SPATIAL-TEMPORAL DISTRIBUTION OF ORGANIC MATTER AND CARBONATE CHEMISTRY PARAMETERS IN TEXAS MID-COAST ESTUARIES: 2014-2015

by

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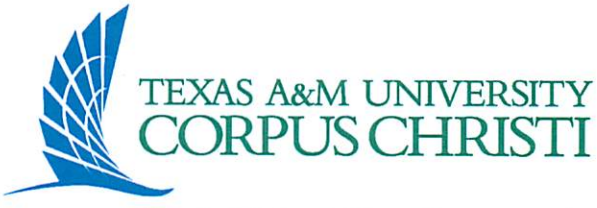

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INTRODUCTION

Many coastal watersheds in Texas are experiencing significant population and economic growth, resulting in increasing demands on freshwater resources that would otherwise flow downstream to coastal waterbodies. Although the general importance of freshwater inflow to estuarine ecological productivity, ecosystem function, and overall ecological health is recognized, there are still significant deficiencies in our understanding of mechanistic linkages, especially for estuaries of the Texas coast. Since 1986, a study supported by the Texas Water Development Board (TWDB) has documented seasonal, interannual and longer-term changes in benthic communities, sediments, nutrients, and chlorophyll in the Matagorda (Lavaca-Colorado Estuary), San Antonio (Guadalupe Estuary), Corpus Christi Bays (Nueces Estuary) and Rincon Bayou. In regards to water quality, several major aspects have been overlooked, specifically effects of freshwater inflow variability on dissolved and particulate organic matter (DOM and POM) and the carbonate system including alkalinity, dissolved inorganic carbon (DIC), and pH. Both allocthonous and autocthonous organic matterare known to be major contributors to the overall productivity of many estuaries. In the case of the carbonate system, a gradual loss of alkalinity (acidification) has been observed in many Texas coastal estuaries presumably due to a reduction of alkalinity export by rivers (Hu et al., 2015), which will have important implications for calcifying organisms in these systems.

Past studies have shown that Texas estuaries respond rapidly to carbon fluxes associated with freshwater inflows, indicating that dissolved and particulate organic matter are a key bio-reactive component of inflow (e.g., Russell & Montagna, 2007; Shank et al., 2009; Bruesewitz et al., 2013). As some fraction of the organic matter is likely to be algal-derived, it is important to discern effects of nutrient-driven algal production versus allochthonous organic matter to project how these systems may change in the future due to climate and or anthropogenic effects. Unfortunately, previous studies have not adequately coupled measures of dissolved organic carbon and nitrogen to inorganic nutrient measurements. In addition, the precipitation/evaporation gradient along the latitude creates a gradient of riverine alkalinity that shows a generally increasing trend from northeast to southwest (TCEQ, 2014; Hu et al., 2015). Another data gap is information on the estuarine carbonate chemistry, which determines the risks of coastal waters to acidification caused by both CO_2 invasion into seawater and estuarine alkalinity reduction caused by reduced freshwater inflow.

As the dominant buffer system in estuaries, the inorganic carbon or the carbonate system (dissolved carbon dioxide or CO_2, alkalinity, carbonate saturation state, pH, and CO_2 partial pressure, or pCO_2) is controlled by river-ocean water mixing and biogeochemical processes. The freshwater endmember river plays a dominant role in the low salinity region of estuaries because freshwater has drastically different composition than seawater (for example, much lower calcium ion (Ca^{2+}) concentration in river water than seawater and much higher pCO_2, Hu and Cai, 2013), which affects carbonate saturation state (Ω) greatly in low salinity waters. In addition, respiration and photosynthesis compete with each other in driving CO_2 release or uptake, which subsequently control pH, Ω, and pCO_2 variations. For example, respiration releases CO_2 and leads to decreases in both pH and Ω but increase in pCO_2, and photosynthesis drives these changes in opposite directions. Finally, the calcification process by calcareous organisms (typically shellfish species in estuaries) consumes alkalinity (HCO_3^- and CO_3^{2-}) and leads to decreases in both pH and Ω but increase in pCO_2. When Ω and pH are sufficiently low, carbonate preserved in estuarine sediment (and live shells) will dissolve and act as a buffer

against the acidifying condition. Shellfish species heavily rely on optimal Ω conditions to survive and reproduce (Waldbusser et al., 2014), thus maintaining these conditions will require well-managed environmental flow in the semi-arid south Texas.

Here we report results from an ongoing study of dissolved and particulate organic carbon/nitrogen, carbonate system parameters that include pCO_2 and Ω of the three estuaries. The goal of the study is to further broaden the view of how freshwater inflow drives water quality and estuarine production along the Texas coast. Results presented here are largely from a period of relatively low rainfall, although a period of heavy spring rainfall was captured in the latter part of the study. It is anticipated that additional sampling in the near future will correspond with a strong El Niño period that has been linked with higher than average rainfall, providing an opportunity to fully elucidate the effects of low versus high freshwater inflow. The study serves as a companion to Dr. Paul Montagna's monitoring of benthic organisms and inorganic nutrients in relation to freshwater inflow to Matagorda Bay (Lavaca-Colorado Estuary), San Antonio Bay (Guadalupe Estuary), and Corpus Christi Bay (Nueces Estuary) as well as Rincon Bayou for carbonate chemistry study only. Results will be used in support of the Senate Bill 3 adaptive management plan for these bay systems.

METHODS

Field sampling was performed in three estuaries in the Texas mid-coastal zone: Corpus Christi (Nueces), San Antonio (Guadalupe), Matagorda (Lavaca-Colorado) Bays, and Rincon Bayou (Fig. 1). The study area is ideal to answer questions related to altered hydrology and climate variability occurring at different temporal scales (e.g., seasonal, annual, multi-annual), and different spatial scales of inflow along climatic (among estuary) and estuarine (within estuary) gradients (Figure 1). For comparison purposes, the organic matter component of the study also includes data collected along the longitudinal axis of Baffin Bay as part of a monthly water quality sampling program. Specifically, data were used from stations CM 36, CM 14, and Central mouth in Baffin Bay (see Wetz 2015 for station details and map).

Stations were located in primary bays closer to the Gulf of Mexico endmember and in secondary bays closer to the freshwater inflow sources. Four stations were sampled for water chemistry in the Guadalupe Estuary, six in the Lavaca-Colorado Estuary, and five in the Nueces Estuary.

Water column samples were collected at all stations in all estuaries at both surface and depth. Sampling occurred eight times: January 2014, April 2014, July 2014, October 2014, January 2015, April 2015, July 2015, and October 2015. Results are also included from organic matter samples collected prior to the start of this study, going back to October 2012.

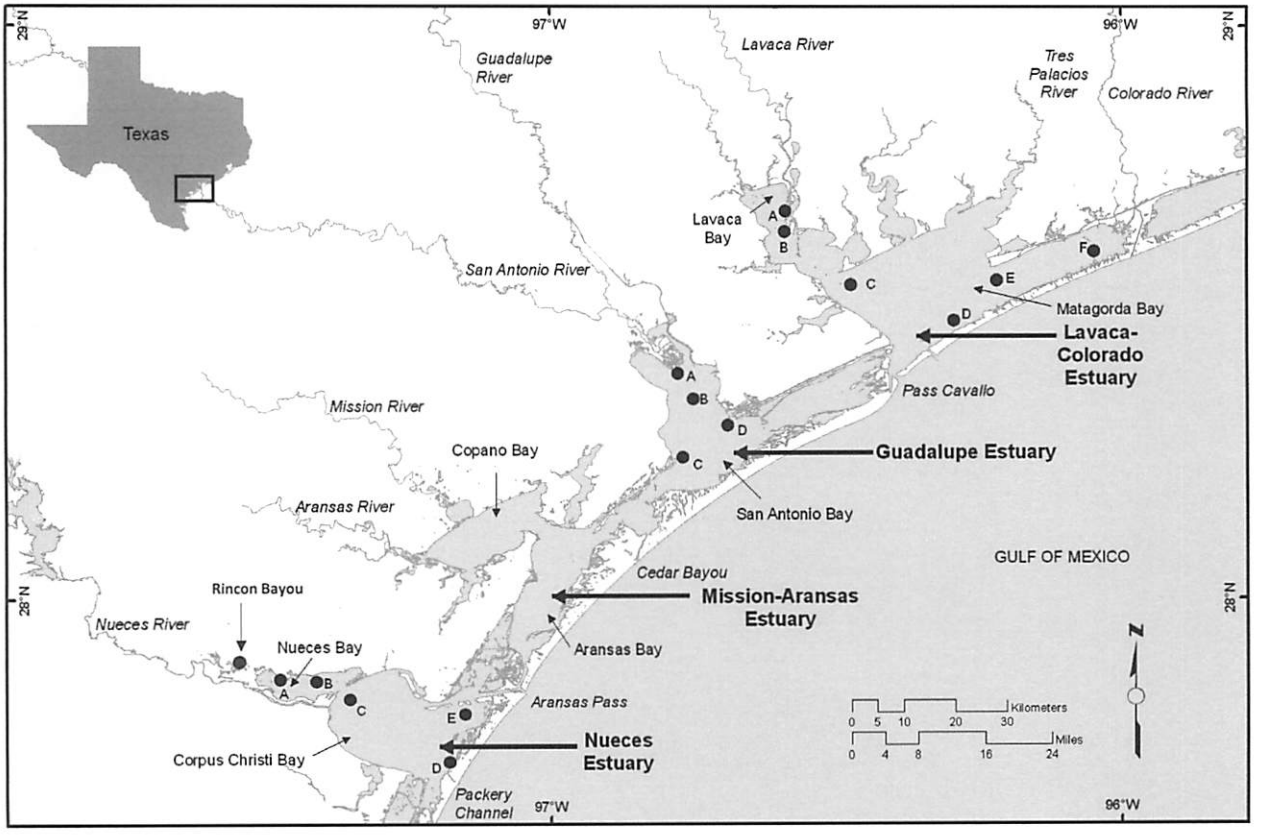

Figure 1. The three Texas mid-coast estuaries sampled. Station locations are along a climatic (among estuaries) and estuarine (within estuaries) gradients. Courtesy of Dr. Paul Montagna.

Hydrographic Measurements - Hydrographic measurements were made at each station with a YSI 6600 multi parameter instrument. The following parameters were read from the digital display unit (accuracy and units): temperature (±0.15°C), pH (±0.1 units), dissolved oxygen (±0.2 mg l^{-1}), depth (±1 m), and salinity. Salinity is automatically corrected to 25°C. In addition, water salinity was also measured at the Hu's lab using a benchtop salinometer to corroborate with field measurements. Based on our observation, slight differences between field and lab salinity may occur, presumably due to density stratification. Thus in our subsequent calculation, we always used lab measured salinity.

Dissolved Organic Carbon and Nitrogen Sample Collection and Analysis - Surface water samples were collected in acid-washed amber polycarbonate bottles. Bottles were stored on ice until return to a shore-based facility where processing of samples occurred. Inorganic nitrogen (nitrate + nitrite, ammonium) was determined from the filtrate of water that passed through GF/F filters using an OI Systems analyzer (see Montagna 2014). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined in the filtrate of water that passed through precombusted (400°C for 4 hours) GF/F filters using a Shimadzu TOC-V analyzer with nitrogen module. Potassium nitrate and potassium hydrogen phthalate were used as standards, and check samples of a known C/N concentration of both Glucosamine and Consensus Reference Water (http://www.rsmas.miami.edu/groups/biogeochem/CRM.html) were routinely injected to insure proper instrument functioning. Dissolved organic nitrogen (DON) was estimated as the difference between TDN and inorganic nitrogen. Total organic carbon (TOC) and Total nitrogen (TN) were estimated as above, except the prefiltration step was omitted.

Carbonate Chemistry Sample Collection and Analysis - Following the standard operating protocol in ocean CO_2 study (Dickson et al., 2007), we used pre-combusted 250 ml Pyrex® ground borosilicate bottles for sample collection. One bottle volume overflow was ensured to completely flush the sampling bottle. 100 µL saturated mercuric chloride ($HgCl_2$) was added into each sample before the bottle was stopped with Apiezon® grease and secured with a rubber band and a nylon clamp to ensure gas tightness.

Upon returning to the lab, sample DIC was analyzed based on acidification, CO_2 extraction, and infrared quantification on an Apollo DIC analyzer. Total alkalinity was analyzed by open cell Gran titration on an Apollo alkalinity titrator. Certified Reference Material purchased from Dr. Andrew Dickson's lab at Scripps Institution of Oceanography was used ensure the accuracy of both analyses. For each sample with added purified m-cresol purple (mCP) solution, absorbance at 434 and 578 nm (after correcting for baseline shift at 730 nm) in a custom-made 10 cm water-jacketed flow-through glass cell (Hellma Optics) was measured on an Agilent 8453 UV-Vis spectrophotometer under strict temperature control using the setup as described in Carter et al. (2013); pH was then calculated using the equation in Liu et al. (2011). Because of the applicable salinity limitation in Liu et al. (2011), pH of all samples with lower than salinity 20 were measured using an Orion® Ross combination glass electrode, which was calibrated using NBS pH buffers (4.01, 7.00, 10.01) at 25°C. Ca^{2+} concentration was analyzed using EGTA titration on a Metrohm automated titrator, and a Ca^{2+} ion-selective electrode was used to determine the titration endpoint (Anderson and Granéli, 1982). Derived carbonate system parameters (pCO_2, carbonate saturation state with respect to aragonite or $\Omega_{aragonite}$) were calculated using a computer program CO2SYS (Lewis and Wallace, 1998). Carbonic acid dissociation constants in Millero (2010) were used in the calculation. $\Omega_{aragonite}$ obtained from CO2SYS was corrected using measured Ca^{2+} concentration.

RESULTS AND DISCUSSION

Spatial-temporal distribution of organic matter

In contrast to long-term historic trends, salinities were similar between Lavaca-Colorado and Guadalupe estuaries due to drought conditions that were in place for the first two years of this study (Fall 2012-2014) (Figure 2). Salinities were higher in Nueces-Corpus Christi Bay, and notably hypersaline in Baffin Bay (Figure 2). No significant differences were observed between estuaries in terms of water temperature (data not shown).

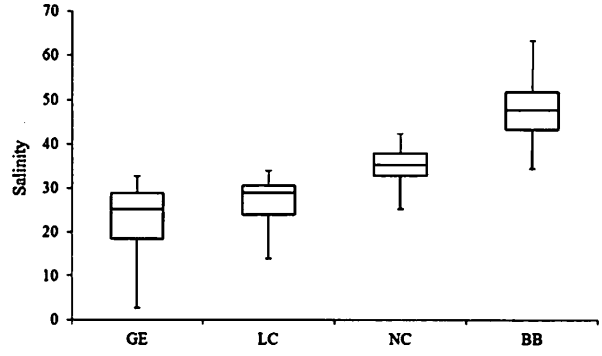

Fig 2. Average salinity in each estuary from October 2012-July 2015. GE = Guadalupe Estuary, LC = Lavaco-Colorado, NC = Nueces-Corpus Christi, BB = Baffin Bay. Note that this labeling scheme is relevant to Figs. 3-7 as well.

It was expected that organic matter concentrations would be higher in the northern, lower salinity estuaries due to historically higher riverine inputs as well as observed differences in this study, yet results showed that dissolved organic carbon and nitrogen concentrations were similar between Lavaca-Colorado, Guadalupe, and Nueces-Corpus Christi bays (Figures 3,4). There are several possible explanations for this deviation from the expected relationship. One possibility is that the riverine endmember DOC concentration was higher for Nueces-Corpus Christi Bay than the other two northern bays. Salinity-DOC relationships extrapolated to zero salinity do not bear this out, at least based on the existing data (data not shown). It is possible that additional collections during a high inflow, wet period may yield the necessary information to explore this further. Another possibility is the DOC in Lavaca-Colorado and Guadalupe Estuary is simply more labile than Nueces-Corpus Christi and is more rapidly removed from the system. One indicator of this would be the ratio of DOC to DON, which in our dataset shows no differences between sites (data not shown). Additional indicators of organic matter lability are currently being explored by collaborators at UTMSI. One final possibility is that internal DOC production rates are higher in Nueces-Corpus Christi Bay than the other sites. We did observe a reasonably strong relationship between DOC and chlorophyll in Nueces-Corpus Christi Bay in contrast to the other sites (see discussion below). This, along with the

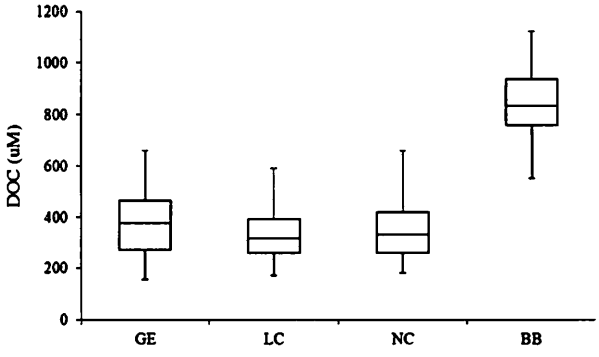

Fig 3. Average dissolved organic carbon concentration in each estuary from October 2012-July 2015.

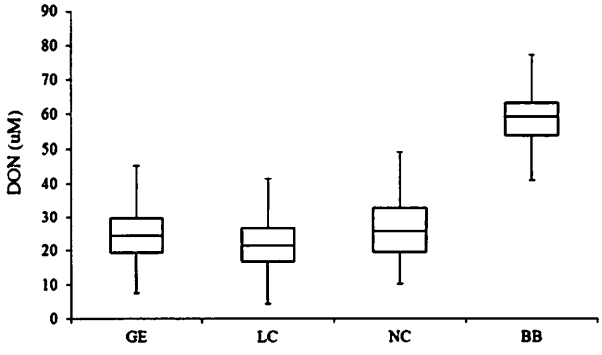

Fig 4. Average dissolved organic nitrogen concentration in each estuary from October 2012-July 2015.

possibility of seagrass contribution, may explain the higher than expected DOC levels in Nueces-Corpus Christi Bay and requires further study. Of the 4 sites included in this study, Baffin Bay stands in stark contrast to the others, with dissolved organic carbon and nitrogen concentrations that were ~3-fold higher in it (Figs. 3,4). This enrichment of organic matter in Baffin Bay is believed to be anthropogenic in nature and is the subject of ongoing studies by P.I. Wetz.

Dissolved organic carbon displayed a strong seasonal cycle in Guadalupe and Nueces-Corpus Christi bays (Figure 5), with DOC concentrations positively correlated with temperature (Table 1). An inverse relationship between DOC and salinity was observed in Lavaca-Colorado (Table 1) and Guadalupe Estuary (Table 1; Figure 5). The strong relationship with salinity, especially in Lavaca-Colorado and to a lesser degree in Guadalupe Estuary, argues that freshwater inflow exerts an important control on DOC in these systems. No relationship was observed for Nueces-Corpus Christi Bay or Baffin Bay in terms of DOC and salinity, suggesting that freshwater inflows may is either too ephemeral to have a noticeable effect given the timescale (quarterly) of our sampling, or simply that the freshwater inflows are not large enough to have an estuary-wide effect. In Nueces-Corpus Christi Bay, a positive relationship was observed between DOC and chlorophyll (Table 1), with chlorophyll also being highest in summer (Figure 5). Thus it is likely that phytoplankton produce the additional dissolved organic matter observed during the warmer months, with additional contribution possibly from decaying seagrass. In Baffin Bay, dissolved organic matter concentrations were high year round (data not shown).

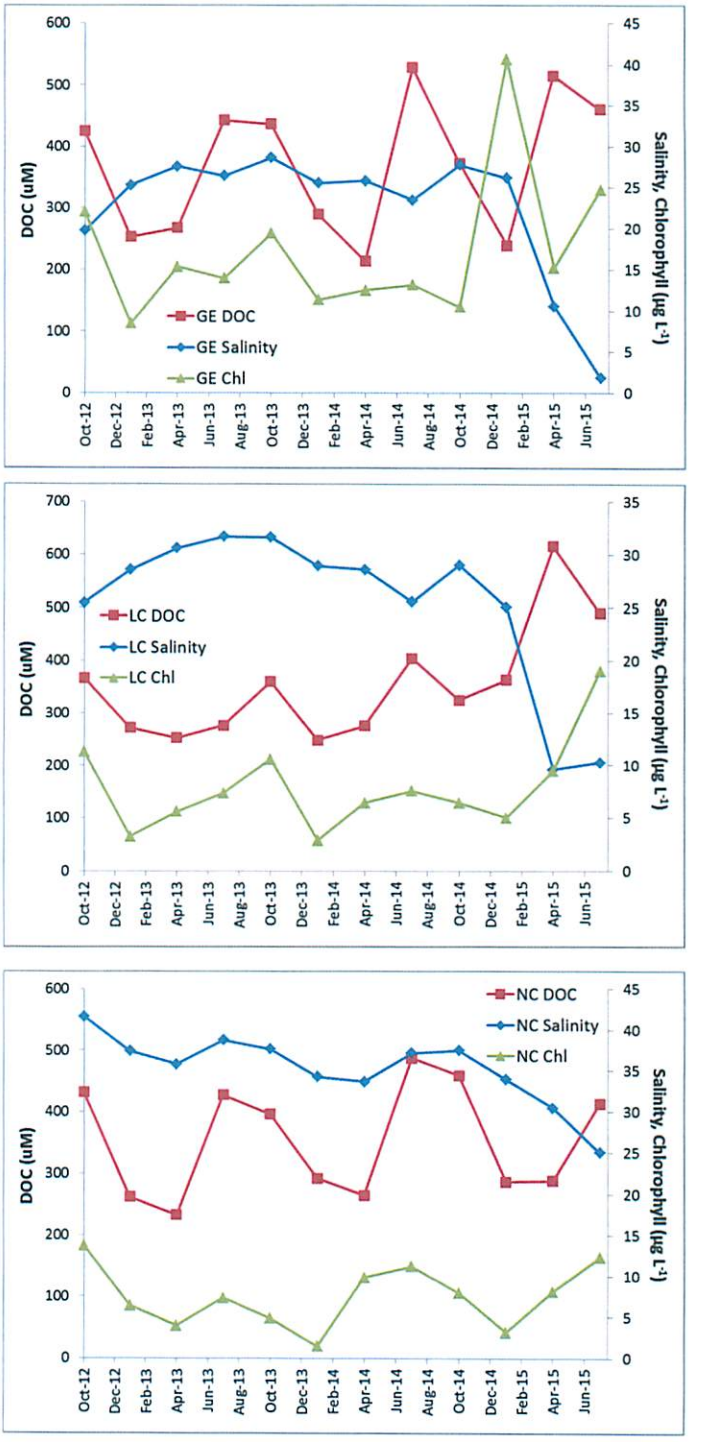

Fig 5. Temporal distribution of salinity, DOC and chlorophyll in Guadalupe (top), Lavaca-Colorado (middle) and Nueces-Corpus Christi (bottom) bays from October 2012-July 2015.

Table 1. Results from correlation analysis of DOC concentrations with relevant environmental parameters.

	Salinity	Temperature	Chlorophyll
Guadalupe DOC	$m = -7.2, r^2 = 0.25$	$m = 10.8, r^2 = 0.37$	$m = 1.6, r^2 = 0.03$
Lavaca-Colorado DOC	$m = -15.0, r^2 = 0.68$	$m = 5.6, r^2 = 0.07$	$m = 10.9, r^2 = 0.16$
Nueces-Corpus Christi DOC	$m = 3.7, r^2 = 0.02$	$m = 10.4, r^2 = 0.31$	$m = 13.3, r^2 = 0.34$
Baffin Bay DOC	$m = 2.2, r^2 = 0.02$	$m = 0.1, r^2 = 0.00$	$m = -0.1, r^2 = 0.00$

With the exception of phytoplankton bloom periods, the ratio of DOC to TOC averaged 62-83% (Figure 6), clearly indicating that dissolved organic carbon is an important driver of ecosystem metabolism (oxygen & CO_2 dynamics, productivity) in these estuaries of the Texas coast. Furthermore, it is important to note that roughly 95% of the dissolved nitrogen in these estuaries was in organic form as opposed to nitrate and ammonium (Figure 7), which (organic nitrogen) has been shown to favor brown tide phytoplankton over ecologically healthy phytoplankton. This prevalence of dissolved organic over inorganic nitrogen, coupled with the very high dissolved organic nitrogen concentrations in Baffin Bay, may explain the persistence of brown tide blooms in the system.

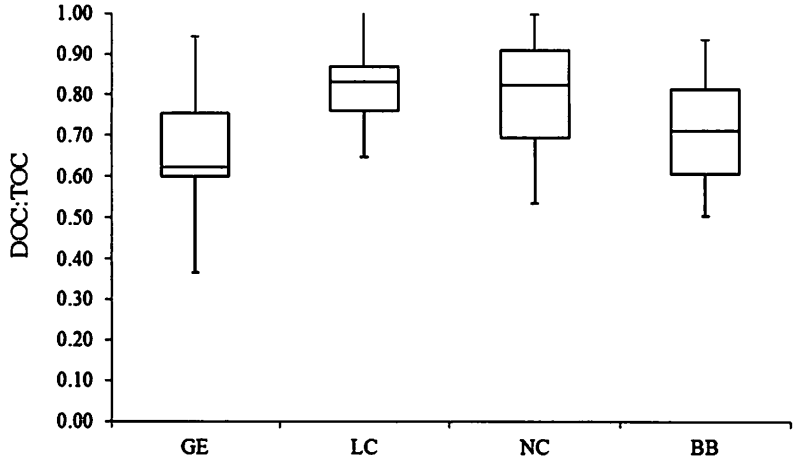

Fig 6. Average ratio of DOC to TOC in each estuary from October 2012-July 2015.

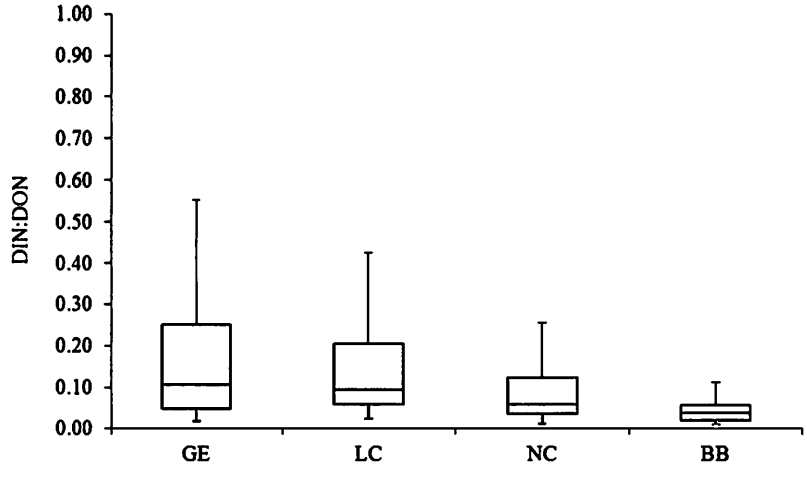

Fig 7. Average ratio of dissolved inorganic nitrogen (DIN; ammonium plus nitrate, nitrite) to DON in each estuary from October 2012-July 2015.

Carbonate chemistry spatial and temporal variations

In general, the surveyed water bodies showed large variability in terms of carbonate system dynamics both among these different systems and across time (Table 2, Figs. 8-9).

Table 2. Estuarine carbonate system characteristics during our surveyed period (01/2014-10/2015). DIC represents measured total dissolved inorganic carbon, TA is titrated total alkalinity.

	T (°C)	Salinity	DIC (μmol/kg)	TA (μmol/kg)	$\Omega_{aragonite}$	pCO_2 (μatm)
San Antonio	21.9±7.9	20.0±9.8	2540+347	2872±311	4.88±2.23	532±451
Matagorda	22.4±7.4	21.6±9.0	2155±397	2395±452	3.05±1.46	631±669
Corpus Christi	23.0±7.1	32.5±4.7	2266±149	2600±196	3.92±1.17	433±115
Rincon	25.1±6.4	10.0±8.6	3175±785	3595±703	8.71±4.01	632±510

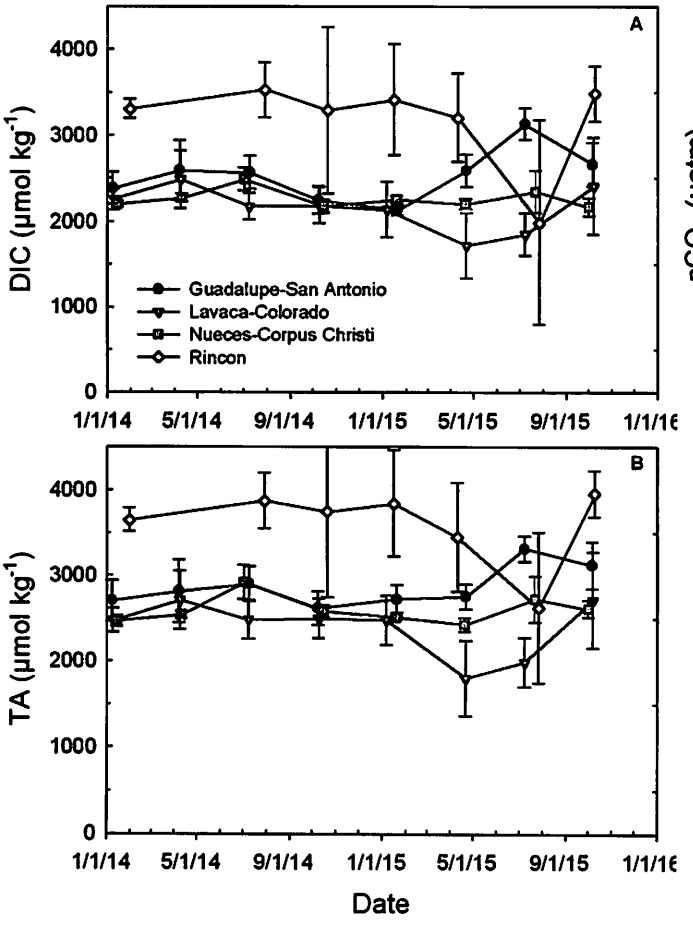

Figure 8. Changes of DIC (A) and TA (B) in the three estuaries and Rincon Bayou.

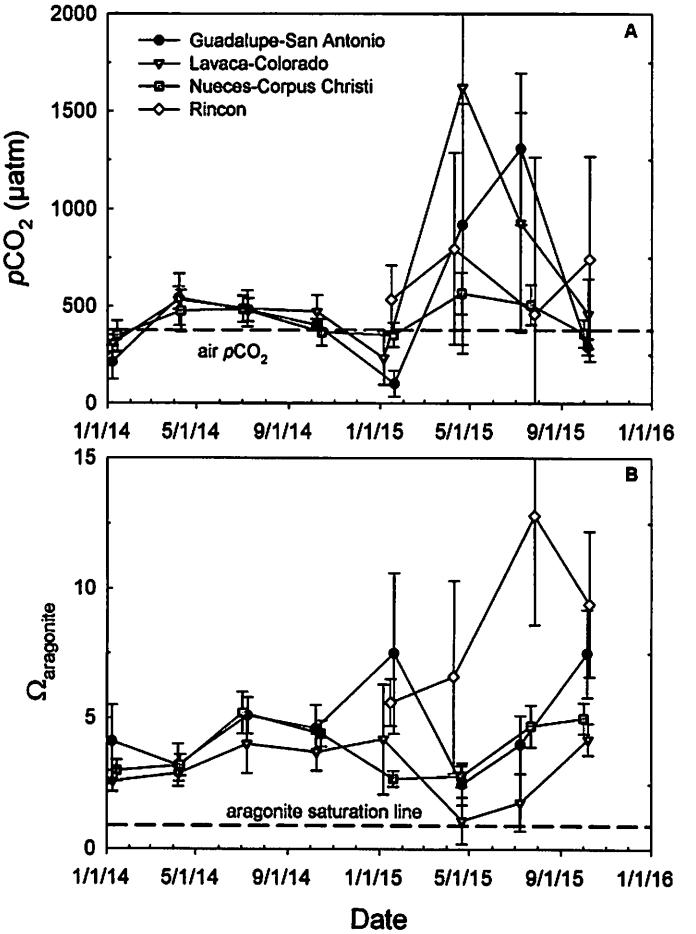

Figure 9. Temporal changes in pCO_2 and $\Omega_{aragonite}$ in the three estuaries and Rincon Bayou.

Salinity appeared to exert the dominant control on the distribution of alkalinity and Ca^{2+} (Fig. 10). However, the two parameters vs. salinity relationships showed distinct patterns. The alkalinity vs. salinity relationship (Fig. 10A) indicates varying freshwater endmember alkalinity from north to south, which represents the level of weathering product (mostly bicarbonate) in the freshwater drainage basin. River endmember alkalinity increased in the order of Lavaca-Colorado, Guadalupe, Nueces (Rincon Bayou receives freshwater inflow from Nueces River), which is consistent with the TCEQ data record (Hu et al. 2015). In addition, both Guadalupe and Nueces Rivers have significantly higher alkalinity levels than their respective receiving estuaries and the coastal Gulf of Mexico (2200-2400 μmol kg^{-1}). On the other hand, calcium concentration showed excellent linear relationship with salinity in all individual water bodies (Fig. 10B). Again, freshwater endmember showed an increasing [Ca^{2+}] in the same order as observed for alkalinity. Note the two panels have different units that differ by a factor of 1000 (μmol kg^{-1} for alkalinity vs. mmol kg^{-1} for Ca^{2+}).

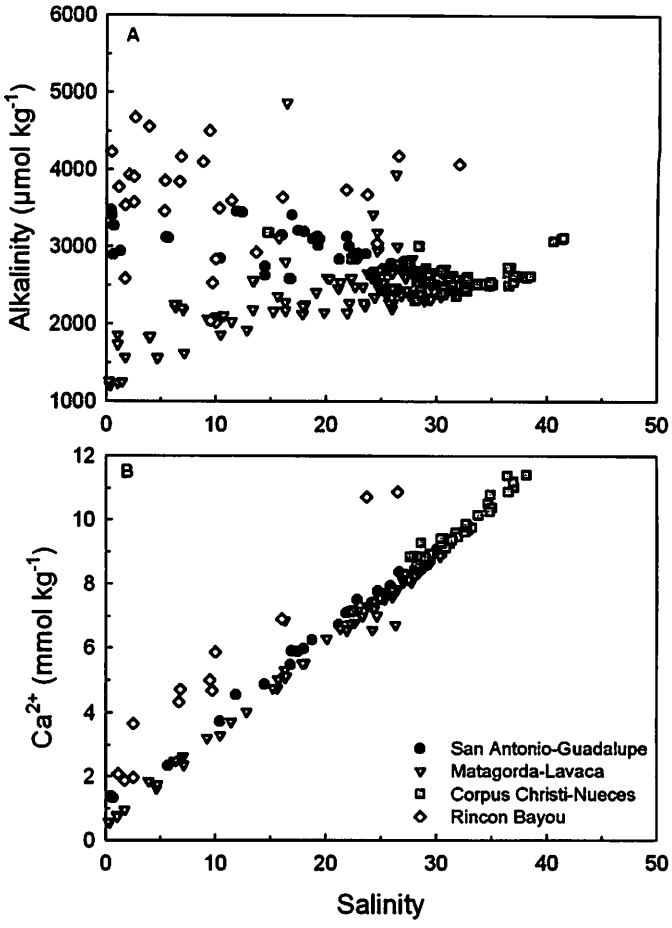

Figure 10. Alkalinity and calcium along the salinity gradient in the three estuaries and Rincon Bayou.

Both alkalinity and Ca^{2+} vs. salinity relationships mostly reflect a mixing scenario between river and estuarine waters. In contrast, pCO_2 and $\Omega_{aragonite}$ along the salinity gradient reflected a more complicated pattern that corresponded to river inflow, primary production, and respiration (Fig. 11). In general, low salinity waters (less than ~15, except that in Rincon Bayou) had much higher pCO_2 than the atmospheric value, consistent with observations in others rivers and river influenced estuaries (Butman and Raymond, 2011; Jiang et al., 2008). In mid salinity waters (15-30), however, pCO_2 was variable, ranging from significant CO_2 undersaturation to significant supersaturation in Matagorda (Lavaca-Colorado) and San Antonio (Guadalupe), respectively. In higher salinity waters (mostly in Corpus Christi (Nueces)), the air-water pCO_2 gradient was much smaller (Fig. 11A). In comparison, carbonate saturation state remained high except in low salinity (less than 11) waters of Matagorda (Lavaca), where the water became undersaturated with respect to aragonite. $\Omega_{aragontite}$ values in both San Antonio (Guadalupe) and Rincon Bayou were all higher than 1 (Fig. 11B). Extreme $\Omega_{aragonite}$ values (up to 18) were observed in Rincon Bayou at salinity of ~10.

In terms of temporal variations, both pCO_2 and $\Omega_{aragonite}$ appeared to have been significantly affected by both seasonal changes and freshwater inflow, as well as the salinity increase after the freshwater inflow (Fig. 9). The dry-wet cycle in 2014-2015 had a significant imprint on the carbonate chemistry in these estuaries. During the entire 2014, which was a dry year, estuarine pCO_2 started from slightly below the atmospheric value (~300 µatm) in winter, then increased to moderately higher than air pCO_2 in spring and summer (up to ~600 µatm) before it decreased to below air pCO_2 level again in winter (Fig. 9A). In 2015 however, pCO_2 exhibited much larger variation despite that it still followed a similar seasonal pattern as that in 2014.

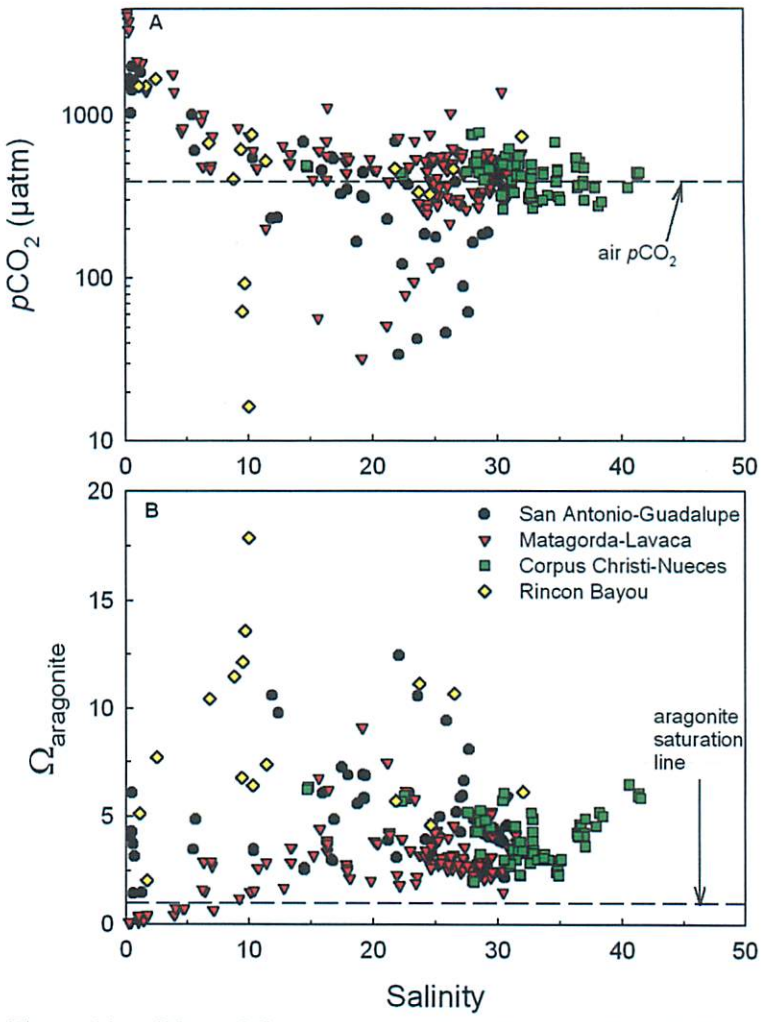

Figure 11. pCO_2 and $\Omega_{aragonite}$ along the salinity gradient in the three estuaries and Rincon Bayou.

The three estuaries had relatively stable $\Omega_{aragonite}$ during 2014 (Fig. 9B). Beginning in 2015, with significantly higher freshwater inflow, two estuaries (San Antonio and Matagorda) first experienced an increase in $\Omega_{aragonite}$, presumably caused by nutrient delivery from the rivers and enhanced estuarine productivity, which consumes CO_2 and lead to a decrease in pCO_2 and moderate increase in $\Omega_{aragonite}$ (01/2015). However, as freshwater continued to strongly affect these estuaries and temperature increased, the respiration signal dominated the carbonate equilibria, as reflected by depressed $\Omega_{aragonite}$ and elevated pCO_2 (starting from May, 2015, Fig. 10A,B). Furthermore, because of low levels of alkalinity in the freshwater endmember of Lavaca-Colorado estuary, the decrease in $\Omega_{aragonite}$ was such that the estuarine water briefly became undersaturated with respect to aragonite (Fig. 10B), implying that these waters could become stressful for shellfish, especially larvae and juveniles. From summer to fall, with a reduction in precipitation/river inflow, both $\Omega_{aragonite}$ and pCO_2 appeared to be returning to the "normal" semi-arid state, along with increasing salinity.

CONCLUSIONS

Results from the first two years of this study have provided novel, important information on organic matter concentrations, speciation (i.e., dissolved vs. particulate) and controls upon its estuarine distributions for several vital mid-coast Texas estuaries. Additional sample collections will be crucial to elucidate the longer-term effects of El Nino-driven rainfall and to test hypotheses outlined above in the previous section in regards to controls on organic carbon. An added advantage of additional collections is that they will correspond with a newly initiated study of ecosystem metabolism and hypoxia formation on the Texas coast (NOAA-funded study by Montagna, Wetz, Hu), providing the most comprehensive opportunity to date to link this bioreactive pool to estuarine biogeochemistry.

The carbonate chemistry parameters collected to date provided a strong first-order view of estuarine metabolism. For example, estuarine pCO_2 levels can be used to study aquatic ecosystem metabolism (Cai, 2011; Crosswell et al., 2012). During the drought conditions of 2014, the estuaries were a small CO_2 sink during cooler months and a small CO_2 source (to the atmosphere) in warmer months. In contrast, during the high rainfall period in early-mid 2015 the estuaries became a large source of CO_2 to the atmosphere (Fig. 9A). This increase in CO_2 source condition is presumably due to significant terrestrial organic matter inputs and subsequent respiration. The dissolved organic matter inputs to estuaries that drive ecosystem metabolism can be strongly affected by climate patterns, as well as water resource and land use changes in coastal watersheds, thus this database provided critical baseline information for these important biogeochemical constituents.

River endmember alkalinity has been shown to affect the buffering capacity of estuarine water itself (Hu and Cai, 2013; Salisbury et al., 2008). Based on our observation, lower alkalinity rivers (such as Lavaca and Colorado) are undersaturated with respect to aragonite while lower latitude rivers (Guadalupe and Nueces) are not. Therefore, river inflow increase due to precipitation increase may have different impacts on these three estuaries and Rincon Bayou (Figs. 10B and 11B). For example, in Lavaca Bay, a decrease in salinity could potentially lead to corrosive conditions for shell-forming organisms in wet seasons, while there will likely be no such condition in Guadalupe and Nueces Bays, the latter derived from Rincon Bayou data. Therefore, as with organic matter distributions, additional sampling of carbonate parameters will be crucial to capture the longer-term effects of El Nino-driven rainfall on estuarine carbonate chemistry in this freshwater-deficient area, and also to allow us to make projections on the potential effects of long-term changes in freshwater inflows to the area.

REFERENCES

American Society for Test Methods. ASTM D5176 - 08 Standard test method for total chemically bound nitrogen in water by pyrolysis and chemiluminescence detection. (Online Reference)

Anderson, L. and Granéli, A., 1982. A compact automated titration system, applied to a high precision determination of calcium in sea-water. Journal of Automatic Chemistry, 4, 75-78.

Bruesewitz, D.A., Gardner, W.S., Mooney, R.F., Pollard, L., and Buskey, E.J. 2013. Estuarine ecosystem function response to flood and drought in a shallow, semiarid estuary: nitrogen cycling and ecosystem metabolism. Limnology and Oceanography 58: 2293-2309

Butman, D. and Raymond, P.A., 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geoscience, 4, 839-842.

Cai, W.-J., 2011. Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration? Annual Review of Marine Science, 3, 123-145.

Carter, B.R., Radich, J.A., Doyle, H.L. and Dickson, A.G., 2013. An automatic system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11, 16-27.

Crosswell, J.R., Wetz, M.S., Hales, B. and Paerl, H.W., 2012. Air-water CO2 fluxes in the microtidal Neuse River Estuary, North Carolina. Journal of Geophysical Research, 117, C08017.

Dickson, A.G., Sabine, C.L. and Christian, J.R., 2007. Guide to Best Practices for Ocean CO_2 Measurements. PICES Special Publication 3.

Hu, X., Beseres Pollack, J., McCutcheon, M.R., Montagna, P.A. and Ouyang, Z., 2015. Long-term alkalinity decrease and acidification of estuaries in Northwestern Gulf of Mexico. Environmental Science & Technology, 49, 3401–3409.

Hu, X. and Cai, W.-J., 2013. Estuarine acidification and minimum buffer zone—A conceptual study. Geophysical Research Letters, 40, 5176-5181.

Jiang, L.-Q., Cai, W.-J. and Wang, Y., 2008. A comparative study of carbon dioxide degassing in river- and marine-dominated estuaries. Limnology and Oceanography, 53, 2603-2615.

Lewis, E. and Wallace, D., 1998. Program Developed for CO_2 System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.

Liu, X., Patsavas, M.C. and Byrne, R.H., 2011. Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements. Environmental Science & Technology, 45, 4862-4868.

Millero, F.J., 2010. Carbonate constants for estuarine waters. Marine and Freshwater Research, 61, 139-142.

Montagna, P.A. 2014. Macrobenthos Monitoring In Mid-Coastal Estuaries - 2014. Final Report to the Texas Water Development Board, Contract # 1448311638. Harte Research Institute, Texas A&M University-Corpus Christi, Corpus Christi, Texas, 39 p.

Russell, M.J., and Montagna, P.A. 2007. Spatial and temporal variability and drivers of net ecosystem metabolism in western Gulf of Mexico estuaries. Estuaries and Coasts 30: 137-153

Salisbury, J., Green, M., Hunt, C. and Campbell, J., 2008. Coastal acidification by rivers: a threat to shellfish? EOS, Transactions, American Geophysical Union, 89, 513-514.

Shank, G.C., Nelson, K., and Montagna, P.A., 2009. Importance of CDOM distribution and photoreactivity in a shallow Texas estuary. Estuaries and Coasts 32: 661-677

TCEQ. (2014, updated daily). Surface Water Quality Monitoring Information System, 09/01/1968-07/16/2014 TAMUCCdr2.xlsx. Compiled by Data Management & Analysis Team. Austin, TX USA. Data Request ID 269.

Waldbusser, G.G., Hales, B., Langdon, C.J., Haley, B.A., Schrader, P., Brunner, E.L., Gray, M.W., Miller, C.A. and Gimenez, I., 2014. Saturation-state sensitivity of marine bivalve larvae to ocean acidification. Nature Climate Change, 5, 273-280.

Wetz, M.S. 2015. Baffin Bay volunteer water quality monitoring study: synthesis of May 2013-July 2015 data. Publication 100 of the Coastal Bend Bays & Estuaries Program (Proj. 1513); available from: http://www.cbbep.org/manager/wp-content/uploads/1513_final_report_August2015.pdf