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# Sedimentary carbon on the continental shelf: Emerging capabilities and research priorities for Blue Carbon

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Continental shelf sediments store large amounts of organic carbon. Protecting this carbon from release back into the marine system and managing the marine environment to maximize its rate of accumulation could both play a role in mitigating climate change. For these reasons, in the context of an expanding “Blue Carbon” concept, research interest in the quantity and vulnerability of carbon stored in continental shelf, slope, and deep ocean sediments is increasing. In these systems, carbon storage is physically distant from carbon sources, altered between source and sink, and disturbed by anthropogenic activities. The methodological approaches needed to obtain the evidence to assess shelf sea sediment carbon manageability and vulnerability within an evolving blue carbon framework cannot be transferred directly from those applied in coastal vegetated “traditional” blue carbon habitats. We present a toolbox of methods which can be applied in marine sediments to provide the evidence needed to establish where and when marine carbon in offshore sediments can contribute to climate mitigation, focusing on continental shelf sediments. These methods are discussed in the context of the marine carbon cycle and how they provide evidence on: (i) stock: how much carbon is there and how is it distributed? (ii) accumulation: how rapidly is carbon being added or removed? and (iii) anthropogenic pressures: is carbon stock and/or accumulation vulnerable to manageable human activities? Our toolbox provides a starting point to inform choice of techniques for future studies alongside consideration of their specific research questions and available resources. Where possible, a stepwise approach to analyses should be applied in which initial parameters are analysed to inform which samples, if any, will provide information of interest from more resource-intensive analyses. As studies increasingly address the knowledge gaps around continental shelf

carbon stocks and accumulation – through both sampling and modelling – the management of this carbon with respect to human pressures will become the key question for understanding where it fits within the blue carbon framework and within the climate mitigation discourse.

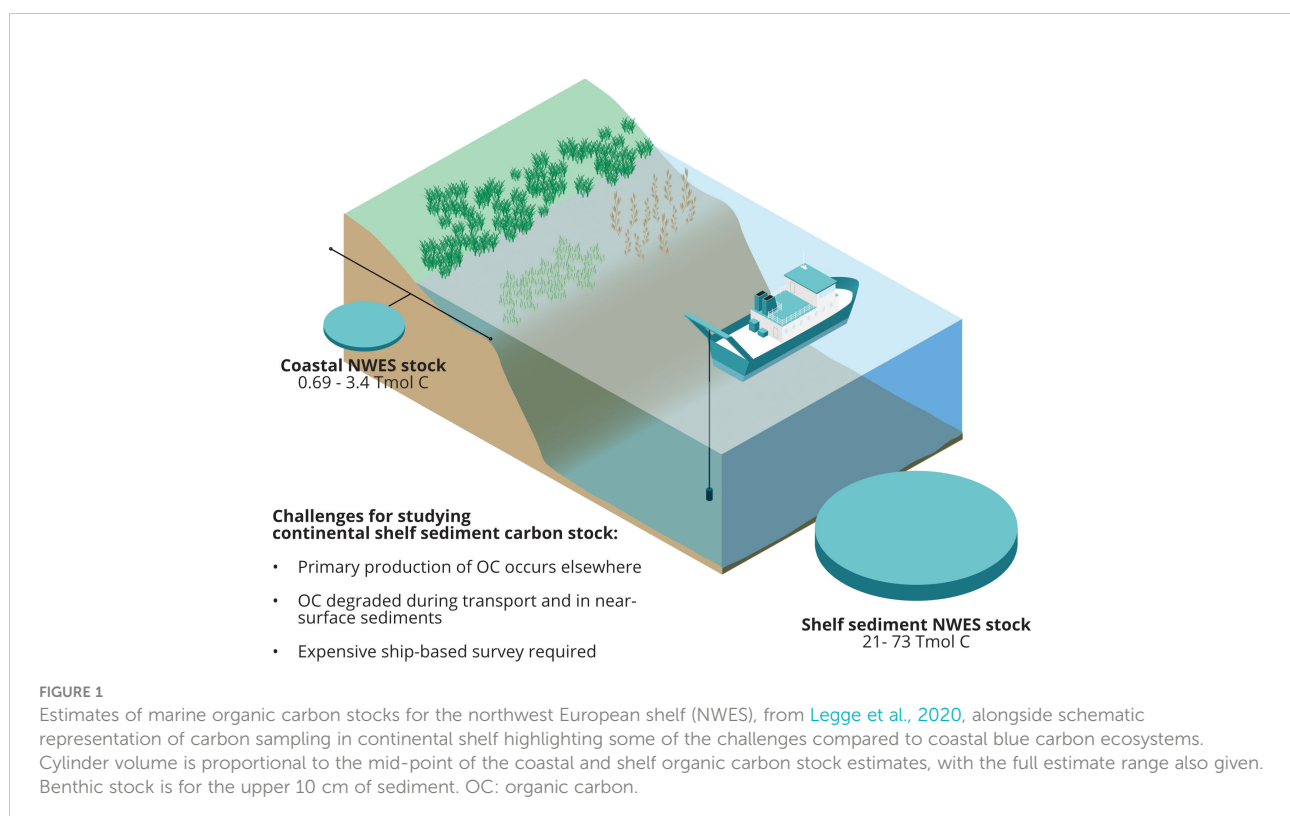
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particulate organic carbon (POC), marine sediment analysis, carbon stock, carbon sequestration, carbon provenance, carbon vulnerability, carbon management

## Introduction

Continental shelf sediments store large amounts of organic carbon (e.g., 21–73 Tmol C in the upper 10 cm of northwest European shelf sediments; Legge et al., 2020; Figure 1). This carbon is both allochthonous, sourced from terrestrial ecosystems (Santos et al., 2021), and autochthonous, derived from marine primary productivity. Organic carbon ( $C_{org}$ ) is transported and transformed in the water column before reaching the seabed where it is further modified or buried (Najjar et al., 2018; LaRowe et al., 2020; Luisetti et al., 2020). Protecting this marine sedimentary carbon from release back into the marine system and managing the marine environment to maximize its accumulation and sequestration would contribute to climate change mitigation.

Blue carbon has become a high-profile topic in conservation and policy discussions, driving the need for a robust scientific evidence base on stocks and accumulation rates of marine carbon (e.g., Lovelock and Duarte, 2019; Macreadie et al., 2019; Christianson et al., 2022). As an emerging research area, blue carbon has been defined differently between studies, and there is ongoing discussion about which elements of marine carbon could and should be included in the blue carbon concept in different contexts (e.g., Krause-Jensen et al., 2018). Lovelock and Duarte (2019) set out criteria to determine if the carbon in a marine ecosystem should be considered as blue carbon from a climate mitigation perspective: removing greenhouse gases at a significant scale, providing long-term storage for fixed carbon dioxide ( $CO_2$ ), the system being negatively impacted by



anthropogenic activities, and the ability to manage the system to maintain or enhance the carbon services without social or environmental harm. Systems which satisfy these conditions are said to be “actionable” if they can be incorporated into existing mitigation policies. Herein, we consider blue carbon to be the organic carbon stored in marine ecosystems which contributes to climate change mitigation in a manageable way.

The traditional blue carbon ecosystems which can currently be included in formal carbon accounting mechanisms (IPCC, 2008; IPCC, 2013) are mangroves, seagrass, and saltmarsh (e.g., Luisetti et al., 2019; Luisetti et al., 2020), but research is increasingly bringing additional systems into the blue carbon discourse, recognising that these habitats (and their carbon) are not isolated from marine carbon cycling in the rest of the ocean (Santos et al., 2021). Macroalgae, for example, are recognized as a significant biomass carbon store, but since carbon is not sequestered long term within the habitat itself it is difficult to include in blue carbon financing frameworks (Krause-Jensen and Duarte, 2016; Krause-Jensen et al., 2018; Dolliver and Connor, 2022; Duarte et al., 2022). Several recent studies and ongoing research aim to improve recognition of the carbon storage ecosystem service macroalgae provide by evidencing their role as a carbon-donor habitat to sediments, such as those considered here (e.g., Trevathan-Tackett et al., 2015; Pessarrodona et al., 2018; Wernberg and Filbee-Dexter, 2018; Kokubu et al., 2019; Ortega et al., 2019; Queirós et al., 2019; Filbee-Dexter et al., 2020).

Similarly, research interest in the quantity and vulnerability of carbon stored in continental shelf, slope and deep ocean sediments is increasing (e.g., Avelar et al., 2017; Atwood et al., 2020; Legge et al., 2020; Smeaton, et al., 2021a; Sala et al., 2021). In these systems, carbon is less directly coupled to primary productivity than in coastal blue carbon habitats. The methodological approaches needed to obtain the evidence to assess shelf sea sediment carbon manageability and vulnerability within an evolving blue carbon framework cannot be transferred directly from those applied in traditional blue carbon habitats: different issues need to be considered, a multi-tool approach taken, and new and emerging techniques used.

Here, we set out how to obtain the evidence needed to establish where and when marine carbon in offshore sediments can contribute to climate mitigation, focusing on continental shelf sediments. The key questions to be addressed in this context are: (i) stock: how much carbon is there and how is it distributed? (ii) accumulation: how rapidly is carbon being added or removed? and (iii) anthropogenic pressures: is carbon stock and/or accumulation vulnerable to manageable human activities? These blue carbon focused questions link directly to the marine carbon cycling questions of carbon provenance and carbon reactivity. This research will provide the foundation upon which to determine if carbon in shelf sediments can be incorporated, without social or environmental harm, into existing climate mitigation

frameworks and policy instruments and thus be considered actionable blue carbon.

Marine scientists have a range of measurement and analysis tools available to provide answers to these questions, from routine, rapid, low-cost analyses to highly specialized techniques which are still in development. We discuss these in turn as they relate to the underlying scientific questions. Together, they make up the marine sediment carbon toolbox from which appropriate sampling and analytical approaches can be chosen for the studies which will fill the evidence gaps identified and enable improved assessment of the role of the seabed in climate change regulation.

## Carbon stocks

### Quantifying stocks

The amount of organic carbon locked away from connection with the atmosphere, or – in the case of sediments, the ocean water column – is the fundamental parameter determining if and where shelf sea sediments satisfy the blue carbon criterion of “significant carbon storage”. The distribution of carbon stocks must be known in order to consider their importance, vulnerability and manageability.

The Blue Carbon Initiative<sup>1</sup>'s manual designed to provide standardized guidance to managers for assessing carbon stocks and emissions factors (Howard et al., 2014), enumerates the three elements required to quantify stocks: (i) (total) organic soil thickness (depth to underlying hard substrate), (ii) dry bulk density, (iii) organic carbon content (%C<sub>org</sub>). In the context of continental shelf sediments, dry bulk density and organic carbon content remain critical, while total soil (sediment) depth is unlikely to be determined and furthermore not immediately relevant in the context of climate mitigation. The depth of interest is that which is likely to be disturbed by human activities, and thus contains “vulnerable” carbon stocks. In traditional blue carbon ecosystems the organic soil thickness is expected to vary from between 10 cm to over 3 m (Howard et al., 2014), and IPCC guidelines recommend the use of 1 m as a standard depth for reporting stocks in the absence of information on total soil depth (IPCC, 2008; IPCC, 2013). In marine sediments, the relevant depth of vulnerability will be influenced by the natural setting (e.g., water depth, sediment type, fauna) and the influence of potential disturbances (bottom trawling, deep-sea mining, dredging and disposal, etc., see *Anthropogenic pressures*). Many, though certainly not all, existing datasets are limited to near-surface sediments (e.g., upper 10 cm; Diesing et al., 2017; Wilson et al., 2018; Smeaton et al., 2021a) due to standard sampling procedures in routine

1 <https://www.thebluecarboninitiative.org>

monitoring programmes. Significant (and unquantifiable) uncertainty in estimated stocks is introduced where data are extrapolated beyond their measurement depth (e.g., to 1 m, [Atwood et al., 2020](#)) as it is not expected that  $C_{org}$  content remains constant between near-surface and deeper sediments. Generally,  $C_{org}$  is expected to decrease with depth due to remineralization/diagenesis (e.g., [Burdige, 2007](#); [Arndt et al., 2013](#); [LaRowe et al., 2020](#)) such that extrapolating near-surface carbon stocks to e.g., 1 meter depth would yield an overestimation of stock, and that deeply buried organic matter may be less labile and less likely to be remineralized to release  $CO_2$  if disturbed (see *Characterising stock reactivity*)

Determination of dry bulk density and organic carbon content in marine sediments are standard analyses which are routinely carried out by geologists, geochemists, and biogeochemists. Dry bulk density is the ratio of the mass of a dried sediment sample to its original volume. Porosity, the ratio of the volume of 'voids' (between sediment grains) to the total (wet) sediment mixture volume, is more frequently reported in marine sediments. Porosity is generally calculated by mass difference of wet and dried sediment, assuming a density for pore fluid (based on salinity) and sediment grains (typically  $2650 \text{ kg cm}^{-3}$  for quartz/feldspar) (e.g., [Jenkins, 2005](#); [Diesing et al., 2017](#)). Empirical relationships have been used to estimate bulk density from sediment grain size (% mud) and  $C_{org}$  content itself (e.g., [Diesing et al., 2017](#); [Silburn et al., 2017](#); [Atwood et al., 2020](#)). The organic carbon content of marine sediments is commonly determined by elemental analyzer, alongside total carbon, inorganic carbon, and organic matter carbon: nitrogen (C:N) ratio ([Verardo et al., 1990](#); [Nieuwenhuize et al., 1994](#); [Harris et al., 2001](#)). This well established method, and its advantages over the lower-cost loss on ignition (LOI) approach, which relies on determining a habitat and/or site-specific conversion between organic matter and organic carbon, is described in detail in [Howard et al. \(2014\)](#) in the context of its application in coastal blue carbon habitats. A methodologically simplified approach based on ramped thermal heating alongside  $CO_2$  detection by infrared spectrometry has recently been applied to marine sedimentary carbon ([Smeaton et al., 2021a](#)).

Total carbon stocks are usually derived by extrapolating spatially limited observations over a relevant spatial area to generate an inventory. The validity of, or numerical uncertainty in, the estimated total stock then depends on how representative the sampled sites are of the larger area of interest ([Howard et al., 2014](#)). Where this is partially addressed by estimating a different stock for different spatial sub-units (e.g., [Burrows et al., 2014](#); [Watson et al., 2020](#); [Gregg et al., 2021](#)), additional uncertainty is introduced by the estimation of the extent of the area for each. It is important to recognize the large uncertainty in values obtained by multiplying estimated stock over a large estimated area (discussed for soil  $C_{org}$  in [Goidts et al., 2009](#)). Since measurements in marine sediments require sampling from a research vessel, at high cost, achieving adequate

spatial resolution for high confidence inventories is particularly challenging. Furthermore, there is a tendency for observations to be biased to near-coast and, because sediment coring is more challenging in coarse sediments, to higher mud-content sediments which are expected to contain high  $C_{org}$  (Figure 5 in [Smeaton et al., 2021a](#)). Linking carbon content to explanatory parameters (e.g., particle size, hydro-acoustic reflectance; [Hunt et al., 2020](#)) and applying statistical models or machine learning approaches to generate spatially resolved maps ([Serpetti et al., 2012](#); [Diesing et al., 2017](#); [Wilson et al., 2018](#); [Atwood et al., 2020](#); [Smeaton et al., 2021a](#)), can help to overcome issues of spatial bias in observations but assumes carbon processing, which controls stock, occurs in the same way across the region of interest. Co-measurement of the key physical and carbon content properties is a fundamental requirement for producing accurate stock assessments therefore determining additional sediment and environment parameters alongside carbon stocks adds significant value to carbon stock measurements.

Marine carbon stocks can also be determined by modelling. Process-based biogeochemical modelling studies focused on shelf sea carbon cycling (e.g., [Kühn et al., 2010](#); [Wakelin et al., 2012](#)) generally assume marine carbon ultimately derives from marine primary production and, crucially, that most organic detrital carbon in the benthic system is remineralized over an annual cycle. With this assumption, models typically predict stocks of benthic  $C_{org}$  one to two orders of magnitude lower than observed ([Aldridge et al., 2017](#)). This discrepancy is resolved if it is assumed the models follow only the relatively labile carbon most important for correctly modelling the annual recycling of carbon and nutrients, whilst most of the observed carbon stock is highly refractory: does not degrade significantly over annual timescales. However, this means that model results do not, at present, provide appropriate stock values for sediment carbon inventories. Long term storage (sequestration) of highly refractory (non-mineralizable) carbon has been implemented within models, for example by explicitly assuming a background flux ([Soetaert et al., 1996](#)) or assuming a fraction of more labile carbon becomes deeply buried and no longer undergoes degradation ([Butenschön et al., 2016](#)).

## Characterising stock provenance

To apply the blue carbon accounting framework, organic carbon in marine sediments must be linked back to the source of photosynthesis to avoid "double-counting". For example: macroalgal carbon being accounted for in a carbon valuation of the coastal macroalgae habitat, and then again in offshore marine sediments where it is eventually buried. To protect or enhance the carbon storage potential of shelf sediments, management measures need to be applied not only locally, but also to the key carbon source ecosystems. Furthermore, the vulnerability of organic carbon in marine sediment to

disturbance, in terms of release back towards the water column, is determined in part by its provenance as this influences how readily it is broken down and remineralized to CO<sub>2</sub>.

The primary production of much of the organic carbon subsequently stored in marine sediments occurred elsewhere: on land or in coastal habitats. In shelf seas marine phytoplankton are an important organic carbon source, though much of this carbon is expected to be recycled back to CO<sub>2</sub> within ocean waters (e.g., [Humphreys et al., 2019](#); [Dang, 2020](#)). In shallow waters, even away from the coast, microphytobenthos also fix carbon at the sediment surface (e.g., [Reiss et al., 2007](#)). Fundamentally, linking stored carbon to its source(s) relies on constraining the properties of the source itself: potential sources should be identified and analysed wherever possible, which is more challenging when carbon storage occurs at a distance from the carbon source and molecular properties are modified between source and sink.

In being transported to marine sediments, and after having been deposited there, organic matter is typically transformed by physical ([Ausín et al., 2021](#)) and biogeochemical processes ([Middelburg, 2018](#); [Kharbush et al., 2020](#)). This chemical alteration makes it more difficult to identify the provenance of different components of sediment organic matter. Moreover, it often renders the organic material molecularly uncharacterizable. Within the sediments, interaction with the mineral surface ([Kleber et al., 2021](#)), and with iron minerals in particular ([Lalonde et al., 2012](#)) have been suggested as a key mechanisms for this. This fraction of the input organic carbon that is sequestered long-term in marine sediments, largely significantly altered from its original molecular form, is that which is largely resistant to remineralization to inorganic carbon. Organic carbon which is less altered, and thus more reactive/vulnerable to disturbance, can also be buried in marine sediments in environments of low biological activity (e.g., under low oxygen or low temperature conditions; [Canfield, 1994](#)).

Methods for determining the provenance of organic carbon in coastal blue carbon ecosystems (tidal marshes, mangrove and seagrass meadows) were recently reviewed by [Geraldi et al., \(2019\)](#). These authors concluded that the more different properties of organic matter that can be determined - in other words: applying a multi-tool approach - the more likely it is a single source can be unambiguously identified. When characterizing organic matter, the methods that provide greater source specificity are those that are performed on the smallest fractions of the bulk material (e.g., compound-specific analyses; see Figure 2.1 in [Bianchi and Canuel, 2011](#)). Here we place relevant methodology in the context of continental shelf sediments and consider issues and sources of uncertainty.

## Bulk organic matter characterization

The majority of organic carbon stored in marine sediments is molecularly uncharacterizable (termed MUC) and thus cannot be characterized in terms of the biochemical classes (such as

proteins or fats) that form living organisms. MUC can often not be extracted from the sediment (e.g., using solvent extraction or acid hydrolysis), and/or cannot be hydrolyzed into recognizable monomers that are amenable to quantification methods; it must be investigated using methods that consider the bulk organic carbon pool. These methods are particularly powerful if they can be related to or calibrated against other established source indicators, or a mechanistic understanding of organic matter transformation and preservation processes.

The most general and routinely used methods, both in marine sediments and in coastal blue carbon habitats, are bulk organic matter carbon to nitrogen ratio [or nitrogen to carbon, see [Perdue and Koprivnjak \(2007\)](#)], and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ . These analyses are typically used in combination as, for example marine sources of organic carbon can have  $\delta^{13}\text{C}$  ratios between -20 ‰ and -30 ‰ which lie within the range of C3 terrestrial plants ([Meyers, 1994](#)), and C:N ratios of soils can fall in the range of those of marine carbon sources (e.g., [Zhao et al., 2015](#)). Information from bulk organic matter characterization can be combined using various mixing models: binary ([Thornton and McManus, 1994](#)), three end-member ([Gordon and Goni, 2003](#)), and Bayesian ([Smeaton and Austin, 2017](#)). Within these models, bulk elemental (C:N) and isotopic ratios of C<sub>org</sub> sources (i.e., terrestrial soils, vegetation and marine algae) are used to constrain, though not unambiguously identify, the proportion of the C<sub>org</sub> originating from each of the sources.

Different isotopic systems (e.g.,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{34}\text{S}$ ) could potentially provide additional specific information on source and transformations of the organic matter in some settings but they have not yet been applied to marine sediment samples even within coastal ecosystems ([Geraldi et al., 2019](#)) and significant methodological development is needed before they can provide additional information in the context of continental shelf carbon sources.

Pyrolysis gas chromatography mass spectrometry (py-GCMS) can be used to investigate the macromolecular composition of sedimentary organic matter, including compound classes such as lignins, cellulose, carbohydrates and proteins. The technique involves heating a sample (e.g., at 700 °C) in an anoxic environment to yield thermal degradation products which are analysed by GCMS. The method has the advantage of not needing solvent extraction, which makes sample preparation less laborious than many biomarker techniques (described in *Biomarkers*), while also looking at the whole organic carbon pool rather than only the extractable pool, which can constitute as little as ~5% of the total organic carbon ([Sparkes et al., 2016](#)).

For example, py-GCMS allowed [Kumar et al. \(2020\)](#) to identify that organic carbon in Ria Formosa Lagoon, Portugal, was dominantly from algal, bacterial and marine macrophyte sources, with very little from terrestrial sources, and that pollution was from spilled petroleum products and sewage. In the Siberian Arctic, py-GCMS allowed differentiation of types of terrestrial organic carbon, with nitriles and alkylbenzenes



derived from humified soils, and furfurals linked to much fresher/less degraded polysaccharides (Guo et al., 2004). In the Barents Sea, Stevenson and Abbott (2019) detected ecosystem shifts with distance from the ice edge, based on changing relative proportions of groups such as alkylphenols, alkylbenzenes, polysaccharides, and alkenes plus alkanes. However, uncertainties about the sources of these groups, and about whether groups are specific to particular sources (e.g., chitin is derived from shrimp and zooplankton, but also from peptidoglycan in bacteria), meant that analysis alongside ecological data was necessary to draw firmer conclusions.

One challenge posed by pyrolysis is that thermal degradation yields hundreds of different compounds, leading to complex chromatograms, and data that are difficult to interpret in terms of organic matter source and degradation state. This challenge has been tackled in some cases (Guo et al., 2004; Guo et al., 2009; Sparkes et al., 2016) by selecting and quantifying a sub-set of compounds (e.g., phenol and pyridine) that can be fairly confidently linked to specific sources (lignin and marine proteins, respectively). Although this means that only a sub-set of total organic carbon is being used to draw conclusions, the full pool is nonetheless being accessed by the analysis, and it does provide a systematic means of making comparisons between samples.

Cross referencing pyrolysis results with more established organic carbon source indicators can help to overcome the challenge of compound classes not being unique to certain organic carbon sources. Sparkes et al. (2016) determined marine versus terrestrial source from the ratio of phenols to pyridines in samples from the East Siberian Arctic Shelf. Through additional analysis of samples along offshore transects they were able to show that phenols were dominantly (although not exclusively) terrestrial, and pyridines were dominantly (but not exclusively) marine. They then showed that their pyrolysis-based index correlated well with other terrestrial versus marine indices, including  $\delta^{13}\text{C}$ ,  $R'_{\text{soil}}$ , and the branched and isoprenoid tetraether (BIT) index, which allowed it's calibration even though the compounds on which it was based were not exclusive to either marine or terrestrial carbon sources.

## Biomarkers

Biomarkers are organic molecules that may be traced unambiguously back to a specific biological origin. They constitute an important source-tracking tool for the characterization of aquatic organic matter (Derrien et al., 2019). Organic matter is a highly complex mixture of different types of compounds with varying physio-chemical properties originating from diverse sources. This includes allochthonous sources outside the aquatic system (e.g., higher plants from the terrestrial environment), autochthonous sources within the aquatic system (e.g., plankton and macrophytes such as seagrasses), and anthropogenic sources (e.g., sewage and oil

spills). The molecular biomarker approach to source-tracking involves targeting specific classes of organic compounds, such as lipids, pigments, lignin-phenols, carbohydrates, and proteins, which can inform on provenance of  $\text{C}_{\text{org}}$  present in marine depositional environments. As a targeted approach, biomarkers are selective by nature and thus represent a specific portion of the bulk organic matter pool.

Some lipids (e.g., sterols, fatty acids) and pigments (chlorophylls and degradation products, carotenoids) produced by specific organisms have been widely used to trace carbon sources within marine particulate organic matter; their recalcitrance makes them good indicators of material exported to marine sediments (Kharbush et al., 2020). Lipid biomarkers are widely considered to hold the most promise as indicators of organic carbon provenance (Derrien et al., 2017; Derrien et al., 2019; Geraldi et al., 2019). The lipids used in this context possess all the necessary qualities of a good biomarker, being ubiquitous, chemically and diagenetically stable, and structurally diverse. Lipids (commonly n-alkanes and fatty acids) have been used to track organic carbon provenance in numerous marine environments from diverse sources including anthropogenic, allochthonous, and autochthonous inputs (Derrien et al., 2019).

The n-alkanes are hugely abundant, simple, straight-chain lipid molecules produced by many lifeforms including terrestrial plants, aquatic plants, plankton, and bacteria. Their chain length provides the key diagnostic feature indicative of biological origin, whilst a predominance of an odd- or even- number of carbon atoms in the structure is also informative. Bacteria, algae, and plankton, for example, all produce short-chain n-alkanes (ca.  $<\text{C}_{20}$ ), while plankton exhibit a predominance of an odd number of carbons (15, 17, or 19), and bacteria, an even number of carbon atoms (16, 18, 20). Mid chain n-alkanes (ca  $\text{C}_{20-25}$ ) are associated with aquatic macrophytes such as seagrasses and saltmarsh plants. Long chain n-alkanes ( $\text{C}_{25-35}$ ) are found in the leaf wax of vascular plants and have a predominance of an odd number of carbons (27, 29, 31) and are largely from terrestrial sources. These variations in the n-alkane structure with associated biological origins led to the development of the carbon preference index (CPI) broadly as an indicator of terrestrial versus petrogenic sources (Bray and Evans, 1961). The CPI has since been adapted and developed alongside many other n-alkane biomarker indices including the average chain length (ACL) and numerous other marine-aquatic-terrestrial discriminating ratios capable of identifying organic matter sources (Derrien et al., 2017). Similar indices also exist for other lipids such as fatty acids and are fully reviewed in Derrien et al. (2017).

Whilst biomarkers can identify a wide range of different inputs to bulk organic matter, including providing high resolution for mixed sources (Derrien et al., 2017), like any analytical tool they also have their limitations. For example, constraining the sources of organic matter using biomarkers can sometimes be a challenge within more complex marine

environments, such as those with significant coastal inputs in addition to marine and terrestrial sources. Advancing analytical methodologies include the very powerful combination of organic biomarkers, such as lipids, alongside the measurement of their specific isotopic signatures (typically stable C, H, N, O, S), termed compound-specific-isotope-analysis (CSIA). This technique imparts added value to the biomarker approach yielding increased specificity and the ability to discriminate between multiple and sometimes overlapping sources of organic matter. It utilizes the difference in isotopic composition of biomarkers from terrestrial, aquatic, and marine sources, which are all distinct and reflective of the CO<sub>2</sub> substrate (e.g., atmospheric, aquatic, marine) used for photosynthesis.

Sikes et al. (2009) combined the n-alkane lipid biomarkers with  $\delta^{13}\text{C}$  to help resolve overlapping and masked sources of organic matter in surface sediments in the Hauraki Gulf, New Zealand. Bulk stable isotope analyses alone could not fully resolve the terrestrial signal, and n-alkane chain length indices were also insufficient due to overlapping and non-unique n-alkane signatures from confounding coastal sources (mangroves, seagrass) alongside the terrestrial and marine inputs. The differences in isotopic composition of biomarkers revealed by CSIA meant that the coastal input could be fully resolved from the terrestrial and marine signals. Sikes et al. (2009) thus demonstrated how an appreciable amount of purely terrestrial-derived organic matter was transported from input locations across the shelf and redistributed and buried in sediments including outer shelf locations towards the continental slope.

The ability to trace and quantify the allochthonous contribution to marine organic matter is essential for accurate carbon accounting (Kharbush et al., 2020). This involves understanding how terrestrial carbon moves through marine ecosystems: the traditional blue carbon ecosystems (mangroves, salt marshes, seagrass), as well as estuaries and continental shelf sediments, and how this carbon may subsequently be sequestered and stored. Lignin biomarkers are a powerful tool to probe the terrestrial contribution. Methodologies that continue to advance our understanding of the various distinct terrestrial inputs include the use of radiocarbon (as an addition to stable carbon and other elements) CSIA of lignin and other biomarkers. Tao et al. (2015) used the abundance and carbon isotope composition ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) of n-alkane and fatty acid lipids and lignin-phenols to characterize source, composition, and age of suspended particulate organic carbon from the Yellow River, China. Natural allochthonous C<sub>org</sub> inputs *via* rivers include recently biosynthesized biomass, pre-aged mineral-associated soil, and 'ancient' sedimentary rock sources. The latter two contain more refractory carbon as they have undergone prior processing and aging, and this has important implications for subsequent carbon cycling and storage in shelf sediments. Tao et al. (2015) found that, while bulk isotope measurements were relatively uniform for  $^{13}\text{C}$  and showed old

$^{14}\text{C}$  ages, it was only the differences in the  $^{14}\text{C}$  ages of individual biomarkers that could fully reveal the various individual and very different terrestrial C<sub>org</sub> sources. Linking the terrestrial C<sub>org</sub> to its distinct source or sources informed on the nature of the exported C<sub>org</sub>. In the case of the Yellow River, the refractory nature of much of the particulate organic carbon supports the high burial rates observed for terrestrial C<sub>org</sub> in the delta area.

## eDNA

Environmental DNA (eDNA) refers to traces of DNA left behind in the environment (soil, water, air, or sediment) by organisms through processes such as sloughing, shedding, or injury (Harrison et al., 2019). Since its first use to detect non-native species (Ficetola et al., 2008), eDNA has been used in a range of applications including rare and cryptic species identification, pathogen monitoring, fisheries stock assessments, diet studies, as well as characterizing the biodiversity of entire communities (Lallias et al., 2015; Deiner et al., 2017; Fonseca et al., 2017; Gilbey et al., 2021). DNA makes up approximately 3% of the cellular C<sub>org</sub> in sediments (Landenmark et al., 2015) and therefore is adept at determining the provenance of marine carbon. Furthermore, eDNA techniques are fast, inexpensive, and capable of identifying carbon provenance to a finer taxonomic rank (species-level) than other techniques such as biomarkers, and stable isotopes (Reef et al., 2017).

At present, we are only aware of three published studies using eDNA to determine sources of C<sub>org</sub> in marine sediments (Reef et al., 2017; Queirós et al., 2019; Ortega et al., 2020). Reef et al. (2017) used eDNA analysis, alongside stable isotope analysis, to identify the origin of C<sub>org</sub> in seagrass meadows. Using a chloroplast gene, Reef et al. (2017) were able to identify traces of 150 plant taxa in the sediment. However, 88% of sequences belonged to seagrass, suggesting most C<sub>org</sub> was autochthonous, originating within the system. Ortega et al. (2020) applied a similar approach using a ribosomal gene, in conjunction with stable isotope analysis, to identify sources of C<sub>org</sub> in seagrass meadows and mangrove forests. A total of 40 plant taxa were identified, showing different communities of plants contributed to blue carbon in mangroves and seagrass meadows. In contrast to seagrass meadows in the Reef et al. (2017) study, Ortega et al. (2020) discovered substantial macroalgal input to stored carbon. The study also investigated if a quantitative relationship existed between i) detected eDNA and sediment eDNA, and ii) detected eDNA and sediment carbon content using mock community experiments. In both instances a high correlation was found, with an R<sup>2</sup> of 76% and 86% found in the sediment DNA and carbon experiments, respectively. This suggests that sedimentary eDNA studies may be able to provide interim information on C<sub>org</sub> if a stable isotope analysis has yet to be conducted. The Queirós et al. (2019) study used a ribosomal gene to detect eDNA in the top centimeter of sediments, alongside stable isotope analysis and benthic-pelagic

process measurements, to understand the contribution of macroalgae to subtidal coastal ocean carbon stocks. One hundred and forty-eight plant taxa from surrounding coastal habitats were detected, suggesting a range of macroalgae species contribute to sedimentary  $C_{org}$ . A method for tracing macroalgal carbon in deeper marine sediments has been developed by the Norwegian Institute for Water Research (NIVA) to investigate long-term sequestration (burial) (d'Auriac et al., 2021). d'Auriac et al. (2021) quantified *L. hyperborea* and *S. latissimi*. eDNA levels in marine sediments down to 1.6 meters below the seafloor to estimate their contribution to the organic carbon stock and understand how it varied with time and since deposition.

Despite established protocols for sediment DNA-based biodiversity assessments (Fonseca and Lallias, 2016; Fonseca, 2018; Pawlowski et al., 2022) there remain technical considerations when conducting a marine carbon study. eDNA biodiversity assessments require the collection of a sediment sample, extracting the DNA from the sediment with no prior organism separation, followed by polymerase chain reaction (PCR) to create copies of the eDNA (called amplicons). These are then sequenced (obtaining the nucleotide composition of the eDNA), and the retrieved sequences are taxonomically assigned using either publicly available genetic databases such as BOLD (Ratnasingham and Hebert, 2007) or GenBank (Clark et al., 2016) or bespoke taxonomic libraries.

Every stage of the workflow has aspects that will affect the outcome of the assessment. Factors associated with sampling such as the body size of organisms in sediment, whereby larger organisms are more likely to be detected (Elbrecht et al., 2017), and seasonality and environmental conditions, which affect how quickly DNA decays (Jo and Minamoto, 2021). Similarly other sources of variation to be considered are habitat heterogeneity and sampling effort i.e., organism ability to disperse and its detectability and representativeness through enough biological replicates (Fonseca, 2018; Grey et al., 2018). Methodological considerations include the DNA extraction method, since different extraction techniques will reflect different components of existing biodiversity (Geraldi et al., 2020). Further considerations of technical replicates are needed, such as the number of DNA extractions or PCR replicates used (more replicates give more robust biodiversity estimates) (Ficetola et al., 2015; Fonseca, 2018; Bruce et al., 2021).

During PCR, the primers (short single stranded sequences of DNA) are used to target the sections of eDNA to copy. DNA is copied more readily if there is greater similarity between the primer and the target eDNA. Therefore, DNA from different taxonomic groups will be copied at different rates (based on similarity to the primers) and the quantity of apparent DNA from each taxon will be distorted. This misrepresentation of biodiversity present is commonly referred to as "primer bias" and is inherent to most PCR-based approaches. In marine sediment carbon this means any given set of primers will not provide a complete picture of  $C_{org}$  origins; an assay to identify

terrestrial-plant DNA may not be capable of detecting phytoplankton DNA (or vice versa). In practice, this means a standardized primer set is unlikely to work for all marine sediment carbon applications, instead primers should be chosen with careful consideration given to the biodiversity present. Fortunately, it is possible to use multiple primers to test different aspects of biodiversity to ameliorate the effects of primer bias, though analysis cost increases with each additional primer.

The selection of genetic reference databases is also a key step in a marine sediment carbon study (Geraldi et al., 2019). In essence, to identify taxa and assign taxonomic identities from DNA, the taxa must already be present, and correctly identified with the relevant DNA region, on a reference database. If absent or mislabeled, the DNA cannot be identified and can lead to an underestimation, or total exclusion, of  $C_{org}$  sources. This can be combatted in some instances by assigning higher taxonomic resolution (i.e., when species level identification is not possible, similarities to a closely related species on the database may facilitate genus or family level identification). Furthermore, a site-specific reference taxonomic database can be constructed but will require additional time and budget.

A final consideration whether or not the number of sequences produced corresponds to the amount of eDNA, biomass or  $C_{org}$  in the sample. Recent meta-analyses suggest that whilst some quantitative relationship between DNA and biomass exists, there is a high degree of variability, likely depending on a combination of the primers used and the community of organisms surveyed, e.g., unicellular or multicellular (Lamb et al., 2019; Yates et al., 2019). Thus, the sequences retrieved from eDNA would not correspond to the total amount of carbon from those taxa. Although molecular techniques are being refined to facilitate quantitative analysis, at present the extent to which sequences correspond to  $C_{org}$  using a mock community (Ortega et al., 2020) should be explicitly tested before molecular data are used in this manner.

## Characterising stock reactivity

Not all organic carbon present in marine sediments at a given time will be stored over timescales greater than weeks to months to years (LaRowe et al., 2020). The total stock of organic carbon can be classified by its biogeochemical reactivity (Alderson et al., 2016), a key biogeochemical model parameter (Arndt et al., 2013). Organic matter reactivity or degradability (which can be defined as susceptibility to removal of a fraction by either biotic or abiotic processes, measured by lifetime e.g., Hansell, 2013) is understood to be a continuum (e.g., LaRowe et al., 2020) from labile (reactive; easily degraded; short lived) to recalcitrant (resistant to rapid microbial degradation; Hansell, 2013) and refractory. The term refractory is defined variability in different studies and used as "a one-fits-all word" for various



properties related to  $C_{org}$  reactivity, typically as the opposite of labile in a certain context, see discussion in [Hansell, 2013](#) and [Baltar et al., 2021](#). Understanding sedimentary organic matter's re-mineralization potential and ability to resist degradation ([Doetterl et al., 2016](#)) is vital in estimating its vulnerability to potential natural or anthropogenic disturbance and remineralization of the associated organic carbon.

The balance of organic carbon fractions with various reactivities determines the biodegradability of sedimentary organic matter and in turn the stability of the associated carbon. The rate of microbially-mediated degradation of organic matter can be impacted by the addition of more or of less labile material to a mixture (the priming effect; [Bianchi and Canuel, 2011](#)). If disturbed, the organic carbon in sediments dominated by labile organic matter is highly likely to be remineralized. Conversely if sediments dominated by recalcitrant organic matter are disturbed this material would likely be re-deposited as particulate organic carbon on or in the seabed. Only organic carbon of some intermediate degradability is thus relevant to the climate mitigation role of marine sediments.

Organic carbon reactivity is fundamentally linked to the organic matter's source, discussed in *Characterising stock provenance*. Black carbon, a refractory carbon fraction formed from incomplete combustion of organic carbon, accounts for 15-30% of the organic matter buried in marine sediments ([Middelburg et al., 1999](#)). The most refractory fraction of the black carbon is highly condensed soot, formed from combustion of fossil fuels at high temperatures ([Masiello, 2004](#)), which may remain in the atmosphere for months before eventually being buried in sediments. More degradable lightly charred black carbon formed during low temperature biomass burning may reach the marine environment *via* rivers through soil leaching or erosion ([Coppola et al., 2014](#)). Once deposited in sediments, factors including the depth of burial, microbial and redox conditions as well as subsequent disturbance influence the degree of black carbon's long-term storage. In general, small soot particles withstand degradation and result in long-term storage whereas lower formation temperature/larger size

fragments are more susceptible to biotic and chemical degradation ([Masiello, 2004](#)).

[Chew and Gallagher \(2018\)](#) show that black carbon can be a major component of organic carbon in seagrass, mangrove and saltmarsh sediment cores and because it is resistant to being re-released back into the atmosphere, as  $CO_2$  for example, assert that it should be discounted from any blue carbon storage mitigations being proposed. Taking a different perspective, [Ren et al. \(2019\)](#) highlight that the relatively slow cycling of black carbon in Arctic Ocean sediments makes it an important fraction of inert carbon representing a significant sink of atmospheric  $CO_2$ , which is likely to increase with global warming and increased melting of permafrost. There is thus a clear need to understand both the overall reactivity of the marine organic matter as well as to identify specific types and sources of organic carbon which are resistant to degradation.

### Thermogravimetric analysis (TGA)

Organic matter recalcitrance can be defined in terms of the temperature at which mass is lost during combustion. TGA is an automated process which continuously measures the mass of a sample during ramped heating (e.g., from 0-1000°C at a rate of  $10^\circ C \text{ min}^{-1}$ ). Thermal decomposition through TGA allows the major organic matter fractions to be quantified. Within the literature, the thermal ranges which define these organic matter fractions are variable depending on environment and methodology ([Table 1](#)). Within marine sediments these organic matter fractions are thermally defined as labile (200 - 400°C), recalcitrant (400 - 550°C) and refractory (550-650°C) ([Capel et al., 2006](#); [Smeaton and Austin, 2022](#)). Focusing on the 200-650°C temperature range removes interference from absorbed water and non-organic material (i.e., calcite).

Most studies using this thermal approach characterize the organic matter into the three fractions, although some studies go further and use the thermal decomposition data to quantify specific components (e.g., hemicellulose, cellulose, lignin) ([Trevathan-Tackett et al., 2015](#); [Trevathan-Tackett et al., 2017](#)) or functional groups such as aliphatic and carboxyl groups ([Lopez-Capel et al., 2005](#); [Manning et al., 2005](#)) potentially

TABLE 1 Temperature ranges defining organic matter recalcitrance by thermogravimetric analysis in different environments.

Environment	Temperature Range (°C)			Reference
	Labile	Recalcitrant	Refractory	
Marine Sediments	200-400	400-550	550-650	( <a href="#">Capel et al., 2006</a> ; <a href="#">Smeaton and Austin, 2022</a> )
Marine Sediment	130-280	280-520		( <a href="#">Kristensen, 1990</a> )
Marine Sediment	160-300	300-400	400-600	( <a href="#">Loh et al., 2008</a> )
Seagrass	200-400	400-500	550-650	( <a href="#">Trevathan-Tackett et al., 2015 and 2017</a> )
Peatland	160-300	300-400	400-600	( <a href="#">Mauquoy et al., 2020</a> )
Plant Material	300-350	400-500	430-530	( <a href="#">Kaloustian et al., 2001</a> )
Soil	300-350	400-500	430-530	( <a href="#">Lopez-Capel et al., 2005</a> ; <a href="#">Manning et al., 2005</a> )

allowing this approach to be applied to determine the provenance of the organic matter.

The quantification of the different thermal fractions allows the lability of organic matter to be estimated (Smeaton and Austin, 2022). A number of indices have been developed for this purpose ranging from the early Rp index (Kristensen, 1990), which used stepwise thermogravimetry (i.e., Loss on Ignition), to the Refractory index (R-index) and Carbon Reactivity Index (CRI), which utilize TGA data and provide an advanced understanding of the thermal characteristics of organic matter in different environments (Trevathan-Tackett, 2016; Smeaton and Austin, 2022). For example, a CRI value of 0 indicates that the material is fully biodegradable (high reactivity), while a value of 1 indicates that the substance is non-biodegradable (low reactivity) (Smeaton and Austin, 2022).

The gases evolved during TGA can be further analysed by coupling the system to an FTIR (Fourier transform infrared spectroscopy) or GCMS to provide greater understanding of (macro) molecular composition. Within marine sediments these approaches are largely focused on detecting and quantifying pollution (Oudghiri et al., 2015; Becker et al., 2020) but they have the potential to be powerful tools in characterizing organic matter. While understanding the recalcitrance of organic matter is one of the main applications of TGA, the continuous nature of the data produced results in their applicability to many areas including provenance studies (Oudghiri et al., 2015; Becker et al., 2020).

### Amino acid index

The amino acid composition of organic matter in marine sediments can be used as an indicator (biomarker) of its degradation state. Total hydrolysable amino acids (THAA) are quantified by reverse-phase HPLC of their fluorescent derivatives (Dauwe and Middelburg, 1998), and their relative abundances used to generate an index for degradation state

which indicates the recalcitrance of the remaining material (Dauwe and Middelburg, 1998; Dauwe et al., 1999). This method was developed for North Sea continental shelf sediments, where phytoplankton primary productivity is the main source of organic matter. It has more recently been applied as part of a study of organic matter in the South Yellow Sea and East China Sea sediments (Chen et al., 2021), and in coastal blue carbon habitats (Vaughn et al., 2021). Recently, compound-specific radiocarbon analysis of amino acids has been proposed as a novel method for improving understanding of food webs and sedimentary organic carbon (Blattmann and Ishikawa, 2020; Blattmann et al., 2020).

### Black carbon quantification

To measure black carbon, traditional methods require the removal of inorganic carbon using the same methodology as that used to prepare samples for organic carbon analysis, with either sulphurous acid (Verardo et al., 1990; Jablonski et al., 2002; Phillips et al., 2011) or hydrochloric acid (Komada, 2008; Brodie et al., 2011). Following removal of inorganic carbon, there are a number of methods used to quantify fractions of black carbon (Hammes et al., 2007; Table 2). Chew and Gallagher (2018) compare chemo-thermal oxidation (CTO) and chemical nitric acid oxidation (NAO) and conclude that the presence of thermally resistant phytoliths was responsible for differences in black carbon results from these two methods.

Newer instrumentation, based on the temperature gradient method is now being applied for carbon measurements (Smeaton, et al., 2021a) with the advantages that no acid carbonate removal is required to remove inorganic carbonates, and that measurements of particulate organic carbon, black carbon (residual oxidizable carbon (ROC)) as well as inorganic carbon can be derived from a single sample. Results have been shown to be comparable with the more traditional methods (Natali et al., 2020).

TABLE 2 Methods used to quantify black carbon, following removal of inorganic carbon (Hammes et al., 2007), including references where these methods have been applied.

Method	Black carbon fraction quantified/comments	Selected references
Chemo-thermal oxidation (CTO)	Refractory soot sediments and particulates. Possible interference from C <sub>org</sub> charring.	Gustafsson et al. (2001), Fang et al. (2016), Chew and Gallagher (2018)
Dichromate/sulphuric acid oxidation	Soot and charring fractions. Variable results and methodology.	Maisello et al. (2002), Ren et al. (2019)
Nitric acid oxidation (NAO)	Degradable char black carbon.	Middelburg et al. (1999), Chew and Gallagher (2018)
BCPA derivatization	Dissolved black carbon especially. Method-inherent errors need correction.	Glaser et al. (1998) Ziolkowski et al. (2011)
$\Delta^{14}\text{C}$ with BCPA	Differentiates fractions from biomass burning and fossil fuel combustion.	Coppola et al. (2014), Coppola et al. (2019)
$\delta^{13}\text{C}$ with BCPA	Differentiates riverine and marine sources.	Wagner et al. (2019), Coppola et al. (2019)

## The priming effect

Priming occurs when the rate of remineralization of stable organic matter is either increased or decreased by addition of labile organic matter (Sanches et al., 2021). As such, simply measuring the recalcitrance of organic matter in marine sediments may not fully capture the vulnerability of stored carbon when the system is disturbed, i.e., if the disturbance mixes stable organic matter with a labile fraction. Sanches et al. (2021) reviewed studies of priming in aquatic systems and found that the observed magnitude and direction of the effect depended on whether a lab or field-based approach was applied and on the proxies used to measure remineralization. Their meta-analysis concluded that, in general, priming has a positive effect (increased remineralization of stable organic matter with the addition of labile organic matter). They recommend using bacterial growth as a proxy (in preference to production or respiration) or CO<sub>2</sub> production as these approaches are most sensitive. For example, van Nugteren et al. (2009) added <sup>13</sup>C-enriched diatoms to marine sediment slurries and measured evolved CO<sub>2</sub> to observe a 31% increase in remineralization.

## Carbon accumulation rates

Quantification of the rate that carbon accumulates in shelf sediments is the key parameter for natural carbon accounting, for which carbon burial is the service of interest (Luisetti et al., 2020). In the context of blue carbon projects, “additionality” must be shown: that management activities lead to an increase in carbon sequestration relative to accumulation rates in the unmanaged system (e.g., Lafratta et al., 2020).

*The Blue Carbon Initiative*<sup>2</sup>'s manual designed to provide standardized guidance to managers for assessing carbon stocks and emissions factors (Howard et al., 2014), discusses carbon accumulation and loss in a chapter entitled ‘how to estimate CO<sub>2</sub> emissions’ – explicitly emphasizing the motivation of assessing impacts on the atmospheric CO<sub>2</sub> budget. The caveat of assuming all, or a given proportion of, sediment carbon accumulation or loss being in connection with the atmosphere is presented therein in this context (Howard et al., 2014). The simple surface elevation table (SET) method often applied in coastal blue carbon ecosystems is not appropriate in marine sediments. Instead, natural radiotracers, including carbon-14 (<sup>14</sup>C, radiocarbon), lead-210 (<sup>210</sup>Pb), and thorium-230 (<sup>230</sup>Th, uranium-thorium dating), are routinely used to determine rates of marine sediment accumulation. <sup>210</sup>Pb and <sup>230</sup>Th are both part of the <sup>238</sup>U decay chain and are deposited from the atmosphere at a relatively constant rate with abundances in marine sediment decreasing with depth as they decay (Appleby and Oldfield, 1978). <sup>14</sup>C is absorbed from the atmosphere into

the tissue of living organisms, and its abundance decays after death (Anderson et al., 1947; Libby et al., 1949). Other dating tools include tephra chronology (Cage et al., 2011; Davies, 2015), optical luminescence (OSL) dating (Madsen et al., 2005) and direct methods to measure the rate of particle accumulation on the seafloor, like sediment traps (which generally underestimate particle fluxes due to particle solubilization, zooplankton swimmers and hydrodynamics; Subha Anand et al., 2017).

Differentiation between radiotracer techniques is based predominantly on the time interval over which their decay rate (half-life) allows material to be dated. Radiocarbon based age-control is typically used to estimate long-term (100s–1000s of years) sediment accumulation rates, while radionuclide dating (i.e., <sup>210</sup>Pb) provides a chronological constraint of modern deposition over the last ~150 years. The limitations of different methods can be partially addressed by combining different radiotracers, but the dates obtained do not always agree (e.g., Jenkins, 2018: shorter-period dates tend to be higher than long-term dates; the Sadler effect; Sadler, 1981). For example, sedimentation rates from <sup>14</sup>C are generally found to be lower (slower) than those derived from <sup>210</sup>Pb (Baskaran et al., 2017; Smeaton et al., 2021b) because of the effects of sediment compaction (Bird et al., 2004) and diagenetic processes (biogeochemical alteration) that can alter the organic matter (Arndt et al., 2013; LaRowe et al., 2020). Baskaran et al. (2017) suggest that short-lived radioisotopes are better suited to determining modern depositional rates than radiocarbon and recommend using <sup>210</sup>Pb where possible when determining sediment accumulation rates.

Radiotracers can also be applied to track carbon through the ocean and or sediment system. While not directly providing organic carbon burial rates, these more focused studies are an integral part of developing a broader understanding of marine carbon cycling. For example: the use of <sup>14</sup>C and <sup>35</sup>S radiolabeling techniques to track microbial recycling of organic carbon in the sediments (Beulig et al., 2017).

## Lead-210-derived sedimentation rates and dating

The process of assigning ages to organic carbon present in specific layers (depth intervals) of marine sediment can be achieved by measuring the activity concentration of co-occurring <sup>210</sup>Pb (Tolosa et al., 1996; Pappa et al., 2019). In relatively undisturbed depositional aquatic ecosystems <sup>210</sup>Pb abundance decreases exponentially with depth from the seawater-sediment interface due to the radioactive decay of the tracer, allowing the <sup>210</sup>Pb depth profile to estimate a sedimentation rate for any substances of interest associated with the sediment. Application of <sup>210</sup>Pb dating remains a challenge because of unresolved issues associated with the variety of radioanalytical methodologies available as well as

<sup>2</sup> <https://www.thebluecarboninitiative.org>

different modelling approaches that play an essential role in deriving sediment accumulation rates from radiotracer measurements (MacKenzie et al., 2011; Garcia-Tenorio et al., 2020).

Disturbances can complicate the straightforward determination of sediment accumulation rates from  $^{210}\text{Pb}$  depth profiles. The surface 10–15 cm of the seabed are likely to be disturbed by, e.g., bioturbation, fishing activities and natural resuspension by bottom water currents (see *Anthropogenic pressures*). Furthermore, dating must account for the additional sources of  $^{210}\text{Pb}$  within the sediment, from the *in-situ* decay of radium-226 ( $^{226}\text{Ra}$ ) and, more problematically, from industrial activities including offshore oil and gas and other mineral processing industries (Sahu et al., 2014; Ahmad et al., 2021). The proportion of  $^{210}\text{Pb}$  present in the sediment and from human activity (termed supported  $^{210}\text{Pb}$ ) does not decay at the same rate as the unsupported  $^{210}\text{Pb}$  fraction from atmospheric deposition (Gulliver et al., 2001; Cook et al., 2004). Measuring  $^{226}\text{Ra}$  in addition to  $^{210}\text{Pb}$  enables the subtraction of supported  $^{210}\text{Pb}$  from the total  $^{210}\text{Pb}$  measured prior to estimating sedimentation rates and dating sediment layers.

With a half-life of 22.3 years,  $^{210}\text{Pb}$  dating is limited to relatively recent sediment ages (up to 150 years). It can therefore be challenging to use this technique in low-sedimentation rate marine environments ( $<0.15\text{ cm y}^{-1}$ ) (De Haas et al., 1997). There are several  $^{210}\text{Pb}$  dating models available, that can be applied and help interpret different  $^{210}\text{Pb}$  core profiles (Arias-Ortiz et al., 2018; Blaauw et al., 2018). These models have been comprehensively described over the last forty years. The Constant Initial Concentration (CIC) (Robbins, 1978), Constant Rate of Supply (CRS) (Appleby and Oldfield, 1978) and Constant Flux: Constant Sedimentation (CF : CS) (Appleby and Oldfield, 1978) models are the most widely used to estimate sedimentation accumulation rates, but they are associated with numerous assumptions that can sometimes limit their appropriateness in more complex and disturbed aquatic ecosystems (Arias-Ortiz et al., 2018). Very often, the mass accumulation rate, expressed in  $\text{mg cm}^{-2}\text{ yr}^{-1}$ , is also estimated to account for compaction effect (Schmidt et al., 2014). More recently the advantages of a Bayesian approach, as applied in radiocarbon dating (Blaauw et al., 2018), is gaining attention (Aquino-López et al., 2020; Blaauw et al., 2021).

$^{210}\text{Pb}$  in environmental matrices, including marine sediments, is commonly determined directly by gamma spectrometry. However, gamma spectrometers equipped with Well-type germanium (Ge) detectors that allow the direct determination of low levels of  $^{210}\text{Pb}$  with little sample mass and preparation required are not commonly available. More common and cheaper flat end Ge detectors with much higher limits of detection can provide insufficient levels of accuracy and precision for measuring the very low levels of  $^{210}\text{Pb}$  naturally present in the environment (Dal Molin et al., 2018). Alternatively,  $^{210}\text{Pb}$  can also be determined indirectly by

measuring polonium-210 ( $^{210}\text{Po}$ ), its granddaughter decay product, *via* alpha spectrometry. Although this alternative traditional radiometric technique requires samples to be digested in strong acid mixtures and treated prior to analysis, the limits of detection and level of accuracy and precision that can be achieved are more appropriate (Hassen et al., 2020). The underlying assumption, that  $^{210}\text{Pb}$  is in secular equilibrium with  $^{210}\text{Po}$  such that both radionuclides are present at the same concentration, can be verified by performing a second analysis of  $^{210}\text{Po}$  at a later stage, i.e., generally, by determining  $^{210}\text{Po}$  ingrowth from the decay of  $^{210}\text{Pb}$  after three to four months.

To determine  $^{226}\text{Ra}$  and correct for supported  $^{210}\text{Pb}$ , gamma spectrometry is the most common technique. The sample must be placed in a radon proof container for a minimum of three weeks prior to analysis to ensure secular equilibrium is established before indirect measurement *via* its two decay products (bismuth-214 and lead-214).  $^{226}\text{Ra}$  can be determined indirectly by either measuring emission of radon-222 gas, or directly by alpha-spectrometry, and more recently by ICP-MS, following appropriate sample preparation steps (IAEA, 2010).

Caesium-137 ( $^{137}\text{Cs}$ ) is commonly used as a complementary tool to validate  $^{210}\text{Pb}$  dating models. Characteristic abundance peaks of  $^{137}\text{Cs}$  observed in marine sediments in the Northern hemisphere can be directly related to nuclear weapon testing events of the late 1950s and early 1960s, and more locally in the UK seas to peak discharges from Sellafield nuclear reprocessing plant in the late 1970s (Environment Agency et al., 2021). Caesium-137 can easily be measured by gamma spectrometry, however, because its concentration is constantly decreasing over time [half-life of 30 years and no major additional characteristic peak since Chernobyl; see Figure 7.9 in Environment Agency et al. (2021)], it is important to optimize the counting time to ensure reliable and accurate results by gamma spectrometry (Garcia-Tenorio et al., 2020).

## Radiocarbon dating

The radioactive  $^{14}\text{C}$  isotope has a half-life of  $5,700 \pm 30$  years (Kutschera, 2013) which allows for the determination of the age of a carbon bearing material formed over the past 55,000 years (Hajdas et al., 2021). Since the detection of  $^{14}\text{C}$  in 1977 using particle accelerators (Bennett et al., 1977), Accelerator Mass Spectrometry (AMS) has become the most used technique in  $^{14}\text{C}$  analysis. In AMS, the  $^{14}\text{C}/^{13}\text{C}$  or  $^{14}\text{C}/^{12}\text{C}$  ratio in the sample is directly measured resulting in shorter measurement times (days to minutes) and reduced sample requirements (g to  $\mu\text{g}$  of C) than previous scintillation methods (Litherland et al., 2011). Recent developments in AMS technologies have resulted in  $^{14}\text{C}$  detections at significantly lower energies (Synal et al., 2000), resulting in the reduction in size of AMS's and the establishment of new sample introduction techniques for direct analysis of  $\text{CO}_2$



resulting from combustion (EA-AMS) (Haghipour et al., 2019), wet oxidation (Leonard et al., 2013), acid hydrolysis (Molnár et al., 2013) and laser ablation (LA-AMS; Welte et al., 2016).

The data produced by the AMS (Fraction  $^{14}\text{C}$  or  $F^{14}\text{C}$ ) allows for conventional  $^{14}\text{C}$  ages to be calculated following the approach of Libby (1955) where conventional  $^{14}\text{C}$  age =  $-8,033 \ln(F^{14}\text{C})$ . To determine the true age of the sample, the conventional  $^{14}\text{C}$  age must be calibrated to a curve based on measurements of  $^{14}\text{C}$  from samples of known age and location (e.g., northern hemisphere, southern hemisphere, or the marine environment). The IntCal radiocarbon calibration curves (Heaton et al., 2020; Hogg et al., 2020; Reimer, 2020) are a resource constructed from measurements of  $^{14}\text{C}$  made in different laboratories on a range of dated samples. The last 13,900 years are constrained by dated tree rings (Reimer, 2020), while beyond this (13,900–55,000 years) lake and marine sediments, speleothems or corals are statistically integrated to create the most accurate representation of past atmospheric  $^{14}\text{C}$  (Reimer, 2020).

Today, conventional  $^{14}\text{C}$  ages are calibrated using advanced Bayesian statistical tools that include dedicated routines for the different calibration curves, the most commonly used modelling tools are OxCal (Ramsey, 1995; Ramsey et al., 2020) and MatCal (Lougheed and Obrochta, 2016). Calibrated  $^{14}\text{C}$  ages are referred to as a calendar age counted backwards from 0 cal BP (before present) which corresponds to 1950 Common Era (CE, previously referred to as AD) or to calendar years Before Common Era (BCE, previously referred to as BC). Post 1950 CE correspond to the age of nuclear testing where atmospheric  $^{14}\text{C}$  concentrations measured in  $\text{CO}_2$  of air and dated tree rings, display significantly elevated  $^{14}\text{C}$  concentration (bomb spike) hindering the use of conventional  $^{14}\text{C}$  dating approaches (Hua et al., 2013; Santos et al., 2020). To calculate sedimentation and accumulation rates an age-depth model is constructed using the calibrated dates. Classical age-depth models can be constructed in software such as CLAM (Blaauw, 2010), but more commonly Bayesian statistical packages such as OxCal (Ramsey, 1995; Ramsey, 2009), and BACON (Blaauw and Christen, 2011), are applied to create models that fully account for uncertainties allowing for the calculation of sedimentation and accumulation rates.

There is a long history of using  $^{14}\text{C}$  to chronologically constrain sedimentary records allowing the calculation of long-term (100s–1000s of years) sedimentation and accumulation rates on the seabed (Kershaw, 1986; Darby et al., 1997; Colman et al., 2002; Santschi and Rowe, 2008; Smeaton et al., 2021c). In marine sediments both organic matter and carbonate (inorganic) material (e.g., shells or foraminifera) can be dated, but organic matter cannot be used to constrain the age of the sediment as the carbon it contains originates from multiple (many unknown) sources with varying compositions and ages. Carbonate material is therefore the preferred sample medium for  $^{14}\text{C}$  analysis and age constraint. Living benthic

foraminifera are found in the upper most layers of most sediments and therefore the shells of foraminifera buried after death provide material ideally suited for dating as they are representative of past surface sediments from their time of deposition. The number of foraminifera required to measure  $^{14}\text{C}$  using a conventional AMS can vary but it is not uncommon to need between 500–1000 individuals, whereas the recent developments in AMS technology (Synal et al., 2000) means that far smaller numbers are now required (<100 individuals) with state-of-the-art systems allowing single foraminifera dating (Wacker et al., 2013; Lougheed et al., 2018). Shells can also be dated but greater care must be taken to ensure they are representative of past surficial sediments and not shells associated with mobile burrowing species (Cage and Austin, 2010; Baltzer et al., 2015).

When calibrating  $^{14}\text{C}$  ages derived from material from the marine environment the marine reservoir effect must be considered. The marine reservoir effect occurs when the C in tissues of organisms or inorganic deposits reflects a mix of C sources and ages (Hajdas et al., 2021). The marine reservoir effect was previously accounted for by adding 400 years to an age calibrated using the northern hemisphere calibration curve (Reimer, 2020) which led to large uncertainties. With the production of the Marine20 calibration curve (Heaton et al., 2020) the marine reservoir age can now be robustly accounted for and is directly integrated into the calibration stage. The Marine20 calibration curve has significantly improved age calibration of marine samples, but it remains a global calibration; for greater accuracy local reservoir age corrections can be applied (i.e., Cage et al., 2006) if available.

## Uranium/thorium paleo-dating of biologically derived fossil carbonates

For 500 to 100,000-year timescales, thorium-230 ( $^{230}\text{Th}$ ) dating, also referred to as U/Th dating or  $^{238}\text{U}$ -uranium-234 ( $^{234}\text{U}$ )- $^{230}\text{Th}$  dating, can be applied. This method relies on the disequilibrium due to solubility differences of uranium and thorium nuclides and involves calculating ages by studying the radioactive relationships between  $^{238}\text{U}$ ,  $^{234}\text{U}$ , and  $^{230}\text{Th}$  (Henderson and Anderson, 2003). It is appropriate in closed carbonate systems with no initial  $^{230}\text{Th}$ , for example, fossil carbonates present within the terrestrial environment (e.g., rocks), but also marine carbonate formations such as corals (Cheng et al., 2000) and authigenic carbonates. It is very often used as a complementary method to  $^{14}\text{C}$  dating of fossil carbonates and for validating results from  $^{14}\text{C}$  dating.

Extending thorium-230 ( $^{230}\text{Th}$ ) dating to marine sediments is challenging mainly due to the presence of additional  $^{230}\text{Th}$  in materials scavenged from the seawater column. In addition, the typical levels of carbonates found in marine sediments as well as the potential post-depositional weathering, transport and



mixing processes can further limit its application (Chen et al., 2020). Nevertheless, modelling and state-of-the-art analytical tools can potentially overcome some of these challenges and thus provide valuable insights into sediment accumulation rates over longer timescales. Geibert et al. (2019) have recently presented an alternative approach using a CRS model, similarly to  $^{210}\text{Pb}$  dating and assuming constant rate of supply of  $^{230}\text{Th}$  from the seawater. Although alpha spectrometry can provide accurate measurement of all relevant U and Th isotopes, these techniques require labor intensive preparation steps and lengthy counting times in comparison to mass-spectrometry coupled with a laser ablation system. These state-of-the-art techniques have become the preferred analytical option (Robinson et al., 2004; Mas et al., 2020).

## Anthropogenic pressures

Only carbon which is subject to manageable “undesirable human impacts”, satisfies the blue carbon criteria of Lovelock and Duarte (2019). The vulnerability of organic carbon in marine sediments to a given disturbance is a function of the organic matter’s source (*Characterising stock provenance*), and recalcitrance (*Characterising stock reactivity*). Pressures on, or conversely management and restoration of, terrestrial or coastal ecosystems which act as remote carbon sources (carbon donors) to marine sediments will affect carbon accumulation (Santos et al., 2021). Physical disturbance of the seabed which resuspends near-surface sediments into the oxic water column will recycle labile organic carbon into the ocean and potentially impact the atmospheric carbon system (Sala et al., 2021), although it can also simply re-distribute and redeposit sediments (Rijnsdorp et al., 2021). Seabed disturbance impacts the benthic faunal community, which plays a key role in the biogeochemical processes determining what fraction of deposited carbon is recycled (remineralized) or buried (stored) (de Borger et al., 2021a; de Borger et al., 2021b).

Bottom trawling is the most spatially significant anthropogenic process physically disturbing shelf sediments (Oberle, et al., 2016b; Rijnsdorp et al., 2021), while wind farms have been shown to locally increase organic matter deposition (and recycling) because of faunal colonization of their structure (de Borger et al., 2021a). Other activities, including pipe and cable laying, aggregate extraction, and dredge disposal, are also expected to impact organic matter storage and deposition, although their impacts are more spatially restricted. Some continental shelf sediments are naturally subject to high disturbance, for example due to high-energy tidal bottom water currents (Thompson et al., 2019), which may locally dominate over bottom fishing disturbance (Diesing et al., 2013); these tend not to be sites with significant carbon stocks or accumulation (Diesing et al., 2021) and are therefore less vulnerable to anthropogenic disturbance from a carbon

perspective and not good sites for the implementation of management measures.

The impacts of trawling on carbon accumulation and storage are complex and differ between shelf and deeper water slope systems (Palanques et al., 2014; Pusceddu et al., 2014; Oberle et al., 2016b; Paradis et al., 2019). See Epstein et al. (2022) for a review. They depend on the properties of the carbon stock, the type of trawling equipment and frequency of trawling, as well as sediment type and faunal community (Legge et al., 2020). More research is required to improve understanding of these factors in the context of carbon storage across a range of settings. Recent work advancing towards this goal includes that of Bradshaw et al. (2021) and Morys et al. (2021) who made field measurements of the biogeochemical impacts of trawl disturbances in the Baltic Sea, and that of de Borger et al. (2021b) who modelled biogeochemical impacts of trawling scenarios at specific sampled sites in the North Sea. Global scale modelling of trawling impact (e.g., Hiddink et al., 2021; Sala et al., 2021) remains limited by the need to make broad-scale assumptions of the underlying processes and carbon characteristics which control carbon response to pressure.

In addition to their use in geochronology (see *Carbon accumulation rates*), radionuclides can also be used to evidence disturbance. In an upper section of mixed (typically bioturbated) sediments,  $^{210}\text{Pb}$  activity is constant before being expected to decrease exponentially with depth (see *Lead-210-derived sedimentation rates and dating*) but this pattern is not observed where sediments have been physically disturbed. Physical seabed disturbance can also be confirmed qualitatively by measuring excess of thorium-234 ( $^{234}\text{Th}$ ).  $^{234}\text{Th}$  has a very short half-life (24.1 days) and is produced directly from the alpha decay of  $^{238}\text{U}$  in the ocean.  $^{238}\text{U}$  is a highly soluble and conservative radionuclide in seawater, whereas  $^{234}\text{Th}$  is highly particle reactive. As  $^{234}\text{Th}$  is preferentially adsorbed onto sinking particles, the natural secular equilibrium between the two radionuclides becomes disturbed. Consequently, an excess of  $^{234}\text{Th}$  is expected in the upper layers of undisturbed sediment. An anthropogenic disturbance (e.g., man-made platforms or trawling) can be qualitatively confirmed if the excess of  $^{234}\text{Th}$  is not as noticeable as in a separate sediment core collected nearby and known to be undisturbed (e.g., in a Marine Protected Area; MPAs).  $^{234}\text{Th}$  can be determined either by beta counting or gamma spectrometry (Buesseler et al., 2001), whereas  $^{238}\text{U}$  is usually measured either by alpha spectrometry or ICP-MS (Forte et al., 2001).

Sampling studies investigating the impact of trawling on carbon accumulation make use of many of the analytical techniques detailed in the sections above. Oberle et al. (2016a) used 3D petroleum fingerprinting alongside  $^{210}\text{Pb}$  dating to quantify the depth of disturbance across sites exposed to different trawling pressure. Paradis et al., (2019; 2021) measured both  $^{210}\text{Pb}$  and  $^{234}\text{Th}$  in a comparison of trawled and un-trawled continental margin sites. Sañé et al. (2013)

compared a number of biomarkers between trawled and un-trawled submarine canyon flank sites and found that labile amino acids in particular were less abundant in the disturbed sediments, providing evidence for increased carbon remineralization as a result of trawling disturbance and resulting differences in vulnerability to subsequent disturbance.

Even if the potential impact of trawling on sediment carbon at a particular site was well understood, data on trawling pressure (gear types, frequency) are often incomplete or not available at an appropriate spatial resolution. Trawling pressure maps are typically compiled from fishing GPS-based vessel track information (e.g., vessel monitoring systems, VMS) (e.g., Oberle et al., 2016b; Eigaard et al., 2017; Sala et al., 2021). These are limited by the temporal (and thus spatial) resolution of the fishing vessel location information, requiring application of interpolation techniques (see Russo et al., 2011) and resulting in estimated trawling intensity within spatial grid cells based on the number of times each was visited. Linking trawling pressure to sediment carbon is also complicated by the non-random distribution of trawling with respect to expected high carbon sites, e.g., trawling pressure tends to be higher in high-mud sediments, which are also highest in organic carbon (see Epstein et al., 2022 for further discussion).

## Discussion

Gaining and improving understanding of the spatial distribution and variability of carbon stocks and accumulation rates and their vulnerability in shelf sea sediments is essential for their monitoring and management. As recent studies demonstrate (e.g., Sañé et al., 2013; Oberle et al., 2016a; Paradis et al., 2019; Paradis et al., 2021), layers of information derived from multiple analytical techniques are required in marine sediments to provide a mechanistic understanding in settings where carbon storage is physically distant from carbon sources, altered between source and sink, and disturbed by anthropogenic activities. We have outlined an extensive multidisciplinary toolbox of analysis techniques which are needed to achieve this understanding, summarized in Table 3.

The choice of techniques applied by any study will be determined by its specific research questions, and also by available resources. Table 3 provides a starting point with which to approach this decision. Where possible a stepwise approach to analyses should be applied by which initial parameters are analysed to inform which samples, if any, will provide information of interest from more resource-intensive analyses. It is important to distinguish between routine measurements and analyses (e.g., particle grain size, total organic carbon and C:N ratios) and emerging techniques and those which have not traditionally been applied in shelf sediments (e.g., eDNA, compound specific isotopic analyses) where ongoing method development must be considered.

Studies should aim to characterize the system by measuring more than the minimum parameters wherever possible to inform a process-level understanding. Associated explanatory parameters such as bottom water properties and pore water chemistry can allow modelling approaches to be applied, adding value to what can be obtained by measurements alone. Biogeochemical modelling can be used in two ways; to help interpret observations, and to allow scaling up and scenario exploration (for example of climate change). However, a clear understanding of which analytical outputs are needed to model a given scenario and which analytical tools can provide these outputs is needed to fully exploit modelling approaches. For example, scenario studies describing the vulnerability of carbon release to a given physical disturbance rely on knowledge of the lability of sediment carbon which must come from observation.

To assess the role of continental shelf sediments in the blue carbon framework, the analyses outlined herein – addressing the fundamental blue carbon questions of stock (its abundance, provenance, recalcitrance) and accumulation rate, and vulnerability – must be considered holistically. A key outstanding question is linking measurements to the physical and biogeochemical processes which control carbon stock and accumulation.

As studies increasingly address the knowledge gaps around continental shelf carbon stocks and accumulation – through both sampling and modelling – the management of this carbon with respect to human pressures will become the key question for understanding where it fits within the blue carbon framework and within the climate mitigation discourse (e.g., Christianson et al., 2022). Can the biogeochemical processes which mediate carbon cycling in near-surface sediments be controlled or protected such that carbon burial is maximized? Improved process understanding is required. Controlling trawling and other human activities which disturb the seabed where it acts as a carbon store appears to be a quick win, yet the impacts of disturbed sediment can extend beyond the trawled area on a regional scale (Palanques et al., 2014). If MPAs are to be used as a management tool to protect carbon stocks and accumulation in continental margin sediments (e.g., Roberts et al., 2017; Sala et al., 2021), their locations must be informed by well-mapped carbon stock and accumulation (e.g., Diesing et al., 2021) and process-level understanding (e.g., de Borger et al., 2021b).

## Conclusions

The marine environment stores organic carbon in offshore as well as coastal ecosystems. In traditional coastal blue carbon habitats (saltmarsh, seagrass, mangrove) organic carbon is locally produced. Organic carbon in marine sediment is more allochthonous: it has largely been transported from terrestrial, coastal or near-surface sources and has been more significantly

**TABLE 3** Summary of analyses presented and considerations for their application to improving understanding of blue carbon in continental shelf sediments.

Parameter or Analysis	Blue Carbon Relevance	Key considerations for application in shelf sediments
(organic) carbon content	fundamental measurement of carbon stock	Typically inter/extrapolated between sampled sites, which is improved by co-measurement of other sediment properties. Typically determined by EA (provides organic carbon) and not LOI (provides organic matter from which OC can be derived) in shelf sediments. Though more expensive than LOI, EA is a routinely applied analysis. In order to derive carbon stocks from percent organic carbon measurements, sediment dry bulk density must also be measured.
carbon to nitrogen ratio (C:N; N:C)	provenance	Informs on provenance only when considered alongside other OM properties. Readily determined by EA alongside OC quantification.
bulk organic matter stable isotopes	provenance	A commonly used analytical approach. When used in tandem with C:N ratios and isotopic mixing models, provides a quantitative method to estimate the proportion OM originating from different sources. Providing accurate estimates of the proportion of OC originating from different sources if (i) OM source values are well defined with minimal overlap, (ii) OM has gone through no decomposition during the transport and burial processes.
pyrolysis	provenance	Allows the whole OC pool to be analysed without requiring solvent extraction. Typically coupled with GC or GCMS to investigate compound classes.
biomarkers	provenance	n-Alkane lipid biomarkers (discussed in detail) and fatty acids, pigments, and lignin phenols (only briefly mentioned herein) provide a targeted approach capable of resolving mixed sources at high resolution. Able to discern source contributions with increased specificity (compared with bulk stable isotopes, for example) in complex environments with overlapping inputs. n-Alkane biomarkers are especially powerful when combined with Compound Specific Isotope Analysis.
eDNA	provenance	Primer choice will determine which taxa can be detected within sediment: it is unlikely that a single primer set will identify all sources of carbon. The availability and quality of reference sequences in genetic databases will affect the ease and accuracy of taxonomic assignment.
black carbon	recalcitrance	May be a significant fraction of the OC, with important implications for discussion of blue carbon. Traditional methods require acid digestion before analysis, which is avoided by temperature gradient methods.
TGA: thermogravimetric analysis	recalcitrance	A rapid low-cost approach to quantify the different OM pools (labile, recalcitrant and refractory) and characterize the reactivity of the OM in marine sediments. Can be used alongside other OM properties to assess the potential vulnerability of the OC within the marine sediments to remineralization.
amino acids	recalcitrance	Provides calculation of an index developed for OM primarily sourced from phytoplankton.
sedimentation rates by Pb-210	accumulation; disturbance (vulnerability)	A heterogeneous mineralogy and granulometry across a core will affect the application of this tool. Fine sieving will help obtain higher absolute Pb-210 concentrations. Depending on the sampling location, other fingerprinting tools from legacy human activities (including non-nuclear activities) might be available to validate any dating or sedimentation rate estimations.
radiocarbon dating ( $^{14}\text{C}$ )	Accumulation; provenance	Primary tool for gaining chronological control over long-term ( $\times 10^3$ year) accumulation rates. In interpreting long-term OC accumulation rates calculated from $^{14}\text{C}$ factors such as compaction, changing C sources and material dated all need to be taken into consideration. Radiocarbon can also be used as a tracer to understand provenance of the OM and processes governing the transport, burial and degradation of the OM.
U/Th dating	accumulation	This approach is not applicable for dating sediment of less than 500 years and is only applicable to authigenic sediments rich in carbonates.
Th-234	disturbance (vulnerability)	Excess of Th-234 should be present only at the sediment-seawater interface. Its depth profile indicates efficient mixing of the upper sediments either by bioturbation or human activities. Comparison with another sediment sample collected from a nearby site and known to be undisturbed by human activities (e.g., MPAs) would be required to confirm a human disturbance qualitatively.

EA, Elemental Analyser; GC, Gas chromatography; GCMS, gas chromatography mass spectrometry; LOI, Loss on ignition; OC, organic carbon; OM, organic matter.

altered from its original form during transport and after deposition in near-surface sediments. Organic carbon stock and accumulation rates are smaller locally in subtidal marine sediment than in coastal blue carbon habitats, but larger when their expansive spatial extent is considered. Shelf sea sediments are subject to different anthropogenic pressures, most notably that of disturbance from bottom trawling, and require different carbon management approaches.

To establish if organic carbon stored in continental shelf sediments contributes to climate change mitigation in a manageable way, thus meeting the criteria for blue carbon,

organic carbon stock and accumulation rates must be determined alongside carbon properties which inform on its sources and stability and control its vulnerability. A multitude of analyses, brought together here as a toolbox, can be applied to answer these questions. Some analyses are already routinely applied in shelf sea sediments (e.g., percent of organic carbon content) while others continue to be developed for offshore sediment blue carbon application (e.g., eDNA). However, even for the relatively simple determination of stock, lack of co-measured dry bulk density or porosity is often a barrier to including legacy data in calculations and spatial modelling is

needed to integrate limited observations and provide a holistic picture. The field is advancing rapidly, with the application of eDNA to link coastal carbon sources to shelf sediment recipient sites and novel carbon reactivity indices being defined to inform on vulnerability. Consistency in methodology between studies through application of the toolbox we present will improve comparability and facilitate data aggregation to develop broad scale understanding.

The link between carbon stored in marine sediments, even at shelf sea water depths, and the atmospheric carbon system is moderated by the oceanic carbon cycle. More sediment carbon data collected alongside explanatory parameters (such as temperature and nutrient concentrations) are needed to better constrain the complex biogeochemical controls on the connectivity between these systems in the context of climate mitigation considerations.

## Author contributions

RP and LB provided initial conceptualization of this work. CAG led a workshop attended by all authors (except SKW) where the manuscript was initiated. Workshop discussions provided the basis for the review. CAG facilitated subsequent manuscript drafting and editing. CAG, JA, FDM, VGF, NH, CH, PDL, CM, CS, SKW, and CW drafted sections of the text. All authors contributed to manuscript revision, read, and approved the submitted version.

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## Conflict of interest

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