Assess Nonpoint Source Nitrogen Contribution to the Texas Coastal Zone from Septic Systems

Final Report

GLO Contract No. 20-047-000-B797

Prepared by:
Esme McMullan, Research Assistant
Lin Zhang, Principal Investigator

and

Gabriele Bonaiti, Co-Principal Investigator

Texas A&M University-Corpus Christi
6300 Ocean Dr., Unit
Corpus Christi, Texas 78412
Phone: 361-825-2095
Email: Lin.Zhang@tamucc.edu

Submitted to:

Texas General Land Office
1700 Congress Ave.
Austin, TX 78701-1495

A report funded by a Texas Coastal Management Program Grant approved by the Texas Land Commissioner pursuant to National Oceanic and Atmospheric Administration Award No. NA19NOS4190106

TABLE OF CONTENTS

EXECUTIVE SUMMARY

The goal of this project was to quantify and compare the amount of nitrogen (NH_4^+, NO_3^-, and NO_2^-) released into water bodies near Corpus Christi, Texas from wastewater treatment plants and septic systems in the surrounding communities. Sample collection began in November 2019 and carried on until September 2021, although it was interrupted during the height of the pandemic in spring of 2020. The sampling occurred at five different wastewater treatment plants ([WWTPs], Oso, Kingsville, Rockport, Portland, and Whitecap) as well as seven different septic systems in Corpus Christi (Oso), Kingsville, Portland, and Rockport near the WWTPs so that the nitrogen loading of these two different sources of treated effluent could be meaningfully compared.

Effluents from WWTPs and on-site septic systems are sources of the nutrients responsible for aquatic nutrient pollution, releasing nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) into local bodies of water, which could lead to eutrophication and hypoxia. Two different sources of effluent were sampled during this study: wastewater treatment plants (WWTP) and septic systems. Both WWTPs and septic systems separate solid waste from liquid wastewater, treat the wastewater, then discharge this cleaned effluent back into the natural environment; however, WWTPs serve a much larger area than septic systems, which collect and treat wastewater from a single home. Each WWTP and septic system may have different methods of treating wastewater and removing excess nutrients, if they are required to. This study detected significant levels of NO_3^-, NO_2^-, and NH_4^+ in bodies of water that served as reservoirs for effluents released by the septic systems and WWTPs. This suggests that further N removal processes would be needed if lower nitrogen concentrations in treated effluents were desired. Rockport WWTP is the only WWTP studied in this project that has a dedicated N removal

process, which incorporates an anoxic tank and discharged the less N per day than other WWTPs studied in this project. The N released by Rockport WWTP was about 50% of the estimated N loading from combined onsite septic systems located in the same county. This suggests that N removal technique employed by WWTP is effective in nitrogen reduction, and N removal techniques should be employed by both WWTPs and septic system to reduce anthropogenic N contribution to local bodies of water.

OUTREACH EFFORTS

Participating Students (Graduate Students):

Lydia Hayes, Charlotte Lee, and Samantha Schiereck

Participating Students (Undergraduate Students):

Jesus Baca, Kaden Harder, NourEldeen Loubani, Marysa McAllister, Esme McMullan, Kaitlin Sams, Catherine Shaw, and Dat Tran

Presentations (Public): 6/13-6/15 Field Trips and Workshop Program for the 2022 REEU Students

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

ACKNOWLEDGEMENTS

Firstly, we would like to thank the Coastal Management Program of the Texas General Land Office for providing support for this project. In addition, we would like to thank the Texas A&M University-Corpus Christi Research and Innovation department for providing funding for the purchase of a nutrient analyzer which allowed us to be able to perform our nutrient analysis in-house.

There were numerous individuals who helped throughout the duration of this project. This study would not have been possible without their dedication, strong work ethic, and ongoing energy and enthusiasm for their work. We would like to thank the following students for all their hard work with countless field sampling, laboratory sample analysis, data analysis, and interpretation: Jesus Baca, Kaden Harder, NourEldeen Loubani, Marysa McAllister, Esme McMullan, Kaitlin Sams, Catherine Shaw, and Dat Tran.

INTRODUCTION

Background Information

Rapid population increase along the Texas coast has led to an estimated 63,000 septic systems, or on-site sewage disposal systems (OSDS), in the coastal zone. Faulty OSDS systems are shown to contribute significant amounts of nitrate to waterways resulting in eutrophication, hypoxia, and red/brown tides, which have harmful effects on ecosystems, fisheries, tourism, and economy. Historically, nonpoint source (NPS) nitrogen input from OSDS systems are poorly understood and more difficult to manage.

Copano-Aransas Bay, Nueces-Corpus Christi Bay, and Baffin Bay have about 14,300 OSDS systems. These bays have a high risk of OSDS pollution due to the shallowness of seasonal groundwater table and sediment texture. Many chemical markers can indicate the presence of OSDS effluents including caffeine, artificial sweeteners, and isotopic ratios of nitrate (d15NO3-). Elevated levels of caffeine, sweeteners, nitrate, and d15NO3- can be used to "fingerprint" NPS inputs of OSDS effluents. N inputs from OSDS can be quantified using an N loading coefficient to convert water (per volume) to mass of N.

While WWTPs are a centralized method of treating waste, onsite septic systems treat waste at a smaller scale, from individual households and commercial locations such as restaurants, to multi-household tracts of land that do not have access to a large-scale wastewater collection system. A conventional onsite septic system consists of two main components: a septic tank, and a soil absorption field (which also goes by many other names such as a weeping field, leaching tile field and subsurface wastewater infiltration system or SWIS). The septic tank collects solid waste as it separates from the liquid portion of the waste, and much like the activated sludge system employed by WWTPs, microorganisms digest some of this organic matter while it is in the tank. The liquid portion of the waste, or the septic tank effluent, is carried by a series of pipes to the designated subsurface wastewater infiltration system, which is a drain field in which gravity causes the effluent to travel from the surface of the field down through the soil where some of the waste is removed from the effluent through organic processes within the soil itself. This naturally treated effluent then becomes part of the groundwater in the area, which can eventually be discharged into surrounding bodies of water (Onsite Wastewater Treatment Systems Manual).

Problems can arise with the onsite septic system method of treating waste when precipitation causes the septic tank effluent to percolate too quickly through the soil without adequate time for organic matter to be removed, or when the precipitation carries the effluent away as surface run-off. Another issue occurs when the natural soil type is not suitable for this type of filtration, or when the volume of septic tank effluent exceeds the capability of adequate soil types to remove organic matter, since subsurface wastewater infiltration systems have a maximum amount of septic tank effluent that they can treat depending on their surface area.

Wastewater treatment plants (WWTP) without N removal capabilities (secondary treatment) are a large source of excess nitrogen in the form of nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) into important bodies of water including rivers, streams, and estuaries (Desimone and Howes 1996; Arachana et al., 2016; McLaughlin et al., 2017). The city of Corpus Christi has five total wastewater treatment plants (WWTPs), two of which were sampled from during the course of this project: the Oso Water Reclamation Plant (WRP) and the Whitecap Wastewater Treatment Plant. The Oso WRP is the largest WWTP in Corpus Christi, treating the wastewater of 50% of the city's inhabitants, while the Whitecap WWTP treats wastewater from the Padre Island collection system. Both plants primarily use the activated sludge method of filtering and treating wastewater (City of Corpus Christi Wastewater Management Plan, 2016).

In the activated sludge method, there are two large collection basins that the influent passes through before it is discharged by the plant as treated effluent. The first is called the aeration tank, which is where the organic matter in the influent is removed due to the metabolism of microbial organisms that rely on the chemical compounds in the sewage for survival. The influent then passes onto the second basin, called the secondary sedimentation tank, in which the liquid portion of the influent separates from the solid biomass. The biomass sticks together and sinks to the bottom of the tank while the liquid is now considered treated and is discharged from the plant as effluent. Some of the biomass, also called activated sludge, is then recirculated back to the aeration tank for the process to begin again while the excess is removed or processed further (Activated Sludge and Aerobic Biofilm Reactors Vol. 5, 2007).

In addition to using activated sludge, the Oso WRP employs breakpoint chlorination in which free chlorine is added to water to oxidize ammonium, which forms a volatile compound known as a chloramine. As more free chlorine is added to react with the chloramine, it eventually reaches a point when the amount of free chlorine added to the water exceeds the amount of chloramine. This is called the breakpoint. However, the city of Corpus Christi specifically states that the plant isn’t intended to or efficient at removing ammonia from the influent that passes through, regardless of using breakpoint chlorination. (Qi, 2018; Moran, 2018; City of Corpus Christi Wastewater Management Plan, 2016). Treated effluent from the Oso WRP is discharged to Blind Oso Bay, which is a shallow bay along the southern shore of Corpus Christi Bay, while treated effluent from Whitecap WWTP is discharged into Laguna Madre, a hypersaline estuary (TCEQ Permit).

This study also sampled effluent from the Portland WWTP, which operates within the city of Portland, Texas. Like Oso and Whitecap, the Portland WWTP also uses the activated sludge method to treat their wastewater. While effective at treating most organic matter, this method may or may not be effective at removing nitrogenous compounds from sewage; studies indicate that it could work with a large aeration tank and a higher age of activated sludge, which is how long the sludge has been removing organic compounds from influent with "high" indicating a longer period of time. These constraints are likely why nitrogenous compounds are rarely removed using the activated sludge method (Bonhomme et. al, 1990). Treated effluent from Portland WWTP is discharged into Nueces Bay, a northwestern part of Corpus Christi Bay (TCEQ Permit).

The Rockport WWTP also uses the activated sludge method of removing organic matter from influent, as well as an anoxic tank built in 2013 specifically for nitrogen removal purposes. Treated effluent is then discharged by the plant into Tulle Ditch in Aransas County. The treated effluent then flows from Tulle Ditch into an unnamed nontidal ditch, then a tidal ditch – which is a ditch that is affected by ocean tides – and from the ditches to Little Bay and lastly into Aransas Bay (TCEQ Permit). Little Bay is a body of water that is to the north of the Rockport coastline, while Aransas Bay is to the east. Like the other WWTPs, Kingsville WWTP uses the activated sludge method. It discharges its treated effluent first into a wetland, then to San Gertrudis Creek, where it flows into the San Fernando Creek and then to Baffin Bay (TCEQ).

The use of N stable isotope ratios ($\delta^{15}N$) in nitrate, nitrite, and ammonium can help discern the differences between N sources and processes in the environment. These sources and processes include synthetic fertilizer, wastewater, soil N, organic matter, atmospheric N, as well as denitrification, nitrification, and ammonification which all have different $\delta^{15}N$ (‰) values

(Kendall 1998; Kendal et al., 2007; BryantMason et al., 2013). The $\delta^{15}N$ of NO_3^-, NO_2^-, and NH_4^+ can be used to pinpoint specific sources of excess N, as well as track the major cycling processes in the environment, enhancing our understanding of how N moves through the ecosystem.

Study Areas

Sampling for this project occurred in twelve different sites: four of which were in Corpus Christi, TX, two in Portland, TX, three in Rockport, TX, and three in Kingsville, TX. The sampling sites included five WWTPs and seven onsite septic disposal sites that were in the same area as the WWTPs for meaningful comparisons between the two sources of N loading.

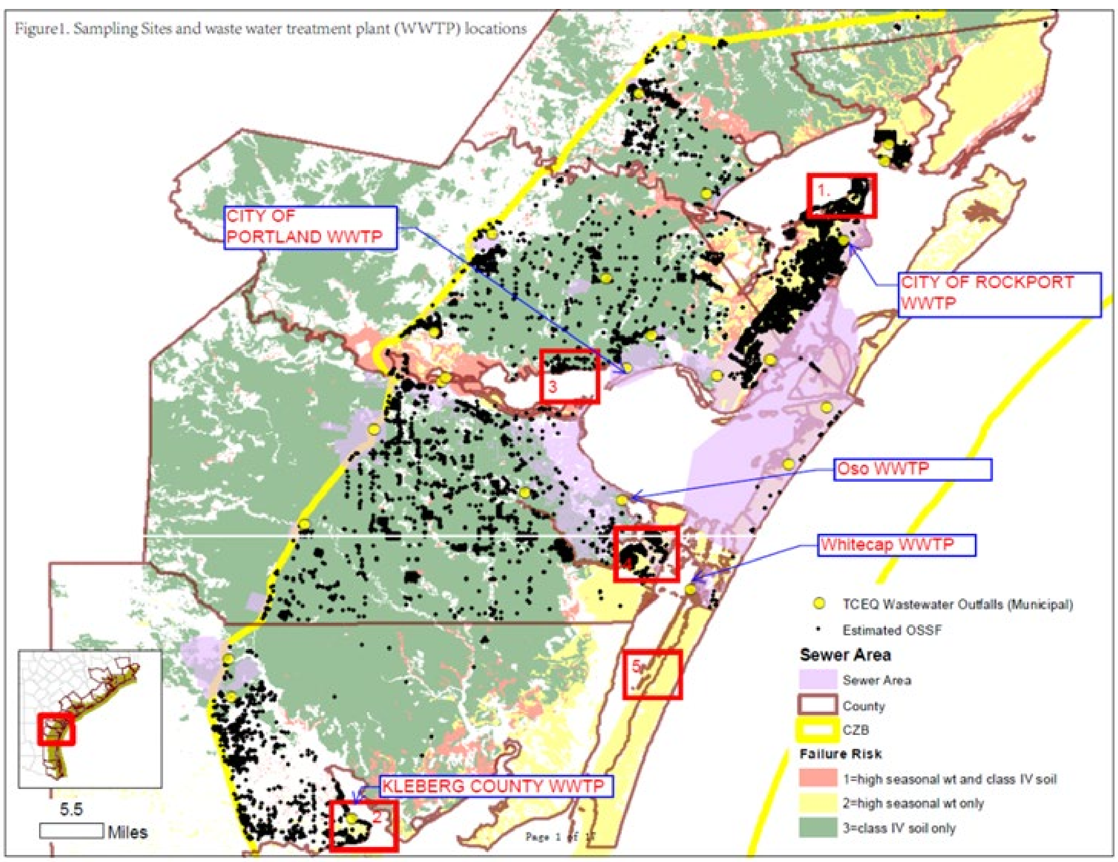


Figure 1. Map of sample sites

METHODS

Sampling

Each of the twelve sites were sampled monthly (although not every month due to complications from the Covid-19 pandemic) from November 2019 through September 2021. For all sites the environmental parameters of pH, water temperature, and salinity were measured. A Thermo Orion Star A324 meter was used for pH measurements. Water temperature and salinity measurements were collected using a Thermo Orion model 135A conductivity meter. All instruments were calibrated monthly before sampling.

Water samples were gathered monthly for nutrient analysis of NO_2^-, NO_3^-, and NH_4^+. Surface water was gathered in 10mL centrifuge tubes filter sterilized with 0.22 μm PES syringe filters and collected in triplicate. Water samples for NO_2^-, NO_3^-, and NH_4^+ nitrogen stable isotopes were collected in triplicate quantities of 15mL for each N species. Water was filtered into 15mL centrifuge tubes using 0.22 μm PES syringe filters, the samples for isotope analysis in NO_2^- and NO_3^- were chemically preserved using 6M NaOH, and 2.5 mM sulfamic acid in 25% HCl, respectively (Bourbonnais et al., 2017).

Nutrient Analysis

For identification and quantification of different N species in water from all sampling locations, nutrient concentrations for NO_3^-, NO_2^-, and NH_4^+ were measured using a SEAL AQ300 Discrete Analyzer. The AQ300 method EPA-148-D Rev 0 was used for NH_4^+ analysis, with a range of 0.21-71 μM. Samples with greater than 71 μM concentration were diluted into the detection range for the method. For this method, 400 μL of water sample reacted with hypochlorite for 40 μL of dichloroisocyanurate. The resulting chloramine reacts with 90 μL of salicylate at alkaline pH in the presence of nitroferricyanide. An indophenol dye, blue-green in color, is formed and measured spectrophotometrically at 660 nm. The concentration is calculated using the measured absorbance unit compared to an eight-point calibration curve (R^2>0.9990).

AQ300 method EPA-115-D Rev A was used to analyze NO_2^- concentrations, this method has a detection range of 0.05 to 107 µM. Samples with concentrations above this range were diluted into the detection range. This method mixes 200 µL of water sample with 200 µL of sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride and 100 µL of a pH buffer solution to form a red-purple dye, measured spectrophotometrically at 520 nm. Concentration is calculated using an eight-point calibration curve (R^2>0.9998).

NO_3^- concentration was measured using the cadmium reduction method, which is the AQ300 method EPA-126-D Rev. This method yields concentrations of NO_3^- + NO_2^-, previously measured NO_2^- concentrations are subtracted to give final NO_3^- concentrations. This method has a detection range of 0.57-257 µM. The method mixes sample with 290 µL of pH buffer and pulls the 430 µL of sample through a 7-turn copper treated cadmium coil, where NO_3^- is reduced to NO_2^-. The reduced sample reacts with 350 µL of sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride giving the mixture a red-purple color, that is then measured using a spectrophotometer at 520 nm. This test uses an eight-point calibration curve (R^2>0.9990).

Quantify N load from OSDS using the water-use approach

The nitrogen load released into local bodies of water from onsite disposal systems (OSDS) was calculated using the same method that was utilized by the Massachusetts Estuary Project. The amount of household water usage was determined via a prior study to be 246 gallons per day (Water Use of Texas Water Utilities, 2015). Using an N loading coefficient of 23.63 mg/L, the water volume was mathematically converted to the mass of corresponding nitrogen per volume. Multiplying the N load per month of one household by the number of septic systems in the study area gave the N load that is released into local bodies of water monthly from these septic systems. Per capita N load was then calculated by dividing the per household N load by the average household occupancy. The N loading coefficient used in this study relied on a previous study that analyzed stream tubes for total dissolved nitrogen from sources such as groundwater, leaching fields and septic effluent (Weiskel and Howes, 1991).

Compare N loads from septic systems to loads from WWTP effluents

The Texas Commission on Environmental Quality (TCEQ) has issued several National Pollutant Discharge Elimination System (NPDES) permits to WWTP plants around the Corpus Christi area, which is stipulated of wastewater treatment systems that discharge more than 5000 gallons of effluent a day. The average monthly effluent flow of the WWTPs was obtained from the plants themselves, and the concentration of nutrients within the treated effluent was calculated via nutrient analysis on a SEAL AQ300 Discrete Analyzer as detailed above. The nutrient concentrations from the WWTPs were then compared to the nutrient concentration data from the OSDS to determine the significance of the OSDS's nitrogen loading and possible ecological effects.

Stable Isotope Analysis

Nitrogen stable isotopes in NO_3^-, NO_2^-, and NH_4^+ were used to identify nitrogen sources and processes in water samples, which have distinctive ^{15}N:^{14}N ratios (‰) (Freyer and Republic 1978). N stable isotopes for NH_4^+ samples were analyzed using an established method (Zhang et al., 2007). Water samples are briefly treated with sulfamic acid and 10% HCl to remove pre-existing NO_2^-, and once NO_2^- is removed, NH_4^+ is oxidized to NO_2^- using hypobromite. Sodium arsenite is then added to remove any additional hypobromite. After this reaction is completed, NO_2^- yield is measured on the SEAL AQ300 Discrete Analyzer. This NO_2^- is then sent to an external isotope lab where it is further reduced to N_2O and measured $\delta^{15}N$ on a Purge-and-Trap IRMS.

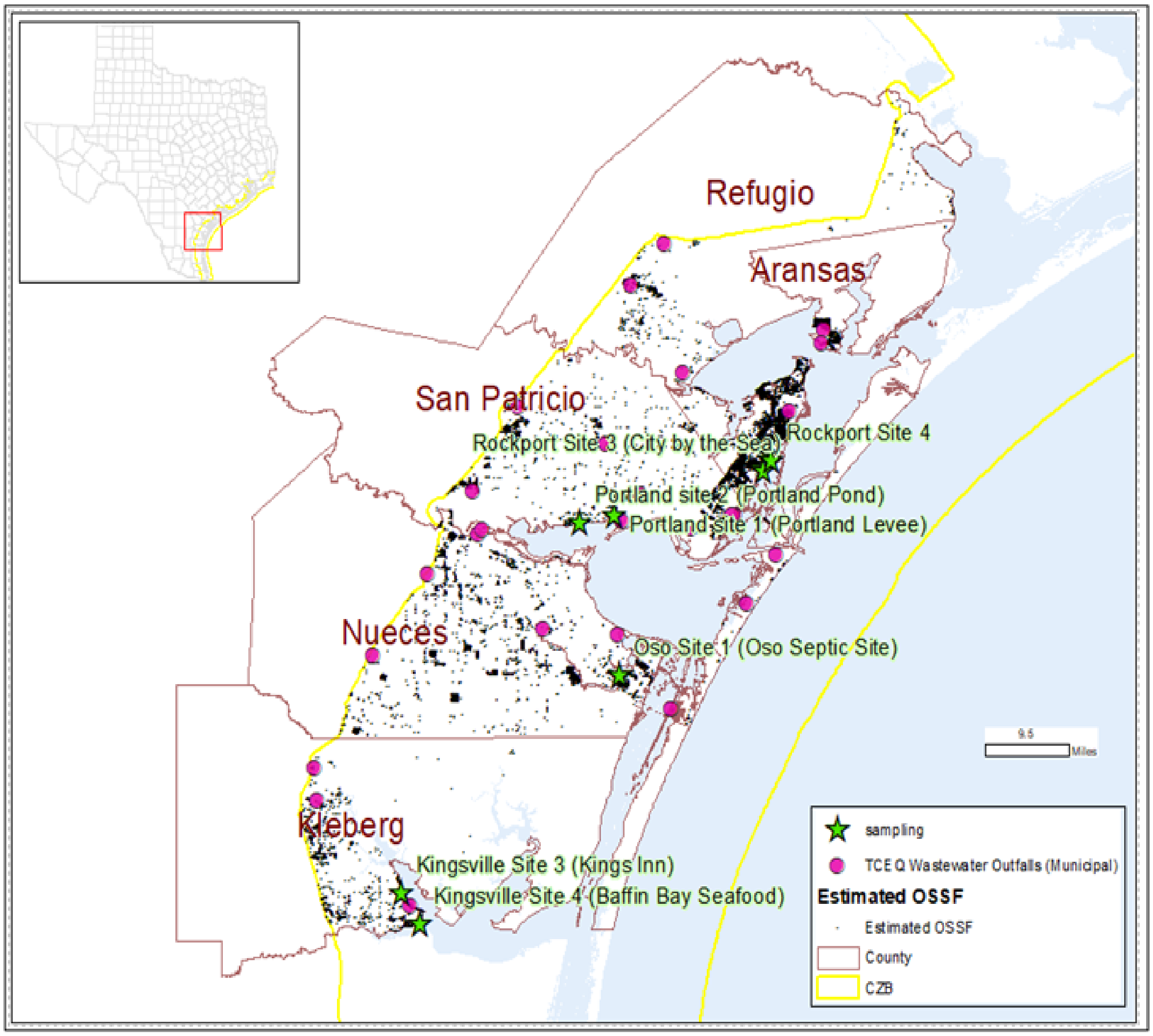


Figure 2. Map of onsite septic system sites in the study area

Nitrate samples were reduced to NO_2^- using cadmium and then to N_2O using the azide method following the procedures outlined in McIlvin and Altabet (2005). $\delta^{15}N$ analysis of produced N_2O was conducted in the same external lab. Along with the NO_3^- samples that were reduced, blanks following the same procedure were also analyzed to account for any N in the water used for reagents. All analyses were performed in triplicates. The equation below was used for calculation of $\delta^{15}N$ ratio in the samples:

$$\delta^{15}\mathrm{N}(‰) = \frac{((^{15}\mathrm{N}/^{14}\mathrm{N})\ \mathrm{sample}) - ((^{15}\mathrm{N}/^{14}\mathrm{N})\ \mathrm{standard})}{((^{15}\mathrm{N}/^{14}\mathrm{N})\ \mathrm{standard})}\ \mathrm{X}\ 1000$$

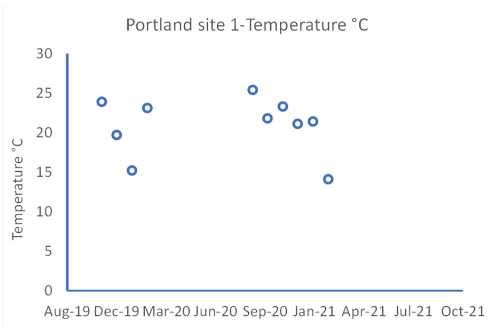
RESULTS

Septic Systems in the Study Area

The average pH of the water at the sites tested ranged from 7.26 to 8.96 in accordance with the normal pH range of freshwater and saltwater bodies. Portland WWTP had the lowest average pH measured while Oso site 1 had the highest average pH measured.

Water temperatures of the sites varied by location and by season. Portland site 1 had an average temperature of 20.9 °C, while Portland WWTP had an average temperature of 24.57 °C. The Oso WWTP had an average temperature of 24.9° C, while Oso site 1 had an average temperature of 23.57° C. Rockport WWTP had an average temperature of 23.19° C, while Rockport sites 3 and 4 had average temperatures of 20.83° and 21.4° C respectively. Whitecap WWTP had an average temperature of 18.47° C and Laguna Madre had an average temperature of 19.36° C. The Kingsville WWTP had an average temperature of 23.9° C while Kingsville sites 3 and 4 had average temperatures of 22.72° and 22.88° C respectively. All averages took all the months in which data was collected into consideration regardless of season, but all locations experienced a dip in temperature from December to April of each year.

Environmental Parameters



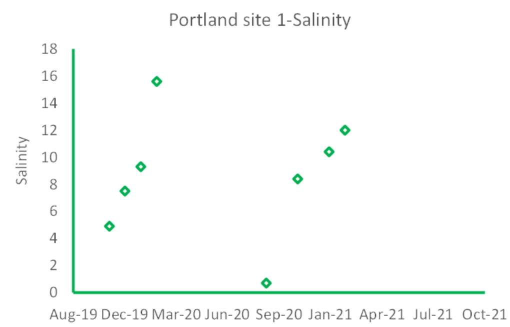
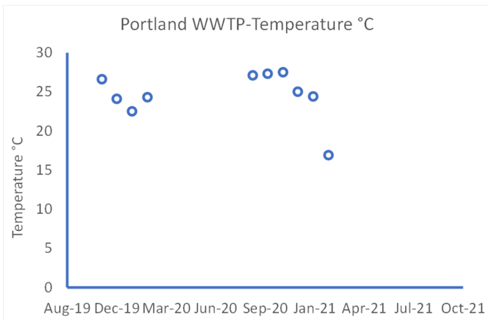


Figure 3. Portland Site 1 temperature and salinity



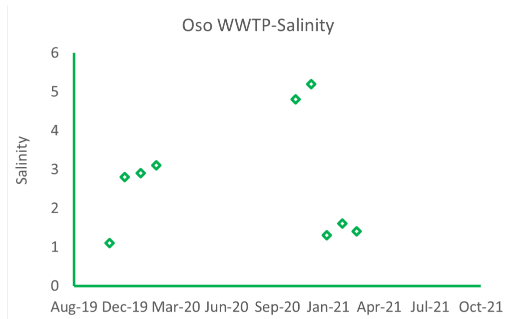
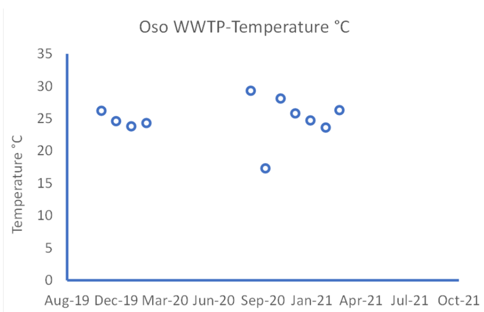


Figure 4. Portland WWTP temperature and salinity



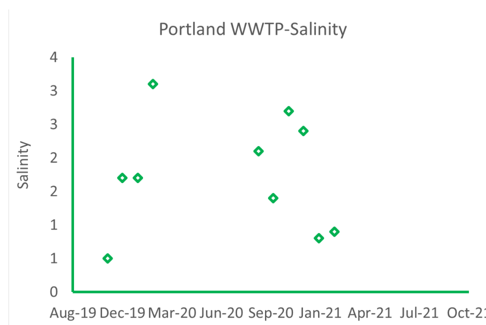
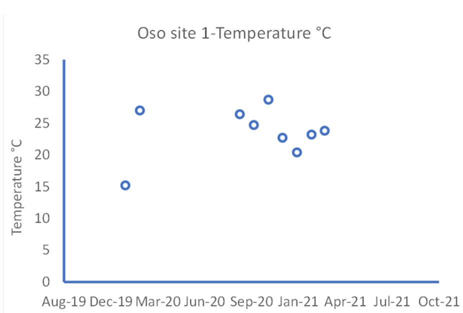


Figure 5. Oso WWTP temperature and salinity.



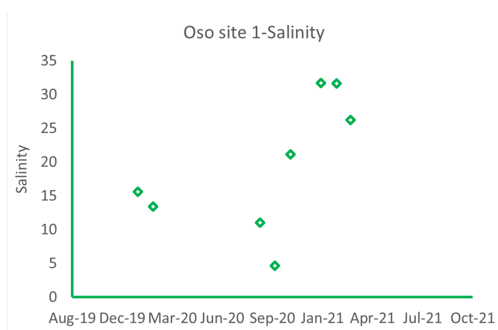


Figure 6. Oso Site 1 temperature and salinity

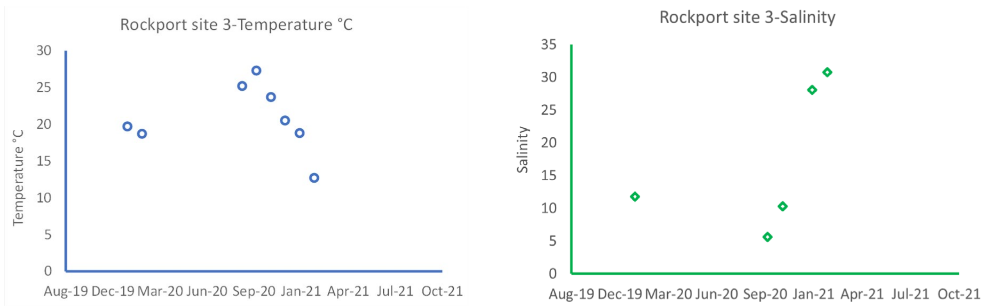


Figure 7. Rockport Site 3 temperature and salinity

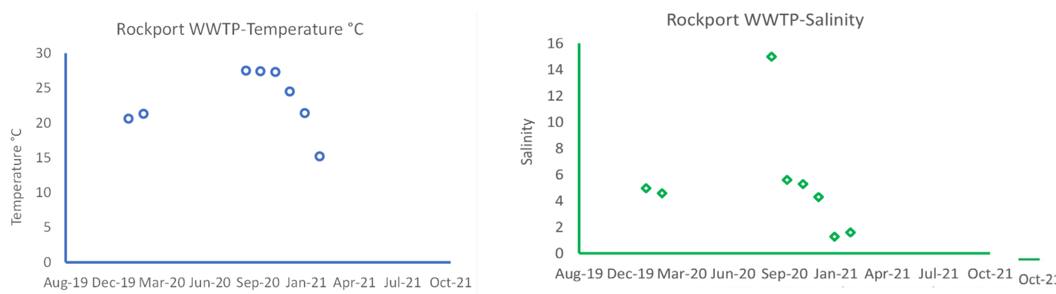


Figure 9. Rockport WWTP temperature and salinity

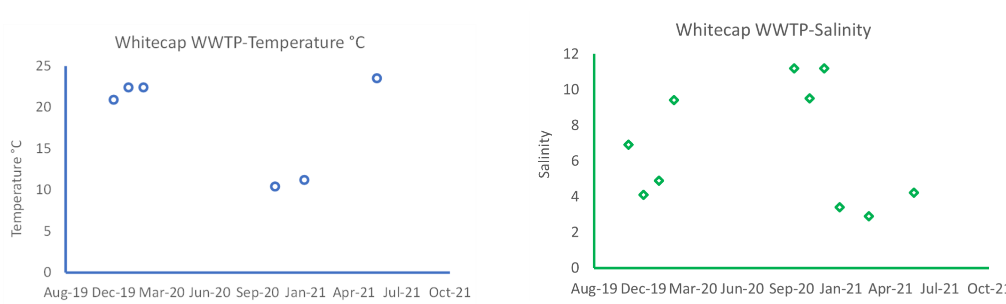


Figure 10. Whitecap WWTP temperature and salinity.

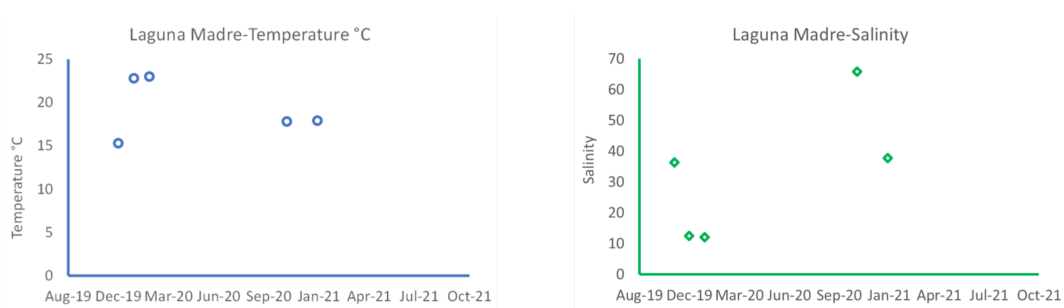


Figure 11. Laguna Madre temperature and salinity

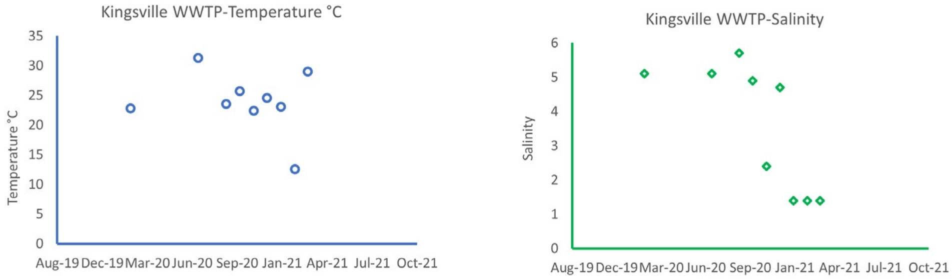


Figure 12. Kingsville WWTP temperature and salinity

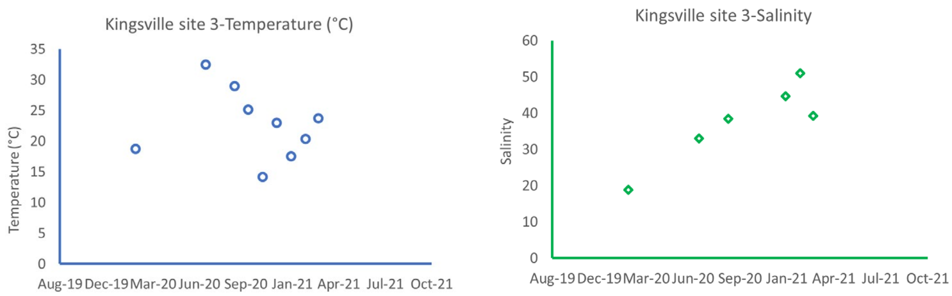


Figure 13. Kingsville Site 3 temperature and salinity

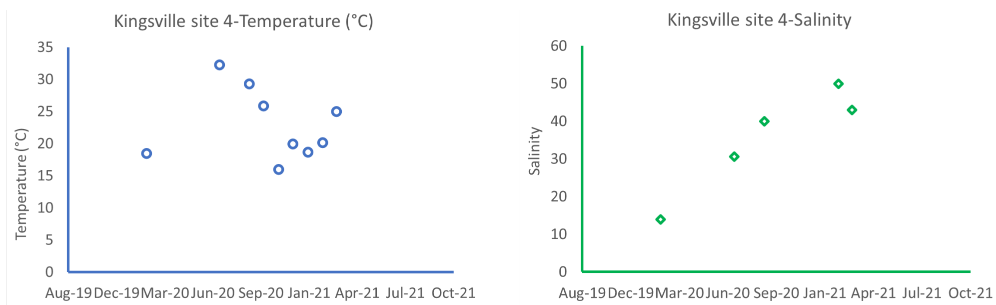


Figure 14. Kingsville Site 4 temperature and salinity

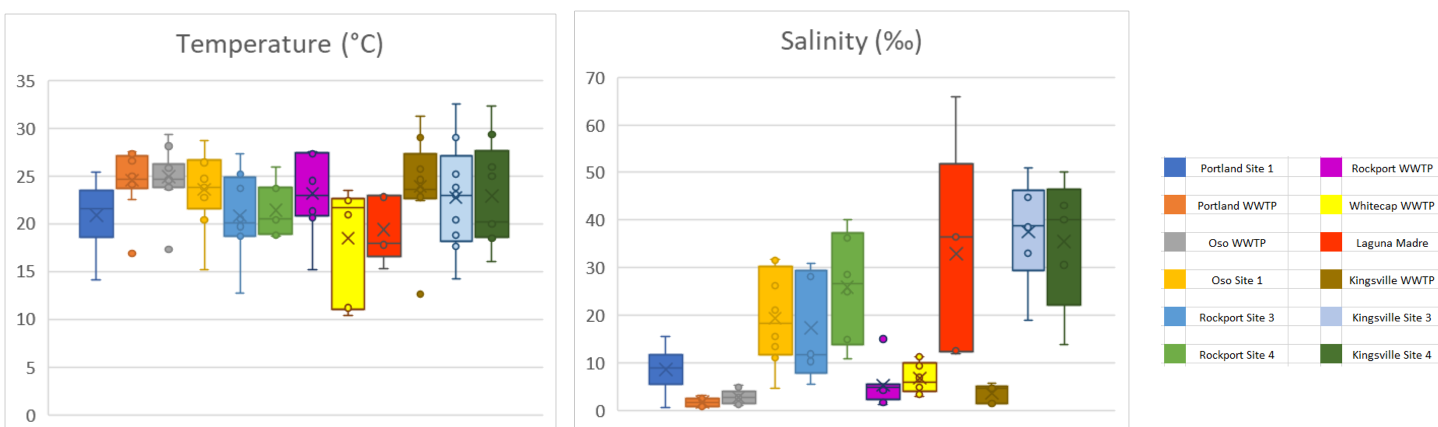


Figure 15. Average temperature and salinity of sample sites

All of the WWTP sites had average salinities that were lower than those of the onsite septic disposal sites: Portland WWTP had an average salinity of 1.73 parts per thousand (‰), Oso WWTP had an average salinity of 2.69 ‰, Rockport WWTP had an average salinity of 5.33 ‰, Whitecap WWTP had an average salinity of 5.9 ‰, and Kingsville WWTP had an average salinity of 3.57 ‰. The average salinities of the onsite septic disposal sites that were sampled from were higher: Portland site 1 had an average salinity of 8.6 ‰, Oso site 1 had an average salinity of 19.4 ‰, Rockport site 3 and 4 had average salinities of 17.32 ‰ and 25.9 ‰ respectively, Laguna Madre had an average salinity of 32.88 ‰, and Kingsville sites 3 and 4 had average salinities of 37.57 ‰ and 35.5 ‰ respectively.

Nutrient Concentrations

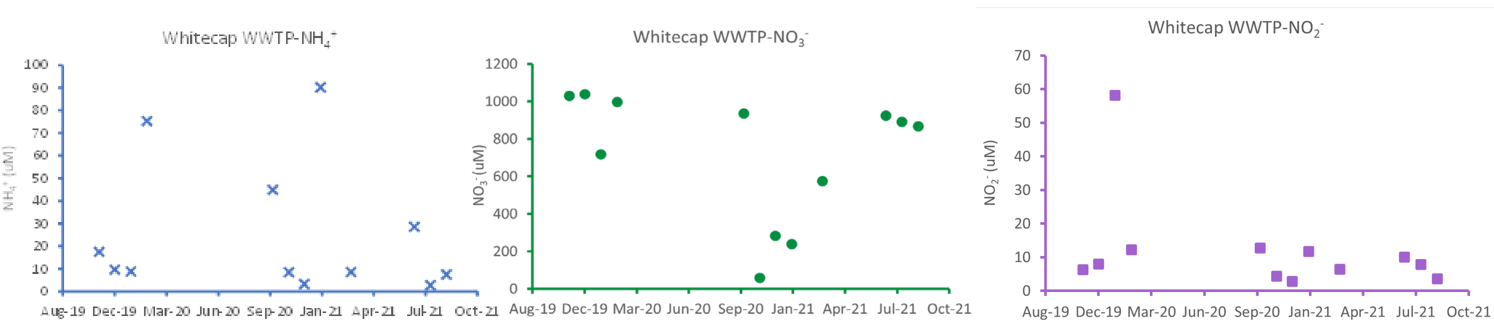


Figure 16. Whitecap WWTP NH_4^+, NO_3^-, and NO_2^- concentrations

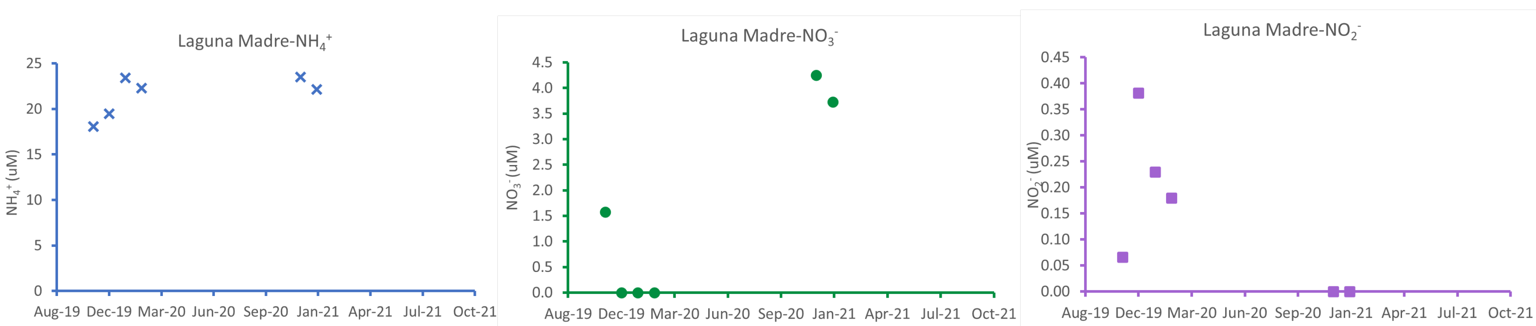


Figure 17. Laguna Madre NH_4^+, NO_3^-, and NO_2^- concentrations

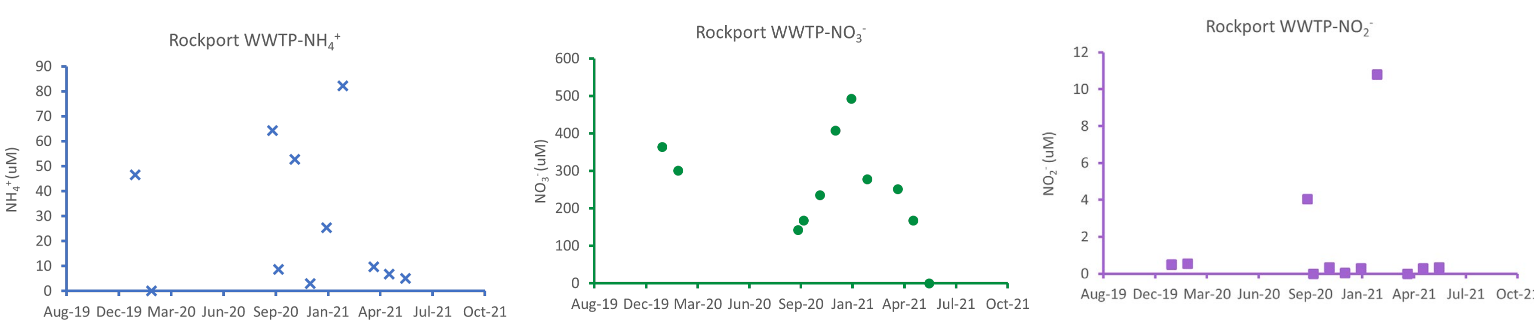


Figure 18. Rockport WWTP NH_4^+, NO_3^-, and NO_2^- concentrations.

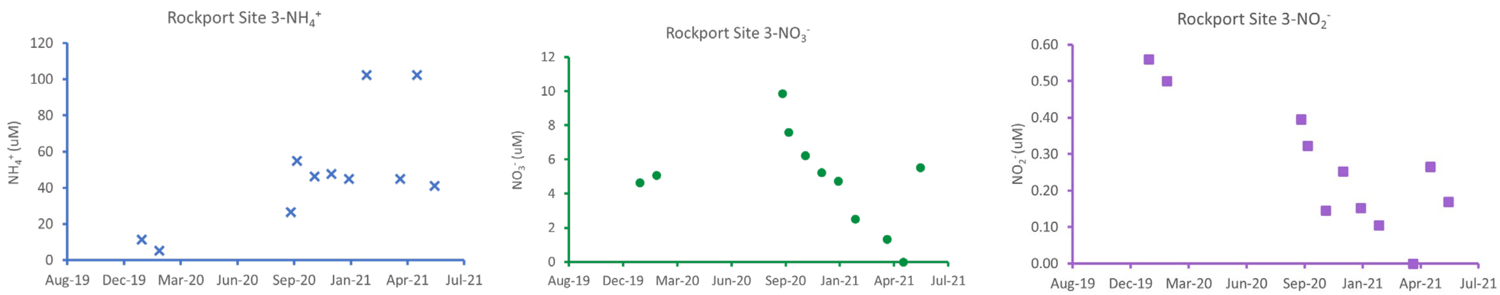


Figure 19. Rockport Site 3 NH_4^+, NO_3^-, and NO_2^- concentrations.

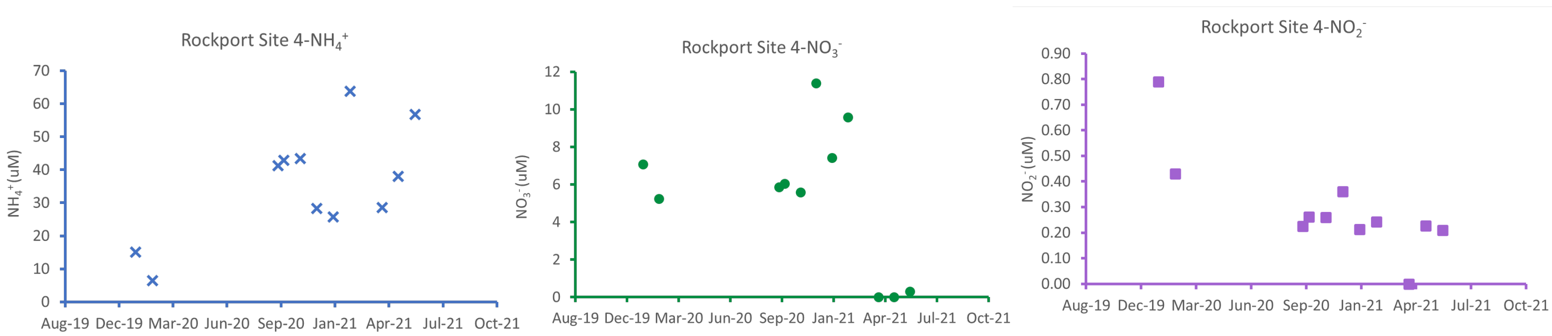


Figure 20. Rockport Site 4 NH_4^+, NO_3^-, and NO_2^- concentrations

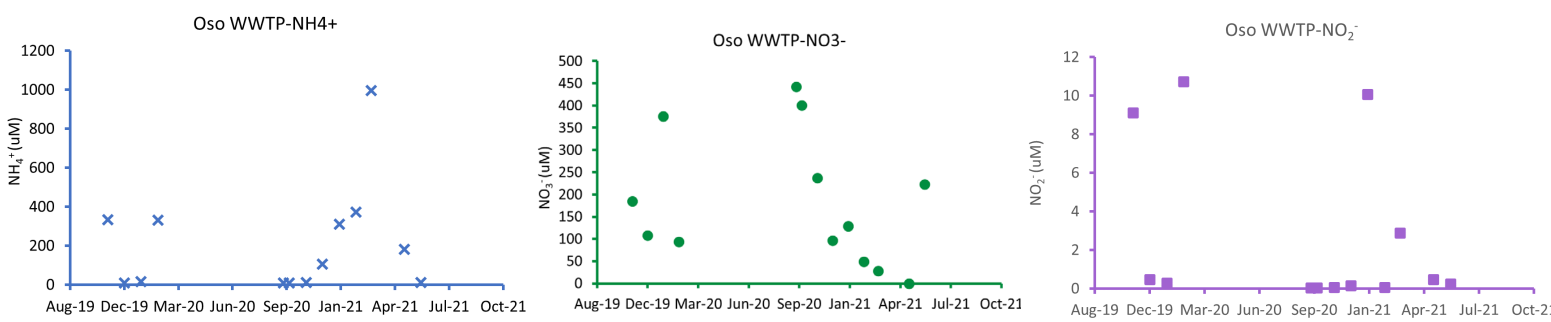


Figure 21. Oso WWTP NH_4^+, NO_3^-, and NO_2^- concentrations

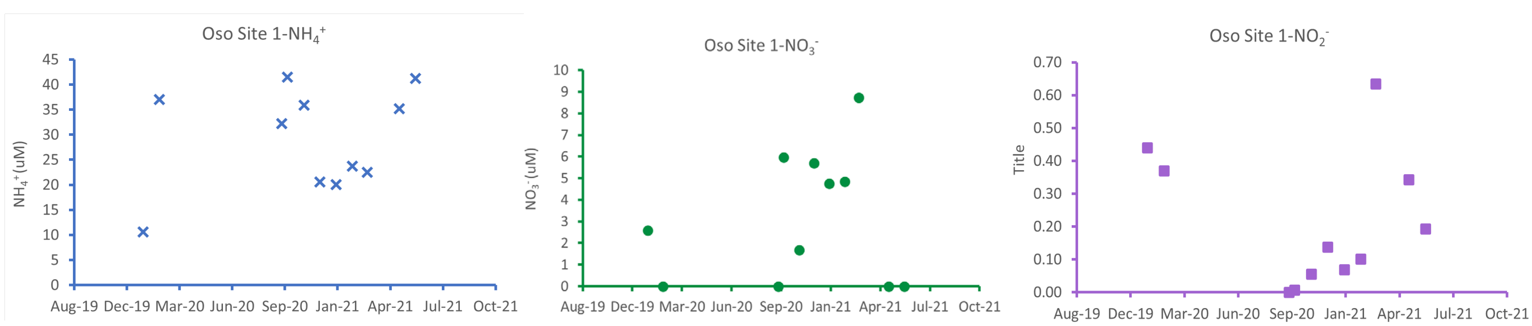


Figure 22. Oso site 1 NH_4^+, NO_3^-, and NO_2^- concentrations

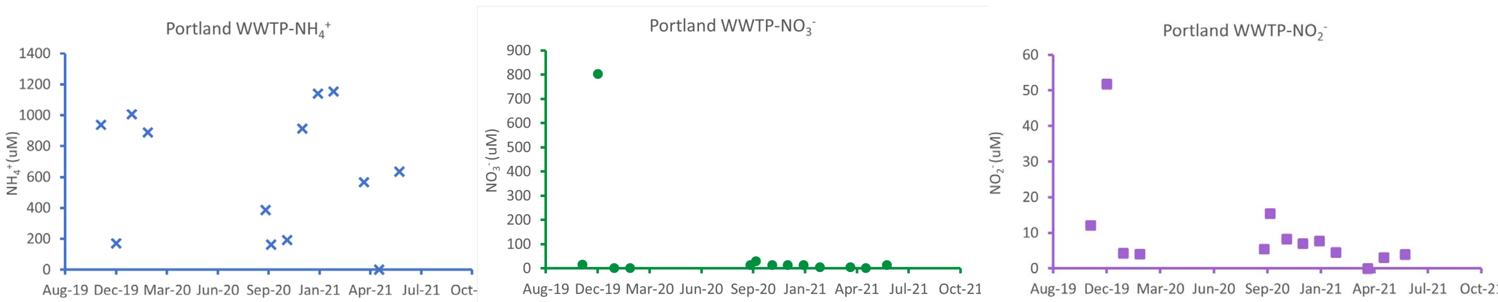


Figure 23. Portland WWTP NH_4^+, NO_3^-, and NO_2^- concentrations

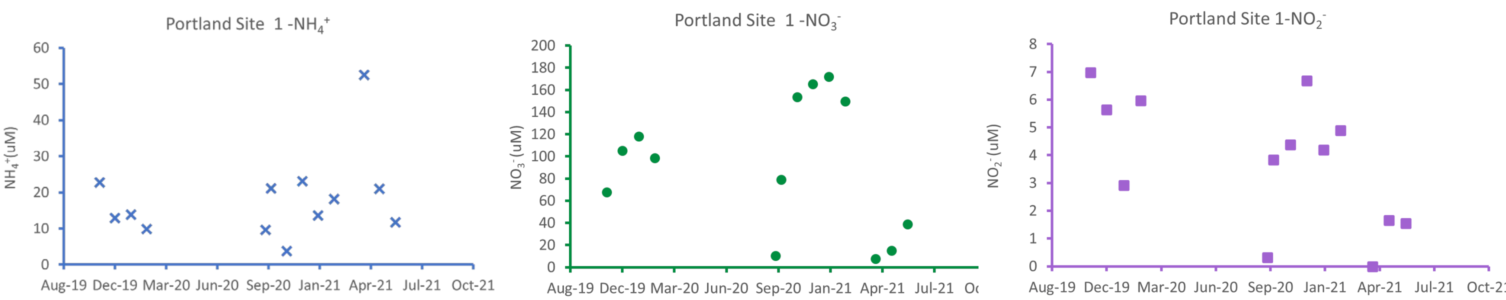


Figure 24. Portland Site 1 NH_4^+, NO_3^-, and NO_2^- concentrations

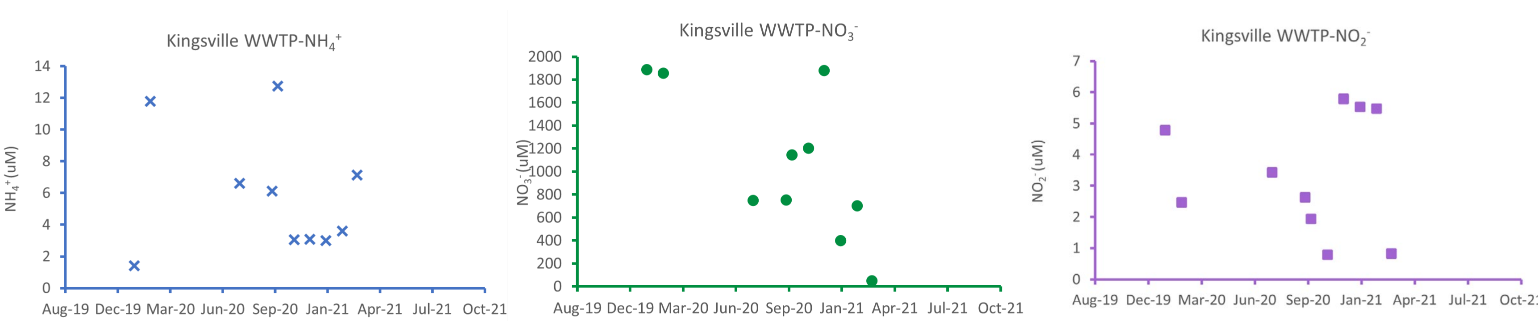


Figure 25. Kingsville WWTP NH_4^+, NO_3^-, and NO_2^- concentrations

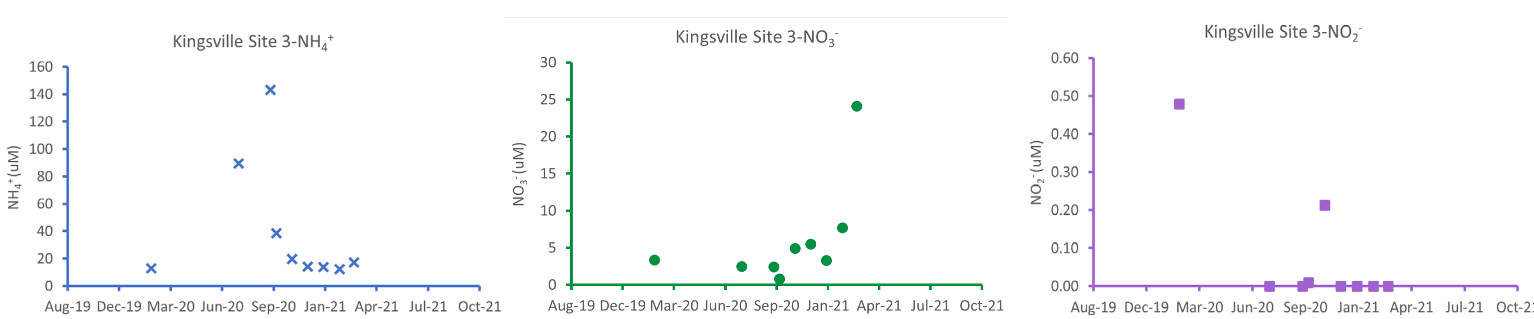


Figure 26. Kingsville Site 3 NH_4^+, NO_3^-, and NO_2^- concentrations

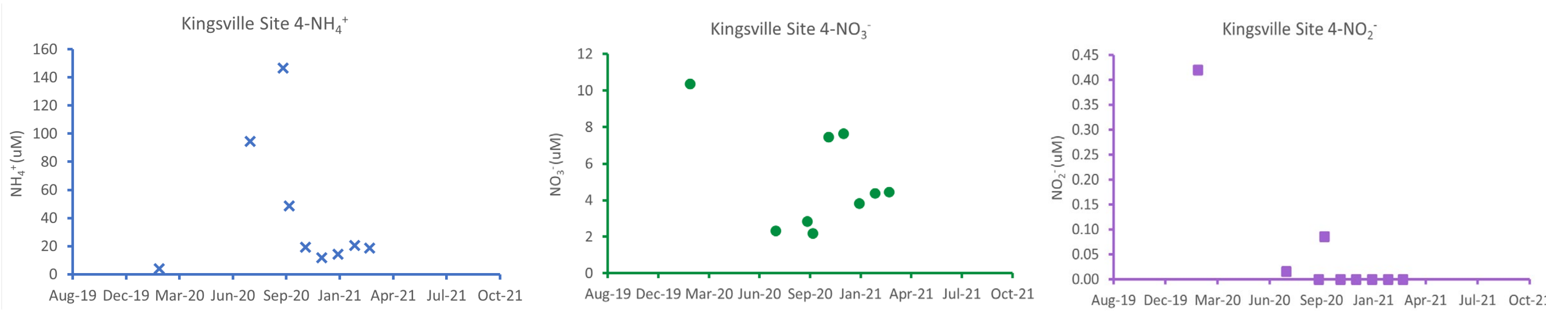


Figure 27. Kingsville Site 4 NH_4^+, NO_3^-, and NO_2^- concentrations

The samples with the highest concentrations of NH_4^+ collected during the study were from the WWTP locations. Whitecap WWTP had an average NH_4^+ concentration of 25.49 uM, Rockport WWTP had an average NH_4^+ concentration of 27.67 uM, and Kingsville WWTP had an average NH_4^+ concentration of 5.86 uM. The last two WWTPs, Oso WWTP and Portland WWTP, had the highest NH_4^+ concentrations of all the areas tested during the course of the study, with average NH_4^+ concentrations of 207.71 uM and 564.81 uM respectively. However, the lowest average NH_4^+ of any of the areas tested was also from a wastewater treatment plant, namely Kingsville WWTP. The average NH_4^+ concentration of the OSDS varied less than that of the WWTPs: Laguna Madre had an average NH_4^+ concentration of 21.47 uM, Rockport sites 3 and 4 had average NH_4^+ concentrations of 47.94 uM and 35.47 uM respectively, Oso site 1 had an average NH_4^+ concentration of 29.14 uM, Portland site 1 had an average NH_4^+ concentration of 18 uM, and Kingsville sites 3 and 4 had average NH_4^+ concentrations of 40.19 uM and 42.04 respectively.

Again, the highest concentration of NO_3^- collected during the study were generally from WWTP sites. The highest average concentration of NO_3^- collected was from Kingsville WWTP with an average NO_3^- of 1064.98 uM. Rockport WWTP had an average NO_3^- concentration of 255.33 uM, and Whitecap WWTP had an average NO_3^- concentration of 714.47 uM. Oso WWTP had an average NO_3^- concentration of 197.3 uM, and Portland WWTP had an average NO_3^-

concentration of 72.31 uM. For the most part, the OSDS had lower NO_3^- concentrations than the WWTPs with the exception of Portland site 1, which had an average NO_3^- concentration of 90.87 uM. The other OSDS had much lower NO_3^- concentrations: Laguna Madre had an average NO_3^- concentration of 1.91 uM, Rockport sites 3 and 4 had average NO_3^- concentrations of 4.80 and 5.32 uM respectively, Oso site 1 had an average NO_3^- concentration of 3.43 uM, and Kingsville sites 3 and 4 had average NO_3^- concentrations of 6.08 and 5.06 uM respectively.

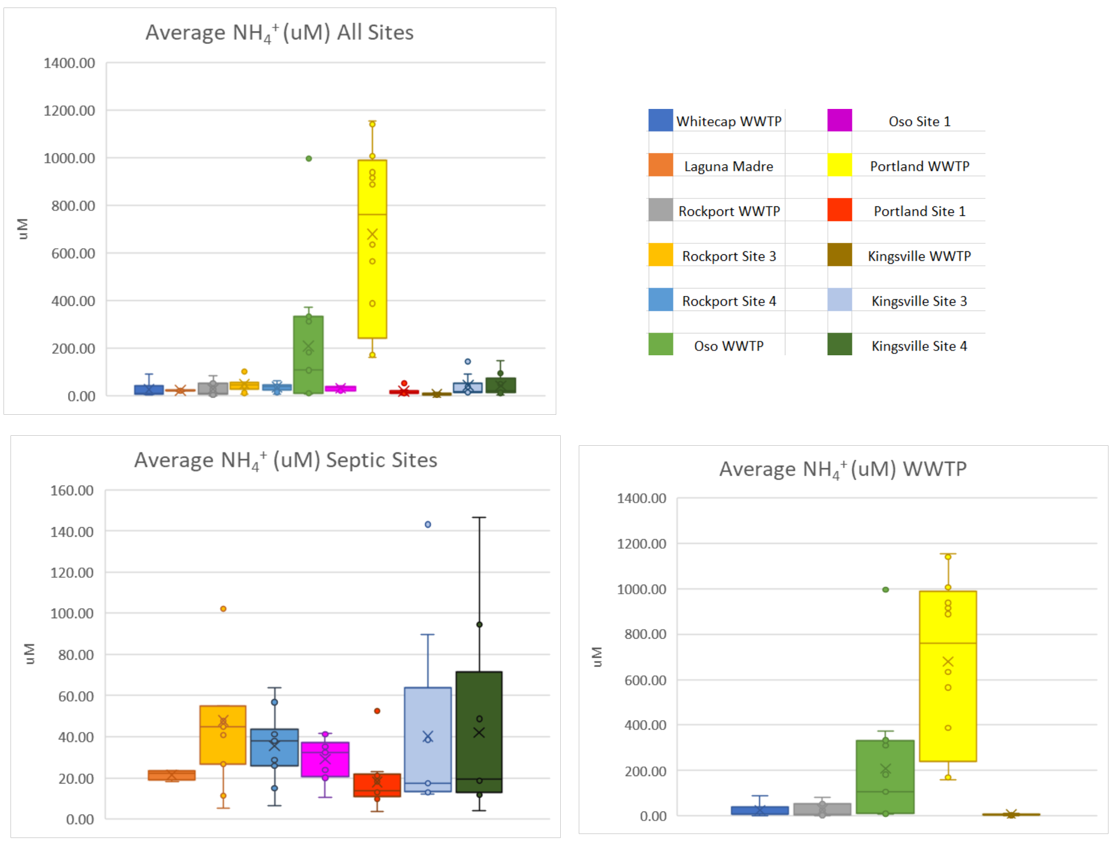


Figure 28. Average NH_4^+ concentrations of sample sites

Like the other two nitrogen-based nutrients, the WWTPs generally had higher NO_2^- concentrations than the OSDS except for one case, Portland site 1. Whitecap WWTP had an average NO_2^- concentration of 12.10 uM, Rockport WWTP had an average NO_2^- concentration of 1.72 uM, Oso WWTP had an average NO_2^- concentration of 2.66 uM, Portland WWTP had an average NO_2^- concentration of 10.66 uM and Kingsville WWTP had an average NO_2^-

concentration of 3.37 uM. The only OSDS that had a higher NO_2^- concentration than any of the WWTPs was Portland site 1, with an average NO_2^- concentration of 4.09 uM. Laguna Madre had an average NO_2^- concentration of 0.14 uM, Rockport site 3 and 4 had average NO_2^- concentrations of 0.29 and 0.32 uM respectively, Oso site 1 had an average NO_2^- concentration of 0.21 uM and Kingsville sites 3 and 4 had average NO_2^- concentrations of 0.08 and 0.06 uM respectively.

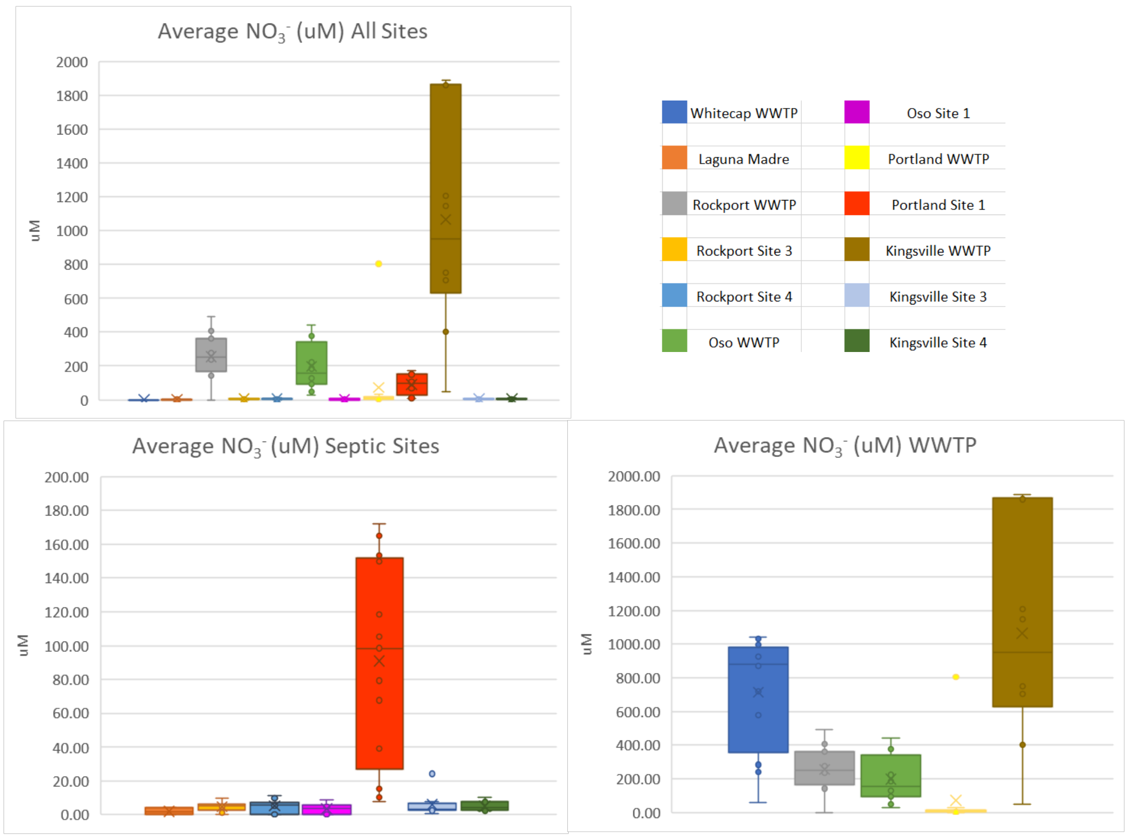


Figure 29. Average NO_3^- concentrations of sample sites

N Loading of Onsite Septic Systems

Figure 30. Average NO_2^- concentrations of sample sites

The average amount of nitrogen discharged daily by the total number of onsite septic systems – or N loading – in a specific county was calculated for the five counties in South Texas encompassing the study areas by multiplying the average daily flow rate of an OSDS system for one household – 246 L/day – by the number of OSDS in a particular county by the N loading coefficient of 23.63 mg/L. Aransas County onsite septic systems were responsible for discharging 167 kg of nitrogen per day, Kleberg County onsite septic systems discharged 27 kg of nitrogen per day, and Nueces County discharged 75 kg of nitrogen per day. Refugio County discharged 11 kg of nitrogen per day, and lastly, San Patricio County was responsible for discharging 54 kg of nitrogen per day.

Row Labels	Count of Inv_County
Aransas	7591
Kleberg	1232
Nueces	3402
Refugio	491
San Patricio	2432
Grand Total	**15148**

Table 1. Number of OSDS per county

N Loading of WWTPs

The average amount of nitrogen discharged daily by – or N loading of – each of the five WWTPs sampled from during this study was also calculated by multiplying the average daily flow rate of each WWTP by the N concentration found at that WWTP. Whitecap WWTP was responsible for discharging 212 kg of nitrogen per day, Rockport WWTP discharged 77 kg of nitrogen per day, and Oso WRP discharged 490 kg of nitrogen per day. The Portland WWTP discharged 79 kg of nitrogen per day, and lastly, Kingsville WWTP was responsible for discharging 125 kg of nitrogen per day.

City	TPDES Permit #	Permitted Annual Average Flow
		MGD
Rockport	WQ0010054001	2.5
OSO	WQ0010401004	16.2
Whitecap	WQ0010401009	2.5
Portland	WQ0010478001	2.5
Kingsville	WQ0010696004	1

Table 2. WWTP flow data

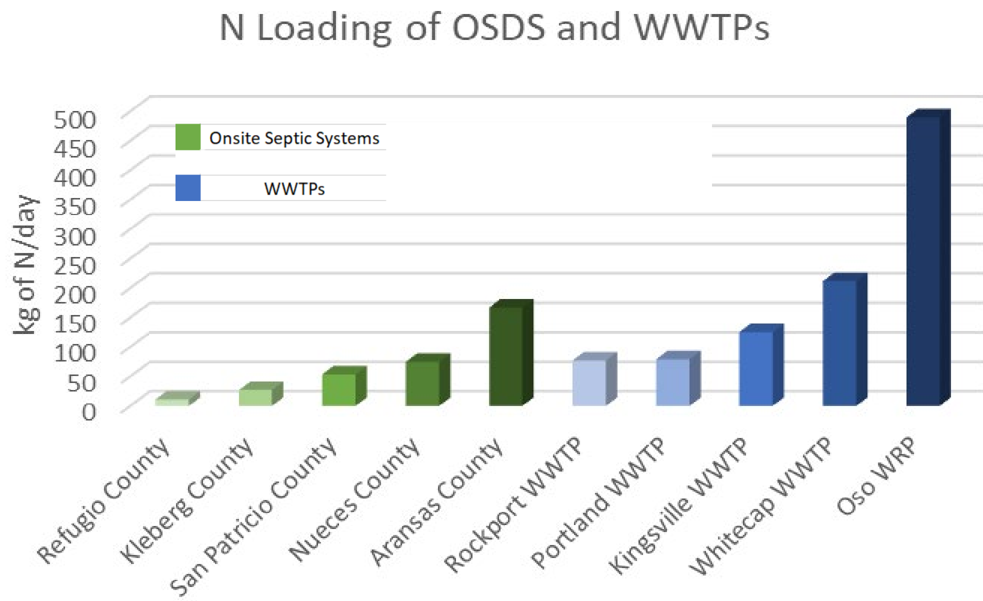


Figure 31. Nitrogen in kg/day discharged by onsite septic systems and WWTPs

Caffeine Concentrations in WWTP and OSDS Areas

Sample Site	Sampling Month	Caffeine Concentration (ng/L)
Rockport WWTP	Feb-20	4.3
Rockport Site 1	Nov-19	0.9
Rockport Site 4	Feb-21	7.3
Portland WWTP	Oct-20	7.3
Portland WWTP	Nov-20	5.5
Portland WWTP	Nov-21	1.7
Portland Site 1	Oct-20	2.3
Portland Site 1	Oct-20	7.4
Portland Site 1	Apr-21	5.8
Whitecap WWTP	Nov-20	16.4
Whitecap WWTP	Dec-20	3
Laguna Madre	Jan-21	7.6
Laguna Madre	Feb-21	1.5
Oso WWTP	Feb-21	3
Oso Site 1	Feb-21	3.5
Kingsville WWTP	Feb-20	7.1
Kingsville WWTP	Sep-20	8.5
Kingsville Site 3	Feb-21	0.7

Table 3. Caffeine concentrations in ng/L

	NO3- (‰)	
Baffin Bay WWTP	08232019	23.2
	11012019	18.3
	01292020	27.2
Whitecap WWTP	11212019	11.4
	12312019	11.9
	03082020	16.2
	11052020	13.0
Rockport WWTP	01202020	6.7
	02292020	6.2

Table 4. Nitrogen isotope ratios in nitrate samples

Site	Date	NH4+ (‰)
Portland WWTP	03042020	8.08
	09222020	6.40
	10272020	7.07
	11232020	5.89
	03052021	8.09
	04122021	4.27
Portland Site 1	03042020	12.58
	10272020	29.94

Table 5. Nitrogen isotope ratios in ammonium samples

DISCUSSION

N Loading of Onsite Septic Systems versus WWTPs

Denitrification is a process in which nitrate and nitrite are reduced to nitrogen gas by microbes, which occurs in the absence of oxygen as fixed forms of N act as electron acceptors during anaerobic respiration (Lindau et al., 2008). Denitrification is utilized by WWTPs as a method by which to remove organic N nutrients from wastewater influent before it is discharged as treated effluent to local bodies of water in an effort to decrease nutrient pollution, which is extremely harmful to aquatic ecosystems. Rockport WWTP is the only wastewater treatment plant sampled from during this project that has a dedicated N removal process. This process directs influent from the aerobic tank present in the activated sludge treatment method to a separate anoxic tank with low levels of dissolved oxygen where denitrification takes place, after which influent can be further treated before it is discharged as effluent (EPA, 2008).

In accordance with their dedicated N removal process, the Rockport WWTP discharges the least amount of kg of nitrogen per day of any of the WWTPs in this study, only 77.115 kg of N/day. The city of Rockport, TX, and its WWTP are located in Aransas County; Aransas County's total onsite septic system N loading is 167.018 kg of N/day. Therefore, the onsite septic systems in the greater Rockport area contribute substantially more nitrogen to local bodies of water than the treated effluent from the WWTP itself, suggesting that dedicated N removal processes are an effective way to mitigate the amount of nitrogen discharged via treated effluents.

The other WWTPs included in the scope of this project – Portland WWTP, Kingsville WWTP, Whitecap WWTP, and Oso WRP – have no dedicated removal method for nitrogen in influent and are not required to. Each of these WWTP discharged more kg of nitrogen per day than Rockport WWTP, and they also surpassed the amount discharged by the total number of onsite septic systems within their respective counties. Portland, TX, is located within Nueces and San Patricio counties; the Portland WWTP discharges 79.140 kg of N/day while Nueces County combined onsite septic systems discharge 74.851 kg of N/day while San Patricio combined onsite septic systems discharge 53.509 kg of N/day. Kingsville, TX, is located within Kleberg County; the Kingsville WWTP discharges 125.170 kg of N/day while Kleberg County combined onsite septic systems discharge 27.107 kg of N/day. Corpus Christi, TX, is located within Nueces County; Oso WRP and Whitecap WWTP discharge 489.923 kg of N/day and 211.771 kg of

N/day respectively while Nueces County combined onsite septic systems discharge 74.851 kg of N/day. Refugio County is located close to the areas studied during this project; its combined onsite septic systems discharge 10.803 kg of N/day.

From these comparisons, it is evident that WWTPs with no dedicated N removal process will discharge more nitrogen into local bodies of water than onsite septic systems located in the same area, likely due to the fact that WWTPs process and treat much more influent on average than onsite septic systems do, even combined. Although not required by regulatory bodies, retrofitting existing WWTPs with N removal processes such as anoxic tanks would greatly minimize the amount of nitrogen discharged into the environment and the ensuing nutrient pollution caused by an influx of effluent with high N concentrations. While this would be a cost burden upfront, poor water quality comes with its own long term negative economic effects (Segerson & Walker, 2002).

SUMMARY

Results suggest that WWTP is the major source of anthropogenic N to the receiving water bodies in most counties in Texas Coastal Bend except in the Aransas County, where the WWTP (Rockport) equips with N removal techniques and there are more septic systems than any other counties studied in this project. As a result, the septic systems in Aransas County contributed about twice as much N as the Rockport WWTP. In other counties, there are fewer septic systems in the coastal zone, which are thus a lesser N polluter than WWTPs. To reduce anthropogenic N loading to critical aquatic ecosystems, it is important to equip both WWTP and septic systems with N removal techniques.

REFERENCES

Archana, A., Li, L., Shuh-Ji, K., Thibodeau, B., & Baker, D. M. (2016). Variations in nitrate isotope composition of wastewater effluents by treatment type in Hong Kong. Marine Pollution Bulletin, 111, 143-152. http://dx.doi.org/10.1016/j.marpolbul.2016.07.019

Bonhomme, M., Rogolla, F., Boisseau, G., & Sibony, J. (1990). Enhancing nitrogen removal in activated sludge with fixed biomass. Water Science and Technology, 22(1), 127-135. https://doi.org/10.2166/wst.1990.0142

Bourbonnais, A., Letscher, R.T., Bange, H.W., Echevin, V., Larkum, J., Mohn, J., Yoshida, N., and Altabet, M.A., 2017. N2O production and consumption from stable isotopic and concentration data in the Peruvian coastal upwelling system. Global Biogeochemical Cycles. 31(4):678-698

BryantMason, A., Xu, J. Y., and Altabet, M., (2013). Isotopic signature of nitrate in river waters of the lower Mississippi and its distributary, the Atchafalaya. Hydrol. Process. 27:2840-2850, doi:10.1002/hyp.9420

Desimone, L. A., & Howes, B. L. (1996). Denitrification and nitrogen transport in a coastal aquifer receiving wastewater discharge. Environmental Science & Technology, 30(4), 1152-1162. https://doi.org/10.1021/es950366p

City of Corpus Christi Wastewater Department. (2016). City of Corpus Christi wastewater management plan (Stantec Consulting Services Inc., Author).

Freyer, B.H.D., and Republic, F., 1978. Seasonal trends of N: and NO, nitrogen isotope composition in rain collected at Jiilich, Germany. Tellus 30:83-92.

Kendall, C., and McDonnell, J. J. 1998. Isotope tracers in catchment hydrology, Ed, Elsevier Science.

Kendall, C., Elliott, E. M., and Wankel, S. D., 2007. Tracing Anthropogenic Inputs of Nitrogen to Ecosystems, p. 375-434. In Michener, R., Lajtha, K., [eds.], Stable Isotopes in Ecology and Environmental Science. Blackwell Publishing Ltd.

Lindau, C. W., Scaroni, A. E., Delaune, R. D., & Nyman, J. A. (2008). Denitrification in cypress swamp within the Atchafalaya River Basin, Louisiana. Chemosphere, 70(5), 886-894. https://doi.org/10.1016/j.chemosphere.2007.06.084

McIlvin, M. R., and Altabet, M. A., 2005. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. Anal. Chem. 77:5589-5595, doi: 10.1021/ac050528s

McLaughlin, K., Nezlin, N. P., Howard, M. D.A., Beck, C. D.A., Kudela, R. M., Mengel, M. J., & Robertson, G. L. (2017). Rapid nitrification of wastewater ammonium near coastal ocean outfalls, Southern California, USA. Estuarine, Coastal and Shelf Science, 186, 263-275. http://dx.doi.org/ 10.1016/j.ecss.2016.05.013

Moran, S. (2018). Dirty water unit operation design: Chemical processes. In An applied guide to water and effluent treatment plant design (pp. 165-169). Elsevier. https://doi.org/10.1016/B978-0-12-811309-7.00013-8

Qi, D. (2018). Treatment of wastewater, off-gas, and waste solid. In Hydrometallurgy of rare earths (pp. 743-777). Elsevier. https://doi.org/10.1016/B978-0-12-813920-2.00008-8

Segerson, K., & Walker, D. (2002). Nutrient pollution: An economic perspective. Estuaries, 25, 797-808. https://doi.org/10.1007/BF02804906

Texas Legislature Texas Water Development Board. (2015). Water use of Texas water utilities. https://www.twdb.texas.gov/publications/reports/special_legislative_reports/doc/2014_WaterUseOfTexasWaterUtilities.pdf

U.S. Environmental Protection Agency. (2002). Onsite wastewater treatment systems manual. U.S. Environmental Protection Agency. https://www.epa.gov/sites/default/files/2015-06/documents/2004_07_07_septics_septic_2002_osdm_all.pdf

U.S. Environmental Protection Agency EPA Office of Wastewater Management. (2008). Municipal nutrient removal technologies reference document (S. Joh Kang, K. Olmstead, K. Takacs, & J. Collins, Authors). https://www.epa.gov/ sites/default/files/2019-08/documents/municipal_nutrient_removal_technologies_vol_i.pdf

von Sperling, M. (2007). Activated sludge process and main variants. In Activated sludge and aerobic biofilm reactors (pp. 1-13). IWA Publishing.

Weiskel, P. K., & Howes, B. L. (1991). Quantifying dissolved nitrogen flux through a coastal watershed. Water Resources Research, 27(2), 2929-2939. https://doi.org/10.1029/91WR01910

APPENDICES

Appendix 1. Photos of field sampling.

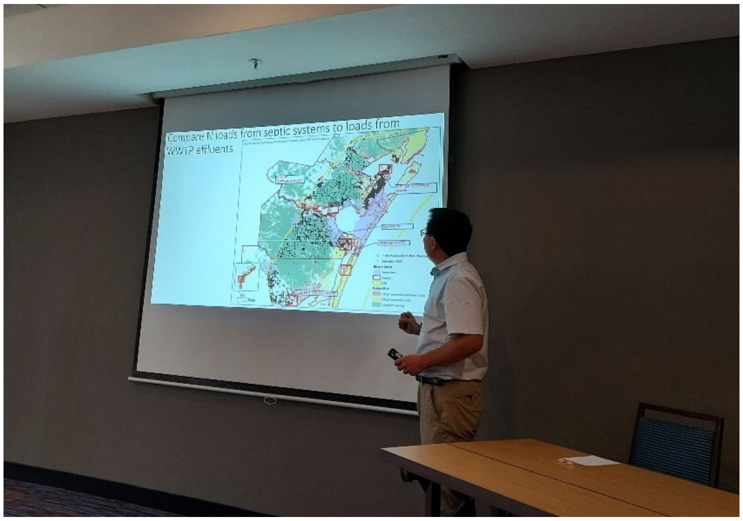
Photo of students Morganne Mier and Daniel Lansidel sampling at the Portland WWTP in November 2019.

Photo of student Morganne Mier sampling at the Portland septic site in November 2019.

Photo of student Daniel Lansidel sampling at the Portland septic site in November 2019.

Photo of student Shahrukh Niazi, Catherine Shaw, and Jesus Baca sampling at the Portland septic site in December 2019.

Appendix 2. Photos of outreach events.



Dr. Lin Zhang (PI) presented results from this project at the 2022 REEU in Jun 2022.

Dr. Anish Jantrania (co-PI) conducted an education and outreach workshop between Jun 13th and 15th in Galveston, TX, which involved 14 students.