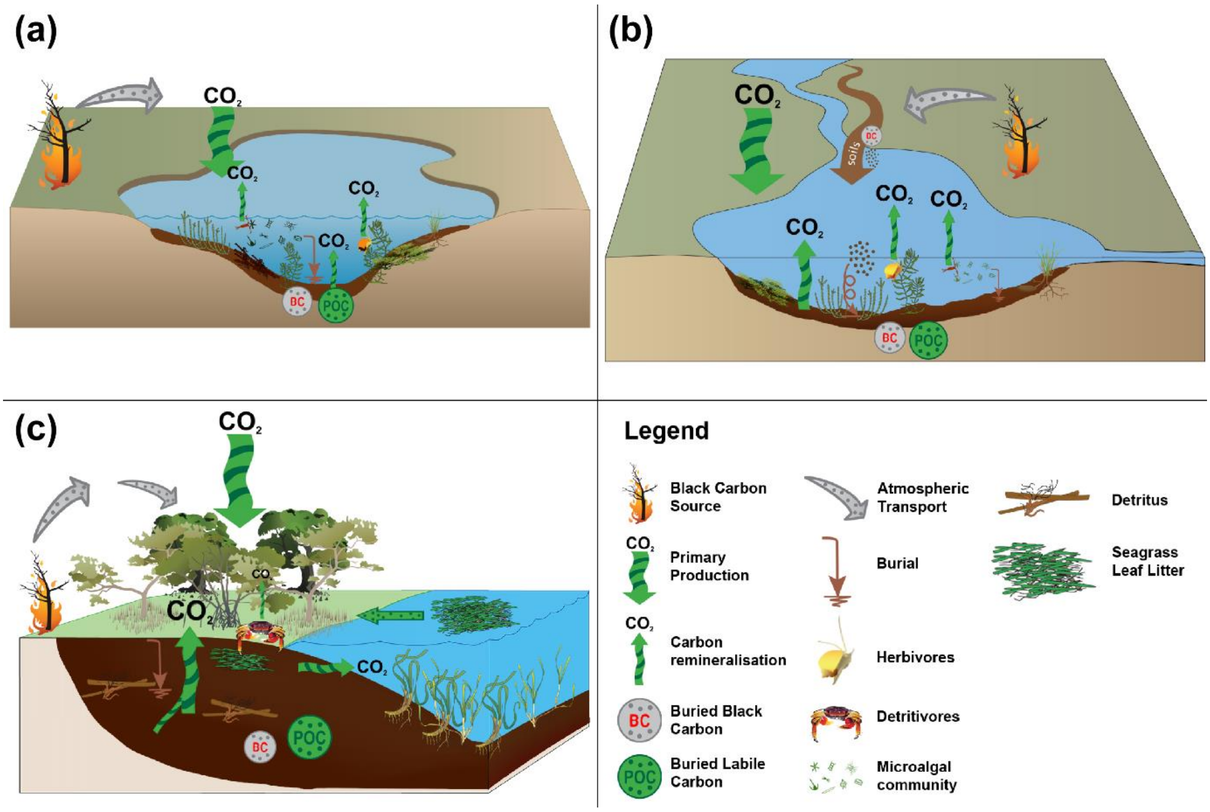

Fig. 1 Conceptual models for ‘a’ Case I; an immature subaquatic wetland pond after one year of deposition and closed to inputs and outputs but impacted by atmospheric deposition of black carbon; ‘b’ Case II; an immature aquatic wetland after one year of deposition, open to river and atmospheric inputs, and outputs; ‘c’ Case III; a mature intertidal mangrove with more than 100 years of deposits and open to atmospheric inputs, litter deposits from an adjacent seagrass ecosystem, with net losses of CO_2 from the canopy from shallow and deep parts of the sediment column vertically, and laterally during tidal exchange. The figure was produced in Abode Illustrator CS6™ with components taken from Media Library Integration and Application Network (https://ian.umces.edu/media-library/).

Case I: An immature closed wetland.

This type of ecosystem approximates the beginning of an established closed wetland pond, or perhaps the start of restoration (Fig. 1a). This scenario was also set out by Prairie (Prairie et al. 2018) but modified here, as after one further year of deposition. Primary production and consumption are at a steady-state and confined within the wetland. The resultant *NEP* then becomes the difference between the annual CO_2 drawdown as it is fixed by the autotrophic assemblage (*GPP*) over the amount respired, as it is consumed by the autotrophic assemblage (*Pr*) and the heterotrophic community. The community is composed of herbivores (*Hr*), benthic detritivores (*Dr*), and decomposers largely confined to sedimentary micro-flora (*Br*). Once organic matter is deposited within the sediments, the microflora continues to consume and remineralise the remaining labile fraction leftover from detritivores over the following year (Cebrian 1999). Thus, the net rate of the remaining carbon accumulated within the sediments after 1 year of deposition is equivalent to the annual *NEP* for that previous year (Eq. 2). *Under these conditions, carbon accumulation does indeed appear to be a proxy for NEP*.

$$NEP = GPP - Pr - Hr - Dr - \int_{1y}^{0y} Br = CAautl \qquad (2)$$

Case II: An immature open wetland.

Most teal and blue carbon ecosystems are not isolated (Fig. 1b). Allochthonous organic carbon is added to wetlands either constantly or sporadically. For freshwater wetlands, this can come from rivers as components of soil and plant debris. On the other hand for coastal wetlands, adjacent seagrass, saltmarsh, and mangrove can also supply material (Chuan et al. 2020; Gonneea et al. 2004). However, BC delivery can be from both soil washout and aerial deposition (Chew & Gallagher 2018). Importantly, unlike a wetlands' innate primary production, allochthonous carbon has been fixed outside as a separate ecosystem service. Consequently, the effect on the *NEP* is then constrained by the amount of allochthonous carbon remineralised (*Ir*) within the ecosystem and not added to the carbon balance (Eq. 3). In other words, including allochthonous production as an ecosystem service will be no more than double accounting. This error appears to have been propagated from the terrestrial assessments, where allochthonous inputs rates were included in the *NEP* term to describe carbon accumulation (Lovett et al. 2006). Assuming most of the allochthonous inputs are rapidly deposited by the canopy into the surface sediments (Bos et al. 2007), their remineralisation is most likely confined within those sediments. The *NEP* then becomes the subtraction of the allochthonous remineralisation term from the autochthonous deposition term. This in turn can be estimated from remains of the autochthonous and net allochthonous carbon accumulated, from the deposition rate of allochthonous organic carbon to the sediments (*I*) from what remains after one year (Il_{1y}) (Eq. 3).

$$NEP = GPP - Pr - Hr - Dr - \int_{1y}^{0y} Br - \int_{1y}^{0y} Ir = \ CAautl_{1y} - (I - Il_{1y}) \quad (3)$$

Eq. 3 Where *Ir* is the fraction of the input of the allochthonous carbon (*I*) that has been consumed and respired; I, is the rate of allochthonous supply of detritus to the ecosystem, and Il_{1y} the remains of that supply after a year of sediment decomposition, and $CAautl_{1y}$ is the accumulation of the remaining organic carbon produced within the ecosystem after a year of sediment decomposition.

$$CA_{1y} = \ CAautl_{1y} + Il_{1y} \quad (4)$$

By subtracting Eq. 4, the elements of carbon accumulation, from the sedimentary and input terms in Eq. 3, its shows that the total organic carbon accumulation will overestimate *NEP* by the rate by which allochthonous organic carbon is initially supplied to the sediments (Eq. 5). To state it in another way, the fraction of allochthonous carbon that has been decomposed is built into the amount remaining for accumulation. For example, should the allochthonous fraction be composed only of recalcitrant BC, then *Il = BC.* Consequently, *NEP* can be calculated by subtracting the sedimentary black carbon fraction from the total organic carbon accumulation rate, because BC is not consumed.

$$NEP = \ CA_{1y} - II_{0y} - BC \quad (5)$$

Case III: A mature intertidal wetland.

Most canopy ecosystems are both open and have been sufficiently established to deposit an extensive sediment column (Fig. 1c). The depth of age of the column produces a legacy of sedimentary organic decay over the past century, albeit faster over decades, thus, further constraining Eq. 3 (Eq. 6). Indeed, for mangroves, it has been found that the mineralisation from century-old carbon deposits is tidally advected into adjacent waters at a rate equivalent to the CO_2 vertical flux (Maher et al. 2018).

$$NEP = NPP - Hr - Dr - \int_{100y}^{0y} Br - \int_{100y}^{0yr} Ir = \ CAautl_{100y} - \left(I_{0y} - Il_{100y}\right) \quad (6)$$

Eq. 6 *NPP* is the net primary production of the autotrophic assemblage (*GPP – Pr*) and CA_{100y} is the carbon accumulation as estimated from what remains after 100 years of decomposition.

By substituting (5) after correcting for remineralisation over climatic scales (100 years) into Eq. 6 and subtracting the allochthonous recalcitrants inputs such as BC (CA_{BC}), the *NEP* becomes the difference between accumulated organic carbon after it has been deposited for 100 years (CA_{100y}) from the sum of the initial deposition rate for allochthonous carbon before consumption (I_{0y}), and the accumulation of allochthonous recalcitrants likely dominated by BC (Eq. 7).

$$NEP = CA_{100y} - (I_{0y} + CA_{BC}) \tag{7}$$

Surface horizons will thus require substantial corrections in the amount of carbon lost after 100 years of deposition, decreasing as the horizons become older. The true rate of mitigation through accumulation then becomes the product of the accretion rate and remaining concentrations after 100 years since it was deposited. Furthermore, the variability and trends for *NEP* can be extracted throughout the sediment column irrespective of the degree of mineralisation or lateral exchange.

Is there a mitigation role for total organic carbon accumulation?

It has been demonstrated that in open systems, the total sedimentary organic carbon accumulation cannot be a measure of carbon sequestration. Yet the concept of locking away the remains organic carbon produced and supplied to the ecosystem within the sediments still ‘feels’ like a sequestration concept. That is true, but only in the sense of what would have not been locked away if the canopy ecosystem had not been there. In other words, carbon accumulation is synonymous with a vulnerable stock concept. The difference with the standing stock is that it only requires the impact of missing canopy service at the time of annual deposition to capture and promote *CA*. Some insights into the differences imposed by the presence of a canopy may be gauged from the population medians between vegetated and non-vegetated ecosystems. For example, in lagoons, the global median non-vegetated carbon accumulation rates were found to be around 62% of coastal wetland accumulation rates (Wilkinson et al. 2018). However, this comparison may need to be tempered. For non-vegetated ecosystems, or the bare patches within a canopy after a disturbance event may support a different mix of allochthonous and autochthonous carbon sources (Macreadie et al. 2014). However, additional stock concepts may be a tautology should they not provide additional information and value on form or function. For example, a larger *CA* rate can separate a near equivalent *Ir* term between an ecosystem assemblage supplied by large amounts of relatively recalcitrant allochthonous carbon from another supplied by smaller amounts of more labile allochthonous carbon. Likewise, is also conceivable that they can also support similar standing stocks, should the larger amount of inorganic mineral material be associated with the supply of the more recalcitrant allochthonous sources. However, it is not clear if *CA* can provide additional value across the remaining supply scenarios.

Putting it all together

Taking into account carbon accumulation, it is proposed that the full value of the carbon sink can now be expressed by (Eq. 8).

$$Annual\ C\ offset\ credit = NEP + \frac{\theta}{\varphi}(Cstock_{1\,m}^{y=1} - BC) + (\theta CA_{y=1} - CA_{BC}) \tag{8}$$

Eq. 8 The components required for ecosystem carbon accreditation, not yet relative to the replacement ecosystem: NEP is the net ecosystem production as calculated down the sedimentary record over time (7); $Cstock_{1\,m}^{y=1}$ the organic carbon stock down the sediment column, and corrected for any decomposition after one year of deposition; θ is the fraction of organic carbon vulnerable to mineralisation; φ the time over which the vulnerable fraction was remineralised after disturbance, to give the equation dimensional integrity; $\theta CA_{y=1}$ vulnerable fraction of organic carbon stock accumulation after one year of production decomposition; and BC represent their respective allochthonous recalcitrant contributions outside of these ecosystem's service.

The above process would seem at first inspection to be less than parsimonious. However, the apparent complexity only arises from the number of arithmetic operations. Notwithstanding accurate geochronologies, in the final analysis, accuracy only requires a robust sedimentary decomposition model for the different sources of organic carbon and a means to estimate the fractions of the autochthonous and allochthonous labile and recalcitrant sources. The model used to both project remineralisation and hindcast allochthonous remains to the original concentration and inputs rates (I_{0y}) (Fig. 2a). For many programs, accurate geochronology and determination of organic sources are part of a best practice (Bindoff et al. 2019). To be useful, however, the decomposition model must account for or dismiss confounding differences in sediment types, redox conditions, temperatures, and organic sources across all time scales. This describes the relative precise and robust power model of Middelberg (1989) (r = 0.987), and its application by Zimmerman and Canuel (2002) to a mixed organic estuarine sediment column. The model describes how the organic mix becomes increasingly recalcitrant over time. The only requirement is a starting point for a continuously recalcitrant first-order decay constant characteristic of the organic mixture, or its organic components (Gallagher 2015). The alternative relies on a collection of cores (> 10) sufficient to normalise models for variability in space as a proxy for time (Strayer et al. 1986; Johannessen et al., 2021), or identifying asymptote concentrations with depth. However, the former is resource-intensive and requires a gradient of sedimentation and source supply rates. For the latter, simple decay with depth requires a constant rate of deposition and unchanging proportions of all organic sources. This is not usual for canopy ecosystems (Callaway et al. 2012; Ellison & Beasy 2018; Gonneea et al. 2004; Rozaimi Jamaludin et al. 2017; Serrano et al. 2014).

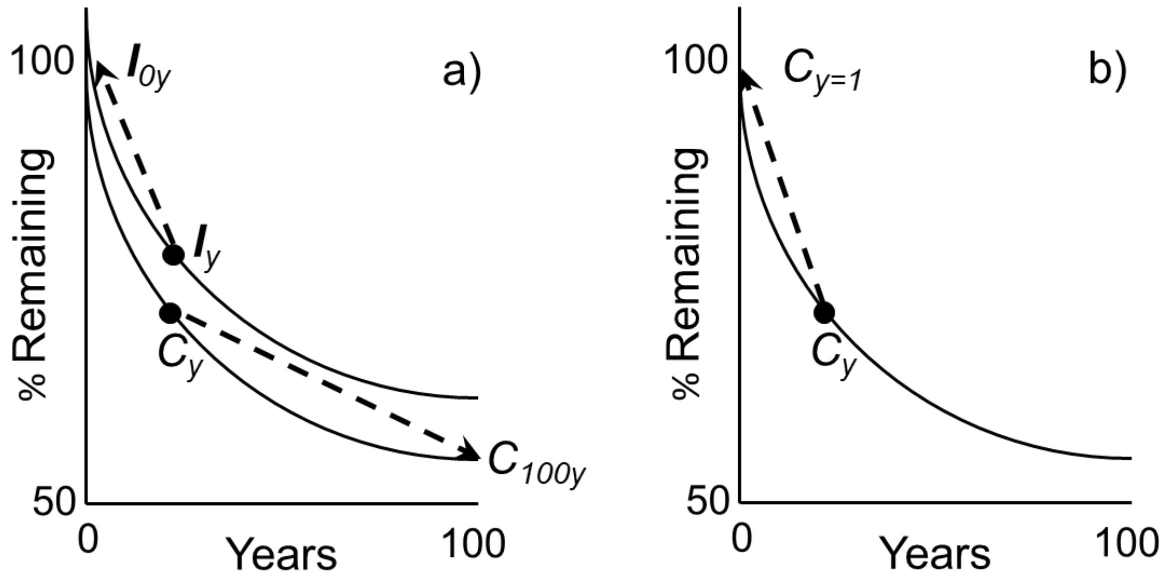

Fig. 2 Hypothetical sedimentary decomposition curves required to estimate *NEP* and carbon accumulation at climatic time scales. Curves within ‘a’ illustrate the process used to estimate the *NEP* (Eq. 5) from carbon accumulation rates, after correcting the component's sedimentary content over times of deposition. The allochthonous content I_y sits on its remineralisation curve as an example of a relatively recalcitrant form. It represents what remains after ‘*y*’ years of deposition from its original content I_{0y} deposited and mixed into the surface sediment layer. The total organic carbon content mixture (C_y) sits on a relatively labile remineralisation curve as the sum of individual organic components decomposition curves, weighted for their respective fractions. It represents what remains after ‘y’ years of deposition and projected to what would remain over climatic time scales (i.e. 100 years). Curve ‘b’ represents the used to hindcast an example of the content *C*y to the time of the original annual deposition C_y=1 (see section “Is there a mitigation role for total organic carbon accumulation?”). The figure was drawn within Microsoft PowerPoint™ 2013.

Testing the accreditation model

Two examples were chosen from the available literature to calculate the annual *NEP* variability over decadal to centennial time scales as determined from (Eq. 7). A mangrove sediment containing moderately labile seagrass litter (Gonneea et al. 2004), using BC estimates from similar systems. A seagrass sediment dominated by relatively recalcitrant mangrove detritus and moderate fractions of BC (Chuan et al. 2020). Full details of the site descriptions, the diagenetic models is found in Supplementary Information (S1) and their successful evaluations. The evaluation was through a convergence of losses after 100 years for total organic carbon (Chuan et al. 2020) and the models’ sum of their weighted components. Templates for the decomposition model decay curves used for the hindcasting and projection of variables (Eq. 7), their stability tests, first-order component decay parameters, the evaluation, along with embedded instructions, and data input heading can be found as Excel™ file Supplementary Information (S2) and (S3).

Case Studies results

Net ecosystem production and carbon accumulation

The sediment accumulation rates were an order of magnitude higher in the mangrove forest than in the seagrass meadow (Fig. 3a, b). There was a considerable disparity between total organic carbon accumulation rates and the calculated *NEP* for both systems. For the mangrove forest, the median *CA* rate was over 33.5 times greater than *NEP*. This was not much less than *CA* rates after correction for decompositional losses (27.5 x) (Fig. 3a). This relative difference, however, was reduced for their respective median *NEP* rates. The seagrass meadow *NEP* (7.2 g C m^{-2} yr^{-1}) was around 4 times less than the mangrove forest *NEP* (27.6 g C m^{-2} yr^{-1}) (Fig. 3a, b). Indeed, from the limited data available, it appears that the seagrass had been essentially carbon-neutral over the last 15 years (geometric mean = 0 g C m^{-2} yr^{-1}). For the seagrass meadow, this likely reflects a respiration assault, due to the high rates of supply of relatively allochthonous mangrove litter (75.4% to 80.4% of organic carbon, Supplementary Information (S3)). However, the differences for the mangrove reflect the smaller allochthonous supply of a more labile phytoplankton assemblage.

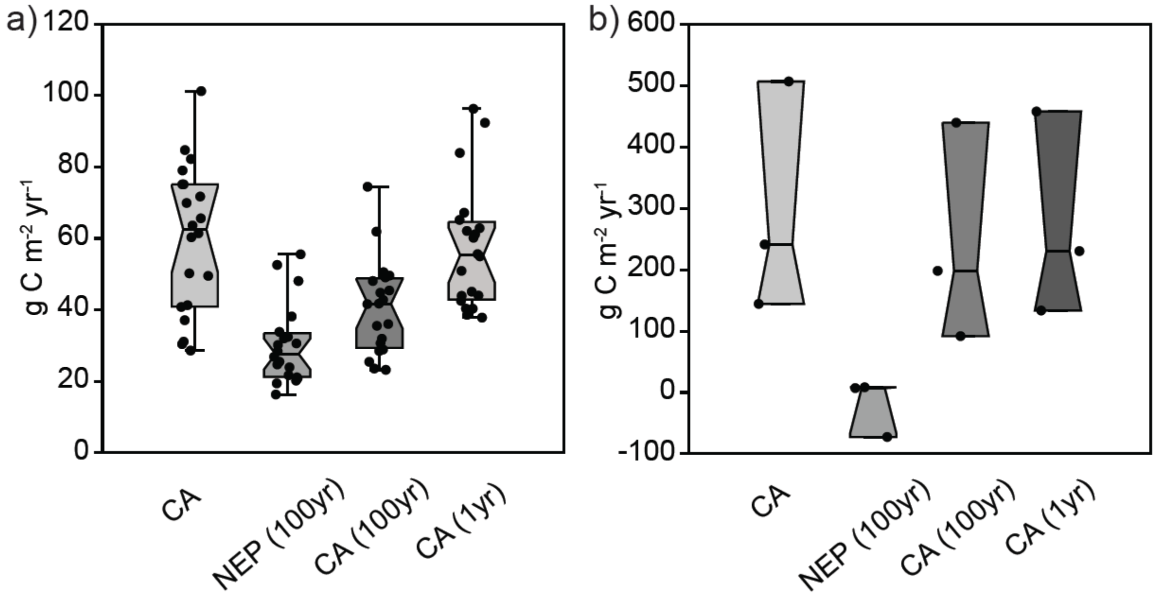

Fig. 3 Carbon sink concepts estimated down the sedimentary record for ‘a’ the seagrass meadow at Salut lagoon; and ‘b’ the mangrove forest at Chelem lagoon. The net ecosystem production after 100 years of deposition (NEP (100yrs)); Sediment carbon accumulation after 100yrs of deposition (CA (100yr)) and without decompositional

corrections (CA); 62% of carbon stock accumulation hindcasted to one year of accumulation (CA(1yr)) if hypothetically it was deposited within a non-vegetated patch (see section "Is there a mitigation role for total organic carbon accumulation?"). The figure was created in the statistical software package PAST™, exported as an svg file then modified and converted to an eps file within Abode Illustrator CS6™.

Interestingly, the overall variability seen in *CA* rates was notably less than the relative variability in their respective *NEP* (Fig. 3a, b). Unlike the mangrove forest, the seagrass meadows' *NEP* switched between heterotrophy (-72.5 g C m^{-2} yr^{-1}) and autotrophy (7.2 and 8.5 g C m^{-2} yr^{-1}). These values are within the range reported from direct measurements also across a lagoon system (-92 to 227 g C m^{-2} yr^{-1}) for the boreal region, and their shallow subtropical counterparts immediately outside a lagoon (-539 to 215 g C m^{-2} yr^{-1}) (Tokoro et al. 2014). For the mangrove forest, the *NEP* maintained a degree of autotrophy through the century of deposition, ranging from 16.3 to 55.5 g C m^{-2} yr^{-1} (median 26.9 g C m^{-2} yr^{-1}). This median and range are notably smaller than reported for global medians of between 628 g C m^{-2} yr^{-1} (Alongi 2020) and 221 g C m^{-2} yr^{-1} (Duarte et al. 2005). However, the estimates were largely based on measurements of gas emissions emanating from the canopy system and could account for the significant lateral transport of remineralisation products during tidal exchange from the deeper parts of the sediment column (Fig. 1d) (Maher et al. 2018). Nevertheless, the examples suggest that *CA* augmented with allochthonous inputs would likely lead to major overestimates of sequestration, irrespective of decompositional corrections (Fig. 3). However, this hierarchy could conceivably be reversed during the early to mid-stages of a restoration. Stocks would not have had sufficient time to accumulate and the canopy and root system may not have been sufficiently developed to fully promote carbon accumulation.

Carbon accredited offsets

The median sediment standing stocks were calculated as a vector component as 732 and 636 g C m^{-2} yr^{-1} for seagrass and mangrove respectively. This assumed that the standing stock today is a good representative of the median over the last century (Supplementary Information (S1)), and after potential disturbance losses around 75% over 20 years, and after correction for a measured BC fraction of 11% for the seagrass and estimated at 5% for the mangrove (Supplementary Information (S1)).

$$\text{Seagrass carbon accreditation } 1\,124 \text{ g C } m^{-2}\ yr^{-1} = 7.2NEP + 732C_{stock} + 385CA_{1y} \quad (9)$$

$$\text{Mangrove carbon accreditation } 1\,783 \text{ g C } m^{-2}\ yr^{-1} = 27.6NEP + 668C_{stock} + 1087CA_{1y} \quad (10)$$

Clearly, stocks in open mature systems appear to dominate the accreditation calculus (Eqs. 9, 10). Indeed the difference is exacerbated by including their respective additional CA_{1yr} concepts, and in doing so, also provides additional convergence for the total accreditation. However, whether this addition is justified will depend on its ability to separate form and function within similar wetland categories; a classification system yet as not explored or its need tested.

Conclusions

A full carbon accrediting assessment for canopy wetlands ideally requires estimates over climatic scales to capture variability and trends relative to a likely replacement. Total *CA* uncorrected or corrected for remineralisation over 100 years is not a measure of sequestration. However, with the use of a robust decomposition model and a means to untangle organic source contributions, the sedimentary record contains sufficient information to determine reasonable estimates of sequestration as the *NEP* that can account for centennial variability and trends. Carbon sink measurements that have employed *CA*, will significantly overestimate the sequestration rate and the total carbon accreditation. This may lead to perverse outcomes. Carbon credits become unnecessarily expensive and it allows for further increases in greenhouse gas emissions larger than the capacity of these ecosystems, would it not be for treating *CA* as an additional non-tautological stock concept.

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Declarations

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Conflict of interest/competing interests

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

Availability of data and material

All data is contained within Supplementary Information (S3) and parameters in Supplementary Information (S2).

Code availability

The Microsoft Excel™ 2013 template for the decomposition model, organic source decomposition parameters and evaluation is found in Supplementary Information (S2) and the Microsoft Excel™ 2013 template for *NEP* estimates in Supplementary Information (S3)

Authors' contributions

All authors contributed to the study conception. Material preparation by [John Barry Gallagher] with contributions and insights from [Ke Zhang], and [Chee Hoe Chuan]. Analysis by [John Barry Gallagher] with contribution from [Chee Hoe Chuan]. The first draft of the manuscript was written by [John Barry Gallagher] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Supplementary Material S1

A re-evaluation of wetland carbon sink concepts and measurements: A diagenetic solution down sediments

John Barry Gallagher[1], Sophia C Johannessen[2], Ke Zhang[3], Chee Hoe Chuan[4]

[1]Institute for Marine and Antarctic Studies, University of Tasmania, Australia, 7000

Orcid ID: 0000-0002-2622-0912.

johnbarry.gallagher@utas.edu.au & johnbarrygallagher@icloud.com

[2]Fisheries and Oceans Canada, Institute of Ocean Sciences, 9860 W. Saanich Rd., PO Box 6000, Sidney, B.C., Canada, V8L 4B2

Orcid ID 0000-0003-3788-2994.

[3]State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, PR China, 210008

Orcid ID 0000-0002-1841-9016.

[4]Borneo Marine Research Institute, Universiti Malaysia Sabah, Jalan UMS, Kota Kinabalu, Sabah, Malaysia, 88400

Orcid ID 0000-0003-4715-5387.A re-evaluation of blue and teal carbon stock and sequestration concepts with solutions for climatic scales

Introduction

The following is a description of the model, evidence of its robustness, and its application used to hindcast and project the losses of sedimentary organic carbon. Two examples with the required data were drawn from the literature (i.e., a geochronology, C concentrations, the fractions of organic sources to the total C content, and black carbon directly or taken from a similar system). The results of the model are then used to estimate net ecosystem production over time, and assert that the same model can be used to estimate changes in stocks of 1 m thickness over time. For stocks, this is provided the depth of the sediment core is sufficient, or the variability in carbon is not captured within a time dictated by the length of the sediment core.

Determining carbon accreditation concepts of a tropical mangrove and seagrass ecosystem

Data acquisition

For the mangrove, Gonneea (Gonneea et al., 2004) kindly supplied the mangrove sediment horizon ages, sediment accretion rates, dry bulk density, and organic carbon contents, required for hindcasting and projection of organic source concentrations. The fractions of mangrove, seagrass and microalgae as surface particulate matter (SPM), were extracted digitally from a pdf (Adobe™) into Graph Grabber™ from a figure within Gonneea et al. (2004) for Chelem Lagoon station 9.

For the tropical seagrass, the organic carbon contents, their carbon stable isotope and N/C molar signatures, dry bulk densities, and accretion rates, horizon ages of the surface 0-2 cm and 20-22 cm, as a mix of 20 cores adjacent cores, came from Chuan et al. (2020). Additional data for the 8-10 cm horizon was taken from an unpublished thesis, supplied by Chew (Swee Theng Chew, 2019). The sediment core had been taken previously within the core sampling site used by Chuan et al. (2020). The proportions of mangrove, seagrass, and microalgal carbon were calculated using a three source carbon stable isotope N/C used across tropical lagoons (Gonneea et al., 2004). The microalgae–SPM source signature was taken from as the microalgal endpoint (Gonneea et al., 2004). The organic source endpoint signatures for mangrove detritus was taken from one of the study lagoons from Gonneea et al (2004). The lagoon supported the mangrove *Avicennia sp.*, consistent with that of surrounding the seagrass meadow. However, the seagrass organic carbon signature endpoints were replaced with local *Enhalus sp.* as the average of three sites from nearby coastal study area from 3 locations within Sepanngar Bay (Kota Kinabalu, Sabah, Malaysia), as supplied by Tzuen Kiat Yap (δ^{13}C -8.6 ‰ and molar N/C 0.0435). This was part of the Ministry of Science, Technology and Innovation grant (FRG0424-SG-1/2015) "Increasing the resilient of sandy beach to erosion by replanting seagrass beds" (Research Supervisor John Barry Gallagher). The dried seagrass shoots (9 to10 shoots per site) were combined and scaped to remove epibionts, dried at 50 ºC, ground with a porcelain mortar and pestle, and fumed with concentrated HCl before. After further drying, the samples were immediately packaged within 5 cm^3 Eppendorf vials and sealed while warm before vacuum sealing all the vials in a plastic bag for transport to the specialised laboratory SINLAB (Canada) (17YAP 001-039 SINLAB.xls). The accuracy was confirmed using standard peach tea and the matrix standard.

All the extracted data can be found in Supplementary Material S4, as inputs for the spreadsheet templates that sets out the calculations for *NEP*, organic carbon accumulation, and stocks.

Site descriptions

The tropical mangrove Chelem lagoon station 9 supported a scrub mangrove forest near the seaward entrance of the lagoon, being impacted by its proximity to a rural population. Its sediments were sandy with relatively low organic carbon contents of around 2.5% dry wt over the last 100 years of deposition, and low carbon accumulation rates (Gonneea et al., 2004). As such, the forest could be expected to support rates of *NEP* within the lower quartile of a global distribution.

The tropical seagrass meadow occupied the upper embayment of the Salut Mengkbong lagoon, located north of Kota Kinabalu, Sabah, a major population centre. The meadow was a subaquatic shallow system composed entirely of *Enhalus sp.*, in which around a quarter of the leaf length could be seen floating on the water surface during spring low tides (Gallagher et al., 2020). The surface waters were generally turbid due to tidal washout out from the surrounding mangrove shoreline. As a consequence, the seagrass sediments supported a relatively high organic content of around 5.5% dry wt to 23 cm deep (Supplementary material S4). Below 23 cm was the remnants of mangrove roots mud and shell detritus deposited from a rare storm surge event (Chuan et al., 2020).

Carbon accreditation model

Hindcasting and projecting sedimentary carbon losses

The advantages of using the sedimentary record for carbon accreditation components for expected variability or trend have been outlined in the manuscript. The question arises can the components within Equation (8) be successfully modeled to produce an accurate estimate? Along with the more familiar geochronology and a discriminatory organic source mixing model, it requires a general decomposition model. The model should be sufficiently robust for hindcasting and projecting organic source losses across different sedimentary environs to determine the *NEP* and carbon accumulation throughout the sediment column. We applied the parameters from the power model constructed by Middelburg (Middelburg, 1989) and modified by Gallagher (2015). Middelburg (1989) found that there was a continuous decrease in the rate of decomposition of sedimentary organic matter that reflected a strong relationship between a first-order decay constant (k), and the sum of deposition time (t) and the apparent age (a) of organic source or sedimentary mixtures of sources (9). The apparent age is a concept of intrinsic time that matches the degree of recalcitrance at the start of decomposition. This starting value is required to determine changes in real-time, that is, the more labile microalgae will have a younger apparent age than the more recalcitrant mangrove leaves containing a higher proportion of lignocelluloses and phenolics. The model was found to be robust as it was constructed from first-order decay constants determined and calculated from a variety of laboratory and *in situ* sediment experiments and sedimentary profiles. Furthermore, these were determined under a variety of anoxic and oxic conditions, temperatures, sediment types, organic sources mixtures, and deposition times over eight orders of magnitude.

The power model has also been successfully (i.e., validated from long-term monitoring data sets) applied by Zimmerman and Canuel (Zimmerman and Canuel, 2002) to disentangle the initial of organic source supply from decomposition sensitive to change of the late Anthropocene. Although, it should be noted that Middelburg did not have access to data for coastal canopy sediments, where the microalgal fraction would not be as dominant. Nevertheless, the work of Janssen on which the model was based (Janssen, 1984), followed the same logarithmic construct, irrespective of large additions of a wide range of more recalcitrant organic sources to soils (i.e., green matter, straw, litter, manure, fir needles, sewage, and various peats).

$$k = 0.16(a + t)^{-0.95} \tag{9}$$

Where the first-order rate constant (k) determines how much of the organic matter with its particular state of recalcitrance remained after a small period (C_t).

$$C_t = C_0\, e^{-kt} \tag{10}$$

Gallagher (Gallagher, 2015) extended the application from sediment organic carbon to individual plant sources deposited to sediments (i.e, phytoplankton, seagrass, macroalgae, deciduous leaves). This was conceptually the same as Janssen's (1984) additions of materials to soils with relatively low organic matter contents. The initial first-order decomposition constants (k) and *cal* associated apparent ages (a), for the plant sources were taken from a compilation of data of decomposition experiments fitted to a first-order rate of decay as a function of their N content (Enríquez et al., 1993). A broad agreement was found with the only two studies that have a sufficient temporal range. A decomposition curve constructed from repeated sampling of sediment cores over 27 years (Gälman et al., 2008) dominated by microalgal supply (*cal* 23.4% remaining after 100 yrs *cf* 22.4% to 29.1% from Gallagher (2015)). A study used diagenetic profiles of dissolved metabolites over depth and time (Alperin et al., 1992). Alperin found the amount of seaweed and phytoplankton carbon remaining after 100 years was 10.2 ± 2% and 21 ± 5% respectively. Although, the remaining seaweed was less than predicted by the power model (22.4% –29.1%). However, the divergence may be specific to seaweeds. Enríquez (Enríquez et al., 1993) also found a greater expected rate of decomposition of the kelp as predicted from its nitrogen content. It was suggested that this may be the result of the bacterial preference of carbohydrate-rich kelps, less chemical alteration before deposition, and a macroscopic surface suitable for bacterial colonisation. These attributes are not shared with seagrass and perennial deciduous leaves, which followed the expected hierarchy of an increasing amount remaining after 100 years of deposition (i.e., between 27.8% to 29.2% and 30.6% to 45.7% respectively) (Gallagher, 2014; Gallagher, 2015).

For this study, the total organic carbon lost after the time of deposition and from the age surface horizons age was calculated from the individual component losses as their weighted fractions. This removes the problem in calculating the apparent age (*a*) of the depositional mixture for non-steady-state accumulation (Middelburg, 1989). The allochthonous component was identified by the nature of the ecosystem and its immediate surroundings and the original amount deposited hindcast along its decomposition curve (Figures 2 and 3).

The model solutions and instructions are presented in three separate Excel™ worksheets.

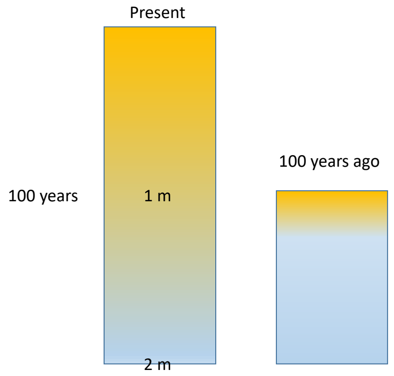
Sequestration and carbon accumulation vectors

- First, the decomposition curves for individual organic components were constructed (Supplementary material S1). The time steps to calculate ‘the first-order decay constants ‘*k’* (9) over 100 years for an apparent age ‘*a* and matching initial ‘*k’* taken from Enrichez (Enríquez et al., 1993). An upland soil decomposition constant was added to the model for future applications (Supplementary Materials S3). The values of *k* were then substituted into (10), and the amount of carbon remaining for that particular organic source was calculated (Supplementary Material S2). Time steps were set to 10 000 for computational stability. The iteration produced 100 000 time steps resulting in additional losses after 100 years < 0.1% (Supplemental Material S?). Instructions on how to start the simulation for individual organic sources and the model’s iteration sensitivity analysis are set out in text boxes within the worksheets (Supplemental S2 and S3).

- Second, the above process for individual allochthonous organic sources and the sum of the fractions of total organic carbon for all organic sources at selected horizon dates can be then used to hindcast and project carbon accumulation after 100 years of deposition for *NEP*. These are set out in stages as inputs within the columns of the Excel™ template (Supplementary Material S4). To run the program, the input data consisted of accretion rates and /or age of the sediment horizon, carbon contents, dry bulk density, the fractions of organic carbon sources, and the results of the individual organic components decompositional losses overtimes that match the ages of the sediment horizons. These are readily filtered out from the decomposition curve simulations (Supplementary Material S2).

Standing stocks over time

An assessment of past stocks may also require extended sampling to should the 100 years of accretion be > 1 m (Fig S1), as it would be unlikely that the rates of supply of organic sources would be constant. Consequently, a correction would also be required to account for losses in carbon contents from those measured today over what the stocks were in the past from a deeper horizon (Figure S1). However, for the core taken from the Salut seagrass meadow, the baseline sedimentation was interrupted by a deposition storm surge event down from 23 cm and likely greater than 52 cm, the bottom core sample (Chuan et al., 2020). Nevertheless, for completeness, we assume that the organic stock to 23 cm today is typical of past values, and around half the stock when integrated to 1 m (Gallagher et al., 2020; Lavery et al., 2013). Similarly, for Mangrove forest at Chelem station 9, it is assumed that the organic stocks today are typical and approximated to twice the amount stored to 42 cm (Donato et al., 2011; Gallagher et al., 2020). Gonneea (2004) recorded a cycle of variability related to oceanographic current changes to around 42 cm over the last 100 years. With the previous cycle seemingly recording organic concentrations marginally elevated over the previous cycle. Corrections for



the fraction vulnerable to mineralisation are set to 0.75 between the range suggested by Pendelton et al (2012) over 20 years. Subtraction of allochthonous carbon faction, as BC within the seagrass meadow (11%) comes from direct measurements. Allochthonous BC for the mangrove sediment was set at 5%, as measured for a similar industrial urban environment (Chew and Gallagher, 2018).

Figure S1. A hypothetical scenario, as measured today and as it was 100 years ago. It shows the stocks to 1 m as a gradient in organic concentrations that fall with depth and time down a sediment column. The illustration implies that 1 m thick stock assessments over time, measured down a sediment column today, require hindcasting the losses over time.

Decompositional model

Convergence between independent decay with time models

The decay parameters of Middelburg’s (1989) power model were constructed from measurements of coastal to deepsea sediment cores but outside of canopy ecosystems. Canopy ecosystems are likely to support greater proportions of macrophytes, woody debris and terrigenous organic sources than non-vegetated sediments. Consequently, the model was evaluated from the convergence from the long-term Salut sediment incubation experiment (Chuan et al., 2020). The decomposition experiment modeled parameters using the reactivity continuum model over 500 days sufficient to describe its decay distribution coefficient as the balance between labile and recalcitrance over time. The projected remaining organic carbon contents of 53.2% after 100 years of deposition from the power model from the seagrass surface horizon (0-2 cm) was in close agreement with the reactivity continuum model projections of 51.2% (Chuan et al., 2020). Although, after correcting for the sediment's BC content (around 11%, Chuan et al., 2020), the reactivity continuum model suggested that the remaining labile organic carbon fractions would amount to 45.6% after 100 years of deposition (Supplementary Information (S2)). Nevertheless, the convergence is good suggesting the results are robust and have a common origin outside of theory, and lie in the real world, confirming each of models’ results (Bycroft, 2010).

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