

The influence of organic alkalinity on the carbonate system in coastal waters

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ABSTRACT

Total alkalinity (TA) is one of the four main carbonate system variables and is a conventionally measured parameter used to characterise marine water carbonate chemistry. It is an important indicator of a waterbody's buffering capacity and a measure of its ability to resist acidification, a matter of growing concern in the marine environment. Although TA is primarily associated with the inorganic components of seawater such as bicarbonate, there is a growing consensus that dissolved organic matter (DOM) can significantly contribute to TA in coastal waters. This organic fraction of TA (OrgAlk) is typically deemed negligible and is not accounted for in conventional TA expressions. However, omission of OrgAlk can lead to the propagation of errors in subsequent carbonate system calculations and to misinterpretation of key carbonate chemistry descriptors such as calcium carbonate saturation states. Here we provide an overview of OrgAlk contributions to TA and investigate the implications of its omission in carbonate system studies conducted in coastal waters. We examine the prevalence of OrgAlk across both coastal and pelagic waters using publicly available carbonate system data products, such as GLODAP and GOMECC. Current measures to account for, incorporate and characterise the contribution of OrgAlk to TA are also critically examined.

1. Introduction: changing carbonate chemistry

The exchange of carbon dioxide (CO₂) between the atmosphere and oceans has been greatly perturbed by anthropogenic carbon release since the industrial revolution. Atmospheric CO₂ levels prior to the industrial era are estimated to be around 270 ppm (Wigley, 1983). This is approximately 50% less than today's value, measured to be around 410 ppm (Dlugokencky et al., 2021). This marked increase in the concentration of atmospheric CO₂ has been mitigated by the oceans, which have absorbed approximately one third of anthropogenically produced CO₂ (Gruber et al., 2019; Sabine et al., 2004), keeping atmospheric levels lower by ~80 ppm (Friedlingstein et al., 2020). This has resulted in dramatic changes in seawater chemistry (Fabricius et al., 2020; Orr et al., 2005; Riebesell and Gattuso, 2015) that have led to a lowering of seawater pH, collectively referred to as ocean acidification. On average, surface ocean pH has fallen by approximately 0.1 pH units (Caldeira and Wickett, 2003; Jiang et al., 2019; Orr et al., 2005). With end-of-century partial pressure of CO₂ (pCO₂) predicted to reach 900–1000 μatm, ocean acidification seriously threatens the stability of ocean ecosystems, fish stocks and food security (Leis, 2018; McNeil and Sasse, 2016).

Ocean acidification is tracked by measuring changes in seawater pH as well saturation state of seawater with respect to aragonite. The latter is commonly used to track ocean acidification because it is a measure of carbonate ion concentration. pH is one of the four main parameters, the other three being dissolved inorganic carbon (DIC), fugacity of CO₂ (fCO₂) and total alkalinity (TA) (Dickson et al., 2007). TA does not change with CO₂ introduction to, or removal from, a waterbody (CO₂ invasion or evasion) and is a conservative parameter with respect to temperature and salinity (Wolf-Gladrow et al., 2007). As TA does not change with ambient CO₂, it is easier to sample for and store compared to other carbonate system parameters such as pH and DIC. As TA can be measured to a good degree of accuracy, within 1–2 μmol.kg⁻¹, it is a preferred tracer variable in numerical models of the oceanic carbon cycle and is the predominantly measured parameter alongside DIC to describe the carbonate system. As advances in spectrophotometric pH analysis have been made in recent years (Ma et al., 2019), more laboratories may opt to use pH and DIC for speciation calculations. However, due to the aforementioned relative ease that TA samples can be collected and stored with, it remains a predominantly measured parameter in many carbonate system studies. TA can be thought of as a measure of a

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waterbody's buffering capacity and is inherently linked to pH (Egleston et al., 2010). Therefore, accurate TA assessment is important in our understanding of the risks associated with the acidification of marine waters. This is especially relevant in littoral systems, as the carbonate chemistry of coastal waters is substantially more dynamic than the open ocean (Borges and Gypens, 2010). These systems exhibit vast temporal and spatial differences in carbonate chemistry due to periodic seasonal cycling (Joesoef et al., 2017; Rheuban et al., 2019) fluctuations in fluvial export and nutrient delivery (Borges and Gypens, 2010; Hydes and Hartman, 2012; Raymond and Cole, 2003), upwelling events (Borges and Frankignoulle, 2002; Millero, 2007) as well as microbial activity (Brewer and Goldman, 1976; Wolf-Gladrow et al., 2007).

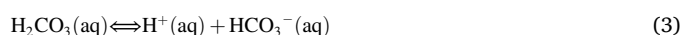
The aforementioned factors add to the overall heterogeneity of carbonate system dynamics in coastal waterbodies and to the uncertainty regarding future impacts of acidification. Only by studying the variability and long-term trends of carbonate chemistry in coastal areas can the natural and anthropogenic processes that affect these systems be delineated (Sutton and Newton, 2020). Furthermore, the global and general circulation models utilised in many predicted ocean acidification scenarios (Carter et al., 2016; Ilyina et al., 2009) do not resolve the intricacies of acidification of the coastal ocean (Duarte et al., 2013). For example, areas such as the north-eastern US coastline are particularly susceptible to acidification due to low TA freshwater discharge (Gledhill et al., 2015; Rheuban et al., 2019), whereas the Baltic Sea is possibly more resistant to acidification due to observed TA increases over the past decades (Gustafsson and Gustafsson, 2020; Müller et al., 2016). These differences in fluvial TA output are typically linked to the bedrock of the river catchment area (McGrath et al., 2016), highlighting the site specificity of TA in coastal systems. Due to this, it is important to ensure that TA dynamics in coastal waters are as accurate and well characterised as possible.

Typically TA is attributed solely to the inorganic components of seawater such as bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and borate (Dyrssen and Sillén, 1967), with other inorganic seawater constituents also making small contributions, as outlined in Table 1. Organic molecules that are present in seawater can also contribute to TA, with this contribution termed organic alkalinity (OrgAlk). There is a growing consensus that OrgAlk can be a significant fraction of TA in coastal waters (Cai et al., 1998; Muller and Bleie, 2008; Patsavas et al., 2015; Song et al., 2020; Yang et al., 2015) and potentially impact carbonate system reference materials (Sharp and Byrne, 2021). Furthermore, questions regarding interferences in TA analysis in coastal environments due to the presence of organic molecules have also been raised (Fong and Dickson, 2019; Hu et al., 2015; Patsavas et al., 2015; Sharp and Byrne, 2020; Song et al., 2020). These compounds, which are thought to be part of dissolved organic carbon (DOC), can possess charged functional groups that can react during TA titrations, thus altering the overall TA signal (Kim and Lee, 2009; Kuliński et al., 2014; Paxéus and Wedborg, 1985). The presence and influence of these organic species are typically omitted in the analysis of TA in the open ocean as they are thought to be present in such small amounts that they can be safely neglected (Dickson et al., 2007) although the consensus view on this is changing (Fong and Dickson, 2019). OrgAlk is not explicitly accounted

for in conventional TA calculations. This presents a two-fold issue, as organic molecules can directly and significantly affect the buffering capacity of a water sample (Hunt et al., 2011) as well as present an analytical interference in TA computation (Sharp and Byrne, 2020). Although the dissociation of organic acids associated with DOM will not affect seawater alkalinity directly, their contribution to alkalinity will proportionally decrease the contributions of other seawater constituents, such as those outlined in Table 1. Any discrepancies in TA analysis induced by OrgAlk can potentially propagate errors in subsequent calculated carbonate system parameters (Abril et al., 2015; Hunt et al., 2011; Koeve and Oschlies, 2012), such as pH and pCO_2 . This is pertinent in coastal systems that can be sensitive to slight changes in carbonate chemistry (Hoppe et al., 2012), such as estuaries in colder northern regions that are particularly at risk of acidification due to higher DIC/TA ratios and increased CO_2 solubility (Cai et al., 2020). Evidently, if the nature of carbonate chemistry in coastal systems is to be accurately depicted, analytical interferences and calculation errors associated with OrgAlk must be mitigated. The purpose of this review is to provide an overview of OrgAlk contributions to TA, how it is quantified, as well as discuss the implications of its omission in carbonate system studies conducted in coastal waters. The relationship between OrgAlk and DOC is investigated through the use of coastal and pelagic large scale carbonate system data sets. Furthermore, methods to evaluate, characterise and account for OrgAlk will be discussed.

2. Alkalinity: the oceans innate buffering ability

Although an understanding of inorganic carbon cycling in the ocean began with the development of appropriate analytical methods in the 1960's (Dyrssen and Sillén, 1967), it is only in more recent years that standardised analytical methods have been documented (Dickson et al., 2007). In order to appreciate OrgAlk, it is necessary to have an understanding of the carbonate system in seawater. The inorganic carbon system can be described by four interlinked parameters: TA, DIC, pH, and fCO_2 . By directly measuring two of these four parameters, utilising equilibrium constants specific to the nature of the aquatic system of study, as well as supplying data on temperature, salinity, pressure and specific inorganic seawater constituents, it is possible to calculate the remaining two parameters and obtain accurate information of carbonate chemistry (Zeebe, 2012). Equilibrium constants for the carbonate system exist for a range of aquatic environments, from the open ocean (Lueker et al., 2000) to brackish coastal waters (Cai and Wang, 1998; Millero, 2010). A substantial portion of the inorganic carbon found on Earth is contained within marine water, estimated to be on the order of 38,000 Pg C (Sundquist and Visser, 2003). The collective sum of all aqueous CO_2 ($\text{CO}_2(\text{aq})$), carbonic acid (H_2CO_3), bicarbonate and carbonate is termed total dissolved inorganic carbon, or DIC. As gaseous CO_2 dissolves into solution, the following equilibrium reactions occur:



The dominant species of inorganic carbon present in seawater is a function of pH, temperature and salinity, with total scale pH (pHT) of surface seawater typically around 8.07 (Jiang et al., 2019). At this pH and within the salinity and pressure ranges of most coastal waters, HCO_3^- and CO_3^{2-} are the dominant species (Raymond and Hamilton, 2018). In a simple seawater system such as that described by Wolf-Gladrow et al. (2007), HCO_3^- and CO_3^{2-} are the dominant proton acceptors; proton acceptors being those negatively charged molecules that can assimilate free positively charged protons. As per the conventional definition of TA, proton acceptors are those bases formed from

Table 1
Contribution of various seawater constituents to open ocean TA (modified from Millero (2001)).

Species	% TA
HCO_3^-	89.8
CO_3^{2-}	6.9
$\text{B}(\text{OH})_4^-$	2.9
$\text{Si}(\text{OH})_3^-$	0.2
MgOH^+	0.1
OH^-	0.1
HPO_4^{2-}	0.1

weak acids with a dissociation constant $K \leq 10^{-4.5}$, whereas proton donors are those acids with $K > 10^{-4.5}$ (Dickson, 1981). As TA is defined as the measure of the amount of proton acceptors per kilogram of seawater (Wolf-Gladrow et al., 2007), HCO_3^- and CO_3^{2-} make up the bulk of TA.

TA was expressed solely in terms of the strong base anions that would react with an added strong acid such as HCl (Rakestraw, 1949). The initial model of TA was further refined by the incorporation of the concepts of the proton condition and subsequently the zero level of protons (Butler, 1964). This is a defined neutral position from which the concentration of H^+ can be measured relative to, and is defined by the species of unionised carbonic acid, boric acid, and water (Dickson, 1992). The TA term was further expanded to include other acid-base components of seawater, such as hydrogen sulfate and hydrogen fluoride. This TA term does not incorporate the influence of additional inorganic proton acceptors which can contribute to total TA such as those outlined in Table 1. A revised TA equation (Dickson et al., 2007) can be represented by the following:

$$[\text{TA}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{BO}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] + [\text{minor bases} - \text{minor acids}] \quad (5)$$

Eq. (5) is the conventional expression used to describe TA in seawater and incorporates the contributions of carbonate and non-carbonate acid-base species to TA. It is within this final term “minor bases – minor acids” in which the impact of OrgAlk arises.

3. Organic alkalinity

The suspected influence of organic species on the accurate analysis of carbonate system parameters was initially reported by Goldman and Brewer (1980), who observed that the presence of organic acids excreted by phytoplankton cultures had an influence on measured TA compared to control samples. As previously stated, the presence and influence of organic species is typically omitted in the analysis of TA in open ocean scenarios. The influence of OrgAlk on discrepancies between calculated and directly measured carbonate system data when using non-OrgAlk adjusted TA as an input parameter have been identified, as outlined in Table 2.

The possibility of discrepancies associated with organic alkalinity has led to a recent study of the carbonate system in estuarine waters to not use TA as an input variable (Yao et al., 2020). Several studies have identified sources of OrgAlk to the coastal ocean (Fig. 1).

As coastal waters are heavily influenced by both nutrient and carbon inputs that stimulate the production and remineralisation of organic matter, they play a significant role in the global carbon cycle (Abril et al., 1999; Bozec et al., 2012; Frankignoulle et al., 1998; Neubauer and

Anderson, 2003). Many shallow coastal ecosystems are considered to be net sources of CO_2 due to the remineralisation of terrestrially sourced or autochthonous organic matter (Borges, 2005). In coastal waters, the connection between net metabolism and nutrient dynamics will change the characteristics of carbon exported to littoral zones (Raymond and Bauer, 2000). The aforementioned processes play an important role in the dynamics of the coastal carbonate system and can have a direct impact on TA. For example, the uptake of inorganic nutrient species by photoautotrophs during primary production, organic matter remineralisation and nitrification can influence TA (Wolf-Gladrow et al., 2007). The sign and magnitude of the effect on TA is governed by the charge of the nutrient species as well as the molar ratios at which marine plankton uptake said nutrient species (Redfield et al., 1963).

Most nutrient species present in seawater are negatively charged and so in order to maintain electroneutrality, photoautotrophs exchange charged non-nutrient ions in the appropriate direction to compensate for the uptake of charged nutrient species. The uptake of a negatively charged nutrient species will result in a net negative charge within the

cell, which in turn is balanced by the uptake or release of H^+ or OH^- respectively. Conversely, the uptake of positively charged nutrient species is balanced by release or uptake of H^+ or OH^- respectively. This loss of H^+ or gain of OH^- increases TA, as per 5. The remineralisation of organic matter will release nutrient species and will have the reverse effect of assimilation during primary production. Bacterially mediated nitrification has been observed to cause TA to display non-conservative behaviour, with respect to salinity, in estuarine waters (Frankignoulle et al., 1996). This is due to the nitrification process consuming 2 mol of TA for every 1 mol of nitrate produced. The net change in TA due to the assimilation or release of nutrient species can be seen in Table 3.

4. Measuring organic alkalinity

Many of the existing methods to quantify OrgAlk operate through conventional methods of TA analysis and calculation, or through modified TA analysis procedures, as can be seen in Fig. 2. TA has been studied for decades (Dickson, 1992; Rakestraw, 1949) and thus throughout the years varying methods of analysis have been developed, such as direct titration (Greenberg et al., 1932), potentiometry (Dyrssen, 1965) and spectrophotometry (Brelund and Byrne, 1993; Yang et al., 2015). A significant bolster to TA analysis was the introduction of certified reference materials (CRMs) that enable the calibration and validation of instruments and analysis methods. CRMs for TA have been available since 1996 from Dr. Andrew G. Dickson of Scripps Institution of Oceanography, University of California, San Diego.

There are two best practice methods to produce directly measured TA (TAM) data, both of which are potentiometric titrations (Dickson et al., 2007). The first method involves an incremental addition of strong acid such as HCl to a precisely known volume of seawater within a closed cell. The pH of the reaction is monitored closely by the use of a pH electrode (Millero et al., 1993). TAM is calculated with titrant volume and electromotive force (emf) data through one of two methods; a non-linear least squares curve fitting (NLSF) technique (Dickson, 1981) or a difference derivative method (Hernández-Ayón et al., 1999). These non-purged, closed cell TA titrations allow for the simultaneous determination of DIC. As DIC can be more accurately determined through coulometric methods (Johnson et al., 1985), coulometry is typically the more routine procedure. The second method involves an open cell purged

Table 2

Errors associated with calculated carbonate parameters when using non-OrgAlk adjusted TA as an input parameter.

Input parameters	$p\text{CO}_2$	pH	DIC
TA - DIC	Underestimated ^{a,b,c}	Overestimated ^{c,d}	N/A
TA - pH	Overestimated ^c	N/A	Overestimated ^d

^a Hu (2020).

^b Koeve and Oschlies (2012).

^c Kuliński et al. (2014).

^d Yang et al. (2015).

^e Hunt et al. (2011).

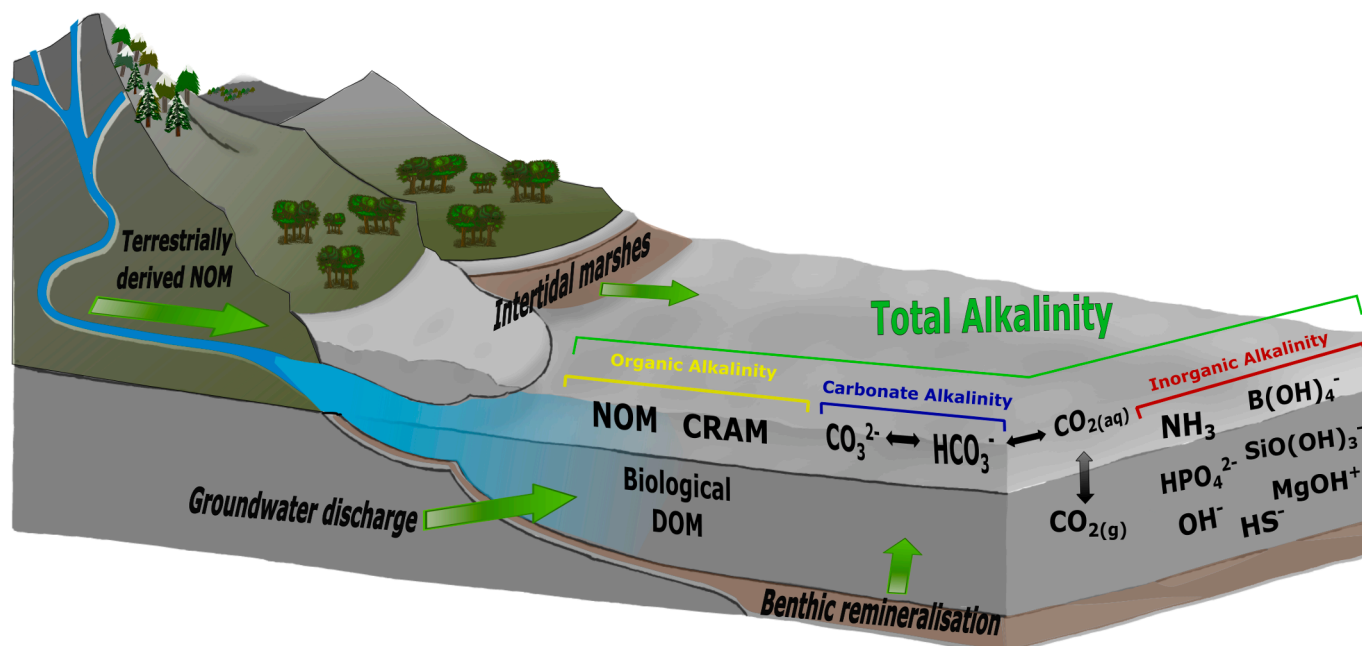


Fig. 1. Simplified diagram illustrating the different components of TA in the coastal ocean; carbonate, inorganic and organic. Green arrows indicate reported sources of OrgAlk, such as intertidal marshes (Cai et al., 1998; Wang et al., 2016), groundwater discharge (Song et al., 2020), terrestrially derived humics (Hunt et al., 2011; Tishchenko et al., 2006) and sediment (Lukawska-Matuszewska, 2016; Lukawska-Matuszewska et al., 2018). NOM - natural organic matter, CRAM - carboxyl rich aliphatic matter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Net change in moles of TA per mole of nutrient assimilated or released (adapted from Wolf-Gladrow et al., 2007).

Nutrient	Assimilation	Release
Sulphate	+2	-2
Phosphate	+1	-1
Nitrate	+1	-1
Nitrite	+1	-1
Ammonia	-1	+1

titration. A single-step addition of strong acid brings the sample to a predetermined pH dependent on suspected alkalinity. Subsequently, CO₂ present in the sample is purged either through sparging with a CO₂ free gas or by stirring. Further incremental acid addition brings sample pH to approximately 3 while pH is continuously measured. Sample pH can be potentiometric or spectrophotometric means (Li et al., 2013). Titration data in the 3.0–3.5 pH range are then used in a NLSF approach to subsequently calculate TAM (Dickson et al., 2003).

In recent years however, concerns over the suitability of potentiometric methods for waters of high dissolved organic material (DOM) concentrations have been raised (Hu et al., 2015; Sharp and Byrne, 2020). The ambiguity which surrounds OrgAlk as a factor impacting the use of TA as an accurate input parameter in carbonate system calculations has been found to vary with the specific method of TA analysis used. In recent work (Sharp and Byrne, 2020), the differences in OrgAlk arising between five different TA analysis methods was investigated. It was found that in a modelled system, the presence of titratable organic molecules elicit responses of differing magnitudes between the different measurement approaches. A notable finding of the study was the apparent unsuitability of open cell multi-step and direct titrations which utilise modified Gran function (MGF) or NLSF techniques when compared to other TA measurement methods in the presence of organic molecules with pK < 6. This is significant as numerous studies have linked this pK range with carboxyl functional groups of DOM present in marine and fluvial waters (Hertkorn et al., 2006; Masini et al., 1998; Muller and Bleie, 2008; Paxéus and Wedborg, 1985; Perdue et al., 1980).

As open cell titrations allow for the incorporation of a back titration procedure to measure OrgAlk, open cell methods may prove beneficial in future investigations.

5. Calculated OrgAlk

TAM is non-discriminatory and incorporates all proton acceptors formed from weak acids, regardless of inorganic or organic nature. Organic molecules that have titratable functional groups with pK values within the titration pH range of the specific analysis method will exert an influence on TA. Using two other carbonate parameter data and software programs that contain accurate carbonate system thermodynamic constants, such as the multi-platform CO₂SYS software program (Lewis and Wallace, 1998), it is possible to calculate alkalinity (TAC). Contributions from organic proton acceptors are not included in TAC and it is assumed that TAC accounts only for the protolytes present in Eq. (5). OrgAlk values are calculated as the difference between TAM and TAC, such that:

$$[OrgAlk_C] = [TAM] - [TAC] \quad (6)$$

This method for calculating OrgAlk has been used by numerous investigators (Delaigue et al., 2020; Hammer et al., 2017; Hernández-Ayon et al., 2007; Kim and Lee, 2009; Kuliński et al., 2014; Patsavas et al., 2015; Song et al., 2020). It is important to note that OrgAlkC values obtained through this method are inherently inclusive of any residual errors associated with TAC, possibly leading to errors in the sign and magnitude of OrgAlkC. These residual errors are likely responsible for the negative OrgAlk values displayed in Figs. 3–5, which were constructed utilising multiple coastal and oceanic carbonate system data products to illustrate relationships between OrgAlk, salinity, DOC and TA, see details below. The residual errors associated with TAM minus TAC are generally attributed to errors in input parameters or with the thermodynamic models which relate them (Fong and Dickson, 2019). TAC errors may be more pronounced in low salinity coastal waters where carbonate system thermodynamic constants have not been as rigorously evaluated (Woosley, 2021). This could translate to large errors in OrgAlkC values observed in lower salinity waters compared to

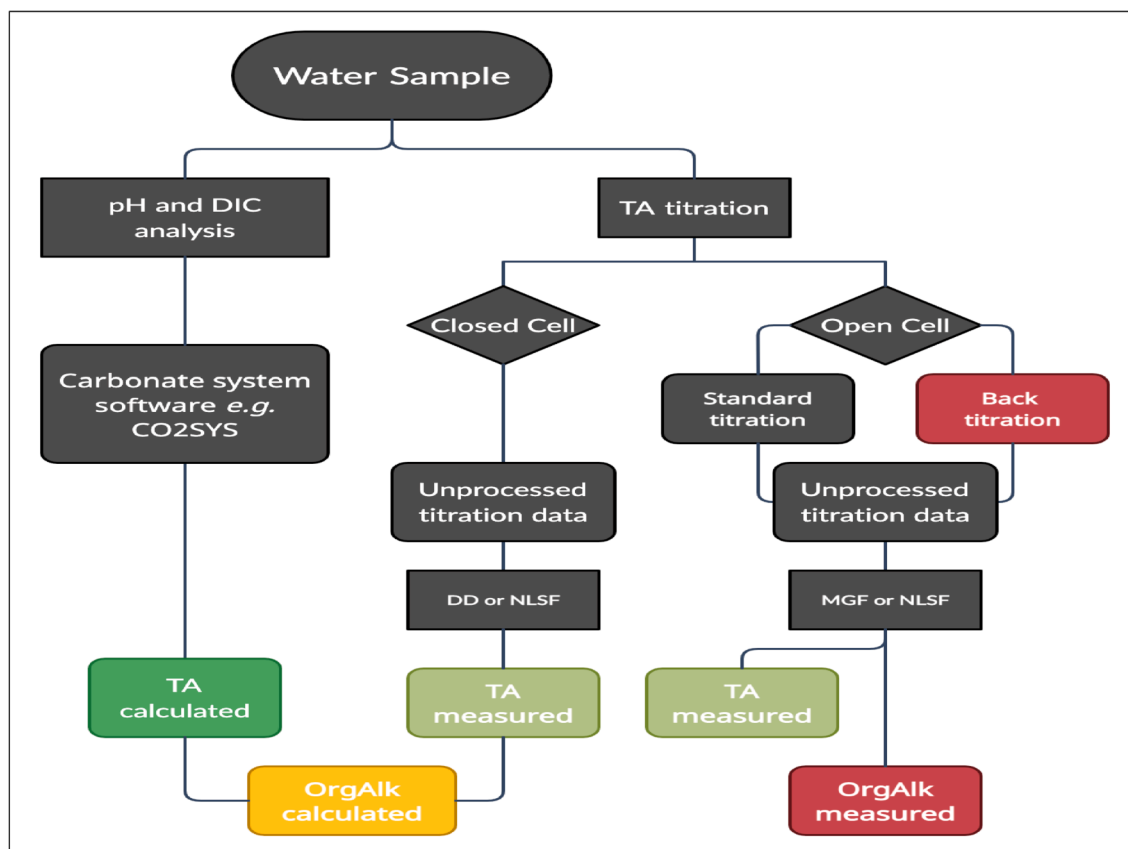


Fig. 2. Flowchart illustrating possible routes for OrgAlk determination. OrgAlk calculated is defined as TA measured minus TA calculated. Calculated OrgAlk values obtained through this method are inherently inclusive of any residual errors associated with calculated TA as well as discrepancies with the carbonate system thermodynamic equilibrium constants used. Note, DD - direct derivative, MGF - modified Gran function, NLSF - non-linear least squares function.

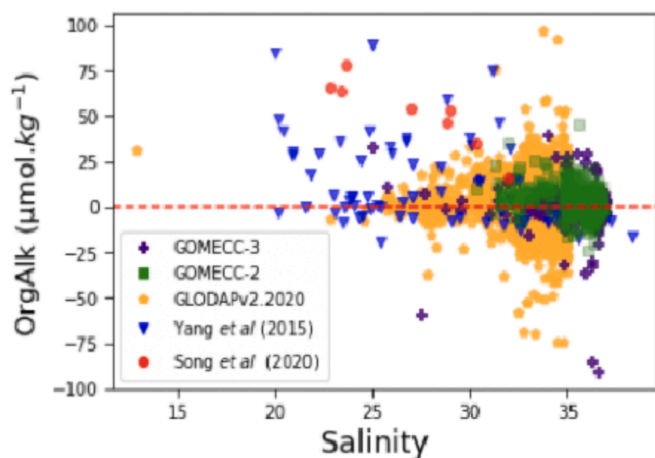


Fig. 3. OrgAlk expressed as a function of salinity for each dataset utilised. OrgAlk_C is reported for all datasets except Song et al. (2020) where OrgAlk_M was reported as OrgAlk directly measured through back titration methods.

those in more saline waters. The carbonate system thermodynamic constants that describe the solubility of CO₂ and dissociation of carbonate species in seawater as a function of temperature and salinity have been determined in a number of studies (Lueker et al., 2000; Millero, 2010; Prieto and Millero, 2002; Woosley, 2021). Each set of constants have their own uncertainties, therefore the specific choice of constants used in carbonate system calculations can introduce bias. Similarly, the choice of constants associated with carbonate system calculations such as the dissociation constants for boric, hydrofluoric, phosphoric and to a minor degree sulfuric acid (Woosley, 2021) can also introduce bias. The

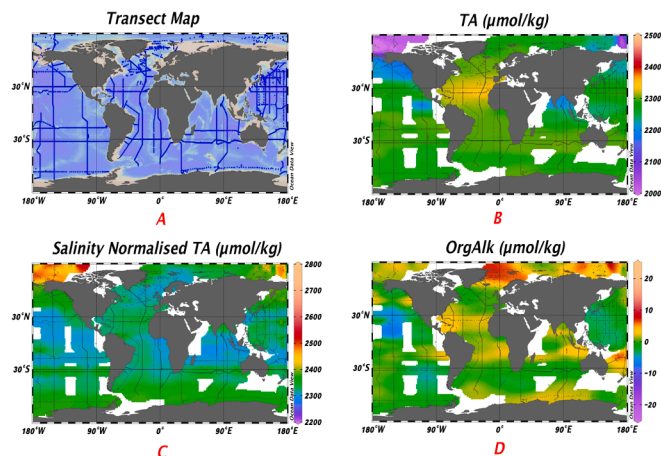


Fig. 4. Surface plots of the GLODAPv2.2020 data product illustrating (a) hydrographic cruises data were taken from (b) TA concentrations, (c) TA normalised to a salinity of 35 and (d) OrgAlk calculated using Eq. (6).

presence of OrgAlk in seawater has been hypothesised as a potential factor in the disparity between directly measured and calculated carbonate system parameters in studies investigating carbonate thermodynamic inconsistency issues (Fong and Dickson, 2019; Millero et al., 2002; Patsavas et al., 2015).

6. Measured OrgAlk

OrgAlk can also be directly measured (OrgAlk_M) by means of back titration (Cai et al., 1998), with this method used and modified in a number of studies (Hunt et al., 2011; Ko et al., 2016; Muller and Bleie,

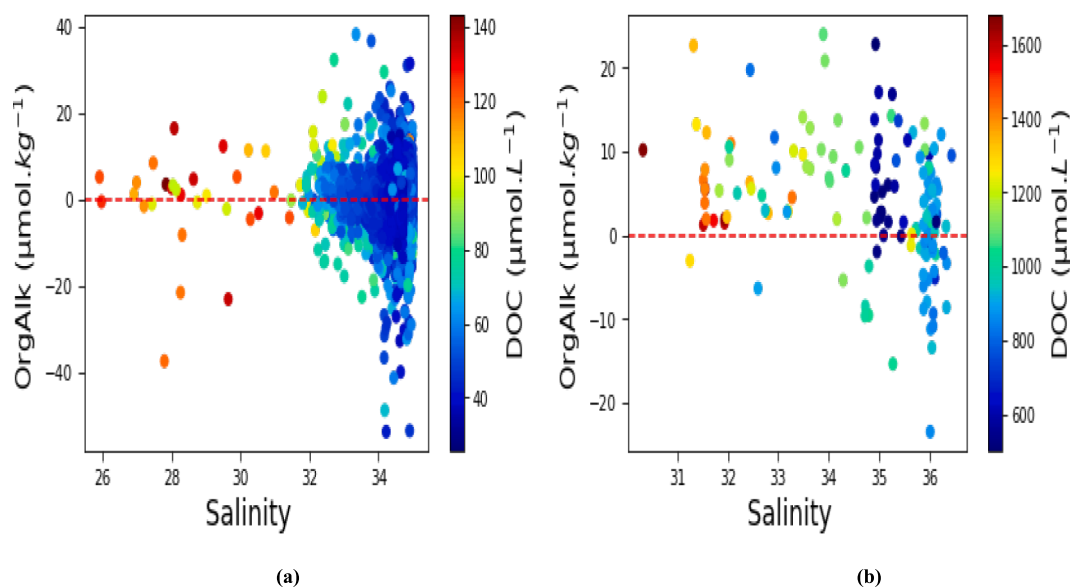


Fig. 5. Calculated OrgAlk values as a function of salinity for (a) GLODAPv2.2020 and (b) GOMECC-2. A positive skew in OrgAlk distributions is observed in less saline waters which coincides with increased DOC concentrations, whereas distributions are largely normal in more saline waters.

2008; Yang et al., 2015). Back titrations are carried out after TA titrations have taken place, thus all carbonate associated TA has been removed. The sample is kept under a N₂ atmosphere to prevent CO₂ invasion and returned to its original pH using a CO₂ free NaOH solution. Re-titration with HCl ensues, with the resultant alkalinity value attributed to OrgAlk_M, minus the contributions of non-carbonate species present. Importantly, as OrgAlk_M is a directly obtained value it should be free from the aforementioned residual errors associated with OrgAlk_C. Good agreement has been found between OrgAlk_M by back titration methods and OrgAlk_C in phytoplankton cultures, although for field samples the agreement was not as pronounced (Ko et al., 2016). Other studies report no strong statistical relationship between OrgAlk_M and OrgAlk_C observed in field samples (Song et al., 2020). Disparity between OrgAlk_M by back titration methods and OrgAlk_C calculated from pH and DIC can potentially be attributed to the bias in chosen carbonate system thermodynamic constants and associated acid-base system constants. Furthermore, in the case of Song et al. (2020), interference to spectrophotometric pH measurement associated with the potential impact of coloured and fine particulate materials could cause errors in pH as an input parameter to TAC and thus OrgAlk_C. More similarity between OrgAlk_M and OrgAlk_C was observed in samples with noticeably less coloured and fine particulate materials (Song et al., 2020). Back titration methods have recently been recommended for implementation on future hydrographic research cruises in order to characterise OrgAlk in spatially heterogeneous oceanic waters (Sharp and Byrne, 2020). The utilisation of back titration methods in studies which overdetermine the carbonate system would glean insights into the magnitude of effect of OrgAlk on the internal consistency of marine carbonate system measurements.

7. Evidence of OrgAlk

Publicly available data sources, such as the Global Ocean Data Analysis Project (GLODAP) (Lauvset et al., 2016; Olsen et al., 2016), and the various Gulf of Mexico and East Coast Carbon Cruises (GOMECC-2, GOMECC-3) (Barbero et al., 2019; Wanninkhof et al., 2012) provide quality controlled information on core oceanic biogeochemical variables and present the opportunity for exploratory investigations of OrgAlk. Any data for which TA along with two other carbonate system parameters have been measured simultaneously allow for the calculation of OrgAlk as per Eq. (6). Based on this, the GLODAPv2.2020, GOMECC-2 and GOMECC-3 data products were filtered to include data for which

DIC, TA, pHT, phosphate and silicate, along with key physiochemical variables were simultaneously and directly measured. TA was then calculated using DIC and pHT as the input parameters through pyCO₂-SYS version 1.6.0 (Humphreys et al., 2020). The carbonate equilibrium constants of Lueker et al. (2000), bisulfate dissociation constant of Dickson (1990) and borate to salinity ratio of Lee et al. (2010) were used throughout all carbonate system calculations. Additionally, the reported calculated OrgAlk and directly measured OrgAlk values were included from the works of Yang et al. (2015) and Song et al. (2020) respectively. The generated and reported OrgAlk_C values were used to illustrate the distributions of OrgAlk in coastal and pelagic zones, as well as investigate the relationship between OrgAlk and organic carbon as shown in Figs. 3–5.

In Fig. 3 OrgAlk values appear normally distributed around 0 μmol.kg⁻¹ in more saline waters. In less saline freshwater influenced waters OrgAlk appears skewed toward positive values. This could be attributed to fluvially discharged organics contributing to OrgAlk in coastal waters with mixing then occurring, subsequently diminishing the OrgAlk signal. Conservative mixing of OrgAlk was indicated in laboratory experiments involving the dilution of organic rich Baltic seawater (Ulfsbo et al., 2015). Furthermore, simulated models have shown that as mixing occurs OrgAlk becomes relatively conservative with respect to salinity (Cai et al., 1998; Hu, 2020).

As OrgAlk is associated with the presence of DOM, oceanic areas that receive inputs of terrestrially derived or autochthonously produced DOM may exhibit significant organic contributions to TA. This is evident in the upper Arctic and tropical ocean zones, as can be seen in Fig. 4. The Arctic Ocean is subject to high DOM loadings arising from fluvial inputs (Cooper et al., 2005; Stedmon et al., 2011), and displays elevated OrgAlk_C values as seen in Fig. 4. It is important to note that the CO₂ system constants and coefficients used for calculation can have spatial biases that can result in larger differences between measured and calculated TA values, and thus OrgAlk_C. It is possible that the higher OrgAlk_C values observed in Arctic waters are due to high DOM inputs. Furthermore, distinct changes in Arctic DOC export have been linked to seasonal cycles (Kaiser et al., 2017), suggesting that OrgAlk may play a more pronounced role in Arctic waters at times of elevated discharge. Here DOC refers to the fraction of DOM that specifically relates to the mass of carbon in the dissolved material. Similarly, the tropics are areas of intense riverine DOC discharge, accounting for 55–62% of the global riverine DOC export (Dai et al., 2012; Li et al., 2017). Although there is not as noticeable an OrgAlk signal associated with the large freshwater

discharge of the Amazon River this could be due to the characteristics of DOM transferred, as the impacts of OrgAlk attributed to DOM have been found to vary spatially across transitional waterbodies (Song et al., 2020).

8. DOM as a contributor to OrgAlk

The magnitude of OrgAlk appears greater in littoral zones due to massive riverine and groundwater discharges of allochthonous organics (Gattuso et al., 1998; Romankevich, 1984). The predominant source of DOM to the coastal ocean arises from riverine inputs that contribute an estimated 0.25 Gt DOC y^{-1} (Cauwet, 2002; Hedges et al., 1997). Although rivers represent a main source of DOM, intertidal salt marshes (Pakulski, 1986; Sousa et al., 2017), autochthonous production by phytoplankton (Hernández-Ayon et al., 2007; Kim and Lee, 2009; Ko et al., 2016) as well as exchanges with adjacent coastal waters (Bianchi, 2007) are all potential sources. As TA_M in coastal waters has been observed to be consistently higher than TA_C (Patsavas et al., 2015), the presence of organic bases in lower salinity coastal waters may present an additional fraction of TA unaccounted for by TA_C . Furthermore, OrgAlk values of up to 45 $\mu\text{mol.kg}^{-1}$ have been attributed to terrigenous organic matter (Tishchenko et al., 2006), indicating evidence of the influence of terrestrial inputs of organics on TA in coastal waters. Although many studies indicate positive OrgAlk values across a range of aquatic environments (Table 4) negative OrgAlk values, ranging from -49 to -18 $\mu\text{mol.kg}^{-1}$, likely associated with humic acids originating from groundwater discharge have been reported (Delaigue et al., 2020). As can be seen in Fig. 5b, higher DOC concentrations are observed in less saline waters, with this coinciding with positively skewed OrgAlk values. This is also observable but to a smaller degrees in Fig. 5a.

DOM in transitional waters is a complex amalgam of both aromatic and aliphatic hydrocarbons that can possess charged functional groups (Leenheer and Croué, 2003). It is well established that terrestrially derived DOM is more aromatic (including lignin) and contains more carboxyl and hydroxyl functional groups than marine DOM (Lam et al., 2007; McCaul et al., 2011; Sleighter and Hatcher, 2008). Carboxyl and phenolic hydroxyl functional groups are thought to be the largest contributors to the acidity of humic substances (Perdue et al., 1980), and display a continuum of pK values within the pH range of TA titrations (Lodeiro et al., 2020; Ritchie and Perdue, 2003). The largest fraction of DOM in the riverine environment is humic in nature (Cauwet, 2002) with the OrgAlk associated with humic-like structures an important fraction of river water buffering capacity, representing 13–66% of TA in some river systems (Hunt et al., 2011). Furthermore, the identification through nuclear magnetic resonance spectroscopy of carboxylic acid groups in carboxyl rich aliphatic matter (CRAM) (Hertkorn et al., 2006; Woods et al., 2010), which comprises a major fraction of refractory

DOC, presents a possible candidate for oceanic OrgAlk (Fong and Dickson, 2019). Functional groups of CRAM with pK_a values ranging from 4.5–6 can contribute significantly to OrgAlk as their basic forms comprise <95% of their total concentration at seawater pH (Fong and Dickson, 2019).

Several studies have observed that OrgAlk increases can be attributed to increases in DOM concentration: in phytoplankton incubation investigations (Kim and Lee, 2009), in natural samples spiked with DOM (Kuliński et al., 2014), in modelled scenarios (Sharp and Byrne, 2020), in coastal seawater (Song et al., 2020) and in sediment pore waters (Lukawska-Matuszewska et al., 2018). Delineation of the relationship between OrgAlk and DOM concentration can only be achieved for organic molecules that have titratable functional groups with pK values within the titration pH range of the specific analysis method. Consistently higher concentrations of DOC in the inner estuaries of several European river systems compared to the marine water they enter have been observed, with DOC concentrations ranging from 55 to 600 μM (Middelburg and Herman, 2007). Consequently, the magnitude of OrgAlk associated with DOM may be accentuated in transitional waterbodies as these systems serve as points of transference between the terrestrial and marine environments (Canuel et al., 2012). It has been found that the magnitude of the impact of OrgAlk attributed to DOM can vary spatially across transitional waterbodies (Song et al., 2020). Mixing of different waterbodies in estuaries appear to be the main factor governing observed DOM characteristics along estuarine gradients (Asmala et al., 2016). Processes such as photochemical and microbial degradation may also impact the organic molecules associated with OrgAlk (Fichot and Benner, 2014). The chemical diversity of DOM has been observed to increase as an aqueous matrix becomes more marine in nature, possibly due to the array of DOM degradation products and influence of autochthonously produced cellular materials (Sleighter and Hatcher, 2008; Zark and Dittmar, 2018).

9. Microbiological associated OrgAlk

In addition with the impact of terrestrially derived organics, as coastal areas are typically sites of intense biological activity, autochthonous organic material can also factor into OrgAlk (Muller and Bleie, 2008). It has been reported that microbiologically produced DOM can have significant contributions to TA (Hernández-Ayon et al., 2007; Kim et al., 2006; Ko et al., 2016). Phytoplankton are known to produce DOM by extracellular excretion (Biddanda and Benner, 1997; Jiao et al., 2010), typically constituting 5 to 30% of their total primary production (Karl et al., 1998), some of which may possess charged functional groups and thus factor in to TA. Incubation studies conducted on three different phytoplankton species (*P. minimum*, *S. costatum* and *C. curvisetus*) indicated that measured OrgAlk was directly related to phytoplankton DOM

Table 4

Contributions of OrgAlk to TA as well as analysis method employed in studies of the carbonate system across various aquatic systems.

Contribution to TA ($\mu\text{mol.kg}^{-1}$)	OrgAlk source	OrgAlk method	Sample matrix	Reference
1–6	Bacteria	Filtration	Coastal seawater	Kim et al. (2006)
0–4	Plankton			
~ 40	Phytoplankton	Calculated	Coastal seawater	Kim and Lee (2009)
< 45	Terrigenous organic matter	Calculated	Coastal seawater	Tishchenko et al. (2006)
160–220	Organic acids	Calculated	River water	Hunt et al. (2011)
~ 56	Organic acids	Calculated	Coastal seawater	Hammer et al. (2017)
14–109				
100–190	Phytoplankton DOM	Calculated	Coastal seawater	Hernández-Ayon et al. (2007)
20–75				
8–73	Organic acids	Calculated	Coastal bottom waters	
2–2953	Organic acids	Calculated	Coastal sediment pore waters	Lukawska-Matuszewska (2016)
104–1505	Organic acids	Calculated	Coastal sediment pore waters	Lukawska-Matuszewska et al. (2018)
22–58	Organic acids	Calculated	Coastal seawater	Kuliński et al. (2014)
≤ 50	Organic acids	Back titration	Estuarine water	Cai et al. (1998)
34 ± 7		Back titration		
32 ± 8	Organic acids	Calculated	Coastal water	Song et al. (2020)
–49 to –18	Humic acids	Calculated	Fjord water	Delaigue et al. (2020)

production, with an organism dependent effect observed (Kim and Lee, 2009). DOM associated OrgAlk produced by phytoplankton has been observed in similar incubation studies (Hernández-Ayon et al., 2007; Kim et al., 2006; Ko et al., 2016; Muller and Bleie, 2008). OrgAlk has displayed a seasonality in surface waters of the Baltic Sea corresponding to Spring bloom events (Hammer et al., 2017), further alluding to the relationship between OrgAlk and phytoplankton produced DOM.

Negatively charged functional groups present on bacterial and phytoplankton cell walls have also been observed to contribute to TA (Kim et al., 2006). These charged functional groups acquire a charge through dissociation and protonation reactions (González-Dávila, 1995). Subsequently, the presence of both positively and negatively

(Fassbender et al., 2018). Direct means of assessing OrgAlk are beneficial in ensuring quantification is as accurate as possible, and free from the errors inherent to OrgAlk_C. Furthermore, direct methods can allow investigators to better ascertain the acid-base characteristics of DOM associated with OrgAlk. Characterisations of the DOM charge groups in a water sample and their associated dissociation constants can be carried out by performing titrations with NaOH. This method of OrgAlk acid-base characterisation can readily be implemented with the same experimental set up as the aforementioned back titration methods to quantify OrgAlk. Using the model of Cai et al. (1998) as adapted by Yang et al. (2015), the dissociation constants of weak organic acids can be ascertained as follows:

$$V_0 \sum_i \frac{X_{iT}}{1 + \frac{[H^+]_T}{K_i}} + V_0 \frac{B_T}{1 + \frac{[H^+]_T}{K_B}} + V_0 \frac{P_T}{1 + \frac{[H^+]_T}{K_P}} + V_0 \frac{Si_T}{1 + \frac{[H^+]_T}{K_{Si}}} - (V_0 + v) \left([H^+]_T - \frac{K'_w}{[H^+]_T} \right) - vC_{HCl} + V_0 \frac{K'_w}{C_H^0} \quad (7)$$

charged functional groups implies a changing net charge, depending on matrix pH (Van Der Wal et al., 1997). The consensus that negatively charged functional groups are predominant over positively charged groups in microbial cell walls is widely accepted (Corpe, 1970; Terayama, 1954). The proton binding capabilities of these functional groups in acidic conditions has been attributed to carboxyl groups (Carstensen and Marquis, 1968). Although recognised as a potential source of OrgAlk, the contributions to TA from bacterial and phytoplankton cell walls are typically small, reported values being between of 1–6 and 0–4 $\mu\text{mol.kg}^{-1}$ respectively (Kim et al., 2006; Ko et al., 2016).

10. Characterising and accounting for OrgAlk

10.1. OrgAlk correction factors

Methods to directly account for OrgAlk in TA calculations have been investigated. Millero et al. (2002) observed that when accounting for a constant amount of organic acids (8 $\mu\text{mol.kg}^{-1}$) and including a single term for an organic acid with a pK_a of 4, discrepancies between calculated and directly determined fCO_2 were lower compared to computed values that omitted the inclusion of the organic acid term. The chosen pK_a of 4 falls within the broad distribution of pK_a values reported for carboxylic acid functional groups on humic and fulvic substances (Masini, 1994; Paxéus and Wedborg, 1985). When accounting for this organic acid, the range was consistent with the uncertainty in computed values resulting from stated uncertainties in the measurements of DIC and TA. Similar bulk corrections to bring directly measured values for carbonate parameters in line with calculated values have been undertaken in related studies (Fong and Dickson, 2019; Patsavas et al., 2015). Comparisons of suggested OrgAlk correction values of 2.4–7.3 $\mu\text{mol.kg}^{-1}$ (Fong and Dickson, 2019) are in agreement with the estimated concentration of carboxylic acids present in CRAM (~ 3 –5 $\mu\text{mol.kg}^{-1}$) (Hertkorn et al., 2013). These methods are applicable only in the post processing correction of large scale data sets and do not offer direct information on OrgAlk. As coastal DOM is a spatially and temporally heterogeneous mixture of terrestrial, autochthonous and marine derived organic materials, the quantity of and acid-base characteristics of OrgAlk may prove too varied to accurately apply post processing corrections.

10.2. Acid-base characteristics of OrgAlk

Discrepancies between OrgAlk_C and OrgAlk_M have been reported to be as large as 8 $\mu\text{mol.kg}^{-1}$ (Yang et al., 2015), and in some cases OrgAlk_C concentrations are not statistically distinguishable from zero

where K_b , K_B , K_P and K_{Si} are the dissociation constants of a weak organic acid X_b , boric acid, phosphate, and silicic acid and X_{iT} , B_T , P_T and Si_T are the total concentrations of organic acid, borate, phosphate and silicate. K'_w is the ion product of seawater, v is the volume of HCl titrant, and V_0 is the volume of sample titrated with NaOH. C_{HCl} and C_H^0 are the concentrations of HCl titrant and hydrogen ion concentration after titration with NaOH, respectively. The values of K_i and C_H^0 are obtained through non-linear least squares fitting techniques. This method allows for the identification of the pK_a values of functional groups on DOM which exert an influence during TA titration.

Another approach to incorporate the contribution of OrgAlk and to minimise subsequent errors in carbonate system calculations was developed by Kuliński et al. (2014) who included a bulk pK value for the acid-base species in DOM (pK_{DOM}). This procedure requires DOC concentrations to be known along with OrgAlk values. By assuming that organic acids (HOrg) present in DOM behave like a weak monoprotic acid, the dissociation constant of said acid can be determined by:

$$K_a = \frac{[H^+][Org^-]}{[HOrg]} \quad (8)$$

Previous work have indicated that the titratable groups associated with DOM can occur in concentrations exceeding that of OrgAlk itself, and that the contribution of DOM to OrgAlk is not quantitative (Muller and Bleie, 2008). This is acknowledged as the fraction of DOM, f , which acts as an acid-base species. Subsequently, Eq. (8) is modified to:

$$K_{DOM} = \frac{[H^+][OrgAlk]}{(f \cdot DOC) - [OrgAlk]} \quad (9)$$

OrgAlk is then defined by:

$$OrgAlk = \frac{K_{DOM} \cdot f \cdot DOC}{[H^+] + K_{DOM}} \quad (10)$$

This method was developed and implemented by Kuliński et al. (2014) and returned a pK_{DOM} of 7.53 and an f value of 0.14 for Baltic seawater. The deviation reported between OrgAlk_C and OrgAlk calculated using Eq. (10) was $\leq 2 \mu\text{mol.kg}^{-1}$. Similar methodology has been applied to further studies of OrgAlk in the Baltic Sea (Hammer et al., 2017), where similar pK_{DOM} and f values were reported, 7.27 ± 0.11 and 0.17 ± 0.02 respectively.

The data produced by Kuliński et al. (2014) was further explored through the use of humic ion-binding model (Tipping et al., 2011) coupled to a specific ion interaction model (Pitzer, 1991) to investigate the contribution of OrgAlk (Ulfsbo et al., 2015). Returned f values of 0.125 show good agreement with the revised f value of 0.12 obtained by

Kuliński et al. (2014), indicating that proton-binding models may be another possible method to characterise OrgAlk.

The aforementioned bulk pK_{DOM} methods are spatiotemporally specific, as the fixed fraction of DOM which exhibits acid-base characteristics during alkalinity titrations has recently been indicated to vary substantially with location and time in coastal waters (Song et al., 2020). DOM characteristics can be drastically modified along estuarine gradients (Asmala et al., 2016; Zhou et al., 2020) and can change with temporal cycles as frequent as tidal (Santos et al., 2009; Tzortziou et al., 2008). Furthermore, coastal systems are subject to loadings of DOM that are specific to the nature of their hydrological and geographic setting. Thus as the acid-base characteristics of DOM will change, the appropriate pK_{DOM} and *f* values will likely vary accordingly. However, it is worth noting that as the components of deep-sea DOM are more universal in nature compared to more site specific DOM of individual biomes (Zark and Dittmar, 2018), a bulk pK_{DOM} term may be applicable to waters with DOM of more uniform characteristics and constant concentration.

11. Recommendations

11.1. Filtration as an inherent step in OrgAlk analysis

Best practice methods for the analysis of carbonate chemistry in the open ocean typically assume filtration is not required (Dickson et al., 2007). Filtration of samples taken from coastal waters is necessary to mitigate interference from high biomass and heavy particulate loads that may interfere with carbonate chemistry analysis. Published methods detail acceptable methods of filtration for TA, pH and DIC analysis (Bockmon and Dickson, 2014), and employ 0.45 µm pore size filters. Such filtration methods should be implemented in studies of OrgAlk as interferences in DIC or pH analysis arising from the presence of particulates can cause inaccuracies in OrgAlk_C (Song et al., 2020). Furthermore, if back titrations or similar are to be pursued, samples for OrgAlk_M determination should be filtered to remove particulates, as particulate organic matter has been shown to contribute non-negligible amounts to TA (Kim et al., 2006). As some studies characterise OrgAlk as a function of DOC (Hammer et al., 2017; Kuliński et al., 2014) yet do not filter samples for TA analysis, the contribution from particulates may be erroneously attributed to DOC and thus lead to overestimations of true OrgAlk values. The incorporation of a filtration step would allow for the characterisation of DOM associated OrgAlk and for direct comparisons with DOC qualitative and quantitative analysis methods. Filter pore size used would depend on the nature of the study, with smaller pore sizes of 0.2 µm used in the characterisation of marine and coastal DOM (Benner et al., 1992; Shimotori et al., 2016).

11.2. Complementary spectroscopic DOM analysis

A possible route by which OrgAlk can be characterised is by linking it to the spectral characteristics of DOC. DOC is routinely measured through wet or high temperature oxidation with subsequent non-dispersive infra-red detection of liberated CO₂. Spectroscopic methods have also been utilised to estimate and characterise DOC in both terrestrial and coastal waters (Carter et al., 2013; Fichot and Benner, 2011). Although susceptible to errors which can be minimised with reparameterization using locally generated data, an advantage inherent to spectroscopic estimations of DOC concentration is that it also offers insights into DOC characteristics (Chin et al., 1994; Helms et al., 2009; Weishaar et al., 2003). Thus, qualitative data on DOM composition derived from such procedures coupled with directly obtained information on the acid-base characteristics of OrgAlk can potentially establish approximate associations between spectral DOM characteristics and pK_{DOM} values. Performed in numerous coastal ecosystems that have similar hydrographic and climatic features, this could allow for the use of ecosystem specific spectral linked bulk pK_{DOM} values. As the content

and characteristics of carboxylic groups in humic substances from a diverse range of systems exhibit only small variations (Huizenga and Kester, 1979; Oliver et al., 1983), coastal areas in which terrestrial organics account for the major share of OrgAlk may be particularly suited to bulk pK_{DOM} utilisation. Furthermore, the acid-base properties of humic substances are not thought to undergo significant alterations arising from changes in matrix ionic strength (Masini, 1994), indicating that bulk humic pK values may be applicable across the ionic strength range in estuarine environments. However, as coastal systems are also subject to autochthonous loadings of DOM through microbiological production, humic like DOM constitutes only a portion of the potential organic contributors to TA. Given the vast array of TA and OrgAlk methodologies available as well as the heterogeneity of coastal DOM, characterising the acid-base properties of OrgAlk is a challenging task.

12. Conclusion

It appears that the remarks of Bradshaw et al. (1981) regarding the presence of unknown protolytes are still reiterated in contemporary research. The recent reevaluation of inconsistencies in carbonate system data from several hydrographic research cruises and subsequent attribution of these discrepancies to the likely influence of OrgAlk reinforces the significance of this alkalinity fraction. The share of TA which is constituted by OrgAlk appears to be larger in littoral zones that are subject to increased loadings of terrestrially discharged DOM. Evidence of a small yet tangible influence of OrgAlk on pelagic TA continues to grow. As the contributions to TA from minor acid-base species in pelagic waters are oftentimes deemed negligible, these findings further reinforce the importance of accounting for OrgAlk. As discussed, there is a growing consensus that neglecting to account for the contribution of OrgAlk when using TA as an input parameter can lead to miscalculation of the remaining carbonate system parameters, as well as important descriptors of the carbonate system such as calcite and aragonite saturation states. Miscalculations of these descriptors can lead to gross misrepresentations of the characteristics of the carbonate system in littoral areas sensitive to slight perturbations in carbonate chemistry. In order to fully account for the impact of OrgAlk, the concentrations, characterisations and associated pK values of the proton accepting portion of DOM must be accurately known. As seasonal events as well as tides can affect DOM characteristics and quantity, the acid-base characteristics attributed to OrgAlk associated molecules may vary accordingly with these cycles. If approaches such as the inclusion of OrgAlk terms in carbonate chemistry calculations are to be pursued, this would require the systematic description of general DOM concentrations and acid-base characteristics in coastal waters with respect to salinity, seasonal and trophic state of a system. Given the heterogeneity in concentration and equilibrium behaviour of OrgAlk components, the inclusion of OrgAlk terms in carbonate system calculations remains a demanding challenge. Given this, the suitability of TA as an appropriate parameter in the derivation of remaining carbonate system parameters in waters subject to enhanced OrgAlk loadings remains questionable, unless matters to incorporate its influence are carried out.

Declaration of Competing Interest

None.

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