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RESEARCH ARTICLE

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Key Points:

- Subannual TA variability is restricted to the upper 150 m of the water column
- Subannual TA variability is controlled by riverine inputs and ocean currents
- A riverine alkalinity input index is used to highlight riverine TA contributions

Supporting Information:

- Supporting Information S1

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Subannual variability of total alkalinity distributions in the northeastern Gulf of Mexico

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Abstract The subannual variability of total alkalinity (TA) distributions in the northeastern Gulf of Mexico was examined through the use of TA data from ship-based water sampling, historical records of riverine TA, and contemporaneous model output of surface currents and salinity. TA variability was restricted to the upper 150 m of the water column, where relationships between salinity and TA were controlled primarily by subannual variations in the extent of mixing between seawater and river water. A transition in TA distribution patterns between the river-dominated northern margin (near the Mississippi-Atchafalaya River System) and the ocean current-dominated eastern margin (West Florida Shelf) was observed. An index for riverine alkalinity input was formulated to provide insights about riverine alkalinity contributions in the upper water column. Spatial and temporal variations of total alkalinity in the northeastern Gulf of Mexico are primarily controlled by riverine TA inputs and ocean currents.

1. Introduction

Total alkalinity (TA) is a keystone variable for investigations of the marine carbonate system. This parameter is defined as “the number of moles of hydrogen ion (H^+) equivalent to the excess of proton acceptors (bases formed from weak acids with dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$)” [Dickson, 1981]. TA can be expressed in terms of component concentrations as follows:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] + \dots - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] - \dots \quad (1)$$

where “...” indicates acids and bases present at low concentrations. As indicated by this definition, TA is not affected by CO_2 exchange between seawater and the atmosphere [Wolf-Gladrow *et al.*, 2007]. Although TA is influenced by primary production, remineralization, and dissolution/precipitation of calcium carbonate [Brewer and Goldman, 1976; Brewer *et al.*, 1975], its distribution in the surface ocean is dominantly controlled by the same factors that govern salinity (e.g., mixing, evaporation) [Millero *et al.*, 1998]. Total alkalinity is, therefore, often treated as a “conservative” variable.

Based on surveys of TA distributions along the western margins of the North Atlantic Ocean, Cai *et al.* [2010] concluded that alkalinity distributions along the margins (0–250 m depth) are dominantly controlled by two types of mixing regimes: (1) river-dominated margins (e.g., Amazon River), where mixing diagrams of total alkalinity versus salinity (TA-S diagrams) are characterized by simple linear relationships, and (2) current-dominated margins (e.g., Labrador Sea, Gulf of Maine), where TA-S diagrams are characterized by segmented mixing lines and a shared midsalinity end-member. These ideal two-member mixing patterns are not always observed, especially along ocean margins where water mass mixing includes the combined effects of river input, alongshore and ocean current transports, and deep water upwelling [Millero *et al.*, 1998]. Using the area of the northeastern Gulf of Mexico that is influenced by the Mississippi-Atchafalaya River System (MARS) as an example, Cai *et al.* [2010] proposed three possible explanations for observed complex TA-S relationships: (a) variations in river end-member alkalinity, (b) mixing among three end-members, and (c) variations in alkalinity losses due to biogenic carbonate production.

Data from the Gulf of Mexico and East Coast Carbon Cruises of July 2007 and July 2012 (GOMECC-1 and GOMECC-2) [Wang *et al.*, 2013; Wanninkhof *et al.*, 2015] suggest that complex TA-S patterns in the MARS-

Figure 1. Northeastern Gulf of Mexico study area. The three research cruises of this work (NEGOM) sampled transects DSH and PCB. A complementary NOAA cruise (GOMECC-2) sampled transects LA and TPA. Colors indicate water depth. The deep bathymetric feature just offshore the PCB transect is the De Soto Canyon.

influenced area can be attributed to TA inputs from multiple riverine sources. Uniformly high TA and salinity on the West Florida Shelf, in contrast, indicates a lack of riverine input and the existence of a high-TA, high-S boundary current. In view of these observations, it is reasonable to propose that alkalinity distribution patterns along the Gulf margin may gradually transition from river dominated in the north to current dominated in the east.

Although prior work has defined the general mechanisms that underlie TA variations in the Gulf of Mexico, there are few observations that can be used to assess TA temporal variability. Moreover, most studies have focused on the MARS-influenced area and the West Florida Shelf [Cai *et al.*, 2010; Wang *et al.*, 2013; Wanninkhof *et al.*, 2015], leaving a data gap in the northeastern Gulf of Mexico.

This study is the first to systematically examine the subannual variability of alkalinity distribution patterns in the northeastern Gulf of Mexico. In combination with prior data and the essential context of ocean current information, our observations over the course of a year help to illuminate the mechanisms responsible for alkalinity distributions in the northeastern Gulf of Mexico.

2. Methodology

2.1. Study Area

Total alkalinity (TA) samples were collected along two shore-normal transects in the northeastern Gulf of Mexico (Figure 1) during three cruises of the *R/V Weatherbird II* (15–24 February 2012, 8–15 May 2012, and 2–12 August 2012). These cruises, collectively labeled “NEGOM,” were primarily focused on impacts of the Deepwater Horizon oil spill, so all hydrographic stations were sited east of the wellhead. The deep-slope hydrocast (DSH) transect, located 150–200 km south of Mobile Bay, consisted of three stations with bottom depths ranging from 1000 to 2500 m. The Panama City Beach (PCB) transect, located 20–130 km southwest of Panama City, Florida, consisted of five stations with bottom depths ranging from 20 to 400 m.

2.2. NEGOM Sample Collection and Analysis

TA samples were collected from 20 L Niskin bottles into 300 mL borosilicate glass bottles (Wheaton Industries, Inc., USA), which were then poisoned with saturated HgCl_2 solution. Depth and salinity data were obtained from an SBE 25 Sealogger (Sea-Bird Electronics, USA) on the CTD rosette. All samples were analyzed in a shore-based laboratory within 2 weeks of sampling. TA was measured using a single-point spectrophotometric titration method [Yao and Byrne, 1998], with a custom automatic titration system consisting of a USB-4000 fiber optic spectrometer (Ocean Optics, Inc., USA), a 665 Dosimat autotitrator with stir plate (Metrohm AG, Switzerland), and a purging system with high-purity N_2 gas. The system was calibrated with certified reference

material (CRM) [Dickson *et al.*, 2003] provided by A.G. Dickson of Scripps Institution of Oceanography. The precision of the TA measurements was determined to be better than $\pm 0.1\%$ ($\pm 2 \mu\text{mol kg}^{-1}$).

2.3. Complementary Data

Additional TA and salinity data were available from the Louisiana (LA) and Tampa (TPA) transects (Figure 1) sampled during the GOMECC-2 (21 July 2012 to 13 August 2012) cruise [Wanninkhof *et al.*, 2014]. TA precision and accuracy were reported to be better than $\pm 0.1\%$ ($\pm 2 \mu\text{mol kg}^{-1}$). Sea-surface salinity and ocean current model output obtained from the Hybrid Coordinate Ocean Model (HYCOM, www.hycom.org) [Chassignet *et al.*, 2007] were expressed as averages over the sampling period of each *R/V Weatherbird II* cruise, using custom MATLAB (The MathWorks, Inc., USA) code. Monthly 2012 riverine alkalinity data were obtained from the USGS "Water Quality Data for the Nation" database (<http://waterdata.usgs.gov/nwis>).

2.4. Mixing Model and Characterization of Riverine Alkalinity Input Index (ΔnTA)

For the case of upper water column mixing involving two end-members, with one being a composite freshwater end-member ($S = 0$ and $\text{TA} = \text{TA}^0$) and the other being an oceanic end-member ($S = S_{\text{oce}}$ and $\text{TA} = \text{TA}_{\text{oce}}$), the TA of any water samples along the mixing line can be expressed as:

$$\text{TA} = \frac{\text{TA}_{\text{oce}} - \text{TA}^0}{S_{\text{oce}}} \times S + \text{TA}^0 \quad (2)$$

Equation (2) can be transformed such that the dependent variable, $\text{TA} \times S_{\text{oce}}/S$, is equivalent to a conventional salinity-normalized total alkalinity (nTA) with the salinity of the oceanic end-member as the reference salinity (S_{oce}):

$$\text{TA} \times \frac{S_{\text{oce}}}{S} = \frac{\text{TA}^0 \times S_{\text{oce}}}{S} + (\text{TA}_{\text{oce}} - \text{TA}^0) \quad (3)$$

Using the relationship described in equation (3), with S_{oce} defined as the highest observed salinity in each plot, regressions of $\text{TA} \times S_{\text{oce}}/S$ against $1/S$ provide TA^0 from the slope of the linear relationship ($\text{TA}^0 \times S_{\text{oce}}$) and TA_{oce} from the intercept ($\text{TA}_{\text{oce}} - \text{TA}^0$). Obtaining TA^0 in this way provides a visual representation of the quality of the TA^0 determinations (i.e., as can be seen from the deviations of individual data points from the regression line). In contrast, obtaining TA^0 from conventional TA-S regressions (i.e., the intercept of equation (2)) requires long-distance extrapolation from a narrow range of high TA and S values and provides no such graphical representation of quality. Nevertheless, as is shown in the supporting information, TA^0 determined from equations (2) and (3) regressions are in very close agreement.

With the conventional salinity normalization concept [Brewer, 1978], wherein TA and S vary only through evaporation and atmospheric precipitation, the TA of any water sample along the mixing line can be expressed as:

$$\text{TA}' = \frac{\text{TA}_{\text{oce}}}{S_{\text{oce}}} \times S \quad (4)$$

This equation ignores contributions from sources with nonzero TA^0 , thereby causing modeled deviations from observed mixing behavior [Friis *et al.*, 2003; Jiang *et al.*, 2014].

To examine freshwater contributions to TA over a range of salinities, for each water sample, we calculated differences between TA, the equation (2) dependent variable, and TA' , the equation (4) dependent variable. As shown in equation (5), the difference between the two forms of salinity-normalized alkalinity (ΔnTA) serves as an index of riverine alkalinity input. The normalization is relative to the oceanic end-member, S_{oce} :

$$\begin{aligned} \Delta\text{nTA} &= \text{TA} - \text{TA}' \\ &= \frac{\text{TA}_{\text{oce}} - \text{TA}^0}{S_{\text{oce}}} \times S + \text{TA}^0 - \frac{\text{TA}_{\text{oce}}}{S_{\text{oce}}} \times S \\ &= \text{TA}^0 \times \left(1 - \frac{S}{S_{\text{oce}}}\right) \end{aligned} \quad (5)$$

Equation (5) shows that water masses with significant inputs of high riverine alkalinity (i.e., large TA^0 and low S) will have appreciable ΔnTA values. Because the factor $(1 - S/S_{\text{oce}})$ is the freshwater fraction of

freshwater/seawater mixtures, ΔnTA is equal to the contribution of alkalinity from the freshwater composite end-member, and $\Delta nTA/TA$ is the fractional contribution of each sample's measured TA that was derived from the composite freshwater end-member.

3. Results and Discussion

3.1. Spatial Distribution of TA in the Northeastern Gulf of Mexico, July to August 2012

With two cruises and four transects, we have a snapshot of alkalinity distributions for the summer of 2012 (July to August). For each transect, Figure 2 shows TA-S relationships (full water column), $TA \times S_{oce}/S$ versus $1/S$ relationships (equation (3), 0–150 m), and vertical profiles of ΔnTA (equation (5), 0–150 m). Regressed TA^0 values obtained in the upper 150 m of each transect, along with standard errors for each TA^0 estimate, are provided in the upper left corners of Figures 2b, 2e, 2h, and 2k.

3.1.1. River-Dominated and Ocean Current-Dominated Mixing Patterns

Data from the study-region boundaries (Figure 1) show two TA-S patterns: the river-dominated mixing of the LA transect (Figure 2a) and the oceanic current-dominated pattern of the TPA transect (Figure 2j). The LA transect (Figure 1) is just offshore of the MARS, the major freshwater source for the Gulf of Mexico. The TPA transect crosses the West Florida Shelf near Tampa Bay, where there is no significant freshwater inflow.

For the LA transect (Figure 2a), the TA-S relationships demonstrate the existence of distinct mixing regimes in upper (0–150 m) and middepth (150–600 m) waters. Both regimes share a common oceanic end-member whose properties ($S \approx 36.7$, $TA \approx 2400 \mu\text{mol}\cdot\text{kg}^{-1}$) are consistent with the properties of Loop Current core water [Wang *et al.*, 2013]. The upper-water regime shows a typical river-dominated mixing pattern, with linear TA variations over $33.5 < S < 36.9$ (Figure 2a) and a composite freshwater end-member TA^0 of $2165.2 \pm 25.7 \mu\text{mol}\cdot\text{kg}^{-1}$ (obtained from the slope of the linear regression of $TA \times S_{oce}/S$ versus $1/S$; Figure 2b). The vertical profile of ΔnTA values (Figure 2c) also demonstrates significant riverine TA input to the upper water column. For middepth waters, the TA-S pattern approximately follows a simple dilution line with a $TA^0 = 0$ (dashed line in Figure 2a), but with a “tongue” of elevated TA in deep water (>600 m) on the continental slope. The TA of this tongue varies between 2320 and 2340 $\mu\text{mol}\cdot\text{kg}^{-1}$ over a very narrow range of salinity (34.8–35.0). This feature is created by the mixing of shelf water with high-TA waters from the deep basin beyond the continental slope [Wang *et al.*, 2013].

Along the TPA transect (Figure 2j), the upper waters show consistently high TA ($2378 \pm 18 \mu\text{mol}\cdot\text{kg}^{-1}$) over a narrow range of S (35.9–36.5). The $TA \times S_{oce}/S$ versus $1/S$ plot for the upper waters (0–150 m; Figure 2k) shows a low slope and weak correlation ($R^2 = 0.2226$) and indicates a low TA^0 value of $616.4 \pm 130.4 \mu\text{mol}\cdot\text{kg}^{-1}$. The TA-S and ΔnTA patterns are both consistent with the limited riverine input in this area. The corresponding ΔnTA profile (Figure 2l) also shows consistently low ΔnTA . The low slope of the $TA \times S_{oce}/S$ versus $1/S$ relationship and the low value of ΔnTA indicate weak riverine end-member contributions to TA, and it seems likely that the nonzero TA^0 was the result of mixing contributions from multiple freshwater inputs with a composite alkalinity lower than that of the MARS system. At depths below 150 m, the TPA transect pattern of TA-S (Figure 2j) is similar to that of the LA transect (Figure 2a). Conservative mixing is indicated at middepths (150–600 m), and elevated TA is observed in deep water (>600 m). Riverine influences along this transect are clearly minimal. TA distributions in this area are instead controlled primarily by ocean currents.

3.1.2. Transitional Mixing Patterns

Data from the August 2012 DSH and PCB transects (Figures 2d–2i) show a transition in TA distribution patterns between the river-dominated north (LA transect) and the ocean current-dominated east (TPA transect). This pattern is consistent with the existence of only minor freshwater inputs between the LA and TPA transects (Figure 1). Compared to the MARS freshwater discharge (average rate of $19,920 \text{ m}^3\cdot\text{s}^{-1}$) [Goolsby *et al.*, 1999], riverine discharges in this part of Gulf Coast are quite small: Mobile Bay, $1800 \text{ m}^3\cdot\text{s}^{-1}$ [Park *et al.*, 2007]; Pensacola Bay, $252 \text{ m}^3\cdot\text{s}^{-1}$ [Thorpe *et al.*, 1997]; and St. Andrews Bay, $28 \text{ m}^3\cdot\text{s}^{-1}$ [Brim *et al.*, 1998].

In the upper water column, the LA-DSH-PCB-TPA sequence of transects (Figures 2b, 2e, 2h, and 2k) demonstrates decreasing composite freshwater end-member alkalinities (TA^0): $TA^0 = 2165.2 \pm 25.7 \mu\text{mol}\cdot\text{kg}^{-1}$ at LA, $2128.5 \pm 74.7 \mu\text{mol}\cdot\text{kg}^{-1}$ at DSH, $1764.7 \pm 85.9 \mu\text{mol}\cdot\text{kg}^{-1}$ at PCB, and $616.4 \pm 130.4 \mu\text{mol}\cdot\text{kg}^{-1}$ at TPA.

Figure 2. TA versus S (full water column), TA $\times$ S_{0ce}/S versus 1/S (0–150 m), and ΔnTA (0–150 m) for four summer 2012 transects in the northeastern Gulf of Mexico. The blue dashed lines are simple dilution lines for the case of end-member mixing with TA⁰ = 0. Regressed TA⁰ values obtained in the upper 150 m of each transect, along with standard errors for each TA⁰ estimate, are provided in the upper left corners of Figures 2b, 2e, 2h, and 2k.

The corresponding ΔnTA profiles between 0 and 150 m (Figures 2c, 2f, 2i, and 2l) also show transitional patterns from the LA transect to the TPA transect.

The PCB stations (Figure 2g) are all too shallow to show middepth or deep water characteristics. For the other three transects, the middepth mixing patterns are highly consistent, with only minor deviations from the lines of simple dilution (dashed lines in Figures 2a, 2d, and 2j). For the deep (>600 m) offshore stations at the DSH transect, elevated TA is observed in continental slope waters, just as for the LA and TPA transects. This elevated TA is attributable to mixing of shelf waters with high-alkalinity deep water from the adjacent basin.

3.2. Subannual Variability of TA Distributions

For two transects, DSH and PCB, data are available from not only August 2012 but also the preceding February and May (Figures 3 and 4).

3.2.1. DSH Transect

Figure 3 shows TA versus S (full water column), $TA \times S_{oce}/S$ versus $1/S$ (0–150 m), and ΔnTA (0–150 m) along the DSH transect (Figure 1) for February, May, and August of 2012. As described in section 3.1, TA distributions at DSH in August (Figure 3g) indicate river-dominated mixing in the upper water column (0–150 m), mixing along a simple dilution line in middepth waters (150–600 m), and a high-TA tongue in deep water (>600 m).

For earlier months of that year (Figures 3a and 3d), significant differences are seen in the upper waters, but not in middepth or deep waters. In February, no water samples with elevated TA are observed for $S \leq 35$. Between February (Figure 3b) and May (Figure 3e), TA^0 increased significantly (from 1618.4 ± 194.8 to $2131.4 \pm 108.3 \mu\text{mol}\cdot\text{kg}^{-1}$), and the range of salinity expanded. These changes can be attributed to increasing high-TA riverine input. This seasonal process is also evident in the ΔnTA profiles (Figures 3c and 3f). Subsequently, from May to August, changes in TA^0 are much smaller (from 2131.4 ± 108.3 to $2128.5 \pm 74.7 \mu\text{mol}\cdot\text{kg}^{-1}$). Minor changes in the slopes and intercepts of $TA \times S_{oce}/S$ versus $1/S$ (Figures 3e and 3h) and similar ΔnTA profiles (Figures 3f and 3i) suggest that riverine influences were similar in these 2 months. The subannual TA^0 patterns obtained from the DSH regression results are also consistent with the riverine TA of the Mississippi River shown in Figure 6a.

3.2.2. PCB Transect

Figure 4 shows TA versus S (full water column), $TA \times S_{oce}/S$ versus $1/S$ (0–150 m), and ΔnTA (0–150 m) along the PCB transect in February, May, and August 2012. Two dominant mixing regimes are observed across these months: (1) above the 150 m depth horizon, significant riverine influence and strong subannual variability are evident, and (2) below 150 m, mixing follows a simple dilution line (dashed line in Figures 4a, 4d, and 4g) that exhibits little variability.

In February (Figure 4a), only small variations in TA or salinity were observed in the upper water column (<150 m). This upper-water homogeneity may be attributable to strong wind-driven mixing associated with a low-pressure system and severe weather that occurred in the area during 18–19 February 2012 [National Weather Service Tallahassee, 2012]. Consistent with this scenario, ΔnTA values of $\sim 20 \mu\text{mol}\cdot\text{kg}^{-1}$ were observed to depths of 80 m. In other months, nonzero ΔnTA values were observed to only 30 m depth. This transect's highest TA^0 value, $1797.7 \pm 205.5 \mu\text{mol}\cdot\text{kg}^{-1}$, was also observed in February (Figure 4b), but this value shows substantial uncertainty due to the small range of salinities encountered in upper waters during this period of strong wind mixing.

Between February and August, the ranges of both TA and salinity increased substantially (Figures 4d and 4g). In May, TA^0 (Figure 4e) was $1361.3 \pm 153.5 \mu\text{mol}\cdot\text{kg}^{-1}$ and the minimum salinity was ~ 35.0 ; in August, TA^0 (Figure 4h) was $1764.7 \pm 85.9 \mu\text{mol}\cdot\text{kg}^{-1}$ and the minimum salinity was 33.5. This increase in TA^0 , along with the accompanying changes in the ΔnTA profiles (Figures 4f and 4i), indicate increasing riverine TA input between May and August. However, the regressed subannual TA^0 patterns at the PCB transect were inconsistent with the temporal TA variations of the Mississippi River (Figure 6a). This suggests that the observed TA^0 "riverine end-members" at PCB were composites of several freshwater components.

Below 150 m, the mixing patterns generally follow a simple dilution line in May and August (Figures 4d and 4g). The February TA- S pattern exhibits a significant deviation from the simple dilution line (Figure 4a). Such deviations may potentially result from the enhanced vertical mixing noted above.

Figure 3. DSH transect: TA versus S (full water column), $\text{TA} \times S_{\text{oce}}/S$ versus $1/S$ (0–150 m), and $\Delta n\text{TA}$ (0–150 m) in February, May, and August 2012. The blue dashed lines are simple dilution lines for the case of end-member mixing with $\text{TA}^0 = 0$. Regressed TA^0 values obtained in the upper 150 m of each transect, along with standard errors for each TA^0 estimate, are provided in the upper left corners of Figures 3b, 3e, and 3h.

3.3. Controls of Upper Water Column Alkalinity in the Northeastern Gulf of Mexico

As shown in sections 3.1–3.2, the most significant subannual TA variability is observed in shallow waters of the northeastern Gulf of Mexico. Therefore, to interpret TA distribution patterns in the context of contemporaneous sea-surface currents and salinities, vertically averaged $\Delta n\text{TA}$ data (0–20 m) were used to explore controls on TA distributions and subannual variability. Figure 5 shows vertically averaged $\Delta n\text{TA}$ (0–20 m) at hydrographic stations sampled during the four summer 2012 transects, along with model (HYCOM) outputs of sea-surface currents and salinities. At the time, a low-salinity plume ($S < 35$) extended southward in two lobes from the northern gulf coast, encompassing the LA, DSH, and PCB transects. The TPA transect ($S > 35$), in contrast, was mainly influenced by the Loop Current eddy periphery. Correspondingly, vertical averages of $\Delta n\text{TA}$ along the LA, DSH, and PCB transects were significantly higher than $\Delta n\text{TA}$ averages for the TPA transect. These patterns (high $\Delta n\text{TA}$ in the freshwater plume and lower $\Delta n\text{TA}$ in the Loop Current-

Figure 4. PCB transect: TA versus S (full water column), $TA \times S_{\text{oce}}/S$ versus $1/S$ (0–150 m), and ΔnTA (0–150 m) in February, May, and August 2012. The blue dashed lines are simple dilution lines for the case of end-member mixing with $TA^0 = 0$. Regressed TA^0 values obtained in the upper 150 m of each transect, along with standard errors for each TA^0 estimate, are provided in the upper left corners of Figures 4b, 4e, and 4h.

dominated area) strongly suggest that riverine inputs exert a dominant control on alkalinity distributions in the northeastern Gulf of Mexico.

At the two central transects, DSH and PCB (Figure 1), we can also look at vertically averaged ΔnTA during the preceding spring and late winter (Figure 6). We compare these temporal patterns to changes in total alkalinity concentrations in the Mississippi River. River TA concentrations (i.e., TA^0) increased continuously, from $1908 \mu\text{mol}\cdot\text{kg}^{-1}$ in February to $2840 \mu\text{mol}\cdot\text{kg}^{-1}$ in August. If upper-water alkalinity distributions at the DSH and PCB transects were controlled solely by riverine input, then continuous increases of average ΔnTA should also be observed at these transects. However, observations along these two transects show intra-annual complexity. At the DSH transect, ΔnTA at the nearshore DSH stations (DSH08 and DSH10) showed patterns (Figure 6b) very similar to the Mississippi River TA pattern. A sizable increase was observed between February and May, and then a smaller increase was seen between May and August. The

Figure 5. Gulf of Mexico surface currents, salinities, and vertically averaged ΔnTA for August 2012. Colors represent salinity. Numbers give the average ΔnTA (0–20 m) for each station (units: $\mu\text{mol}\cdot\text{kg}^{-1}$).

seawardmost station (DSH09), however, showed a different (increasing) pattern, with most of the increase in ΔnTA occurring between May and August (Figure 6b). Along the PCB transect (Figure 6c), average ΔnTA at the four inner stations (PCB01–PCB04) decreased or remained nearly constant from February to May, but then ΔnTA greatly increased between May and August. At the seawardmost station (PCB05), average ΔnTA increased continuously from February to August. These contrasting characteristics, with continuously increasing riverine TA concentrations but more complex average ΔnTA patterns in some Gulf areas, indicate that riverine input is not the sole control on TA distributions in the northeastern Gulf of Mexico.

The accompanying Gulf of Mexico surface conditions, along with vertically averaged (0–20 m) ΔnTA , are shown in Figure 7. In February (Figures 7a and 7d), a low-salinity plume ($S < 35$) was observed along the Gulf Coast from the Mississippi River estuary to as far as 85°W (including the inner stations of the PCB transect). At the DSH transect, DSH08 and DSH10 were impacted by the eastward Mississippi freshwater plume, but DSH09 was controlled by the high-salinity periphery of the Loop Current and Loop Current eddy (note the high-salinity tongue extending northward between 85°W and 89°W). Therefore, within the DSH transect, ΔnTA values also declined as distance from shore increased and the impact from riverine input decreased (Figures 6b and 7a). For the PCB transect, because the alongshore current was weak during this period, the extra TA input was from the local freshwater inputs with low TA^0 . Therefore, ΔnTA values declined from PCB01 to PCB05 (except PCB04), as distance from shore increased and the impact from local freshwater input decreased. The depressed salinities observed for the PCB04 samples (0.4–0.7 lower than PCB03 and PCB05) are not consistent with the time-averaged salinity field shown in Figure 7a. The high ΔnTA observed at PCB04 ($33.4 \mu\text{mol}\cdot\text{kg}^{-1}$) was possibly spurious, caused by low-salinity values from the rosette's CTD. (Surface S from the rosette CTD was 0.7 lower than S obtained from the ship's underway CTD at this station.)

In May (Figures 7b and 7e), as the Loop Current eddy weakened and moved off to the southwest, the northern-Gulf freshwater plume stretched offshore, forming a low-salinity tongue ($S \approx 35$) between the DSH and PCB transects (Figure 7b). As the riverine TA was much higher than in February (Figure 6a), ΔnTA at the DSH and PCB transects increased substantially in May (Figures 6b and 7b). Surface current from the Mississippi River mouth went southeast across the upper DSH transect (DSH08 and DSH10); part of this current turned northeast and went through the PCB transect, from PCB05 to PCB01. As was the case in February, ΔnTA values at the DSH transect declined spatially from DSH08 to DSH09 as the distance from the Mississippi River mouth increased (Figure 7b). At the PCB transect, as the Mississippi River freshwater plume became the major source of extra TA input, ΔnTA values generally declined from PCB05 to PCB01, along the path of the surface current from the Mississippi River mouth.

In August (Figures 7c and 7f), the high-salinity peripheries of the Loop Current and Loop Current eddy exerted minimal influences on the northeastern Gulf of Mexico, and the surface current field was more

Figure 6. Seasonal changes in riverine TA and vertically averaged ΔnTA (0–20 m) at hydrographic stations in the northeastern Gulf of Mexico, February to August 2012. (a) Mississippi River TA at Belle Chasse, LA (USGS Site 07374525). (b) Average ΔnTA at DSH stations. (c) Average ΔnTA at PCB stations.

complicated. During this time, the study area was mostly covered by low-salinity ($S < 35$) water, and the influence of riverine TA input was strongest. Therefore, average ΔnTA values for both the DSH and the PCB transects substantially increased, reaching their maximum values observed during the 6 month study period (Figures 6b and 6c). Surface currents from the mouth of the Mississippi River moved clockwise across the DSH transect from the northeast to southwest, resulting in decreasing ΔnTA from DSH08 to DSH09. At the PCB transect, the nearshore surface current brought extra TA input from the northern Gulf Coast. As the surface current went clockwise to the southwest from PCB02 to PCB05, ΔnTA values decreased as the distance from shore increased. However, no significant surface current activity was observed at the most inshore station, so ΔnTA at PCB01 was lowest among the PCB stations.

Figure 7. Evolution of surface conditions in the northeastern Gulf of Mexico in (a and d) February, (b and e) May, and (c and f) August 2012: average surface salinities (indicated by colors), surface currents (indicated by vectors), and vertically averaged ΔnTA (0–20 m, indicated by numbers in parentheses; units are $\mu\text{mol}\cdot\text{kg}^{-1}$). White arrows indicate the approximate paths of surface current from the riverine sources. In Figures 7d–7f, the white lines show the locations of transects DSH and PCB, and the white boxes show the location of the northeastern Gulf area shown in Figures 7a–7c. The locations of the Loop Current (LC) and Loop Current eddy (LCE), as inferred from surface currents and salinities, are also shown in Figures 7d–7f.

4. Summary and Conclusions

In the northeastern Gulf of Mexico, significant subannual TA variability was observed in the upper water column (0–150 m). Linear changes in TA were observed over a 33.5–36.8 range of salinity, and TA^0 and ΔnTA increased sharply between February and August 2012. This pattern, which is consistent with observations of increasing Mississippi River TA concentrations over the same period, indicates the importance of riverine

input as a control on the subannual variability of TA distributions in this area. Riverine influence declined along the Gulf Coast from the MARS-influenced area toward the West Florida Shelf, as well as from near-shore to offshore locations. The subannual variability of the changes was strongly modulated by variations in ocean currents in the region. Simultaneous consideration of surface currents, salinity, Δ TA, and riverine TA conditions (Figures 6 and 7) shows that interactions of riverine inputs (TA^0 values) with ocean currents dominate subannual total alkalinity distributions in the northeastern Gulf of Mexico. Based on the present findings, we suggest that Δ TA, determined from equations (3) to (5), is a useful indicator of riverine alkalinity input in the upper water column.

TA distributions in the upper water column are attributable, in part, to biogeochemical processes (respiration, photosynthesis, and calcification). Because the regressions used here account for variations attributable to physical mixing, influences from biogeochemical processes should be revealed as systematic deviations from the linear TA versus $1/S$ and TA versus S relationships provided by equations (2) and (3). Our work suggests that with more frequent CO_2 system observations, better accounts of freshwater discharges, and high temporal resolution ocean models for surface currents, the mechanisms that underlie TA distributions, including both physical mixing and biogeochemical processes, can be increasingly well defined.

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