Baffin Bay Volunteer Water Quality Monitoring Study: Synthesis of May 2013-July 2014 Data

Final Report

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Executive Summary

The goal of this study was to establish a spatially-temporally intensive water quality monitoring program in Baffin Bay, relying heavily on volunteer citizen scientists for data collection. Sample collection began in May 2013 from 9 sites throughout Baffin Bay and continues to present. At the beginning of the study period, Baffin Bay was experiencing a significant, prolonged drought. In early fall 2013, the drought began to lessen and precipitation patterns more in accordance with long-term monthly averages developed. Salinities were very high at the start of the sampling period (>60-70), but over the course of the study salinity tended to decrease through June 2014. Results show distinct seasonal and spatial patterns in key water quality parameters. Of particular interest is chlorophyll *a*, an indicator of algal biomass. Findings show persistent, excessive levels of chlorophyll in a large portion of Baffin Bay throughout the year that often exceeded TCEQ criteria for estuaries, indicative of a nutrient enriched system. Levels of inorganic nutrients capable of supporting algal growth (ammonium, nitrate, orthophosphate) were relatively high at the beginning of the record, but decreased thereafter. However, concentrations of ammonium and orthophosphate remained elevated in near bottom waters through the end of summer 2013, indicating continued availability of nutrients via recycling to support algal growth. Dissolved organic nitrogen levels were very high in the system, with concentrations consistently exceeding 35 µM throughout the study. Dissolved organic carbon levels were also very high in spring-early summer of 2013 (718 to >2400 µM) and declined thereafter, but still consistently exceeding 400 µM. Dissolved oxygen levels showed a distinct seasonal cycle that is temperature dependent. Undersaturated dissolved oxygen levels were noted each summer in Baffin Bay, indicative of high biological oxygen demand that is supported by labile organic matter. Interestingly, dissolved oxygen reached much lower (i.e., hypoxic) levels in summer 2013 compared to summer 2014. The cause of this interannual variability is unclear, though salinity stratification of the water column was much less pronounced in summer 2014, indicating an influence of physical dynamics on oxygen levels. These results highlight the necessity of additional data collections in order to fully elucidate seasonal and interannual nutrient and oxygen dynamics in Baffin Bay, as well as to begin to determine potential sources of nutrients.

Acknowledgements

First and foremost, we thank the many volunteers who dedicated 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 entities who provided funding for the first year of this study, including Kleberg County, Celanese Corporation, the Coastal Bend Bays & Estuaries Program, Coastal Conservation Association and the Saltwater Fisheries Enhancement Association.

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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 including 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 five 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 criteria, 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

1990 (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 criteria for water quality standards 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. The goal of this study was to establish a spatially-temporally intensive water quality monitoring program in Baffin Bay, relying heavily on volunteer citizen scientists for data collection.

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 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.

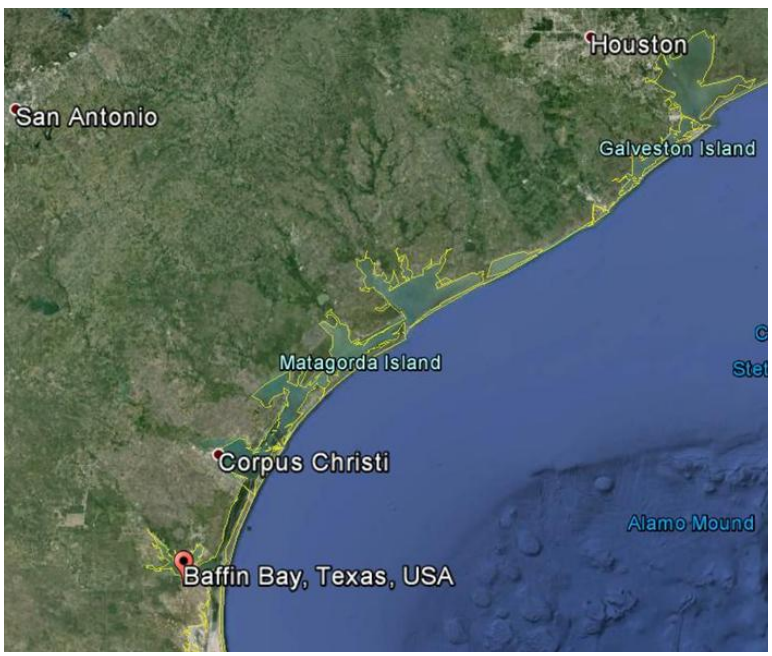

Figure 1. Map of Baffin Bay, located ~50 km southwest of Corpus Christi, TX.

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 heretofore referred to as precipitation "anomaly".

Sample collection – Water samples were collected on a monthly basis from May 2013 through July 2014 at 5-12 sites in Baffin Bay, weather permitting (Table 1). This included 9 permanent sites (Figure 2) and 3 additional sites in the head of each tributary (Cayo del Grullo, Laguna Salada, Alazan) following significant rain events. Water samples were collected by volunteer citizen scientists. 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

Sampling Date	Sites
May 15th and 16th, 2013	8
June 13th, 2013	9
July 18th, 2013	12
August 15th, 2013	9
September 18th, 2013	9
October 18th, 2013	5; adverse weather at other sites
November 15th, 2013	9
December 13th, 2013	9
January 16th, 2014	9
February 13th, 2014	9
March 19th, 2014	9
April 16th, 2014	9
May 16th, 2014	12
June 27th, 2014	9
July 17th, 2014	9

Table 1. Sampling events completed to date.

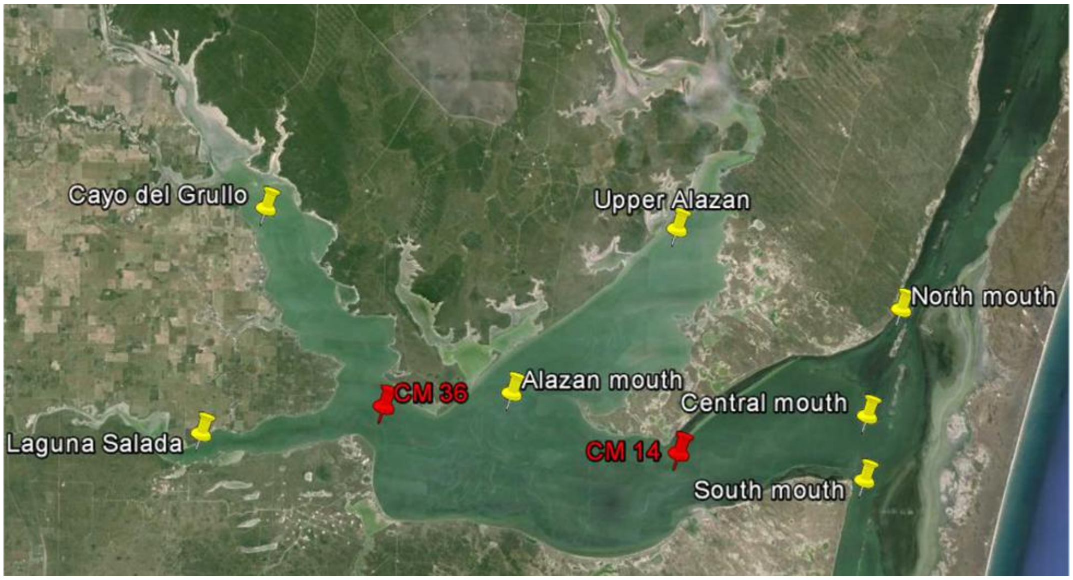

Figure 2. Map of permanent sampling locations in Baffin Bay. Red markers indicate two sites that are visited as part of TCEQ's quarterly monitoring program.

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. Michael Wetz.

Results

At the beginning of the study period, Baffin Bay was experiencing a significant, prolonged drought (Fig. 3). In early fall 2013, the drought began to lessen and precipitation patterns more in accordance with long-term monthly averages developed (Fig. 3).

Physical setting - Temperature followed a distinct seasonal pattern, with temperatures increasing in late winter-early spring, peaking during summer, and then decreasing in early fall (Fig. 4). There were no obvious differences between sites in terms of temperature. Salinities were very high at the start of the sampling period in May 2013, exceeding 70 in the upper Alazan and Laguna Salada (Fig. 5). Highest salinities were consistently recorded in western Baffin Bay, particularly in the three tributaries, while lowest salinities were observed near the mouth of Baffin Bay. Over the course of the study, salinities in general tended to decrease until June 2014, when salinities began to increase again in most of the western portion of Baffin Bay (Fig.

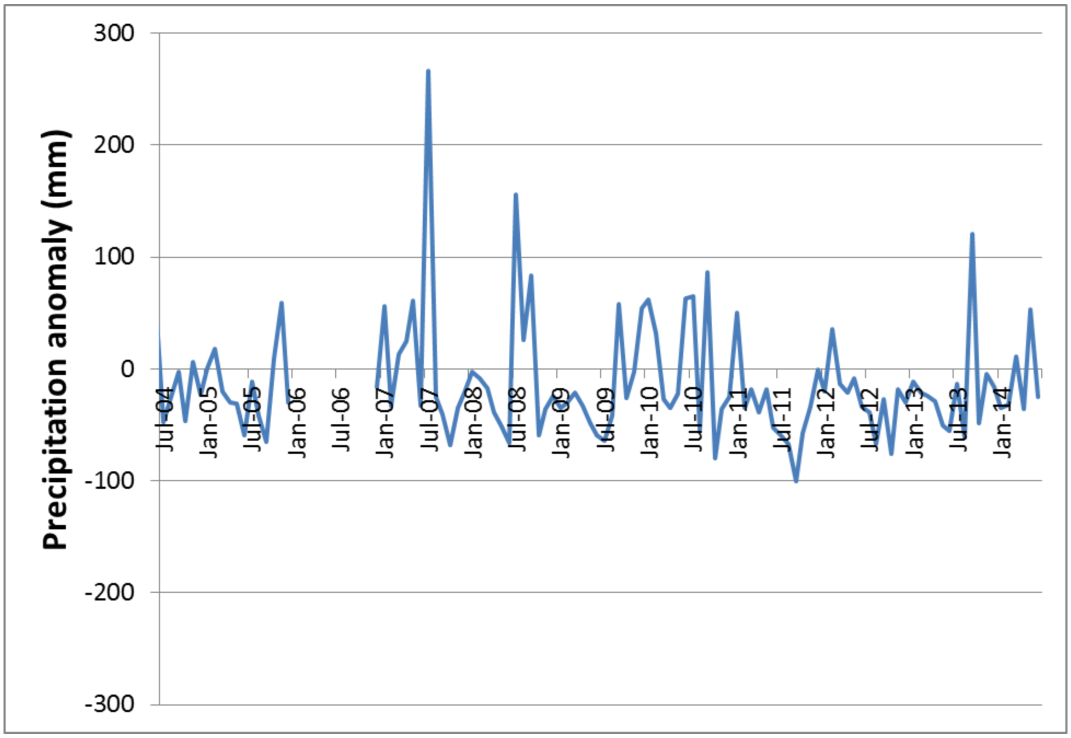

Figure 3. Precipitation anomaly (deviation from 1974-2014 monthly mean) at Kingsville Naval Air Station from 2004 to 2014.

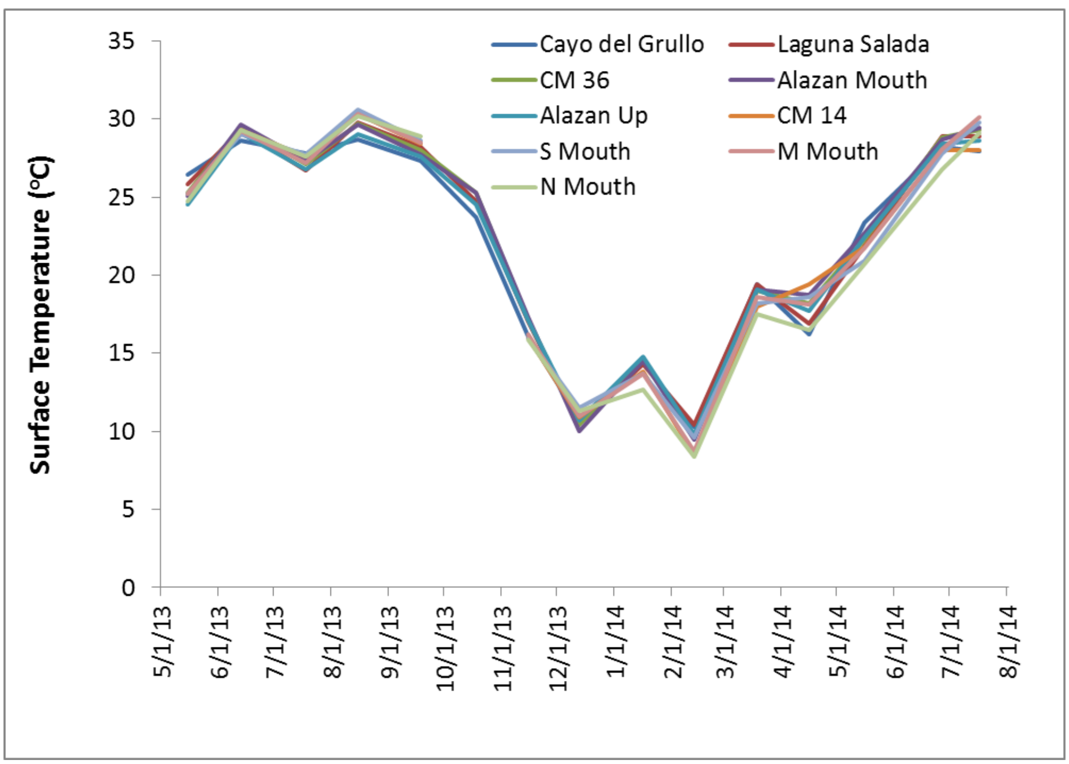

Figure 4. Surface temperature in Baffin Bay.

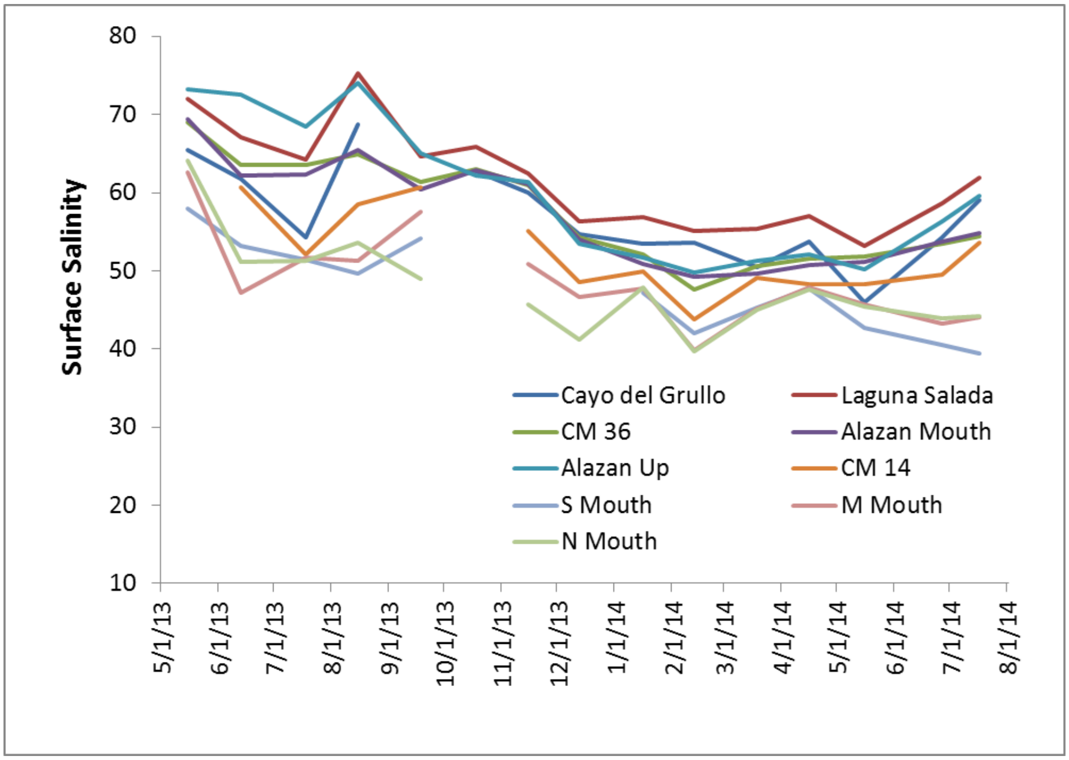

Figure 5. Surface salinity in Baffin Bay.

Figure 6. Surface salinity in western compared to eastern Baffin Bay. "West" includes upper Alazan, lower Alazan, CM 36, Laguna Salada and Cayo del Grullo sites. "East" includes CM 14, north/central/south mouth sites.

5). In early summer of both 2013 and 2014, intrusion of lower salinity water from Laguna Madre is apparent, particularly in the eastern portion of Baffin Bay where salinities decreased during this time (Fig. 5,6). This influence of lower salinity Laguna Madre water did not extend into western Baffin Bay however. Strong salinity stratification (i.e., higher salinity in subpycnocline waters than surface waters) of the water column was observed in summer 2013, but was not as noticeable in summer 2014 (Fig. 7).

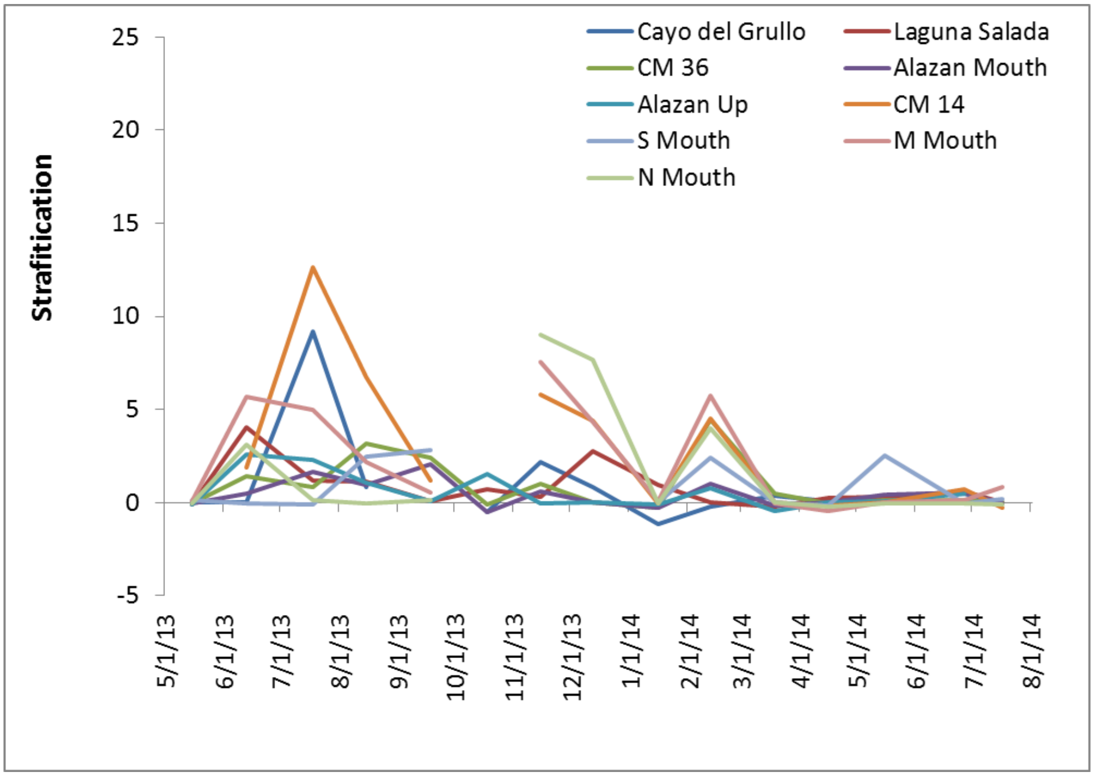

Figure 7. Stratification index (=Bottom minus surface salinity) in Baffin Bay.

Biological-chemical dynamics – Chlorophyll *a* concentrations tended to be very high in Baffin Bay during this study, exceeding the TCEQ criteria (11.6 µg/l) in 109 of 130 sample collections (83%). Using a slightly more relaxed National Coastal Condition Report for "poor" condition (20 µg/l; NCCR 2012), chlorophyll *a* was still in excess in 78 of 130 sample collections (60%). A distinct seasonal pattern was observed in terms of chlorophyll *a*, with very high levels noted in May-September 2013, after which chlorophyll decreased to a wintertime low in January and February (Fig. 8). Chlorophyll began to increase again thereafter, peaking in June-July 2014. During the observed intrusion of lower salinity Laguna Madre water in early summer of both years, chlorophyll tended to decrease in the eastern portion of Baffin Bay, but

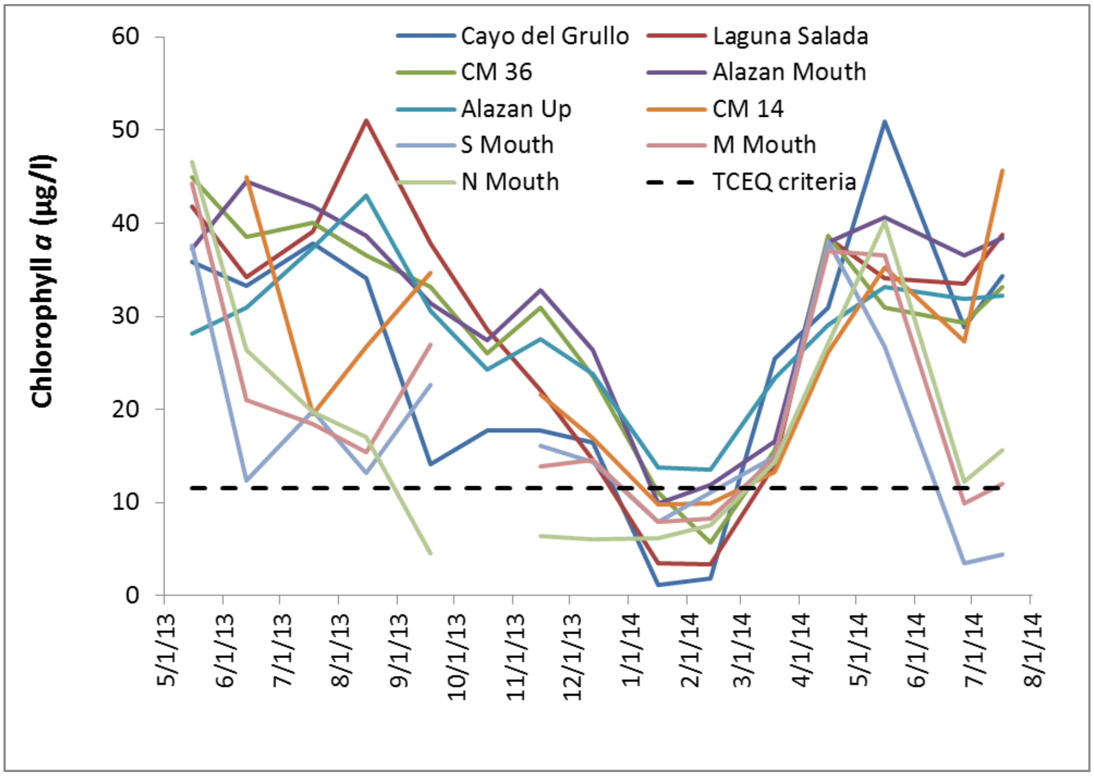

Figure 8. Chlorophyll *a* in Baffin Bay.

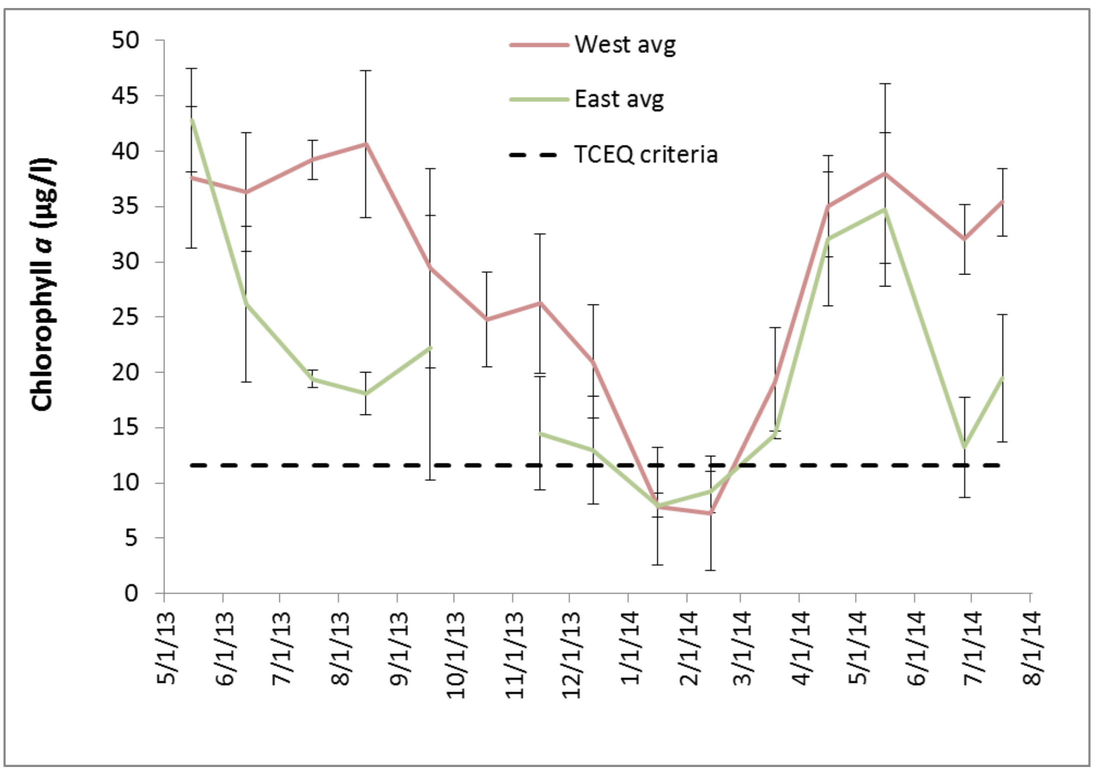

Figure 9. Chlorophyll *a* in western compared to eastern Baffin Bay. "West" includes upper Alazan, lower Alazan, CM 36, Laguna Salada and Cayo del Grullo sites. "East" includes CM 14, north/central/south mouth sites.

remained elevated in the western portion (Fig. 8,9).

In terms of the inorganic nutrients that may support phytoplankton growth, surface nitrate plus nitrite (N+N) concentrations exceeded 5 µM at the beginning of the study period at all sites except Cayo del Grullo (4.4 µM), and the north and central sites at the mouth (< 1 µM) (Fig. 10).

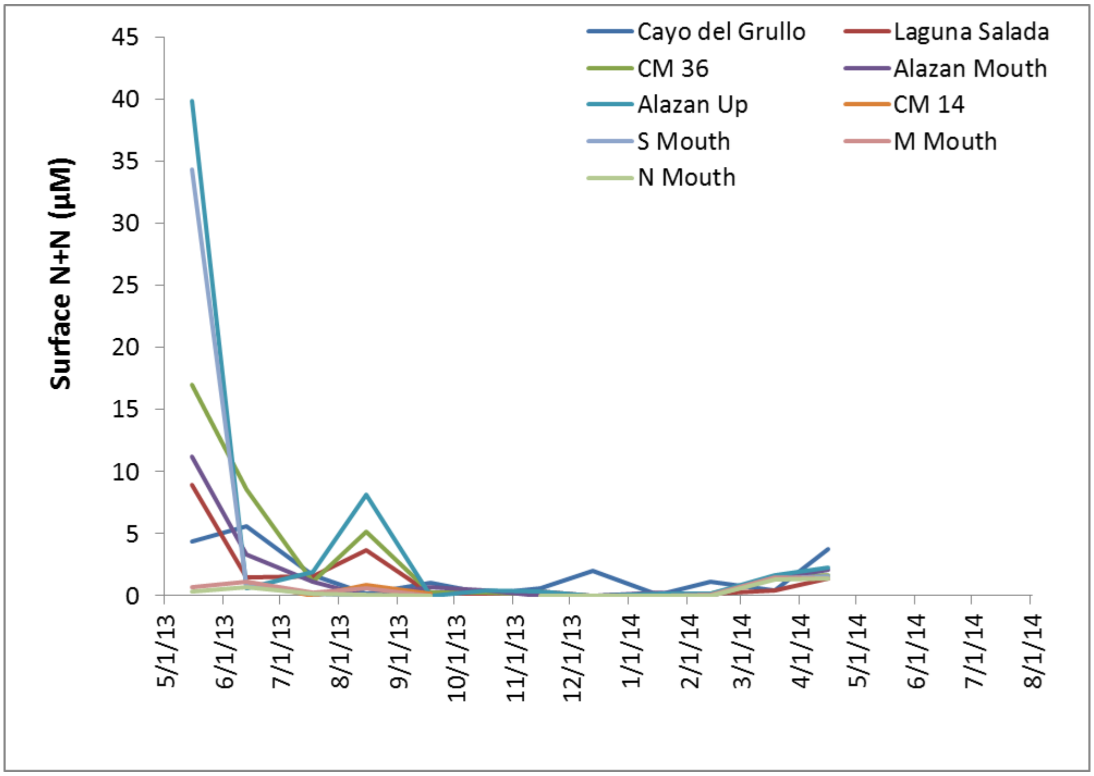

Figure 10. Surface N+N in Baffin Bay.

Very high N+N concentrations (>35 µM) were noted at both the upper Alazan site and south site at the mouth. N+N concentrations decreased after May 2013 and were generally <4 µM thereafter through April 2014, with the exception of a small secondary peak in August 2013 at the upper Alazan, CM 36 and Laguna Salada sites. N+N concentrations were occasionally elevated in near bottom waters, especially during May through August 2013 (Fig. 11). Surface ammonium concentrations peaked in July-August 2013, with highest concentrations observed at the upper Alazan and Laguna Salada sites, and declined thereafter (Fig. 12). Elevated ammonium concentrations were also observed from May through August in near bottom waters at most sites (Fig. 13). Ammonium concentrations in near bottom water declined thereafter and remained low through April 2014 except for episodic increases. By far, the dominant form of

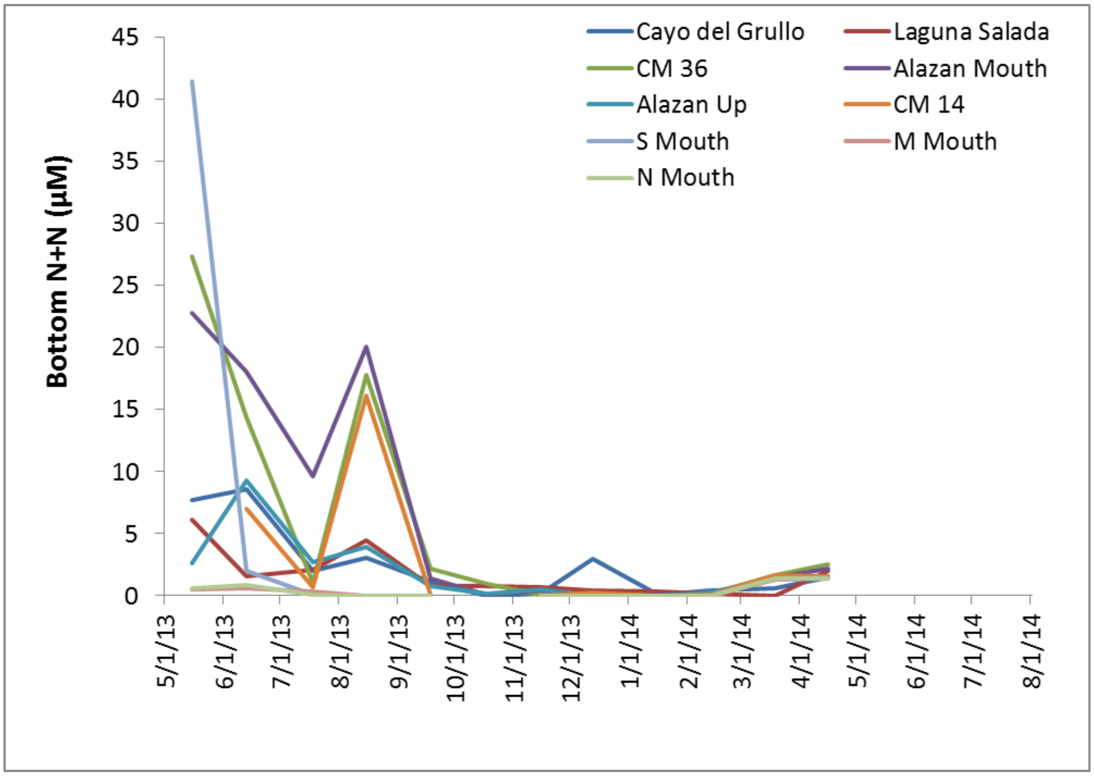

Figure 11. Bottom N+N in Baffin Bay.

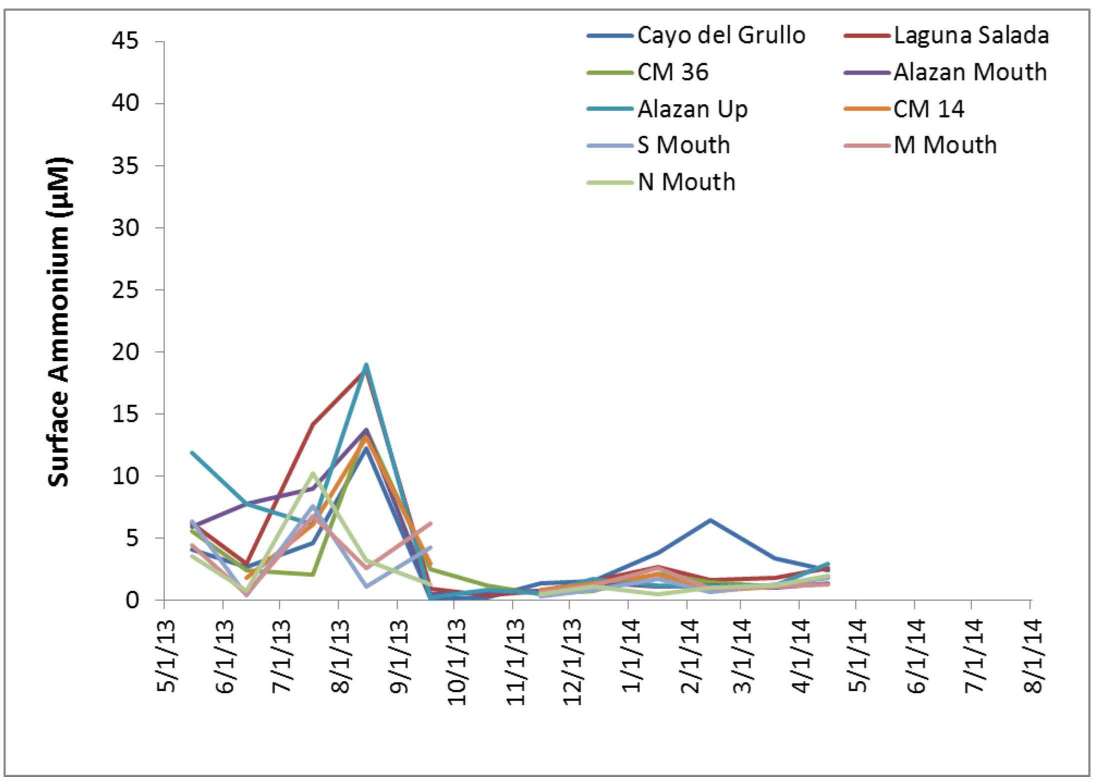

Figure 12. Surface ammonium in Baffin Bay.

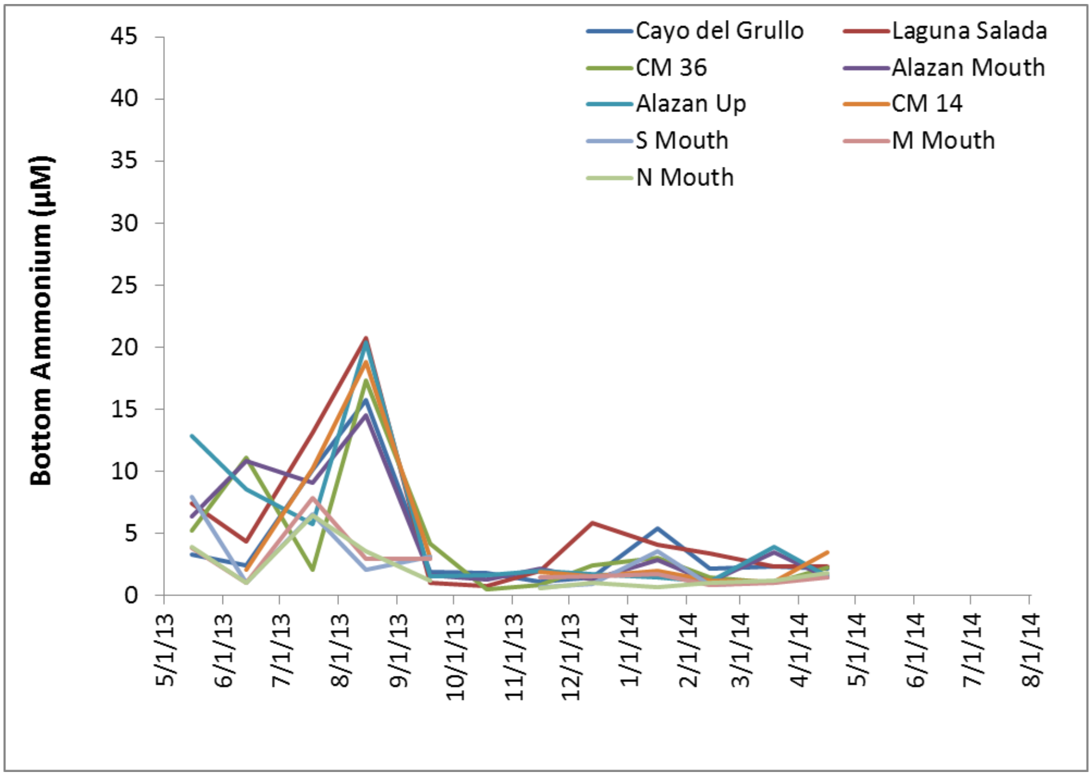

Figure 13. Bottom ammonium in Baffin Bay.

nitrogen during the study period was as dissolved organic nitrogen (DON), with DON concentrations regularly exceeding 35 µM (Fig. 14). No clear seasonal pattern was observed in terms of DON. At the time of this report, total nitrogen data had not been QA/QC'd and is not included. However, initial screening of that data indicates that at times, a fraction of the organic nitrogen equivalent to that found as DON is in the form of particulate organic nitrogen in Baffin Bay. Surface orthophosphate concentrations exceeded 1 µM at the beginning of the study period at all sites except the north and central sites at the mouth (< 0.5 µM) (Fig. 15). Very high surface orthophosphate concentrations (>5 µM) were noted at CM 36, upper Alazan, and south site at the mouth (Fig. 15). Orthophosphate concentrations decreased after May 2013 and were generally <1 µM thereafter through April 2014, with the exception of a small secondary peak in July-August 2013 in western Baffin Bay. Orthophosphate concentrations were periodically elevated in near bottom waters, especially in May, June and August 2013, and exceeded surface orthophosphate concentrations at times (Fig. 16). The inorganic nitrogen to phosphorus ratio, one indicator of the limiting nutrient (i.e., N or P), exceeded the threshold level (16) for P-

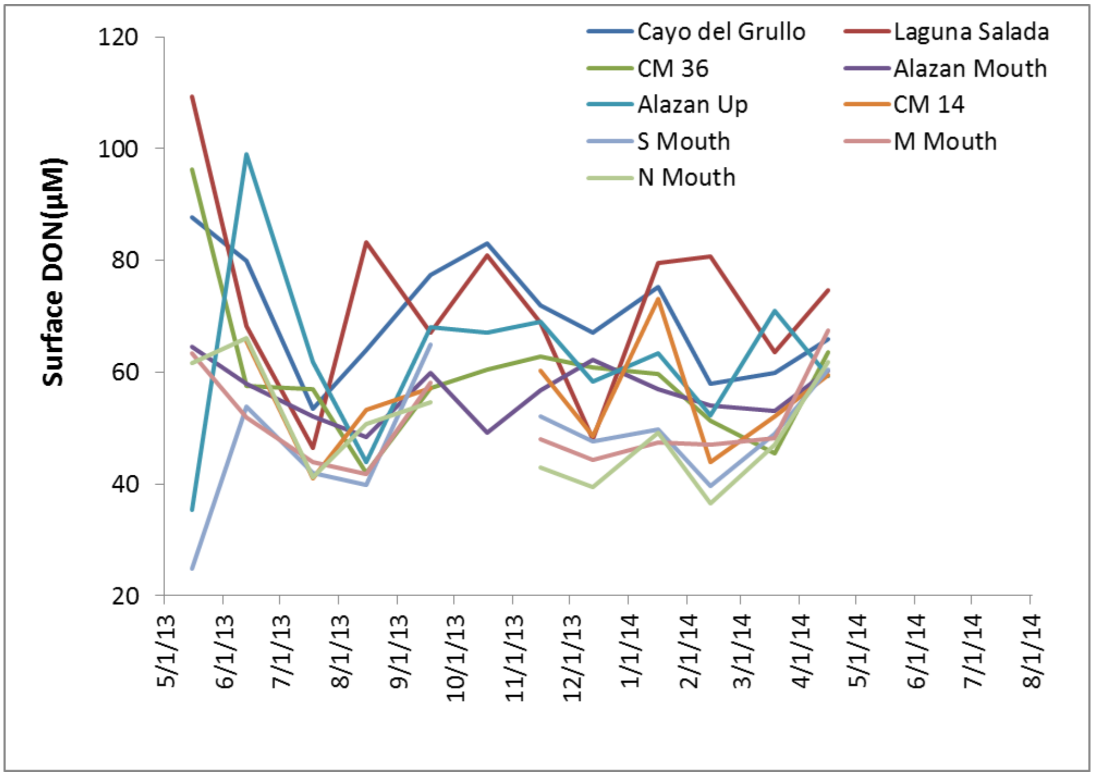

Figure 14. Surface dissolved organic nitrogen in Baffin Bay.

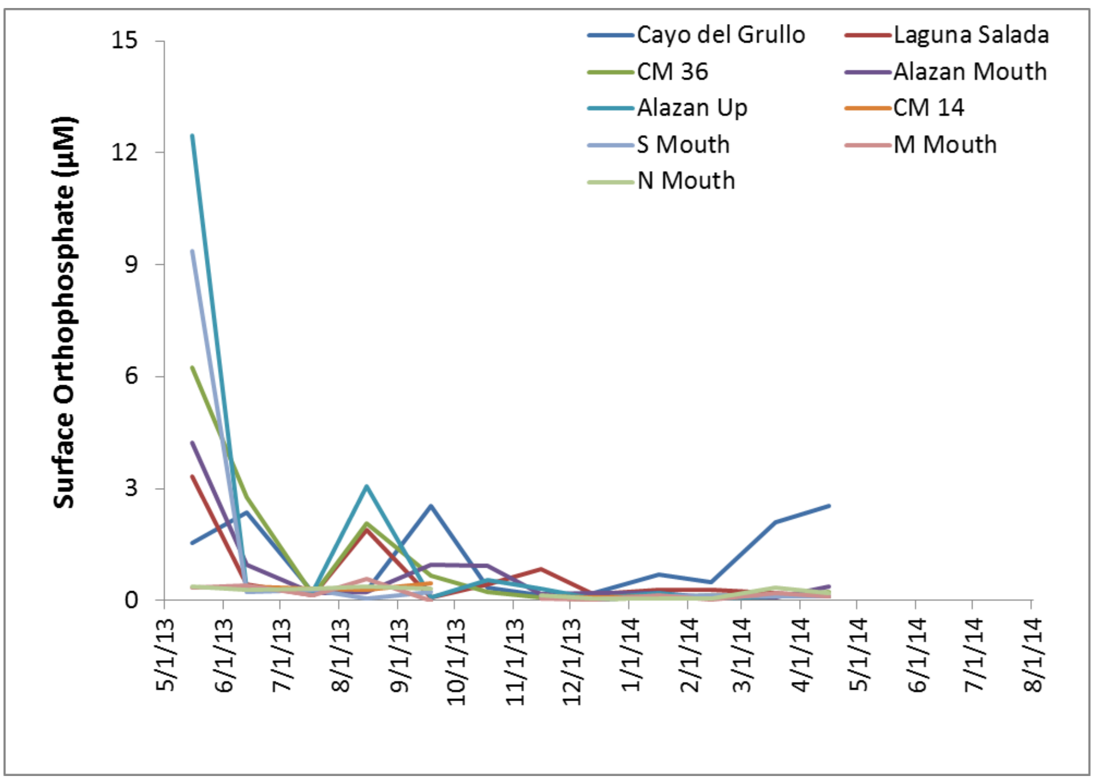

Figure 15. Surface orthophosphate in Baffin Bay.

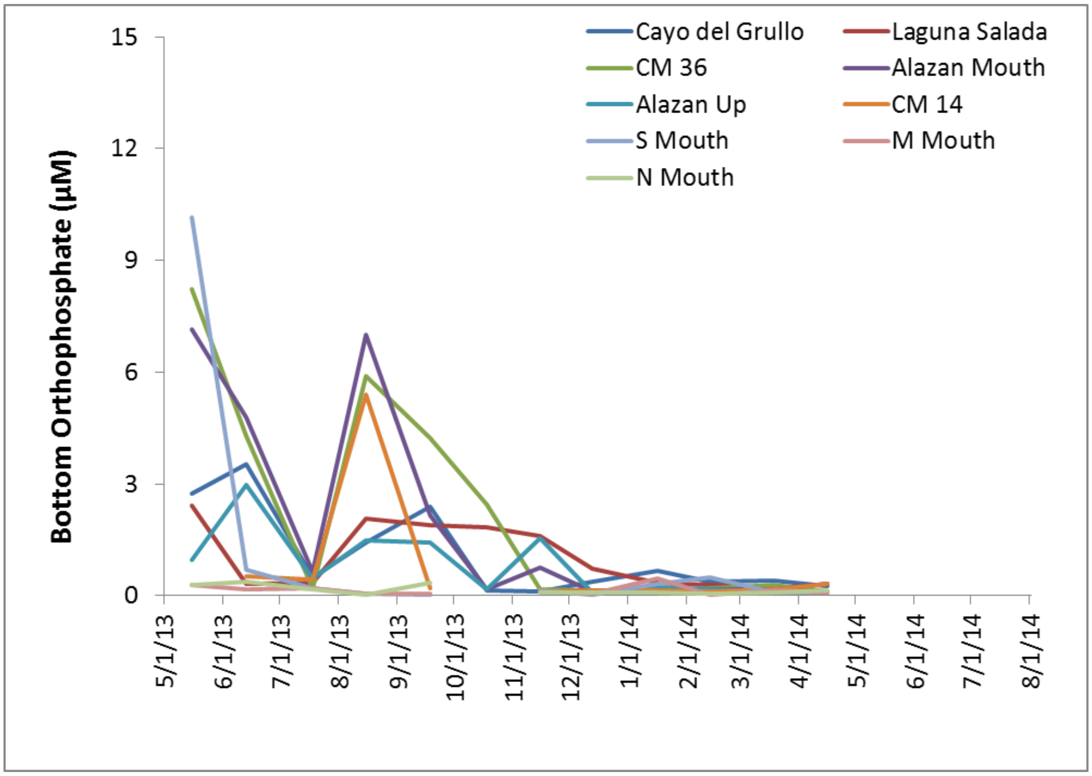

Figure 16. Bottom orthophosphate in Baffin Bay.

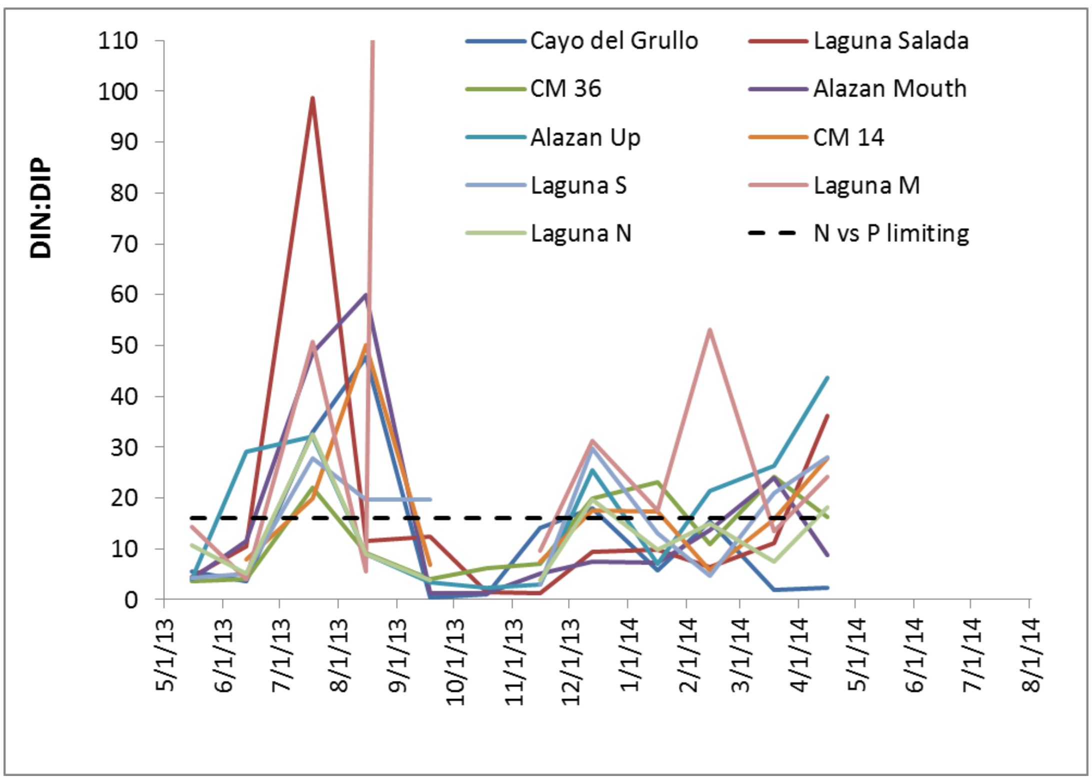

Figure 17. Ratio of dissolved inorganic nitrogen to orthophosphate in surface waters of Baffin Bay. Dashed line at N:P of 16 is the Redfield ratio, above which P is believed to be limiting to algal growth and below which N is believed to be limiting.

limiting conditions in summer 2013, and then fell below this threshold in fall, indicating N-limiting conditions (Fig. 17). For the remainder of the study period, not clear pattern was observed. Silicate concentrations were generally >20 µM, with the exception of sites at the mouth where concentrations as low as <1 µM were occasionally observed, especially during fall-winter (Fig. 18).

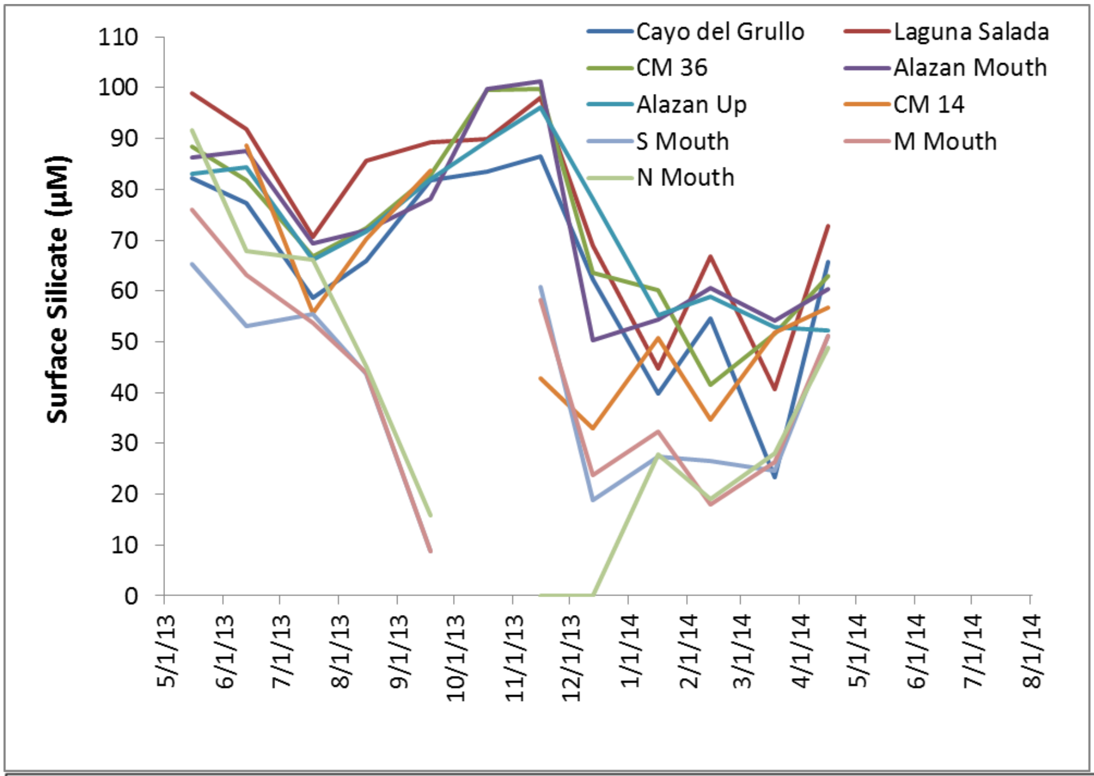

Figure 18. Surface silicate in Baffin Bay.

Dissolved organic carbon (DOC) represents a biogeochemically important constituent of coastal waters, where it supports bacterial respiration (an aerobic process). DOC concentrations were exceptionally high at the beginning of this study, exceeding 1000 µM at all locations (Fig. 19). DOC subsequently decreased at most locations and remained fairly constant after summer 2013. Highest DOC concentrations tended to be found in the western portion of Baffin Bay. At the time of this report, total organic carbon data had not been QA/QC'd and is not included. However, initial screening of that data indicates that at times, a fraction of the organic carbon equivalent to that found as DOC is in the form of particulate organic carbon in Baffin Bay.

Dissolved oxygen displayed a clear seasonal pattern that can be linked to temperature, with lowest levels being observed in the warmer summer months and highest levels in winter (Fig.

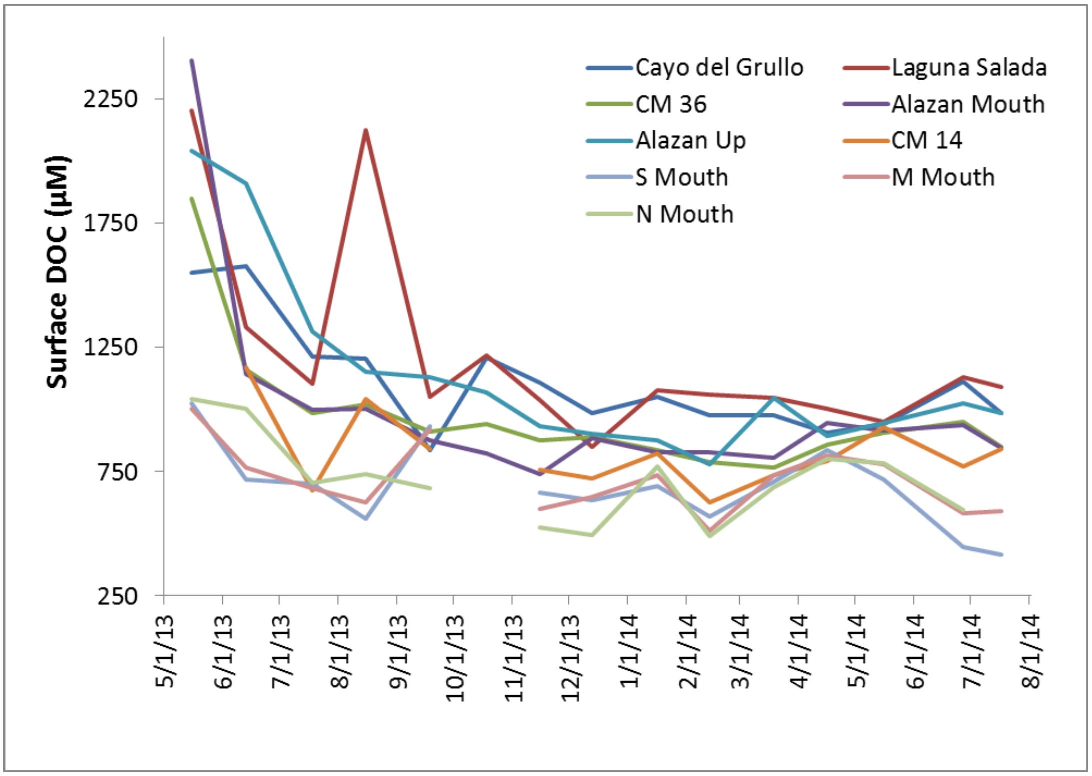

Figure 19. Surface dissolved organic carbon in Baffin Bay.

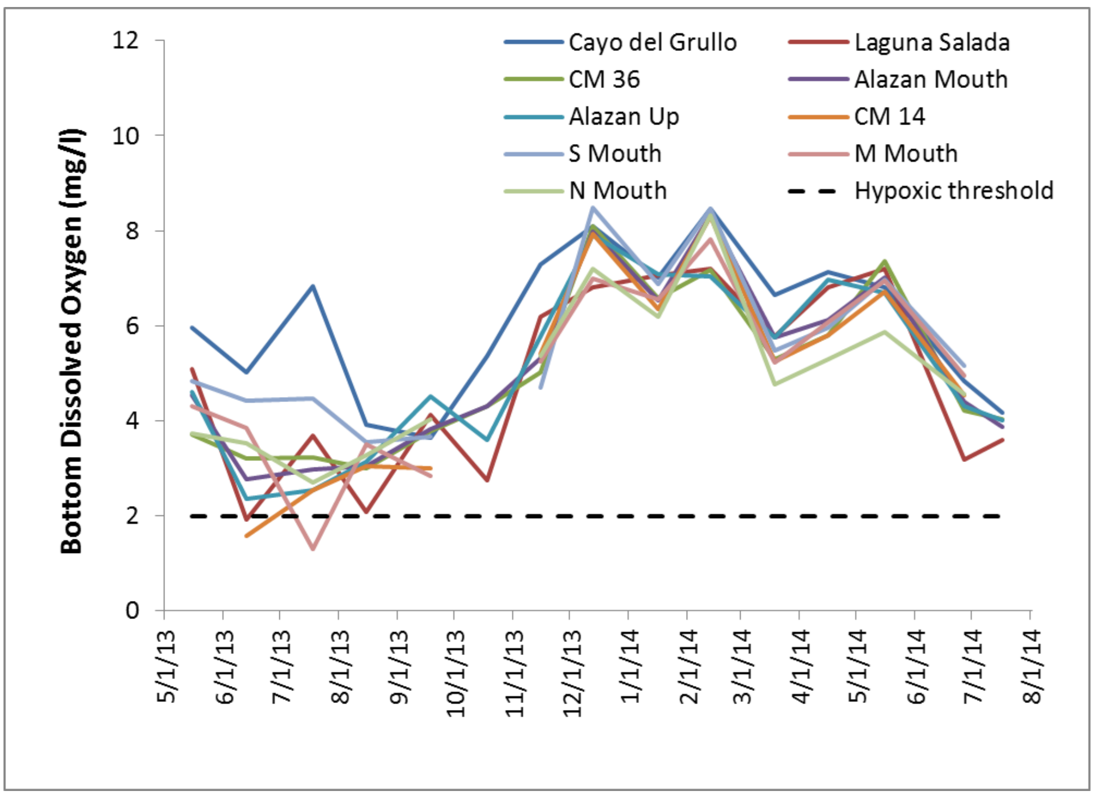

Figure 20. Bottom dissolved oxygen in Baffin Bay. Dashed line indicates the hypoxia threshold.

20). In summer 2013, several instances of sub-hypoxic bottom waters were observed. Yet in 2014, despite similarly high water temperatures, hypoxia was not observed. No clear spatial patterns are evident, though the dataset is far too limited to determine this.

Discussion

Results from the first year of a multi-year water quality data collection effort in Baffin Bay show the presence of seasonal patterns in terms of water quality dynamics and sources/fate of nutrients and organic matter in the system. Ultimately, this data, in conjunction with ongoing collections over the next two years 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). Chlorophyll *a*, a key indicator of phytoplankton (algal) biomass, exceeded TCEQ criteria throughout much of the study period and was frequently at levels that would be considered excessive even by National Coastal Condition Report (EPA, 2012) standards. The strong seasonal pattern of high chlorophyll in spring through fall can be explained in part by light and temperature. That is, phytoplankton growth is dependent on ample light levels for photosynthesis, and is often correlated with water temperature as well. Thus the wintertime low levels of chlorophyll may be indicative of either low light, low temperatures, or both.

From early fall 2013 and continuing to the end of the study period, precipitation patterns developed that were more in accordance with long-term monthly averages, and salinities decreased. Nonetheless, as light and temperature began to increase between February and March 2014, a corresponding increase in chlorophyll occurred and overall, very high chlorophyll levels were noted through mid-2014. An interesting feature in terms of chlorophyll, observed in both 2013 and 2014, is a sharp decrease in chlorophyll between May and June in the eastern portion of Baffin Bay. In both years, this appeared to correlate with an intrusion of lower salinity, oligotrophic water from Laguna Madre in Baffin Bay. We believe this is due to the seasonal shift in wind direction along the Texas coast, which results in southeasterly winds becoming established during this time of year. Interestingly, salinity and chlorophyll levels were largely unaffected in the western Baffin Bay. A TAMU-CC Ph.D. student (Emily Cira) will be conducting a study of this phenomenon beginning in 2015. If confirmed, this finding highlights the importance of water exchange with Laguna Madre in terms of water quality dynamics in Baffin Bay.

In addition to light and temperature, nutrient (primarily nitrogen and phosphorus) availability is a major control on phytoplankton growth. Results from this study show that the nitrogenous nutrients available to phytoplankton are primarily reduced species, including DON and secondarily ammonium. During this study period, surface N+N levels were relatively low except in May 2013. As in other estuarine systems, it appears that nutrient cycling and availability is strongly influenced by water temperature in Baffin Bay. For example, during summer 2013, relatively high concentrations of ammonium were prevalent compared to oxidized N+N, and may result from such processes as fluxes out of near bottom waters, recycling within the water column, and photochemical alterations, among others. Furthermore, elevated concentrations of ammonium were observed during summer in near 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). These reducing conditions became less prevalent as temperatures decreased during fall and winter, and consequently ammonium levels in both surface and bottom waters decreased considerably. Despite this, DON concentrations remained elevated throughout the year. 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). 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). Orthophosphate concentrations in surface waters were only episodically elevated, though like ammonium, high near bottom water concentrations were occasionally observed during summer. Our group has collected additional samples to determine total dissolved phosphorus and dissolved organic phosphorus concentrations, and will report that data in future syntheses. A previous study (Cotner et al. 2004) highlighted the potential for phosphorus to become limiting (to phytoplankton growth) in Baffin Bay, and our initial findings based on inorganic nitrogen to phosphorus ratios supports this notion. As part of a GLO-funded study, we will conduct nutrient addition bioassays beginning in early 2015 to further test for nutrient limitation of phytoplankton growth in Baffin Bay.

A longer term goal of this study is to begin to identify sources of nutrients to Baffin Bay. Clearly the sediments in this system are a potentially important source of nutrients to the water column, at least on a seasonal basis. At this point, the role of watershed derived nutrients remains enigmatic and will require additional data collection. However, the finding of relatively low N+N concentrations in surface waters does not discount the potential importance of watershed-derived nutrients. For instance, An and Gardner (2002) reported high rates of dissimilatory nitrate reduction to ammonium in Baffin Bay, which can result in nitrate being transformed to ammonium, a process that may mask the influence of watershed inputs. Furthermore, results from our rain event samplings, which will be reported in future syntheses, suggests that episodic events, not captured by monthly sampling, may be important for delivering nutrients from the watershed to Baffin Bay. Other sources of nutrients, such as groundwater and atmospheric deposition, must be considered in future nutrient budgeting efforts as well.

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. Additionally, DOC concentrations were occasionally high in near bottom waters (data not presented). High particulate organic matter concentrations were also observed and tended to mirror chlorophyll levels, indicating significant contribution of phytoplankton carbon to water column particulate organic matter. These high levels of organic matter 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 routinely observed below saturation oxygen levels, especially during the summer, indicative of intensive microbial respiration and utilization of labile organic matter. Dissolved oxygen occasionally reached hypoxic (<2 mg/) levels in summer 2013, and were generally <4 mg/l during that time. Previous studies have shown hypoxic dissolved oxygen levels, and in some cases oxygen levels of <3 mg/l, to have sublethal and/or lethal effects on benthic organisms (e.g., Ritter and Montagna 1999; Diaz and Rosenberg 2008). Interestingly, to date it appears that bottom dissolved oxygen levels during summer 2014 are not approaching the low levels observed in summer 2013. Although the cause of this year-to-year difference is as of yet unexplained, one possible cause is the apparently much weaker stratification (i.e., stronger or more persistent mixing and/or less freshwater inflow) observed during summer 2014 compared to summer 2013. Without discounting the obvious role that the high organic matter concentrations play in terms of driving biological oxygen demand, this finding of interannual differences in oxygen levels would again highlight the important role that physical processes play in Baffin Bay water quality dynamics.

In the second year of this study (June 2014-May 2015), we will continue to focus on additional data collection to verify previously observed patterns and to begin to develop an ecosystem health index following previously established protocols (i.e., NCCR 2012). This additional data will be necessary to begin to explore interannual variability in more detail. Additionally, we plan to deploy Hydrolab sensors in Baffin Bay in early 2015 for continuous monitoring of water quality, allowing for better determination of daily to weekly timescales of water quality change. Finally, research will be undertaken to explore in much greater detail the interactions between physical drivers (circulation, winds) and water quality dynamics in the system.

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