



Methods to measure lateral carbon flow

A review for application in coastal wetlands

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Acronyms

DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
FDOM	Fluorescent Dissolved Organic Matter
IPCC	Intergovernmental Panel on Climate Change
IRGA	Infrared Gas Analyser
LOI	Loss on Ignition
NDIC	Non-Dispersive Infrared
NEE	Net Ecosystem Exchange
ORP	Oxidation Reduction Potential
PIC	Particulate Inorganic Carbon
POC	Particulate Organic Carbon
POM	Particulate Organic Matter
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UVVR	Unvegetated-Vegetated Ratio



1. Introduction

Coastal habitats such as saltmarshes, mangroves and seagrass beds have a much higher sediment carbon burial rate than terrestrial forest ecosystems (Mcleod et al., 2011), which is coupled with high primary productivity, particularly under increased nutrient loads (Valiela & Valiela, 1995; Valiela et al., 1997; Bogard et al., 2020). They have therefore received much attention as potential nature-based solutions to mitigate against anthropogenic climate change. However, many aspects of the carbon balance in these ecosystems are still uncertain, including their actual potential to sequester the stored carbon over a long period of time and the overall net balance of their carbon budget (Williamson & Gattuso, 2022).

Methods to determine full carbon balances from coastal habitats are still emerging and developing, whereas carbon balances in terrestrial systems have been studied for much longer. Experience and methodologies from the development of terrestrial and inland freshwater ecosystems are an ideal starting point for fine scaling approaches to measuring carbon balances in coastal and tidal environments. Peatlands in particular provide many useful resources as they incorporate a mixture of soil, vegetation and water, which need to be considered in coastal ecosystems as well.

An ecosystem's carbon budget is comprised of vertical (gaseous) carbon flux and lateral carbon (dissolved and particulate matter) (Richardson et al., 2020). The inclusion of lateral carbon flow is vital for estimating accurate carbon budgets in all systems. Originally, terrestrial carbon budgets often focussed on just terrestrial ecosystems, such as forests, grasslands, arable lands and peatlands due to lack of data from aquatic systems (Janssens et al., 2005). The intergovernmental panel on climate Change (IPCC) report from 2001 (IPCC, 2001) assessed the carbon cycle for land and oceans separately. Whilst it considered carbon export from land to the oceans, actual inland aquatic carbon processes in lakes and rivers were not included, neither was the distinction of coastal systems, such as tidal marshes and estuaries. The inclusion of inland freshwater ecosystems in carbon budgets has shown that aquatic carbon flux can be greater per unit area than terrestrial fluxes and carbon budgets now include both types of ecosystems (Cole et al., 2007).

In peatland ecosystems the overall carbon loss through runoff can be higher than a third of the annual net CO₂-C uptake of the system (Nilsson, 2008). This is dominated by dissolved organic carbon (DOC) (Billett et al., 2010), which on its own can lead to a loss of around a third of the net ecosystem exchange (NEE) (Dinsmore et al., 2010;



Roulet et al., 2007). Other significant pathways for aquatic C loss are dissolved inorganic carbon (DIC) export (Richardson et al., 2020) and CO₂ outgassing (Müller et al., 2015).

Measuring lateral carbon flow in peatlands at a catchment scale is much easier compared to measuring the soil-air NEE because fluvial carbon only goes in one direction: export from the system (disregarding minor atmospheric DOC deposits). Provided the catchment is well-defined and watertight, this can be measured at one single point (Billett et al., 2010). Within catchments, however, fluxes can be spatially variable (Richardson et al., 2020). Within coastal ecosystems measurements of lateral carbon flow is much more challenging because fluvial carbon regularly moves into and out of the system due to the tides, introducing much higher variability (Najjar et al., 2018).

Nonetheless, lateral carbon flow also plays a major role in overall carbon budgets in coastal ecosystems (Akhand et al., 2021). Export can be higher than in terrestrial systems (Bogard et al., 2020), but these vary in magnitude and major pathways between ecosystems. Whilst coastal ecosystems have a high productivity and carbon burial rate (Mcleod et al., 2011; Bogard et al., 2020), a significant proportion of the in-situ fixed C is exported to other systems such as the coastal ocean. Bogard et al. (2020) estimated that as much as 41% of in-situ fixed C can be exported to other systems from coastal wetlands in general. In a study reviewing tidal wetlands of North America, Najjar et al. (2018) estimated that up to 80% of the net atmospheric uptake can be exported from tidal wetlands to estuaries and shelf waters, whilst only 20% are stored through burial.

The pathway through which C is exported also varies between the different types of coastal ecosystems. Santos et al. (2021) reviewed carbon outwelling pathways for mangroves, saltmarshes, seagrass and macroalgae (e.g. kelp forests) and concluded that lateral carbon loss in saltmarshes and mangroves is dominated by DIC and by particulate organic carbon (POC) in seagrass meadows and macroalgae forests. Even within ecosystems high variability can be the case for carbon retention and export, which may be dependent on factors such as ecosystem stability linked to vegetation cover (Ganju et al., 2019) and vegetation type present (Tan et al., 2020). Childers et al. (2002) reviewed saltmarsh literature and showed that the majority of saltmarshes studied were net sinks for POC, and net sources for DOC, but not all reviewed studies showed this trend highlighting the variability within ecosystems.



Whilst carbon outwelling may be higher than in-situ burial (Santos et al., 2021) and the ecosystem may be losing more carbon than fixing it, this does not necessarily mean that this carbon is lost as oceanic carbon and returned to the atmosphere. Santos et al. (2021) propose that carbon outwelling from coastal systems to the wider ocean is a major carbon sequestration mechanism, but Williamson & Gattuso (2022) note that the fate and sequestration rate of laterally exported C from coastal ecosystems to the open ocean can currently not be determined and quantified with routine monitoring.

Due to tidal connectivity to other habitats, saltmarshes also have inputs of carbon brought in on the tide, and the balance of carbon inputs to locally-derived carbon is a known knowledge gap in saltmarsh research. This is highly significant within carbon accounting for true carbon sequestration, and therefore climate change mitigation, due to the need to separate autochthonous (originating from within the saltmarsh) and allochthonous (originating from outside the saltmarsh and then washed in) carbon. All autochthonous carbon is carbon removed from the atmosphere via primary productivity, and is therefore considered a real carbon gain due to the saltmarsh habitat and management activity. Allochthonous carbon is only considered a gain if it can be demonstrated it would have been returned to the atmosphere if it had not been buried in the saltmarsh – a level of understating we currently do not have. This review does not consider the source of the carbon measured. However, the authors felt it was important to acknowledge the two origins of carbon (autochthonous and allochthonous) due to the impact this has for carbon accounting both in the voluntary carbon market, and for potential inclusion of saltmarsh habitat in the UK Greenhouse Gas Inventory (GHGI).

Lateral carbon is mainly comprised of POC, DOC and DIC with most aquatic carbon balances focussing on these three parameters (e.g. Worrall et al., 2009; Evans et al., 2016a; Tank et al., 2018; Richardson et al., 2020). Other carbon fractions present in aquatic systems are dissolved CH₄ and particulate inorganic carbon (PIC), but these are rarely measured even when they are acknowledged as a component of the aquatic carbon balance (Wang et al., 2019; Rantakari et al., 2010) or a full carbon balance is assessed (Peacock et al., 2019).

This review will cover the three main components of lateral carbon flow (POC, DOC and DIC) by explaining their role in coastal ecosystem processes and exploring different methods to capture these. As will be evident throughout the review all carbon budget components are linked to one another through various processes and each component – even though presented individually – cannot be viewed in isolation.



2. Lateral carbon flow components and measurement methods

2.1 Particulate organic carbon (POC)

2.1.1 Background

Particulate organic matter (POM) exists either in the form of living organisms, detrital particles or vegetation material (Hyndes et al., 2014). POM is defined by particle size, which depends on the filter pore size used to collect POM material and is usually between 0.45 and 1,000 μm (Hutchens et al., 2017). Particulate organic carbon is the carbon component of particulate organic matter, which is approximately 50% (Evans et al., 2016b; Richardson et al., 2020).

POM in coastal waters comes from in-situ primary production, land run-off from nearby terrestrial systems and primary production in other coastal ecosystems (Hyndes et al., 2014). For example seagrass beds and kelp forests can export a large amount of their total primary production (Mateo et al., 2006; Krumhansi & Scheibling, 2012). POM is also derived from living animals in the form of faeces or body parts, including plankton and nekton, both in-situ or migrating (Hyndes et al., 2014). POM is moved into coastal waters through riverine and tidal transport, direct run-off from land, landslides, plankton and nekton migration, crab burrowing activities, and storm events causing erosion in nearby ecosystems (Hyndes et al., 2014).

Natural variations in POM concentrations are linked to the tidal amplitude, river flow, terrestrial rainstorm events or drought periods. Other factors are the actual geomorphology of the coastal ecosystem, its location, distance and type of neighbouring ecosystem. Particle size and buoyancy of particles also play a role – this affects how they are transported – as does palatability to grazers and the abundance of grazers. Any of these can be altered by human interference such as habitat destruction (loss of source material), climate change (changes in precipitation, temperature, storm events), development (barrier construction) and fisheries (changes in trophic transfers) (Hyndes et al., 2014).

Galy et al. (2015) state that a “*significant fraction of riverine POC*” is stored long-term in marine sediments, whereas Dymond (2010) assumes this is true for 80% of terrestrial POC. It is clear that some coastal POC is exported to other ocean ecosystems, and some is stored in-situ, but to what extent this actually happens depends on the coastal ecosystem’s environmental setting (Santos et al., 2021). In saltmarshes, for instance, POC is mainly buried in sediment and only makes up a small fraction of the exported carbon, whereas in seagrass beds and kelp forests



POC is the main constituent of exported C (Santos et al., 2021). POC that is not exported can form an in-situ carbon sink, either buried in marine sediment, transformed to refractory DOC (i.e. DOC that resists microbial degradation (Baltar et al., 2021)), or can be turned into bicarbonate through anaerobic respiration. However, POC can also be returned to the atmosphere as CO₂ through oxic respiration (Santos et al., 2021).

2.1.2 Methods

Low frequency POC data

The principle of POC measurements involves the collection of water samples, filtering these to collect particulate matter, storing the filter papers appropriately, and then determining the fraction of organic matter in the collected particles and estimating the carbon component of these. Commonly, the loss on ignition method is applied, where a certain volume of water is filtered through pre-combusted and pre-weighed glass fibre filter papers. The filter papers are then dried in an oven, weighed, then placed in a furnace and weighed again. The difference in weight between oven-dried material and residue material after combustion gives the loss on ignition (LOI) weight (e.g. Evans et al. 2016b, Chapman et al., 2022). The LOI method by Ball (1964) is often applied (e.g. Gaffney et al., 2020; Pickard et al., 2022), who uses the following equation to calculate POC:

$$Y = (0.458 \times X) - 0.4 \quad (1)$$

Where Y is the organic carbon in % and X is the LOI (%). This can then be converted to mg/L.

In most studies 500 ml of water are filtered (e.g. Rosset et al., 2019; Regensburg et al., 2021) but some filter up to 5 or 10 litres (Akhand et al., 2021; Bjarnadottir et al., 2021), which might be required when POM concentrations are low. The actual filtered volume needs to be noted for each sample to ensure that the conversion to mg/L is correct. Dinsmore et al. (2010) note that the LOI method gives a 15% error margin in water samples with low POC concentrations. Inorganic carbon can be removed by acid fumigation of collected particles (e.g. Santos et al., 2019; Knobloch et al., 2021; Yau et al., 2022) but this is not applied by all. Salts can be removed by washing filters with ultrapure water (Turnewitsch et al., 2007; Obernosterer et al., 2008).

An alternative to the LOI method is the Dumas combustion method, by which samples are burnt and the carbon released is measured as a gas. Bjarnadottir et al., (2021) compress the collected particles in the filter paper with a hydraulic press and then apply the Dumas combustion method with a macro elemental analyser.



Unspecified combustion methods are also applied by Santos et al. (2019) and Yau et al., (2022) with a flash elemental analyser. Osburn et al., (2015) use a wet chemical oxidation method with a total organic carbon (TOC) analyser.

Richardson et al. (2020) determined total suspended sediments (TSS) by weight and estimated POM and POC from TSS, assuming that 75% of TSS is POM and that 50% of POM is POC.

High frequency / continuous POC data with proxies

Knobloch et al., (2021) obtained continuous TSS data for a tidal marsh creek system by using turbidity measurements as a proxy. Continuous turbidity measurements were logged by a YSI multi-parameter sonde. A linear regression between turbidity and TSS with 140 data points had a r^2 value of 0.8. The TSS data could then potentially be converted to POC data by the Richardson et al. (2020) approach as outlined above.

Rosset et al. (2019) used turbidity as a direct proxy for POC concentrations in a fen peatland. They had 30 data points for both parameters and achieved an r^2 value of 0.65 with a linear regression. The same approach was used by Hou et al. (2023) investigating wastewater discharge of an aquaculture farm. Here 35 data points of turbidity and POC data produced a linear relationship with an r^2 value of 0.51.

High frequency / continuous POC data with aerial imagery and remote sensing

To monitor POM and POC levels in a tidal wetland Ganju et al. (2019) established a relationship between POM and marsh stability, which was defined by an unvegetated-vegetated ratio (UVVR) combined with elevation. The UVVR was determined through aerial imagery. Water samples were collected and POM concentrations were determined for all and POC concentrations for some sites. An average of 45% POC of POM was applied to sites without any POC data. The correlation between POM and UVVR was $r^2 = 0.78$. This was improved by a multiple regression between POM and POC with UVVR and elevation; the r^2 values were 0.95 and 0.96, respectively.

POC for coastal waters can also be sufficiently estimated directly from satellite imagery as demonstrated by Tran et al. (2019). Relationships between the different band ratios and POC (derived from lab analyses) expressed in r^2 values ranged



between 0.59 and 0.68. Overall, the study found that POC estimates differed between mineral-dominated and organic-dominated waters, with an overestimation for the first type and an underestimation for the latter.

2.2 Dissolved organic carbon (DOC)

2.2.1 Background

Dissolved organic carbon is the carbon component of dissolved organic matter (DOM), which is approximately 55% of DOM (Bourbonniere, 2009). The distinction between DOM and POM is made by particle size, determined by filter pore sizes applied, which ranges between 0.2 and 0.7 μm (see section 2.2.2. Methods).

In coastal ecosystems, DOC has several sources. As part of primary productivity DOC is leached from vegetation. This can happen in-situ, or in neighbouring ecosystem, from which DOC can be imported through water movement (Hyndes et al., 2014; Shelton et al., 2022). On a global scale, seagrasses can release up to 46 % of their net community production to the water column as DOC, although some of this may derive from trapped allochthonous sediment (Barrón et al., 2014). Once vegetation becomes detached and starts to decompose further DOC is released; in mangrove systems this can mean a release of up to 75 % of organic carbon in leaf matter within just a few weeks (Kristensen et al., 2008). DOC is also excreted from animals and leached from POM (Hyndes et al., 2014). Additionally, DOC can also be of terrestrial origin, where run-off is either directly washed into coastal ecosystems from immediate terrestrial sources or arrives through riverine and estuarine transport (Hyndes et al., 2014). This has profound effects on the biogeochemistry of coastal waters (e.g. Frigstad et al., 2013; Traving et al., 2017).

Movement of DOC is largely facilitated by riverine and tidal transport, but also influenced by weather (e.g. through storm surges), land run-off and migration of nekton as part of the trophic food chain (Hyndes et al., 2014). DOC concentrations can be increased by an increase in river flow or tidal amplitude. Increased rainfall also causes an increase in terrestrial DOC export to coastal areas. A decrease in DOC concentration can occur during periods of increased microbial activity. As DOC production is partially linked to POC concentrations, factors influencing POC concentrations also relate to DOC (Hyndes et al., 2014).

DOC can have different fates in coastal environments. It can be turned into DIC compounds either through biodegradation (i.e. absorption by microbes) or



photodegradation (i.e. breakdown of organic components by solar irradiance) (Bauer & Bianchi, 2011). DOC also flocculates in coastal waters and produces POC in the process (Sholkovitz, 1976; St. Pierre et al., 2020). Additionally, DOC is also exported to other aquatic ecosystems (Hyndes et al., 2014; Shelton et al., 2022).

2.2.2 Methods

Low frequency DOC data

The principle of DOC measurements involves the collection of water sample, filtering this to remove particulate matter, storing the sample appropriately, and then analysing the sample in the lab with an analyser. The approach is consistent across terrestrial and coastal studies. Differences do occur in the overall methods and techniques, but this does not seem to be connected to the ecosystem, but to the choices made by principal investigators or research institute protocols. Filtering of samples involves filter papers with different pore sizes, such as 0.22 μm (Watanabe et al., 2020; Richardson et al., 2020), 0.3 μm (Saraceno et al., 2009), 0.45 μm (Müller et al., 2015; Chapman et al., 2022) and 0.7 μm (Santos et al., 2019; Gaffney et al., 2020). Some pre-filter the water sample with a 0.7 μm filter, followed by a 0.22 μm filter (Cao & Tzortziou, 2021; Shelton et al., 2022). The filter size is important to note as it ultimately defines the definition of DOC. Results from studies utilising different filter pore sizes may not necessarily be comparable.

Filter material differs and includes polytetrafluoroethylene (Watanabe et al., 2020), glass fibre (Yau et al., 2022), cellulose nitrate (Evans et al., 2016b), nylon (Regensburg et al., 2021), cellulose acetate (Rosset et al., 2019), nucleopore (Menendez et al., 2022) and polycarbonate (Cao & Tzortziou, 2021). Most studies used the filters without any pre-treatment but some pre-combusted (Gaffney et al., 2020) or pre-washed (Regensburg et al., 2020). The filtrate is then added to bottles or vials, which are either pre-combusted (Akhand et al., 2021), pre-washed (Pickard et al., 2022) or un-modified (Taillardat et al., 2022). Some protocols require acidification of filtrates (e.g. Evans et al., 2016b; Schiebel et al., 2020) and sparge them with oxygen (Regensburg et al., 2021) to remove inorganic carbon and to stabilise the sample, whilst others do not require treatment of the filtrate (e.g. Watanabe et al., 2020). Filtrates are then stored until analysis either in a fridge below 4 °C (Shelton et al., 2022), are frozen (Müller et al., 2015) or mixed with mercury chloride (HgCl₂) (Santos et al., 2019). Analyses methods include the non-purgeable organic carbon method (Shelton et al., 2022), high-temperature catalytic oxidation



(Akhand et al., 2021) and high temperature combustion (Menendez et al., 2022) with a range of analysers.

High frequency / continuous DOC data with proxies

In a tidal marsh Menendez et al., (2022) collected measurements for fluorescent dissolved organic matter (fDOM), chlorophyll-a fluorescence, turbidity, pH, dissolved oxygen, temperature, conductivity and water depth every 15 minutes with an EXO2 multiparameter sonde (manufacturer YSI Inc.) fitted with the relevant sensors. Additionally, they collected water samples once a month with an autosampler every hour for a 24-hour period. These were analysed for DOC in the lab as outlined above. In total they used 256 data points, for which they had both DOC lab analysis values and data records from the EXO2 sonde. Linear regression with fDOM yielded an r^2 value of 0.6, which was improved to $r^2 = 0.71$ by the inclusion of turbidity, dissolved oxygen, pH and salinity data. Data gaps in between water sample collection was interpolated by the multiple regression model equation.

Bogard et al. (2020) applied a similar approach (major axis regression approach) for a different tidal marsh and achieved an r^2 value of 0.87 with 440 data points between fDOM and DOC. A linear regression also showed a close relationship between fDOM and DOC for Rosset et al., (2019) in a fen peatland with an r^2 value of 0.93 and 167 observations. These examples illustrate that continuous DOC data can be obtained by logging the appropriate proxy variables.

High frequency / continuous DOC data with remote sensing

Cao & Tzortziou (2021) used a combination of Landsat-8 and Sentinel-2/MSI and DOC data from water samples tested in the lab (as above) to develop a DOC algorithm through multiple regression for a tidal estuarine wetland. This had an error value of 23 %, which the authors judged as a good outcome. DOC export from a peatland river to coastal waters was successfully estimated by ChunHock et al. (2020) with Landsat-8 imagery. The relationship between Landsat-8 Red to Green bands and DOC had an r^2 value of 0.77 and a mean error of 5.71 %. This is reviewed in more detail by Mohseni et al., (2022).



2.3 Dissolved inorganic carbon (DIC)

2.3.1 Background

DIC is made up of three fractions: Dissolved CO₂, bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). Dissolved CO₂ consists of two pools (free CO₂ and H₂CO₃) but because they behave as one pool and cannot be easily distinguished analytically, they are usually just referred to as dissolved or aqueous CO₂. Dissolved CO₂ is the most dominant acid, whereas bicarbonate and carbonate are the major buffers with the most acid neutralising capacity, also referred to as alkalinity. The ratio of dissolved CO₂ to bicarbonate and carbonate is the main control of pH in water. (Cole & Prairie, 2014; Cole et al., 2021). In acidic waters DIC is mainly dissolved CO₂ but in water with a pH > 5.5 the other constituents also need to be considered (Cole & Prairie, 2014). In seawater dissolved CO₂ makes up only approximately 1% of DIC, the rest is mainly bicarbonate and carbonate (Bakker et al., 1996). Dissolved CO₂ is the key variable to understand overall DIC. It is produced through a variety of processes (after Cole & Prairie, 2014):

- respiration (biological oxidation of organic matter to CO₂) by primary producers, consumers and microbes
- Photooxidation of organic matter
- precipitation of dissolved carbonate ion into solid phase carbonate, which takes place during formation of corals and shells of molluscs
- Soil respiration that is not degassed into air but dissolved into water creates high levels of dissolved CO₂ in ground water
- Addition of acid (e.g. through rain) increases the amount of CO₂ at the expense of HCO₃ and CO₃
- Abiotic carbonate precipitation in oceans

In freshwater systems dissolved CO₂ dissolves the parent rock material and thereby releases bicarbonates and carbonates, subsequently regulating water pH and the entire chemical balance in surface water (Cole & Prairie, 2014). Dissolved CO₂ in surface waters also exchanges with CO₂ in the atmosphere. If no other controls were present, the CO₂ concentration in water would be the same as in the atmosphere as stated by Henry's Law. In reality, dissolved CO₂ is very dynamic and differs greatly between ecosystems. When respiration exceeds gross primary productivity, then surface waters are supersaturated with dissolved CO₂, which is often the case with inland freshwater bodies such as rivers and lakes. This supersaturation then results in CO₂ outgassing to the atmosphere (Cole & Prairie, 2014).

The main fate of riverine DIC is CO₂ outgassing to the atmosphere and transport to estuaries and coastal ecosystems (Li et al., 2017, Yin et al., 2020). Coastal wetlands



therefore receive terrestrial DIC but additionally also produce DIC in situ through both aerobic and anaerobic respiration (Wang et al., 2016). These processes are particularly complicated in tidal environments where waters with different pH and salinity mix. DIC present in coastal wetlands is either outgassed to the atmosphere or outwelled to the coastal ocean (Wang et al., 2016), where photosynthesis converts it into organic matter, which eventually is drawn down to the deeper ocean (Passow et al., 2012). Outwelling of DIC from coastal wetlands to the coastal ocean may be a significant contribution to long-term carbon storage in the ocean (Santos et al., 2019).

A variety of terms are used for dissolved CO₂, which in the literature are often used interchangeably, all of which refer to gaseous CO₂ dissolved in liquid, examples include: partial pressure CO₂, pCO_{2(water)}, pCO_{2(aq)}, CO₂* (precisely referring to the combined pool of free CO₂ and H₂CO₃) and fCO₂, where f stands for fugacity.

pCO_{2(air)} refers to the partial pressure of CO₂ in the air, which alongside pCO_{2(aq)} can be used to calculate the flux between water and air in combination with the gas exchange velocity *k*, which is mainly influenced by wind and water turbulence (Cole & Prairie, 2014; Rosentreter et al., 2017) but can be quite variable between ecosystems. The gas exchange velocity *k* can either be derived from existing literature (e.g. Jiang et al. (2008) compute their own equation for *k* based on reported *k* for a range of coastal ecosystems) or estimated directly at the study site through a combination of floating chamber CO₂ flux measurements, water column pCO₂ measurements and atmospheric pCO₂ measurements (Rosentreter et al., 2017).

2.3.2 Methods

2.3.2.1 pCO₂ – direct measurements

Low frequency pCO₂ data

Direct measurement of pCO₂ is more accurate compared to estimating or calculating pCO₂ from other parameters (Cole & Prairie, 2014, Golub et al., 2017). Direct measurements can take place through active equilibration (e.g. bottle head space method), passive equilibration (a sensor enclosed in a waterproof and gas permeable membrane) (Yoon et al., 2016) or with a pCO₂ sensor submersed in the water column.

Measurements of pCO₂ with an equilibrator involves pumping water into an equilibrator fitted with a gas permeable membrane at a certain specified flow rate



(e.g. 3 L min⁻¹ (Yau et al., (2022)), where the water equilibrates with the ambient air. The CO₂ concentration in the head space is then measured with a portable infra-red gas analyser such as the Los Gatos (e.g. Yau et al. 2022) or LI-COR (e.g. Ho et al., 2013; Müller et al., 2015) analysers. Alternatively, a known volume of sample water can also be added to a bottle with a known volume of remaining head space filled either ambient air (Chapman et al., 2022) or hydrocarbon free zero air (Taillardat et al., 2022). Once the water sample is equilibrated with the head space, which can be accelerated by shaking, a sample of the head space gas is taken and the gas concentration is determined with spectroscopy (Taillardat et al., 2022) or gas chromatography (Chapman et al., 2022). For both methods the water temperature must be kept at a known constant (ideally the same as the waterbody temperature) because changes in temperature mean changes in gas concentrations (Cole & Prairie, 2014). An additional option can be to use the bottle method and measure the gas concentration in the equilibrated head space directly with a portable infra-red gas analyser (Liu et al., 2021).

A restriction to both methods (equilibrator and head space bottle) is that the measurements are labour intensive and low frequency.

High frequency / continuous pCO₂ data – submersible sensors

Methods for direct and continuous in-situ measurements were developed by Johnson et al. (2010), Blackstock et al. (2019) and Turner et al. (2022). Johnson et al. (2010) enclose the sensor head of an infrared gas analyser (IRGA, Vaisala, Helsinki, Finland, GMT220 and GMM 220 series) into a waterproof but gas permeable membrane and deploy this directly into the water column. The deployed IRGA is connected to external power and a data logger on a mounted or floating platform.

Blackstock et al. (2019) used a similar approach with a Senseair AB (Delsbo, Sweden) K30 1 and K30 10% IRGA. Turner et al. (2022) refined the Blackstock et al. (2019) method for tidal environments with the waterproofed K30 10% IRGA floating up and down with the tide. All three approaches measure pCO₂ directly and continuously but still require above-surface connections to a power source and data logger, which provides a challenge in tidal environments.

A different but more expensive approach is an in-situ pCO₂ logger with an internal data logger such as the HydroC (Contros GmbH, Germany) or the C-Sense (Turner Designs, USA). The C-Sense probe uses temperature-compensated non-dispersive infrared (NDIC) to measure pCO₂. Do Vale et al. (2019) compared the probe to measurements with the head space method and found that the C-Sense probe overestimated pCO₂ due to biofouling. They recommend periodic cleaning of immersed sensors for long-term deployment. The HydroC is a flow-through sensor which uses infrared absorption spectrometry to measure pCO₂. Müller et al., (2015) note that the sensor is only calibrated to 1500 µatm and nonlinear at high concentrations. They performed measurements with the head space method



alongside sensor deployment and used the additional measurements to correct the HydroC.

A portable meter is available from Oxyguard International in Denmark designed for aquaculture. It measures $p\text{CO}_2$ with a gas-permeable membrane and infra-red absorption cell and converts the measured pressure into mg L^{-1} through with a solubility factor (Moran et al., 2010; Pfeiffer et al., 2011). Pfeiffer et al. (2011) compared the meter with four other methods of $p\text{CO}_2$ determination including direct measurements with a head space unit and an IRGA and calculations of $p\text{CO}_2$ from other parameters. They concluded that the Oxyguard probe was the only method close to that with the head space and IRGA, but they do concede that the calibration time for the Oxyguard probe was lengthy. Moran et al. (2010) also assessed the Oxyguard probe and concluded that the meter is not appropriate for measuring low CO_2 concentrations such as in surface water in equilibration with the atmosphere. Low accuracy levels of $0.5 \text{ mg L}^{-1} \text{ CO}_{2(\text{aq})}$ for the Oxyguard probe, means direct measurement of $p\text{CO}_2$ with gas stream infra-red detection has an accuracy two orders of magnitude higher than the Oxyguard meter. The meter also has a slow reaction time at low water velocity, requiring up to 60 minutes in still water. The response time is also temperature dependent with lower temperatures requiring longer response time. Depending on the actual response time taken, some CO_2 loss may occur and needs to be accounted for. However, the authors also suggest that the Oxyguard probe may be useful in situations where pH and alkalinity cannot be measured accurately (Moran et al., 2010).

2.3.2.2 $p\text{CO}_2$ – indirect (determination from other measured parameters)

Nomographic determination

Dissolved carbon dioxide can be determined nomographically (i.e. several measured parameters are lined up alongside each other, and the unknown parameter can be determined by intersecting the known parameters with a straight line) if pH, total alkalinity, temperature and total mineral content are known. The accuracy of this method is only as good as the accuracy of the measured parameters (APHA, 2017). This method is not recommended for seawater because of high total dissolved solids (Pfeiffer et al., 2011).

Calculation

Dissolved CO_2 can be calculated from measured DIC and alkalinity, DIC and pH or alkalinity and pH and in combination with two dissociation constants K_1 and K_2 . K_1 expresses the ratio between bicarbonate and dissolved CO_2 , which is temperature dependent. K_2 expresses the ratio between carbonate and bicarbonate. In water with a $\text{pH} < 7.5$ K_2 can be ignored because the amount of carbonate is small enough to



ignore (Cole & Prairie, 2014). There are two main problems with the calculation method:

1. Generally, the method is unsuitable for seawater because the high concentration of ions affects the constants K1 and K2 (Cole & Prairie, 2014; APHA, 2017). A solution to this was to determine new K1 and K2 constants as a function of temperature and salinity, which was developed by Mehrbach et al. (1973) and further refined by other studies such as Lueker et al., (2000) and Sulpis et al. (2020). According to Sulpis et al. (2020) there are at least 15 expressions for K1 and K2 in existence. Despite these improvements Pfeiffer et al. (2011) and Moran et al. (2010) disregard the calculation method for application in seawater.
2. The second problem is the accuracy of the required parameters for calculations, such as DIC, alkalinity and pH. Analytical uncertainties for DIC and alkalinity lead automatically to uncertainties in dissolved CO₂ (Lueker et al., 2000). Accurate measurements of pH can be problematic because of constant drift in electrodes if they are not regularly calibrated. A pH error of 0.1 (bearing in mind that pH is logarithmic) can lead to a pCO₂ error of 20% or higher (Moran et al., 2010).

Nonetheless, the calculation method is applied in studies of saline waters (e.g. Baumann et al., 2015; Endo et al., 2019) and programs such as CO₂SYS (Lewis et al., 1998) and seacarb R package (Gattuso et al., 2022) assist with calculations.

2.3.2.3 pCO₂ – titration

Free dissolved CO₂ reacts with sodium carbonate or sodium hydroxide. Either one of these is added to collected water until the reaction of the free CO₂ with either one of the substances is completed. This is indicated by either a pink colour of an indicator paper or recording of a pH end point of 8.3. The amount of sodium carbonate or sodium hydroxide added to the water to reach the end point is used to calculate dissolved CO₂ in mg L⁻¹ (APHA, 2017). Measuring dissolved CO₂ by titration is not suitable for seawater because of the high total dissolved solids (APHA, 2017; Pfeiffer et al., 2011).

2.3.2.4 DIC

Low frequency DIC data

DIC (the combined pool of pCO₂ and alkalinity) can be measured by collecting a water sample and then analysing it in the lab with a DIC analyzer. Water samples are



usually filtered (e.g. Gaffney et al., 2020; Yau et al., 2022) but not all studies mention filtering of water (e.g. Akhand et al., 2021; Baumann et al., 2015), which questions the definition of DIC as opposed to PIC. Filter material is usually glass fibre (e.g. Santos et al., 2019; Yau et al., 2022) but can also be polycarbonate (Golub et al., 2017). Filter pore sizes tend to be 0.7 μm (e.g. Gaffney et al., 2020; Santos et al., 2019; Yau et al., 2022) but can also be 0.45 μm (Tan et al., 2020) or 0.4 (Golub et al., 2017), which will determine DIC definition. Filtrates are collected in glass bottles and poisoned with mercuric chloride to stop all biological activity (e.g. Santos et al., 2019; Richardson et al., 2020; Yau et al., 2022). Analysers vary and include the OI Aurora 1030W (Santos et al., 2019; Yau et al., 2022), Shimadzu TOC-L (Gaffney et al., 2020) and Kimoto Electric ATT-05 and ATT-15 (Watanabe et al., 2020).

High frequency / continuous DIC data with proxies

Continuous high frequency data for DIC can be obtained through modelling with high frequency data-logged parameters. Wang et al., (2016) logged pH and oxidation reduction potential (ORP) with an EXO2 sonde and combined the data with hourly discrete bottle samples analysed for DIC as outlined above as well as tidal flow and water fluxes. A multilinear regression model with 80 observations produced an r^2 value of 0.74. The combination of high-resolution measurements and modelling estimated a DIC export from their saltmarsh twice as high as previous estimates (Wang et al., 2016). The same approach at the same study site with a different set of data produced an r^2 value of 0.91 with 104 observations (Chu et al., 2018). For Bogard et al., (2020) the best multiple linear regression model for predicting DIC included water level, temperature and salinity for which they obtained an r^2 value of 0.88 with 31 observations.



3. Summary

Table 1 provides an overview of all methods discussed and their applicability to coastal wetland systems. Generally, most methods developed in terrestrial environments can be directly applied in saltmarshes or other coastal and tidal wetlands. The main constraint and difference to terrestrial environments is the salinity of the water, which provides challenges for some methods. Biofouling of submerged sensors can also be problematic in coastal wetlands but can be mitigated by using anti-fouling guards and regular cleaning of devices. A further challenge is the tidal environment. Waterbodies in terrestrial settings tend to stay in one place and sampling methods requiring external power, e.g. for a water pump, can set up a power station (battery or solar panels) adjacent to the water body. In saltmarshes, however, dry ground for power stations may be hundreds of meters away from water during low tide and may be submerged during very high spring tides if the sea wall is breached. This, however, does not make the method itself unsuitable but provides challenges in adjusting the set-up.



Table 1: Summary of the methods reviewed for lateral carbon flow.

Parameter	Method	Suitability for coastal wetlands	Comment	Applied in coastal wetlands
POC	Collection of water samples, filtering, determine LOI weight after Ball (1964) or with a combustion method or wet oxidation method	Yes	-	LOI: Ganju et al. (2019) Combustion: Knobloch et al. (2021) Wet oxidation: Osburn et al. (2015)
POC	Estimation from TSS	Yes	To improve accuracy, the relationship between TSS and POC can be established by POC analysis of a subsample.	n/a
POC	Modelling from proxy parameter (turbidity)	Yes	The relationship between turbidity and POC is likely to be more robust with higher numbers of POC observations.	Knobloch et al. (2021)
POC	Aerial imagery / remote sensing	Yes	Imagery resolution may not be high enough for small wetlands.	Ganju et al. (2019) Tran et al. (2019)



Parameter	Method	Suitability for coastal wetlands	Comment	Applied in coastal wetlands
DOC	Collection of water samples, filtering, analysis of filtrate with appropriate analyser	Yes	-	e.g. Santos et al. (2019) Schiebel et al. (2020) Yau et al. (2022)
DOC	Modelling from proxy parameter (fDOM)	Yes	The relationship between fDOM and DOC is likely to be more robust with higher numbers of DOC observations.	Bogard et al. (2020) Menendez et al. (2022)
DOC	Aerial imagery / remote sensing	Yes	Imagery resolution may not be high enough for small wetlands.	Cao & Tzortziou (2021) ChunHock et al. (2020)
pCO ₂	Head space method	Yes	-	Ho et al. (2013) Yau et al. (2022)
pCO ₂	Submerged pCO ₂ sensors	Yes	Provided regular cleaning prevents biofouling, sensor has high accuracy and sensor is calibrated to high concentrations	Baumann et al. (2015) Turner et al. (2022)
pCO ₂	Nomographic determination	No	High total dissolved solids in seawater are not compatible with this method	n/a



Parameter	Method	Suitability for coastal wetlands	Comment	Applied in coastal wetlands
pCO ₂	Calculation	(Yes)	This method is prone to errors in sea water but can be an applied method provided the potential error of pCO ₂ is stated.	Baumann et al. (2015) Endo et al. (2019)
pCO ₂	Titration	No	High total dissolved solids in seawater are not compatible with this method	n/a
DIC	Collection of water samples, filtering, analysis of filtrate with appropriate analyser	Yes	-	e.g. Baumann et al. (2015) Santos et al. (2019) Yau et al. (2022)
DIC	Modelling from proxy parameters (pH, ORP, water level, temperature, salinity)	Yes	The relationship between the proxy variables and DIC is likely to be more robust with higher numbers of DIC observations.	Chu et al. (2018) Bogard et al. (2020) Wang et al. (2016)



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