Baffin Bay Volunteer Water Quality Monitoring Study: Synthesis of May 2013-January 2019 Data

Annual Report

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Executive Summary

The goal of this study is to quantify spatial-temporal distribution of key water quality variables in Baffin Bay. Sample collection began in May 2013 from 9 sites throughout Baffin Bay and continues to present, albeit from a reduced number of sites (6) since May 2017. Since the beginning of the study, Baffin Bay has undergone two distinct drought and wet cycles. From May 2013-March 2015, Baffin Bay experienced a significant, prolonged drought and hypersaline conditions. Chlorophyll $a$ concentrations were very high in the system, owing to the presence of a “brown tide” phytoplankton bloom. Nutrient ratios suggest alternating periods of nitrogen and phosphorus limitation of phytoplankton growth during this timeframe, although bioassays conducted as part of another study indicated that nitrogen was the primary nutrient limiting phytoplankton growth. In spring 2015, several periods of intense rainfall occurred in the Baffin Bay watershed and salinities dropped sharply to < 27. Chlorophyll decreased throughout the bay following this rainfall despite generally higher inorganic nutrient concentrations. One exception was at site 2 (Laguna Salada), where the brown tide bloom persisted. From summer 2015 to summer 2016, salinity gradually increased to the mid-30’s at most locations. This increase accelerated thereafter and salinity was ≥40 by October 2016. During this time, chlorophyll was lower on average than during the previous drought period. Although not presented here, brown tide abundances were also low. Nutrient data suggests that phosphorus may have limited the growth of non-brown tide phytoplankton. Salinity remained ≥ 40 until June 2018, after which rainfall increased and salinities decreased in the bay. Unlike during the prior wet period, chlorophyll increased during the most recent period and was relatively high (>20 µg/l) at many locations in Baffin Bay. Nutrient ratios were indicative of nitrogen limitation of phytoplankton growth, and interestingly dissolved organic nitrogen (DON) decreased concomitant with the chlorophyll increase, suggesting utilization by the phytoplankton. Overall, chlorophyll $a$ exceeded TCEQ screening levels for impairment throughout much of the study period and was frequently at levels that would be considered excessive by National Coastal Condition Report (EPA, 2012) standards.
Acknowledgements

First and foremost, we thank the many volunteers who dedicated four years of their time and resources to the collection of this water quality data in Baffin Bay. This study would not have been possible without their efforts. We are also grateful to the Celanese Corporation for funding. Finally, we thank our partners at the Coastal Bend Bays & Estuaries Program for their ongoing support and interest.
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Introduction

Cultural eutrophication is a major environmental threat facing coastal ecosystems worldwide (Nixon 1995; Diaz and Rosenberg 2008). Over the past 50 years, there has been a substantial increase in nutrient loading to the coastal zone, resulting in growing expression of symptoms such as persistent algal blooms, hypoxia/anoxia formation, and microbial pathogen growth among others (Nixon 1995; Boesch 2002; Rabalais et al. 2009). These symptoms often have deleterious consequences for ecosystem structure and function, resulting in such visible effects as fish kills and other animal mortalities, alteration of food webs and economic losses (Diaz and Rosenberg 1995; Boesch 2002). The most recent synthesis of data from the U.S. indicates that as of 2007, at least 30% of estuaries were considered moderately to highly eutrophic, with eutrophication pressures expected to grow in 65% of estuaries over the next decade (Bricker et al. 2007). Unfortunately, Texas estuaries have been poorly represented in national eutrophication assessments such as the aforementioned report, largely due to lack of sampling efforts and data coverage. Nonetheless, there is growing concern fueled by public observations and recent scientific assessments that several systems in South Texas are indeed undergoing significant eutrophication. One example is Baffin Bay, which represents critical habitat for several economically- and ecologically-important fish species and is popular with recreational fishermen.

In the past 1-2 decades, growing expression of symptoms of eutrophication such as hypoxia and dense algal (phytoplankton) blooms have been noted in Baffin Bay. Hypoxia and excessive phytoplankton growth, which are quite possibly intricately linked, are concerning because of their potential effects on ecosystem health and fisheries in coastal embayments. For instance, hypoxia has been linked to several large fish kills in Baffin Bay over the past 5-10 years (unpubl. Texas Parks & Wildlife Spills & Kills Team reports). Hypoxia formation tends to occur during warm summer-fall months, often following freshwater pulses that inject allochthonous nutrients and organic matter and induce stratification in the bays (unpubl. Texas Parks & Wildlife Spills & Kills Team reports). Co-occurrence of phytoplankton blooms and hypoxia have been noted in Baffin Bay as well (unpubl. Texas Parks & Wildlife Spills & Kills Team reports), and overall phytoplankton biomass frequently exceeds state screening levels, raising concerns about the potential role of nutrient-laden runoff (Montagna and Palmer 2012; this study). For instance, Baffin Bay has experienced prolonged, dense blooms of the brown tide organism, *Aureoumbra lagunensis*, since 1989 (Buskey et al. 1997; Buskey et al. 2001). More recently, a fish kill occurred
in 2010 and coincided not only with hypoxia, but also with a dense phytoplankton bloom of the dinoflagellate *Pyrodinium bahamense* and the diatom *Thalassiothrix sp.* (unpubl. Texas Parks & Wildlife Spills & Kills Team report).

Using data obtained primarily from TCEQ quarterly sampling, Montagna and Palmer (2012) documented a long-term increase in Kjehldahl nitrogen, nitrate and orthophosphate in Baffin Bay. Ammonium, chlorophyll *a* and nitrate also regularly exceeded state screening levels in a number of years. While state agency sampling efforts in Baffin Bay have been valuable for documenting long-term water quality changes in the system, their limited spatial-temporal coverage hinders determination of the timing and location of symptoms of water quality degradation, and also preclude determination of the main cause(s) of water quality degradation in the system. Here results are presented from an ongoing water quality monitoring study, the goals of which are to quantify spatial-temporal distributions of key water quality parameters in Baffin Bay, and to increase our understanding of the drivers of water quality change in this system.

**Methods**

*Study location* – Baffin Bay is a shallow (≤ 2-3 m depth) South Texas coastal embayment adjacent to the Laguna Madre (Figure 1). Residence time of water in Baffin Bay typically exceeds 1 year due to minimal tidal influence and freshwater inflows, and the system is prone to hypersaline conditions due to evaporation exceeding precipitation (Shormann 1992). Circulation in Baffin Bay is primarily driven by winds.

*Meteorological data* – Monthly mean precipitation data from the Naval Air Station Kingsville was obtained from the National Climatic Data Center. Using data from January 1973 through June 2014, monthly mean precipitation was calculated. The monthly deviation from this long-term monthly mean was then calculated, and is referred to as precipitation “anomaly”.

*Sample collection* – Water samples were collected on a monthly basis from May 2013 through October 2017 at 5-12 sites in Baffin Bay (Figure 2). Water samples were collected by volunteer citizen scientists from the start of the study until May 2017. In order to qualify for this program, volunteers had to undergo rigorous training in the lab of Dr. Michael Wetz (Texas A&M University - Corpus Christi) and demonstrate competency in field sample collection (documentation retained in Wetz lab). At each site, a profile of salinity, temperature, conductivity, dissolved oxygen and pH was obtained by lowering a YSI ProPlus sonde at 0.5 m increments through the water column.
Surface and near bottom discrete water samples were collected in a Van Dorn sampling device and transferred to acid-washed amber polycarbonate bottles. Bottles were stored on ice until return to a shore-based facility where processing of samples occurred.

Sample analyses – Chlorophyll *a* was determined from samples collected on, and extracted from Whatman GF/F filters (nominal pore size 0.7 µm). Chlorophyll was extracted using 90% acetone and analyzed fluorometrically. Inorganic nutrients (nitrate + nitrite (N+N), nitrite, silicate, orthophosphate, ammonium) were determined in the filtrate of water that passed through GF/F filters using a Seal QuAAtro autoanalyzer. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined in the filtrate of water that passed through GF/F filters using a Shimadzu TOC-V analyzer with nitrogen module. Dissolved organic nitrogen (DON) was estimated as the difference between TDN and inorganic nitrogen. Complete methodological details on wet chemical and YSI analyses can be obtained from Dr. Wetz.

Results

At the beginning of the study period in spring 2013, Baffin Bay was experiencing a significant, prolonged drought (Figure 3). In early fall 2013, the drought began to lessen and precipitation patterns more in accordance with long-term monthly averages developed. By spring 2015, several periods of intense rainfall occurred in the Baffin Bay watershed. These conditions reoccurred in spring 2016. From summer 2016-summer 2018, average to below average rainfall was observed. In fall 2018, several months of above average rainfall were noted.

Physical setting – Water temperature varied little between sampling locations. A distinct seasonal pattern was observed, with temperatures increasing in late winter-early spring, peaking during summer, and then decreasing in early fall (Figure 4). Salinity was very high at the start of the sampling period in May 2013, exceeding 70 at site 5 (upper Alazan) and site 2 (Laguna Salada) (Figure 5). Salinity tended to decrease through the middle of 2015, with the decrease accelerating in spring 2015 as a result of heavy rainfall in the watershed. From summer 2015 to summer 2016, salinity gradually increased to the mid-30’s at most locations. This increase accelerated thereafter and salinity was ≥40 by October 2016. Salinity remained ≥40 until June 2018, after which rainfall increased and salinities decreased in the bay. Strong salinity stratification (i.e., higher salinity in bottom waters than surface waters) of the water column was observed only episodically, being
most pronounced at tributary sites that were influenced by runoff, especially during 2015-2016 (Figure 6).

**Biological-chemical dynamics** – Chlorophyll \( a \) concentrations tended to be very high in Baffin Bay during this study, exceeding the TCEQ screening level (11.6 µg/l) in 305 of 529 samples (58%). Using a slightly more relaxed National Coastal Condition Report for “poor” condition (20 µg/l; NCCR 2012), chlorophyll \( a \) was still in excess in 155 of 529 sample collections (29%). Highest chlorophyll concentrations tended to be found in spring-summer coincident with higher water temperatures, especially when brown tide was the dominant phytoplankton taxa from 2013-early 2015 (Figure 7). Thereafter, the pattern became less pronounced, with occasional spring (2018) and even winter blooms (2018-2019) being noted. Distinct interannual variability was observed in addition to the seasonal patterns. For example, chlorophyll \( a \) tended to be lower during the lower salinity, “wet” conditions in spring-summer 2015 and 2016 compared to prior drought years, although localized very high chlorophyll was still observed. This pattern was reversed in the subsequent drought-wet cycle, with chlorophyll remaining low during the 2017 drought/high salinity conditions, and increasing substantially in 2018 during high rainfall, low salinity conditions. From a spatial standpoint, chlorophyll concentrations tended to be highest in the tributaries of western Baffin Bay, with much lower concentrations typically observed towards the mouth. In particular, site 2 (Laguna Salada) appears to be particularly susceptible to high phytoplankton biomass.

N+\( N \) concentration exceeded 5 µM at the beginning of the study period at all sites except 1 (4.4 µM), 8 and 9 (north and central mouth; < 1 µM) (Figure 8). Very high N+\( N \) concentrations (>35 µM) were noted at both sites 5 and 7. N+\( N \) concentrations decreased after May 2013 and were generally <1-4 µM thereafter through February 2015. In April 2015, N+\( N \) was 15.9 µM at site 1, but <0.6 µM at the other sites. In May 2015, two relatively N+\( N \) values were observed, 6.8 µM at site 3 and 28.3 µM at site 5, while other sites had N+\( N \) <1.5 µM. N+\( N \) concentrations were low again (<5 µM) at all sites from summer 2015 through early spring 2016. In March 2016, high N+\( N \) concentrations were observed at site 5 (48.5 µM) and site 1 (13.8 µM), concurrent with low salinity conditions, while other sites had N+\( N \) <5 µM. High N+\( N \) concentration was observed at site 5 in May 2016 (24.4 µM). Thereafter, surface N+\( N \) concentrations were generally low, with the exception of modest increases in December 2016 at sites 1 and 5. N+\( N \) concentrations in
bottom waters were typically less than in surface waters (Figure 9), likely due to lower oxygen levels in the bottom waters. Surface ammonium concentrations were high in July-August 2013, with highest concentrations observed at sites 2 and 5 (Figure 10). Ammonium declined thereafter, remaining relatively low through April 2015. In May and June 2015, high (>10 µM) ammonium concentrations were once again observed, this time at multiple sites coincident with relatively low salinity conditions. After decreasing at most sites through October 2015, high ammonium concentrations were observed in November 2015 at sites 3-6, though this was not associated with a salinity decrease or rainfall event. Ammonium concentrations moderated from December 2015-February 2016; thereafter, high ammonium concentrations were observed at sites 1, 2 and 5 in March and sites 1-5 in May 2016, coincident with high rainfall, lower salinity conditions. In July-August 2016, relatively high ammonium concentrations were observed in Alazan Bay extending out to the mouth. Thereafter, only ephemeral increases in ammonium were observed, primarily in the western part of the bay but occasionally at the mouth as well. Overall, ammonium concentrations tended to be much higher in the system during the “wet” period of 2015-2016 than during the earlier drought years. However, this pattern was not repeated with the wet conditions in 2018, when ammonium concentrations were relatively low. Bottom water ammonium concentrations tended to mirror patterns observed at the surface, although concentrations were frequently higher in the bottom waters (Figure 11). By far, the dominant form of nitrogen during the study period was dissolved organic nitrogen (DON), with DON concentrations regularly exceeding 35 µM (Figure 12). No clear seasonal pattern was observed in terms of DON. However, DON concentrations began to increase in the high rainfall, low salinity summer of 2015, peaking in late 2016. Since then, it appears as if the DON has been decreasing. Highest concentrations tended to be in the western part of Baffin Bay and tributaries, decreasing towards the mouth.

Surface orthophosphate concentrations exceeded 1 µM at the beginning of the study period at all sites except 8 and 9 (< 0.5 µM) (Figure 13). Very high surface orthophosphate concentrations (>5 µM) were noted at sites 3, 5 and 7. Orthophosphate concentrations were generally low after May 2013, with the exception of a small secondary peak in July-August 2013 in western Baffin Bay and concentrations of 2.1-2.6 µM at site 1 from March-May 2014. In April-June 2015, very high concentrations were observed at site 1, ranging from 9.6-10.7 µM. Likewise, in May and June 2015, the orthophosphate concentration at site 5 ranged from 5.3-6.2 µM. Orthophosphate concentrations were <0.6 µM from August-October 2015. Persistent high (0.9-12.0 µM)
orthophosphate concentrations were again observed at site 1 from November 2015-December 2016, and at site 5 in March, May and June 2016 (2.0-5.2 µM). Orthophosphate concentrations were generally low thereafter until summer 2018, when concentrations increased at all sites coincident with higher rainfall conditions. Orthophosphate concentrations were periodically elevated in near bottom waters, especially in May, June and August 2013 at various sites throughout Baffin Bay, and April-June 2015 and November 2015-June 2016 at site 1 (Figure 14). Silicate concentrations were highly variable between sites and dates in Baffin Bay. The most notable observations were very low silicate levels at various sites in 2015-2016, and much higher levels thereafter (Figure 15). Also assessed were two nutrient ratios (dissolved inorganic nitrogen:orthophosphate, dissolved inorganic nitrogen:silicate) that can give an indication of which element is limiting to phytoplankton growth. Early on in the study period, DIN:DIP varied from indicating nitrogen limitation (N:P<16) to indicating phosphorus limitation (N:P>16)(Figure 16). After the high rainfall period in spring 2015, DIN:DIP was more frequently indicative of phosphorus limitation until early 2018, when nitrogen limitation became more frequently observed. In general, silicate did not appear to be limiting, except episodically from spring 2015-spring 2016, when DIN:Si was >1 (Figure 17).

Dissolved organic carbon (DOC) concentrations were exceptionally high at the beginning of this study, exceeding 1000 µM at all locations (Figure 18). DOC subsequently decreased at most locations and was lower, but variable through spring 2016. Thereafter, it appears as if DOC increased concurrent with the return of higher salinity conditions. From late 2016 onward, a trend towards decreasing DOC was again observed. Overall, highest DOC concentrations tended to be found in the tributaries.

Dissolved oxygen (DO) displayed a clear seasonal pattern that can be linked to temperature, with lowest levels being observed in the warmer months and highest levels in winter (Figure 19). In summer 2013, several instances of hypoxic (<2 mg/l) bottom waters were observed. Yet in 2014, despite similarly high water temperatures, hypoxia was only observed at site 2 in July. The overall higher bottom DO levels in summer 2014 compared to summer 2013 may have been due to strong mixing (and less stratification; Fig. 7) in summer 2014. Hypoxia was observed again in May-June 2015, but only at site 5 coinciding with very low salinity conditions. Hypoxia was observed on two dates during summer 2017, but only at site 2. In September 2018, hypoxia was observed at site 1.
Discussion

Results from this study show the presence of significant spatial-temporal variability in terms of water quality dynamics in the system. Ultimately, this data, in conjunction with ongoing collections and a reanalysis of historical TCEQ data should provide a comprehensive understanding of water quality conditions, as well as environmental drivers that affect water quality in Baffin Bay.

At the beginning of the study period, Baffin Bay was experiencing a significant, prolonged drought and concurrently a major bloom of the brown tide organism *Aureoumbra lagunensis* (Wetz, unpubl. data). Hypersaline conditions associated with drought have previously been shown to favor brown tide blooms in the system (e.g., Buskey et al. 1997, 2001). One factor that has been overlooked is the role of nutrients. During the early part of this study (2013-early 2015), nutrient ratios suggested alternating conditions of nitrogen and phosphorus limitation of phytoplankton growth. However, nutrient addition bioassays conducted in 2014-2015 showed that only nitrogen addition stimulated phytoplankton growth. Sun et al. (2012) found that *A. lagunensis* has the ability to use organic forms of phosphorus, and thus may be less susceptible than other phytoplankton taxa to phosphorus limitation. Furthermore, Cira et al. (in prep) has determined that *A. lagunensis* abundances were negatively correlated with DON, implying that it was utilizing some fraction of the DON, further highlighting the importance of nitrogen. The strong seasonal pattern of high chlorophyll in spring-summer during 2013-early 2015, when *A. lagunensis* dominated the phytoplankton community, can be explained in part by water temperature. Recently, Cira et al. (in prep) determined that water temperature is an important factor regulating the growth of *A. lagunensis*. Thus the lower levels of chlorophyll in winter may be indicative of the effects of low temperatures.

From early fall 2013 through spring 2015, precipitation patterns developed that were more in accordance with long-term monthly averages, and salinities decreased. Despite the lower salinity levels, very high chlorophyll levels were noted in spring-summer 2014 as in spring-summer 2013. In spring 2015, chlorophyll noticeably decreased concurrent with several heavy precipitation events and lower salinity conditions, despite higher inorganic nutrient concentrations than during the earlier timeframe. Chlorophyll remained relatively low for an extended period thereafter. There are several possible explanations for the decrease in chlorophyll. First, it is likely that there
was significant flushing as well as reduced light from high turbidity that accompanied the spring 2015 rains in Baffin Bay. Another explanation (not mutually exclusive) is that microzooplankton grazing (e.g., Buskey et al. 1997, 2001) and/or benthic filter feeder removal of phytoplankton may have been depressed during the hypersaline conditions, but became important again with lower salinities. Finally, based on DIN:Si during that time, it is possible that silicate availability was limiting to the growth of diatoms in the system, but this would not have prevented other phytoplankton from growing.

During the most recent drought-wet cycle (2017-2018), chlorophyll concentrations behaved opposite what they did at the start of the study. For example, chlorophyll was lower on average during the drought of mid-2016 to early 2018 than during the previous drought period. Although not presented here, *A. lagunensis* abundances were also low. Nutrient data suggests that phosphorus may have limited the growth of non-brown tide phytoplankton. Salinity remained ≥ 40 until June 2018, after which rainfall increased and salinities decreased in the bay. Unlike during the prior wet period, chlorophyll increased during the most recent period and was relatively high (>20 µg/l) at many locations in Baffin Bay. Nutrient ratios were indicative of nitrogen limitation of phytoplankton growth, and interestingly dissolved organic nitrogen (DON) decreased concomitant with the chlorophyll increase, suggesting utilization by the phytoplankton.

A longer-term goal of researchers working on Baffin Bay-related water quality issues is to identify sources of nutrients to Baffin Bay. During the study period, surface N+N and ammonium levels were generally low except during wet periods, when high concentrations were commonly observed at the tributary sites. Similarly, high orthophosphate concentrations were observed during these periods in the Cayo del Grullo and upper Alazan Bay. Elevated concentrations of ammonium were also occasionally observed during summer in bottom waters, consistent with studies from this and other systems showing release of reduced nitrogen from suboxic sediments under warm conditions (e.g., An and Gardner 2002). DON concentrations were elevated throughout the year and in fact, the total dissolved nitrogen (i.e., DON + ammonium, N+N) and DON concentrations observed in Baffin Bay are consistently higher than many other estuaries in the Gulf of Mexico, including those of the central Texas coast (e.g., Bianchi 2007; Mooney & McClelland 2012; Wetz et al. 2017). DON concentrations began to increase in the high rainfall, low salinity summer of 2015, peaking in late 2016. Furthermore, highest concentrations tended to be in the western part of Baffin Bay and tributaries, decreasing towards the mouth. These findings
point to runoff from the watershed as a possible source of DON. Prevalence of high concentrations of reduced nitrogen such as ammonium and DON are important because they have been implicated as potentially favoring dominance by the brown tide organism over other healthy phytoplankton (Gobler et al. 2013). Output from the SPARROW nutrient loading model indicates that fertilizers and atmospheric deposition are the dominant sources of nitrogen to Baffin Bay, while fertilizer was the dominant source of phosphorus (Rebich et al. 2011). Internal loading from sediments in this system appear to another important source of inorganic nutrients to the water column, at least during the warm summer months. In terms of the source(s) of organic nitrogen, Ockerman and Petri (2001) pointed to crop residue as a major source of organic nitrogen during runoff events to Petronila Creek, a stream that flows into Baffin Bay. Alternatively, we have found very high (and increasing) chlorophyll levels in Petronila Creek based on TCEQ data (Wetz, unpubl. data), suggesting that this algal biomass may be flushed downstream to Baffin Bay during rain events and contribute to the organic nitrogen. During drought years however, other sources of organic nitrogen must be considered. Examples may include wastewater discharge from Kingsville, Alice and NAS Kingsville, septic from surrounding communities, as well as biotic sources (e.g., algal and seagrass exudation).

Organic matter concentrations in Baffin Bay tended to be very high during the study period. Sources of DOC are unclear, though DOC concentrations tended to be much higher in the western portion of Baffin Bay, possibly indicating tributary sources and/or internal sources such as phytoplankton exudation. In support of this, Cira et al. (in prep.) has found a strong correlation between *A. lagunensis* abundance and DOC, suggesting that exudate from the brown tide blooms contributes to the DOC pool in Baffin Bay. Regardless of source, these high levels of DOC as well as algal biomass are important because they may fuel microbial respiration and biological oxygen demand. Near bottom oxygen levels showed a distinct seasonal cycle that is undoubtedly temperature related, with lower temperatures capable of holding more oxygen than higher temperatures. Nonetheless, we occasionally observed hypoxic (<2 mg/l) conditions, and oxygen levels and were generally <4 mg/l throughout summer, indicative of intensive microbial respiration and utilization of labile organic matter. Previous studies have shown that hypoxic dissolved oxygen levels, and in some cases oxygen levels of <3-5 mg/l, can have sublethal and/or lethal effects on benthic organisms (e.g., Ritter and Montagna 1999; Diaz and Rosenberg 2008).
Overall, Baffin Bay is displaying multiple symptoms of eutrophication including very high organic carbon, organic nitrogen and chlorophyll concentrations, episodic hypoxia as well as symptoms not quantified here such as fish kills. Given the strong linkage between total nitrogen and chlorophyll along the Texas coast (e.g., Wetz et al. 2017), 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 eutrophic conditions in Baffin Bay and needs to be a focus of targeted reductions in the future.

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