





Organic Alkalinity as an Important Constituent of Total Alkalinity and the Buffering System in River-To-Coast Transition Zones

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Key Points:

- Organic alkalinity can greatly affect seawater acidity and the carbonate system in six southeast Chinese estuaries
- Organic acids with low- pK_a values caused significant uncertainties in different total alkalinity measurement approaches in southeastern Chinese estuaries
- River input is a major source of organic alkalinity in the study estuaries

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Organic acid-base species in the dissolved organic carbon pool have been shown to make an important contribution (i.e., organic alkalinity; OrgAlk) to the total alkalinity (TA) in many coastal systems. This study documents an intensive investigation of OrgAlk characteristics in the river-to-coast transition zones of six southeast Chinese rivers. OrgAlk, mainly originating from river input, accounted for an important proportion of TA (0.3%–12%) in six estuaries. Carboxylic acid groups were commonly present in all estuaries. Notable differences in the TA values (1–18 $\mu\text{mol kg}^{-1}$) determined by several established TA measurement approaches were identified in estuaries where organic acids with $pK_a < 5.2$ were abundant. The most widely used open-cell titration method, in comparison with closed-cell titration and single-step titration, is the best approach to incorporate OrgAlk in titrated TA when the pK_a values of organic acids were > 5 in the study estuaries. Across our study sites, OrgAlk might modify H^+ concentrations by 3%–69% (i.e., pH by 0.01–0.78) and aragonite saturation states by 1%–72%, indicating that OrgAlk can play a significant role in the coastal carbonate buffering system. It is essential to improve current TA measurement approaches to more accurately represent OrgAlk in the coastal system and assess impacts of OrgAlk on coastal carbonate chemistry.

Plain Language Summary Organic acid-base species have been shown to make an important contribution (i.e., organic alkalinity; OrgAlk) to total alkalinity (TA) in the coastal systems. However, the established aquatic TA model generally does not consider OrgAlk as a significant term. In this study, we assessed the influence of OrgAlk on TA measurements and the role it plays in the carbonate buffering system in six southeastern Chinese estuaries. Some of the established TA measurement approaches could not fully incorporate OrgAlk according to the definition of TA, resulting in differences in the TA values determined by different TA measurement approaches in the study estuaries, where large quantities of organic acids with $pK_a < 5.2$ were present. OrgAlk was estimated to affect H^+ concentration and aragonite saturation state considerably across our study sites, thus playing an important role in the coastal carbonate buffering system. Improving the current TA measurement approaches to better include OrgAlk in the TA model is greatly needed to avoid misinterpretation of key carbonate system indicators. This requires a comprehensive understanding of the characteristics of organic acid-base species and their cycling across coastal systems.

1. Introduction

River-to-coast transition zones, including estuaries and their adjacent coastal areas, are influenced by terrestrial inputs, coastal hydrological and biogeochemical processes, and anthropogenic activities. Estuaries play a critical role in the coastal carbon budget by modifying organic and inorganic carbon from rivers and tidal wetlands, and ultimately transporting part of the received carbon to continental shelves (Cai, 2011; Fichot et al., 2014; Herrmann et al., 2015; Najjar et al., 2018). Organic acid-base species have been reported to be abundant in organic carbon-rich coastal waters (e.g., Cai et al., 1998; Hinckley, 2021; Kerr et al., 2021; Liang et al., 2020), and originate from allochthonous sources, such as rivers, wetlands, and groundwater discharge (Cai et al., 1998; Hinckley, 2021; Song et al., 2020). They may also have autochthonous sources, such as in situ production by phytoplankton and bacteria (Dulaquais et al., 2018; Ko et al., 2016; Sarma et al., 2018). These organic acid-base species may contribute to total alkalinity (TA) in the form of organic alkalinity (OrgAlk), which is an important control on carbonate

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chemistry and CO₂ fluxes in coastal waters (Liang et al., 2020; Song et al., 2020; Yang et al., 2015). However, the biogeochemical characteristics and mixing behaviors of OrgAlk in coastal systems have only been reported by a limited number of studies (Cai et al., 1998; Kuliński et al., 2014; Song et al., 2020; Yang et al., 2015). A comparative study of OrgAlk across different coastal systems may reveal important commonalities, and improve our understanding of the environmental factors controlling variations in OrgAlk across coastal systems.

According to the definition of TA, acids with a dissociation constant $K > 10^{-4.5}$ are treated as proton donors, while those bases dissociated from weak acids with $K \leq 10^{-4.5}$ are considered as proton acceptors (Dickson, 1981). The presence of OrgAlk has been reported to impact the interpretations of traditional TA titrations and pose challenges regarding how to best determine TA under the current TA definition (Sharp & Byrne, 2020; Ulfsbo et al., 2015). Sharp and Byrne (2020) showed that the presence of low-pK_a organic acids (pK_a < 6) may result in large inconsistencies in TA values measured by open-cell and closed-cell titration methods and by a single-step titration approach. The open-cell and closed-cell titration methods determine TA values by stepwise acid addition, fitting the titration curve at pH 3.0–3.5 (or 3.8) using different approaches (e.g., Dickson, 1981; Dickson et al., 2003; Herández-Ayón et al., 1999; Millero et al., 1993), while in single-step titration (e.g., X. Liu et al., 2015; Yao & Byrne, 1998), a single addition of acid is performed to titrate the sample to the final pH (normally between pH 3.0–4.2). The distinct strategies to determine TA used by these established TA measurement approaches likely result in their different capabilities in accurately quantifying TA in the presence of low-pK_a organic acids. In particular, the conjugate bases of organic acids with pK_a < 4.5, which do not positively contribute to TA according to the TA definition (Dickson, 1981), may still be titrated by current titration methods (Sharp & Byrne, 2020), resulting in a mismatch between the titrated TA value and the TA definition. However, the importance of the presence of low-pK_a organic acids (especially those with a pK_a < 4.5) with respect to TA titration is still not well determined across different coastal systems.

Previous studies have reported that large errors might exist in the calculated carbonate system parameters if OrgAlk was ignored in organic carbon-rich coastal waters (e.g., Hunt et al., 2011; Kerr et al., 2021; Kuliński et al., 2014; Yang et al., 2015). However, the biogeochemical influence of OrgAlk on the carbonate speciation and saturation state of calcium carbonate (Ω_{Ar}) and the variation of this influence across different types of estuaries has not been thoroughly studied. This effect of OrgAlk may represent an important mechanism by which organic carbon cycling regulates the carbonate buffering system and its response to coastal acidification.

Herein, an intensive study on OrgAlk was conducted in the river-to-coast transition zones of six rivers in south-eastern China. OrgAlk concentrations and compositions were compared in six estuaries with specific hydrological and biogeochemical features to explore commonalities and differences in OrgAlk characteristics between these systems. A numerical titration model was used to estimate the uncertainties in TA values determined by open-cell, closed-cell, and single-step titration approaches in the presence of OrgAlk in each estuary. The effects of OrgAlk on the carbonate buffering system were estimated across these six estuaries to gain insight into the important role that OrgAlk plays in various coastal carbonate systems.

2. Methods

2.1. Study Sites

Water sampling was conducted in six estuaries, including the Changjiang (CJ) Estuary, Zhujiang (ZJ) Estuary, Jiaojiang (JJ) Estuary, Oujiang (OJ) Estuary, Minjiang (MJ) Estuary, Jiulongjiang (JLJ) Estuary, and their adjacent coastal areas in the Southeast of China (Figure 1). The CJ and ZJ are the first and second largest rivers in terms of annual freshwater discharge in China, respectively. The CJ and ZJ catchment areas are abundant in carbonate rocks, resulting in high HCO₃⁻ concentrations (1,500–1,800 μmol kg⁻¹) and thus high TA concentrations in CJ and ZJ freshwater (Cai et al., 2008). As opposed to CJ and ZJ, rivers that flow into the four small estuaries, including the JJ Estuary, OJ Estuary, MJ Estuary, and JLJ Estuary, have low HCO₃⁻ concentrations (300–1,000 μmol kg⁻¹) due to the relatively low carbonate weathering rates in these river catchments (Qi et al., 2014; Wu et al., 2011).

2.2. Sampling and Measurements

Samples for OrgAlk, TA, dissolved inorganic carbon (DIC), pH, dissolved organic carbon (DOC), nutrients, and salinity were collected by Niskin bottles from surface water across the freshwater-seawater mixing zones

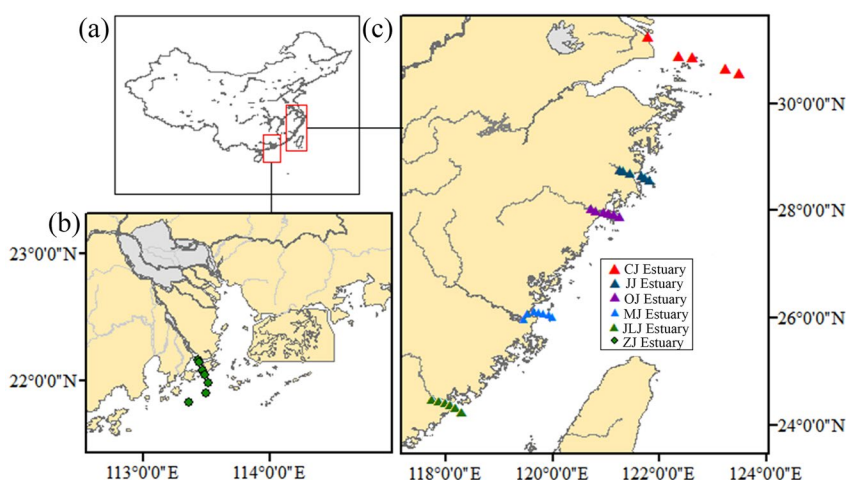


Figure 1. Sampling sites in six river-to-coast transition zones. CJ Estuary, JJ Estuary, OJ Estuary, MJ Estuary, JLJ Estuary, and ZJ Estuary represent Changjiang, Jiaojiang, Oujiang, Minjiang, Jiulongjiang, and Zhujiang Estuaries in the Southeast of China.

in ZJ, MJ, OJ, JLJ, and JJ Estuaries in August 2019 (Figure 1). Samples of the same parameters were collected in the surface water of the CJ Estuary in August 2020 (Figure 1). Temperature of water samples was measured with a handheld digital thermometer (HH800, Omega, USA). Sample salinity was analyzed in the lab with a Guildline AutoSal instrument (8400B, Guildline, Canada) with a precision of 0.01. Unfiltered water samples for TA, DIC, pH, and OrgAlk measurements were collected into 250 mL borosilicate glass bottles and poisoned with 100 μL of a saturated mercuric chloride solution for preservation. DOC and nutrient samples were filtered through pre-combusted GF/F filters (0.75 μm pore size). Filtered DOC samples were acidified to pH <2 with hydrochloric acid and stored in the refrigerator until analysis. Filtered nutrient samples were preserved with 25 μL of a saturated mercuric chloride solution and stored at 4°C until analysis.

DOC samples were measured using a total organic carbon analyzer (TOC-VCPN, Shimadzu Co., Japan) with the precision of DOC measurements <2%. Nutrient samples were measured by a segmented flow analyzer (Sanplus System, Skalar Analytical, The Netherlands). DIC samples were measured with a DIC auto-analyzer (AS-C3, Apollo SciTech Inc., USA). During the DIC measurements, aliquots for DIC analysis were sampled from the surface layer of each bottle after the unopened sample bottle had been left standing for 2 hr, to avoid the influence of settled carbonate particles. The precision and accuracy of DIC measurement was $\pm 2 \mu\text{mol kg}^{-1}$.

pH samples were measured with a Ross glass pH electrode (Orion 81208B, Thermo Fisher Scientific, USA) at a constant temperature (25°C) when salinity was ≤ 5 . The measurement accuracy was ± 0.01 . When salinity was >5, pH samples were measured using an automated flow-through system for embedded spectrophotometry (Reggiani et al., 2016). The salinity range for potentiometric and spectrophotometric pH measurements was suggested by Dinauer and Mucci (2017). Thymol blue sodium salt (TCI #FCP01, Tokyo chemical industry) was used as an indicator for spectrophotometric pH measurements. The thymol blue has been suggested to have low impurities as an indicator (Hudson-Heck & Byrne, 2019). J. Liu et al. (2022) reported limited influence of impurity in thymol blue on pH measurement. The accuracy of spectrophotometric pH measurements of certified reference material (CRM; Scripps Institution of Oceanography) was ± 0.0024 . Given that particles might interfere with the accuracy of spectrophotometric pH measurements and the JJ Estuarine water remained highly turbid when salinity reached high values (salinity >20), pH values of the JJ Estuarine water were measured by pH electrode, instead of by embedded spectrophotometry, when salinity was >5. The pH values measured at NBS scale were transferred to the total proton concentration scale by CO2SYS program (Matlab version; van Heuven et al., 2011). In this study, all pH values are reported on the total proton concentration scale (pH_T) at in situ temperature.

TA samples were filtered using 0.45 μm syringe filters (Pall, USA) before determination of TA concentration by a modified Gran titration method using a ROSSTM combination pH electrode. During the titration process, a Kloehn syringe pump (V6, Norgren, USA) was used to control the volume of hydrochloric acid (HCl) solution added into the sample. The concentration of HCl was calibrated with a certified reference material from Dr. A. G.

Dickson's lab (Scripps Institution of Oceanography, USA). The precision of TA measurement was $\pm 2 \mu\text{mol kg}^{-1}$. The measured TA values were used to estimate the proportions of OrgAlk in TA and calculate the influence of OrgAlk on H^+ and Ω_{Ar} across different coastal systems in this study. It should be noted that we likely underestimated TA values as a result of adding HgCl_2 into the TA samples for preservation. Mos et al. (2021) reported that the addition of HgCl_2 was likely associated with a $\sim 0.8\%$ reduction of measured TA values in estuarine water samples after 1–6 months of collection. The potential underestimation of TA likely caused an overestimation of the proportions of OrgAlk in TA. However, the magnitude of this overestimate was likely rather small ($\sim 0.8\%$). Moreover, if the measured TA values were increased by 0.8%, the estimated mean OrgAlk effects on H^+ and Ω_{Ar} would change by $\sim 5\%$. This small deviation caused by potential TA uncertainties would not change our conclusion on the importance of OrgAlk effects on the carbonate buffering system in this study.

OrgAlk samples were filtered by $0.45 \mu\text{m}$ syringe filters (Pall, USA) before measurement. OrgAlk measurements were performed according to the methods of Cai et al. (1998) and Song et al. (2020). In brief, each OrgAlk sample was titrated from its initial pH to $\text{pH} < 3$ with a calibrated HCl solution. After CO_2 was removed from the acidified sample by bubbling high purity nitrogen gas, the sample was titrated with a NaOH solution ($\sim 0.1 \text{ M}$) back to its initial pH. The NaOH solution was prepared with DI water bubbled with high purity nitrogen gas for $\sim 3 \text{ hr}$ to remove dissolved CO_2 . Lastly, the second open-cell titration was conducted on the sample to determine the remaining non-carbonate alkalinity concentration after the removal of carbonate alkalinity. OrgAlk was determined by subtracting the borate alkalinity and nutrient alkalinity from the non-carbonate alkalinity. Borate alkalinity was calculated from salinity and pH according to Lee et al. (2010). Nutrient alkalinity contributed from silicate, phosphate, and ammonium was calculated based on nutrient concentrations and pH according to Dickson et al. (2007). Despite bubbling with nitrogen gas, the NaOH solution may dissolve some air CO_2 , which will result in uncertainties in OrgAlk measurements. The DIC concentration in the NaOH solution was determined as the difference in TA values of carbonate-free artificial seawater between the first and second titrations following the method of Song et al. (2020). The OrgAlk concentrations were corrected for the presence of carbonate alkalinity ($13\text{--}19 \mu\text{mol kg}^{-1}$) introduced by the NaOH solution titration. The mean difference in OrgAlk concentrations between duplicate samples ($n = 38$) was $3 \pm 2 \mu\text{mol kg}^{-1}$. Although the OrgAlk concentration was corrected for introduced carbonate alkalinity, the removal of or accounting for carbonate alkalinity in titration bases needs to be further studied to improve the accuracy of OrgAlk measurements.

Previous studies have used the excess TA (ΔTA) approach to estimate the contribution of OrgAlk, which involves calculating the difference between the measured TA and the calculated TA from DIC-pH or DIC- $p\text{CO}_2$ pair that presumably does not include OrgAlk (e.g., Lukawska-Matuszewska et al., 2018; Yang et al., 2015). However, a significant disparity observed between ΔTA and measured OrgAlk (Figure S1 in Supporting Information S1) highlights the need for further research to better quantify OrgAlk.

We defined the freshest (salinity < 2.5) and most saline (salinity > 29) samples in each estuary as the freshwater and seawater endmembers of the corresponding estuary, respectively. Full titrations were conducted on the freshwater and seawater endmembers of each estuary to determine the dissociation constants and total concentrations of organic acids in the six estuaries. The total concentration of a specific organic acid (HA_T) represents the sum of the concentrations of the organic acid (HA) and its conjugate base (A^-). Samples for full titration were first titrated with HCl solution to $\text{pH} < 3.0$. After removing CO_2 with high purity nitrogen gas, the acidified sample was titrated to $\text{pH} > 10.0$ with ~ 200 stepwise additions of calibrated NaOH solution to obtain a full titration curve. The full titration curve was used to derive the apparent pK_a values and total concentrations of organic acids by a charge balance model elaborated below.

2.3. Charge Balance Model

The pK_a values and total concentrations of organic acids in a given sample were determined by a charge balance model according to Cai et al. (1998) and Song et al. (2020). To account for the residual CO_2 concentration in the NaOH solution, its introduced carbonate alkalinity was added into the charge balance equation (Song et al., 2020):

$$V_0 \sum_i \frac{\text{HA}_{iT}}{1 + \frac{[\text{H}^+]}{K_i}} + \frac{V_0 \text{B}_T}{1 + \frac{[\text{H}^+]}{K_B}} + \frac{V_0 \text{Si}_T}{1 + \frac{[\text{H}^+]}{K_{\text{Si}}}} + \text{P}_{\text{Alk}} + \frac{V \text{C}_{\text{TNa}}}{1 + \frac{[\text{H}^+]}{K_{\text{C1}}} + \frac{K_{\text{C2}}}{[\text{H}^+]}} \quad (1)$$

$$+ \frac{2V \text{C}_{\text{TNa}}}{1 + \frac{[\text{H}^+]^2}{K_{\text{C1}} K_{\text{C2}}} + \frac{[\text{H}^+]}{K_{\text{C2}}}} - (V + V_a)([\text{H}^+] - [\text{OH}^-]) + V_a \text{C}_{\text{H}}^0 - V \text{C}_{\text{B}} = 0$$

where,

$$P_{\text{Alk}} = \frac{2V_0P_TK_{P1}K_{P2}K_{P3} + V_0P_TK_{P1}K_{P2}[H^+] - V_0P_T[H^+]^3}{[H^+]^3 + K_{P1}[H^+]^2 + K_{P1}K_{P2}[H^+] + K_{P1}K_{P2}K_{P3}} \quad (2)$$

where V_0 is the initial volume of the sample; HA_{iT} is the total concentration of organic acid i ($HA_{iT} = [HA_i] + [A_i^-]$); K_i is the dissociation constant of organic acid i . B_T , Si_T , and P_T are the total concentrations of borate, silicate, and phosphate, respectively, which were determined by nutrient measurements; K_B , K_{Si} , K_{C1} , K_{C2} , K_{P1} , K_{P2} , and K_{P3} are the dissociation constants of boric acid, silicic acid, carbonic acid, and phosphoric acid, respectively. V is the volume of NaOH solution added into the sample. C_{TNa} is the concentration of DIC in the NaOH solution. V_a is the volume of the acidified sample. C_H^0 is the hydrogen ion concentration after the first titration. C_B is the concentration of NaOH, determined by calibrated HCl titration. K_B , K_{Si} , K_{P1} , K_{P2} , K_{P3} , K_{C1} , and K_{C2} were calculated using the parameterizations of Cai and Wang (1998), Dickson (1990), and Millero (1995), respectively. X_{IT} , K_i , C_H^0 , and C_{TNa} were determined by fitting Equation 1 using the Matlab™ function “leastsq.”

A previous study has reported that the OrgAlk values calculated using pK_a values and total concentrations of organic acids estimated from the charge balance model were generally higher compared to the measured OrgAlk concentrations obtained through the two-step Gran titration approach (Song et al., 2020). The charge balance model assumed zero ionic strength in the samples, which likely caused uncertainties in the estimated pK_a values and total concentrations of organic acids. Masini et al. (1998) reported a maximum organic acid pK_a variation of 0.75 over a range of ionic strengths from 0.01 to 1.0 M. To quantify the uncertainties in estimated pK_a values due to ignoring ionic strength, we assumed that the variation in the pK_a value of a given organic acid is proportional to the change in ionic strength. The potential maximum uncertainty in the estimated pK_a of organic acids in a given sample with ionic strength I was then calculated as $I/(1.0-0.01) \times 0.75$, according to the report of Masini et al. (1998). This pK_a uncertainty was used in the following uncertainty analysis.

Given the potential uncertainties in the estimated total concentrations of organic acids from the charge balance model, and the challenge to determine these uncertainties, we refrained from using the total concentrations of organic acids estimated by the model to assess the influence of OrgAlk in full titration samples. Instead, we used the measured OrgAlk values, pK_a values, and total concentration ratio of organic acids derived from the charge balance model to re-estimate the total concentrations of organic acids in each full titration sample (Equation S1 in Supporting Information S1), and employed these values for the subsequent estimation of OrgAlk influence on the TA measurements and carbonate buffering system. This approach ensures that the estimated contributions of OrgAlk to TA in full titration samples, when assessing the influence of OrgAlk based on pK_a values and re-estimated total concentrations of organic acids, are consistent with the measured OrgAlk concentrations. Since full titrations were conducted only on the freshwater and seawater endmembers in each estuary, we assumed that the concentrations of organic acids were conservative and that the apparent pK_a values of organic acids remained constant during the mixing of freshwater and seawater. Thus, the total concentrations of freshwater-sourced and seawater-sourced organic acids in a given estuarine sample were calculated by multiplying the re-estimated total concentrations of organic acids at the freshwater (T_f) and seawater endmembers (T_s) of that estuary by the proportion of freshwater (P_f) and seawater (P_s) in the sample, that is, $T_f \times P_f$ and $T_s \times P_s$, respectively. The estimated pK_a values and total concentrations of organic acids in each sample of an estuary were then used to estimate the effects of OrgAlk on the TA measurements and the carbonate buffering system, as described in the following sections.

2.4. Evaluation of the Agreement in Established TA Measurement Approaches

The agreement in different TA measurement approaches in the presence of OrgAlk in each estuary, was determined using a numerical titration model (Sharp & Byrne, 2020). This model simulates five distinct TA measurement approaches to estimate the resulting TA values in the presence of OrgAlk. The measurement methods include open-cell titration with modified Gran function analysis of titration data (MGF open-cell), open-cell titration with nonlinear least squares fit of titration data (NLSF open-cell), closed-cell titration with nonlinear least squares fit of titration data (NLSF closed-cell), closed-cell titration with difference derivative analysis of titration data (DD closed-cell) and single-step titration. The pH, DIC, estimated pK_a values, and total concentrations of organic acids in each sample were used as input parameters to run the titration model. We define the difference between measured TA values and inorganic alkalinity (including carbonate, borate, and nutrient alkalinity) due to the presence of organic acids as titratable OrgAlk (OrgAlk_T). OrgAlk_T represents the concentration of OrgAlk that each TA measurement approach could interpret in the presence of given organic acids. The concentration of OrgAlk_T in each sample was

estimated by subtracting the inorganic alkalinity derived by the model titration when the organic acid concentration is set to zero from the corresponding model-derived TA value for each of the five TA measurement approaches.

According to Dickson's TA definition (Dickson, 1981), in the presence of organic acids with $pK_a \geq 4.5$, conjugate bases of these organic acids are included in TA as a positive term, whereas if organic acids have pK_a values < 4.5 , organic acids are included as a negative term in the TA calculation equation. Therefore, the OrgAlk concentration according to TA's definition could be calculated as:

$$\text{OrgAlk}_D = \sum_i \frac{HX_{iT}}{1 + \frac{[H^+]}{K_{Xi}}} - \sum_i \frac{HY_{iT}}{1 + \frac{K_{Yi}}{[H^+]}} \quad (3)$$

where HX_{iT} and K_{Xi} represent the total concentration and dissociation constant of organic acid HX_i with $pK_a \geq 4.5$, respectively; HY_{iT} and K_{Yi} represent the total concentration and dissociation constant of organic acid HY_i with $pK_a < 4.5$, respectively. The OrgAlk concentrations calculated by Equation 3 were termed "defined OrgAlk" (OrgAlk_D) in this study. The pK_a values and total concentrations of organic acids used to estimate OrgAlk_T and OrgAlk_D in each sample was derived in Section 2.3. The difference between OrgAlk_T and OrgAlk_D indicates the uncertainty in each TA measurement approach caused by the presence of organic acids, according to the current definition of TA.

2.5. Evaluation of the Influence of OrgAlk on the Carbonate Buffering System

The influence of OrgAlk on H^+ concentration and Ω_{Ar} was evaluated by incorporating the pK_a values and total concentrations (i.e., HA_T) of organic acids in each sample, as estimated in Section 2.3, into the CO2SYS calculation program (van Heuven et al., 2011) according to Song et al. (2020). We assumed that all conjugate bases of organic acids are produced or removed simultaneously with protons (i.e., from the dissociation of organic acids or the reverse association process). When the conjugate bases of organic acids have a positive contribution to TA, that is, their pK_a values ≥ 4.5 according to the definition of TA, any changes in their concentrations would be offset by simultaneous changes in protons, resulting in no change in TA. Note that certain organic acids with pK_a values < 4.5 may negatively contribute to TA according to the TA definition (Dickson, 1981; Equation 3). The production of these organic acids would thus decrease TA (Equation 3). However, all identified conjugate bases of organic acids in the study estuaries were suggested to positively contribute to TA, except for those organic acids that were excluded for data analysis (see Section 3.2 for detailed information). OrgAlk influence was thus estimated as the differences of pH_T (ΔpH_T), H^+ concentrations (ΔH^+), and Ω_{Ar} ($\Delta \Omega_{Ar}$) between the values calculated from the OrgAlk-incorporated CO2SYS program with TA, DIC, and OrgAlk as input parameters and the values derived from the same program but with OrgAlk = 0. Note that some conjugate bases of organic acids might also be produced with other cations, such as Zn^{2+} or Cu^{2+} (Garcia-Mina, 2006; Shi et al., 2016), resulting in the net gain or loss of TA. However, the current knowledge is limited for our understanding of how conjugate bases of organic acids cycle with H^+ versus with other cations. In this study, we estimated OrgAlk effects by assuming that all conjugate bases of organic acids are produced concurrently with H^+ to constrain TA variation, which is required to resolve the OrgAlk-incorporated CO2SYS program. To explicitly estimate OrgAlk effects on the buffering system, future studies on the cycling of organic acid-base species in the aquatic environment are needed.

The combined uncertainties of ΔpH_T , ΔH^+ , and $\Delta \Omega_{Ar}$, including uncertainties in pK_a values of silicic acid, carbonic acid, phosphoric acid, boric acid, and organic acids and uncertainties in OrgAlk, TA, and DIC measurements, were also estimated based on a modified error propagation program (Orr et al., 2018; Song et al., 2020).

3. Results

3.1. OrgAlk Concentrations in Estuaries of Southeast China

To gain insight into the variability of the carbonate systems and OrgAlk concentrations in different types of rivers emptying into the south-eastern coastal area, the OrgAlk, pH_T , TA, DIC, and DOC concentrations in freshwater endmembers (freshest sample with salinity < 2.5) of six estuaries were compared (Figure 2). ZJ and CJ had lower OrgAlk concentrations and higher TA and DIC values than OJ, JJ, JLJ, and MJ (Figure 2). The maximum OrgAlk concentration was observed in JJ, while the maximum DOC concentration was observed in JLJ (Figure 2).

The measured OrgAlk concentrations ranged from 6 to 62 $\mu\text{mol kg}^{-1}$ across the six estuaries with the maximum observed at the freshwater endmember of the JJ Estuary and the minimum at the seawater endmembers of the JJ and JLJ Estuaries (Table S1 in Supporting Information S1). The measured OrgAlk concentrations generally

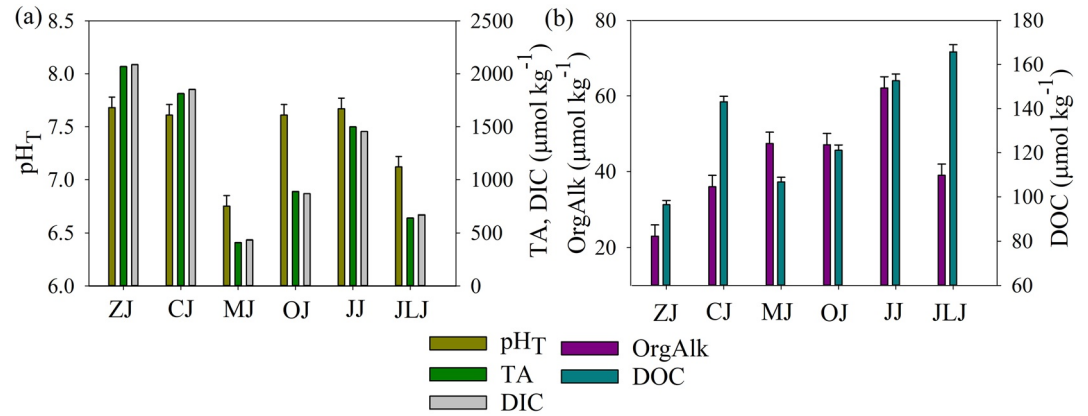


Figure 2. The pH_T, DIC, TA, OrgAlk, and DOC values at the freshwater endmembers of six estuaries. The error bars indicate the uncertainties in the corresponding parameters.

decreased with increasing salinity and pH_T in all of the study estuaries, except in the ZJ Estuary (Figure 3 and Figure S2 in Supporting Information S1). OrgAlk concentrations were significantly negatively correlated with salinity ($p < 0.05$) in the JLJ, MJ, OJ, and JJ Estuaries, while no significant correlation between the measured OrgAlk and salinity was observed in the CJ and ZJ Estuaries (Figures 3a and 3b). OrgAlk accounted for 0.3%–12% of TA, was an important proportion of TA in all six estuaries (Figures 3c and 3d). The maximum proportion of OrgAlk was observed at the freshwater endmember of MJ Estuary, while the minimum was observed at the seawater endmember of ZJ Estuary (Figures 3c and 3d).

The variations in DOC concentrations were significantly correlated with salinity ($p < 0.05$) in the JLJ, MJ, OJ, and JJ Estuaries (Figures 4a and 4b). In comparison, there was no significant correlation between the DOC concentrations and salinity in the ZJ and CJ Estuaries (Figures 4a and 4b). The OrgAlk:DOC ratios varied from 6% to 44% and decreased with increasing salinity in most estuaries, except for the CJ Estuary (Figures 4c and 4d). This indicated that organic acids were an important component of DOC in the estuaries of this study, and river freshwater was likely a major source of organic acids to these estuaries.

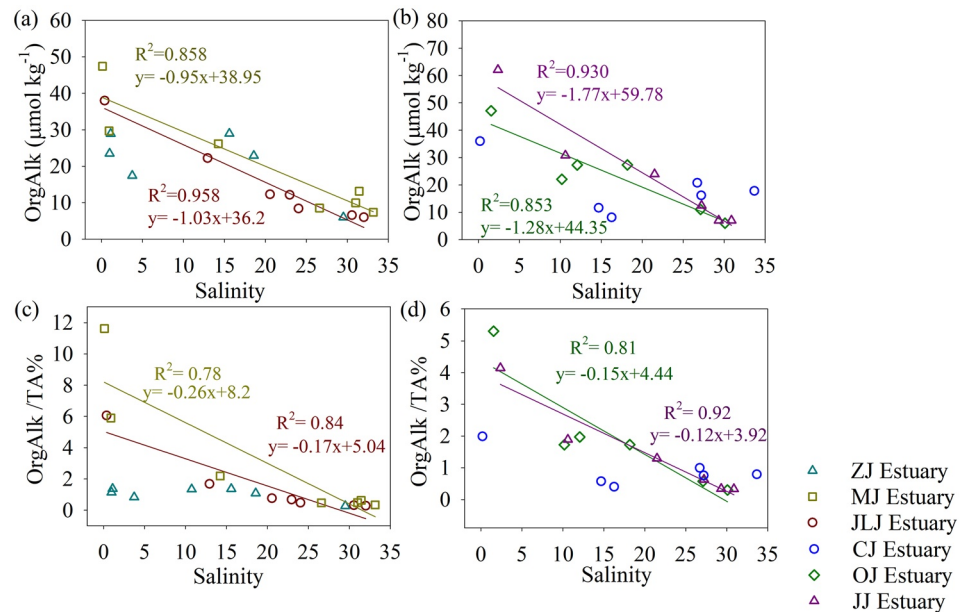


Figure 3. The variations in measured OrgAlk concentrations (a, b) and proportions of OrgAlk in TA (c, d) in six estuaries. The solid lines represent the best-linear regression lines between OrgAlk or OrgAlk/TA% and salinity when the correlation is significant for a given estuary ($p < 0.05$). The colors of the regression lines are the same as the corresponding data symbols of the estuaries.

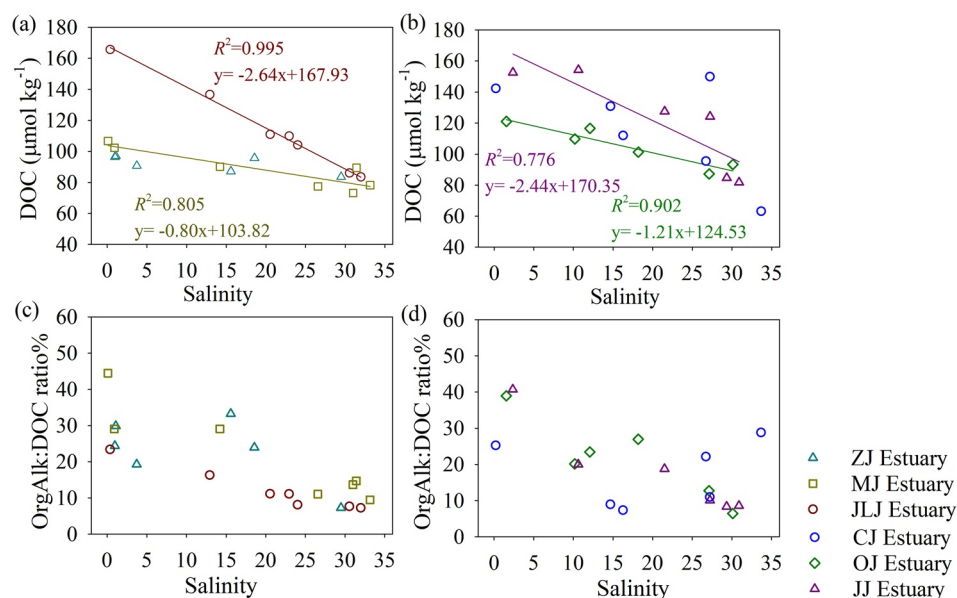


Figure 4. Variations in DOC (a, b) and OrgAlk:DOC ratios (c, d) with salinity in six estuaries. The solid lines represent the regression lines between DOC and salinity, between which there is a significant correlation for a given estuary ($p < 0.05$). The colors of the regression lines are the same as the corresponding data symbols of the estuaries.

3.2. Characteristics of Organic Acid Groups

The pK_a values of organic acids at the freshwater and seawater endmembers of the study estuaries ranged between 4.4 and 9.6 (Table 1). Three groups of organic acids were identified at the seawater endmembers of the JLJ, MJ, and JJ Estuaries, while two groups of organic acids were identified at the seawater endmembers of the remaining estuaries and the freshwater endmembers of all study estuaries (Table 1), which were defined as the second and third groups of organic acids. The pK_{a1} value of the first group (pK_{a1}) at the seawater endmember of the MJ Estuary was estimated to be ~ 5.0 (Table 1), which was relatively high compared to the groups with pK_{a1} of 2.8–3.0 identified at the seawater endmembers of the JJ and JLJ Estuaries. However, the full titration of samples was conducted over a pH range of ~ 3.0 –10.0. At the boundary of this range, the pK_{a1} values (~ 3.0) derived from the full titration curves potentially have large uncertainties. Therefore, these pK_{a1} values for JJ and JLJ Estuaries were not considered in further data analysis but are still presented in Table 1. Given the low OrgAlk concentrations ($< 7 \mu\text{mol kg}^{-1}$) at the seawater endmembers of JJ and JLJ Estuaries, ignoring these organic acids will likely have limited impacts on our results. The pK_a values of the second group of organic acids (pK_{a2}) were in the range of 4.4–6.8 at the freshwater endmembers and 5.0–6.1 at the seawater endmembers of all six estuaries (Table 1). Similar pK_{a2} values (in the range of 5.0–6.1) were observed at the freshwater and seawater endmembers of all the study estuaries, except for the ZJ and CJ Estuaries (Table 1). The pK_a values of the third group (pK_{a3}) (Table 1) were above 7.9 at the freshwater and seawater endmembers of all estuaries, except for the JJ Estuary, where the pK_{a3} was 6.6.

It should be noted that the OrgAlk values derived from the pK_a values and total concentrations of organic acids estimated by the charge balance model were generally higher than the corresponding OrgAlk concentrations derived from the two-step titration method, particularly at the seawater endmembers of the study estuaries (Table 1). The mismatch between these two values can likely be attributed, at least in part, to uncertainties in the estimated pK_a values and total concentrations of organic acids caused by the omission of ionic strength in the charge balance model.

3.3. Agreement in TA Measurement Approaches

The agreement in TA values determined by different TA measurement approaches in the presence of OrgAlk was evaluated in each estuary using a numerical titration model (Sharp & Byrne, 2020). Given that the inorganic alkalinity values determined by distinct TA measurement approaches through the titration model were virtually identical (Sharp & Byrne, 2020), the deviations in titratable OrgAlk (i.e., OrgAlk_T), calculated as the difference between

Table 1
The Primary Groups of Organic Acids Estimated at the Freshwater and Seawater Endmembers of ZJ, CJ, JLJ, MJ, OJ, and JJ Estuaries

Sample	Salinity	pH _T	OrgAlk (μmol kg ⁻¹)	pK _{a1}	pK _{a2}	pK _{a3}	HA _{1T} (μmol kg ⁻¹)	HA _{2T} (μmol kg ⁻¹)	HA _{3T} (μmol kg ⁻¹)
Freshwater endmember									
ZJ Estuary	1.0	7.68	34	–	6.8	8.1	–	8	138
CJ Estuary	0.2	7.61	36	–	4.4	8.9	–	64	95
JLJ Estuary	0.4	7.12	39	–	5.0	8.4	–	79	21
MJ Estuary	0.1	6.75	45	–	5.2	7.9	–	9	204
OJ Estuary	1.5	7.61	44	–	5.2	8.5	–	7	80
JJ Estuary	2.4	7.67	59	–	5.1	8.6	–	19	23
Seawater endmember									
ZJ Estuary	29.5	8.03	6	–	6.0	8.7	–	90	74
CJ Estuary	33.7	7.96	18	–	5.0	7.9	–	40	123
JLJ Estuary	32.0	7.88	6	3.0 ^a	5.8	9.6	32 ^a	9	17
MJ Estuary	33.1	8.00	10	5.0	6.1	9.1	10	52	41
OJ Estuary	30.1	7.98	6	–	5.7	8.7	–	90	122
JJ Estuary	30.9	7.90	7	2.8 ^a	5.2	6.6	46 ^a	30	60

Note. OrgAlk concentrations were measured by two-step Gran titration method. pK_{a1}, pK_{a2}, and pK_{a3} represent the pK_a values of groups 1–3 estimated using the charge balance model in full titration samples. HA_{1T}, HA_{2T}, and HA_{3T} denote the total concentrations of groups 1–3 estimated using the charge balance model.

^aMeans organic acids with pK_a around 2.8–3.0, which were not considered in the subsequent analysis of the influence of OrgAlk on TA measurements and the carbonate system.

titrated TA values and the corresponding inorganic alkalinity values determined by each TA measurement approach, could indicate the consistency of the current TA measurement approaches in the presence of OrgAlk (Figure 5).

Noticeable deviations (1–18 μmol kg⁻¹) in OrgAlk_T values derived from open-cell titration, closed-cell titration, and single-step titration approaches were observed in low salinity waters (salinity ≤27) of the JJ, JLJ, and CJ Estuaries, where organic acids with pK_a <5.2 were observed (Figure 5 and Table 1). These deviations were estimated to account for ~1–10% of the TA values determined by the open-cell titration approach, and the magnitude of these deviations decreased as salinity increased (Figure 5). There was almost no difference (<3 μmol kg⁻¹) in OrgAlk_T values derived from different TA measurement approaches in the high-salinity coastal zones (salinity >27; Figure 5).

The OrgAlk_T values derived from the established TA measurement approaches were much closer (deviation <2 μmol kg⁻¹) to the concentrations of defined OrgAlk (i.e., OrgAlk_D) determined by the current definition of TA in the ZJ, MJ, and OJ Estuaries, except for the OrgAlk_T values derived from the DD closed-cell titration approach (Figure 5 and Table 2). In the JJ and JLJ Estuaries, the concentrations of OrgAlk_D were nearly equal to the OrgAlk_T values derived from the MGF and NSLF open-cell titration measurements but were generally higher than the OrgAlk_T values derived from the NSLF and DD closed-cell titration approaches, and the single-step titration approach by a maximum of 13 μmol kg⁻¹ (Figure 5 and Table 2). Large deviations (~0–30 μmol kg⁻¹) were observed between OrgAlk_T values derived from all TA measurement approaches and the concentrations of OrgAlk_D in the CJ Estuary (Figure 5b and Table 2).

3.4. Effects of OrgAlk on H⁺ and Ω_{Ar}

The impact of OrgAlk on H⁺, pH_T, and Ω_{Ar} (i.e., ΔH⁺, ΔpH_T, and ΔΩ_{Ar} defined in the Methods section) was derived by incorporating the pK_a values and total concentrations of organic acids in each sample into the CO2SYS program as described in Section 2.5 (Figure 6). It is worth noting that we identified a group of organic acids with a pK_a value of 4.4 at the freshwater endmember of the CJ Estuary (Table 1). Given the uncertainties associated with the derived pK_a values, it can be challenging to determine whether these particular organic acids should be considered as a positive or negative term in TA. However, based on the findings of our study (Figure 5) and the study conducted by Sharp and Byrne (2020), the conjugate bases of this group of organic acids might be

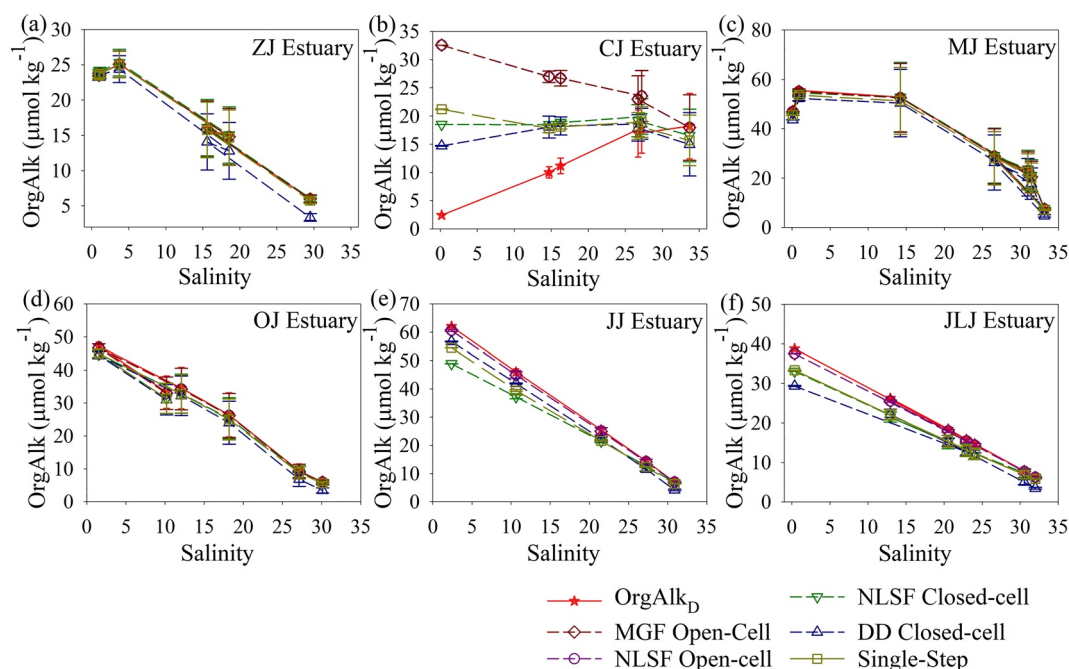


Figure 5. The concentrations of titratable OrgAlk (OrgAlk_T) and defined OrgAlk (OrgAlk_D) in six estuaries. The OrgAlk_T values were determined by subtracting inorganic alkalinity (carbonate alkalinity, borate alkalinity, and nutrient alkalinity) from total alkalinity (TA) values derived from modeled MGF open-cell, NLSF open-cell, NLSF closed-cell, DD closed-cell, and single-step titration methods according to Sharp and Byrne (2020). OrgAlk_D was calculated based on Dickson's definition on TA. The error bars indicate uncertainties in OrgAlk_T and OrgAlk_D due to uncertainties in pK_a values of organic acids.

incorporated into the measured TA values through open-cell titration methods. Therefore, to maintain consistency with the measured TA values, the conjugate bases of this group of organic acids were included as a positive contribution to TA when estimating the influence of OrgAlk.

The presence of OrgAlk changed the H^+ concentration by 0.4–115 nmol kg^{-1} and the pH_T by 0.01–0.78, and the effects were smaller at higher salinities (Figures 6a and 6b). The influence of OrgAlk on the H^+ concentration was greater in the JJ, MJ, OJ, and JLJ Estuaries than in the CJ and ZJ Estuaries (Figures 6a

Table 2
The Comparison Between Mean Defined OrgAlk (OrgAlk_D) and Titratable OrgAlk (OrgAlk_T) Derived From the MGF and NLSF Open-Cell Titration Methods, NLSF and DD Closed-Cell Titration Methods, and Single Step Titration Method Across Six Estuaries

Study sites	OrgAlk_D ($\mu\text{mol kg}^{-1}$)	OrgAlk_T ($\mu\text{mol kg}^{-1}$)				
		MGF open-cell	NLSF closed-cell	NLSF open-cell	DD closed-cell	Single-step
ZJ Estuary	18	18 (0)	18 (0)	18 (0)	17 (0-2)	18 (0)
MJ Estuary	34	34 (0)	34 (0-1)	34 (0)	31 (2-4)	33 (0-2)
OJ Estuary	26	26 (0)	25 (0-2)	26 (0)	24 (2-3)	25 (1-2)
JJ Estuary	31	30 (0-1)	25 (2-13)	30 (0-1)	27 (3-5)	27 (2-8)
JLJ Estuary	18	18 (0-2)	16 (0-6)	18 (0-2)	14 (3-9)	16 (0-5)
CJ Estuary	13	25 (0-30)	18 (2-16)	25 (0-30)	17 (0-12)	18 (1-18)

Note. The numbers in parentheses indicate the range of differences between OrgAlk_D and OrgAlk_T .

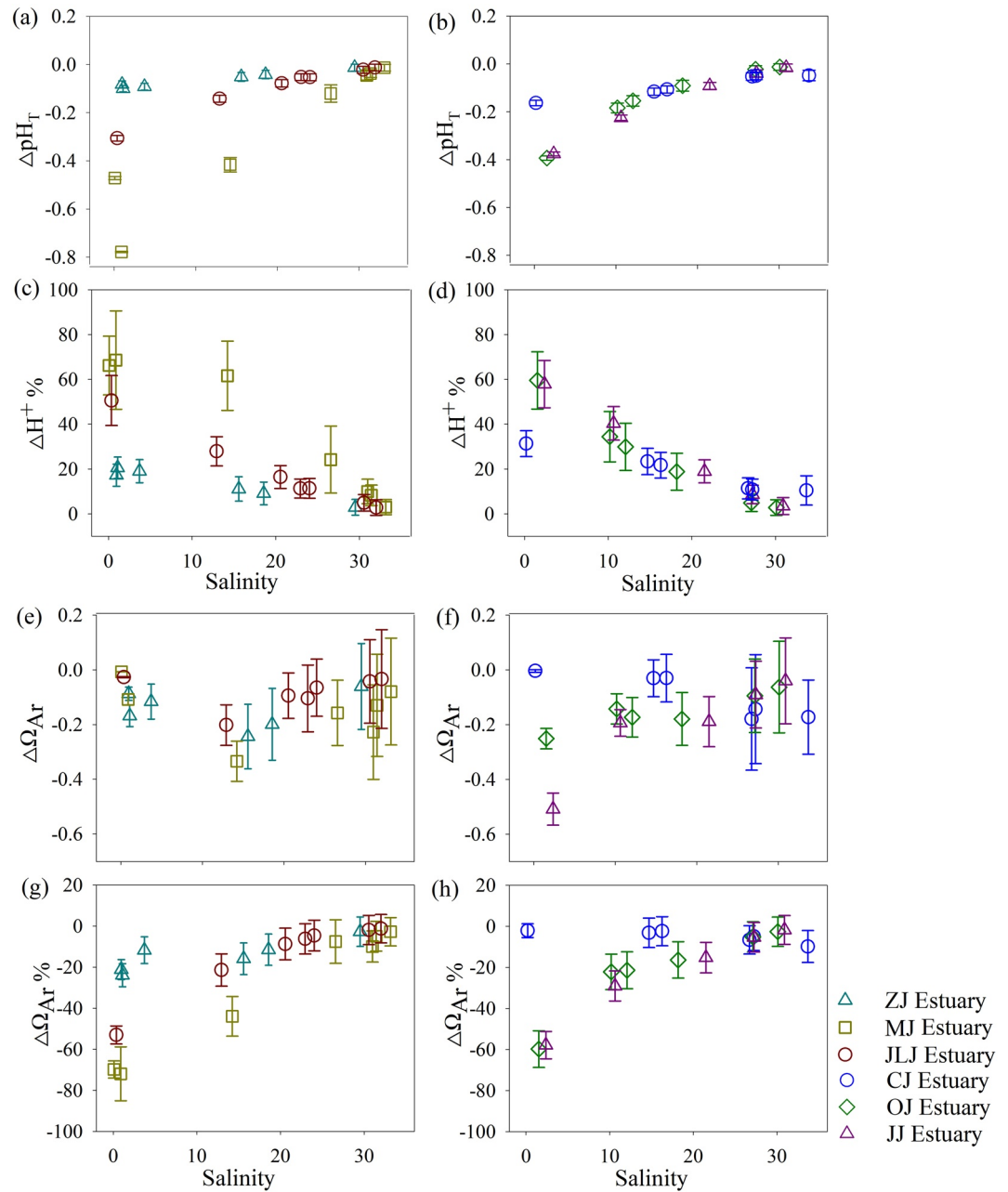


Figure 6. Variations in OrgAlk influence on pH_T (ΔpH_T ; a and b), Ω_{Ar} ($\Delta\Omega_{Ar}$; e and f) and the percentage of ΔH^+ and $\Delta\Omega_{Ar}$ in H^+ concentration (c and d) and Ω_{Ar} values (g and h) calculated with consideration of OrgAlk in six estuaries. The error bars indicate uncertainties in OrgAlk effects.

and 6b). In total, variations in the H^+ concentrations resulting from the influence of OrgAlk might account for 3%–69% of the H^+ concentrations calculated by the modified CO2SYS program considering OrgAlk (Figures 6c and 6d).

Compared to ΔH^+ , the differences in calculated Ω_{Ar} due to OrgAlk exhibited a complex relationship with salinity (Figure 6). At low salinities, $\Delta\Omega_{Ar}$ generally decreased (became more negative) with increasing salinity; however, $\Delta\Omega_{Ar}$ increased (became less negative) as salinity increased when salinity reached higher values in the ZJ, MJ, and JLJ Estuaries (Figure 6e). For the OJ and JJ Estuaries, $\Delta\Omega_{Ar}$ generally increased with increasing salinity, with the maximum $\Delta\Omega_{Ar}$ values occurring at the seawater endmembers of these estuaries (Figure 6f). The variations in $\Delta\Omega_{Ar}$ might account for –72% to –1% of Ω_{Ar} values calculated by the modified CO2SYS program considering

OrgAlk, with the minimum observed at the freshwater endmember of the MJ Estuary and the maximum observed in the offshore coastal waters (Figures 6g and 6h).

4. Discussion

4.1. OrgAlk Variations in Estuaries of Southeast China

All the study estuaries were rich in OrgAlk with river input as its primary source (Figure 3). The CJ and ZJ, which have abundant carbonate rocks within their catchments, showed lower OrgAlk concentrations than other rivers (JLJ, JJ, MJ, and OJ) with low carbonate weathering rates. However, given the high discharge of the CJ and ZJ, their input fluxes of organic acids into the adjacent coastal zones were still considerable. The significant correlation between OrgAlk and salinity suggested the mixing between freshwater and seawater was likely a dominant factor controlling variations in concentrations of OrgAlk in the MJ, OJ, JJ, and JLJ Estuaries. Besides physical mixing, photochemical and microbial degradation of humic acids might lead to the removal of organic acids in coastal waters (Cory et al., 2007; Logozzo et al., 2021). Otherwise, organic acid anions adsorbing to particles or aggregating into large molecules could also contribute to the variations in OrgAlk concentrations (Dulaquais et al., 2018; Mantoura & Woodward, 1983).

The pK_a values of organic acids at the freshwater and seawater endmembers of the six estuaries (Table 1) indicated that the carboxylic acid groups, phenolic or amine species were likely the dominant organic acid species in the estuaries of this study (Cai et al., 1998; Ritchie & Perdue, 2003). The similar pK_{a1} and pK_{a2} values at the freshwater endmembers of JJ, MJ, OJ, and JLJ Estuaries (Table 1) suggested similar compositions of organic acids in the JJ, MJ, OJ, and JLJ. However, the organic acid species in the large rivers ZJ and CJ were quite different from those in the small rivers (JJ, MJ, OJ, and JLJ). A large difference in pK_{a3} values of the seawater endmembers of six estuaries was observed (Table 1), likely suggesting different phenolic or amine species in different coastal waters.

4.2. The Effect of Low- pK_a Organic Acids on TA Measurements

According to this study, low- pK_a organic acids ($pK_a < 6.0$) were commonly found in both river freshwater and coastal seawater (Table 1). Apparent differences were observed in the OrgAlk_T values derived by five established TA measurement approaches in the low salinity waters (salinity ≤ 27) of the JJ, JLJ, and CJ Estuaries where organic acids with $pK_a < 5.2$ were present (Table 1 and Figure 5). However, the differences in OrgAlk_T concentrations were negligible in each estuary when salinity was high (salinity > 27) due to their relatively low OrgAlk concentrations (Figure 5). Therefore, we propose that for certain types of TA-related research, such as those using measured TA to calculate the CO₂ flux and compare it to historical data in low-salinity estuarine waters, the inconsistency in the TA measurement approaches should be considered.

The MGF and NSLF open-cell titration approaches-derived OrgAlk_T concentrations matched well with the concentrations of OrgAlk_D in the ZJ, MJ, OJ, JJ, and JLJ Estuaries where the pK_a values of organic acids were ≥ 5.0 (Figure 5 and Table 2). This indicates that the open-cell titration method could protonate nearly all conjugate bases of organic acids with $pK_a \geq 5.0$, thus providing an accurate interpretation of the TA definition in the presence of these kinds of organic acids. Similar to Sharp and Byrne (2020), we observed that the closed-cell titration and single-step titration approaches-derived OrgAlk_T concentrations were lower than the concentrations of OrgAlk_D in the JJ and JLJ Estuaries where organic acids with pK_a values < 5.2 were abundant. This suggested that closed-cell and single-step titration approaches may fail to represent Dickson's definition of TA with high accuracy in the presence of low- pK_a organic acids.

Moreover, some of the organic acids with $pK_a < 4.5$, which are expected to have a negative contribution to alkalinity according to the TA definition, might have been considered as a positive contribution in the titrated TA, because most TA measurement approaches are performed at pH < 4.5 . This is indicated by higher OrgAlk_T values (15–33 $\mu\text{mol kg}^{-1}$) determined by the five TA measurement approaches (i.e., MGF open-cell, NLSF open-cell, NLSF closed-cell, DD closed-cell, and single-step titration approaches) than the OrgAlk_D values (2–18 $\mu\text{mol kg}^{-1}$) in the CJ Estuary where the pK_a value of one group of organic acids was < 4.5 (Figure 5). Moreover, some organic acids with $pK_a < 4.5$ might interfere with the estimation of alkalinity using the MGF or nonlinear least squares fit approach over the pH range of 3.0–3.5. This interference can lead to additional uncertainties in the measurements of TA. Given that OrgAlk concentrations were determined by the open-cell titration

method in this study, the presence of organic acids with $pK_a < 4.5$ might also cause uncertainties in the reported OrgAlk measurements. The full-range titrations suggest the potential presence of organic acids with pK_{a1} values ranging from 2.8 to 3.0 at the seawater endmembers of the JJ and JLJ Estuaries (Table 1), which might interfere with the TA and OrgAlk measurements. However, the influence of these organic acids on sample measurements is not expected to affect the data analysis significantly due to the low OrgAlk concentrations in these seawater endmembers ($6\text{--}7 \mu\text{mol kg}^{-1}$). Future studies are warranted to determine how to improve TA and OrgAlk measurement approaches to better include low- pK_a organic acids and fit the TA definition in coastal systems. Importantly, an organic acid binding model that is able to explicitly identify organic acids in seawater will facilitate the improvement of OrgAlk and TA measurement approaches.

4.3. Importance of OrgAlk in the Coastal Carbonate Buffering System

The influence of OrgAlk on the natural water H^+ concentration in the coastal system was suggested to be primarily determined by both OrgAlk concentration and water pH (Song et al., 2020). OrgAlk had a stronger influence on the H^+ value in river freshwater than in coastal seawater due to the high OrgAlk concentrations, low pH, and low buffer capacity values in rivers (Figure 6). Similarly, the ZJ and CJ Estuaries showed smaller variations in H^+ values than other river estuaries due to their relatively lower concentrations of OrgAlk (Figure 6). Generally, OrgAlk might change H^+ by $\sim 3\%$ – 69% with the maximum changes occurring at the freshwater endmember of each estuary (Figure 6). This indicates a significant influence of OrgAlk on the carbonate system in estuarine and coastal zones, especially in low salinity waters.

Theoretically, OrgAlk influences Ω_{Ar} by changing the CO_3^{2-} concentration. The variation in CO_3^{2-} concentration caused by the influence of OrgAlk is primarily determined by the buffer capacity and OrgAlk concentrations in coastal systems. At the minimum buffer capacity ($pH \approx 7.5$), the CO_3^{2-} concentration was most sensitive to pH changes driven by variations in OrgAlk. This might be the reason why the largest magnitude of $\Delta\Omega_{Ar}$ occurred when the pH was near 7.5 in the MJ and JLJ Estuaries (Figure 6 and Figure S3 in Supporting Information S1). Meanwhile, high OrgAlk concentrations likely resulted in large variations in Ω_{Ar} in the low salinity waters of the OJ and JJ Estuaries. OrgAlk might change Ω_{Ar} by 1% – 72% (Figure 6), suggesting that OrgAlk was an important factor influencing the aragonite saturation state in coastal systems. Generally, low-salinity estuarine zones were more influenced by OrgAlk than high-salinity coastal waters due to their higher OrgAlk concentrations.

Previous studies typically calculated the aragonite saturation state in coastal systems by using a carbonate system calculation program with TA-DIC, TA- pCO_2 , or TA-pH pairs as input parameters without including OrgAlk (e.g., Azetsu-Scott et al., 2014; Chierici et al., 2011; Mathis et al., 2011). Our results imply that previous estimates of Ω_{Ar} ignoring OrgAlk in coastal systems, especially in low salinity waters, might incur large uncertainties. It is worth noting that pH values include the influence of OrgAlk, whereas DIC is not directly affected by OrgAlk. Therefore, the Ω_{Ar} value calculated by pH and DIC as input parameters accounts for the OrgAlk effect and is expected to result in a smaller calculation error. More importantly, our results indicate that OrgAlk can considerably influence the H^+ concentration and Ω_{Ar} , representing an important mechanism by which organic carbon cycling controls the coastal carbonate buffering system.

Given the reduced precision compared to TA measurements and the lack of a standard reference material for OrgAlk measurements, it was likely difficult for the two-step titration method to accurately determine OrgAlk concentrations in seawaters where OrgAlk concentrations were rather small ($6\text{--}7 \mu\text{mol kg}^{-1}$). Moreover, the low OrgAlk concentrations at the seawater endmembers of most estuaries in this study likely prevented the charge balance model from accurately interpreting organic acids through full titration curves. However, the potential uncertainties in OrgAlk measurements and estimates of organic acids in seawater are unlikely to change the main conclusion of this study, given that our conclusion on OrgAlk effects was primarily based on the high OrgAlk concentrations in low-salinity estuarine water.

5. Conclusions

Organic acid-base species are important components of DOC in the six southeastern Chinese estuaries examined in this study. These species contribute significantly to TA and originated, mainly, from river input. This study investigated the agreement among various TA measurement approaches in the presence of OrgAlk across a diverse range of Chinese estuaries. The open-cell titration method, the most commonly used approach, in comparison with the closed-cell and single-step titration methods, fits the TA definition best when pK_a values of

organic acids were $> \sim 5.0$ in estuaries. However, when organic acids with $pK_a < 4.5$ were abundant, large uncertainties in TA values existed for all TA titration approaches tested. The considerable influence of OrgAlk on H^+ and Ω_{Ar} across the six estuaries implies that OrgAlk plays an important role in the coastal carbonate buffering system. This highlights the necessity to include OrgAlk in TA measurements and TA model to avoid misinterpretation of key coastal carbonate system parameters in further studies.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data reported in this study can be accessed at [figshare.com](https://doi.org/10.6084/m9.figshare.20965759.v5) (<https://doi.org/10.6084/m9.figshare.20965759.v5>; Song et al., 2023a). The modified CO2SYS calculation program, which includes the contribution of OrgAlk, is available for download at <https://doi.org/10.6084/m9.figshare.23582301.v1> (Song et al., 2023b).

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Erratum

The originally published version of this article contained typographical errors in Table 2. The heading for column 2 should be “OrgAlk_D (μmol kg⁻¹),” and the heading spanning columns 3 through 7 should be “OrgAlk_T (μmol kg⁻¹).” These errors have been corrected, and this may be considered the authoritative version of record.