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Final Report

I. Title Page

Project Title: The Hydrological Switch: A Novel Mechanism Explains Eutrophication and Acidification of Estuaries

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The Hydrological Switch: A Novel Mechanism Explains Eutrophication and Acidification of Estuaries

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II. Executive Summary

Humans have a significant influence on estuaries through land use change, freshwater diversions, climate change, and increased use of fertilizers. These drivers cause harmful algal blooms, hypoxia, and acidification. The hypothesis for the current study is that hydrological control acts as a switch, where increased flows cause episodic hypoxia and short-term acidification) due to increased loads of organic matter, and reduced flows cause long-term acidification due to reduced loads of riverine alkalinity and benthic calcification. We have named this the "hydrological switch hypothesis"

The research outputs supported by this project generated 21 peer-reviewed publications and 53 presentations at meetings. The project has had an enormous impact on student development, training 3 postdocs, 16 graduate students, and 3 undergraduate students. Interaction with other NOAA programs such as the Educational Partnership Program and the Gulf of Mexico Coastal Ocean Observing System helped to advance the NOAA mission overall.

Overall, field sampling covered wide spatial and temporal ranges. Sampling occurred in the five coastal estuaries from the wetter north (Colorado-Lavaca Estuary) to the drier south (Baffin Bay) covering a linear distance of over 200 km. A total of 105 trips were executed to perform discrete grab sampling between October 2015 and July 2019 covering a period of 3.8 years. Sampling from October 2017 through July 2019 was made possible through additional funds to define the response after Hurricane Harvey, which occurred 25 August 2017. Continuous data collection was executed over 278 days.

Research results show that hydrological change is the over-arching driver of estuary change because: estuaries are transition zones where sea water is diluted by fresh water, climate change is manifested in precipitation change and thus change in creek and river flow regimes, and these flow regimes drive chemical and particulate loading from watersheds to the coasts. Thus, rivers act as a switch where increased flows cause episodic hypoxia (hence short-term acidification or dealkalization) due to increased loads of organic matter, and reduced flows cause long-term acidification due to reduced loads of riverine alkalinity.

Water column alkalinity levels were controlled by both the river end member composition and the freshwater inflow balance. In estuaries where evaporation and high salinities are dominant, , alkalinity always remains higher than in seawater. There is a long-term (multidecadal) decrease in pH in western Gulf of Mexico estuaries concomitant with increasing salinity levels.

Dissolved inorganic nitrogen (DIN) concentrations were low when inflow rates were low and salinity was high., again demonstrating that river hydrology is controlling estuary dynamics. In low-flow systems, such as the Nueces Estuary, salinity was highest at the river-mouth locations relative to the oceanic-side stations, indicating that the system was a ‘‘reverse estuary’’ where evaporation exceeds freshwater inflow, resulting in net inflow of marine water into the estuary.

The most surprising finding was the dominant role dissolved organic carbon and nitrogen (DOC and DON) were playing, particularly in the evaporation dominated estuaries. Dissolved organic matter (DOM) molecules from riverine and coastal waters are more compact than standard biomolecules with the same molecular weights, and about 10% of the molecules identified have isomers. DOC in the water column accounts for about 67 - 73% of overall dissolved oxygen consumption in these bays and is highest during flood periods. Existing ecological models were modified to incorporate this new role of DON in biogeochemical cycling and productivity.

Hypoxia occurs in the southeastern region of Corpus Christi Bay every summer. This has a negative impact on natural living resources such as benthos, which can not escape the low oxygen waters because they are relatively immobile. However, the are multiple stressors because salinity and temperature are also highest in summer when hypoxia is most common. Because of the high water temperatures, and despite hypoxia induced acidification, water chemistry does not reach aragonite undersaturation and hypercapnia (CO_2 partial pressure > 1000 µatm).

Hurricane Harvey made landfall in Texas, USA on 25 August 2017 as a category 4 storm and we extended our NOAA-funded studies to capture the signature of this extreme event. Wind-driven disturbances were most severe along the coastal barrier islands and lower estuaries, damaging mangroves and seagrass and increasing sediment coarseness. Rain-driven disturbances were most pronounced within freshwater streams and the upper estuaries. Sharp, but short-lived water quality changes were noted in the estuaries such as zero salinities and oxygen concentrations. DOM shifted from a protein-like and lipid-like dominated community before the storm to a lignin, tannin and condensed aromatic structure dominated during the high flow event. The water quality changes led to a near collapse of benthic fauna. While the water column returned to baseline levels after 10 days, the benthic fauna did not recover for 9 months but the community structure took nearly two years to recover.

The outputs of this research have resulted in significant outcomes that will engender environmental benefits. Texas has a legislatively mandated process to ensure that environmental flows to the coast are sufficient to maintain a “sound ecological environment that maintains the productivity, extent, and persistence of key aquatic habitats in bays and estuaries.” Environmental flow standards were set State-wide between 2011 and 2013, and through an adaptive management process must be reviewed every 10 years. Public outreach activities included publications in newspapers and magazines, meetings with stakeholder groups, and recommendations to management teams. The project team is involved in many management level activities and will remain engaged in these for many years to come.

III. Purpose

A. Overarching Goals

Humans are having a significant influence on estuaries through land use change, hydrological change, climate change, and increased use of fertilizers. These drivers are causing a proliferation of harmful algal blooms, hypoxia, and acidification. The goal of the current project is to examine the relationships among multiple stressors (i.e., estuarine acidification, reduced freshwater inflow, hypoxia, and nutrient loading) and hydrological change. Hydrological change is the over-arching driver of estuary change because: estuaries are transition zones where sea water is diluted by fresh water, climate change is manifested in precipitation change and thus change in creek and river flow regimes, and these flow regimes drive chemical and particulate loading from watersheds to the coasts. The final goal is for the products of the research to be translated into outcomes in environmental management of coastal living resources.

B. Hypotheses

The hypothesis for the current study is that hydrological control acts as a switch, where increased flows cause episodic hypoxia (hence short-term acidification or dealkalization) due to increased loads of organic matter (Fig. 1A), and reduced flows cause long-term acidification due to reduced loads of riverine alkalinity and benthic calcification (Fig. 1B). We have named this the "hydrological switch hypothesis" (Fig.1).

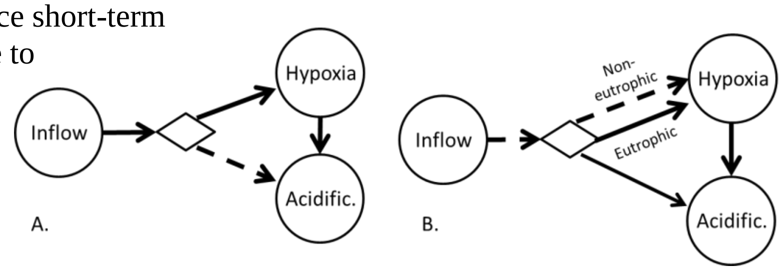

Figure 1. Freshwater inflow switch hypothesis. (A) High flow condition, (B) Low flow condition.

IV. Approach

The hypothesis was tested through a series of field studies to measure water quality response over space and time. The spatial aspect takes the form of an estuary comparison experiment. Four estuaries were studied: Baffin Bay (BB), Nueces Estuary (NC), Guadalupe Estuary (GE), and Lavaca-Colorado Estuary (LC) (Fig. 2). Although the estuaries share common geomorphological characteristics with one another, they are different in historical hydrology and long-term average salinity. Within NC, GE and LC, there is a positive salinity gradient from secondary bays to primary bays. In contrast, BB is typically a negative estuary where evaporation rates are greater than freshwater runoff into the system, and during drought, salinity may increase from the mouth to upper estuary. Thus, the hydrological switch hypothesis is tested by comparing estuaries with different long-term hydrology characteristics.

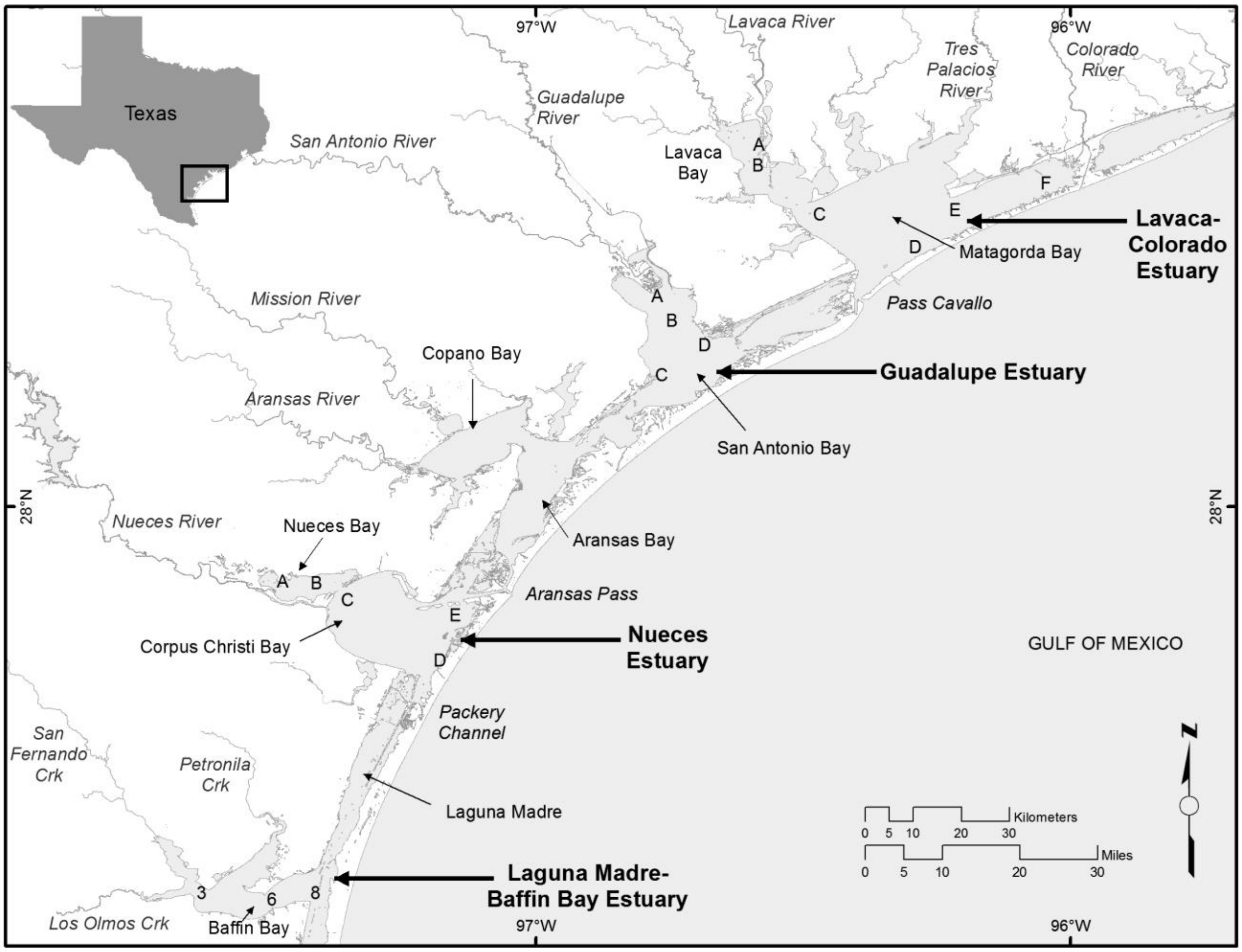

Figure 2. Study area with 18 stations and 8 bays within four estuaries along the Texas coast.

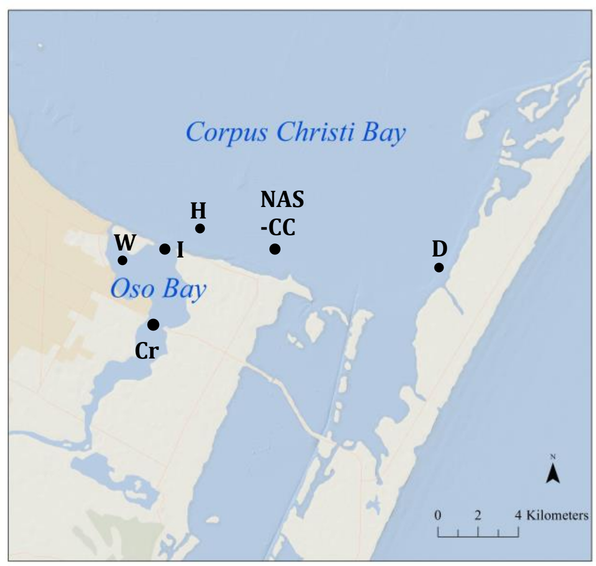

Figure 3. Location for Corpus Christi Bay hypoxia/acidification study.

In wastewater-influenced systems such as the Oso Bay-Corpus Christi Bay complex, reduced flows out of the watershed may also lead to long-term acidification and chronic hypoxia due to influence by low pH, high nutrient/organic matter wastewater. High frequency spatial and temporal sampling to unravel the relationships between eutrophication, hypoxia and acidification was performed in Corpus Christi Bay at the mouth of Oso Bay (Fig. 3). Six sites were established for deployment of continuously measuring water quality sensors and/or collection of discrete samples; two in Oso Bay (in the wastewater influenced zone, “W”; and at the intersection of Oso Creek and Oso Bay, “Cr”) to quantify conditions at end-member locations, one at Oso Inlet (“I”), one in the core of the Corpus Christi hypoxic zone ("H"), one to the east of the hypoxia zone and closer to the exchange point with Laguna Madre ("NAS-CC), and one overlapping with another zone of consistent summer hypoxia ("D") that is also part of a long-term quarterly sampling program. Also, TAMUCC is located on the island where the letter "W" occurs.

The temporal aspect of the study is important because precipitation, and thus hydrology, changes over time allowing us to test for differences between dry and wet periods. In fact, our last sampling period was planned for July 2017, but Hurricane Harvey hit the study area in August 25, 2017 (Fig. 4). We were able to secure funding from the National Science Foundation to incorporate this extreme event data into our analyses. So, our sampling continued through 2018 and we were also able to incorporate storm effects and recovery.

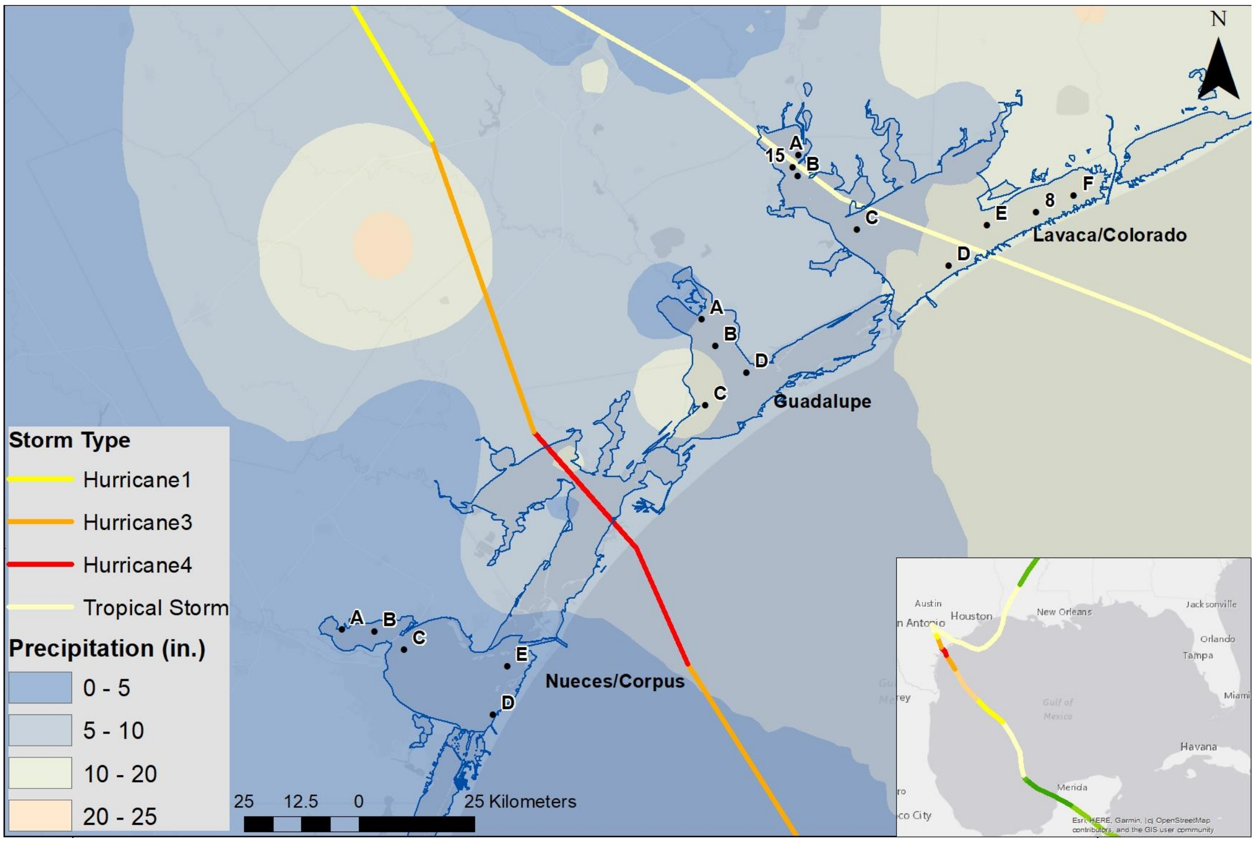

Figure 4. Long-term sampling stations overlaid with the track of Hurricane Harvey and precipitation amounts (August 2017).

Both continuous and discrete and measurements were made. Continuous measurements were made by deploying multi-parameter water quality sondes at two sites in Baffin Bay (sites 3 and 6 on Figure 2; 2/15-11/17 with some breaks due to weather and instrument failure) and one site in San Antonio Bay (site A on Figure 2; 5/17-12/17). Discrete measurements occurred on specific sampling trips where we measured inorganic nutrients (ammonia, nitrate, nitrite, phosphate, and silicate), chlorophyll, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), total organic carbon (TOC), total nitrogen (TN), alkalinity, dissolved inorganic carbon (DIC), calcium concentration, particulate organic matter (POM), dissolved organic matter (DOM), dissolved free amino acids (DFAA), dissolved combined amino acids (DCAA), bulk organic compounds, dissolved oxygen (DO), salinity, and pH. Bioavailability of dissolved organic nitrogen (DON) were also evaluated using microcosm incubations. Benthic abundance, biomass, and community structure was measured as an indicator of sediment quality and biological response of a living marine resource.

Results of all the field measurements were integrated into an ecological model.

A. Work Performed

Discrete grab sample collection: We successfully completed 16 quarterly field sampling expeditions (October 2015, January 2016, April 2016, July 2016, October 2016, January 2017, April 2017, July 2017, October 2017, January 2018, April 2018, July 2018, October 2018, January 2019, April 2019, and July 2019) to Lavaca/Matagorda, Guadalupe/San Antonio, and Nueces/Corpus Christi estuaries. Baffin Bay was sampled monthly from September 2015 to August 2019. In addition, 69 trips to the Mission-Aransas Estuary were also conducted using the boat-of-opportunity from the Mission-Aransas Estuarine Research Reserve, and 20 trips to Lavaca, San Antonio, Mission, Aransas and Nueces Rivers to sample the zero salinity waters for nutrient and organic matter analyses.

Continuous data collection by sondes: We successfully completed sonde deployments in in Corpus Christi Bay from June - August, 2016, and San Antonio Bay from 31 May 2017 through 5 December 2017. The sondes measure dissolved oxygen, salinity, temperature, depth, and pH.

The University of South Florida set up SEAS instruments for paired measurement of pH and DIC. The measurement design was intended to characterize CO_2 system diurnal cycles over a two-week period with bihourly sampling at the benthic boundary and below the surface in order to characterize observed fluxes of CO_2. In the summer of 2016, we conducted the first instrumental deployment. However, due to mechanical failure of an O-ring, the DIC instrument flooded, which also eliminated power to the timing device that controlled both the pH and the DIC instruments. During the second deployment we deployed pH SEAS and also the Sunburst pH sensor. The data produced by these deployments are currently under evaluation. We found that the water in Corpus Christi Bay had a heavy sediment load, so that the performance of optical systems, like SEAS-pH, may be somewhat diminished by light scattering and even blockage of the optical channel. Remedies for this problem are being developed. It should be noted, in contrast, that the SEAS-DIC instrument is not directly affected by high sediment loads because the optical path is a synthetic solution that is equilibrated with acidified seawater.

B. Project Management

Organizations and individuals performing work and roles.

1. **Texas A&M University – Corpus Christi, Corpus Christi, Texas. Lead Institution.**
   - 1.1. Paul Montagna, Ph.D., Principal Investigator. Project management, field logistics, benthic indicators, ecological modeling, statistical analyses, reporting, management.
     - 1.1.1. Leslie Adams, M.S., Research Assistant. Nutrient analyses, data management.
     - 1.1.2. Rick Kalke, M.S., Research Assistant. Field work, benthic sample analysis.
     - 1.1.3. Larry Hyde, M.S., Research Assistant. Field work, benthic sample analysis.

- 1.1.4. Elani Morgan, M.S., Research Assistant. Field work, data management.
- 1.1.5. Terry Palmer M.S., Research Assistant. GIS, graphical analyses, reports.
- 1.1.6. Evan Turner, Ph.D., Postdoctoral Associate. Ecological modeling.
- 1.1.7. Melissa Rohal, Ph.D., Postdoctoral Associate. Ecological modeling.
- 1.1.8. Bhanu Paudel, M.S., Graduate Research Assistant. Nutrient dynamics.
- 1.1.9. Cameron Page, B.S., Graduate Research Assistant. Hypoxia studies.
- 1.1.10. Jaime Smith, B.S., Graduate Research Assistant.

1.2. Xinping Hu, Ph.D., Co-Principal Investigator.

- 1.2.1. Cory Staryck, M.S., Research Assistant. Field work, sample analysis, data management.
- 1.2.2. Hongming Yao, M.S., Graduate Research Assistant. Field work, sample analysis.
- 1.2.3. Hongjie Wang, M.S., Graduate Research Assistant. Field work, sample analysis.
- 1.2.4. Melissa McCutcheon, M.S., Graduate Research Assistant. Field work, sample analysis.

1.3. Michael Wetz, Ph.D., Co-Principal Investigator.

- 1.3.1. Ken Hayes, M.S., Research Assistant. Nutrient, DOC, DON, analyses.
- 1.3.2. Lily Walker, B.S., Graduate Research Assistant. Field work, sample analysis, dissertation research on dissolved oxygen dynamics.
- 1.3.3. Tiffany Chin, B.S., Graduate Research Assistant. Field work, sample analysis.
- 1.3.4. Emily Cira, M.S., Graduate Research Assistant. Field work, sample analysis.
- 1.3.5. Kelsey Fisher, M.S., Graduate Research Assistant. Field work, sample analysis.
- 1.3.6. Jennifer Hemphill, M.S., Graduate Research Assistant. Field work, sample analysis.
- 1.3.7. Elizabeth Obst, B.S., Undergraduate Assistant. Field work, sample analysis.
- 1.3.8. Jessica Tolan, B.S., Undergraduate Assistant. Field work, sample analysis.
- 1.3.9. Sarah Tominack, M.S. Graduate Research Assistant. Field work, sample analysis.

2. University of South Florida, College of Marine Science, St. Petersburg, Florida

2.1. Robert Byrne, Ph.D., Co-Principal Investigator. In situ carbonate measurement.

- 2.1.1. Sherwood Liu, Ph.D., Research Associate. Development of in situ carbonate measurement systems.
- 2.1.2. Michelle Platz, Ph.D. student. Deployment of in situ carbonate measurement systems.
- 2.1.3. Chris Moore, M.S. student. Performs pH surveys.

3. University of Texas at Austin, Marine Science Institute, Port Aransas, Texas

3.1. Zhanfei Liu, Ph.D., Co-Principal Investigator. Measurement of POM, DOM, DFA, DCAA, bulk organic compounds.

- 3.1.1. Jianhong Xue, Ph.D., Research Associate. Sample analysis.
- 3.1.2. Kaijun Lu, PhD student and now Postdoctoral Research Associate. Field work, sample analysis.
- 3.1.3. John O’Connor, M.S., Graduate Research Assistant. Field work, sample analysis.
- 3.1.4. Kai Wu, Ph.D. student, Visiting Student. Field work, sample analysis.
- 3.1.5. Jason Jenkins, M.S., Graduate Research Assistant. Field work.
- 3.1.6. Xianbiao Lin, Ph.D. student, Visiting Student. Field work, sample analysis.
- 3.1.7. Lucas Martinez, B.S., NSF REU student. Field work, sample analysis.

4. NOAA, National Centers for Environmental Prediction Environmental Modeling Center, College Park, Maryland

4.1. Hae-Cheol Kim, Ph.D., Co-Principal Investigator. Development of ecological models.

V. Findings

A. Actual Accomplishments and Findings

Accomplishments are summarized by topic below. References to work supported here are underlined and listed in Section VI.A.ii. Other references that are not supported by this project text are listed in Section V.D.

i. Acidification

Carbonate chemistry variation was measured in the five coastal estuaries from the wetter north (Colorado-Lavaca Estuary) to the drier south (Baffin Bay). Water column alkalinity levels were found to be controlled by both the river end member composition and the freshwater inflow balance. For example, Guadalupe River and Lavaca River had distinctly different levels of alkalinity with the former having much elevated values than the later, hence alkalinity level always stayed higher than the seawater in Guadalupe Estuary. In comparison, Lavaca Bay and Matagorda Bay (of Colorado-Lavaca Estuary) had varying degrees of TA changes that correspond to the freshwater inflow balance conditions. The upper (secondary) bay (Lavaca) had lower alkalinity but the lower (primary) bay (Matagorda) had similar alkalinity as the seawater (Montagna et al. 2018). In Mission-Aransas Estuary, alkalinity was higher than the seawater value under low freshwater inflow conditions and lower during high inflow conditions (Yao and Hu 2017), similar to that in Lavaca Bay. For the two evaporation-dominated estuaries (Nueces Estuary and Baffin Bay), alkalinity always remained higher than the seawater although due to different mechanisms, i.e., Nueces River had higher alkalinity levels, but Baffin Bay did not have significant riverine discharge hence was evaporation controlled (Montagna et al. 2018).

Lower river inflow would lead to increasing estuarine water residence time. In estuaries without significant hypersalinity stress, alkalinity decrease actually occurred along with increasing salinity during two periods of low river inflow in Mission-Aransas Estuary (Hu et al. submitted). Calcification by calcareous organisms and exchange with coastal water that has lower alkalinity were thought to contribute to the decreasing alkalinity level during the low river inflow period. On the other hand, increasing river inflow in Guadalupe River, especially during the latter half of the project period, helped to increase alkalinity levels in Guadalupe Estuary (Yao et al. in revision). These observations are consistent with our hypothesis that river inflow reduction would cause alkalinity decline in these semiarid estuaries. Findings from an analysis of coastwide water quality trends also are consistent with this hypothesis, as those results show a long-term (multidecadal) decrease in pH in Nueces, Guadalupe and Lavaca-Colorado estuaries concomitant with increasing salinity levels (Bugica et al. in review).

Carbonate saturation state with respect to aragonite (Ω_{arag}) mostly remained higher than 1, the critical level for the dissolution of this mineral. However, the only times when Ω_{arag} was lower than 1 occurred in Lavaca Bay and Copano Bay (the secondary bay in Mission-Aransas Estuary).

These low Ω_{arag} values were driven by river inflow that had low alkalinity levels as well as low calcium ion concentration (Montagna et al. 2018; Yao and Hu 2017).

The relationship between hypoxia and acidification was examined in a highly evaporative environment in southeast Corpus Christi Bay. The findings are noted in the **Hypoxia** section below.

ii. Dissolved Inorganic Matter/Nutrients

The hypothesis that ‘‘freshwater inflow variability over space and time can drive suspended solids and nutrient concentrations’’ was tested by comparing three micro-tidal estuaries (Guadalupe, Lavaca- Colorado, and Nueces) in Texas with different hydrologic flow regimes over three years with wet and dry conditions (Paudel et al. 2019a, Paudel et al. 2019b). In all three estuaries, Total suspended solids (TSS) was less than 50 mg/L most of the time. In the Nueces Estuary, TSS of higher than 100 mg/L occurred during frontal events. Dissolved inorganic nitrogen (ammonia+nitrite+nitrate) concentrations were most of the time lowest in the Nueces Estuary (i.e. $\leq$0.5 μmol/L), with low inflow rates and high average salinity of 37.6. Salinity was highest in the river-estuary mouth (average salinity 38.3) of the Nueces Estuary relative to the other oceanic-side stations (average salinity 37), indicating that the system was a ‘‘reverse estuary’’ where evaporation exceeds freshwater inflow, resulting in net inflow of marine water into the estuary. The inverse correlation between ammonium and salinity in all three estuaries and the corresponding negative correlation between nitrite+nitrate concentrations and salinity in the Guadalupe Estuary indicate that the quantity of inflow controls nitrogen concentrations and transformations in the three estuaries. Drought conditions limited riverine transport of nitrogen and sediment to the three estuaries, demonstrating the importance of freshwater inflow to maintaining these constituents. Average silica and orthophosphate concentrations correlated positively with chlorophyll-a in combined data from all three estuaries. Silica and orthophosphate concentrations remained constant over the study period but correlated with chlorophyll-a when suspended solid was low. Therefore, inflow dynamics drive changes in the salinity regime, suspended solids, and act to maintain nutrient concentrations.

Estimates were made to determine dissolved inorganic nitrogen (DIN = ammonium (NH4) and nitrite+nitrate (NO_2+ NO_3) release from aerobic sediment slurry at two different hydrologic flow regimes (Paudel et al. 2017). The watershed of the Guadalupe River–Estuary system receives more freshwater inflow than does the watershed of the Nueces River–Estuary system; thus, the Nueces Estuary is more saline than is the Guadalupe Estuary. Sediment samples were collected using cores, analyzed for organic matter and grain size, and used to perform laboratory experiments to measure DIN release. During the experiments, DIN concentrations in overlying water were measured for 48 h in five different salinity treatments. Ammonium concentrations were higher in the Nueces River and Estuary treatments than in similarly treated samples from the Guadalupe River and Estuary. An increase in NO_2+NO_3 concentrations along salinity gradients of the Nueces Estuary treatments indicated favorable condition for nitrification. The Guadalupe River sediments that were not exposed to salinity had an increase in NH_4 concentration at 7.5 psu. The different DIN release among salinity treatments indicated that hydrologic forcing on organic matter deposition and salinity have an important role on the retention and release of inorganic nitrogen at the sediment–water aerobic layers in rivers and estuaries.

iii. Dissolved Organic Matter/Nutrients

Dissolved organic matter (DOM) and DON was characterized using advanced mass spectrometry, and we found that natural DOM molecules from riverine and coastal waters are more compact than standard biomolecules with same molecular weights; about 10% of the molecules identified have isomers (Lu et al. 2018). This result moves our understanding of DON formation and lability to a new level.

Organic carbon sources on interannual timescales were examined in both Baffin Bay and Oso Bay (Wang et al. 2018). Results indicate that the water column accounts for ~67 - 73% of overall dissolved oxygen consumption in these bays. The organic carbon responsible for dissolved oxygen consumption in Baffin Bay water column is influenced by hydrological conditions, ranging from recycled organic carbon, terrestrial organic carbon, and algal carbon, corresponding to drought, flooding and flooding relaxation period, respectively. Meanwhile, algal carbon is the dominant organic carbon source that drives benthic respiration in Baffin Bay and water column respiration in Oso Bay, whereas sedimentary respiration in Oso Bay is mainly controlled by organic carbon produced from benthic macrophytes. The comparison of these two systems indicates that Baffin Bay hypoxia is more controlled by agricultural influence while Oso Bay hypoxia is mainly from a wastewater treatment plant.

iv. Hypoxia

In the southeastern region of Corpus Christi Bay that experiences frequent summer hypoxia, we observed positive correlation between dissolved oxygen concentration and bottom water pH, similar to those in other coastal hypoxic system (McCutcheon et al. 2019). However, due to warm water temperature and the presence of the seagrasses in the vicinity of the studied area (Laguna Madre), inflowing waters from the latter had relatively higher buffering capacity. Therefore, despite hypoxia induced acidification, water chemistry does not reach aragonite undersaturation and hypercapnia (CO_2 partial pressure > 1000 μatm).

However, at any moment in nature, organisms are exposed to multiple stressors, the effects of which are difficult to separate (Smith and Montagna in revision). In southeastern Corpus Christi Bay, TX, declines in benthic macrofaunal community abundance, biomass, diversity, species richness, and species evenness have largely been attributed to the occurrence of hypoxia. We also aimed to determine if other, confounding stressors contribute to benthic macrofaunal declines. A 30-year time series of water quality data (salinity, temperature, DO, pH, phosphate, ammonium, nitrite+nitrate, silicate) and benthic community data (abundance, biomass, species richness, species evenness) was analyzed to examine 1) water quality dynamics of the region, and 2) relationships between water quality dynamics and benthic macrofaunal response. Principal component analysis of the water quality dataset finds there are three principal components representing a multiple stressor index, a nutrient index, and an acidification index. Seasonality was confounded with the multiple stressor index, but not the nutrient or acidification indexes. Spearman rank-order correlations indicated both the multiple stressor and acidification indexes were inversely related to benthic macrofaunal community abundance, biomass, and species richness. A stepwise multiple linear regression analysis on individual water quality variables identified DO, and possibly temperature, to be leading explanatory variables for predicting benthic abundance. Temperature, pH, and nitrite+nitrate were leading explanatory variables for predicting benthic biomass. Temperature was the only leading explanatory variable for predicting species richness. These results demonstrate that multiple stressors, including high temperature, high salinity, and low DO concentrations, are collectively acting on benthic communities in southeastern Corpus Christi Bay. Therefore, future studies of hypoxia effects should consider the effects of confounding variables.

v. Hurricane Harvey

Hurricanes represent a major disturbance for coastal systems. Hurricane Harvey made landfall in Texas, USA on 25 August 2017 as a category 4 storm and we extended our NOAA-funded studies to capture this extreme event (Patrick et al. in revision). There were two distinct disturbances associated with this storm that were spatially decoupled: 1) high wind and storm surge, and 2) scouring floods and significant discharge of fresh water carrying carbon and nutrients to estuaries. We combined with other Harvey researchers to provide a comprehensive synthesis of the impacts of Hurricane Harvey on biogeochemical, hydrographic, and biotic components of freshwater and estuarine systems and their comparative resistance and resilience.

Wind-driven disturbances were most severe along the coastal barrier islands and lower estuaries, damaging mangroves and seagrass and increasing sediment coarseness. Erosion along the coastal wetlands occurred but was lower where mangroves were present compared to marsh plants. Rain-driven disturbances were most pronounced within freshwater streams and the upper estuaries. Sharp, but short-lived water quality changes were noted in the estuaries. For example, in Guadalupe Estuary, average surface salinity was ~ 10 at station A during the week prior to Harvey, and 17 ± 7 at four sites along the estuary axis. Bottom water DO at site A ranged from 3.6 to 8.3 mg L^{-1} over the course of the diel cycle, while the bay wide average was 6.5 ± 0.7. As Harvey neared landfall, storm surge from the Gulf of Mexico tripled the salinity, but it quickly dropped as rainfall and runoff from the storm intensified. By 5 d post-storm, salinity dropped to zero at site A and took 37 d to return to pre-storm conditions. During and immediately following the storm, the diel DO cycle was briefly disrupted by high winds and mixing of the water column. Approximately 5 d after the storm, bottom water hypoxia-/anoxia developed at site A and DO remained low for one week, concurrent with high river inflow and low salinity conditions. It took approximately 10 d for bottom DO to return to the pre-storm average. Overall, there were no obvious effects Harvey on water quality in Guadalupe Estuary beyond Fall 2017.

Large volumes of freshwater run-off and subsequent decreases in salinity and DO affected benthic fauna in the estuary, but there was negligible impact on fishes. While hydrographic and biogeochemical components returned to baseline conditions quickly, biotic components demonstrated lower magnitude changes, but appear to require longer time-scales to return to pre-storm conditions. Thus, the more resistant components of systems are not necessarily the most resilient, and biotic components sensitive to physical impacts may be among the most vulnerable to hurricanes.

To further evaluate the impacts of high flow events on riverine DOM, multidimensional molecular level information of DOM from four south Texas Rivers (Aransas, Lavaca, Mission, and Nueces Rivers) was acquired using high-resolution Ion Mobility Quadrupole Time of Flight Liquid Chromatography Mass Spectrometry (IM Q-TOF LCMS) (Lu et al in review). Base-flow samples were collected in May, July and October of 2016, June of 2017, and March of 2018, while high-flow samples were collected in September of 2017 (after Harvey), and June and September of 2018. DOM shifted from a protein-like and lipid-like dominated community at base flow condition, to a lignin, tannin and condensed aromatic structure dominated one during high flow event based on MS and tandem MS data. These changes in high-flow riverine DOM indicate an increase of terrestrial signal, which likely is a result of mobilization of terrestrial organic matter from the watersheds by flooding. These results provide insights into structural changes of riverine DOM in response to extreme climate events in subtropical regions and have implications in understanding biogeochemical changes in estuaries under a changing climate.

vi. Ecological Modeling

A major finding of this research was the importance of dissolved organic nitrogen (DON) in controlling the biogeochemistry of estuaries that suffer from very low freshwater inflow rates (Montagna et al. 2018). This implies that our past biogeochemical modeling (Arismendez et al. 2009, Turner et al. 2014), which modeled only dissolved inorganic nitrogen (DIN), such as nitrite + nitrate (NO2+3), is insufficient because DON was not included in those models. High levels of DIN occur in areas of low salinity and DIN levels decrease with increasing salinity. High levels of DON occur in areas of high salinity and hypersalinity, then DON decreases with decreasing salinity. This implies that a Nitrogen form is being built, not consumed, in high salinity estuaries. Chlorophyll-a (Chl) has the same pattern of both DIN and DON on both ends of the salinity spectrum (Montagna et al. 2018). The relationship between nutrients and chlorophyll is often modeled using nutrient-phytoplankton-zooplankton (NPZ) formulations. In estuaries, filter and suspension feeding benthos (particularly bivalves) are important consumers of phytoplankton, so a benthic component was added to the model and renamed the nitrogen-phytoplankton-consumer (NPC) model (Turner et al. 2014). However, even though DON is now thought to be important in controlling primary productivity in Texas estuaries, it is not included in NPC models. A new NPC model was created with a DON component and flows (Fig. 5).

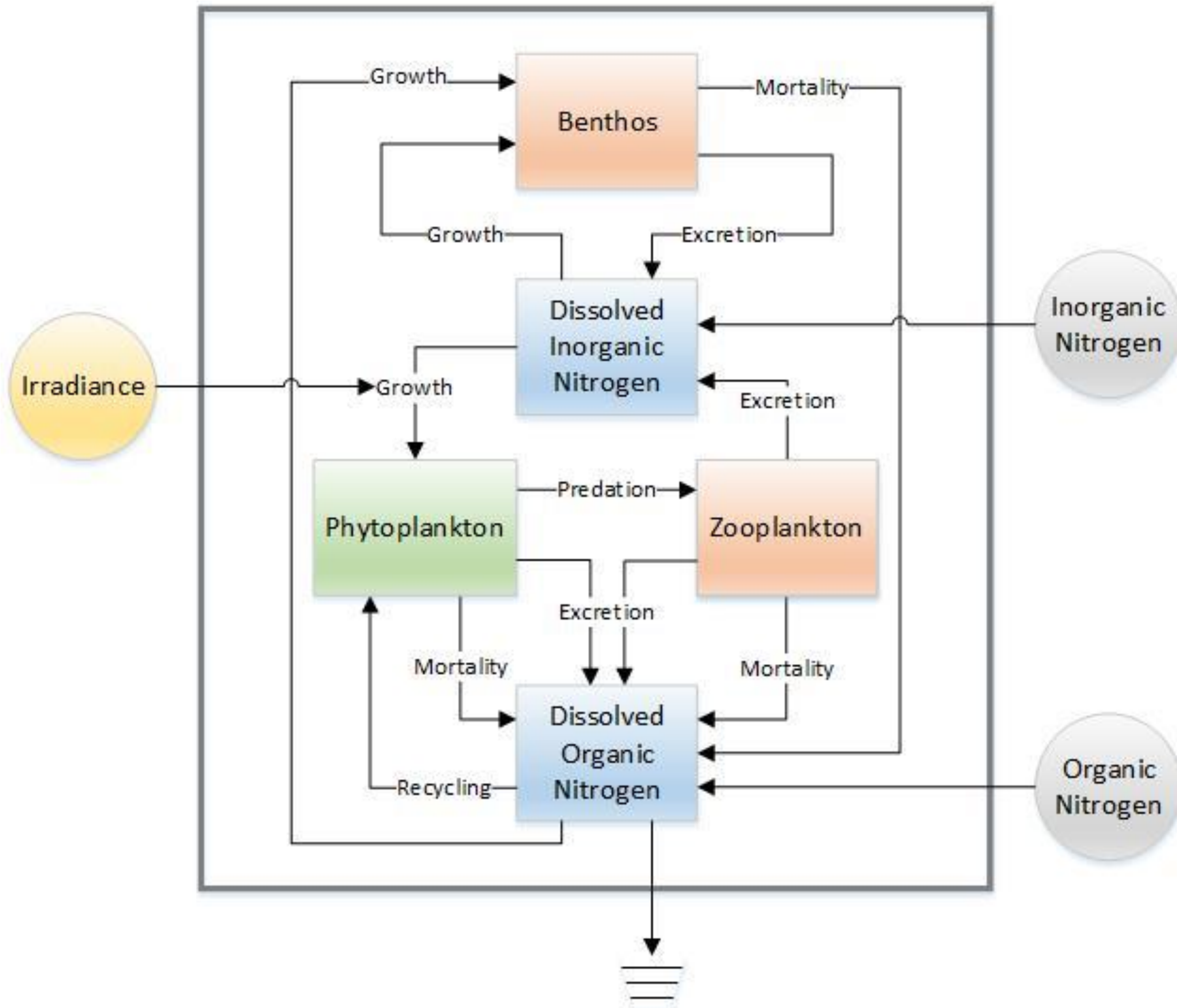

Figure 5. Nitrogen-Phytoplankton-Consumer (NPC) model structure.

For the NPC model to run, the system requires inputs of DON and DIN (Figure 1). These concentrations have been calculated using the USGS EGRET model, which is based on a Weighted Regressions on Time Discharge and Season (WRTDS) model (Hirsch and DeCicco 2015). The WRTDS model requires discharge values and nutrient concentrations to run which were downloaded from the USGS and TCEQ websites. The nitrogen inputs have been calculated and integrated into the NPC model. We are currently calibrating the model using data from our long-term field studies that includes benthic, chlorophyll, zooplankton, and in bay nitrogen concentrations. All datasets have been converted to mg N/L. For calibration 2/3 of the data is being used leaving 1/3 for validation.

B. Significant Problems

Hurricane Harvey made landfall on 25 August 2017 about 30 miles northeast of Corpus Christi, Texas as a Category 4 hurricane with winds up to 130 mph. This is the strongest hurricane to hit the middle Texas coast since Carla in 1961. While Texas A&M University-Corpus Christi suffered little damage in Corpus Christi, but our neighbors at the University of Texas Marine Science Institute (UTMSI) in Port Aransas were devastated, and Co-PI Zhanfei Liu lost his lab. Dr. Liu, and many of his colleagues, were working out of laboratories at the Harte Research Institute. We lost a water quality sonde that was moored on the UTMSI dock during the storm, but overall we are mostly intact at TAMUCC. Co-PI Hu obtained a grant from the Gulf Research Program at the National Academy to replace the equipment. PI Montagna, and Co-PIs Hu and Wetz obtained a Rapid Response Research (RAPID) grant from the National Science Foundation to study storm impacts. Co-PI Liu also obtained a RAPID grant to study the impacts on Mission Aransas Estuary. The storm was both a setback and an opportunity. While our research progress was hampered, there were opportunities to extend the sampling and capture an extreme event. A no-cost extension to 31 August 2019 was granted.

The storm also provided a unique scientific opportunity. As the title of our project implies, we are studying how river flow affects acidification and hypoxia in coastal environments. Harvey produced one of the largest floods ever to hit the Texas coast, and it is estimated that the flood will be a 1:1000 year event.

C. Need for Additional Work

Long-term increases in salinity, a consequence of reductions in freshwater inflow caused by diversion for human use, pose a unique challenge to coastal ecosystems in this region because they drive decreases in the buffering capacity of estuaries as well as in nutrient loads that would otherwise fuel their productivity. The quantity of freshwater input to coastal estuaries will continue to be a chronic problem for the northwestern Gulf of Mexico coastal zone due to growing human water demands. The problem will be exacerbated by the potential changes in the alternating flood and drought conditions under a changing global climate, i.e., the duration of drought could get longer and flood may become more intense, and the latter may be influenced by the increasing frequency of tropical storms (Emanuel, 2005; Emanuel, 2013; Webster et al., 2005). Therefore, what the future holds for the estuaries in our study region remains to be seen. To continue our research effort, sustained studies that integrate routine sampling like we have been doing and high frequency monitoring are still needed. In addition, hydrodynamic studies that include in situ measurement of estuary-ocean exchange, numerical modeling of both physical circulation and biogeochemical reactions are also needed to better understand the estuarine biogeochemistry in the changing global environment.

Another important discovery was the importance of DOM, DON, and DOC in responding to river flow and evaporation, and how those biogeochemical dynamics is driving biological and water quality responses. However, the focus remains on dissolved inorganic nutrients and carbon, and dissolved organic nutrients and carbon are usually ignored in surveys and monitoring studies. We now believe that organic alkalinity is also important in controlling overall alkalinity and pH, yet we have yet to perform sufficient sampling to prove this hypothesis.

D. References Cited in Section V.

Arismendez, S.S, H.-C. Kim, J. Brenner and P.A. Montagna. 2009. Application of watershed analyses and ecosystem modeling to investigate land–water nutrient coupling processes in the Guadalupe Estuary, Texas. *Ecological Informatics* 4: 243-253.

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Turner, E.L., D.A. Bruesewitz, R.F. Mooney, P.A. Montagna, J.W. McClelland, A. Sadovski, E.J. Buskey. 2014. Comparing performance of five nutrient phytoplankton zooplankton (NPZ) models in coastal lagoons. *Ecological Modelling* 277: 13–26.

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VI. Applications

A. Outputs:

i. New Fundamental or Applied Knowledge

We now know that dissolved organic nitrogen and dissolved organic carbon play much more important roles in coastal eutrophication than previously thought. We demonstrated the link between concentrations of these compounds and hydrology.

ii. Scientific Publications

Underline indicates student author, bold indicates **Co-PI**.

Hu, X., 2019. Ocean acidification studies in the Gulf of Mexico: Current status and future research needs. In: L. McKinney, M. Besonen and K. Withers (Editors), *Proceedings: The Gulf of Mexico Workshop on International Research*. U.S. Department of the Interior Bureau of Ocean Energy Management, New Orleans, LA, pp. 97-110.

Hu, X., Yao, H., Staryk, C.J., McCutcheon, M.R., Walker, L. and Wetz, M.S. 2020. Disparate responses of two adjacent subtropical estuaries to the influence of Hurricane Harvey – A case study. *Frontiers in Marine Science* (submitted)

Li X., **Liu Z.**, Chen W., Wang L., He B., Wu K., Gu S., Jiang P., Huang, B., Dai M., 2018. Production and transformation of dissolved and particulate organic matter as indicated by amino acids in the Pearl River Estuary, China. *Journal of Geophysical Research: Biogeosciences* 123:3523-3537. doi: 10.1029/2018JG004690.

Lu K. **Liu Z.** 2019. Molecular level analysis reveals changes in the chemical composition of dissolved organic matter from south Texas rivers after high flow events. *Frontier in Marine Science* (in review)

Lu K., Gardner, W.S., **Liu Z**. 2018. Molecular structure characterization of riverine and coastal dissolved organic matter with ion mobility quadrupole time-of-flight LCMS (IM Q-TOF LCMS). *Environmental Science & Technology* 52: 7182-7191. doi: 10.1021/acs.est.8b00999

McCutcheon, M.R., Staryk, C.J. and **Hu, X.**, 2019. Characteristics of the Carbonate System in a Semiarid Estuary that Experiences Summertime Hypoxia. *Estuaries and Coasts* 42: 1509-1523. doi: 10.1007/s12237-019-00588-0

Montagna, P. 2018. Nature's Vital Signs: Using Bioindicators to Understand Ecosystem Health. *Scientia*, 5 pages, https://doi.org/10.26320/SCIENTIA243

Montagna, P.A. 2018. Customizing ODS graphics to publish visualizations. *South Central SAS Users Group Proceedings*. http://www.scsug.org/wp-content/uploads/2019/01/Montagna-Customizing-ODS-Graphics-to-Publish-Visualizations.pdf

Montagna, P.A., **X. Hu**, T.A. Palmer, and **M. Wetz**. 2018. Effect of hydrological variability on the biogeochemistry of estuaries across a regional climatic gradient. *Limnology and Oceanography* 63:2465-2478. doi: 10.10MPMP02/lno.10953.

O'Connor J. A., Guo L., Liu Z. 2019. Characterization of riverine dissolved organic matter using thermal slicing pyrolysis gas chromatography mass spectrometry: Implications for anthropogenic influence and organic matter lability. *Organic Geochemistry* (ready for submission)

Patrick, C.J., Yeager, L., Armitage, A.R., Carvallo, F., Congdon, V., Dunton, K.H., Fisher, M., Hardison, A., Hogan, J., Hosen, J., **Hu, X.**, Kiel Reese, B., Kinard, S., Kominoski, J.S., Lin, X., **Liu, Z.**, **Montagna, P.A.**, Pennings, S. C., Walker, L., Weaver, C.A., **Wetz, M.** 2020. A systems level analysis of ecosystem responses to hurricane impacts on a coastal region. *Estuaries and Coasts* (in revision)

Paudel, B., P.A. Montagna and L. Adams. 2019b. Water quality data from estuarine variable hydrologic flow regimes during frequent drought. *Data in Brief* 25:104178, 18 pp. doi: 10.1016/j.dib.2019.104178

Paudel, B., **P.A. Montagna**, L. Adams. 2019a. The relationship between suspended solids and nutrients with variable hydrologic flow regimes. *Regional Studies in Marine Science* 29:9 pp. doi: 10.1016/j.rsma.2019.100657

Paudel, B., **P.A. Montagna**, M. Besonen and L. Adams. 2017. Inorganic nitrogen release from sediment slurry of riverine and estuarine ecosystems located at different river regimes. *Marine and Freshwater Research* 68(7) 1282-1291. doi: /10.1071/MF16260

Reyna N.E., Hardison A., **Liu Z.** 2017. Influence of major storm events on the quantity and composition of particulate organic matter and the phytoplankton community in a subtropical estuary, Texas. *Frontiers in Marine Science* doi: 10.3389/fmars.2017.00043

Smith, J.K. and P.A. Montagna. 2019. Distinguishing between hypoxia and other confounding stressor effects on macrobenthic communities. *Journal of Experimental Marine Biology and Ecology* (in revision).

Wang, H., **Hu, X.**, **Wetz, M.S.** and Hayes, K.C., 2018. Oxygen consumption and organic matter remineralization in two subtropical, eutrophic coastal embayments. *Environmental Science & Technology* 52: 13004-13014. doi: 10.1021/acs.est.8b02971

Wetz, M.S., E.K. Cira, B. Sterba-Boatwright, P.A. Montagna, T.A. Palmer, and K.C. Hayes. 2017. Exceptionally high organic nitrogen concentrations in a semi-arid South Texas estuary susceptible to brown tide blooms. *Estuarine Coastal and Shelf Science* 188: 27-37. doi: 10.1016/j.ecss.2017.02.001

Wu K., Lu K., Dai M., **Liu Z.** 2019. Seasonal variations of bioavailable dissolved organic matter of south Texas rivers in coastal waters. *Estuarine, Coastal and Shelf Science* (in review)

Yao, H. and **Hu, X.** Responses of carbonate system CO_2 flux to extended flooding in a semiarid subtropical estuary. *Limnology and Oceanography* 62: S112-S130. doi: 10.1002/lno.10646

Yao, H., McCutcheon, M.R., Staryk, C.J. and **Hu, X.**. Hydrologic controls on CO_2 chemistry and flux in subtropical lagoonal estuaries of the northwestern Gulf of Mexico. *Limnology & Oceanography* (in revision)

iii. Patents

No patents resulted from this study.

iv. New Methods and Technology

We developed methods for characterizing dissolved organic matter using advanced mass spectrometry (Lu et al., 2018), and thermal slicing pyrolysis coupled with gas chromatography mass spectrometry (O'Connor et al., in prep.)

The new ecological model (Fig. 5) is both an extension of existing models, but also a new formulation of biogeochemical dynamics.

v. New or Advance Tools

Montagna, P.A. 2018. Customizing ODS graphics to publish visualizations. South Central SAS Users Group (SCSUG) Proceedings, Austin, TX, 4-7 November 2018. http://www.scsug.org/wp-content/uploads/2019/01/Montagna-Customizing-ODS-Graphics-to-Publish-Visualizations.pdf

vi. Workshops

No workshops were organized under this study.

vii. Presentations

Underline indicate student author, bold indicates **Co-PI**.

Hu, X. Estuarine Acidification, A Subtropical (Texas) Flavor, Gulf of Mexico Coastal Ocean Observing Network (G-CAN) Webinar, May 18, 2017.

Hu, X. Two tales of one storm. Harvey Research Symposium. Port Aransas, TX. Aug. 23, 2018.

Hu, X., C.J. Staryk, M.R. McCutcheon, H. Yao, M.S. Wetz, P.A. Montagna. 2018. Extreme weather event induced changes in estuarine CO_2 flux and carbon cycle. Ocean Sciences Meeting, Portland, OR, 12-16 February 2018.

Hu, X. Dealkalization of estuaries in the northwestern Gulf of Mexico. NOAA Ocean Acidification Program PI meeting, Seattle, WA., 2017.

Liu Z, Lu K. The number of isomers in molecules of marine dissolved organic matter is constrained: Insights from ion mobility mass spectrometry. Gordon Research Conference: Chemical Oceanography. Holderness, NH, July 14-19, 2019.

Liu Z. Phosphate (P) is key affecting remineralization of labile organic matter in estuarine and coastal waters. 2017 Estuary Research Workshop, University of Rhode Island, September 13, 2017.

Liu Z., Lin X., Lu K., Xu X., Douglas S.V., Xue J., Hardison. The impact of Hurricane Harvey on water column and sediment biogeochemistry of the Mission-Aransas Estuary in south Texas. Ocean Science Meeting, Portland OR, Feb 11-16, 2018.

Liu Z., Liu S. Phosphorus is key to affecting decomposition of labile organic matter in hypoxic coastal waters. Santa Fe, NM, ASLO Summer Meeting, June 5-10, 2016.

Liu Z., Lu, K., O'Connor, J. Elucidating molecular level information of dissolved organic matter in aquatic environments using advanced analytical instrumentation. The Fourth Xiamen Symposium on Marine Environmental Sciences, Xiamen, China, January 6-9, 2019.

Lu K., Liu Z. Molecular level analysis reveals changes in recalcitrance and isomeric composition of dissolve organic matter from south Texas rivers after high flow events. Gordon Research Conference: Chemical Oceanography. Holderness, NH, July 14-19, 2019.

Lu K., **Liu Z**., Gardner W.S. Using ion mobility quadrupole time of flight (Q-TOF) LC/MS to characterize molecular structure of riverine and coastal dissolved organic matter. Aquatic Science Meeting, Honolulu, Hawaii, Feb 26-Mar 3, 2017.

Lu K., Wu K., Gardner W.S., **Liu Z**. Elucidating structural and isomer information of natural dissolved organic matter in South Texas Rivers by a new ion mobility quadrupole time of flight (IM Q-TOF) LC/MS technique. Ocean Science Meeting, Portland, OR, Feb 11-16 2018.

Lu K., Wu K., Gardner W.S., **Liu Z**. Using ion mobility quadrupole time of flight (Q-TOF) LC/MS to characterize molecular structure of riverine and coastal dissolved organic matter. Aquatic Science Meeting, Honolulu, Hawaii, Feb 26-Mar 3, 2017.

Lu K., Wu K., **Liu Z**. Bioavailability and molecular structure of dissolved organic matter in five south Texas rivers. Texas Bays and Estuaries Meeting, Port Aransas, Texas, April 12-13, 2017.

Lu, K., **Liu Z.**, Molecular characteristics of dissolved organic matter from three South Texas Rivers: Insights provided by thermal slicing pyrolysis gas chromatography mass spectrometry and amino acid analysis, Gulf Estuarine Research Society, Galveston, TX, November 8, 2018.

Lu, K., **Liu Z.**, The number of isomers in molecules of marine dissolved organic matter is constrained: Insights from ion mobility mass spectrometry. Marine Organic Geochemistry Workshop, Hanse-Wissenschaftskolleg, Delmenhorst, Germany, April 27-30, 2019.

Lu, K., **Liu, Z**. Bioavailability and molecular level characterization of dissolved organic matter in south Texas rivers. Coastal and Ocean Science at Work for Texans, Texas Sea Grant, April 9, 2019.

Lu, K., Wu, K., **Liu, Z**. Bioavailability and molecular structure of dissolved organic matter (DOM) in five south Texas rivers. The Fourth Xiamen Symposium on Marine Environmental Sciences, Xiamen, China, January 6-9, 2019.

McCutcheon M.R. and **Hu, X.** Temporal variability and driving factors of the carbonate system in the tidal inlet of a semiarid estuary. Gulf Estuarine Research Society Fall Meeting, Galveston, TX. Nov 8-10, 2018.

McCutcheon, M.R. and **Hu, X**. Understanding uncertainties in the changing carbon budget of estuaries: A case study in the northwestern Gulf of Mexico. ASLO 2018 Summer Meeting. Victoria, Canada. Jun 10-15, 2018.

McCutcheon, M.R. and **X. Hu**. CO_2 flux and long-term $p$$CO_2$ trends of the estuaries of the Northwestern Gulf of Mexico. Coastal Estuarine Research Federation biennial meeting, Providence, RI, 5-9 November 2017.

McCutcheon, M.R. and **X. Hu**. Estimating air-sea CO_2 flux and long-term $p$$CO_2$ trends of the northwestern Gulf of Mexico estuaries. Gulf Estuarine Research Society, Pensacola, FL, 2016.

McCutcheon, M.R., and **X. Hu**. CO_2 flux and long-term $p$$CO_2$ trends of the estuaries of the Northwestern Gulf of Mexico. Gordon Research Conference on Chemical Oceanography, New London, NH, 2017.

McCutcheon, M.R., Yao, H., Staryk, C.J. and **Hu, X.** Temporal variability and driving factors of the carbonate system in the tidal inlet of a semiarid estuary. 2019 ASLO Aquatic Sciences Meeting, San Juan, Puerto Rico, Feb 23-Mar 2, 2019.

Montagna, P. Fundamentals of Ecological Modeling and Deep Sea Research for Place-Based Conservation. Center for Coastal and Marine Ecosystems (CCME), Center Wide Core Competency Course, Gulf Coast Research Laboratory, Ocean Springs, MS, 1-3 August 2017.

Montagna, P.A. Designation of a National Estuarine Research Reserve for Conservation. NERRS/NERRA Annual Meeting, Corpus Christi, TX, 13 November 2017.

Montagna, P.A. Ecosystem Services Provided by Benthic Habitats. Coastal Estuarine Research Federation Biennial Meeting, Providence, RI, 5-9 November 2017.

Montagna, P.A. Effect of freshwater inflow on biogeochemistry of estuaries across a climatic gradient. NOAA Educational Partnership Program, Howard University, Washington, DC, 19-22 March 2018.

Montagna, P.A. Importance of freshwater inflows. CLE Coastal Law Conference, Houston, TX 8-9 June 2017.

Montagna, P.A. Policy and science framework for freshwater inflow determinations under Texas SB3, Restore America's Estuaries, 8th National Summit on Coastal and Estuarine Restoration and 25th Biennial Meeting of The Coastal Society, New Orleans, LA, 10-15 December 2016.

Montagna, P.A. X. Hu, and **M. Wetz**. Biogeochemical Impact of Hurricane Harvey on Texas Coastal Lagoons. Ocean Sciences Meeting, Portland, OR, 12-16 February 2018.

Montagna, P.A., C. Chaloupka, E. DelRosario, A. Gordon, R. Kalke, T. Palmer, and E. Turner. Managing environmental flows and water resources, Environmental Impact 2018, Naples, Italy, 20-22 June 2018.

Montagna, P.A., M. Hardegree. Long-term changes in estuarine benthos and fish are related to climate change. Association for Science of Limnology and Oceanography Meeting, Victoria, Canada, June 11-15, 2018.

Montagna, P.A., **X. Hu**, T. Palmer, and **M. Wetz**. Effect of Freshwater Inflow on Biogeochemistry of Estuaries at Regional and Local Scales, Aquatic Sciences Meeting (ASLO 2017), Honolulu, HI, 26 February – 3 March 2017.

Montagna, PA., C. Chaloupka, E. DelRosario, A. Gordon, T. Palmer, and E. Turner. Using Benthic Indicators to Determine Freshwater Inflow Requirements for Hydrological Restoration of a Salt Marsh. Benthic Ecology Meeting, St. John's, Newfoundland, Canada, 4 April 2019.

O'Connor J., Guo L., **Liu Z**. Characterizing riverine dissolved organic matter (DOM) using a novel thermal slice pyrolysis gas chromatography mass spectrometry technique. Texas Bays and Estuaries Meeting, Port Aransas, Texas, April 12-13, 2017.

O'Connor J., Guo L., **Liu Z**. Using a unique thermal slice pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) technique to reveal chemical structures of DOM from nine north American rivers. Ocean Science Meeting, Portland, OR, Feb 11-16 2018.

O'Connor, J., Guo L., **Liu Z**. Characterization of riverine DOM using thermal slicing pyrolysis GC-MS: implications for anthropogenic influence and organic matter lability. XV International Estuarine Biogeochemistry Symposium. Vigo, Spain, June 04-05, 2019.

O'Connor, J., Xue, J., Guo L., **Liu Z.** Molecular characteristics of dissolved organic matter from three South Texas Rivers: Insights provided by thermal slicing pyrolysis gas chromatography mass spectrometry and amino acid analysis. Gulf Estuarine Research Society, Galveston, TX, November 8, 2018.

Smith, J.K., **P.A. Montagna.** "Multiple stressor effects on macrobenthic communities in Southeastern Corpus Christi Bay, Texas, U.S.A." Benthic Ecology Meeting, Corpus Christi, TX, 28-30 March 2018.

Staryk, C.J., M.R. McCutcheon, and **X. Hu**. Seasonal hypoxia and high buffer capacity in a shallow subtropical estuary. Coastal Estuarine Research Federation biennial meeting, Providence, RI, 5-9 November 2017.

Walker, L. Hypoxia Dynamics in a Semiarid South Texas Estuary. Association for Science of Limnology and Oceanography Meeting, Victoria, Canada, June 11-15, 2018.

Walker, L. The Effects of Hurricane Harvey on South Texas Water Quality. NOAA EPP/MSI Education and Science Forum 2018

Walker, L. Timescales of Dissolved Oxygen Variability in a Semiarid South Texas Estuary (Baffin Bay). Coastal Estuarine Research Federation biennial meeting, Providence, RI, 5-9 November 2017.

Walker, L., and **M. Wetz**. Hypoxia dynamics in a semiarid South Texas estuary. ASLO Summer Meeting, Victoria, BC, June 2018.

Walker, L., **M. Wetz**, K. Hayes, and P. Montagna. Impact of Hurricane Harvey on the water quality of Texas estuaries. ASLO Aquatic Sciences Meeting, San Juan, Puerto Rico, 2019.

Wang, H., K. Hayes, **M. Wetz**, and **X. Hu**. A stable isotope study on organic matter driving oxygen consumption in two south Texas estuaries. Texas Bays & Estuaries Meeting, Port Aransas, TX, 2016

Wetz, M., E. Cira, K. Hayes, L. Walker, X. Hu, and H. Wang. Hypoxia in a hypersaline, lagoonal South Texas estuary (Baffin Bay). Restore America's Estuaries Meeting, New Orleans, LA, 2016

Xue, J., K. Wu, **M. Wetz**, and **Z. Liu**. Spatial and seasonal patterns of total dissolved amino acids in Lavaca and San Antonio Bays, Texas. Texas Bays & Estuaries Meeting, Port Aransas, TX, 2017.

Yao, H. and **X. Hu**. Hydrologic control on subtropical estuarine CO_2 fluxes. 2017 Texas Bays and Estuaries Meeting, Port Aransas, TX, 2017.

Yao, H. and **X. Hu**. Hydrologic control on subtropical estuarine CO_2 fluxes. Joint NACP and AmeriFlux Principal Investigators Meeting, North Bethesda, MD, 2017.

Yao, H. and **X. Hu**. Hydrologic control on CO_2 fluxes in subtropical estuaries. Coastal Estuarine Research Federation biennial meeting, Providence, RI, 5-9 November 2017.

Yao, H., **Hu, X.**, **Montagna, P.A.**. CO_2 flux in northwestern Gulf of Mexico estuaries - a hydrological control? ASLO 2018 Summer Meeting. Victoria, Canada. Jun 10-15, 2018.

B. Management outcomes – I. Management applications:

i. New fundamental or Applied Knowledge

The role of rivers in buffering pH and contributing dissolved and particulate organic matter to estuaries is an important new contribution to the management of environmental flows and eutrophication. The information has already been incorporated in reviewing environmental flow standards in Texas.

ii. New or improved skills

TAMUCC is part of the NOAA Center for Coastal and Marine Ecosystems (CCME) was established in 2016 as a Cooperative Science Center through a competitive award funded by the NOAA Educational Partnership Program with Minority Serving Institutions (EPP/MSI). The goal of the NOAA Center for Coastal and Marine Ecosystems (CCME) cooperative agreement (NA16SEC4810009) is to educate and train a new generation of scientists, particularly from underrepresented minority communities, in NOAA-relevant STEM disciplines and social sciences, equipped to utilize interdisciplinary approaches to address issues confronting marine and coastal communities. Lily Walker is a doctoral student funded by the CCME and has worked extensively on the current project. Her experiences here and with CCME has enhanced her education and training.

iii Publications, Workshops, Presentations, Outreach Products

McKinney, L. and **P. Montagna**. 2017. "One way or another we must protect our bay." Corpus Christi Caller Times. Online 20 October 2017 http://www.caller.com/story/opinion/forums/2017/10/20/one-way-another-we-must-protect-our-bay/785705001/

Montagna, P.A. "Importance of freshwater inflows." CLE Coastal Law Conference, Houston, TX 8-9 June 2017. This presentation was included in a conference that enable lawyers to meet continuing education credits. Thus, the work from this project was used to educate the legal community about hydrological control of coastal environments.

Montagna, P.A. and J. Trungale. "Assessment of the Relationship Between Freshwater Inflow and Biological Indicators in Lavaca Bay." Colorado-Lavaca Bay & Basin Stakeholder Committee Meeting, LaGrange, TX, 1 March 2019. This stakeholder group will review and revise environmental flow regulations in Lavaca and Matagorda Bays. This presentation educated them on the project results.

Montagna, P.A. "Focused Flows for Environmental Benefit." Texas Environmental Flows Funders Briefing, Meadows Foundation, Dallas, TX, 26 March 2019. This group of NGO's is funding research on environmental flow benefits.

Montagna, P.A. "Importance of Environmental Flows to Lavaca Bay." Lavaca Bay Foundation, Port Lavaca, TX, 18 April 2019. This new NGO was formed to monitor Lavaca Bay health, and this presentation educated the members on the inflow/hydrology issue.

Montagna, P.A. "Estuary Desal Issues: Intakes and Discharges." Coastal Bend Bays Foundation, Corpus Christi, TX, 12 May 2019. This forum was to identify issues related to siting desalination plants along the Texas coast, and the presentation incorporated results from this project to inform the siting process.

Montagna, P.A. "Importance of Freshwater Inflow to Lavaca Bay." Formosa Plastics, Point Comfort, TX, 26 June 2019. The plastic plant discharges into Lavaca Bay near where the Lavaca River enters the bay, this presentation educated the plant management on the inflow/hydrology issue.

Montagna, P.A. "People, Climate, and the Importance of Freshwater Inflow to Estuaries." University of Texas, Research Experiences for Undergraduates, Corpus Christi, TX, 28 June 2019. Educated undergraduates on the role of hydrology in estuaries.

Montagna, P.A. "Development of Freshwater Inflow/Biological Indicator Relationship" and "Using Comparative Long-Term Benthic Data for Adaptive Management of Freshwater Inflow to Three Estuaries (Colorado-Lavaca, Guadalupe, and Nueces)." Colorado-Lavaca Bay and Basin Area Stakeholder Committee, LaGrange, TX, 2 August 2019. This stakeholder group will review and revise environmental flow regulations in Lavaca and Matagorda Bays. This presentation educated them on the project results.

iv. New Methods and Technology

The new ecological model (Fig. 5) is being used at the Texas Water Development Board to organize data and review inflow standards.

v. New or Advanced Tools (e.g. models, biomarkers)

The incorporation of dissolved organic nitrogen in biogeochemical models will advance prediction of harmful algal blooms.

vi. Workshops

On Sept 13, 2017, Dr. Liu was invited to give a talk entitled, “Phosphate (P) is key affecting remineralization of labile organic matter in estuarine and coastal waters” at the 2017 Estuary Research Workshop at University of Rhode Island, and about 200 people attended.

vii. Presentations

On Feb. 17, 2017, Dr. Liu was invited to give a public talk entitle, “Does organic matter have anything to do with the health of coastal ecosystems” at the Rockport Bay Education Center, and about 20 people attended, enhancing public conscience about eutrophication and hypoxia in coastal waters. We also communicated with Mission-Aransas National Estuarine Research Reserve (NERR) about our finding of cyanobacterial bloom in the bay after the 2015 Texas storms.

viii. Outreach Activities/Products (e.g. website, newsletter articles)

Middleton, B.A., and **P.A. Montagna**. 2018. Turning on the faucet to a healthy coast. The Solutions Journal 9(3) https://www.thesolutionsjournal.com/article/turning-faucet-healthy-coast/

C. Management outcomes - II. Societal condition improved due to management action resulting from output:

Paul Montagna is working with several local groups to implement findings, these include the San Antonio Bay Partnership, the Coastal Bend Bays & Estuaries Program, and the Texas Water Development Board.

Paul Montagna is working with three Basin and Bay Area Stakeholder Committees (BBASC) review standards, prescribe monitoring, and validate flow regimes. The BBASCs are for the Nueces, Guadalupe, and Lavaca-Colorado estuaries. Under the Texas Legislature, 2007 Senate Bill 3 (SB3), rules and regulations, the BBASCs must review standards every 10 years during an adaptive management process. This process is overseen by two state agencies, the Texas Water Development Board and the Texas Commission on Environmental Quality. Montagna works closely with both of these groups as well.

Paul Montagna has a continued collaborative relationship with the Bay and Estuaries Program at the Texas Water Development Board, which is also providing funding that is being used to enhance the NOAA program. He also has been building on collaborations with NOAA scientists at the Fort Johnson laboratory in Charleston, SC. He has also received grants from three private foundations to enhance the freshwater inflow work.

Xinping Hu is working with the Texas Commission on Environmental Quality to review dissolved oxygen standards in Oso Bay and Corpus Christi Bay.

Xinping Hu initiated monitoring of pCO2 and pH in the Aransas Ship Channel from November 8, 2016. High resolution (hourly) data are being collected continuously. complementary part of this project and funded by Coastal Bend Bays and Estuaries Program (EPA direct funding).

Xinping Hu also started investigating the effect of groundwater, specifically fluxes of alkalinity and reduced sulfur, on carbonate chemistry in the Mission-Aransas Estuary since October 2016. This project is funded by the Coastal Management Program of the Texas General Land Office.

Xinping Hu also initiated a project funded by the National Science Foundation from May 2017 to examine the effect of hydrologic control on CO2 fluxes and acidification in subtropical estuaries using the Mission-Aransas Estuary as a case study.

Michael Wetz recently completed an analysis of historic water quality data for all bays on the Texas coast to quantify water quality trends and explore the mechanistic relationships between documented water quality trends and relevant drivers (i.e., land use coverage/change, climate and hydrologic patterns and variability). This analysis complements our ongoing NOAA-funded research by placing it in a larger context of environmental changes occurring on the Texas coast. The trend analysis study was funded by the NOAA Coastal Management Program (via Texas General Land Office) and the Texas ONEGulf Center of Excellence.

Zhanfei Liu initiated a project funded by Texas Sea Grant from Feb 2018 to examine quality of particulate organic matter in Mission Aransas Estuary.

Zhanfei Liu initiated a project funded by NSF from Oct 2017 to trace the impact of Hurricane Harvey on biogeochemical processes in the water column and sediment in Mission Aransas Estuary.

Zhanfei Liu is working with the Mission Aransas NERR for outreach activities to disseminate results from this project. For example, Liu is involved in preparing the coming 2018 Teachers on the Estuary Workshop in July 20, 2018.

VII. Evaluation

Overall, this project was 100% successful in meeting the proposed project goals and objectives. The project proved to be more timely than we anticipate during the proposal process. As the project was ending in August 2017, Hurricane Harvey hit the study area, so the only modification of the goals and objectives was to follow-up with additional sampling to capture the signature of the event. Because the project goal was to identify the role of hydrological drivers, the most significant disturbance by Harvey was the extreme rain, which was categorized as a 1 in 1000 year event. This allowed us to capture the full dynamic range of potential biogeochemical responses in an estuary.

Prepared by:

____ August 30, 2019________

Paul Montagna, Principal Investigator   Date