Exceptionally high organic nitrogen concentrations in a semi-arid South Texas estuary

susceptible to brown tide blooms

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Abstract

Studies of estuarine eutrophication have tended to focus on systems with continually flowing rivers, while little is known about estuaries from semi-arid/arid regions. Here we report results from an assessment of water quality conditions in Baffin Bay, Texas, a shallow (<2-3 m) subtropical estuary located in a semi-arid region that has agriculture as the dominant (44%) watershed land use. Chlorophyll a averaged 28-30 µg/l in Baffin Bay from 2003-2013 and total Kjeldahl nitrogen (TKN) concentrations were also very high (116-120 µM), with concentrations of both variables exceeding those of most other Texas estuaries by 2-5 fold. More recent field sampling (2013-2015) showed that dissolved organic nitrogen concentrations in Baffin Bay ($62 \pm$ $14 \,\mu$ M) were >2 fold higher than in three other Texas estuaries. In contrast, inorganic nitrogen (ammonium, nitrate) and phosphate concentrations were relatively low. Statistically significant long-term annual increases in chlorophyll a and salinity were observed in Baffin Bay, while long-term seasonal increases were observed for water temperature and TKN. Overall, Baffin Bay is displaying multiple symptoms of eutrophication, namely very high organic carbon, organic nitrogen and chlorophyll concentrations, as well as symptoms not quantified here such as fish kills and episodic hypoxia. Much of the increase in chlorophyll in Baffin Bay, at least since ~1990, have coincided with blooms of the mixotrophic phytoplankton species, Aureoumbra lagunensis, which is thought to be favored under high proportions of organic to inorganic nitrogen. Thus the high and possibly increasing organic nitrogen concentrations, coupled with a long-term annual increase in salinity and a long-term seasonal increase in water temperature are likely to promote additional brown tide blooms in this system in the future.

<u>1. Introduction</u>

Estuaries provide critical habitat for important fish and shellfish species and play a vital role in the economy of coastal states, including Texas (Lacson and Lee 1997; Jones and Tanyeri-Abu 2001). Water quality is a major determinant of the health of estuaries, and consequently affects the ability of these systems to support healthy fisheries (Whitfield and Elliott 2002; Eby et al. 2005). Texas has seven primary estuarine systems from its eastern border with Louisiana to its southern border with Mexico, along with numerous smaller bays within these systems. Texas' coastal counties have experienced human population growth over the past two decades, with future growth expected to contribute to an additional 26-82% increase by 2050 (Texas State Data Center, http://txsdc.utsa.edu/Data/TPEPP/Projections/Index.aspx). Along with this growing urban footprint on coastal land use coverage, agriculture remains a significant land use in many Texas watersheds (NOAA Coastal Change Analysis Program). Worldwide, both urban and agricultural land uses have been shown to contribute to water quality degradation through pollutant (i.e., nutrients, bacteria) inputs to receiving waterbodies (Hopkinson and Vallino 1995; Handler et al. 2006).

Despite the pronounced presence of urbanization and agriculture in Texas coastal watersheds, widespread negative effects on water quality have not been reported to date. Wetz et al. (2016) found localized negative effects of municipal wastewater discharge on a small secondary bay system (Oso Bay), but the ecosystem impacts were unclear. Thronson and Quigg (2008) summarized fish kill records for Texas estuaries from 1970-2006 and found that low dissolved oxygen during warmer months was believed to be an important cause of fish kills, yet the driver(s) of this low dissolved oxygen, whether natural or human-induced, were not determined. In the most recent National Estuarine Eutrophication Assessment, five of nine Texas estuaries

assessed had moderate or moderate to low eutrophication condition, while four others lacked sufficient data for assessment (Bricker et al. 2007).

Although widespread water quality degradation is not apparent on the Texas coast, localized concerns have arisen over the past few decades. One area of concern is the Baffin Bay-Upper Laguna Madre complex. Since 1990, Baffin Bay and adjacent Upper Laguna Madre have experienced large, prolonged blooms of the "brown tide" phytoplankton species, Aureoumbra lagunensis (Buskey et al. 1998, 2001). The first reported bloom began in early 1990 in tributaries of Baffin Bay, but eventually spread to both the Upper and Lower Laguna Madre (Stockwell et al. 1993), resulting in seagrass die-off (Onuf 1996; Onuf 2000). Remnants of this bloom persisted for nearly seven years in the Baffin Bay-Laguna Madre complex (Buskey et al. 2001). Since then, several additional brown tide blooms have occurred in the same area (unpubl. Texas Parks & Wildlife reports; Wetz et al. unpubl. data). Previous studies have attributed development of the 1990 brown tide bloom to both lack of top-down control and a concurrent pulse of nutrients that stimulated growth. Microzooplankton grazer abundances as well as benthic filter feeder abundances were very low during bloom development, coincident with a period of drought and hypersaline conditions (Montagna et al. 1993; Buskey et al. 1997). As for the nutrient pulse, it was speculated that this was derived from agricultural runoff and/or decay of fish that died during the freeze (e.g., Stockwell et al. 1993; Whitledge et al. 1993), but the main source has never been identified. Likewise, virtually nothing is known about the nutrient source(s) that have allowed for brown tide bloom persistence and/or redevelopment in subsequent years. Experimental studies have determined that A. lagunensis is a mixotroph that relies on reduced nitrogen (ammonium, organic nitrogen) for growth, but it cannot utilize nitrate (DeYoe and Suttle 1994; Muhlstein and Villareal 2007; Agostoni and Erdner 2011)

Brown tide is not the only issue of concern in terms of water quality in Baffin Bay. For example, hypoxia has been documented, including on several occasions that coincided with large fish kills over the past decade (unpubl. Texas Parks & Wildlife reports). In addition, a large fish kill occurred in late 2010 coincident with hypoxia as well as a bloom of the dinoflagellate *Pyrodinium bahamense* (unpubl. Texas Parks & Wildlife reports). *P. bahamense* is known to produce toxins under certain conditions (Phlips et al. 2015), and has been implicated in low dissolved oxygen events that led to fish kills elsewhere (e.g., Morrison and Greening 2011). Recent studies suggest that *P. bahamense* is typically most competitive under relatively high nutrient input conditions (Phlips et al. 2015). As with the prevalence of brown tide blooms, it is unclear as to whether the hypoxic events as well as *P. bahamense* bloom represent symptoms of larger-scale water quality degradation or simply natural variability.

Here we report results from an assessment of water quality conditions in Baffin Bay, Texas. The primary focus is on the spatial extent of, and long-term changes in, select water quality indicators. Differences are also highlighted between Baffin Bay and other estuarine systems along the Texas coast that have not experienced brown tide blooms, offering new insight into potential drivers of brown tide bloom formation and persistence.

2. Methods

2.1. Baffin Bay characteristics

Baffin Bay is a shallow (<2-3 m) subtropical estuary located in a semi-arid region (Figure 1). Land use in the Baffin Bay watershed is dominated by agriculture (44%), with urban contribution limited to small cities such as Kingsville (pop. 26,213) and Alice (pop. 19,576) (NOAA Coastal Change Assessment Program). The semi-arid climate coupled with high evaporation rates in the region can lead to hypersaline conditions in Baffin Bay. Winds can be relatively strong in the region and are thought to play a dominant role in hydrography of the system (Tunnell and Judd 2002). The nearest inlets that allow for exchange between Baffin Bay and Gulf of Mexico are Packery Channel (~41 km north of Baffin Bay), Aransas Pass (~70 km north of Baffin Bay) and Port Mansfield (~80 km south of Baffin Bay). These distances, along with diurnal tidal ranges of only ~2-3 cm, results in minimal overall tidal influence on Baffin Bay. As such, Baffin Bay has a long mean residence time (>1 year).

2.2. Data sources

Data for this study were obtained from historic databases as well as ongoing sampling programs. In order to quantify intra- or inter-estuary patterns in select water quality variables, data were obtained from two sources; 1) Texas Commission on Environmental Quality's Surface Water Quality Monitoring (SWQM) program

(https://www.tceq.texas.gov/waterquality/monitoring, and 2) ongoing investigator-led sampling programs. In order to examine long-term changes in select variables, data were utilized from the SWQM program as well as from Ward and Armstrong (1997), who compiled historic data (ca. 1960's-early 1990's) from numerous sampling programs conducted in south-central Texas estuaries.

2.3. Sampling procedures

The SWQM program involves water sample collection from numerous sites along the Texas coast on a quarterly basis (Figure 1). Details on SWQM sampling procedures and analytical methodologies are available at: https://www.tceq.texas.gov/waterquality/monitoring. Briefly,

current methods employed in SWQM include the following: Standard Methods 2520 (for Salinity), Standard Methods 2500 B (for Water Temperature), EPA 446.0 (for Chlorophyll *a*), Standard Methods 4500 (for Total Kjeldahl Nitrogen), EPA 350.1 (for Ammonium), EPA 365.3 (for Orthophosphate), and EPA 365.3 (for Total Phosphorus). Method detection limits for each have changed over time and are dealt with appropriately in statistical approaches (see below). For the historic data, Ward and Armstrong (1997) provide additional information on methodological approaches and data sources.

Data collected from investigator-led field programs in Lavaca-Colorado, Guadalupe, Nueces and Baffin Bay Estuaries were used to quantify broad-scale patterns in dissolved organic carbon (DOC) and dissolved organic nitrogen (DON). Samples were collected from 4-9 sites along the salinity gradient of each system from July 2013 to June 2015 (Figure 1). Surface water samples were collected in acid-washed amber polycarbonate bottles. Bottles were stored on ice until return to a shore-based facility where processing of samples occurred. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined using the filtrate of water samples that were passed through precombusted 25 mm GF/F filters and stored frozen (-20°C) until analysis. Samples were subsequently analyzed using the High Temperature Catalytic Oxidation method on a Shimadzu TOC-Vs analyzer with nitrogen module. Standard curves were run twice daily using a DIW blank and five concentrations of either acid potassium phthalate solution or potassium nitrate for DOC and TDN, respectively. Three to five subsamples were taken from each standard and water sample and injected in sequence. Reagent grade glucosamine was used as a laboratory check standard and inserted throughout each run, as were Certified Reference Material Program (CRMP) deep-water standards of known DOC/TDN concentration. Average daily CRMP DOC and TDN concentrations were $48.1 \pm 7.4 \mu mol L^{-1}$ and $31.9 \pm 2.7 \mu mol L^{-1}$

respectively. Dissolved organic nitrogen (DON) was determined by subtracting dissolved inorganic nitrogen (ammonium, nitrate + nitrite (N+N)) from TDN. For Lavaca-Colorado, Guadalupe, Nueces Estuaries, inorganic nitrogen (N+N, ammonium) was determined from the filtrate of water that passed through a 0.4 μ m polycarbonate filter and stored frozen (-20° C) until analysis, typically within one month of collection. Samples were analyzed with an O.I. Analytical Flow Solution IV analyzer. Check standards of known concentration, as well as matrix spikes and laboratory duplicates were run after every 10 samples. Method detection limit for both ammonium and nitrate + nitrite was $0.25 \,\mu$ M. For Baffin Bay, inorganic nitrogen (N+N, ammonium) was determined from the filtrate of water samples that were passed through a 25 mm GF/F filters and stored frozen (-20°C) until analysis. After thawing to room temperature, samples were analyzed on a Seal QuAAtro autoanalyzer. Standard curves with five different concentrations were run daily at the beginning of each run. Fresh standards were made prior to each run by diluting a primary standard with low nutrient surface seawater. Deionized water (DIW) was used as a blank, and DIW blanks were run at the beginning and end of each run, as well as after every 8-10 samples to correct for baseline shifts. Method detection limit for both ammonium and nitrate + nitrite was $0.02 \,\mu$ M.

2.4. Statistical analysis of long-term trends

Kendall's τ_a (Kendall 1955) was used to measure the monotonic association between time and variables. In cases where the SWQM data included time periods with collections that were more frequent than quarterly, a seasonal (winter = DJF, spring = MAM, summer = JJA, autumn = SON) average was computed from the existing data to avoid biasing towards a particular year or season that may have higher frequency data. The SWQM database also contained censored data for certain variables. In the aforementioned analysis, a comparison between a censored and an uncensored value was treated as a tie if no specific ranking was possible, but was treated as any other comparison if a ranking was possible. Comparisons between two censored values were always treated as ties. The computation of the variance of τ_a for the test statistic was adjusted for all ties arising both from censored and uncensored data. The hypotheses tested were

$$H_0: \tau_a = 0$$

versus

$$H_0: \tau_a \neq 0$$

Slopes for trend lines were computed using the method of Akritas et al. (1995). The slope *m* of the trend line is chosen so that the association between *x* and the residuals y - m * x has Kendall's $\tau_a = 0$. *m* is reported as the midpoint of all *m*'s satisfying this criterion. The intercept is chosen to be the median residual, where for censored data the residuals are computed using the method of Turnbull (1976). All calculations and graphs were made in R version 3.3.0 (R Core Team 2016), including the NADA package version 1.5-6 (Lee 2013).

2.5. Nutrient addition bioassays

Nutrient addition bioassays were conducted with water collected from the Alazan and Cayo del Grullo tributaries of Baffin Bay on March 28, May 23, August 21, and November 20, 2015 (Figure 1). Surface water was collected in 10-20 L carboys (pre-washed with 10% HCL) and covered with black bags until transferred into acid-washed 1 L Cubitainers (Hedwin Co.; ~80% transparent to ambient photosynthetically active radiation, PAR) for nutrient amendments. Four treatments were run per site in triplicate, including; 1) Control (no nutrient addition), 2) 10 μ M-N as ammonium chloride, 3) 0.6 μ M-P as monopotassium phosphate, and 4) 10 μ M-N and 0.6

 μ M-P. Cubitainers were subsequently incubated at the surface ~10 m from shore in the Cayo del Grullo to maintain ambient temperature and light levels. These environmental conditions were monitored with equipment secured to a nearby pier. PAR reaching the surface water was monitored with a LI-COR LI-190SA quantum sensor at ~ 1 m above the water's surface, and surface water temperature was monitored with a Hydrolab DS5X submerged to ~0.5 m depth. Subsamples (~100-250 ml) for chlorophyll *a* were taken immediately after experimental set-up, at 24 hours, and at 48 hours. Results are presented from the 0 and 24 hour time points, as phytoplankton growth (when stimulated) ceased after 24 hours.

3. Results

3.1. Spatial patterns

Broad spatial patterns in water quality variables along the Texas coast were determined by calculating the 10-year average (from 2003-2013) of each relevant variable from all available SWQM estuarine sites. There is a strong salinity gradient on the Texas coast, with lower salinities in the northern estuaries and much higher salinities to the south (Figure 2). This coincides with well-documented precipitation and freshwater inflow gradients (Montagna et al. 2013). Chlorophyll *a* concentrations averaged $\leq 10 \,\mu g/l$ at many sites along the Texas coast. Exceptions include two small secondary bays (Carancahua Bay, 29 $\mu g/l$; Oso Bay, 24 $\mu g/l$), a site adjacent to the Arroyo Colorado outflow in the Lower Laguna Madre (18 $\mu g/l$), both sites in Baffin Bay (28-30 $\mu g/l$) and an adjacent site in the Laguna Madre (24 $\mu g/l$) (Figure 2). Nitrate plus nitrite (N+N) concentrations were $\leq 5 \,\mu$ M along much of the coast, with the exception of Carancahua Bay (12 μ M), Oso Bay (14 μ M) and a site in the lower Laguna Madre adjacent to the Arroyo Colorado outflow (38 μ M) (Figure 2). Ammonium concentrations were $\leq 6 \,\mu$ M

along the entire coast (Figure 2). Total Kjeldahl Nitrogen (TKN) concentrations averaged ≥ 24 μ M at all sites along the Texas coast (Figure 2), and very high concentrations were noted in Carancahua Bay (154 μ M), Oso Bay (110 μ M), Baffin Bay (116-120 μ M) and adjacent sites in the upper Laguna Madre (Figure 2). Given the low ammonium concentrations, it appears that the majority of the TKN was as organic nitrogen. Total phosphorus (TP) concentrations were generally $\leq 5 \mu$ M, with relatively low concentrations observed throughout much of the Laguna Madre (Figure 2). Exceptions include Oso Bay (5.5 μ M) and Carancahua Bay (9.6 μ M).

Data from studies focused on the four specific estuarine systems confirm the aforementioned pattern of very high organic matter concentrations in Baffin Bay. Mean DOC concentrations were higher in Baffin Bay ($850 \pm 105 \mu$ M) than in the Guadalupe ($380 \pm 121 \mu$ M), Lavaca-Colorado ($358 \pm 117 \mu$ M), and Nueces ($362 \pm 89 \mu$ M) Estuaries (Table 1). Similarly, mean DON concentrations were higher in Baffin Bay ($62 \pm 14 \mu$ M) than in the Guadalupe ($26 \pm 8 \mu$ M), Lavaca-Colorado ($25 \pm 7 \mu$ M), and Nueces ($28 \pm 6 \mu$ M) Estuaries (Table 1). Within Baffin Bay, the highest DOC and DON concentrations were found in the three main tributaries and decreased towards the mouth (Figure 3).

Overall, chlorophyll *a* concentrations were strongly correlated with total nitrogen (TKN + N+N) concentrations (m = 0.21, $r^2 = 0.89$) along the Texas coast, whereas the relationship with TP was not nearly as strong (m = 2.57, $r^2 = 0.30$) (Figure 4). Nutrient addition bioassays conducted at two sites in Baffin Bay confirm that phytoplankton growth in this system is largely nitrogen limited throughout the year. A statistically significant increase in chlorophyll occurred in the ammonium and ammonium plus phosphate addition treatments compared to the control (t-test, p < 0.01) at both sites in March and May 2015 (Figure 5). In contrast, the change in chlorophyll in the phosphate addition was not different from that of the control treatment (Figure

5). It is important to note that the March experiment was conducted during an active brown tide bloom (E. Cira, unpubl. data). In August 2015, chlorophyll decreased in the control and phosphate treatments, whereas it remained elevated in the ammonium and ammonium plus phosphate addition treatments at the Alazan site, and in the ammonium treatment at the Cayo del Grullo site (Figure 5). In November 2015, a statistically significant increase in chlorophyll occurred in the phosphate addition treatment compared to the control (t-test, p < 0.01) at the Alazan site, but high variability in chlorophyll in the ammonium and ammonium plus phosphate treatments rendered it impossible to reach any firm conclusion about their effect (Figure 5). No statistically significant effect of ammonium and/or phosphate were observed at the Cayo del Grullo site (Figure 5).

3.2. Temporal trends

Statistically significant long-term increases in chlorophyll *a* (p < 0.02; 0.2-0.3 µg L⁻¹ yr⁻¹) and salinity (p < 0.02; 0.3 yr⁻¹) were observed at both Baffin Bay SWQM sites (Figure 6; Table 2). Although a statistically significant long-term increase in water temperature was not detected when using all SWQM data (Table 2), a seasonally significant increase was observed for station 13450 in spring (p < 0.01; 0.1° C yr⁻¹), and borderline significant increases were observed in summer at station 13450 (p = 0.06; 0.03° C yr⁻¹) as well as spring and summer at station 13452 (p= 0.07; 0.03-0.06° C yr⁻¹) (Table 2). Detection of trends in TKN is complicated because of large gaps in data prior to 1990. A significant increase was observed in spring at station 13450 (p = 0.02; 1.6 µM yr⁻¹). When comparing pre-1990 (prior to onset of brown tide blooms in the system) and post-1990 TKN data, pre-1990 TKN was significantly lower (t-test, p = 0.01; 99 ± 19 μ M) at station 13450 compared to 118 ± 37 μ M for post-1990 data. No significant trends annual or seasonal trends were observed for ammonium, N+N, orthophosphate or TP.

In addition to analysis of SWQM data from within Baffin Bay, data were also analyzed from two of the three streams that feed into Baffin Bay (San Fernando Creek, Petronila Creek). No data were available from a third stream (Los Olmos Creek). A statistically significant long-term increase (1989-2013) in chlorophyll *a* (p < 0.01; 1.8 µg L⁻¹ yr⁻¹) was observed in the tidal section of Petronila Creek (Table 2), while no trends were observed for ammonium, TKN, N+N, TP or orthophosphate. It should be noted that TKN data is only available from late 1993 onward in Petronila Creek. San Fernando Creek exhibited a long-term increase in orthophosphate (p =0.05; 1.0 µM yr⁻¹), a decrease in ammonium (p < 0.01; 0.2 µM yr⁻¹) and no change in TKN, N+N or TP (Table 2). Overall, TKN (161 ± 98 µM) and chlorophyll *a* (50 ± 43 µg L⁻¹) concentrations were high but variable in the tidal section of the agricultural dominated Petronila Creek, whereas inorganic nutrient concentrations were low over the period from 2003-2013. In the wastewater influenced San Fernando Creek, relatively high concentrations of N+N (174 ± 131 µM), orthophosphate (90 ± 74 µM) and TP (94 ± 77 µM) were observed over the period from 2003-2013, while chlorophyll *a* (24 ± 24 µg L⁻¹) and TKN (130 ± 61 µM) concentrations were slightly lower than in Petronila Creek.

<u>4. Discussion</u>

For the central-south Texas coast as a whole, symptoms of water quality degradation were generally limited to a few small systems (e.g., Carancahua Bay and Oso Bay) and a site adjacent to the Arroyo Colorado outflow in the Lower Laguna Madre. In fact, most of the estuarine systems examined in this analysis displayed low nutrient and chlorophyll concentrations. Baffin Bay was a notable exception, as it is displaying multiple symptoms of eutrophication including very high organic carbon and organic nitrogen concentrations, high and increasing chlorophyll concentrations, as well as symptoms not quantified here such as fish kills and episodic hypoxia. Given the strong linkage between total nitrogen and chlorophyll along the Texas coast, as well as the stimulatory effects of nitrogen on Baffin Bay phytoplankton growth in bioassays, it is reasonable to conclude that nitrogen is an important driver of the eutrophication of Baffin Bay. Furthermore, because of its long residence time, Baffin Bay is undoubtedly sensitive to nitrogen inputs (Bricker et al. 2008). In contrast, the relationship between phosphorus and phytoplankton growth in the system is less clear. Periods of very high (>16) inorganic nitrogen to phosphorus ratios have been observed in the system (Rhudy et al. 1999; Wetz, unpubl. data), yet the brown tide organism *A. lagunensis* has been shown to thrive under these otherwise phosphorus limiting conditions (Liu et al. 2001; Cotner et al. 2004), presumably due to its ability to utilize organic phosphorus (Sun et al. 2012). Thus effects of phosphorus limitation may not be expressed equally across all phytoplankton taxa, and it would appear that *A. lagunensis* growth is not controlled by phosphorus.

Based on SWQM data, inorganic nitrogen concentrations are low on average in Baffin Bay. This is consistent with data from more intensive sampling programs in Baffin Bay (Wetz et al. unpubl. data) and nearby systems (e.g., Mooney and McClelland 2012), which have shown only ephemeral increases in inorganic nitrogen, typically as a result of high rainfall periods or storm events. In contrast, organic nitrogen concentrations are consistently very high in the system compared to not only other Texas estuaries but estuaries worldwide (this study; Berman and Bronk 2003; Mulholland et al. 2009). Although limited by availability of data prior to 1990, there are indications that TKN concentrations have also increased between the pre-1990 to post1990 period, most noticeably during the spring. Similarly, chlorophyll increased on an annual basis at both sites, mainly during summer at station 13450 and during spring at station 13452. A strong seasonal cycle in terms of chlorophyll is present in Baffin Bay, with chlorophyll typically peaking in May-July coincident with seasonal water temperature increase (Cira and Wetz, unpubl. data). One possible explanation for the temporal disconnect between the TKN increase (spring) and chlorophyll increase (summer) at station 13450 is that, on a seasonal basis, the TKN is retained until late spring-summer due to the system's long residence time, and is ultimately drawn down by phytoplankton as water temperatures warm and biomass accumulates. Ongoing studies are underway to quantify the seasonal dynamics of nutrients and phytoplankton growth in Baffin Bay, and should provide further insight into these dynamics. It is important to note that much of the increase in chlorophyll concentrations in Baffin Bay, at least since ~1990, has coincided with blooms of the mixotroph *Aureoumbra lagunensis* that is thought to be favored under high proportions of organic to inorganic nitrogen (Muhlstein and Villareal 2007; Gobler et al. 2013; Kang et al. 2015).

One important consideration in terms of the role of organic nitrogen as a driver of phytoplankton growth, and specifically that of brown tide, is the lability of the DON. We are aware of no studies that have quantified the chemical makeup of the DON in Baffin Bay-Laguna Madre, but this will undoubtedly affect its overall availability to the phytoplankton and their subsequent growth rates (Bronk et al. 2007). For example, Muhlstein and Villareal (2007) found that *A. lagunensis* exhibited growth rates using urea that were roughly 75% of those on ammonium, suggesting that urea is relatively lability. Samples have been collected from Baffin Bay for urea determination and will be reported in the future. In contrast to urea, the numerous other organic nitrogen compounds that could conceivably make up the overall pool may exhibit a

wider range of labilities, in some cases being very difficult to utilize (Bronk et al. 2007). External factors, such as light levels and water temperature, will play a role in terms of DON availability and recycling. For example, Baffin Bay is subjected to very high light levels for a large part of the year that could promote photo-oxidation of the DON to ammonium, as seen in other systems (Vahatalo et al. 2003; Stedmon et al. 2007). Warm water temperatures are also likely promote intensive bacterial remineralization of the DON to ammonium (Badr et al. 2008). Studies are underway now to discern the lability of the DON pool, and also to determine the influence of interannual variability in freshwater inflow on nitrogen forms/concentrations and phytoplankton growth/composition.

In terms of the main sources of nitrogen to Baffin Bay, both external and internal sources must be considered because the system often experiences prolonged (multi-year) drought conditions that are punctuated by above average rainfall during El Nino events (Tolan 2007). SPARROW model output suggests that, on average, fertilizers and atmospheric deposition are the largest external nitrogen sources, followed by manure from pastures, urban runoff and wastewater discharge (Rebich et al. 2011). Groundwater was not included in the model, although two recent studies suggest that groundwater inputs to Baffin Bay are comparable to other coastal regions, albeit possibly exhibiting considerable spatial-temporal variability (e.g., Breier et al. 2010; Uddameri et al. 2014). The relative contribution of each source will depend on hydrologic conditions, as it is not uncommon for the agricultural-dominated streams in the Baffin Bay watershed to become stagnant during drought conditions. Thus sources of more consistent flows (i.e., wastewater or septic) may represent a larger fraction of external loadings during drought conditions. Indeed, one of the three streams that flows into Baffin Bay (San Fernando Creek) has 12 permitted wastewater facilities that discharge into it, and overall this

stream has very high nitrate and TKN concentrations. In contrast, during episodic rainfall events and/or periods of above average rainfall, agricultural-dominated streams would represent important contributors to loadings given the large areal extent of agriculture in the watershed (Rebich et al. 2011).

As for organic nitrogen sources to Baffin Bay, Ockerman and Petri (2001) examined runoff from agricultural land in the watershed and found that \geq 70% of runoff-derived loadings to a stream that flows into Baffin Bay (Petronila Creek) were in the form of organic nitrogen. They further speculated that this organic nitrogen was derived from crop residue, as "no till" practices are commonly employed in the area. Here we offer an alternative explanation for the high proportion of organic nitrogen loadings from agricultural-dominated lands in the Baffin Bay watershed. Petronila Creek has become highly enriched in terms of algal biomass since late 1989 when water quality monitoring began, with the SWQM data showing exceptionally high and increasing chlorophyll levels as well as relatively high TKN levels. We speculate that during episodic high rainfall periods, this labile, organic rich algal biomass and its degradation products are flushed into Baffin Bay. However, it is difficult to make a firm judgement on the relative importance of agricultural practices on the loadings of organic nitrogen to Baffin Bay, as other external and internal sources (e.g., wastewater, septic, algal exudation, etc.) have yet to be quantified. It is clear that the watershed sources of nitrogen, including but not limited to organic nitrogen, and the conditions that facilitate loadings to Baffin Bay require more attention in order to develop robust management strategies.

Regardless of external source, it seems likely that any nitrogen that is added to the system will undergo multiple transformations and be retained for a prolonged period, a phenomenon that is common to long residence time systems such as Baffin Bay (Cloern 2001; Pinckney et al. 2001). As such, internal nitrogen loadings are likely to be important in Baffin Bay as well, especially during the prolonged drought conditions. An and Gardner (2002) found evidence of high potential rates of dissimilatory nitrate reduction to ammonium (DNRA) at the sediment-water interface in Baffin Bay, leading to high potential rates of ammonium flux to the water column. This, along with the overall high DON concentrations, may provide the reduced nitrogen necessary to promote brown tide persistence once blooms are established. Other possible internal nitrogen sources include algal exudation, release from biota such as fish, and nitrogen fixation. Unfortunately, we are aware of no studies that have fully quantified internal nitrogen loading rates in the system, including over the course of a drought-wet cycle.

Overall, the importance of the aforementioned symptoms of eutrophication on Baffin Bay ecosystem health cannot be overstated. Baffin Bay has long been known for its ability to support commercial and recreational fishing opportunities (Lacson and Lee 1997). Because of its isolation from major population centers, it has traditionally been overlooked from a water quality assessment standpoint due to a perception that human influence on the system is minimal. Data presented in this study indicates that the system is currently experiencing symptoms of water quality degradation, presumably due to human influence on the watershed. This trend toward eutrophication may be the end product of even longer processes that have changed the system and its watershed. For example, Besonen et al. (2016) presented data from sediment cores collected throughout Baffin Bay. They observed an increase in chlorophyll concentrations that began around ~AD 1860 when land use change first became pronounced in the watershed. Their data also indicates a much sharper increase in chlorophyll over the past half-century, when human influence on the watershed has accelerated. The long term water temperature and salinity increases may also play a role in the recent water quality changes, as phytoplankton growth rate

typically increases with water temperature increase (Eppley 1972), while high salinities are particularly important for brown tide dominance by eliminating grazers (Buskey et al. 1998). Overall, the high and possibly increasing organic nitrogen concentrations, coupled with a longterm annual increase in salinity and a long-term seasonal increase in water temperature are likely to promote additional brown tide blooms in this and similar systems in the future (see also Buskey et al. 1998; Koch et al. 2014; Kang et al. 2015).

Evidence from previous brown tide events suggests that the ability of the ecosystem to support the aforementioned fisheries may eventually be compromised by multiple stressors, namely those associated with eutrophication (hypoxia; food web collapse due to brown tide, e.g., Gobler and Sunda 2012), climate change (i.e., long-term water temperature increase), and hypersaline conditions that develop during drought periods. Aside from the previously mentioned fish kills involving important species (i.e., trout, red drum, black drum) over the past decade in Baffin Bay, anecdotal evidence suggests that a dramatic decline in abundances of the dominant filter-feeding clam (Mulinia lateralis) occurred during the most recent drought that ended in 2013-2014 (S. Murray, pers. comm.), similar to events that occurred just prior to the first brown tide bloom in 1989 during drought (Montagna et al. 1993). The cause of the recent decline is unclear, though an ongoing study of benthic macrofauna biomass and diversity has demonstrated strong negative relationships with both dissolved oxygen and salinity (Pollack et al., unpubl. data). Regardless of the cause, the loss of benthic filter feeders, which are an important food source for the commercially-important black drum (Pogonas cromis), has been speculated to play a role in a recent (2012-2013) decline in the health of black drum (Pogonas *cromis*) in the system (J. Pollack, pers. comm.). Additional work is clearly needed to

characterize the ecological consequences of water quality degradation in the system, especially in light of the temperature and salinity increases.

On a broader scale, process studies of estuarine eutrophication have tended to focus on systems with continually flowing rivers from which nutrients and organic matter are derived. In contrast, little is known about estuaries from semi-arid/arid regions. Estuaries in these regions only receive freshwater input via episodic rainfall and flow from ephemeral streams, implying that traditional views of nutrient management may not be fully applicable in them. In addition, these systems can also be hypersaline at times, and typically have a long residence time which allows for prolonged retention and cycling of nutrients. Despite the lack of attention from the research community, the cumulative number of these systems approaches that of classic riverdominated estuaries and they can have a significant areal footprint (e.g., Largier et al. 2010; Potter et al. 2010). Most importantly, climate models suggest that there will likely be a significant expansion of arid regions in the near future (Chan and Wu 2015), which when coupled with increasing freshwater demands due to human population growth in coastal watersheds, may lead to more estuarine systems demonstrating characteristics typical of those in present day arid/semi-arid region. As demonstrated in this study, these systems can still be susceptible to the process of eutrophication and its associated symptoms (Bricker et al. 2008). Thus additional emphasis should be placed on quantifying and understanding water quality and nutrient-phytoplankton dynamics in similar systems.

5. Acknowledgements

We thank the dedicated citizen scientist volunteers who were integral in the Baffin Bay data collections, including: Jim Atkins, Frank Baumann, Jerry Bjork, Jan Cannamore, Al Gordon,

Michael Henry, Carl Hooker, Thomas Mullenix, Scott Murray, David Rowsey, Ron Ryon, Jim Scoggins, Charles Sellers, Diane Sellers, John Sutton and Paul Wimberly. We also thank the following individuals for assistance with sample processing: Victor Batres, Kalman Bugica, Kelsey Fisher, Anne-Marie Gavlas, Cory Staryk, Jessica Tolan, Sarah Tominack, Lily Walker and Hongjie Wang. This work was supported in part by an Institutional Grant (award no. NA14OAR4170102) to the Texas Sea Grant College Program from the National Sea Grant Office, by a Texas Coastal Management Program Grant approved by the Texas Land Commissioner pursuant to National Oceanic and Atmospheric Administration award no. NA14NOS4190139, by NOAA's National Center for Coastal Ocean Science (award no. NA15NOS4780185), and by the Texas Water Development Board (award no. 1600011924). All views, opinions, findings, conclusions, and recommendations expressed in this material are those of the author(s) and do not necessarily reflect the opinions of the Texas Sea Grant College Program, the National Oceanic and Atmospheric Administration or any of its subagencies. Additional funding was provided by the Celanese Corporation, Kleberg County, Coastal Conservation Association, Saltwater Fisheries Enhancement Association, and Coastal Bend Bays & Estuaries Program.

<u>6. References</u>

Agostoni, M., and D.L. Erdner. 2011. Analysis of ammonium transporter and urease gene expression in *Aureoumbra lagunensis*. Harmful Algae 10: 549-556

Akritas, M.G., S.A. Murphy, and M.P. Lavalley. 1995. The Theil-Sen estimator with doubly censored data and applications to astronomy. J. American Statistical Assoc. 90: 170–77

An, S., and W. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Mar. Ecol. Prog. Ser. 237: 41-50

Badr, E.S.A., A.D. Tappin, and E.P. Achterberg. 2008. Distributions and seasonal variability of dissolved organic nitrogen in two estuaries in SW England. Mar. Chem. 110: 153-164

Berman, T., and D. Bronk. 2003. Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. Aquat. Microb. Ecol. 31: 279-305

Besonen, M., E.M. Hill, and P. Tissot. 2016. Baffin Bay sediment core profiling for historical water quality. Publication 109 of the Coastal Bend Bays & Estuaries Program. 76 pp.

Breier, J.A., C.F. Breier, and H.N. Edmonds. 2010. Seasonal dynamics of dissolved Ra isotopes in the semi-arid bays of south Texas. Mar. Chem. 122: 39-50

Bricker, S., B. Longstaff, W. Dennison, A. Jones, K. Boicourt, C. Wicks, and J. Woerner. 2007.Effects of nutrient enrichment in the nation's estuaries: a decade of change. NOAA CoastalOcean Program Decision Analysis Series No. 26. National Centers for Costal Ocean Science,Silver Spring, MD. 328 pp.

Bricker, S.B., B. Longstaff, W. Dennison, A. Jones, K. Boicourt, C. Wicks, and J. Woerner.

2008. Effects of nutrient enrichment in the nation's estuaries: a decade of change. Harmful Algae8: 21-32

Bronk, D.A., J.H. See, P. Bradley, and L. Killberg. 2007. DON as a source of bioavailable nitrogen for phytoplankton. Biogeosciences 4: 283-296

Buskey, E.J., P.A. Montagna, A.F. Amos, and T.E. Whitledge. 1997. Disruption of grazer populations as a contributing factor to the initiation of the Texas brown tide algal bloom. Limnol. Oceanogr. 42: 1215-1222

Buskey, E.J., B. Wysor, and C. Hyatt. 1998. The role of hypersalinity in the persistence of the Texas "brown tide" in the Laguna Madre. J. Plankton Res. 20: 1553-1565

Buskey, E.J., H. Liu, C. Collumb, and J.G.F. Bersano. 2001. The decline and recovery of a persistent Texas brown tidal algal bloom in the Laguna Madre (Texas, USA). Estuaries 24: 337-346

Chan, D., and Q. Wu. 2015. Significant anthropogenic-induced changes of climate classes since 1950. Scientific Reports 5: Article No. 13487.

Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210: 223-253

Cotner, J.B., M.W. Suplee, N.W. Chen, and D.E. Shormann. 2004. Nutrient, sulfur and carbon dynamics in a hypersaline lagoon. Estuar. Coast Shelf Sci. 59: 639-652

DeYoe, H.R., and C.A. Suttle. 1994. The inability of the Texas "brown tide" alga to use nitrate and the role of nitrogen in the initiation of a persistent bloom of this organism. J. Phycol. 30: 800-806

Eby, L.A., L.B. Crowder, C.M. McClellan, C.H. Peterson, and M.J. Powers. 2005. Habitat degradation from intermittent hypoxia: impacts on demersal fishes. Mar. Ecol. Prog. Ser. 291: 249-261

Eppley, R.W. 1972. Temperature and phytoplankton growth in the sea. Fishery Bulletin 70: 1063-1085

Gobler, C.J., and W.G. Sunda. 2012. Ecosystem disruptive algal blooms of the brown tide species, *Aureococcus anophagefferens* and *Aureoumbra lagunensis*. Harmful Algae 14: 36-45

Gobler, C.J., F. Koch, Y. Kang, D.L. Berry, Y.Z. Tang, M. Lasi, L. Walters, L. Hall, and J.D.Miller. 2013. Expansion of harmful brown tides caused by the pelagophyte, *Aureoumbra lagunensis* DeYoe et Stockwell, to the US east coast. Harmful Algae 27: 29-41

Handler, N.B., A. Paytan, C.P. Higgins, R.G. Luthy, and A.B. Boehm. 2006. Humandevelopment is linked to multiple water body impairments along the California coast. Estuar.Coasts 29: 860-870

Hopkinson, C.S., and J.J. Vallino. 1995. The relationships among man's activities in watershed and estuaries: a model of runoff effects on patterns of estuarine community metabolism. Estuaries 18: 598-621

Jones, L.L., and A. Tanyeri-Abur. 2001. Impacts of recreational and commercial fishing and coastal resource-based tourism on regional and state economies. Report TR-184 of the Texas Water Resources Institute.

Kang, Y., F. Koch, and C.J. Gobler. 2015. The interactive roles of nutrient loading and zooplankton grazing in facilitating the expansion of harmful algal blooms caused by the pelagophyte, *Aureoumbra lagunensis*, to the Indian River Lagoon, FL, USA. Harmful Algae 49: 162-173

Kendall, M.G. 1955. Rank correlation methods. 2nd ed. Charles Griffin & Company.

Koch, F., Y. Kang, T.A. Villareal, D.M. Anderson, and C.J. Gobler. 2014. A novel immunofluorescence flow cytometry technique detects expansion of brown tides caused by *Aureoumbra lagunensis* to the Caribbean Sea. Appl. Env. Microbiol. 80: 4947-4957

Lacson, J.M., and W.Y. Lee. 1997. Status and trends of selected marine fauna in the Corpus Christi Bay National Estuary Program study area. Publication 24 of the Corpus Christi National Estuary Program.

Largier, J. L. 2010. Low-inflow estuaries: hypersaline, inverse and thermal scenarios. In: Contemporary Issues in Estuarine Physics. A. Valle-Levinson (editor), Cambridge University Press, Cambridge. Pp. 247-272.

Lee, L. 2013. NADA: Nondetects and Data Analysis for Environmental Data. https://CRAN.R-project.org/package=NADA.

Liu, H., E.A. Laws, T.A. Villareal, and E.J. Buskey. 2001. Nutrient-limited growth of *Aureoumbra lagunensis* (Pelagophyceae), with implications for its capability to outgrow other phytoplankton species in phosphate-limited environments. J. Phycol. 37: 500-508

Montagna, P.A., D.A. Stockwell, and R.D. Kalke. 1993. Dwarf surfclam *Mulinia lateralis* (Say, 1822) populations and feeding during the Texas brown tide event. J. Shellfish Res. 12: 433-442

Montagna, P.A., T.A. Palmer, and J. Pollack. 2013. Hydrological changes and estuarine dynamics. Springer-Verlag New York, 94 pp.

Mooney, R.F., and J.W. McClelland. 2012. Watershed export events and ecosystem responses in the Mission-Aransas National Estuarine Research Reserve, South Texas. Estuar. Coasts 35: 1468-1485

Morrison, G., and H. Greening. 2011. Water quality. In: Yates, K.K., H. Greening, and G. Morrison (eds.). Integrating science and resource management in Tampa Bay, Florida: U.S. Geological Survey Circular 1348, 280 pp.

Muhlstein, H.I., and T.A. Villareal. 2007. Organic and inorganic nutrient effects on growth rateirradiance relationships in the Texas brown tide alga *Aureoumbra lagunensis* (Pelagophyceae).J. Phycol. 43: 1223-1226

Mulholland, M.R., G.E. Boneillo, P.W. Bernhardt, and E.C. Minor. 2009. Comparison of nutrient and microbial dynamics over a seasonal cycle in a mid-Atlantic coastal lagoon prone to Aureococcus anophagefferens (brown tide) blooms. Estuar. Coasts 32: 1176-1194

Nance, H.S. 2006. Tracking salinity sources to Texas streams: Examples from West Texas and the Texas Gulf Coastal Plain. Gulf Coast Assoc. of Geological Societies Transactions 56: 675-693

Ockerman, D.J., and B.L. Petri. 2001. Hydrologic conditions and water quality in an agricultural area in Kleberg and Nueces counties, Texas, 1996-1998. U.S. Geological Survey Water Resources Investigations Report 01-4101

Onuf, C.P. 1996. Seagrass responses to long-term light reduction by brown tide in upper Laguna Madre, Texas: distribution and biomass pattern. Mar. Ecol. Prog. Ser. 138: 219-231

Onuf, C.P. 2000. Seagrass responses to and recovery from seven years of brown tide. Pacific Conservation Biol. 5: 306-313

Phlips, E.J., S. Badylak, M.A. Lasi, R. Chamberlain, W.C. Green, L.M. Hall, J.A. Hart, J.C
Lockwood, J.D. Miller, L.J. Morris, and J.S. Steward. 2015. From red tides to green and brown
tides: bloom dynamics in a restricted subtropical lagoon under shifting climatic conditions.
Estuar. Coasts 38: 886-904

Pinckney, J.L., H.W. Paerl, P. Tester, and T.L. Richardson. 2001. The role of nutrient loading and eutrophication in estuarine ecology. Environ. Health Perspectives 109: 699-706

Potter, I.C., Chuwen, B.M., Hoeksema, S.D., and M. Elliott. 2010. The concept of an estuary: A definition that incorporates systems which can become closed to the ocean and hypersaline. Estuar. Coastal Shelf Sci. 87: 497-500

Rebich, R.A., N.A. Houston, S.V. Mize, D.K. Pearson, P.B. Ging, and C.E. Hornig. 2011. Sources and delivery of nutrients to the northwestern Gulf of Mexico from streams in the southcentral United States. J. American Water Resources Assoc. 47: 1061-1086 Rhudy, K.B., V.K. Sharma, R.L. Lehman, and D.A. McKee. 1999. Seasonal variability of the Texas "brown tide" (*Aureoumbra lagunensis*) in relation to environmental parameters. Estuar. Coast Shelf Sci. 48: 565-574

Stedmon, C.A., S. Markager, L. Tranvik, L. Kronberg, T. Slatis, and W. Martinsen. 2007.Photochemical production of ammonium and transformation of dissolved organic matter in theBaltic Sea. Mar. Chem. 227-240

Stockwell, D.A., E.J. Buskey, and T.E. Whitledge. 1993. Studies on conditions conducive to the development and maintenance of a persistent "brown tide" in Laguna Madre, Texas. In: T.J. Smayda and Y. Shimizu (eds.), Toxic phytoplankton blooms in the sea, Elsevier Science Publishers, pp. 693-698

Sun, M.M., J. Sun, J.W. Qiu, H.M. Jing, and H.B. Liu. 2012. Characterization of the proteomic profiles of the brown tide alga *Aureoumbra lagunensis* under phosphate- and nitrogen-limiting conditions and of its phosphate limitation-specific protein with Alkaline Phosphatase activity. Appl. Environ. Microbiol. 78: 2025-2033

Thronson, A., and A. Quigg. 2008. Fifty-five years of fish kills in coastal Texas. Estuar. Coasts 31: 802-813

Tolan, J.M. 2007. El Niño-Southern Oscillation impacts translated to the watershed scale:Estuarine salinity patterns along the Texas Gulf Coast, 1982 to 2004. Estuar. Coastal Shelf Sci.72: 247-260

Tunnell, J.W., and F.W. Judd. 2002. The Laguna Madre of Texas and Tamaulipas. Texas A&M University Press, College Station. 346 pp.

Turnbull, B.W. 1976. The empirical distribution function with arbitrarily grouped, censored and truncated data. J. Royal Statistical Society. Series B (Methodological): 290–95.

Turner, E.L., B. Paudel, and P.A. Montagna. 2015. Baseline nutrient dynamics in shallow well mixed coastal lagoon with seasonal harmful algal blooms and hypoxia formation. Mar. Poll. Bull. 96: 456-462

Uddameri, V., S. Singaraju, and E.A. Hernandez. 2014. Temporal variability of freshwater and pore water recirculation components of submarine groundwater discharges at Baffin Bay, Texas. Environ. Earth Sci. 71: 2517-2533

Vahatalo, A.V., K. Salonen, U. Munster, M. Jarvinen, and R.G. Wetzel. 2003. Photochemical transformation of allochthonous organic matter provides bioavailable nutrients in a humic lake. Archiv. Fur Hydrobiol. 156: 287-314

Ward, G.H., and N.E. Armstrong. 1997. Current status and historical trends of ambient water, sediment, fish and shellfish tissue quality in the Corpus Christi Bay National Estuary Program study area. Publication 13 of the Corpus Christi Bay National Estuary Program. 270 pp.

Wetz, M.S., K. Fisher, L. Price, K. Hayes, and B. Sterba-Boatwright. 2016. Water quality dynamics in an urbanizing South Texas estuary: relationships with watershed land use coverage. Mar. Poll. Bull. 104: 44-53

Whitfield, A.K., and A. Elliott. 2002. Fishes as indicators of environmental and ecological changes within estuaries: a review of progress and some suggestions for the future. J. Fish Biol. 61: 229-250

Whitledge, T.E. 1993. The nutrient and hydrographic conditions prevailing in Laguna Madre, Texas, before and during a brown tide bloom. In: T.J. Smayda and Y. Shimizu (eds.), Toxic phytoplankton blooms in the sea, Elsevier Science Publishers, pp. 693-698 Table 1. Mean \pm SD for dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations (μ M) measured in four estuaries of the Texas coast from July 2013 to June 2015 (Figure 1).

Estuary	DOC	DON	
Lavaca-Colorado	358 ± 117	25 ± 7	
Guadalupe	380 ± 121	26 ± 8	
Nueces-Corpus Christi	362 ± 89	28 ± 6	
Baffin Bay	850 ± 105	62 ± 14	

Table 2. Temporal trends of water quality parameters in Baffin Bay where statistically significant annual or seasonal trends were observed. Bold, italicized values are significant (p < 0.05).

Site	Parameter	Time period	Year of first	<i>p</i> -value	Annual
			collection		trend
13450 (Baffin	Salinity	Annual	1968	<0.01	0.3
Bay)		Winter		0.36	0.2
		Spring		0.06	0.4
		Summer		0.07	0.4
		Autumn		0.24	0.2
	Water	Annual	1968	0.12	0.05
	temperature	Winter		0.68	-0.02
	(°C)	Spring		<0.01	0.10
		Summer		0.06	0.03
		Autumn		0.27	0.05
	Chlorophyll a	Annual	1973	<0.01	0.3
	(µg/l)	Winter		0.19	0.3
		Spring		0.71	0.1
		Summer		0.01	0.5
		Autumn		0.06	0.4
	TKN (µM)	Annual	1975	0.61	0.0
	. ,	Winter		0.44	-0.7
		Spring		0.02	1.6
		Summer		0.33	-0.8
		Autumn		0.56	-0.3
13452 (Baffin	Salinity	Annual	1968	0.02	0.3
Bay)		Winter		0.51	0.2
		Spring		0.33	0.2
		Summer		0.49	0.2
		Autumn		0.18	0.3
	Chlorophyll a	Annual	1973	0.02	0.2
	(µg/l)	Winter		0.46	0.3
	_	Spring		0.02	0.4
		Summer		0.72	0.1
		Autumn		0.33	0.2
13090	Chlorophyll a	Annual	1989	<0.01	1.8
(Petronila	(µg/l)	Winter		0.09	3.8
Creek)	_	Spring		0.13	1.8
		Summer		0.05	2.2
		Autumn		0.03	1.3
13033 (San	Ammonium	Annual	1969	<0.01	-0.2
Fernando	(µM)	Winter		<0.01	-0.6
Creek)		Spring		0.01	-0.2

	Summer		0.16	-0.1
	Autumn		0.20	-0.1
Orthophosph	nate Annual	1973	0.05	1.0
(µM)	Winter		0.71	-0.6
	Spring		0.42	0.5
	Summer		<0.01	4.2
	Autumn		0.19	1.4
ТР	Annual	1969	0.13	0.5
	Winter		0.44	-0.5
	Spring		0.29	0.8
	Summer		<0.01	2.1
	Autumn		0.96	0.0

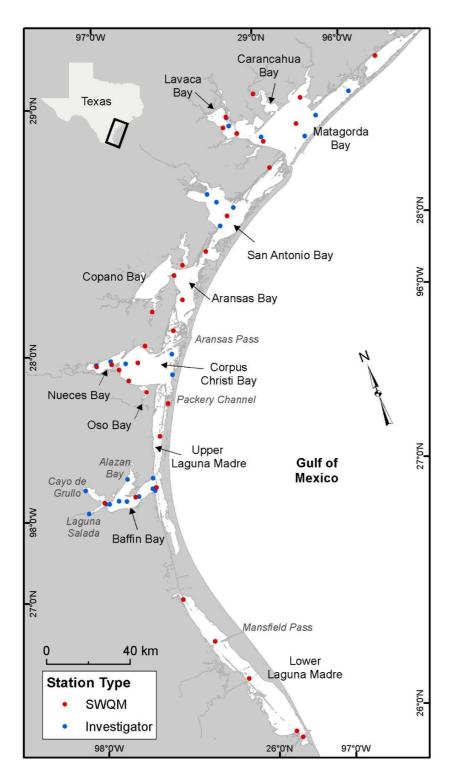


Figure 1. Location of SWQM long-term sampling locations (red dots) and investigator-led sampling locations (blue dots).

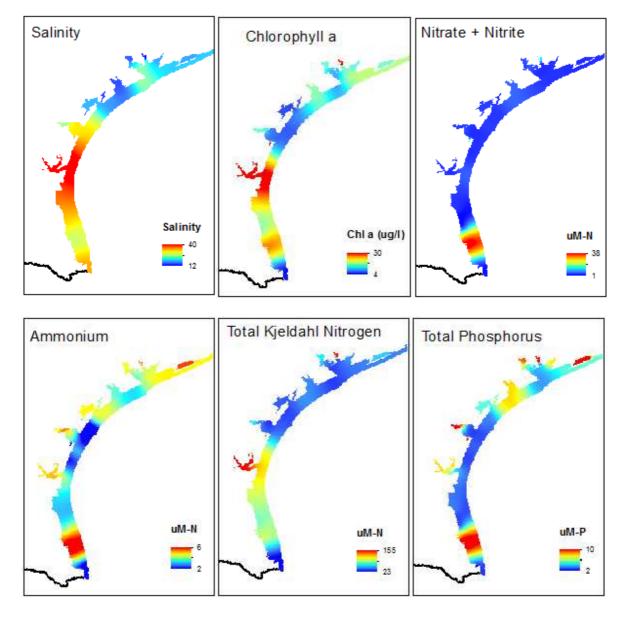


Figure 2. Mean concentrations of select water quality parameters in Texas estuaries, based on SWQM data from samples collected on a quarterly basis from 2003-2013.

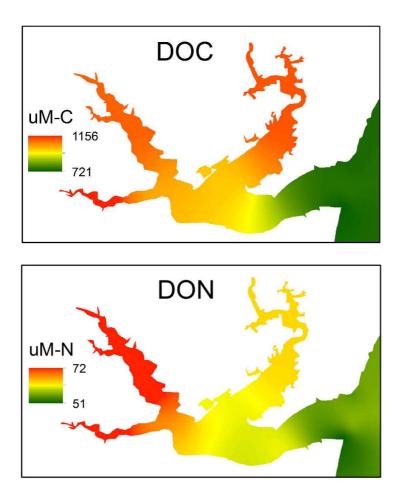


Figure 3. Mean dissolved organic carbon and dissolved organic nitrogen concentrations (μ M) in Baffin Bay, July 2013-June 2015.

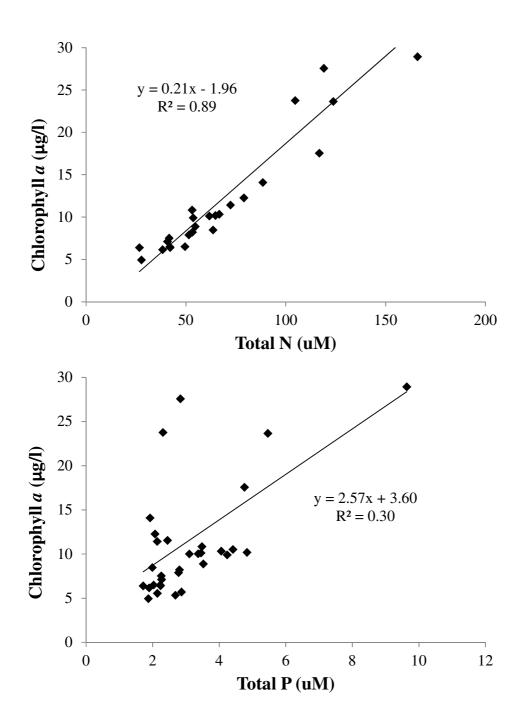


Figure 4. Relationship between Chlorophyll *a* (μ g/l) and Total Nitrogen (μ M) or Total P based on 2003-2013 mean for all Texas coast SWQM stations.

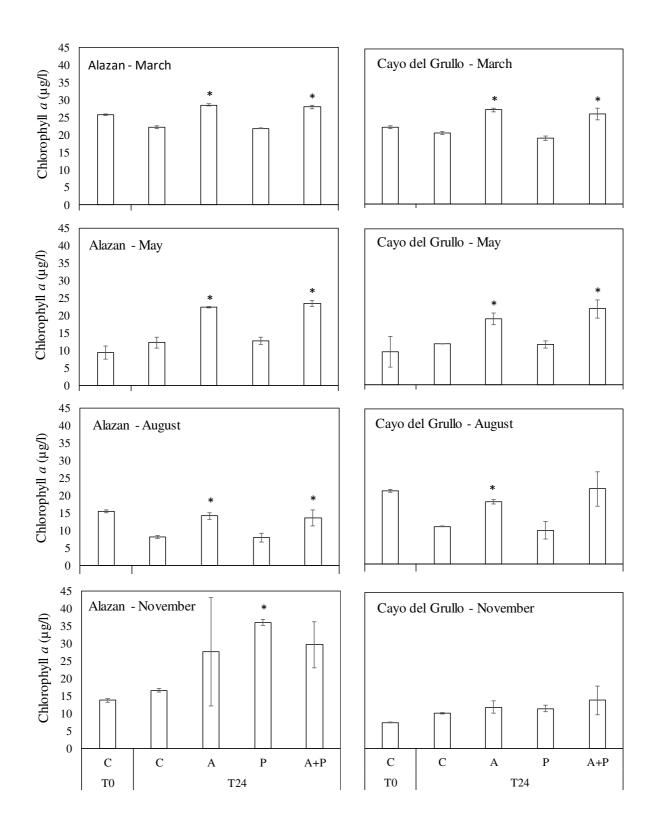


Figure 5. Results from nutrient addition bioassays conducted at two sites in Baffin Bay in 2015. Shown are the 0 and 24 hour chlorophyll *a* concentrations (μ g/l). "C" = Control, "A" =

ammonium addition, "P" = phosphate addition, and "A+P" = ammonium + phosphate addition. Asterisk above a treatment indicates that chlorophyll in that treatment was significantly different from chlorophyll in the control at 24 hours.

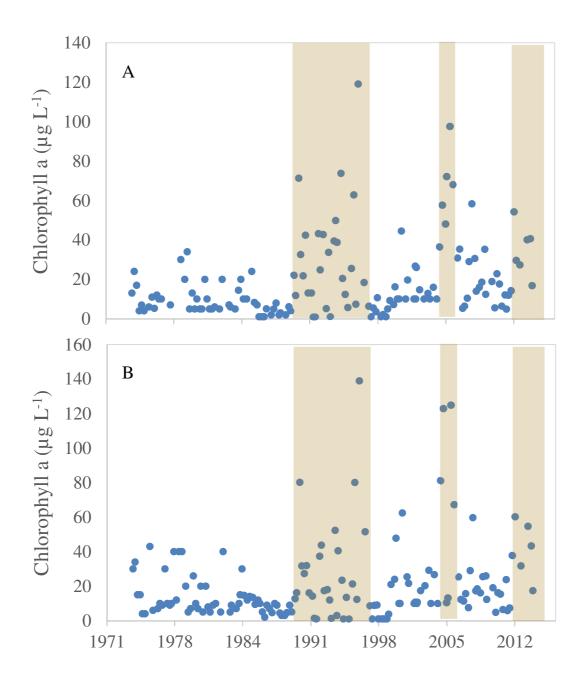


Figure 6. Change in chlorophyll *a* over time at station 13450 (A) and 13452 (B) in Baffin Bay, Texas. Periods of known "brown tide" blooms, as corroborated by peer reviewed publications or Texas Parks & Wildlife reports, are denoted by brown shaded areas.