

Evaluation of factors contributing to water quality degradation in an urbanizing estuary (Oso Bay, Texas)

Final Report

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Table of Contents

Executive Summary.....	3
Outreach Efforts.....	5
<i>Research Findings:</i>	
Introduction.....	7
Methods.....	9
Results.....	14
Discussion.....	21
References.....	26
Figures.....	31
Tables.....	37

Executive Summary

Here we report results from a 3-year study of the spatial-temporal dynamics of select water quality parameters in a subtropical estuary, Oso Bay, which has a watershed that has undergone extensive urbanization in the past decade. Results show presence of very high inorganic nutrient (N, P) and organic matter (C, N) concentrations year round, prolonged and dense phytoplankton blooms, and episodic hypoxia/anoxia in western Oso Bay, which is subject to discharge from a municipal wastewater treatment facility. Aside from relatively high dissolved organic carbon (DOC) levels, these conditions were not present in the main portion of Oso Bay. There were a number of instances when signatures of wastewater were present at the mouth of Oso Bay, suggesting that water and associated organic matter may be advected from western Oso Bay to the mouth and potentially into Corpus Christi Bay. These findings are significant because the region of Corpus Christi Bay adjacent to the mouth of Oso Bay has been shown to experience episodic hypoxia from spring-fall, causing negative effects on benthic communities in this area, yet until now there have been no studies that have identified the source(s) of organic matter fueling hypoxia in Corpus Christi Bay. Results from nutrient addition bioassays show that nitrogen availability is an important control on phytoplankton growth in western Oso Bay. Overall, these results argue that the direct (senescing phytoplankton blooms, wastewater-derived DOC) and indirect (phytoplankton-derived DOC) effects of the eutrophication of western Oso Bay have farther reaching implications than just that part of Oso Bay, and suggest that nitrogen inputs from a local wastewater treatment plant may need to be reduced in order to alleviate the symptoms of eutrophication. In addition to the research component of this study, efforts were made to translate findings to stakeholders and students who may have an interest in the Oso

watershed. These efforts included classroom presentations, public seminars, and development of a brochure on Oso Bay/Creek water quality, and are detailed in the “Outreach Efforts” section of this report.

Outreach Efforts

Education and outreach were vital components of this study. Ten undergraduates participated in the field or bioassay research components of this study, and one M.S. student conducted research as part of this study. Results from this study, as well as more general information on the significance of Oso Bay, were presented in a number of venues including classroom presentations, public seminars, and via a brochure that was developed in collaboration with 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, excluding the brochure. A copy of the brochure is attached to this final report, as are copies of these presentations wherever available.

News articles:

“Texas A&M University-Corpus Christi students identify potentially toxic plankton in Oso Bay”; Corpus Christi Caller Times; June 14th, 2012 edition;
(<http://www.caller.com/news/2012/jun/14/students-identify-potentially-toxic-plankton-in/>)

“Texas A&M University-Corpus Christi professor awarded \$70K grant for Oso Bay water quality study”; Corpus Christi Caller Times; April 30th, 2012 edition;
(<http://www.caller.com/news/2012/apr/30/texas-am-university-corpus-christi-professor-70k/>)

Presentations (scientific conferences):

Wetz, M., K. Fisher, L. Price, D. Sokoly, and K. Hayes. 2013. Symptoms and causes of water quality degradation in an urbanizing estuary (Oso Bay, TX). Benthic Ecology Meeting, Savannah, GA.

Sokoly, D., J. Pollack, and M. Wetz. 2013. Relationships between land use, water quality and benthic meiofauna community structure and abundance in Oso Bay (Corpus Christi, Texas). Benthic Ecology Meeting, Savannah, GA.

Price, L., K. Fisher, M. Wetz. 2013. Causes and symptoms of eutrophication in an urbanizing estuary (Oso Bay, Corpus Christi, TX). ASLO Aquatic Sciences Meeting, New Orleans, LA.

Fisher, K., Wetz M. 2013. Phytoplankton and nutrient dynamics in an urbanizing, eutrophic subtropical estuary (Oso Bay, Texas). 2013 Coastal & Estuarine Research Federation Meeting, San Diego, CA.

- Smith, B., M. Wetz, and K. Hayes. 2014. Spatial-temporal distribution of heterotrophic bacteria in a eutrophic, lagoonal estuary (Oso Bay, Texas). Joint Aquatic Sciences Meeting, Portland, OR
- Fisher, K., L. Price, K. Hayes, M. Wetz. 2014. Nutrient and Phytoplankton Dynamics in Oso Bay, Texas. 2014 Gulf Estuarine Research Society Meeting, Port Aransas, TX
- Hayes, K., E. Cira, K. Fisher, L. Price, B. Smith, M. Wetz. 2014. Organic Matter Loading and Heterotrophic Bacterial Abundance in a Eutrophic, Lagoonal Estuary (Oso Bay, Corpus Christi, TX). 2014 Gulf Estuarine Research Society Meeting, Port Aransas, TX

Presentations (universities):

- Wetz, M. 2013. Effects of severe drought on estuarine planktonic food webs. University of Texas Marine Science Institute (invited seminar)
- Wetz, M. 2014. Systems approaches to understanding the eutrophication of two South Texas estuaries. Coastal Carolina University School of Coastal & Marine Sciences (invited seminar).
- Wetz, M. 2014. Eutrophication dynamics in two South Texas estuaries. Texas A&M University-Galveston (invited seminar).

Presentations (public, local):

- Wetz, M. 2013. Eutrophication of South Texas estuaries: Oso Bay & Baffin Bay. Coastal Issues Forum (Coastal Bend Bays Foundation), Corpus Christi, TX (invited seminar).
- Wetz, M. 2014. Does Oso Bay have a nitrogen problem? Coastal Issues Forum of the Coastal Bend Bays Foundation, Corpus Christi, TX (invited seminar)
- Wetz, M. 2013. Estuarine and coastal ecosystem dynamics lab. Beta-Beta-Beta Honor Society, TAMU-CC

Internet:

“Water quality studies conducted in Baffin Bay raising awareness of importance of good water quality for all local estuaries”; TAMU-CC Office of Research, Commercialization and Outreach homepage, March 2013; http://research.tamucc.edu/news/baffin_bay.html

University Classes:

In mid-April 2013 and 2014, Wetz utilized data obtained from this study as part of a case study on eutrophication in two classes that he taught at TAMU-CC, “Global Change Ecology” and “Global Change and It’s Effects on Aquatic Ecosystems”. Enrollment was as follows:

2013, Global Change: 14 undergraduates

2013, Global Change and It’s Effects on Aquatic Ecosystems: 12 graduate students

2014, Global Change: 6 undergraduates

Introduction

Estuaries are critical habitat for many important fish and shellfish species, and provide a multitude of ecosystem services that benefit humans (Costanza et al. 1997; Barbier et al. 2011). These vital ecological attributes are highly dependent on overall ecosystem health, and water quality in particular is a major determinant of an estuary's ability to support healthy food webs (Deegan et al. 1997; Hobbie 2000; Breitburg et al. 2009). Roughly 40% of the world's population, or 2.8 billion people, currently live within 100 km of the coast (CIESIN 2012). By 2100, it is estimated that 4 billion people could be living along the world's coasts (CIESIN 2012). As such, humans are having a significant and growing impact on the landscape of coastal watersheds, as well as hydrologic and biogeochemical cycles occurring within them (Kennish 2002). Consequently, water quality has deteriorated in a number of systems over the past century as a result of these transformations in watersheds (Paerl et al. 1998; Kemp et al. 2005; Rabalais et al. 2009).

Human population growth imparts a trajectory that includes increasing impervious surface coverage and wastewater treatment facilities in coastal watersheds. Consequences include increased point- and non-point source pollutant discharge and alteration of natural pathways for runoff dispersal and pollutant removal, all of which may ultimately affect estuarine water quality (Hopkinson and Vallino 1995). For example, numerous studies have shown that urbanization and increasing impervious surface coverage, as well as discharge from wastewater facilities, leads to enhanced inputs of inorganic nutrients (Vernberg et al. 1992; Bowen and Valiela 2001; Howarth et al. 2002; Handler et al. 2006; Kaushal et al. 2008; Mallin et al. 2009; Rothenberger et al. 2009; Nagy et al. 2012), microbial pathogens (Vernberg et al. 1992; Mallin et al. 2000, 2009; Holland et al. 2004; Handler et al. 2006; Campos and Cachola 2007; DiDonato et al. 2009; Nagy

et al. 2012), and biological oxygen demand-stimulating materials (e.g., Mallin et al. 2009; Andrade et al. 2011) to receiving water bodies. Presence of impervious surface may also alter the timing, duration, magnitude and pathways of runoff and associated pollutants during runoff events to the extent that the ability of a system to process pollutants such as nutrients can be inhibited (Hopkinson and Vallino 1995; Nagy et al. 2012). External climate forcing represents an additional driver of estuarine water quality dynamics, namely through effects on precipitation and temperature patterns (Cloern 2001; Paerl et al. 2006). Climate projections suggest that high precipitation events, drought and heat waves may become more frequent and/or intense in certain world regions (including coastal areas) in the near future as a result of anthropogenic greenhouse gas emissions (Meehl et al. 2007). It is possible, if not likely, that these changes on land and in the atmosphere will lead to unwelcome shifts in estuarine water quality (i.e., eutrophication), with negative impacts on ecosystem structure and trophic dynamics (Scavia et al. 2002; Flemer and Champ 2006; Wetz and Yoskowitz 2013).

South Texas supports a number of productive estuarine ecosystems. For example, recreational fishing in the Nueces Estuary, Mission-Aransas Estuary and Laguna Madre contributes ~\$1.87 billion annually to the Texas economy. When combined with the seafood industry and nature tourism, these three systems contribute ~\$3.2 billion to the state economy (Nueces River and Corpus Christi and Baffin Bay Basin and Bay Area Stakeholder Committee 2012). In recent years, the watersheds of these systems have experienced significant population growth as a result of jobs created by expanding energy and shipping sectors, among others. For example, the population of Nueces County, home to one of the largest cities in south Texas (Corpus Christi), increased by 8.5% from 2000 to 2010 (U.S. Census Bureau), and recent population scenarios suggest that it may increase by up to 34% by 2050 (Texas State Data

Center, <http://txsdc.utsa.edu/Data/TPEPP/Projections/Index.aspx>, accessed 10/28/2014). Despite the obvious potential for these changes to affect the ecological health of the aforementioned systems, many gaps exist in terms of assessments of water quality change in local bays. For example, the most recent National Estuarine Eutrophication Assessment reported water quality trends for only 5 of 9 estuarine systems of interest on the Texas coast largely due to lack of data from the other systems (Bricker et al. 2007). Here we report results from a 3-year study of the spatial-temporal dynamics of select water quality parameters in Oso Bay, which borders the city of Corpus Christi and has a watershed that has undergone extensive urbanization in the past decade.

Methods

Site description - Oso Bay is a shallow (<1-2 m), microtidal estuary in which circulation is primarily driven by winds (Nicolau 2001). For the larger south Corpus Christi Bay watershed (which encompasses Oso Bay), watershed land cover is agriculture dominated (~48%), though in the past several decades, significant urbanization has occurred concomitant with population growth. For example, high and low density development increased by ~12% between 1996 and 2010 (NOAA Coastal Change Analysis Program). This trend is projected to continue for the foreseeable future due to population growth projections for the area (Texas State Data Center, <http://txsdc.utsa.edu/Data/TPEPP/Projections/Index.aspx>, accessed 10/28/2014).

Sampling program – Water samples were collected on a biweekly (March-October) to monthly (November-February) basis, weather permitting, from August 2011 to May 2014. Six sites were chosen, including the head of Oso Bay at Yorktown Bridge (YB) and the mouth at Oso Inlet (OI;

Fig. 1). Four other sites, representing the main tributaries of Oso Bay, were also chosen and each varied considerably in terms of land cover type that it drained. Examples include: 1) a tributary from an active golf course that uses reclaimed wastewater for course watering (“AG”), 2) a tributary that receives effluent from a municipal wastewater treatment plant (“WP”), 3) a tributary that drains a mix of agricultural land and impervious surface on the south side of Oso Bay (“AI”), and 4) a tributary from a defunct golf course (“DG”). At WP, AI and DG, samples were collected from the mouth of each tributary where it enters Oso Bay. Due to limited accessibility, samples at AG were collected ~300 m upstream of the tributary mouth. Sample collection did not begin at AI and DG until June 2012. Sampling occurred at the same time of day (morning) on each date. Vertical profiles of conductivity (salinity), dissolved oxygen (DO), pH and temperature were conducted at each site using a calibrated YSI ProPlus sonde. Surface water was collected in acid-washed 1-L amber polycarbonate bottles that were rinsed four times with deionized water prior to each sampling trip. This water was subsequently analyzed for: chlorophyll *a*, inorganic nutrients (silicate; ammonium; nitrate plus nitrite, N+N; orthophosphate, PO₄³⁻), dissolved organic carbon (DOC) and total dissolved nitrogen (TDN). Details on sample processing and analyses are provided below in Biological and Chemical Analyses.

Daily average wind speed and rainfall data from the study period were obtained from two sites that are close to our study area; Corpus Christi International Airport for watershed rainfall, and Naval Air Station-Corpus Christi for localized rainfall (Fig. 1). Data were retrieved from the National Climatic Data Center (www.ncdc.noaa.gov).

Biological-chemical analyses – Prior to subsampling from 1-L amber bottles, the bottles were gently inverted several times to ensure homogenization of water and materials contained therein.

For chlorophyll *a* determination, 25 ml of sample was gently filtered (≤ 5 mm Hg) through 25 mm Whatman GF/F filters. Filters were stored frozen (-20°C) in sealed Vacutainers until analysis. Chlorophyll was extracted from the filters by soaking for 18-24 hours in 90% HPLC-grade acetone at -20°C , after which chlorophyll *a* was determined fluorometrically with a Turner Trilogy fluorometer without acidification. Inorganic nutrients were determined using the filtrate of water samples that were passed through a 25 mm GF/F filter and stored frozen (-20°C) until analysis. After thawing to room temperature, samples were analyzed on a Seal Quattro autoanalyzer. Standard curves with five different concentrations were run daily at the beginning of each run. Fresh standards were made prior to each run by diluting a primary standard with low nutrient surface seawater. Deionized water (DIW) was used as a blank, and DIW blanks were run at the beginning and end of each run, as well as after every 8-10 samples to correct for baseline shifts. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined using the filtrate of water samples that were passed through precombusted 25 mm GF/F filters and stored frozen (-20°C) until analysis. Samples were subsequently analyzed using the High Temperature Catalytic Combustion method on a Shimadzu TOC-Vs analyzer with nitrogen module. Standard curves were run twice daily using a DIW blank and five concentrations of acid potassium phthalate solution (for DOC) and five concentrations of potassium nitrate (for TDN). Three to five subsamples were taken from each standard and water sample and injected in sequence. Reagent grade glucosamine was used as a laboratory check standard and inserted throughout each run, as were Certified Reference Material Program (CRMP) deep-water standards of known DOC/TDN concentration. Average daily CRMP DOC and TDN concentrations were $44.1 \pm 5.2 \mu\text{mol L}^{-1}$ and $32.8 \pm 2.4 \mu\text{mol L}^{-1}$ respectively. Dissolved organic nitrogen (DON) was determined by subtracting dissolved inorganic nitrogen

(ammonium, nitrate plus nitrite) from TDN. For the entire dataset, there were 5 cases where the calculated DON concentration was negative (1 from DG, 2 each from AG, WP). It is suspected that this was due to incomplete oxidation of organic nitrogen in these samples, but regardless, this DON data was excluded from site-specific DON estimates and comparisons.

Statistical analyses – Differences in water quality parameters by location were analyzed using salinity as a covariate. Water quality parameters were first transformed using natural logarithms to improve normality. When necessary, weighted least squares were used to explicitly model any remaining heteroscedasticity in the data. Relationships between water quality parameters and salinity at each site were initially characterized as linear; if there was significant evidence of non-linearity, a quadratic model was used instead. For all parameters, a straightforward analysis by ANCOVA was not possible, due both to the non-linear models used for some sites and to interactions between site and salinities. Therefore, for salinities between 0 and 20, and for each pair of sites, the differences in a predicted water quality parameter and simultaneous 95% confidence intervals for those differences were calculated (Bretz et al. 2011). If the confidence intervals did not contain zero, the differences were considered statistically significant for that salinity at a significance level of $\alpha = 0.05$. The use of simultaneous confidence intervals protects against family-wise Type I error in this procedure.

To model associations between chlorophyll and various environmental parameters, multiple regression was used. As above, natural logarithms were used to transform chlorophyll and environmental parameters to improve normality, and weighted least squares were used to model heteroscedasticity. Seasonal patterns in chlorophyll were modeled using a cyclic penalized spline based on day-of-the-year (DOY). Then models involving the seasonal spline and the

environmental parameters were used to examine if any of the environmental parameters explained significant variation after any seasonal effects were taken into account. An exhaustive search of all parameter combinations was not possible due to missing data in some parameters. Instead, correlation between $\ln(\text{chlorophyll})$ and environmental parameters, as well as between $\ln(\text{chlorophyll})$ and environmental parameters from the previous time period, was used to identify possible relationships, and an initial model was built. Backward regression with a significance level of $\alpha = 0.05$ and adjusted R^2 were used to assess retention of individual variables in the model.

All statistical analyses were performed in R (version 3.1.1, R Core Team, 2014), including the nlme package (version 3.1-117, Pinheiro et al, 2014), the mgcv package (version 1.8-3, Wood, 2011), and the multcomp package (version 1.3-6, Hothorn et al, 2008).

Nutrient addition bioassays - The interaction between nutrient supply and phytoplankton growth in Oso Bay were examined seasonally using nutrient addition bioassays. Bioassay water was obtained from two sites; the head of Oso Bay where Oso Creek enters the system (YB), and western Oso Bay (MG). At each site, a control and three treatments were performed in triplicate as follows:

- No addition (Control)
- 120 μM $\text{NO}_3^- \text{N}$ (as KNO_3)
- 8 μM PO_4^{3-} (as KPO_4^{3-})
- 120 μM $\text{NO}_3^- \text{N}$, 8 μM PO_4^{3-}

Water was transferred into 1-L transparent polyethylene Cubitainers, amended with the nutrients outlined above, and incubated in situ at the TAMU-CC beach. Cubitainers were incubated for 72

h, and samples were drawn at daily intervals to establish statistical relationships between nutrient supply and phytoplankton growth responses as determined from chlorophyll *a* measurements.

Results

Spatial trends - Salinity was highest at the head of Oso Bay (Table 1), averaging 39 ± 13 . This site is immediately downstream of where cooling water, originating from the hypersaline Laguna Madre, is discharged from a local power plant. Lower salinities were noted at tributaries AI, DG, and AG, averaging 27 ± 17 , 26 ± 14 and 14 ± 11 respectively. The lowest salinities were observed at WP, averaging 6 ± 8 (Table 1). Average water temperatures did not vary considerably between sites (Table 1), though temperature at WP was consistently higher than at any other site by 3-10°C from November/December through March/April (data not shown). pH on average was equivalent between sites with the exception WP, which was 0.8-1.0 units lower than the other sites (Table 1).

N+N concentrations were highest at WP, averaging $495 \pm 295 \mu\text{M-N}$, followed by AG which averaged $125 \pm 126 \mu\text{M-N}$ (Table 1). N+N concentrations were intermediate at AI and DG, averaging $23 \pm 56 \mu\text{M-N}$ and $26 \pm 41 \mu\text{M-N}$, respectively (Table 1). The differences in $\ln(\text{N+N})$ between WP and AG were significant at salinities <15 , and the differences in $\ln(\text{N+N})$ between WP and AI, and WP and DG were statistically significant across all tested salinity levels. Lowest N+N concentrations were observed at YB and OI, averaging $4 \pm 12 \mu\text{M-N}$ and $2 \pm 6 \mu\text{M-N}$ respectively (Table 1).

Ammonium concentrations were highest at WP, averaging $383 \pm 231 \mu\text{M-N}$, followed by AG which averaged $96 \pm 128 \mu\text{M-N}$ (Table 1). Ammonium concentrations were intermediate at AI and DG, averaging $10 \pm 18 \mu\text{M-N}$ and $18 \pm 30 \mu\text{M-N}$, respectively (Table 1). The difference in

ln(ammonium) between WP and AG was significant at salinities <11, and the differences in ln(ammonium) between WP and AI and WP and DG were statistically significant across all tested salinity levels. Lowest concentrations of ammonium were observed at YB and OI, averaging $3 \pm 3 \mu\text{M-N}$ and $2 \pm 3 \mu\text{M-N}$ respectively (Table 1).

PO_4^{3-} concentrations were highest at WP, averaging $58 \pm 27 \mu\text{M-P}$, followed by AG which averaged $33 \pm 28 \mu\text{M-P}$ (Table 1). PO_4^{3-} concentrations were intermediate at AI and DG, averaging $5 \pm 7 \mu\text{M-P}$ and $7 \pm 6 \mu\text{M-P}$, respectively (Table 1). The difference in ln(PO_4^{3-}) between WP and AG was significant at salinities <4, and the differences between WP and AI and WP and DG were statistically significant across all salinity levels. Lowest concentrations were observed at YB and OI, averaging $1 \pm 3 \mu\text{M-P}$ and $1 \pm 1 \mu\text{M-P}$ respectively (Table 1).

DOC concentrations were highest at AG, averaging $879 \pm 218 \mu\text{M}$, followed by DG ($773 \pm 185 \mu\text{M}$) and WP ($768 \pm 80 \mu\text{M}$) (Table 1). DOC concentrations were intermediate at YB and AI, averaging $699 \pm 254 \mu\text{M}$ and $682 \pm 205 \mu\text{M}$, respectively (Table 1). Lowest concentrations were observed at OI, averaging $463 \pm 133 \mu\text{M}$ (Table 1). Ln(DOC) concentrations were significantly higher at AG than at AI or WP across all tested salinity levels. DON concentrations were highest at WP, averaging $151 \pm 195 \mu\text{M-N}$, followed by AG ($84 \pm 37 \mu\text{M-N}$) (Table 1). Intermediate DON concentrations were found at DG ($61 \pm 15 \mu\text{M-N}$), AI ($53 \pm 18 \mu\text{M-N}$) and YB ($52 \pm 18 \mu\text{M-N}$). Lowest DON concentrations were found at OI, averaging $35 \pm 10 \mu\text{M-N}$ (Table 1). Ln(DON) concentrations were significantly different between AG and DG, and AG and AI at all tested salinity levels.

Highest chlorophyll concentrations were found at AG, which averaged $44 \pm 41 \mu\text{g L}^{-1}$, followed by DG ($27 \pm 18 \mu\text{g L}^{-1}$) and AI ($27 \pm 21 \mu\text{g L}^{-1}$) (Table 1). Lower chlorophyll levels were found at YB ($11 \pm 13 \mu\text{g L}^{-1}$), OI ($10 \pm 9 \mu\text{g L}^{-1}$) and WP ($5 \pm 6 \mu\text{g L}^{-1}$) (Table 1). DO

levels averaged 6.2-7.0 mg L⁻¹ at YB, OI, AI and DG, but were lower at WP (4.3 ± 2.0 mg L⁻¹) and AG (4.8 ± 2.8 mg L⁻¹) (Table 1). Hypoxic conditions (<2.0 mg L⁻¹) were occasionally observed at AG, WP and DG (Fig. 2). In 2012 for example, hypoxia was observed at AG on two consecutive sampling trips in late March-April (spanning a 3-week period), mid-June (spanning a 2-week period), and on three consecutive sampling trips in August (spanning a 4-week period) (Fig. 2).

Evidence of export from Oso Bay to Corpus Christi Bay – There are indications that water and associated materials are occasionally exported out of Oso Bay to OI, presumably into Corpus Christi Bay. This includes low salinity water from three different sources; municipal wastewater, local tributaries in Oso Bay and Oso Creek. For example, in mid-August through mid-September 2011, salinities were nearly fresh (0.1-2.7) at OI, pH was below average (7.86-8.07), DOC and DON concentrations (432-467 μM, 32 μM respectively) were relatively high, and inorganic nitrogen concentrations were <1 μM (Fig. 3). This low salinity was not preceded by a significant rain event in the region (Fig. 4), suggesting influence of wastewater from western Oso Bay. It is important to note that in early August 2011, a very large phytoplankton bloom (152 μg L⁻¹ Chl *a*) was in place at AG, which may have depleted nutrients from the water column prior to water from this region being advected to OI (Fig. 5). Low salinities were again noted at OI (0.2-3.2) from February through late April 2012, accompanied by relatively high DOC (312-781 μM) and DON concentrations (26-56 μM), and variable but generally high inorganic nitrogen (primarily as ammonium, 0.8-55.1 μM) and orthophosphate concentrations (0.2-4.7 μM) (Fig. 3). During this time several rainfall events >25 mm occurred (Fig. 4). At the beginning of the period in early February 2012, salinity was low at YB (Fig. 6), indicating that the source of low salinity water at OI could have been runoff from Oso Creek. From mid-

February through mid-April 2012, salinity had increased considerably at YB (Fig. 6), indicating that the source of low salinity water at OI switched to either runoff from local tributaries and/or wastewater from western Oso Bay. Later, from mid-April through early May 2012, salinity decreased again at YB concurrent with several watershed rainfall events (Figs. 4, 6), suggesting that flow of low salinity water out of Oso Creek may have contributed to the low salinity water at OI. In early June 2012, another brief episode of low salinity water (Salinity = 2.7) was observed at OI, accompanied by below average pH (8.02), high DOC (534 μM) and DON (39 μM) concentrations, and low inorganic nutrient concentrations (Fig. 3). No significant rainfall occurred in the watershed prior to this event (Fig. 4), pointing to wastewater as the source of the low salinity. Large, prolonged phytoplankton blooms occurred throughout much of western Oso Bay, which may have depleted the inorganic nutrients prior to the water mass reaching OI (e.g., Fig. 5). Another example of low salinity at OI comes from July 2012, when a sharp salinity decrease (from 37.7 to 19.9) over a two week period was accompanied by an increase in chlorophyll from 4 to 35 $\mu\text{g L}^{-1}$, a DOC increase from 375 to 706 μM , and a DON increase from 22 to 51 μM (Fig. 3). Inorganic nitrogen levels at this time were $<0.2 \mu\text{M}$ however (Fig. 3). This appearance of low salinity water at OI was concurrent with a rainfall event of 20 mm on July 13th in the watershed as well as a drop in salinity at YB (Figs. 4,6), pointing to influence of runoff from Oso Creek as contributing to the low salinity at OI. Finally, low salinity (0.1-0.2) was again noted at OI on August 17th and 31st, 2012. Accompanying this low salinity was low pH (7.40-7.53), relatively high DOC (440-744 μM) and DON concentrations (32-60 μM), and low inorganic nitrogen concentrations ($<0.2 \mu\text{M}$) (Fig. 3). No rainfall was observed during this timeframe (Fig. 4), pointing to the influence of wastewater from the western Oso Bay. In late July 2012, a very large phytoplankton bloom (122 $\mu\text{g L}^{-1}$ Chl *a*) was in place at AG, and

throughout August 2012 chlorophyll concentrations were $>40 \mu\text{g L}^{-1}$, which may have depleted nutrients from the water column prior to water from this region being advected to OI (Fig. 5).

In addition to export of low salinity water to OI and Corpus Christi Bay, there are also indications of export of hypersaline water out of Oso Bay as well. For example, from mid-September through mid-December 2012, salinity >40 was observed at OI (Fig. 3). Further upstream at YB, salinities were generally even higher (Fig. 6), suggesting that discharge of high salinity cooling water from the nearby power plant and its subsequent downstream advection to OI was the source of the hypersaline water. At OI, inorganic nutrient concentrations were low ($<3 \mu\text{M}$), while DOC (396-599 μM) and DON concentrations (32-44 μM) were relatively high (Fig. 3). From late June to late August 2013, salinity >40 was observed again at OI, and upstream salinities were higher, pointing to discharge of high salinity power plant cooling water as the source of the hypersaline conditions. The water at OI tended to have low inorganic nitrogen concentrations, while DOC (403-685 μM) and DON concentrations were high (34-49 μM) (Fig. 3).

Seasonal trends- Distinct seasonal patterns were noted in terms of several key water quality parameters in Oso Bay, but not for all parameters. For example, no obvious seasonal pattern in salinity was observed (Figs. 3,5,6), likely due to the minimal influence of freshwater sources other than wastewater and runoff during ephemeral high rainfall events. Likewise, no obvious season pattern was observed for pH (Figs. 3,5,6). In contrast, water temperature displayed a typical seasonal cycle, being lowest in winter and peaking during summer (data not shown).

At YB, which is representative of the larger portion of Oso Bay that is influenced by both Oso Creek and discharge of high salinity water from the local power plant, chlorophyll tended to peak during spring through early summer (Fig. 6). In contrast, no clear seasonal pattern in nutrient

concentrations was observed (Fig. 6), except silicate which was frequently $<10 \mu\text{M}$ during winter-spring but much higher during the rest of the year (data not shown). Of all of the environmental parameters measured in this study, only silicate (coefficient 0.0102, $p = 0.0002$) and watershed rainfall (coefficient 0.3734, $p = 0.0198$) had a statistically significant relationship with chlorophyll at this site after the seasonal pattern was taken into account. For example, several large rain events occurred in March-April 2012 (Fig. 4). Chlorophyll began to increase in late-March and peaked at $59 \mu\text{g L}^{-1}$ in late June, remaining above $20 \mu\text{g L}^{-1}$ for over two months from mid-April through late June (Fig. 6). During the initial phase of the bloom in early March 2012, salinity was high (39-42), nitrate concentration was $12.2 \mu\text{M}$ and increased to $40.7 \mu\text{M}$ by late March, and phosphate concentration was $2.1 \mu\text{M}$ (Fig. 6), which could have supported bloom development. By late April, salinity dropped to <3 and inorganic nutrients decreased considerably, yet the bloom remained in place, pointing to either phytoplankton growth on recycled and/or organic nutrients or import of phytoplankton from the eutrophic Oso Creek (Fig. 6). By late May 2012, salinities increased dramatically and nutrient concentrations reached limiting levels, suggesting a shift towards import of phytoplankton from Laguna Madre via discharge from the local power plant. In spring 2013, watershed rainfall was low compared to spring 2012 (Fig. 4), and the phytoplankton bloom was much less pronounced, with chl concentrations $>20 \mu\text{g L}^{-1}$ lasting for <1 month compared to 2.5 months in 2012 (Fig. 6). Salinity increased from 39 to 60 while nutrient concentrations were low at the start of the 2013 bloom (Fig. 6), pointing to import of an already initiated phytoplankton bloom from Laguna Madre as the source of the bloom. DOC and DON concentrations tend to be lowest during the winter at YB, and subsequently peak during late spring-early summer (Fig. 6). In general, DOC

concentrations mirrored chlorophyll concentrations at this site. Dissolved oxygen was highest during winter and lowest during summer, but never reached hypoxic levels (data not shown).

At AG, which is representative of the eutrophied western Oso Bay, chlorophyll tended to peak in spring-summer, though blooms (defined as chlorophyll $>20 \mu\text{g L}^{-1}$) were observed year round (Fig. 5). Of all of the environmental parameters measured, only average 2-d wind speed (coefficient 0.244, $p = 0.034$) and average 2-d wind speed from the previous sampling trip (coefficient 0.309, $p = 0.008$) had a statistically significant relationship with chlorophyll at this site. Inorganic nutrient concentrations were elevated year round at AG (Fig. 5), though oscillations between ammonium and nitrate as the dominant inorganic nitrogen form were pronounced (data not shown). DOC and DON concentrations tend to be lowest during the winter at AG, and subsequently peaked during spring-early summer, concurrent with the seasonal peak in chlorophyll (Fig. 5). Dissolved oxygen was highly variable at AG, displaying a tendency toward hypoxic levels during summer that was occasionally reversed to supersaturated conditions during phytoplankton blooms (Fig. 2).

Nutrient addition bioassays – At the head of the estuary (YB), there was no obvious effect of orthophosphate addition on phytoplankton growth relative to the control (ambient nutrient treatments) in any of the experiments (Table 2), indicating that phosphorus (P) alone is not a limiting factor for phytoplankton growth at this location. However, there was a modest stimulatory effect of nitrate on phytoplankton growth in September and December 2012, indicating that nitrogen (N) can be an important factor controlling phytoplankton growth (Table 2). The most stimulatory effect was noted in treatments where nitrate and orthophosphate were added in combination in September and December (Table 2), indicating that phytoplankton growth may at times be co-limited by both N and P. In March, phytoplankton in all treatments,

including the control, grew at nearly the same rate, indicating that neither N nor P were limiting to phytoplankton growth at this time (Table 2). In July, there was virtually no difference between treatments. Unfortunately, seagrass detritus covered the incubation vessels after 24 hours, making interpretation of the results difficult due to the potential for this to have created artificial light limitation.

In western Oso Bay (MG), there was no obvious effect of orthophosphate addition on phytoplankton growth relative to the control in any of the experiments (Table 2). This indicates that phosphorus (P) alone is not a controlling factor for phytoplankton growth at this location. However, there was a very strong stimulatory effect of nitrate on phytoplankton growth in September 2012, December 2012, July 2013 and March 2014, indicating that nitrogen (N) is an important factor controlling phytoplankton growth in this region (Table 2). There was no difference in response between the nitrate-amended treatments and nitrate + phosphate-amended treatments in September 2012, December 2012 or March 2014, indicating that phytoplankton growth was not co-limited by N and P. In July 2013, there was a slightly greater response to N and P compared to N alone, suggesting the possibility for co-limitation by N and P. In March 2013, phytoplankton growth declined in all treatments. This is almost certainly due to the fact that the experiment was initiated during the declining phase of a very large phytoplankton bloom, hence the nutrient levels were insufficient for supporting a bloom of that magnitude.

Discussion

Coastal eutrophication is a global phenomenon resulting from human activity in watersheds as well as climate change (Cloern 2001; Paerl et al. 2006; Rabalais et al. 2009). To date, there has been limited evidence of eutrophication-related concerns in Texas estuaries, though recent

trends in population growth and land use change have the potential to contribute to long-term deterioration of coastal water quality in the absence of mitigation activities. Findings from this study demonstrate water quality degradation in an urbanizing South Texas estuary, Oso Bay. Previous studies have documented episodic hypoxia in this system (e.g., Nicolau 2001), though primary focus from a water quality standpoint has been on pathogenic bacterial levels in both Oso Creek and Oso Bay, which exceed regulatory agency criteria and are now the focus of a total maximum daily load process (Texas Commission on Environmental Quality, www.tceq.texas.gov). Results presented here indicate localized presence of very high nutrient concentrations year round, dense phytoplankton blooms, and episodic hypoxia/anoxia. However, the overall effects of this eutrophication may not be isolated to a specific region of Oso Bay, considering both the connectivity that Oso Bay has with the larger Corpus Christi Bay system as well as evidence presented here of export of this eutrophied water to a region of Corpus Christi Bay that is prone to hypoxia. Thus from a management standpoint, the potential broader-scale implications of the localized eutrophication should be given consideration.

At the local level (i.e., western Oso Bay), clear effects of wastewater effluent discharge were observed on several water quality parameters, consistent with results from prior studies in other systems (Anderson et al. 2002; Mallin et al. 2005). In particular, very high inorganic nutrient (N, P) and DON concentrations were observed virtually year round, and dense phytoplankton blooms were observed for a large portion of the year at AG. High phytoplankton biomass (chlorophyll) was only observed episodically at the wastewater site (WP) however, presumably a result of chlorination of the effluent which would prevent significant phytoplankton growth. Nonetheless, results from another study that took place in 2013 showed that the high chlorophyll conditions observed at AG often extend well out into the center of Oso Bay, and occasionally to

OI (Schroer 2014). The presence of hypoxia/anoxia was somewhat surprising given the shallow water column (<1 m) and persistent wind-driven mixing in western Oso Bay. This phenomenon is not unheard however, as Verity et al. (2006) observed a long term decrease in dissolved oxygen as well as presence of hypoxia in shallow, well mixed estuaries in Georgia that were experiencing eutrophication. The high phytoplankton biomass in western Oso Bay would represent an obvious source of labile organic matter fueling bacterial oxygen demand (Paerl et al. 1998; Kemp et al. 2005). Another source of organic matter that may contribute to biological oxygen demand is DOC, which reached very high concentrations and was apparently derived from both the wastewater effluent and phytoplankton exudation, as noted by the strong correlation between DOC and chlorophyll. Both wastewater-derived DOC (Servais et al. 1987; Abril et al. 2002; Petrone et al. 2009) and phytoplankton-derived DOC can be labile (Wetz et al. 2008; Lonborg et al. 2010). In short, the western region of Oso Bay appears to be prone to low oxygen conditions as a result of elevated organic matter loads. Overall, the combination of episodic low oxygen conditions as well as presence of low pH water (<8) has potential to impose stress on organisms in this part of Oso Bay, as has been shown elsewhere (Ringwood and Keppler 2002; Sunda and Cai 2012). A complementary study is underway looking at benthic diversity and biomass in Oso Bay, with preliminary results showing low diversity in the wastewater-influenced region of Oso Bay (K. DeSantiago and J. Pollack, unpubl. data).

Differences were observed in certain water quality parameters between AG and WP that are worth mentioning, despite the fact that both sites are fed by the same source water (i.e., treated wastewater effluent). For example, N+N and ammonium levels were ca. 75% lower on average and orthophosphate levels were 43% lower at AG compared to WP despite similar source water (i.e., wastewater effluent). This may be partially explained by greater uptake potential by

phytoplankton at AG, although based on the differences in chlorophyll between sites and a conservative estimate of cellular N:chl ratio (10:1), phytoplankton uptake would only account for ~5% of the observed nitrogen difference between sites. This indicates that other factors are primarily responsible for this difference in nutrient concentrations between sites. One argument could be that the pronounced presence of wetland plants in the AG tributary as well as potential for nutrient processing in an on-site pond may have contributed to significant nutrient capture. Furthermore, whereas the plant-lined AG tributary is ca. 900 m long and contains several meanders that could aid in water and material retention, the WP tributary is only ca. 200 m long and follows a nearly straight path into Oso Bay. These findings point to the importance of effective management practices for aiding in nutrient removal on golf courses (cf. Mallin et al. 2000), and further suggest that redesign of the WP tributary may have beneficial results in terms of pollutant removal if modeled after the neighboring AG tributary.

Based solely on nutrient concentrations and frequency of phytoplankton blooms at OI compared to the western Oso Bay sites, it could be concluded that the most direct effects of wastewater-derived eutrophication (i.e., nutrients-phytoplankton-hypoxia) were limited to the western subregion of the bay. In other words, there appears to be significant internal nutrient processing as water masses move away from western Oso Bay towards the mouth. These results are consistent with findings from Schroer (2014), who observed sharp gradients in nutrients and chlorophyll from western Oso Bay to the mouth. Nonetheless, in this study's much longer time series, there were a number of instances when signatures of wastewater were present at OI. Although this water was frequently devoid of inorganic nutrients, it typically contained relatively high DOC concentrations and occasionally high chlorophyll. These findings are significant because the region of Corpus Christi Bay adjacent to the mouth of Oso Bay has been shown to

experience episodic hypoxia from spring-fall, causing negative effects on benthic communities in this area (Montagna and Ritter 2006; Montagna and Froeschke 2009). To date, no studies have identified the source(s) of organic matter fueling hypoxia in Corpus Christi Bay, though physical mechanisms have been proposed. In one example, Hodges et al. (2011) describe the advection of hypersaline water near the bottom out of Oso Bay. This water mass remains isolated from the overlying water once in Corpus Christi Bay, triggering hypoxic conditions due to lack of reoxygenation. Indeed, hypersaline water was observed on several instances at the mouth of Oso Bay in the present study. More frequently however, very low salinity conditions were observed at the mouth and were often not explainable without invoking wastewater advection. In the case of both hypersaline and low salinity conditions, these water masses were accompanied by relatively high DOC and occasionally high chlorophyll concentrations. Thus it could be theorized that Oso Bay is an important source of organic matter driving microbial respiration in the hypoxic zone of Corpus Christi Bay. Furthermore, these results argue that the direct (senescing phytoplankton blooms, wastewater-derived DOC) and indirect (phytoplankton-derived DOC) effects of the eutrophication of western Oso Bay have farther reaching implications than just that part of Oso Bay.

It is not unreasonable to conclude that Oso Bay represents a sentinel for the future of Texas estuaries as well as other estuaries worldwide that may experience significant urbanization. Developing nations in particular are expected to see a major increase in wastewater facilities and associated nutrient loadings over the coming decades due to population growth (van Drecht et al. 2009), and the effects of wastewater discharge are readily evident in Oso Bay. In Oso Bay, an argument can be made that the symptoms of eutrophication as well as possible linkages to Corpus Christi Bay hypoxia necessitates efforts to control nutrient loading to the bay. Given the

correlation between nitrogen concentrations and chlorophyll in western Oso Bay, as well as the growth response of phytoplankton in this region to nitrogen additions in bioassays, this suggests that nitrogen inputs from wastewater discharge may need to be reduced to alleviate the symptoms of eutrophication in Oso Bay.

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Figure Legends

Figure 1. (A) Location of Oso Bay along the Texas coast. (B) Location of two rainfall measurement sites, Corpus Christi International Airport (CCIA) and Naval Air Station-Corpus Christi (NAS-CC), in relation to Oso Bay. (C) Location of six sampling sites in this study.

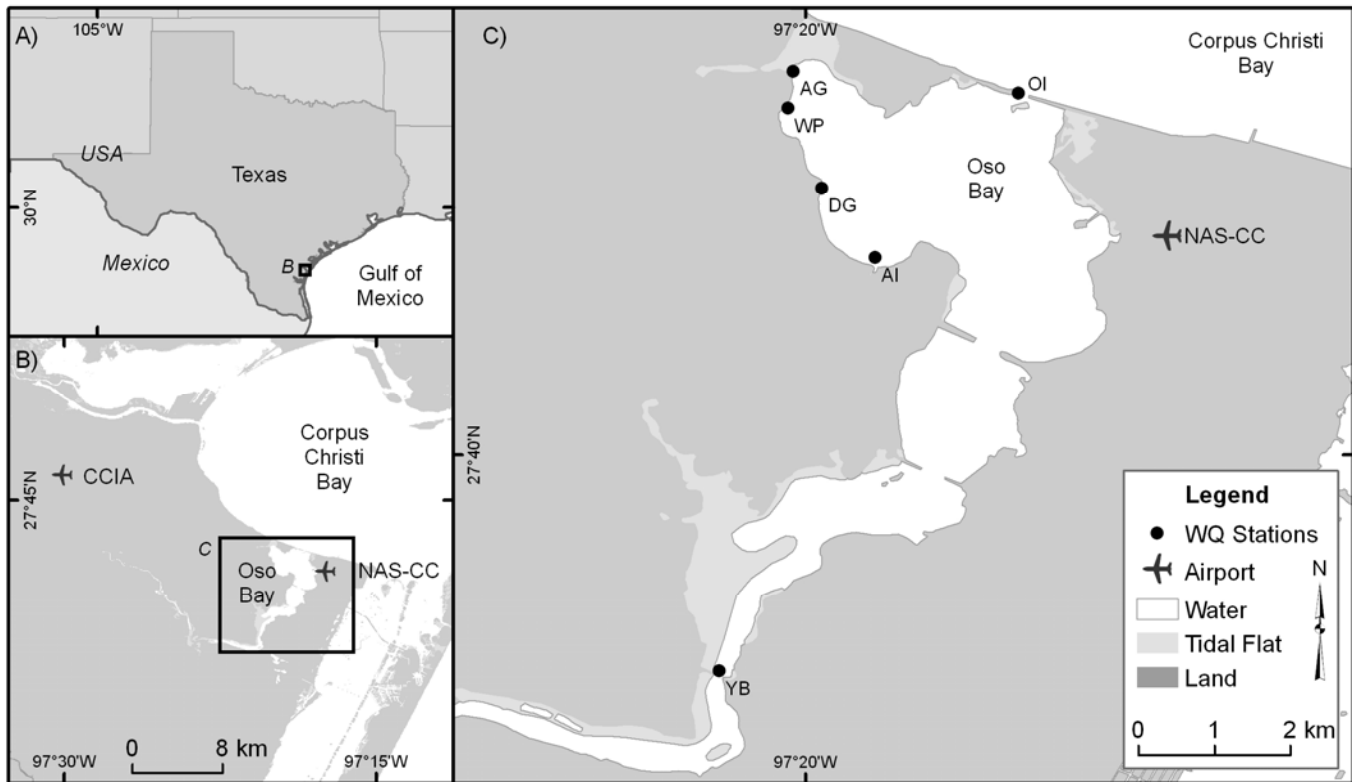
Figure 2. Dissolved oxygen concentration (mg L^{-1}) at (A) AG, WP, and (B) AI, DG sites in Oso Bay.

Figure 3. Temporal pattern of select water quality parameters at site OI (mouth) in Oso Bay. (A) Salinity and chlorophyll, (B) dissolved organic carbon, (C) dissolved inorganic nitrogen and dissolved organic nitrogen, and (D) orthophosphate and pH.

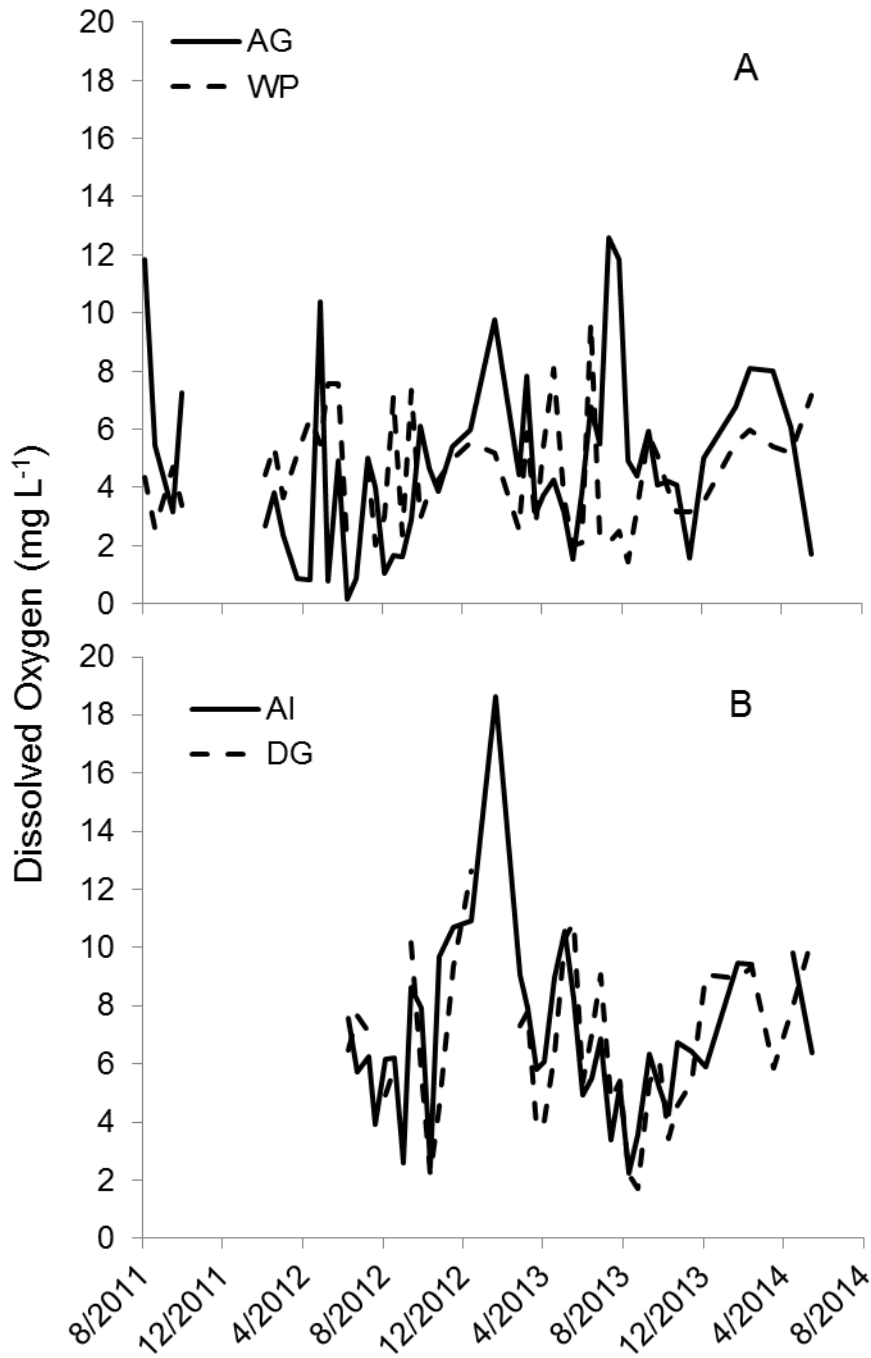
Figure 4. Rainfall (mm) as measured at (Top) CCIA and (Bottom) NAS-CC.

Figure 5. Temporal pattern of select water quality parameters at site AG in western Oso Bay. (A) Salinity and chlorophyll, (B) dissolved organic carbon, (C) dissolved inorganic nitrogen and dissolved organic nitrogen, and (D) orthophosphate and pH.

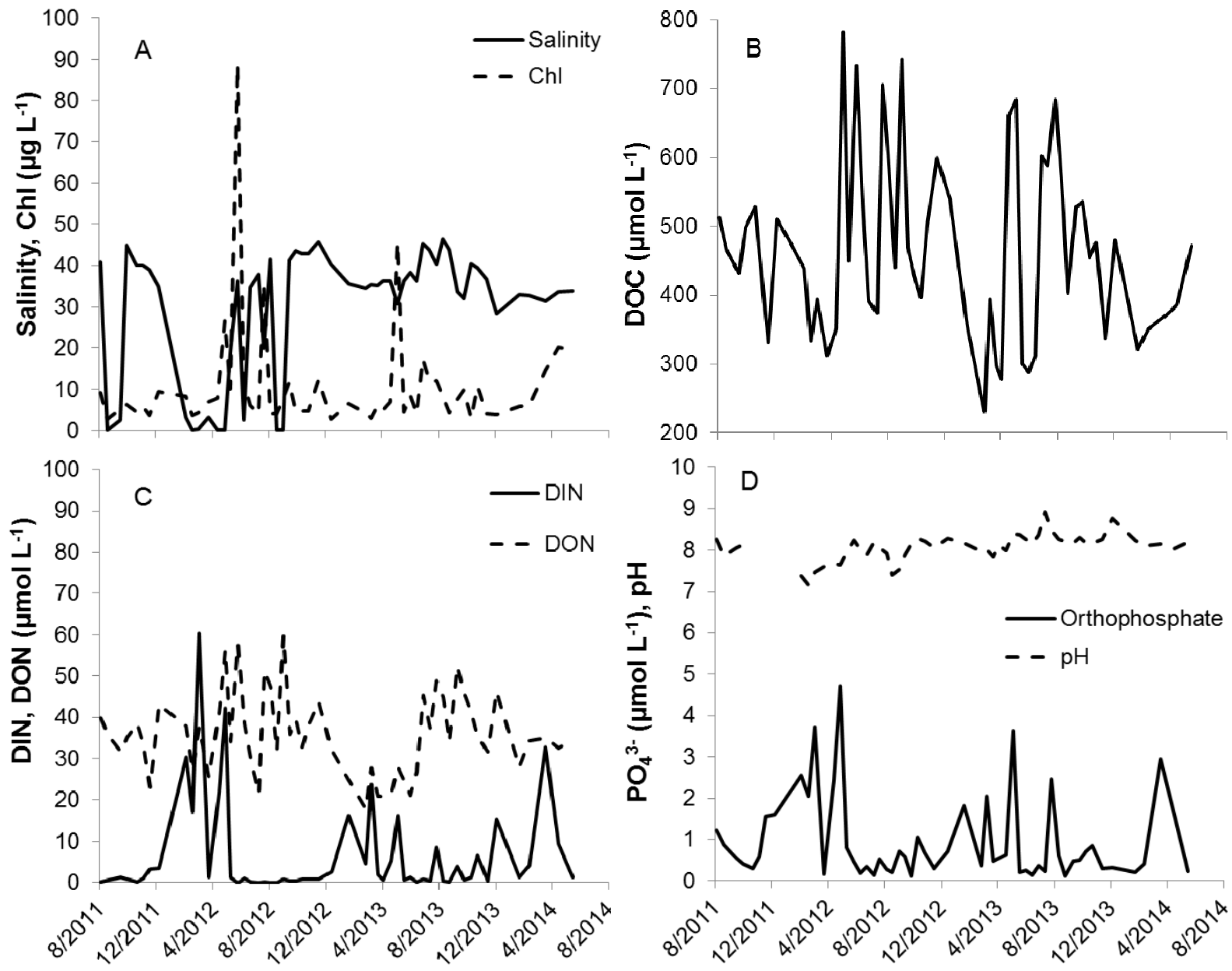
Figure 6. Temporal pattern of select water quality parameters at site YB (head) in Oso Bay. (A) Salinity and chlorophyll, (B) dissolved organic carbon, (C) dissolved inorganic nitrogen and dissolved organic nitrogen, and (D) orthophosphate and pH.



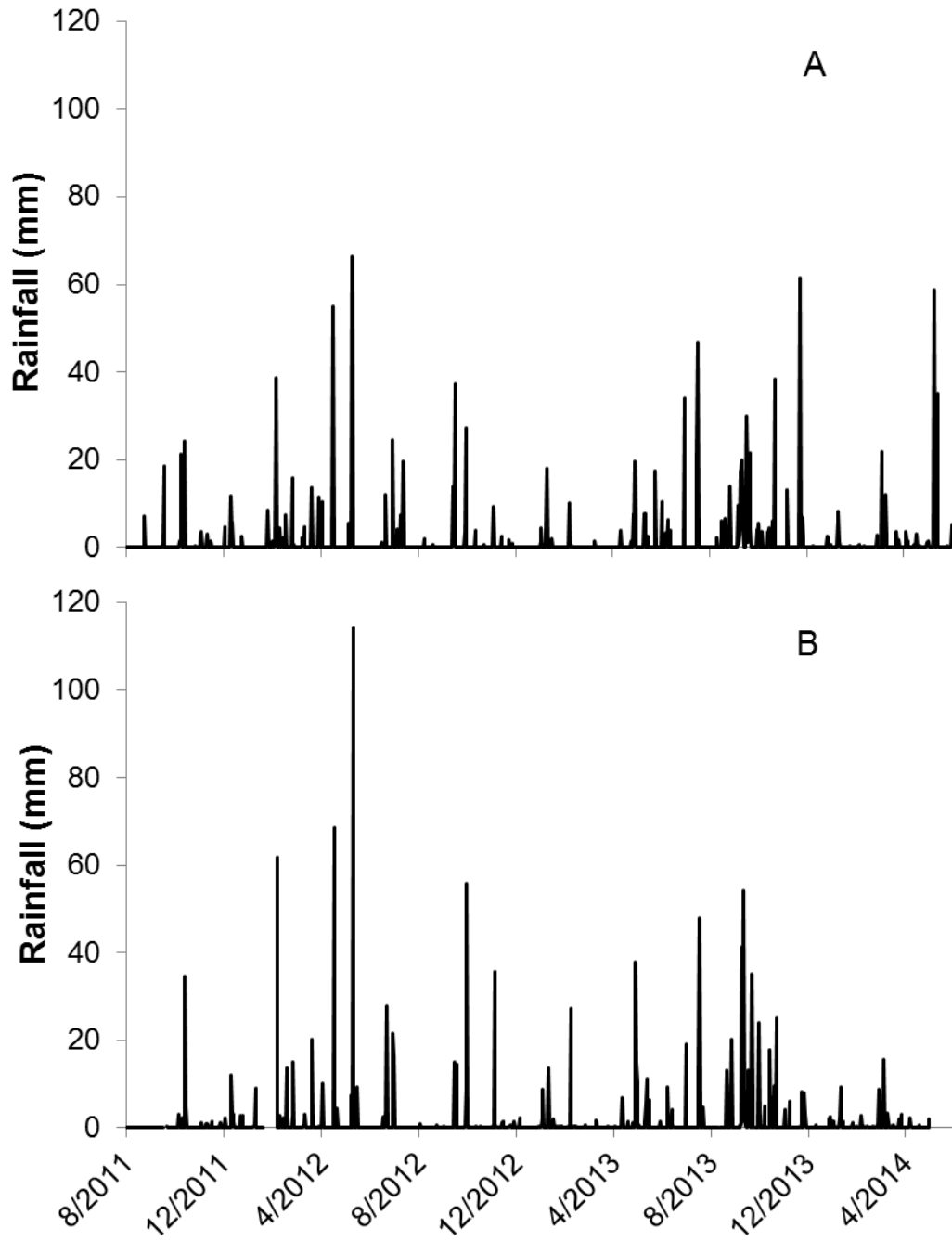
Wetz et al. Figure 1.



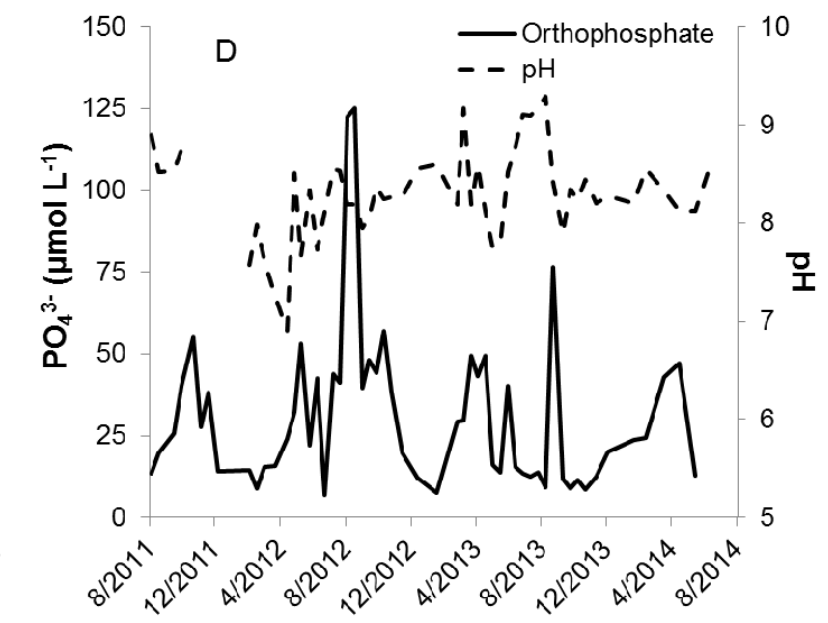
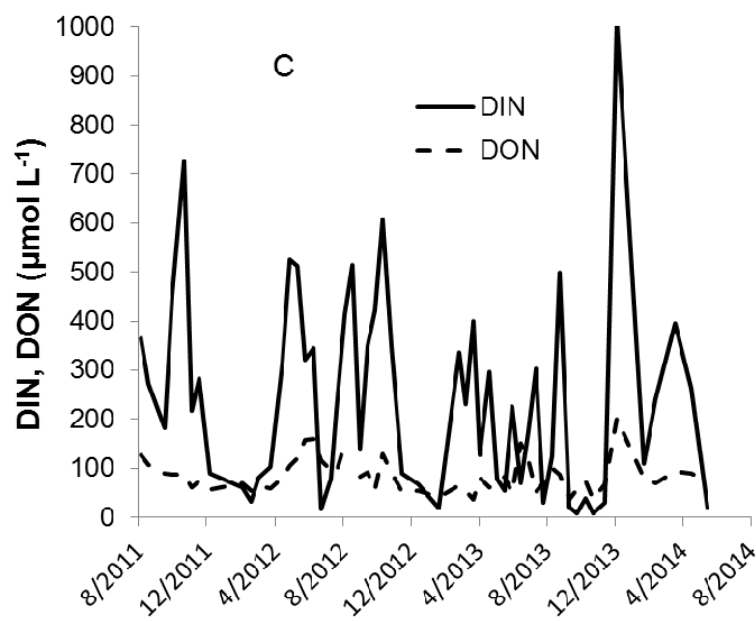
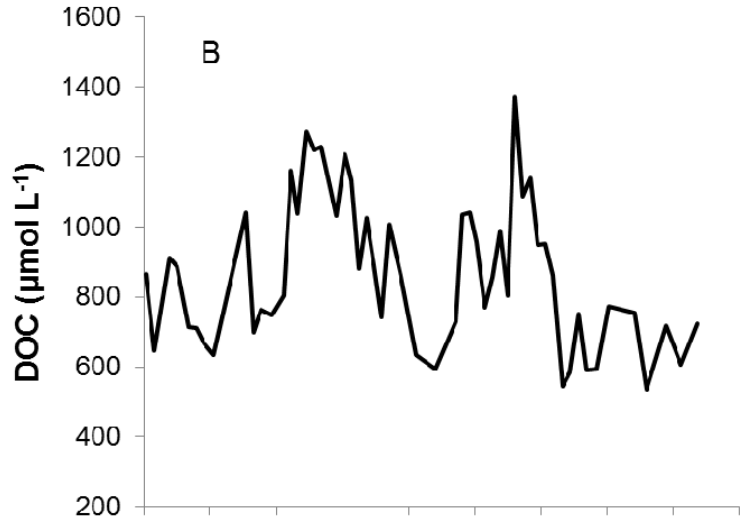
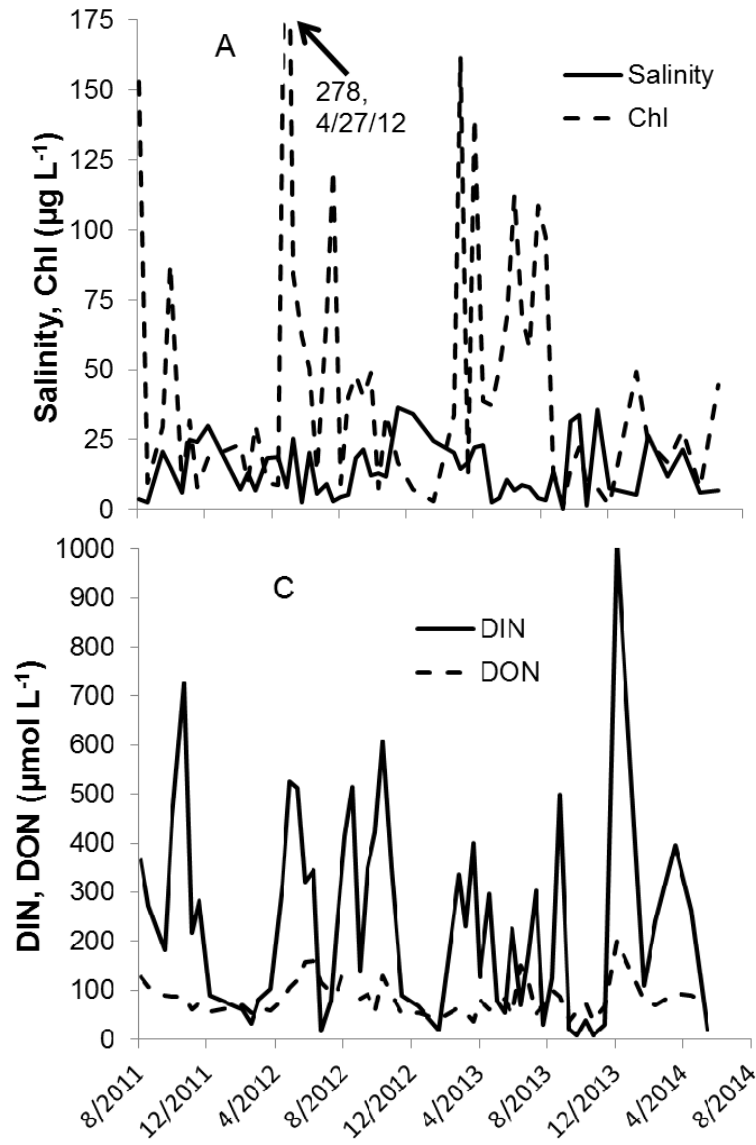
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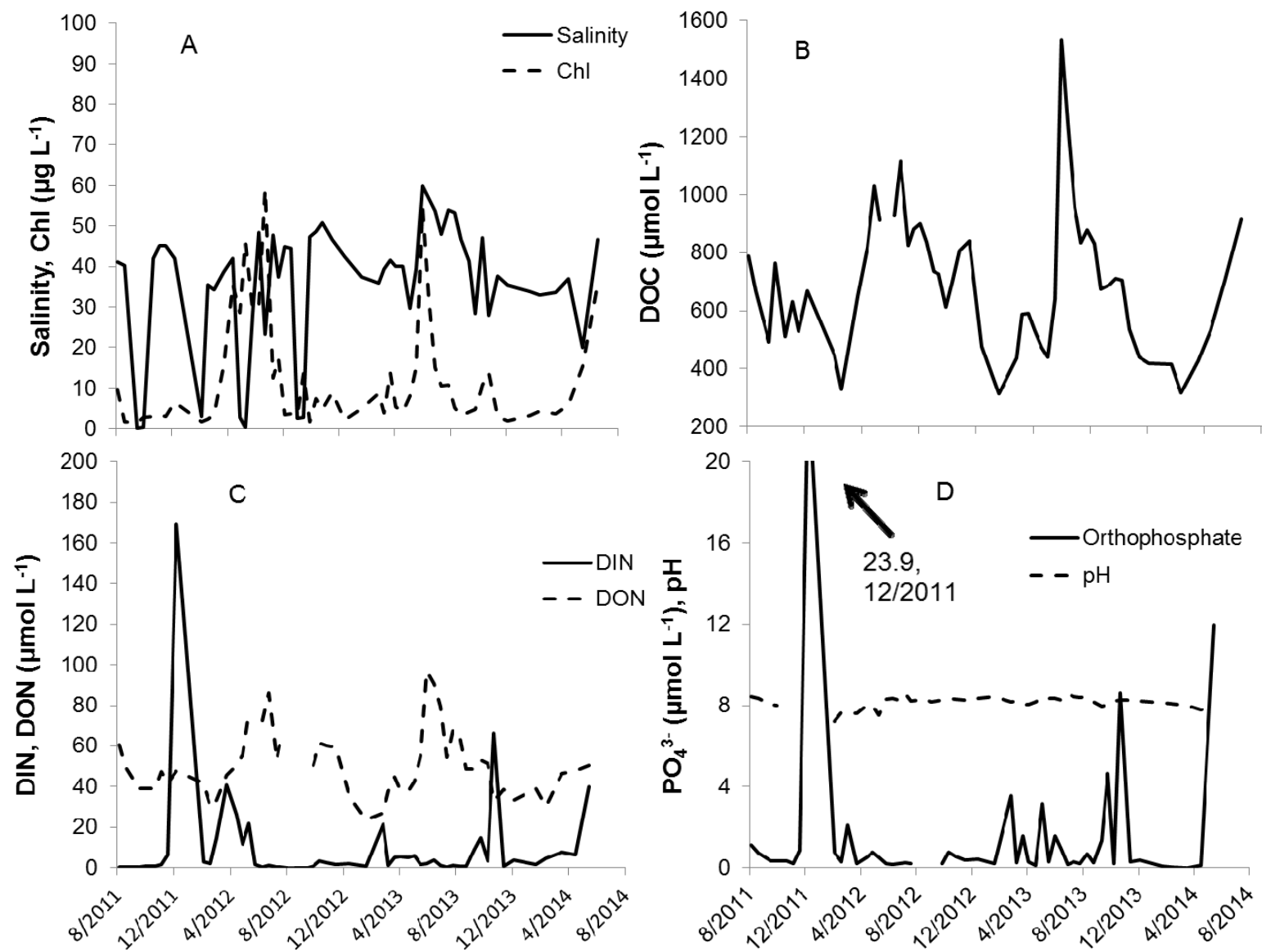
Wetz et al. Figure 3



Wetz Figure 4



Wetz et al. Figure 5



Wetz et al. Figure 6

Table 1. Mean \pm SD for a select set of water quality parameters from six Oso Bay sampling sites from 6/8/2012 to 5/15/2014.

	Salinity	Temp.	pH	N+N	NH₄⁺	PO₄³⁻	DOC	DON	Chl a	D.O.
AG	14 \pm 11	24 \pm 6	8.4 \pm 0.4	125 \pm 126	96 \pm 128	33 \pm 28	879 \pm 218	84 \pm 37	44 \pm 41	4.8 \pm 2.8
WP	6 \pm 8	26 \pm 4	7.4 \pm 0.4	495 \pm 295	383 \pm 231	58 \pm 27	768 \pm 80	151 \pm 195	5 \pm 6	4.3 \pm 2.0
OI	34 \pm 11	23 \pm 6	8.2 \pm 0.3	2 \pm 6	2 \pm 3	1 \pm 1	463 \pm 133	35 \pm 10	10 \pm 9	6.4 \pm 1.8
YB	39 \pm 13	24 \pm 6	8.2 \pm 0.2	4 \pm 12	3 \pm 3	1 \pm 3	699 \pm 254	52 \pm 18	11 \pm 13	6.2 \pm 1.5
AI	27 \pm 17	23 \pm 7	8.2 \pm 0.3	23 \pm 56	10 \pm 18	5 \pm 7	682 \pm 205	53 \pm 18	27 \pm 21	7.0 \pm 3.1
DG	26 \pm 14	23 \pm 6	8.3 \pm 0.3	26 \pm 41	18 \pm 30	7 \pm 6	773 \pm 185	61 \pm 15	27 \pm 18	6.6 \pm 2.6

Table 2. Results from nutrient addition bioassays. “No” indicates no phytoplankton growth response, “+” indicates a positive growth response, and “++” indicates a positive growth response that exceeds another positive growth response in the same experiment.

Site	Treatment	Sept. 2012	Dec. 2012	March 2013	March 2014	July 2013	July 2014
YB	N	+	+	No		No	
	P	No	No	No		No	
	N+P	++	++	No		No	
AG	N	+	+	No	+	+	No
	P	No	No	No	No	No	No
	N+P	+	+	No	+	++	No