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The relationship between suspended solids and nutrients with variable hydrologic flow regimes

Bhanu Paudel[a,*], Paul A. Montagna[b], Leslie Adams[b]

[a] *Delaware Department of Natural Resources and Environmental Control, 100 W Water Street, Suite 10B Dover, DE 19904, United States*
[b] *Texas A&M University-Corpus Christi, Harte Research Institute for Gulf of Mexico Studies, 6300 Ocean Drive, Unit 5869 Corpus Christi, TX 78412, United States*

HIGHLIGHTS

- Spatial and temporal variability in TSS and nutrients along hydrologic gradient were tested.
- Inflow dynamics drive changes in salinity regime, TSS concentrations, and nutrients.
- Limited inflow to estuaries curtailed inorganic nitrogen and TSS concentrations transport.
- In Nueces Estuary, salinity near river-estuary mouth was higher during low inflow.
- In Nueces Estuary, there was sign of Reverse Estuary condition.

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ABSTRACT

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. 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.

1. Introduction

Climate data over the past 50 years reveals increased drought frequency with rising temperature in the southern United States (Karl et al., 2009). Most of the southern United States may have twice as many days with temperatures above 32 °C (~90 F) by the end of this century, based on lower and higher greenhouse gases emissions scenarios (Karl et al., 2009). Occurrence of frequent drought exacerbates low inflow conditions, which are also affected by water diversions, and affecting estuarine health (Palmer and Montagna, 2015). Freshwater inflow is important to maintaining healthy estuarine condition, because rivers transport nutrients and sediments to estuaries, and dilute salinity from the ocean (Montagna et al., 2002, 2013a), assuming that nutrients drive primary production, wetlands accrete sediments, and salinity gradients affect biological community structure. Thus if lower flows occur due to climate change, estuary health could be affected.

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[*] Corresponding author.
E-mail address: Bhanu.Paudel@state.de.us (B. Paudel).

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In addition to river transport, essential nutrients are recycled by organisms or released and adsorbed from inorganic sediment particles, thus suspended solids act as nutrient carriers changing the amount of water-column nutrients. In addition to the biological recycling of organic compounds (Bruesewitz et al., 2017, 2015), nutrients are released into the water column from suspended particulate matter and resuspended particles in estuaries with changing salinities (Ding and Henrichs, 2002; Tappin et al., 2010). In the Ogeechee River Estuary, GA, sediments that remained in the suspended fraction were high in particulate organic nitrogen (Alber, 2000). Laguna Madre, TX, a hypersaline estuarine system, sediments with minimal freshwater input, released NH_4^+ from resuspended sediments (Morin and Morse, 1999). These studies demonstrate that total suspended solid (TSS), either carried by inflow or resuspended, affects nitrogen concentrations in estuaries.

Phosphorus in organic rich freshwater sediments forms complexes with cations, e.g. iron and aluminum ions and adsorbs to sediments. As organic rich sediments move from freshwater into saline water, phosphorus desorbs due to the increase in electrolytes and negatively charged metal oxides (Sundareshwar and Morris, 1999). Resuspension is important because phosphorus released from resuspended sediments was 20–30 times greater than from undisturbed lake sediments (Sondergaard et al., 1992). Phosphorus has a tendency to adsorb and bond with calcium carbonate rich sediments (McGlathery et al., 1994), and release during resuspension (Spagnoli and Bergamini, 1997).

Silica in estuaries is primarily carried by sediments transported by freshwater inflow to estuaries (Humborg et al., 2000). Silica minerals in estuary sediments can control dissolved silica concentration (Rickert, 2000; Rickert et al., 2001). In laboratory experiments, release of silica from sediments containing silica minerals maintains the silica concentration in the overlying water column in the Guadalupe, Lavaca-Colorado, and Nueces Estuaries (Paudel et al., 2015).

The emerging paradigm is that the link between sediments, TSS, and transport of dissolved inorganic matter from rivers, is a synergistic and complex interaction that regulates nutrient supplies and affects cycling processes in estuaries. One factor that drives these interactions is hydrological flow regimes because hydrology controls both transport of materials to the estuaries and salinity gradients within estuaries. We hypothesized that variability in climate and hydrologic regimes are responsible for differences in nutrient supply and transformation processes in different estuaries. This hypothesis is examined by comparing nutrient, TSS, and chlorophyll-a concentrations among estuaries with different hydrologic regimes, and how changes occur over time due to a cycle of wet and dry periods.

2. Methods

2.1. Study sites and sampling design

Three South Texas estuaries, Lavaca-Colorado, Guadalupe and Nueces, were compared to examine TSS and inorganic nutrients variability with flow. The estuaries have similar geographic structure (Fig. 1), but have different inflow regimes (Montagna et al., 2013a; Montagna and Li, 2010; Montagna et al., 2011a,b). River inflow decreases from the northeast to the southwest; the average inflow for the Lavaca-Colorado, Guadalupe and Nueces Estuaries are 3679×10^6 m^3yr^{-1}, 2677×10^6 m^3yr^{-1}, and 348×10^6 m^3yr^{-1} respectively (Montagna et al., 2013a). The Nueces River discharges into the Nueces Estuary, the Guadalupe River discharges into the Guadalupe Estuary, and the Lavaca River and Colorado River discharges into the Lavaca-Colorado Estuary (Fig. 1). During the current study, 2012 had the highest river flow rates, followed by 2013, and 2011 had the lowest flow rates.

Stations in the Lavaca-Colorado, Guadalupe and Nueces Estuaries were located along salinity gradients from the major freshwater sources to the tidal inlets of the Gulf of Mexico. Stations A, B, and F were closer to the river mouth in the estuaries compared to stations C, D, and E, which were closer to the Gulf of Mexico (Fig. 1). The stations closer to freshwater sources are in the secondary bays and are called “near” treatment stations and those further from freshwater sources are in primary bays and are called “far” treatment stations. This spatial difference between primary and secondary bays controls biological community structure (Montagna and Kalke, 1995; Palmer and Montagna, 2015; Van Diggelen and Montagna, 2016).

The stations were sampled quarterly from April 2011 to Oct 2013 in all three estuaries to collect water samples for TSS, chlorophyll-a and inorganic nutrients. Dissolved oxygen (DO), pH, temperature, salinity and conductivity were measured at each sampling event using an YSI Sonde (YSI Model 556 MPS, Yellow Spring, OH, USA). Results from past studies indicate quarterly sampling is sufficient for studying long-term water quality dynamics because of the low variability of nutrient and TSS concentrations in the three estuaries throughout the year, except during peak flow events, in long-term sampling since 1987 (Montagna and Li, 2010; Kim and Montagna, 2012), and weekly sampling between October 2011 to October 2012 (Turner et al., 2015). Generally, inorganic nitrogen and phosphorus were less than 1 μmol/L in the long-term and weekly studies. The three estuaries are shallow and well mixed, and the surface and bottom water quality values are similar. One exception is station D in Corpus Christi Bay where summer hypoxia is associated directly with stratification (Ritter and Montagna, 1999; Applebaum et al., 2005; Montagna and Froeschke, 2009).

2.2. Total suspended solid (TSS)

Surface water samples were collected using 500 ml brown Nalgene bottles. Bottom water samples, i.e., 20 cm above sediment, were collected using Van Dorn sampler. Two replicate water samples were taken at each station. Water samples were kept on ice after collection and filtered within 24 h of collection using GF/F filter paper. Filtered sediment samples were dried and weighed to determine TSS.

2.3. Chlorophyll-a and inorganic nutrients

Water samples were collected from surface water, filtered (GF/F filter paper) on site and then stored frozen. Chlorophyll-a was determined using non-acidic extraction method. A Turner Design Trilogy fluorometer was used to measure chlorophyll-a concentration using a methanol extract method (Krauk et al., 2006). Analysis was performed within 12 to 16 h of methanol addition.

Nutrient samples were filtered on site using 0.45 μm polycarbonate filter paper and kept on ice until stored frozen, and were processed for analysis within two weeks. Nutrient analysis was conducted using the O.I. Analytical Flow Solution IV® (FS IV®) auto analyzer that combines both segmented flow analysis and flow injection analysis techniques with computer controlled sample selection and peak processing. Nutrient chemistries were measured as specified by the manufacturer. The range of method detection limits (MDL) are 0.1-10 μmol/L for ammonium (NH_4^+), 0.02-10 μmol/L for orthophosphate (o-PO_4), 0.35-35 μmol/L for silica (SiO_2), and 0.02-40 μmol/L for nitrite+nitrate (NO_3^- + NO_2^-, here also referred as NO_x). Silica in samples reacts with molybdate in acid medium and is detected as silicic acid or silicate. Matrix matching between the carrier, standards and the sample matrix minimizes refractive index effects on absorbance, which

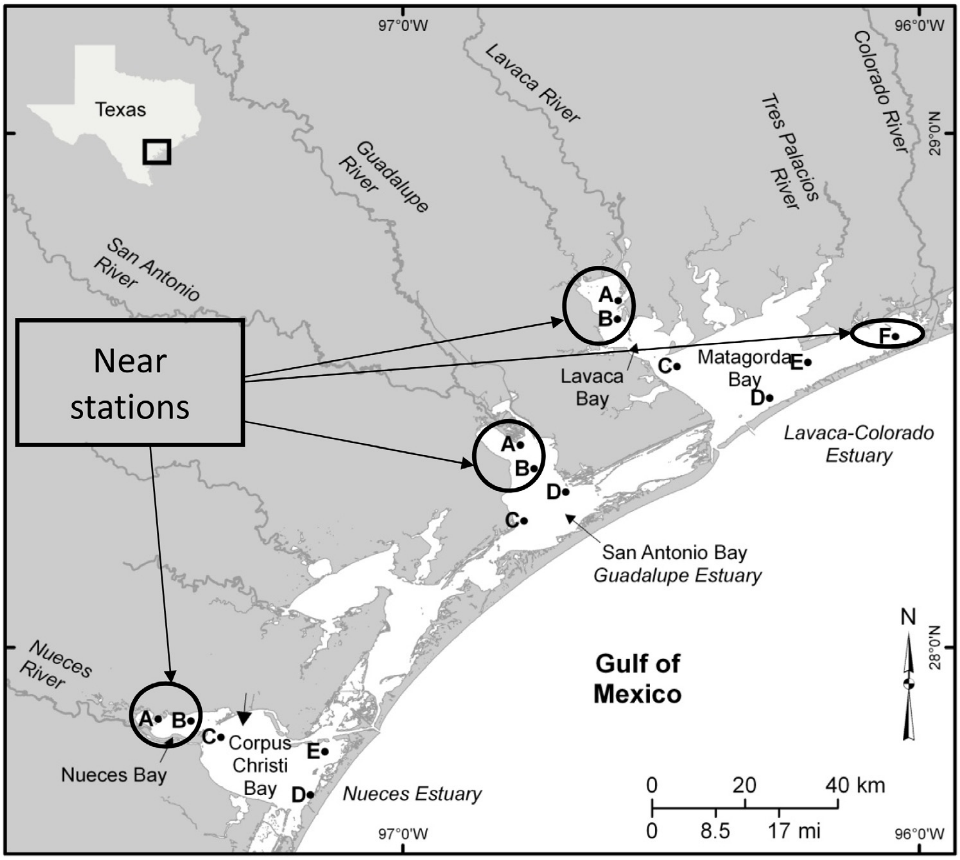

Fig. 1. Study area and sampling locations in each estuary. Stations are grouped into "near" the river source (A, B, and F) and "far: from the river source (C, D, and E).

are caused in part by salinity. Artificial seawater is adequate for the analysis of both o-PO_4 and SiO_2, but matrix matching is important for dissolved nitrogen (N) chemistries and requires the use of low nutrient seawater (LNSW) to accurately detect low (μmol) levels of N in samples. The typical lowest concentration minimum reportable levels (LCMRL) are: 0.25–10.0 μmol NO_x (O.I. Analytical method 15040908, OIA, 2008), 10.0–300.0 μmol SiO_2 (O.I. Analytical method 15061001, OIA, 2001a), and 0.25–10.0 μmol NH_4^+ (O.I. Analytical method 15031107, OIA, 2007). The o-PO_4 method has a LCMRL of 0.10–10.0 μmol (Perstorp Analytical method 000589 OIA, 2001b), but is a modification of the Alpkem chemistries method (Alpkem, 1993). In the present study LCMRL was used to prepare standard curve for the analyses.

2.4. Statistical analysis

The goal was to test for near versus far treatment differences within and among estuaries over time. A weighted average value was calculated prior to running statistical analyses. This was necessary because there were many missing values and the number of stations in the treatments was unbalanced. Samples were first average by date-estuary-treatment-station-depth, then averaged by date-estuary-treatment-station, and then average by date-estuary-treatment. The date-estuary-treatment-station data set was used for analysis of variance (ANOVA) where stations were replicates, and the average by date-estuary-treatment data set was used in the principal components analysis (PCA). The data was then transformed by the natural logarithm (ln) to help normalize the distribution of the residuals.

ANOVA was performed to analyze for differences in inorganic nutrients, and TSS between near and far stations using a 2-way model where sampling date and treatment were the two main effects and stations were replicates. Tukey post hoc multiple comparisons test was performed to identify the difference among sample groups. Pearson's correlation was performed between TSS and inorganic nutrient concentrations in all the three estuaries to identify the link between these variables.

Principal component analysis (PCA) was performed to analyze the relationship between TSS, inorganic nutrients and other water quality variables. Before the PCA analysis data were standardized to a normal distribution using STANDARD so that scales were the same for all variables. The FACTOR procedure was used to perform PCA (Long et al., 2003). From here on in the text, factor 1 or first principal component was represented by PC1 and factor 2 or second principal component was represented as PC2. Axis rotation was done by VARIMAX rotation.

ANOVA was performed using the GLM procedure (SAS Institute Inc, 2013), and all plots were created using SGPLOT, SGSCATTER and SAS ODS graphics designer (SAS Institute Inc, 2016).

3. Results

3.1. Salinity and flow

The Guadalupe Estuary salinities were significantly different ($p \leq 0.0001$) between near and far stations. Post hoc test confirmed higher average salinities in the far stations, i.e., the difference between near and far stations were 6.3 salinity units, compared to near stations. In the Guadalupe Estuary, salinities in near and far stations increased from January 2011 to October 2011, then dropped, with near station salinity dropped close to zero (Fig. 2). Inflow to the Guadalupe Estuary decreased from

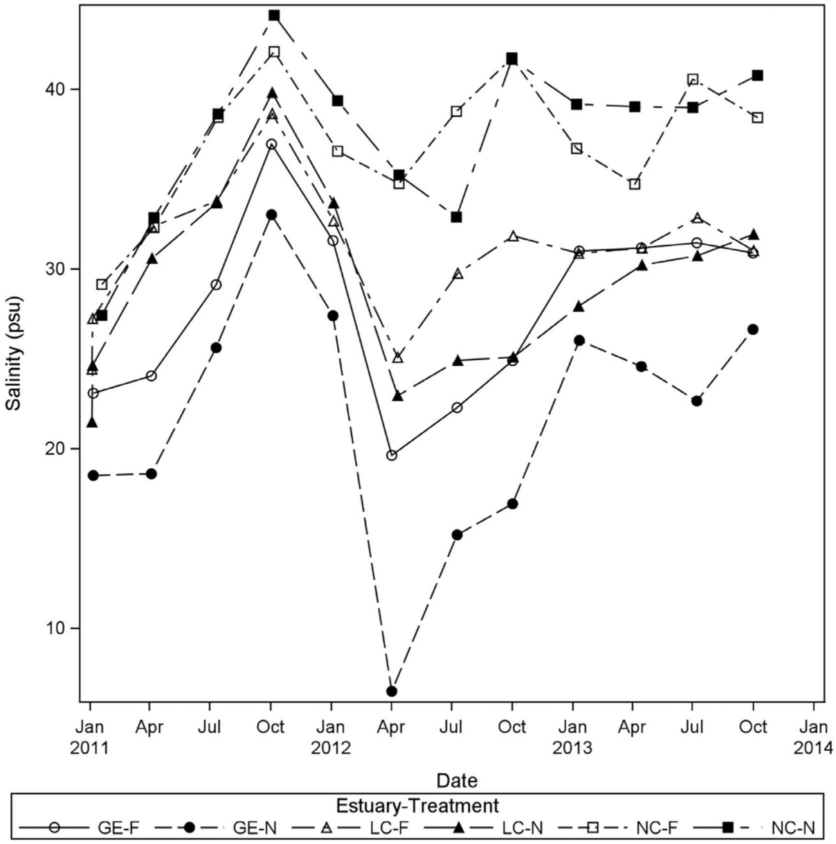

Fig. 2. Average salinity during the study period among treatments. Treatment abbreviations: GE-F = far stations in Guadalupe Estuary, GE-N = near stations in Guadalupe Estuary, NC-F = far stations in Nueces Estuary, NC-N = near stations in Nueces Estuary, LC-F = far stations in Lavaca-Colorado Estuary, LC-N = near stations in Guadalupe Estuary.

January 2011 to July, August 2011 and then inflow increased from October 2011 to the end of March and beginning of April 2012 (Fig. 3H). Salinity changed inversely with the inflow.

The Nueces Estuary salinities were similar between near and far stations; no peak inflow into the estuary occurred (Figs. 2 and 3H). Although similar, mean near- and far-salinities were significantly different, i.e. $p = 0.02$ in the Nueces Estuary.

The Lavaca-Colorado Estuary salinities differed significantly between near and far stations ($p = 0.0065$). This result was confirmed using post hoc test that far stations in the Lavaca-Colorado Estuary were more saline than near stations. Salinity increased in the estuary from January 2011 to October 2011, then after that salinity decreased with the increase in inflow to the estuary (Figs. 2 and 3H).

3.2. Inorganic nutrients and total suspended solids

Ammonium concentrations were higher in the Guadalupe and Lavaca-Colorado estuaries than in the Nueces Estuary (Fig. 3A). In the Nueces Estuary, NH_4^+concentration was below the detection limit (0.25 μmol/L) during July 2011, October 2011, and January 2012 (Fig. 3A) and decreased along increasing salinity gradients (Fig. 4A). In the Nueces and Lavaca-Colorado Estuaries, concentrations ranged from below detection limit to 5.07 μmol/L and 6.15 μmol/L respectively, but were often ≤ 1 μmol/L. In April 2012 and July 2012, the Lavaca-Colorado Estuary NH_4^+ concentration peaked at >3 μmol/L, and then dropped to ca. 1 μmol/L. Concentrations in the Guadalupe Estuary ranged from below detection limit to 4.90 μmol/L, with most of the values falling between 1 and 3 μmol/L. NH_4^+ concentrations were not significantly different between near and far stations in all but Nueces Estuary (Table 1).

Nitrite and nitrate concentrations ranged from below detection limit (0.25 μmol/L) to 1.80 μmol/L in Nueces, 27.8 μmol/L in Guadalupe and 11.265 μmol/L in Lavaca-Colorado Estuaries. The highest NO_x concentration of 27.8 μmol/L was found in the Guadalupe Estuary during April 2012. Most of the time, NOx concentrations were lower than 1 μmol/L, in all three estuaries (Fig. 3B). Nitrite+nitrate concentrations (NO_x) decreased along increasing salinity gradient of the Guadalupe and Lavaca-Colorado Estuaries and were similar in the two, while NO_x concentrations were around 0.5 μmol/L along the Nueces Estuary increasing salinity gradient (Fig. 4B). In Guadalupe and Nueces estuaries, NO_x concentration was significantly different between near and far stations (Table 1). In the Guadalupe Estuary, most of the higher concentrations were from near stations (Fig. 4B).

In all three estuaries, the highest o-PO_4 concentration was identified in October 2012 (Fig. 3C). The o-PO_4 concentration ranged from below detection limit (0.1 μmol/L) to 1.76 μmol/L in Nueces, 0.15 to 3.03 μmol/L in Guadalupe, and below detection limit to 1.30 μmol/L in Lavaca-Colorado Estuaries. In the Nueces Estuary's far stations, o-PO_4 concentration was <0.5 μmol/L. Orthophosphate concentrations were distributed evenly along salinity gradients of the three estuaries (Fig. 3C). Orthophosphate concentration was significantly different between near and far stations in the Nueces and Guadalupe estuaries but not in the Lavaca-Colorado Estuary (Table 1). Near stations in the Lavaca-Colorado Estuary had higher o-PO_4 concentration compared to the far stations (Fig. 4C).

In January 2012, SiO_2 concentration was the lowest in all three estuaries (Fig. 3D). In the Guadalupe and Lavaca-Colorado Estuaries, SiO_2 concentration was the highest in October 2012, whereas the highest SiO_2 concentration in the Nueces Estuary was in July

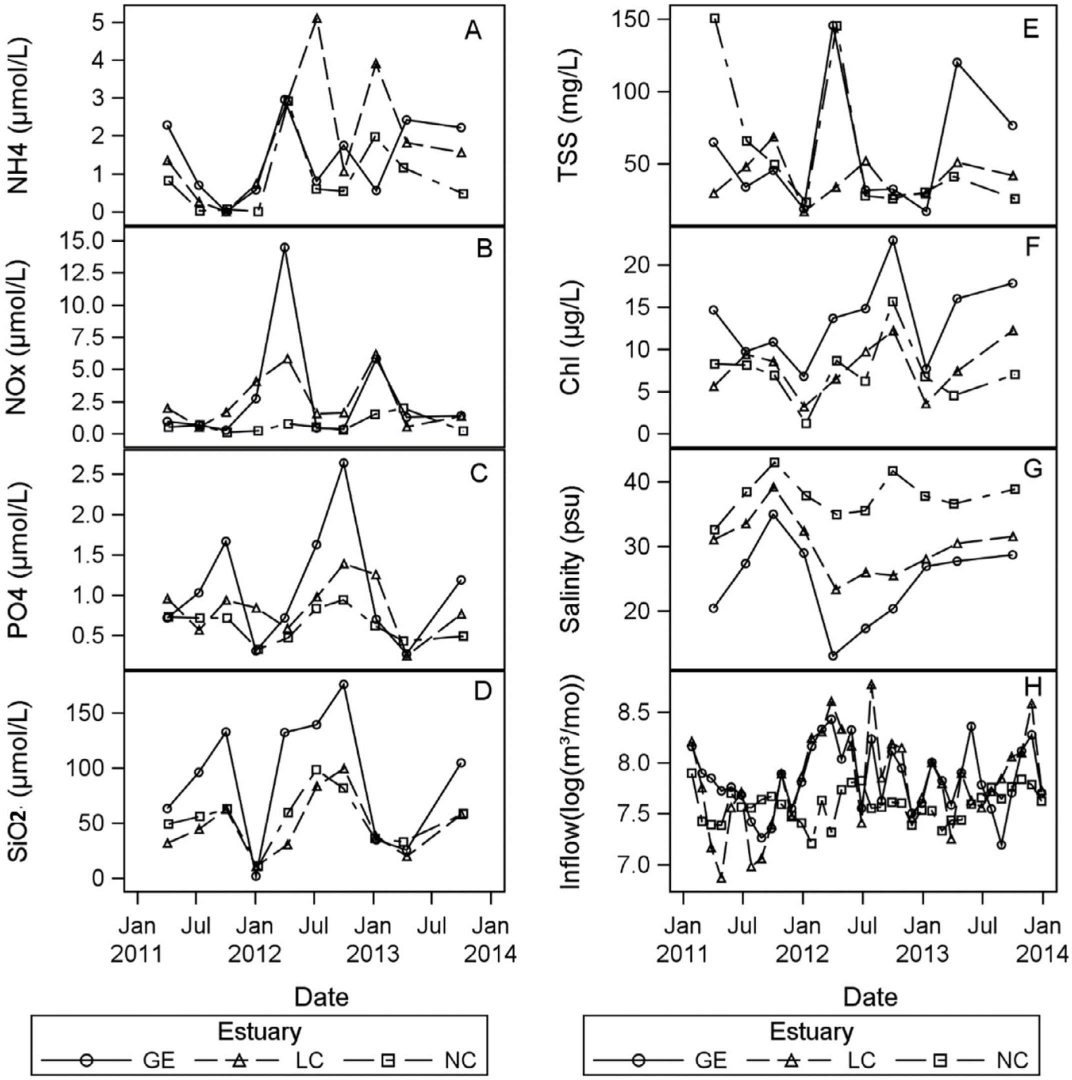

Fig. 3. Average estuary-wide concentrations of nutrients and particulates over time compared to inflow. (A) Ammonium. (B) Nitrite plus nitrate (NOx). (C) Orthophosphate. (D) Silica. (E) Total suspended solids. (F) Chlorophyll-α. (G) Salinity. (H) Inflow log scale. Estuary abbreviations: GE = Guadalupe, LC = Lavaca-Colorado, NC = Nueces.

Table 1
Analysis of variance to test significant difference between near and far stations in the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces (NC) estuaries. Abbreviation: Temp = temperature, Chl-α = chlorophyll-α, TRT = Treatment (i.e. near vs far).

Variable	Source								
	GE			LC			NC		
	Date	TRT	Date*TRT	Date	TRT	Date*TRT	Date	TRT	Date*TRT
Temp	<0.0001	0.0026	0.2681	<0.0001	0.0031	0.0004	<0.0001	0.4067	0.2037
Salinity	<0.0001	0.0004	0.1158	<0.0001	0.0003	0.0060	<0.0001	0.0105	0.0001
DO	<0.0001	<0.0001	0.1642	<0.0001	<0.0001	0.8772	<0.0001	0.0036	0.0028
pH	<0.0001	<0.0001	0.0848	0.0250	0.3543	0.4992	<0.0001	<0.0001	0.0029
Secchi	<0.0001	0.0597	0.5825	<0.0001	0.1884	0.0026	<0.0001	<0.0001	0.2534
TSS	<0.0001	0.0307	0.7945	<0.0001	0.2155	0.0278	<0.0001	<0.0001	0.0127
NH_4^+	<0.0001	0.1819	0.5340	<0.0001	0.2259	0.8138	<0.0001	0.0411	0.0021
NOx	0.1520	0.0057	0.0566	0.0003	0.9916	0.5131	<0.0001	<0.0001	<0.0001
SiO_2	<0.0001	<0.0001	0.0212	<0.0001	0.0002	0.3640	<0.0001	<0.0001	0.0037
o-PO_4	<0.0001	0.0016	0.0048	0.0002	0.0982	0.9093	0.1257	<0.0001	0.3234
Chl-α	0.0043	<0.0001	0.1146	<0.0001	0.0264	0.6362	<0.0001	0.0188	0.1611

2012 (Fig. 3D). The SiO_2concentrations ranged from below detection limit (10 µmol/L) to 135.94 µmol/L in Nueces 206.21 µmol/L in Guadalupe, and 120.31 µmol/L in Lavaca-Colorado Estuaries. Silica concentrations decreased along the increasing salinity gradients of the three estuaries. The decrease was more pronounced in the Guadalupe Estuary compared to the other two estuaries (Fig. 4D). In all three estuaries, SiO_2 concentration differed significantly between near and far stations (Table 1). The SiO_2 concentrations ranged between 15 and 45 µmol/L at far stations in the Nueces and Lavaca-Colorado Estuaries, compared to far

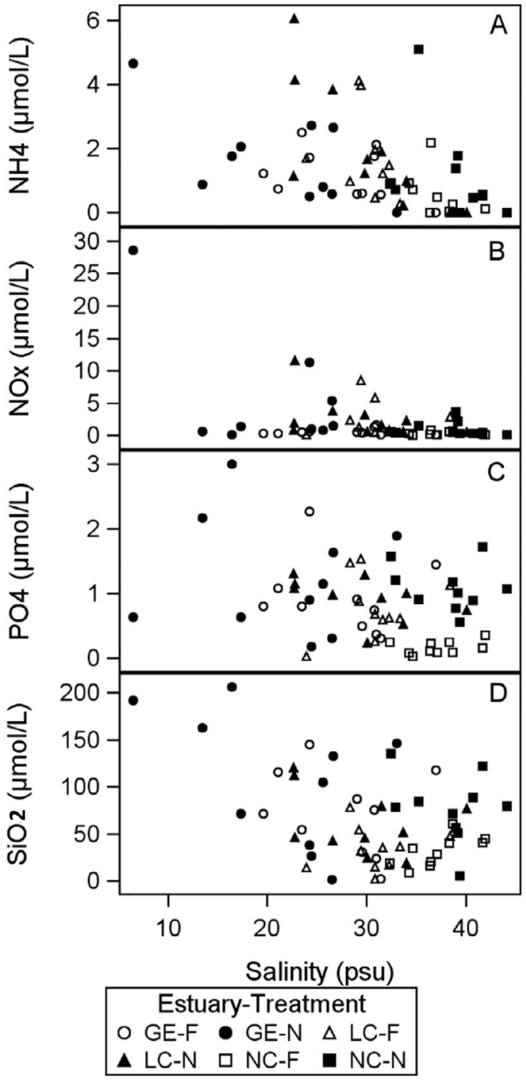

Fig. 4. Average inorganic nutrient concentrations along salinity gradients among estuary-treatment samples. (A) Ammonium. (B) Nitrite plus nitrate. (C) Orthophosphate. (D) Silica. Treatment abbreviations: GE-F = far stations in Guadalupe Estuary, GE-N = near stations in Guadalupe Estuary, NC-F = far stations in Nueces Estuary, NC-N = near stations in Nueces Estuary, LC-F = far stations in Lavaca-Colorado Estuary, LC-N = near stations in Guadalupe Estuary.

stations in the Guadalupe Estuary with concentrations greater than 80 µmol/L.

The highest suspended solid concentrations in the Nueces estuary occurred during April 2011 and April 2012, whereas in the Guadalupe and Lavaca-Colorado Estuaries highest suspended solid was in April 2012 and October 2011 respectively (Fig. 3E). The highest suspended solid concentrations occurred during cold front events, i.e. windy days with >9 m/s, and during peak flow events. Suspended solid concentrations differed between near and far stations in the Guadalupe and Nueces estuaries but not in the Lavaca-Colorado Estuary (Table 1). Suspended solids ranged from 16.59 mg/L to 249.31 mg/L, 17.16 to 182.88 mg/L and 16.48 to 80.24 mg/L in the Nueces, Guadalupe and Lavaca-Colorado estuaries respectively.

The highest chlorophyll-a concentration, in Guadalupe and Nueces Estuaries, occurred in October 2012, whereas they were elevated in the Lavaca-Colorado Estuary in October 2013, (Fig. 3F). Chlorophyll-a (—g/L) ranged from 0.62 to 21.0 in Nueces, 2.37 to 29.2 in Guadalupe and 2.25 to 15.23 in Lavaca-Colorado estuaries. In all three estuaries, chlorophyll-a concentrations differed significantly between near and far stations (Table 1). In the Lavaca-Colorado estuary, stations closer to the Colorado River had more chlorophyll-a and the *p*-value for significant is also marginally higher. In the Nueces estuary, the far stations had lower chlorophyll-a concentrations than the near stations in the months of April 2012 and July 2012.

Throughout the sampling periods, salinity ranged from ca 31 to 45 in Nueces, 1.9 to 37 in Guadalupe, and 7.9 to 40 in Lavaca-Colorado estuaries. Oct 2011 was the highest salinity month for the three respective estuaries (Fig. 3G).

3.3. Relation between inorganic nutrients, chlorophyll-a and total suspended solids

The first and second principal components (PC1 and PC2) explained 39% and 21% of the variation in all estuaries (Fig. 5A). PC1 had the highest positive values for TSS, SiO_2, and Chl, but the highest negative values for secchi and DO. PC2 had the highest positive values for NOx and the highest negative values for salinity. Temporal change was important driver in all three estuaries. PC1 had the highest positive values for July and October, whereas the highest negative values for January (Fig. 5B).

4. Discussion

4.1. Salinity, inorganic nutrients, and total suspended solids

Salinity fluctuated with the amount of inflow to the respective in the Guadalupe and Lavaca-Colorado Estuaries. In April 2012, dissolved nitrogen in both estuaries increased with flow, which may suggest that inflow transports dissolved nitrogen. However, there was no evident change in inflow to the Nueces Estuary likewise any observed change in dissolved nitrogen. One explanation is that a large proportion of the ammonium is formed and taken up very rapidly by ecosystem organisms. These processes may include, uptake by plants and microbes, animal excretion, microbial mineralization, leaving minimal concentrations or recognizable trends, especially in warm subtropical environments (Bruesewitz et al., 2015). In the Nueces Estuary, higher salinities were observed in the near stations for most of the time and the average salinity in the near stations was higher than the average salinity in the far stations by 1.17 units. These characteristics reflect those of a reverse estuary.

The long-term (1977–2009) average turbidity (measured as NTU with an YSI sonde) was higher in the secondary bays (i.e., near stations) than in the primary bays (i.e., far stations) of the Guadalupe, Nueces, and Lavaca-Colorado Estuaries (Montagna et al., 2013b). However, TSS was not significantly different between near and far stations in the Lavaca-Colorado Estuary during the current study period (Table 1). Most of the present study occurred during low flow conditions, which may help explain the similar TSS concentration in the near and far stations.

Ammonium was not significantly different between near and far stations in the Guadalupe and Lavaca-Colorado estuaries (Table 1). Silica was only significantly different between near and far stations in all three estuaries. Ortho-phosphate and NO_x were significantly different between near and far stations in the Nueces and Guadalupe Estuaries (Table 1). The low river inflow to the estuaries, along with ecological processes, during the present study may help explain reasons for almost similar nutrients concentrations (except silica) between near and far stations. A recent modeling study indicated that high inflow events can increase inorganic nutrients in the Guadalupe, Nueces, and Lavaca-Colorado Estuaries (Paudel and Montagna, 2014).

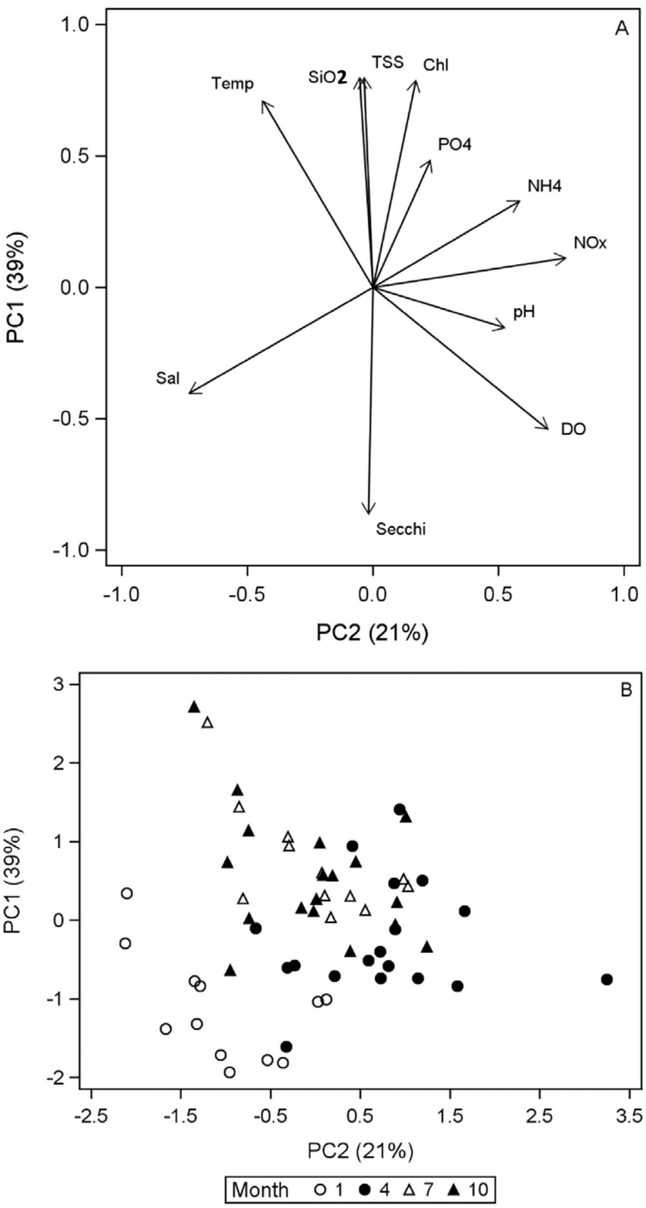

Fig. 5. Principal components analysis of mean water quality variables for each sampling period in each Estuary. (A) Variable loads. (B) Sample scores by month in all three estuaries, where 1 = January, 4 = April, 7 = July, and 10 = October. Abbreviations: Sal = salinity, Temp = temperature, Chl = chlorophyll-α.

In the past, a half saturation constant (HSC) nutrient concentration was used as a standard of inorganic nutrient concentrations to identify inorganic nutrient limitations in the estuaries. The HSC nutrient concentration is defined as the amount at which nutrient uptake is half of the maximum value and can be used as a first approach to identify nutrient limitation (Fisher et al., 1988). Below the HSC, the uptake rate is reduced and is limiting algal growth (Fisher et al., 1988). The HSC concentration for nitrate, nitrite and NH_4^+ to grow coastal phytoplankton is 1-2 µmol/L each, whereas for o-PO_4 it is 0.1–0.5 µmol/L (Fisher et al., 1988; Sanders et al., 2001). Samples of 13 NO_x concentrations out of 56 in the Guadalupe, 6 out of 70 in the Nueces, and 25 out of 84 in the Lavaca-Colorado Estuaries were equal to or greater than HSC. Most importantly those samples equal to or greater than half saturation constant were from near stations only. In contrast to NO_x concentrations, most of the o-PO_4 concentrations were equal to or greater than HSC with the exceptions of far stations in the Nueces and Lavaca-Colorado Estuaries. In the Nueces Estuary, most of the average NH_4^+ and NO_x concentrations in the near and far stations were less than 1 µmol/L (Figs. 4A and 4B). Oxidized forms of inorganic nitrogen, especially nitrate, were found to be abundant in Texas estuaries (Hou et al., 2012). Nitrite+nitrate and NH_4^+concentrations in the present study were found to be limiting to grow coastal phytoplankton in all three estuaries using HSC as the standard concentration. Orthophosphate may be limiting in the far stations of the Nueces Estuary. A follow up nutrients limitation study is recommended to affirm nutrients limitation in the three estuaries. The new approach of using nutrient (e.g. for ammonium) demand to help define limitation may be useful for selected nutrients (Bruesewitz et al., 2015, 2017; Gardner et al., 2017). This simple approach resembles the short (e.g. 24 h) incubation techniques as used for biological demand and do not require use of isotopes (Gardner et al., 2017).

The HSC concentration to grow coastal phytoplankton for SiO_2 is 1-5 µmol/L (Fisher et al., 1988). Based on that, the SiO_2 concentration in all three estuaries was not limiting to coastal phytoplankton growth (Fig. 3D). The significant difference in SiO_2 concentrations at near and far stations in all three estuaries indicates freshwater inflow was supplying SiO_2 in the near stations (Table 1). In all three estuaries, SiO_2 concentration was close to 100 µmol/L in salinities greater than 20 and TSS less than or equal to 50 mg/L. This result may result from the release of SiO_2 from mineralization. A laboratory experiment using the Guadalupe and Nueces Estuary sediments identified that resuspension can release SiO_2 concentration in the water (Paudel et al., 2015). Hence inflow and mineralization maintain SiO_2 concentrations in these estuaries.

4.2. Relationship between flow, total suspended solids and nutrients

Nitrogen and phosphorus concentrations increase with the increasing suspended solid concentrations in the Humber Estuary, UK (Jickells et al., 2000). Average TSS concentrations in the estuary were greater than 100 mg/L during extreme peak flow (observed in the Guadalupe and Nueces Estuaries) during frontal events. It is likely that high inflow accompanied by transport of high suspended solids and dissolved NO_x from the watershed to estuary, which is evident as Guadalupe River transport loads from urban and agricultural land. High inflow and channel disturbance by wind can also bring NH_4^+ ions into the water column, which is then oxidized and resulted in higher NO_x concentrations.

The o-PO_4 concentration ranged from below detection limits to 3 µmol/L. The presence of organic matter and calcite minerals in the sediment of the estuaries may have enhanced adsorption of o-PO_4 to the sediments resulting low water column concentration (Paudel et al., 2015). An increase of o-PO_4 concentration was related to chlorophyll-a and TSS concentration. At TSS lower than 50 mg/L, o-PO4 was correlated with chlorophyll-a (Montagna and Paudel data). This result indicates that at lower turbidity remineralization was active and controlling o-PO_4 concentration.

Similar to o-PO_4, SiO_2 was correlated with chlorophyll-a when TSS was lower than 50 mg/L. In the Guadalupe Estuary, during peak flow events, the average SiO_2 concentration was more than 500 µmol/L (Montagna unpublished data). The relationship of SiO_2 with chlorophyll-a and TSS concentrations indicates the presence of diatoms and SiO_2 minerals in the estuaries could maintain SiO_2 concentration. The presence of SiO_2 minerals in the sediments can maintain SiO_2 concentration in the water column (Rickert et al., 2001). High inflow events accompanied by high TSS and churning of bottom sediment increased SiO_2 concentration in the water, as low grade SiO_2 species and SiO_2 minerals were present in the sediments of Guadalupe and Nueces Estuaries (Paudel et al., 2015).

Nitrogen limitation relative to phosphorus is possible if there is no human influence on excess sediment transport to the estuary (Paerl, 2009; Nixon, 1995; Howarth and Marino, 2006). However, nitrogen limitation in all the three estuaries studied here resulted from reduced sediment to the estuaries because of water diversions — a different type of human influence compared to the fore mentioned studies. The decrease in sediment transport to the Nueces Estuary is due to the sedimentation in Lake Corpus Christi (Ockerman et al., 2013). In the Nueces estuary, the low variability of TSS, salinity, and NH_4^+ indicates low freshwater input, as those variables changes with variability in inflow to the estuary. Low NH_4^+ concentration in the Nueces Estuary, where nitrogen limitation was the greatest among the three estuaries, might be the result of low sediment supply. The low NH_4^+ and NO_x concentrations found in the present study supports previous studies that showed nitrogen limitation in Texas Estuaries (Gardner et al., 2006; Hou et al., 2012).

Freshwater inflow and temporal changes were the main drivers in the three estuaries. We have noticed NH_4^+ and NO_x concentrations changes with the inflow amount in all three estuaries (Fig. 3A), whereas SiO_2 and PO_4 concentrations were affected by seasonal variation and recycle release from sediments. As sediment bottom churned up with seasons, turbidity in water increases (Fig. 3A), which helps in releasing silica and phosphorus in the water (Paudel et al., 2015). It was also noticed that nutrients, suspended solids and water quality parameters changed with time. The highest positive values in the July and October indicate the possibility of high nutrients and sediments in the estuaries during those periods (Fig. 3B). That was because of high inflow volume observed during that period (Fig. 3H). In addition, the lowest concentrations in January could also be associated with low temperature that in turns affect recycle and release in the water.

5. Conclusion

Prolonged drought and water diversions limit supply of freshwater, thus could promote the formation of "reverse estuary". There had been extended drought in South Texas during this study and our salinity data in the near and far stations of Nueces Estuary indicate the presence of "reverse estuary" conditions. Decreases in precipitation have decreased inflow to the three estuaries, which curtail sediment and nutrient transport to the estuaries. We have identified river inflow as a major source of dissolved nitrogen to the three estuaries. Based on the half saturation constant, the Nueces Estuary with the least inflow was limiting dissolved inorganic nitrogen. Compared to the Guadalupe and Lavaca-Colorado Estuaries, where dissolved nitrogen concentrations increased with the river inflow, there was no change in dissolved nitrogen in the Nueces Estuary as there was no evidence of inflow. Our study revealed that dissolved silica, orthophosphate and ammonium concentration all correlated with suspended solid concentrations. Additionally, dissolved silica and orthophosphate correlated with chlorophyll-a when TSS was less than 50 mg/L. The study identifies changes in salinity regime with the inflow dynamics are important for the TSS concentration in the estuaries and can help maintain nutrients.

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