Particle triggered reactions as an important mechanism of alkalinity and inorganic carbon removal in river plumes

E. Wurgaft^{1,2}, Z.A. Wang¹, J. H. Churchill³, T. Dellapenna⁴, S. Song^{1,5}, J. Du⁶, M.C. Ringham^{1,7}, T. Rivlin^{8,9} and B. Lazar⁹

¹Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.

²Avinoam Adam Department of Natural Sciences, The Israeli Open University, Ra'anana, Israel.

³Department of Physical Oceanography, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.

⁴Department of Marine and Coastal Environmental Sciences, Texas A&M University at Galveston.

⁵State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai, China.

⁶Department of Applied Ocean Physics and Engineering, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.

⁷Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA.

⁸The Interuniversity Institute for Marine Sciences, The H. Steinitz Marine Biology Laboratory, The Hebrew University of Jerusalem, Eilat, Israel.

⁹Freddy and Nadine Herrmann Institute of Earth Science, The Hebrew University of Jerusalem, Jerusalem, Israel.

Corresponding author: Eyal Wurgaft (wurgaft@openu.ac.il)

Key Points:

- The effect of particle-induced, heterogeneous reactions on the carbonate system was measured in the Brazos and Mississippi river plumes.
- Heterogeneous reactions may cause 10-90% of alkalinity and dissolved inorganic carbon removal in the Brazos and Mississippi river plumes.
- Heterogeneous reactions may be an important mechanism in coastal carbonate chemistry worldwide.

Abstract

The effects of heterogeneous reactions between river-borne particles and the carbonate system were studied in the plumes of the Mississippi and the 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 removal of 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*, 2012; *Berner et al.*, 1983; *Emerson and 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 non-conservative changes in TA and DIC across the salinity gradient between river and seawater endmembers (e.g., *Cai*, 2003; *Fennel and 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 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 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.*, 2003; *Morse et al.*, 1985; *Tribble and 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 Eq. 1, precipitation of $CaCO_3$ in a closed-system (without CO_2 gas-exchange) decreases TA versus DIC on a straight line with a slope of 2. Opening the system for gas-exchange decreases this slope towards 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 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 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 and Mangelsdorf*, 1977; 1979; *Sayles et al.*, 1978]:

$$(\alpha H^{+})_{adsorbed} + (X^{\alpha +})_{dissolved} \leftrightarrow (\alpha H^{+})_{dissolved} + (X^{\alpha +})_{adsorbed}$$
(2)

where α is the charge of the dissolved cation X (e.g, Na⁺ or Mg²⁺) exchanged with H⁺ on particles. According to Eq. 2, TA will decrease by the same amount as protons desorbed $((X^{\alpha+})_{adsorbed})$ 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 significant removal of TA and DIC by heterogeneous reactions in major river plumes. Beyond the river plumes studied (from the Mississippi and the 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 9-18 September 2017 from the *R/V Pelican*, focused on the plumes of the Mississippi and the Brazos rivers (Figure 1), the two major suppliers of suspended solids to the nGoM [Carlin and Dellapenna, 2014; Milliman and 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 [Savles and 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, TSS ranged between 10 and 40 mg l⁻¹ (Figure S3) and increased gradually towards the river mouth.



Figure 1. Sampling area and stations in the northern Gulf of Mexico (nGoM). (a) Area map of the nGoM, with red rectangles indicating the sampling areas of the Mississippi and Brazos river plumes. The figure was generated by Ocean Data View software [*Schlitzer*, 2002].

2.2 Underway measurements, seawater sampling and analysis

During the cruise, seawater was pumped from ~ 3 m below 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, USA) and by an automatic Infrared DIC analyzer (AS-C3, Apollo Sci Tech, USA) [Wang et al., 2017]. Org-Alk was measured according to 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. Sample pH was measured spectrophotometrically based on 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 Sr^{2+}) 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 pre-weighed 0.45 µm filters, which were then dried at 60 °C for 48 hours 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 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 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, as the plume residence time in both systems, as estimated from ADCP data and drifter tracks, is short (< 2 days, Text S4), while the riverine variations in DIC and TA are on a seasonal scale (measured at USGS 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 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 TA and DIC are expressed as:

$\Delta TA_{HET} = TA_{OBS} - TA_{CON} - \Delta TA_{OTH}$	(3))
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 $\Delta DIC_{HET} = DIC_{OBS} - DIC_{CON} - \Delta DIC_{OTH,}$ (4)

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

Determination of ΔTA_{OTH} and ΔDIC_{OTH} was done according to:

 $\Delta TA_{OTH} = 2\Delta CaCO_{3,BIO} + \Delta TA_{SED} + \Delta DIN + \Delta SRP - \Delta OrgAlk$ (5)

 $\Delta DIC_{OTH} = \Delta CaCO_{3,BIO} + \Delta DIC_{SED} + \Delta DIC_{air-sea} + 5\Delta DIN,$

· (6)

where $\Delta CaCO_{3,BIO}$ is the DIC change due to biogenic CaCO₃ production, ΔTA_{SED} and ΔDIC_{SED} denote the fluxes of TA and DIC from the sediment, $\Delta DIC_{air-sea}$ 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 TA [*Brewer and Goldman*, 1976; *Wolf-Gladrow et al.*, 2007] was estimated based on the deviations of DIN and SRP from the conservative mixing (Δ DIN and Δ SRP). The impact of photosynthesis and respiration on DIC was estimated based on Δ DIN, as converted to DIC changes according to the Redfield ratio Δ DIC: Δ DIN =5 [*Huang et al.*, 2012]. Δ DIN was chosen over Δ 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 Eqs. 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 DIC, was not accounted for in our two-endmember mixing model. Since the NH₄⁺ concentrations in the Mississippi and Brazos are typically 3-5 μ mol kg⁻¹ or less [*Guo et al.*, 2012], the potential of nitrification to reduce TA is limited to 6 μ mol kg⁻¹. As will be shown below, this is insignificant compared to other terms in equations 5-6. Biological CaCO₃ precipitation (Δ CaCO_{3,BIO}) was also estimated to be insignificant (5 ±7 μ mol kg⁻¹, Table S2) in both river plumes. This is in agreement with previous studies [*Warwrik and*

Paul, 2004; *Green et al.*, 2006] who estimated that calcifiers are numerically unimportant within the plume, and 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 TA and DIC, a series of controlled experiments was conducted in which a set of borosilicate bottles with HDPE 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 hours), 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 ~ 27 °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 µm filter (see Text S2 for more details).

3 Results and discussion

Three lines of evidence suggest that heterogeneous reactions removed TA and DIC from seawater in the two river plumes studied. Firstly, the values of ΔTA_{HET} and ΔDIC_{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, ΔTA_{HET} and ΔDIC_{HET} reached mean values of -85 and -40 µmol kg⁻¹, respectively (negative values indicate TA and DIC removal). In the Brazos plume, ΔTA_{HET} and ΔDIC_{HET} were multifold larger, both reaching approximately -300 µmol kg⁻¹. Secondly, Ca:Na ratios in the Brazos river plume (Figure 4) were lower than ratios expected from conservative mixing, suggesting that Ca²⁺ was removed as CaCO₃ from the river plume. No systematic deviation from conservative mixing was observed for any other major elements measured in the plume (Figure S4). Thirdly, in the laboratory seeding experiments, TA and DIC in the nGoM seawater decreased by roughly 50 and 20 µmol kg⁻¹, respectively, in response to introduction of particles from the Mississippi and Brazos plume regions, whereas no significant changes in TA or DIC were measured in the control bottles (with no particles introduced) (Figure 5). The timescale of decline for both 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 ΔTA_{HET} signal in the Mississippi plume (85 versus 300 µmol kg⁻¹ in the Brazos plume), which is equivalent to a Ca²⁺ decrease due to HCP of ~ 40 µmol kg⁻¹ ($\Delta TA_{HET}/2$), below the precision of ICP-MS Ca²⁺ measurements (± 0.5% of the 2-10 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 CaCO₃ 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 CaCO₃ precipitation play an insignificant role in removing TA and DIC from the Brazos and Mississippi plumes. Our measurements indicate that although DIC removal in the Mississippi plume was dominated by NCP, Δ DIC_{HET} was a prominent DIC removal mechanism, amounting to a mean of 27 ± 28 % (1SD) of the DIC removal by NCP (5 Δ DIN in equation 6). Furthermore, DIC removal in the Brazos plume was dominated by Δ DIC_{HET}, which exceeded DIC removal by NCP by roughly a factor of 80 and Δ DIC_{air-sea} (the largest term of equation 6) by roughly a factor of 25 (Tables S1 and S2).



Figure 2. TA (a) and DIC (b) deviations from the two-endmember conservative mixing, as well as their deviations from conservative behavior due to heterogeneous reactions (c) in the Mississippi River plume. The blue '+' markers are the measured values, and the green circles are

the values corrected for all biogeochemical processes except heterogeneous reactions (equations 5 and 6). The red lines represent the two-endmember (Mississippi River and nGoM) conservative mixing line. The dashed line denotes a linear extrapolation of the green circle values in the high to mid salinity range to the measured minimal salinity endmember (S=15.7). Color scale in (c) represents sample salinity. For the sake of clarity, the maximal error bars (see Text S5 for details) are shown for representative points.



Figure 3. Same as Figure 2 except for the Brazos River plume The error is smaller than the markers, and is shown in the right corner of panel C.



Figure 4. Ca:Na ratios versus Na concentrations in the Mississippi (left panel) and Brazos (right panel) river plumes. The red line indicates conservative mixing between the river and seawater endmembers.



Figure 5. TA and DIC versus time, and TA versus DIC observed during seeding experiments in which seawater from the nGoM was seeded with particles from the Mississippi (a-c) and Brazos (d-f) 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.

Differences between the $\Delta TA_{HET}:\Delta DIC_{HET}$ ratios in the laboratory experiments and in situ studies are notable. Values of ΔTA_{HET} versus ΔDIC_{HET} from the Mississippi plume mostly fall below a 2:1 line (Figure 2), indicating influence of both HCP and cation-exchange on TA and DIC (equations 1 and 2). By contrast, TA versus 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 of 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 HCP being the dominant mechanism affecting TA and DIC in the laboratory closedsystem.

The Δ TA_{HET} and Δ DIC_{HET} values derived from the Brazos plume samples fall on a 1:1 slope (Figure 3), whereas values of TA and DIC determined in the laboratory experiments seeded with 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 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 Δ TA_{HET} and Δ DIC_{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 Δ DIC_{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 Δ TA_{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.

5 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 μ mol kg⁻¹) is on the same order of magnitude as that measured during a "whiting" event over the Little Bahama Banks (~ 400 μ mol 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 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 TA and DIC. To estimate the plume-scale effect, the corrected values were linearly extrapolated between the high 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 rivermouth TA and DIC endmembers (Table S1), which represent the incoming fluxes of these properties into the nGoM, is an estimate of the removal of TA and DIC due to heterogeneous reactions in the plumes [*Boyle et al.*, 1974; *Officer*, 1979]. This difference accounted for 6 % and 2 % of TA and DIC concentrations, respectively, in the Mississippi and up to 20 % of 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 seawater in river plumes, in particular 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 4 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 S3). This TSS ratio is comparable to the ratios of maximum ΔTA_{HET} and ΔDIC_{HET} found in the two plumes (Figures 2, 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 TA and DIC in the Mississippi river plume, we assume that the ratios between TSS and the respective mean values of ΔTA_{HET} and ΔDIC_{HET} 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 ΔTA_{HET} and ΔDIC_{HET} 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.

Acknowledgments

We are indebted to the captain and crew of the R/V Pelican for their assistance during the cruise. We thank Alex Ren from Louisiana Universities Marine Consortium for his help before and after the cruise, and Chana Krenzler for reading and commenting on the first draft. This research was funded by the National Science Foundation (NSF) and the Bi-National Science Foundation U.S-Israel award number OCE-BSF 1635388. All data used in this work is available through the NSF data depository [*Wang and Churchill*, 2020].

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