PROGRESS REPORT

(Project Name) Baffin Bay volunteer water quality study: Data collection and outreach to address water quality concerns

(GLO Contract No.) 15-044-000-8389

(Reporting Period) 10/1/2014-9/30/2016

Task 1: Water quality sampling

- Status of the task during this reporting period: ☐ in progress **X** completed

- Briefly describe major accomplishments for this reporting period.

  Water samples were collected from nine sites in Baffin Bay monthly through June 2016.

- List the deliverable(s)/milestone(s) completed during this reporting period. (Submit a copy of your completed deliverable(s)/milestone(s) with this report.)

  A final data report was submitted to the GLO, as was a file containing all raw data. In addition, copies of all presentations (4 total) made at scientific conferences have been provided to GLO. One peer reviewed manuscript is currently under review (in the journal *Estuarine, Coastal and Shelf Science*) and another will be submitted in late 2016. The first manuscript highlights the very high levels of organic nitrogen in Baffin Bay compared to other bays, which (organic nitrogen) has been shown elsewhere to be a significant contributor to brown tide blooms. The second manuscript will focus on the effects of freshwater inflow on water quality in Baffin Bay and other Texas estuaries. Copies of all manuscripts will be provided to GLO as they are published.

- Were there any problems or obstacles encountered during this reporting period (e.g., delays, remedial action taken, schedule revision). ☐ Yes **X** No If yes, please explain:

Task 2: Nutrient addition bioassays

- Status of the task during this reporting period: ☐ in progress **X** completed

- Briefly describe major accomplishments for this reporting period.

  Bioassays were conducted on a quarterly basis in Baffin Bay in 2015.

- List the deliverable(s)/milestone(s) completed during this reporting period. (Submit a copy of your completed deliverable(s)/milestone(s) with this report.)

A final data report was submitted to GLO, as was a file containing all raw data. In addition, copies of all presentations (4 total) made at scientific conferences have been provided to GLO. One peer reviewed manuscript is currently under review (in the journal *Estuarine, Coastal and Shelf Science*) and another will be submitted in late 2016. Copies of all manuscripts will be provided to GLO as they are published.

- Were there any problems or obstacles encountered during this reporting period (e.g., delays, remedial action taken, schedule revision). ☐ Yes **X** No If yes, please explain:

  N/A

Task 3: Outreach

- Status of the task during this reporting period: ☐ in progress **X** completed

- Briefly describe major accomplishments for this reporting period.

  Education and outreach were vital components of this study. Four undergraduates, one M.S. student, and one Ph.D. student participated in the field or bioassay research components of this study. Results from this study, as well as more general information on the significance of Baffin Bay, were presented in a number of venues including classroom presentations (2 total), public seminars (5 total), and a public "Baffin Bay research" symposium held in conjunction with the Coastal Bend Bays Foundation (www.baysfoundation.org). Results were also discussed to various degrees in 9 television or newspaper interviews.

- List the deliverable(s)/milestone(s) completed during this reporting period. (Submit a copy of your completed deliverable(s)/milestone(s) with this report.)

  Copies of all classroom and public presentations, as well as flyers, sign in sheets and photos from the Baffin Bay symposium were provided to GLO.

- Were there any problems or obstacles encountered during this reporting period (e.g., delays, remedial action taken, schedule revision). ☐ Yes **X** No If yes, please explain:

  N/A

Baffin Bay volunteer water quality study: Data collection and outreach to address water quality concerns

Final Report

GLO Contract No. 15-044-000-8389
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Table of Contents

Research Findings:

Executive Summary

Here we report results from a 3-year study of the spatial-temporal distribution of select water quality parameters in a subtropical estuary, Baffin Bay (Texas). Sample collection began in May 2013 from 9 sites throughout Baffin Bay and relied on volunteer citizen scientists for collections.

At the beginning of the study period, Baffin Bay was experiencing a significant, prolonged drought and hypersaline conditions. Chlorophyll *a* concentrations were very high in the system, owing to the presence of a brown tide bloom. By spring 2015, El Niño-like conditions developed, which led to several periods of intense rainfall in the Baffin Bay watershed and a sharp decrease in salinities. Since then, chlorophyll has decreased possibly due to flushing, reduced light from runoff-derived high turbidity, and/or increased consumption by microzooplankton and benthic filter feeders. 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 even by National Coastal Condition Report (EPA, 2012) standards. A strong seasonal pattern of high chlorophyll in spring-summer and low chlorophyll in winter was observed, which can be explained by light availability and water temperature. An interesting feature in terms of chlorophyll, observed in all three summers, is a sharp decrease in chlorophyll between May and June in the eastern portion of Baffin Bay. In each case, this appeared to correlate with an intrusion of oligotrophic water from Laguna Madre in Baffin Bay.

During the study period, surface nitrate + nitrite (N+N) and phosphate concentrations were relatively low except in May 2013 at several sites, and at the Cayo del Grullo and upper Alazan sites following the spring 2015 and 2016 rains. Very high ammonium concentrations were observed from spring 2015-onward, especially at the tributary sites, pointing to watershed sources for both N+N and ammonium. Elevated concentrations of ammonium and phosphate were observed during summer in near bottom waters, consistent with studies from this and other systems showing release of nutrients from suboxic sediments under warm conditions. Dissolved organic nitrogen (DON) concentrations were elevated throughout the year, especially at the tributary sites, and accounted for the largest pool of nitrogen in the system. In fact, the total dissolved nitrogen 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. The spatial distribution of DON within Baffin Bay argues for tributary sources and/or internal sources such as phytoplankton exudation. 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.

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 at both sites in March and May 2015. 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. In November 2015, a statistically significant increase in chlorophyll occurred in the phosphate addition treatment compared to the control 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. No statistically significant effect of ammonium and/or phosphate was observed at the Cayo del Grullo site.

DOC concentrations were very high in Baffin Bay and tended to be much higher in the western portion of Baffin Bay, indicating tributary sources and/or internal sources such as phytoplankton exudation. 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 routinely observed undersaturated oxygen levels, especially during the summer, indicative of intensive microbial respiration and utilization of labile organic matter.

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, 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 may need to be a focus of targeted reductions in the future.

Outreach Efforts

Education and outreach were vital components of this study. Four undergraduates, one M.S. student, and one Ph.D. student participated in the field or bioassay research components of this study. Results from this study, as well as more general information on the significance of Baffin Bay, were presented in a number of venues including classroom presentations, public seminars, and a public "Baffin Bay research" symposium held in conjunction with the Coastal Bend Bays Foundation (www.baysfoundation.org). Below is a complete list of outreach and education efforts that were undertaken as part of this study. Supporting documents will be provided to GLO separately.

News articles:

"Studying a bay: focus goes from sensational to scientific as data found; Corpus Christi Caller Times; November 23rd, 2014 edition; http://www.caller.com/sports/outdoors/sikes-baffin-bay-focus-goes-from-sensational-to-science_36546222

"Brown tide study gets closer to answers"; Corpus Christi Caller Times; April 22nd, 2015 edition; http://www.caller.com/sports/outdoors/brown-tide-study-gets-closer-to-answers_27777629

"Special report: state of the bay"; KIII-TV (Corpus Christi); aired on evening newscast, April 23rd, 2015; http://www.kiiitv.com/story/28887126/special-report-state-of-the-bay

"The lure of Baffin in summer"; Corpus Christi Caller Times; August 22nd, 2015 edition; http://www.caller.com/sports/outdoors/the-lure-of-baffin-in-summer-1def52a3-075b-0679-e053-0100007f55f4-322604381.html

"Science students become stewards through research"; Corpus Christi Caller Times; January 22nd, 2016 edition; http://www.caller.com/news/local/science-students-become-stewards-through-research-295196cd-1fef-04c1-e053-0100007f1fe7-365942821.html

"Abandon the bait and take the plastic plunge"; Corpus Christi Caller Times; December 12th, 2015 edition; http://www.caller.com/sports/outdoors/abandon-the-bait-and-take-the-plastic-plunge-2665e7c1-7858-2535-e053-0100007fe2df-361691051.html

"Rain helped bays but did little for lakes"; Corpus Christi Caller Times; May 18th, 2016; http://www.caller.com/sports/outdoors/rain-helped-bays-but-did-little-for-lakes-330bf587-f6f2-

3375-e053-0100007feeed--380039641.html

"Baffin Bay symposium"; KRIS-TV (Corpus Christi); aired on evening newscast, June 28th, 2016; http://www.kristv.com/story/32322273/baffin-bay-symposium

"Research on Baffin Bay reaches historic high"; Corpus Christi Caller Times; June 27th, 2016; http://www.caller.com/news/local/research-on-baffin-bay-reaches-historic-high-3642b5e7-8244-4ff6-e053-0100007fb595-384592111.html

Presentations (scientific conferences):

1. Ph.D. student Emily Cira gave a talk at the 2015 Coastal & Estuarine Research Federation conference in Portland, Oregon, in November. Title: Nutrient controls upon phytoplankton growth in a eutrophying, brown tide-dominated South Texas estuary (Baffin Bay).

2. M.S. student Kenneth Hayes gave a poster presentation at the 2015 Coastal & Estuarine Research Federation conference in Portland, Oregon, in November. Title: Spatial-temporal distribution of organic carbon and nitrogen in a eutrophic estuary (Baffin Bay, TX).

3. M.S. student Kenneth Hayes gave a poster presentation at the 2016 Texas Bays & Estuaries meeting in Port Aransas, TX, in April. Title: Spatial-temporal distribution of organic carbon and nitrogen in a eutrophic estuary (Baffin Bay, TX).

4. Wetz gave a talk at the 2016 Texas Bays & Estuaries meeting in Port Aransas, TX, in April. Title: Three years of water quality sampling in Baffin Bay by "citizen scientists": what have we learned?

Presentations (public, local):

1. Riviera, TX (Hubert-Kaufer Park), April 24th, 2015. At this "data conference", Wetz shared results from the study with project volunteers as well as representatives from the Coastal Bend Bays & Estuaries Program.

2. Bishop, TX (Celanese Corp.), June 8th, 2015. At this public meeting, Wetz shared results from the study with >40 members of the public. This meeting was sponsored by the Celanese Corp. as well as the Coastal Bend Bays & Estuaries Program.

3. Wetz gave a talk to the Texas Ag Industries Group on October 2nd, 2015.

4. Wetz gave a talk to Ms. Rosana Ryan's class at Riviera High School on October 9th about project results.

5. Wetz gave a talk on the project at the Baffin Bay research symposium held on June 28th, 2016, in Corpus Christi, TX.

University Classes:

In mid-April 2015 and 2016, Wetz utilized data obtained from this study as part of a case study on eutrophication in a class that he taught at TAMU-CC, “Global Change Ecology”. Enrollment was as follows:

2015: Global Change Ecology: 14 undergraduates
2016: Global Change Ecology: 24 undergraduates

Other:

1. On June 2nd, 2015, Wetz reviewed presentations from senior high school students in Mrs. Ryan’s class at Riviera High School (Riviera, TX) and provided feedback to them. Their presentations were about water quality sampling that they had conducted in Baffin Bay.

2. A public symposium was held on Baffin Bay research on June 28th, 2016, at the Del Mar Center for Economic Development in Corpus Christi, Texas. The event was heavily publicized through flyers, roadside billboards and media advertisements. 101 people signed in for the symposium. The TAMU-CC homepage provided a nice synopsis of the event, which can be found here: http://www.tamucc.edu/news/2016/06/070116%20baffin%20bay%20symposium%20post%20event.html#.V-QlezVGxp5

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 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. Here results are presented from the first three years of a volunteer 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 heretofore referred to as precipitation “anomaly”.

Sample collection – Water samples were collected on a monthly basis from May 2013 through July 2016 at 5-9 sites (Fig. 2). 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 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.

Nutrient addition bioassays - Nutrient addition bioassays were conducted with water from the Alazan and Cayo del Grullo tributaries of Baffin Bay on March 28, May 23, August 21, and November 20, 2015 (Figure 1). For each event, surface water was collected in 10-20 L carboys (pre-washed with 10% HCL) and covered with black bags until transferred into 1 L Cubitainers (Hedwin Co.; ~80% transparent to ambient photosynthetically active radiation, PAR; pre-washed with 10% HCL) for nutrient amendments. Four treatments were run per site in triplicate, including; 1) Control (no nutrient addition), 2) 10 µM-N as ammonium chloride, 3) 0.6 µM-P as monopotassium phosphate, and 4) 10 µM-N and 0.6 µM-P. Cubitainers were subsequently incubated at the surface ~10m 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 ~ 1m above the water's surface, and surface water temperature was monitored with a Hydrolab DS5X submerged to ~0.5m 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.

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). By spring 2015, El Niño-like conditions developed, which led to several periods of intense rainfall in the Baffin Bay watershed. These conditions persisted through spring 2016, during which several additional high rainfall periods were observed (Fig. 3).

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 (Fig. 4). It is interesting to note that winter (December-January-February; DJF) water temperature increased in a step-wise manner from winter 2013-2014 to winter 2015-2016. For example, the winter 2013-2014 average was 11.4^{o}C compared to winter 2014-2015 (16.9^{o}C) and winter 2015-2016 (19.1^{o}C) (Fig. 4). Salinity was very high at the start of the sampling period in May 2013, exceeding 70 in the upper Alazan and Laguna Salada (Fig. 5). Salinity tended to decrease over the course of the study, with the decrease accelerating in spring 2015 as a result of heavy rainfall in the watershed (Fig. 5). Prior to that, the highest salinity was consistently recorded in western Baffin Bay, particularly in the tributaries, while lowest salinity was observed near the mouth. Following the heavy rainfall in spring 2015, the pattern reversed, with highest salinities typically observed in near the mouth of Baffin Bay and much lower salinities observed in western Baffin Bay (Fig. 5). In late spring-early summer of both 2013 and 2014, intrusion of lower salinity water from Laguna Madre was apparent, particularly in the eastern portion of Baffin Bay (Fig. 5,6). This influence of lower salinity Laguna Madre water did not extend into western Baffin Bay however. Strong salinity stratification of the water column was observed in summer 2013 and 2015, but was not as noticeable in summer 2014 (Fig. 7).

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 218 of 336 samples (65%). Using a slightly more relaxed National Coastal Condition Report for “poor” condition (20 µg/l; NCCR 2012), chlorophyll *a* was still in excess in 129 of 336 sample collections (38%). A distinct seasonal pattern was observed in terms of chlorophyll *a*, with highest concentrations found in spring-summer, decreasing through fall-winter (Fig. 8). Interestingly, chlorophyll *a* concentrations were nearly 2-fold higher in winter (DJF) 2014-2015 compared to winter 2013-2014, coincident with water temperatures that were ca. 5^{o}C warmer in winter 2014-2015 (Figs. 4, 8). Yet in winter 2015-2016 when water temperatures were warmer than both prior winters, chlorophyll *a* concentrations were relatively low (cf. 2013-2014) (Fig. 8). During the observed intrusion of lower salinity Laguna Madre water in early summer of 2013 and 2014, chlorophyll tended to decrease in the eastern portion of Baffin Bay, but remained elevated in the western portion (Fig. 9).

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). 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 <1-4 µM thereafter through February 2015 (Fig. 10). In April 2015, N+N was 15.9 µM at the Cayo del Grullo, but <0.6 µM at the other sites (Fig. 10). In May 2015, two relatively high N+N values were observed, 6.8 µM at CM 36 and 28.3 µM at the upper Alazan site (Fig. 10), 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 the upper Alazan site (48.5 µM) and Cayo del Grullo (13.8 µM), concurrent with low salinity conditions, while other sites had N+N <5 µM (Fig. 10). Finally, high N+N concentration was observed at the upper Alazan site in May 2016 (24.4 µM) (Fig. 10). N+N concentrations were elevated in near bottom waters in summer 2013, but not summer 2014 (Fig. 11). Relatively high bottom water N+N was also observed at Cayo del Grullo in March 2016, coinciding with low salinity at the site.

Surface ammonium concentrations were high in July-August 2013, with highest concentrations observed at the upper Alazan and Laguna Salada sites. Ammonium declined thereafter, remaining relatively low through April 2015 (Fig. 12). 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 (Fig. 12). After decreasing at most sites through October 2015, high ammonium concentrations were observed in November 2015 at the Alazan and mid-channel sites, though this was not associated with a salinity decrease or rainfall event (Fig. 12). Ammonium concentrations moderated from December 2015-February 2016; thereafter, high ammonium concentrations were observed primarily at the tributary sites and the western part of the bay in March and May 2016, coincident with high rainfall, lower salinity conditions (Fig. 12). Overall, ammonium concentrations tended to be much higher in the system during the “wet” period of 2015-2016 than earlier years. Elevated ammonium concentrations were also observed from May through August 2013 in bottom water at most sites (Fig. 13). Ammonium concentrations in bottom water declined thereafter and were generally low until spring 2015, during which bottom water concentrations periodically reached very high levels and often at multiple locations (Fig. 13).

By far, the dominant form of nitrogen during the study period was dissolved organic nitrogen (DON), with DON concentrations regularly exceeding 35 µM (Fig. 14). No clear seasonal pattern or interannual patterns have been observed in terms of DON. Highest concentrations tend to be found in the tributaries, decreasing towards the mouth of Baffin Bay (Fig. 14).

Surface orthophosphate concentrations exceeded 1 µM at the beginning of the study period at all sites except the north and central mouth sites (< 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 until April 2015 with the exception of a small secondary peak in July-August 2013 in western Baffin Bay and concentrations of 2.1-2.6 µM in Cayo del Grullo from March-May 2014 (Fig. 15). In April-June 2015, very high concentrations were observed in Cayo del Grullo, ranging from 9.6-10.7 µM (Fig. 15). Likewise, in May and June 2015, the orthophosphate concentration at the upper Alazan site ranged from 5.3-6.2 µM (Fig. 15). Orthophosphate concentrations were <0.6 µM from August-October 2015. Persistent high (1.6-8.1 µM) orthophosphate concentrations were again observed at Cayo del Grullo from November 2015-June 2016, and at the upper Alazan site in March, May and June 2016 (2.0-5.2 µM) (Fig. 15). Orthophosphate concentrations were periodically elevated in near bottom waters, especially in May, June and August 2013 at various sites throughout Baffin Bay, April-May 2015 and November 2015-June 2016 in Cayo del Grullo (Fig. 16).

The inorganic nitrogen to phosphorus ratio, one indicator of the limiting nutrient (i.e., N or P), displayed P-limiting conditions (above Redfield ratio, N:P>16) in summer of 2013, 2014 and 2015, as well as November-December 2015 and spring 2016 (Fig. 17). In contrast, N-limiting conditions (N:P<16) were observed for the remainder of the time (Fig. 17).

Dissolved organic carbon (DOC) represents a biogeochemically important constituent of coastal waters, where it supports bacterial respiration. DOC concentrations were exceptionally high at the beginning of this study, exceeding 1000 µM at all locations (Fig. 18). DOC subsequently decreased at most locations and remained fairly constant after summer 2013, with the exception of a brief increase in October 2014 (Fig. 18). Highest DOC concentrations tended to be found in the western portion of Baffin Bay (Fig. 18).

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 (Fig. 19). In summer 2013, several instances of sub-hypoxic (<2 mg/l) bottom waters were observed. Yet in 2014, despite similarly high water temperatures, hypoxia was only observed in one location (Laguna Salada) 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, this time at the upper Alazan site coinciding with very low salinity conditions (Figs. 5, 19).

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 20). In contrast, the change in chlorophyll in the phosphate addition was not different from that of the control treatment (Fig. 20). 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 (Fig. 20). 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 (Fig. 20). No statistically significant effect of ammonium and/or phosphate were observed at the Cayo del Grullo site (Fig. 20).

Discussion

Results from the first three years of a multi-year water quality data collection effort in Baffin Bay show the presence of significant spatial-temporal variability in terms of water quality dynamics in the system. Ultimately, this data, in conjunction with a reanalysis of historical TCEQ data provides 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-summer 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 lower levels of chlorophyll in winter may be indicative of either low light, low temperatures, or both. As a case in point, chlorophyll levels were nearly 2-fold higher in winter 2014-2015 compared to winter 2013-2014, possibly due to water temperatures that were 5^{o}C warmer in 2014-2015. This suggests that future warming trends in terms of winter air and water temperatures, as is projected to occur due to climate change (Nielsen-Gammon 2011), may lead to an extended growing season for phytoplankton in the system. Yet in winter 2015-2016, which was warmer than both prior winter periods, chlorophyll was at lower levels similar to winter 2013-2014. One possibility is that high turbidity associated with lower salinity conditions, coupled with strong water column mixing (e.g., Fig. 7), prevent significant phytoplankton growth in winter 2015-2016 despite high water temperatures. If confirmed, this would highlight the complexity of physical factors regulating wintertime phytoplankton growth in the system. Additional experimental and field studies are underway to better discern controls on wintertime phytoplankton growth in Baffin Bay.

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. Only since spring 2015 has chlorophyll noticeably decreased concurrent with several heavy precipitation events and lower salinity conditions, despite higher inorganic nutrient concentrations than during the earlier timeframe. Although speculative at this point, it is possible that the recent decrease in chlorophyll may be attributed to significant flushing as well as reduced light from high turbidity that accompanied the spring 2015 rains in Baffin Bay. An alternative explanation 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 have become important again with lower salinities. Our group recently completed several experiments to quantify microzooplankton grazing during the recent lower salinity conditions and will be in a position to address this issue at a later date. In terms of benthic filter feeders, anecdotal visual evidence suggests that significant mortality occurred during the hypersaline conditions, though in 2015-2016 benthic filter feeders appear to be abundant again (J. Pollack, unpubl. data).

An interesting feature in terms of chlorophyll, observed in all three summers, is a sharp decrease in chlorophyll between May and June in the eastern portion of Baffin Bay. In each case, this appeared to correlate with an intrusion of oligotrophic water from Laguna Madre in Baffin Bay. This is likely 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. 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 DON and secondarily ammonium. During the study period, surface N+N levels were relatively low except in May 2013 and at Cayo del Grullo and upper Alazan sites following the spring 2015 and 2016 rains. Likewise, very high ammonium concentrations were observed from spring 2015-onward, especially in at the tributary sites, pointing to watershed sources for both N+N and ammonium. 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). DON concentrations were 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; Wetz unpubl. data). 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 typically low, although high concentrations were observed at the Cayo del Grullo and upper Alazan sites in spring 2015 and 2016. High bottom water orthophosphate concentrations were occasionally observed during summer as well. 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. However, findings from our nutrient addition bioassays showed that despite the potential for P-limiting conditions based on nutrient ratios, nitrogen was the main element limiting phytoplankton growth. This is consistent with numerous studies from other estuarine systems, and highlights the difficulty in relying on nutrient ratios to determine the major limiting element.

A longer term goal of this study is to begin to identify sources of nutrients to Baffin Bay. The sharp increase in inorganic nutrient concentrations in both the upper Cayo del Grullo and Alazan Bay after heavy rain events in 2015 and 2016 point to watershed source(s). 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 Petronilla Creek, a stream that flows into Baffin Bay. Alternatively, we have found very high (and increasing) chlorophyll levels in Petronilla 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, 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. 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 routinely observed undersaturated 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 and were generally <4 mg/l during summer. 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). Unfortunately, monthly sampling is insufficient to quantify dissolved oxygen "mean state" as well as timescales of change in a dynamic system such as Baffin Bay. Consequently, our lab has been deploying sondes along the longitudinal axis of Baffin Bay since February 2015 to characterize these aspects of dissolved oxygen dynamics in Baffin Bay.

Because of the strong interannual variability observed in water quality in the system, there is a need to continue sampling, at least for another two years. This will be crucial given that as of 9 June 2016, NOAA's Climate Prediction Center declared that El Niño had officially dissipated. Dissipation of El Niño will likely lead to a return to low precipitation, high salinity conditions in South Texas over the coming year. Thus there is now an opportunity to capitalize on this natural, predictable climatic regime to gain a more complete understanding of the influence of hydrological and climatic variability on water quality and brown tide blooms in the system.

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, 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 may need to be a focus of targeted reductions in the future.

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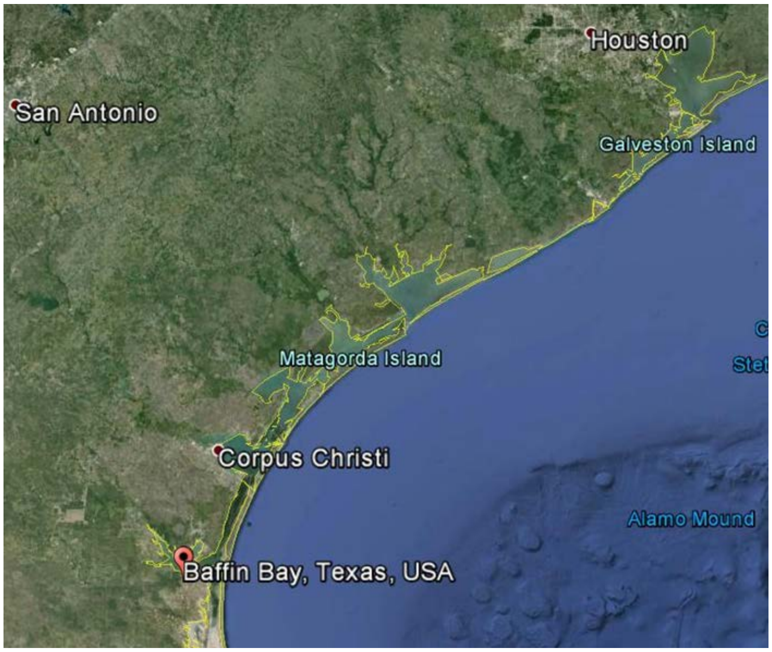

Figure 1. Map of Baffin Bay, located ~50 km southwest of Corpus Christi, TX.

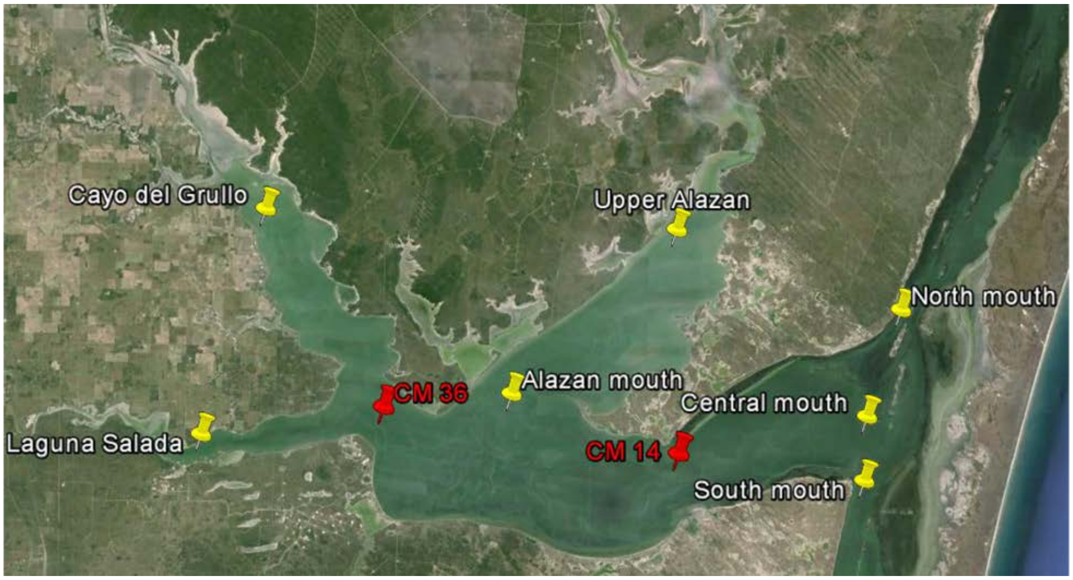

Figure 2. Map of permanent sampling locations in Baffin Bay. Red markers indicate two sites that are visited as part of TCEQ's quarterly monitoring program.

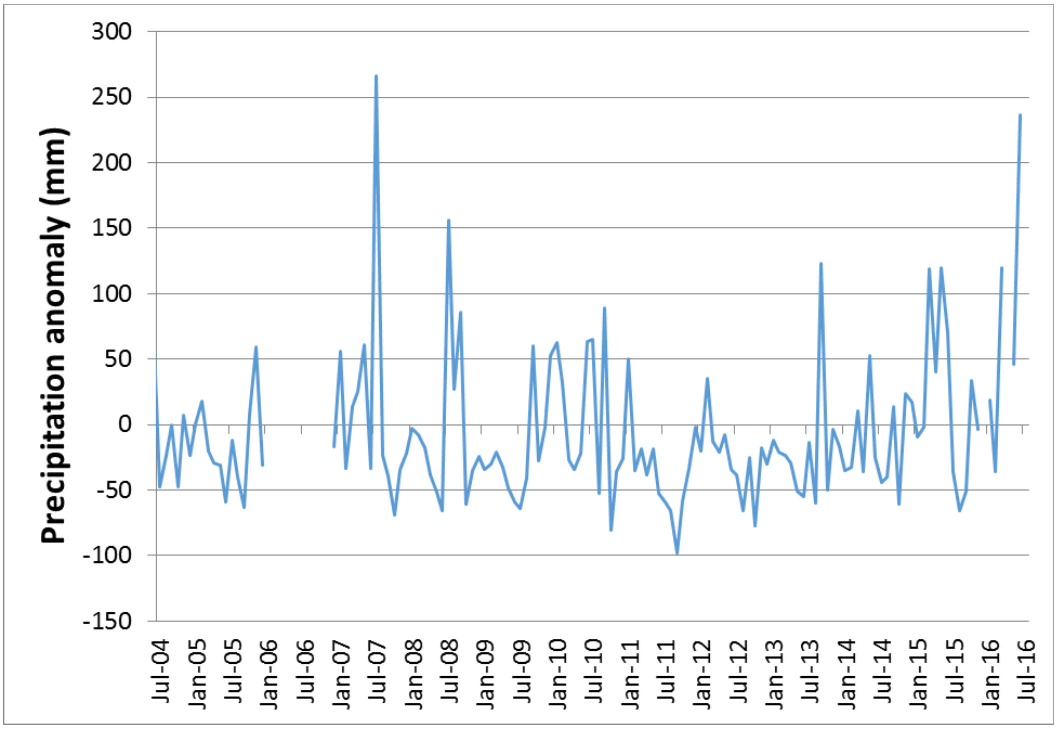

Figure 3. Precipitation anomaly (deviation from 1974-2014 monthly mean) at Kingsville Naval Air Station from 2004 to 2016.

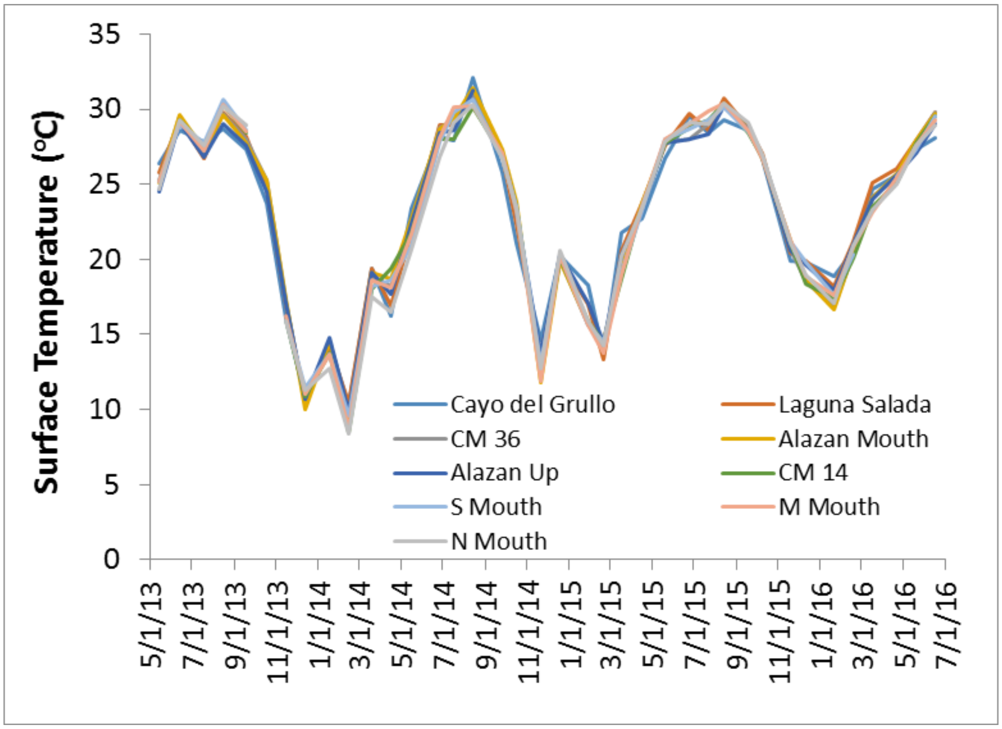

Figure 4. Surface temperature in Baffin Bay.

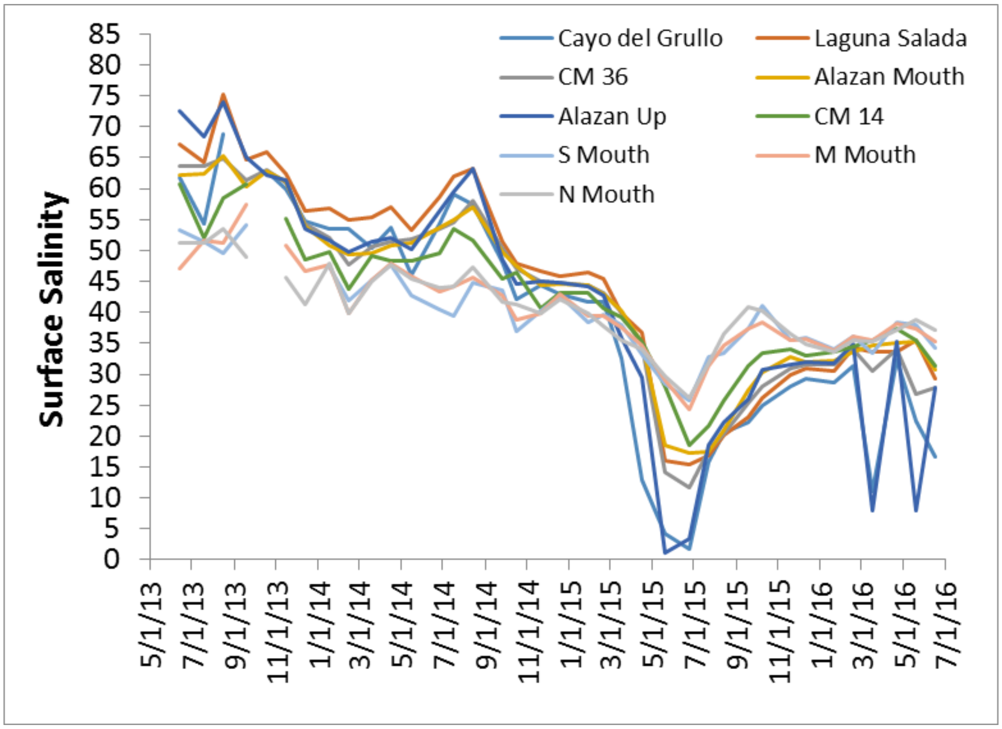

Figure 5. Surface salinity in Baffin Bay.

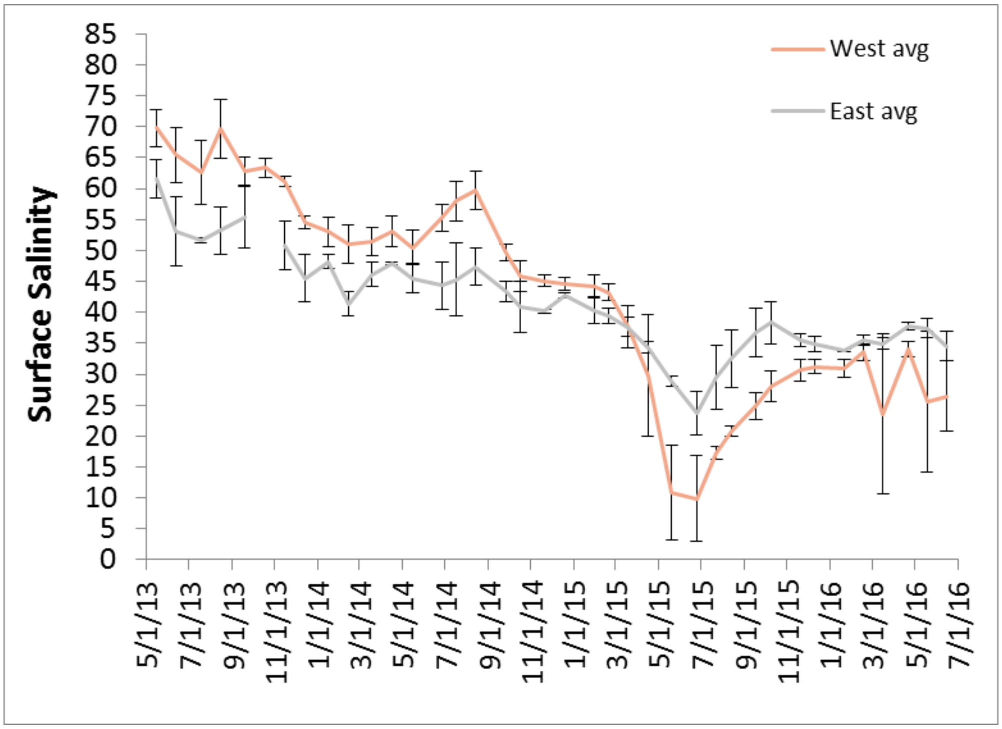

Figure 6. Surface salinity in western compared to eastern Baffin Bay. "West" includes upper Alazan, lower Alazan, CM 36, Laguna Salada, and Cayo del Grullo sites. "East" includes CM 14, north/central/south mouth sites.

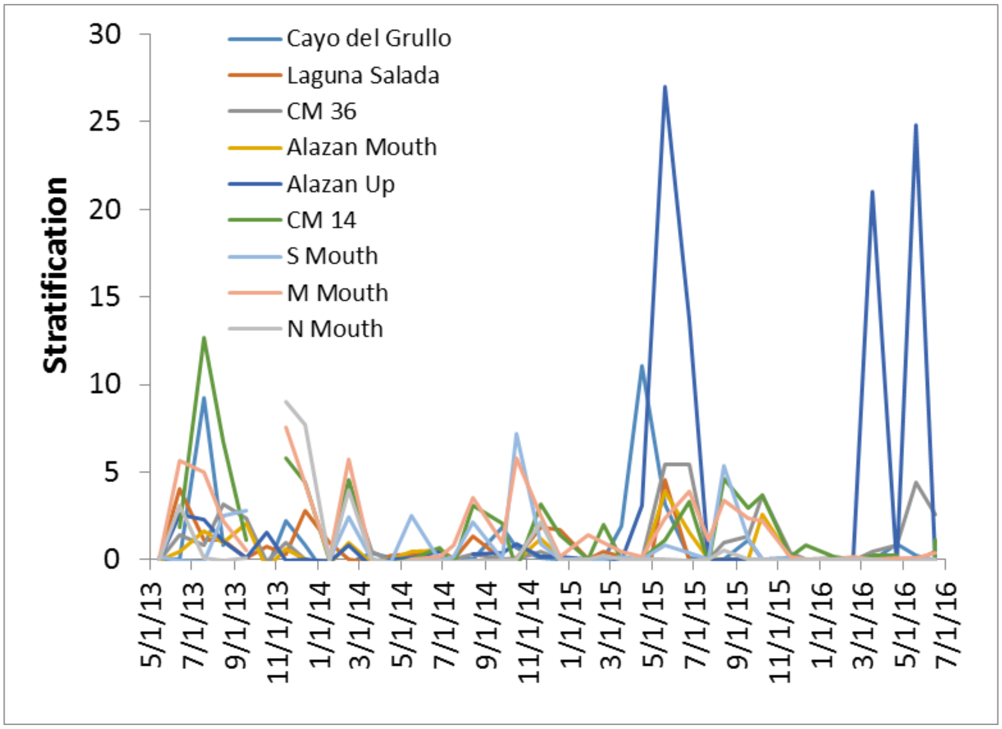

Figure 7. Stratification index (=Bottom minus surface salinity) in Baffin Bay.

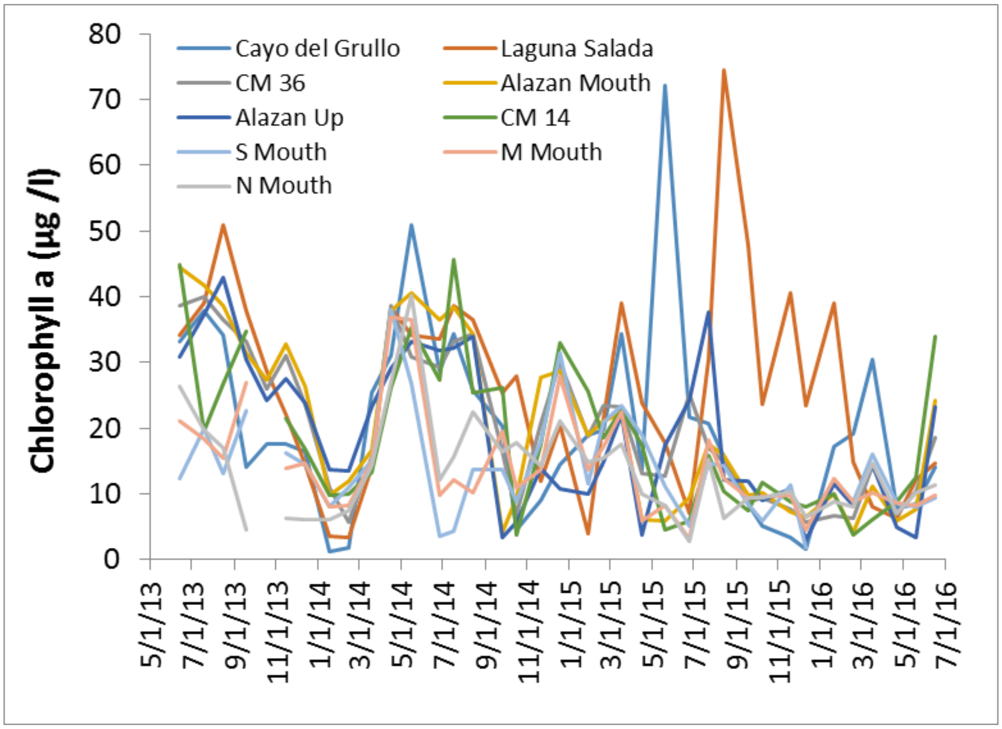

Figure 8. Chlorophyll *a* in Baffin Bay.

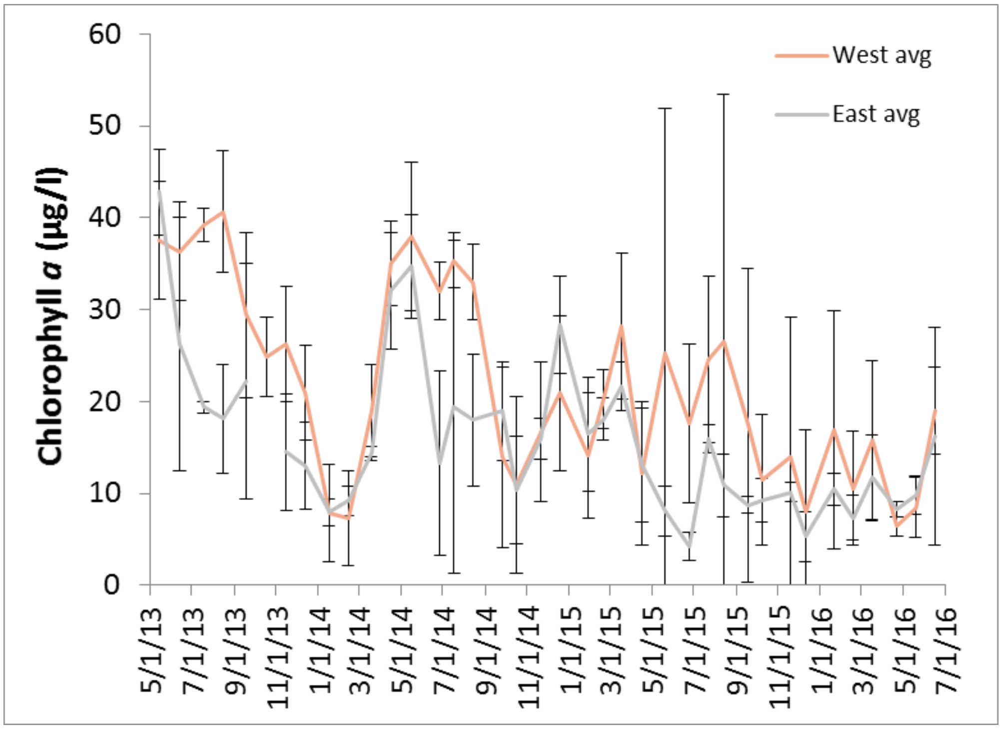

Figure 9. Chlorophyll *a* in western compared to eastern Baffin Bay. "West" includes upper Alazan, lower Alazan, CM 36, Laguna Salada and Cayo del Grullo sites. "East" includes CM 14, north/central/south mouth sites.

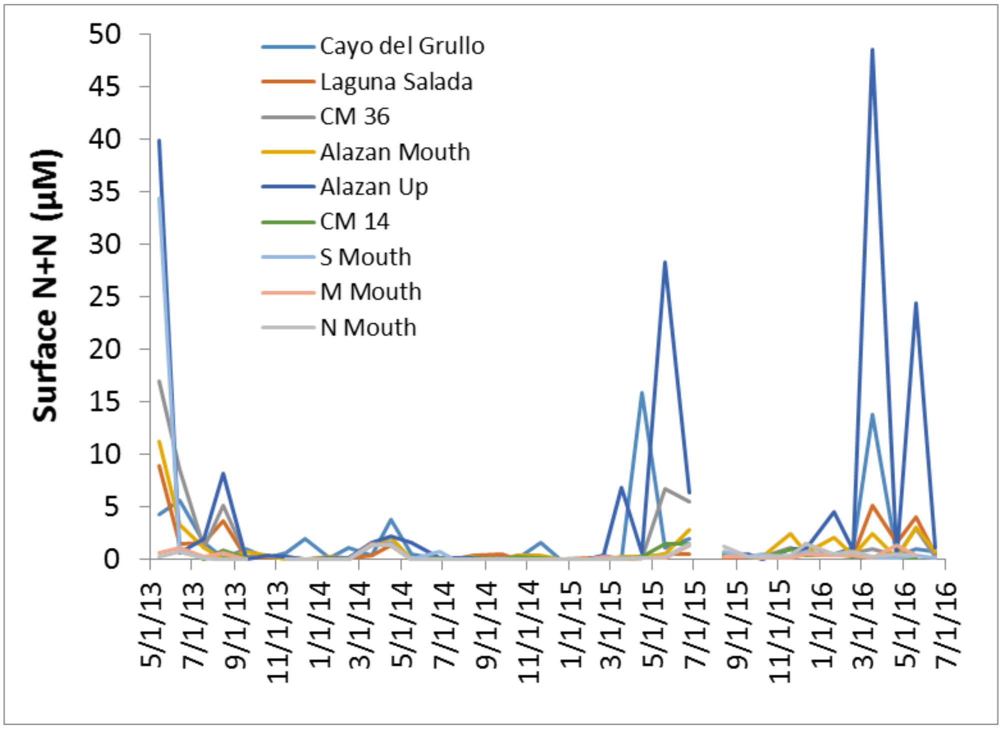

Figure 10. Surface N+N in Baffin Bay.

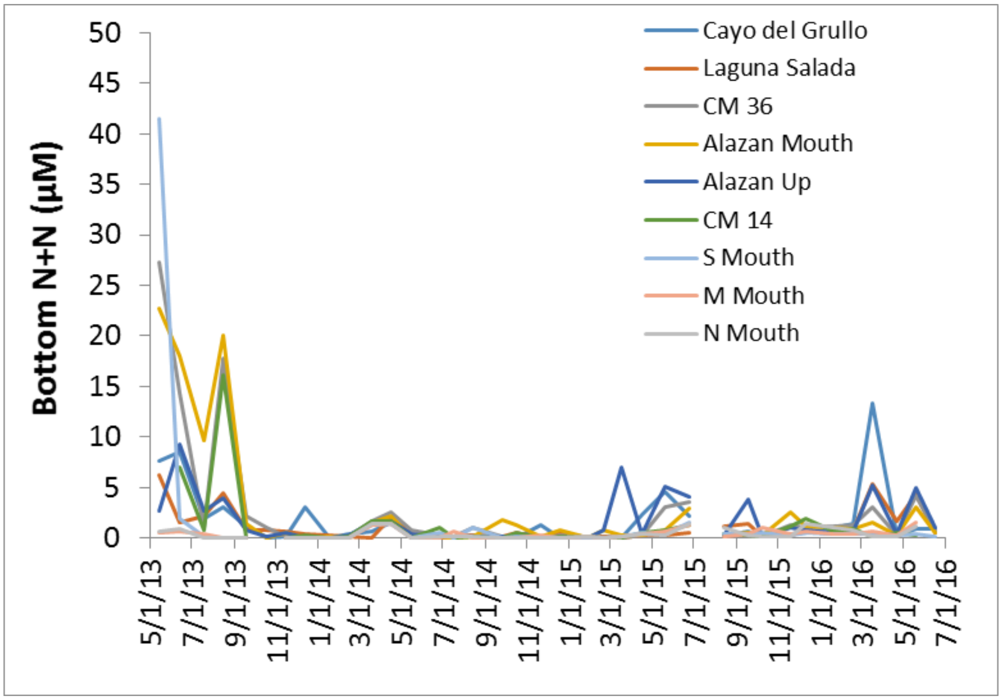

Figure 11. Bottom N+N in Baffin Bay.

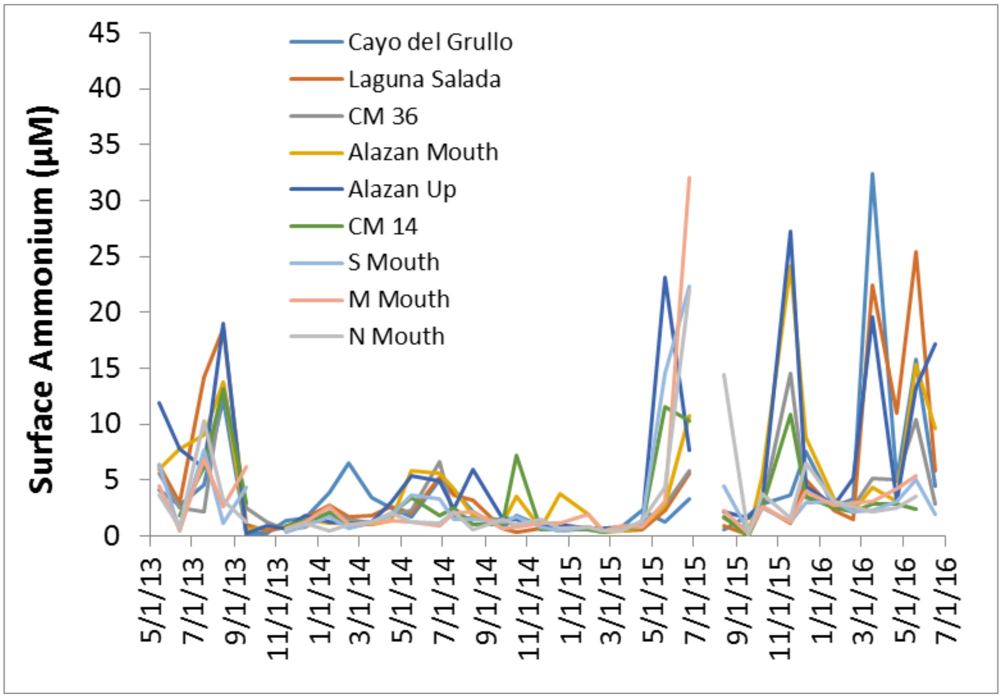

Figure 12. Surface ammonium in Baffin Bay.

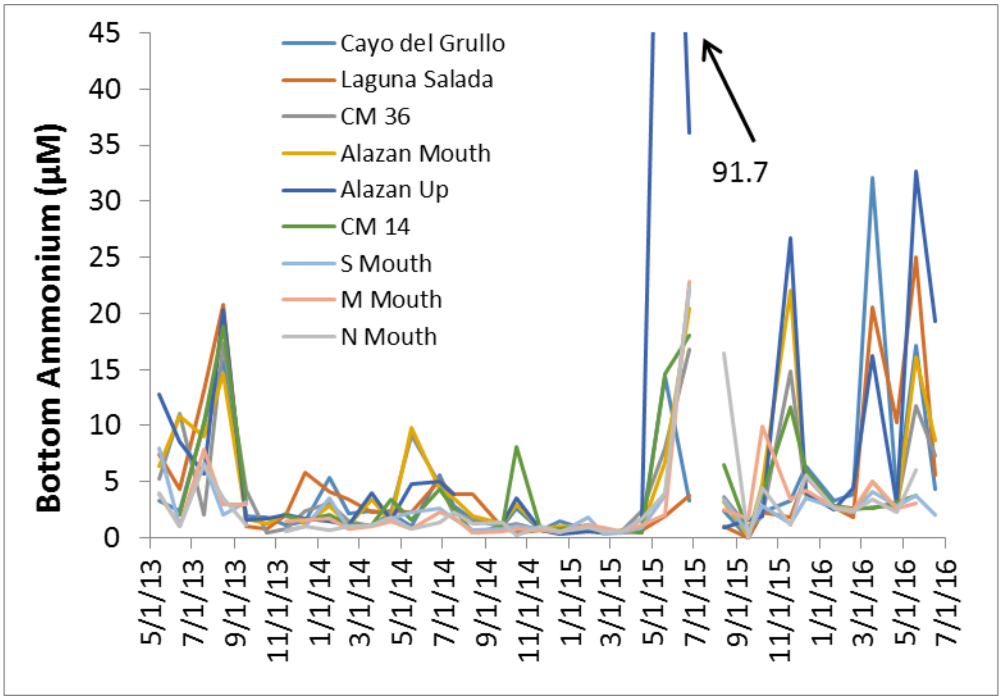

Figure 13. Bottom ammonium in Baffin Bay.

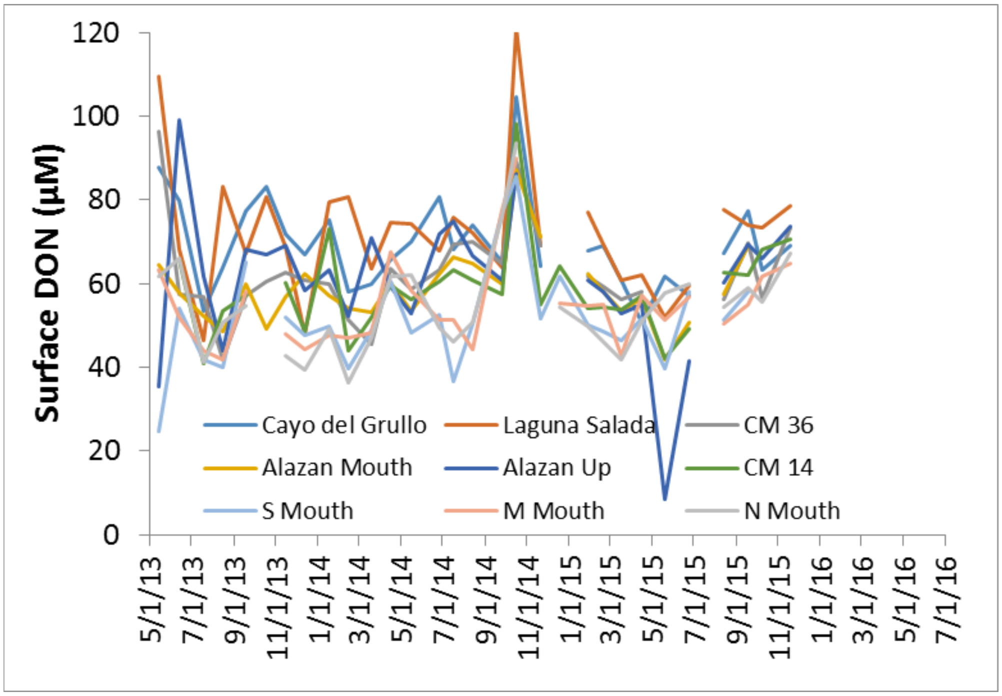

Figure 14. Surface dissolved organic nitrogen in Baffin Bay.

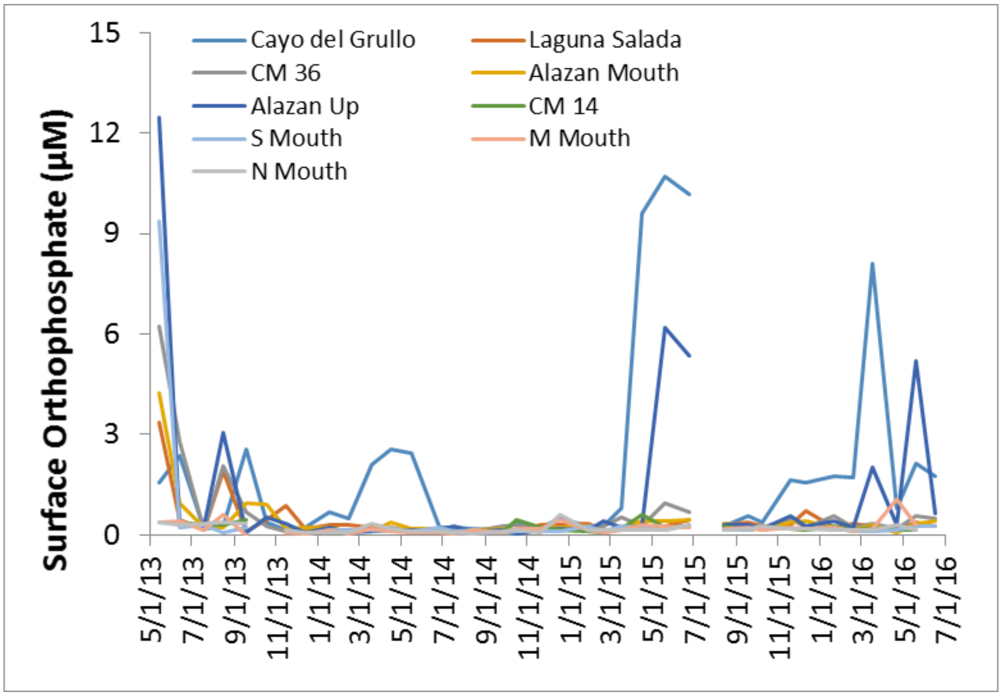

Figure 15. Surface orthophosphate in Baffin Bay.

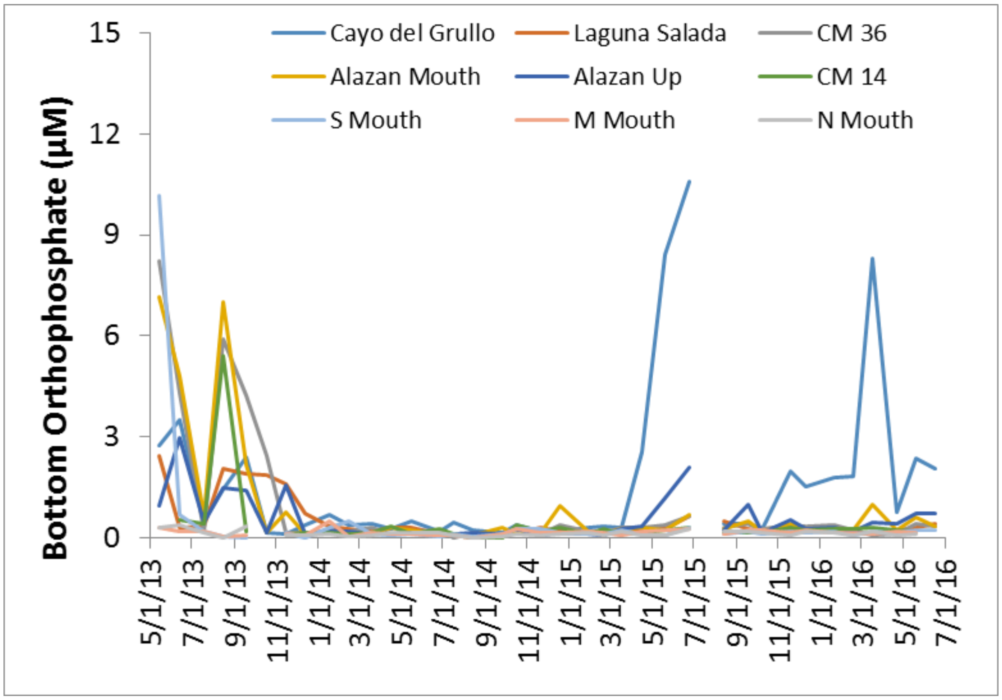

Figure 16. Bottom orthophosphate in Baffin Bay.

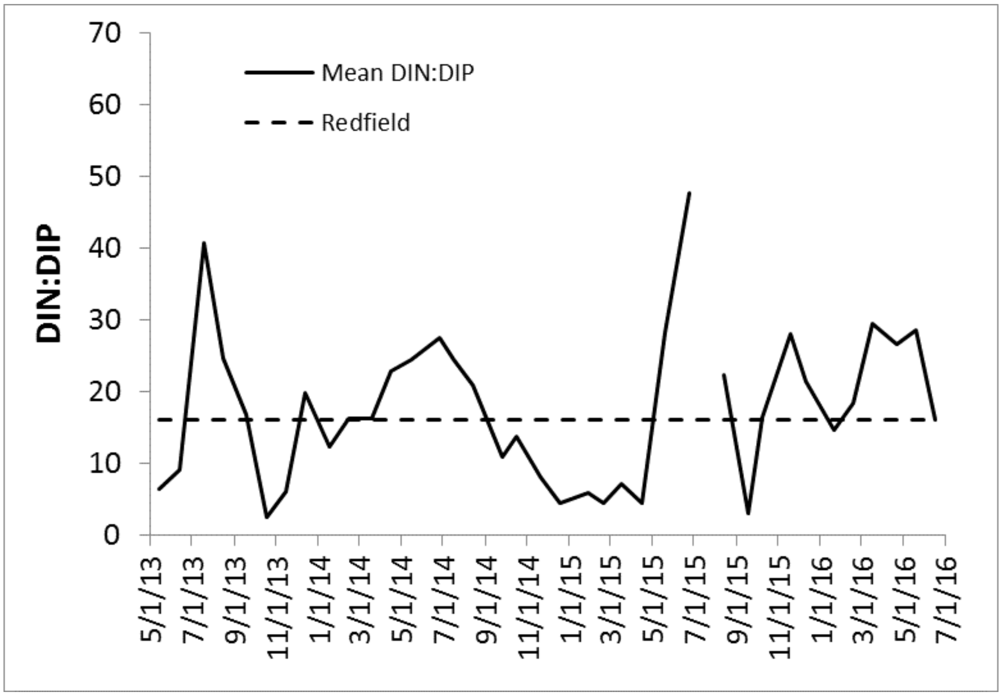

Figure 17. Ratio of dissolved inorganic nitrogen to orthophosphate in surface waters of Baffin Bay. Dashed line is the theoretical boundary between P limiting (>16) and N limiting (<16) conditions.

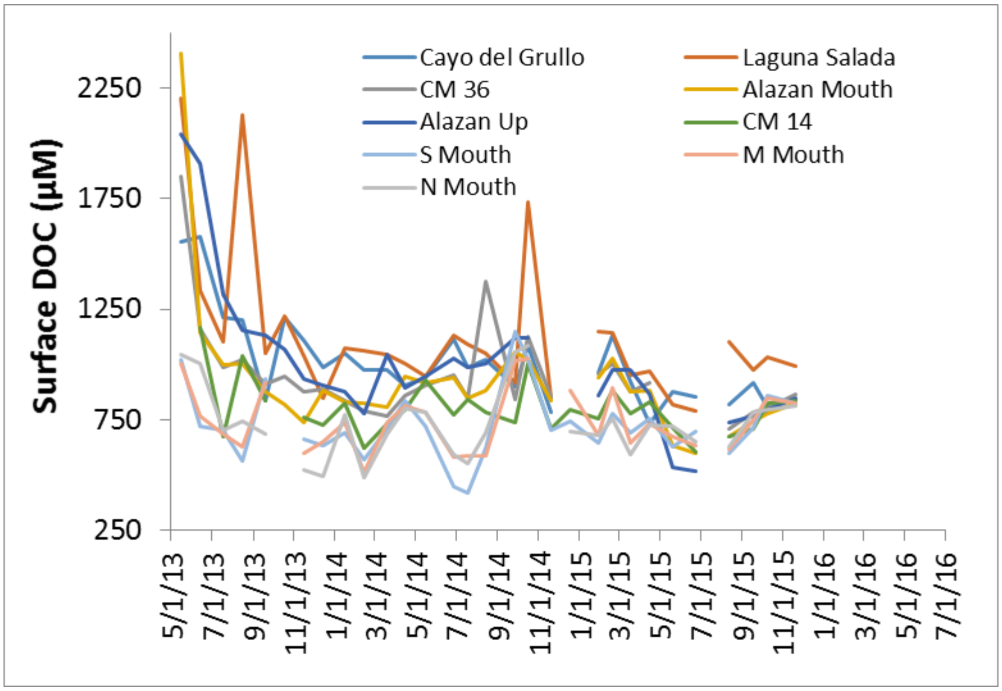

Figure 18. Surface dissolved organic carbon in Baffin Bay.

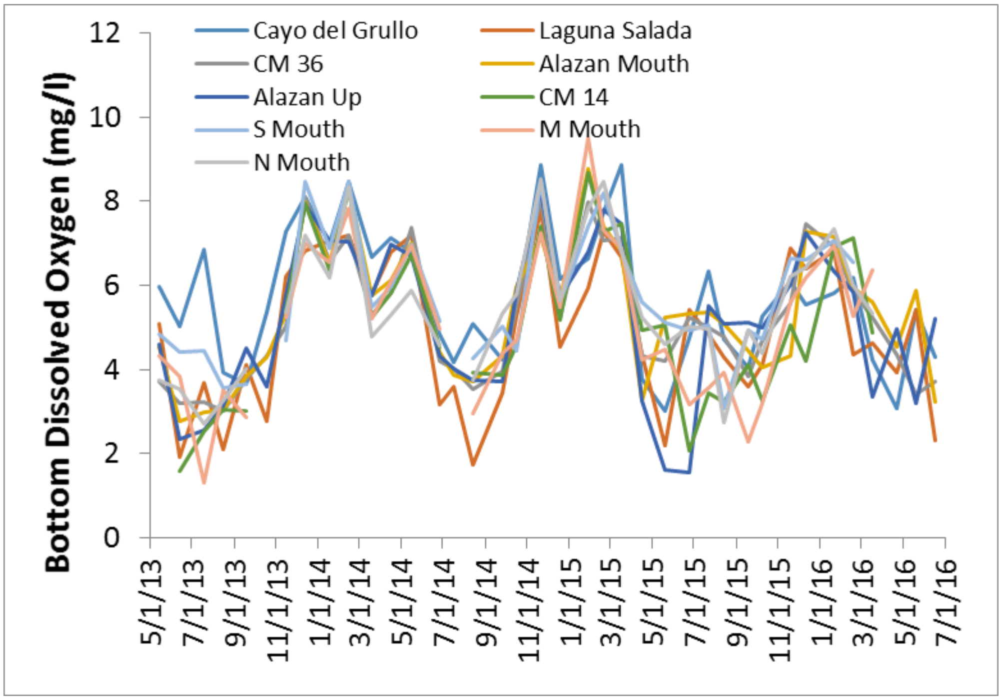

Figure 19. Bottom dissolved oxygen in Baffin Bay.

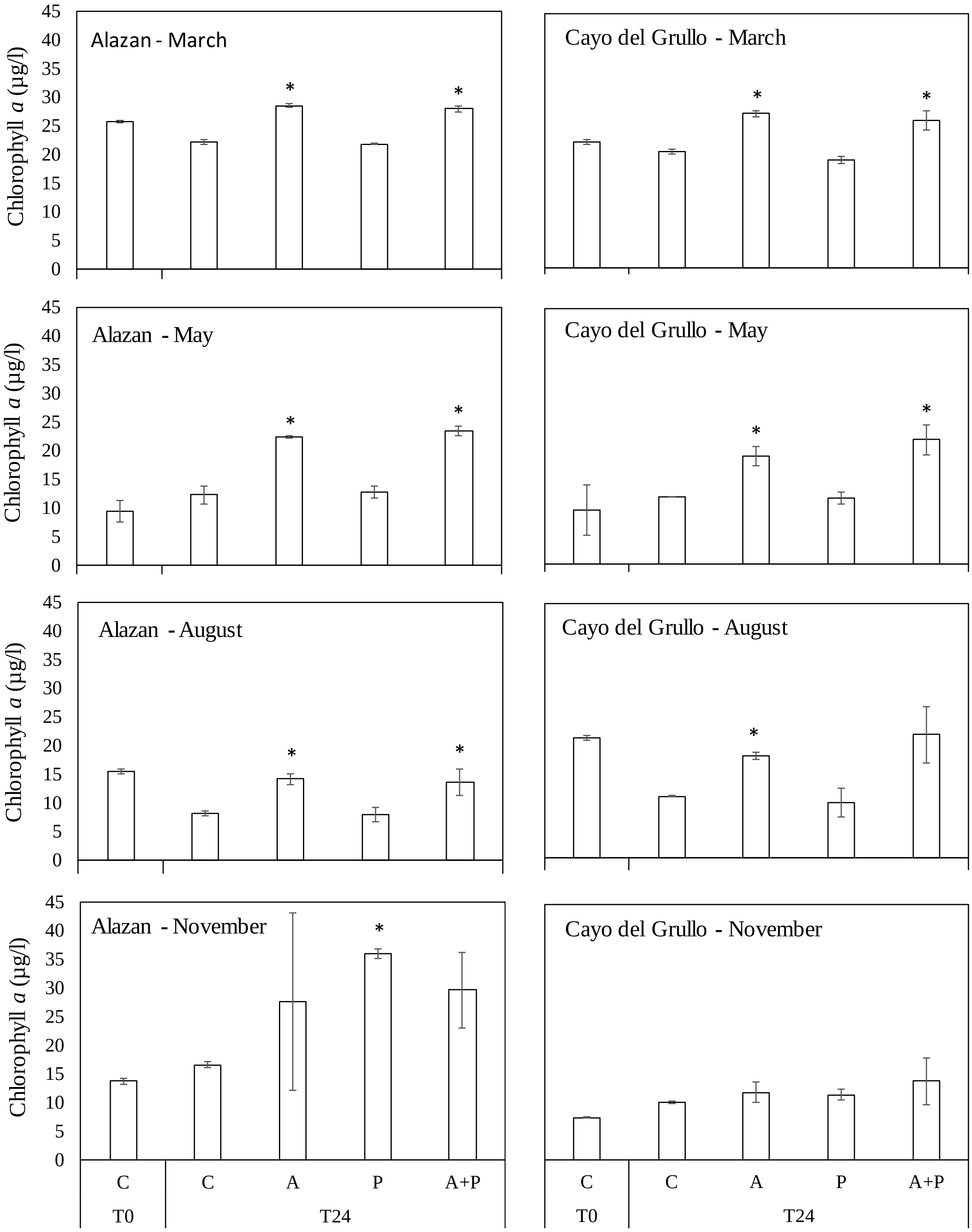

Figure 20. Results from nutrient addition bioassays conducted at two sites in Baffin Bay in 2015. Shown are the 0 and 24 hour chlorophyll *a* concentrations (µg/l). "C" = Control,

“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.