Aquatic Geochemistry
https://doi.org/10.1007/s10498-020-09375-x

ORIGINAL ARTICLE

Effect of Organic Alkalinity on Seawater Buffer Capacity: A Numerical Exploration

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Received: 18 September 2019 / Accepted: 9 April 2020

Abstract

Organic alkalinity is a poorly understood component of total titration alkalinity in aquatic environments. Using a numerical method, the effects of organic acid (HOA) and its conjugate base (OA^-) on seawater carbonate chemistry and buffer behaviors, as well as those in a hypothetical estuarine mixing zone, are explored under both closed- and open-system conditions. The simulation results show that HOA addition leads to pCO_2 increase and pH decrease in a closed system when total dissolved inorganic carbon (DIC) remains the same. If opened to the atmosphere ($pCO_2 = 400$ µatm), CO_2 degassing and re-equilibration would cause depressed pH compared to the unperturbed seawater, but the seawater buffer to pH change $\left(\beta_{DIC} = \left(\frac{\partial \ln([H^+])}{\partial DIC}\right)^{-1}\right)$ indicates that weaker organic acid (i.e., higher pK_a) results in higher buffer capacity (greater β_{DIC}) than the unperturbed seawater. In comparison, OA^- (with accompanying cations) in the form of net alkalinity addition leads to pCO_2 decrease in a closed system. After re-equilibrating with the atmosphere, the resulting perturbed seawater has higher pH and β_{DIC} than the unperturbed seawater. If river water has organic alkalinity, pH in the estuarine mixing zone is always lower than those caused by a mixing between organic alkalinity-free river (at constant total alkalinity) and ocean waters, regardless of the pK_a values. On the other hand, organic alkalinity with higher pK_a provides slightly greater β_{DIC} in the mixing zone, and that with lower pK_a either results in large CO_2 oversaturation (closed system) or reduced β_{DIC} (in mid to high salinity in the closed system or the entire mixing zone in the open system). Finally, despite the various effects on seawater buffer through either HOA or OA^- addition, destruction of organic molecules including organic alkalinity via biogeochemical reactions should result in a net CO_2 loss from seawater. Nevertheless, the significance of this organic alkalinity, especially that comes from organic acids that are not accounted for under the currently recognized "zero proton level" (Dickson in Deep Sea Res 28:609–623, 1981), remains unknown thus a potentially interesting and relevant research topic in studying oceanic alkalinity cycle.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10498-020-09375-x) contains supplementary material, which is available to authorized users.

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Keywords Organic alkalinity · Buffer · Carbonate chemistry · Ocean acidification

1 Introduction

Numerous studies (e.g., Hagens et al. 2014; Hofmann et al. 2010) have investigated the responses of the seawater acid–base buffer system to environmental perturbations such as the ocean acidification following the classic work by Revelle and Suess (1957). As pH is the "master variable" in the seawater media (Jourabchi et al. 2005) and can be measured directly, determining how proton concentration changes as a result of ocean acidification has been one of the focal points in numerous studies (Egleston et al. 2010; Frankignoulle 1994; Hagens and Middelburg 2016; Hofmann et al. 2010). Therefore, elucidating the buffer mechanisms that control the magnitude of proton concentration changes due to biogeochemical reactions is important for understanding the seawater acid–base properties under the changing ocean conditions.

Among the many acid–base pairs that contribute to seawater buffer under normal oxic conditions, carbonate, borate, and nutrients (ammonia, phosphate, and silicate) have been studied extensively and are well documented (Hagens and Middelburg 2016). It is known that the carbonate species (HCO_3^- and CO_3^{2-}) contribute the most to the buffer capacity in seawater and borate ($B(OH)_4^-$ and H_3BO_3) follows (Stumm and Morgan 1995). With the exception of anoxic environments (sediment porewater or water column in anoxic basins), nutrients and sulfide do not provide significant buffer (Ben-Yaakov 1973; Boudreau and Canfield 1993). In addition to the inorganic acid–base pairs, organic acids, their dissociation products (the conjugate bases of organic acids are considered as organic alkalinity), plankton, and bacteria cells have all been proposed to provide buffer in seawater (Kim et al. 2006). Hence, while the global oceans are under the threat of ocean acidification, organic alkalinity is also proposed to provide additional buffer, at least in the coastal ocean where organic levels are high relative to the open ocean (Sippo et al. 2016).

Organic alkalinity is not a new concept and has long been recognized as a possible component of total titration alkalinity in seawater (e.g., Dickson 1992). As rivers are known to carry non-trivial amounts of organic acids (e.g., Perdue et al. 1980; Ritchie and Perdue 2003), their conjugate bases contribute to alkalinity in both river and coastal waters (Cai et al. 1998; Hunt et al. 2011). In recent years, organic alkalinity has been receiving increasing attention in not only the water column (Hammer et al. 2017; Hernández-Ayon et al. 2007; Kim and Lee 2009; Ko et al. 2016; Kuliński et al. 2014; Muller and Bleie 2008; Wang et al. 2013; Yang et al. 2015), but also sediment pore waters (Lukawska-Matuszewska 2016). Historically, the combination of alkalinity and pH has been used to estimate CO_2 partial pressure (pCO_2) in inland waters (Butman and Raymond 2011). However, several studies pointed out that this type of calculation may overestimate pCO_2 because the CO_2 system speciation calculations assume that the major components of alkalinity are the carbonate species (Abril et al. 2015; Hunt et al. 2011; Nydahl et al. 2017).

Given its wide presence in estuarine and coastal waters, it is desirable to explore the significance of organic alkalinity in buffering against pH change, and whether such buffer would facilitate atmospheric CO_2 uptake by seawater. In addition, how terrestrially derived organic alkalinity behaves in estuarine zone is also worth investigating. This work presents a MatLab®-based framework that interested readers can utilize in their own investigations.

2 Methods

Based on the operational definition of TA—"the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kg of sample" (Dickson 1981), if an organic acid has $pK_a < 4.5$, addition of this acid would lead to a titration of alkalinity thus decrease its value. Therefore, in this simulation, total organic acid ($T_{HOA} = HOA + OA^-$, i.e., the organic acid and its conjugate base, the latter being organic alkalinity) at a concentration of 0–400 µmol kg^{-1} (in 100 µmol kg^{-1} increment) with the pK_a value ranging between 4.5 and 10.0 and pH ranging between 7.0 and 8.5 are chosen. The 400 µmol kg^{-1} upper limit is arbitrarily decided as algal culture can have 400–800 µmol kg^{-1} organic base while coastal seawater has been observed to have up to 200 µmol kg^{-1} organic base (Hernández-Ayon et al. 2007). The simulated pK_a range includes the vast majority of natural pK_a values found in natural waters (Table 1, the discussion on organic acid with $pK_a < 4.5$ can be found in Sect. 4.6). The pH range for the simulation encompasses the majority of natural seawater pH values including those highly productive coastal waters (Hofmann et al. 2011). The combination of T_{HOA} concentration, pK_a, and pH should generate reasonable concentration ranges of organic alkalinity (OA^-) (Table 1). For the sake of simplicity, here a single organic acid with varying pK_a value is used in the calculations, but the readers can add any number of the acids in their buffer calculations by modifying the supplied MatLab script (Supplementary Material) with predetermined acid dissociation constants. Similarly, nutrient influence (ammonia, phosphate, and silicate) can also be examined but is not discussed here. In this simulation, two forms of organic acid addition are considered. First, organic acid with $4.5 < pK_a \leq 10.0$ is added into seawater in the molecular form (i.e., HOA) with no change to TA (Ko et al. 2016).

Table 1 Literature reported organic alkalinity concentrations and dissociation constants pK_a

Environment	Org-A (µM)[a]	pK_a	References
Phytoplankton culture	30–60	–	Kim and Lee (2009)
Phytoplankton culture	15–40	4.4–4.9 and 6.1–6.9[b]	Ko et al. (2016)
Phytoplankton culture	5–20	4.0, 9.1[b]	Muller and Bleie (2008)
Phytoplankton culture	200–800	5–7[c]	Hernández-Ayon et al. (2007)
Coastal	22–58	5.86–7.53[c]	Kuliński et al. (2014) and Ulfsbo et al. (2015)
Coastal	≤ 15	–	Ko et al. (2016)
Estuarine and coastal	14–190	–	Hernández-Ayon et al. (2007)
Estuarine and coastal	0–56	7.27[c]	Hammer et al. (2017)
Estuarine	16–34	–	Yang et al. (2015)
River	15–56	–	Wang et al. (2013)
River and Estuarine	~ 10–100[d]	4.46–10[d]	Cai et al. (1998)

[a]All organic alkalinity concentrations except those in Cai et al. (1998) were calculated using measured TA minus that calculated using DIC and pH (or pCO_2, Ulfsbo et al. 2015)

[b]pK_a values were obtained via NaOH back titration and curve fitting

[c]pK_a values were obtained via titration curve modeling

[d]Organic alkalinity was analyzed using NaOH back titration; pK_a values were obtained via titration curve fitting

Second, a conjugate base of HOA is added into seawater in the ionic form (i.e., OA^-) along with a cation (M^{n+}) to maintain charge balance, resulting in a net increase in TA. It is noted that even though this simulation uses the term "organic acid", conceptually this acid can be either an organic or a mineral acid. Therefore, the results of the simulation should apply to any acid or its conjugate base addition within the defined pK_a range, despite the fact that there are only a few known inorganic acids (mostly of inorganic nutrients) that have pK_a values within this range under oxic conditions (e.g., Millero 2001).

The initial simulation condition includes TA = 2350 μmol kg^{-1} and pCO_2 = 400 μatm at air-seawater equilibrium. At salinity 35 and temperature 15 °C, the equilibrium DIC concentration is 2124 μmol kg^{-1}, which is calculated using the carbonic acid dissociation constants (K_1 and K_2) reported in Mehrbach et al. (1973) and refit by Dickson and Millero (1987), the bisulfate dissociation constant reported in Dickson et al. (1990), and the total boron concentration in Uppström (1974). Even though bisulfate is considered as negative alkalinity in the TA definition (Dickson 1981), the values are negligible at the simulation pH range (i.e., 0.019 μmol kg^{-1} at pH 7.0 and < 0.001 μmol kg^{-1} at pH 8.5, note pH on the free scale (pH_F) is used here), so this negative contribution to TA is not included in the simulations. Note the refitted constants presented in Dickson and Millero (1987) are on the seawater scale (SWS), and the MatLab version of the program CO2SYS (Ver. 1.1) converts these constants to be based on the free scale (Line 1806–1807 in the function FindpHOnAllScales, van Heuven et al. 2011). All constants at the simulation temperature and salinity are taken from the CO2SYS program.

To calculate the perturbations of organic acid to seawater, two scenarios are simulated for both HOA and OA^- additions. Both changes in pCO_2 under a closed-system condition (i.e., constant DIC) and the expected DIC concentration changes to "restore" the perturbed seawater back to air-seawater equilibrium (pCO_2 = 400 μatm) under an open-system condition are calculated. These two scenarios are included to reflect seawater that is not subject to air-sea gas exchange (below the mixed layer) and that freely exchanges with the atmosphere. For each T_{HOA} level (0–400 μmol kg^{-1}), a two-dimensional matrix (pH vs. pK_a) is calculated using the MatLab scripts in Supplementary Material (Organic_Alkalinity_HOA.m and Organic_Alkalinity_OA.m). Next, for each pK_a value, a search for the speciation solution after the HOA or OA^- addition for a closed system with fixed DIC (pCO_2, β_{DIC}, and organic alkalinity or [OA^-]) and for an open system that allows air-sea re-equilibration at pCO_2 = 400 μatm (DIC, β_{DIC}, and [OA^-]) is done using the MatLab command "*interp1*" and the "*pchip*" interpolating algorithm (i.e., shape-preserving piecewise cubic interpolation). Using this approach, complex analytical solution of the multiple nonlinear equations of the acid–base buffer system can be avoided.

To evaluate the effect of organic alkalinity on buffer capacity changes, an extended buffer factor based on Egleston et al. (2010) was obtained:

$$\beta_{DIC} = \left(\frac{\partial \ln\left(\left[H^+\right]\right)}{\partial DIC} \right)^{-1} = \frac{DIC \times S - TA_C^2}{TA_C} \tag{1}$$

In Eq. (1) TA_C is carbonate alkalinity, $S = \left[HCO_3^-\right] + 4\left[CO_3^{2-}\right] + \frac{\left[B(OH)_4^-\right]\left[H^+\right]}{K_B + \left[H^+\right]} + \frac{\left[OA^-\right]\left[H^+\right]}{K_{HOA} + \left[H^+\right]} + \left[H^+\right] + \left[OH^-\right]$ (see Supplementary Material for the detailed derivation steps), in which K_B, and K_{HOA} are dissociation constants of boric and organic acids, respectively.

β_{DIC} reflects the change of $[H^+]$ (or pH) in response to the addition of CO_2. Lower values indicate less buffer and higher values indicate stronger buffer, although see below (Sect. 4.4) for a discussion on high β_{DIC} values at higher pCO_2 and low pH conditions.

Finally, in addition to calculating buffer effect of organic acid on the seawater endmember, the influence of organic alkalinity in estuarine mixing zone using the same seawater but without organic alkalinity and a river endmember is also evaluated. River water has varying levels of weathering products due to many factors including drainage basin mineralogy, river hydrology, and biogeochemical reactions. For simplicity, a DIC concentration of 1050 µmol kg^{-1} and a TA value of 1000 µmol kg^{-1} are selected for this simulation. These values are bracketed by rivers with high levels of weathering products (for example, the Mississippi River), and those that have little (for example, Amazon) (Hu and Cai 2013). Similar to the method above, multiple river T_{HOA} levels (at constant river alkalinity) are used in the mixing simulations. As little is known regarding the salinity-dependent dissociation constant of natural organic acids, here simulations using only two fixed "boundary" pK_a values are presented (4.50 and 8.20, the latter being the calculated pK_a that provides the greatest buffer to seawater, see Sect. 3.2) across the estuarine mixing zone. The readers can use the supplied MatLab scripts to examine other pK_a values found in natural organic acids and their respective concentrations (see Table 1), as well as rivers with different inorganic carbon system parameters. Similar to the simulations on the seawater-only cases above, both closed- and open-systems are also considered.

3 Results

3.1 Changes to pCO_2, pH, and DIC Under Closed- and Open-System Conditions due to Organic Acid Addition

If DIC concentration is maintained after the addition of HOA under a closed-system condition, seawater pCO_2 would be higher than the starting conditions (400 µatm, Fig. 1a). In contrast, if OA^- is added into the system (with accompanying cations), pCO_2 would decrease (Fig. 1b). Furthermore, both pK_a and T_{HOA} determine the magnitude of pCO_2 increase or decrease. Generally, at fixed level of T_{HOA}, pCO_2 is higher following HOA addition at a lower pK_a (i.e., stronger acid leads to greater pCO_2 increase, Fig. 1a). For OA^- addition however, pCO_2 is lower at a higher pK_a (i.e., stronger conjugate base of a weaker acid leads to greater pCO_2 decline, Fig. 1b). On the other hand, higher T_{HOA} concentration leads to higher pCO_2 (HOA) or lower pCO_2 (OA^-) at fixed pK_a (Fig. 1a, b). Because the addition of HOA (without changing TA) increases pCO_2, one would expect to see CO_2 degassing if this perturbed seawater is exposed to the air, which would result in a decrease in DIC concentration compared to the original value (excess DIC in Fig. 1c). Conversely, an addition of OA^- increases TA but does not change DIC, resulting in pCO_2 decrease. Subsequent CO_2 uptake would result in DIC increase after air-seawater re-equilibration under the open-system condition (DIC deficiency in Fig. 1d). From the calculation results, as much as 339 µmol kg^{-1} DIC would need to be degassed (from the initial 2124 µmol kg^{-1}) or 334 µmol kg^{-1} DIC needs to be taken up from the atmosphere to restore seawater pCO_2 back to the starting condition when $T_{HOA} = 400$ µmol kg^{-1} (Fig. 1c, d) following HOA addition or OA- addition, respectively.

As expected, organic acid with lower pK_a (stronger acid) would have more complete dissociation hence higher levels of OA^- (within TA = 2350 µmol kg^{-1}, Fig. 1e). Because

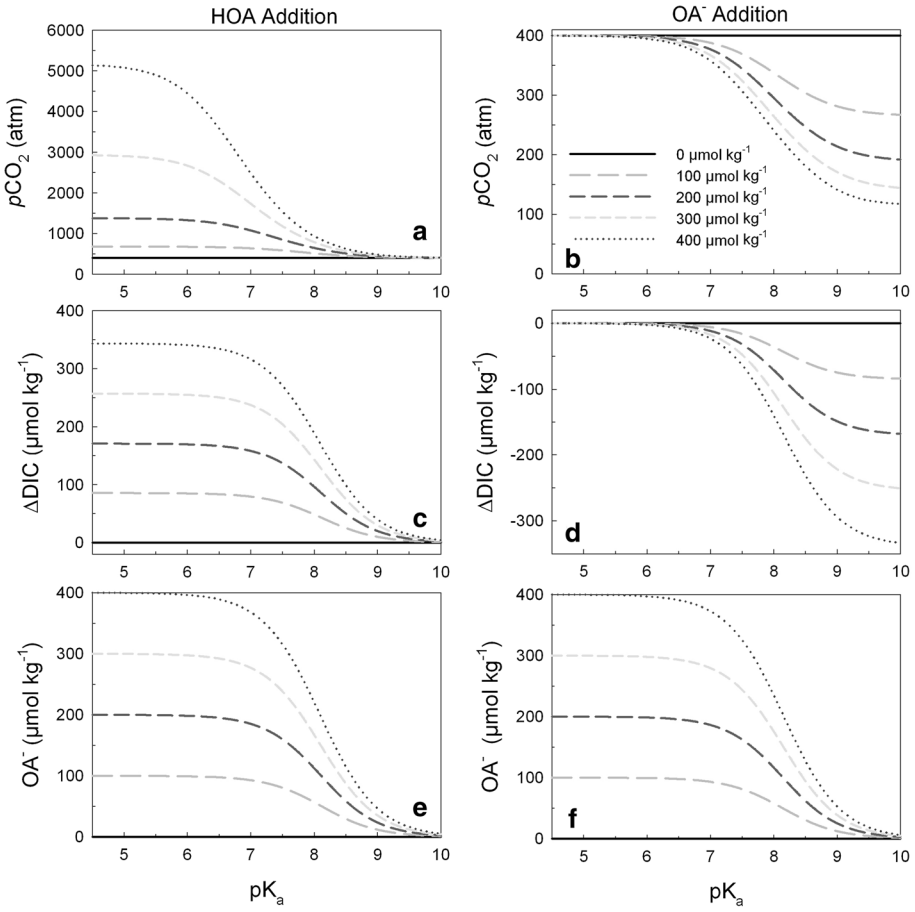

Fig. 1 Seawater pCO_2 after the addition of organic acid (HOA, **a**) or organic base (OA^-, **b**) at constant DIC = 2123.6 μmol kg^{-1} in a closed system. Expected DIC loss due to CO_2 degassing after HOA addition (**c**, excess DIC) and CO_2 uptake (**d**, DIC deficiency) after the perturbed seawater reach equilibration with atmosphere at 400 μatm (open system). Concentrations of OA^- at pCO_2 400 μatm for both HOA and OA^- addition (**e**, **f**). Simulation initial condition, TA = 2350 μmol kg^{-1}, $S = 35$, $T = 15$ °C. The legend shows total concentrations of organic acid (undissociated HOA and its conjugate base OA^-, or T_{HOA}). Note that the panels e and f show similar patterns because the differences in $[OA^-]$ at each T_{HOA} concentration across the simulated pK_a range are small relative to the scale of the *y*-axis

of their overall higher pH conditions for each level of simulated T_{HOA} addition (Fig. 2a, b), final $[OA^-]$ concentrations following the OA^- addition in the open system (Fig. 1f) are slightly higher (by up to 11 μmol kg^{-1}) than those in the scenarios with HOA addition (Fig. 1e) at the same pK_a.

3.2 Buffer Capacity Under Closed- and Open-System Conditions due to Organic Acid Addition

Contrary to the readily apparent "acidification" effect caused by either HOA addition in seawater (i.e., pH decreases for all levels of organic acid addition, Fig. 2a) or the "basification"

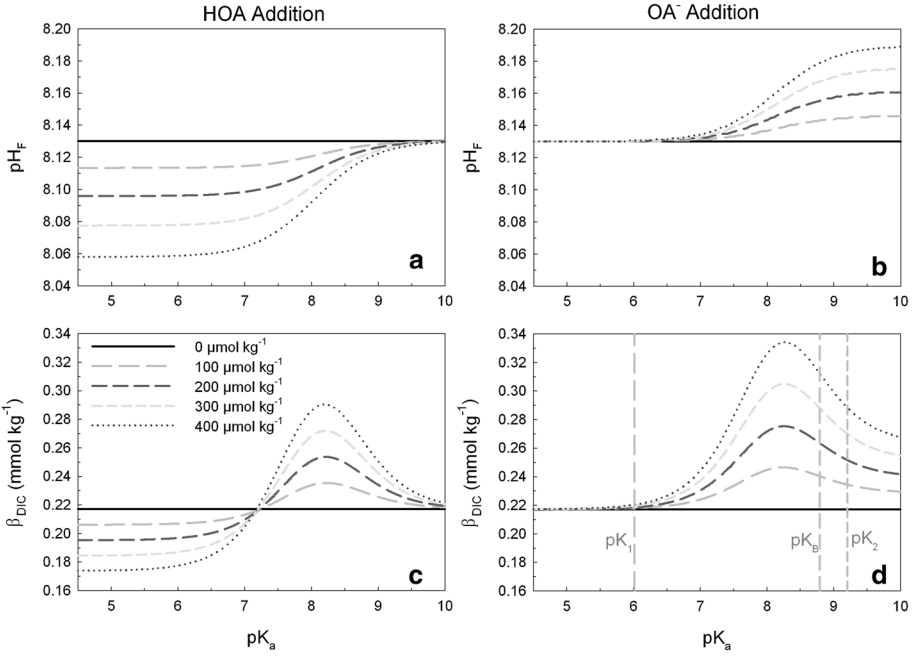

Fig. 2 Seawater pH (**a**, **b**) and β_{DIC} (**c**, **d**) following HOA (or OA^-) addition and subsequent degassing (or CO_2 uptake) in an open system. All values are calculated at $pCO_2 = 400$ μatm. Simulation condition, TA = 2350 μmol kg^{-1}, $S = 35$, $T = 15$ °C

effect caused by OA^- addition (i.e., pH increases, Fig. 2b), after the perturbed water is re-equilibrated with the same atmosphere pCO_2 of 400 μatm, buffer capacity β_{DIC} exhibits rather complex behaviors (Fig. 2c, d). For the HOA addition scenario, if pK_a of organic acid is lower than a certain threshold (i.e., ~ 7.15 for the model seawater at $T = 15$ °C and $S = 35$, Fig. 2c), β_{DIC} of organic acid-perturbed seawater is lower than that of the original seawater (note the intercepts between the various T_{HOA} levels and the unperturbed seawater are close but not exactly the same, Fig. 2c). However, when pK_a is greater than this threshold, organic acid-perturbed seawater appears to have greater buffer capacity than that of the original seawater, i.e., $[H^+]$ is less sensitive to DIC addition than the unperturbed seawater (see β_{DIC} definition in Eq. 1), despite that this perturbed seawater has lower pH than the unperturbed one (Fig. 2a). The maximum buffer appears when $pK_a = 8.20$ at the simulation condition (Fig. 2c). For the OA^- addition scenario, β_{DIC} increases in all cases. Similar to HOA addition, the highest buffer also appears at the higher pK_a range, here 8.25 (Fig. 2d), slightly higher than that for HOA addition (Fig. 2c).

3.3 Changes in pH of Maximum β_{DIC} due to Organic Acid Addition

For a monoprotic acid (HOA), the maximum buffer occurs at its pK_a value as the concentrations of the undissociated acid (HOA) and its conjugate base (OA^-) are the same, i.e., the equivalence point, where $pH = pK_a$ (provided that the acid concentration is not too low, otherwise water dissociation would become more important). Whereas for a diaprotic acid (H_2OA), maximum buffer occurs at two equivalence points, i.e., $[H_2OA] = [HOA^-]$

(pH = $pK_{a,1}$, i.e., the first dissociation constant) and [HOA^-] = [OA^{2-}] (pH = $pK_{a,2}$, i.e., the second dissociation constant) (Stumm and Morgan 1995). Addition of other acid–base pairs into the diprotic acid solution would alter the pH where the buffer maxima (as well as minima) appear. For example, in the seawater used in this simulation (i.e., TA = 2350 µmol kg^{-1}, S = 35, T = 15 °C), pK_1 = 6.02, pK_2 = 9.20 (again, these values are on the free pH scale), the buffer maximum that corresponds to [CO_3^{2-}] = [HCO_3^-] would have been pH = pK_2 = 9.20 provided there are no other acid–base pairs (pH = pK_1 is the other maximum buffer at lower pH, Fig. 3). Although because of the presence of borate, maximum β_{DIC} appears at lower pH (8.82) than pK_2 (note pK_B = 8.79). The same applies to the adjacent minimum β_{DIC} when DIC = TA, i.e., instead of pH = (pK_1 + pK_2)/2 = 7.61, the minimum β_{DIC} appears at pH 7.58 (Egleston et al. 2010; Hu and Cai 2013) (Fig. 3). Assuming that pK_a of HOA is 8.20, the maximum buffer occurs as pH 8.66 when HOA is added (or pH 8.69 if OA^- is added), which is a further decrease from the organic alkalinity-free seawater (pH 8.82, see above) (Fig. 3). Note that β_{DIC} at the assumed air pCO_2 condition (400 µatm) is not at its maximum in the simulated pH range and will decrease further with continued ocean acidification (Fig. 3).

3.4 Influence of Organic Alkalinity in Estuarine Mixing Zone

At the given river endmember DIC and TA values and assuming that the river water is organic free, pCO_2 is 1147 µatm at 15 °C using the carbonate dissociation constants in Millero (1979). This pCO_2 level is realistic (i.e., higher than the atmospheric pCO_2) and falls within the natural river pCO_2 range (Butman and Raymond 2011).

Clearly, both pK_a value and organic acid concentration play important roles in the speciation of the buffer system in the estuarine zone (Figs. 4, 5). Compared to the zero T_{HOA} condition (the dark red curves in Figs. 4, 5), the presence of organic acid–base in river water always increases pCO_2 and decrease pH_F in the mixing zone for the closed system (Fig. 4a, b), and upon complete air–water equilibration (open system), DIC decreases due to CO_2 degassing (Fig. 5a) and pH is nevertheless still lower than the mixing between zero T_{HOA} condition (Fig. 5b). This result is similar to the situation where HOA is added into seawater (Fig. 2a).

Based on the simulation, stronger organic acid leads to more acidified estuarine water (solid curves in Figs. 4a, b and 5b). Furthermore, in the closed system the concentration of the conjugate base (OA^-) of the stronger organic acid (pK_a = 4.5) exhibits a close to linear

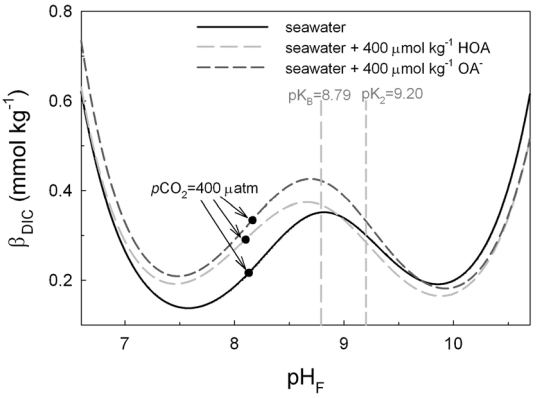

Fig. 3 Simulated β_{DIC} in seawater, seawater + 400 µmol kg^{-1} HOA, and seawater + 400 µmol kg^{-1} OA^-. Simulation initial condition, TA = 2350 µmol kg^{-1}, S = 35, T = 15 °C, HOA pK_a = 8.20. The three closed circles represent pCO_2 = 400 µatm for the three simulations. Maximum β_{DIC} appears at pH 8.82, 8.66, and 8.69 for these three simulations, respectively

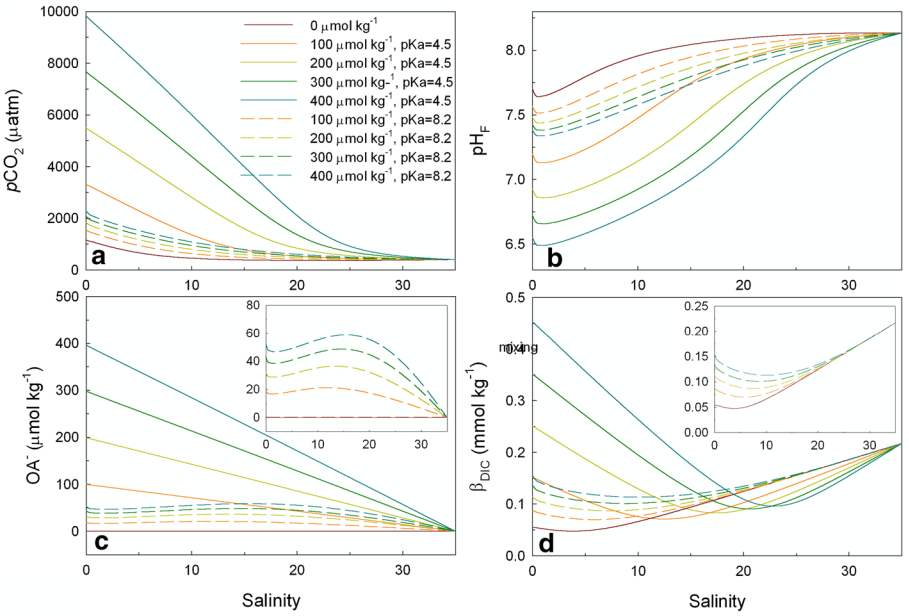

Fig. 4 pCO_2 (**a**), pH_F (**b**), [OA^-] (**c**) and β_{DIC} (**d**) as a function of salinity in the river-ocean mixing zone in a closed system. The inserts in panels **c** and **d** are blown-up views of results calculated with $pK_a = 8.20$. The river endmember has DIC = 1050 μmol kg^{-1}, TA = 1000 μmol kg^{-1} with various levels of total organic acid (0, 100, 200, 300, 400 μmol kg^{-1}). The ocean endmember is set to be the same as that in seawater simulation with zero organic acid, i.e., TA = 2350 μmol kg^{-1}, pCO_2 = 400 μatm, $S = 35$, $T = 15$ °C. Conservative mixing of TA and DIC is assumed in this calculation. See text for details

relationship with salinity (Fig. 4c), while the weaker organic acid ($pK_a = 8.2$) yield a mid-salinity maximum in [OA^-] (the insert in Fig. 4c). In the open system, such distinction is less clear as [OA^-] shows a nearly linear relationship with salinity across most of the mixing zone (Fig. 5c).

In the close system, β_{DIC} of the two organic acids both show a mid-salinity β_{DIC} minimum, and the salinity at which the β_{DIC} minimum appears is lower for the weaker acid (dashed curves in Fig. 4d). Despite this commonality, the weaker organic acid increased β_{DIC} value across all salinity range compared to the no zero T_{HOA} condition (the dark red curve), while the stronger organic acid depresses the β_{DIC} value at mid to high salinity relative to the zero T_{HOA} condition, although at lower salinities β_{DIC} values are higher (Fig. 4d). In the open system however, the stronger acid depresses β_{DIC} across all salinity range while the weaker acid elevates β_{DIC} slightly (Fig. 5d) relative to the zero T_{HOA} river condition. This again is similar to HOA addition into seawater and β_{DIC} is elevated for organic acid with high pK_a values (Fig. 2c).

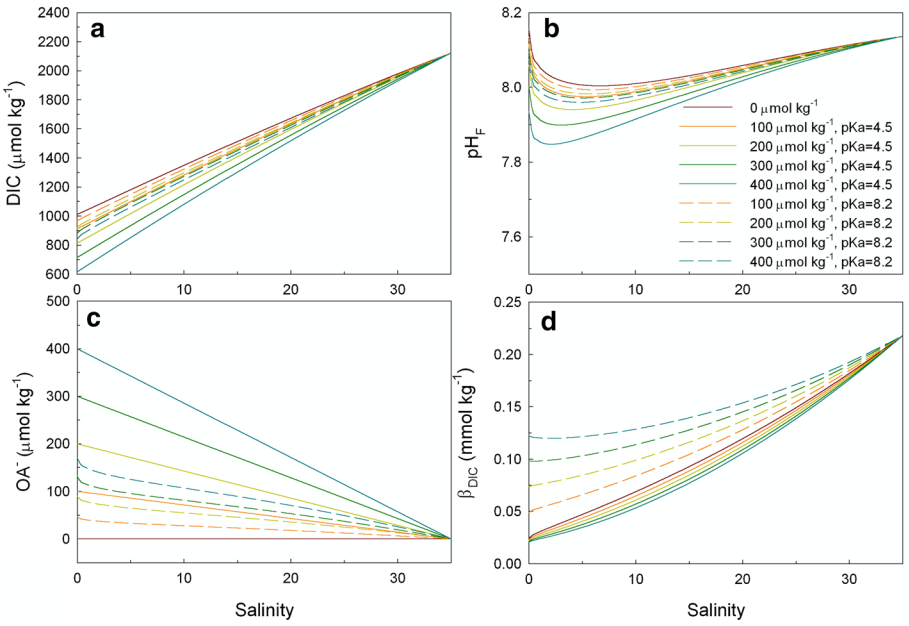

Fig. 5 pCO_2 (**a**), pH_F (**b**), [OA^-] (**c**) and β_{DIC} (**d**) as a function of salinity in the river-ocean mixing zone in an open system. The river and ocean endmember compositions are the same as those in Fig. 4. Since the entire mixing zone is assumed to be an open system, pCO_2 across the salinity gradient is uniformly 400 μatm

4 Discussion

4.1 Controls on pK_a that Corresponds to Maximum β_{DIC}

Not only is the seawater β_{DIC} maximum affected by the form of organic acid added (i.e., HOA and OA^-), but pK_a that corresponds to the maximum β_{DIC} is also a function of the equilibrium pCO_2. For both HOA and OA^- additions, pK_a that corresponds to maximum β_{DIC} (Fig. 2c, d) decreases with increasing pCO_2, the same also applies to the threshold pK_a (defined here as the "transition pK_a," Fig. 6), i.e., the intercept pK_a value between the perturbed and unperturbed seawater for HOA addition (see Fig. 2c). The physical meaning of these shifts is that stronger organic acid (lower pK_a) and its conjugate base play a more important role controlling seawater buffer capacity at higher pCO_2 levels. Compared to the equilibrium pCO_2 control, temperature and salinity have less influence on the value of pK_a at the β_{DIC} maximum. For example, at $S = 35$ and 25 °C with $pCO_2 = 400$ μatm (TA is 2350 μmol kg^{-1} for HOA addition or 2750 μmol kg^{-1} with OA^- addition) and 400 μmol kg^{-1} T_{HOA} concentration, pK_a at maximum β_{DIC} is only greater by 0.05 than the value at 15 °C, when all other conditions are kept the same (Figs. S1 and S2). Similarly, changing salinity from 35 to 20 while maintaining the same TA (for simplicity assuming river TA and ocean TA equal each other), pK_a only increases by 0.02 (Figs. S1 and S2). These differences indicate that weaker organic acid–base pair exerts stronger control at higher temperature and lower salinity, although the changes are smaller than the changes caused by seawater pCO_2 change (Fig. 6). On the other hand, fluctuating seawater pCO_2

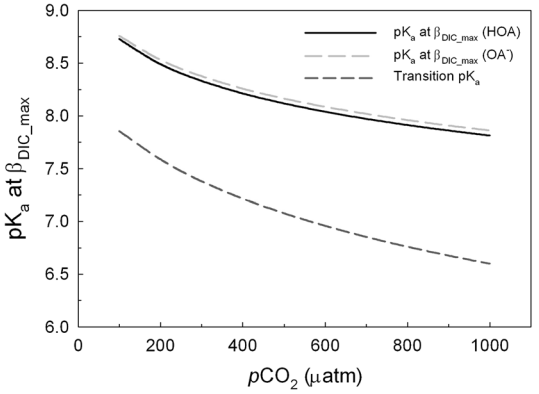

Fig. 6 pK_a values that correspond maximum β_{DIC} for HOA addition (solid curve), OA^- addition (dashed grey curve), and the threshold condition (cf. Fig. 2c, dashed black curve) as a function of equilibrating pCO_2. Each curve represents an average of four T_{HOA} scenarios (100 μmol kg^{-1}, 200 μmol kg^{-1}, 300 μmol kg^{-1}, and 400 μmol kg^{-1}). Average standard deviations of these scenarios are 0.01 (both HOA and OA^- addition) and 0.03 (the threshold value) and are not shown in the figure. Simulation initial condition, TA = 2350 μmol kg^{-1}, $S = 35$, $T = 15$ °C

under natural conditions means that not a single organic acid may provide the maximum amount of buffer, but a collection of these acids that have relatively high pK_a values would be responsible for this buffer effect. It is also worth noting that other buffer factors should exhibit similar behaviors as they all show similar patterns in the seawater system (Egleston et al. 2010).

4.2 Effect of Organic Alkalinity Addition on Seawater Uptake of Atmospheric CO_2

Following HOA addition, pCO_2 increase and CO_2 degassing would occur (Fig. 1c). This CO_2 loss in an open system is expected, as HOA addition into a seawater is essentially the same as ocean acidification or adding any other acid. However, the dissociation of the organic acid produces its corresponding conjugate base, OA^-, rather than bicarbonate or carbonate (the conjugate bases for carbonic acid); hence, OA^- replaces these two carbonate species, causing overall DIC decrease due to CO_2 loss (Fig. 1c).

Using the literature reported pK_a values found in various seawater media (Table 1), phytoplankton culture or other environments may produce relatively strong organic acids in the form of HOA, as most calculated pK_a values are less than 7.15 (i.e., the transition pK_a in Fig. 2c). Hypothetically, if the perturbed seawater following the addition of these organic acids is equilibrated with the atmosphere, then it has lower buffer capacity than the unperturbed seawater.

In contrast to net HOA addition, if OA^- is added into seawater in a net sense, CO_2 uptake would occur (Fig. 1d). In this scenario, a weak base (OA^-) combines with proton to form HOA. This process leads to an increase in pH (not shown) and decrease in pCO_2 (Fig. 1b) in a closed system. However, before answering the question whether net OA^- addition is a process that helps seawater take up CO_2, it is worth exploring whether organic alkalinity represents a net addition to the inorganic acid–base system in seawater and what the fates are for organic molecules in the seawater.

4.3 Is Organic Alkalinity an "Extra" Source of Seawater Alkalinity in Nature?

In the literature, there are conflicting views on whether organic alkalinity contributes to net TA increases in seawater. First, Kim et al. (2006) suggested that phytoplankton cells contribute to TA when particulate organic carbon level is greater than 200 μmol kg^{-1} (the cells have alkalinity of 3–5 μmol kg^{-1}), and bacteria contribute 1–6 μmol kg^{-1}. However, Hernández-Ayon et al. (2007) compared filtered and unfiltered phytoplankton culture and did not observe significant difference within a 5 μmol kg^{-1} uncertainty. It is worth noting that the later study does not necessarily invalidate the earlier findings as the two studies have different levels of analytical precision, i.e., ± 1 μmol kg^{-1} in Kim et al. (2006) and ± 4–5 μmol kg^{-1} in Hernández-Ayon et al. (2007). Nevertheless, the contribution from live cells appears to have a much smaller influence on TA compared to organic alkalinity discussed below.

Kim and Lee (2009) used phytoplankton culture under high nutrient conditions to study the potential organic alkalinity production. These authors used cultured media, in which TA increase exceeds the extent of nitrate consumption with a $-(\Delta TA/\Delta NO_3)$ ratio of 1.11–1.45, indicating "excess" alkalinity production (11–45% more than the nitrate taken up by the phytoplankton) that cannot be explained by simple reaction stoichiometry of anion uptake, because one unit of nitrate utilization theoretically produces one unit of alkalinity. In these phytoplankton cultures (10^4–10^5 cell ml^{-1}), organic alkalinity ranges 30–60 μmol kg^{-1} with similar increase in the dissolved organic carbon (DOC) concentrations. However, in a follow-up study that investigated phytoplankton cultures by the same group (Ko et al. 2016), organic acid addition into seawater was not found to influence TA. These authors interpreted that the weak acid addition only shifts acid–base equilibria and not total amount of acid neutralizing capacity, making it essentially equivalent to HOA addition to seawater as discussed above.

Despite that both HOA and OA^- additions are considered in the perturbation simulations, to add organic alkalinity in a net sense (i.e., increase TA), the anion OA^- needs to enter the seawater along with cation(s) to maintain a charge balance. To achieve this, organic acids in the molecular form produced through biogeochemical reactions need to react with minerals to produce the conjugate base anion along with cations from mineral dissolution (for example carbonate or silicate) (e.g., Lundegard and Land 1989; Welch and Ullman 1993), although this type of reaction is far more complex than a simple dissolution of minerals. Nevertheless, it is likely that environments with significant presence of minerals (such as wetlands, shallow estuaries, and coastal areas) that allow organic acid-mineral reactions may have the capacity to increase total alkalinity in a net sense.

4.4 Organic Alkalinity and Its Buffer Effect in the Estuarine Zone

When river water carries organic acid and enters estuarine mixing zone, the presence of organic acid and its conjugate base not only shifts the acid–base equilibria across the salinity gradient, but also the buffer behavior of the estuarine water, compared with the scenario that river water has only carbonate alkalinity (i.e., the zero-T_{HOA} river, the dark red curves in Figs. 4, 5). Clearly, not accounting for the presence of organic alkalinity would underestimate pCO_2 if using TA and DIC as the input pair for the CO_2 system speciation calculations (Fig. 4a), regardless of the dissociation constant. Similarly, using pH and TA as the input pair without considering the contribution of organic alkalinity (Fig. 4c)

would overestimate pCO_2 as what previous studies have shown (Abril et al. 2015; Hunt et al. 2011; Nydahl et al. 2017).

Replacing carbonate alkalinity with organic alkalinity (i.e., maintain the constant alkalinity level) alters buffer capacity of estuarine water (Figs. 4d, 5d). It is clear that organic acid with lower pK_a causes greater deviation in β_{DIC} compared with mixing between zero-T_{HOA} river water and seawater in a closed system (Fig. 4d). At higher salinity, β_{DIC} values are lower than values from this mixing scenario, and at lower salinity β_{DIC} increases (Fig. 4d). This reversal in β_{DIC} values is because carbonate and borate ion concentrations are very low at high pCO_2 and low pH conditions; hence, the buffer is provided by diluting CO_2 into existing DIC (Egleston et al. 2010), while less proton concentration change would occur at given CO_2 addition, yielding greater β_{DIC}. In other words, this increase in β_{DIC} with decreasing salinity does not translate to resistance to acidification by any means because water pCO_2 level is already high (Fig. 4a). Instead, this high pCO_2 water would acidify seawater with lower pCO_2 levels upon mixing. This type of elevated β_{DIC} values along with high DIC and pCO_2 levels were also observed in other estuarine settings (e.g., Wang et al. 2016). Similar to the seawater endmember simulation, organic acid with higher pK_a always results in elevated buffer regardless of whether the system is open or not (Figs. 4d, 5d).

As pK_a increases, all calculated pCO_2, pH_F, OA^-, and β_{DIC} values approach the results from mixing between carbonate zero-T_{HOA} river water and seawater (Figs. 4d, 5d). This result is reasonable, because as the organic acid is weaker, it would play a less important role in regulating the buffer system. Using this simulation, it is clear that the effect of organic alkalinity on estuarine buffer diminishes with increasing salinity, regardless of the pK_a values.

In reality, estuarine mixing and river export to the coastal ocean occur on vastly different time scales, and depending on these time scales, various extent of degassing due to high-CO_2 river water discharge would occur (Borges et al. 2006; Jiang et al. 2008), to the extent that all excess DIC is lost through air–water equilibrium in an open system (Fig. 5a). Therefore, organic alkalinity in an estuarine mixing zone may be expected to behave between the two extreme scenarios, i.e., closed vs. open (Figs. 4, 5), as a function of estuarine residence time.

4.5 The Fate of Organic Alkalinity

In the literature, higher organic alkalinity levels are commonly found in rivers, and its contribution to TA diminishes in higher salinity waters (Cai et al. 1998; Hunt et al. 2011; Wang et al. 2013; Yao and Hu 2017), just like what the simple numerical simulations above suggest. Certainly, in reality the decrease of organic alkalinity concentration across a salinity gradient are only partially attributed to dilution, as both photochemical and microbial processes may also break down these organic molecules (e.g., Amon and Benner 1996; Fichot and Benner 2014). To the best of the author's knowledge, there is currently no study investigating the degradation of organic alkalinity on seawater acid–base chemistry.

To explore the theoretical effect of organic alkalinity degradation, it is reasonable to consider a simplistic scenario using a "model compound". The simplest organic acid–formic acid (HCOOH) has pK_a lower than 4; thus, it is not an ideal representative for this simulation. Acetic acid (CH_3COOH, or HAc) ($pK_a = 4.76$ in freshwater at 25 °C, Serjeant and Dempsey 1979) is taken as an example to illustrate the organic acid perturbation, and the conjugate base of acetic acid—acetate (Ac^-)—is used as a model species to represent

organic alkalinity. Note that pK_a decreases by ~0.15 at seawater ionic strength (Millero 1983). Although for the sake of simplicity, the freshwater value pK_a value is used here, because even after the salting coefficient correction, pK_a would still be greater than 4.5. A complete degradation of the acetate can be represented as:

$$CH_3COO^- + 2O_2 \rightarrow HCO_3^- + CO_2 + H_2O \quad (2)$$

Clearly, this reaction produces DIC but does not change TA, a process equivalent to the "charge transfer" mechanism in an earlier seawater alkalinity dynamics discussion (Hu and Cai 2011). In other words, the addition of HAc into seawater and subsequent complete breakdown to CO_2 has no effect on TA but leads to a net increase in DIC, while the addition of an acetate salt (Ac^-) increases TA by the amount of acetate added, and the breakdown of acetate also increases DIC. Simulations of both HAc and Ac^- additions and final remineralization indicate that pCO_2 increases for both cases (Fig. 7). Moreover, even though the final DIC concentration is higher for the Ac^- addition (due to the initial CO_2 uptake in an open system after the Ac^- addition, Fig. 7b) than the addition of HAc (Fig. 7a), the pCO_2 level is lower at any given amount of HAc because of higher TA level caused by the net Ac^- addition (Fig. 7). Similar to the acetate addition, it is common knowledge among the saltwater aquarium hobbyists that vinegar and a "limewater" (i.e., $Ca(OH)_2$ solution) can be used together to increase alkalinity and calcium levels in tanks that host hard corals, a process that is equivalent to the simulation of Ac^- addition here.

In natural waters, humic substances represent the largest dissolved organic matter fraction, and carboxyl and phenolic hydroxyl groups in the complex humic "molecules" give rise to their acidity (Perdue et al. 1980). Based on the above discussion, it is likely that

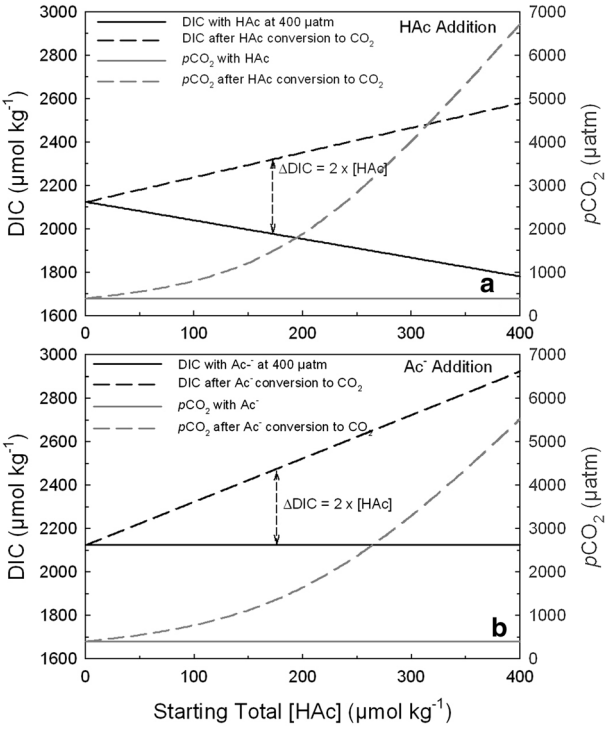

Fig. 7 Two hypothetical scenarios of acetic acid (HAc, **a**) and acetate (Ac^-, **b**) perturbation and subsequent respiration on seawater DIC and pCO_2 changes. The solid lines are DIC (black) and pCO_2 (grey horizontal) after the perturbation of acetic acid and equilibration with 400 µatm atmosphere. The dashed lines are DIC (black) and pCO_2 (grey) after the added HAc (or Ac^-) is converted to CO_2 (or carbonate alkalinity) in a closed system. Simulation condition, TA = 2350 µmol kg^{-1}, $S = 35$, $T = 15$ °C, acetic acid $pK_a = 4.76$

degradation of large organic acid molecules that have carboxyl groups, including their conjugate bases, would lead to an initial seawater pCO_2 increase and CO_2 degassing, irrespective of the degradation mechanism. The same conclusion may also be drawn for phenolic compounds (another type of proton donor among natural organic acids) because their degradation may involve production of aliphatic acids as the intermediates (van Schie and Young 2000), and subsequent reaction would then have the same effect on seawater CO_2 system, as DIC production from decarboxylation reactions may occur.

4.6 Caveats

In natural waters, organic acids often appear in clusters with a wide range of pK_a values, some of which can be lower than 4.5 (Table 1). This study only deals with minimum pK_a at 4.5, at which pH a hypothetical acid would have equal concentrations of HOA and OA^- at the empirically defined "zero proton level" (Dickson 1981), which is widely used in determining alkalinity of natural waters. However, in cases that involve organic acids that have lower pK_a things become more challenging especially from the analytical point of view. Current curve fitting of the potentiometric titration data for alkalinity analysis uses the final pH of ~ 3.0, at which the concentrations of the major conjugate anions (HCO_3^-) common in seawater or freshwater with little organic matter is minimal (Dickson et al. 2007). If significant quantities of organic acids are present in seawater, the species with lower pK_a (≤ 4.5) will continue to protonate after the empirical zero proton level is reached through acid titration (Ulfsbo et al. 2015). For example, at the lower pH limit of current curve fitting scheme (pH 3.0), the unprotonated conjugate base would be about 1/32 of its protonated counterpart (if $pK_a = 4.5$), and the ratio would be 1/10 at pH 3.5. Hence, the currently accepted zero proton level theoretically prevents the inclusion of the bases of stronger conjugate acids. However, if these "protonation capacities" that are not included in current alkalinity titration results are present in the anionic form, upon transformation in the ocean water, it will turn out to be "excess" alkalinity through charge transfer (Hu and Cai 2011), a process in which even the conjugate base (SO_4^{2-}) of the strong sulfuric acid can be converted to bicarbonate upon complete reduction and removal from the water column. Therefore, the problem now is how much this unrecognized protonation capacity due to the presence of conjugate bases of stronger acids (with $pK_a < 4.5$) is present in river waters, which then contributes to the oceanic alkalinity cycle. This could be a potentially interesting topic for future studies.

The simple simulations using the model compounds in Sect. 4.5 do not necessarily reflect what occurs under natural conditions, and it is also widely recognized that organic alkalinity may be present even in oligotrophic ocean waters, even though their levels can be very low (Fong and Dickson 2019). However, from the buffer examination and the potential transformation to organic alkalinity in the ocean, it is unlikely that the contribution of organic alkalinity would exert major control on seawater CO_2 uptake capacity.

5 Conclusions

Using numerical simulation, two types of organic alkalinity input (direct organic acid input, HOA, or that of its conjugate base, OA^-) are explored for the effects on seawater carbonate chemistry under both closed-system and open-system conditions. Addition of HOA would increase seawater pCO_2 in a closed system, and degassing would occur if the system

is then open to the atmosphere. In the open system scenario, if the pK_a of HOA is above a threshold value (7.15 for the simulated seawater in this work), the organic acid-perturbed seawater will have higher buffer capacity than the unperturbed one despite its lower pH. On the other hand, addition of conjugate base OA^- increases pH and decreases pCO_2. The resulting seawater will have higher buffer capacity than the unperturbed one across all simulating pK_a.

Simulations on both HOA and OA^- perturbations suggest that highest buffer occurs at organic acid pK_a 8.2–8.3 when the seawater is exposed to atmospheric pCO_2 of 400 µatm. pK_a for maximum buffer is slightly dependent on the physical conditions (temperature and salinity). However, stronger organic acid (lower pK_a) and conjugate base would play a more important role in regulating seawater buffer when pCO_2 increases, or ocean acidification progresses further.

In the estuarine zone, terrestrially derived organic acids, regardless of their dissociation constants, all lead to a more acidified condition (CO_2 degassing and lower pH) than the scenario in which mixing occurs between zero-T_{HOA} river water and seawater. This effect diminishes with increasing salinity. Nevertheless, organic alkalinity with pK_a that provides maximum buffer in seawater would provide greater buffer in the estuarine mixing zone, while that from a stronger acid either substantially increases pCO_2 at low salinity or decreases buffer against further pH change at mid to high salinity conditions.

Despite that HOA or OA^- addition could enhance seawater buffer capacity to various extents, degradation of organic acid should have a net increase in DIC. Therefore, organic alkalinity likely should not be considered as a mechanism for enhancing long-term seawater buffer or facilitating additional atmospheric CO_2 uptake. Regardless, there are still many unknowns with organic alkalinity; thus, it is worth continuing investigation on how much of this alkalinity, both those organics that have been included by the current analytical approaches and those that are not (i.e., pK_a below the currently defined zero proton level), contribute to the oceanic alkalinity cycle.

Acknowledgements This study is funded by the National Science Foundation Chemical Oceanography Program (OCE-1654232). The author wishes to thank Drs. David Burdige and Robert Byrne for their helpful comments on an earlier draft of this manuscript, and Melissa McCutcheon for her editorial help. Three reviewers and the associate editor provided critical insights on an earlier version of this manuscript, which helped to improve the quality of the work.

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