Water quality dynamics in an urbanizing subtropical estuary (Oso Bay, Texas)

Michael S. Wetz[*,a]

Kenneth C. Hayes[a]

Kelsey V.B. Fisher[a]

Lynn Price[a,1]

Blair Sterba-Boatwright[b]

*Corresponding author

[a]Department of Life Sciences
Texas A&M University-Corpus Christi
6300 Ocean Dr., Unit 5860
Corpus Christi, TX 78412
Email: michael.wetz@tamucc.edu
Phone: 361-825-2132
Fax: 361-825-2025

[b]Department of Mathematics and Statistics
Texas A&M University-Corpus Christi
6300 Ocean Dr.
Corpus Christi, TX 78412

[1]Present address:
Department of Ocean, Earth and Atmospheric Sciences
Old Dominion University
406 Oceanography
Norfolk, VA 23529

Abstract

Results are presented from a study of water quality dynamics in a shallow subtropical estuary, Oso Bay, Texas, which has a watershed that has undergone extensive urbanization in recent decades. High inorganic nutrient, dissolved organic matter and chlorophyll concentrations, as well as low pH (<8), were observed in a region of Oso Bay that receives wastewater effluent. Despite being shallow (<1 m) and subjected to strong winds on a regular basis, this region also exhibited episodic hypoxia/anoxia. The low oxygen and pH conditions are likely to impose significant stress on benthic organisms and nekton in the affected area. Signatures of eutrophied water were occasionally observed at the mouth of Oso Bay, suggesting that it may be exported to adjacent Corpus Christi Bay and contribute to seasonal hypoxia development in that system as well. These results argue for wastewater nutrient input reductions in order to alleviate the symptoms of eutrophication.

Keywords: Estuary, water quality, eutrophication, phytoplankton, hypoxia, wastewater

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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 coastal watershed hydrology and biogeochemistry (Kennish 2002).

Human population growth often results in increasing impervious surface coverage and wastewater discharge 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 ultimately affect estuarine water quality (Hopkinson and Vallino 1995; Hutchins et al. 2014). For example, numerous studies have shown that increasing impervious surface coverage and wastewater discharge lead to increased inputs of inorganic nutrients (Bowen and Valiela 2001; Howarth et al. 2002; Handler et al. 2006; Mallin et al. 2009; Rothenberger et al. 2009; Jang et al. 2011) and microbial pathogens (Mallin et al. 2000, 2009; Holland et al. 2004; Handler et al. 2006; Campos and Cachola 2007), as well as high rates of microbial respiration and/or low oxygen conditions in receiving waters (Brosnan and O'shea 1996; Mallin et al. 2009; Andrade et al. 2011; Jang et al. 2011). Presence of impervious surface also alters the timing, magnitude and pathways of runoff and associated pollutants to the extent that the ability of a system to process pollutants such as nutrients can be inhibited (Hopkinson

and Vallino 1995). 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) 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 accelerate estuarine water quality degradation, with negative impacts on ecosystem structure and trophic dynamics (Flemer and Champ 2006; Wetz and Yoskowitz 2013).

South Texas supports a number of ecologically and economically productive estuarine ecosystems. Agriculture represents the dominant land use coverage in many South Texas coastal watersheds. However, there is a growing trend of urbanization as well. For example, the most populous coastal county in the region, Nueces, experienced an 8.5% increase in human population 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). Despite the prevalence of agricultural land use coverage as well as the obvious potential for urbanization to affect the ecological health of the aforementioned systems, many gaps exist in terms of water quality assessments in Texas 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).

Oso Bay, in Nueces County, Texas, is a secondary embayment that flows into Corpus Christi Bay. There are indications that water quality degradation is occurring in Oso Bay, including: 1) localized presence of high concentrations of pathogenic bacteria for which a total maximum

daily load (TMDL) has been recommended, and 2) episodic low dissolved oxygen levels resulting in the bay being placed on the U.S. EPA "impaired" waters list. While recent attention has begun to focus on pathogenic bacteria sources/dynamics as a result of the TMDL process, little is known about the drivers of phytoplankton blooms or hypoxia/anoxia in the system. Here we report results from a 3-year study of the spatial-temporal dynamics of select water quality parameters in Oso Bay, and evaluate mechanisms that control these important water quality indicators. We conclude that Oso Bay is a case study for the future of many warm subtropical estuaries worldwide that are expected to undergo significant urbanization and experience growing influence of wastewater.

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).

Sampling program – Water samples were collected on a biweekly (March-October) to monthly (November-February) basis, weather permitting, from August 2011 to December 2013, and monthly from January 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). YB integrates flows coming out

of not only Oso Creek, but also discharge from a power plant cooling pond that can far exceed volumetric flows from Oso Creek (Wetz, unpubl. data). Four other sites, representing the main tributaries of Oso Bay, were also chosen. These 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). Samples were collected near the mouth of each tributary where they enter Oso Bay. Sample collection did not begin at AI and DG until June 2012. Sampling occurred in the morning on each date. Conductivity (salinity), dissolved oxygen, pH and temperature were measured 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. Samples were stored on ice until return to the laboratory for processing, which occurred 1-3 hours after collection. This water was subsequently analyzed for: chlorophyll *a*, inorganic nutrients (silicate; ammonium; nitrate plus nitrite, N+N; nitrite; orthophosphate, PO_4^{3-}), 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 watershed rainfall and cloud cover data for the study period were obtained from the Corpus Christi International Airport, while daily average wind speed was obtained from Naval Air Station-Corpus Christi (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 homogenize the water and materials contained therein. For

chlorophyll *a* determination, a known volume of sample water was gently filtered (≤ 5 mm Hg) through 25 mm Whatman GF/F filters. Filters were stored frozen (-20ºC) in sealed Vacutainers until analysis. Chlorophyll *a* was extracted from the filters by soaking for 18-24 hours in 90% HPLC-grade acetone at -20ºC, 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 (-20ºC) until analysis. After thawing to room temperature, samples were analyzed on a Seal QuAAtro autoanalyzer. Standard curves with five different concentrations were run daily at the beginning of each run. Fresh standards were made prior to each run by diluting a primary standard with low nutrient surface seawater. Deionized water (DIW) was used as a blank, and DIW blanks were run at the beginning and end of each run, as well as after every 8-10 samples to correct for baseline shifts. 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 (-20ºC) until analysis. Samples were subsequently analyzed using the High Temperature Catalytic Oxidation method on a Shimadzu TOC-Vs analyzer with nitrogen module. Standard curves were run twice daily using a DIW blank and five concentrations of either acid potassium phthalate solution or potassium nitrate for DOC and TDN, respectively. Three to five subsamples were taken from each standard and water sample and injected in sequence. Reagent grade glucosamine was used as a laboratory check standard and inserted throughout each run, as were Certified Reference Material Program (CRMP) deep-water standards of known DOC/TDN concentration. Average daily CRMP DOC and TDN concentrations were 44.1 ± 5.2 μmol L^{-1} and 32.8 ± 2.4 μmol L^{-1} respectively. Dissolved organic nitrogen (DON) was determined by subtracting dissolved inorganic nitrogen (ammonium, N+N)

from TDN. For the entire dataset, calculated DON concentration was negative and outside of analytical error for 5 out of 210 samples (1 each from DG and MP, 3 from 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.

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 were calculated 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. Seasonal patterns in chlorophyll were modeled using a cyclic penalized spline based on day-of-the-year. 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.

Correlation between ln(chlorophyll) and environmental parameters, as well as between ln(chlorophyll) and environmental parameters from the previous time period, was used to eliminate environmental parameters not related to chlorophyll. An exhaustive search of models using the combinations of the remaining parameters was performed, with models ranked by adjusted R^2. An initial model was built using the variables that occurred most frequently in the highest-ranking models. Forward and backward regression with a significance level of $\alpha = 0.05$ and changes in adjusted R^2 were used to assess addition or retention of individual variables in the model. To model associations between dissolved oxygen and various environmental parameters, the same process was used for site YB. For site MP, there was no annual trend and hence no spline component of the resulting models. The removal of the spline allowed us to use deleted residuals in the exhaustive search to focus on the models' predictive strength.

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).

Results

Spatial trends – Salinity was highest at the head of Oso Bay (YB; 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. Intermediate 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 the other sites by 3-10^{o}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 ± 295 μM-N, followed by AG which averaged 125 ± 126 μM-N (Table 1). Intermediate N+N concentrations were observed at AI and DG, averaging 23 ± 56 μM-N and 26 ± 41 μM-N, respectively (Table 1). The differences in ln(N+N) between WP and AG were significant at salinities <15, and the differences in ln(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 ± 12 μM-N and 2 ± 6 μM-N respectively (Table 1).

Ammonium concentrations were highest at WP, averaging 383 ± 231 μM-N, followed by AG which averaged 96 ± 128 μM-N (Table 1). Ammonium concentrations were intermediate at AI and DG, averaging 10 ± 18 μM-N and 18 ± 30 μM-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 ± 3 μM-N and 2 ± 3 μM-N respectively (Table 1).

PO_4^{3-} concentrations were highest at WP, averaging 58 ± 27 μM-P, followed by AG which averaged 33 ± 28 μM-P (Table 1). Intermediate PO_4^{3-} concentrations were observed at AI and DG, averaging 5 ± 7 μM-P and 7 ± 6 μM-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 ± 3 μM-P and 1 ± 1 μM-P respectively (Table 1).

DOC concentrations were highest at AG, averaging 879 ± 218 μM, followed by DG (773 ± 185 μM) and WP (768 ± 80 μM) (Table 1). DOC concentrations were intermediate at YB and AI, averaging 699 ± 254 μM and 682 ± 205 μM, respectively (Table 1). Lowest concentrations were observed at OI, averaging 463 ± 133 μM (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 144 ± 191 μM-N, followed by AG (84 ± 37 μM-N) (Table 1). Intermediate DON concentrations were found at DG (61 ± 15 μM-N), AI (53 ± 18 μM-N) and YB (52 ± 18 μM-N). Lowest DON concentrations were found at OI, averaging 35 ± 10 μM-N (Table 1). Ln(DON) concentrations were significantly different between AG and DG, and AG and AI at all tested salinity levels.

Highest chlorophyll *a* concentrations were found at AG, which averaged 44 ± 41 μg L^{-1}, followed by DG (27 ± 18 μg L^{-1}) and AI (27 ± 21 μg L^{-1}) (Table 1). Intermediate chlorophyll *a* levels were found at YB (11 ± 13 μg L^{-1}) and OI (10 ± 9 μg L^{-1}), while the lowest levels were found at WP (5 ± 6 μg L^{-1}) (Table 1). Dissolved oxygen 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). Dissolved oxygen < 3 mg L^{-1} were observed in 27% of samples at AG, 28% of samples at WP and 8% of samples at DG, while hypoxic levels (<2 mg L^{-1}) were observed in 22% of samples at AG, 6% of samples at WP, and 3% of samples at DG (Fig. 2).

Temporal dynamics of chlorophyll a and dissolved oxygen- At YB, chlorophyll tended to peak during spring through early summer (Fig. 3). On an interannual basis, the spring-summer phytoplankton bloom (defined as chlorophyll *a* concentration >20 μg L^{-1}) was much less pronounced in 2013 when it lasted for <1 month, compared to 2012 when it lasted 2.5 months (Fig. 3). In spring 2013, watershed rainfall was low compared to spring 2012 (Fig. 4), April

mean water temperature averaged 6.4 ºC cooler than in 2012 (Fig. 3), and April cloud cover was nearly 2-fold higher than in 2012 (data not shown). These results are consistent with statistical findings that show a strong seasonal influence on chlorophyll *a* at YB, presumably due to temperature. In addition, watershed rainfall (coefficient = 0.20, $p = 0.02$), cloud cover from the previous sampling period (coefficient = -0.10, $p = 0.03$), DON (coefficient = 0.02, $p = 0.02$) and silicate (coefficient = 0.26, $p = 0.002$) had a significant relationship with chlorophyll *a*. Silicate concentrations were typically <10 µM during winter-spring but much higher during the rest of the year (Fig. 3). Silicate showed no relationship with salinity at YB, but had a positive linear relationship with temperature (data not shown). No clear patterns were observed in terms of N+N, ammonium or phosphate concentrations, and no relationships between these parameters and salinity or temperature were detected (Fig. 3).

At AG, which is representative of the eutrophied western Oso Bay, chlorophyll *a* tended to peak in spring-summer, though blooms (defined as chlorophyll *a* >20 µg L^{-1}) were observed year round (Fig. 5). Orthophosphate concentrations were consistently > 5 µM-P year round, and appeared to peak during spring-fall (Fig. 5). While a seasonal pattern was observed for total dissolved inorganic nitrogen concentrations, with highest concentrations typically in spring-fall (Fig. 5), no clear pattern was observed for individual constituents (i.e., N+N, ammonium; Fig. 5). Of all of the environmental parameters measured, salinity (coefficient = 0.03, $p = 0.04$), wind speed (coefficient = 0.37, $p = 0.01$), wind speed from the prior sampling date (coefficient = 0.37, $p = 0.02$) and ammonium from the prior sampling date (coefficient = 0.19, $p = 0.03$) had a statistically significant relationship with chlorophyll *a* at this site.

Dissolved oxygen at YB was highest during winter and lowest during summer, but never reached hypoxic levels (data not shown). Only salinity (coefficient = -0.04, $p = 0.003$) had a

statistically significant relationship with dissolved oxygen at YB after the seasonal pattern was taken into account. In contrast to YB, dissolved oxygen was highly variable at AG, with hypoxia and even anoxia occasionally observed as well as supersaturated conditions during phytoplankton blooms (Fig. 2). Dissolved oxygen <2 mg L^{-1} was particularly noticeable in 2012, such as during 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). Several environmental parameters correlated with dissolved oxygen at AG, including orthophosphate (coefficient = -1.53, $p = 0.02$), local rainfall (coefficient = -1.04, $p < 0.01$), ammonium (coefficient = -1.66, $p < 0.001$), dissolved inorganic nitrogen (coefficient = 2.17, $p < 0.001$), chlorophyll *a* (coefficient = 0.63, $p = 0.02$), and salinity from the previous sampling date (coefficient = 0.09, $p < 0.01$).

Evidence of potential export from Oso Bay to Corpus Christi Bay – This study yielded circumstantial evidence that water and associated materials are occasionally exported out of Oso Bay into Corpus Christi Bay, based on water quality data from site OI at the mouth of Oso Bay. For example, the presence of low salinity at OI can only arise from Oso Bay, as there are no obvious sources of freshwater in the region of Corpus Christi Bay adjacent to OI. Likewise, the presence of hypersaline water from OI is indicative of power plant cooling water that has been advected from upper Oso Bay to the mouth.

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 <2 μM (Fig. 6). No rainfall was recorded in early-mid August (Fig. 4) and salinity was initially high at YB (40; Fig. 3), thus the first appearance of low salinity water at OI in mid-August was likely due to

advection 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} chlorophyll *a*) was in place at AG, which could have depleted nutrients from the water column prior to water from this region being advected to OI (Fig. 5). Between mid-August and mid-September 2011, several small rain events were noted and the salinity dropped at YB from 40.3 to 0.3 (Figs. 3,4). Thus we cannot rule out discharge of freshwater from Oso Creek as contributing to the continued presence of low salinity water at OI in mid-September 2011.

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. 6). 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. 3), indicating that the source of low salinity water at OI could have been discharge from Oso Creek. From mid-February through mid-April 2012, salinity increased considerably at YB (Fig. 3), indicating that the source of low salinity water at OI switched to either runoff from local tributaries and/or wastewater from western Oso Bay. From mid-April through early May 2012, salinity decreased again at YB concurrent with several watershed rainfall events (Figs. 3,4), suggesting that flow of low salinity water out of Oso Creek could 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 (<2 μM) inorganic nutrient concentrations (Fig. 6). No significant rainfall occurred in the watershed prior to this event and salinity was high (48.4) at YB (Figs.

3,4), pointing to wastewater as the source of the low salinity. Salinities were also relatively low at AI and DG (2.8-5.0; data not shown), which may further highlight the expansive coverage of wastewater in Oso Bay. Large, prolonged phytoplankton blooms occurred throughout much of western Oso Bay (i.e., >50 μg L^{-1} Chl *a* at AG, AI, DG), which could 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 μg L^{-1}, a DOC increase from 375 to 706 μM, and a DON increase from 22 to 51 μM (Fig. 6). Inorganic nitrogen levels at this time were <1 μM however (Fig. 6). 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. 3,4), pointing to influence of discharge from Oso Creek or runoff from local tributaries 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 (<1 μM) (Fig. 6). No rainfall was recorded in early-mid August and salinity at YB was initially high (44.5) (Figs. 3,4), thus the appearance of low salinity water at OI in mid-August was likely due to advection of wastewater from western Oso Bay. In late July 2012, a very large phytoplankton bloom (122 μg L^{-1} chlorophyll *a*) was in place at AG, and throughout August 2012 chlorophyll *a* concentrations were >40 μg L^{-1}, which could have depleted nutrients from the water column prior to water from this region being advected to OI (Fig. 5). Between mid- and late August, one small rain event occurred (Fig. 4) and salinity dropped at YB from 44.5 to 2.6 (Fig. 3).

Consequently we cannot rule out discharge of freshwater out of Oso Creek as contributing to the continued presence of low salinity water at OI in late August 2012.

In addition to the presence of low salinity water at OI, hypersaline water was occasionally observed at OI as well. For example, from mid-September through mid-December 2012, salinity >40 was observed at OI (Fig. 6). Further upstream at YB, salinities were even higher (Fig. 3), 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 μM), while DOC (396-599 μM) and DON concentrations (32-44 μM) were relatively high (Fig. 6). From late June to late August 2013, salinity >40 was again observed 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. 6).

Discussion

Coastal eutrophication is a global phenomenon resulting from human activity in watersheds as well as from 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 (but see Thronson and Quigg 2008), 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 localized water quality degradation in an urbanizing South Texas estuary, Oso Bay. However, through water mass advection the overall effects of this eutrophication may extend to a region of adjacent Corpus Christi Bay that

is prone to hypoxia. Thus from a management standpoint, the broader-scale implications of the eutrophication should be given consideration.

Data collected from the head of the estuary, where water quality is influenced by discharge from both Oso Creek and the power plant cooling ponds, showed minimal evidence of eutrophication-related issues. Hypoxia was not observed and chlorophyll *a* >20 μg L^{-1} was rarely observed, typically only during the annual spring bloom. Chlorophyll *a* appeared to be controlled by seasonal temperature and/or light increase, as well as physical-chemical mechanisms. The positive relationship with rainfall could indicate either the importance of runoff-derived nutrients or import of phytoplankton blooms from Oso Creek. Since nitrate, ammonium or phosphate did not display a relationship with salinity, this seemingly rules out a significant effect of runoff on nutrient availability. Thus it is plausible that rain events deposit freshwater phytoplankton blooms into Upper Oso Bay, which is not entirely surprising given the eutrophied nature of the heavily wastewater-influenced Oso Creek. For example, at one site in Oso Creek (#13028) that is subject to quarterly water quality monitoring by a state agency, the mean chlorophyll *a* in 2012-2013 was 61 μg L^{-1} (Wetz, unpubl. data). Ambient light availability (denoted by the negative relationship with prior cloud coverage), and silicate availability (denoted by the positive relationship with silicate concentration) may also be important controls on phytoplankton in upper Oso Bay. Silicate correlated with water temperature, which has been shown to control the regeneration of biogenic silica in sediments (Aller and Benninger 1981; Yamada and D'Elia 1984).

In contrast to upper Oso Bay, western Oso Bay displayed clear effects of wastewater discharge, consistent with results from studies in other systems (Anderson et al. 2002; Mallin et al. 2005). In particular, very high inorganic nutrient (N, P) and DON concentrations were

common at AG, WP, AI and DG, dense phytoplankton blooms were frequently observed at AG, AI and DG, and episodic hypoxia/anoxia occurred at AG, WP, and DG. Chlorophyll *a* was positively correlated with prior ammonium concentrations at AG, suggesting that N availability is important for controlling phytoplankton growth. These findings are consistent with DIN:DIP ratios at AG, DG, and AI that were predominately <16, and with strong phytoplankton growth responses to inorganic N but not inorganic P in seasonal nutrient addition bioassays conducted at AG from 2012-2014 (Wetz, unpubl. data). Chlorophyll *a* at AG was also correlated with winds, which could have: 1) injected nutrients into the water column from sediments, thereby stimulating phytoplankton growth, or 2) resuspended benthic microalgae. Benthic nutrient fluxes have not been measured in Oso Bay, though the shallow water column and extensive mudflats in western Oso Bay would undoubtedly be conducive for strong benthic-pelagic linkages. The mudflats are a known reservoir for benthic diatoms (Withers and Tunnell 1998), which were occasionally the dominant phytoplankton taxa during blooms at AG (Wetz, unpubl. data). However, blooms of pelagic taxa (e.g., *Chroomonas sp.*) were also observed (Wetz, unpubl. data), thus presence of blooms cannot be attributed solely to resuspension. High chlorophyll *a* concentrations were also observed on a routine basis at AI and DG, and another study that took place in 2013 showed high chlorophyll *a* extending from AG well out into the center of Oso Bay (Schroer 2014), and occasionally to OI (Schroer 2014; this study). This highlights the broader-scale influence of nutrient-rich wastewater on phytoplankton in Oso Bay.

The presence of hypoxia/anoxia was somewhat surprising given the shallow water column (<1 m) and persistent wind-driven mixing in western Oso Bay. Shallow water hypoxia has been previously observed in systems such as Waquoit Bay (D'avanzo and Kremer 1994) and several Delaware creeks (Tyler et al. 2009), primarily during warm periods that coincided with cloudy

days. Verity et al. (2006) also observed hypoxia in shallow, well mixed estuaries in Georgia that were experiencing eutrophication. In our study, dissolved oxygen at AG correlated with a number of environmental variables. The negative correlation with rainfall could be explained by inputs of allochthonous organic matter during rain events that fueled biological oxygen demand and/or development of stratification that prevents reoxygenation of the water column. The negative correlation with nutrients such as ammonium and orthophosphate is not surprising, given that low oxygen conditions are well known to enhance fluxes of these analytes (e.g., Cowan and Boynton 1996). The positive relationship between dissolved oxygen and phytoplankton biomass (chlorophyll *a*) is indicative of the potential for active photosynthesis to lead to oxygen increases, particularly in this eutrophied portion of Oso Bay. The persistent high phytoplankton biomass and oxygen production may explain the surprising lack of correlation between dissolved oxygen and water temperature, especially considering that the majority of blooms occurred during the warmer seasons when dissolved oxygen would otherwise be expected to be lower than observed (spring-fall).

Given the relatively high phytoplankton biomass in parts of Oso Bay, phytoplankton production clearly plays an important role in dissolved oxygen dynamics. Although active blooms can increase dissolved oxygen levels, the relationship is less clear as the phytoplankton reach senescence and are affected by microbial degradation. Phytoplankton biomass can be highly labile and would represent a significant source of organic matter for bacterial respiration (Biddanda 1988; Paerl et al. 1998). Studies in temperate systems have found a temporal lag between peak phytoplankton production, its subsequent degradation and onset of hypoxia, which has been attributed to temperature regulation of both stratification and respiration by microbes and benthic organisms (e.g., Malone et al. 1988; Rabalais et al. 2009). In Oso Bay, the

timescales of microbial degradation and conditions leading to the breakdown of phytoplankton biomass are not known, though with the majority of bloom activity occurring during the warmer seasons (spring-fall), any time lag between phytoplankton senescence and microbial degradation may be short. Dissolved organic carbon may also contribute to biological oxygen demand and reached very high concentrations in Oso Bay. Wastewater effluent and allochthonous inputs during rain events are obvious sources of the DOC. In addition, the correlation between DOC and chlorophyll *a* suggests that phytoplankton exudation could have been an important source. 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 persistent high organic matter loads from point-source wastewater discharge, surrounding land during rain events, and phytoplankton blooms. 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).

Despite the fact that both AG and WP receive treated wastewater effluent, differences were observed in certain water quality parameters that are worth mentioning. For example, N+N and ammonium levels were ca. 75% lower on average and orthophosphate levels were 43% lower at AG compared to WP. This is partially explained by greater uptake potential by phytoplankton at AG, although based on the differences in chlorophyll *a* between sites and a conservative estimate of cellular N:chl *a* 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 removal. Furthermore, whereas the wetland 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 could be beneficial in terms of pollutant removal if modeled after the neighboring AG tributary.

In addition to the localized indicators of eutrophication, there were several instances when signatures of wastewater were present at the mouth of Oso Bay. Previous work by Flint (1984) documented 3-6 fold higher ammonium concentrations at a Corpus Christi Bay station located immediately outside the mouth of Oso Bay compared to other stations in Corpus Christi Bay, and attributed this to wastewater export from Oso Bay. They further showed the stimulatory effect of this ammonium on phytoplankton productivity in Corpus Christi Bay. In our study, OI water frequently contained high DOC concentrations, along with occasional high nutrient and chlorophyll *a* concentrations. 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 (Ritter and Montagna 1999), causing negative effects on benthic communities (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, but our data suggests that export out of Oso Bay may be an important mechanism for providing organic matter to the

hypoxic zone of Corpus Christi Bay. Although the rates and mechanisms of export are beyond the scope of this study, additional field sampling is planned to quantify both aspects of exchange with Corpus Christi Bay. The low salinity conditions occasionally observed at OI were often not explainable without invoking wastewater advection. We were able to rule out watershed runoff as a source of the low salinity water on several occasions due to lack of co-occurring or recent previous rainfall, and there are no known freshwater sources in the near field region of Corpus Christi Bay. Given that the tidal range in Corpus Christi Bay is very small (Hodges et al. 2011), it is likely that winds and/or gravity-driven flow play a significant role in advection of this freshwater to OI, though this requires verification as noted above. Others (e.g., Ritter and Montagna 1999; Hodges et al. 2011) have documented conditions leading to advection of hypersaline water from upper Oso Bay along the bottom through the mouth of Oso Bay. When present, this hypersaline water mass remains isolated from the overlying water once in Corpus Christi Bay, triggering hypoxic conditions due to lack of reoxygenation. Indeed, we also observed hypersaline water on several instances at the mouth of Oso Bay in both surface and near bottom waters, though it is unclear if the mechanisms leading to the advection of this hypersaline water out of the mouth of Oso Bay are similar to those for freshwater.

It is not unreasonable to conclude that Oso Bay could be a case study for the future of many other warm subtropical estuaries worldwide that are expected to undergo significant urbanization and experience growing influence of wastewater. 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 point-source wastewater discharge are readily evident in Oso Bay. Furthermore, as has been demonstrated in numerous other studies, there is often a strong linkage between water temperature, phytoplankton

bloom development, and hypoxia (Rabalais et al. 2009; Najjar et al. 2010). Thus global climate change may exacerbate the deleterious effects of increases in untreated or minimally treated wastewater discharge. Results from this study indicate that the eutrophication of western Oso Bay has farther reaching implications through advection of chlorophyll *a* and/or DOC-rich water to the estuary mouth and possibly into neighboring Corpus Christi Bay. Consequently, both the localized and potential farther afield negative effects necessitate efforts to control nutrient loading to Oso Bay. In particular, multiple lines of evidence (correlation between ammonium and chlorophyll, DIN:DIP ratios showing predominance of N-limitation, nutrient addition bioassays) argue for a need to reduce wastewater-derived nitrogen loading, which (nitrogen) appears to be the dominant nutrient controlling phytoplankton growth in the eutrophied region of Oso Bay.

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Figure Legends

Figure 1. (A) Location of Oso Bay along the Texas coast. (B) Location of 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.

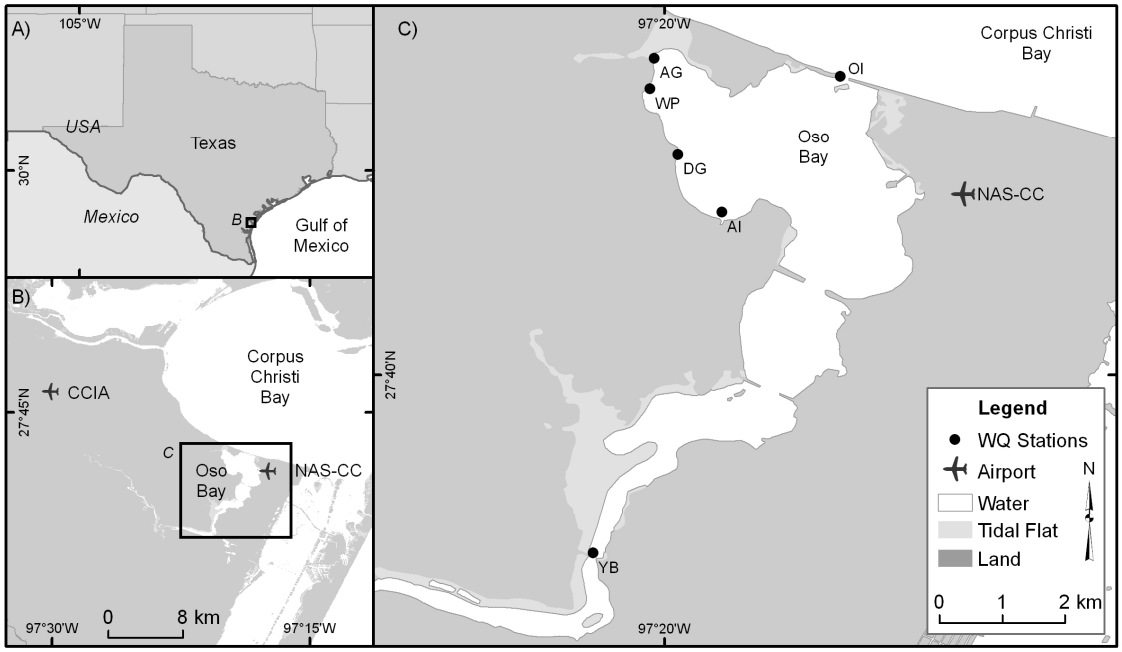
Figure 2. Dissolved oxygen concentration (mg L^{-1}) at (A) AG, WP, and (B) AI, DG sites in Oso Bay.

Figure 3. Temporal distribution of select water quality parameters at site YB (head) in Oso Bay. (A) Salinity and temperature, (B) dissolved organic carbon, (C) dissolved inorganic nitrogen and silicate, and (D) orthophosphate and chlorophyll.

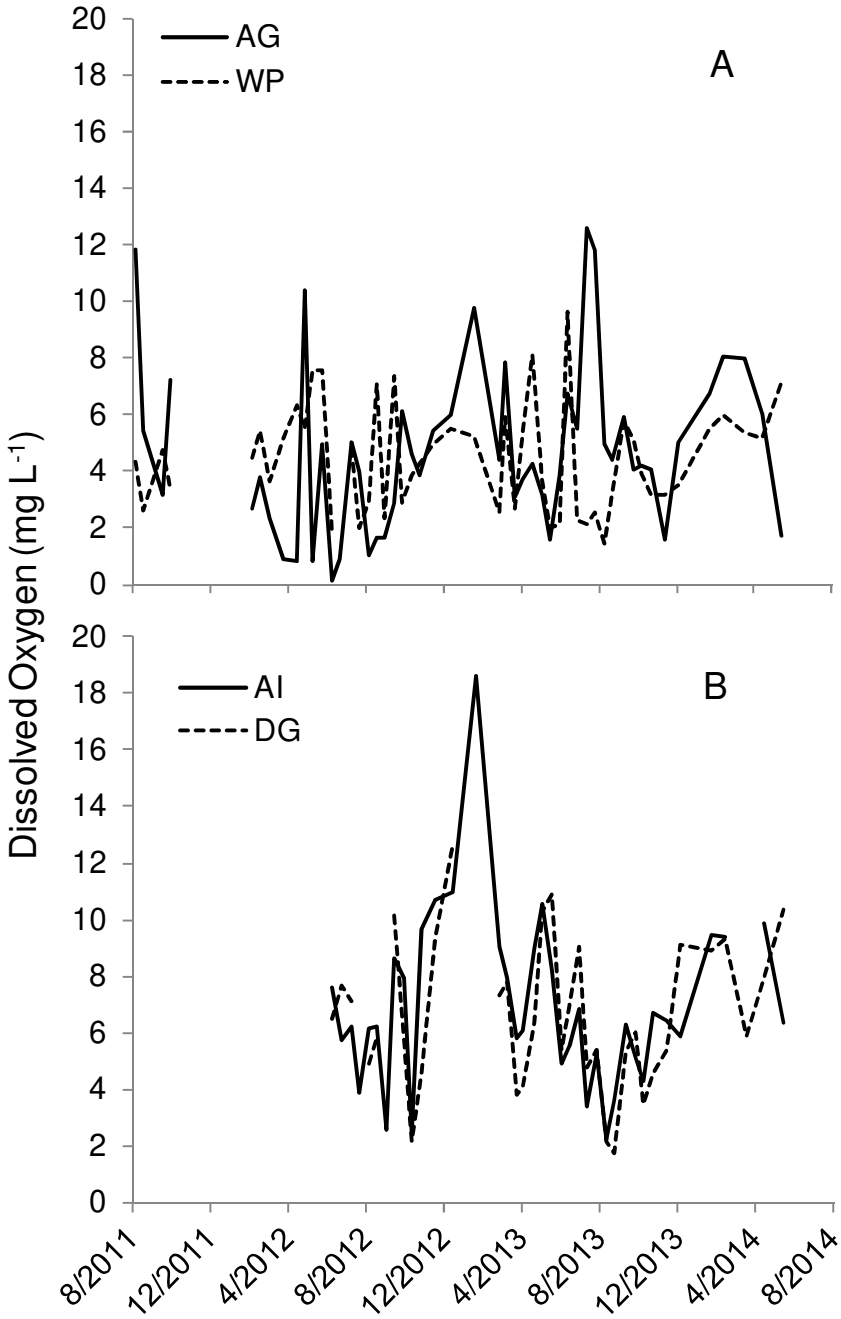
Figure 4. Rainfall (mm) at CCIA.

Figure 5. Temporal distribution of select water quality parameters at site AG in western Oso Bay. (A) Salinity and temperature, (B) dissolved organic carbon and chlorophyll, (C) N+N and ammonium, and (D) orthophosphate and pH.

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



Wetz et al. Figure 1



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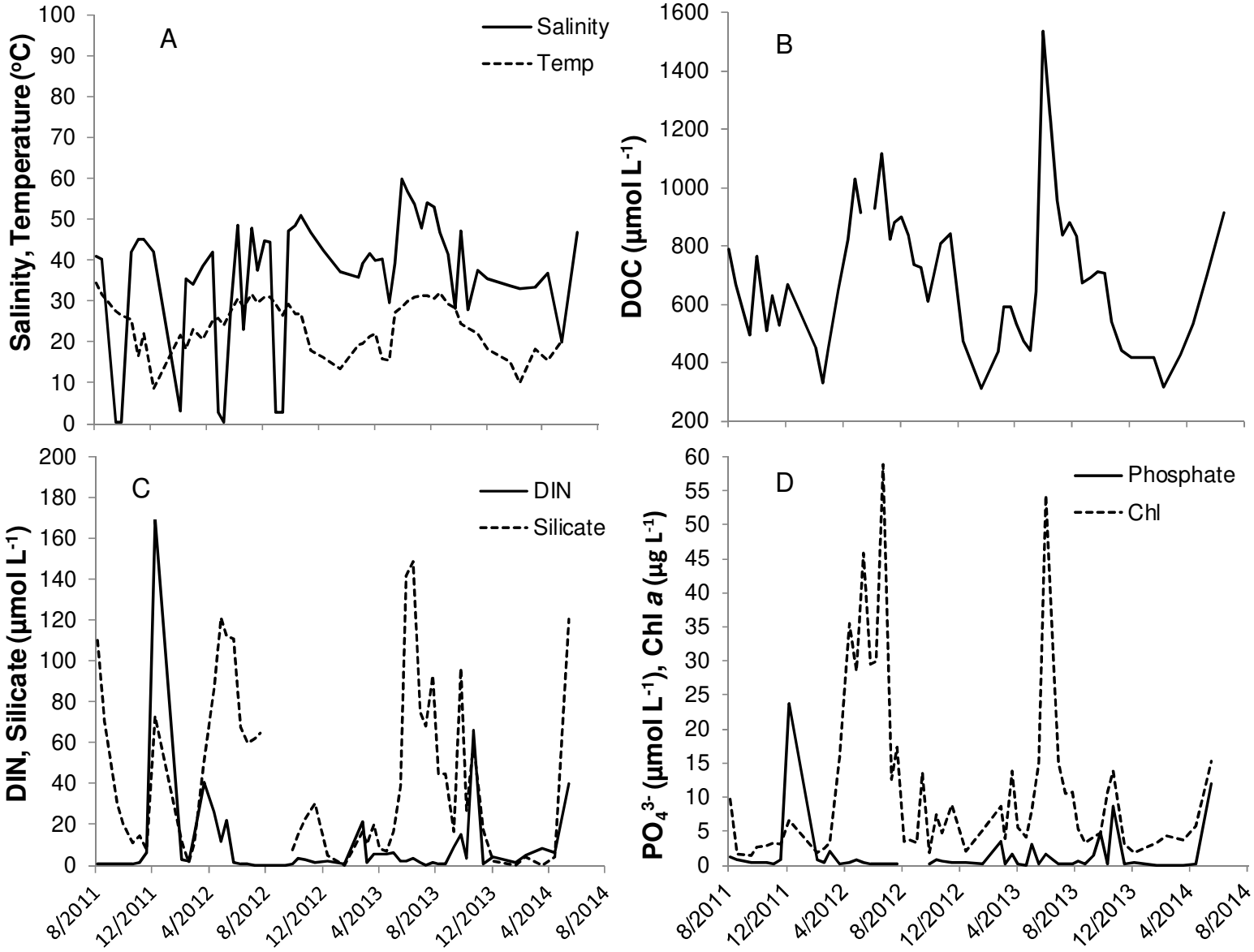
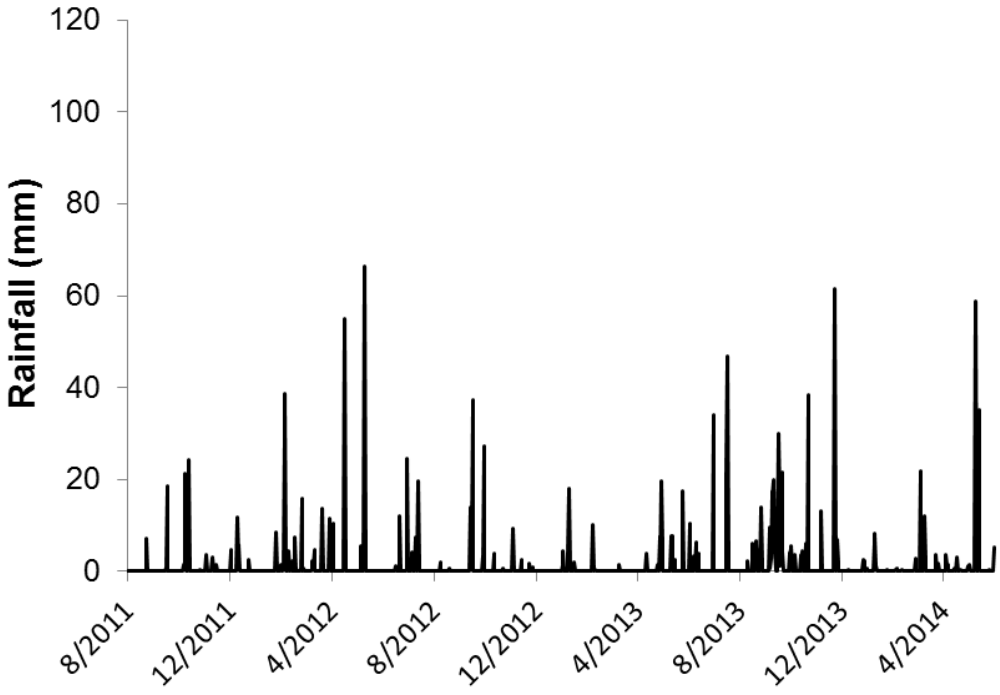
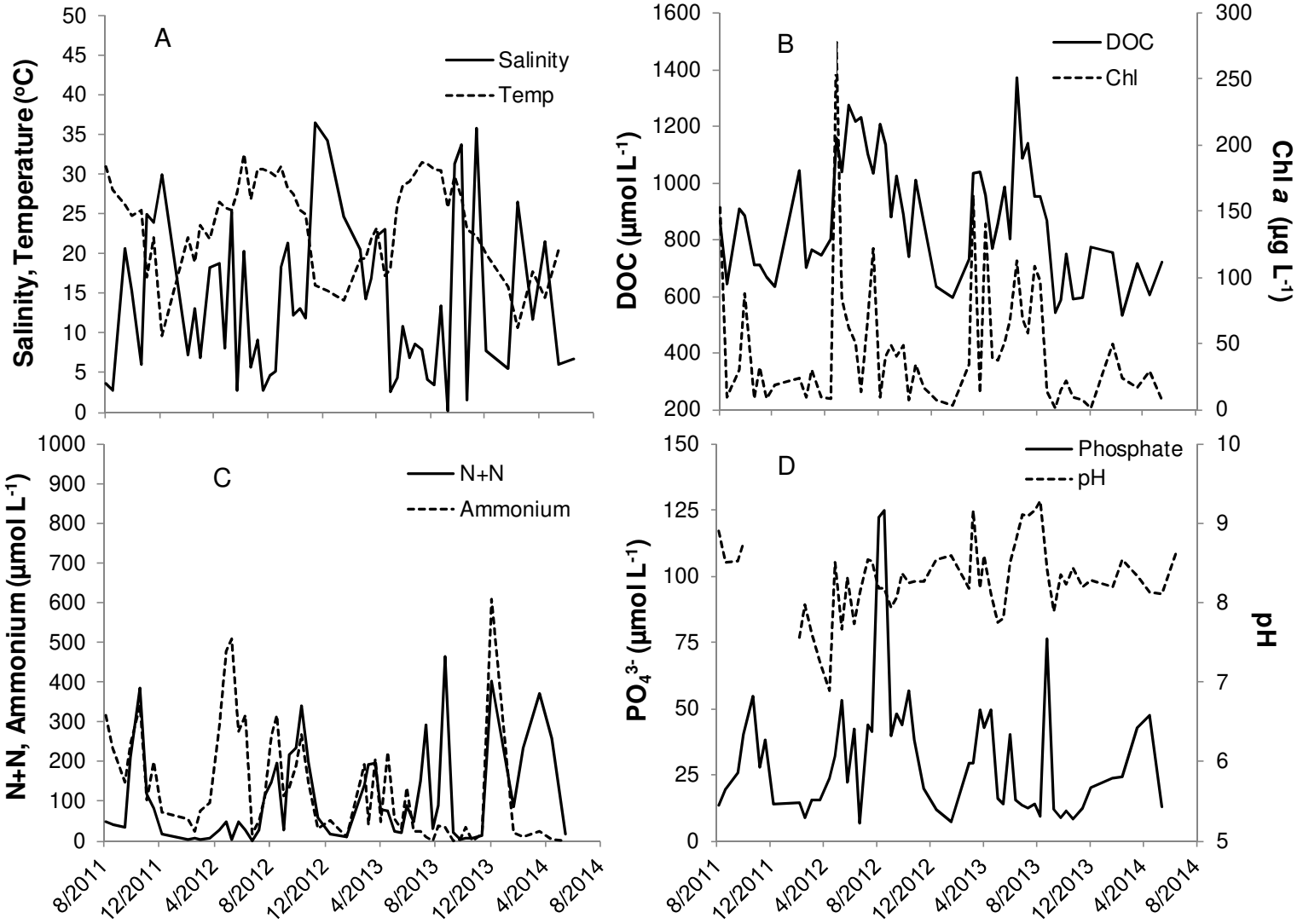


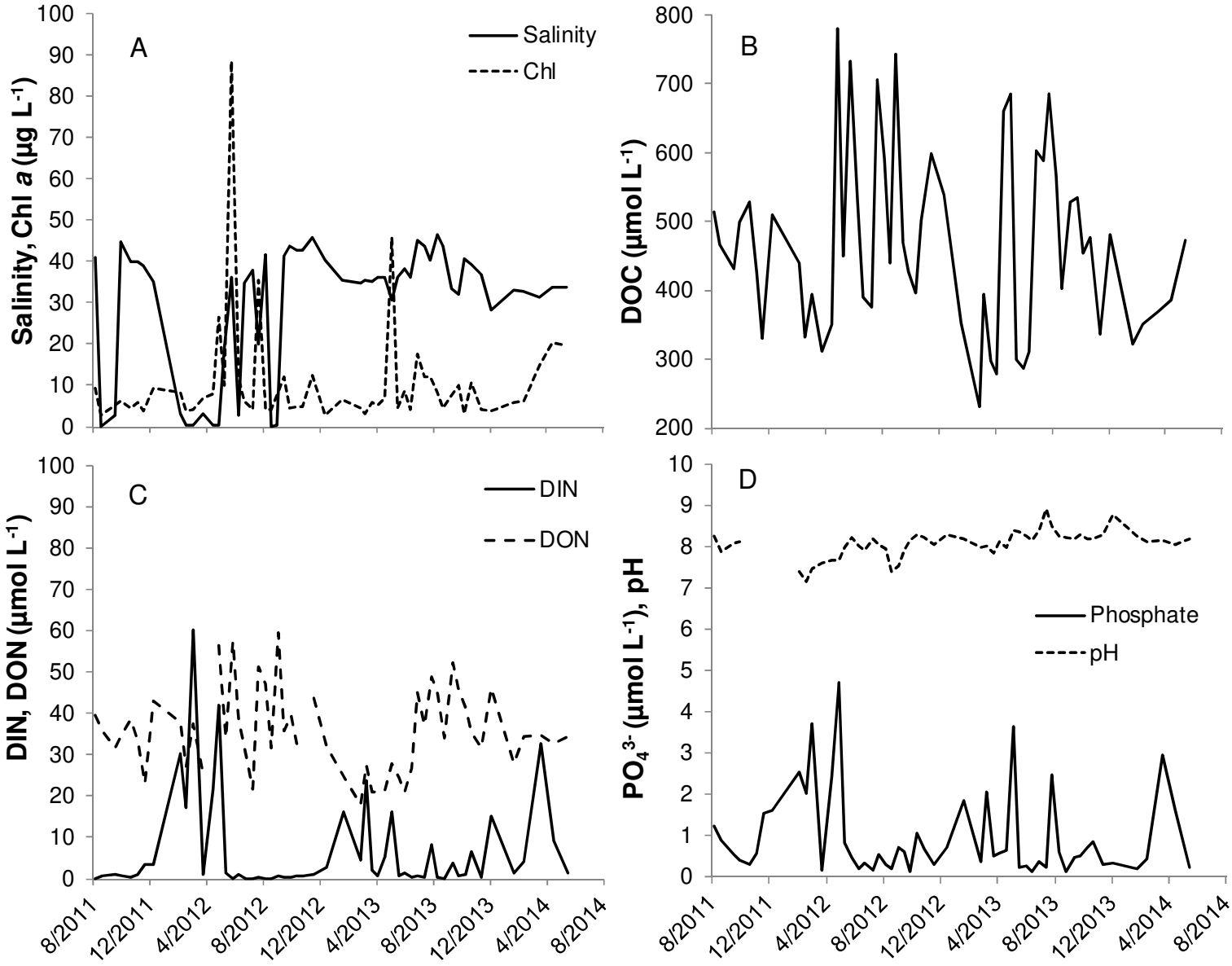
Wetz et al. Figure 3



Wetz Figure 4



Wetz et al. Figure 5



Wetz et al. Figure 6

Table 1. Mean ± SD for water quality parameters from six Oso Bay sampling sites from 6/8/2012 (when sampling began at AI, DG) to 5/15/2014.

	Salinity	**Temp. (^{o}C)**	**pH**	**N+N (μM)**	**NH_4^+ (μM)**	**PO_4^{3-} (μM)**	**DOC (μM)**	**DON (μM)**	**Chl *a* (μg L^{-1})**	**D.O. (mg L^{-1})**
AG	14 ± 11	24 ± 6	8.4 ± 0.4	125 ± 126	96 ± 128	33 ± 28	879 ± 218	84 ± 37	44 ± 41	4.8 ± 2.8
WP	6 ± 8	26 ± 4	7.4 ± 0.4	495 ± 295	383 ± 231	58 ± 27	768 ± 80	144 ± 191	5 ± 6	4.3 ± 2.0
OI	34 ± 11	23 ± 6	8.2 ± 0.3	2 ± 6	2 ± 3	1 ± 1	463 ± 133	35 ± 10	10 ± 9	6.4 ± 1.8
YB	39 ± 13	24 ± 6	8.2 ± 0.2	4 ± 12	3 ± 3	1 ± 3	699 ± 254	52 ± 18	11 ± 13	6.2 ± 1.5
AI	27 ± 17	23 ± 7	8.2 ± 0.3	23 ± 56	10 ± 18	5 ± 7	682 ± 205	53 ± 18	27 ± 21	7.0 ± 3.1
DG	26 ± 14	23 ± 6	8.3 ± 0.3	26 ± 41	18 ± 30	7 ± 6	773 ± 185	61 ± 15	27 ± 18	6.6 ± 2.6