**Particle Triggered Reactions as an Important Mechanism of Alkalinity and Inorganic Carbon Removal in River Plumes**

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**Abstract** The effects of heterogeneous reactions between river-borne particles and the carbonate system were measured in the plumes of the Mississippi and Brazos rivers. Measurements within these plumes revealed significant removal of dissolved inorganic carbon (DIC) and total alkalinity (TA). After accounting for all known DIC and TA sinks and sources, heterogeneous reactions (i.e., heterogeneous CaCO₃ precipitation and cation exchange between adsorbed and dissolved ions) were found to be responsible for a significant fraction of DIC and TA removal, exceeding 10% and 90%, respectively, in the Mississippi and Brazos plume waters. This finding was corroborated by laboratory experiments, in which the seeding of seawater with the riverine particles induced the removal of the DIC and TA. The combined results demonstrate that heterogeneous reactions may represent an important controlling mechanism of the seawater carbonate system in particle-rich coastal areas and may significantly impact the coastal carbon cycle.

1. **Introduction**

Riverine input carrying the continental weathering products of rock materials is a primary source of total alkalinity (TA) and dissolved inorganic carbon (DIC) to the ocean, and therefore, has a major influence on the seawater carbonate system (Berner & Berner, 2012; Berner et al., 1983; Emerson & Hedges, 2008; Meybeck, 2003; Sabine et al., 2004). Within the coastal ocean, the carbonate system is controlled by a suite of physical (e.g., mixing, circulation, and air-sea gas exchange) and biogeochemical (e.g., photosynthesis, respiration, and seawater interactions with sediments and/or suspended particles) processes (Bauer et al., 2013; Cai et al., 2020; Wang et al., 2013). Numerous studies have shown that in a river plume environment, these biogeochemical processes often cause nonconservative changes in the TA and DIC across the salinity gradient between river and seawater endmembers (e.g., Cai, 2003; Fennel & Wilkin, 2009; Guo et al., 2012; Hofmann et al., 2011; Huang et al., 2012).

A potentially important, but thus far largely ignored, chemical process affecting the coastal carbonate system is the heterogeneous reaction on surfaces of particles suspended in seawater. It is well known that heterogeneous CaCO₃ precipitation (HCP) can occur on suspended particles, which provide nucleation seeds for crystal growth and lead to a decrease in the TA and DIC. In fact, seeding seawater with solid CaCO₃ is a common laboratory procedure for induction of CaCO₃ precipitation (DeBoer, 1977; Millero et al., 2001; Morse et al., 1985, 2003; Tribble & Mackenzie, 1998; Troy et al., 1997; Wollast et al., 1980).

CaCO₃ precipitation can be described by the reaction:

\[ Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \] (1)
According to Equation 1, precipitation of CaCO₃ in a closed-system (without CO₂ gas-exchange) decreases the TA versus the DIC on a straight line with a slope of 2. Opening the system for gas-exchange decreases this slope toward 1.

HCP has been observed on biogenic CaCO₃ surfaces such as coral fragments (Enmar et al., 2000) and gastropod nacre (Nassif et al., 2005). However, very few studies have examined the importance of HCP on the carbonate system in situ. Morse et al. (2003) hypothesized that HCP on suspended sediment may be the main mode of TA and DIC removal over the Bahama Banks. This hypothesis was supported by measurements showing a decrease in both the TA and DIC within a plume of suspended CaCO₃-rich sediment over the Little Bahama Banks (Bustos-Serrano et al., 2009). Wurgaft et al. (2016) presented evidence that HCP on resuspended sediment and particles from flash flood deposition caused a decrease in the TA and DIC within the Red Sea. On a global scale, Tribble and Mackenzie (1998) suggested that HCP on sinking foraminiferal skeletons may induce a carbon flux from the photic zone comparable to the riverine carbon flux to the ocean, making HCP a potentially important process in the oceanic carbon cycle.

Another heterogeneous reaction mechanism that has been shown to result in a decrease in TA (but not in DIC) is cation exchange between dissolved cations in seawater and adsorbed protons on natural particles (Sayles & Mangelsdorf, 1977, 1979; Sayles et al., 1978):

\[
\alpha H^+_{\text{adsorbed}} + X_{\text{dissolved}}^{a+} \leftrightarrow \alpha H^+_{\text{dissolved}} + X_{\text{adsorbed}}^{a+}
\]  

where \( \alpha \) is the charge of the dissolved cation X (e.g., Na⁺ or Mg²⁺) exchanged with H⁺ on particles. According to Equation 2, the TA will decrease by the same amount as protons desorbed \((X^{a+}_{\text{adsorbed}})\) and is limited by the cation exchange capacity of the particles.

HCP and cation exchange may be particularly important in influencing the carbonate system of coastal areas with riverine influx, due to the abundance of river-borne particles serving as nuclei for these processes. Thus far, however, the in situ effects of HCP and cation exchange on the carbonate system in a river plume environment have not been explicitly examined.

In this study, we combine data from field observations in the northern Gulf of Mexico (nGoM) with measurements from laboratory experiments to provide the first in situ evidence for the significant removal of TA and DIC by heterogeneous reactions in major river plumes. Beyond the river plumes studied (from the Mississippi and Brazos rivers), the findings have significant implications for the role of heterogeneous reactions on the coastal carbon cycle and the global marine carbonate system.

2. Materials and Methods

2.1. Field Campaign

The field observations, acquired over September 9–18, 2017 from the R/V Pelican, focused on the plumes of the Mississippi and Brazos rivers (Figure 1), the two major suppliers of suspended solids to the nGoM (Carlin & DellaPenna, 2014; Milliman & Meade, 1983). Because both rivers drain carbonate platforms (Cai et al., 2008; Zeng et al., 2011), they are supersaturated with respect to carbonate minerals (2–5 times higher than the solubility product for calcite) and carry a suspended load rich in carbonate particles, which can serve as precipitation nuclei for marine HCP (Millero et al., 2001; Morse et al., 2003; Mucci, 1981; Wurgaft et al., 2016). The suspended particle loads of these rivers also contain large amounts of clay minerals, which can act as precursors for cation exchange (Sayles & Mangelsdorf, 1977, 1979; Sayles et al., 1978). The cruise occurred shortly after the Brazos experienced record high discharge due to flooding caused by Hurricane Harvey (Figure S1), which reached the Texas shore 14 days before sampling commenced. The heavy particle load carried by the Brazos floodwaters resulted in a well-defined front separating the sediment-laden river plume water from the clearer seawater of the nGoM (Figure S2). Moving shoreward, the total suspended solid (TSS) concentration increased sharply from 10 to 40 mg l⁻¹, crossing the front (Figure S3) to...
>150 mg l⁻¹ near the river mouth. In the Mississippi plume, which was not affected by Hurricane Harvey, the TSS ranged between 10 and 40 mg l⁻¹ (Figure S3) and increased gradually toward the river mouth.

2.2. Underway Measurements, Seawater Sampling and Analysis

During the cruise, seawater was pumped from ∼3 m below the sea surface and used for underway measurements of temperature, salinity, and TSS (from a 10-cm path-length WETLabs transmissometer). In addition, seawater samples were collected at various depths using a Niskin Rosette equipped with a SeaBird electronics CTD. Water samples were extracted from selected Niskin bottles and used for determination of carbonate system parameters (TA, DIC and pH), following procedures described by Dickson et al. (2007). The TA and DIC of water samples were determined, respectively, by modified Gran titration on an automated titrator (AS-ALK2, Apollo Sci Tech) and by an automatic Infrared DIC analyzer (AS-C3, Apollo Sci Tech) (Wang et al., 2017). Org-Alk was measured according to procedures by Cai et al. (1998) and Song et al. (2020). All measurements of carbonate system parameters were calibrated with Certified Reference Material provided by Dr. A.G. Dickson of the Scripps Institution of Oceanography. The sample pH was measured spectrophotometrically based on procedures by Liu et al. (2011). Colorimetric methods (Grasshoff et al., 2009) were used for determination of dissolved inorganic nitrogen (DIN = NO₃ + NO₂), silica, and soluble reactive phosphate (SRP) concentrations. Concentrations of the major ions (Na⁺, Cl⁻, Mg²⁺, Ca²⁺, K⁺ and Sr²⁺) were determined with an inductively coupled plasma mass spectrometer. TSS samples used for calibration of the transmissometer beam attenuation were acquired by filtering 4 L of seawater through preweighed 0.45 µm filters, which were then dried at 60 °C for 48 h and reweighed. Further details of the analytical analyses of bottle samples can be found in the supporting information (Text S1).

2.3. Assessment of Heterogeneous Reactions

In assessing the effect of heterogeneous reactions of particles on the TA and DIC in the Brazos and Mississippi plumes, it was assumed that the plumes comprise two endmembers, river water and seawater. In the Mississippi plume, the two-endmember mixing scenario has long been established for the DIC and TA (Cai, 2003; Guo et al., 2012). For the Brazos plume, there is no evidence in the literature suggesting multiple endmember mixing within the plume. Moreover, the record flooding of Hurricane Harvey (Figure S1) caused an overflow of the Brazos, such that its waters were flowing from the neighboring canals and estuaries, further reducing the possibility of a nearby third, or other, endmember. In both plume systems, the correlation between the major ions and salinity also supports the two-endmember mixing assumption (Figure S4). Finally, because the plume residence time in both systems, as estimated from acoustic Doppler current profiler data and drifter tracks, is short (<2 days, Text S4), while the riverine variations in DIC and
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TA are on a seasonal scale (measured at United States Geological Survey gauge stations, Text S5), we consider the river endmembers to be invariant. Nevertheless, the effects of changes in the chemical properties of the river endmembers were considered in the error estimation of the results (Text S5).

Under the two-endmember mixing, the deviations of DIC and TA from the conservative mixing line in plume water are caused by biogeochemical processes, including photosynthesis and respiration, biogenic CaCO₃ production, gas exchange, benthic fluxes, and heterogeneous reactions. The effect of heterogeneous reactions on the TA and DIC are expressed as follows:

$$\Delta T_{AHET} = T_{OBS} - T_{CON} - \Delta T_{OTH}$$

$$\Delta D_{IC} = D_{OBS} - D_{CON} - \Delta D_{OTH},$$

where $\Delta T_{AHET}$ is the change in TA due to heterogeneous reactions, $T_{OBS}$ is the observed TA, $T_{CON}$ is the TA that would be expected for strictly conservative mixing between the two endmembers, and $\Delta T_{OTH}$ is the change in TA due to biogeochemical processes other than heterogeneous reactions (with the DIC terms similarly defined in Equation 4).

Determination of $\Delta T_{OTH}$ and $\Delta D_{OTH}$ was done according to the following:

$$\Delta T_{OTH} = 2\Delta C_{aCO3,BIO} + \Delta T_{SED} + \Delta D_{IN} + \Delta SRP - \Delta OrgAlk$$

$$\Delta D_{IC} = 6\Delta C_{aCO3,BIO} + \Delta D_{IC,SED} + \Delta D_{IC,air-sea} + 5\Delta D_{IN},$$

where $\Delta C_{aCO3,BIO}$ is the DIC change due to biogenic CaCO₃ production, $\Delta T_{SED}$ and $\Delta D_{IC,SED}$ denote the fluxes of TA and DIC from the sediment, $\Delta D_{IC,air-sea}$ is the air-water CO₂ flux, and $\Delta OrgAlk$ is the contribution of organic alkalinity to TA. The net effect of photosynthesis and respiration on the TA (Brewer & Goldman, 1976; Wolf-Gladrow et al., 2007) was estimated based on the deviations of DIN and SRP from the conservative mixing ($\Delta D_{IN}$ and $\Delta SRP$). The impact of photosynthesis and respiration on the DIC was estimated based on $\Delta D_{IN}$ and converted to DIC changes according to the Redfield ratio $\Delta D_{IC}/\Delta D_{IN} = 5$ (Huang et al., 2012). $\Delta D_{IN}$ was chosen over $\Delta SRP$ for this purpose because phosphate tends to adsorb on the surface of suspended particles (Millero et al., 2001; Pan et al., 2002). See supporting information for details of the endmembers (Text S3 and Table S1) and the estimation and values of the terms in Equations 5 and 6 (Table S2).

Nitrification, which removes 2 moles of TA per 1 mole of NH₄⁺ (Soetaert et al., 2007; Wolf-Gladrow et al., 2007) without affecting the DIC, was not accounted for in our two-endmember mixing model. Since the NH₄⁺ concentrations in the Mississippi and Brazos are typically 3–5 µmol kg⁻¹ or less (Guo et al., 2012), the potential of nitrification to reduce the TA is limited to 6 µmol kg⁻¹. As will be shown below, this is insignificant compared to the other terms in Equations 5 and 6. Biological CaCO₃ precipitation ($\Delta C_{aCO3,BIO}$) was also estimated to be insignificant (5 ± 7 µmol kg⁻¹, Table S2) in both the river plumes. This is in agreement with previous studies (Green et al., 2006; Wawrik & Paul, 2004) which estimated that calcifiers are numerically unimportant within the plume, and this estimation was confirmed by the absence of foraminiferal skeletons and coccolithophorids on the solids in filter samples collected for TSS measurements. Finally, since our focus was on the biogeochemical processes which occur outside the river-mouths, we used the data from $S = 15$ as the river endmember, which eliminates the effects of processes occurring in the rivers.

2.4. Seeding Experiments

To further study the effects of suspended particles on the TA and DIC, a series of controlled experiments was conducted in which a set of borosilicate bottles with high-density polyethylene caps were filled with surface seawater from the southernmost station in the Mississippi transect and seeded with riverine particles (at 4 ± 0.2 g l⁻¹) from sediment cores acquired in areas of the Mississippi and Brazos river plumes. Each bottle was poisoned with HgCl₂ to arrest biological activity. Throughout the experiment (200–400 h), each bottle was kept in the dark on a table shaker, at ~80 RPM, keeping the particles in suspension. The seawater temperature ranged over 20–22°C throughout the experiment, whereas the in situ temperatures...
were \( \sim 27^\circ\text{C} \). As this temperature difference is equivalent to a decrease of less than 5% in the saturation levels for calcite and aragonite, the results were not corrected to in situ conditions. At selected times, a pair of bottles containing seeded seawater and/or a pair of control bottles was removed from the table shaker and sampled by filtering the water through a 0.2 \( \mu \text{m} \) filter (see Text S2 for more details).

### 3. Results and Discussion

Three lines of evidence suggest that heterogeneous reactions removed the TA and DIC from the seawater in the two river plumes studied. First, the values of \( \Delta\text{TA}_{\text{HET}} \) and \( \Delta\text{DIC}_{\text{HET}} \) (the effects of heterogeneous reactions on TA and DIC) fall well below the conservative mixing line (Figures 2 and 3) in both plumes. In the Mississippi plume, \( \Delta\text{TA}_{\text{HET}} \) and \( \Delta\text{DIC}_{\text{HET}} \) reached mean values of \(-85\) and \(-40\ \mu\text{mol kg}^{-1}\), respectively (negative values indicate TA and DIC removal). In the Brazos plume, \( \Delta\text{TA}_{\text{HET}} \) and \( \Delta\text{DIC}_{\text{HET}} \) were multifold larger, both reaching approximately \(-300\ \mu\text{mol kg}^{-1}\). Second, Ca:Na ratios in the Brazos river plume (Figure 4) were lower than the ratios expected from conservative mixing, suggesting that \( \text{Ca}^{2+} \) was removed as \( \text{CaCO}_3 \) from the river plume. No systematic deviation from conservative mixing was observed for any other major elements measured in the plume (Figure S4). Third, in the laboratory seeding experiments, TA and DIC in the nGoM seawater decreased by roughly 50 and 20 \( \mu\text{mol kg}^{-1} \), respectively, in response to the introduction of particles from the Mississippi and Brazos plume regions, whereas no significant changes in the TA or DIC were measured in the control bottles (with no particles introduced) (Figure 5). The timescale of decline for both the TA and DIC was of order 50 h, which is similar to the residence time of the plumes (Text S4).

Regarding the second point above, it is noteworthy that the effect of HCP was not apparent in the Ca:Na ratios in the Mississippi plume (Figure 4). This is most likely due to the small \( \Delta\text{TA}_{\text{HET}} \) signal in the Mississippi plume (85 vs. 300 \( \mu\text{mol kg}^{-1} \) in the Brazos plume), which is equivalent to a \( \text{Ca}^{2+} \) decrease due to an HCP of \( \sim 40\ \mu\text{mol kg}^{-1} \) (\( \Delta\text{TA}_{\text{HET}}/2 \)), below the precision of ICP-MS \( \text{Ca}^{2+} \) measurements (\( \pm 0.5\% \) of the 2–10 \( \text{mmol kg}^{-1} \) signal in the Mississippi plume).

A number of studies have observed TA and DIC deviations from conservative mixing within the Mississippi plume and attributed these to nitrification, biological \( \text{CaCO}_3 \) precipitation, and net community production (NCP: Photosynthesis-respiration) (Cai, 2003; Guo et al., 2012; Keul et al., 2010). As noted in section 2.3, nitrification and biological \( \text{CaCO}_3 \) precipitation play an insignificant role in removing the TA and DIC from the Brazos and Mississippi plumes. Our measurements indicate that although DIC removal in the Mississippi plume was dominated by NCP, \( \Delta\text{DIC}_{\text{HET}} \) was a prominent DIC removal mechanism, amounting to a mean of \( 27 \pm 28\% \) (1 SD) of the DIC removal by NCP (5\( \Delta\text{DIN} \) in Equation 6). Furthermore, DIC removal in the Brazos plume was dominated by \( \Delta\text{DIC}_{\text{HET}} \), which exceeded DIC removal by NCP by roughly a factor of 80 and \( \Delta\text{DIC}_{\text{air-sea}} \) (the largest term of Equation 6) by roughly a factor of 25 (Tables S1 and S2).

Differences between the \( \Delta\text{TA}_{\text{HET}}:\Delta\text{DIC}_{\text{HET}} \) ratios in the laboratory experiments and in situ studies are notable. Values of \( \Delta\text{TA}_{\text{HET}} \) versus \( \Delta\text{DIC}_{\text{HET}} \) from the Mississippi plume mostly fall below a 2:1 line (Figure 2), indicating the influence of both HCP and cation exchange on the TA and DIC (Equations 1 and 2). By contrast, the TA versus the DIC derived from the closed-system laboratory experiments seeded with Mississippi
plume sediments decline at a ratio of 2.1:1 (Figure 5), close to the expected HCP ratio. One possible explanation for this difference is that the particles used for the seeding experiment, collected from the top section of a core, were likely to have been in seawater longer than the particles suspended in the plume. The cation-exchange sites of the core-derived particles may have equilibrated with seawater prior to collection, resulting in the HCP being the dominant mechanism affecting the TA and DIC in the laboratory closed system.

The \( \Delta \text{TA}_{\text{HET}} \) and \( \Delta \text{DIC}_{\text{HET}} \) values derived from the Brazos plume samples fall on a 1:1 slope (Figure 3), whereas the values of TA and DIC determined in the laboratory experiments seeded with the Brazos plume sediments decline along a slope of 2.9 (Figure 5). While the TA:DIC slope of the experimental results may be attributed to the HCP and cation exchange, the in situ slope of 1 warrants explanation. Based on the Ca:Na trend (Figure 4), the mixing model estimates (Table S2), and the experimental results, we expect that the main process affecting \( \Delta \text{TA}_{\text{HET}} \) and \( \Delta \text{DIC}_{\text{HET}} \) in the Brazos is HCP, which is characterized by a slope of 2:1. A slope of 1:1 may result from an underestimate of the DIC changes due to gas-exchange and/or uptake by NCP (Table S1), which may cause an overestimate of \( \Delta \text{DIC}_{\text{HET}} \). An additional mechanism that can explain the low in-situ TA:DIC ratio relative to that of HCP may be desorption of dissolution products of minerals such as hydroxyapatite (Longo et al., 2014; Nenes et al., 2011; Stockdale et al., 2016), which would increase TA (and thus lower \( \Delta \text{TA}_{\text{HET}} \)) without affecting DIC. Further research is required to determine the mechanisms responsible for the observed TA and DIC removal and their changing ratios in river plumes and other high particle-load coastal systems.

4. Significance and Implications

This study shows that heterogeneous chemical reactions between suspended particles and seawater, including both HCP and cation ion exchange, may result in significant TA and DIC removal from two major river plumes in the nGoM. Under the high particle-load conditions encountered in the Brazos River plume (Figures S2 and S3), the magnitude of the removal (~250–350 \( \mu \text{mol kg}^{-1} \)) is on the same order of magnitude as that measured during a
"whiting" event over the Little Bahama Banks (~400 μmol kg$^{-1}$ (Bustos-Serrano et al., 2009)). The results from this study suggest that processes that introduce large, suspended particle loads to the coastal ocean, such as riverine inputs, sediment resuspension, and flash flooding, may cause substantial removal of water-column TA and DIC. Such particle-seeding processes may have important, yet not fully understood, effects on the coastal carbonate chemistry and the coastal carbon cycle.

To evaluate the scale of the TA and DIC removal by heterogeneous reactions in the two river plumes, we applied the approach employed in a number of studies (Boyle et al., 1974; Cai, 2003; Officer, 1979). This involved correcting the observed TA and DIC concentrations for all biogeochemical processes except heterogeneous reactions (green circles in Figures 2 and 3). The difference between the “corrected” concentrations and the concentrations expected from conservative mixing represents the effect of heterogeneous reactions on the TA and DIC. To estimate the plume-scale effect, the corrected values were linearly extrapolated between the high-salinity to mid-salinity plume region ($S > 21$ in the Mississippi and $S > 18$ in the Brazos) and the minimum salinity measured ($S = 15$ and $S = 12$ in the Mississippi and Brazos, respectively; black dash lines in Figures 2 and 3). The difference between the extrapolated values and the river-mouth TA and DIC endmembers (Table S1), which represent the incoming fluxes of these properties into the nGoM, is an

Figure 5. Total alkalinity (TA) and dissolved inorganic carbon (DIC) versus time, and TA versus DIC observed during seeding experiments in which seawater from the nGoM was seeded with particles from (a–c) the Mississippi and (d–f) Brazos plume regions. The filled blue circles are from the seeding treatment and the red circles are from the control treatment in which no particles were added. Each data point is the mean of two duplicate experimental bottles. The overall mean difference between the duplicate bottles is ±8 μmol kg$^{-1}$, which is smaller than the marker size. The dashed lines in (c) and (f) are the linear best-fit lines of TA versus DIC (filled blue circles) observed during the experiments.
estimate of the removal of the TA and DIC due to heterogeneous reactions in the plumes (Boyle et al., 1974; Officer, 1979). This difference accounted for 6% and 2% of the TA and DIC concentrations, respectively, in the Mississippi, and up to 20% of the TA and DIC in the Brazos. By comparison, NCP in the Mississippi plume is estimated to remove approximately 50% of the DIC from the riverine input (Cai, 2003). These estimates highlight the significance of heterogeneous chemical reactions between suspended particles and the seawater in river plumes, particularly for those where, or when, particle loading is significant.

The substantial losses of TA and DIC in the Brazos plume are likely due to the exceptionally high particle load carried by the Brazos in the wake of Hurricane Harvey. The maximum TSS measured in the Brazos plume (>200 mg l⁻¹) is roughly four times the maximum measured TSS in the Mississippi (50 mg l⁻¹), which was not impacted by recent heavy rains during the time of our sampling (Figures S2). This TSS ratio is comparable to the ratios of maximum ΔTAHET and ΔDICHET found in the two plumes (Figures 2 and 3), suggesting that there might be a close relationship between the particle load and heterogeneous removal of TA and DIC from the seawater.

To gain a first-order estimate of the long-term effects of heterogeneous reactions on the TA and DIC in the Mississippi River plume, we assume that the ratios between TSS and the respective mean values of ΔTAHET and ΔDICHET are constant and identical to the ratios measured during our cruise. Multiplying these ratios by the 2011–2019 average TSS from the Mississippi’s gauge station 07374000 near Baton Rouge, LA, yields ΔTAHET and ΔDICHET values of 90 and 40 µmol kg⁻¹, respectively. When integrated over a plume thickness of 5 m and divided by a residence time of 2 days (Cai, 2003; Guo et al., 2012; Lohrenz et al., 1997), these values indicate a TA and a DIC sink of 180 mmol m⁻² d⁻¹ and 80 mmol m⁻² d⁻¹, respectively. For comparison, the DIC uptake resulting from NCP was estimated to be 170–330 mmol m⁻² d⁻¹ (Cai, 2003; Guo et al., 2012). Even though these estimates are preliminary, the field data and laboratory results in this study suggest that TA and DIC removal via heterogeneous reactions is likely to be an important component of the carbon cycle in the two river plumes studies and may play an important role in controlling the carbonate system in river plumes. More generally, heterogeneous reactions may be a ubiquitous phenomenon that need to be taken into account when studying carbonate chemistry and the carbon cycle in particle-laden marine environments worldwide.

Data Availability Statement

All data used in this work are available through the NSF data depository (Wang & Churchill, 2020).

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References

Bauer, J. E., Cai, W. J., Raymond, P. A., Bianchi, T. S., Hopkinson, C. S., & Regnier, P. A. G. (2013). The changing carbon cycle of the coastal ocean. Nature, 504(7478), 61–70. https://doi.org/10.1038/nature12857

Berner, E. K., & Berner, R. A. (2012). Global environment: Water, air and geochemical cycles. Princeton University Press.

Berner, R. A., Lasaga, A. C., & Garrels, R. M. (1983). The carbonate-silicate geochemical cycle and its effect on atmospheric carbon-dioxide Global environment: Water, air, and geochemical cycles. Princeton University Press.

Berner, R. A., & Lasaga, A. C. (1984). The fate of chemical components in the environment. Geochimica et Cosmochimica Acta, 48(2), 159–173. https://doi.org/10.1016/0016-7037(84)90166-0

Berner, R. A., Lasaga, A. C., & Garrels, R. M. (1983). The carbonate-silicate geochemical cycle and its effect on atmospheric carbon-dioxide Global environment: Water, air, and geochemical cycles. Princeton University Press.

Berner, R. A., & Lasaga, A. C. (1984). The fate of chemical components in the environment. Geochimica et Cosmochimica Acta, 48(2), 159–173. https://doi.org/10.1016/0016-7037(84)90166-0

283(3), 473–483. https://doi.org/10.1016/0016-7037(74)90188-4

Bustos-Serrano, H., Morse, J. W., & Millero, F. J. (2009). The formation of whitings on the Little Bahama Bank. Marine Chemistry, 113(1–2), 1–8. https://doi.org/10.1016/j.marchem.2008.10.006

Cai, W. J. (2003). Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume. Geophysical Research Letters, 30(2), 1032. https://doi.org/10.1029/2002GL016312

Cai, W. J., Guo, X., Chen, C., Dai, M., Zhang, L., Zhai, W., et al. (2008). A comparative overview of weathering intensity and HCO₃⁻ flux in the world’s major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers. Continental Shelf Research, 28(12), 1538–1549. https://doi.org/10.1016/j.csr.2007.10.014

Cai, W. J., Wang, Y. C., & Hodgson, R. E. (1998). Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA. Geochimica et Cosmochimica Acta, 62(3), 473–483. https://doi.org/10.1016/s0016-7037(97)00363-3

Cai, W. J., Xu, Y. Y., Feely, R. A., Wanninkhof, R., Alin, S. R., Barbero, L., et al. (2020). Controls on surface water carbonate chemistry along North American ocean margins. Nature Communications, 11(1), 2691.

Carlin, J. A., & Dellapenna, T. M. (2014). Event-driven deltaic sedimentation on a low-gradient, low-energy shelf: The Brazos River subaqueous delta, northwestern Gulf of Mexico. Marine Geology, 353, 21–30. https://doi.org/10.1016/j.margeo.2014.03.017

DeBoer, R. (1977). Influence of seed crystals on the precipitation of calcite and aragonite. American Journal of Science, 277(1), 38.

Dickson, A. G., Sabine, C. L., & Christian, J. R. (2007). Guide to best Practices for ocean CO₂ measurements. PICES special publication.
Emerson, S., & Hedges, J. (2008). Chemical oceanography and the marine carbon cycle. Cambridge University Press. https://doi.org/10.1017/cbo9780511979320

Ennmar, R., Stein, M., Bar-Matthews, M., Sass, E., Katz, A., & Lazar, B. (2000). Diagenesis in live corals from the Gulf of Aqaba. I. The effect on paleo-oceanography tracers. Geochimica et Cosmochimica Acta, 64(18), 3123–3132. https://doi.org/10.1016/s0016-7037(00)00417-8

Fennel, K., & Wilkin, J. (2009). Quantifying biological carbon export for the northwest North Atlantic continental shelves. Geophysical Research Letters, 36(18). https://doi.org/10.1029/2009gl039818

Grasshoff, K., Kremling, K., & Ehrhardt, M. (2000). Methods of seawater analysis. John Wiley & Sons.

Green, R. E., Bianchi, T. S., Dagg, M. J., Walker, N. D., & Breed, G. A. (2006). An organic carbon budget for the Mississippi River turbidity plume and plume contributions to air-sea CO2 fluxes and bottom water hypoxia. Estuaries and Coasts, 29(4), 579–597. https://doi.org/10.1007/bf02784284

Guo, X., Cai, W.-J., Huang, W.-J., Wang, Y., Chen, F., Murrell, M. C., et al. (2012). Carbon dynamics and community production in the Mississippi River plume. Limnology and Oceanography, 57(1), 1–17. https://doi.org/10.4319/lo.2012.57.1.0001

Hofmann, E. E., Cahill, B., Fennel, K., Friedrichs, M. A., Hyde, K., Lee, C., et al. (2011). Modeling the dynamics of continental shelf carbon. Annual Review of Marine Science, 3, 93–122. https://doi.org/10.1146/annurev-marine-120709-142740

Huang, W.-J., Cai, W.-J., Powell, R., Wang, Y., Jiang, L.-Q., & Hopkinson, C. (2012). The stoichiometry of inorganic carbon and nutrient removal in the Mississippi River plume and adjacent continental shelf. Biogeosciences, 9(7), 2781–2792. https://doi.org/10.5194/bg-9-2781-2012

Keul, N., Morse, J. W., Wanninkhof, R., Gledhill, D. K., & Bianchi, T. S. (2010). Carbonate chemistry dynamics of surface waters in the northern Gulf of Mexico. Aquatic Geochemistry, 16(3), 337–351. https://doi.org/10.1007/s10498-010-9061-2

Liu, X. W., Patasova, M. C., & Byrne, R. H. (2011). Purification and characterization of meta-cresol purple for spectrophotometric seawater pH measurements. Environmental Technology & Environment, 45(11), 4862–4868. https://doi.org/10.1080/13648176.2011.592879

Lohrenz, E. E., Cahill, B., Fennel, K., Friedrichs, M. A., Hyde, K., Lee, C., et al. (2011). Modeling the dynamics of continental shelf carbon. Annual Review of Marine Science, 3, 93–122. https://doi.org/10.1146/annurev-marine-120709-142740

Meybeck, M. (2003). Global occurrence of major elements in rivers. Geochemistry, 41(7), 951–960. https://doi.org/10.1016/S0016-7037(03)00154-5

Millero, F., Huang, F., Zhu, X. R., Liu, X. W., & Zhang, J. Z. (2001). Adsorption and desorption of phosphate on calcite and aragonite in seawater. Aquatic Geochemistry, 7(1), 33–56. https://doi.org/10.1023/a:101134417092

Munro, J. D., & Meade, R. H. (1983). World-wide delivery of river sediment to the ocean. The Journal of Geology, 91(1), 1–21. https://doi.org/10.1086/628741

Morse, J. W., Gledhill, D. K., & Millero, F. J. (2003). CaCO3 precipitation kinetics in waters from the Great Bahama bank: Implications for the relationship between bulk chemistry and whittings. Geochimica et Cosmochimica Acta, 67(15), 2819–2826. https://doi.org/10.1016/S0016-7037(03)00103-0

Nassen, N., Pinna, N., Gehrke, N., Antonietti, M., Jager, C., & Colfen, H. (2005). Amorphous layer around aragonite platelets in nacre. Geochimica et Cosmochimica Acta, 69(11), 4043–4049. https://doi.org/10.1016/j.gca.2005.06.055

Nees, A., Krom, M., Mihalopoulos, N., Van Cappellen, P., Shi, Z., Bougiatioti, A., et al. (2011). Atmospheric acidification of mineral aerosols: A source of bioavailable phosphorus for the oceans. Atmospheric Chemistry and Physics, 11(13), 6265–6272. https://doi.org/10.5194/acp-11-6265-2011

Officer, C. B. (1979). Discussion of the behaviour of nonconservative dissolved constituents in estuaries. Estuarine and Coastal Marine Science, 9(1), 91–94. https://doi.org/10.1016/0012-6827(79)90009-4

Pan, G., Krom, M. D., & Herut, B. (2002). Adsorption-desorption of phosphate on airborne dust and riverborne particulates in East Mediterranean seawater. Environmental Science & Technology, 36(15), 3519–3524. https://doi.org/10.1021/es020516d

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., et al. (2004). The oceanic sink for anthropogenic CO2, Science, 305(5682), 367–371. https://doi.org/10.1126/science.1097403

Sayles, F. L., & Mangelsdorf, P. C. (1977). Equilibration of clay-minerals with seawater - exchange - reactions. Geochimica et Cosmochimica Acta, 41(7), 951–960. https://doi.org/10.1016/0016-7037(77)90154-5

Sayles, F. L., & Mangelsdorf, P. C. (1979). Cation-exchange characteristics of Amazon River suspended sediment and its reaction with seawater. Geochimica et Cosmochimica Acta, 43(5), 767–779. https://doi.org/10.1016/0016-7037(79)90260-6

Schlitzer, R. (2002). Interactive analysis and visualization of geoscience data with Ocean Data View. Computers & Geosciences, 28(10), 1211–1218. https://doi.org/10.1016/s0098-3004(02)009040-7

Song, S., Wang, Z. A., Gonmea, M. E., Kroeger, K. D., Chu, S. N., Li, D., & Liang, H. (2020). An important biogeochemical link between organic and inorganic carbon cycling: Effects of organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt marshes. Geochimica et Cosmochimica Acta, 275, 123–139. https://doi.org/10.1016/j.gca.2020.02.013

Stockdale, A., Krom, M., Mortimer, R., Benning, L., Carslaw, K., Herbert, R., et al. (2016). Understanding the nature of atmospheric acid processing of mineral dusts in supplying bioavailable phosphorus to the oceans. Proceedings of the National Academy of Sciences of the United States of America, 113(51), 14639–14644. https://doi.org/10.1073/pnas.1608136113

Tribble, J. S., & Mackenzie, F. T. (1998). Recrystallization of magnesian calcite overgrowths on calcite seeds suspended in seawater. Aquatic Geochemistry, 4(3–4), 337–360. https://doi.org/10.1023/a:1009636331784

Troy, P. F., Li, Y.-H., & Mackenzie, F. T. (1997). Changes in surface morphology of calcite exposed to the oceanic water column. Aquatic Geochemistry, 3(1), 1–20. https://doi.org/10.1023/a:1009652821575
Wang, Z. A., & Churchill, J. (2020). CO₂-system and auxiliary data from the Northern Gulf of Mexico from samples collected during R/V Pelican cruise PE18-09 in September of 2017. Biological and Chemical Oceanography Data Management Office (BCO-DMO). https://doi.org/10.26008/1912/bco-dmo.821117.1

Wang, Z. A., Lawson, G. L., Pilskaln, C. H., & Maas, A. E. (2017). Seasonal controls of aragonite saturation states in the Gulf of Maine. Journal of Geophysical Research: Oceans, 122(1), 372–389. https://doi.org/10.1002/2016jc012373

Wang, Z. A., Wanninkhof, R., Cai, W. J., Byrne, R. H., Hu, X. F., Peng, T. H., & Huang, W. J. (2013). The marine inorganic carbon system along the Gulf of Mexico and Atlantic coasts of the United States: Insights from a transregional coastal carbon study. Limnology and Oceanography, 58(1), 325–342. https://doi.org/10.4319/lo.2013.58.1.0325

Wawrik, B., & Paul, J. H. (2004). Phytoplankton community structure and productivity along the axis of the Mississippi River plume in oligotrophic Gulf of Mexico waters, Aquatic Microbial Ecology, 35(2), 185–196. https://doi.org/10.3354/Ame035185

Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Koertzinger, A., & Dickson, A. G. (2007). Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Marine Chemistry, 106(1–2), 287–300. https://doi.org/10.1016/j.marchem.2007.01.006

Wollast, R., Garrels, R., & Mackenzie, F. (1980). Calcite-seawater reactions in ocean surface waters. American Journal of Science, 280(9), 831–848. https://doi.org/10.2475/ajs.280.9.831

Wurgaft, E., Steiner, Z., Luz, B., & Lazar, B. (2016). Evidence for inorganic precipitation of CaCO₃ on suspended solids in the open water of the Red Sea. Marine Chemistry, 186, 145–155. https://doi.org/10.1016/j.marchem.2016.09.006

Zeng, F.-W., Masiello, C. A., & Hockaday, W. C. (2011). Controls on the origin and cycling of riverine dissolved inorganic carbon in the Brazos River, Texas. Biogeochemistry, 104(1), 275–291. https://doi.org/10.1007/s10533-010-9501-y

Reference From the Supporting Information

Hitchcock, G., Wiseman, W. J., Boicourt, W., Mariano, A. J., Walker, N., Nelsen, T., & Ryan, E. (1997). Property fields in an effluent plume of the Mississippi River. Journal of Marine Systems, 12(1–4), 109–126.